Geochemistry and Mineralogy of the Colorado Plateau Uranium Ores

Compiled by ROBERT M. GARRELS *and* ESPER S. LARSEN 3D

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A summary of the results of field and laboratory studies concerned with the nature of the ores and the alteration processes affecting them.
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FOREWORD

The urgency and magnitude of the uranium resources program have provided an unequaled opportunity to investigate the Colorado Plateau uranium ores. This volume summarizes the results of field and laboratory studies concerned with the nature of the ores and the alteration processes affecting them. Thirty scientists have contributed directly; they include specialists in structural geology, sedimentation, sedimentary petrology, groundwater geology, mineralogy, nuclear geology, crystal chemistry, structural crystallography, physical chemistry, and analytical chemistry. The studies are aimed at understanding the ores from these varied points of view.

With such a diversity of effort at work, speculation becomes more and more restricted by the empirical and experimental facts that are developed. Thus the facts, combined with only modest speculation, have led the writers of this volume to a number of important conclusions, not all new, but certainly better founded than heretofore, concerning the Plateau ores. Among the most important are: (1) the carnotite and similar ores that have yielded the great bulk of the production up to now are the weathering products of a different sort of primary ore; and (2) the primary ores are a lower valence assemblage, the predominant type consisting of vanadium clay minerals together with uraninite, coffinite, and montroseite present in rocks containing organic remains chiefly of wood. The geologic environment and the chemical course of the weathering process are now well understood in general outline, although much detail is still lacking.

The data and conclusions presented should prove helpful in future exploration for uranium on the Plateau, particularly in exploration at greater depth and in primary ores. For example, in districts in which abundant vanadium is associated with uranium, the stratigraphic and structural controls, the size, and the tenor of primary ore bodies should be comparable to the weathered ore bodies; where vanadium is scarce, the primary ore body may be smaller but richer than its weathered counterpart.

In addition many of the data have direct application to other types of uranium deposits than those represented on the Colorado Plateau. The general patterns of the oxidation of uranium (and of vanadium) are sufficiently determined so that they apply to any natural environment, although the details of structure and chemistry may vary widely.

Perhaps the greatest value, in the long run, is the establishment of the nature and environment of the primary ores. Knowing their habitat and their nature, we can speculate upon their origin: the source of the uranium and associated elements, the nature and course of the fluids that carried them, and the environmental changes that caused their precipitation. We are proceeding now to collect data that will give limits to our speculation.

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September 6, 1956

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CONTENTS

GEOCHEMISTRY AND MINERALOGY OF THE COLORADO PLATEAU URANIUM ORES

Compiled by ROBERT M. GARRELS and ESPER S. LARSEN 3d

INTRODUCTION

The uranium ores on the Colorado Plateau, which covers parts of Colorado, Utah, Arizona, and New Mexico, are the principal domestic source of uranium. A very great effort has been devoted to unraveling the geologic relations of the ores to the enclosing rocks, and a great effort has gone into geochemical investigations of the ores.

Until very recently, most of the uranium came from ores in which uranium was in its highest valence state—U(VI), such as carnotite—and was commonly associated with minerals containing vanadium in its highest valence state—V(V). These are the typical carnotite ores. In the past few years, an increasingly large part of the uranium has come from ores in which the uranium is present in uraninite and coffinite; that is, the uranium is in part at least in its lowest stable valence state, U(IV), and the minerals accompanying it are low-valence vanadium oxides or hydrated oxides, pyrite, marcasite, and other base-metal sulfides. These are the typical "black ores." In recent years, too, the carnotite-type ores have been found to grade downward in a number of deposits, through a zone of minerals of intermediate valence state, into the typical "black ores." Many workers were convinced, on the basis of the geologic relations in the field and the mineralogic character of the ores, that the "black ores" were the primary materials from which the high-valence (carnotite-type) ores were derived by oxidation during weathering. This concept is now widely accepted.

The studies reported here have been aimed at (1) testing this oxidation concept, (2) developing a knowledge of the stability relations of vanadium and uranium minerals under varying conditions of pH and oxidation-reduction potentials (Eh), and (3) defining the nature and equilibrium conditions of the "primary" (low-valent) ores. The origin of the primary ores is not specifically considered in these reports.

The parts that follow are summary reports of more extensive studies, many of which are still in progress. The first 5 parts present topical data of general application to the Colorado Plateau deposits; parts 6 through 15 cover the results of theoretical, experimental, or empirical studies relating to the chemical and physical nature of the ores and their oxidation; in parts 16 through 19 are described the geological relationships between oxidized and unoxidized ore in several ore deposits on the Plateau; part 20 concerns the broad geochemical relationships of vanadium and uranium throughout the world. The final part summarizes conclusions and particularly emphasizes the salient problems requiring further study.

Part 1 contains no new or original data; it presents a background for the work reported on and a brief summary of the geology of the Colorado Plateau to serve as a setting for the parts that follow. No authorship is given for "The Known and the Unknown," which represents the conclusions of a large number of collaborators, a good many of whom are not authors of parts of this paper; it would be impossible to credit individuals with most of the ideas presented.

Semiquantitative spectrographic data are presented in several parts of this volume. Table 1 shows the limits of sensitivity of the method for the elements determined. These values are only approximate, as the

TABLE 1.—*Limits of sensitivity for elements determined by the semiquantitative spectrographic method*

Element	Percent	Element	Percent	Element	Percent
Si	0.005	Eu	0.003	Ru	0.008
Al	.0001	F	.08	Sb	.01
Fe	.0008	Ga	.001	Sc	.0005
Mg	.00003	Gd	.006	Sn	.001
Ca	.01	Ge	.001	Sr	.001
Na	.01	Hf	.007	Sm	.008
K	.1	Hg	.08	Ta	.1
Ti	.0005	Ho	.001	Tb	.01
P	.07	In	.0004	Te	.08
Mn	.0007	Ir	.03	Th	.05
Ag	.00001	La	.003	Tl	.04
As	.01	Li	.01	Tm	.001
Au	.001	Lu	.005	U	.08
B	.005	Mo	.0005	V	.001
Ba	.0005	Nb	.001	W	.05
Be	.00005	Nd	.006	Y	.001
Bi	.005	Ni	.001	Yb	.0001
Cd	.005	Os	.1	Zn	.008
Ce	.03	Pb	.001	Zr	.0008
Co	.001	Pd	.003		
Cr	.0006	Pr	.01		
Cs	.8	Pt	.003		
Cu	.00005	Rb	7		
Dy	.006	Re	.04		
Er	.003	Rh	.004		

data reported have been collected at two laboratories over a period of years, during which the method has been refined and modified.

The major part of the work represented by this publication was sponsored by the Division of Raw Materials of the U. S. Atomic Energy Commission; smaller segments of the work were supported by the Division of Research of the Atomic Energy Commission and by the Geological Survey.

Many geologists of both the Atomic Energy Commission (including their contractors) and the Geological Survey have contributed ideas, materials, and courtesies without which the studies reported herein could not have been undertaken. Particular appreciation must be expressed to the staff of many of the mines. Their continuing cooperation permitted many and repeated mine examinations and extensive mineral collecting.

Part 1. GEOLOGIC SETTING OF THE COLORADO PLATEAU ORES

By Alice D. Weeks and R. M. Garrels

CONTENTS

ILLUSTRATION

TABLE

GEOLOGY OF THE URANIUM-ORE REGION

Many reports on the geomorphology, stratigraphy, structure, and regional geology of the Colorado Plateau or various parts of it are available. Extensive bibliographies are given in many of these reports (Fenneman, 1931; Gregory, 1917, and 1938; Gillully and Reeside, 1928; Craig and others, 1955; Kelley, 1955a; Hunt and others, 1953, and Hunt, 1956). Most of the uranium deposits are in the east-central part of the Colorado Plateau and, therefore, the description which follows will be limited generally to a broad belt trending northwestward through the "Four Corners" area, the common corner of Colorado, Utah, Arizona, and New Mexico, and extending from the San Rafael Swell in Utah to the Grants district in New Mexico.

Figure 1 shows the general location of the uranium-bearing region of the Colorado Plateau (the Colorado Plateaus province of Fenneman) and its relation to the principal physiographic divisions and structural features of the Plateau. It also serves as a location map for places or mines receiving significant mention in the text; many place names used in the text are not shown, but they can be found on more detailed maps such as those of Finch (1955) and Kelley (1955) and on the geologic quadrangle maps[1] recently published by the U. S. Geological Survey. Other maps, including photogeologic maps, are listed in Wallace and Smith (1955).

TOPOGRAPHY AND CLIMATE

The uranium region occupies most of the Canyon Lands, and a part of the Navajo and Datil sections of the Colorado Plateaus province (Fenneman, 1931). The Canyon Lands consist of young to mature canyoned plateaus of high relief. The area is deeply dissected by the Colorado River and its tributaries which rise in the mountains bordering the plateaus. Most of the Canyon Lands lie between 5,000 and 7,500

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[1] These include the following quadrangles of western Colorado: Gateway, Map GQ55; Pine Mountain, Map GQ60; Juanita Arch, Map GQ81; Calamity Mesa, Map GQ61; Roc Creek, Map GQ83; Red Canyon, Map GQ58; Atkinson Creek, Map GQ57; Paradox, Map GQ72; Davis Mesa, Map GQ71; Uravan, Map GQ78; Anderson Mesa, Map GQ77; Bull Canyon, Map GQ33; Naturita N. W., Map GQ65; Horse Range Mesa, Map GQ64; Hamm Canyon, Map GQ69; Gypsum Gap, Map GQ59; Egnar, Map GQ68; and Joe Davis Hill, Map GQ66.

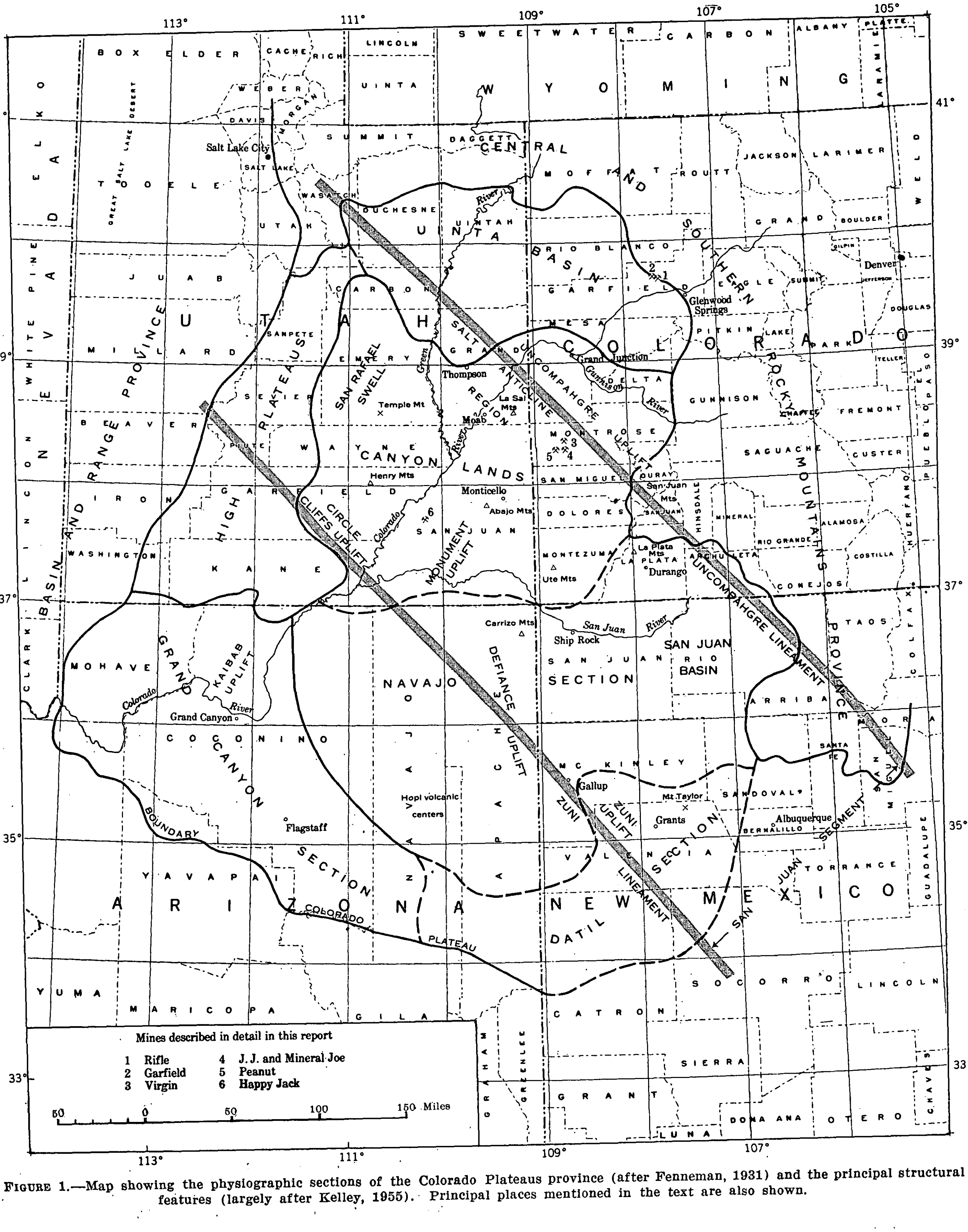

FIGURE 1.—Map showing the physiographic sections of the Colorado Plateaus province (after Fenneman, 1931) and the principal structural features (largely after Kelley, 1955). Principal places mentioned in the text are also shown.

feet above sea level and little of the area is below 5,000 feet except the canyon bottoms. Stocks and laccolithic mountains rise several thousand feet above the surrounding plateaus and the highest point is in the LaSal Mountains, more than 13,000 feet above sea level. The climate is arid in the western and southern parts of the Canyon Lands (about 5 inches average annual rainfall at Hanksville, Emery County, Utah) and the vegetation is mainly bunch grass, saltbush, cactus, and sage. The higher mesas and plateaus receive more precipitation and support a growth of piñon and juniper. In the uranium region of western Colorado the average annual precipitation ranges between approximately 11 inches at Paradox, Montrose County, and 16 inches at Norwood, San Miguel County. The highest mountains and plateaus have 20 inches or more average annual precipitation and a forest cover of spruce, pine, or aspen.

The northeastern part of Arizona and northwestern part of New Mexico in the Navajo section of the Colorado Plateaus province (Fenneman, 1931) is a dry country not as deeply dissected as the Canyon Lands because it has no large stream except the San Juan River along the northern border of the Navajo country. Bedrock consists mainly of sandstone and shale strata having gentle dip. A few large volcanic plugs and many small plugs and dikes intrude the sedimentary rocks and are conspicuous in the topography; buttes, mesas, and hogback ridges are also common land forms.

The northern part of the Datil section in New Mexico is characterized by extensive lava flows in addition to the gently dipping sedimentary rocks.

The topography, climate, and vegetation of the Henry Mountains region, Utah, are described by Hunt and others (1953); that of the Navajo country and the San Juan country by Gregory (1917 and 1938).

SEDIMENTARY ROCKS

The rocks of the Colorado Plateau, and particularly the uranium ore region of the Plateau, are predominantly sedimentary, ranging in age from Precambrian to Tertiary. Precambrian metamorphic rocks are exposed along the Grand Canyon of the Colorado River, in the Central portion of the Zuni uplift, in valleys eroded in the Uncompahgre Plateau, and in the Black Canyon of the Gunnison River. Sedimentary rocks of Paleozoic age are exposed in the central part of the San Rafael, Monument, Kaibab, Defiance, and Zuni uplifts and in the salt anticline region (Wengerd and Strickland, 1954). Sedimentary rocks of Mesozoic age, the chief host rocks of the uranium and vanadium deposits, are exposed over large areas on the flanks of the uplifts and on the structural platforms and in some of the basins between uplifts (McKee, 1951 and 1954; Stokes, 1950; Baker, Dane, and Reeside, 1936; Craig and others, 1955; and Young, 1955). Tertiary sedimentary rocks occur in considerable thickness in the San Juan, the Uinta, and the Piceance basins (the last two are chiefly outside the uranium region) and in lesser thickness in the Chuska Mountains, capping an unconformity on the Defiance monocline. The Mesozoic sedimentary rocks (table 1) include strata of fluviatile, lacustrine, eolian, volcanic, and marine origin and range from conglomerate, through sandstone, siltstone, and shale to limestone.

IGNEOUS ROCKS

Precambrian intrusive rocks are exposed in the Uncompahgre uplift, in the Black Canyon of the Gunnison River, and along the Grand Canyon of the Colorado River. In the central part of the Plateau are many small areas of younger intrusives. These include the stocks and laccoliths of the LaSal, Abajo, and Henry Mountains in Utah, the Ute Mountains in Colorado, and the Carrizo Mountains in Arizona. They are composed mostly of diorite porphyry and range in composition from diorite to syenite (Gould, 1927; Hunt and others, 1953; Waters, 1955, p. 715–716); the age is probably early Tertiary. The Navajo country has many volcanic plugs, dikes, diatremes, and lava-capped mesas (Williams, 1936; Hack, 1942). Many of these are alkaline basalts, including chiefly minette in the Monument Valley and Shiprock areas and limburgite, monchiquite, and other unusual rock types in the Hopi Buttes volcanic field, and are probably younger than the stocks and laccoliths. Extensive Tertiary and Quaternary lava flows occur chiefly in the areas outside the principal uranium-producing districts, except those occurring near ore in the Mount Taylor region of New Mexico (Hunt, 1938).

STRUCTURE

The Colorado Plateau has about one-third of its total area occupied by basins ranging in structural relief from 700 to 14,000 feet, about one-fifth the area occupied by uplifts ranging in structural relief from 500 to 5,000 feet, and nearly one-half the area is occupied by platforms, benches, gently dipping slopes, saddles, arches, sags (Kelley, 1955a). The strata of the Plateau as a whole dip eastward and northeastward toward the deep basins that were filled during the Tertiary.

The chief structural features of the uranium-producing area are the Uncompahgre Plateau on the northeast of the salt anticline region (Dane, 1935; Cater and McKay, 1955; and Stokes, 1948), and the broad upwarps known as the San Rafael Swell, Circle Cliffs, Monument, Defiance, and Zuni uplifts—each bordered

TABLE 1.—*Generalized section of upper Paleozoic to lower Tertiary strata in southwestern Colorado and adjoining parts of Utah, Arizona, and New Mexico*

System	Group, formation, or member	Thickness (feet)	Character and distribution
Eocene	Wasatch formation	3,000+	Varicolored shale, sandstone, and limestone; widespread.
Cretaceous	Mesaverde group	1,000±	Light-colored sandstone and gray shale; coal bearing; cliff forming; widespread.
	Mancos shale	2,000–5,000	Gray shale; forms valleys and steep slopes; widespread.
	Dakota sandstone	50–200	Gray and brown sandstone and shale; mesa capping; widespread.
	Burro Canyon formation	50–250	Light-colored conglomeratic sandstone and green and maroon mudstone; mesa capping.
Jurassic	Morrison formation	300–500 200–400	Brushy Basin shale member: varicolored shale (or mudstone), some sandstone lenses; forms slopes; widespread. Salt Wash sandstone member: light-colored sandstone and red mudstone; forms cliffs and benches; widespread.
	Summerville formation	50–400	Red and gray shale, thin sandstone; forms slopes; thickens westward.
	Curtis formation	0–250	Glauconitic sandstone, greenish shale, gypsum; present only in central Utah. Todilto limestone in New Mexico.
	Entrada sandstone	50–1,000	Light-colored massive cliff-forming sandstone in Colorado and eastern Utah; thickens westward and becomes red earthy sandstone.
	Carmel formation	0–600	Red earthy sandstone in Colorado and eastern Utah; thickens westward and becomes gray and red shale, limestone, and gypsum.
? Jurassic(?)	Navajo sandstone	0–2,000	Light-colored massive sandstone; cliff forming; generally absent in Colorado, thickens westward.
	Kayenta formation	0–300	Red sandstone, irregularly bedded; bench forming; absent in eastern part of region.
Triassic	Wingate sandstone	0–400	Red massive sandstone; cliff forming, absent in eastern part of region.
	Chinle formation	100–500	Red shale and sandstone; forms slopes; widespread (called Dolores in Colorado).
	Shinarump member	0–100	Light-colored conglomeratic sandstone and shale; bench forming; absent in Colorado.
	Moenkopi formation	0–1,000	Red-brown shale and sandstone; forms slopes; absent in eastern part of region.
Permian ?	Cutler and Rico formations	0–6,000	Red and gray shale, arkose, and conglomerate; thickest in Colorado though absent in places; thins gradually westward.
Pennsylvanian	Hermosa formation (Paradox member)	0–10,000	Gray limestone, black shale, salt, dolomite, anhydrite, gypsum; coarse clastic facies near Uncompahgre front in Colorado.

by a sharp monocline (Kelley, 1955b). Stocks and laccolithic intrusions (the LaSal, Abajo, Ute, Carrizo, La Plata, and Henry Mountains) dome the sediments around them. These stocks and laccoliths all intrude platform or basin areas and may have been controlled by lines of weakness adjacent to sunken sedimentary blocks. Kelley (1955a) notes the locations of these intrusives along three northwest lines parallel to the strike of the salt anticlines, the Uncompahgre uplift, and the lineaments of the Rocky Mountains.

GENERAL DESCRIPTION OF THE URANIUM DEPOSITS

STRATIGRAPHIC DISTRIBUTION

Uranium deposits have been recognized in nearly all the sedimentary formations from Pennsylvanian to Tertiary age in the Colorado Plateau (Finch, 1955; Isachsen, Mitchum, and Wood, 1955), but the major uranium and vanadium production has come from strata of Triassic age, especially the Shinarump member and other beds in the lower part of the Chinle formation, and from Jurassic rocks, particularly the Entrada sandstone, Todilto limestone, and Morrison formation.

Although many occurrences of uranium were known in Triassic formations in Utah long ago (Hess, 1914 and 1925; and Butler, Loughlin, and Heikes, 1920) the chief production was from the Salt Wash member of the Morrison formation in southwestern Colorado (Coffin, 1921; Fischer, 1942) until after World War II. During the period 1948–53 several large mines—the Monument No. 2 mine, Apache County, Ariz.; the Happy Jack and the MiVida mines, San Juan County; and the Delta (Hidden Splendor) mine, Emery County, Utah—and many smaller mines were opened in Triassic formations. Several large deposits have been found recently in the Morrison formation in New Mexico, one at the Jackpile mine in Valencia County and the others in the Ambrosia Lake area, McKinley County. All deposits in the Todilto limestone are in McKinley and Valencia Counties, New Mex., and all have been found since 1950. Deposits in the Entrada sandstone along the west side of the San Juan Mountains, southwestern Colorado, and in the Wingate(?) and Entrada sandstones near Rifle, Garfield County, Colo., are moderately large, but they are low in uranium and valuable mainly for their vanadium content.

In the Maybell-Lay area, Rio Blanco County, Colo., just north of the Colorado Plateau, deposits have been recently found in the Browns Park formations of late Tertiary age.

In some areas the principal deposits are restricted to one favorable stratigraphic zone, sandstone lens, or channel filling; in other areas ore is found at more than one horizon; in still others it crosses stratigraphic boundaries at a low angle. In the Uravan and Gateway districts, Colo. (McKay, 1955), all the large mines of the two districts are in the upper sandstone lens of the Salt Wash member of the Morrison formation, but small mines have been developed in the lower part of the Salt Wash member, or in the base of the overlying Brushy Basin member of the Morrison formation. In the Slick Rock district, San Miguel County, Colo., ore is mined from more than one horizon in the Salt Wash member, but almost all of it has come from the uppermost sandstone. In the Big Indian-Lisbon Valley area ore is mined from the Cutler formation (Permian), the Chinle (Triassic), and the Morrison (Jurassic). In the Grants-Laguna area in New Mexico, ore is mined from the Todilto limestone, the Morrison formation (chiefly Brushy Basin member) of Jurassic age and the Dakota sandstone (Cretaceous). At the Rifle vanadium mine, Garfield County, Colo., the ore dips more steeply than the sedimentary host rocks and crosses two formation boundaries.

DISTRIBUTION OF THE PRINCIPAL METALS

The relative abundance of uranium, vanadium, and copper in the ores varies both geographically and stratigraphically. More detailed information is given in the parts that follow, particularly in Part 3; also in Fischer (1955). In general, the Entrada sandstone on the eastern margin of the Plateau has deposits of vanadium with little uranium. The Morrison formation, particularly the Salt Wash member, has vanadium-uranium deposits with the V:U ratio commonly between 5:1 and 10:1 in the Uravan mineral belt of western Colorado. The vanadium-uranium ratio is slightly lower in the Green River and the Henry Mountains districts in Utah, and is much lower toward the south in New Mexico. The deposits in the Shinarump member and other parts of the Chinle formation have a much wider range in composition than those in the Entrada and Morrison formations. Vanadiferous uranium deposits with a V:U ratio between 5:1 and 1:1 occur at Monument Valley, Ariz.; Big Indian Valley, San Juan County, and Temple Mountain, Emery County, Utah. Copper-uranium deposits occur in the White Canyon area on the west flank of the Monument uplift in Utah, and uranium deposits with traces of other metals in many mines of the San Rafael Swell, Circle Cliffs uplift, Monument uplift, and in the Interriver district north of Moab, Utah. The Todilto limestone in the Grants-Laguna area of New Mexico has uranium ore with the V:U ratio about 1:2. Although traces of silver occur in several districts the only commercial silver deposits in the Plateau were those of the Silver Reef district, Washington County, Utah, where small amounts of uranium, vanadium, and copper were associated with the silver; and at the Cashin copper mine on LaSal Creek, Montrose County, Colo., where little or no uranium or vanadium is known. However, galena from the Cashin mine contains abnormal amounts of radiogenic lead and the lead is similar in isotopic composition to that in galena samples from the uranium-vanadium deposits.

CHARACTERISTICS OF THE ORE

The commonest type of host rock is the lenticular sandstone and mudstone facies of fluviatile sediments. Conglomerate, massive sandstone, limestone, and shale also contain ore in some areas. Volcanic debris, now largely altered to clay minerals, is associated with the principal ore zones; it is abundant in certain zones in the Chinle formation close above the basal Shinarump member and in the Brushy Basin shale member above the Salt Wash sandstone member of the Morrison formation, and lesser amounts are present within the ore-bearing sandstones. These relationships were studied by Waters and Granger (1953) who suggested the possible bearing of the volcanic material on the origin and precipitation of uranium.

The deposits are tabular, elongate, or podlike, in general parallel to the bedding but commonly with a gently undulant surface, or locally the ore boundary crosses the bedding in steep curved surfaces referred to as "rolls" by the miners. In length the ore bodies range from a few feet to thousands of feet, and in thickness they range generally from a few inches to 10 or 15 feet, rarely more than 50 feet. The ore may follow the bottom of a channel or sandstone lens or the top of a lens or sedimentary structure (as in a petroleum trap) or may appear to "float" midway in a permeable layer. A single deposit may range in grade from weakly mineralized rock below 0.10 percent U_3O_8 (the lower grade of ores at present purchased by the Atomic Energy Commission) to strongly mineralized massive or disseminated ore. Locally high-grade ore consists of or is associated with richly mineralized fossil wood fragments or logs. The logs may be 75 feet or more in length and contain small pockets of ore with 50 percent U_3O_8. The ore boundary ranges from a sharp distinct cutoff within a fraction of an inch to a broad transition zone grading into rock below ore grade.

Guides to ore in the Uravan mineral belt are organic matter, lenticular sandstone and mudstone strata, light-brown sandstone and thick gray mudstone (altered from red to gray) under the ore-bearing sandstone (Fischer, 1950, and Weir, 1952). McKay (1955) shows that coincidence of lenticularity, favorable color of sandstone, and continuous gray mudstone underlying the sandstone are necessary for large deposits; and that lenticularity without the other characteristics (or vice versa) is unfavorable in the Gateway-Uravan district in Colorado. At the surface the favorable sandstone is buff with scattered brown speckles and at depth it is white or light gray with disseminated pyrite grains, in contrast to the average red sandstone of the Salt Wash member of the Morrison. Further description of the Morrison stratigraphy and guides to carnotite deposits in western Colorado are given by Craig and others (1955).

In the Shinarump member and other basal sandstones of the Chinle formation most of the uranium deposits are found in channels cut into the underlying formations near irregular pinch outs of the formation (Finch, 1955). Carbonized wood fragments or logs, "altered" gray mudstone, and lenticular sandstone and mudstone in the channel filling indicate a favorable environment. Copper and iron stain, altered clay, and alunite and jarosite are common at the surface of the sulfide-rich deposits. Those uranium deposits low in vanadium or copper, and in sulfide minerals are more difficult to prospect than are either vanadium-uranium or copper-uranium deposits, because recognizable secondary minerals are sparse.

Ore minerals are typically fine grained and fill the pore space of the sandstone, impregnate clay pellets and fossil wood, or replace the cell walls of the wood. Commonly, interstitial clay has been replaced or recrystallized and locally quartz grains have been corroded. Some zones of sandstone have an overgrowth of silica on the quartz grains that ranges from a thin coating giving the grains a crystal outline to a complete filling of the interstices with silica. Calcite is probably the commonest cementing material in the sandstones except near the salt anticlines where gypsum is locally predominant.

Sedimentary control of mineralization is common, and vein filling or fracture control is rare except in mines such as the Cashin or Big Indian copper mines. Secondary minerals coating joints should not be confused with primary fracture control. There is no indication that the temperature during ore deposition was significantly higher than that expected from the normal geothermal gradient at a depth of several thousand feet.

AGE OF THE DEPOSITS

Although many questions arise in making age determinations of these uranium ores, the problem has been approached from several angles, including a thorough isotopic study of all the major types of ore and the associated lead minerals and study of the various aspects of differential leaching or enrichment. These lines of evidence indicate that the ores were deposited not earlier than the Late Cretaceous or the early Tertiary (Stieff, Girhard, and Stern, 1950; Stieff and Stern, 1952; Stieff, Stern, and Milkey, 1953). Oxidation of ores above the zone of saturation has taken place during Quaternary time (see Part 13), and those ores that have remained below the zone of oxidation (saturated with water) are still relatively unoxidized.

CONDITIONS AT THE TIME OF ORE DEPOSITION

Assuming that the deposits were formed in Late Cretaceous time, estimates of the approximate thickness of cover of the ore zones were made, based on isopach maps of the Mesozoic formations (McKee, 1951, pls. 2 and 3). Although the thickness of the different formations varies considerably across the broad expanse of the uranium region the cover of the Shinarump member and lower part of the Chinle formation was probably 6,500 to 10,000 feet thick, and the cover of the Salt Wash member of the Morrison formation was probably 5,000 to 8,000 feet thick. Levorsen (1954, p. 401) gives the average geothermal gradient in sedimentary rocks as 1.11° C. per 100 feet, abnormally high gradients about twice as great, and abnormally low gradients about one-third the average. At a depth of 5,000 feet the average temperature would be at 71° C with a possible range from 35° to 127° C, and at 10,000 feet depth the average temperature would be 127° C. with a possible range from 53° to 238° C.

Another important condition at the time of deposition was the composition of the pore water in the various formations. Although we cannot determine specifically the composition in Late Cretaceous time, it seems fairly certain however, that the composition of the water differed considerably from one formation to another, as has been demonstrated in an extensive study of oil-field waters from Paleozoic and Mesozoic formations in Wyoming (Crawford, 1940). The assemblage of lithologic types in the uranium region of the Colorado Plateau includes limestones, dolomites, evaporites interbedded with black shales, fluvial deposits, volcanic ash, coal, and marine shales and sandstones. Such a wide variety of environments of deposition suggests a wide range in composition of formation waters. The Paradox member of the Hermosa formation of Pennsylvanian age contains salt, gypsum, anhydrite, and pyritic black shale (Wengerd and Strickland, 1954), and recent wells drilled into this member in the Boundary Butte oil field on the Arizona-Utah border have found black sulfur water. Springs emerging from an intrusive plug of evaporite and black shale strata of the Paradox member at Onion Creek in T. 24 S., R. 24 E. between Fisher Valley and the Colorado River, Grand County, Utah (Dane, 1935, pl. 1), are highly saline and contain H_2S gas that is effectively bleaching the red color of shale pebbles along Onion Creek. In other areas, H_2S gas is associated typically with salt intrusions (Dobbin, 1935, p. 1069), and with limestones, such as the Madison limestone (Mississippian) of Wyoming, and in large quantity with the Rundle limestone in the Pincher Creek gas field in southwestern Alberta.

By Late Cretaceous time the volcanic ash in the Chinle and Morrison formations was probably devitrified and altered to bentonite. The waters in and near the bentonitic beds may have contained sodium bicarbonate derived by base exchange as Crawford (1940) postulated for the bentonitic beds in Cretaceous formations in Wyoming. Water bearing sodium bicarbonate is an effective solvent and carrier of uranium. The water in the fluvial deposits probably contained little, if any, H_2S gas and was less saline than that in the typical marine deposits, which, in turn, was less saline than the water in the evaporite series.

During the Cretaceous period the waters of the deeper formations probably reached equilibrium with their environments, but as regional deformation began in Late Cretaceous time this equilibrium was disturbed by migration of oil and gas toward structural highs and by displacement and movement of water. Reaction would take place between clays and water of changing salinity as water moved through a formation or especially along the borders of the Paradox salt intrusions where waters of quite different composition would come in contact. Zones of reducing environment favorable for ore deposition were present in the vicinity of carbonized logs and accumulations of plant fragments referred to in the field as "trash piles." They also may have been produced by H_2S gas from the Hermosa or other formations, or along paths of migrating oil and gas. That oil and gas may have migrated through these rocks is suggested by the fact that the Morrison formation, Entrada sandstone, Shinarump member of the Chinle, and Hermosa formation all produce oil and gas (or either) in areas of Colorado and Utah where these strata are less strongly deformed than the salt anticline area and the steep monoclines (Grand Hogback, Comb Ridge, or San Rafael Reef) of the uranium region.

Work in progress in 1956 on the age of the stocks and laccoliths has not yet established their age relative to that of the uranium deposits. The importance of these intrusions as a factor influencing the deposition of the uranium ores has been considered but awaits proper evaluation.

HISTORY AND STATEMENT OF THE OXIDATION PROBLEM

The earliest workers on the Colorado Plateau (Hillebrand and Ransome, 1905, p. 17) recognized the possibility that the carnotite might represent the secondary product of some "material already existent in the sandstone" and that its deposition was determined by proximity to the surface, and was probably partly dependent upon a semiarid climate. Hess (1914 and 1933) thought that solutions were reduced on contact with vegetation in the sediment, and that later, upon the raising, draining, and oxidation of the rocks the minerals now found were formed. Butler and others (1920, p. 120) regarded all the deposits in the sandstone of the Plateau as of one type, whether mined for silver, copper, uranium, or vanadium. They believed the deposits were formed by circulating waters that collected the metals disseminated through the sedimentary rocks and deposited them on contact with carbonaceous matter or earlier sulfides, or other precipitating agents; and that most of the minerals at present exposed are the products of alteration of the original minerals by surface solutions. In White Canyon and in Capitol Reef, Utah, Hess (1925) and Butler and others (1920) observed uranium sulfate associated with copper sulfates that were forming around chalcopyrite and, although pitchblende was not identified, they concluded that the uranyl sulfates were developing from some primary uranium mineral.

In the years that followed, many geologists whose investigations were concentrated in western Colorado described vanadium silicates, carnotite, and tyuyamunite as the predominant minerals in the shallow deposits. Fischer (1950) and Stokes (1952) did not interpret the carnotite deposits as secondary, or the oxidation product of low-valent primary ores because so little low-valent or "black ore" was known at that time. Many mines were less than 50 feet beneath the surface of the ground and few were as much as 100 feet deep. Detailed field work on carnotite and roscoelite ores in the late 1930's and 1940's demonstrated the remarkable dependence of ore occurrence on sedimentary structures, and its apparent independence of larger structural features (Fischer 1942), except perhaps on a regional basis. A widely held concept in the late 1940's was that the ores were contemporaneous, or nearly so, with the enclosing sediments, and that carnotite and tyuyamunite were primary minerals.

In the early 1950's, when many new mines were developed during the prospecting boom encouraged by the government exploration program, new occurrences of black (unoxidized) ore began to appear. Uraninite was found in vanadium-uranium ore (Rasor, 1952) and copper-uranium ore. Montroseite [VO(OH)] and coffinite [$U(SiO_4)_{1-x}(OH)_{4x}$] were also found to be typical of unoxidized ore.

The age-determination studies of the early 1950's indicating a Late Cretaceous or early Tertiary age, the finding of many uraninite occurrences, and the development of the uraninite-copper sulfide deposit at the Happy Jack mine, San Juan County, Utah, suggested to some geologists a hydrothermal origin and a deep source for the metals, but such an origin for typical carnotite deposits was untenable to many geologists.

In the controversy over a hydrothermal origin *versus* a primary sedimentary or ground-water origin the problem of oxidation soon was recognized as a hurdle to be overcome before the problem of origin could be satisfactorily discussed and attacked. The contrast between the chemical behavior and mineralogical character (Part 5) of vanadium-uranium ores and those of copper-uranium ores confused the discussion of origin.

Actually, it is quite possible that all the ore existed in a reduced state before oxidation during the Quaternary, quite independently of origin. The ores could have been (1) reduced at the time of primary sedimentary deposition, (2) deposited as a reduced-mineral suite at a later time by ground waters, or (3) deposited by ascending hydrothermal fluids. Thus it appeared that the problem of oxidation could be attacked without regard to these controversial issues.

If a reduced-ore stage preceded Quaternary oxidation, predictions can be made concerning mineralogic, chemical, and geologic relations.

1. Ores protected from air should contain an equilibrium mineral assemblage under reducing conditions.
2. As a deposit is followed from the surface to places of more and more limited access of air, the assemblage should converge toward the original reduced assemblage.
3. High-valent minerals should be clearly related to post-ore features, such as jointing; high-valent minerals should always be later in the sequence than reduced ones.
4. The texture and composition of some high-valent ores should resemble those clearly developed from reduced ores.

If there were two kinds of ore, a primary low-valent suite, and a primary high-valent suite, it might well be expected that oxidation of the low-valent suite would produce ore with textural character and mineralogic or elemental composition different from that of primary high-valent ore.

With such tests in mind, many investigators worked on various aspects of the problem. Studies were made of predicted *versus* observed sequences of minerals, assuming that all ore was once reduced. Minerals were synthesized to see if their conditions of formation corresponded to those expected in an oxidizing environment superimposed on the original ore suite. In general the attack was based on the premise that all ore originally was a reduced suite, and the hypothesis was tested by its ability or inability to explain field and laboratory observations. The following parts of this volume are devoted to many facets of the oxidation problem.

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Part 2. CHARACTERISTICS OF THE HOST ROCK

By Robert A. Cadigan

CONTENTS

ILLUSTRATION

TABLE

ABSTRACT

Uranium deposits in the sedimentary rocks of the Colorado Plateau are distributed throughout most of the lithologic units which make up the regional stratigraphic column. The Morrison formation of Jurassic age and the Shinarump member and sandstones in the lower part of the Chinle formation of Triassic age yield at least 90 percent of current uranium ore production. The Todilto limestone and Entrada sandstone of Jurassic age together yield about 5 percent of current production.

The host rocks of the Morrison and Chinle formations are noted for ledge-forming lenticular fine- to coarse-grained, cross-stratified sandstone bodies which occupy trough-shaped erosional features known as channels. Associated with the channel sandstones, particularly in the lower parts, are green clay strata and pellets; petrified, carbonized, and coalified plant material; bone; and pebbles derived from metamorphic, igneous, and sedimentary rocks. Interbedded with the sandstones are red, green, or variegated siltstone and claystone strata.

The sandstones vary regionally in composition and can usually be classified as arkose, sedimentary tuff, or orthoquartzite depending on the location. The clay minerals of the sandstones as well as those of the siltstones and claystones belong to the hydromica, montmorillonite, and kaolinite groups. The kaolinitic clays are mostly of detrital origin. The montmorillonite and hydromica clays were mostly derived from volcanic ash.

The Todilto limestone is a 10- to 30-foot-thick moderately pure limestone unit, extending throughout the southeastern part of the Colorado Plateau. The Entrada sandstone, typically a 50- to 300-foot-thick massive partly cross-stratified, fine-grained sandstone varies regionally in composition, but in western Colorado it is an orthoquartzite or a feldspathic orthoquartzite.

Generally, ore deposition in the Morrison formation, Shinarump member, and sandstones of the lower part of the Chinle formation appears to be influenced locally by the sedimentary structures, plant material, bone, clay, and certain textural zones in certain parts of the sandstone strata. Ore deposition appears

to be favored regionally in the Salt Wash member of the Morrison formation by certain lithofacies characteristics.

Ore deposition in the Entrada sandstone appears to be related to the Dolores-Entrada and Entrada-Pony Express contacts. Ore deposition in the Todilto shows a relationship to joints and fractures.

STRATIGRAPHIC LOCATION OF MAJOR URANIUM-ORE DEPOSITS

The uranium deposits in the sedimentary rocks of the Colorado Plateau region are distributed throughout most of the lithologic units which make up the regional stratigraphic column. At this time (1955) the major part, at least 90 percent, of the production of ore is from the Morrison formation of Jurassic age, and the Shinarump member and sandstones in the lower part of the Chinle formation of Triassic age. An additional 5 percent of the production is from the Todilto limestone and underlying Entrada sandstone of Jurassic age (Fischer, R. P., 1955, oral communication). Figure 2 illustrates the regional distribution of ore deposits in excess of 1,000 tons for each of the stratigraphic units named above.

METHODS AND DEFINITIONS

The petrographic study of the uranium ore-producing formations has been carried on by means of thin section study, grain-size analyses and the field examination of sedimentary structures. Most of the work has

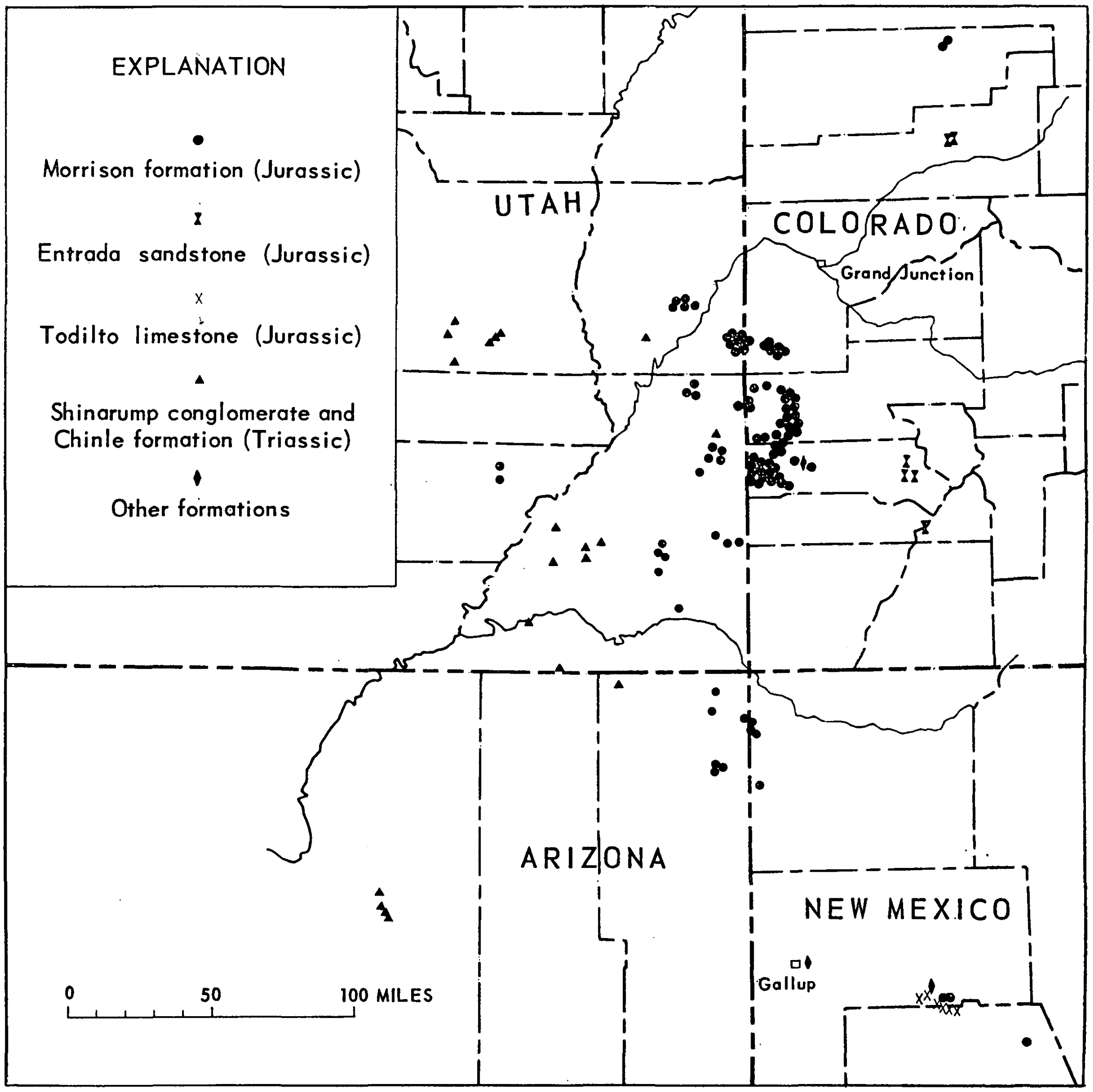

FIGURE 2.—Regional occurrence of uranium-ore deposits of 1,000 tons or more in the major and minor producing formations of the Colorado Plateau. (Prepared by R. P. Fischer, R. T. Chew III, and H. S. Johnson for the paper, "Uranium-vanadium-copper deposits on the Colorado Plateau," International Conference on Peaceful Uses of Atomic Energy, Geneva, Switzerland, 1955, from a map by W. I. Finch.)

been done on the major producing formations and lithologic types.

TABLE 1.—*The petrologic classification of detrital sedimentary rocks*

[After Pettijohn, 1949, and Krynine, personal communication, 1952; exclusive of the treatment of tuff [1]]

Classification	Quartz plus tuff [1] (percent)		Feldspar plus kaolin (percent)		Micas (percent)	
	Limits	Typical	Limits	Typical	Limits	Typical
Orthoquartzite	70–100	85	0–10	5	0–20	10
Feldspathic orthoquartzite	55–90	75	10–25	15	0–20	10
Graywacke	0–70	50	10–80	20	20–75	30
Subgraywacke	15–80	60	0–10	5	20–75	35
Arkose	0–75	50	25–100	40	0–20	10

[1] The amount of tuff present affects the rock classification in the following manner:

1. If there is less than 10 percent tuff, the rock classification is not affected.
2. If there is 10 to 25 percent tuff, the rock name is modified by the word "tuffaceous"—that is, tuffaceous arkose.
3. If there is 25 to 75 percent tuff, the rock name designates a variety of tuff—that is, graywacke tuff.
4. If there is 75 percent or more of tuff, the rock is an unmodified tuff.

Classification of the rocks generally follows the system proposed by Krynine (1948) but was modified as illustrated by table 1. The rocks studied represent various intermixtures of three end products: arkoses, orthoquartzites, and tuffs. Some sandstone strata of restricted occurrence could be classified as graywackes on the basis of their hydromica content, but due to a lack of other essential components such as basic rock fragments and alkalic-calcic feldspars, these rocks are not considered as true graywackes.

The classification of sandstones in specific stratigraphic units was based on point count analyses of an aggregate of 119 thin sections, including 66 for the Morrison formation, 28 for the Shinarump member, and 25 for the lower sandstones of the Chinle formation. The Entrada composition studies were restricted to the examination of a few thin sections supported by loose grain studies including mineral grain counts on 15 samples. The Todilto limestone and the correlative Pony Express member of the Wanakah formation composition studies were restricted to examination of a few thin sections and insoluble residue studies of two samples (one each).

The data on clay minerals in the formation studied was obtained from the thin section studies; from X-ray diffraction analyses of clay and silt separates; and from unpublished work of, and informal communications with, Alice Weeks, W. D. Keller, and others of the U. S. Geological Survey, and J. C. Griffiths of the Pennsylvania State University. Further data on the unmineralized clay minerals are given by Keller in Part 9.

Microscopic arrangements of the grains, matrix, and cement of the sandstones as they appear in thin section were termed the microstructure of the rock. If the detrital grains are in contact with each other to a maximum extent, with a minimum of interstitial cement and matrix, the microstructure is classified as homogeneous. If the detrital grains are suspended in matrix and cement, with some grains in contact, but most separated from other grains by intervals of varying widths, the microstructure is classified as heterogeneous.

The ore-producing formations were studied on the outcrop to determine small-scale lithologic relationships, to obtain information pertinent to stratigraphic problems, and to collect representative samples for laboratory investigations. The conspicuous bedding features and forms produced by the sedimentation processes of cyclic deposition which included intervals of erosion, are referred to by the general all-inclusive term "sedimentary structures." The erosional features are referred to in this paper as erosion surfaces, cuts, or channels in ascending order of magnitude of relief. The writer was fortunate to be associated with a number of geologists who have done detailed studies of sedimentary structures and their orientations. These include L. C. Craig, G. W. Weir, G. A. Williams, and O. B. Raup, all of the U. S. Geological Survey.

This part of the present report is aimed at describing the petrographic framework of the ore deposits. That the ore is stratigraphically controlled is quite obvious; rocks of the favored strata are therefore referred to as host rocks whether or not they contain ore.

In the following pages, the stratigraphic and lithologic units defined above as host rocks are described so as to emphasize the more general or average characteristics. No attempt is made to give the detailed petrography, or sedimentary structure characteristics of any unit in these descriptions. The general outline to which all the descriptions are fitted seeks to bring out the following points for each unit: (1) Stratigraphic relations, (2) textural types present and their arrangement, (3) structural features of erosion and deposition, (4) rock composition and classification, and (5) microscopic arrangement of constituents. These are variations of the three main properties of rocks: composition, texture, and structure.

TRIASSIC HOST ROCKS

SHINARUMP MEMBER OF THE CHINLE FORMATION

[Uranium-production rank, third]

Stratigraphic relations.—The white to pale-brown Shinarump member of the Chinle formation of Late Triassic age occupies a position in the stratigraphic column of the Colorado Plateau at the base of the Chinle formation and above the Moenkopi formation of Triassic age. The Shinarump is restricted in occurrence to the southern half of the Colorado Plateau region (Stewart and Williams, 1954). The lower contact of the Shinarump is an erosional disconformity; the upper contact is conformable at most places but is disconformable or undefinable at a few places.

Textural types and their arrangement.—The Shinarump member is in most places a medium-grained sandstone unit with persistent and conspicuous zones of very coarse grained sandstone, pebbly sandstone, and pebble conglomerate. The sandstones and conglomerates are usually moderately to poorly sorted. This general texture is characteristic throughout the whole area in which the formation is present. Green claystone or mudstone strata are above, below, and within the sandstone strata. In many places in the southern and central parts of the Plateau, as the result of a lateral facies change, the Shinarump is represented by green claystone strata containing a 1- to 3-foot clay and pebble zone. Where the sandstone facies is locally absent the greenish kaolin mudstone (part 9 of this volume) equivalent will, in most instances, contain coarse sand grains and granules dispersed throughout the mud. The sandstone facies and siltstone facies contain the same mineral components, but in different proportions.

A variegated red, purple, and white mudstone facies is found in the upper part of the Shinarump in many areas of the northern part of the Plateau including the Moab, White Canyon, and San Rafael Swell areas in Utah. Beyond the range of the sandstone facies it may be a regional equivalent of the Shinarump member. However, this coarse-sand-filled kaolinitic mudstone stratum is referred to as the "purple-white zone" (Finch, 1953) in areas where it separates the Chinle and the Moenkopi formations, and is usually assigned to the Chinle.

Structural features of erosion and deposition.—The sandstone strata of the Shinarump tend to form a single composite ledge-forming sandstone bed which extends many square miles laterally, but which is elongated in the direction parallel to the channel trends in the area. The broad areal extent is the result of the junction or coalescence of adjacent channel fills to form a uniform upper surface for the single conspicuous ledge. The channel fills of the Shinarump may have an average cross-sectional area in the order of 2,500 to 10,000 square yards. The deeper channels contain abundant petrified, coalified and crushed logs, and disseminated plant material (Witkind, 1954).

Rock composition and classification.—The Shinarump member may be classified typically as an arkose, although in some areas it grades into orthoquartzites and tuffs. The common detrital components are grains of quartz, potash feldspar, plagioclase, altered tuff, and quartzite; the kaolinite, hydromica, and montmorillonite groups of clays; and included pebbles of quartz, quartzite, feldspar, chert, granite, and silicic-alkalic volcanic rocks (Stewart, J. H., and Albee, H. F., 1955, oral communication).

The chief interstitial clay minerals are of the kaolinite group with minor amounts of hydromica. Where there is a significant increase in the proportion of tuff, the chief clay minerals are of the montmorillonite group. Much of the bedded clays in the Shinarump are of the hydromica group.

The clay minerals in the sandstone are well crystallized. The kaolinite clays appear as detrital clay in white interstitial wads and as decomposition products in the cleavage cracks of weathered feldspar grains.

The main cementing materials of the Shinarump consist, in order of importance, of silica in the form of overgrowths on quartz grains, iron oxides, and calcite and other carbonates. The rocks are, on the average, only moderately indurated. Other nondetrital components include ore and gangue minerals and authigenic silica present in the altered tuff.

The major regional change in composition occurs in the southwestern part of the Colorado Plateau, in north-central Arizona and south-central Utah, where the sandstones can be classified as tuffaceous arkoses or tuffs. The rocks contain enough potash feldspar to support a hypothesis that they were derived from silicic-alkalic igneous rocks. Regional variations in feldspar content are also present with recognized high feldspar areas in the southeastern and northern parts of the Plateau.

Microstructure.—The sandstones of the Shinarump contain both heterogeneous and homogeneous microstructures. The kaolin-mud matrix comprises about 10 percent of the moderately sorted sandstones and about 30 percent of the poorly sorted sandstones. The mud is distributed throughout the rock in interstitial films or in wads of about 1 millimeter in size.

SANDSTONES IN THE LOWER PART OF THE CHINLE FORMATION

[Uranium-production rank, second]

Stratigraphic relations. — The light-colored sandstones of the lower part of the Chinle formation occupy a position in the stratigraphic column immediately above the Shinarump member. They are easily confused with the Shinarump member where it is absent. The sandstones are found in the Monitor Butte, and the overlying Moss Back (Stewart and Smith, 1954) members of the Chinle formation. The peculiar sandstones considered to be typical of the respective units are not confined within the member boundaries. Thus the Moss Back-type sandstones are frequently found in the Monitor Butte member and vice versa. For this reason the lower sandstones of the Chinle will be referred to as the Monitor Butte-type and the Moss Back-type sandstones.

The Monitor Butte type of sandstone is similar in composition to the Shinarump type sandstone, but differs greatly in texture and structure. The Monitor Butte type is pale green to gray fine grained to very fine grained, and is tightly cemented with calcite or silica. The greenish beds are in most cases only a few feet thick, and are evenly bedded with parallel ripple laminations in which thin laminae of well-sorted sand are separated by laminae of greenish chloritic or hydromica clay. On weathering, the beds are much subjected to jointing, slumping, and separating along their laminae, as in beds of shale. Penecontemporaneous slumping is abundant; however, the general bedding and depositional structures are commonly preserved. The sandstones of the Monitor Butte are associated with hydromica or bentonitic claystone strata.

The white to pale-brown Moss Back-type sandstone of the lower part of the Chinle more nearly resembles the Shinarump and is almost exclusively the host rock for ore deposits in the lower part of the Chinle. The Moss Back type is the host rock in those areas in the northern and northwestern parts of the Colorado Plateau where the sandstone and conglomerate facies of the Shinarump is absent.

Textural types and their arrangement.—The Moss Back-type sandstones are fine grained with pebbly and conglomeratic zones. They contain claystone and mudstone seams, lenses, and fragments. Individual samples show predominantly moderate sorting with poor sorting in the coarse-grained sands.

Structural features of erosion and deposition.—The erosional and depositional structures of the sandstones of the lower part of the Chinle are generally of the same scale and frequency as those of the sandstones of the Shinarump. The sandstone strata of the Moss Back member tend to form a single thick composite ledge-forming sandstone bed or a closely spaced sequence of beds, averaging about 50 feet thick. The unit extends over an area of about 9,000 square miles (Stewart and Williams, 1954). The unit fills erosion channels which, in extreme cases, increases the thickness of the sandstone strata to 100 to 150 feet. Thick-bedded ledge-forming channel-filling sandstone strata of the Moss Back type are frequently found below and separated by thick mudstone strata from the prominent sandstone unit of the Moss Back member.

Lithified, mineralized, or coalified logs and wood fragments may be found in the bottoms of channels in the same manner as those found in the Shinarump, or scattered throughout bedded gray claystones or mudstones associated with the channel deposits.

Rock composition and classification.—The Moss Back-type sandstone is an arkose but shows enough variation in composition to be classified as a feldspathic orthoquartzite in some locations. The common detrital components are grains of quartz, potash feldspar, plagioclase feldspar, altered tuff, quartzite fragments, and clays of the kaolinite, montmorillonite, and hydromica groups. Pebbles of chert, quartz, and quartzite are also present. The Moss Back-type sandstone shows an increase in feldspar to the north or northwest.

The chief interstitial clay minerals in the sandstones are of the kaolinite group with minor amounts of hydromica and montmorillonite. Montmorillonite clays increase with the amount of tuff. The bedded clays in and around Moss Back-type sandstones are hydromicas, montmorillonites, and mixed layer clays. The clay minerals in the sandstones are well crystallized. The kaolinite clays appear as detrital clay in white interstitial wads and as decomposition products in the cleavage cracks of weathered feldspar grains. The "purple-white" mudstone zone underlies the Moss Back member in the absence of the Monitor Butte member and the sandstone-conglomerate facies of the Shinarump.

The suite of clay minerals present in the lower part of the Chinle lithologic units is influenced by larger amounts of altered alkalic-silicic volcanic ash in the southern and western part of the Colorado Plateau and becomes dominantly montmorillonite.

The cementing material of the Moss Back type of sandstone consists, in order of importance, of silica in the form of overgrowths on quartz grains, calcite and other carbonates, and iron oxides. The sandstones range from highly indurated to poorly indurated. Other nondetrital components include ore and gangue minerals.

Microstructure.—The microscopic arrangement of the Moss Back-type sandstones is heterogeneous, becoming more so in the coarse-grained sandstones and conglomerates.

General comparison of ore-bearing sandstone of the Shinarump member and lower part of the Chinle.—Sandstones of the Shinarump and Moss Back members of the Chinle formation are similar in average composition. Pebble assemblages of the two show a significantly higher percentage of quartz for the Shinarump (Albee, H. F., oral communication). The main differences in appearance between the two types of sandstone are due to the finer texture of the Moss Back type and the multiple ledges in the lower part of the

Chinle formation where the Monitor Butte member is present as compared with the single composite ledge commonly observed in the Shinarump member.

JURASSIC HOST ROCKS

ENTRADA SANDSTONE

[Uranium-production rank, eighth]

Stratigraphic relations.—The Entrada sandstone, a formation in the San Rafael group of Jurassic age, extends with various facies changes over almost the entire Colorado Plateau. It immediately underlies the Todilto limestone, in the southeast; the Curtis formation of Jurassic age, in the north; the Cow Springs formation of Jurassic age, in the south; and the Summerville formation of Jurassic age, in much of the rest of the Plateau. In western Colorado, where uranium ore is produced from the Entrada, it overlies the Dolores formation of Triassic age (Fischer, 1942), which is equivalent at least in part to the Chinle formation. Elsewhere it overlies the Carmel formation of Jurassic age conformably where this unit is present, or it forms the base of the San Rafael group of Jurassic age and disconformably overlies the Glen Canyon group of Triassic and Jurassic age.

Textural types and their arrangement.—The sandstone units that make up the Entrada are well to moderately sorted and range from fine- to very fine-grained. Some strata contain medium and coarse well-rounded grains of chert, quartz, and potash feldspar. These coarse grains are concentrated along laminations or disseminated throughout the sandstone in some parts of the formation. In west-central Colorado, east of the Plateau, the basal part of the Entrada is medium to coarse grained, similar to the underlying Pennsylvanian sedimentary rocks.

Structural features of erosion and deposition.—The Entrada sandstone consists of a number of very thick to thin cross-stratified and horizontally stratified sandstone beds separated by what may be referred to as horizontal truncation planes or partings. In most areas the formation weathers on exposure to form a white, gray or pale-brown to orange massive convex sandstone ledge 50 to 300 feet thick which is colloquially called the "slick rim." Cross-stratification in some of the beds is of the dimensions associated with eolian deposition.

Rock composition and classification.—In the northeastern part of the Plateau where the Entrada is a host rock for uranium deposits, it may be classified as an orthoquartzite or a feldspathic orthoquartzite. It is composed of quartz, chert, potash and sodic feldspar, and a heavy-mineral suite consisting of zircon, tourmaline, rutile, anatase, muscovite, epidote, ilmenite, magnetite, and leucoxene. The Entrada is highly feldspathic in west-central Colorado, where it appears to contain material derived from underlying arkoses and possibly Precambrian granites. The feldspathic Entrada contains clays formed of ground-up mica and hydromica. In southwestern Colorado the Entrada contains much less feldspar and more clays formed of recrystallized hydromica and possibly some chlorite. Nondetrital minerals include calcite and barite, and euhedral anatase crystals probably of authigenic origin.

Microstructure.—The microstructure of the sandstones is nearly all of the homogeneous type. The clay matrix is interstitial especially when the rock is rich in ground-up mica, but also forms authigenic rims around the quartz and feldspar grains. Grains of feldspar, particularly albite, are speckled with calcite and hydromica which may be accepted as evidence of replacement of the detrital grains by carbonates and authigenic clay minerals. Some unidentified hydromica clay minerals occupy positions which strongly suggest ghosts of detrital grains. The rock is only moderately well cemented by carbonates and clay matrix.

TODILTO LIMESTONE

[Uranium-production rank, seventh]

Stratigraphic relations.—The Todilto limestone, a formation in the San Rafael group of Jurassic age, is restricted in extent to the southeastern part of the Colorado Plateau region. It is conformable with underlying Entrada sandstone and may be separated from the Summerville by a disconformity. The Pony Express limestone member of the Wanakah formation of southwestern Colorado is probably equivalent to the Todilto and has generally the same stratigraphic relations.

Textural and structural features.—The Todilto is characterized in outcrop by a 10- to 30-foot limestone ledge and has a gypsiferous facies in some localities. The depositional structures are dominantly flat bedded. The flat-bedded features may be emphasized by a banded appearance; the horizontal parallel bands are in the order of magnitude of 1 to 4 inches or less thick. Parallel distorted bands may be seen in the upper part of the limestone unit. The formation exhibits typical limestone jointing influenced by the closely spaced bedding and degree of local structural activity. The Todilto limestone contains crystalline textures ranging from microcrystalline to macrocrystalline. Ore deposits in the Todilto show some relation to structure and jointing (Bucher, 1953).

Rock composition and classification.—The Todilto limestone and the Pony Express limestone member are composed of an acid-soluble carbonate fraction, which constitutes about 90 percent of the rock, and an insoluble fraction. The insoluble fraction consists of authigenic quartz crystals with many bubblelike inclusions, allogenic grains of quartz, orthoclase, microcline, chert, and in very small proportions barite, tourmaline, apatite, biotite, muscovite, rutile, and others. Considering the heavy minerals as index minerals, the proportion of apatite is higher in the Todilto and the Pony Express than in adjacent rocks. The color of the limestone facies changes from dark gray in Colorado to pale-yellowish gray in New Mexico. The color probably is related to the amount of fine carbon disseminated in the rock. A gypsum facies assigned to the Todilto makes up most of the unit in parts of northwestern and north-central New Mexico.

Microstructure.—Microscopic examination shows that the banded appearance results from layers of macrocrystalline mosaic-structured euhedral calcite crystals separated by bands of microcrystalline anhedral sutured calcite crystals. Scattered within the microcrystalline bands are parallel-oriented lenses of mesocrystalline to macrocrystalline subhedral calcite crystals in mosaic arrangement. Detrital grains are scattered throughout but are more plentiful in the microcrystalline bands.

MORRISON FORMATION

Stratigraphic relations.—The Morrison formation of Jurassic age is made up of light-colored, lens-shaped, cross-stratified sandstones and reddish, greenish-gray, and variegated claystones, siltstones, and mudstones. On the Colorado Plateau, the Morrison is divisable into four members. The uppermost member, the Brushy Basin, is composed dominantly of variegated, red, green, and purple bentonitic mudstone strata and lesser amounts of pebbly sandstone. The basal member, which lies just below the Brushy Basin member in the northern half of the Plateau, is the Salt Wash member. The Salt Wash is characterized by light-gray and light-brown ledge-forming sandstones interbedded with red and green siltstone and mudstone strata; the Salt Wash is the chief uranium ore-producing member of the Morrison formation.

In the southeastern part of the Plateau, the Westwater Canyon and underlying Recapture members tongue in between the Brushy Basin and the Salt Wash members and replace the Salt Wash member and the lower part of the Brushy Basin member (Craig and others, 1955). The Westwater Canyon member is characterized by moderately lensing, moderately cross-stratified pale-yellow ledge-forming sandstones and brown and brownish-gray siltstone and bentonitic mudstone strata.

Facies changes.—Facies changes of both local and regional scale are the rule in members of the Morrison formation. The host rock favored by uranium ore deposits in the Salt Wash member of the Morrison formation in southwestern Colorado and southeastern Utah seems closely related to certain local lithologic facies characteristics (Mullens and Freeman, 1952). Significant facies characteristics include: an optimum ratio of sandstone to mudstone in a vertical sequence (about 50 percent), an optimum thickness "stream deposit-type" to "nonstream deposit-type" sedimentary units (90 to 200 feet), and an optimum degree of average size and continuity of sandstone strata.

In localities in an area from south to southwest of the Four Corners area (juncture of Colorado, Utah, Arizona, and New Mexico, see fig. 2), the Morrison consists of a sequence of convex weathering, massive sandstones of the Westwater Canyon and Recapture members separated by silty sandstone partings. This sandy facies apparently is not a favorable host rock for uranium ore in the Morrison formation. The favorable facies appears to be the sequence of lenticular ledge-forming sandstone units interstratified with mudstone, siltstone, and claystone units to the west, north, and southeast of the Four Corners area.

SALT WASH MEMBER OF THE MORRISON FORMATION

[Uranium-production rank, first]

Stratigraphic relations.—The Salt Wash member is the basal member of the Morrison formation in the central, northern, and western part of the Plateau.

Textural types and their arrangement.—The Salt Wash member, like the Brushy Basin member, is composed of mudstone strata and ledge-forming sandstone beds; however, in most localities there is much more sandstone in proportion to mudstone than is observed in the Brushy Basin member. Volumetrically, the Salt Wash contains more sandstone than any other member (Freeman, V. L., oral communication).

The sandstones of the Salt Wash member are, on the average, fine grained and well to moderately sorted. The basal or lower parts of the "channel" sandstones are of coarse sand; moderately to poorly sorted; contain green clay chip conglomerates, quartzite, silicified tuff, chert, and silicified limestone pebbles, wood, and bone.

Structural features of erosion and deposition.—The ledge-forming sandstone beds are lenticular composite cross-stratified units. The Salt Wash in any ore locality commonly has from 3 to 6 ledge-forming sandstone units separated by silty sandstone or mudstone. The larger resistant beds form composite ledges that are less continuous than the single composite ledge of the Shinarump and are of smaller dimensions with an average cross-sectional area in the order of 1,000 to 5,000 square yards.

Rock composition and classification.—The sandstone strata of the Salt Wash vary in classification over the Plateau region, and include orthoquartzites, tuffs, and arkoses, together with all possible modifications. The sandstones are composed of quartz, potash feldspar, sodic feldspar, silicified and altered tuff, chert, metamorphic rock fragments, and rhyolitelike igneous rock fragments and hydromica, montmorillonite, and kaolinite clay minerals. The dominant clay minerals in both the mudstone and in the sandstone strata are of the hydromica group, but with a high proportion of mixed-layer clays which were possibly derived from montmorillonite or volcanic ash. Analyses of the tuff suggest a silicic-alkalic igneous source. Heavy minerals represent less than 0.5 percent, by weight, of the average sandstone, and consist largely of varieties of zircon, tourmaline, garnet, staurolite, epidote, rutile, apatite, magnetite-ilmenite, miscellaneous titanium minerals, and minor amounts of biotite. This general assemblage is common for all sandstones of the Morrison formation but with regional variations in proportions.

The composition of sandstones of the Salt Wash varies over the region similarly to the sandstones of the Brushy Basin member, with high feldspar content to the southeast and high tuff content to the northwest.

Wood in the form of petrified, mineralized, or coalified logs or fragments is present at the base of channels. Bone in various degrees of alteration or replacement is present in the Salt Wash mudstone and sandstone strata.

Nondetrital components are calcite, dolomite, and other carbonates, iron oxides, silica, and gangue and ore minerals. Calcite is the dominant cement but much silica cement is present as overgrowths on the quartz grains. Iron oxides are not significant as cements.

Microstructure.—The arrangement of components as observed under the microscope shows the sandstone to have microstructures of two general types, the heterogeneous type where a significant amount of clay matrix and little cement is present and a homogeneous type where the sandstone is made up of grains and cement with a minimum of matrix. The heterogeneous type appears to be the microstructure in which primary uranium ore mineralization is more often found.

RECAPTURE MEMBER OF THE MORRISON FORMATION

[Uranium-production rank, sixth]

Stratigraphic relations.—The Recapture member intertongues with the Salt Wash member in the Four Corners area of the Plateau and replaces it to become the basal member of the Morrison formation in the south and southeast. In contrast to the pale yellow of the overlying Westwater Canyon member, the Recapture member is characterized by browns and whites in both claystone and sandstone facies.

Textural types and their arrangement.—The sandstones of the Recapture member are, on the average, moderately sorted and very fine grained but contain some medium- and fine-grained sands with granules and small pebbles of quartz, feldspar, granite, and chert. In general it is finer textured than the overlying Westwater Canyon member and contains a much higher proportion of bedded mudstone, siltstone, and claystone. Nondetrital components include calcite and other carbonates, secondary silica, and iron oxides.

Structural features of erosion and deposition.—Structures of erosion and deposition in the Recapture member are similar to those of the Salt Wash member, particularly in the Four Corners area, with similar debris-filled, deep channels, and lenticular ledge-forming sandstone units. Although the size and shape of individual sandstone units are similar to those of the Salt Wash, there are fewer of them in the average vertical sequence of Recapture member strata, and they show less resistance to weathering.

Rock composition and classification.—The sandstones of the Recapture member may be classified as feldspathic orthoquartzites and arkoses with the feldspar and kaolin content increasing to the southeast. They contain detrital grains of quartz, potash feldspar, plagioclase, silicified altered tuff, igneous rock, quartzite, and heavy minerals. The clay minerals present are of the hydromica, montmorillonite, and kaolinite groups, with the hydromica group dominant. Most of the sandstones contain the mixed layer clays common to many of the sandstone units described as host rocks. The bedded mudstones, siltstones, and claystones in the Recapture member contain these same clay minerals. In many localities the Recapture is characterized by thick strata of montmorillonite-rich swelling grayish-green and brown mudstone. Woody debris is present particularly in the Four Corners area.

Microstructure.—The sandstones of the Recapture member show both homogeneous and heterogeneous microstructure. The detrital grains are associated with different amounts of hydromica and montmorillonite clays which form the matrix, and are cemented by varying amounts of carbonate minerals, iron oxide, and silica in the form of secondary overgrowths on quartz grains. Kaolinite is present chiefly as the alteration product of weathered feldspar grains.

WESTWATER CANYON MEMBER OF THE MORRISON FORMATION

[Uranium-production rank including arkoses of the Brushy Basin member, fourth]

Stratigraphic relation.—The Westwater Canyon member is an arkosic facies of the Morrison formation and underlies and is interbedded with the Brushy Basin member in the southeastern part of the Colorado Plateau region. The ore-bearing Jackpile sandstone, although assigned to the Brushy Basin member, is essentially the same facies as the Westwater Canyon member.

Textural types and arrangement.—The sandstones of the Westwater Canyon member are, on the average, moderately sorted, medium-grained and contain zones of granule conglomerate and pebbly sandstone which are characterized by fresh-looking cleavage fragments of pink feldspar. Like other members of the Morrison, the sandstone units are associated with bedded mudstone, siltstone, and claystone strata.

Structures of erosion and deposition.—Erosional and depositional structures in the sandstones are similar to those of the thick ledges of the Shinarump and Brushy Basin, but show less scouring and are less lenticular. The channels are few and inconspicuous, and contain little woody material in the Four Corners area, but become more prominent and more "trashy" to the southeast. The erosional and depositional structures of the ore-bearing Jackpile sandstone resemble those of the Salt Wash member of the central part of the Plateau region in that they are highly lenticular and show more erosion and truncation surfaces.

In much of the Westwater Canyon outcrop, the sandstone beds form composite ledges which pile up in closely spaced vertical sequence to form a single massive bed or a thick sandstone interval of 2 or 3 ledges separated by thin yellowish-green and rare red mudstone strata. These thick composite sandstone strata appear in continuous exposures over wide areas.

Rock composition and classification.—The yellowish sandstones of the Westwater Canyon member may be classified as arkoses and are composed of detrital grains of quartz, potash feldspar, altered and silicified tuff, plagioclase, igneous rock, quartzite, heavy minerals, and clay minerals of the kaolinite, montmorillonite, and hydromica groups. Much coarse material is present as pebble-sized fragments of quartz, potash feldspar, granite, quartzite, and chert. Nondetrital components include calcite and other carbonates, silica in the form of overgrowths on quartz grains, and in silicified tuff.

Although hydromica or mixed-layer clays are probably dominant, kaolin forms the matrix of many sandstone units and in this respect the sandstones of the Westwater Canyon differ in composition from the other sandstones of the Morrison formation.

Microstructure.—The sandstones of the Westwater Canyon member have both homogeneous and heterogeneous microstructures. The sandstones of heterogeneous texture, which are in the minority, are characterized by abundant kaolin in the matrix. Sandstones with the more homogeneous structures have much less matrix which is in most cases dominantly hydromica with some montmorillonite and kaolin.

BRUSHY BASIN MEMBER OF THE MORRISON FORMATION

[Uranium-production rank exclusive of arkose beds, fifth]

Stratigraphic relations.—The Brushy Basin member is the most regionally extensive stratigraphic unit within the Morrison formation and forms the top of the formation except in areas where pre-Dakota erosion has removed it.

Textural types and their arrangement.—The texture of the sandstones of the Brushy Basin is generally fine- to medium-grained with coarse to conglomeratic zones in the basal parts; thick lenses of sandy coarse conglomerate are common in many localities. The bedded mudstone which is the dominant lithologic type in the average exposure of the Brushy Basin member, characteristically contains granules and coarse sand grains of red chert or silicified tuff scattered throughout.

Structural features of erosion and deposition.—The resistant sandstone beds are ledge-forming and were deposited in erosional scours. One or two of these sandstone units are commonly present in the lower third of the member. The basal contacts show erosion surfaces. Petrified wood, bone, mud and clay lenses, disturbed bedding, and conglomerates are characteristic of the first sediments deposited above the eroded surfaces. The bedded mudstone contains some thinner, evenly bedded very fine grained limy sandstones which are seldom of the ledge-forming type except in the southeastern part of the Plateau region. In northeastern and central New Mexico, thick lenses of medium-grained kaolin-rich arkose are present in the middle and upper parts of the Brushy Basin. The ore-bearing Jackpile sandstone (Hilpert, L. S., and Freeman, V. L., 1955, written communication), in New Mexico is a ledge-forming composite arkosic sandstone unit that was deposited in close association with the mudstone strata occurring in the middle of the Brushy Basin member.

Rock composition and classification.—The Brushy Basin is a tuffaceous unit composed chiefly of montmorillonite-rich mudstones, fragments or grains of silicified altered tuff, and lesser amounts of thick lensing ledge-forming pebbly sandstone and conglomerate beds. The sandstone strata vary over the Colorado Plateau region from arkose to orthoquartzite to tuff with many gradations and modifications. From the center of the Plateau the tuffaceous material increases northwestward, and the arkosic material increases southeastward.

The sandstone units are composed of detrital grains of quartz, altered tuff, potash feldspar, plagioclase, quartzite, and a volumetrically insignificant amount of heavy minerals. Clay minerals include hydromica, montmorillonite, and mixed layer clays; some kaolinite clays are present in the southeastern part of the Plateau region. The nondetrital constituents include secondary silica in the form of overgrowths on quartz grains, zoned interstitial chalcedony, calcite and other carbonates, localized occurrences of gypsum, and iron oxides in the form of interstitial cement and staining on grains. The white angular sand grains observed in hand specimens in the central, northern, and western parts of the Plateau are probably silicified tuff; they are generally slightly coarser than accompanying quartz grains. Red and green pebbles of chert, which also are probably derived from material of volcanic origin, dominate the pebble assemblage which includes also fragments of quartzite, silicified limestone, and silicified metamorphosed shale. Bones and bone fragments are common in both mudstone, sandstone, and conglomerate units.

Microstructure.—The sandstones of the Brushy Basin contain both homogeneous and heterogeneous microstructures.

MISCELLANEOUS FEATURES OF THE MAJOR URANIUM-PRODUCING HOST ROCKS

DETRITAL MINERALS

Quartz, the principal detritial mineral, is of two main types; igneous and metamorphic. The grains are usually rounded to subrounded, but the shape is changed in most samples by euhedral overgrowths which form perfect terminations on many grains. The original rounded quartz grains show moderate to slight replacement by calcite; however, the quartz overgrowths on the original grains are replaced readily.

The feldspar varieties are, in order of quantity, orthoclase, albite, oligoclase, microcline, andesine, and sanidine. The feldspars show various degrees of alteration and weathering, but albite appears as the most weathered of the varieties. In many calcite-bearing sandstones albite grains are commonly replaced in part or wholly by calcite leaving peculiarly oriented ghosts.

The three major varieties of tuff are present, including vitric, crystal, and lithic tuffs, each in various degrees of alteration and silicification. The typical vitric tuff grain contains a mixture of amorphous and slightly hydrous silica, spherical microgranular crystals of quartz, and voids. The outside surfaces of the angular grains are, in most instances, white and soft, like chalk. Variation in the proportions of the mixture mentioned above results in variation of the index of refraction from that of opal to that of quartz. The more highly silicified vitric tuff may be highly colored and may comprise the red or green "chert" pebbles and granules found in the Morrison formation.

The crystal tuff grains differ from the vitric only in that they include a fourth component which consists of microphenocrysts of potash feldspar, biotite, quartz, and other minerals.

The lithic tuffs are the most difficult to recognize; they resemble very fine grained rhyolite, or at worst, a practically unclassifiable rock fragment.

The heavy-mineral suites present are moderately large; however, they constitute only 0.1 to 1.0 percent of the rock. Exclusive of unique occurrences of unusual minerals, the suites are composed of varieties of the nonopaque minerals zircon, tourmaline, staurolite, epidote, apatite, rutile, anatase, brookite, garnet, biotite, muscovite, and spinel, and the opaque minerals magnetite, ilmenite, leucoxene, magnetite-ilmenite, and ilmenite-leucoxene-anatase intermixtures.

Clay minerals include the hydromica, montmorillonite, and kaolinite groups. The term hydromica is used broadly to include sericite, in part, and chlorite, in part. In addition to the conventional groups, there are also mixed-layer clays and other undefined clay minerals which suggest instability in many of the clays. The clays occur in both well-crystallized and poorly crystallized form. The hydromica clays are well crystallized when they form the borders around detrital grains of quartz. The kaolinite clays that occur in isolated interstitial wads are usually well crystallized. Some kaolinite crystals occur in well-developed accordion-shaped systems in the matrix. Montmorillonite is usually poorly crystallized.

The evidence suggests that recrystallization of some clays has occurred or is occurring. The well-crystallized detrital kaolinite in the interstitial wads may be allogenic and not due to recrystallization; however, the accordion-shaped crystals in the matrix appear to be the result of recrystallization. The hydromica clays are probably nearly all authigenic.

Aside from the kaolinite composing parts of weathered feldspar grains, the clays are nearly all a part of, or were derived from the matrix. At the time the host rocks were deposited it is conceivable that the matrix consisted of a mixture of detrital clays, fine volcanic ash, and ground-up feldspar, quartz, and igneous and metamorphic rock fragments.

The nondetrital components of the host rocks include much material which acts as a cement and some that does not. Isolated euhedral calcite crystals commonly seen in the matrix or in grains of albite, exert little influence as a cement; when calcite is an effective cement it forms continuous bands or zones which fill the interstices and extend through the rock. Siderite, dolomite, barite, gypsum, and the iron oxides are volumetrically less important than calcite, but also have respectively similar roles as isolated crystals and cement. Silica cement takes two forms: as overgrowths on quartz grains and as zoned interstitial chalcedony. The ore and gangue minerals in the uranium-ore deposits are also among the nondetrital minerals.

SUMMARY OF LITHOLOGIC CHARACTERISTICS

The lens-shaped cross-stratified sandstone units of the Chinle and Morrison formations characteristically weather to form conspicuous ledges which contrast with the less resistant siltier strata above, below, and lateral to them. The associated red and green claystone and mudstone strata, where sufficiently thick, form variegated, slightly concave slopes. If the fine-textured strata contain bentonite the slopes are slightly convex. Mostly the ledge-forming sandstones have an erosional disconformity at the base but are conformable with the sediments above; however, the upper contact may be a disconformity if overlying conformable siltstones have been removed by subsequent erosion prior to another depositional cycle.

Most of the ledge-forming sandstones are a composite of many smaller cross-stratified units which are nearly all separated from each other by erosional truncations. The bottom of a typical ledge-forming unit is coarse textured and poorly sorted and may contain a conglomerate zone of clay galls and chips, and pebbles of sedimentary, metamorphic, and igneous rocks. Pebbly zones may be observed also along some truncation planes within the major unit. Other accumulated material found in the basal part of many of the units includes disturbed claystone strata, petrified wood, and various kinds of carbonaceous material either concentrated in pockets or disseminated in the accompanying nonorganic sediments.

The dimensions of each of these major sandstone lenses are a function of the dimensions of the respective erosional cut or cuts which they occupy. The cuts resemble erosional features such as are produced by present-day water currents, and for this reason the deeper parts of the erosional cuts are referred to as "channels." The size of single continuous ledge-forming sandstone units ranges in order of magnitude from several miles to 100 feet or less in breadth and from 1 foot to 200 feet in thickness.

Any single major unit may include a large number of complex sedimentary and erosional structures or may consist entirely of a single cross-stratified set. The average size of the units and average scale of structures of deposition and erosion vary from formation to formation and within formations vary from area to area.

INTERPRETATION OF ENVIRONMENT WHICH PRODUCED THE HOST ROCKS

The majority of geologists who have worked in the Plateau region believe that the rocks discussed above were derived from sediment deposited in an alluvial environmental complex in a broad continental basin (see Mook, 1916; Longwell, 1924; Baker, 1936; Craig and others, 1955). This hypothesis is supported by evidence of contemporaneous deposition and erosion, the widespread extent of the dominant facies, the nature of the interbedding of mudstone strata with lenses of sandstone strata, the high degree of cross-stratification in the sandstone units, the plant remains in the bottoms of channels, and the overall resemblance to present-day stream deposits of the sedimentary deposits which form the Morrison formation, the Shinarump member and lower sandstone units of the Chinle formation.

CONCLUSIONS

The sedimentary rocks which rank as the major producers of uranium ore have certain characteristics which probably are related to the occurrence of uranium ore.

Unique characteristics of composition are (1) a combination of potash and sodic feldspar-rich sands; (2) large quantities of silicic-alkalic tuff and ash, wood, vegetable material, and bone, all of which produce a wide variety of chemical environments and the resulting variety of clay minerals and other alteration products; and (3) an apparent restriction of the mineralization to the sandstone and mudstone strata containing hydromica and kaolinite as the dominant clay mineral groups to the exclusion of the montmorillonite clays.

Unique characteristics of combined composition and structure are (1) the presence of channels; (2) sedimentary traps and confined aquifers; (3) the presence of clays, vegetable material, and conglomerates concentrated in the bottoms of channels, and (4) the region-wide association of restricted permeable sandstones with impermeable claystone strata, containing a trace to moderate amounts of slightly to very soluble salts and compounds.

Critical features of the minor producing formations are less apparent. Uranium production from the Entrada sandstone and Todilto limestone is restricted to a narrow 60-foot zone in the stratigraphic column which straddles the Entrada-Todilto contact, and to a 20- to 30-foot zone above the Entrada-Dolores contact (Fischer, 1942). The special characteristics of these zones include jointed limestone, well-sorted sandstone, and evaporite lithologic types. The Entrada-Todilto contact, though inconspicuous, is wide in extent and represents an important stratigraphic reference plane in the southeastern part of the Colorado Plateau region. All, some, or none of these factors may be related to the deposition of uranium in these two formations.

The stratigraphic units of Triassic and Jurassic age described are not in their entirety classifiable as host rocks, but they do contain the particular facies which favor the occurrence of deposits of uranium ore.

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Part 3. ELEMENTAL COMPOSITION OF THE SANDSTONE-TYPE DEPOSITS

By E. M. Shoemaker, A. T. Miesch, W. L. Newman, and L. B. Riley

CONTENTS

ILLUSTRATIONS

TABLES

ABSTRACT

The chemical composition of sandstone-type uranium ores and unmineralized sandstones from the Colorado Plateau has been determined chiefly by spectrographic analysis. More than 400 samples of ore and nearly 300 samples of unmineralized sandstone were analysed for about 60 elements by a rapid semiquantitative technique, and more restricted suites of samples were analysed for 5 elements by chemical techniques. The spectrographic and chemical analyses were treated by conventional mathematical methods for grouped data.

The average chemical composition of sandstones from the principal host rocks of Colorado Plateau uranium deposits—the Shinarump and Moss Back members of the Chinle formation, both of Late Triassic age, and the Salt Wash member of the Morrison formation, of Late Jurassic age—differ only moderately from the average composition of sandstones from most of the formations of Paleozoic and Mesozoic age on the Colorado Plateau. Average sandstones of the Shinarump and Moss Back members appear to contain significantly more aluminum, iron, titanium, zirconium, vanadium, chromium, copper, and probably more cobalt and nickel than average Colorado Plateau sandstones and less magnesium, calcium, barium, and probably less potassium. Average sandstones of the Salt Wash contain significantly more calcium, manganese, and copper than average Colorado Plateau sandstones and significantly less iron and probably less potassium, boron, cobalt, nickel, and yttrium.

A sandstone-type uranium deposit may be considered as composed of two fundamental parts: an indigenous part, and a foreign part which was added to the indigenous part to form the deposit. The indigenous part comprises all elements that would have occupied the space of the uranium deposit had uranium mineralization never occurred; these elemental components are called intrinsic. The foreign part comprises all elements that were added to the indigenous part by the processes of mineralization; these elemental components are called extrinsic. Almost all elements in sandstone-type uranium deposits are probably partly intrinsic and partly extrinsic, but each element may be classified according to the dominant role it plays in a majority of the deposits.

Elements detected by the analyses used in this study that are interpreted as dominantly intrinsic in the uranium deposits of both Upper Triassic rocks and the Morrison formation include silicon, aluminum, iron, magnesium, calcium, sodium, potassium, titanium, zirconium, barium, strontium, manganese, beryllium, boron, scandium, chromium, zinc, gallium, silver, lanthanum, and antimony. Dominantly extrinsic elements in the deposits of both the Morrison formation and the Upper Triassic rocks include uranium, vanadium, cobalt, nickel, copper, arsenic, molybdenum, and lead. Two elements, selenium and yttrium, are interpreted as dominantly extrinsic in the deposits of the Morrison formation, but dominantly intrinsic in the deposits of the Upper Triassic rocks. Other elements—not determined in the analyses used in this study, but known from other work—which may be extrinsic components of some of the sandstone-type uranium ores on the Colorado Plateau include sulfur, phosphorus, ytterbium, tin, cadmium, tellurium, and thallium.

INTRODUCTION

A regional study of the distribution of elements in the rocks and ores of the Colorado Plateau was begun in 1951 to provide information on the geochemical environment of the uranium deposits. Study of the gross elemental composition of the uranium ores provides a broad basis, and for some problems a starting point, for more detailed geochemical and mineralogical investigations. This paper summarizes information obtained to date on the gross elemental composition of the uranium deposits and the role or roles played by each element in the history and composition of the ore. The investigation is still in progress and all histograms and averages given are subject to minor revision.

METHODS OF SAMPLING AND SAMPLE PREPARATION

Two general types of samples have been used in the study of the composition of the rocks and ores. Most samples of unmineralized sandstones from formations under study were collected from outcrops during detailed stratigraphic investigations (Craig and others, 1955; Williams, 1954, p. 33–35) and were supplied by R. A. Cadigan of the U. S. Geological Survey. Some samples were collected by the writers from drill core and from outcrops. Samples of uranium ore were obtained from mechanical splits of ores shipped to mills and buying stations.

The samples of unmineralized sandstones are essentially grab samples selected to be representative of randomly distributed individual sandstone strata or parts of strata. Samples were taken without regard to proximity to known uranium deposits, but no samples that were visibly mineralized or found to have a radioactivity greater than 0.005 percent eU were incorporated in this study of unmineralized rocks. Two to five pounds of rock, as fresh as could be obtained, were originally collected, from which about 250 grams of fragments were picked out by hand. Where further crushing before grinding was necessary, the samples were crushed in a jaw crusher with iron jaws, and all samples were ground to minus 80-mesh in a disk grinder with ceramic plates (Barnett and others, 1955).

The samples of uranium ores obtained from mills and buying stations are pulverized quarters of splits or pulps that were assayed to determine payment to the shippers. Most of the samples studied were obtained from the U. S. Atomic Energy Commission's Monticello plant, operated by the American Smelting and Refining Co. (For description of sampling process see Colorado School of Mines Research Foundation, 1954, p. 46–49.) The pulps were ultimately ground to minus 120-mesh in cast-iron disk grinders. Nearly all the pulps are probably contaminated slightly with tramp iron. The average introduced amount of iron is estimated to be about 0.1 percent by weight. If the composition of the tramp iron is similar to that analyzed by Myers and Barnett (1953, table 2), the amounts of spectrographically detectable minor elements introduced with the iron are probably below or near the spectrographic limit of sensitivity.

Samples representing individual shipments or suites of shipments were combined, according to weight of ore represented, into composite samples for each mine. Final samples submitted for analysis consisted of 100- to 250-gram splits of the composite pulps. Samples from some mines were divided into two or more groups, and two or more composite pulps were prepared, representing different grades of ore or ore shipped from different parts of the mine. The amount of ore represented by the samples from each mine ranges from 1 to more than 5,000 tons and averages about 250 tons.

The term "ore" in this report refers to mineralized rock mined and shipped to the mills for payment. A surprising proportion, about 20 percent, of the shipments studied contained less than 0.10 percent U_3O_8, the minimum grade for ore established by the U. S. Atomic Energy Commission (1948). Not all of the material mined and classed as ore in this report, therefore, is of ore grade under present economic conditions.

ANALYTICAL METHODS

Most of the analyses were done by a rapid semiquantitative spectrographic method in the Denver spectrographic laboratory of the U. S. Geological Survey. R. G. Havens was the principal analyst, but large numbers of analyses were made by P. R. Barnett, G. W. Boyes, Jr., and P. J. Dunton; 428 samples of ore pulps and 289 samples of unmineralized sandstones were analyzed spectrographically.

Sixty elements are detectable with one exposure by the spectrographic method employed for this study. Of these elements, 22 are present in more than 65 percent of the ores in concentrations[3] above the spectrographic limits of sensitivity, and 9 elements are present in less than half of the ores in concentrations above the limits of sensitivity. The remaining 29 elements looked for were not detected in either the ores or the unmineralized sandstones. Study of the composition of the ores by the rapid spectrographic method is thus limited to about 30 elements.

The limits of sensitivity for each element are in general those listed by Myers (1954, p. 195). As the analytical work has extended over a period of 3 years and some changes were made in the details of the technique during this time, and as the individual analysts followed slightly different practices in reporting elements near the limit of sensitivity, the limit of sensitivity actually attained or reported for each element has varied slightly. Histograms given in figures 5 to 9 are cut off at the highest limits of sensitivity reported, but averages given in tables 1 and 2 and the correlation coefficients shown in figure 4 incorporate some determinations below the highest limit used. A majority of the statistics are subject to minor revision, pending review of some analyses and incorporation of additional samples.

Spectrographic data on arsenic, antimony, and zinc have been supplemented by colorimetric analyses (Lakin, Almond, and Ward, 1952, p. 14–16; Ward and Lakin, written communication, 1953; Almond, written communication, 1953) because these elements are generally present in the sandstones and ores in concentrations below the spectrographic limit of sensitivity. Selenium analyses were done by colorimetric methods (Lovering, and others, 1955). The colorimetric analyses were done by H. E. Crow, J. H. McCarthy, A. P. Marranzino, J. Meadows, and J. L. Silverly under the supervision of H. W. Lakin and L. F. Rader.

MATHEMATICAL TREATMENT OF ANALYSES

The concentrations of the elements, as determined by semiquantitative spectrographic analysis in this study,

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[3] The term "concentration" is used throughout this chapter in the conventional sense of fractional weight contained.

are reported in a series of 15 equal logarithmic classes that span the range from 0.0001 to 10 percent. Concentrations greater than 10 percent or less than 0.0001 percent are generally beyond the range of sensitivity of the spectrographic technique employed and are noted but not classified. Each class interval is equal to 0.3333 in $\log_{10}$ values, and the class limits form a geometric series that may be generated by integral powers of the cube root of 10 (2.154). After log transformation the analytical data may be treated with conventional mathematical methods for grouped data described in elementary statistics texts (see, for example, Waugh, 1943, p. 81–154, 372–430; Snedecor, 1946, p. 31–74, 137–168; or Hoel, 1947, p. 3–20, 78–92, 128–166).

The formulas used are as follows:

$$\bar{x}=\frac{1}{n}\Sigma f_i x_i, \tag{1}$$

where $\bar{x}$ = mean log,
n = total number of samples,
x_i = class midpoint of the ith class in logs,
f_i = frequency of ith class.

$$s=\left[\frac{\Sigma f_i(\bar{x}-x_i)^2}{n-1}\right]^{1/2}=\left[\frac{1}{n-1}\left(\Sigma f_i x_i^2-\frac{[\Sigma f_i x_i]^2}{n}\right)\right]^{1/2} \tag{2}$$

where s = log standard deviation.

$$r=\frac{n\Sigma f_i x_i y_i-(\Sigma f_i x_i)(\Sigma f_i y_i)}{[n\Sigma f_i x_i^2-(\Sigma f_i x_i)^2]^{1/2}[n\Sigma f_i y_i^2-(\Sigma f_i y_i)^2]^{1/2}} \tag{3}$$

where
r = linear correlation coefficient between x and y, which are the logs of the concentration of two elements.

The number of significant figures that may be retained for $\bar{x}$ and s is a function of the number of samples and the magnitude of s up to a limit determined by the precision with which the standards used in the analysis were prepared. No assumptions or judgments on the precision or accuracy of the analyses or on the frequency distribution of the analytical results are involved in the statistical theory of the formulae employed. The computed values of $\bar{x}$ and s may be assigned some probability determined by the precision and accuracy of the analyses. If an analyst can assign the correct class to an element in 60 percent of the determinations (a conservative estimate), the minimum probability for the computed value of $\bar{x}$ recorded to the maximum number of allowable significant figures is 60 percent. By dropping one significant figure the probability of $\bar{x}$ and s is greatly increased.

Statistical comparison of some of the semiquantitative spectrographic determinations with chemical analyses of the same material indicates the absolute error of the spectrographic analysis is proportional to the concentration, over the range of sensitivity, and analysis of replicate spectrographic determinations shows that deviations from the geometric mean are approximately lognormally distributed. The frequency distribution of most elements that lie above the spectrographic limit of sensitivity in the various groups of samples studied has been found by chi-square test to be approximately lognormal both in unmineralized sandstones and in the uranium ores. Thus the statistical theory for normal or Gaussian distribution may be applied to the spectrographic data with the least bias after log transformation. This transformation is based on the results obtained from the samples and is not concerned with the underlying causes of the form of the distribution.

If some determinations fall below the spectrographic limit of sensitivity the population mean log and log standard deviation can be estimated with least bias from the probability function for the truncated normal distribution (Fisher, 1931, p. xxxiii).

$$df=\frac{1}{\sigma\sqrt{2\pi}I_o(\xi)}e^{-\frac{(x-m)^2}{2\sigma}}dx$$

where σ = population standard deviation
m = population mean
ξ = difference between m and limit of sensitivity in σ values, limit of sensivity $= m+\sigma\,\xi$

and the I_O function has the form

$$I_o=\frac{1}{\sqrt{2\pi}}\int_x^\infty e-\frac{1}{2}t^2\,dt$$

Hald (1952, p. 62–63) gives tables derived from this probability function for estimating the sample mean and log standard deviation as well as tables for the one-sided censored normal distribution with which account may be taken of the number of analyses below the limit of sensitivity. Though the use of these table (for the truncated or censored normal distribution) introduces the least bias in the calculation of mean log and log standard deviation, several other methods of approximate calculation give closely comparable results. Where a majority of analyses are below the limit of sensitivity a rough estimate of the mean log may be obtained from the percent above the limit of sensitivity by use of the area tables for the normal curve and by assuming an average value for the log standard deviation. The means obtained by use of the area tables and an assumed standard deviation should be considered only as indicating the probable order of magnitude of the mean of the samples analyzed.

The simplest and generally most useful measure of central tendency that may be computed from the spectrographic analyses is the arithmetic mean of the logs, the antilog of which is the geometric mean. For a lognormal distribution the geometric mean is an estimate of the population median or true median. The most efficient (Fisher, 1921, p. 309–310) estimate of the true or population arithmetic mean may also be obtained from the geometric mean by methods given by Sichel (1952, p. 265–285). For purposes of comparison the geometric mean is generally the most satisfactory measure of central tendency for lognormal or approximately lognormal distributions, because the logarithmic variance of geometric means of small sets of samples drawn from a lognormally distributed population is less than the logarithmic variance of the arithmetic means (the geometric mean is a more efficient or more stable statistic). All means given in this paper are geometric except where otherwise noted.

It must be emphasized that the geometric means given in this paper should not be compared directly with published estimates of element abundance which are reported as arithmetic means. The geometric means for all the elements reported are invariably less than the estimated true arithmetic means by an amount that is a function of the log standard deviation (see footnote table 2). For a majority of distributions studied the arithmetic mean is 2 to 3 times greater than the geometric mean.

COMPOSITION OF SANDSTONES OF THE COLORADO PLATEAU AND SANDSTONE-TYPE URANIUM ORES

Uranium deposits have been found on the Colorado Plateau in most of the principal formations of Permian through Tertiary age and in three kinds of sedimentary rocks: limestone, mudstone, and sandstone. Some uranium deposits are also known in igneous rocks of Tertiary and possible Cretaceous age. More than 85 percent of the known uranium deposits are in sandstone and conglomeratic sandstone strata of the Shinarump and Moss Back members of the Chinle formation of Late Triassic age and of the Morrison formation of Late Jurassic age. Most of the ore produced from the Morrison formation has come from the Salt Wash member, and most of the known uranium deposits are in the central part of the Colorado Plateau where the Salt Wash member is well exposed.

COMPOSITION OF UNMINERALIZED SANDSTONE FROM THE PRINCIPAL URANIUM ORE-PRODUCING STRATA

Two principal uranium ore-producing groups of strata are distinguished for purposes of discussion. The first group comprises the Shinarump and the Moss Back members of the Chinle formation. Nearly all the uranium ores from Upper Triassic rocks included in this study are from these two units. The second group of strata, which make up the Salt Wash member of the Morrison formation, contain most of the ore deposits in the Morrison formation included in this study. Only 32 samples of sandstones from the Shinarump and Moss Back members from the central part of the Colorado Plateau (fig. 3) are included in the study and averages calculated for this group of samples should be considered preliminary. The statistics for sandstones from the Salt Wash member, on the other hand, are based on 96 samples from localities distributed over the area occupied by the Salt Wash member. At many of the sample localities in the Morrison formation unmineralized sandstone samples were taken from several different sandstone strata in the Salt Wash member, and, in general, the samples of the several sandstone units taken from a single stratigraphic section are similar in major and minor element composition. The samples taken from the Salt Wash are thought to be fairly representative of the sandstones of this member.

The chemical composition of the principal ore-bearing strata differs moderately from the average chemical composition of Colorado Plateau sandstones (table 1). The average sandstones from the Shinarump and Moss Back members appear to contain significantly[3] more aluminum, iron, titanium, zirconium, vanadium, chromium, copper, and probably more cobalt and nickel than the average Colorado Plateau sandstones. Aluminum in the unmineralized sandstones is contained chiefly in feldspar and clay minerals (for description of mineralogy see Part 2), and the greater content of aluminum in the sandstones of the Shinarump and Moss Back members indicates a greater content of feldspar and clay than is found in average sandstones of the Colorado Plateau (Part 2). Iron, titanium, and zirconium have a moderate-to-high correlation and vanadium, chromium, and copper a low-to-moderate correlation with aluminum in unmineralized Salt Wash sandstone (fig. 4) and probably have similar correlations in the sandstones of the Shinarump and Moss Back. The above-average amounts of iron, titanium, and zirconium and perhaps also of cobalt and nickel in the sandstones of the Shinarump and Moss Back members probably is in part a reflection of the above-average content of feldspar and clay. The concentration of

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[3] For large sample sets drawn from normal populations the standard deviation of the difference between two means may be approximated without serious bias from the equation

$$\sigma_{\bar{x}-\bar{y}} \approx s_{\bar{x}-\bar{y}} \approx \sqrt{\frac{s_x^2}{n_x}+\frac{s_y^2}{n_y}},$$

and the significance of $\bar{x}-\bar{y}$ may be determined from ordinate tables for the normal curve of error. The precise determination of significance of the difference between two means for small sample sets, in the general case that the variances are not equal, is mathematically more complex. In this paper, for purposes of simplicity, a difference is judged significant if one mean lies outside the 99 percent confidence interval of another mean. (See table 2 for confidence intervals of the means.)

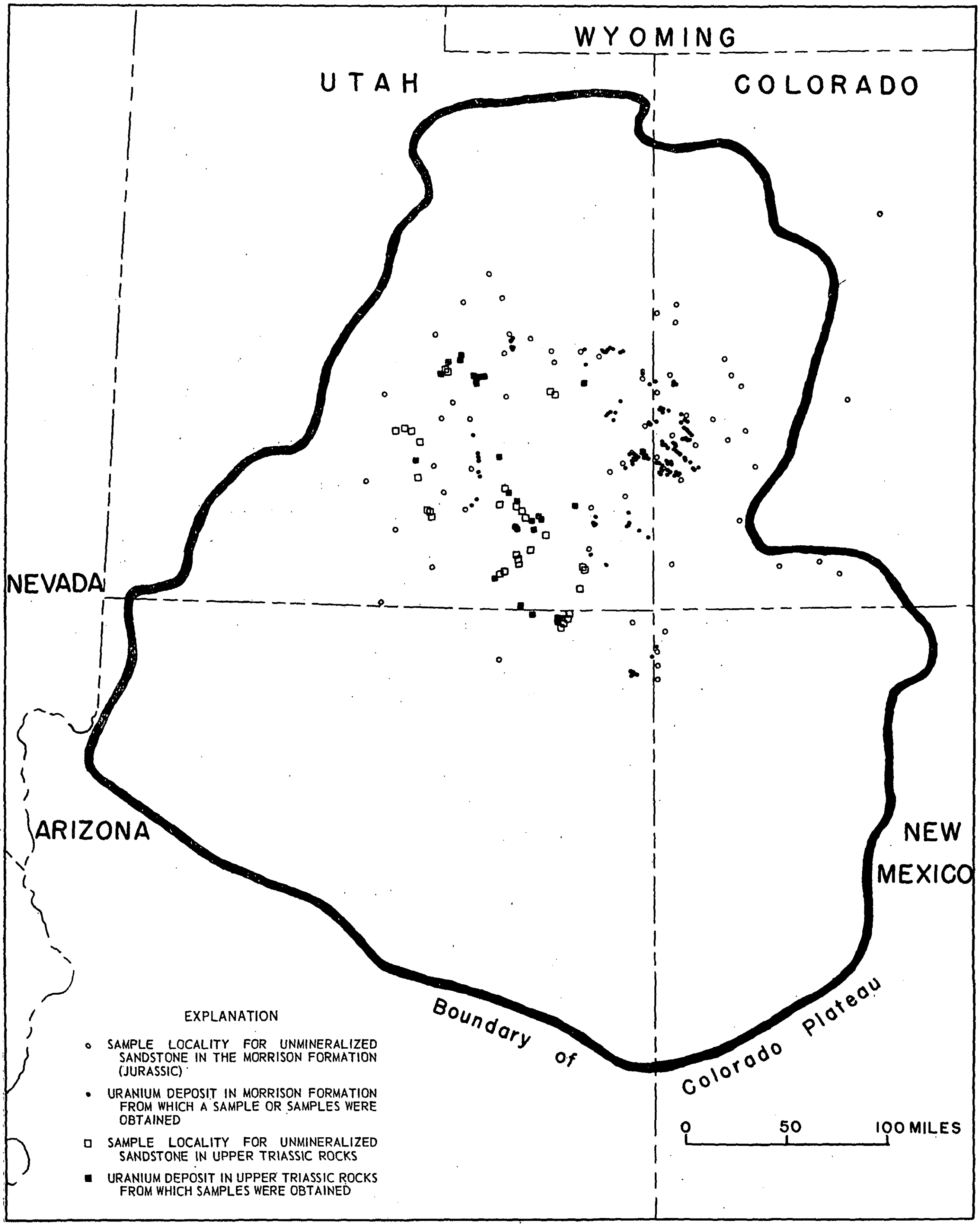


FIGURE 3.—Map of the Colorado Plateau showing localities for samples of unmineralized sandstone and uranium deposits from which samples were obtained.

copper in the average of sandstones of the Shinarump and Moss Back members, which is more than 10 times, is noteworthy. Visible traces of copper carbonates are widespread in Shinarump and Moss Back members.

Magnesium, calcium, barium, and probably potassium appear to be significantly lower in sandstones of the Shinarump and Moss Back than in average Plateau sandstones. The low concentration of magnesium and calcium reflects a less-than-average content of carbonate in sandstones of the Shinarump and Moss Back members.

Average sandstones of the Salt Wash contain significantly more calcium, manganese, and copper than average Colorado Plateau sandstones. Calcium and manganese have a high correlation (fig. 4) and are contained mainly in carbonates, which are the principal cements of the sandstone of the Salt Wash (according to Cadigan in Part 2). Sandstones of the Salt Wash are significantly lower than average in iron and probably lower in potassium, boron, cobalt, nickel, and yttrium.

TABLE 1.—*Average chemical composition of Colorado Plateau sandstones and sandstones from the principal uranium ore-bearing strata*

[Composition shown in parts per million]

Element	Sandstones of Paleozoic and Mesozoic age from the Colorado Plateau [1]	Unmineralized sandstones of the—	
		Shinarump and Moss Back members of the Chinle formation [2]	Salt Wash member of the Morrison formation [3]
Si	>100,000	>100,000	>100,000
Al	10,000	33,000	11,900
Fe	3,700	12,000	2,400
Mg	2,700	1,300	2,300
Ca	12,000	2,500	33,000
Na	690	900	890
K	4,300	≈2,000	≈3,000
Ti	580	1,800	510
Zr	88	250	103
Mn	140	120	220
Ba	280	520	340
Sr	45	60	49
B	16	≈16	≈8
V	11	30	10
Cr	7	14	6.6
Co	1	≈5	≈.5
Ni	2	≈9	≈.5
Cu	9	100	13
Y	4	16	≈2
U			[4] ≈1

[1] Geometric mean of the geometric-mean composition of sandstones in each of 24 formations on the Colorado Pleateau ranging in age from Cambrian through Cretaceous (289 samples, averaged by formations).

[2] Geometric mean composition (32 samples).

[3] Geometric mean composition (96 samples).

[4] Geometric mean of 23 samples analysed by fluorimetric method (Grimaldi, May, and Fletcher, 1952).

Sandstones of the Salt Wash, in general, are more like the average Colorado Plateau sandstones than are the sandstones of the Shinarump and Moss Back members. Only two elements show a similar significant departure from the Colorado Plateau sandstone average in both major groups of ore-bearing strata. Copper is significantly higher in both the sandstones of the Salt Wash and the sandstones of the Shinarump and Moss Back than in the average Plateau sandstones, and potassium appears to be significantly lower in both. In comparing sandstones of the important ore-bearing formations with other sandstones it should be noted that the estimates of geometric-mean concentrations of each of the elements in unmineralized sandstones of the Salt Wash would fall within the confidence interval of the mean (table 2) for all elements, if the elements contained in all the ore estimated to have been present in the Morrison formation were dispersed in sandstones. In other words, the estimate of average concentration of elements in the sandstones of a given formation is not significantly changed if the ore deposits are included with the unmineralized sandstones, even in the most intensely mineralized formation.

COMPOSITION OF SANDSTONE-TYPE URANIUM ORES FROM UPPER TRIASSIC ROCKS AND FROM THE MORRISON FORMATION

Most of the uranium deposits of the Colorado Plateau consist of sandstone and minor amounts of mudstone impregnated with and partly replaced by minerals of uranium, vanadium, and in some cases by copper or other heavy metals. To this kind of deposit the name sandstone-type uranium deposit has been applied. The discussion of uranium deposits in this paper is restricted to sandstone-type deposits in Upper Triassic rocks and in the Morrison formation.

All the deposits studied in the Morrison formation are in the Salt Wash member except for a small number that are in sandstone lenses near the base of the overlying Brushy Basin member. More than 200 deposits, or approximately 10 percent of the known deposits, in the Morrison formation and about 40,000 tons of ore from the Morrison formation are represented by the samples studied. The arithmetic-mean grade of uranium and vanadium in 211 deposits, averaged by tonnage, is very close to the weighted-arithmetic-mean grade for all ore produced from the Morrison formation for successive 6 months periods in 1953 and 1954 (see section "Uranium and vanadium"). The samples of ores from the Morrison are therefore considered representative of producing deposits in uranium and vanadium content and are thought to be probably representative in their content of most other elements as well.

All but two of the sampled deposits in Upper Triassic rocks are in the Shinarump or Moss Back members of the Chinle formation, and the remainder are in other members of the Chinle formation. Only 38 deposits in Upper Triassic rocks, about 6 percent of the known deposits in these rocks, have been studied, and these may not be fully representative of the deposits now producing ore from the Chinle formation. A disproportionate number of deposits in Upper Triassic rocks studied are in one relatively small area at Temple Mountain, in central Utah.

The average composition of sandstone-type uranium ores from the Chinle formation and from the Morrison formation is given in table 2 along with the average composition of the unmineralized sandstones. The frequency distributions on which these averages are based are shown in figures 5 to 9. Class intervals used in the histograms for spectrographic analyses are the same as the class intervals by which the analyses were reported, and the class intervals used in the histograms for colorimetric analyses are approximately the same as those used for the spectrographic analyses.

Table 2.—*Average composition of uranium ores and unmineralized sandstones of the principal uranium ore-bearing formations on the Colorado Plateau*

[All elements except Zn, As, Se, and Sb were determined by semiquantitative spectrographic analyses, thus: (1) 211 deposits, (2) 96 samples, (3) 38 deposits, (4) 32 samples

Element	Morrison formation—Chiefly Salt Wash member						Upper Triassic rocks—Chiefly Shinarump and Moss Back members of the Chinle formation					
	Uranium ores (1)			Unmineralized sandstones (2)			Uranium ores (3)			Unmineralized sandstones (4)		
	Range of geometric mean		Geometric deviation [2]	Range of geometric mean		Geometric deviation [2]	Range of geometric mean		Geometric deviation [2]	Range of geometric mean		Geometric deviation
	Geometric mean	×÷ Confidence interval [1]		Geometric mean	×÷ Confidence interval [1]		Geometric mean	×÷ Confidence interval [1]		Geometric mean	×÷ Confidence interval [1]	
Al	2.48	1.14	2.03	1.2	1.18	1.89	2.2	1.42	2.21	3.3	1.66	2.85
Fe	.90	1.12	1.89	.24	1.19	1.91	1.5	1.33	1.90	1.2	1.81	3.40
Mg	.68	1.19	2.60	.23	1.33	2.85	.17	1.61	2.99	.13	2.12	4.72
Ca	1.97	1.22	3.07	3.3	1.40	3.47	.7	1.87	4.14	.25	2.60	7.19
Na	.091	1.23	3.19	.089	1.42	3.73	.08	1.63	3.04	≈.1	---	---
K	≈.27	---	---	.37 [3]≈.3	---	---	≈.48	---	---	.15 [3]≈.2	---	---
Ti	.104	1.13	1.95	.051	1.20	1.96	.13	1.43	2.26	.18	1.56	2.50
Zr	.0237	1.14	2.11	.0103	1.27	2.40	.018	1.36	2.03	.025	1.81	3.39
Mn	.031	1.15	2.17	.022	1.33	2.89	.024	1.58	2.85	.012	3.05	10.00
Ba	.084	1.16	2.32	.034	1.34	3.00	.07	1.67	3.22	.05	1.97	4.06
Sr	.0122	1.13	2.00	.0049	1.28	2.50	.014	1.52	2.59	.006	2.21	5.13
Be	<.0001	---	---	<.0001	---	---	[3]≈.00007	---	---	<.0001	---	---
B	≈.0015	---	---	<.001 [3]≈.0008	---	---	.0014	---	---	≈.0016	---	---
Sc	<.001	---	---	<.001	---	---	<.001 [3]≈.0006	---	---	<.001 [3]≈.0004	---	---
V	.49	1.15	2.14	.0010	1.32	2.81	.063	1.92	4.40	.0030	2.08	4.52
Cr	.00169	1.14	2.03	.00066	1.25	2.27	.0030	1.56	2.74	.0014	1.54	2.44
Co	.00104	1.27	3.77	<.0002 [1]≈.0005	---	---	.0025	2.00	4.16	≈.0005	---	---
Ni	.00084	1.28	4.02	<.0002 [3]≈.00005	---	---	.0025	1.67	3.22	≈.0009	---	---
Cu	.0086	1.30	4.34	.0013	1.28	2.49	.030	2.76	10.10	.010	1.79	3.33
Zn [4]	.0116	1.44	2.58	.0053	1.53	2.09	.031	3.11	4.16	---	---	---
Ga	<.0005	---	---	<.0005	---	---	<.0005 [3]≈.0002	---	---	<.0005 [3]≈.0001	---	---
As [4]	.0168	1.42	2.48	<.001	---	---	.020	1.85	2.16	---	---	---
Se [5]	.00118	1.48	4.45	<.0002	---	---	≈.0006	---	---	≈.0003	---	---
Y	.00129	1.21	2.86	<.0005 [3]≈.0002	---	---	.0017	1.76	3.61	.0016	1.50	2.31
Mo	≈.0013	---	---	<.0005	---	---	≈.0017	---	---	<.0005 [3]≈.0002	---	---
Ag	<.0001 [3]≈.00005	---	---	<.0001 [3]≈.00003	---	---	<.0001 [3]≈.00004	---	---	<.0001	---	---
Sb [4]	≈.0001	---	---	≈.0002	---	---	≈.0002	---	---	---	---	---
La	<.002	---	---	<.002	---	---	<.002 [3]≈.001	---	---	<.002 [3]≈.0008	---	---
Yb	---	---	---	<.0001 [3]≈.00003	---	---	---	---	---	.00024	1.68	2.42
Pb	.0088	1.29	4.10	<.0001	---	---	.0064	1.66	3.16	[3]≈.001	---	---

[1] The 99 percent confidence interval for the population geometric mean: the limits of the confidence interval are determined from Student's *t* distribution (Fisher and Yates, 1953, p. 1 and 40) where *t* is the deviation (or range of the population mean), in units of estimated standard error. For a normal distribution

$$\text{confidence interval of the mean} = \pm t \frac{s}{\sqrt{n-1}}$$

or for a lognormal distribution

$$\text{confidence interval of GM} = \overset{\times}{\div} \text{antilog } t \left[\frac{(\log \text{GD})}{\sqrt{n-1}}\right]$$

The most efficient estimate of the arithmetic mean of a lognormal population may be obtained from the following equation if n is large:

$$\log_{10} \text{estimated arithmetic mean} = \log_{10} \text{GM} + 1.1513 (\log_{10} \text{GD})^2$$

[2] Geometric deviation or antilog of the log standard deviation.

[3] Estimated geometric mean. Estimated by assuming the part of the frequency distribution below the limit of sensitivity conforms to part of a lognormal distribution. Where a majority of analyses are below the limit of sensitivity the geometric mean is estimated from the frequency above the limit of sensitivity by assuming a lognormal distribution for the total frequency and by assuming for the element in question an average log-standard deviation computed for elements in the type of rock or ore analyzed.

[4] Colorimetric analyses (1) 49 deposits, (2) 23 samples, (3) 14 deposits.

[5] Colorimetric analyses (1) 102 deposits, (2) 8 samples, (3) 30 deposits, (4) 30 samples.

In table 2 a factor is given for each mean that lies above the analytical limits of sensitivity which defines the limits of the 99-percent confidence interval for the true geometric mean of the type of rock from which the samples were taken. For the elements that lie mainly or entirely above the analytical limits of sensitivity, a measure of the dispersion or variation of concentration of each element in the ores and rocks (the geometric deviation) is also given. The geometric deviation is the antilog of the logarithmic standard deviation and is a measure of dispersion that is independent of the order of magnitude of the mean concentration. If the frequency distribution of an element is approximately lognormal the range of concentration between the limits defined by the geometric mean divided by the geometric deviation and the geometric mean multiplied by the geometric deviation will include about 68 percent of the analyses.

As an example, the table may be read for aluminum as follows: the geometric-mean concentration of aluminum in 211 sandstone-type uranium ores from the Morrison formation is 2.48 percent. Assuming the selection of deposits studied to be representative and the spectrographic analyses unbiased, then the true geometric mean of the aluminum concentration in all uranium deposits in the Salt Wash member and overlying parts of the Brushy Basin member of the Morrison formation, of which there are about 2,000 known at the present time, would lie (with 99 percent confidence) betwen 2.83 percent (2.48×1.14) and 2.18 percent (2.48÷1.14). About 68 percent of the deposits may be expected to have an aluminum concentration between 5.0 percent (2.48×2.03) and 1.22 percent (2.48÷2.03). The calculated geometric-mean concentration of aluminum in 96 samples of the unmineralized sandstone host rocks in the Salt Wash member of the Morrison formation is 1.2 percent, and, if the samples are representative, the geometric mean of all sandstone of the Salt Wash lies between the limits of 1.40 percent and 1.01 percent at 99 percent probability. About 68 percent of the sandstone of the Salt Wash member may be expected to have between 0.63 percent and 2.25 percent aluminum. The estimated geometric mean or median concentration of aluminum in uranium deposits of the Morrison formation is 2.08 times as great as the estimated median concentration in unmineralized sandstone of the Salt Wash member, and the median concentration of aluminum in all Morrison uranium deposits may be expected (with about 99 percent confidence) to be between 1.77 and 2.46 times as great as the median concentration in sandstone of the Salt Wash.

The correlation of elements in unmineralized sandstones of the Salt Wash member of the Morrison formation and in sandstone-type uranium deposits of the Morrison formation is given in chart form in figure 4. Each number on the chart is a linear correlation coefficient between the logs of the concentration of two elements. The distribution of the logs of most pairs of elements in the samples studied approximates a normal correlation surface. The pair of elements for which each correlation coefficient stands is determined, as in a mileage chart, by the headings of the column and row in which the coefficient is found. In figure 4 the correlation between pairs of elements is given for all elements that occur above the spectrographic limit of sensitivity in more than 63 percent of the 211 uranium deposits of the Morrison studied.

The correlation coefficient may be taken as a measure of the geochemical coherence (Rankama and Sahama, 1950, p. 48) between two elements in a given type of rock. The coefficients may range in value from minus one to plus one. Values near either plus or minus one indicate a nearly linear relation or proportional variation between the concentration logs of two elements, a positive linear relation or direct proportionality if the coefficient is positive and a negative linear relation or inverse proportionality if the coefficient is negative. A coefficient near zero indicates there is no linear relation between two elements (that the covariation is essentially random). In general terms the correlation coefficients on the chart show which elements vary sympathetically, which elements vary antipathetically, and which elements show no significant correlation. The lowest significant value for the correlation coefficient for a normal correlation surface is a function of the number of samples and may be determined from tables (Fisher and Yates, 1953, p. 54) for a given probability.

Study of figure 4 will reveal the general degrees of association or coherence of the elements in Morrison uranium deposits and unmineralized sandstones of the Salt Wash member. No negative correlation coefficients that are significant at 99 percent confidence were found. All significant correlations are positive and the correlation of most elements with aluminum in both the ores and the unmineralized rocks is significant or nearly significant. The causes of some of the element associations are fairly well understood at the present time; for others they are largely unknown. Interpretation of some of the correlations is given in the discussion that follows. For purposes of discussion a significant correlation below 0.35 will be spoken of as low, from 0.35 to 0.49 as moderate, from 0.50 to 0.74 as high, and above 0.74 it will be spoken of as very high. These designations are purely relative and are used merely to distinguish the ranges of correlation observed on the chart.

CLASSIFICATION OF ELEMENTS IN SANDSTONE-TYPE URANIUM DEPOSITS

GENERAL FEATURES

For convenience of discussion the following classification has been adopted for the elemental components of the sandstone-type uranium deposits.

Intrinsic elemental components	Syngenetic components Epigenetic (diagenetic) components
Extrinsic elemental components	Ore components Accessory components

CORRELATION OF ELEMENTS IN URANIUM DEPOSITS

CORRELATION OF ELEMENTS IN UNMINERALIZED SANDSTONES

	V	Ni	Cu	Pb	Mo	Cr	Y	Ti	Zr	B	Mn	Ba	Sr	K	Na	Ca	Mg	Fe	Al	U
V	**V**	+.07	+.23	+.35	+.07	+.22	+.26	+.15	+.37	+.27	+.07	+.34	+.34	+.15	+.09	+.03	+.36	+.28	+.50	+.32
Ni		**Ni**	+.08	+.14	+.49	+.10	+.27	+.14	+.08	+.12	.00	+.02	+.08	+.03	+.05	–.04	–.06	+.37	+.11	+.10
Cu	+.06		**Cu**	+.56	+.16	+.30	+.04	+.27	+.29	+.23	+.26	+.15	+.31	+.27	+.26	+.32	+.36	+.07	+.36	–.04
Pb				**Pb**	+.14	+.33	+.07	+.21	+.25	+.15	+.26	+.14	+.23	+.29	+.21	+.23	+.39	+.25	+.49	+.11
Mo					**Mo**	+.25	+.24	+.04	+.22	–.09	.00	+.01	+.13	+.14	+.10	+.04	.00	+.34	–.13	+.06
Cr	+.38		.00			**Cr**	+.12	+.22	+.20	+.32	+.21	+.20	+.25	+.38	+.21	+.20	+.27	+.20	+.36	+.10
Y							**Y**	+.25	+.39	+.39	+.05	+.25	+.11	+.08	+.15	–.04	+.11	+.31	+.22	+.18
Ti	+.17		+.28			+.21		**Ti**	+.41	+.22	+.37	+.26	+.34	+.44	+.39	+.35	+.25	+.17	+.50	+.19
Zr	+.28		+.01			+.42		+.50	**Zr**	+.26	+.35	+.25	+.14	+.19	+.43	+.39	+.38	+.31	+.46	+.15
B										**B**	+.10	+.21	+.17	+.28	+.21	+.13	+.23	+.16	+.35	+.11
Mn	+.16		+.22			+.24		+.02	–.05		**Mn**	+.19	+.28	+.37	+.56	+.75	+.30	+.20	+.47	–.09
Ba	+.11		–.08			+.20		+.08	+.16		–.03	**Ba**	+.37	+.27	+.19	+.11	+.15	+.15	+.28	+.05
Sr	–.04		+.39			+.15		+.31	+.05		+.34	+.34	**Sr**	+.42	+.26	+.36	+.19	+.10	+.40	+.10
K														**K**	+.34	+.45	+.22	+.02	+.45	+.06
Na	+.04		–.22			+.26		+.35	+.14		+.47	–.09	+.31		**Na**	+.56	+.45	+.37	+.47	+.08
Ca	+.08		+.26			+.22		–.12	–.12		+.83	–.05	+.41		+.39	**Ca**	+.48	+.12	+.46	–.14
Mg	+.30		+.20			+.16		+.09	+.14		+.22	+.19	+.07		+.19	+.17	**Mg**	+.34	+.58	+.11
Fe	+.20		+.32			+.29		+.30	+.20		+.21	+.19	+.16		+.27	+.05	+.44	**Fe**	+.30	+.23
Al	+.24		+.35			+.25		+.60	+.40		+.12	+.23	+.24		+.30	+.04	+.16	+.48	**Al**	+.14
U																				**U**

CORRELATION OF ELEMENTS IN URANIUM DEPOSITS

CORRELATION OF ELEMENTS IN UNMINERALIZED SANDSTONES

NUMBERS ARE LINEAR CORRELATION COEFFICIENTS CALCULATED AFTER LOG TRANSFORMATION.

LOWEST SIGNIFICANT VALUE AT 99 PERCENT CONFIDENCE IS 0.19 FOR CORRELATION OF ELEMENTS IN URANIUM DEPOSITS AND 0.26 FOR CORRELATION OF ELEMENTS IN UNMINERALIZED SANDSTONES.

FIGURE 4.—Correlation of elements in uranium ores and in unmineralized sandstones from the Salt Wash member of the Morrison formation (Jurassic).

This classification applies and has meaning only for ore or mineralized rock. The purpose of the classification is to provide a simple framework of concepts with which the role of each element in the mineralogy and history of the ore deposits may be discussed.

Two basic assumptions are involved in this classification system.

1. The minerals that contain the bulk of the elements of economic importance, the ore elements, are assumed to be epigenetic components of the ores, in the strict sense of the term epigenetic (Lindgren, 1933, p. 154) that the minerals are introduced or formed in a preexisting rock or sediment. Because the distribution of ore minerals does not follow in detail the lamination of

the sedimentary rocks in which the ore is contained, the emplacement of the ore minerals probably was later than the deposition of the individual laminae in which the ore minerals are now found. This interpretation has been explicitly stated by Lindgren (1911, p. 568), Coffin (1921, p. 159 and 176), and Fischer (1937, p. 943). The ore deposits are thus conceived as composed of two fundamental parts: (1) a mass of sediment or rock formed prior to emplacement of the ore minerals and (2) minerals carrying the bulk of the ore elements and other associated minerals introduced or formed in the mass of sediment or rock that today constitutes the ore deposit. The first part may be thought of as the indigenous or intrinsic part of the ore deposits, corresponding approximately in composition to the rocks that would have occupied the space of the ore deposits had mineralization never occurred; the second part may be thought of as foreign or extrinsic to the individual rock masses that constitute the deposits. The concepts of intrinsic and extrinsic, as here defined, are restricted in their application to mineral deposits of epigenetic origin.

2. It is assumed that the processes by which the minerals carrying the bulk of ore elements were emplaced in the ore deposit are distinct and can be distinguished from other processes which induced postdepositional changes in the sedimentary beds in which the ore deposits are located, processes that are commonly lumped under the broad ill-defined category of diagenesis. Empirically, the distinction between uranium mineralization and diagenesis is largely based on the spatial distribution of the products of the two processes; the uranium deposits are localized whereas diagenetic minerals such as calcite and authigenic quartz are widely distributed in the sediments, apparently irrespective of the distribution of uranium deposits. Such products are in both cases epigenetic. It is entirely possible, and even likely, that the processes of uranium mineralization may have affected rocks away from the uranium deposits and produced minerals indistinguishable from the minerals formed by unrelated diagenetic processes, but the distinction between intrinsic and extrinsic components applies only to rock that is recognizably mineralized with uranium.

Intrinsic elements are defined as the elements whose presence in the ore is unrelated to processes of uranium mineralization. Empirically, they are defined as elements found in the ores in amounts comparable to the amounts found in the unmineralized parts of the strata that contain the ore deposits. The intrinsic elements fall into two broad groups, (1) the syngenetic elements, or those elements contained originally in the clastic components and the elements contained originally in precipitates in the mineralized rock that were strictly simultaneous in deposition with the clastic components and, (2) epigenetic elements or elements introduced (during diagenesis) into the locus of the ore deposit after deposition of the ore-bearing strata by processes unrelated to uranium mineralization. Both syngenetic and epigenetic intrinsic elements may have been partly rearranged during uranium mineralization and incorporated in ore minerals or other minerals formed during mineralization.

Depending upon the stage in the history of the mineralized rock that the uranium was introduced into the deposits, the introduction of epigenetic intrinsic elements may have either preceded or followed the introduction of uranium. Calcium, for example, which is contained largely in the abundant calcite cement of the sandstones of the Salt Wash may have been introduced and precipitated in the individual bodies of ore or mineralized rock early in the history of the rock, prior to the introduction of extrinsic uranium (Waters and Granger, 1953, p. 15–20), but may also have been partly introduced, rearranged, or leached away after uranium mineralization.

The extrinsic elements of a uranium deposit are elements that have been introduced by processes of or related to uranium mineralization into the body of sediment or rock that became the uranium deposit. The extrinsic elements are contained largely in minerals formed or crystallized in place, though some may be merely adsorbed on or absorbed in preexisting minerals. No sources for the extrinsic elements are implied by this definition nor does it imply that all the extrinsic elements had the same source as the uranium. In particular, no implication is intended that the extrinsic elements were derived either from the beds that enclose the uranium deposits or from sources external to these beds. Neither is it implied that all the extrinsic elements were necessarily introduced into the uranium deposit at the same time, though the simultaneous introduction of extrinsic elements into most of the uranium deposits seems likely. The extrinsic elements are further subdivided for discussion into ore elements and accessory elements on the somewhat arbitrary basis of whether a given element contributes to the economic value of the ore.

The extrinsic elements are empirically defined as those elements that are more abundant in the uranium ores than in the equivalent unmineralized rocks. Because of selectivity of uranium mineralization for certain parts of the host strata the average intrinsic composition of mineralized rock in the sandstone-type uranium deposits differs somewhat from the average composition of unmineralized sandstone. Uranium ore in the Morrison formation contains, on the average, twice as much aluminum as the unmineralized sandstones of the Morrison, probably because the ore is localized in sandstone units that initially contained on the average twice as much clay or mudstone. All other intrinsic elements in the ore that correlate positively with aluminum in the unmineralized sandstones are, as may be expected, higher in the average ore than in the average unmineralized sandstone.

Probably no single chemical element in the sandstone-type uranium ores belongs exclusively to either the intrinsic or extrinsic components of any given ore, as each element is present in some concentration, however small, in the detrital minerals of the sandstone and a certain amount, however small, was probably carried in the solutions that introduced the uranium. The problem of classification, therefore, is to assess the relative importance of the roles played by each element in the ores. An element is here tentatively considered dominantly of one classification or another if the major part of the element is believed to fall in a given classification in a majority of the deposits studied. The classification of individual elements in the following discussion is based mainly on the comparison of the averages given in table 2.

No consideration has been given in this investigation to the radioactive daughter products of uranium that are present in the sandstone-type uranium ores. Paired radiometric and fluorimetric uranium analyses of thousands of samples of the sandstone-type ores from the Morrison formation indicate that the great majority of the ores are nearly in equilibrium on a hand-specimen scale. The content of radioactive daughter elements, therefore, tends to be proportional to the content of uranium in the ores. In the theoretical terms of the proposed classification of elements the radioactive daughter elements are neither intrinsic nor extrinsic. They are neither an indigenous part of the uranium deposits, nor were they introduced by the processes of mineralization, but were generated in place. They could be spoken of as authigenic elements in the prime sense of the word.

DOMINANTLY INTRINSIC ELEMENTS

SILICON

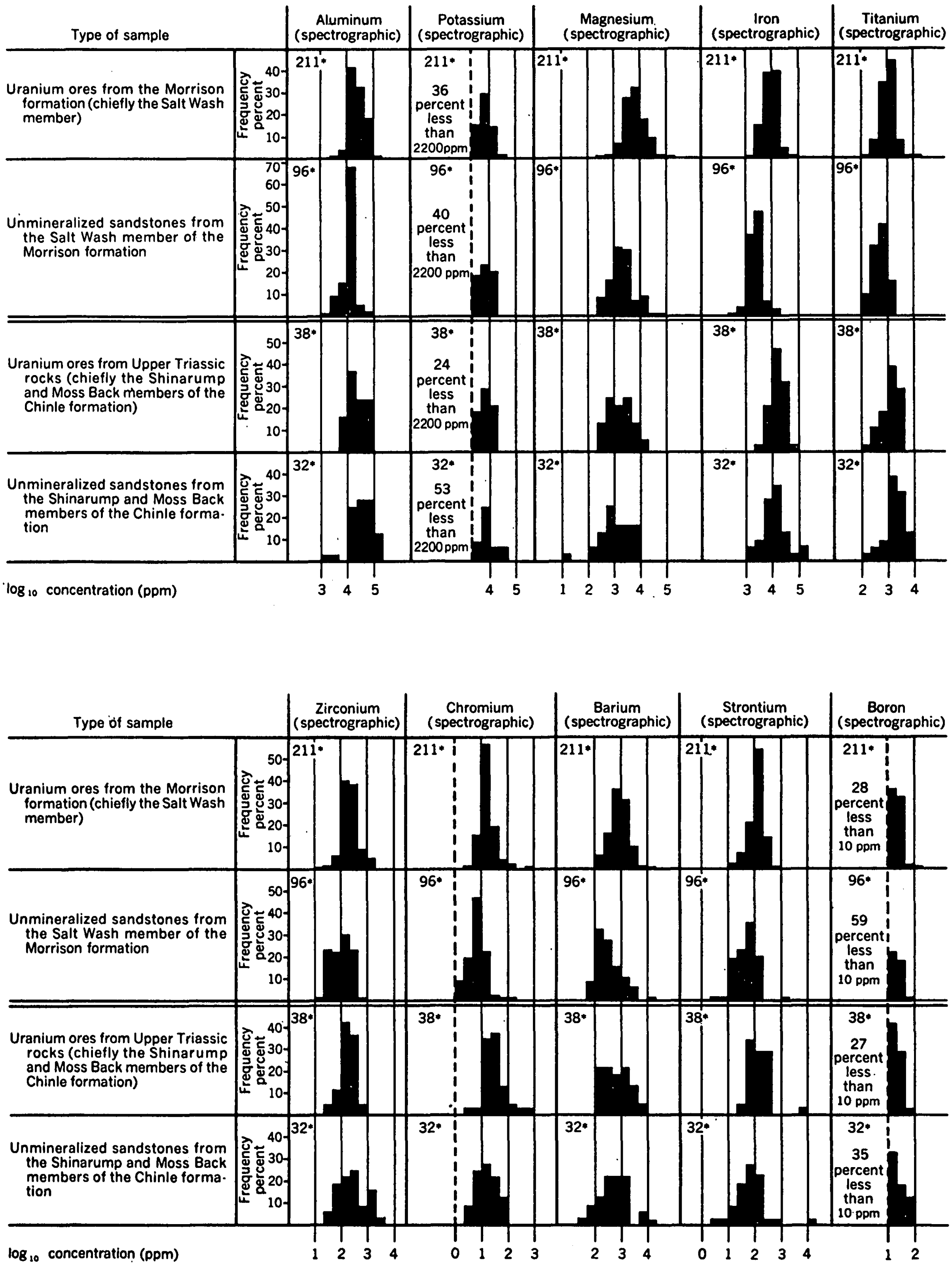
Silicon and oxygen occur mainly in the various mineral forms of silica and constitute the large bulk of the sandstone-type uranium deposits as well as the unmineralized rocks that enclose the deposits. The concentration of silicon in both the ores and unmineralized rocks is too high to be estimated by semiquantitative spectrographic analysis, but an approximation of the arithmetic mean concentration of silica may be obtained by subtraction of the oxide equivalents of the arithmetic means of all other elemental constituents from 100 percent. If carbonate is assigned to all the calcium a fair estimate of the arithmetic-mean silicon concentration in unmineralized Salt Wash sandstone may be obtained by this method, and it has been found to be approximately 36 percent (77 percent SiO_2). No account of sulfate, sulfide, phosphate, carbonates other than calcium carbonate, or organic carbon is taken in such an estimate, but since the estimated arithmetic-mean concentration of only two spectrographically detectable elements (Al and Ca) other than silicon are greater than 1 percent, the estimate for silicon is probably correct to within 1 or 2 percent silicon.

The concentrations of nearly all elements other than silicon and oxygen tend to be higher in ores from the Morrison than in the unmineralized sandstones of the Salt Wash member, but calcium, the second most abundant metallic element in the sandstones, is less abundant in the average ores. Because of the uncertainties involved in the estimations by subtraction it cannot be definitely said whether the silicon content of the ores is significantly different from that of the unmineralized sandstones of the Salt Wash. In any event the difference is probably very small in proportion to the total silicon content and the great bulk of silicon is intrinsic in the ore deposits.

Fischer (1942, p. 380) and Waters and Granger (1953, p. 15–20) have shown that quartz has been dissolved and locally removed in apparently significant amounts in parts of some Morrison ore deposits, probably during mineralization. These observations suggest that some loss of total silica from the sandstone-type uranium deposits may have commonly taken place during mineralization. Differences in silicon content between host rocks and ores in Triassic formations are expected to be similar to the relations observed in the deposits in the Morrison.

ALUMINUM

Aluminum (figs. 4 and 5) in the unmineralized sedimentary rocks and in the uranium deposits is contained largely in various kinds of clay and claylike micaceous minerals (Parts 2 and 10) and in detrital feldspars (Part 2). Rough estimates of the distribution of aluminum between the clay and feldspar components of unmineralized sandstones of the Salt Wash, based on size and mineralogical analyses by R. A. Cadigan (unpublished data), suggest that about one-third to one-half of the aluminum is generally contained in the clay-silt size fraction and the remainder is contained largely in sand size detrital feldspar. The twofold difference between the concentration of aluminum in the



•Number of uranium deposits or number of samples of sandstone

FIGURE 5.—Frequency distribution of the dominantly intrinsic elements (aluminum through boron) of uranium ores, contained in uranium ores and in unmineralized sandstones of the Colorado Plateau.

Morrison ores and the concentration in unmineralized sandstones of the Salt Wash is probably due almost entirely to the presence of higher initial amounts of mudstone in the ores, mainly in the form of interstitial clay and silt, mudstone pebbles, and thin mudstone beds. Selective mineralization of mudstone-bearing parts of the sandstone strata in the Morrison formation has been recognized for some time (Fischer, 1942, p. 380–381; Waters and Granger, 1953, p. 10).

Aluminum is an essential constituent of some of the major vanadium-ore minerals, which include clays and micaceous claylike minerals (Fischer, 1942, p. 370). (See Parts 5 and 10.) Some of the vanadium in the ore appears to have been taken up in preore clay minerals, but some is also present in more coarsely crystalline claylike or micacous minerals that appear to have crystallized in the ore (Hess, 1933, fig. 2; Fischer, 1942, p. 377 and fig. 54*A*; Waters and Granger, 1953, p. 12–20). Even though aluminum is an essential constituent of some of the major vanadium-ore minerals, most or nearly all of the aluminum in the ores probably was contained originally in the detrital components of the host sandstones, because the ratio of aluminum in ore to aluminum in unmineralized sandstone is closely comparable to similar ratios for titanium and zirconium, elements that are not known to be significant constituents of the ore minerals crystallized in place. (See section on titanium and zirconium in this chapter.)

The average concentration of aluminum in 38 ores from Triassic rocks is lower than the average obtained for unmineralized sandstones of the Shinarump and Moss Back members. As in the deposits of the Morrison this difference may be interpreted as due to selective mineralization, but in these rocks the selectivity would be for parts of the ore-bearing strata that contain less than average amounts of aluminum. The difference in aluminum concentration between the ores and the unmineralized sandstones is close to the limit of significance at 99 percent probability. The average aluminum content of the ores from Upper Triassic rocks is closely comparable to the average of the ores from the Morrison.

POTASSIUM

Potassium (figs. 4 and 5), like aluminum, is contained chiefly in feldspars and clay minerals, both in unmineralized sandstones and in the uranium ores. The distribution of potassium between the clay and feldspar components of unmineralized sandstones of the Salt Wash is estimated to be closely similar to the distribution of aluminum, approximately one-fourth to one-third in the clay fraction and the remainder mainly in the feldspars. Unlike aluminum, however, potassium appears to have nearly the same concentration in the ores as in the unmineralized rocks. Some factor such as selectivity of mineralization for potassium-lean but clay-bearing rocks or leaching of potassium by mineralizing solutions may be required to explain the observed differences in the potassium-aluminum ratios between ores from the Morrison and unmineralized rocks. Part of the observed difference between the potassium-aluminum ratio in the ore and the ratio in the unmineralized sandstones is probably due to the fact that most of the ores studied are from the uppermost sandstone strata of the Salt Wash member of the Morrison formation which appear to contain less potassium on the average than the remainder of sandstones of the Salt Wash.

The reverse differences between the potassium-aluminum ratios are represented in the ores and unmineralized sandstones from Upper Triassic rocks; the average of the samples studied suggests the ores contain slightly less aluminum whereas potassium appears to be higher in the ores than in the unmineralized sandstones. In a majority of the sandstones potassium is below the limit of sensitivity, however, and the apparent reversal of the aluminum-potassium relations in the Triassic rocks compared with the relations in the Morrison formation may be partly due to uncertainties of estimation or inadequate sampling of the ores and unmineralized rocks from the Upper Triassic. Potassium is considered to be almost entirely an intrinsic component of the ores in both the Upper Triassic rocks and the Morrison formation.

IRON

Iron (figs. 4 and 5) in unmineralized sandstones of the Salt Wash is contained largely in clay minerals and oxides physically inseparable from clay minerals, in detrital heavy minerals, and in authigenic sulfides, oxides, and carbonates. The average iron content of 14 chemically analysed claystones from the Salt Wash (Weeks, 1951, table 2) is 2.4 percent (arithmetic mean of average for 6 gray clays and average for 8 red clays). If the arithmetic-mean content of silt and clay (corresponding approximately to claystone or mudstone in composition) in the sandstones of the Salt Wash is about 6.5 percent (R. A. Cadigan, unpublished data), the arithmetic-mean content of iron attributable to the clay would be about 0.15 percent. The estimated arithmetic-mean content of iron in sandstones of the Salt Wash calculated from table 2 is 0.30 percent (see footnote 1, table 2). Iron directly associated with clay may thus account for about one-half of the total iron in sandstones of the Salt Wash, and this association is brought out by the moderately high iron-aluminum correlation (fig. 2). Part of the iron with the clay is contained in the clay-mineral lattices and part in the red clays as an extremely finely divided pigment, possibly hematite, which evidently imparts the red color (Weeks, 1951, p. 11–12). Perhaps one-fourth to one-third of the remaining iron may be attributable to opaque detrital heavy minerals and the rest mainly to authigenic iron minerals—pyrite, marcasite, hematite, goethite, and ferriferous carbonates.

Iron is nearly four times as abundant[4] in the samples of ores from the Morrison as in the unmineralized sandstones of the Salt Wash. Roughly a twofold difference would be expected from the correlation of iron with aluminum, leaving about half of the iron in the ores or about 0.4 percent in the median case to be accounted for. On the order of 0.1 percent of this "excess" iron is estimated to be tramp iron introduced into the samples during grinding. The proportions of tramp iron might vary considerably but the majority of "excess" iron appears to represent a real difference between the ores and equivalent unmineralized rocks and is considered an extrinsic component of the ores. If about 0.3 percent iron in the average ore is extrinsic and about 0.4 percent intrinsic, the bulk of the iron would be intrinsic but the extrinsic part of the iron would be the second most abundant extrinsic component of the Morrison ores. In many ore deposits from the Morrison iron may be dominantly extrinsic.

The estimated mean concentration of iron in the ores from Triassic rocks is greater than the estimated mean concentration in the unmineralized sandstones, but the difference is within the limits of confidence at 99 percent probability. It is possible that about the same quantity of iron is extrinsic in the average ore from Triassic rocks as in the average deposit from the Morrison, but the bulk of iron in ores from Triassic rocks is clearly intrinsic.

MAGNESIUM

The distribution of magnesium (figs. 4 and 5) among the mineral components of unmineralized sandstone of the Salt Wash is probably similar in some respects to the distribution of iron, with which magnesium has a moderate correlation. If two clays of the Salt Wash for which chemical analyses are available (Weeks, 1951, table 1) may be considered typical, about one-third of the magnesium in the average sandstone of the Salt Wash could be directly associated with the clay. About the same proportion is obtained if the geometric mean concentration of spectrographically determined magnesium in 32 mudstones (Newman, 1954, p. 44) is used as a basis of estimation. Part of this magnesium is in the clay lattice, but part may also be commonly present as very fine grained dolomite (Weeks, 1951, p. 8). The association of magnesium with clay, however, is much less strong than that of iron with clay, as is brought out by the subsignificant magnesium-aluminum correlation coefficient. The greater part of the magnesium in a majority of the sandstones is probably contained in dolomite independent of the clay, perhaps some of detrital origin but most of it probably in authigenic form. The lack of significant correlation (fig. 4) between magnesium and calcium, which is the principal cation associated with carbonate in sandstones of the Salt Wash, indicates that the amount of magnesium is largely independent of the total carbonate content of the rocks. The magnesium-calcium scatter diagram (not illustrated) reveals that the concentration of magnesium never exceeds the concentration of calcium, and the bulk of magnesium in any sample could, therefore, be contained in dolomite. If all the magnesium and calcium in the median unmineralized sandstone of the Salt Wash were calculated as dolomite and calcite the proportion of dolomite to calcite would be about 1 to 4. The moderate correlation of magesium with iron suggests that much of the dolomite may be ankeritic.

Magnesium is three times as abundant in the average of the ores from the Morrison as in the sandstones of the Salt Wash, and in the ores it has a high correlation with aluminum and a moderate correlation with calcium. Part of the observed difference may be due to selective mineralization of rocks with above-average magnesium content. The studies of Waters and Granger (1953, p. 14–15) suggest a possible selectivity of mineralization for rocks rich in the magnesian group of clays, the montmorillonites and chlorites, and the high correlation of magnesium with aluminum in the ores might be considered as suggestive that a major part of the magnesium in the ores was contained originally as an essential component of the original clays. On the other hand, Keller (Part 9) does not find an association of mineralized rock with montmorillonite, and three other elements—calcium, manganese, and sodium—thought to be contained or associated largely with carbonates also have a moderately high correlation with aluminum in ores from the Morrison. The bulk of the magnesium in a majority of ores from the Morrison is considered to be present as a carbonate, probably in the mineral form dolomite, as suggested by the moderately high magnesium-calcium correlation in the ores. The reason that magnesium has a moderately high cor-

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[4] The term "abundance" is generally reserved for the arithmetic-mean concentration in conventional geochemical usage. In this report relative abundances or abundance ratios are computed from the geometric means because the abundance ratios are sensitive to small errors of estimation and the geometric mean is a more stable statistic than the arithmetic mean. If the log-standard deviation is the same for two distributions for which an abundance ratio is calculated, then the same ratio is obtained for the geometric means as would be found for the arithmetic means. The standard deviations for most pairs of distributions compared in this report are closely similar.

relation with calcium in the ores from the Morrison and not in the unmineralized sandstones of the Salt Wash is probably because a much higher fraction of calcium is present in dolomite in the ores than in the unmineralized sandstone. If all the magnesium and calcium in the median ore were calculated as dolomite and calcite the proportion of dolomite to calcite would be greater than 2 to 1, as contrasted with 1 to 4 in the unmineralized sandstones. Because of the threefold higher concentration of magnesium in the ores it seems likely that a considerable part of the magnesium is extrinsic, though how much cannot at present be estimated. As in the case of iron, probably less than half of the magnesium in the average ore is extrinsic.

The difference in magnesium concentration between ores and unmineralized sandstones in Upper Triassic rocks is well within the 99 percent confidence interval of the means, and magnesium may be considered a dominantly intrinsic element in the majority of these ores with reasonable confidence.

TITANIUM AND ZIRCONIUM

Titanium and zirconium (figs. 4 and 5) exhibit high and moderate correlation in the unmineralized sandstones of the Salt Wash and in the ores from the Morrison respectively, and their manner of occurrence in both sandstones and ores is probably similar. Titanium has a high correlation and zirconium a moderate correlation with aluminum in both the ores and unmineralized sandstones, and the ratio of abundance of each element in the ores to the abundance in the sandstones is essentially the same as the ratio for aluminum in both the Upper Triassic rocks and the Morrison formation. This high degree of coherence suggests that the factors controlling the distribution of titanium and zirconium are essentially the same as those controlling aluminum, and both titanium and zirconium as well as aluminum are considered to be almost entirely intrinsic in the sandstone-type ores. Neither titanium nor zirconium are known to be essential or major constituents of any of the ore minerals in the sandstone-type uranium deposits and only rarely are they reported even as trace constituents in qualitative spectrographic analysis of the ore minerals (Weeks and Thompson, 1954).

Titanium in the unmineralized sandstones is associated closely with the clay component. The arithmetic-mean titanium content of 14 chemically analyzed claystones and siltstones from the Salt Wash (Weeks, 1951, table 2) is 0.32 percent, and the geometric-mean titanium content of 32 mudstones of the Salt Wash analyzed by semiquantitative spectrographic methods (Newman, 1954) is 0.1 percent. On this basis about one-fifth to one-fourth of the titanium in average unmineralized sandstones of the Salt Wash would be contained in the clay-silt component of sandstones. Whether any of this titanium is present in the clay lattice or whether most of it is present as a minutely divided titania polymorph, perhaps anatase, is not clear (Grim 1953, p. 49), but titania in amounts found in claystones of the Salt Wash are commonly found in kaolin group clays (Ross and Kerr, 1931, p. 163). The bulk of the remainder of the titanium is probably present in detrital heavy minerals such as ilmenite, ilmenomagnetite and ilmenohematite, and rutile, or in alteration products of these heavy minerals, mainly leucoxene and anatase. The high correlation of titanium with aluminum suggests that perhaps a major part of these heavy minerals is contained in the fine-grained fraction of the sandstones along with the clays.

Some zirconium is closely associated with the clay fraction of the sandstones, perhaps partly as a trace constituent of the clay minerals, but the bulk of the zirconium is evidently contained as zircon, about half of which can be separated as sand-sized detrital grains. As with the titanium heavy minerals, probably much of the rest of the zircon present in the sandstones is in the fine fraction, which may partly account for the correlation of zircon with aluminum; but some zircon could also be enclosed as minute inclusions in the light sand-sized mineral fractions, perhaps in feldspars.

BARIUM, STRONTIUM, AND CHROMIUM

The distribution of barium, strontium, and chromium (figs. 4 and 5) in the sandstones of the Salt Wash has been partially evaluated from analyses of the clay-silt- and sand-sized fractions and of heavy mineral separates. An appreciable part of the barium is in the fine fraction of the sandstones, though the bulk is evidently contained in coarser-grained interstitial barite, a large part of which is recovered in heavy mineral separates (R. A. Cadigan, personal communication). About one-third part of the strontium may commonly be associated with the fine fraction of the sandstones and the bulk of the remainder possibly substitutes as a trace constituent for calcium in the abundant calcite cement and for barium in the interstitial barite, as suggested by moderate strontium-calcium and strontium-barium correlation coefficients in the standstones of the Salt Wash member and the ores from the Morrison formation. Chromium occurs in such low concentrations in the unmineralized sandstones that its distribution is difficult to account for. Analyses of heavy minerals indicate that perhaps one-fifth to one-third of the chromium is in the heavy mineral fraction, which probably accounts for the moderate chromium-zirconium correlation in sandstones of the Salt Wash, and another part of the chromium, perhaps one-tenth to one-fifth is in the clay-silt fraction. The remainder of the chromium is dispersed in an unknown way in the sandstones.

Barium, strontium, and chromium each have a correlation with aluminum in unmineralized sandstones of the Salt Wash that is close to the lowest significant value at 99 percent confidence, and each element has a low to moderate correlation with aluminum in the Morrison ores. The ratio of abundance of the barium, strontium, and chromium, in the unmineralized sandstones of the Salt Wash to their abundance in the ores from the Morrison is nearly the same for each element and is somewhat greater than the ratio for aluminum. In the Triassic rocks all three elements are more abundant in the ores than in the unmineralized sandstones in contrast to aluminum, which is lower in the ores, though the difference in barium concentration between ore and unmineralized sandstone is within the confidence intervals of the means. A part of the barium, strontium, and chromium, in both the ores from the Morrison formation and Triassic rocks is interpreted as extrinsic, though the bulk of these elements in the majority of ores is probably intrinsic.

In a few sandstone-type uranium deposits in the Triassic rocks and the Morrison formation any one of the three elements, barium, strontium, or chromium may possibly be a major extrinsic component of the ores. Barium has been found to be a major extrinsic element in uraniferous and nonuraniferous deposits along faults in sandstones of Jurassic age and in the Brushy Basin member of the Morrison formation north of the Ute Mountains, Colorado, and Garrels and others (Part 15) have found barium to be locally enriched within a uranium deposit in the Salt Wash. Similarly, strontium has been found to be a major constituent of a uraniferous vein deposit in the vicinity of sandstone-type uranium deposits in the Morrison formation and has been found to be locally enriched within a ore deposit in the Salt Wash (Part 15). Sandstone with more than average chromium is closely associated with vanadium-uranium deposits in the Entrada sandstone of Jurassic age on the eastern margin of the Colorado Plateau[5] (Fischer, Haff, and Rominger, 1947, p. 125 and plate 1; Part 19). In Sinbad Valley, in westernmost Colorado, chromium-rich sandstone has been found in an unidentified formation (Hillebrand and Ransome, 1905, p. 21), probably the Wingate sandstone of Triassic age, in the vicinity of uranium and copper deposits. Chromium has also been found in a conspicuous concentration associated with uranium deposits in the Wingate sandstone of Temple Mountain, in central Utah, and near uranium deposits in the Morrison formation in the vicinity of Grants in northwestern New Mexico (L. S. Hilpert, personal communication).

BORON

On the basis of spectrographic analysis of heavy-mineral and clay-fraction separates and of mudstones, about half or more of the boron (figs. 4 and 5) in sandstones of the Salt Wash is estimated to be contained in the heavy-mineral fraction of the sandstones and a significant part of the remainder in the fine fraction. Probably the bulk of the boron is carried in tourmaline, which is the only detrital mineral identified in the sandstones of the Salt Wash that contains boron as an essential constituent (see part 2 for commonly occurring heavy minerals). Some of the boron associated with the fine fraction is probably present in soluble borates (A. D. Weeks, personal communication). In ores from the Morrison boron has a moderate correlation with aluminum and a low to moderate correlation with a number of other elements that are associated with aluminum probably because of association of detrital heavy minerals and soluble salts with the clay-silt fraction of the rocks. The estimated mean boron content of the ores is about twice the estimated mean boron content of the unmineralized sandstones, a difference that could be attributed to the higher mudstone content of the ores. The boron content of ores from Upper Triassic rocks is estimated to be essentially the same as the content of the unmineralized sandstones. In ores from both Upper Triassic rocks and the Morrison formation boron is considered almost entirely intrinsic.

BERYLLIUM

The distribution of beryllium (fig. 6) in the unmineralized sandstone can be inferred only from indirect evidence. Beryllium has not been detected by spectrographic methods in the sandstones of the Salt Wash and only rarely in sandstones of the Shinarump and Moss Back, but it has been detected in many mudstones of the Salt Wash. The bulk of the beryllium may be contained in the clay fraction of the unmineralized rocks. A few ores from the Morrison and about one-third of the ores from Upper Triassic rocks contain beryllium in detectable concentrations. The occurrence of detectable beryllium in the few ores from the Morrison can probably be attributed to high mudstone content of the ores in which beryllium is detected. About 75 percent of the ores from Triassic rocks which contain detectable beryllium have more than average concentrations of aluminum. The bulk of beryllium may be intrinsic in ores both from Triassic rocks and from the Morrison, but a significant part of the beryllium in ores from Triassic rocks could also be extrinsic.

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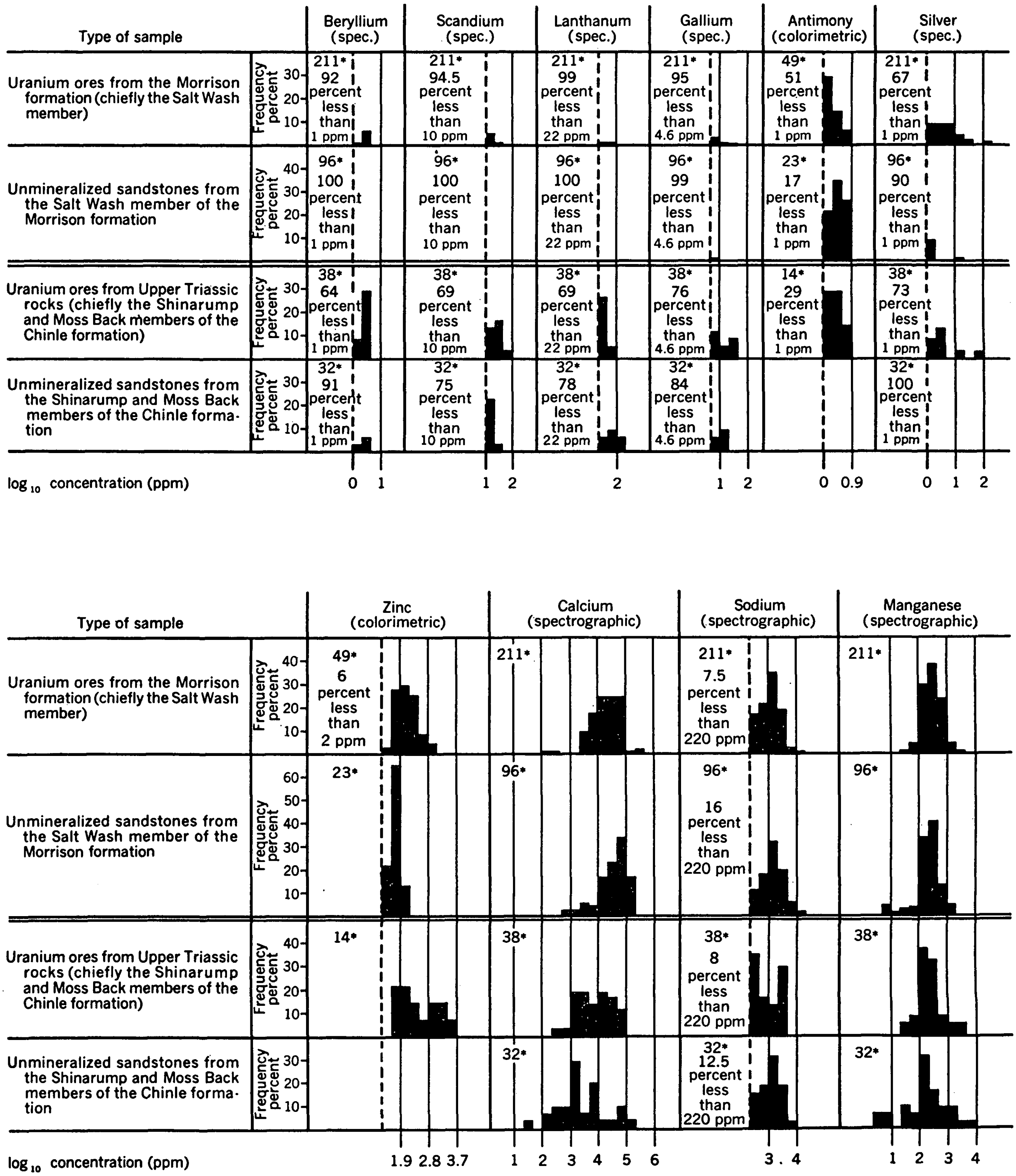
[5] Bush, A. L., and Bryner, Lenold, written communication, 1953.



*Number of uranium deposits or number of samples of sandstone

FIGURE 6.—Frequency distribution of the dominantly intrinsic elements of uranium ores that are contained in uranium ores and in unmineralized sandstones of the Colorado Plateau (beryllium through manganese).

SCANDIUM, LANTHANUM, AND GALLIUM

Scandium and lanthanum have not been detected and gallium only rarely detected in unmineralized sandstones of the Salt Wash (fig. 4). Although each of these elements occurs in concentrations above the spectrographic limits of sensitivity in only a few of the ores from the Morrison studied, gallium was detected in trace amounts (less than 4.6 parts per million (ppm)) in more than 50 percent of the ores; hence its median concentration is essentially at the limit of sensitivity. The mean content of scandium and gallium of 32 mudstones from the Salt Wash, on the other hand, is above the spectrographic limit of sensitivity (Newman, 1954, p. 44); lanthanum has been detected in many mudstones and has been found in concentrations considerably above the limit of sensitivity in heavy-mineral separates. Most of the scandium, lanthanum, and gallium may be contained in the fine fraction of the sandstones, either in clays or associated heavy minerals. These elements occur in concentrations above the spectrographic limit of sensitivity mainly in the more aluminous Morrison ores in which their infrequent occurrence is probably accounted for by above-average mudstone content.

In Upper Triassic rocks scandium, lanthanum, and gallium occur in concentrations above the spectrographic limit of sensitivity in 15 to 25 percent of the sandstones studied and are found in the ores with somewhat greater frequency. Lanthanum and gallium are high mainly in high-aluminum ores and scandium appears to have a moderate tendency to accompany high-aluminum ores. The abundance of these elements is probably related to the initial mudstone content of the ores. All three elements are considered mainly intrinsic in ores both from Upper Triassic rocks and from the Morrison formation.

ANTIMONY

The distribution of antimony (fig. 6) has been studied by colorimetric analyses of about one-fourth of the samples of ores and of sandstones of the Salt Wash member; no analyses have been completed for unmineralized sandstones of the Shinarump and Moss Back members. The estimated mean concentration of antimony in 49 ores from the Morrison is about half the estimated mean for 23 samples of sandstone of the Salt Wash and the estimated mean for 14 ores from Upper Triassic rocks is about the same as the mean for sandstones of the Salt Wash. These data, though incomplete, strongly suggest that antimony is almost entirely intrinsic in the ores.

SILVER AND ZINC

The distribution of silver and zinc (fig. 6) in the unmineralized sandstones is largely unknown. Silver has been reported in concentrations above the spectrographic limits of sensitivity in a few percent of the unmineralized sandstones of the Salt Wash, but most of the analyses in which silver was detected may be slightly biased. Zinc has not been detected by spectrographic methods in the unmineralized sandstones and the statistics on zinc are based entirely on colorimetric analyses of a limited suite of samples. Rankama and Sahama (1950, p. 713) reported concentrations of zinc in clays and shales that are considerably higher than the estimated arithmetic-mean zinc content of 24 sandstones of the Salt Wash (calculated from table 2). An appreciable part of the zinc in the sandstones may be in the clay fraction, though zinc does not appear to correlate with aluminum in the samples studied. Rankama and Sahama (1950, p. 706), also, reported that silver is enriched in some argillaceous rocks, and clays could be the dominant carriers of silver in the sandstones of the Salt Wash member.

The estimated mean concentration of silver in 211 ores and the mean concentration of zinc in 49 ores from the Morrison formation are each about twice as great as the corresponding means for unmineralized sandstones of the Salt Wash, though little confidence should be attached to the ratio for silver. If silver and zinc are contained largely in the clay fraction of the sandstones this difference could be largely due to selective mineralization of mudstone-bearing sandstone. On the other hand, the higher concentrations of both silver and zinc in the ores from the Morrison tend to occur with high concentrations of copper and lead, elements which are interpreted as mainly extrinsic, and silver occurs locally in concentrations from 10 to more than 100 times higher than the spectrographic limit of sensitivity. In a majority of ores from the Morrison silver and zinc may be mainly intrinsic but in those deposits that contain high concentrations of silver and zinc both elements are probably mainly extrinsic. The ratios of abundance of silver and zinc in ores from Upper Triassic rocks to their abundance in the unmineralized sandstones is unknown, but both elements could be mainly extrinsic in these ores. Silver has been the principal ore element in sandstone-type uranium deposits in the Chinle formation at Leeds in southwestern Utah (Hess, 1933, p. 452–455; Proctor, 1953, p. 78–96).

CALCIUM, SODIUM, AND MANGANESE

Calcium and manganese are contained principally as carbonates and sodium, partly as a bicarbonate in the unmineralized sandstones of the Salt Wash (figs. 4 and 6). Calcium, the second most abundant element in the sandstones, occurs mainly in calcite, which is the dominant cement of the sandstones in the Salt Wash

(Part 2), but a significant part is also contained in dolomite. Locally, in the vicinity of salt structures, a major part of the calcium is also present as the sulfate, gypsum. Traces of calcium are present in soluble bicarbonate form, in plagioclase, and in other detrital minerals. Most of the calcite in the sandstones forms a relatively coarse grained interstitial cement, but some is also fine grained and associated with the clay (Weeks, 1951, p. 8–10; 1953, table 1). On the order of one-tenth to one-fifth of the calcium may be contained in the fine fraction of the sandstones.

Manganese has a very high correlation with calcium both in the unmineralized sandstones and in the ores from the Morrison and is probably contained largely in calcite which it enters readily in solid solution. The proportion of manganese to calcium in the sandstones is so low that if all the calcium and manganese were calculated as carbonate less than 1 percent of the combined carbonate would be rhodocrosite in the average sandstone. A minor proportion of the manganese is probably present in the oxide form, perhaps mainly as pyrolusite, and a trace of manganese is contained in heavy minerals. Locally the Morrison formation contains ore-grade deposits of manganese oxides in the sandstones (Baker, Duncan, and Hunt, 1952, p. 66–68).

Sodium is contained principally in plagioclase feldspars and in nonsilicate sodium salts in the sandstones of the Salt Wash. Flame photometric analyses of the sand-sized fraction of 14 sandstones of the Salt Wash (R. A. Cadigan, written communication) suggest that the sodium in the feldspars represents about half of the total sodium in the sandstones of the Salt Wash. The remainder of the sodium is thought to be contained mainly in soluble salts, principally sodium bicarbonate. Extraction of salts by water at 100° C. from a core of carnotite ore in the sandstone of the Salt Wash yielded 28,900 ppm soluble solids per unit volume of pore water, of which 1,330 ppm, or about 0.006 percent by weight of the total rock was sodium (calculated from data by Manger, 1954a, p. 62 and 63). The principal anion was bicarbonate, but carbonate, sulfate and a trace of chloride were also present. Similar quantities of soluble solids were extracted from other segments of sandstone core, both mineralized and unmineralized (Manger, 1954b, p. 92). Weeks (1953, table 1) reports extracting burkeite, $Na(CO_3)\ (SO_4)_2$; Thenardite, Na_2SO_4; halite; and soda niter, $NaNO_3$, from clays of the Salt Wash. The present ground waters in the Salt Wash member are principally bicarbonate solutions (Part 4), and it is likely that the bulk of the soluble sodium is combined with bicarbonate. A moderate correlation of sodium with calcium and with manganese in the sandstones and a high correlation in the ores suggest that the bulk of the sodium (as bicarbonate) is physically associated with the carbonates. Some of the soluble sodium may also be contained in montmorillonite clays (Weeks, 1953, p. 10). Probably only a fraction of the soluble sodium is extracted by a hot-water leach if the bulk of the sodium salts is intimately mixed with the carbonate cement of the sandstones.

The ratio of abundance in the Morrison ores to the abundance in unmineralized sandstones of the Salt Wash is about 0.6 for calcium, approximately 1.0 for sodium, and 1.4 for manganese. Calcium is the only element that is lower in the ores from the Morrison than in the unmineralized sandstones. Among the various factors that have contributed to the apparent "deficiency" of calcium in the ores, two are probably the most important. It is possible that the present milling practice on the Colorado Plateau, which has resulted in a penalty for high-lime ores from which vanadium is extracted (U. S. Atomic Energy Commission, 1948), has caused ore producers to mine and ship ore preferentially from deposits with low calcium content, and has introduced bias into the sampling of ore deposits with respect to calcium and closely associated elements. The effect of this bias is thought to be negligible. The principal factor contributing to the apparent "deficiency" is probably selective mineralization of sandstones with low content of carbonate cement. The samples studied of unmineralized sandstone from the uppermost sandstone strata of the Salt Wash, the principal host of the producing ore deposits, have an average calcium content only half as great as the average for the remainder of sandstones of the Salt Wash. Another likely significant factor may have been actual leaching of calcite from the ore deposits either during or after mineralization. Leaching of the calcite cement during intermediate stages of oxidation of the ores, owing to low-pH conditions produced by alteration of sulfides, has been suggested by Weeks and Coleman (personal communication) and in Part 14. Most of the ores studied from the Morrison are at least partially oxidized and many are nearly completely oxidized. In the ores, but not in the unmineralized sandstones, calcium and manganese have a moderate correlation with titanium, zirconium, potassium, and aluminum, elements associated with the clay-silt fraction, suggesting that a significant part of the carbonate left in the ores is contained in the mudstone component where it would be the least subject to leaching.

Despite the fact that calcium content is lower in the Morrison ores than in the unmineralized sandstones, manganese, which has a very high correlation with calcium in both the ores and sandstones, has a higher value in the ores. The explanation for this apparently anomalous relation may lie partly in the redistribution of calcium and manganese during oxidation. Calcium may tend to be flushed out of the deposits by acid oxidizing solutions, whereas, the manganese originally contained in carbonate probably would tend to reprecipitate as the relatively insoluble tetravalent oxide. Some of the manganese may also be extrinsic. However, the bulk of manganese, as well as calcium and sodium, is considered intrinsic in the Morrison ores.

In the ores from Upper Triassic rocks calcium and manganese are 3 and 2 times respectively more abundant than they are in the unmineralized sandstones. Whether this indicates introduction of carbonate into the ores or perhaps selective mineralization of carbonate-rich sandstones is not clear. It should be noted that the confidence interval of the mean is fairly high for calcium in the ores and exceptionally high for manganese in the sandstones. Though the observed differences are probably significant, too great a weight should not be placed on the calculated abundance ratios.

ORE ELEMENTS

Uranium contributes the bulk of the value to the ores now mined on the Colorado Plateau, though in a few ores, vanadium, which is also extracted, may be the principal ore element in terms of its contribution to the price of the ore. In all ores produced from the Morrison formation vanadium as well as uranium is an ore element. Copper is paid for by uranium ore buyers in a few uranium ores produced from the Shinarump member in southeastern Utah. Selenium has been considered as a possible byproduct of some ores, but to date it has not been extracted. In a few sandstone-type ores mainly from Triassic beds, and in limestone ores from northwestern New Mexico uranium is the only element that contributes to the value of the ore.

URANIUM AND VANADIUM

Uranium and vanadium (figs. 4, 7, and 8) are not only the principal ore elements but are also the elements that have the highest ratios of abundance in the ores to their abundance in unmineralized sandstones in both Upper Triassic rocks and the Morrison formation. The minimum acceptable grade established by U. S. Atomic Energy Commission (1948) is about 1,000 times as great as the mean concentration of uranium in 23 samples of unmineralized sandstone of the Salt Wash (table 1). The ratio of the mean for vanadium in ores and in unmineralized sandstones is about 500 in the samples from the Morrison formation and about 20 in

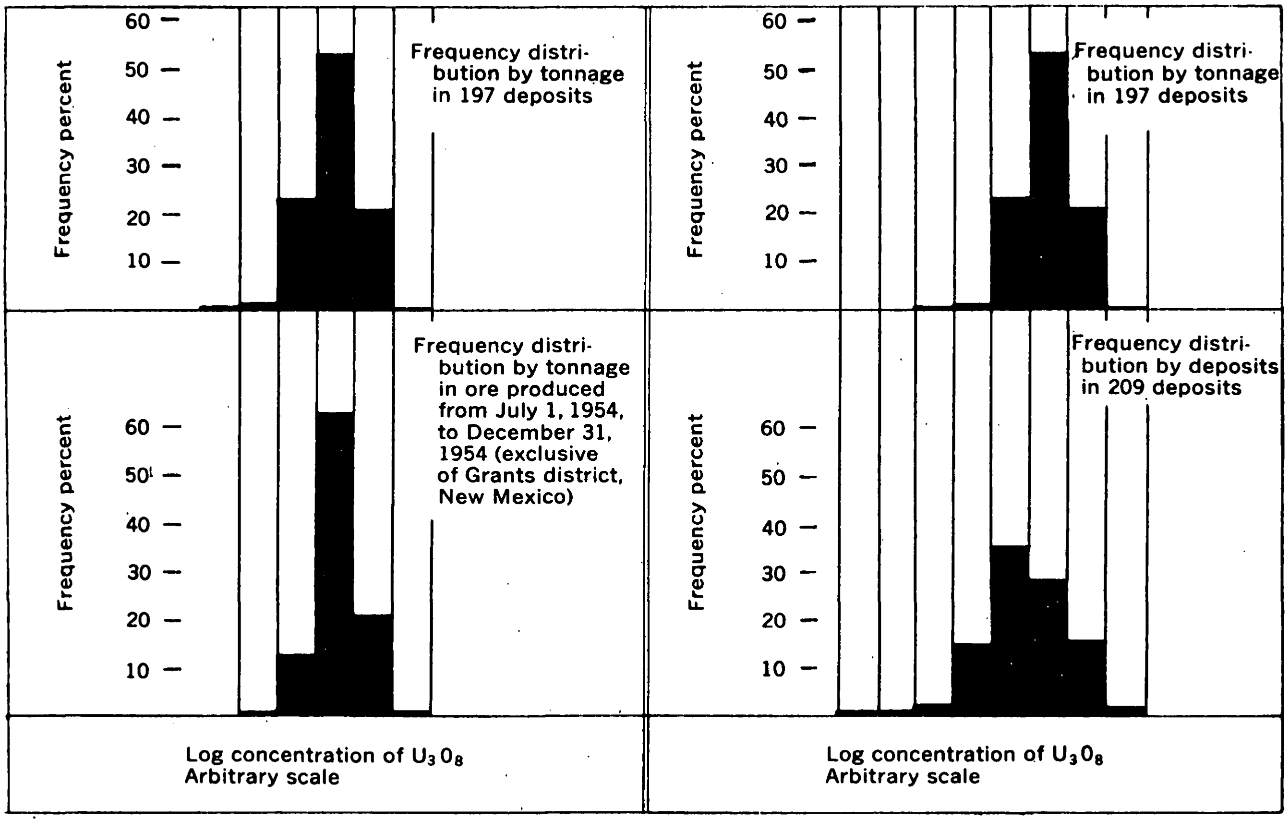


FIGURE 7.—Frequency distribution of U_3O_8, as determined by fluorimetric analysis, in uranium ores from the Morrison formation.

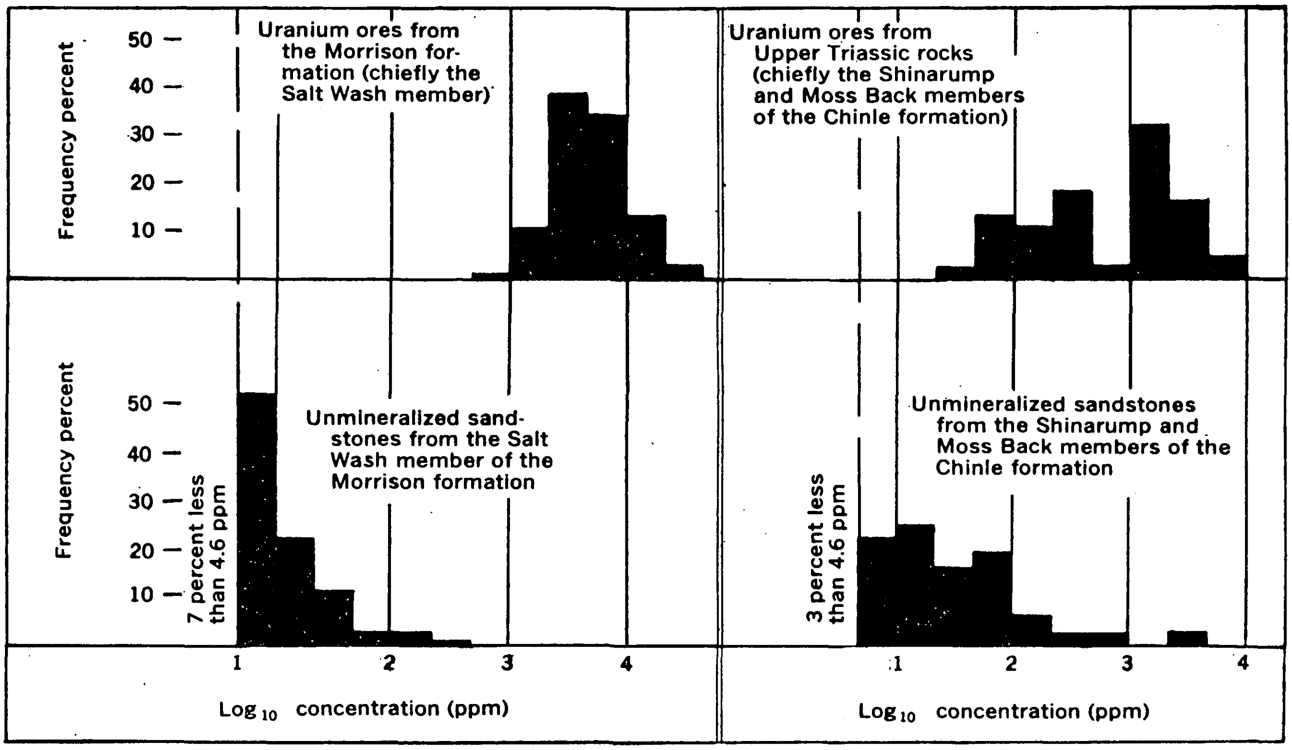


FIGURE 8.—Frequency distribution of vanadium, as determined by spectrographic analysis, in uranium ores and unmineralized sandstones of the Colorado Plateau.

the Upper Triassic rocks. Though the ratio is less for vanadium than for uranium, vanadium is the most abundant extrinsic element in the Morrison ores.

Some comparisons can be drawn between the uranium content of the samples studied and the uranium content of the ore produced over a considerable period without specifying arithmetic-mean concentrations, which are withheld for security reasons. The arithmetic-mean concentration of uranium, weighted according to tonnage, in all ore represented by the samples for which tonnage data are available from 197 deposits in the Morrison formation, is identical (to two significant figures) to the arithmetic-mean concentration of uranium in all ore produced from the Morrison formation for each of four 6-month periods in 1953 and 1954—exclusive of ore produced from the Grants district of New Mexico, for the period July 1 to December 31, 1954. The frequency distribution of U_3O_8 by tonnage—calculated from total tonnage and weighted-average uranium content of ore from each deposit—for the 197 deposits is closely similar to the frequency distribution by tonnage of all ore produced from the Morrison formation, exclusive of the Grants district—calculated from total tonnage and weighted average uranium content of ore produced from each deposit per month or semimonthly settlement—for the period July 1 to December 31, 1954 (fig. 7).

The arithmetic-mean concentration of uranium, weighted according to tonnage, in all ore represented by the samples from 38 deposits in Upper Triassic rocks is 12 percent less than the arithmetic-mean concentration of uranium in all ore produced from the Chinle formation in 1953 and 1954, but it is identical (to two significant figures) to the arithmetic-mean concentration of uranium in all ore produced from the Chinle formation in the latter half of 1954.

The frequency distribution of U_3O_8 by tonnage in the 197 deposits from the Morrison formation may be compared in figure 7 with the frequency distribution of U_3O_8 by deposits in 209 of the deposits studied for which fluorimetric assays are available. The first distribution weights the frequency heavily in favor of large producers; whereas, in the second distribution each of the 209 deposits is given equal weight, whether the amount of ore represented is large or small. It is the second type of distribution that is represented by all the histograms given for spectrographic and colorimetric analyses. The two types of distributions provide estimates of two entirely different parameters of the uranium distribution which should be carefully distinguished: the arithmetic mean of the distribution by tonnage, when multiplied by the total tonnage, gives the total quantity of U_3O_8 produced, whereas the geometric mean of the distribution by deposits gives an estimate of the median grade of uranium in randomly selected deposits. It is of interest that, though the modes of the two types of distribution are significantly displaced, the estimated arithmetic-mean concentration of U_3O_8 calculated from the distribution by deposits is only 15 percent less than the estimated arithmetic mean calculated from distribution of tonnage.

Concentrations of most elements in the ores from the Morrison formation are virtually independent of the grade of uranium. Only vanadium, iron, and titanium correlate significantly with uranium, and all three of the correlations are low, that of titanium at the limit of significance. Even though deposition of the uranium ore appears to have been selective with respect to mudstone content and other lithologic features of the host sandstone strata, and although several accessory elements appear to have been introduced by the mineralizing processes, uranium exhibits no strong affinities in its grade distribution among deposits either for detectable intrinsic elements or for accessory extrinsic elements. The distribution of uranium may, however, have been strongly influenced by the distribution of organic carbon (Parts 5, 12, and 14), analyses for which are not yet available. The mineral forms taken by uranium in the deposits are listed in Part 5.

The arithmetic mean grade of V_2O_5, weighted according to tonnage, for the samples of Morrison ores studied is 6 percent less than the mean of all the ore from the Morrison (exclusive of ore from the Grants district) produced in 1953 and 1954 (table 3). This small difference may be due to weight given among the samples studied to deposits in the Slick Rock district of southwestern Colorado. The weighted mean for the samples from 38 deposits in Upper Triassic strata is significantly lower than the mean of ore produced from Upper Triassic rocks in 1953 and 1954. Ore produced from the Upper Triassic during this period is heavily weighted toward one large mine in the Shinarump member, whereas more than half of the tonnage represented by the samples studied is from mines in a small area around Temple Mountain in central Utah, all producing from the Moss Back member of the Chinle formation. The mean for the samples studied from deposits in the Upper Triassic is nearly the same as the mean for ore produced from the Chinle formation in the latter half of 1954, both for V_2O_5 and U_3O_8.

TABLE 3.—*Comparison of weighted arithmetic-mean grade of vanadium pentoxide in ores produced in 1953 and 1954 and in ores represented by samples studied*

[Arithmetic-mean grade of V_2O_5 weighted according to tonnage; based on chemical assays by ore buyers]

Formation from which ore is produced	6-month period ending—	V_2O_5 (percent)
Undifferentiated Triassic rocks	June 30, 1953	1.08
Shinarump member	Jan. 1, 1954	1.25
	July 1, 1954	1.07
	Dec. 31, 1954	.92
Chinle formation (excluding Shinarump member)	Jan. 1, 1954	.87
	July 1, 1954	.72
	Dec. 31, 1954	.58
Weighted mean for all Triassic rocks, Jan. 1, 1953, to Dec. 31, 1954		0.85
Weighted mean for samples from 38 deposits in Triassic rocks		.59
Morrison formation [1]	June 30, 1953	1.65
	Jan. 1, 1954	1.66
	July 1, 1954	1.64
	Dec. 31, 1954	1.67
Weighted mean for Morrison formation [1] Jan. 1, 1953 to Dec. 31, 1954		1.65
Weighted mean for samples for 197 deposits in Morrison formation		1.55

[1] Exclusive of ores produced from Grants district, in New Mexico, during period ending December 31, 1954.

The frequency distribution of vanadium in the ores and unmineralized sandstones, based on semiquantitative spectrographic analyses, is given in figure 8. Histograms given for the ores are for frequency by deposits, not by tonnage, and as with uranium, neither these histograms nor the means computed from them given in table 2 can be compared directly with production data. In the histograms for deposits given in figure 8 equal weight is given to all deposits, whether large or small, whereas the great bulk of production from deposits in Upper Triassic rocks, in particular, is from only a small percentage of the mines producing at present.

Vanadium in the ores from the Morrison formation has a high correlation with aluminum, a moderate correlation with lead, zirconium, magnesium, and uranium, and a low correlation with many other elements including several that tend to correlate with aluminum. The high correlation with aluminum illustrates a strong tendency for vanadium to be more abundant in the more aluminous ores of the Morrison formation, a relation interpreted as due to selective precipitation of vanadium by clay minerals in the rocks that received the ore elements. The minerals in which vanadium is primarily contained in the deposits are given in part 5. In the oxidized deposits the bulk of the vanadium is contained in micaceous or claylike silicates.

ACCESSORY EXTRINSIC ELEMENTS

Most of the accessory extrinsic elements in the sandstone-type uranium ores of the Colorado Plateau were recognized more than 30 years ago. With reference to the Colorado Plateau uranium-vanadium deposits Lindgren wrote (1923, p. 440–441):

> The ores are later than the beds which they follow, and are characterized by a very strange assortment of elements among which, besides the two already mentioned, are copper, lead, silver, barium, chromium, nickel, molybdenum, and selenium.

To this list can be added only three other elements, cobalt, arsenic, and possibly yttrium, which can be shown from the present study to be characteristic extrinsic elements in the sandstone-type uranium ores. The principal elements detectable by the spectrographic method that are extrinsic in a large majority of ores from both the Upper Triassic rocks and the Morrison formations are uranium, vanadium, cobalt, nickel, copper, arsenic, molybdenum, and lead.

COPPER AND LEAD

The abundance of copper (figs. 4 and 9) is about 7 times greater in Morrison ores than in unmineralized sandstones of the Salt Wash and about 3 times greater in ores from Upper Triassic rocks than in unmineralized sandstones of the Shinarump and Moss Back. Lead is more than 9 times as abundant in ores from the Morrison as in the unmineralized sandstones and about 6 times as abundant in the ores as in the sandstones in Upper Triassic rocks. Though the ratio of abundances for copper is lower for ores and rocks from the Triassic than for the Morrison formation, because of the unusually high concentration of copper in the unmineralized sandstones of Triassic age, the amount of copper that has probably been introduced into the average ore in the Triassic strata is more than twice as great as the amount probably introduced into average Morrison ores.

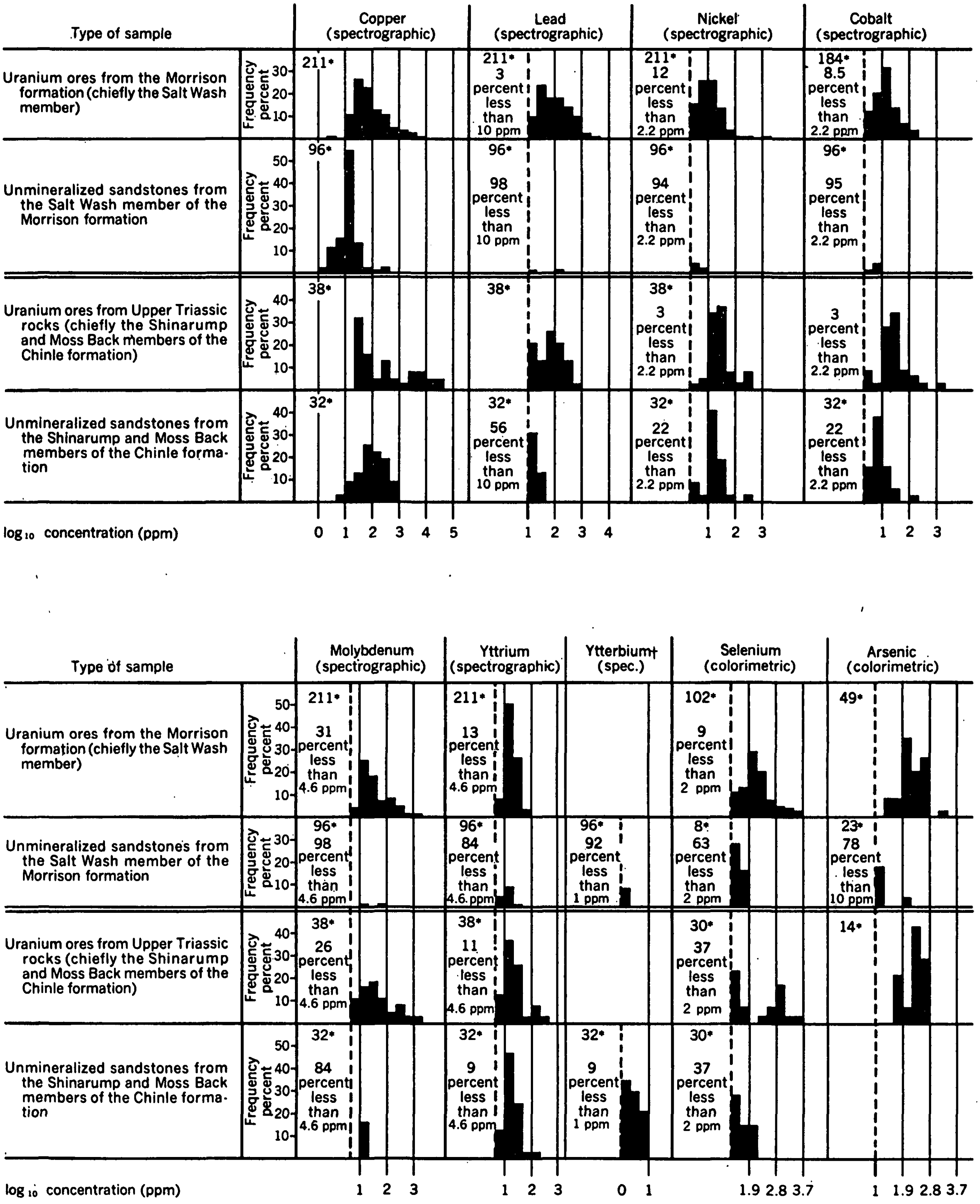
Lead (figs. 4 and 9) in the sandstone-type uranium ores is of at least three origins: (1) intrinsic lead contained in the rocks just prior to mineralization, (2) extrinsic lead introduced into the deposits, probably at the time of initial uranium mineralization, and (3) radiogenic lead derived in the deposits by decay of the uranium in the deposits since initial mineralization. Isotopic analyses of lead extracted from some of the pulp samples included in this study (Stieff, Stern, and Milkey, 1953, p. 19, samples GS–40, 41, 42, 47, 48, and 49) indicate that the proportion of radiogenic lead derived in place, in bulk samples of ore from the Morrison, ranges from about 5 to more than 80 percent of the total lead. The content of radiogenic lead derived in place tends to be proportional to the uranium content of the ores, and the highest proportions of radiogenic lead derived in place generally are found in ores that have the lowest concentrations of total lead. On the basis of the analyses given by Stieff, Stern, and Milkey (1953, p. 18 and 19) it is estimated that less than half of the lead in ores from the Upper Triassic rocks and the Morrison formation with average grade and average lead content is derived by decay of uranium at the locus of the present deposits.

In the ores from the Morrison formation copper and lead are closely related, as is shown by a high correlation. Both copper and lead have low to moderate correlation with the elements associated with carbonates in the ores. A moderate correlation of copper and lead with aluminum, and low to moderate correlation of copper with some elements associated with aluminum and calcium in the unmineralized sandstones of the Salt Wash also suggests some affinity of copper and lead both for the aluminous or clay-silt fraction of the rocks and for the carbonate cement. The distribution of lead in the unmineralized sandstones is largely unknown, but lead is generally present in detectable concentrations in mudstones of the Salt Wash (Newman, 1954, p. 44) even though rarely reported in sandstones of the Salt Wash, suggesting that much of it may be contained in the clay-silt fraction. Higher frequency of detectable lead in the sandstones of the Shinarump and Moss Back members may be due to higher average content of clay. In the low-valent ores extrinsic copper and lead are probably contained primarily as sulfides (Part 5).

Copper and lead correspond closely in their regional distribution in the ores. Both elements have greater frequency of high concentration in uranium deposits, mainly in the Morrison formation, in an area partially coincident with a region of salt structures that lies athwart the Colorado-Utah State line (Shoemaker, 1954, p. 71 and 76). Both elements also have a greater frequency of high concentrations in uranium deposits, mainly in Upper Triassic strata, in an area between the San Juan and Colorado Rivers in southeastern Utah and in an area on the San Rafael Swell in central Utah. The regional distribution of above average concentrations of silver (Shoemaker, 1954, p. 77) and zinc in the ores resembles that of copper and lead.

NICKEL, COBALT, AND MOLYBDENUM

Nickel and cobalt (figs. 4 and 9) are estimated to be about 20 times as abundant in ores from the Morrison formation as in unmineralized sandstones of the Salt Wash, though so few samples of the sandstones contain detectable concentrations of nickel and cobalt that these estimates should be regarded only as indicating the order of magnitude of the ratio. Molybdenum (figs 4 and 9) is more than three times as abundant in the ores from the Morrison as in the sandstones and the ratio of abundance for molybdenum is probably as large as the ratios for nickel and cobalt. In the Upper Triassic



•Number of uranium deposits or number of samples of sandstone

†Spectrographic analysis of ytterbium in uranium ore is interfered with by vanadium

FIGURE 9.—Frequency distribution of the dominantly accessory extrinsic elements of uranium ores contained in uranium ores and in unmineralized sandstones on the Colorado Plateau.

rocks the estimated ratios of abundance between ores and unmineralized sandstones are about 3 for nickel, 5 for cobalt, and 9 for molybdenum. Again, the estimated ratio for molybdenum should be regarded as indicating only the order of magnitude. The ratios of abundance for nickel and cobalt are low in the Triassic rocks because of the much higher concentrations of these two elements in unmineralized sandstones of the Shinarump and Moss Back members as compared with sandstones of the Salt Wash.

Nickel and molybdenum have a moderately high correlation in Morrison ores. Like uranium and unlike all other elements for which the correlation in the ores has been calculated, nickel and molybdenum show no significant correlation with aluminum. Both nickel and molybdenum exhibit a moderate correlation with iron and low correlation with yttrium; molybdenum has a significant but low correlation with chromium and zirconium as well. The correlation of cobalt has not been calculated because of interference by uranium in some of the cobalt analyses, but cobalt is known to correlate highly with nickel and probably has associations similar to those of nickel in the ores. The correlation of nickel with iron probably reflects an association with iron sulfides, which commonly contain appreciable concentrations of nickel and cobalt (Hegemann, 1942, p. 125–138) and which are known to contain relatively high concentrations of nickel and cobalt in some of the sandstone-type uranium deposits of the Colorado Plateau (Part 5). The bulk of nickel and cobalt in the low-valent ores may be contained in bravoite or nickeliferous and cobaltian pyrite. Molybdenum may enter the iron sulfides to some extent but the molybdenum sulfides molybdenite and jordisite have also been found (Part 5).

The concentration of nickel and cobalt in the uranium deposits tends to be broadly zoned across the central part of the Colorado Plateau. Nickel and cobalt tend to be higher in ores from both the Upper Triassic rocks and the Morrison formation toward the west or northwest part of the region and lower toward the east or southeast (Shoemaker, 1954, p. 75). Molybdenum appears to follow a similar pattern in deposits in the Morrison formation but is more erratically distributed in the deposits in Upper Triassic rocks (Shoemaker, 1954, p. 74).

YTTRIUM AND YTTERBIUM

Yttrium (figs. 4 and 9) is tentatively considered a dominantly extrinsic element in the ores from the Morrison formation. It is estimated to be about eight times more abundant in the ores than in unmineralized sandstones of the Salt Wash. This estimate is subject to large uncertainties because the large majority of sandstones analyzed did not contain detectable yttrium and because some variation exists in the limit of sensitivity as estimated by individual analysts. In the ores yttrium has a moderate correlation with iron, nickel, molybdenum, vanadium, titanium, barium, and aluminum. The correlations with zirconium, boron, and titanium suggest that a part of the yttrium in the ores is in detrital heavy minerals, which spectrographic analyses show to be the principal carriers of yttrium in the unmineralized Salt Wash sandstones. The correlations with iron, nickel, and molybdenum suggest some affinity of yttrium with the nickel-cobalt-molybdenum group of extrinsic elements. As in the case of iron, about half of the yttrium in Morrison ores may be intrinsic and about half extrinsic. In Upper Triassic rocks the concentration of yttrium in ores and in unmineralized sandstones is practically identical, and yttrium is considered largely intrinsic in the ores. The regional distribution of yttrium in all ores is similar to the distribution of nickel, cobalt, and molybdenum, but is more erratic (Shoemaker, 1954, p. 72).

Spectrographic analyses of ytterbium (figs. 4 and 9) in the ores has been prevented by interference from high concentrations of vanadium. Ytterbium has a very high correlation with yttrium in heavy-mineral separates from sandstones of the Salt Wash and is a member of the yttrium group of rare earths which are generally associated in nature (Rankama and Sahama, 1950, p. 517). Ytterbium may, like yttrium, be partly extrinsic in ores in the Morrison formation.

SELENIUM

Selenium (fig. 9) is more than six times as abundant in the average of the ores from the Morrison as in the unmineralized sandstones of the Salt Wash and about twice as abundant in the average of ores from Upper Triassic rocks as in the unmineralized sandstones of the Shinarump and Moss Back members. Unlike the distribution of all other elements investigated, the distribution of selenium in the ores studied from Triassic rocks is bimodal. One mode corresponds with the probable modal concentration in the unmineralized sandstones and the other mode is about 50 times higher. This unusual distribution is due to the high proportion of deposits represented from one small area, at Temple Mountain in central Utah, where the uranium deposits are unusually rich in selenium. Nearly all other ores studied from Triassic rocks are comparable in selenium content to the unmineralized sandstones. The distribution of selenium in Morrison ores is more nearly lognormal. Selenium is considered dominantly extrinsic in Morrison ores and in ores from Upper Triassic strata at Temple Mountain but dominantly intrinsic in most other ores from Upper Triassic rocks.

The regional distribution of selenium in ores of the Morrison formation (Shoemaker, 1954, p. 73) is similar to the regional distribution of nickel, cobalt, and molybdenum. A majority of the more richly seleniferous ores are found northwest of the Colorado River. The association of selenium with elements that may be contained mainly in sulfides in low-valent ores is an expectable one. Iron sulfides, into which selenium will enter by substitution for sulfur (Williams and Byers, 1934), locally contain as much as 1 percent selenium in the Colorado Plateau ores (Part 5) and appear to be the most likely hosts for the bulk of extrinsic selenium in low-valent ores. Some ores also contain traces of such selenides as eucairite (CuAgSe) and clausthalite (PbSe) and also native selenium (Part 5).

ARSENIC

Arsenic (fig. 9), as determined by colorimetric analyses of a limited suite of samples, is more than 17 times as abundant in ores from the Morrison formation as in the unmineralized sandstones of the Salt Wash member. The content of arsenic in ores from Upper Triassic rocks appears to be similar to the content in ores from the Morrison, but no data are yet available on the arsenic content of unmineralized sandstones of the Shinarump and Moss Back members. In terms of abundance ratio, arsenic may be the third or fourth most important extrinsic element in the sandstone-type uranium ores, and in terms of actual amount or quantity contained it is the fifth most important extrinsic element, among those studied, in Morrison ores.

The manner in which arsenic is contained in the ores is not fully known. In low-valent ores the arsenides domeykite and arsenopyrite and realgar, as well as, native arsenic have been reported (Part 5) but appear to be rare. Arsenic has been found associated with coffinite, one of the major uranium minerals in low-valent ores, but apparently it is not an essential constituent of the mineral (Stieff, Stern, and Sherwood, 1955, p. 609). In oxidized ores arsenic occurs in the arsenates zeunerite and metazeunerite and in rare occurrences in abernathyite, novacekite, and conichalcite (Part 5; Weeks and Thompson, 1954, p. 59); it also enters into such phosphates as autunite and torbernite (Weeks and Thompson, 1954, p. 24 and 36) and into vanadates similar to calciovolborthite. Most of these minerals are extremely rare in vanadiferous ores, however, and the bulk of arsenic in oxidized ore may be contained as a minor constituent in some of the common vanadates.

The regional distribution of arsenic in the ores appears to be nearly or essentially random, in contrast to the relatively systematic distribution of most other accessory extrinsic elements. Probably the distribution of arsenic is more closely related to the distribution of uranium than any other extrinsic element.

ELEMENTS NOT DETECTED

Table 4 gives the spectrographic limits of sensitivity for 29 elements that, with the exceptions of neodymium and niobium, have not been detected in samples representing more than 1 ton of ore from sandstone-type uranium deposits in the Upper Triassic rocks and the Morrison formation or in whole samples of unmineralized sandstones from these formations. Traces of niobium have been detected in the ores of 8 and neodymium in the ores of 1 of 211 deposits from the Morrison formation, but neither element has been detected in unmineralized sandstones of the Salt Wash or in ore or unmineralized sandstone in Upper Triassic rocks.

TABLE 4.—*Elements looked for but not detected in pulp samples of ores from 249 uranium deposits and in 128 grab samples of unmineralized sandstones from the Upper Triassic rocks and the Morrison formation*

Element	Spectrographic limit of sensitivity (percent)	Element	Spectrographic limit of sensitivity (percent)
Au	0.005	Os	0.005
Bi	.001	P	.5
Cd	.005	Pd	.0005
Ce	.05	Pt	.005
Dy	.05	Re	.005
Er	.005	Rh	.005
Gd	.05	Ru	.005
Ge	.0005	Sm	.01
Hf	.1	Sn	.001
Hg	1.0	Ta	.05
In	.001	Te	.5
Ir	.005	Th	.05
Li	.01	Tl	.05
Nb[1]	.001	W	.01
Nd[2]	.01		

[1] Traces found in ores from 8 uranium deposits in the Morrison formation.
[2] Trace found in ore from 1 uranium deposit in the Morrison formation.

A number of the elements not detected in pulp samples of the ores or in whole samples of the sandstones have been found in detectable quantities in heavy minerals or in clay fractions of the sandstones. These include cerium, erbium, hafnium, tin, and phosphorous in the heavy minerals and lithium in the clay fractions. Bismuth has been detected in samples of gypsum from salt intrusions in southwestern Colorado and has been found in gypsiferous sandstones of the Salt Wash and in gypsum from the sandstones in places where the Salt Wash sandstone member is adjacent to the salt intrusions. Indium has also been detected in gypsiferous Salt Wash sandstones and mudstones associated with the bismuth. Any of these elements might be detected spectrographically in small samples and perhaps even in pulp samples of the uranium ores. Some of these and other elements are probably partly extrinsic in a number or perhaps even in most of the sandstone-type uranium deposits. Tin occurs locally in moderate concentration in the uranium ore at the Peanut mine, in southwestern Colorado (Roach and Thompson, written communication, 1955), and phosphorous may be a significant constituent of some sandstone-type uranium deposits where it forms phosphates in the oxidized ore (Part 5). Cadmium has been noted in the mineral greenockite (Part 5) and may be widespread in the ores in concentrations slightly below the spectrographic limit of sensitivity. Mercury has been reported from shales in the Chinle formation in northern Arizona (Lausen, 1936) and could possibly be an extrinsic component in the uranium ores. Tellurium has been reported from highly vanadiferous and seleniferous "alluvium" overlying ore in the Morrison formation at Thompson in southeastern Utah, by Beath (1943, p. 701 and 704). Thallium was detected spectrographically in a grab sample of uranium ore from the Navajo sandstone of Jurassic and Jurassic (?) age in northern Arizona (Shoemaker, 1955), and might also be an extrinsic component of ores in the Morrison and Upper Triassic rocks.

SUMMARY

A sandstone-type uranium deposit may be considered as composed of two fundamental parts: an indigenous part and a foreign part which was added to the indigenous part to form the deposit. The indigenous part consists of all elements that would have occupied the space of the uranium deposit had uranium mineralization never occurred; these elements of the uranium deposit are called intrinsic. The foreign part consists of all elements that were added to the indigenous part by processes of mineralization; these elemental components are called extrinsic. Nearly all elements in sandstone-type uranium deposits are probably in part intrinsic and in part extrinsic, but each element may be classified according to the dominant role it plays in a majority of the deposits.

The classification of elements studied in this investigation in the uranium deposits of the Morrison formation and the Chinle formation is given in table 5.

TABLE 5.—*Classification of elements in sandstone-type uranium deposits from Upper Triassic rocks and from the Morrison formation*

			Abundance ratio [1]	
		Element	*Morrison formation*	*Upper Triassic rocks*
Dominantly intrinsic.	Dominantly syngenetic.	Si	≈1	≈1
		Al	2. 1	. 7
		Fe	3. 7	1. 3
		K	≈1	≈2
		Ti	2. 0	. 7
		Zr	2. 3	. 7
		Be	------------	------------
		B	≈2	≈1
		Sc	------------	≈2
		Cr	2. 6	2. 1
		Zn	2. 2	------------
		Ga	------------	≈2
				1
		Ag	≈2 (?)	------------
		Sb	≈0. 5	------------
		La	------------	≈1
	Dominantly epigenetic.	Mg	3. 0	1. 3
		Ca	0. 6	3
		Na	≈1	≈1
		Mn	1. 4	2
		Ba	2. 4	1. 4
		Sr	2. 5	2
Dominantly extrinsic.	Ore elements	U	>1000	------------
		V	500	20
	Accessory elements.	Co	≈20	≈5
		Ni	≈20	≈3
		Cu	7	3
		As	>17	------------
		Se	>6	≈2
		Y	≈8	------------
		Mo	>3	≈9
		Yb	------------	------------
		Pb	>9	≈6

[1] Ratio of estimated geometric-mean concentration in uranium ores to estimated geometric-mean concentration in unmineralized sandstones.

Dominantly intrinsic elements are further subdivided according to whether they are contained principally in syngenetic minerals in the uranium deposits or whether they are contained principally in authigenic minerals formed after the deposition of the sediments that ultimately were transformed into uranium deposits. Dominantly extrinsic elements are subdivided according to their economic importance into ore elements and accessory elements. The classification of elements as intrinsic or extrinsic rests primarily on the ratios of their abundance in unmineralized sandstones to their abundance in the uranium deposits. Because of selectivity of mineralization, account must be taken of the fact that the average intrinsic composition of the rocks or sediments mineralized is not equivalent to the average composition of unmineralized sandstones. In uranium deposits in the Morrison formation most of the dominantly intrinsic elements are more abundant than they are in the unmineralized sandstones.

Several elements not detected by the spectrographic method in the sandstone-type uranium ores are probably present as dominantly extrinsic elemental components of the ores. Two of possible importance in the composition of the ores are sulfur and phosphorous. Iron, though dominantly intrinsic, is also present as one of the most abundant extrinsic elemental components of the ores, and the extrinsic iron is probably contained mainly in the sulfides pyrite and marcasite in low-valent ores. Much of the sulfur combined with extrinsic iron in the sulfides may have been introduced into the ores with the iron. On oxidation the sulfur may tend to be lost from the ore, but some is retained as sulfate. Phosphorous is identified in some ores in various phosphorous minerals. Among other elements that could be dominantly extrinsic in the ores but are below the spectrographic limit of sensitivity in bulk samples are tin, cadmium, tellurium, and thallium.

Though all elements were probably carried in some concentration, however small, in the solutions that introduced uranium into the ores, only a limited suite of elements form the recognizable extrinsic components of the ores. Those elements that are now thought to be or are likely to prove to be identifiable members of the extrinsic suite of elements are listed in table 6 in the estimated order of abundance of their extrinsic fraction in the average ore from the Morrison formation. No great weight should be placed on the exact position of each element in the order given; in particular, the positions of sulfur and phosphorus, which have been estimated for relatively oxidized ore mainly from indirect lines of mineralogical evidence, are in considerable doubt. The list of possible extrinsic elements whose concentrations are below the spectrographic limit of sensitivity shows only those elements suggested by some specific analytical or mineralogical evidence and should not be considered inclusive.

TABLE 6.—*Extrinsic elemental components of average uranium ore from the Morrison formation, in their estimated order of abundance*

	Component
Probably extrinsic in more than half of the uranium deposits	Vanadium
	Iron
	Magnesium
	Uranium
	Sulfur
	Arsenic
	Phosphorous
	Copper
	Lead
	Molybdenum
	Selenium
	Cobalt
	Nickel
	Yttrium
Probably extrinsic in less than half of the uranium deposits	(Barium)
	(Strontium)
	(Zinc)
	(Chromium)
	(Silver)
Possibly extrinsic in the uranium deposits but not detected spectrographically in bulk samples of the ores	Ytterbium(?)
	Tin(?)
	Cadmium(?)
	Tellurium(?)
	Thallium(?)

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Part 4. OCCURRENCE AND CHEMICAL CHARACTER OF GROUND WATER IN THE MORRISON FORMATION

By David A. Phoenix

CONTENTS

ILLUSTRATIONS

TABLES

ABSTRACT

Ground water in the Morrison formation of Late Jurassic age is in juxtaposition with deposits of uranium-vanadium ore minerals. This water is under water-table conditions in most of the region, but locally it is confined by impermeable clay strata. It is mostly derived from the infiltration of precipitation and surface runoff. Some water is contained in pore spaces in sandstone but most is in joints. Movement of this water is, at first, downward from the land surface, but bedding planes, mudstone seams, and other places where the rocks have a low permeability act as barriers and divert its path usually toward the direction of regional dip. Under water-table conditions the permeable sediments are usually saturated for a few inches to a few feet above each extensive barrier; under artesian conditions the ore-bearing sandstone is entirely saturated. The amount of water contained in the rocks is not great and its movement is slow. Evaporation from the land surface and transpiration by plants is sufficiently high to dispose of most of the discharge, but discharge is great enough to form springs and seeps locally.

Samples of ground water from the Salt Wash and Brushy Basin members of the Morrison formation have been analyzed to determine their chemical character and metal content. The ground water in the Salt Wash member is largely a bicarbonate solution with variable amounts of calcium and magnesium ions; the ground water in the Brushy Basin member is either a sulfate or bicarbonate solution with sodium. The ground water from the Salt Wash and Brushy Basin members is generally weakly alkaline. In most samples uranium, vanadium, copper, lead, and selenium are present in amounts less than 1 ppm (part per million).

It is concluded that if ground water was responsible for introduction of the uranium and vanadium metals into the Salt Wash and if it was comparable to present ground water, it contained very small concentrations of the metal ions.

INTRODUCTION

This paper is concerned with the occurrence and chemical composition of ground water in the uranium-vanadium-bearing Morrison formation in southwestern Colorado and southeastern Utah (fig. 10). The study was undertaken to determine the influence similar ground water might have had on genesis of the ore deposits. Water-level measurements in numerous boreholes have been used to determine the mode of occurrence of ground water in ore-bearing sandstone of the Morrison formation. Chemical analyses of ground water from 23 sample points in the Morrison

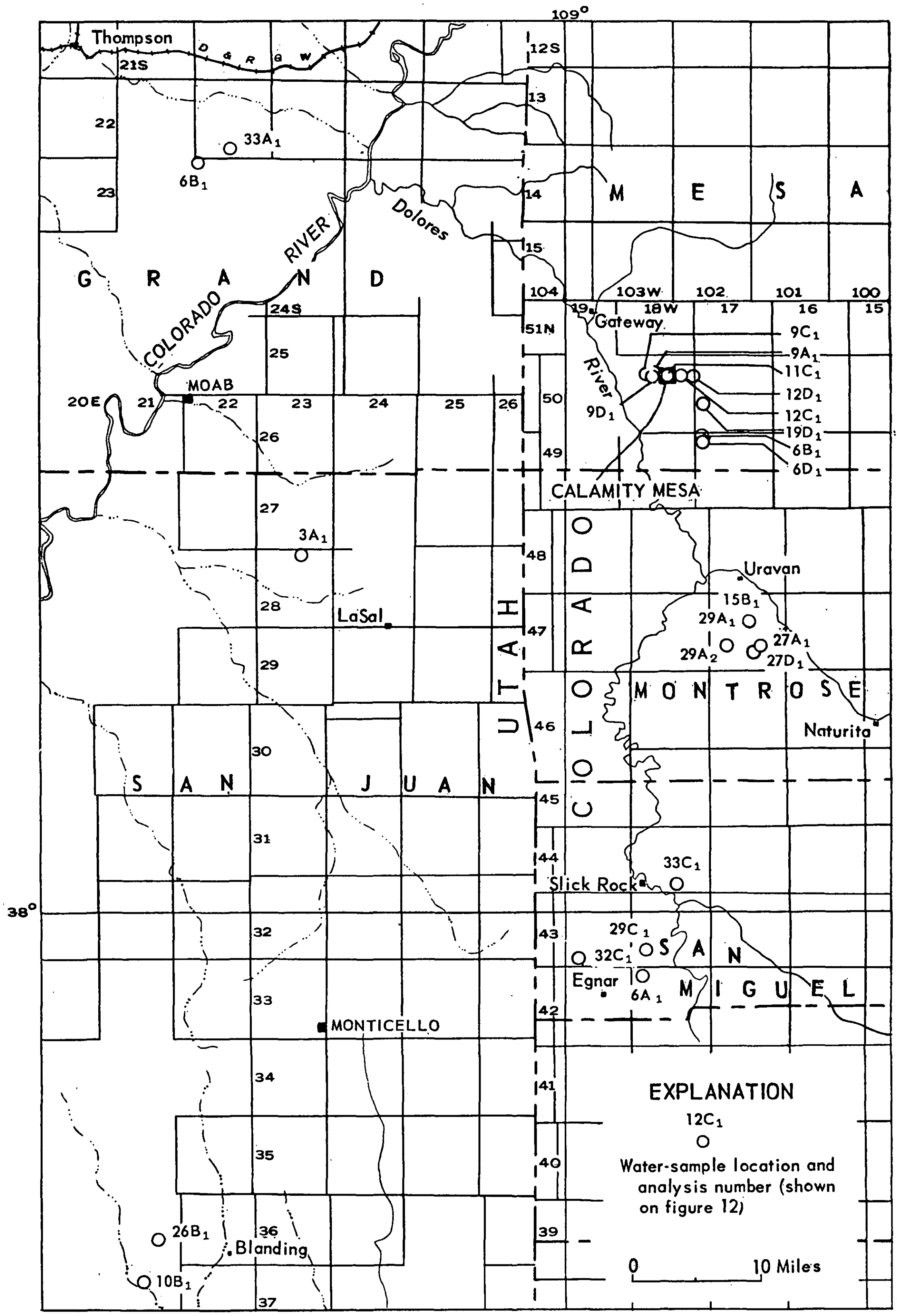

FIGURE 10.—Index map of southwestern Colorado and southeastern Utah, showing water-sample locations.

formation established its chemical characteristics and metal-ion content.

The number assigned to a well or spring in this report is both an identification and location number. It is based on the base and meridian system of the General Land Office. A typical number consists of three units. The first unit is the number of the township north or south of the base line. The second unit, separated from the first by a slant, is the number of the range east or west of the meridian. The third unit, separated from the other two units by a dash, lists the number of the section and is followed by a letter designating the quarter section, and finally a number to show the order in which the well or spring was recorded within the subdivision. The letters A, B, C, and D designate, respectively, the northeast, northwest, southwest, and southeast quarters of the section. On figure 10, owing to space limitation, only that part of the number designating the subdivision of the section and the order in which the well or spring was recorded in that subdivision is shown.

CLIMATE

The climate of the region is semiarid, but the average annual precipitation differs from place to place. The average monthly and annual precipitation in different geographic and topographic localities is summarized in table 1. In Colorado the Norwood and Northdale stations are on upland mesas, the Paradox and Gateway stations are in the bottoms of steep-walled canyons. The station at Monticello, Utah, is on the east flank of the Abajo Mountains, and precipitation here is probably duplicated on the upland mesas east of the La Sal Mountains. Thompson, Utah, is on the eastern edge of the Green River desert; this region receives less rainfall than most areas in southwestern Colorado and southeastern Utah. The average annual precipitation in the area of detailed ground-water study (fig. 10) is probably not as great as that at the Norwood or Northdale stations or as little as that at the Gateway station. The average precipitation in the area of detailed ground-water study is probably about 12 inches a year.

MORRISON FORMATION

The Morrison formation of Late Jurassic age is divided into two members: a lower member, the Salt Wash, and an upper member, the Brushy Basin. The Salt Wash member is composed of lenticular strata of sandstone and mudstone. Near the top of this member the strata of sandstone give the appearance of a persistent layer because the strata overlap. In detail, however, they are separated by beds of mudstone or local disconformities. The Brushy Basin member is varicolored bentonitic shale and mudstone interbedded with lenticular strata of sandstone and conglomeratic sandstone. Discrete strata of conglomeratic sandstone occur sporadically near the base of the member. The uranium-vanadium ore deposits are largely confined to the uppermost sandstone strata of the Salt Wash member.

Erosion has dissected the Morrison formation so that it now forms the midslopes of many mesas in southwestern Colorado and southeastern Utah. Outcrops of the Brushy Basin member are sparse except in the most arid regions. The beds are usually covered by landslide debris or talus blocks of more resistant and younger formations. Outcrops of sandstone in the Salt Wash member are resistant and they usually form cliffs and broad benches. Because the Morrison formation has been dissected by erosion and also broadly folded, outcrops of the ore-bearing sandstone of the Salt Wash member differ in altitude from area to area, so that the opportunity for ground-water recharge in the member depends on local structural and topographic features as well as on the average annual rainfall.

GROUND WATER IN THE AREA

OCCURRENCE

The main aquifer in the Morrison formation is composed of lenticular sandstone strata near the top of the

TABLE 1.—*Average monthly and annual precipitation, in inches, at eight climatological stations in southwestern Colorado and southeastern Utah*

[Data from U. S. Department of Commerce, Weather Bureau. Record from establishment of station to 1954, inclusive. Altitude in feet; precipitation in inches]

Station	Altitude	Number of years	Jan.	Feb.	Mar.	Apr.	May	June	July	Aug.	Sept.	Oct.	Nov.	Dec.	Average annual
Blanding, Utah	6,036	46	1.05	1.20	1.08	0.94	0.76	0.58	0.99	1.24	1.47	1.29	0.82	1.35	12.77
Monticello, Utah	7,066	32	1.25	1.44	1.57	1.09	.87	.72	1.51	1.88	1.62	1.86	1.09	1.36	16.26
Moab, Utah	4,125	61	.73	.69	.88	.73	.72	.43	.81	.79	.98	.99	.65	.86	9.26
Thompson, Utah	5,150	30	.59	.56	.73	.67	.51	.51	.85	.90	.97	1.10	.49	.72	8.60
Norwood, Colo	7,017	26	1.00	1.27	1.45	1.56	1.10	.96	1.78	1.97	1.52	1.32	.82	1.11	15.86
Northdale, Colo	6,842	24	1.10	1.16	1.31	1.18	.82	.63	1.15	1.45	1.91	1.52	1.35	1.19	14.20
Paradox, Colo.,[1] 2 mi. SE	5,300	13	.74	.53	.59	.74	.57	.64	1.09	1.04	.66	1.14	.75	.82	8.71
Gateway, Colo.,[2] 4 mi. NE	4,903	7	.93	.61	.67	.87	.82	.48	.90	1.29	.89	1.33	.59	.54	9.57

[1] Averages based on incomplete record, 1942–54, inclusive.

[2] Averages based on incomplete record, 1947–54, inclusive.

Salt Wash member. This aquifer is locally called the ore-bearing sandstone because it contains most of the uranium-vanadium deposits in the Morrison formation. From a distance its appearance is often that of a continuous layer. Other strata of sandstone lower in the Salt Wash member as well as strata of conglomeratic sandstone at the base of the Brushy Basin member sometimes contain ground water, but generally they do not yield water to wells or springs.

Although ground water in the ore-bearing sandstone is confined in some areas, it is unconfined in most of the region. It has been studied in the Calamity Mesa area, Mesa County, Colo. (fig. 10) in an area where the ore-bearing sandstone is exposed for about 2 square miles and where it has been explored by mine workings and cut by several hundred diamond-drill holes. Several months after drilling had stopped the depth to water was measured in 246 uncased diamond-drill holes. These drill holes are distributed throughout the Calamity Mesa area and they penetrate the ore-bearing sandstone as well as several feet of mudstone below. Water was encountered in all but 20 of the diamond-drill holes. In drill holes near the central part of the mesa, water levels, in places, stand 20 or 30 feet above the base of the ore-bearing sandstone; in drill holes nearer the edge of the mesa, water levels are only 2 or 3 feet above the base of the ore-bearing sandstone, and those that do not contain water are along the edge of Calamity Mesa where the ore-bearing sandstone is exposed as a cliff and where it is jointed.

Confined ground water has been found in synclinal structures where erosion has not destroyed the nearly impermeable cover of the Brushy Basin member. Diamond-drill holes to the ore-bearing sandstone have encountered water under sufficient hydrostatic pressure to flow at the land surface near Uravan, Montrose County, Colo., near Slick Rock, Montrose County, Colo., near La Sal, San Juan County, Utah, and 6 miles west of Blanding, San Juan County, Utah. In these places the lenticular ore-bearing sandstone is probably saturated, and the lenses are sufficiently connected hydraulically to be capable of transmitting ground water to drill holes for at least 2 or 3 miles from the nearest recharge area. Flows of 30 gpm at the land surface and pressures sufficient to raise water levels 20 feet above the land surface have been recorded in the La Sal Creek and Uravan areas. However, the amount of ground water flowing from these drill holes and the hydraulic pressure usually has decreased substantially within a few months after the hole was drilled. This indicates that the beds are not very permeable and, hence, that movement of water from the outcrop to the drill holes is slow.

Some of the characteristics of ground-water occurrence were determined from a contour map of the water table based on the measured water levels referred to a sea-level datum. The contour map indicates that ground water in the ore-bearing sandstone is perched on mudstone at the base of the ore-bearing sandstone and that the water table has a general slope of about 3° SW., approximately the same as the dip of the rocks. However, the contact between the ore-bearing sandstone and the mudstone below is an irregular surface with locally as much as 6 feet of relief. The water-table map is in places a subdued replica of a map of this surface. The direction and rate of ground-water movement probably are controlled in part by irregularities in the contact. The "lows" in the contact may act as "channelways" along which the greater amount of the present day ground water moves.

The measurement of water levels was sometimes hindered by the presence of moisture on the walls of the diamond-drill holes. This moisture persisted throughout the 21 months of observation and probably is ground water. Where it was detected, the upper level of moisture always was above a lenticular stratum of mudstone or above some similar impermeable zone contained within the ore-bearing sandstone. It is difficult to evaluate the influence that leakage from these local zones of saturated rocks may have had on water-level measurements in the diamond-drill holes, for the rate of leakage could not be determined.

The movement of water into the rocks is at first downward from the surface. A large part of this water gains entry to the ore-bearing sandstone through joints, but some probably moves through the intergranular interstices in the more permeable places. The portion of this water that exceeds soil-moisture requirements is free to percolate to the water table and migrate laterally in the direction of the hydraulic gradient as ground water. The path of ground-water movement generally follows the direction of regional dip, but in detail it is devious, for the ore-bearing sandstone contains numerous barriers in the form of lenticular clay strata, local disconformities, and bedding planes. The ore-bearing sandstone may thus be saturated above each impermeable zone for a few inches or even a few feet and in more than one place. It is believed that ground water "cascades" from the extremity of each lenticular barrier to eventually reach the impermeable mudstone at the base of the ore-bearing sandstone.

The water levels in 22 of the holes were measured at monthly intervals from late in 1949 through July 1951. The monthly measurements of 10 of these holes are plotted on figure 11 to show the water-level fluctuations. Although the water levels in some of the holes, notably CA–125, CA–501, CA–505, and CA–678, show fluctuations through the period of observation, water in other

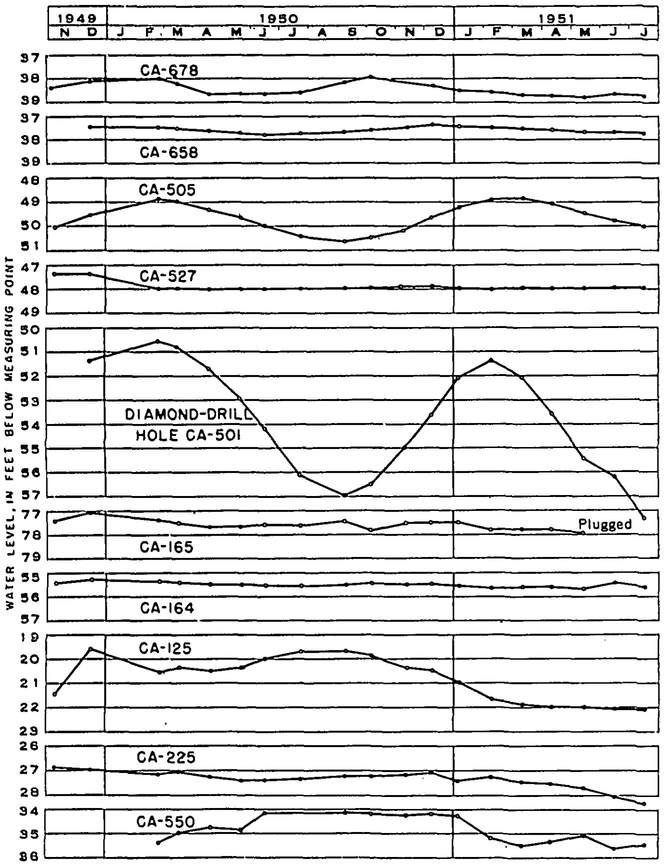

FIGURE 11.—Hydrographs of water-level measurements in 10 diamond-drill holes, Calamity Mesa area, Mesa County, Colo., November 1949 to July 1951.

holes shows little or no fluctuation. These data suggest that the water in the sandstone strata is being recharged locally by the infiltration of surface water and precipitation, probably introduced into the sandstone through fractures that are open to the surface. The lack of response of the water level in other holes to seasonal variations in precipitation suggests that sandstone in the immediate vicinity of these holes is not fractured and has a relatively low permeability; in places pore spaces in the ore-bearing sandstone may be plugged with drill mud.

Discharge of ground water from the ore-bearing sandstone is by springs or seeps, by evaporation, and by transpiration. The fact that some drill holes in the ore-bearing sandstone are "breathing" air suggests that locally there is atmospheric circulation in the rocks; therefore, some ground water is probably lost by evaporation within the rocks. In places, the roots of juniper and piñon and probably the roots of other plants as well reach several tens of feet into the rocks and these plants act as miniature pumps to discharge ground water. Along the edge of Calamity Mesa plant roots penetrate joints to depths of about 20 feet below the top of the ore-bearing sandstone, but mine workings in the interior of the mesa have encountered roots along prominent joints to a depth of about 50 feet. The amount of ground water discharged from within the ore-bearing sandstone by plant transpiration is probably small, except near the outcrop or where the rocks are jointed and plant roots can easily penetrate to the zone of saturation or to its capillary fringe. Ground-water discharge is most active along the downdip or southwest edge of the mesa where the base of the ore-bearing sandstone is exposed. The total amount of ground water discharged from the Calamity Mesa area cannot be measured but it is probably only a small fraction of the average annual rainfall.

CHEMICAL CHARACTER

The chemical analyses of 23 samples of ground water from the Morrison formation are shown in table 2. These samples were collected from mines, springs, and wells in the Salt Wash and Brushy Basin members of the Morrison formation. All samples from the Salt Wash member were collected near ground known to contain uranium-bearing minerals. Samples from the overlying Brushy Basin member presumably had not percolated through or near rocks containing these minerals.

The milligram equivalents, or reacting values (Palmer, 1911, p. 5)—called equivalents per million (epm) in this report—of the soluble ions, have been computed for all the analyzed samples. The equivalents per million for 22 of the samples are shown graphically on figure 12 and indicate the chemical character of the water from each locality at the time the water was sampled for analysis. Of the 22 samples, 12 are classed as calcium, magnesium bicarbonate water; 3 as calcium, magnesium sulfate water; 3 as sodium sulfate water; and 4 as sodium bicarbonate water. These differences in character are probably determined in part by the duration of time the ground water has been in contact with the rocks, by the composition and physical properties of the rocks, by the presence or absence of soluble salts in the paths of ground-water movement, and by the degree to which the solution has been concentrated by evaporation and plant transpiration. For sample 50/18W–9A (table 2), the total iron, sum of total dissolved solids, and tons per acre-foot appear to be questionable determinations and their application should be used with reservation. The sample was turbid when collected and the iron probably includes that from ferruginous sediments. Although total iron should include iron both in solution and precipitated, it is based on the premise of a clear sample at the time of collection. This, however, does not disqualify it as a calcium, magnesium sulfate water.

TABLE 2.—*Chemical analyses, in parts per million, of ground water*

[Analyses for U, V, Cu, Pb, and Se, and of sediment, by George J. Petretic or Lewis F. Rader, Jr., U. S. Geol. Survey.

Field data (U. S. G. S.)					Silica (SiO_2)	Iron (Fe)		Calcium (Ca)	Magnesium (Mg)	Sodium (Na)	Potassium (K)	Manganese (Mn)	Bicarbonate (HCO_3)	Sulfate (SO_4)	Chloride (Cl)
Field location No.[1]	Salt Lake City lab. No.	Denver lab. No.	Source of sample	Date of collection		In solution	Iron (Fe) total								
Samples from the Brushey															
50/18W-9D$_1$	6402	4/51	Maverick mines area; spring.	4/9/51	15	0.01	--------	41	36	123	9.6	0.00	[6] 509	63	24
49/17W-6D$_1$	6322	3/51	Blue Mesa; spring.	3/31/51	9.6	.07	0.18	5.8	12	847	11.0	.00	[8] 1,900	296	55
47/17W-27A$_1$	6317	----------	Long Park area; dug well.	3/23/51	15	.03	.07	97	104	318	16.0	.00	354	798	171
44/18W-33C$_1$	6318	----------	Joe Davis Canyon; spring.	3/24/51	9.9	.04	--------	41	13	360	8.8	.00	528	435	61
43/19W-32C$_1$	6319	1/51	Bishop Canyon; Strawberry Spring.	3/24/51	16	.05	--------	88	34	203	4.4	.00	506	212	113
42/18W-6A$_1$	6320	----------	Spud Patch; dug well.	3/24/51	20	.07	--------	98	103	118	6.6	.29	554	158	198
Samples from the															
50/17W-19D$_1$	3812	B-2	Outlaw Mesa; dug well.	11/15/49	23	0.10	0.16	84	88	65	7.6	0.00	620	105	64
50/18W-9A$_1$	3811	B-4 [10] B-17 [11]	Maverick mines area, Matchless mine; sump.	11/16/49 7/29/50	[12] 22	.07	99	524	389	58	--------	.00	479	2,310	165
50/18W-9C$_1$	3810	B-3	Maverick mines area; spring.	11/16/49	15	.05	.12	56	50	129	13.0	.00	483	119	69
50/18W-11C$_1$	4536	B-5	Calamity Mesa; spring.	4/18/50	16	.03	.04	62	57	33	4.8	.00	408	65	40
50/18W-12C$_1$	3813	B-1	Outlaw Mesa; spring.	11/16/49	20	.05	.06	82	49	32	4.2	.00	417	59	36
50/18W-12D$_1$	4537	B-6	Outlaw Mesa; Ronnie No. 1 mine; underground spring.	4/19/50	13	.03	--------	62	35	11	3.0	.00	344	23	14
49/17W-6B$_1$	6321	2/51	Blue Mesa; spring.	3/31/51	11	.02	--------	30	37	68	8.0	.00	[16] 391	32	18
47/17W-15B$_1$	4686	B-8	Long Park area; spring.	5/28/50	12	.07	.19	50	67	92	8.7	.00	425	192	33
47/17W-27D$_1$	4685	B-7	Long Park, Long Park No. 10 mine; ore chute.	5/28/50	13	.82	1.24	62	33	17	3.2	.00	245	77	18
47/17W-29A$_1$	4687	B-10	Long Park, Henry Clay mine; underground spring.	5/27/50	14	.09	.15	86	43	19	5.9	.00	406	43	34
47/17W-29A$_2$	4688	B-9	Long Park, Henry Clay mine; sump.	5/27/50	10	.11	.26	59	43	20	6.1	.00	317	48	37
43/18W-29C$_1$	4733	B-11	Spud Patch, May Day mine; sump.	6/26/50	17	.04	--------	64	16	27	4.8	.00	226	42	30
37/21E-10B$_1$	4735	B-13	Blanding mines area, East Bank mine; sump.	6/24/50	13	.11	.25	116	114	179	10.0	.00	480	631	91
36/21E-26B$_1$	4734	B-12	Blanding mines area; AEC diamond-drill hole No. BA-6.	6/24/50	13	.02	--------	77	53	128	6.4	.00	378	353	27
28/23E-3A$_1$	4779	B-16	Yellow Circle mine area; spring.	6/28/50	12	.03	--------	38	59	10	4.6	.00	[18] 351	28	24
23/22E-6B$_1$	4777	B-15	Yellow Cat mines area, Telluride No. 18 mine; sump.	6/29/50	11	.20	--------	89	20	129	6.1	.00	202	388	13
22/22E-33A$_1$	4778	B-14	Yellow Cat mines area, Cactus Rat mine; 20 foot adit.	6/29/50	10	.03	--------	101	15	343	3.4	.00	205	806	47
Threshold of detection.		----------	------------------------------	---------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------

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[1] Field No., example: 50/17W-19D, indicates T. 50 N., R. 17 W., sec. 19, and the quarter section (A, B, C, or D, lettered counterclockwise from the NE¼).

[2] Method of determination: Fluorimetric.

[3] Method of determination: Colorimetric.

[4] Noncarbonate hardness or "permanent" hardness refers to hardness exceeding the equivalence with carbonate and bicarbonate. The two hardnesses are, by common practice, expressed as "Hardness as $CaCO_3$."

[5] Percent sodium: Obtained by dividing the milligram equivalents of sodium by total milligram equivalents of cations and multiplying by 100.

[6] Includes 8 ppm CO_3.

[7] gpm: Gallons per minute.

[8] Includes 311 ppm CO_3.

[9] See following table for analyses, in percent:

Lab. No.	Precipitate (ppm)	UO_3	V_2O_5	Fe_2O_3*	CaO**	K_2O**
B-1	5.4	0.05	1.7	4.9	1.0	1.4
B-2	2.2	.11	1.4	9.4	5.6	2.5
B-3	7.7	.1	1.8	1.7	.2	.5
B-4	39.5	6.4	14.4	3.9	.2	1.3

*Method of determination: Colorimetric.

**Method of determination: Flame photometric.

from wells, springs, and mines in the Morrison formation

Analyses for other constituents by E. L. Singleton, W. M. Webster, and E. F. Williams, U. S. Geol. Survey]

Fluoride (F)	Nitrate (NO_3)	Boron (B)	Uranium (U)[3]	Vanadium (V)[3]	Copper (Cu)[3]	Lead (Pb)[3]	Selenium (Se)	Dissolved solids		Hardness[4] as $CaCO_3$		Other data			Remarks
								Residue on evaporation at 180° C. (ppm)	Tons per acre-ft	Calcium magnesium	Noncarbonate	Specific conductance (Micromhos at 25° C.)	Per cent sodium[5]	pH (laboratory)	
Basin shale member															
0.7	3.3	0.03	0.05	0.09	0.00	0.00	0.05	566	0.77	250	0	908	50	8.1	Basal conglomerate of Brushy Basin member. Yield<1 gpm.[7] Temp. 54° F.
2.6	3.8	.40	.06	.30	.05	.00	<.05	2,180	2.96	64	0	3,270	96	9.4	Sandstone of the Brushy Basin member. Yield <1 gpm. Temp. 43° F. Field pH 9.
.7	.2	.06	--------	--------	--------	--------	--------	1,690	2.30	670	380	2,360	50	8.0	Sandstone of the Brushy Basin member. Temp. 38° F. Field pH 6–7.
1.0	.3	.07	--------	--------	--------	--------	--------	1,190	1.62	156	0	1,730	82	8.1	Sandy shale of the Brushy Basin member. Field pH 7. Temp. 42° F.
.3	.1	.09	.02	.12	.00	.00	<.05	920	1.25	360	0	1,420	55	7.9	Basal conglomerate of Brushy Basin member. Field pH 7. Temp. 43° F.
.3	14.0	.03	--------	--------	--------	--------	--------	989	1.35	668	214	1,610	27	7.7	Quaternary alluvium derived from Brushy Basin (?) member. Field pH 7.
Salt Wash sandstone member															
0.7	0.2	0.04	0.0	<0.1	0.06	0.03	0.00	743	1.01	572	64	1,230	20	7.5	Ore-bearing sandstone, 30 feet downdip from mined ore body. Sediment analyzed.[9]
.9	(13)	(14)	18.0 .82	95.0 11.8	.01 .00	.03 .00	12.50 3.13	3,700	5.03	2,910	2,510	4,410	4	6.8	Seep from mineralized sandstone. B–4 sediment analyzed.[9]
.6	.9	.08	.1	<.1	.03	.17	.00	690	.94	345	0	1,100	44	8.0	Ore-bearing sandstone(?). Sediment analyzed.[9]
.5	4.7	.06	.3	<.1	.00	.00	.00	484	.66	389	54	820	15	7.5	Base of ore-bearing sandstone. Yield 1 gpm. Temp. 50° F.
.5	5.6	.02	.2	<.1	.07	.06	.00	494	.67	406	64	807	14	7.7	Ore-bearing sandstone 100 feet downdip from mined ore body. Sediment analyzed.[9]
.3	4.1	.04	.0	.1	.00	.00	.00	335	.46	298	16	584	7	7.9	Top of ore-bearing sandstone. Yield 100 gpd.[15] Temp. 50° F.
.4	4.1	.03	.02	.16	.00	.00	<.05	401	.55	227	0	669	38	8.1	Ore-bearing sandstone, 2,000 feet downdip from nearest known ore body. Yield <1 gpm. Field pH 6.[17]
.2	1.2	.02	.6	<.1	.00	.00	.00	666	.91	400	52	1,030	33	7.9	Base of ore-bearing sandstone. Yield 84 gpd. Temp. 52° F.
.4	15.0	.00	.3	1.2	.00	.00	.00	360	.49	290	89	576	11	7.7	Ore-bearing sandstone. Yield <25 gpd. Temp. 53½° F.
.3	6.1	.01	.2	<.1	.00	.00	.00	451	.61	392	59	740	9	7.7	Mineralized sandstone. Yield 120 gpd. Temp. 45½° F.
.3	6.2	.02	.6	<.1	.00	.00	.00	386	.52	324	64	655	12	7.7	Mine sump.
.4	1.7	.04	<.1	<.1	.00	.33	.00	314	.43	226	40	523	20	7.7	Mineralized sandstone. Temp. 44° F. Field pH 6.
.4	1.9	--------	8.7	22.8	.00	.00	.00	1,400	1.90	758	364	1,990	34	7.4	Mine sump. Temp. 47° F. Field pH 7.
.2	.2	.00	<.1	.1	.00	.00	.00	844	1.15	410	100	1,250	40	7.7	Ore-bearing sandstone. Yield 15 gpm. Temp. 56° F. Field pH 6.5.
.4	5.4	.02	.2	<.1	.00.	.50	.00	361	.49	338	38	647	6	8.3	Mineralized sandstone. Yield 50 gpd. Temp. 58° F.
.4	2.6	.04	.8	<.1	.00	.04	1.00	759	1.03	304	138	1,100	47	7.9	Mineralized sandstone. Yield 300 gpd. Temp. 50° F.
.3	5.8	.02	.2	<.1	.00	.02	7.87	1,430	1.94	314	146	2,030	70	7.9	Ore-bearing sandstone, 50 feet below mineralized sandstone. Temp. 56° F. Field pH 6.5–7.
--------	--------	--------	.01	.01	.01	.01	.05								

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[10] Sample collected from sludge pit in drift. Water contaminated by drill sludge. Source: Underground seep from face of ore.

[11] Sample collected from flooded winze. Water uncontaminated by drill sludge. Source: Underground seep from face of ore.

[12] On addition of HCl, yellow color developed, but faded after standing.

[13] Deep-blue color developed on addition of phenodisulfonic acid to evaporated sample. Color disappears with addition of H_2O. Deep yellow developed with NH_4OH.

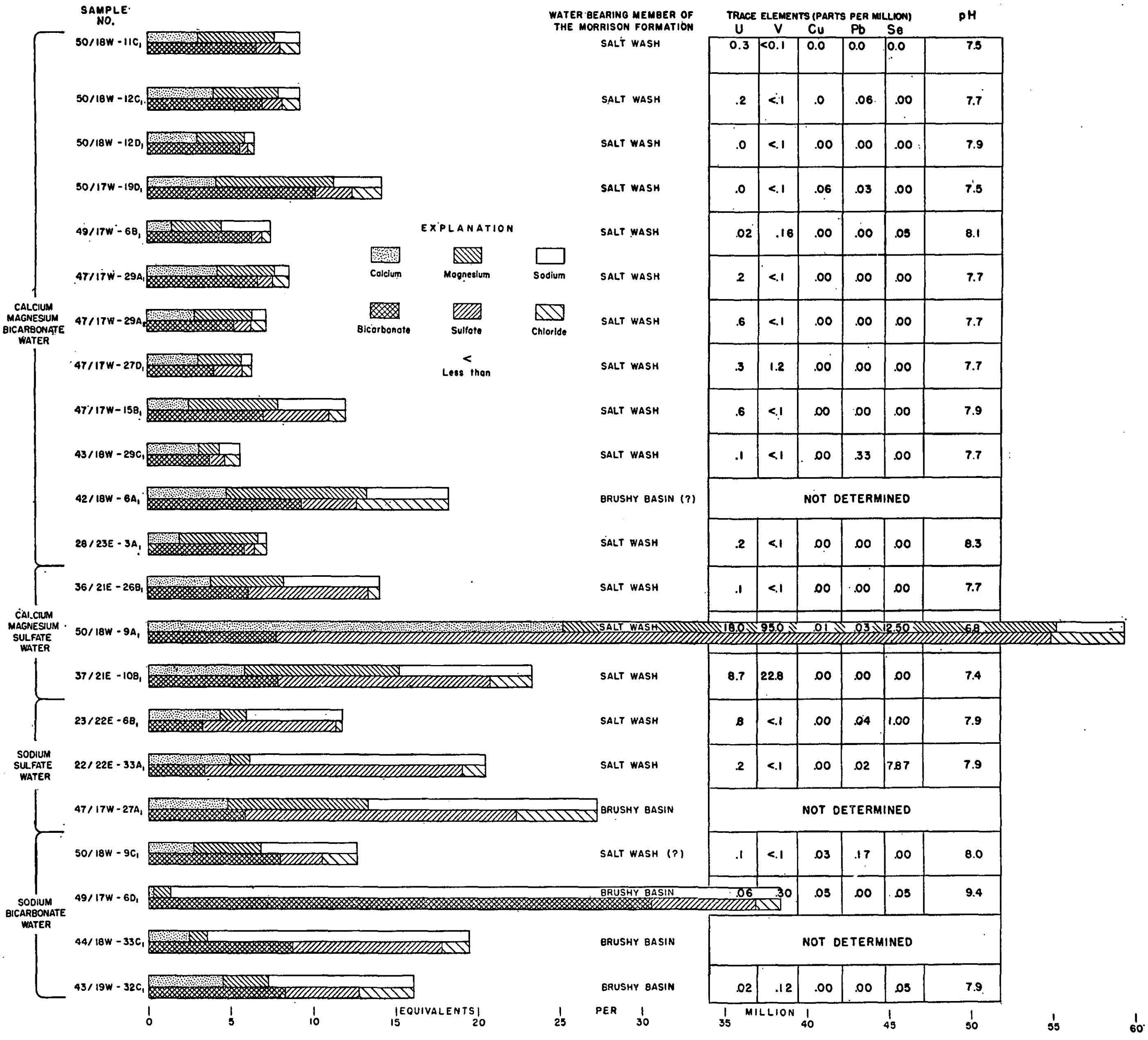
[14] Unable to detect green-yellow color of boron.

[15] gpd: Gallons per day.

[16] Contains 14 ppm CO_3.

[17] All field pH determinations were by "Hydrion" paper.

[18] Contains 7 ppm CO_3.



SAMPLE NO.	WATER BEARING MEMBER OF THE MORRISON FORMATION	TRACE ELEMENTS (PARTS PER MILLION) U	V	Cu	Pb	Se	pH
50/18W-11C$_1$	SALT WASH	0.3	<0.1	0.0	0.0	0.0	7.5
50/18W-12C$_1$	SALT WASH	.2	<.1	.0	.06	.00	7.7
50/18W-12D$_1$	SALT WASH	.0	<.1	.00	.00	.00	7.9
50/17W-19D$_1$	SALT WASH	.0	<.1	.06	.03	.00	7.5
49/17W-6B$_1$	SALT WASH	.02	.16	.00	.00	.05	8.1
47/17W-29A$_1$	SALT WASH	2	<.1	.00	.00	.00	7.7
47/17W-29A$_2$	SALT WASH	.6	<.1	.00	.00	.00	7.7
47/17W-27D$_1$	SALT WASH	.3	1.2	.00	.00	.00	7.7
47/17W-15B$_1$	SALT WASH	.6	<.1	.00	.00	.00	7.9
43/18W-29C$_1$	SALT WASH	.1	<.1	.00	.33	.00	7.7
42/18W-6A$_1$	BRUSHY BASIN (?)	NOT DETERMINED					
28/23E-3A$_1$	SALT WASH	.2	<.1	.00	.00	.00	8.3
36/21E-26B$_1$	SALT WASH	.1	<.1	.00	.00	.00	7.7
50/18W-9A$_1$	SALT WASH	18.0	95.0	.01	.03	12.50	6.8
37/21E-10B$_1$	SALT WASH	8.7	22.8	.00	.00	.00	7.4
23/22E-6B$_1$	SALT WASH	.8	<.1	.00	.04	1.00	7.9
22/22E-33A$_1$	SALT WASH	.2	<.1	.00	.02	7.87	7.9
47/17W-27A$_1$	BRUSHY BASIN	NOT DETERMINED					
50/18W-9C$_1$	SALT WASH (?)	.1	<.1	.03	.17	.00	8.0
49/17W-6D$_1$	BRUSHY BASIN	.06	30	.05	.00	.05	9.4
44/18W-33C$_1$	BRUSHY BASIN	NOT DETERMINED					
43/19W-32C$_1$	BRUSHY BASIN	.02	.12	.00	.00	.05	7.9

Compiled from analyses by C. S. Howard, G. J. Petretic, and L. F. Rader

FIGURE 12.—Bar graph showing analyses of ground water from the Morrison formation in equivalents per million and the concentration of trace elements in parts per million. Sample locations shown on figure 10.

Water from the Brushy Basin member has a high concentration of sodium ions, whereas, water from Salt Wash sandstone has a high calcium- and magnesium-ion concentration. This difference in chemical quality probably is due largely to gross differences in mineralogic composition between the Salt Wash and Brushy Basin sedimentary rocks.

The uranium, vanadium, copper, lead, and selenium content of 19 of the 22 water samples is also shown on figure 12. The concentration of uranium, vanadium, copper, and lead at the threshold of detection is about 0.01 ppm, whereas, the concentration of selenium at the threshold of detection is 0.05 ppm. Where 0.00 ppm is reported for selenium, it indicates less than 0.05 ppm; for the other metals 0.00 ppm indicates a concentration of less than 0.01 ppm. As a general rule, these metals were found in amounts of less than 1 ppm, and some are present in such small amounts that they are just above the threshold of detection as determined by quantitative methods used at the time these solutions were analyzed. Although the concentration of these metals differed within these limits, the amounts present do not seem to correspond to the variations of total dissolved solids in the ground waters.

Lead was detected in trace amounts in some of the samples collected from the ore-bearing sandstone. At the localities from which these waters were collected this metal is known to occur in minor amounts in the uranium-vanadium ore.

Selenium and copper, common in many ore deposits in the Salt Wash member, were detected in water from the Brushy Basin member, even though this member contains very few ore deposits.

Fluoride in ground water from ore-bearing sandstone in the Salt Wash member is usually present in amounts ranging from 0.20 ppm to 0.90 ppm. However, samples 49/17W–6D_1 and 44/18W–33C_1, collected from the Brushy Basin member, have 2.60 ppm and 1.00 ppm fluoride, respectively. The significance of these differences cannot be determined from the few analyses available.

Detectable amounts of boron are present in most of the ground waters sampled for analysis. The average concentration of boron in all the samples analyzed is 0.05 ppm.

Uranium and vanadium were detected in all the water samples that were analyzed for these metals. The greatest amount of uranium and vanadium was detected in ground water from mine sumps (samples 50/18W–9A_1 and 37/21E–10B_1). Either the metals in these samples were present as colloids or else the ore minerals from these mines were more soluble in this ground water than elsewhere. It might be significant that these water samples have a higher magnesium-ion and hydrogen-ion concentration than those from any other locality. It is also suggested that the oxidation potential of these waters might differ from the ordinary ground-water solution from the Salt Wash member. In the remaining 17 samples, none contained uranium or vanadium in amounts greater than 1.20 ppm, and the median amount of uranium or vanadium in the normal ground water is about 0.10 ppm. As observed by Phoenix and reported by Judson and Osmond (1955), these amounts are appreciably higher than can be expected from nonmineralized areas.

Observed secondary uranium and vanadium minerals on fractures suggest that the concentration of the uranium and vanadium ions in the ground water might bear some spatial relationship to the ore deposits. To test this, sample 49/17W–6B_1 was collected at a spring issuing from ore-bearing sandstone of the Salt Wash at a point approximately 2,000 feet downdip from the nearest ore body, and sample 47/17W–29A_1 was collected from a mine stope in the immediate vicinity of sandstone that contained carnotite ore. The first sample contained 0.02 ppm uranium and 0.16 ppm vanadium, whereas, the second contained 0.20 ppm uranium and $<$0.10 ppm vanadium. The higher concentration of the uranium ions in the sample of ground water collected near an ore body suggests a difference that may be directly related to the proximity of the deposits.

It was expected that there might be a major difference in the uranium and vanadium content between the waters collected from the Salt Wash member and those collected from the overlying Brushy Basin member, as the Salt Wash contains practically all the ore deposits found in the Morrison formation. Differences, however, are not too striking. Three water samples from the Brushy Basin average 0.04 ppm uranium and 0.17 ppm vanadium. Samples of ground water from the Salt Wash and from the Brushy Basin together, excluding samples reported from ore or from mine sumps, and exclusive of those for which a "less than" value is given, have the following average content: 0.24 ppm uranium in 5 samples (50/18W–9C_1 50/18W–11C_1, 50/18W–12C_1, 49/17W–6B_1, and 47/17W–27D_1), and 0.45 ppm vanadium in 4 samples (49/17W–6B_1, 47/17W–27D_1, 49/17W–6D_1, and 43/19W–32C_1).

The relation of metal concentration to the hydrogen-ion concentration in the ground-water solutions cannot be determined with certainty from the few analyses available. Within the determined limits of hydrogen-ion concentration—that is, a pH of 6.8 to 9.4—uranium concentrations are between 18.9 ppm for the most acid solution to 0.06 ppm for those that are most alkaline; whereas, vanadium concentrations are between 95 ppm for the most acid solutions to 0.3 ppm for the most alkaline. These data would suggest a rather direct correlation with pH and the solubility of the uranium and vanadium. However, as Garrels (1953; 1954, written communication) has shown, the stability of uranium and vanadium in aqueous solutions is not only dependent upon the pH of the solution, but upon the Eh of the solution and upon the oxidation state of the uranium and vanadium compounds as well. Unfortunately, it has not been possible to measure Eh in natural solutions with consistent results, and thus no direct correlation between the amount of the uranium and vanadium in the ground-water solution and pH alone should be made until more data become available. The water samples that contain high concentrations of uranium and vanadium were collected from places where ores are undergoing active oxidation, thus giving maximum opportunity for solution of unstable phases formed during the oxidation process.

The efflorescent coatings of bicarbonate and sulfate salts around the rims of springs or seep outlets distant from known ore deposits are not radioactive. There is thus no indication that carnotite, or some similar uranium mineral, is being precipitated from the normal ground water at these places. On the other hand, the carnotite observed coating many fracture surfaces in the ore-bearing sandstone near the ore deposits above the present water table, as well as the efflorescent coatings of uranium and vanadium salts on mine walls, show that uranium and vanadium are migrating. Uranium minerals coating fractures may have formed from earlier ground water. It also seems likely that capillary water in the zone of aeration dissolves previously deposited minerals and carries uranium and vanadium only a short distance before precipitating them as salts on the mine walls.

CONCLUSIONS

Ground water is contained in sandstone strata of the Morrison formation that are ore bearing. This water is usually perched on mudstone and is free to fluctuate with seasonal variations in precipitation. Locally, where structural conditions prevent drainage, ground water is confined and the sandstone strata are saturated. The occurrence and chemical character of ground water in the Morrison formation are thus dependent upon a number of factors including variation in climate, the geomorphic history of the region, and upon the structure and composition of the rocks.

The analyses of the samples of ground water collected from the Salt Wash and Brushy Basin members of the Morrison formation probably represent the chemical character of the ground water contained in these rocks. The ground water in the Salt Wash is a weakly alkaline bicarbonate solution with variable amounts of calcium and magnesium ions; the ground water in the Brushy Basin is likewise weakly alkaline but is either a sulfate or bicarbonate solution with sodium.

The ground water in the Salt Wash, regardless of its chemical character, generally contains less than 1 ppm of uranium, vanadium, copper, lead, and selenium ions. Uranium, vanadium, and selenium ions, in amounts of less than 1 ppm, probably are also typical constituents of ground water in the Brushy Basin. The significance of the amounts of these ions present in ground water in both Salt Wash and Brushy Basin members in regard to spatial relationships to the ore bodies cannot be determined with certainty from the number of samples analyzed, but significant differences may exist. If the fluid responsible for introduction of the uranium and vanadium metals into the Salt Wash was comparable to the recent ground water, it contained very small amounts of the metal ions.

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Part 5. SUMMARY OF THE ORE MINERALOGY

By ALICE D. WEEKS, ROBERT G. COLEMAN, and MARY E. THOMPSON

CONTENTS

ILLUSTRATIONS

TABLES

ABSTRACT

In the Colorado Plateau uranium has been produced chiefly from very shallow mines in carnotite ores (oxidized vanadiferous uranium ores). Recent deeper mining has penetrated black unoxidized ores in water-saturated rocks, and extensive exploration has discovered many deposits of low vanadiferous to nonvanadiferous ores. The uranium ores include a wide range from highly vanadiferous to nonvanadiferous and from as much as 1 percent to a trace of copper, and they contain a small amount of iron and traces of lead, zinc, molybdenum, cobalt, nickel, silver, manganese, and other metals.

Recent investigation indicates that the carnotite ores have been derived by progressive oxidation of primary (unoxidized) black ores that contain low-valent uranium and vanadium oxides and silicates. The uranium minerals uraninite and coffinite are associated with coalified wood or other carbonaceous material. The vanadium minerals, chiefly montroseite, roscoelite, and other vanadium silicates, occur in the interstices of the sandstone and in siltstone and clay pellets as well as associated with fossil wood. Calcite, dolomite, barite and minor amounts of sulfides, arsenides, and selenides occur in the unoxidized ore.

Partly oxidized vanadiferous ore is blue black, purplish brown, or greenish black in contrast to the black or dark-gray unoxidized ore. Vanadium combines with uranium to form rauvite. The excess vanadium is present in corvusite, fernandinite, melanovanadite and many other quadrivalent and quinquevalent vanadium minerals as well as in vanadium silicates. Pyrite and part or all of the calcite are replaced by iron oxides and gypsum.

In oxidized vanadiferous uranium ores the uranium is fixed in the relatively insoluble minerals carnotite and tyuyamunite, and the excess vanadium commonly combines with one or more of the following: Calcium, sodium, potassium, magnesium, aluminum, iron, copper, manganese, strontium, or barium, or rarely it forms the hydrated pentoxide. The relatively stable vanadium silicates are little affected by oxidation.

The unoxidized nonvanadiferous ores contain uraninite and coffinite in close association with coalified wood and iron and copper sulfides, and traces of many other sulfides, arsenides and selenides. The oxidized nonvanadiferous ores differ from the vanadiferous ores because, in the absence of vanadium to form a uranyl vanadate complex, a great variety of secondary yellow and greenish-yellow uranyl minerals are formed. The uranyl sulfates and carbonates are more common than the oxides, phosphates, arsenates, and silicates. Because the sulfates and carbonates are much less stable than carnotite, the oxidized nonvanadiferous ores occur only as halos around cores of unoxidized ore and do not form large oxidized deposits close to the surface of the ground as do carnotite ores.

Oxidation has taken place since the lowering of the water table in the present erosion cycle. Because of local structures and the highly lenticular character of the fluviatile host rocks perched water tables and water-saturated lenses of sandstone are common high above the regional water table. Unoxidized ore has been preserved in these water-saturated rocks and the boundary between oxidized and unoxidized ore is very irregular.

INTRODUCTION

Vanadiferous uranium ores were discovered in sandstones in western Colorado in 1898 and carnotite, a yellow secondary uranyl vanadate mineral, was named the following year (Friedel and Cumenge, 1899). At first the ores were mined chiefly for radium, later for vanadium, and recently for uranium (Coffin, 1921; Fischer, 1942; Fischer, 1950). For many years the production was from oxidized ore in shallow mines, and the Colorado Plateau ores became characterized as carnotite ores (Hillebrand and Ransome, 1905; Hess, 1933). Recent extensive exploration and deeper mining, in many places in the Colorado Plateau, have penetrated black unoxidized vanadiferous ore below perched water tables or close to the main water table. Also nonvanadiferous ores, both oxidized and unoxidized, have been found. Much of the present uranium produced in the Plateau is from relatively unoxidized, or primary, ore. The deposits are now generally referred to as sandstone-type uranium deposits rather than carnotite deposits.

The chief uranium-producing beds in the Colorado Plateau are in the Morrison formation of Late Jurassic age and contain vanadiferous uranium ore. Important production also comes from the Shinarump member and other basal sandstones of the Chinle formation of Late Triassic age. These contain vanadiferous uranium ore in Monument Valley, Ariz.; Big Indian Valley, San Juan County, and the Temple Mountain area, Emery County, Utah; copper-uranium ore in the White Canyon and Red Canyon areas of San Juan County, Utah; and uranium ore in other areas of Utah and Arizona. The Todilto limestone of Late Jurassic age on the northeast and east of the Zuni uplift in New Mexico contains uranium and a little vanadium. The Entrada formation of Late Jurassic age along the eastern margin of the Plateau in Colorado contains vanadium ore with low uranium content. Both a geographic and stratigraphic variation in metal ratios occurs in the Plateau ores (Part 3 of this volume).

Thanks are due many of our colleagues on the Geological Survey—especially the authors of the other parts of this volume—who have advised or participated in this study. Chemists, spectrographers, and X-ray crystallographers have done much analytical work, and many field geologists, both of the U. S. Geological Survey and the U. S. Atomic Energy Commission, and mining company employees have aided us in this study. References to the geology and mineralogy of various uranium deposits on the Colorado Plateau by J. W. Gruner, P. F. Kerr, and many others have been compiled by Cooper (1953, 1954).

CLASSIFICATION

The Plateau uranium ores are classified on the basis of whether or not a significant amount of vanadium is associated with the uranium (Weeks and Thompson, 1954). The presence of vanadium has an important chemical and mineralogic control on the uranium during the oxidation of the ore. Vanadiferous uranium ore ranges in V : U ratio (weight percent) from more than 15 : 1 to 1 : 1 and contains traces of copper and other metals, but in general the copper content is less than in nonvanadiferous ores. The uranium ores referred to in this report as nonvanadiferous may contain traces of vanadium and commonly contain minor amounts of copper and other metals, locally as much as 1 percent of copper. The two main types may be subdivided according to the degree of oxidation that has taken place. Mineralogically the types differ greatly because the affinity of vanadium for uranium tends to make the uranyl vanadates carnotite and tyuyamunite the chief uranium minerals in oxidized vanadiferous ore, whereas the oxidation of uraninite in nonvanadiferous ore produces a greater variety of secondary yellow and greenish-yellow uranyl minerals such as hydrated oxides, carbonates, sulfates, phosphates, arsenates, and silicates (tables 1 and 2). Subdivision of the nonvanadiferous uranium ores on the basis of copper content (Finch, 1954) is unnecessary because the copper is unimportant commercially and it does not control the uranium during oxidation by complexing as does vanadium. The uranium ore at Temple Mountain in the eastern part of the San Rafael Swell in Utah has been referred to as asphaltite ore (Hess, 1922) because of the abundance of asphaltic or other carbonaceous material. However, higher-than-average carbon content does not prevent classifying this ore on the basis of mineral assemblage with the other vanadiferous uranium ores. All the Plateau uranium deposits have associated carbonaceous material, and the Temple Mountain ores differ more in degree than in kind.

Much more vanadiferous than nonvanadiferous uranium ore has been mined on the Colorado Plateau. This is due to the influence of intensive mining of vanadium just prior to the recent interest in uranium mining. Seven of the nine processing plants on the Plateau in 1955 handled vanadiferous ore and recovered both vanadium and uranium (Ritter, 1955). Recently the production of low vanadiferous and nonvanadiferous ores has increased rapidly. The sandstone-type uranium deposits on the south and west flanks of the Black Hills, in South Dakota and Wyoming, are moderately vanadiferous and resemble the carnotite ores of the Colorado Plateau. However, the sandstone-type uranium deposits in the Ambrosia Lake district of McKinley County, New Mexico and in the Powder River basin of Wyoming seem to be low vanadiferous and those in the Wind River basin of Wyoming and in Karnes County, Tex., many contain more uranyl phosphates and arsenates than uranyl vanadates.

TABLE 1.—*Uranium minerals found on the Colorado Plateau*

Oxides:
- Uraninite, UO_2+
- Becquerelite, $2UO_3 \cdot 3H_2O$
- Schoepite, $UO_2(OH)_2 \cdot H_2O$
- Fourmarierite, $PbU_4O_{13} \cdot 7H_2O$ (?)
- Gummite (fine-grained mixture consisting in part of hydrated oxides)

Carbonates:
- Rutherfordine, $(UO_2)(CO_3)$
- Schroeckingerite, $NaCa_3(UO_2)(CO_3)_3(SO_4)F \cdot 10H_2O$
- Bayleyite, $Mg_2(UO_2)(CO_3)_3 \cdot 18H_2O$
- Swartzite, $CaMg(UO_2)(CO_3)_3 \cdot 12H_2O$
- Andersonite, $Na_2Ca(UO_2)(CO_3)_3 \cdot 6H_2O$
- Liebigite, $Ca_2(UO_2)(CO_3)_3 \cdot 10\text{–}11H_2O$
- Rabbittite, $Ca_3Mg_3(UO_2)_2(CO_3)_6(OH)_4 \cdot 18H_2O$

Sulfates:
- Uranopilite, $(UO_2)_6(SO_4)(OH)_{10} \cdot 12H_2O$
- Johannite, $Cu(UO_2)_2(SO_4)_2(OH)_2 \cdot 6H_2O$
- Zippeite, $K_4(UO_2)_6(SO_4)_3(OH)_{10} \cdot H_2O$ [1]
- Zippeite-like minerals containing Na; Co, Ni, Fe, or Mg

Phosphates:
- Autunite, $Ca(UO_2)_2(PO_4)_2 \cdot 10\text{–}12H_2O$
- Torbernite, $Cu(UO_2)_2(PO_4)_2 \cdot 12H_2O$
- Bassetite, $Fe(UO_2)_2(PO_4)_2 \cdot 8H_2O$
- Meta-autunite, $Ca(UO_2)_2(PO_4)_2 \cdot 8H_2O$
- Metatorbernite, $Cu(UO_2)_2(PO_4)_2 \cdot 8H_2O$
- Phosphuranylite, $Ca(UO_2)_4(PO_4)_2(OH)_4 \cdot 7H_2O$
- Sabugalite, $HAl(UO_2)_4(PO_4)_4 \cdot 16H_2O$
- Saléeite, $Mg(UO_2)_2(PO_4)_2 \cdot 8H_2O$

Arsenates:
- Zeunerite, $Cu(UO_2)_2(AsO_4)_2 \cdot 10\text{–}12H_2O$
- Abernathyite, $K_2(UO_2)_2(AsO_4)_2 \cdot 8H_2O$
- Metazeunerite, $Cu(UO_2)_2(AsO_4)_2 \cdot 8H_2O$
- Novacekite, $Mg(UO_2)_2(AsO_4)_2 \cdot 8\text{–}10H_2O$

Silicates:
- Coffinite, $U(SiO_4)_{1-x}(OH)_{4x}$
- Uranophane,[2] $Ca(H_3O)_2(UO_2)_2(SiO_4)_2 \cdot 3H_2O$
- Beta-uranophane, $Ca(H_3O)_2(UO_2)_2(SiO_4)_2 \cdot 3H_2O$
- Boltwoodite, $K_2(UO_2)_2(SiO_3)_2(OH)_2 \cdot 5H_2O$
- Cuprosklodowskite, $Cu(UO_2)_2(SiO_3)_2(OH)_2 \cdot 5H_2O$
- Sklodowskite, $Mg(UO_2)_2(SiO_3)_2(OH)_2 \cdot 6H_2O$
- Soddyite, $(UO_2)_5(SiO_4)_2(OH)_2 \cdot 5H_2O$

Vanadates:
- Carnotite,[3] $K_2(UO_2)_2V_2O_8 \cdot 1\text{–}3H_2O$
- Tyuyamunite, $Ca(UO_2)V_2O_8 \cdot 5\text{–}8\tfrac{1}{2}H_2O$
- Metatyuyamunite, $Ca(UO_2)_2V_2O_8 \cdot 3\text{–}5H_2O$
- Rauvite, $CaO \cdot 2UO_3 \cdot 5V_2O_5 \cdot 16H_2O$
- Uvanite, $2UO_3 \cdot 3V_2O_5 \cdot 15H_2O$

Unknowns: Several carbonates, sulfates, phosphates, and silicates

[1] Written communication, Clifford Frondel.

[2] Structural formula, Smith, Gruner, and Lipscomb, 1957.

[3] Structural formula, Appleman and Evans, 1957.

TABLE 2.—*Vanadium minerals found on the Colorado Plateau*

Oxides:
- Montroseite, $VO(OH)$
- Häggite, $V_2O_2(OH)_3$
- Paramontroseite, VO_2
- Doloresite, $3V_2O_4 \cdot 4H_2O$
- Duttonite, $VO(OH)_2$
- Navajoite, $V_2O_5 \cdot 3H_2O$

Phosphates:
- Sincosite, $CaV_2O_2(PO_4)_2 \cdot 5H_2O$

Vanadite:
- Simplotite, $CaV_4O_9 \cdot 5H_2O$

Vanadyl vanadates:
- Melanovanadite, $2CaO \cdot 2V_2O_4 \cdot 3V_2O_5 \cdot H_2O$ (?)
- Sherwoodite, $Ca_3V_8O_{22} \cdot 15H_2O$
- Fernandinite, $CaO \cdot V_2O_4 \cdot 5V_2O_5 \cdot 14H_2O$
- Corvusite, $V_2O_4 \cdot 6V_2O_5 \cdot nH_2O$
- Corvusite-like mineral, $V_2O_4 \cdot 5V_2O_5 \cdot 12H_2O$
- New calcium vanadyl vanadate
- New sodium calcium vanadyl vanadate
- New potassium iron vanadyl vanadate

Vanadates:
- Descloisite, $(Zn,Cu)Pb(VO_4)(OH)$
- Santafeite, $Na_2O \cdot 3MnO_2 \cdot 6(Mn,Ca,Sr)O \cdot 3(V,As)_2O_5 \cdot 8H_2O$
- Tangeite, $CuCa(VO_4)(OH)$
- Vésigniéite, $Cu_3Ba(VO_4)_2 \cdot (OH)_2$
- Volborthite, $Cu_3(VO_4)_2 \cdot 3H_2O$
- Vanadinite, $Pb_5(VO_4)_3Cl$
- Carnotite,[1] $K_2(UO_2)_2V_2O_8 \cdot 3H_2O$
- Tyuyamunite, $Ca(UO_2)_2V_2O_8 \cdot 5\text{–}8\tfrac{1}{2}H_2O$
- Metatyuyamunite, $Ca(UO_2)_2V_2O_8 \cdot 3\text{–}5H_2O$
- Fervanite, $Fe_2(VO_4)_2 \cdot 2\tfrac{1}{2}H_2O$
- Steigerite, $Al_2(VO_4)_2 \cdot 6\tfrac{1}{2}H_2O$
- Brackebuschite, $Pb_4MnFe(VO_4)_4 \cdot 2H_2O$
- New vanadate, $SrO \cdot CaO \cdot V_2O_5 \cdot 3H_2O$
- Rossite, $CaV_2O_6 \cdot 4H_2O$
- Metarossite, $CaV_2O_6 \cdot 2H_2O$
- Pascoite, $Ca_3V_{10}O_{28} \cdot 16H_2O$
- Hummerite, $K_2Mg_2V_{10}O_{28} \cdot 16H_2O$
- Uvanite, $2UO_3 \cdot 3V_2O_5 \cdot 15H_2O$ (?)
- Rauvite, $CaO \cdot 2UO_3 \cdot 6V_2O_5 \cdot 20H_2O$ (?)
- Hewettite, $CaV_6O_{16} \cdot 9H_2O$
- Metahewettite,[2] $CaV_6O_{16} \cdot 3H_2O$
- Barnesite, $Na_2V_6O_{16} \cdot 3H_2O$

Silicates:
- Roscoelite, $K(Al,V)_2(Al,Si_3)O_{10}(OH,F)_2$
- Vanadium-bearing hydrous mica
- Vanadium-bearing chlorite

[1] Appleman and Evans, 1957.

[2] Barnes, 1955.

MINERALOGY OF THE PRIMARY (UNOXIDIZED) ORES

VANADIFEROUS ORES

The primary vanadium-uranium ores are characterized in general by their black color and by the presence of low-valent uranium and vanadium oxides and silicates, and by copper, iron, lead, and zinc sulfides, arsenides, and selenides (table 3). These ores should not be confused with the blue-black or corvusite ores which represent an intermediate stage of oxidation. The ores have a wide range of vanadium content and for convenience in description they have been divided into groups on the basis of their vanadium-uranium ratios.

TABLE 3.—*Sulfides, arsenides, selenides, and other accessory metallic minerals found on the Colorado Plateau*

Elements:
- Native arsenic
- Native selenium

Sulfides:
- Pyrite, FeS_2
- Cobaltian pyrite $(Fe,Co)S_2$. As much as 1 percent Co.
- Selenian pyrite, $Fe(S,Se)_2$. As much as 5 percent Se.
- Marcasite, FeS_2
- Selenian marcasite, $Fe(S,Se)_2$. As much as 1 percent Se.
- Galena, PbS.
- Sphalerite, ZnS
- Chalcocite, Cu_2S
- Digenite, $Cu_{2-x}S$
- Bornite, Cu_5FeS_4
- Chalcopyrite, $CuFeS_2$
- Greenockite, CdS
- Covellite, CuS
- Molybdenite, MoS_2
- Jordisite,[1] Mo sulfide (?)
- Realgar, AsS
- Tennantite $(Cu,Fe)_{12}As_4S_{13}$

Arsenides:
- Domeykite, Cu_3As

Selenides:
- Clausthalite, PbSe
- Eucairite, CuAgSe
- Ferroselite, $FeSe_2$

[1] Gruner and Gardiner (1952).

VANADIUM-URANIUM RATIO GREATER THAN 15 : 1

Vanadiferous ores with low uranium content are characterized by the dominance of vanadium silicates over vanadium oxides and by the general lack of fossil wood. The unoxidized ores in the Entrada sandstone (Jurassic) of the Rifle and Placerville districts in western Colorado are repesentative of this group and appear to have a monotonous and simple mineralogic composition (pl. 1). At Placerville roscoelite is the dominant vanadium mineral occupying the intergranular areas as fine-grained micaceous aggregates, and at Rifle it is accompanied by some vanadium-bearing chlorite and mixed layer mica-montmorillonite (or so-called hydrous mica). No vanadium hydrous mica is present in the primary roscoelite ore at Placerville. The chemical analyses of Placerville samples (table 4) indicate that vanadium substitutes for aluminum; the high potassium and low water content are characteristic of roscoelite and not of vanadium hydromica. In roscoelite-rich thin layers either concordant with or cutting across bedding planes the quartz is strongly corroded and microstylolites (Fischer, 1942, p. 380) develop where the quartz grains are in juxtaposition.

TABLE 4.—*Chemical analyses of roscoelite*

	1	2	Metal atoms		
SiO_2	44.81	40.40	3.045		4.000
TiO_2	.56	.20	.011		
Al_2O_3	18.42	18.31	1.626	0.944 .682	
V_2O_3	20.41	17.57	1.061		1.967
V_2O_4	--------	1.69	.092		
FeO	1.58	.61	.039		
MgO	.83	.83	.093		
K_2O	8.28	11.26	1.081		1.081
Na_2O	.07	--------			
H_2O+	3.87	3.54			
H_2O-	.53	.40			
CaO	.20	3.10	Calcite impurity		
CO_2	--------	2.42			
Cr_2O_3	.02	--------			
MnO	.01	--------			
LiO_2	None	--------			
F	.15	<0.10			
P_2O_5	.01	--------			
	99.75	100.33			
Less O=F	0.06				
	99.69				

1. Roscoelite from Placerville, Colo. (Fischer, Haff, and Rominger, 1947, p. 124). Analyst, V. North.
2. Roscoelite from Fall Creek mine, Placerville, Colo., collected by A. L. Bush. Analyst, H. Levine.

TABLE 5.—*Analyses of uraninites* [1] [2]

	1	2
UO_3	31.08	20.58
UO_2	52.28	42.49
ThO_2	nil	--------
PbO	.74	1.48
CuO	2.96	--------
Ni_2O_3	--------	.40
Co_2O_3	--------	.64
Fe_2O_3	1.21	1.93
TiO_2	--------	.29
Al_2O_3	.30	1.18
ZnO	--------	4.09
MnO	--------	.22
SiO_2	2.87	4.35
CaO	2.22	2.40
BaO	.15	5.21
SrO		.34
H_2O+	.99	1.17
H_2O-	.28	.70
V_2O_5	.54	.22
S	1.70	4.35
As	.005	.013
Se	nil	.003
F	.21	.28
	97.54	92.34
O for F	.11	.12
Total	97.43	92.22
Specific gravity	9.1	8.6
Unit cell	$a_0=5.43$	$a_0=5.43$

[1] Analyst: Glen Edgington, U. S. Geological Survey.

[2] Age determinations on these uraninites have been published by Stieff and Stern (1952).

1. Happy Jack mine, White Canyon, Utah. Probably contains quartz, pyrite chalcocite, and chalcopyrite as minor impurities.
2. Shinarump No. 1 mine, Seven Mile Canyon, Grand County, Utah. Probably contains pyrite, quartz, calcite, and barite as minor impurities.

Montroseite (Weeks, Cisney, and Sherwood, 1953) is interleaved with the roscoelite aggregates as small discrete crystalline rosettes. Paramontroseite (Evans and Mrose, 1955) may locally supersede montroseite where oxidation has commenced. Calcite or dolomite commonly accompanies the montroseite and roscoelite and appears to be contemporaneous with the vanadium mineralization. Minor but persistent galena-clausthalite (selenium and sulfur in solid solution) and chalcopyrite are accompanied by sparse pyrite and marcasite. Small amounts of uranium are present, but its mineralogic occurrence has not been determined completely. The deposits at Rifle, Colo., are more fully described in Part 19 of this volume.

VANADIUM-URANIUM RATIO BETWEEN 15:1 AND 1:1

Ores with vanadium-uranium ratios ranging between 15:1 and 1:1 occur extensively in the Salt Wash sandstone member of the Morrison formation (Late Jurassic) and to a lesser extent in the Shinarump member and other basal sandstones of the Chinle formation (Triassic) and in other formations.

The uranium occurs in uraninite and coffinite (Stieff, Stern, and Sherwood, 1956) in the primary ore and almost without exception is associated with coalified wood or other carbonaceous material and with pyrite or other sulfides. Thorium and rare earths are conspicuously absent in analyzed uraninites (table 5) from the Colorado Plateau and the U(IV) is found to be in excess of U(VI). Various stages of uranium saturation of the coalified wood have been observed. An ordinary X-ray diffraction powder photograph of mineralized wood may not detect uraninite or coffinite unless several percent uranium is present.

Uraninite preferentially replaces the cell walls of the wood structure (pl. 1*C*). Commonly the cell lumens (cavities) are filled by sulfides (pl. 1*D*), but if the lumens are vacant the uraninite also forms in this area. Where the original wood structure was collapsed or vitrainized or both during diagenesis, the uraninite intimately impregnates or replaces the coal and faithfully retains the coaly structures. Uraninite deposited in the sandstone bordering fossil wood may show replacement of earlier sulfides, or detrital quartz, or be intimately intergrown with calcite or dolomite. Coffinite is found within coalified wood where it fills the cell cavities. Most of the occurrences of coffinite are in vanadiferous ores, and many of these are in the Salt Wash sandstone member of the Morrison formation in the Uravan mineral belt of western Colorado (Fischer and Hilpert, 1952).

Detailed study of polished sections of mineralized carbonaceous material indicates that much of the so-called asphaltite ore is sandstone containing many small detrital fragments of coalified wood with some interstitial insoluble carbonaceous matter that is anisotropic and does not show any cell structure. The quartz grains in the impregnated sandstone bordering the wood are commonly corroded. Particularly in the Temple Mountain area this type of ore is further impregnated or coated along joint surfaces with thick brown crude oil. The chemical character of these carbonaceous materials is discussed in Part 12 of this volume.

In the primary ores of this group vanadium oxides appear to be more abundant locally than vanadium silicates. The chief primary oxide, montroseite VO(OH), is easily oxidized to the more commonly observed paramontroseite. Another primary vanadium oxide häggite $V_2O_2(OH)_3$ has been identified from near Carlile, Wyo. (Evans and Mrose, 1958) and from several mines in McKinley and Valencia Counties, N. Mex. In places montroseite impregnates the fossil wood by filling cell cavities, but the growth of its elongate crystals soon obscures the wood structure. Typically its strong crystallinity causes the formation of rosettes and bands of intricate and sinuous nature either on contraction fractures in fossil wood (pl. 2*A*, *B*) or in interstitial areas of the sandstone (Weeks, Cisney, and Sherwood, 1953, p. 1237).

Associated with the montroseite and paramontroseite in the intergranular matrix are vanadium silicate minerals. Vanadium-bearing chlorite may be one of the most important vanadium silicates in the primary ores. Intensive study of a small number of samples by Hathaway (Part 11 of this volume) indicates that roscoelite is not an important mineral in this group, but that vanadium hydromica, characterized as a mixed layer mica-montmorillonite clay, is commonly present and may contain considerable amounts of vanadium. The vanadium silicates impart a deep greenish or brownish color to the rock and in thin section show a moderate birefringence and a marked pleochroism. Kaolinite is common in the ores of the Grants district in New Mexico but only a small amount is present locally in the Uravan district of Colorado. Kaolinite does not contain substituted vanadium.

Pyrite and marcasite are the most common sulfides associated with the primary ores and two distinct generations of iron sulfides have been recognized. Sulfides formed during diagenesis impregnate or form pseudomorphs of wood or occur as nodules and are considered pre-ore. Euhedral and massive pyrite associated with uraninite and galena are considered penecontemporaneous with the mineralization (pl. 2*C*). Detailed study of the iron sulfides shows that those associated with mineralization have been enriched in cobalt and nickel relative to the diagenetic sulfides. Galena is commonly present within the uraninite and as later vein material cutting uraninite, indicating two generations. Chalcopyrite, chalcocite, digenite, sphalerite, molybdenite, greenockite, native arsenic, and realgar occur sparingly in the primary vanadiferous ores.

Minor amounts of selenides including clausthalite, eucairite, and ferroselite are found along ore boundaries or associated with coalified logs in the Salt Wash member of the Morrison formation. Selenian marcasite, pyrite, and chalcocite are also common in the Salt Wash and may contain as much as 5 percent selenium substituting for sulfur. Although selenium has been detected in many ore bodies from other stratigraphic horizons, the only primary selenide identified as yet in the Chinle formation is ferroselite from a mine at Temple Mountain, Emery County, Utah. Ferroselite is a new mineral named by Buryanova and Komkov (1955) from Tuvinsk Autonomous Territory.

In addition to galena and clausthalite, lead occurs in small quantity in several unusual minerals. The rare lead vanadates—descloizite, vanadinite, and brackebuschite—form thin bands along ore borders in several mines in the Uravan district (Weeks, Truesdell, and Haffty, 1957). Also in this district the lead molybdate, wulfenite, was found in a mineralized log.

Calcite and dolomite or either with a smaller amount of barite make up a large part of the gangue. The primary ore from some mines contains less than 6 percent $CaCO_3$, the limit allowed in the mill processing of low-lime ores, but some primary ore contains much more calcite. At Mi Vida mine, San Juan County, Utah, coarsely crystalline white calcite is intimately associated with both montroseite and uraninite and fills spaces originally occupied by flattened branches and twigs of fossil wood. Small remnants of coalified wood as well as the shape of the calcite masses indicate that wood was replaced by calcite. The outer border of the calcite mass is commonly penetrated by montroseite needles forming a thing black shell. Gross (1956) estimates that the calcite content of Mi Vida ore averages 16 percent or higher and that the calcite content of the host rock (Chinle formation) averages between 22 and 28 percent. Samples of barren Salt Wash sandstone from drill core at depths of several hundred feet have a wide range of calcite content (oral communication, N. Archbold, 1955). Locally the sandstone host rock is cemented with pre-ore gypsum as in the Jo Dandy area on the faulted margin of the Paradox salt anticline, Montrose County, Colo. Detailed descriptions of ores from the J. J. and Mineral Joe mines in the Jo Dandy area are given in Parts 18 and 15 of this volume.

NONVANADIFEROUS ORES

Deposits in which vanadium is negligible and uranium is the only metal of importance—except where copper may be locally of commercial value—occur chiefly in the Shinarump member and other basal sandstones in the Chinle formation (Triassic). The ore is found mainly in channels that contain carbonaceous material and mudstone beds; these channels are along the thin edge (pinch-out) of the formation where conglomerate and sandstone beds fill cuts in the underlying formation (Finch, 1955). The Happy Jack mine, San Juan County, and the Delta (Hidden Splendor) mine, Emery County, Utah, are good examples of nonvanadiferous ore.

In general these primary ores are lighter in color than the vanadiferous ores because the black vanadium oxide, montroseite, is lacking, but a few ores with high sulfide content are dark colored. Uranium is contained chiefly in uraninite, and coffinite is scarce or lacking. Coalified wood and diagenetic sulfides are the main controls of uraninite deposition, and the wood is replaced in the same manner as described above.

Abundant sulfides are associated with uraninite in some of these ores— for example, the Happy Jack mine, in Utah—and a more complicated mineralization sequence is evidenced by ambiguous relations between the uraninite and the sulfides. Two generations of pyrite have been established in these primary ores with the pyrite in the uraninite showing rims of unidentified nickel and cobalt minerals—further evidence of nickel-cobalt enrichment accompanying the uranium mineralization (pl. 2D). Copper sulfides, including chalcopyrite, bornite, chalcocite, and covellite are dominant in some mines and lead, zinc, and iron sulfides dominate in others. Galena is commonly associated with uraninite either as early euhedral cubes or as late vein material. Sphalerite is very light colored with a low iron content (as at Happy Jack and Delta mines), indicating a temperature of formation below 138° C according to the method of Kullerud (1953). Molybdenum sulfide(?) in trace amount commonly occurs in mineralized wood. Silver has been noted in spectrographic analyses of sulfide concentrates, but no silver minerals—other than those previously known at Silver Reef, Washington County, Utah, and the eucairite at Cougar mine, San Miguel County, Colo.—have been identified. Some uraninite ores have very little accompanying sulfide; these ores are difficult to recognize in the field and must be prospected by careful search with a Geiger or scintillation counter.

Calcite content is high in some mines as at Sevenmile Canyon, north of Moab, Utah. Barite is present in small quantity in some nonvanadiferous ore, as at Dirty Devil No. 6 mine, Emery County, Utah, and seems to be less common than in the vanadiferous ores of the Morrison formation.

OXIDATION SEQUENCE AND MINERALOGY OF VANADIFEROUS URANIUM ORES

EARLY STAGE OF OXIDATION

The primary ores are stable in reducing environments after emplacement and generally retain their original minerals and textures if they are not exposed to oxidizing conditions. Those ores which have remained below the zone of oxidation (water table) retain their primary character. In the Colorado Plateau various stages of oxidation may be found superimposed on the primary ores because the deposits occur in many different situations with respect to the water table and also because of variable water-retention capacities of the pore space of the ore sandstones.

The numerous nonsilicate vanadium minerals are very sensitive to changes in oxidation potential and pH. Most of them have small fields of stability (Garrels, 1953; also Parts 6 and 7 of this volume) and therefore serve as convenient indicators of the degree of oxidation and the pH of the environment during oxidation. Montroseite, VO(OH), oxidizes readily to paramontroseite, VO_2, (Evans and Mrose, 1955) when exposed to air, as evidenced by the fact that montroseite specimens in the laboratory commonly alter to VO_2 in a few months' time. Other new vanadium (IV) minerals—doloresite, duttonite, and simplotite—are possibly all alteration products of montroseite (Stern and others, 1957, and Thompson, Roach, and Meyrowitz, 1958). Detailed study of these minerals has been made at the Peanut mine, Montrose County, Colo. (Part 17 of this volume).

Uraninite is altered, uranium (IV) oxidizing to uranium (VI), without producing any megascopically observable change. Coffinite seems to be slightly more resistant to oxidation than uraninite. The early oxidation of the primary uranium minerals apparently disperses the uranium into a black amorphous colloidal phase, an intermediate step between uraninite or coffinite and the yellow uranyl minerals. No X-ray pattern of any uranium minerals can be obtained from slightly oxidized ore. Considerable oxidation of vanadium takes place between the time of alteration of uraninite and coffinite and the appearance of uranyl vanadates in corvusite ore. The sulfides are still fresh and unaltered after oxidation of uraninite and montroseite has begun.

CORVUSITE ORE, PARTLY OXIDIZED

Further oxidation of the ores causes a change in color from black to blue black in ores of the corvusite stage. Some greenish-black and brown also appear at this stage. As soon as all the vanadium (III) has oxidized to vanadium (IV), the vanadium (IV) minerals alter to a group of compounds containing various proportions of vanadium (IV) and (V) with some calcium, iron, sodium, or potassium.

Available vanadium (V) combines with uranium (VI) to form the widespread but ill-defined and sometimes inconspicuous mineral rauvite (Hess, 1925) which may be dispersed in microscopic grains in massive corvusite or form glassy or gel-like coatings on quartz grains, pebbles, or contraction fractures in mineralized wood. Rauvite ranges in color from purplish black and brownish red in the gell-like varieties to orange red in the powdery aggregates. Its chemical formula is uncertain because samples giving the same X-ray powder pattern have slightly different chemical compositions. The calcium content may not be essential but all rauvite samples have a higher V: U ratio than carnotite and tyuyamunite. The rare and even less well known mineral uvanite is intermediate in V: U ratio between rauvite and carnotite and was found with rauvite at Temple Mountain, Utah, by Hess (1925).

Small amounts of several uranyl minerals including meta-autunite, phosphuranglite, saléeite, novacekite, uranophane, and boltwoodite, have been found in corvusite ore. These minerals form locally where uranyl ions are present and where the vanadium has not reached the quinquevalent state or where the pH is too low for formation of carnotite.

The best crystallized of the vanadium (IV–V) minerals is melanovanadite, for many years known only from the type locality in Peru and now recognized in a number of mines in the Plateau. A new calcium vanadyl vanadate from the J. J. mine, Montrose County, Colo., and from Eastside Carrizo mines, San Juan County, N. Mex., occurs in black bladed microscopic crystals and is under investigation. Microscopic tetragonal crystals of a bluish-black to greenish-black vanadate sherwoodite (Thompson, Roach, and Meyrowitz, 1958) have been noted in many mines. Most of the vanadium (IV–V) material, however, is poorly crystallized and shows a very complex and intimate mixture of minerals quite similar in appearance and generally referred to in the field as "corvusite" or fernandinite. A common feature associated with the growth of corvusite between quartz sand grains is microscopic fracturing of the quartz parallel to the corvusite-rich band or normal to the columnarlike aggregates of corvusite; this was noted especially in corvusite-rich nodules at the Monument No. 2 mine, Apache County, Ariz., and in many mines in the Uravan mineral belt of western Colorado. The molecular ratio of vanadium (V) to (IV) ranges from 6 in the corvusite originally described (Henderson and Hess, 1933) to somewhat lower values in other corvusitelike minerals (analyzed by A. M. Sherwood and R. Meyrowitz, 1954). The vanadium (V) to (IV) ratio decreases in this group of minerals as the calcium content increases, with a possible series from corvusite (6) through fernandinite (5) to melanovanadite (1½), somewhat like the navajoite-hewettite-pascoite-rossite series described below. A new vanadium (IV) and (V) mineral containing some iron and potassium occurs in the Hummer, Van, and Peanut mines, all in Montrose County, Colo. It is a dark-red fibrous mineral similar in appearance to hewettite and is being studied. A new sodium calcium vanadyl vanadate found in the Section 33 mine near Grants, N. Mex. and in the Bowen and LaSalle mines near Uravan, Colo., occurs in thin seams of dark green fibrous or bladed microscopic crystals.

By the time the corvusite stage is reached, some of the associated minerals begin also to show a response to the oxidizing conditions. The sulfides alter to oxides and sulfates, and the selenides alter either directly or indirectly to native selenium. Occurrences of native selenium have been described from South Dakota, Colorado, and Utah (Thompson, Roach, and Braddock, 1956) and many additional occurrences in Wyoming, Utah, New Mexico, and Colorado are known. Depending on the relative abundance of calcite with respect to pyrite in the primary ore, a wide range of pH is possible when the pyrite oxidizes during the corvusite stage and the oxidizing solutions may remain acid or be neutralized by calcite. Part or all of the calcite gangue and cement in the sandstone may be dissolved and the sandstone may be partly recemented by gypsum and iron oxides. (The possible addition of calcium carbonate as recent caliche is noted below.)

CARNOTITE ORE, HIGHLY OXIDIZED

As oxidation progresses, carnotite and tyuyamunite develop chiefly from rauvite, and some may form in other ways (investigation in progress). Once crystallized, the carnotite is remarkably stable and fixes the uranium very effectively. The minerals containing vanadium (IV) and (V) of the corvusite stage oxidize to form vanadium (V) minerals. The specific ones formed depend closely on pH conditions (see Parts 6, 7, and 8 of this volume), on the presence of certain cations to combine with vanadium, and on several other factors. Vanadium fixes all available uranium in uranyl vanadates, and the excess vanadium may form the hydrated pentoxide, navajoite (Weeks, Thompson, and Sherwood, 1955), or much more commonly it combines with other elements—these include calcium to form hewettite and pascoite (Hillebrand, Merwin, and Wright, 1914) and rossite (Foshag and Hess, 1927), potassium and magnesium to form hummerite (Weeks and Thompson, 1954), sodium for sodium vanadate (Weeks and Thompson, 1954), aluminum for steigerite (Henderson, 1935), iron for fervanite (Hess and Henderson, 1931), copper for volborthite and tangeite (formerly known as calciovolborthite), or barium and copper for vesignieite (Guillemin, 1955). These vanadates range in color from brown through red, orange, yellow, and green to nearly colorless. Hewettite readily dehydrates to metahewettite (Barnes, 1955) and rossite dehydrates to metarossite. Other new vanadates include santafeite, a manganese vanadate (Sun and Weber, 1957), and a strontium calcium vanadate being studied by M. E. Thompson.

Although the presence of tyuyamunite in the "carnotite ores" of the Colorado Plateau has been known for many years (Hillebrand, 1913 and 1924), the relative abundance of the two minerals is not known quantitatively. Neither is it known how much tyuyamunite has been converted to carnotite (or vice versa) by cation exchange (Hillebrand, 1913, 1924; Murata, Cisney, Stieff, and Zworykin, 1951). The common assumption that carnotite is more abundant than tyuyamunite in the Uravan mineral belt of Colorado is difficult to evaluate in this mineralogic study, because more identifications have been made of mineral specimens from joint coatings and mineralized logs than of average ore sandstone with fine-grained uranyl vanadates disseminated interstitially between the quartz grains and impregnated in clay. Most of the yellow coatings on joints and some of the richly mineralized logs (such as those found in 1950 in the Charles-T No. 2 mine in the Slickrock district, San Miguel County, Colo.) are tyuyamunite, but these account for a small part of the total uranium that has been mined from oxidized ore, and carnotite may be the dominant mineral in the Uravan belt. However, in the Lukachukai group of mines, Apache County, Ariz., and especially in the mines in Todilto limestone in the Grants district, McKinley and Valencia Counties, N. Mex., tyuyamunite seems to be more abundant than carnotite. The recent formation of tyuyamunite on joints and fractures is related to the calcium content and alkaline nature of the ground water caused by the present semiarid climate and to the high calcite content of the country rock (as at Mi Vida mine, p. 70). Phoenix (Part 4 of this volume) classed most of the ground-water samples from the Salt Wash sandstone member of the Morrison as calcium bicarbonate waters. He found these water samples were alkaline as did R. F. Marvin during fieldwork in 1954 and 1955 with the senior author.

Although in the laboratory, tyuyamunite is readily base-exchanged to carnotite in the presence of potassium-bearing solutions, evidence is lacking that the bulk of Plateau carnotite has undergone exchange. A general rule for the Plateau is that carnotite is typically finer grained than tyuyamunite although some exceptions to this rule are known. If much of the carnotite had formed by exchange, one would expect the grain size and habit to be similar to that of tyuyamunite. Carnotite apparently occurs where potassium is available in the interstitial hydrous mica of the sandstone, and tyuyamunite forms where calcium is available from the host rock or ground water. Tyuyamunite contains more water than carnotite, and when tyuyamunite ores are mined, the mineral readily dehydrates to metatyuyamunite (Stern, Stieff, Girhard, and Meyrowitz, 1956).

In the oxidized ores of the Uravan belt carnotite, tyuyamunite, and the various brightly colored vanadates are locally abundant but in the bulk of the ore are actually less abundant than the fine-grained greenish-gray and light-brown vanadium silicates that contributed much of the vanadium mined in the Plateau (Fischer, 1942) previous to World War II. Mineralogic and chemical study of these vanadium silicates by the Geological Survey, is in progress and therefore the present description of these minerals is tentative. The outcrop of ore sandstone is commonly gray with little or none of the brightly colored minerals. The probable leaching of the vanadates from the outcrop is discussed below. These gray sandstone ores have commonly been termed roscoelite ores in contrast to carnotite ores, but preliminary study suggests that true roscoelite is common only in the Rifle and Placerville districts of Colorado. In the Uravan belt vanadium-bearing chlorite, and hydrous mica or mixed-layer clays seem to be more abundant than true roscoelite. Some of the vanadium silicate interstitial in the sandstone probably has persisted practically unchanged from the unoxidized ore, whereas some clay may have become impregnated with vanadium solutions migrating during oxidation.

At the Rifle mine near Rifle, Colo., where the vanadium silicate ore is affected very little by oxidation, small amounts of the uranyl carbonates bayleyite and swartzite form efflorescences on the mine walls. Here probably little or no soluble vanadium is available to combine with the uranium.

In areas where the vanadium-uranium ratio is low or the vanadium is moderately low and irregularly distributed, small amounts of other uranium minerals may occur, as uranophane near Grants, N. Mex., and autunite, andersonite, schroeckingerite, and zippeite in the Thompsons district, Grand County, Utah. Study is in progress on the uranium deposits in the Morrison formation and in the Todilto limestone of the Grants and Laguna areas in New Mexico which range from low to nonvanadiferous.

MINERALOGY OF OXIDIZED NONVANADIFEROUS URANIUM ORES

URANIUM MINERALS

The nonvanadiferous uranium ores differ notably from the vanadiferous because oxidation of uraninite in the absence of a significant amount of vanadium produces a greater variety of secondary uranium minerals. These include hydrated oxides, carbonates, sulfates, phosphates, arsenates, and silicates. They are microcrystalline or massive and range in color from orange through yellow, and greenish yellow to green. They fill pore spaces or minute fractures in sandstone, conglomerate, or fossil wood and coat joint surfaces and mine walls. Among these minerals none is as predominant as carnotite and tyuyamunite are in the oxidized vanadiferous ore (Weeks and Thompson, 1954). In general these secondary minerals form irregular rims around unoxidized remnants of the primary minerals. They develop next to the core of unoxidized minerals and are removed from the outside of the rim until the source is gone. These secondary uranium minerals generally do not form large deposits of completely oxidized ore as does carnotite, because their relative solubilities are much greater than that of carnotite.

The hydrated uranium oxides are small in quantity and found in only a few mines because sulfate, carbonate, or some other anion is usually present to combine with uranium. Small amounts of becquerelite, schoepite, and fourmarierite are closely associated with oxidizing uraninite.

In the oxidation of sulfide-rich uraninite ore the most abundant secondary uranium minerals are the uranyl sulfates: johannite, uranopilite, zippeite, and other unidentified zippeitelike minerals. These green, yellowish-green, and deep-yellow minerals are beautifully developed by evaporation on the walls of Happy Jack mine in White Canyon, San Juan County, Utah (Part 16 of this volume; and Trites and Chew, 1955).

The uranyl carbonates are commonly developed wherever the sulfide content of the ore is low and host rock, or gangue, contains sufficient carbonate, as at Shinarump No. 1 mine, Utah (Finch, 1954), or where the ground water is carbonate rich. Seven uranyl carbonates have been identified on the Colorado Plateau, including rutherfordine (rare), liebigite, and schroeckingerite; and four new carbonates—andersonite (Axelrod and others, 1951), bayleyite (Axelrod and others, 1951; Stern and Weeks, 1952), rabbittite (Thompson, Weeks, and Sherwood, 1955), and swartzite (Axelrod and others, 1951). Two additional uranyl carbonates were unidentified. Small amounts of rutherfordine are found associated directly with uraninite. All the uranyl carbonates except rutherfordine form on mine walls and on fracture surfaces by evaporation of uranyl carbonate solutions. Only because of the semiarid climate on the Plateau are these carbonates temporarily preserved. Occasional heavy rains wash away the carbonates, such as bayleyite at Hideout mine and andersonite at the Atomic King mine in San Juan County, Utah, and then they gradually accumulate again during a dry season.

The uranyl phosphates are rare in the Plateau, because the sandstone host rock is low in phosphate except very locally where fossil bones are preserved. Small amounts of autunite, meta-autunite, phosphuranylite (possibly an alteration product of autunite), torbernite, metatorbernite, and bassetite have been found. Small amounts of uranyl arsenates are present: metazeunerite at a number of localities in White Canyon and in the San Rafael Swell, in Utah; and novacekite (Stern and Annell, 1954), abernathyite (Thompson, Ingram, and Gross, 1956), and zeunerite at one locality each. The uranyl silicates—uranophane, boltwoodite (Frondel and Ito, 1956) sklodowskite, and cuprosklodowskite— are not abundant in the Plateau. The unknown sulfates, phosphates, and silicates that are being studied probably include several new minerals.

SECONDARY MINERALS OF COPPER AND OTHER METALS

Copper, the chief associated metal in some of the nonvanadiferous ore as well as in some of the vanadiferous deposits, occurs in many secondary minerals, commonly as malachite, azurite, chalcanthite, antlerite, brochantite, and chyrsocolla, and rarely as conichalcite, chalcoalumite, and volborthite. Several other metals differ in abundance from one mine to another: iron and manganese in limonite and wad; cobalt in bieberite (commonly dehydrated), cobaltocalcite, cobaltomenite, erythrite, or cobaltoan pickeringite; molybdenum in ilsemannite, powellite, or ferrimolybdite; and traces of lead, zinc, nickel, and silver.

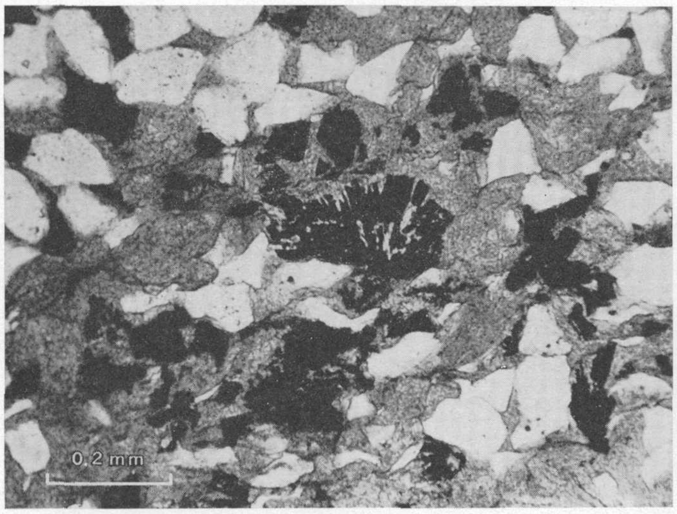
The presence of brightly colored copper, cobalt, and molybdenum secondary minerals on the rock outcrop or on joint surfaces within a few feet of the cliff face is helpful to the prospector, but many small copper deposits on the Plateau do not contain commercial quantities of uranium.

ASSOCIATED MINERALS

Clay lenses in the ore and mudstone or shale underlying ore are commonly bleached. During oxidation, especially of the sulfide-rich ores, the clays are altered further by development of one or more of the following: Kaolinite, jarosite, alunite, or gibbsite. Fluorescent uraniferous opal and allophane coat some joint surfaces and serve as prospecting guides.

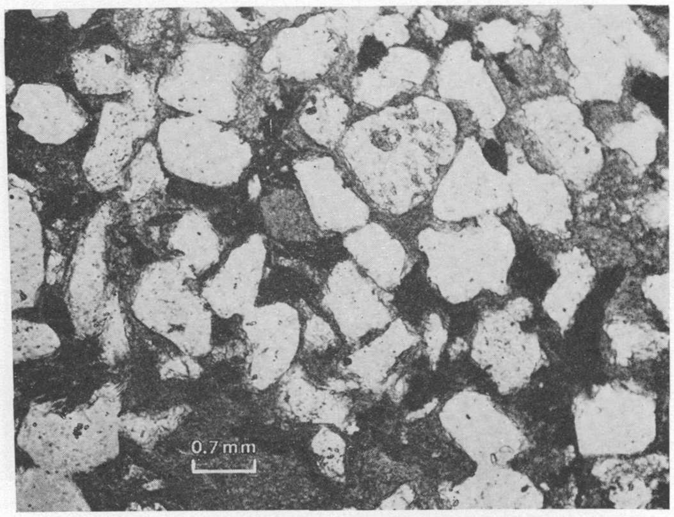
RELATION OF OXIDATION TO WATER SATURATION OF ORE

Second only in importance to the range of primary composition of the Colorado Plateau uranium ores is



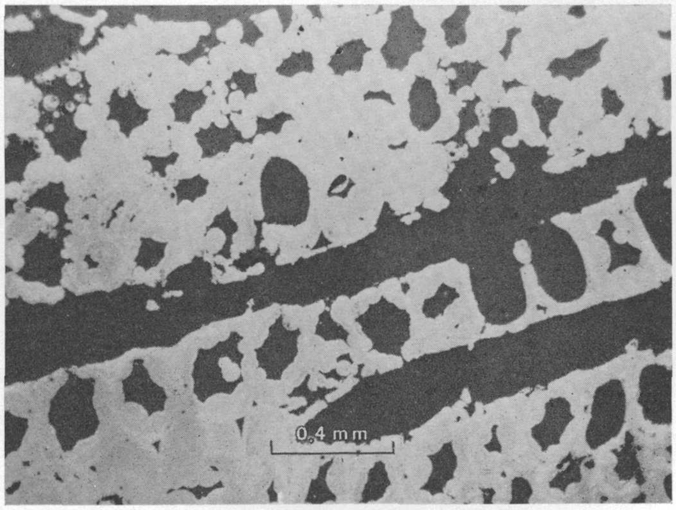
A. PRIMARY VANADIFEROUS ORE, 1,700 FT IN FROM THE PORTAL, FALL CREEK MINE, PLACERVILLE, COLO.

The irregular white areas are strongly corroded quartz-sand grains. The gray groundmass is roscoelite and the black opaque areas are montroseite, some showing radiating bladed crystals. Thin section.



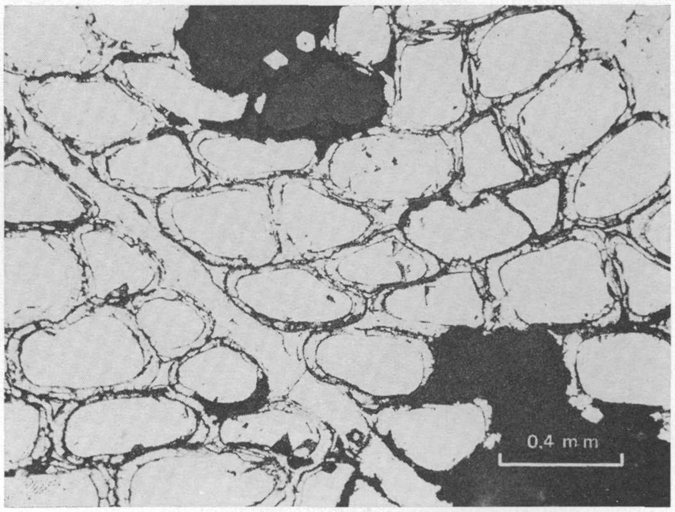
B. PRIMARY VANADIFEROUS ORE, 7,000 FT IN FROM THE PORTAL, GARFIELD MINE, RIFLE, COLO.

The irregular white areas are quartz grains showing some corrosion. The gray intergranular areas are roscoelite and the black opaque grains are montroseite. Thin section.



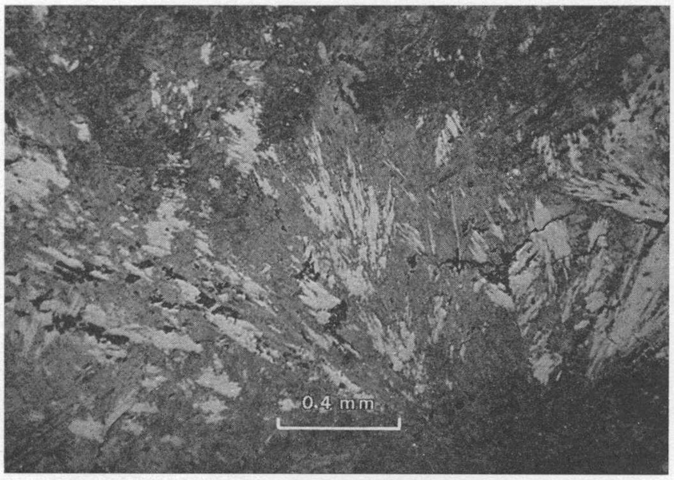
C. PRIMARY VANADIUM-URANIUM ORE, MI VIDA MINE, SAN JUAN COUNTY, UTAH.

Uraninite (light gray) replaced cell walls of coalified wood and partially infilled the lumens. Calcite (dark gray) filled the remainder of the lumens and fractures along the wood rays. Polished section.



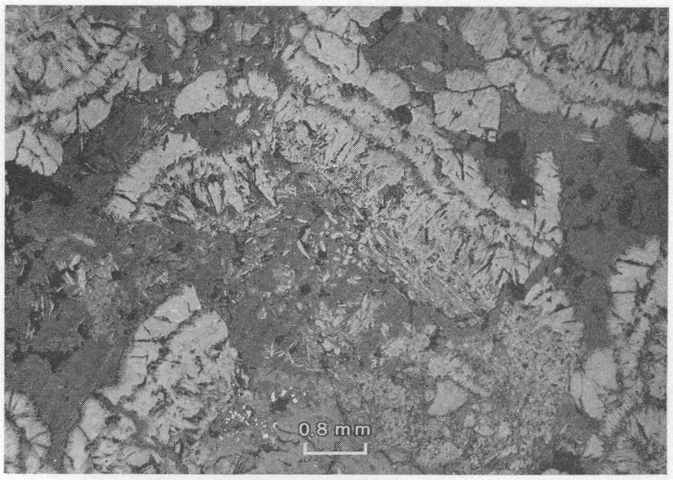
D. PYRITE ASSOCIATED WITH PRIMARY ORE, MARSHBANK CANYON MINE, TEMPLE MOUNTAIN, EMERY COUNTY, UTAH.

Pyrite (white) replaced the cell walls of coalified wood and impregnated the lumens. The dark particles are quartz. Polished section.



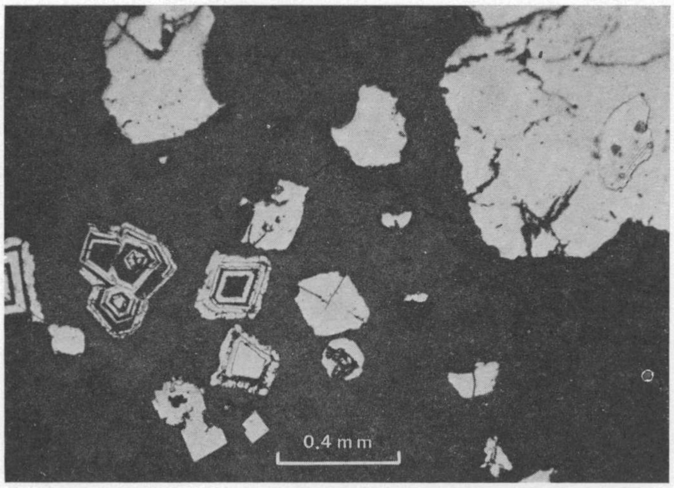
A. PARTLY OXIDIZED URANIUM-VANADIUM ORE, MI VIDA MINE, SAN JUAN COUNTY, UTAH.

Light-colored needlelike paramontroseite crystals replaced by dark-gray massive doloresite. Polished section.



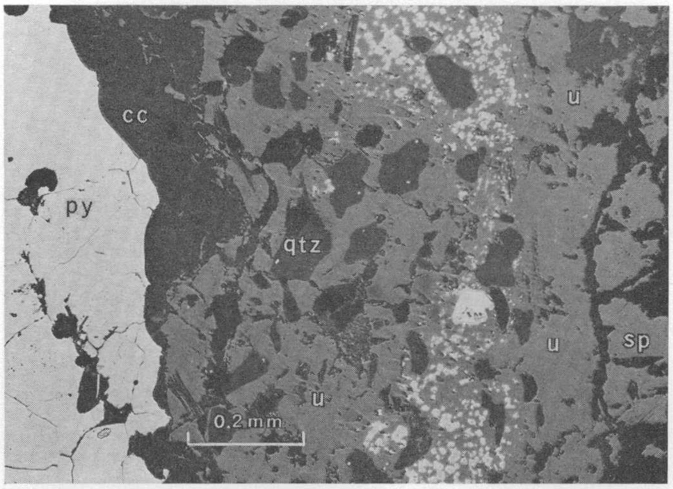
B. PRIMARY URANIUM-VANADIUM ORE, OVERSIGHT MINE, MONTROSE COUNTY, COLO.

Banded aggregates of montroseite fractured and healed later by calcite (dark gray). The medium-gray patch along the bottom is coalified wood. Polished section.



C. PRIMARY URANIUM-VANADIUM ORE, MI VIDA MINE, SAN JUAN COUNTY, UTAH.

The mottled dark-gray groundmass is an intimate mixture of uraninite and coffinite. Zoned crystals of pyrite show selective replacement by galena, uraninite, and coffinite. Two well-developed crystals of galena are in the lower left of the picture. The light irregular patches also are pyrite, and they show strong corrosion by the uranium minerals. Polished section.



D. PRIMARY NONVANADIFEROUS ORE, DELTA MINE, EMERY COUNTY, UTAH.

Detrital quartz (*qtz*) and massive pyrite (*py*) replaced by calcite (*cc*). The light-colored zone crystals in the uraninite (*u*) are second generation cobalt-rich pyrite. A band of sphalerite (*sp*) is along the right-hand border of the picture. Polished section.

their range in degree and depth of oxidation. Oxidation depends on access of air to the ore, as in exposed rocks with no soil cover and where evaporation is high, in relatively continuous permeable sandstone beds above the water table, and in strata truncated downdip by a canyon. Oxidation has been prevented or retarded where water is held in the pore space of the ore sandstone, as in strata protected by thick soil cover, in lenticular sandstone beds surrounded by clay, in strata below a perched water table or the main water table, and in strata that dip away from the valley wall.

UNOXIDIZED ORE IN WET MINES AT OR CLOSE TO THE WATER TABLE

A good example of wet unoxidized ore is at the School Section No. 36 mine, T. 30 S., R. 25 E., near the south end of the floor of Lisbon Valley, San Juan County, Utah. At a depth of about 70 feet a relatively sharp boundary occurs between partly oxidized ore and wet unoxidized ore containing fossil wood replaced by uraninite and calcite. The mine is at the foot of a long northward-facing slope that rises nearly 2,000 feet to the Monticello Plateau; the slope is covered with vegetation and holds considerable moisture.

The Basin No. 1 mine on the east side of Cottonwood Creek, west of Blanding, San Juan County, Utah, is wet because it is below the level of the creek bed. The mine is in a blanket-type deposit and the wettest and least oxidized ore is spotted, cemented with calcite, and contains small coalified wood fragments. Updip, above the west side of the creek, are many old mines in more oxidized ore.

The unoxidized ore at the Peanut mine, Montrose County, Colo., is described in Part 17 of this volume. During mining operations at the Peanut mine, the School Section No. 36, and many other mines in unoxidized ore, considerable water was released from saturated sandstone lenses that contained unoxidized ore.

PARTLY OXIDIZED DEPOSITS, ABOVE THE MAIN WATER TABLE BUT IN PROTECTED LOCATIONS WHERE SOME MOISTURE IS HELD

The Corvusite mine on Beaver Mesa, Grand County, Utah, is a good example of partly oxidized ore with small remnants of unoxidized ore. The deposit was mined intermittently for more than 40 years and was the type locality for the mineral corvusite (Henderson and Hess, 1933). The mine is located on the updip side of the mesa toward the La Sal Mountains, and the ore is in richly mineralized fossil trees and relatively small sandstone lenses interbedded with thick clay so that the ore remains saturated with water. The mesa is more than 7,500 feet above sea level, has considerable soil cover and vegetation, cool temperature, low evaporation, and possibly more rainfall than the lower parts of the Plateau. These factors all contribute to the continued dampness of the ore and they have prevented more than partial oxidation although the mine is high above the main regional water table.

At the Bitter Creek mine on the north side of Paradox Valley, Montrose County, Colo., the Salt Wash sandstone member of the Morrison formation dips 15° to the northeast, away from Paradox Valley. These strata are truncated by the San Miguel River some distance to the north, and water in the mine drains slowly downdip. At Bitter Creek the ore at the surface of the ground is oxidized, is lower than average grade in both vanadium and uranium, and contains gypsum. Mining has progressed several hundred feet downdip through a thick transition zone of partly oxidized ore consisting chiefly of corvusite and rauvite with remnants of unoxidized montroseite or paramontroseite and pyrite. The water-soluble efflorescence, pascoite, forms on the moist corvusite-rich layers. At depth, gypsum and iron oxides are absent and the barren rock is gray rather than buff. Partly oxidized rich ore pockets commonly contain a small amount of radioactive barite. This indicates that recent oxidation of the primary uranium minerals separated trace amounts of radium which, probably as sulfate, formed a coating on the crystals of barite in the gangue. Inasmuch as radium has a half-life of about 1,500 years, the radioactive coating on the barite would lose more than 99 percent of its radioactivity in 15,000 years. Possibly the radioactive coating was formed considerably less than 15,000 years ago. The lower grade of the ore in the old open-pit workings is probably due to leaching at the outcrop rather than to dissemination or spreading of small high-grade ore bodies as proposed by Heyl (1956).

The J. J. mine, Montrose County, Colo., described in Part 18 of this volume, shows the transition from unoxidized to oxidized ore at a perched water table.

DRY MINES WITH OXIDIZED VANADIFEROUS ORE

The dry mines with highly oxidized ore may be classified in three groups. Many carnotite deposits apparently have been oxidized in place with practically no movement of material. Some have been modified during an intermediate stage of oxidation by downdip migration of vanadium and possibly of uranium. Ore sandstone directly at the surface of the ground probably has been leached of some uranium and vanadium by alkaline surface and ground water.

OXIDATION IN PLACE

Where there is little or no catchment area to supply ground water to the ore sandstone, moist-air oxidation takes place without significant migration of vanadium and uranium. The supply of ground water is small or negligible in isolated knolls, in small fault blocks along the borders of the collapsed salt anticlines, or where strata dip away from a valley wall. Examples of mines situated thus are the Rattlesnake mine in the north end of Lisbon Valley, San Juan County, Utah; several mines in the Jo Dandy group along Paradox Valley; and the Dolores group of mines on the bench of Atkinson Mesa above the Dolores River, Montrose County, Colo.

The Rattlesnake mine in Lisbon Valley had (in 1954) highly oxidized ore in dry friable sandstone. The yellow and brown ore had spotted and banded textures resembling those in unoxidized ore and giving the appearance of oxidation with little or no movement of material. Hewettite, the red calcium vanadate, seems to be more abundant in the ores of the Jo Dandy and Dolores groups of mines than in the ores of the Club group (see below) of mines through which oxidizing solutions probably have migrated. In general, if the vanadium-uranium ratio is high, ores that have been oxidized in place by moist air have more of the brightly colored vanadates than other ores.

The carnotite- and tyuyamunite-rich logs found in various mines appear to be the oxidized product of fossil wood partly replaced with uraninite and impregnated with montroseite. Some of these have been oxidized with very little spreading or dissemination of uranium and vanadium. The detailed wood cell structure so commonly observed in polished sections of uraninite (pl. 1C) is destroyed by volume changes during oxidation, and carnotite logs show only the gross feature of the wood. Only one instance of wood cell structure preserved in secondary minerals has been noted—that of a narrow rim of becquerelite around uraninite-replaced fossil wood at Monument No. 2 mine, Apache County, Ariz. (oral communication, D. H. Johnson).

MODIFICATION DURING OXIDATION

Ores in strata that have a ground-water catchment area updip and that are truncated downdip by a canyon may have been modified during oxidation by migration of water-soluble vanadium and possibly selenium and other constituents, especially if the strata are moderately permeable. Vanadium is readily leached from partly oxidized ore by water; 50-g samples of blue-black ore (from the Bitter Creek mine, Montrose County, Colo., and the Corvusite mine, Grand County, Utah) in 500 ml of distilled water yielded solutions with pH below 2 which contained uranium as well as vanadium. Oxidizing ground water moving downdip through ore would leach vanadium from the vanadyl vanadates more easily than from the vanadium silicates. The water would be acid until neutralized by solution of carbonate cement.

The Club group of mines (Fischer, 1942, p. 386) on the bench formed by the Salt Wash sandstone member of the Morrison formation above the San Miguel Canyon at Uravan, Montrose County, Colo., are dry with chiefly oxidized ore and the ore rolls have "breakaway surfaces." The strata dip toward the canyon allowing water to drain through the more permeable sandstone beds. Higher on Club Mesa the Lasalle Mining Co.'s 260-foot shaft mine also is dry and has well-developed rolls in oxidized ore; a little corvusite ore and radioactive barite in mineralized logs; and some blanketlike spotted ore with calcite cement in the deepest, least oxidized part of the mine. The barite is coated with radioactive daughter products, probably radium sulfate, precipitated from recently oxidized primary ore minerals. Evaporation of moisture on certain beds of sandstone along the mine walls forms pascoite. Still higher on Club Mesa the Shattuck Denn Co.'s 500-foot shaft mine is moderately dry although certain horizons in the Brushy Basin shale member of the Morrison formation had considerable water when the operators were sinking the mine shaft. The ore is partly oxidized with a few remnants of coffinite and montroseite and a trace of secondary yellow appearing on the joint surfaces. The ore has an undulating surface but no typical "breakaway roll surfaces."

The Cougar mine in the Lower Group at Slickrock, San Miguel County, Colo., is on a bench of sandstone of the Salt Wash that dips toward the Dolores River canyon and has the same structural situation as the Club mines. Around the rim of the bench are many old adits and on top of the bench old open-pit workings which show mined-out rolls with "breakaway surfaces." The underground workings have numerous rolls in several sandstone lenses separated by thin clay beds. Away from the surface and cliff face some less-oxidized patches of ore persist and locally copper sulfides and copper, lead, and silver selenides occur, and the vanadiferous ore is in the corvusite stage. Up the hill a few hundred yards from the Cougar mine is the Little Muriel shaft about 35 or 40 feet deep. In the summer of 1954 after the mine had been abandoned for a time, about a foot of water had accumulated and seepage from a layer of corvusite ore had formed a thick coating of pascoite on the mine wall. Also, alteration of selenides had produced a pink efflorescence, the unstable monoclinic form of native selenium. Here is indication that water seeping through a partly oxidized deposit can transport vanadium, selenium, and probably other constituents.

Both the Cougar and Club mines are on the downdip side of areas that would feed water intermittently through them, spreading the vanadium and modifying its distribution. Vanadium silicate ore seems to predominate over vanadate ore in these mines probably because of leaching of corvusite. The ore rolls have well-developed "breakaway surfaces" that have been accentuated during oxidation by one or more of the following processes: solution of pyrite, the vanadates, and some of the carbonate cement, and volume changes due to oxidation and changes in hydration. These mines illustrate the gradation from oxidized ore near the surface to less oxidized ore back from the outcrop.

ORE SANDSTONE DIRECTLY AT THE SURFACE OF MESAS

Where small dry mesas are capped by ore sandstone as at the Eastside Carrizo mines, west of Shiprock, N. Mex., the chief vanadium mineral is vanadium chlorite, hydromica, or other vanadium silicate mineral. The uniformly light-gray ore is low in uranium, which is present in thinly disseminated yellow grains of tyuyamunite in the sandstone or as a coating of tyuyamunite on the joint surfaces below a thick calichelike crust. Uranium seems to have been leached from these surface deposits probably by recent alkaline ground water. Hewettite, also, probably has been leached from the surface by alkaline ground water; only a few remnants of hewettite and vanadyl vanadates occur under a hard cemented sandstone bed in the deepest part of one of the abandoned mines in the Eastside Carrizo group.

Other areas having vanadium silicates with very little carnotite or other vanadium minerals in ore exposed on top of mesas or broad benches include Flat Top Mesa in the middle of the syncline south of Gateway, Colo., and another Flat Top Mesa (also called Shinarump Mesa), west-southwest of Temple Mountain, Emery County, Utah.

A salt crust consisting principally of sodium sulfate, with some carbonate and other salts, accumulates near the foot of the Brushy Basin shale outcrops at the Cactus Rat mines in the Thompsons district, Utah. The surface water saturated with these salts has affected the recent oxidation of the ore in this area, causing the development of sodium vanadate, schroeckingerite, andersonite, zippeite, and other minerals not typical in vanadiferous ores.

The highly alkaline condition of the ground water and the thick salt crusts probably has affected the ore since Altithermal time in the Recent epoch—a warm dry period of great caliche formation from Wyoming (Leopold and Miller, 1954) south to Texas and Mexico (A. W. Weeks, 1945). In some areas—as in Monument Valley, Arizona and Utah—arid conditions were present in pre-Wisconsin time.

RELATIVE STABILITY AND SIZE OF OXIDIZED DEPOSITS

Because of the stability of carnotite, large oxidized deposits of carnotite have developed at shallow depth in the Colorado Plateau. In the progressive alteration of the black low-valent ores, the corvusite stage is the critical stage when the minerals are rather unstable and vanadium or uranium or both could be leached if water moved through. As soon as the carnotite stage is reached the deposit becomes relatively stable under shallow-depth conditions and little happens to it until, uncovered by erosion, it reaches the caliche zone at or close to the outcrop. Then in the alkaline environment carnotite appears to be slowly leached.

During oxidation of nonvanadiferous uranium ores on the Plateau, uranyl carbonates and sulfates seem to be more common than hydrated uranyl oxides, phosphates, arsenates, and silicates. The carbonates and sulfates are the least stable of the secondary uranium minerals (Garrels and Christ, Part 6 of this volume) and do not accumulate to form large oxidized deposits in place as does carnotite. The secondary minerals form around oxidizing uraninite and spread into joint fractures or along bedding planes but do not remain if water moves through the fractures.

Preservation of nonvanadiferous deposits in a dissected plateau such as the Canyon Lands of Utah depends on local structural and sedimentary features. Ore in a channel that is parallel to the regional strike has a better chance of preservation than ore in a channel parallel to the dip, especially if the channel is in strata that dip away from a canyon wall rather than toward the canyon. In addition to conditions favoring original deposition of ore, the prospector should consider the favorable conditions for preservation of nonvanadiferous ore. The Happy Jack mine on the southwest side of White Canyon is in a much more favorable situation for preservation of ore than are some of the mines on the southwest end of Deer Flats where there is less cover and the strata dip toward the canyon; these are on the west flank of the Monument Uplift in San Juan County, Utah. The ore of the Delta (Hidden Splendor) mine is protected in its location under the steeply dipping Wingate sandstone of Triassic age along the monocline of the southeast side of the San Rafael Swell in Utah.

SECONDARY ENRICHMENT

Secondary enrichment is unlikely in most of the vanadiferous uranium ore bodies for the following reasons: (1) the ore bodies are small tabular or podlike bodies with their long dimension parallel to the bedding; (2) the thickness is rarely more than 25 feet and commonly less than 10 feet; (3) in moist-air oxidation little if any migration takes place; (4) oxidation of the small ore bodies is rapid; (5) carnotite, the chief oxidized-uranium mineral has very low solubility; and (6) the sulfide content of vanadiferous ore generally is low.

Only a few nonvanadiferous uranium ore bodies in the Plateau, such as that at Happy Jack mine, Utah, (see Part 16 of this volume) have abundant sulfides and a favorable structure for migration of solutions from oxidized into unoxidized ore where sooty pitchblende, chalcocite, and covellite are deposited to form a zone of secondary enrichment. The chief oxidized products of nonvanadiferous uranium ore are much more soluble than carnotite and are generally washed away rather than redeposited.

TIME AND DEPTH OF OXIDATION

The oxidation of the Colorado Plateau uranium ores took place since the water table was lowered following the canyon cutting of the present erosion cycle. As the regional water table dropped, water was retained in the pore spaces of many rocks high above the main water table. This is particularly true in the fluvial-type sediments that are the common host rocks of the Plateau uranium ores. Tolman (1937, p. 156–157) states that the so-called capillary fringe zone may be much thicker above a sinking water table than above a rising water table.

Detailed study in the Uravan mineral belt shows that interbedding of shales, shaly sandstones, and lenticular sands together with a folded and faulted structure allows many varied situations with respect to perched water tables, retention of moisture, and the location of preserved unoxidized ore. The depth to unoxidized ore ranges from a few feet to many hundreds of feet. Because of the moderately low rainfall and the wide range of permeability of the sediments some deposits have had almost no water moving through and others have had enough to modify the deposit appreciably.

Bateman (1950, p. 265–269) states that submerged oxidized zones are common in western United States. Possibly when more detailed knowledge of the oxidation pattern of the Colorado Plateau ores is obtained, a history of fluctuating water tables may be found, but as yet no submerged oxidized zones have been recognized in Plateau ores. The irregular boundary of oxidation high above the regional water table more closely fits his description of stranded oxidized zones (Bateman, 1950, p. 265), "If the water table is depressed rapidly, oxidation may not be able to keep pace with it and the bottom of oxidation may become stranded above the water table." The oxidation history of the Plateau ores appears to be a one-way process following a lowered water table.

The small amount of radioactive barite found in several mines near Thompsons, Utah, and between Uravan and Paradox Valley in Colorado indicates that some of the oxidation is Recent. Studies of the Ra–U equilibrium of several high-grade carnotite and tyuyamunite samples by Stieff and Stern (Part 13 of this volume) indicate that in some mines oxidation occurred during the Pleistocene.

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Part 6. BEHAVIOR OF URANIUM MINERALS DURING OXIDATION

By R. M. Garrels and C. L. Christ

CONTENTS

ILLUSTRATIONS

ABSTRACT

Uranium occurs as U(VI) and U(IV) in minerals of the Colorado Plateau ores. The number of species containing U(VI) is large, but only two U(IV) minerals are known from the Plateau: uraninite, an oxide, and coffinite, a hydroxy-silicate. These oxidize to yield U(VI) before reacting significantly with other mineral constituents. Crystal-structure analysis has shown that U(VI) invariably occurs as uranyl ion, UO_2^{+2}. Uranyl ion may form complex carbonate or sulfate ions with resulting soluble compounds, but only in the absence of pentavalent vanadium, arsenic, or phosphorus. In the presence of these elements in the +5 valence state, the uranyl ion is fixed in insoluble layer compounds formed by union of uranyl ion with orthovanadate, orthophosphate, or orthoarsenate. Under favorable conditions UO_2^{+2} may react to form the relatively insoluble rutherfordine, UO_2CO_3, or hydrated uranyl hydroxides. These are rarely found on the Colorado Plateau as opposed to their excellent development in other areas, a condition which is apparently related to the semiarid climate and low water table of the Plateau. Uranium may also be fixed as uranyl silicate, but little is known about minerals of this kind. In the present study, emphasis has been placed on a detailing of the chemical and crystal-structure changes which occur in the oxidation paragenetic sequence.

INTRODUCTION

Uranium occurs in two valence states in minerals from the Colorado Plateau uranium ores: as U(VI) and U(IV). The number of species containing U(VI) is large, but only two minerals containing U(IV) have been isolated and characterized. They are uraninite, an oxide, and coffinite, a silicate or hydroxy-silicate. As has been documented in other parts of this volume (see especially Parts 5, 14 and 15), the occurrences of uranium minerals are quite consistent with the view that these two minerals are the progenitors of all the U(VI) phases. That interpretation will be accepted for the purposes of this discussion, and emphasis will be on a detailing of the chemical and structural changes that result in the production of many-hued and chemically diversified later generations from these two parent materials. These relations are shown in figures 13 and 14; the text is best followed by continuous reference to them.

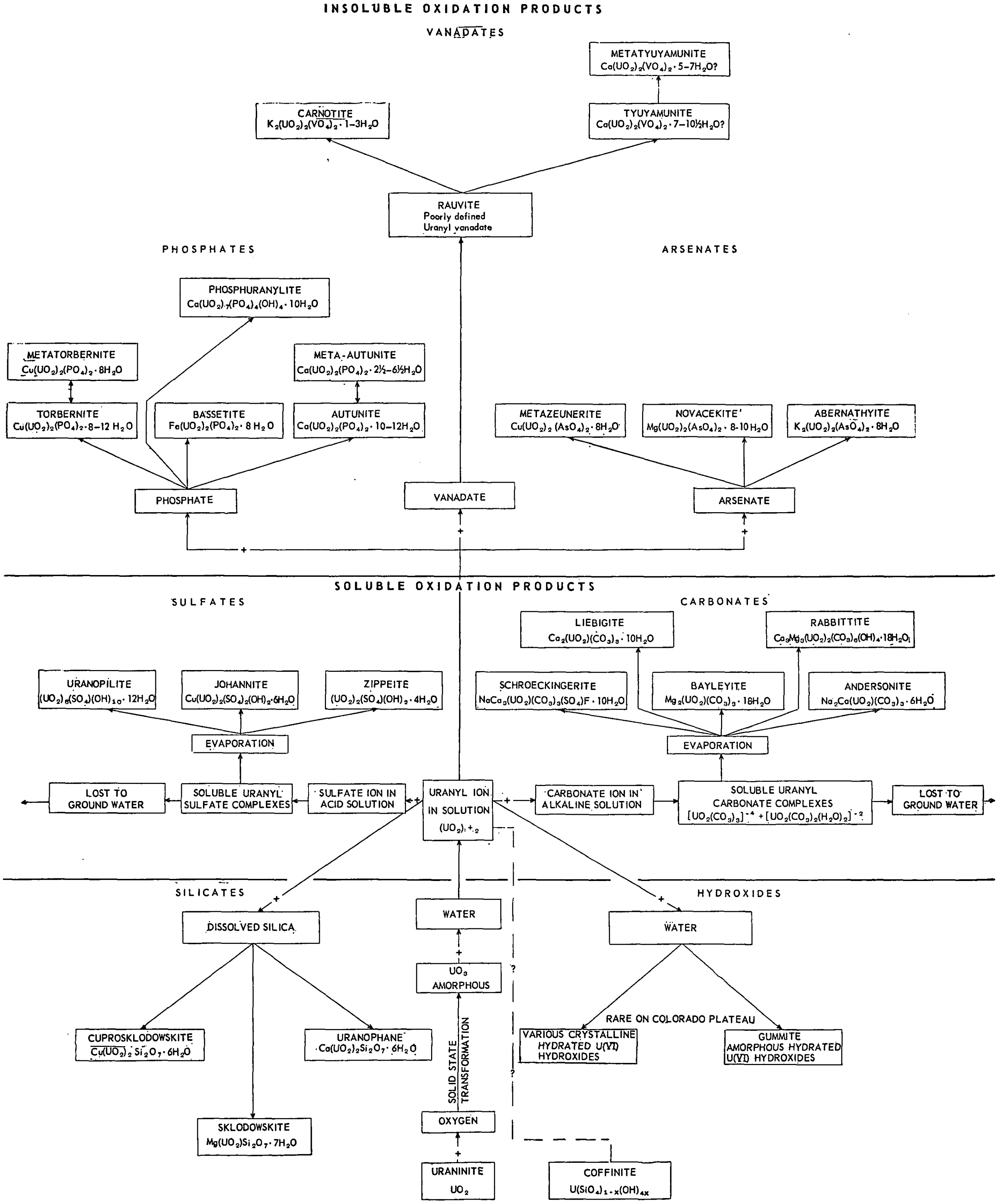
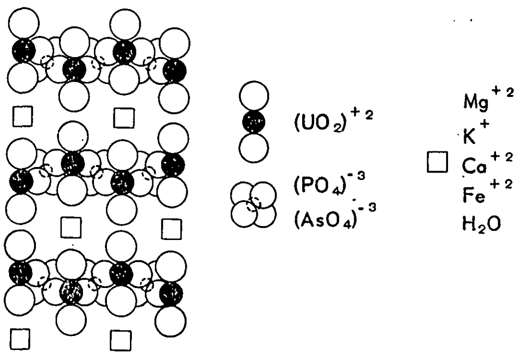


FIGURE 13.—Reactions and products in the weathering of uraninite and coffinite. Data on minerals from Weeks and Thompson (1954), Gruner (1954), and Weeks (oral communication).



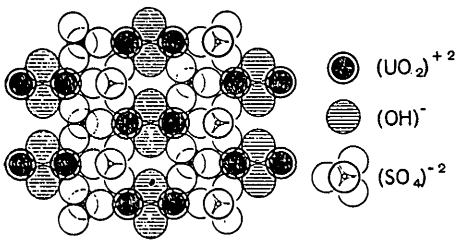
$M^{+2}(UO_2)_2(XO_4)_2 \cdot n\,H_2O$

(Illustrated by autunite $Ca(UO_2)_2(PO_4)_2 \cdot n\,H_2O$, after Beintema, 1938)

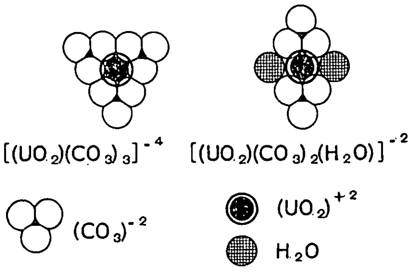
INSOLUBLE OXIDATION PRODUCTS

Phosphates and arsenates

(Vanadates are similar but see Part 7)

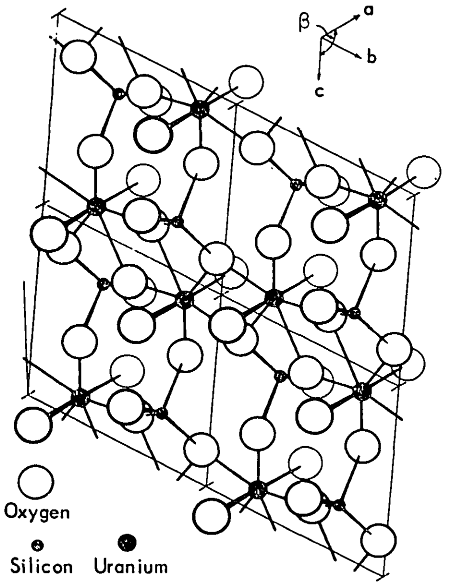


SULFATES



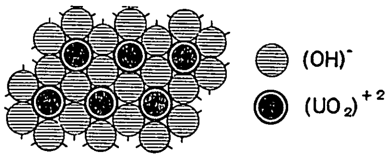
CARBONATE COMPLEX IONS

$(UO_2)^{+2}$ ion normal to plane)



SILICATES

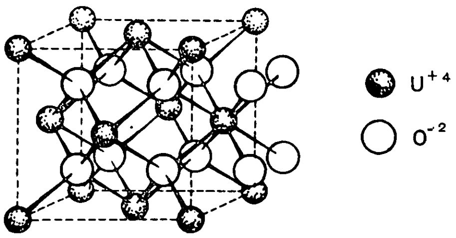
$[(UO_2)_2(SiO_4)_2]^{-4}$ Sheet structure in uranophane, according to Smith, Gruner, and Lipscomb, 1957



$UO_2(OH)_2$

URANYL HYDROXIDES

$(UO_2)^{+2}$ ion normal to plane



URANINITE UO_2

Figure 14.—Some structures involved in oxidation of uraninite.

URANINITE

Uraninite from Plateau deposits is fine grained. Analysis of carefully purified materials invariably shows UO_2 and UO_3 in various ratios, with a tendency for the maximum ratio to occur in massive specimens collected from sites protected from the atmosphere until mining operations took place. Presumably the material originally precipitated was largely UO_2, and most of the UO_3 reported is a product of the radioactive decay of uranium to lead, plus that from oxidation by the atmosphere (Palache and others, 1944).

Synthetic preparations of UO_2 give sharp X-ray diffraction powder patterns (Kerr and others, 1954) corresponding to the fluorite structure (fig. 14). Uraninite samples from the Plateau give essentially the same powder patterns, but the definition of the patterns varies widely. The diffuseness of the patterns increases with increasing UO_3. The reasons for this have been studied by many investigators (Brooker and Nuffield, 1952; Kerr and others, 1954). Apparently, the loss of definition in the patterns results from a variety of causes including a reduction in crystallite size of the UO_2 and nonuniform oxidation throughout the sample. No pattern corresponding to a U(VI) compound is found; presumably the U(VI) exists as UO_3 in the amorphous state.

During radioactive decay, uranium atoms disintegrate through a series of daughter products to lead, leaving an excess of oxygen atoms relative to uranium atoms; hence chemical analysis reports UO_2, UO_3, and PbO. As an equation (for 50 percent disintegration):

$$2UO_2 \longrightarrow PbO + UO_3$$

Plateau uraninites are not older than 60 to 70 million years (Stieff and Stern, 1952); the analytical UO_3 content from development of lead in that time span would be about 2 percent by weight. The least altered uraninite so far analyzed for UO_2 and UO_3 has a UO_3 content of about 30 percent (Stern, T. W., oral communication) showing that no entirely fresh material has been obtained.

The structural pattern of uraninite can still be discerned in X-ray powder photographs of material containing as much as 80 percent UO_3 (Brooker and Nuffield, 1952, p. 366), and no trace of a UO_3 pattern can be seen.

The development of UO_3 by atmospheric oxidation is clearly as pseudomorphic process; the original grain shapes of UO_2 are retained, and there are no characteristic changes in color or texture. However, UO_3 percentage of a given specimen does agree with position relative to access to oxygen; cores of massive specimens are lower in UO_3 content than the rims.

Thus the first stage of supergene oxidation of uraninite is essentially a solid-state phenomenon and gives rise to material that analyzes as UO_3 but that still resembles the parent UO_2, megascopically. This new material is amorphous under X-rays.

The probable reaction is:

$$UO_2 + \tfrac{1}{2}O_2 \longrightarrow UO_3 \quad \Delta F = -36.4 \text{ kcal}$$

The free-energy change probably is somewhat less negative than that calculated here for the crystalline materials because the UO_3 is amorphous.

Solution of UO_2 without oxidation is not an important process because of the extremely low solubility of UO_2 in deaerated water. Instead, it oxidizes much more rapidly and effectively in the solid state.

COFFINITE

The new mineral, coffinite (Stieff and Stern, 1955), is not well characterized, but is a U(IV) silicate, with some hydroxyl substitution for the silicate ion. Presumably its formula ranges between $U_2(SiO_4)_2$ and $U_2(OH)_4(SiO_4)$. It occurs typically as a replacement of woody material, or in intimate association with carbonaceous material, mostly of woody origin (Part 5). Very serious problems have arisen in attempting to separate a pure phase from the environment, owing to many causes such as the usual extreme fineness of grain and the intimate intergrowth with other materials. However, X-ray, infrared, and electron-diffraction studies show it to be an analogue of zircon and thorite, with the same kind of transition to an hydroxy-substituted species. It is probably a primary mineral, although Weeks and Coleman (oral communication) suspect that it is nearly always late in the paragenetic sequence, and may result from complex reactions among uranium in solution, woody material, and silica released into solution by the action of the ore fluid on sand grains.

Its intimate intergrowth with uraninite indicates similar very low solubility relations in a reducing environment, and there is a suggestion that it is somewhat more resistant to oxidation than uraninite. Nevertheless, it probably oxidizes much more rapidly than it dissolves, so that, as in the case of uraninite, mineralogic changes involving a quadrivalent uranium ion in solution are an unimportant aspect of its postdepositional history.

The importance of coffinite as an ore mineral is difficult to assess, chiefly because of the short time that has elapsed since its recognition; the number of occurrences already recorded, however (Gruner and Smith, 1954, p. 8; Stieff and Stern, oral communication), suggests that it makes up a significant proportion of the uranium content of many primary Plateau ores.

In summary, the uranium of coffinite, like that of uraninite, alters rapidly to U(VI) in the presence of air; the mineral structure is destroyed and the greater part of the postdepositional history involves U(VI).

REACTION OF URANINITE WITH GROUND WATER WITHOUT OXIDATION

One of the major questions concerning the postdepositional history of the Plateau ores is the possibility of migration of uranium by solution and redeposition as a result of the action of moving ground water. Inasmuch as ground waters below the water table are usually reducing and slightly alkaline, the problem in that environment appears to be related to direct solubility of uraninite and coffinite in such media rather than to transport by a combined oxidation-transport-reduction process.

Uraninite is so extremely stable, in terms of giving up U(IV) to water solutions, that it appears doubtful if much movement can take place without oxidation. The same is probably true of coffinite. No good data are available on the solubility of UO_2 in water, although some work has been done on $U(OH)_4$, the less stable hydroxide (Leider, 1954). Values reported for the solubility of the hydroxide in water and NaOH solutions range around 10^{-6} moles per liter at average ground water pH values (7–9). There is, however, a strong likelihood that this measured value is that of U(VI), rather than U(IV), inasmuch as oxidation occurs very easily, and the amount of soluble uranium involved is so small. Also, Leider's results (1954) for the solubility of $UO_3 \cdot H_2O$ and $U(OH)_4$ are strikingly similar, both in acid and alkaline solution. UO_2 is notably difficult to dissolve even in very strong nonoxidizing acids. According to Phair and Levine (1953, p. 367),

> The results of these investigations show that unaltered pitchblende is itself relatively insoluble in even the most concentrated solutions of H_2SO_4 at room temperature. Once, however, it has become partly oxidized by contact with oxygen * * *.

Further indirect evidence on the solubility of UO_2 comes from the tendency of U(IV) in solution to behave as a moderately strong basic cation with little tendency to form stable soluble complexes. In other words, it is quite certain the UO_2 will not dissolve appreciably without oxidation unless very stable complexes exist. We are always in the quandary of not being sure of the composition of ancient ground waters, but at least there is no current reason to expect that they contained any effective U(IV) complexing agents.

REACTIONS OF UO_3 WITH GROUND WATER

UO_3 HYDRATES AND RELATED COMPOUNDS

As shown before, the first stage of alteration of uraninite is to amorphous UO_3, apparently by an essentially solid state reaction, without the intervention of a solution step. UO_3 is unstable relative to uranyl hydroxide hydrate in water solution (Garrels, 1955), and the reaction

$$UO_3+2H_2O \rightarrow UO_2(OH)_2 \cdot H_2O \qquad \Delta F=-13 \text{ kcal}$$

takes places in a pure water solution.

There is a family of uranyl hydroxide hydrates, including $UO_2(OH)_2 \cdot H_2O$, $UO_2(OH)_2 \cdot \frac{1}{2}H_2O$, and $UO_2(OH)_2$ (Katz and Rabinowitch, 1951, p. 281–294), but they are not common minerals on the Colorado Plateau. They differ from each other by small increments of free energy, which probably explains their coexistence. It appears that the hydroxide monohydrate ($UO_2(OH)_2 \cdot H_2O$) is in fact the stable species in water at 25° C and atmospheric pressure (Bullwinkel, 1954, p. 8).

The sparsity of uranyl hydroxide hydrates on the Plateau, as opposed to their abundance and striking development in other areas, perhaps is related to the semiarid climate and low water table of the Plateau. Oxidation takes place in thin films of water on the mineral grains after the water table has dropped, and concentration of ions is high in these films, so that compounds other than the oxides develop. The uranyl hydroxide hydrates probably form and persist only in the virtual absence of carbonate species.

Structurally the uranyl hydroxide hydrates are members of the more general class of compounds represented by the formula $xMeO \cdot yUO_3 \cdot zH_2O$ where Me is Pb or Ba, and perhaps Ca (Christ and Clark, 1955). Among the minerals included in this class are becquerelite, schoepite, billietite, masuyite, fourmarierite, and vandendriesscheite. The structure common to all these minerals is shown in figure 14. It consists of a pseudohexagonal arrangement of linear vertical uranyl ions linked together into infinite horizontal sheets by the hydroxyl ions, with the sheets held together in the crystal in the vertical direction by water molecules or by metal ions and hydroxyl ions. Thus, the formula $xMeO \cdot yUO_3 \cdot zH_2O$ should be written as

$$xMe(OH)_2 \cdot yUO_2(OH)_2 \cdot (z-x-y)H_2O$$

UO_3 CARBONATE COMPLEXES

Uranyl ions form soluble complexes with carbonate ions. In many ores calcite is an abundant constituent of the rocks, and during oxidation of accompanying pyrite the calcite is dissolved to give a solution high in HCO_3^--ion. Unless there is an excess of pyrite relative to calcite, the resultant solution eventually reaches a pH between 6 and 8, representing ideal conditions for the formation of uranyl carbonate complexes (Bullwinkel, 1954).

The following discussion of the carbonate complexes in water is based largely on the work of Bullwinkel (1954).

Both a di- and a tri-carbonate complex are formed:

$$UO_2^{++}+3CO_3^{-2}\rightarrow[UO_2(CO_3)_3]^{-4}$$

and

$$UO_2^{++}+2CO_3^{-2}+2H_2O\rightarrow[UO_2(CO_3)_2(H_2O)_2]^{-2}$$

These complexes are most effective in the intermediate pH range because they are destroyed both by H^+ and OH^-. Addition of H^+ to the tricarbonate complex in solution gives successively the dicarbonate complex and the uranyl ion:

$$[UO_2(CO_3)_3]^{-4}+2H_2O+H^+\rightarrow[UO_2(CO_3)_2(H_2O)_2]^{-2}+HCO^-_3$$

$$[UO_2(CO_3)_2(H_2O)_2]^{-2}+2H^+\rightarrow UO_2^{++}+2H_2O+2HCO_3^-$$

Further acid addition will form H_2CO_3.

Addition of OH^- to the tricarbonate complex tends to form insoluble metal uranates with available cations:

$$[UO_2(CO_3)_3]^{-4}+4OH^-+Me^{++}\rightarrow MeUO_4+2H_2O+3CO_3^{-2}$$

Thus either acid or alkaline conditions tend to break up the carbonate complexes and reduce the solubility of uranium in solution. Evaporation, on the other hand, tends to precipitate the solid uranyl carbonates. Five of these are known from the Plateau: liebigite, schroeckingerite, bayleyite, andersonite, and rabbittite. Their compositions are shown in figure 13. The particular species formed depends chiefly on the relative abundance of Na^+, Ca^{++}, or Mg^{++}.

All these carbonates are hydrated. The crystals contain the complex carbonate ions (fig. 14) as discrete units and, accordingly, are all easily soluble in water; their geologic behavior reflects this high solubility. The minerals form as efflorescences on mine walls and in the zone of evaporation near the ground surface. Their existence is transitory even by human standards. Changes in the distribution of the carbonates can be observed almost from day to day. With the exception of an occurrence in the Thompsons district, Utah (Weeks, A. D., oral communication) uranyl carbonates are known only from nonvanadiferous ores.

Anhydrous uranyl carbonate UO_2CO_3 (rutherfordine) is very rare on the Plateau, although it is relatively abundant in other uraniferous terranes. Some insight into the reason for its rarity can be interpreted from Bullwinkel's observations (1954, p. 35) on the conversion of $UO_2(OH)_2\cdot H_2O$ to $UO_2\cdot CO_3$ by bubbling of air through a water suspension of the hydrated oxide. The small amount of CO_2 in air is sufficient to cause the change. On the other hand, if excess carbonate or bicarbonate is added to the solution (as Na_2CO_3 or $NaHCO_3$) rutherfordine dissolves as uranyl carbonate complexes are formed. Although the experiment has not been performed, it appears likely that evaporation would yield hydrated compounds with a $UO_2^{++}:CO_3^=$ of 1:3, like those observed on the Plateau. Thus rutherfordine probably forms under humid climatic conditions, where relatively pure water is draining through the zone of oxidation; whether it or uranyl hydroxide hydrates forms depends on the partial pressure of CO_2 in the atmosphere. On the Plateau, where the ground waters contain much carbonate and bicarbonate, rutherfordine, if formed, would dissolve, and the only carbonates are those formed by evaporation, which record their genesis from the soluble carbonate complex by the universal $UO_2^{++}:CO_3^=$ of 1:3, as opposed to the 1:1 in rutherfordine. Furthermore the structure of rutherfordine is similar to that of the uranyl hydroxide hydrates, rather than to the hydrated uranyl carbonates (Christ, Clark, and Evans, 1955).

URANYL SULFATES

When pitchblende or coffinite oxidizes in the presence of iron sulfides or copper-iron sulfides, or both, and in the absence of appreciable amounts of vanadium, phosphorus, or arsenic, small amounts of the sulfates uranopilite, johannite, and zippeite may form. The genesis of the sulfates is similar to that of the carbonates. Oxidation of accompanying sulfides yields sulfate ion in acid solution. Sulfate, like carbonate, forms a complex with the uranyl ion. The sulfate complexes are not nearly so stable as the carbonate but are sufficiently stable to increase the solubility of U(VI) markedly. According to Brown (Brown and others, 1954) the "complex" is undissociated UO_2SO_4. The dissociation constant of the reaction

$$UO_2SO_4\rightarrow UO_2^{++}+SO_4^=$$

is approximately 7×10^{-4} at room temperature, indicating that uranyl sulfate dissolved in water would have a few percent of its uranium available as uranyl ion. In the presence of excess sulfate, as in the oxidation of an ore containing sulfide, the fraction of uranium tied up would be much greater.

Like the carbonates, solid uranyl sulfates apparently form only by evaporation of ground water. The resultant compounds are poorly characterized. They form crystals of appreciable size only with great difficulty; in most occurrences they form colloform precipitates. They are somewhat analogous to the basic copper sulfates, such as brochantite, for the originally precipitated material is essentially a gel of indefinite composition. Upon aging, composition changes progressively with water loss, and continuous recrystallization of a whole series of solid phases takes place. It is likely then that the compositions given in figure 13 are not truly representative of most natural uranyl sulfates inasmuch as they have been determined from the best crystallized minerals available. The natural materials found as crusts and efflorescences are probably more hydrated than the selected materials studied in the laboratory. Only the structure of johannite is known (D. Appleman, oral communication). A sketch of the structure is shown in figure 14.

SUMMARY OF THE OXIDATION-REDUCTION RELATIONS IN URANIUM ORES LOW IN VANADIUM, PHOSPHORUS, OR ARSENIC

As indicated in figure 13 oxidation of primary uranium ores in the absence of vanadium, phosphorus, and arsenic may well result in rapid loss of uranium to ground water. The absence of any "fixing elements", plus complexing of the uranyl ion by sulfate or carbonate ion, provides optimum conditions for retaining uranium in solution. If the primary association is uraninite plus pyrite in a noncarbonate gangue, oxidation produces a strongly acid sulfate solution in which UO_3 dissolves as fast as it is formed by solid-state oxidation of the original UO_2. Unless evaporation essentially to dryness takes place the dissolved uranium is carried away.

Uranium is even more soluble in the presence of carbonates. The hydrogen ion developed by oxidation of the sulfides is neutralized by reaction with the calcite of the gangue and a neutral or slightly alkaline solution high in sulfate, bicarbonate, and carbonate is formed under these conditions. The complexing action of the carbonate ion is added to that of the sulfate ion producing conditions of maximum uranium solubility.

In the presence of reactive silica, uranium can be fixed into the relatively insoluble silicates. Unfortunately, little is known of the environment in which they can form, or even concerning their stability after crystallization. Locally, however, they are important factors in the fixation of uranium in nonvanadiferous ores.

In nonvanadiferous ores, then, there is commonly abundant evidence of the migration of uranium in the zone of oxidation. For example, the outcrop itself may be almost entirely free of uranium, and its former presence may be suggested only by traces of oxidized copper minerals. Behind the outcrop, a zone measured usually in a few feet or a few tens of feet may be found in which uranyl sulfates and carbonates are intermixed with iron oxides and oxidized copper minerals. In this zone chemical uranium values may differ markedly and erratically from equivalent uranium, inasmuch as the daughter products of radioactive disintegration are generally less soluble and uranium tends to move differentially. At the margin of oxidation a rather abrupt change to essentially unaltered pitchblende-sulfide ore may take place. The extent and effects of oxidation differ markedly, of course, from place to place, depending upon the details of the geology, but movement, redistribution, and loss of uranium are characteristic. Loss of uranium is retarded by adsorption of uranyl ion on hydrous ferric oxides, and similar colloidal materials, but the efficiency of the process is incompletely understood (Lovering, 1955).

THE URANIUM LAYER COMPOUNDS—VANADATES, PHOSPHATES, AND ARSENATES

In the upper part of figure 13 a large number of mineral species are listed under the headings of vanadates, phosphates, and arsenates. There is, however, a single structural theme that unifies them so that their genesis can be discussed almost as if they were but a single mineral. Inspection of their formulas and of their basic structure, as shown in figure 14, shows that they are composed of sheets made up by a combination of uranyl ion with vanadate, phosphate, or arsenate ion and that various metal ions and (or) water are rather loosely bound between the sheets. The vanadate, arsenate, and phosphate ions are coordinated around the uranium of the uranyl ion in similar manner, except that in the arsenates and phosphates the ortho-ion, $(XO_4)^{-3}$, is the coordinating unit, whereas in the vanadates the metavanadate ion, $(V_2O_8)^{-6}$, is the coordinating unit (Daniel Appleman, oral communication). The $(V_2O_8)^{-6}$ ion has essentially the same structure as a segment of the vanadium-oxygen chain found in $KVO_3 \cdot H_2O$ (Christ, Clark, and Evans, 1954). The bonds within a layer are very strong. In addition, as can be seen from figure 14, the planar structure can be extended essentially indefinitely. This possibility of a development of "infinite" sheets explains why the vanadates, phosphates, and arsenates are so slightly soluble, whereas the carbonates and sulfates, which contain finite groups, are so soluble.

The picture emerges that primary uranium minerals oxidize to UO_3. UO_3 in turn reacts with water to provide a certain amount of uranyl ion. As soon as uranyl ion encounters pentavalent vanadium, phosphorus, or arsenic in solution, there is a tendency to build up the claylike sheets which are held together loosely by whatever cations happen to be in solution and by water molecules. Neither phosphorus nor arsenic occurs in important amounts in the Plateau deposits except locally. Therefore, the reactions of uranium with vanadium will be discussed at length and the corresponding phosphates and arsenates will be treated only by implied analogy.

The two major uranium vanadates are carnotite and tyuyamunite—or metatyuyamunite, which has a lower degree of hydration. The vanadium in these compounds is 5-valent vanadium. Because the primary oxidizable vanadium mineral apparently is montroseite, V(III) oxide, neither carnotite nor tyuyamunite can form until uranium has achieved a +6 valence and vanadium has gone all the way from +3 to +5. Various studies (see Part 5) have shown that pitchblende and coffinite are among the first minerals to oxidize. Usually uranium reaches +6 valence before all the vanadium has been oxidized to vanadium (IV). Consequently there is a stage during the oxidation of a given uranium-vanadium deposit in which the uranium occurs as uranium (VI) but in which there is no vanadium (V) with which it can combine. Little is known concerning the solid phase in which uranium occurs at this stage. Some specimens have been examined that contain several percent uranium as (VI) but in which there is no identifiable uranium mineral. It is conceivable that at this stage the uranium exists as amorphous black UO_3, although it is difficult to understand why some hydration to give brightly colored UO_3 hydrates has not occurred, but they seem to be absent. Also, at this stage the uranium is readily leachable in very dilute acid solution if precautions are taken to prevent any oxidation of vanadium to vanadium (V). Numerous speculations could be made concerning the phases containing uranium at this stage, but so little real evidence is available that these probably should be deferred.

In studies of the system involving UO_3, V_2O_5, K_2O, and H_2O a uranyl vanadate with a higher vanadium-uranium ratio than carnotite or tyuyamunite has a rather wide field of stability (see Part 8). It is possible, therefore, that carnotite and tyuyamunite do not precipitate directly at pH below about 6, but are preceded by a solid phase of different composition which reconstitutes by a decomposition reaction. The presumed intermediary compound is shown in figure 13 as rauvite. The necessity for such an intermediary, together with the extreme insolubility of the minerals, may explain the extreme fineness of grain of most natural carnotite and tyuyamunite.

The solubility of carnotite in normal ground waters is very small, perhaps even in the presence of appreciable carbonate. The solubility of tyuyamunite is considerably greater although no quantitative values are available. This difference can be attributed to the excellent "fit" of potassium ion into the positions between the uranyl vanadate sheets. The calcium ion is smaller than the potassium ion and even though it is doubly charged it does not bind the sheets together with equal effectiveness. A good parallel can be drawn between the uranyl vanadates, phosphates, and arsenates and the ordinary clay minerals. The cations are held in exchange positions. As in the clays, potassium and calcium are held very firmly, whereas sodium and magnesium are more easily exchanged.

Therefore, even in the presence of abundant calcium and sodium a small amount of potassium ion in solution is preferentially taken up in the interlayer positions to form carnotite, so that carnotite is a widespread and extremely important ore mineral even in environments in which calcium ion is more concentrated than potassium in the ground waters. On the other hand, a great deal of yellow powdery material probably has been called carnotite that is in fact tyuyamunite.

The very low solubility of carnotite under most earth-surface conditions is shown by the presence of equilibrium between uranium and daughter products in most bulk samples of carnotite-bearing ores. If there were substantial active leaching, relative movement of uranium and daughter products should have disrupted this equilibrium. Furthermore, lead-uranium ages of many carnotite-bearing samples are in good agreement with those containing pitchblende, showing oxidation in place without migration. On the other hand, near the outcrop, or more generally in the zone in which there is active entrance of water into and evaporation from uranium-vanadium ores, it appears possible that considerable movement of uranium may occur. The thin soils in most of the Plateau area are very high in carbonates, attesting the continuous upward migration of carbonates by a capillary process. Under these optimum conditions for the formation of soluble uranyl carbonate complexes uranium may be leached even from carnotite.

Oxidation of a primary uraninite-montroseite (or coffinite-montroseite) ore probably follows these steps: First, uranium minerals oxidize to uranium (VI). The solid species of this stage are unknown. At a slower rate the vanadium oxidizes to vanadium (IV) and then to vanadium (V). As soon as any vanadium (V) is available it unites with uranyl ion to form a uranyl vanadate. The nature of original uranyl vanadate formed is not well defined and perhaps is best described under the general term of rauvite. Then, through decomposition, typical uranyl metavanadate sheet structure develops and available ions in the solution take up interlayer positions. If there is any appreciable potassium, it is taken up preferentially and binds the sheets together into the very insoluble carnotite. After potassium is essentially used up in forming carnotite, tyuyamunite is formed. Carnotite or tyuyamunite, once formed, tend to be stable under the semiarid conditions of the Colorado Plateau, although local movement and recrystallization along cracks and fractures is observed commonly, and it is not unlikely that there is considerable movement at or near the present ground surface. This near-surface movement undoubtedly is promoted chiefly by the presence of carbonates.

No quantitative data are available on the relative solubilities of the uranyl vanadates, arsenates, and phosphates, although from their general geologic behavior the sequence as given probably is in order of increasing solubility.

SUMMARY

In summary, primary uranium minerals are essentially insoluble under reducing conditions. As soon as oxygen is added to the system, however, direct oxidation of the solid uranium (IV) phases apparently takes place to give amorphous UO_3. In the absence of vanadium, phosphorus, or arsenic the UO_3 dissolves very easily in ground waters, especially those containing carbonate or sulfate. Deposition of the dissolved uranium takes place only as a result of evaporation of the ground water to form crusts and efflorescences of uranyl carbonates or basic uranyl sulfates, or locally by reaction with dissolved silica to form uranyl silicates. Uranium (VI) is fixed by arsenic and phosphorus and especially by vanadium. It apparently becomes fixed as a uranyl vanadate of transitory existence by reaction with almost any anionic species containing vanadium (V). Decomposition of this intermediate, plus reaction with potassium or calcium produces insoluble carnotite or tyuyamunite. Once precipitated these minerals persist except where exposed at the outcrop.

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Part 7. THE CRYSTAL CHEMISTRY AND MINERALOGY OF VANADIUM

By Howard T. Evans, Jr.

CONTENTS

ILLUSTRATIONS

ABSTRACT

Many recent crystal structure investigations on vanadium oxides and compounds are reviewed in terms of the over-all chemistry and mineralogy of the element. The structure studies are compared with the oxidation potential-pH phase diagram which is constructed from the best available thermodynamic data for the element. From these correlative studies, an alteration sequence is derived for the weathering process of the vanadium ores of the Colorado Plateau. Accordingly, montroseite [VO(OH)] is treated as the primary vanadium mineral. During weathering, montroseite is converted to various insoluble tetravalent and pentavalent oxide minerals, including paramontroseite and "corvusite." Final oxidation of "corvusite" yields soluble polyvanadate complexes from which crystallize pascoite, hummerite, hewettite, and other pentavalent vanadate minerals. Under more alkaline environments, duttonite [$VO(OH)_2$] is formed, from which may be derived simplotite, melanovanadite, and rossite. If uranium is present these are converted to rauvite, tyuyamunite, and carnotite. Generally speaking, in its lower valence states vanadium is similar to manganese in behavior, but in the higher states of oxidation it resembles phosphorus (in strongly alkaline media) and molybdenum and tungsten (in acid media).

INTRODUCTION

Until recently, vanadium had played a minor role in mineralogy. Lately, interest in vanadium mineralogy has been increased because vanadium plays a key role in the paragenetic relationships in the sandstone-type uranium deposits, such as those of the Colorado Plateau. Recent geologic studies have raised many questions concerning the time, mechanism, and mode of deposition of the uranium and vanadium ores in the sandstones, shales, and conglomerates, and their subsequent weathering and transport. Extensive recent studies on the chemistry and crystallography of vanadium compounds and minerals in various laboratories has led to a greater understanding of the behavior of vanadium under varying conditions of oxidation potential and pH, which give promise to provide valuable clues to the solution of these problems.

An important vanadium ore mineral (at Globe, Ariz., for example) is vanadinite, a member of the apatite group of minerals. A second important type is vanadium silicate, as mica, as clay minerals, and as chlorites. Vanadium forms a host of other minerals, many of which are as yet undescribed or poorly characterized. They are listed in a miscellaneous group in Dana's System of Mineralogy (Palache, Berman, and Frondel, 1951, p. 1042) and also in a U. S. Geological Survey publication by Weeks and Thompson (1954). Phases involving oxygen are numerous and very complex, mainly because of the variability of the valence state of vanadium.

A fair amount of information concerning the chemical and mineralogical behavior of vanadium is available in a widely dispersed and somewhat conflicting literature. In addition, recent work in X-ray crystallography by members of the U. S. Geological Survey has revealed new and significant structural relationships among vanadium compounds and those of other elements. It is the purpose of this report to review briefly present knowledge of the behavior of vanadium in the solid state.

The emphasis in this paper will be on the structure and nature of the known minerals as they are found in nature, in relation to each other and to artificial solid compounds, and to the solution studies of Garrels (1953), Ducret (1951), Jander and Jahr (1933), and others. While the methods of electrometric and pH titration have proved to be the most informative in the study of the solution phases, the most powerful approach to the problem of the constitution of the solids has been through the medium of X-ray diffraction and crystal-structure analysis. As the body of information on structure increases, it is often possible to infer the nature of the solution components through various interrelationships and characteristic physical properties of the solids.

The ideas and information presented in this paper have resulted from the concerted efforts of many workers at the U. S. Geological Survey, some of whom are mentioned in the text, as well as many other independent workers outside the Survey. Especial thanks are due to R. M. Garrels, of the Geological Survey, who has continuously urged and encouraged the compilation of this report on vanadium chemistry and mineralogy and who has contributed in no small way directly to its makeup. Finally, the author wishes to express his gratitude to W. H. Barnes and his colleagues, of the National Research Council of Canada, who in personal discussions from time to time have provided much valuable information.

ELECTROCHEMISTRY OF VANADIUM

Before entering upon a discussion of the various minerals containing vanadium, let us review briefly the equilibrium behavior of vanadium under various conditions of pH and oxidation potential as it has been revealed in recent studies by Souchet and Carpeni (1946), Ducret (1951), Garrels (1953), and others. The best thermodynamic information available to us is summarized in figure 15, in the manner described by Pourbaix (1949). The tabulated data of Latimer (1952) have been used in the construction of the diagram.

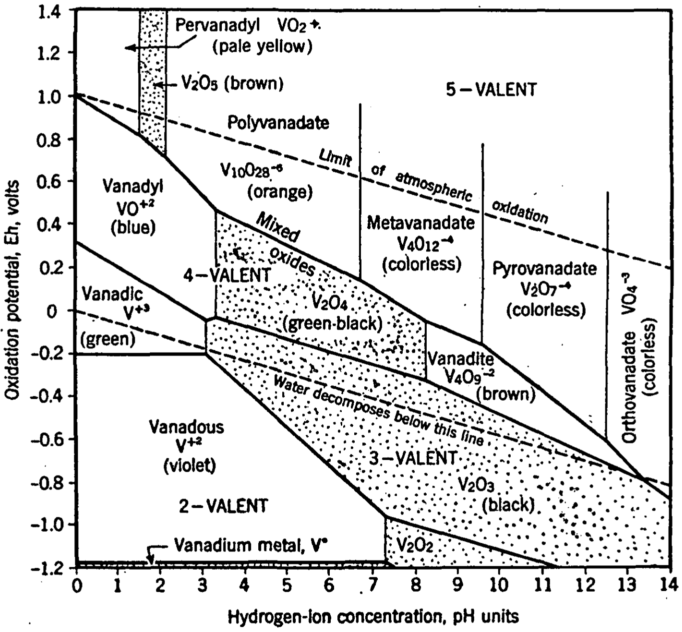

FIGURE 15.—Oxidation potential—pH phase diagram for vanadium in aqueous solutions. Stippled fields represent solids (solubility of V<0.01 mol. per l.). Phases may be hydrated or hydrogenated to an unknown degree.

In the diagram of figure 15, all conditions of pH (hydrogen-ion concentration) and Eh (oxidation potential) are represented. The diagram is divided into regions which are labeled with the species that predominates in that region. Two sloping dashed lines are shown: the lower one represents the limit below which hydrogen ion is reduced to hydrogen, a condition which ordinarily does not occur in nature; the upper line is the limit above which water or hydroxyl ion is oxidized to oxygen, and toward which all systems below the line trend under terrestrial weathering conditions.

The areas between the heavy lines represent the four valence states of vanadium. They correspond roughly to the regions of stability of $V(OH)_3$, $VO(OH)_2$ and $V_2O_5 \cdot nH_2O$ as determined by Garrels (1953). The slope of these heavy lines is determined by the way in which H^+ ions are involved in the oxidation reaction. Thus, the oxidation potential required to convert V^{+2} to V^{+3} is independent of pH since no H^+ ions are involved in the oxidation reaction; but when V^{+2} is converted to V_2O_3, H^+ is liberated in the reaction, and the potential boundary falls with increasing pH. When no oxidation or reduction takes place, changes in pH will effect profound changes in the constitution of the vanadium-bearing ion or solid; these changes are marked by vertical lines on the diagram. The formula species indicated may actually be replaced by hydrates, without changing the phase boundaries significantly. The presence of hydrogenated ions such as $HV_2O_7^{-3}$ may affect the boundary distributions to a small degree.

In the following discussion, reference will be made to figure 15 to clarify relationships among minerals and artificial compounds under consideration. Thus, the diagram will serve as a "road map" in our survey of the mineralogy and chemistry of vanadium.

REDUCED FORMS OF VANADIUM

VANADIUM (II)

Bivalent vanadium is unstable and releases hydrogen from water. This behavior is consistent with the diagram of figure 15, which shows that the conditions under which V^{+2} ions are stable are well below the limit below which water decomposes. The artificial compound VO is known; like MnO, it has the rocksalt structure. Thermodynamic considerations have shown that bivalent vanadium probably does not occur in nature (Garrels. 1953, p. 1263).

VANADIUM (III) AND VANADIUM (IV): THE MONTROSEITE GROUP

Trivalent vanadium is also relatively unstable, and has a short life in the presence of air. Unlike the bivalent ion, V^{+3} is stable in oxygen-free acid water solution, from which, characteristically, vanadium alums may be crystallized—for example, $CsV(SO_4)_2 \cdot 12H_2O$. V_2O_3 has the corundum type of structure but is not yet known in nature. $VO(OH)$ is the mineral monotroseite (Weeks, Cisney, and Sherwood, 1953), which occurs as steel-black prismatic lath-shaped crystals, or as a brittle, crystalline, jet black mass. Paramontroseite, V_2O_4, is a common alteration product resulting from the atmospheric alteration of montroseite. Another distinct oxide species (Weeks and Thompson, 1954, p. 54), now designated doloresite, which is closely associated with paramontroseite, forms dark brown, nonmetallic crystalline masses when pure and is probably a quadrivalent hydrous oxide. Still another quadrivalent oxide species, duttonite, has been identified recently, occurring as pale brown flaky crystals, but it is found in more alkaline environments. The oxide minerals have proved to be difficult to separate and characterize by the usual chemical and mineralogical methods, but their interrelationships and essential constitution have been revealed by the methods of X-ray diffraction and crystal structure analysis.

Montroseite and paramontroseite both have the diaspore ($Al_2O_3 \cdot H_2O$) structure. The details of these structures have been given by Evans and Block (1953), and Evans and Mrose (1954). The structure contains double chains of VO_6 octahedra sharing edges, the chains being linked to each other by sharing octahedron corners (see the pictorial view in fig. 16).

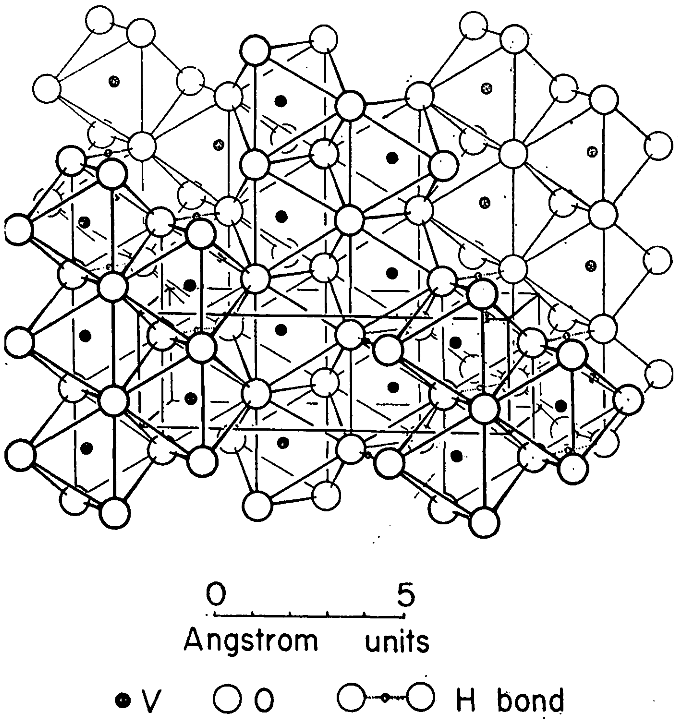

FIGURE 16.—Pictorial view of montroseite structure (diaspore type).

Evans and Mrose found that montroseite single crystals give multiple diffraction patterns showing the presence of two intimately mixed phases, but whose crystal structures are similar and are in parallel position throughout the crystal mass. By means of Fourier analyses of the electron density distribution in each of the two phases separately, they were able to show conclusively that hydrogen is present in one and absent in the other. These two structures, which are montroseite and paramontroseite, respectively, are illustrated in figure 17, projected along the chain axis. The chains are visible in end view in both drawings. Comparison of the two structures leads unequivocally to the conclusion that the original host mineral is montroseite (VO(OH)) and that the paramontrosite (V_2O_4 or VO_2) has originated by the solid state oxidation of montroseite. The oxidation process has taken place by the diffusion of hydrogen out of the structure without breaking the vanadium-oxygen bonds or disrupting the hexagonal close-packed oxygen framework.

Artificial vanadium dioxide, V_2O_4, has a slightly distorted rutile type of structure (Andersson, 1953). This structure is characterized by straight octahedron chains as shown in the pictorial view of figure 18. It is very probable that the diasporelike form of V_2O_4, paramontroseite, is entirely metastable and can only be formed through the low-temperature alteration mechanism just described, controlled by the original montroseite structure. Similar alteration mechanisms have been observed for certain of the iron oxides (Evans and Mrose, 1954). Montroseite is a highly insoluble stable mineral under reduced conditions, but by its conversion to the metastable paramontroseite, it becomes readily decomposable and subject to further oxidation.

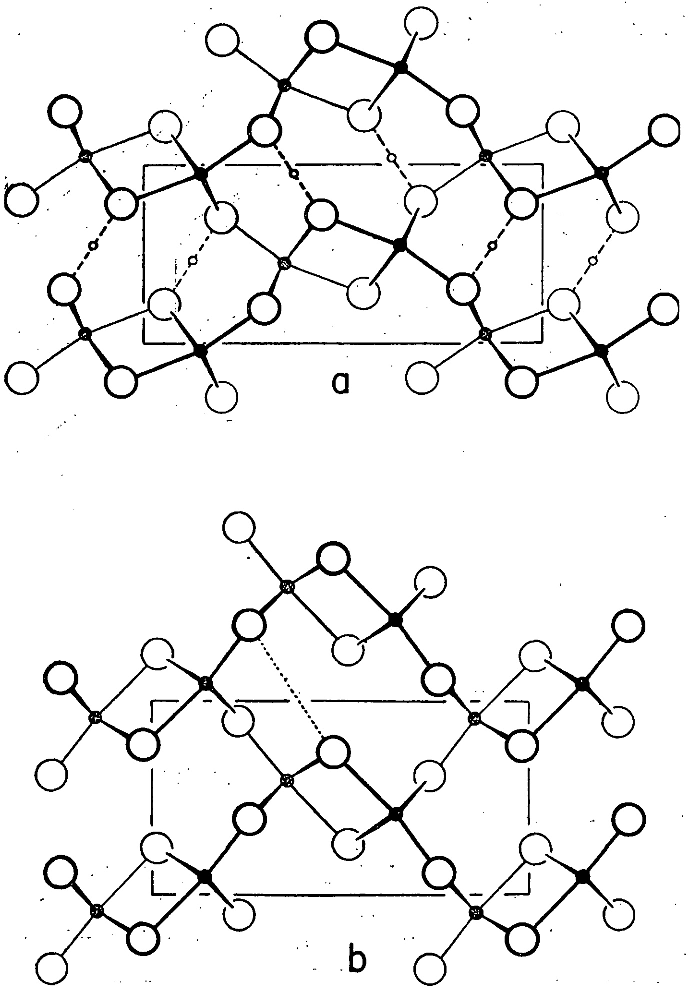

FIGURE 17.—Projections along the *c*-axis of the crystal structure of (a) montroseite and (b) paramontroseite. Large circles are oxygen atoms, dark circles vanadium, small open circles hydrogen. Note absence of hydrogen bond in paramontroseite.

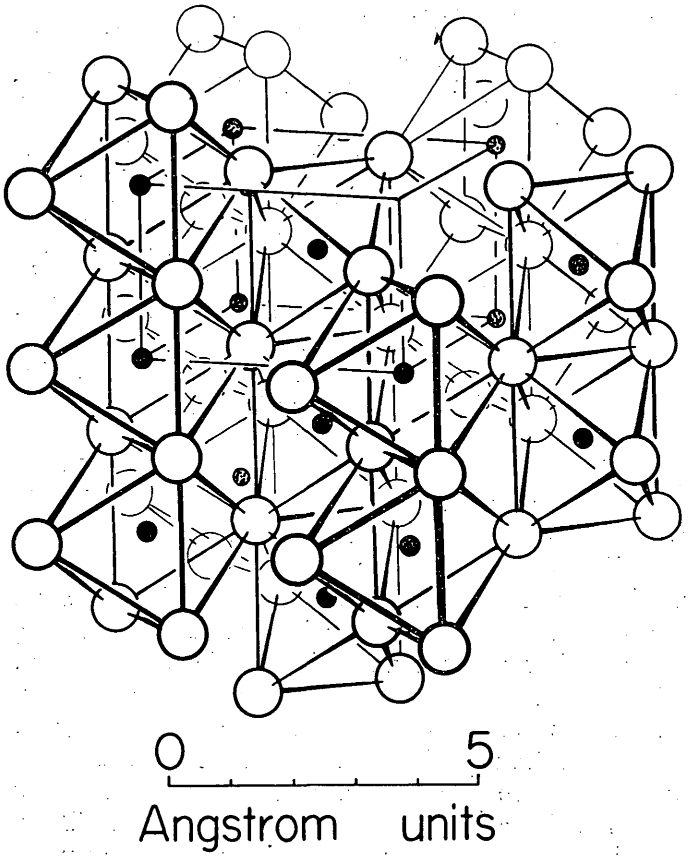

FIGURE 18.—Pictorial view of V_2O_4 structure (distorted rutile type). Large circles are oxygen atoms, small circles vanadium.

Paramontroseite (pseudomorph after montroseite) is sometimes intimately mixed with another vanadium oxide mineral, doloresite. Petrographic studies (Coleman, oral communication) indicate that doloresite replaces montroseite or paramontroseite. Since any remnant montroseite is oxidized to paramontroseite on atmospheric exposure, the mixture probably represents a close association of stable and a metastable form of the tetravalent oxide. Crystalline fragments of doloresite give exceedingly poor single crystal diffraction patterns, but it has been possible to index them on an orthorhombic lattice which is obviously related to montroseite and artificial V_2O_4. These oxides all share a fiber axis spacing of 3.0 A, which is characteristic of the octahedron chain.

All evidence indicates that montroseite is probably the chief primary vanadium mineral, aside from the vanadium silicates, of the Colorado Plateau sandstone deposits. The conditions of formation are not known, but possibly they are hydrothermal in type. Figure 15 shows that a portion of the V_2O_3 field extends above the water decomposition line in the vicinity of pH 3–5. While the room temperature conditions represented by the diagram will be altered somewhat at elevated temperatures, montroseite may be considered to have formed somewhere in this region.

Recently, the new mineral duttonite (Thompson, Roach, and Meyrowitz, 1956b) has been found at the Peanut mine, Bull Canyon, Montrose County, Colo., where more alkaline conditions prevail. Crystal structure studies have shown that it is the dioxide hydrate, $V_2O_4 \cdot 2H_2O$. The structure consists of strings of VO_6 octahedra linked vertically by their apices to form sheets, which are then tied together with hydrogen bonds (fig. 19). An unusual feature of the structure is the close approach of the vanadium atom to the apical oxygen atom to form a strong V–O bond, corresponding to a VO^{+2} ion. Since this ion is well known from chemical studies, its appearance in the solid is not surprising. In fact, it is probably present in the artificial V_2O_4 structure, in which the ideal tetragonal cell is doubled in volume and reduced to monoclinic symmetry. If the octahedron chains (vertically arranged in fig. 18) contain the VO^{+2} bond pointing in alternate directions as in duttonite, such a distortion would readily be accounted for.

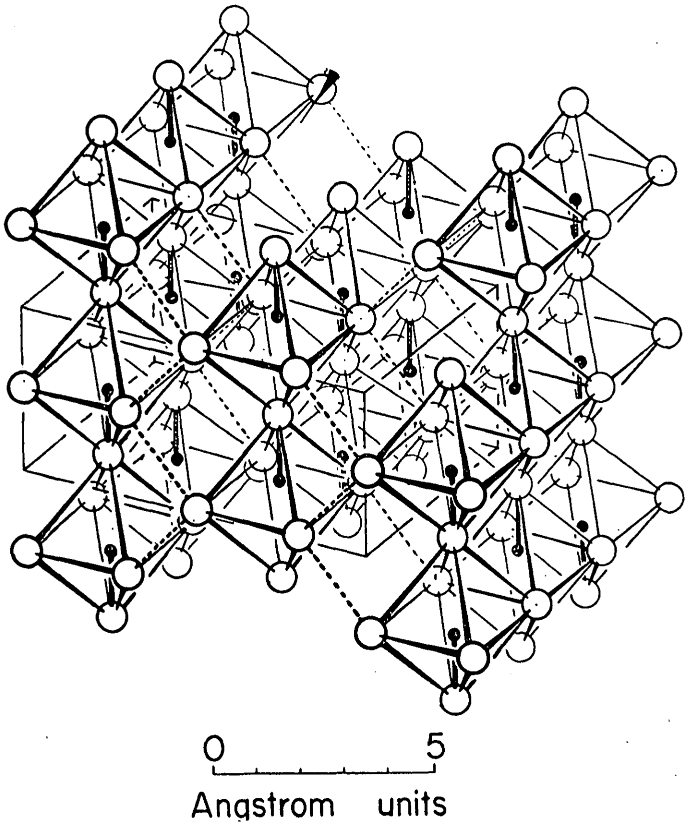

FIGURE 19.—Pictorial view of duttonite. Large circles are oxygen atoms, small circles vanadium, and dashed lines are hydrogen bonds.

In its valence states three and four, vanadium is similar to manganese in its behavior. Single and double and even triple octahedron chains have been found in several manganese oxide minerals—for example, pyrolusite, coronadite, hollandite, and psilomelane (Wilson, Structure Reports, 1949, 1950). Indeed, groutite, $Mn_2O_3 \cdot H_2O$, and ramsdellite, Mn_2O_4 (Wilson, Structure Reports, 1949, 1950), are completely analogous to montroseite and paramontroseite, respectively. Unfortunately, very little work has been done on the phase relations of manganese oxide minerals in the natural environment, so that we are not at present able to compare any similarities there may be to vanadium systems. On the other hand, the tendency of vanadium to form asymmetric oxygen bonds in its coordination environment when it attains the quadrivalent or higher state is in contrast to manganese.

OXIDIZED FORMS OF VANADIUM

OXIDATION OF QUADRIVALENT VANADIUM

Weathering action ultimately raises vanadium oxide minerals to the highest oxidation state—that is, +5. This oxidation process is evident from the sequence of minerals in the Colorado Plateau region, and is also predicted by the thermodynamic studies which are summarized in figure 15. The oxidation process is very complex, passing through numerous intermediate stages. Many take place in the solid state, like the conversion of montroseite to paramontroseite described in the previous section. When vanadium passes above the tetravalent state, its oxides are still relatively insoluble (above pH 3), but the oxide structures are completely reconstituted.

A number of phases, changing one into another, probably exist between $V_2O_4 \cdot nH_2O$ and $V_2O_5 \cdot nH_2O$. These phases are the principal constituents of the so-called "blue-black ore." None of these phases has been isolated and uniquely characterized as yet. "Corvusite" is a name associated with a fibrous vanadium oxide hydrate which yields a blue-black powder on scratching or crushing. Its essential constitution and nature are unknown (it may be a mixture) and "corvusite" cannot yet be regarded as a well-established species. Other oxide phases in this range have a green streak and all are commonly coated with an almost iridescent blue tarnish.

During oxidation the pH of the environment tends to drop, especially if much pyrite is present. The vanadium then becomes relatively soluble and is leached out of the oxide bodies as VO^{+2} and $V_{10}O_{28}^{-6}$ ions as would be expected by reference to figure 15. As soon as the solutions reach the surrounding rock, they become diluted and react with the calcium carbonate cement. The pH is thus raised sharply again, causing the remaining VO^{+2} ions to be completely oxidized by atmospheric action.

Complete oxidation of vanadium to vanadium (V) is marked by a distinct color change from the blue-black associated with the vanadium (IV)-(V) complexes to brown, red, or orange shades associated with derivatives of V_2O_5. The presence of uranium introduces yellow and yellow-green phases in this oxidized zone.

pH DISPERSION OF VANADIUM (V) COMPLEXES IN SOLUTION

Vanadium pentoxide is strongly amphoteric, dissolving readily to form cations in strong acid solutions, and anions in weakly acid and alkaline solutions. In these solutions, vanadium forms a great variety of oxygen ion complexes. The relative concentrations of the various complexes depend critically upon the acidity and concentration of the solution, the presence of other complexing ions (UO_2^{+2} or PO_4^{-3}), and, because of the slow rate of many of the reactions, the history of the solution. Some insight into the constitution of V_2O_5 solutions as a function of pH has been gained by Jander and Jahr (1933) by means of diffusion-rate studies. In figure 20 is shown their plot of diffusion rate of vanadium in solution (corrected for viscosity) against pH. The presence of plateaus in this curve suggests that at certain critical pH values the ions present in the solution react to form other more complex ions (with decreasing pH), but that between these critical values, the solutions are relatively stable. Assuming very approximately that ion molecular weight is proportional to the square of the diffusion rate, Jander and Jahr suggested that above pH 12.6 only VO_4^{-3} ions are present; in the range pH 9.6 to 12.6, $V_2O_7^{-4}$ ions are present; in the range pH 6.7 to 9.6 ions like $V_4O_{13}^{-6}$ exist; and between pH 6 and the oxide precipitation point at pH 2.2 ions similar to $V_6O_{16}^{-7}$ predominate. A study of solutions in the system K_2O–V_2O_5–H_2O by R. Marvin (Part 8 of this volume), of the U. S. Geological Survey, has produced a large number of crystallized products. Crystal structure studies of these products suggest that the constitution of all solutions of pH below 12 are somewhat more complex than is suggested by Jander and Jahr's diffusion studies.

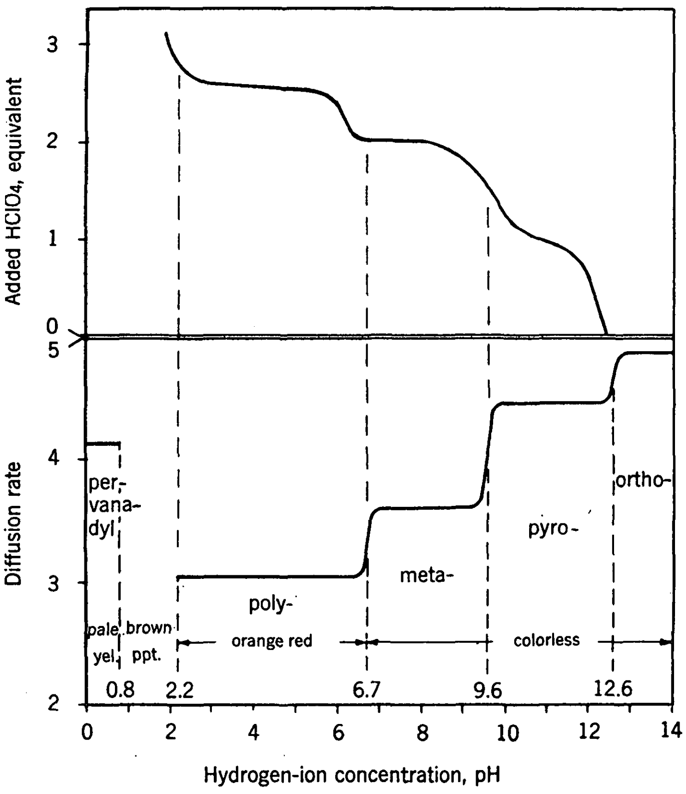

FIGURE 20.—Dispersion of vanadium phases with pH. Upper diagram, titration curve for sodium vanadate solution after Ducret (1951). Lower diagram, diffusion rate curve for sodium vanadate solution after Jander and Jahr (1933).

Similar plateaus are also observed on titration curves of pH versus added acid. Such a curve is shown in the upper half of figure 20 as measured by Ducret (1951). The breaks in such curves between plateaus correspond to the vertical boundaries in the quinquevalent field at the top of figure 15. Souchet and Carpeni (1946) and previous workers have associated the indicated stability fields with complexes similar to those proposed by Jander and Jahr, but Ducret, basing his conclusions on the shape of the titration curves in the vicinity of the breaks, repudiates the idea of successive condensation to higher molecular-weight groups. Only in the orange "polyvanadate" region does he postulate the existence of a $H_3V_2O_7^-$ ion; in the "meta-" and "pyro-" regions the ions $H_2VO_4^-$ and HVO_4^{-2}, respectively, are supposed to predominate. Nevertheless, all the structures that have been worked out related to this system show that there is a powerful tendency for the orthovanadate ion to condense into complex groups, and it seems very likely that such complexes are important constituents of the solutions.

In view of all the evidence that is now available, we may propose the following reactions as taking place over the whole pH range:

At—

pH 12.6: $2VO_4^{-3}+2H^+\rightarrow V_2O_7^{-4}+H_2O$
pH 9.6: $2V_2O_7^{-4}+4H^+\rightarrow V_4O_{12}^{-4}+2H_2O$
(or $H_2V_4O_{13}^{-4}+H_2O$)
pH 6.7: $5V_4O_{12}^{-4}+8H^+\rightarrow 2V_{10}O_{28}^{-6}+4H_2O$
pH 2.2: $V_{10}O_{28}^{-6}+6H^+\rightarrow 5V_2O_5+3H_2O$
pH 0.8: $V_2O_5+2H^+\rightarrow 2VO_2^{+}+H_2O$

All the vanadium groups written in these equations may be for the most part hydrated. Some of the ions may also form hydrogenated ions like $HV_2O_7^{-3}$ or $H_2V_2O_7^{-2}$.

These reactions are based primarily on the concept of condensation, that is, the linking together of small coordination groups to form larger ones, by splitting out H_2O. The behavior of quinquevalent vanadium with respect to the stepwise formation of more condensed complexes with increasing coordination as pH decreases greatly resembles that of molybdenum and tungsten.

ORTHOVANADATES AND PYROVANADATES

At pH levels above 12.6, the tetrahedral orthovanadate ion VO_4^{-3} appears to be stable in solution. Although no crystal structures of orthovanadates prepared from such solutions have been studied in detail a number of highly soluble, deliquescent salts have been obtained which are clearly isostructural with the corresponding phosphates and arsenates. Thus, H. Baker (1885) demonstrated by crystallographic and optical means the following isomorphous groups:

Hexagonal:
  $Na_3VO_4\cdot 12H_2O$
  $Na_3PO_4\cdot 12H_2O$
  $Na_3AsO_4\cdot 12H_2O$
Cubic:
  $Na_3VO_4\cdot 10H_2O$
  $Na_3PO_4\cdot 10H_2O$
  $Na_3AsO_4\cdot 10H_2O$
Orthorhombic:
  $Na_3VO_4\cdot 8H_2O$
  $Na_3PO_4\cdot 8H_2O$
  $Na_3AsO_4\cdot 8H_2O$
Cubic:
  $2Na_3VO_4\cdot NaF\cdot 19H_2O$
  $2Na_3PO_4\cdot NaF\cdot 19H_2O$
  $2Na_3AsO_4\cdot NaF\cdot 19H_2O$

This strong evidence by analogy for the prevalence of the VO_4^{-3} ion in solution is in direct contradiction to Ducret's conclusion (1951) that this ion cannot exist in the presence of water.

Several orthovanadate mineral types are well known: vanadinite, isostructural with apatite. These minerals are usually characterized by the presence of a complexing amphoteric element such as Pb, Zn or Bi, and are formed under hydrothermal conditions. Truly ionic compounds such as the sodium salts mentioned above are not known in nature, as is to be expected from their strong basic character and high solubility.

The properties of V_2O_5 solutions in the range of pH 9.6 to 12.6 suggest that a pyrovanadate ion, $V_2O_7^{-4}$ may be stable. No crystal structure evidence is available to establish its existence definitely, although colorless crystalline salts such as $Ca_2V_2O_7\cdot 2H_2O$ are readily formed in this pH range.

METAVANADATES

The range from pH 6.7 to pH 9.6 represents a stability field corresponding to the so-called metavanadates. The crystal structures of the colorless compounds KVO_3 (Evans and Block, 1953) and $KVO_3\cdot H_2O$ (Christ, Clark, and Evans, 1954), which readily crystallize in this range of pH, have been worked out. These crystals both have chain structures, which means that the actual ion present in the solution is still unknown. In the pyrovanadate range we see the tendency for the single VO_4^{-3} tetrahedra to condense into coordination complexes, containing several vanadium atoms, as the pH is lowered. In KVO_3 (fig. 21), tetrahedra link into endless zigzag chains of composition $(VO_3)_n^{-n}$, by sharing corners. These chains are very similar to the silicate chains in diopside, $CaMg(SiO_3)_2$; indeed, the compound $NaVO_3$ appears to be isostructural with diopside.

At low temperatures, prisms of $KVO_3\cdot H_2O$ are also formed, and these have an entirely different structure (fig. 22). In the monohydrate, the vanadium is in strict fivefold coordination with oxygen, forming a trigonal bipyramid configuration which links into endless chains of composition $(VO_3)_n^{-n}$ by sharing edges. A similar type of chain has been confirmed for V_2O_5 by Byström, Wilhelmi, and Brotzen (1950), but the chains are linked laterally to form sheets, and the vanadium coordination is distorted so that it approaches sixfold. The two structures are compared in figure 23, in which the end views of the chain elements are projected on the (001) planes. In this compound, vanadium shows the tendency to increase its oxygen coordination as the pH is lowered. Although the two types of chain appear to be completely different, it is not hard to imagine that the fivefold chain could be formed by an accordionlike pleating of the fourfold chain along its length, while

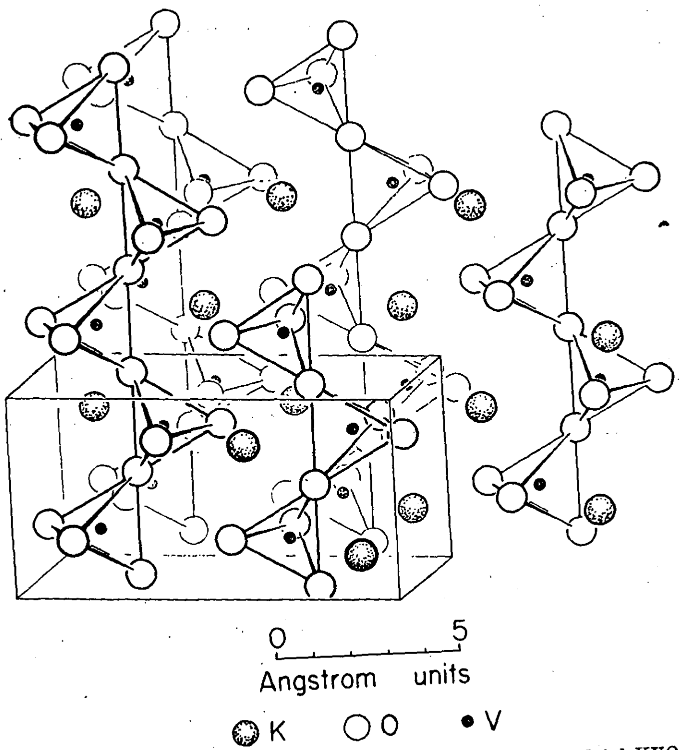

FIGURE 21.—Pictorial view of the crystal structure of artificial KVO_3.

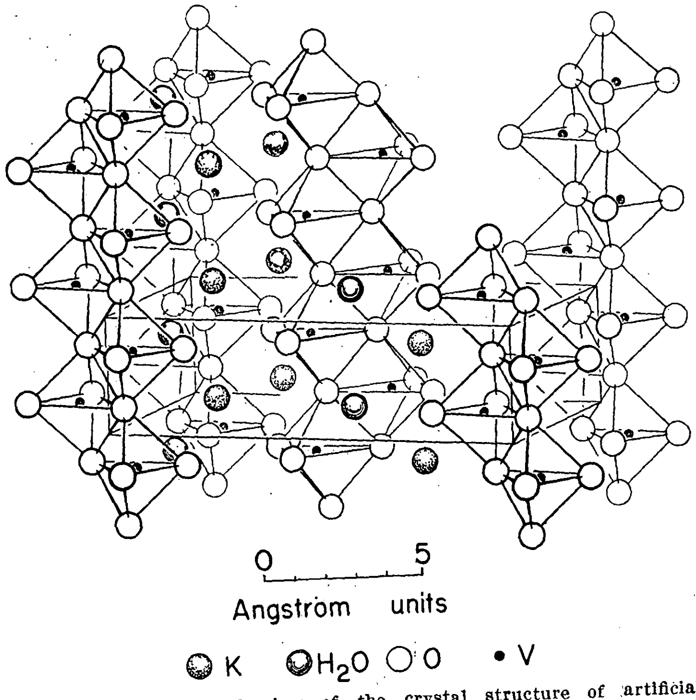

FIGURE 22.—Pictorial view of the crystal structure of artificial $KVO_3 \cdot H_2O$.

each vanadium atom picks up an extra oxygen bond from an adjacent tetrahedron (fig. 24). Apparently, little energy is involved in this process, because there is evidence to show that simply grinding the $KVO_3 \cdot H_2O$ will convert it partly to KVO_3 (Christ, Clark, and Evans, 1954).

$KVO_3 \cdot H_2O$ has a prism axis (chain direction) spacing of 3.70 A. This spacing is the fundamental fivefold chain link unit length, and is a characteristic feature, often easily recognized as a fibre spacing, of many vanadate compounds and minerals formed in an acid environment of low temperature which is characteristic of present day Colorado Plateau deposits. Apparently, this fivefold chain in one or another modification is a common fundamental structure motif of such compounds.

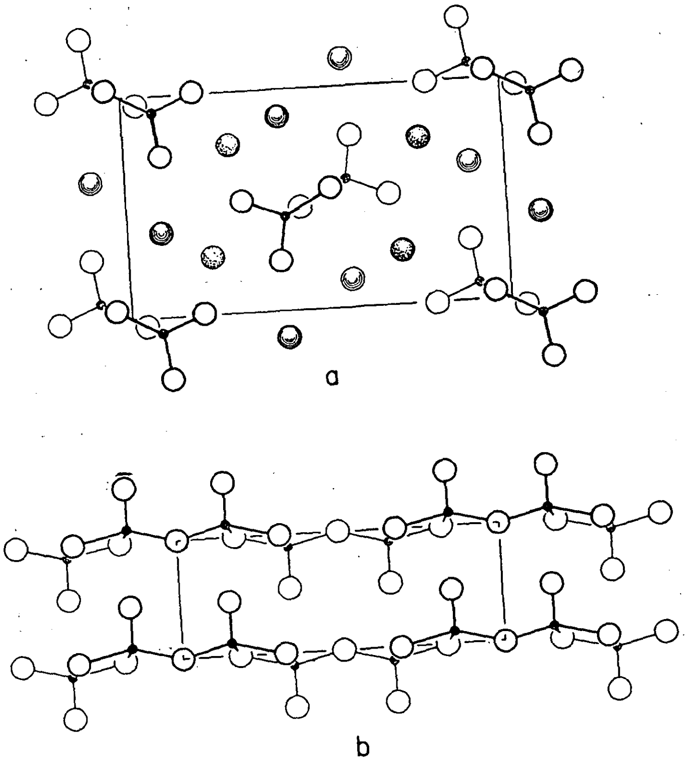

FIGURE 23.—Projections along the *c*-axis of the crystal structure of (a) $KVO_3 \cdot H_2O$ and (b) V_2O_5. Large circles are oxygen atoms, small circles vanadium, large arc-shaded circles H_2O, and large stippled circles K^+ ions.

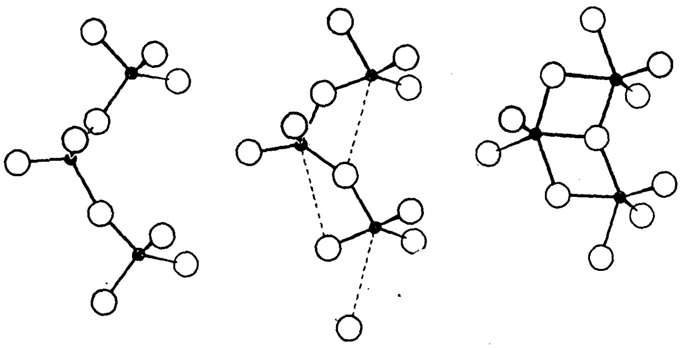

FIGURE 24.—Possible mechanism for transformation from fivefold to fourfold coordinated metavanadate chain. Large circles are oxygen atoms, small circles vanadium.

Minerals which correspond to the metavanadate range are rare, the only ones likely to belong here being rossite $Ca(VO_3)_2 \cdot 4H_2O$ and metarossite $Ca(VO_3)_2 \cdot 2H_2O$. Their true character is not certain because their structures are not yet known.

Regarding the nature of the ion which is stable in the metavanadate solutions, it seems reasonable to suppose that it consists of either a trivanadate, $V_3O_{10}^{-5}$, or a tetravanadate, $V_4O_{13}^{-6}$, or probably both in addition to others. These would be threefold and fourfold links from the KVO_3 chain. Analogous phosphate complexes are known to exist in solution, in equilibrium with the HPO_4^{-2} and $H_2PO_4^-$ ions, but apparently HVO_4^{-2} and $H_2VO_4^-$ ions are much less stable than the corresponding acid phosphate ions.

POLYVANADATES: THE PASCOITE GROUP

If a V_2O_5 solution is acidified below pH 6.7, the solution suddenly turns orange, and it enters a new stability field covering the range from pH 6.7 to 2.2, corresponding to the so-called polyvanadates. These solutions yield a variety of different orange and red crystalline products of complex composition. Marvin (Part 8) has prepared, among others, the following compounds, which have been characterized crystallographically (Evans, Mrose, and Marvin, 1955):

I. $K_6V_{10}O_{28} \cdot 10H_2O$, triclinic (pseudomonoclinic).
II. $K_6V_{10}O_{28} \cdot 9H_2O$, monoclinic.
III. $Ca_3V_{10}O_{28} \cdot 16H_2O$ (pascoite), monoclinic.[6]
IV. $K_2Mg_2V_{10}O_{28} \cdot 16H_2O$ (hummerite), triclinic.
V. KV_3O_8, monoclinic.

The appearance of the tenfold group $V_{10}O_{28}^{-6}$ in the first four compounds strongly indicates, since the compounds are quite soluble, that such a polycomplex is an important component of the solution. The strong inference from the crystal structure studies that poly-ions of high molecular weight are stable in these solutions supports generally the views of Jander and Jahr (1933), Souchet and Carpeni (1946) and most other chemical workers, but stands opposed to the hypotheses of Ducret (1951) who maintains that the orange solutions contain mostly $H_3V_2O_7^-$ ions.

Neither the crystals nor the solutions are stable for any length of time. The crystals tend to dehydrate, falling to a yellow powder after some weeks at ordinary temperatures. The potassium polyvanadate solutions after some weeks at room temperature, or rapidly at higher temperatures, deposit light orange insoluble crystals of KV_3O_8 while any crystals of $K_6V_{10}O_{28} \cdot 9H_2O$ present in the solution disappear. KV_3O_8 is apparently a stable end product of a series of competitive condensation reactions going on in the solution. In the same way, hewettite, $CaV_6O_{16} \cdot 9H_2O$, is formed from solutions of pascoite.

A recent structure determination of KV_3O_8 (Block, 1954) indicates that it contains chains built of segments of the fivefold chain of $KVO_3 \cdot H_2O$. These bent chains are linked laterally to form sheets of composition $(V_3O_8)_n^{-n}$ which are interleaved with K^+ ions. The interesting thing about this structure is that two out of three vanadium atoms in the sheet have fivefold coordination while the third approaches sixfold. The structure of the decavanadate complex ion is not yet known, but it also probably consists of some linkage based on the fivefold chain, and acts as an intermediate step in the formation of the more highly condensed phases such as KV_3O_8, hewettite, and others which are referred to below.

The minerals hummerite (Weeks and Thompson, 1954; and Marvin and Magin, Part 8 of this volume) and pascoite (Palache, Berman, and Frondel, 1951; and Marvin and Magin, Part 8) are true representatives of the polyvanadate stability field. When the vanadium oxides reach the highest valence state, the acid ground waters dissolve them as the polyvanadate, in which form the vanadium moves into the surrounding rock. The brilliant orange crusts of pascoite that form on the blue-black vanadium oxide pockets in the Colorado mines make a striking underground display under the miner's lamp.

HEWETTITE GROUP

When the vanadate solutions are brought to a pH below 3, the vanadium is almost entirely precipitated as brown and red-brown solids. These products have a constitution that has not been revealed in detail, but they undoubtedly correspond to the natural minerals hewettite and navajoite. The complexes containing large cations like hewettite are apparently stable with respect to the decavanadate ion, and may be formed at somewhat higher pH than that allowed for the pure oxide (navajoite). These minerals are fibrous, with the fiber axis invariably exhibiting the characteristic 3.7 A spacing. Recent structure studies by Barnes and his coworkers (Barnes and Qurashi, 1952; Barnes, written communication) have revealed the fivefold chains tied together by oxygen links to form sheets of composition $(VO_3)_n^{-n}$. The details of these structures have not yet been described, but apparently the vanadium atoms are more nearly sixfold in coordination than fivefold. The sheets are loosely held together by Ca^{+2} ions (in hewettite), Na^+ ions (in a new undescribed mineral)

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[6] Pascoite has been incorrectly described as triclinic and having the composition $Ca_3V_6O_{17} \cdot 11H_2O$ in Dana's System of Mineralogy (Palache, Berman, and Frondel, 1951).

or H^+ ions (in navajoite), and varying amounts of water. The variety of discrete phases that readily transform from one to another by base exchange or change in vapor pressure has made the study of this group of minerals and compounds especially involved.

MIXED VANADIUM (IV) AND VANADIUM (V): THE CORVUSITE GROUP

The picture is made even more confusing at lower oxidation potentials. This brings us again to the group of minerals now designated loosely and collectively as "corvusite." No distinct species has yet been isolated from these dark green or blue-black mixtures. Recently, specimens have been found in which a good fibrous development is apparent, and such fibrous samples always show a fiber spacing of 3.7 A by X-ray diffraction. The close relation between the "corvusite" and hewettite groups is further emphasized by the existence of specimens showing the fibrous seams of blue-black "corvusite" partly altered to navajoite, the fibrous structure being maintained from one phase to the other. Artificial compounds which possibly are related to the "corvusite" group are: $2V_2O_4 \cdot V_2O_5$; $Na_2O \cdot V_2O_4 \cdot 5V_2O_5$; $Na_2O \cdot V_2O_4 \cdot 11V_2O_5$. All these are prismatic or fibrous in habit, and have a 3.7 A fiber spacing. The last two, described by Flood and Sørum (1943), illustrate the way in which a relatively small amount of alkali can play an essential stoichiometric role to balance corresponding amounts of reduced vanadium in V_2O_5-like structures. "Corvusite" usually contains small but appreciable amounts of calcium. $2V_2O_4 \cdot V_2O_5$ actually has a V_2O_5 structure with certain oxygen atoms removed (Aebi, 1948). All these observations indicate that the valence range four to five in vanadium is represented in the "corvusite" group by many structures based on the fivefold chain of $KVO_3 \cdot H_2O$ in generally condensed lateral linkages, all retaining the characteristic 3.7-A fiber habit of the chain. The complexity of the group is increased by the incorporation of alkali and alkaline-earth ions and water into these structures. These phases grade into the fully oxidized species of the hewettite group. The fact that the transition from vanadium (IV) to vanadium (V) takes place with little change in structure accounts in part for the fact that the natural vanadates frequently contain 1 or 2 percent V_2O_4. Some specimens of pascoite have been found which are dark green because of a relatively high V_2O_4 content.

Another mixed quadrivalent and quinquevalent oxide is the mineral melanovanadite. Its structural constitution is unknown at present, but it is apparently unrelated to "corvusite." Its mineralogical associations suggest that possibly it represents an intervalent complex phase adjacent to the metavanadate field, analogous to the "corvusite" phase which is adjacent to the polyvanadate field.

METAVANADATE LAYER COMPLEXES: CARNOTITE, TYUYAMUNITE, AND RAUVITE

The uranyl vanadate complexes carnotite, $K_2(UO_2)_2V_2O_8 \cdot nH_2O$, and tyuyamunite, $Ca(UO_2)_2V_2O_8 \cdot nH_2O$, play a special role in the vanadate systems into which uranium is introduced. A tentative structure for anhydrous carnotite (KUO_2VO_4) has been proposed by Sundberg and Sillén (1949), but recent crystal structure studies (Appleman and Evans, 1957) have shown this structure to be incorrect. The sheet complex does not contain discrete orthovanadate VO_4^{-3} groups, but is made up of double $V_2O_8^{-6}$ groups linked to the uranyl UO_2^{+2} groups, so that the latter have a uniform fivefold coordination about their equators (fig. 25). The vanadium atoms are in fivefold coordination with oxygen, and the $V_2O_8^{-6}$ group corresponds closely to two links in the five-coordinated metavanadate chain found in $KVO_3 \cdot H_2O$. The strong layer structure is common to the autunite and carnotite groups of minerals, and accounts for their outstanding hydration-dehydration and base exchange properties.

Recent chemical studies (Paul Barton, written communication) indicate that carnotite is formed most readily in the pH range 7 to 9, but precipitates slug-

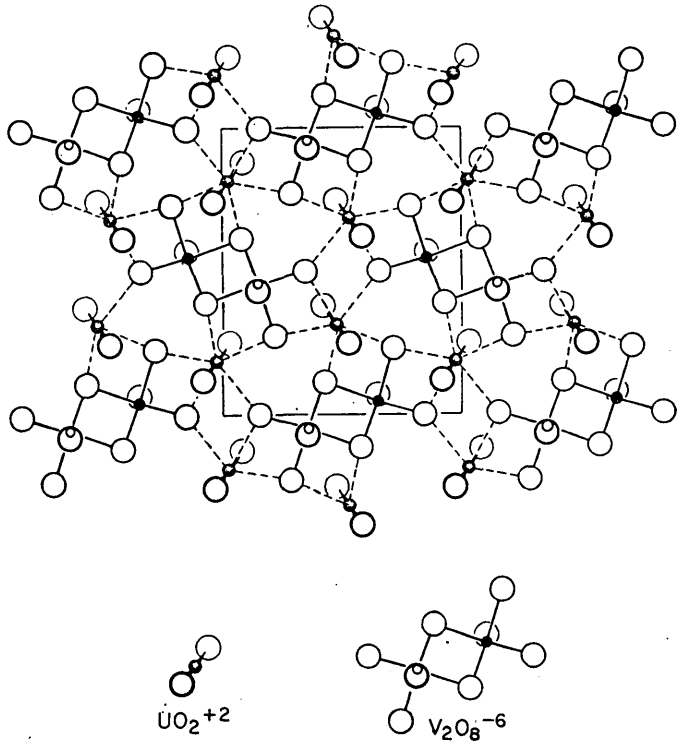

FIGURE 25.—Sheet structure of carnotite (after Daniel Appleman) showing linkage of uranyl and divanadate groups (interlayer K^+ ions not shown).

gishly from more acid solutions. This observation confirms the close relationship of carnotite to the metavanadate series indicated by its crystal structure. The solubility of carnotite is very low and removes practically all vanadium or uranium (whichever is less) from the solution.

Rauvite is a red to reddish-brown resinous mineral of variable composition which may be represented by the formula $x\mathrm{UO_3} \cdot y\mathrm{V_2O_5} \cdot n\mathrm{H_2O}$, with y usually somewhat greater than x. While calcium is frequently present in natural rauvite, it is apparently not an essential constituent. It gives a characteristic powder X-ray diffraction pattern, but instead of sharp lines, the pattern consists of a number of bands. These bands are characteristic of partial crystalline order, such as would be found for a layer structure in which the stacking and orientation of the layers is completely random. Mineralogic associations suggest that rauvite may be a precursor to the formation of carnotite under very acid conditions. Rauvite can be prepared artificially from acid potassium vanadate solutions, especially when the relative potassium ion concentration is low. Much work needs to be done in order to determine the relation between rauvite and carnotite and the mechanism of their formation.

The special characteristics of these layer structures has been further emphasized by the recent new green calcium vanadite mineral, simplotite (Thompson, Roach, and Meyrowitz, 1956a). Preliminary single crystal work on this species has brought out an unusual crystal chemical relationship among the following series of minerals:

Mineral	*Formula*	*V valence*
Meta-autunite	$\mathrm{CaU_2P_2O_{12} \cdot 4H_2O}$	--
Metatyuyamunite	$\mathrm{CaU_2V_2O_{12} \cdot 3\text{–}4H_2O}$	5
Sincosite (Peru)	$\mathrm{CaV_2P_2O_{10} \cdot 5H_2O}$	4
Simplotite	$\mathrm{CaV_2V_2O_9 \cdot 5H_2O}$	4

These minerals all have the basic layer structure referred to above, and form yellow or green plates with a micaceous cleavage and a pseudotetragonal aspect. Apparently, in addition to its similarity to phosphorus, vanadium can also play a role similar to that of uranium in these layer complexes. The implied relationship between the $\mathrm{VO^{+2}}$ and $\mathrm{UO_2^{+2}}$ ions will be clearer when detailed crystal structure analyses of these minerals become available.

GENERAL CHARACTERISTICS OF VANADIUM (V)

In retrospect, we see that the behavior of vanadium (V) varies markedly with conditions of acidity. In basic media, it resembles phosphorus and forms phosphatelike structures—for example, vanadinite, isostructural with apatite. In acid media, vanadium (V) increases its oxygen coordination to five, tending toward six, and the vanadate groups show a strong tendency to polymerize. In this respect, vanadium is very similar to molybdenum and tungsten. Vanadium is most soluble in the pH ranges 2.2 to 6.7, and below 0.8 (where the vanadyl ion $\mathrm{VO_2^+}$ is formed), with a gap near the isoelectric point near pH 1.5 where $\mathrm{V_2O_5}$ hydrates precipitate even from moderately dilute solutions.

Since the lower valence vanadium minerals are generally insoluble, we may conclude that vanadium is transported during weathering in the Colorado sandstones only in the fully oxidized polyvanadate or metavanadate form under acid or weakly alkaline conditions. Some vanadium (IV) may also be released by the acid waters, but this will be quickly oxidized by atmospheric action. If uranium and vanadium are oxidized in the same environment, carnotite or tyuyamunite will be precipitated until the uranium or vanadium is used up. No uranium-vanadium complexes are known at lower valence states; apparently these elements interact only in the fully oxidized state. Excess vanadium in the form of polyvanadate may be temporarily deposited as pascoite-type or hewettite-type minerals, or be taken up in a silicate hydromica or clay structure, or be washed away altogether.

SUMMARY AND CONCLUSIONS

Referring once more to figure 15, it is useful to indicate on the Eh-pH diagram the regions in which the various minerals which have been discussed are stable.

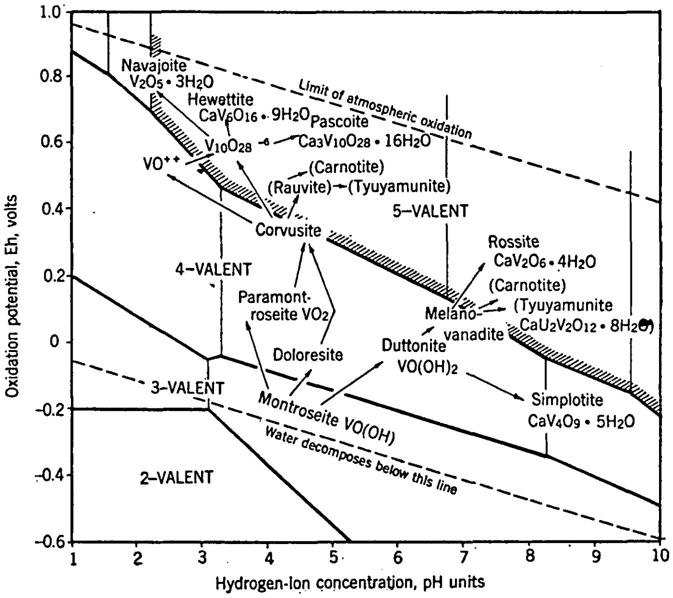

FIGURE 26.—Portion of the Eh-pH phase diagram of figure 15, showing positions of various vanadium mineral species and probable alteration sequences.

This has been done in figure 26, in which the direction of alteration is also suggested by means of arrows. The focal point is montroseite, the most reduced state of vanadium oxide minerals. The alteration under weathering then moves upward on the diagram, with excursions to higher or lower pH conditions, depending upon mineral associations and environment. In the region of complete oxidation, the presence of uranium causes the various complex fields above the shaded boundary to be completely replaced by carnotite.

Broadly speaking, the following generalizations may be made in conclusion:

1. Trivalent vanadium is represented by the primary mineral montroseite (VO(OH)), and is readily oxidized by the atmosphere to the quadrivalent form. Vanadium is similar in its crystal chemistry to manganese in the three- and four-valent state.
2. Mixed vanadium (IV) and (V) oxides comprise the "blue-black ores," and probably are derived to a considerable extent from oxidation of montroseite.
3. Vanadium (V) oxide and its derivatives form the final stage of oxidation. In alkaline media, vanadates behave structurally like phosphates; in acid media, vanadates condense successively to form colorless and orange-red soluble complexes, and finally slightly soluble red or brown fibrous hewettite-type compounds. Vanadium (V) is similar to molybdenum and tungsten in behavior with regard to the tendency to polymerize with decreasing pH.
4. An important structural property of pentavalent vanadium is the formation of the five-coordinated chain which appears between pH 2 and 8. This structure motif appears to play an important role in the formation of the mixed vanadium (IV) and vanadium (V) oxides and hydrates.
5. Carnotite covers a wide pH range of stability for vanadium (V). Pentavalent vanadium will precipitate any uranium present as carnotite or tyuyamunite. Excess vanadium may be temporarily deposited as hewettite or pascoite, or bound up in a silicate mica or clay.

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Part 8. SYNTHESIS OF CALCIUM VANADATE MINERALS AND RELATED COMPOUNDS

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CONTENTS

ILLUSTRATIONS

TABLE

ABSTRACT

Synthesis of natural vanadates shows that most of them are stable in an acid environment. Phase studies of a portion of the system CaO–V_2O_5–H_2O indicate that calcium vanadates are an indicator of environmental pH conditions. Some minerals such as pascoite indicate rapid evaporation of vanadate solutions; other minerals such as hewettite show that slow evaporation took place. Cursory examination of systems K_2O–$UO_2(NO_3)_2$–V_2O_5 and CaO–$UO_2(NO_3)_2$–V_2O_5, both in aqueous solution, has yielded information on the relationships among carnotite, tyuyamunite, and rauvite.

INTRODUCTION

The weathering of primary vanadium and uranium minerals leads to the formation of many secondary minerals, some containing both uranium and vanadium. Synthesis of some of the secondary minerals was undertaken to obtain knowledge of the environment of formation. The synthesis of vanadium minerals containing only fully oxidized vanadium (V) was first undertaken. Then uranium (VI) was added to solutions to obtain uranium-containing vanadates. In this way, the pH range, temperature, and saturation conditions under which some of these minerals can be synthesized are now known.

Since these minerals presumably result from the attack of ground water and air on primary uranium and vanadium minerals, resulting in their oxidation and solution, synthesis was attempted from aqueous solutions containing the desired ions at temperatures between 20° and 90° C. The pH of a solution was varied by adding either acetic or nitric acid. The solid phases were identified by X-ray diffraction patterns and, when possible, by optical methods. The fine-grained habit of some precipitates made optical identification unreliable.

The authors acknowledge the help and advice of many of their colleagues in the U. S. Geological Survey, especially that of Daphne R. Ross, who made the X-ray identifications, and Robert Meyrowitz, who performed the chemical analyses.

CALCIUM VANADATES

One- to two-liter stock solutions containing calcium and vanadate ions were prepared from dry reagents, CaO and V_2O_5 (containing a small amount of V_2O_4), in the following way. The V_2O_5 was powdered and stirred into a liter of water containing 100 ml of 30 percent H_2O_2 which increased the solubility of V_2O_5 and oxidized any V (IV) to V (V). The powdered CaO was then added. The mixture was agitated and slowly heated to boiling to rid the solution of excess H_2O_2. Care was taken in boiling the solution, as the release of O_2 from the H_2O_2 was very rapid and as the solution was violently agitated. The ratio of V_2O_5 to CaO should not be smaller than 3:1 by weight unless the solution is very dilute, as a fairly insoluble hydrated pyrovanadate will precipitate when the solution is heated. After the excess H_2O_2 was destroyed, the solution was cooled, filtered, and analyzed. A useful stock solution has a concentration of 0.04M CaO and 0.08M V_2O_5. More concentrated solutions are saturated at room temperature.

After the stock solution was prepared and analyzed, an aliquot was taken (generally not less than 20 ml). The pH was adjusted to the desired value by adding dilute (1:10) nitric acid, dropwise (dilute acetic acid was sometimes used). The solution was then placed in an oven set at the desired temperature, and evaporated until a solid phase or phases separated out. Table 1 illustrates the actual handling of two aliquots (runs).

TABLE 1.—*The preparation and handling of two runs (aliquots) used in construction of parts of $CaO–V_2O_5–H_2O$ phase diagram*

	Run Ca-17-18	Run Ca-17-19	Remarks
$CaO–V_2O_5$ solution [1] ml	20	20	Dilute HNO_3 added to each run to adjust to initial pH.
pH of run at start	5.15	4.0	Beakers were covered with watchglasses and placed in oven at 56° C.
pH on 3d day	5.0	3.9	Hewettite forming in each beaker.
pH on 5th day	4.95	3.9	Hewettite recovered from solution Ca-17-19.
pH on 7th day	4.85	----------	Hewettite plus a few pascoite crystals recovered from solution Ca-17-18.
			Phases were separated from the mother liquor in a Buchner funnel, washed with water and acetone or alcohol, and air dried.

[1] 8.4 g/l CaO+27.9 g/l V_2O_5.

As can be seen from samples in table 1, the pH of a solution varies with time. Such variations are probably the result of ionic adjustments or changes in volume, and, if precipitation occurs, changes in concentration. The direction of change in pH may be erratic, but generally solutions having pH values above 3.0 have a pH drift towards the pH value representing the phase boundary between the polyvanadates and metavanadates. Solutions having a pH value below 3.0 tend to become more acid. Highly alkaline solutions absorb atmospheric CO_2; this lowers the pH and causes calcite crystals to form.

Since stock solutions with a pH value greater than 8 necessarily have a very low concentration of V_2O_5 and CaO to prevent precipitation during preparation, large aliquots must be taken to provide sufficient solid phase for proper identification. To facilitate matters an aliquot of a more concentrated stock solution (pH less than 7.5) was placed in a beaker and diluted sufficiently with H_2O to prevent immediate precipitation of a solid phase at the basic pH which was to be explored. The electrodes of the pH meter were then placed in the diluted aliquot and the pH raised to the desired value by adding freshly prepared $Ca(OH)_2$ solution or 100 to 200 mg of powdered CaO. In the latter case, the solution was vigorously stirred until the pH rose to the desired value; the solution was then filtered to remove excess solid CaO and then evaporated at the desired temperature.

The addition of CaO or $Ca(OH)_2$ changed the known V_2O_5/CaO ratio. Since it was impractical to analyze each solution prepared in the above manner, the approximate ratio was determined as a function of the pH. From the analyses of stock solutions and their pH values, a graph of pH plotted against V_2O_5/CaO ratio was constructed. Then the approximate ratio in a solution can be determined from its pH by using this graph if the solutions are approximately the same dilution. Knowledge of the exact ratio is not necessary as it has been found that the phase boundaries are not sensitive to this variable.

Figure 27 shows three sections of the $CaO–V_2O_5–H_2O$ system; pH is plotted on the ordinate axis, V_2O_5/CaO ratio in grams on the abscissa. The pH and the temperature determine the solid phase to be formed. The V_2O_5/CaO ratio seems relatively unimportant. The phase boundaries are primarily controlled by pH and secondarily by temperature; this can be seen in Figure 28.

As mentioned before, HNO_3 was added to solutions so as to explore the system at lower pH values than could be obtained with dissolved $CaO–V_2O_5$ alone. As solutions with a V_2O_5/CaO ratio of four or greater are acid, the alkaline region could not be explored without adding a soluble base, the cation of which might form new solid phases, further complicating the phase diagram. Therefore this area has been left blank although it seems reasonable to assume that the phase boundaries would remain the same if extended to the right.

Figure 28 shows the five stability areas found in the examined portion of the $CaO–V_2O_5–H_2O$ system. No phase boundary is shown for the $Ca_3(VO_4)_2 \cdot Ca(OH)_2$; its formation is dependent on the concentration of CaO and V_2O_5 in solution but not their ratio.

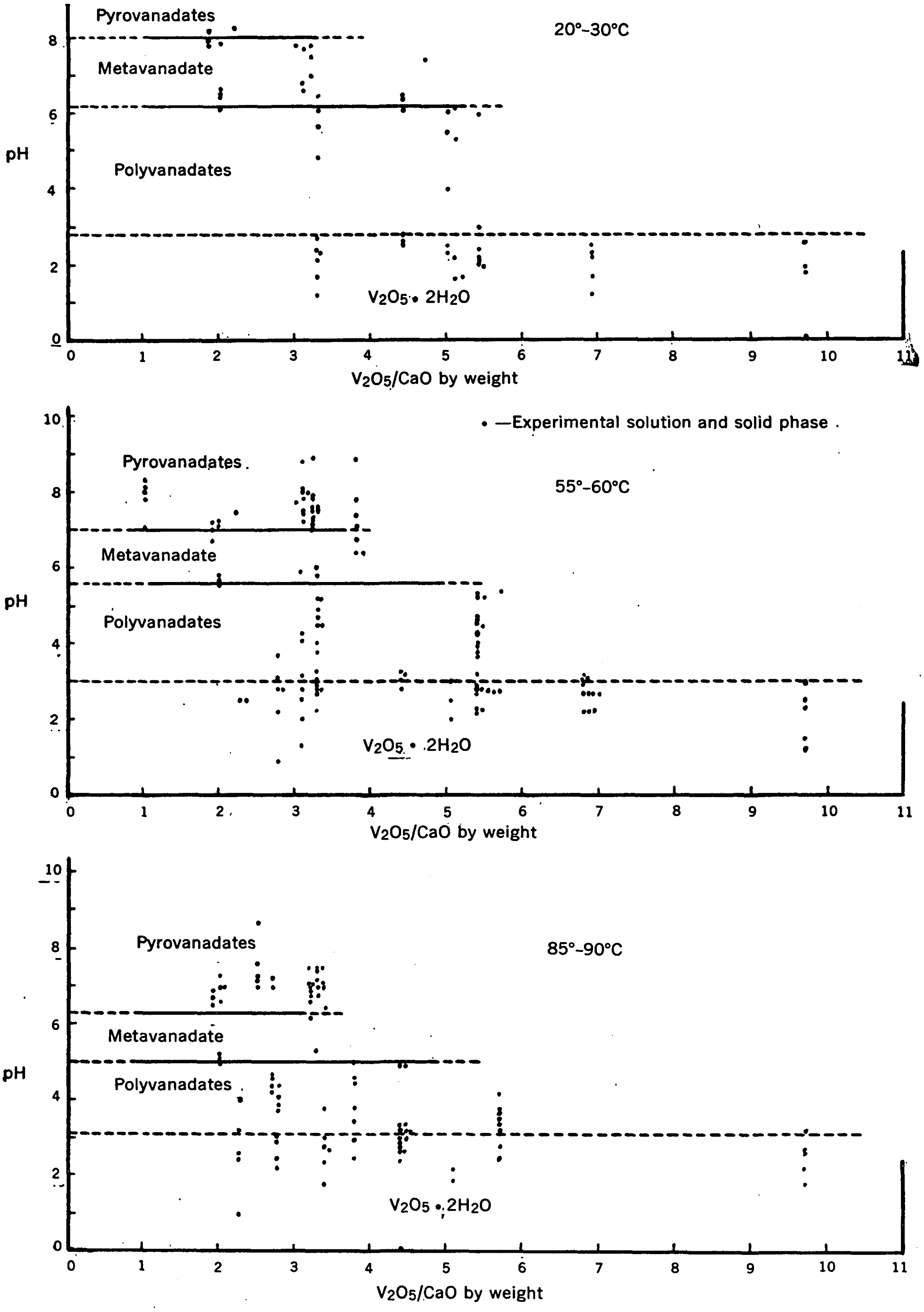

FIGURE 27.—Sections of the $CaO–V_2O_5–H_2O$ system.

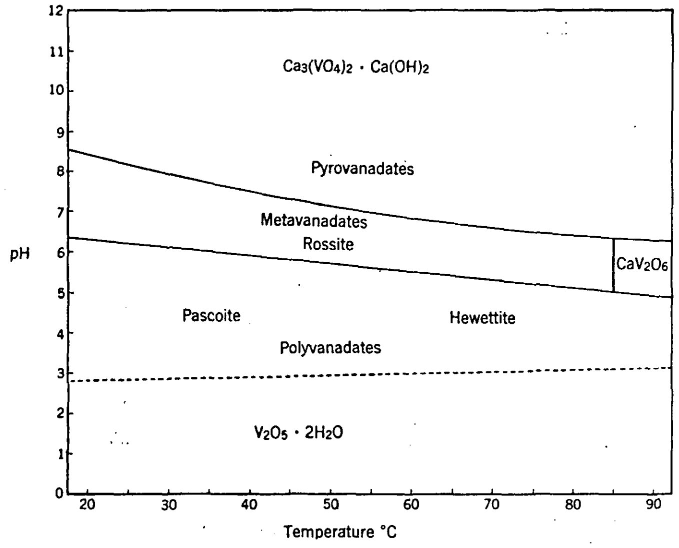

FIGURE 28.—Diagram showing the relationship of calcium vanadates to pH and temperature.

If the solution is nearly saturated, $Ca_3(VO_4)_2 \cdot Ca(OH)_2$ may precipitate in the metavanadate region; while in a dilute solution, precipitation may not occur until the pH approaches 11. This basic salt precipitates very rapidly as a flocculent, white material which if heated to boiling or left at room temperature for a few days, may become crystalline or revert to a pyrovanadate.

Under the $Ca_3(VO_4)_2 \cdot Ca(OH)_2$ precipitation region and sometimes covered by it, is the stability area for pyrovanadates; no orthovanadates were discovered. Two pyrovanadates, $Ca_2V_2O_7 \cdot 2H_2O$ and $Ca_2V_2O_7$, were found. Neither has been established as a mineral although Hess and Schaller (1914) reported a mineral which they called pintadoite ($Ca_2V_2O_7 \cdot 9H_2O$), a hydrated pyrovanadate. Neither of the synthetic pyrovanadates agrees with the description of pintadoite.

At room temperature, the metavanadate stability area which adjoins the pyrovanadate area is mostly in an alkaline environment but at higher temperatures gradually shifts toward the acid side. The hydrated metavanadate, $CaV_2O_6 \cdot 4H_2O$, corresponding to the mineral rossite, is stable up to 85° C. The stable phase then is anhydrous calcium metavanadate, CaV_2O_6. The high temperature metavanadate is not known to occur in nature.

The next stability area contains the hydrated polyvanadates, $Ca_3V_{10}O_{28} \cdot 16H_2O$ and $CaV_6O_{16} \cdot 9H_2O$, corresponding respectively to pascoite and hewettite. Their formation depends not only on pH and temperature but also on the rate of evaporation. A calcium vanadate solution at 40° C with a pH value between 5.9 and 3.0 produces pascoite if rapidly evaporated and hewettite if very slowly evaporated. Increasing the temperature of the solution favors the crystallization of hewettite. Sometimes hewettite will start crystallizing, then pascoite crystals will also appear, and the two will grow simultaneously.

Potassium polyvanadates, like the calcium polyvanadates, are dependent on temperature and rate of evaporation. Various evaporation rates at room temperatures will cause metastable polyvanadates of composition $K_2V_4O_{11} \cdot 7H_2O$, $K_6V_{10}O_{28} \cdot 10H_2O$, and $K_6V_{10}O_{28} \cdot 8H_2O$ to crystallize. Then if further evaporation is prevented, the existing polyvanadates will redissolve as the stable phase $K_2V_6O_{16}$ or $K_2(OH)_2V_6O_{15}$ crystallizes. By analogy, pascoite, $Ca_3V_{10}O_{28} \cdot 16H_2O$, is considered the metastable phase and hewettite, $CaV_6O_{16} \cdot 9H_2O$, the stable phase, although pascoite cannot be redissolved and hewettite crystallized in its place merely by stoppering the solution, as is possible with potassium vanadate solutions.

Solutions having a low pH, below 3, are thought to be in the stability area for $V_2O_5 \cdot 2H_2O$. The phase boundary between the $V_2O_5 \cdot 2H_2O$ and the polyvanadates is dotted to show uncertainty. Generally, $V_2O_5 \cdot 2H_2O$ will crystallize below this boundary but occasionally it will be above it. Similarly, the polyvanadates will occur above this boundary but pascoite has occasionally formed at pH 2.2. Furthermore, another phase which is similar to hewettite in appearance and composition may possibly be present in this pH region.

No $V_2O_5 \cdot 3H_2O$, corresponding to the mineral navajoite, has been found in the study of this system.

Synthetic rossite and pascoite are identical to the natural minerals in physical properties and appearance, but the synthetic materials are better crystallized. Synthetic hewettite is like the natural hewettite in fibrous habit, silky luster, and hardness, but differs in color. Natural hewettite is a vivid deep red; synthetic hewettite is a light to dark brown. Like their natural counterparts, synthetic rossite and hewettite dehydrate on exposure to the atmosphere to metarossite and metahewettite, respectively.

Below are the optical properties determined for synthetic rossite and pascoite using phosphorus-sulfur-methylene iodide index liquids with white light.

SYNTHETIC ROSSITE ($CaV_2O_6 \cdot 4H_2O$)

Optical properties

$\alpha = 1.720 \pm 0.003$ at 28° C	triclinic[1]
$\beta = 1.783 \pm 0.003$	biaxial negative
$\gamma = 1.842 \pm 0.003$	$2V = 85°$ (calc.)
	colorless, nonpleochroic
	$r < v$ (?) dispersion, faint

Chemical analysis

[Analyst, George B. Magin, Jr.]

	CaO	*V_2O_5*	*H_2O*	*Total*
Found	18.58	58.43	22.89	99.90
Calc	18.09	58.67	23.24	100.00

SYNTHETIC PASCOITE ($Ca_3V_{10}O_{28} \cdot 16H_2O$)

Optical properties

$\alpha = 1.771 \pm 0.003$ at 27° C
$\beta = 1.824 \pm 0.003$
$\gamma = 1.826 \pm 0.003$

monoclinic [2]
biaxial negative
$2V = 30°$ (calc.)
pleochroic
  X = light cadmium yellow
  Y = orange
  Z = cadmium yellow
absorption $X < Z < Y$
$r > v$ dispersion, very strong

Chemical analysis

[Analyst, George B. Magin, Jr.]

	CaO	*V_2O_5*	*H_2O*	*Total*
Found	12.56	65.23	22.23	100.02
Calc	12.32	66.58	21.10	100.00

[1] As reported by Weeks and Thompson, 1954.
[2] As reported by Evans, Mrose, and Marvin, 1954.

Pascoite has been heretofore listed as

$$Ca_2V_6O_{17} \cdot 11H_2O$$

(Hillebrand, Merwin, and Wright, 1914; Palache, Berman, and Frondel, 1951), but crystallographic and density studies (Evans, Mrose, and Marvin, 1954) on synthetic pascoite plus chemical analyses show that its formula should be $Ca_3V_{10}O_{28} \cdot 16\text{–}17H_2O$. The formula as determined from the chemical analysis alone requires 17 molecules of water, but 16 molecules of water to agree best with density measurements (Evans, Mrose, and Marvin, 1954). The exact amount of water will not be known until the crystal structure has been determined. The extra water revealed by chemical analysis may be due to included water in rapidly formed crystals.

Synthetic hewettite was not identified optically because of its fine fibrous habit, its high indices of refraction (above 2.0), and its reaction with high-index oils which changed the color of the fibers from a yellow or red to a dark green or black. Nonreacting index oils show that the fibers have a yellow to red color, parallel extinction, and are nonpleochroic. Identification was made by X-ray powder diffraction films.

The $V_2O_5 \cdot 2H_2O$ phase is usually very fine grained, occasionally fibrous. It is dark reddish brown in the mother liquor but changes on washing and drying to a dull brown or green. Solutions with pH values less than 1 sometimes produce a black, hydrated vanadium pentoxide. The $V_2O_5 \cdot 2H_2O$ is soft with a dull, sometimes velvetine, luster. Examination with a petrographic microscope reveals an anisotropic, yellowish green material with indices of refraction greater than 1.9; high index oils react with the material. Identification is made by X-ray powder diffraction patterns and chemical analyses.

The solubilities of synthetic rossite, pascoite, hewettite, and $V_2O_5 \cdot 2H_2O$ as determined in doubly distilled water at 30° C are as follows:

Rossite	4.55 g/l, pH of solution 6.8
Pascoite	More than 20 g/l, pH of solution 6.1
Hewettite	0.03 g/l, pH of solution 4.5
$V_2O_5 \cdot 2H_2O$	0.03 g/l, pH of solution 4.1

The solubility figure of the pascoite is approximate. Hewettite crystallized within a short time from the nearly saturated or saturated pascoite solution and changed the ratio and concentration of dissolved $CaO\text{–}V_2O_5$.

To apply the information of the phase diagram to field conditions, one must understand what happens during the attack by air and ground water on the primary mineral assemblage. Thus, the breakdown of sulfides, predominantly pyrite, produces acid conditions. The acid conditions and available oxygen facilitate the solution and oxidation of vanadium. The pH of such a solution is affected by the solution of vanadium minerals and associated calcite, dilution by other ground waters which may be slightly basic, and movement through the sediments. When the solution is saturated, rossite will crystallize if the pH is above 6.2, assuming the temperature is near 30° C. It is doubtful if the pH ever rises much above 8, as no indisputable evidence of natural pyrovanadates has been found. Hewettite will develop if the pH value is below 6.2 and concentration is very slow. The necessity of very slow concentration in the formation of hewettite is shown by the fact that it does not form as an efflorescence on mine walls or surface exposure where evaporation is rapid, as does pascoite. Hewettite is found in porous or fractured sediments where evaporation is greatly retarded.

If the ground water is quite acid, below pH 3.0, hydrated vanadium pentoxide should form. It is possible that if only a very minor amount of calcium ions or other cations were present in the ground water, hydrated V_2O_5 would also form at higher pH values, since hydrated V_2O_5 has formed at pH values up to 4 in the laboratory.

The presence of rossite in a deposit may indicate a maximum temperature limit as rossite is not formed above 90° C.

URANIUM-CONTAINING VANADATES

In an attempt to learn about the formation of carnotite, $K_2(UO_2)_2(VO_4)_2 \cdot 1\text{–}3H_2O$, and tyuyamunite, $Ca(UO)_2(VO_4)_2 \cdot 7\text{–}10.5H_2O$, exploration of the systems

$K_2O\text{-}UO_2(NO_3)_2\text{-}V_2O_5$ and $CaO\text{-}UO_2(NO_3)_2\text{-}V_2O_5$, both in aqueous solution, was started.

The method of exploration was much the same as in the $CaO\text{-}V_2O_5\text{-}H_2O$ system. Thus, in the $K_2O\text{-}UO_2(NO_3)_2\text{-}V_2O_5$ system, stock solutions were prepared from the dry reagents, KOH, V_2O_5 (containing some V_2O_4), and $UO_2(NO_3)_2 \cdot 6H_2O$. Since KOH and

$UO_2(NO_3)_2 \cdot 6H_2O$ are readily soluble in water, stock solutions of 5.5M KOH and 0.127M $UO_2(NO_3)_2$ were easily prepared. A colloidal solution of V_2O_5 (0.0015M) was prepared by dissolving V_2O_5 in water containing H_2O_2. A KOH-V_2O_5 stock solution was prepared by dissolving KOH in a liter of H_2O, adding powdered V_2O_5 and 50 ml of 30 percent H_2O_2, and heating to boiling to rid the solution of excess H_2O_2. The solution was then cooled, filtered, and analyzed. Concentrations ranged between 0.18 to 0.32M KOH and 0.23 to 0.62M V_2O_5.

Solutions for evaporation are prepared from aliquots of the stock solutions. These aliquots have to be diluted approximately 100 fold to prevent instant precipitation on mixing. The KOH-V_2O_5 aliquot is first diluted, then any additional KOH or V_2O_5 which is needed to obtain the desired ratio is added from the prepared stock solutions. The $UO_2(NO_3)_2$ aliquot is put in another beaker and diluted. The two solutions are then mixed by pouring the uranium nitrate into the KOH-V_2O_5 solution. The reverse procedure results in initially cloudy solutions. The pH is adjusted by adding HNO_3 (1:10). Solutions are evaporated at room temperature (24° to 30°C) or on a hot plate at 80°C.

The precipitated phases are usually so finegrained that identification is made by X-ray powder diffraction patterns, rather than by optical methods.

Figure 29 shows a section containing the KOH axis and midpoint of the opposite side of the triangular phase diagram of the KOH-V_2O_5-$UO_2(NO_3)_2$ system. This section shows the tentative relationship between carnotite, rauvite, and hydrated vanadium pentoxide. Phase boundaries are dependent on pH and concentration of reacting ions; temperature has no appreciable effect on these phase boundaries. The dashed line across the top of the diagram indicates the limits of exploration. No experimental solution had an initial pH above the dashed line. The area below the line was explored by depressing the pH of a solution with HNO_3.

The yellow synthetic carnotite, as identified by X-ray diffraction patterns, has a fairly large area of stability. The only noticeable difference between carnotite formed in the basic environment as against that formed in an acid environment, is in the degree of crystallinity. The carnotite formed in the basic region is of finer grain, giving broad, diffuse X-ray diffraction lines. No chemical analyses are available as yet on these synthetic carnotites. A solubility study on synthetic carnotite has indicated that its solubility is near 0.15 ppm in distilled water and increases to 4 ppm at pH 3.3 (NO_3^- present).

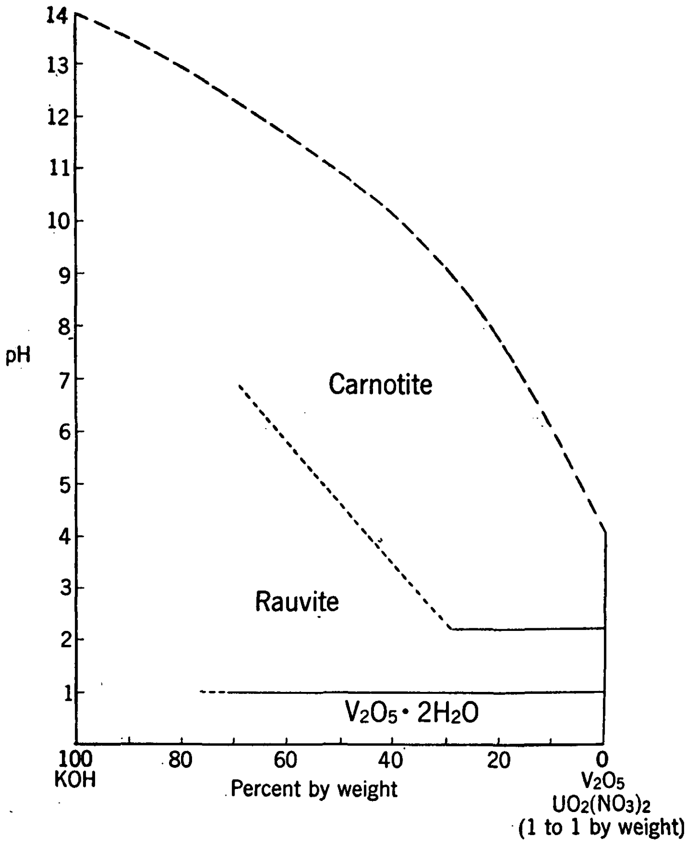

FIGURE 29.—Section of the KOH-V_2O_5-$UO_2(NO_3)_2$ aqueous solution phase diagram showing the relative positions of the initial phases formed upon evaporation of solutions.

Synthetic rauvite or rauvite-like material forms under acid conditions as a bright yellow precipitate which dries to a dull yellow, orange, or brown material. The bright yellow color usually returns when the material is returned to water. The X-ray diffraction pattern of this material is distinctive, but the lines are broad and diffuse, due to very fine grain size, and possibly to a disordered structure. Malcolm Ross, of the Geological Survey, after examining natural rauvite with the electron microscope, suggests that it has a platy or claylike character. His examination of synthetic rauvite showed it to consist of very fine crystalline aggregates.

Although natural rauvite has been listed as $CaO \cdot 2UO_3 \cdot 5V_2O_5 \cdot 16H_2O$(?) (Weeks and Thompson, 1954), some doubt remains as to its real composition. No analysis on rauvite or rauvite-like material precipitated from solutions containing potassium ion is available. But synthetic rauvite, as identified by X-ray powder diffraction pattern, was precipitated as a bright yellow material from a solution containing only $UO_2(NO_3)_2$ and V_2O_5, no calcium or potassium ions present. A chemical analysis of this material, by George B. Magin, Jr., gave the following composition (in percent):

UO_3	V_2O_5	H_2O	Total
47.08	37.72	15.49	100.29

This composition gives the tentative formula, $UO_3 \cdot V_2O_5 \cdot 5H_2O$.

When a solution is prepared containing relatively high concentrations of uranium and vanadium ions, rauvite is sometimes precipitated in the stability region of carnotite. This action suggests that rauvite may form as a metastable phase and later convert to the stable phase, carnotite.

Results of solubility runs with synthetic rauvite are not available, but its solubility is thought to be comparable to carnotite.

Solutions with pH values less than 1 precipitate dark brown to black $V_2O_5 \cdot 2H_2O$, as identified by X-ray methods. Precipitation of the $V_2O_5 \cdot 2H_2O$ continues until the vanadium pentoxide in solution is depleted. Then green crystals of $UO_2(NO_3)_2 \cdot xH_2O$ crystallize if the solution is at room temperature. At 80° C a fine-grained yellow material forms, tentatively identified by X-ray powder diffraction patterns as a hydrated uranium oxide. The last material to come out of solution is KNO_3, colorless crystals. As the solutions increase in KOH and V_2O_5 concentration, golden crystals of $K_2V_6O_{16}$ may form after the precipitation of the carnotite or rauvite at 80° C.

Examination of the CaO-$UO_2(NO_3)_2$-V_2O_5 system in aqueous solution has been started but not enough data have been collected to delineate phase boundaries. From what data are known, the phase diagram will probably be similar to that of the K_2O-$UO_2(NO_3)_2$-V_2O_5 system in aqueous solution, with tyuyamunite appearing in place of carnotite.

Preparation of stock solutions of CaO-V_2O_5, V_2O_5, and $UO_2(NO_3)_2$ used in this study has been described above. Small aliquots of CaO-V_2O_5 and $UO_2(NO_3)_2$ stock solutions are placed in separate beakers and diluted with water. The diluted CaO-V_2O_5 is brought to the desired ratio by adding the necessary milliliters of V_2O_5 stock solution or freshly prepared $Ca(OH)_2$ solution (approx. 0.015M). Then the diluted $UO_2(NO_3)_2$ is poured into the CaO-V_2O_5 solution. As mentioned before, this method of mixing prevents immediate precipitation. The pH of a solution is adjusted with HNO_3. Solutions are then evaporated at 30°, 55°, or 90° C in ovens.

The phases so far encountered are tyuyamunite, $Ca(UO_2)_2(VO_4)_2 \cdot 5$–$10.5H_2O$, rauvite, and $V_2O_5 \cdot 2H_2O$. They are fine grained and identification is made by X-ray methods. The tyuyamunite phase corresponds to the carnotite phase of the K_2O-$UO_2(NO_3)_2$-V_2O_5 system. The synthetic rauvite and $V_2O_5 \cdot 2H_2O$ are similar to previously synthesized phases. However, in one case, the rauvite remained quite yellow in color instead of changing to a dull orange or brownish color.

Again pH, concentration of reacting ions, and temperature are factors affecting stability of the solid phase. Thus far, no tyuyamunite has been synthesized below 90°C at the few points explored on the phase diagram. It may be possible that at lower temperatures rauvite forms as a metastable phase which will slowly convert to tyuyamunite. Most of the rauvite was precipitated under conditions similar to its formation shown by the K_2O–$UO_2(NO_3)_2$–V_2O_5 phase diagram. The same also applies to $V_2O_5 \cdot 2H_2O$. Again, as in the above system, the exact relationship of rauvite to tyuyamunite (or carnotite) is not known. Rauvite may be either a metastable or a stable phase, depending on the pH of the environment.

The study of synthetic carnotite and tyuyamunite shows that carnotite and probably also tyuyamunite can be formed under either acid or basic conditions. However, the attack on the primary mineral assemblage, as previously related, presumably took place in an acid environment, oxidizing and dissolving both uranium and vanadium. Since uranium-containing vanadates are quite insoluble above pH 3 and precipitate quite readily, they should form in preference to other vanadates if the fully oxidized uranium and vanadium ions came together in solution. Highly acid conditions, pH 1 or below, would prevent the formation of uranium vanadates and redissolve those already formed. Hydrated V_2O_5 would probably be the first phase to appear under such conditions.

MISCELLANEOUS VANADATES

Some of the rarer vanadates found on the Colorado Plateau have been synthesized.

The sodium analog of hewettite, $Na_2V_6O_{16} \cdot 3H_2O$, which has recently been found in nature (A. D. Weeks, oral communication), can be synthesized either by direct precipitation or by base exchange. At 55° C, $Na_2V_6O_{16} \cdot 3H_2O$ formed directly from slowly evaporated $NaOH$-V_2O_5 solutions (0.22M NaOH, 0.11M V_2O_5) with pH values between 3.0 and 6.0, adjusted with glacial acetic acid. $Na_2V_6O_{16} \cdot 3H_2O$ was identified by X-ray diffraction patterns and chemical analyses. It would probably form at 20° C if the solution were evaporated very slowly; more rapid evaporation would produce a metastable polyvanadate analogous to $K_6V_{10}O_{28} \cdot 9H_2O$ and $Ca_3V_{10}O_{28} \cdot 16H_2O$ (pascoite). In forming $Na_2V_6O_{16} \cdot 3H_2O$ by base exchange, hewettite

($CaV_6O_{16}\cdot 9H_2O$) or one of its lower hydrates is placed in a sodium-bearing solution with a pH between 3.0 and 6.0 for an appropriate length of time. Several grams of synthetic hewettite were converted to the sodium analog in Na_2SO_4 solutions (Na_2SO_4 concentration varied from 0.1N to 0.7N) in three weeks. Identification was made by X-ray diffraction patterns. Natural $Na_2V_6O_{16}\cdot 3H_2O$ could have formed in either way.

Hummerite, $K_2Mg_2V_{10}O_{28}\cdot 16H_2O$, is easily crystallized from solutions containing stoichiometric amounts of potassium, magnesium, and vanadium at pH 5 by rapid evaporation at room temperatures. Variation in the relative ratios of potassium, magnesium, and vanadium concentrations, if not extreme, does not prohibit hummerite formation. A KOH-V_2O_5 solution 0.00676M KOH, 0.0165M V_2O_5) was made by dissolving dry KOH and V_2O_5 in water. H_2O_2 was used to dissolve the V_2O_5; excess H_2O_2 was boiled off. One tenth of a gram of $Mg(NO_3)_2$ was then dissolved in 100 ml of KOH-V_2O_5 solution. The pH was raised to the desired pH by adding concentrated KOH solution. The solution was placed in an open, shallow evaporating dish, and crystals soon formed. Synthetic hummerite crystals are sensitive to heat, dehydrating readily.

Volborthite, $Cu_3V_2O_8\cdot 3H_2O$, will slowly crystallize out of a solution having a pH between 2.0 and 4.7. Above pH 4.7, it becomes very insoluble and precipitates as a flocculent material which will crystallize if the solution is boiled for a few minutes. In synthesizing volborthite, 20 ml of 0.0855M NH_4VO_3 solution were added to 200 ml of H_2O. The pH was adjusted to 2 with concentrated HNO_3 to prevent an immediate precipitation from forming on addition of 2 ml of 2.5M $Cu(NO_3)_2$. The solution was stirred and NH_4OH (1:10) added to raise the pH to the desired value. Heating the solution before the addition of the NH_4OH increases the grain size of volborthite if precipitated at a pH value above 4.7. Identification of the volborthite was made by X-ray diffraction pattern and chemical analysis. Chemical analysis was done by Robert Meyrowitz, U. S. Geological Survey, by microchemical techniques.

Several attempts were made to synthesize calciovolborthite, $(Cu,Ca)_2VO_4OH$, by adding various amounts of 1.25M $Cu(NO_3)_2$ to 40 ml portions of CaO-V_2O_5 solution (0.0365M CaO, 0.0412M V_2O_5). HNO_3 (1:50) was added to the CaO-V_2O_5 solutions before the $Cu(NO_3)_2$ to lower the pH to 5, then again after the addition of the $Cu(NO_3)_2$ to give a pH value between 4.5 and 4.0. No calciovolborthite was formed; dark brown crystalline aggregates of volborthite appeared.

To determine if calciovolborthite was stable at high pH values, the $Cu(NO_3)_2$ solution was diluted to approximately 0.005M and then made ammoniacal with NH_4OH. This solution was added to 100 ml of CaO-V_2O_5 (approximately 0.0035M CaO, 0.0005M V_2O_5) solution and placed in an oven at 90° C. A light green, fine-grained precipitate formed which gave an X-ray powder diffraction pattern tentatively identified as tangeite (calciovolborthite, Guillemin, 1956) by Daphne Ross (written communication). Chemical analyses of three precipitates by George B. Magin, Jr., reveal calcium, copper, and vanadium present in major amounts. Samples were apparently not pure tangeite as the analyses did not agree with the theoretical composition. Both copper and calcium are thought to be essential components of the material as it is not formed if either copper or calcium ions are absent. Heating the precipitate in its mother liquor for several days at an elevated temperature also seems to be required to crystallize the tangeite. It formed at pH values between 8.5 and 10. Volborthite was sometimes present as a contaminant in precipitates formed near pH 8.5.

Several attempts have been made to synthesize fervanite, $Fe_4(VO_4)\cdot 5H_2O$, and steigerite, $Al_2(VO_4)_2\cdot 6.5H_2O$. The procedure is similar to the synthesis of volborthite except $Fe(NO_3)_3$ or $Al(NO_3)_3$ were substituted for $Cu(NO_3)_2$. A very insoluble, brown, flocculent iron vanadate precipitated near pH 1.6; an insoluble, yellow, flocculent aluminum vanadate precipitated near pH 4. Even though the flocculent materials were boiled for several minutes or precipitated from near-boiling solutions or precipitated by very slowly increasing the pH of the solution (urea, $CO(NH_2)_2$, was added; then the solution was heated to cause decomposition of urea and formation of NH_4OH); no indication of crystallinity was detected by X-ray powder diffraction. Chemical analyses by Robert Meyrowitz, U. S. Geological Survey, using microchemical techniques, give the following empirical formulas: $Fe_2(VO_4)_2\cdot 5H_2O$ and $AlVO_4\cdot 4H_2O$.

CONCLUSIONS

Synthesis of many of the vanadates found on the Colorado Plateau, study of the system CaO-V_2O_5-H_2O, and cursory examination of systems K_2O-$UO_2(NO_3)_2$-V_2O_5 and CaO-$UO_2(NO_3)_2$-V_2O_5, both in aqueous solution, show that the natural vanadates can form over a wide range of pH conditions. The best pH indicators are the calcium vanadates; rossite forms under slightly alkaline or acid conditions, depending on the temperature; pascoite and hewettite crystallize in a weak to moderate acid environment. Carnotite indicates pH values above 2.2; rauvite and navajoite indicate acid conditions. While it has not been possible to duplicate actual natural conditions, especially the presence of other ions and their influence on vanadium (V) concentration and precipitation, the presence of pascoite seems to indicate rapid evaporation of ground water carrying vanadate ions; hewettite and probably Na-hewettite seem to indicate slow evaporation.

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Part 9. CLAY MINERALS IN THE MUDSTONES OF THE ORE-BEARING FORMATIONS

By W. D. Keller

CONTENTS

ILLUSTRATIONS

TABLES

ABSTRACT

Mudstone samples were collected from uranium-vanadium ore-bearing sedimentary formations on the Colorado Plateau to determine if differences could be detected in the gross clay mineralogy between red- and green-colored mudstones which are otherwise stratigraphically equivalent, between ore-bearing and barren mudstone, and within other relationships referred to in the conclusions below. Clay mineral identifications, which were made by the use of X-ray powder diffraction patterns, differential thermal analyses, and petrographic examinations, lead to the following conclusions concerning the gross clay mineralogy of the mudstones.

Red and green (also purple and white) counterparts of mudstone do not show a significant difference in gross clay mineralogy in the Rico formation of Pennsylvanian and Permian (?) age, the Cutler formation of Permian age, the Moenkopi, and Chinle formations of Triassic age, and the Salt Wash and Brushy Basin members of the Morrison formation of Jurassic age. Clay minerals within all the common clay mineral groups may be constituents of red and green mudstone without regard to color. No difference was detected in the gross clay mineralogy of red-green counterparts whether the green color was developed along mineralized fault planes which transected the red beds long after lithification or in isolated spots within thick, relatively impermeable mudstones whose color change may have occurred during diagenesis.

Mudstones may be ore bearing or barren without necessary difference in their clay mineral components.

Alunitization of red mudstone of the Moenkopi formation at the Oyler mine in Capitol Reef National Monument was preceded by bleaching of the red ferric oxide pigment, mobilization of the iron as sulphate and the formation of jarosite, removal of calcite, and formation of some gypsum.

It is difficult to find unequivocal evidence of effects on the rocks from the solutions which carried uranium-vanadium ore minerals apart from the ore minerals themselves.

INTRODUCTION

Mudstones, of which clay minerals are major components, constitute an integral part of the sequence of sedimentary rocks which contain uranium and vanadium ore on the Colorado Plateau. It is probable that the mudstones have played an essential role, one way or another, in the precipitation, localization, and concentration of many of the ore deposits. For example, the bulk properties of mudstones, especially low permeability, have made them important as barriers, traps, and guides for ore-bearing solutions.[7] The chemical and mineralogical properties of the clay minerals, on the other hand, are probably more important where replacements by ore minerals occur. The color of the mudstones also has been of special interest because it has been observed that a high ratio of green to red mudstone and sandstone can be successfully used as an indicator of favorable ground (Weir, 1952) on the Plateau.

In consequence of the close association of mudstone with ore deposits, and of the red-green (similarly, purple-white) color relationship to ore-bearing ground, at least two major questions have arisen regarding their mineralogic composition. Does the clay mineralogy of mudstones in localities productive of ore differ from that in barren country, and does the clay mineralogy of the green mudstone differ from that of the red which is stratigraphically equivalent?

This report is concerned with the above questions. It does not include consideration of the clay minerals finely disseminated in the sandstones or of the vanadiferous clay minerals which are ore minerals.

ACKNOWLEDGMENTS

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THE PROBLEM OF CLAY MINERALS IN RED AND GREEN MUDSTONES

To answer the question whether the clay minerals in red and green stratigraphically equivalent mudstones are different, it is relatively simple to collect specimens from red and green counterparts at one locality and analyze them mineralogically. An analysis from a single locality merely opens up the geologic problem, however, because green and red clay-bearing rocks occur in contact over a wide variety of geologic conditions which bear on the deposition and concentration of ore.

For example, although the ratio of green to red mudstones and sandstones is higher in favorable ground, it is also recognized that apparently similar green-red pairs, except for ratios of green to red, occur in red beds far removed from localities in which uranium-vanadium mineralization occurs. The problem enlarges thereby: are red-green counterparts from within ore deposits different from those in barren ground? Next, where green mudstones are mineralized, were the ore-transporting solutions responsible for the green color within red beds, or were the chemical and mineral environments within the green rock the causes for deposition of the ore minerals? Hence, a single question is immediately doubled or tripled.

Green spots may occur isolated within the interior of relatively impermeable thick mudstone layers indicating color differentiation probably during diagenesis—that is, early in the history of the rock, but in contrast to this relationship elsewhere, green zones occur alongside joints and fault planes which clearly transect the primary stratification structures in red beds. Some of the fault and joint planes are mineralized, others are not. Was the mineralization the the cause or the effect of the secondarily developed green color, and what clay minerals are present across the color contact in these red-green rocks?

In a similar way, it may be asked if the clay minerals, and possibly other minerals except the iron-oxide minerals, differ in red-green counterparts in rocks of different geologic ages, in those deposited under different sedimentational environments, in those composed of different clay mineral groups, in occurrences where the uranium-vanadium ore minerals are dark and low in oxidation state as against those higher in oxidation state, and in various other combinations. With the introduction of each new variable to the problem the number of questions increases geometrically to the point where it becomes impossible practically to collect red-green pairs for analysis in such a way as to eliminate all variables except color in the many combinations referred to above. Specimens were collected and analyzed, however, from the relationships encountered most commonly in field work and these will be described subsequently.

FIELD AND LABORATORY WORK

Approximately 400 samples of mudstone and clayey sandstone were collected from localities on the Colorado

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[7] Mullens, T. E., and Freeman, V. L., Lithofacies of the Salt Wash member of the Morrison formation. (Written communication.)

Plateau during parts of the summers of 1953 and 1954. Where red and green counterparts were taken, they were always obtained from the same stratigraphic level and within a few inches apart across the color contact, unless otherwise stated. The clay minerals were identified mainly from X-ray powder diffraction patterns, but differential thermal analysis and the petrographic microscope were also used.

The clay fraction was extracted from sandstones by gently disaggregating in distilled water by rolling (not grinding) in a ball mill, and then recovering from sedimentation the particles having settling velocities equivalent to and less than 2-micron spheres according to Stoke's Law. Some muds rich in gypsum or other soluble flocculating salts required repeated stirring with distilled water, settling, and decantation before the clay remained in a dispersed state, but no dispersing chemical, other than very dilute NH_4OH, was added.

During the first stages of the laboratory work all samples were dispersed and only minus 2-micron fractions analyzed, some in random orientation and others as oriented aggregates (clay films). The oriented-aggregate technique greatly enhances the X-ray reflections from the basal planes of platy minerals, making it possible to detect small amounts of platy clay minerals which might otherwise be missed, particularly mixed-layer types which characteristically give weak reflections.

After comparing the diffraction patterns of those minus 2-micron fractions from mudstones with patterns from the bulk or entire mudstone it was concluded that more or less mineral segregation and concentration occurred during sedimentation. Minerals heavier than the clay minerals, like iron oxides, iron sulfides, and some uranium-vanadium ore minerals, were removed to a significant degree from the minus 2-micron fraction of clay minerals owing to the more rapid settling of the heavier minerals, and, therefore, the minus 2-micron fraction was not always representative of the original rock.

It is obvious that geologic conclusions based on mineral identifications of nonrepresentative fractions of a rock may be dangerously erroneous. It was necessary then to choose in this study between sacrificing either some sensitivity in clay mineral identification or of fidelity in representation of the outcrop by the specimen. Because the first objective of the problem was to look for possible differences between the red and green counterparts of mudstones which might be utilized in geologic interpretation or as a guide to ore, it seemed of paramount importance that the sample which was analyzed must represent the rock.

Therefore, the considered decision was made to identify primarily the dominant clay mineral constituents in the whole mudstones—that is, the bulk samples, although it is possible that small amounts of some clay minerals detectible only by more refined methods, may have remained unreported. Many samples were still fractionated, however, to check observations on the bulk samples. A truly refined clay mineral analysis requires determinations of ion exchange and perhaps even chemical analysis, which become so costly in terms of both time and money that the limit of diminishing returns is quickly reached in a geologic study where many clay samples are involved, as in this one.

Physical methods of clay mineral analysis, as were used, rarely permit recognition, at our present stage of knowledge, of the nature of cationic population in the octahedral, tetrahedral, and interlayers of the clay minerals. It is possible that chemical differences of this type occur between clay minerals, but which would escape detection by the physical analytical techniques employed. This reservation must be made on the conclusions to be reached later in this report.

For the purposes of identification by X-ray, a 001 interplanar spacing of approximately 7A in the clay mineral was taken to indicate a member of the kaolin group. The reflections of kaolin-type minerals were regularly more characteristic of the "fire-clay type of kaolinite," one with layers stacked partially at random, than of well-crystallized kaolinite (Grim, 1953). The fire-clay type of kaolin is commonly developed in argillaceous sedimentary rocks whose source material is not previously well-crystallized kaolinite.

Hydrous mica, which has also been called illite, is identified by an interplanar spacing of approximately 10A. This is commonly a broader (platykurtic) peak than the sharper one provided by clastic muscovite. Some diffraction patterns showed broad 10A bases which abruptly narrowed to a sharp peak, as if pierced by a sharp 10A shaft. Such patterns were interpreted as coming from both hydrous mica clay and clastic muscovite flakes. The presence of muscovite in mudstones showing this type of pattern was confirmed by microscopic examination.

Chloritic minerals were identified by a spacing of approximately 14A. Because chlorite peaks persisted regularly after heating several of these clays to 500° C. for 6 hours, which destroys the structure of kaolinite, it was assumed that the ancient sediments under study did not contain chlorite whose structure is destroyed at a lower temperature than that which wrecks kaolinite. This assumption may be incorrect because chlorite which was destroyed below 500° C. has been found in ore clays (Part 11) from the Colorado Plateau. Even if this assumption should prove to be incorrect, it does not invalidate the results obtained by comparing red and green counterparts, because the samples of both colors were treated the same.

Montmorillonite minerals were identified by swelling along the *c* axis to approximately 17A upon solvating with ethylene glycol.

These criteria for clay mineral identification, using the 001 spacings, are in general use currently, although they are vulnerable to criticism (Weaver, 1953). The 060 peaks of clay minerals also were regularly checked. X-ray equipment used was a North American Philips unit at the University of Missouri. A wide-range Geiger-Muller goniometer and nickel-filtered copper Kα radiation were employed.

CLAY MINERALS IN REPRESENTATIVE SAMPLES OF MUDSTONE

Mineral analyses of representative mudstone samples have been organized in terms of stratigraphic sequence, productive (uranium-vanadium ore) and nonproductive localities, occurrence along faults, and a deposit where bleaching and alteration to alunite (the Oyler mine) has occurred. Many more mineral analyses were run than reported on herein, but these described will represent the data which have lead to the final conclusions.

CLAY MINERALS IN RED-GREEN MUDSTONE SAMPLES

A tabulated record of representative red and green stratigraphically equivalent samples of mudstones from red-bed ore-bearing formations on the Colorado Plateau is given in table 1.

Many samples were collected and analyzed from the Moenkopi formation of Triassic age, especially near its contact with the Shinarump member of the Chinle formation of Triassic age (or other overlying sandstone) primarily at mining localities from Monument Valley, Arizona, to the north end of the San Rafael Swell in Utah. Hydrous mica and muscovite characterize this zone in the Moenkopi, and kaolinite may, or may not, be present in it.

In figure 30 are shown X-ray diffractograms of stratigraphically equivalent green (No. 234) and red (No. 235) Moenkopi from a mineralized zone near the Oyler mine, Capitol Reef National Monument, Utah. Hydrous mica, muscovite, kaolinite, quartz, and probably calcite are represented in the diffractograms. No significant difference is found between the patterns of the clay minerals in the red and green counterparts.

The Shinarump member of the Chinle formation exposed on Dille Butte in the San Rafael Swell, which is the source of samples Nos. 519 and 520 described herein,

TABLE 1.—*Clay minerals in mudstone samples from selected formations*

Sample No.	Formation or member and locality	Color, red (R) or green (G)	Clay-size minerals
451 R	Rico formation, Hercules mine, Kane Springs district, Utah.	R	Hydrous mica, muscovite quartz, calcite, hematite.
451 G	Rico formation, Hercules mine, Kane Springs district, Utah.	G	Hydrous mica, muscovite, quartz, calcite.
270 R	Moenkopi formation, Capitol Reef Nat. Monument.	R	Kaolinite, hydrous mica, dolomite.
270 G	Moenkopi formation, Capitol Reef Nat. Monument.	G	Kaolinite, hydrous mica, dolomite.
519	Shinarump member of the Chinle formation, Dille Butte, N. end San Rafael Swell.	Purple	Kaolinite, hematite, quartz.
520	Shinarump member of the Chinle formation, Dille Butte, N. end San Rafael Swell.	White	Kaolinite, quartz.
273 R	Chinle formation, Pick's Delta mine, San Rafael Swell.	R	Hydrous mica, muscovite, kaolinite, quartz, hematite.
273 G	Chinle formation, Pick's Delta mine, San Rafael Swell.	G	Hydrous mica, muscovite, kaolinite, quartz.
15 R	Salt Wash member of Morrison formation, Uravan, Colo.	R	Hydrous mica, quartz.
15 G	Salt Wash member of Morrison formation, Uravan, Colo. See table 3, for other Salt Wash samples.	G	Hydrous mica, quartz.
5 R	Brushy Basin member of Morrison formation, Uravan, Colo.	R	Montmorillonite, hydrous mica (?).
6 G	Brushy Basin member of Morrison formation, Uravan, Colo.	G	Montmorillonite, hydrous mica (?).

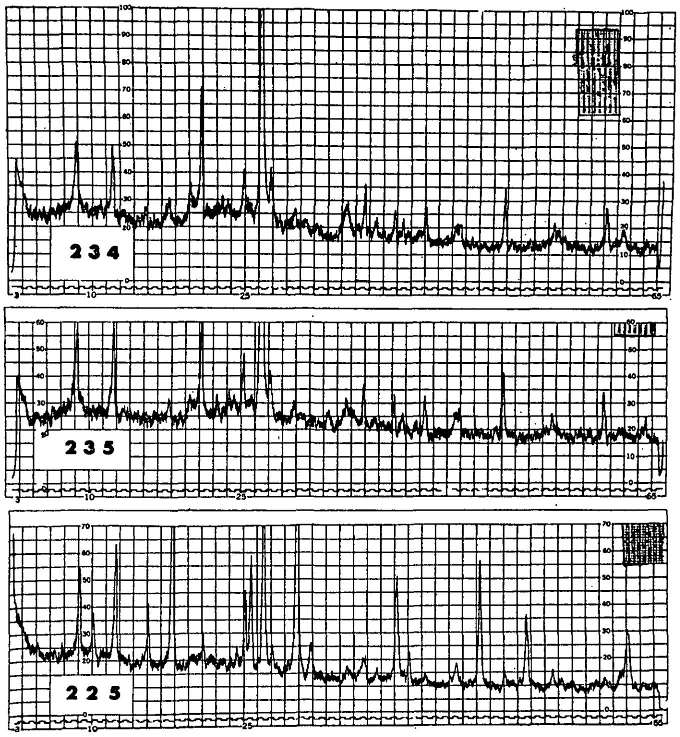

FIGURE 30.—X-ray powder diffractograms of red mudstone of the Moenkopi formation ,Triassic) (No. 235) collected about 600 feet west of the entrance to the Oyler mine in Capitol Reef National Monument, Utah, and a green counterpart (No. 234), stratigraphically equivalent 6 inches from sample 235. Diffractogram 225 is of an alunitized seam in bleached Moenkopi at what appears to be the same stratigraphic zone as that of samples 234 and 235.

exhibits a purple-white mudstone zone which is probably representative of other purple-white occurrences, presumably parallels in color relationship the red-green pairs of red beds.

The X-ray pattern (fig. 31) of the white Shinarump mudstone (No. 520) shows peaks of kaolinite and quartz while that of the purple counterpart (No. 519) shows hematite in addition to kaolinite and quartz. The hematite pattern of the purple sample is more nearly complete for hematite than are those of the hematite-red rocks of the red beds. The purple color (very dusky red purple 5RP 2/2; Goddard, and others, 1948) is reminiscent of certain specular hematite, but when the rock is finely pulverized for analysis it becomes red (pale reddish brown, 10R 5/4; Goddard and others, 1948) that is typical of red-bed sedimentary hematite. Because the X-ray patterns of the purple and white counterparts of the mudstone of the Shinarump member are practically superimposable, except for the additional hematite peaks in the purple sample, it is concluded that the clay mineral in the purple and white counterparts is the same.

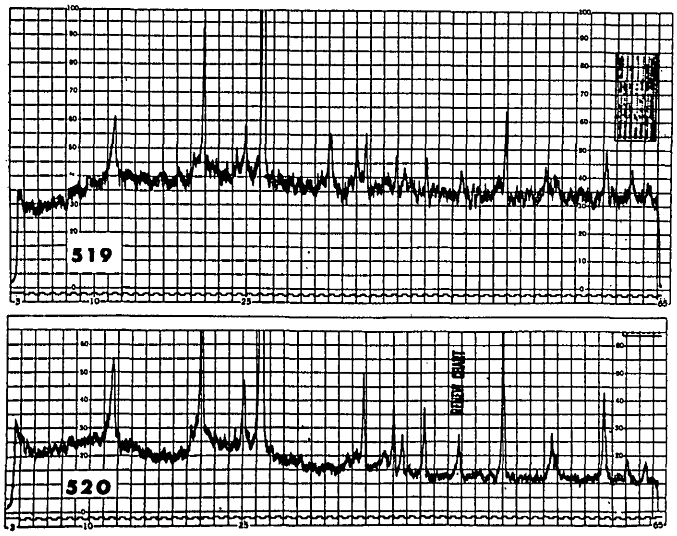

FIGURE 31.—X-ray powder diffractograms of purple (No. 519) and white (No. 520) Shinarump member of the Chinle formation (Triassic) from Dille Butte, north end of San Rafael Swell, Utah. North American Philips wide-range goniometer, Ni-filtered Cu-Kα radiation. Degrees 2θ are shown along base lines of diffractograms.

The mineral composition of No. 520 was computed from its chemical composition (table 2) to be approximately, as follows:

	Percent		*Percent*
Kaolinite	37	Hematite	10
Quartz	51	TiO_2 (rutile, anatase?)	2
			100

Extended studies with the microscope and differential thermal analysis of bulk and fine fractions of samples 519 and 520 support the clay-mineral analysis as given above.

The samples from the Chinle contained hydrous mica and kaolinite, except that tuffaceous portions of the Chinle contained montmorillonite. The Brushy Basin member of the Morrison formation of Jurassic age contains montmorillonitic zones (fig. 32), and zones in which hydrous mica is dominant. The diffractograms of the montmorillonite in the red (No. 5) and green (No. 6) counterparts of the Brushy Basin samples are as nearly alike as are duplicate runs of the same sample. It is concluded, therefore, that the gross clay mineralogy of the two samples is the same.

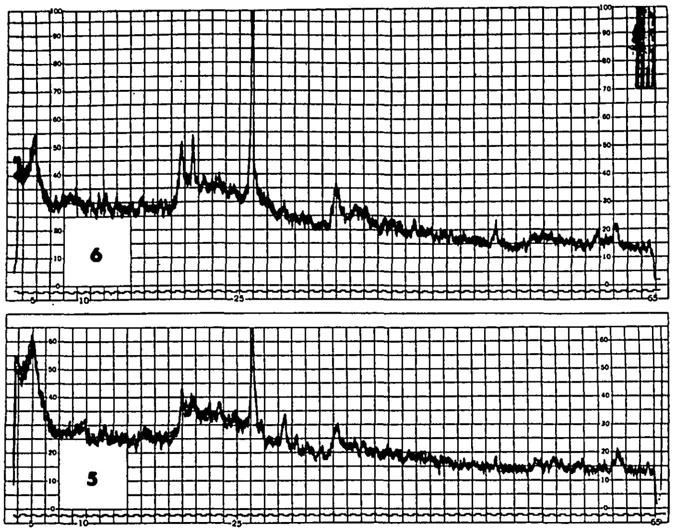

FIGURE 32.—X-ray powder diffractograms of green (No. 6) and red mudstone (No. 5) stratigraphically equivalent to the Brushy Basin member of the Morrison formation (Jurassic) from near Uravan, Colo.

The data in table 1 may be summarized in the following conclusions. No significant difference was found between the clay minerals in stratigraphically equivalent red and green counterparts of mudstones collected from

TABLE 2.—*Chemical composition of purple (no. 519) and white (no. 520) silty mudstones from Dille Butte, north end of San Rafael Swell, Utah*

[Analyst, Lois Trumbull, U. S. Geological Survey.]

	Sample 519	Sample 520
SiO_2	68.03	78.75
Al_2O_3	14.31	13.42
Fe_2O_3	10.29	1.14
FeO	.10	.04
MgO	.04	.05
CaO	.06	.05
Na_2O	.06	.01
K_2O	.16	.15
H_2O-	.55	.44
H_2O+	5.09	4.62
TiO_2	1.06	1.03
CO_2	.02	.02
P_2O_5	.04	.03
MnO	.01	.00
	99.82	99.75

the Rico, Cutler, Moenkopi, and Chinle formations, and the Salt Wash and Brushy Basin members of the Morrison formation, or within clay mineral groups including the kaolin group, the hydrous micas, the montmorillonites, and probably chlorite. The red color of mudstone red beds disappears with removal or absence of the ferric oxide; it need not, and ordinarily does not involve a change in the clay minerals.

CLAY MINERALS IN THE SALT WASH MEMBER OF THE MORRISON FORMATION FROM PRODUCTIVE AND BARREN LOCALITIES

Mudstone samples from the Salt Wash member of the Morrison formation were collected to study the following relationships of clay minerals to ore mineralization: productive mudstone, which was enriched with uranium-vanadium minerals of ore grade, taken from generally favorable districts (Club group, Uravan, Colo.; Lower group, Slick Rock, Colo.); nonproductive mudstone from generally favorable districts (Uravan, Slick Rock, and Long Park, Colo.); productive mudstone from a less favorable to generally unfavorable district (Yellow Cat, Utah); and nonproductive mudstone from a generally unfavorable district (Salt Wash member type section, Emery Co., Utah). Red and green counterparts were collected from the nonproductive localities, but the productive mudstone was found in only green or gray colors. The results of the clay mineral analyses are shown in table 3.

TABLE 3.—*Clay minerals in selected productive and nonproductive samples of the Salt Wash member of the Morrison formation from the Colorado Plateau*

Sample No.	Locality	Productive clay	Nonproductive clay	Favorable district	Unfavorable district	Red	Green or gray	Clay minerals
10	Club group Uravan, Colo	X		X			X	Hydrous mica, kaolinite.
15R	Club group, Uravan, Colo		X	X		X		Hydrous mica.
15G	Club group, Uravan, Colo		X	X			X	Hydrous mica.
25	Lower group, Slick Rock, Colo	X		X			X	Hydrous mica, kaolinite, chlorite.
28G	Lower group, Slick Rock, Colo		X	X			X	Hydrous mica.
29R	Lower group, Slick Rock, Colo		X	X		X		Hydrous mica.
LP-954G	Long Park, Colo		X	X			X	Hydrous mica.
LP-954R	Long Park, Colo		X	X		X		Hydrous mica, unidentified.
47	Yellow Cat, Utah	X			X		X	Hydrous mica, chlorite(?).
52R	Salt Wash member type section, Emery County, Utah.		X		X	X		Hydrous mica.
53G	Salt Wash member type section, Emery Country, Utah.		X		X		X	Hydrous mica.
54R	Salt Wash member type section, Emery County, Utah.		X		X	X		Hydrous mica.
55G	Salt Wash member type section, Emery County, Utah.		X		X		X	Hydrous mica.

It is concluded from this study that the clay minerals are not significantly different between the productive and nonproductive mudstones, with one possible reservation. Productive mudstones are usually more likely to contain kaolinite and (or) chlorite(?) in addition to hydrous mica, than are nonproductive mudstone. It is doubted, however, that kaolinite per se, is responsible for deposition of ore minerals, because the same kaolinite-containing beds elsewhere along the strike may be nonproductive. It appears, therefore, that kaolinite-containing mudstones represent a set of physical, chemical, or stratigraphic environments which are more likely to favor deposition of uranium-vanadium ore minerals than those in which hydrous mica alone, of the clay minerals, was deposited.

No significant difference was noted between the clay minerals in green and red mudstone counterparts examined in the foregoing study. Hydrous mica is the common clay mineral in the Salt Wash member, as was found also by Weeks (1953).

RED-GREEN MUDSTONE ALONG FAULTS

Mudstone samples were collected from red-green counterparts along faults in the Kane Springs district, Utah, in the Cutler formation of Pennsylvanian and Permian(?) age (Atomic King No. 2 mine), the Rico formation of Permian age (Hercules mine), and the Moenkopi formation of Triassic age (supplied by Otis McRae); the faults are now mineralized by oxidized-type minerals. The green zone along the fault plane ranges from a few inches to 2 feet wide on each side. Clay mineral identifications are shown in table 4.

No significant differences were noted between the clay minerals in bleached mineralized zones along the fault planes, in their red counterparts, and in control samples collected nearby from barren rocks in the same stratigraphic beds as those containing ore minerals. From this lack of difference it is inferred that solutions which carried oxidized-type minerals did not necessarily bleach the red beds, and that they did not necessarily modify the gross clay mineralogy of the mudstones.

It is possible, however, for solutions to react with and modify clay minerals in association with uranium-vanadium ore deposits.

TABLE 4.—*Clay minerals in mudstone samples from mineralized faults and nearby barren rocks in the Kane Springs district, Utah*

Sample No.	Locality	Red	Green or gray	Clay-size minerals
448 G	Hercules mine, fault in Rico formation mineralized.		X	Hydrous mica, muscovite, quartz, calcite, dolomite.
449 R	Counterpart of 448 G	X		Hydrous mica, muscovite, quartz.
451 G	Barren, control sample for 448 G.		X	Hydrous mica, muscovite, quartz, calcite.
451 R	Counterpart of 451 G	X		Hydrous mica, muscovite, quartz, calcite, hematite.
447	Atomic King No. 2 mine, fault in Cutler formation, mineralized.		X	Mixed layer hydrous mica and montmorillonite.
446	Control sample for 447, collected 60 feet away.		X	Mixed layer hydrous mica and montmorillonite.
530-4	Altered, mineralized Moenkopi along fault.		X	Hydrous mica, kaolinite quartz.
530-1	Unaltered Moenkopi, 1 foot from altered zone (No. 530-4).	X		Hydrous mica, kaolinite quartz.

ALUNITIZATION AT THE OYLER MINE, CAPITOL REEF NATIONAL MONUMENT

A sequence of four samples of mudstone of the Moenkopi formation collected at the Oyler mine in Capitol Reef National Monument, Utah, illustrate the effect of sulfate reaction on the clay and carbonate minerals in the mudstone (table 5). Red, barren Moenkopi (No. 235) occurring 600 feet west of the mine, contains hydrous mica, muscovite, kaolinite, quartz, calcite, and hematite. The same stratigraphic zone at the entrance to the mine is bleached of iron oxide but contains gypsum. A mineralized seam in the mine contains alunite and metatorbernite (fig. 1, diffractogram 225). The metatorbernite peak is marked "Me."

It is inferred from this sequence that sulfate-bearing solutions, probably acidic, at the Oyler mine locality reacted with the ferric oxide in the red mudstone of the Moenkopi formation to bleach the pigment. Jarosite has been found at the mine and it is probable that the iron was moved, and partially removed, as iron sulfate. The sulfate reaction converted the calcite (and dolomite?) to gypsum. Further reaction of sulfate with aluminous clay minerals resulted in the development of alunite.

TABLE 5.—*Samples collected at the Oyler mine, Capitol Reef National Monument, Utah*

Sample No.	Description	Minerals present
225	White clay filling seams in bleached mudstone, Oyler mine entrance.	Kaolinite, hydrous mica, quartz, alunite, metatorbernite.
227	Bluish laminated mudstone, contains metatorbernite, Oyler mine entrance.	Kaolinite, hydrous mica, quartz.
229	Bleached Moenkopi, contains ore minerals, Oyler mine entrance.	Kaolinite, hydrous mica, quartz, dolomite, gypsum.
235	Red Moenkopi, 600 feet west of Oyler mine entrance. Essentially equivalent stratigraphically to above samples, as nearly as can be observed.	Hydrous mica, muscovite, kaolinite, quartz, calcite, hematite.

The presence of metatorbernite in the bleached portion of the Moenkopi and in the alunite-rich seams may be interpreted as follows: (1) that the sulfate solutions also carried in the metatorbernite, or alternatively, that (2) metatorbernite-bearing solutions followed the same avenues previously traversed by sulfate solutions. Spatial association of the minerals is permissive toward the first alternative, but the writer has not found compelling evidence that alunite and metatorbernite were genetically associated. It is difficult to find unequivocal evidence of effects from the solutions which carried the ore minerals apart from the ore minerals themselves.

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Part 10. CHEMICAL STUDY OF THE MINERALIZED CLAYS

By Margaret D. Foster

CONTENTS

ILLUSTRATIONS

TABLES

ABSTRACT

In the vanadium-bearing sandstones on the Colorado Plateau the principal vanadium mineral is a clay, which coats and replaces sand grains and partly or completely fills the pore spaces of the sandstone and imparts a dark color to it, the depth of color being deeper the greater the vanadium content.

Of the eight samples used in studying the composition and character of the mineralized clays and their relation to the unmineralized clays, three were mineralized clay pellets, two pairs were clay fractions from adjacent mineralized and unmineralized (dark and light) zones in sandstone, and one was an unmineralized clay fraction from a light-colored zone in sandstone. All were from the Salt Wash member of the Morrison formation.

Chemical analyses show that the samples are similar in composition except for vanadium content, and that increase in vanadium content is accompanied by decrease in alumina and silica content, the content of the other constituents remaining relatively constant throughout. In composition the samples are similar to hydrous micas, but X-ray diffraction studies show that they are mixtures principally of mica and interlayered mica-montmorillonite, with usually a small amount of chlorite and quartz. Vanadium is present in all the phases making up the clays, except quartz, as is shown by differential solution studies.

The samples differ in degree of oxidation. In the least oxidized sample some vanadium is present in the trivalent state, and all the iron is present as divalent iron; in the most highly oxidized sample there is some free V_2O_5 and all the iron is trivalent. In the other six samples all vanadium is present as V_2O_4 and the iron is present in different proportions as ferrous and ferric.

Structural formulas derived from the analyses show that seven of the samples form a suite in which the sum of the octa-

hedral positions occupied by Al and V^{+4} and the sum of the positions occupied by Fe and Mg are remarkably constant. Increase in the number of positions occupied by V is accompanied by decrease in Al positions, the number of positions occupied by Fe and Mg remaining constant throughout. As substitution of V^{+4} for Al^{+3} decreases the negative charge on the octahedral layer, increase in V^{+4} content and consequent decrease in octahedral charge is accompanied by increase in tetrahedral charge; the total charge and the potassium content remain fairly constant.

The chemical and mineralogical similarity of the mineralized and unmineralized clays suggest that the unmineralized clays became mineralized simply by the replacement of some of the octahedral aluminum by quadrivalent vanadium, with the necessary charge adjustments in the tetrahedral layer. However, other deposits are known where the vanadium clay was deposited by the mineralizing solutions.

INTRODUCTION

Deposits of vanadium-bearing sandstone, widely distributed on the Colorado Plateau, have been the principal domestic source of vanadium and uranium. As described by Fischer (p. 377, 1942), the ore occurs mainly as an impregnation of the sandstone, coating and replacing the sand grains and partly or completely filling the pore spaces of the sandstone. The principal vanadium mineral is micaceous and was thought to be roscoelite until X-ray studies by S. B. Hendricks (as cited by Fischer, 1942) showed that in some formations—as in the Morrison of Jurassic age—the principal vanadium mineral is a clay mineral of the hydrous mica group. The mineral imparts a dark color to the sandstone, the depth of color being greater the higher the vanadium content. Richly mineralized clay pellets, which occur in some places, are black and brittle.

This study of the vanadium-bearing clays was undertaken to determine whether vanadium is present as a superficial impregnation of the clay or whether it is in the clay structure, and if so, its position and valence.

COMPOSITION AND CHARACTER OF THE VANADIFEROUS CLAYS

CHEMICAL ANALYSES

Of the suite of eight samples used in this study, three (AW-22-52, AW-144-52, and AW-146-52) are clay pellets collected by A. D. Weeks, and five are clays separated from sandstone collected by Robert M. Garrels. Samples G-43M-53 and G-43UM-53, and G-29M-53 and G-29UM-53, are paired samples representing mineralized and relatively unmineralized clay from dark and light colored zones in the same specimen. Sample G-27UM-53 is a relatively unmineralized clay from a light colored zone in sandstone. The suite of samples studied, therefore, includes five mineralized and three relatively unmineralized samples. The three latter were included in order to study the differences in composition brought about in the clay by mineralization. For this purpose the two pairs of samples, G-43UM-53 and G-43M-53, and G-29UM-53 and G-29M-53, are of particular interest. All samples are from the Salt Wash member of the Morrison formation of Jurassic age. Chemical analyses of these samples, together with their locality, are given in table 1. The chemical analyses were made by the writer according to the usual methods of rock analysis as described by Hillebrand and Lundell (1929) except for sodium and potassium, which were determined with the flame photometer by Paul Elmore, of the U. S. Geological Survey, and vanadium. In this study the state or states of valence in which vanadium is present was of especial interest. For this determination, the following procedure was used:

TABLE 1.—*Unadjusted chemical analyses of vanadium clays*

[M. D. Foster, analyst. K_2O and Na_2O determined by Paul Elmore by flame photometer]

	G-27UM-53	G-43UM-53	G-29UM-53	G-29M-53	G-43M-53	AW-146-52	AW-22-52	AW-144-52
SiO_2	52.78	52.22	53.36	50.24	47.32	48.10	45.46	43.68
Al_2O_3	20.48	20.96	20.44	17.38	19.36	17.62	16.02	15.32
Fe_2O_3	2.06	1.19	1.90	.00	.00	2.61	2.93	7.70
FeO	2.32	2.56	1.85	3.58	3.49	1.03	2.00	.00
V_2O_5	.00	.00	.00	.00	.00	.00	.00	2.39
V_2O_4	.75	1.02	1.16	8.38	7.60	12.36	16.07	10.55
V_2O_3	.00	.00	.00	.00	1.34	.00	.00	.00
TiO_2	.90	.92	.82	.46	.52	.52	.64	.32
CaO	.62	.48	.64	.48	.62	.74	.62	1.60
MgO	4.61	4.00	4.47	4.43	5.01	4.09	2.13	3.75
Na_2O	.31	.23	.25	.27	.23	.30	.24	.30
K_2O	6.30	6.18	5.94	5.86	5.40	4.96	6.58	4.67
MnO	.03	.02	.02	------	.02	.01	.02	.05
H_2O	8.43	9.86	8.92	9.12	9.14	7.92	8.00	9.96
Total	99.59	99.64	99.77	100.20	100.05	100.26	100.71	100.29

G-27UM-53. Mineral Joe Mine, Jo Dandy group, Paradox Valley, Montrose Co., Colorado.

G-29UM-53, G-29M-53. Mineral Joe Mine, Jo Dandy group, Paradox Valley, Montrose Co., Colorado.

G-43UM-53, G-43M-53. Virgin Mine, Long Park area, Montrose Co., Colorado.

AW-146-52. Cougar Mine, Slick Rock, San Miguel Co., Colorado.

AW-144-52. Sunnyside Mine, east side of Carrizo Mountains, San Juan Co., New Mexico.

AW-22-52. Little Peter Claim, La Sal Creek, San Juan Co., Utah.

15 ml of 1–2 H_2SO_4 was added to 0.50 g of the sample in a 50-ml Erlenmeyer flask, the air in the flask was then displaced with CO_2 and the flask was stoppered. This mixture was digested on a steam bath (at about 95° C) for a week or ten days—that is, until the clay appeared to have been decomposed and all the Fe and V extracted. After transferring the mixture to a 500-ml Erlenmeyer flask, it was diluted to 250 ml with distilled water, heated to 80° C, and titrated to the first permanent pink with 0.05 $KMnO_4$ solution. The mixture was then filtered to remove the undissolved residue (quartz and silica released from the clay on decomposition). A second 500-ml Erlenmeyer flask containing the filtrate was placed on an electric radiator and SO_2 gas was passed through the solution for 10 minutes. Still keeping the solution hot, a rapid stream of CO_2 was passed through the solution until it was free of SO_2, as tested by bubbling the exit gases from the flask through a hot, very dilute solution of $KMnO_4$. Lack of fading of the permanganate indicates the absence of SO_2. When the solution was free of SO_2 and had cooled to about 80° C it was again titrated to a pink end-point with $KMnO_4$. The amount of iron in solution was then determined. From the relationships between the first and second titrations and the $KMnO_4$ equivalent of the iron present, the amounts of V_2O_3, V_2O_4, V_2O_5, FeO, and Fe_2O_3 can be calculated as follows:

1. If the second titration is the same as the first titration, all the vanadium was originally present in the solution as V(IV) and all the iron as Fe(II). The $KMnO_4$ equivalent of the iron present is subtracted from the first titration (or second titration, as they are the same) to obtain the $KMnO_4$ equivalent of the V(IV) present.

Example:

	1st titration (ml)	*2d titration (ml)*	*Iron titration (ml)*
$KMnO_4$ used	13.10	13.10	6.35
Blank	.10	.10	.10
Reduced by SO_2	--------	13.00	--------
Originally reduced	13.00 →	13.00	
FeO	6.25 ←		6.25
Originally oxidized	--------	.00	--------
V_2O_4	6.75	--------	--------

NOTE.—No V_2O_3 or Fe_2O_3 because 1st titration equals 2d titration.

2. If the 2d titration is greater than the 1st titration some or all of the Fe and V were present in the original solution as Fe (III) and V (V) depending on the relations between the 1st, 2d, and iron titrations.

Example 1:

	1st titration (ml)	*2d titration (ml)*	*Iron titration (ml)*
$KMnO_4$ used	6.20	12.50	3.45
Blank	.10	.10	.10
Reduced by SO_2	--------	12.40	--------
Originally reduced (=V_2O_4)	6.10 →	6.10	
Originally oxidized (=Fe_2O_3+V_2O_5)	--------	6.30	--------
Total iron (=Fe_2O_3)	--------	3.35 ←	3.35
V_2O_5	--------	2.95	--------

NOTE.—No FeO or V_2O_3 because V_2O_5 is present.

Example 2:

	1st titration (ml)	*2d titration (ml)*	*Iron titration (ml)*
$KMnO_4$ used	8.20	9.85	2.35
Blank	.10	.10	.10
Reduced by SO_2	--------	9.75	--------
Originally reduced	8.10 →	8.10	
Total iron	--------	--------	2.25
Originally oxidized (=Fe_2O_3)	--------	1.65 →	1.65
FeO	.60 ←		.60
V_2O_4	7.50	--------	--------

NOTE.—No V_2O_5 because FeO is present; no V_2O_3 because 2d titration is larger than 1st titration.

Example 3:

	1st titration (ml)	*2d titration (ml)*	*Iron titration (ml)*
$KMnO_4$ used	0.10	8.30	3.80
Blank	.10	.10	.10
Originally oxidized	--------	8.20	--------
Originally reduced	.00 →	.00	
Fe_2O_3+V_2O_5	--------	8.20	--------
Total iron (=Fe_2O_3)	--------	3.70 ←	3.70
V_2O_5	--------	4.50	--------

NOTE.—No FeO, V_2O_4, or V_2O_3 because 1st titration is zero.

3. If the 2d titration is less than the 1st titration some or all of the V was originally present as V (III); if only part of the V was present as V (III), the rest was present as V (IV). Either way, all the Fe was present originally as Fe (II). In the 1st titration, therefore, some or all of the V had to be oxidized from V (III) to V (IV) to V (V), resulting in a higher 1st than 2d titration.

Example:

	1st titration (ml)	*2d titration (ml)*	*Iron titration (ml)*
$KMnO_4$ used	17.70	15.90	4.40
Blank	.10	.10	.10
Originally reduced	17.60	--------	--------
Reduced by SO_2	15.80 ←	15.80	
V_2O_3	1.80 →	1.80	
V_2O_4+FeO	--------	14.00	--------
Total iron (=FeO)	--------	4.30 ←	4.30
V_2O_4	--------	9.70	--------

NOTE.—No V_2O_5 or Fe_2O_3 because 1st titration exceeds 2d titration.

X-ray powder patterns by F. A. Hildebrand, of the U. S. Geological Survey, showed that all the samples contained quartz. It was also possible that part of the

Al_2O_3, Fe_2O_3, V_2O_4, and V_2O_5 found on analysis was not in the clay structure. Consequently to determine as nearly as possible the composition of the clay itself, it was necessary, in addition to the usual chemical analysis, to make use of several special tests. The amount of quartz present was determined by digesting the residue from the vanadium-iron acid extraction with 0.5*N* NaOH, which dissolves silica freshly released by the decomposition of the clay but leaves the quartz present untouched. Soluble silica and alumina were determined by digestion with NaOH, as described by Foster (1953, p. 151), using a separate portion of each sample. V_2O_4, V_2O_5, FeO, and Fe_2O_3 not in the clay structure were determined by digesting another portion of each sample in 1–2 H_2SO_4 (1 part of H_2SO_4 to 2 parts of distilled water) for 1 hour at room temperature, filtering, and determining the amounts of these constituents that had gone into solution in that time. Preliminary studies had shown that the clay materials making up these samples are very stable under acid treatment and that in a 1-hour digestion period there is little or no attack on the clay structure, whereas the vanadium and iron compounds present but not in the clay structure are dissolved. This treatment also effects solution of any "free" alumina present, providing a check on "free" alumina determined by digestion with NaOH.

All the samples were found to contain some quartz, "free" alumina, "free" iron oxide, and vanadium oxide, either V_2O_4 or V_2O_5, that apparently did not belong in the clay structure. However, it is of particular interest in this study that the amount of "free" vanadium oxide present, especially in the mineralized clays, was small in comparison with the amount that seemed to belong in the clay structure.

Adjusted analyses of the clays, after making allowances for quartz, and for aluminum, vanadium, and iron compounds not in the clay structure, are shown in table 2. TiO_2 was also deducted in adjusting the analyses as X-ray studies indicated TiO_2 to be present as anatase.

It should be pointed out that the procedure used for determining the valence states of vanadium and iron apply rigorously only to the valence states of the ions present in solution, and not in the original clay minerals. At the low pH used, vanadium (V) will be reduced to vanadium (IV) by any ferrous iron going into solution, and the iron thus oxidizing to ferric. However, inspection of table 2 indicates that the analyses must approximate closely the composition of the clays. Sample G–27UM–53 contains very little vanadium, but contains a significant amount of ferric iron. Thus ferric iron must be present in the clay. Similarly, samples G–29M–53 and G–43M–53 contain no ferric iron but abundant vanadium (IV); thus neither ferric iron nor vanadium (V) were present in the clay and the analysis must be correct as stated. In the other samples, no large deviations from the reported values seem likely.

TABLE 2.—*Adjusted chemical analyses of vanadium clays*

[M. D. Foster, analyst. K_2O and Na_2O determined by Paul Elmore]

	G–27UM–53	G–43UM–53	G–29UM–53	G–29M–53	G–43M–53	AW–146–52	AW–22–52	AW–144–52
SiO_2	53.26	52.36	52.46	49.12	46.94	47.39	44.87	45.86
Al_2O_3	20.74	21.40	21.15	17.62	19.84	18.51	16.84	15.40
Fe_2O_3	2.12	1.23	1.95	.00	.00	2.41	2.65	5.80
FeO	1.76	2.04	1.95	3.54	3.23	.91	1.10	.00
V_2O_4	.51	1.06	.99	8.52	7.36	11.73	16.03	10.15
V_2O_5	.00	.00	.00	.00	1.40	.00	.00	.00
CaO	.65	.50	.67	.50	.67	.79	.68	1.36
MgO	4.82	4.15	4.71	4.66	5.23	4.38	2.33	4.35
Na_2O	.32	.24	.26	.28	.24	.32	.27	.35
K_2O	6.59	6.42	6.25	6.16	5.63	5.32	7.19	5.42
H_2O	8.82	10.24	9.39	9.59	9.54	8.49	8.74	11.56
Total	99.59	99.64	99.78	99.99	100.08	100.25	100.70	100.25

COMPARATIVE COMPOSITION OF MINERALIZED AND UNMINERALIZED CLAYS

The principal differences in the chemical composition of the clays studied are in their content of SiO_2, Al_2O_3, and V_2O_4. Their content of all other constituents is remarkably uniform. The three (relatively) unmineralized clays (G–27UM–53, G–29UM–53, and G–43UM–53) have essentially the same content of SiO_2 (52.37 to 53.26 percent) and of Al_2O_3 (20.74 to 21.41 percent). In the mineralized clays greater V_2O_4 content is accompanied by lower SiO_2 and Al_2O_3 content, as shown in figure 33. Comparison of the adjusted analyses for G–29UM–53 and G–29M–53 (table 2), which represent light and dark layers of the same specimen, shows that an increase of 7.53 percent in V_2O_4 content is accompanied by a decrease of 3.31 percent in SiO_2 content and 3.54 percent in Al_2O_3 content; the content of all other constituents remains essentially the same. In terms of molecular ratios this amounts to a loss of 0.43 in SiO_2 plus Al_2O_3 and a gain of 0.36 in V_2O_4. The fact that

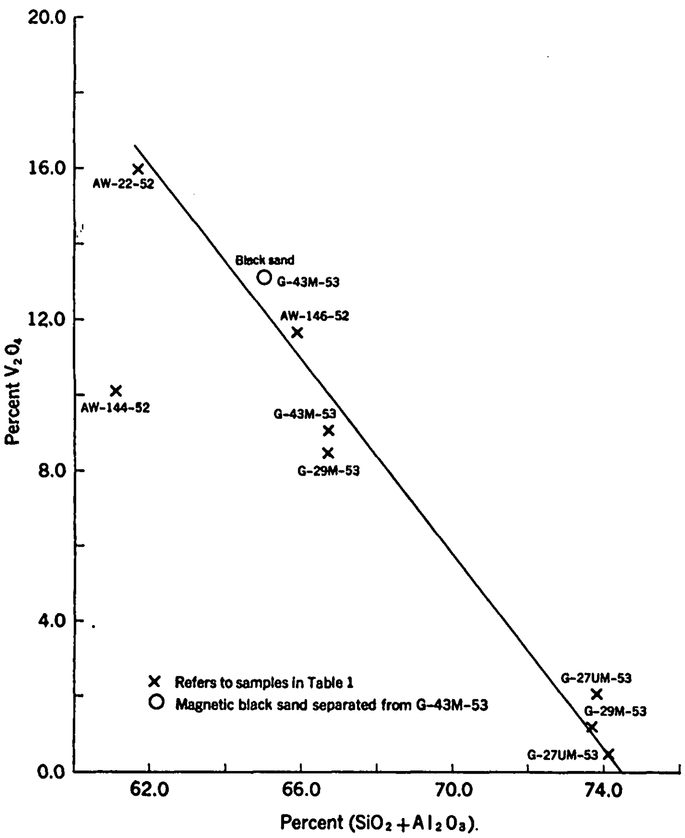

FIGURE 83.—Relation between V_2O_4 and (SiO_2 plus Al_2O_3) in mineralized and unmineralized clays.

increase in V_2O_4 content is accompanied by a proportionate decrease in the content of these two constituents only, without altering the content of any of the other constituents, suggests that V_2O_4 has not simply impregnated the clay as such, but that it is actually a part of the clay structure; thus V^{+4} affects both Si and Al but not other cations in the structure.

MINOR ELEMENTS

Quantitative spectrographic analyses for minor elements in these clays, by K. J. Murata, of the U. S. Geological Survey, are given in table 3. The most important of the minor elements are uranium and lead. Two of the unmineralized samples, G-27UM-53 and G-29UM-53, and one mineralized sample, AW-146-52, contained no uranium. All the other samples contained from 0.1 to 0.2 percent of uranium except for AW-144-52, which contained 0.6 percent. All of the samples contained lead, the amount present ranging from 0.06 to 0.3 percent, but there was no correlation between the amount of lead and the amount of uranium present—nor was there any correlation between the amount of vanadium and the amount of uranium or lead present. Other minor elements are present in the low hundredths or thousandths of a percent except for 0.1 percent of Ba in G-43UM-53 and AW-144-52, and 0.1 percent of Zr in the latter sample.

TABLE 3.—*Quantitative spectrographic analyses of vanadium clays for minor elements*

[K. J. Murata, analyst. Looked for but not found: Au, Pd, Pt, W, Ge, As, Sb, Bi, Cd, Tl, In, Th, Nb, P]

	G-27UM-53	G-43UM-53	G-29UM-53	G-29M-53	G-43M-53	AW-144-52	AW-146-52	AW-22-52
Cu	0.003	0.002	0.005	0.005	0.003	0.009	0.2	0.06
Ag	.0004	0	0	0	.0004	0	.0005	.004
Mo	0	0	0	0	0	.003	0	0
Sn	0	0	0	0	0	0	0	0
Pb	.06	.07	.1	.08	.08	.2	.06	.3
Zn	0	0	0	0	0	0	0	.04
Co	.002	.005	.004	.008	.005	.002	.001	.01
Ni	.003	.002	.003	.005	.004	.002	.003	.005
Cr	.005	.01	.007	.004	.007	.005	.01	.006
Sc	.004	.002	.003	.001	.001	.001	.002	.001
Y	0	0	0	.009	.008	0	.008	0
La	0	.01	0	0	0	0	0	0
Zr	.03	.02	.03	.02	.01	.01	.01	.009
U	0	.1	0	.1	.2	.6	0	.2
Be	.0005	.0004	.0005	.0005	.0004	.0003	.0004	.0005
Sr	.02	.03	.04	.02	.01	.1	.01	.05
Ba	.009	.1	.02	.01	.01	.1	.02	.07
B	.009	.008	.007	.005	.004	.002	.003	.004

STAGES OF OXIDATION

At the time of analysis all vanadium in the structure of the clays was present as V_2O_4, except for 1.40 percent of V_2O_3 in G-43M-52. All the samples had had opportunity for oxidation, as they had been collected from mine walls, and had been exposed to the air. In many mines the assemblage of minerals indicates that oxidation had taken place before the mine was opened. If all vanadium had been originally present as V^{+3}, all iron must have been present as Fe^{+2}. The first step in the oxidation of such a mixture is oxidation of V^{+3} to V^{+4}. The V^{+3}–V^{+4}–Fe^{+2} relationship of G-43M-52 and of G-29M-52 indicates that, if all the vanadium had once been present as V^{+3}, the former is now near the end of this stage of oxidation and the latter has completed it but has not yet progressed to the second stage of oxidation of Fe^{+2} to Fe^{+3}. All the other samples, except for AW-144-52, are in this second stage of oxidation. AW-22-52, in which two-thirds of the iron is present as Fe^{+2}, has progressed least in this stage and

AW-146-52, in which two-thirds of the iron is present as Fe^{+3}, has progressed farthest. The Fe^{+2}–Fe^{+3} relationship of the three (relatively) unmineralized samples falls between these two samples in degree of oxidation. In AW-144-52 all the iron is present as Fe^{+3}. The final stage in the oxidation process is oxidation of V^{+4} to V^{+5}. The presence of 2.39 percent of free V_2O_5 in AW-144-52 (table 1) may indicate that some of the vanadium originally in this clay has been oxidized to the pentavalent stage and has been ejected from the structure because V^{+5} does not take octahedral coordination.

X-RAY DIFFRACTION STUDIES

X-ray diffraction studies of the suite of vanadium clays under consideration were made by John Hathaway, of the U. S. Geological Survey, and his methods and data are presented in Part 11. Part of his data are summarized here.

All the samples gave diffraction patterns showing lines in the 10A region that broaden and shift on treatment with ethylene glycol and shift again on heating to 500° C. This is interpreted as an indication of the presence of montmorillonitic layers randomly interstratified with mica layers.

All the samples except AW-22-52 contain chlorite in various amounts with some mixed-layered chlorite-montmorillonite exhibited by sample G-29UM-53. The fine-grained material in these samples contains less chlorite than the coarser material.

The composition of each sample is tabulated below with quantitative estimates given as parts in ten. Inasmuch as these estimates are derived from the intensities of the diffracted lines and many factors in addition to quantity of a mineral affect diffraction intensity, these estimates are not intended to give more than a general indication of the relative amounts of the various minerals present.

Field No.	Minerals present	Quantitative estimates (parts in 10)
AW-146-52	Mica and mixed-layered mica-montmorillonite	9
	Chlorite	Tr.
	Quartz	Tr.
AW-144-52	Mica and mixed-layered mica-montmorillonite	8
	Metatyuyamunite	1
	Quartz	Tr.
AW-22-52	Mica and mixed-layered mica-montmorillonite	9
	Quartz	Tr.
G-27UM-53	Mica and mixed-layered mica-montmorillonite	9
	Chlorite (possibly mixed-layered)	<1
G-29UM-53	Mica and mixed-layered mica-montmorillonite	8
	Mixed-layered chlorite-montmorillonite	1
	Quartz	<1
G-29M-53	Mica and mixed-layered mica-montmorillonite	8
	Chlorite	2
	Quartz	Tr.
G-43UM-53	Mica and mixed-layered mica-montmorillonite	9
	Chlorite	Tr.
G-43M-53	Mica and mixed-layered mica-montmorillonite	6
	Chlorite	3

NOTE.—The above samples might be grouped as follows:

1. Mica ——→ Increasing mixed-layering
AW-22-52
G-43M-53
G-43UM-53
G-29M-53
G-29UM-53
G-27UM-53
AW-146-52
AW-144-52

2. Mica ——→ Increasing chlorite content
AW-144-52
AW-22-52
G-43UM-53
G-27UM-53
AW-146-52
G-29UM-53
G-29M-53
G-43M-53

Chlorite decomposition temperature (loss of 14A line):

Below 500° C	*Above 500° C*
	G-27UM-53 coarse
	G-27UM-53 fine
G-29UM-53 fine	G-29UM-53 coarse
G-29M-53 fine	G-29M-53 coarse
G-43UM-53 coarse	
G-43UM-53 fine	
G-43M-53 fine	G-43M-53 coarse
	AW-146-52 (whole sample)

All of the samples except AW-22-52 showed approximately the same intensity relationships among the 001 reflections with a 002 reflection of greater intensity than that exhibited by roscoelite. This suggests a lesser degree of substitution in these samples of V for Al than that encountered in roscoelite. Sample AW-22-52 on the other hand shows a very weak 002 reflection suggesting that this material approaches roscoelite in octahedral composition.

DIFFERENTIAL-SOLUTION ANALYSIS

OCTAHEDRAL-TETRAHEDRAL ION DIFFERENTIATION

In the foregoing discussion it has been assumed that V^{+4} proxies for octahedral aluminum in the mineralized clays. In order to determine definitely the position of vanadium in these clays a modification of Brindley's (1951) procedure for determining tetrahedral and octahedral aluminum in silicates was used. Separate 0.50 gram samples of a given clay were digested in 1-2 H_2SO_4 on a magnetic stirrer for different periods of time at room temperature; the residue was then filtered off and the solution was analyzed for Al_2O_3, MgO, vanadium oxides, and iron oxides. For each specimen a few widely separated time runs were first made; additional runs were then made to establish critical points in the curve more definitely. The amount (in percent) of Al_2O_3, V_2O_4, Fe_2O_3, and MgO extracted from AW-144-52 plotted against time is shown in figure 34. The curve for V_2O_4 has the same shape as those for Fe_2O_3 and MgO, known to be octahedral constituents. Like the curves for these constituents, the V_2O_4 curve flattens after 20 hours of acid treatment, when extraction of

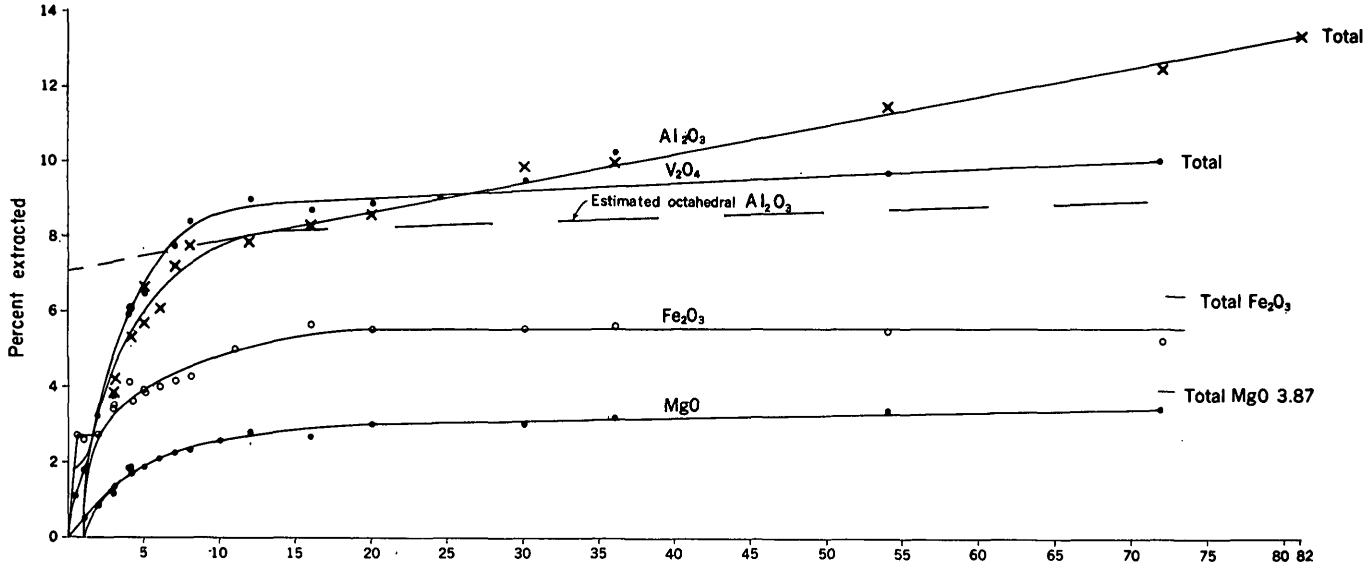

FIGURE 34.—Differential-solution analysis of AW–144–52.

octahedral ions is essentially complete. The similarity between the Fe_2O_3, MgO, and V_2O_4 curves suggests very strongly that V_2O_4 is, like Fe_2O_3 and MgO, an octahedral constituent.

For as long as 20 hours of treatment the Al_2O_3 curve has the same shape as the other curves, but instead of flattening out at this point, it swings upward. Complete extraction of Al_2O_3 required 62 more hours of treatment. The shape of the curve suggests that octahedral Al_2O_3 is extracted first, with the other octahedral constituents, and that only when extraction of octahedral constituents is complete, or nearly so, does extraction of tetrahedral constituents begin. This stepwise extraction permits differentiation of octahedral and tetrahedral ions, particularly of Al_2O_3, as well as that of "free" constituents—such as Fe_2O_3 and Al_2O_3—that are not in the clay structure and that dissolve very quickly compared with ions that are in the clay or mica structure.

AW–144–52 broke down much more rapidly on acid treatment than any of the other clays in this study. That it is also the most highly oxidized and that its formula is deficient in octahedral positions occupied (see table 4) all suggest that the structure is under considerable strain and may be to some extent disorganized.

FORMULAS AND THEIR INTERPRETATION

As shown by Foster (1955) mixtures of dioctahedral micas and montmorillonites are similar in composition to materials that have been called hydrous micas and illites and rational formulas may be derived from analyses. This is to be expected, as dioctahedral micas, dioctahedral hydrous micas, and montmorillonites have the same 2:1 layer structure, in which only two positions are occupied in the octahedral layer and in which the charge induced on the structure by the proxying of lower valence cations for higher valence cations is balanced by large cations, such as K, Ca, Mg, or Na, located between the composite layers. Structural formulas may, therefore, be derived for materials like these vanadium clays that are composed predominantly of interlayered mica and montmorillonite, as if they were hydrous micas.

The formulas for the clays studied were derived by the method devised by Marshall (1949, p. 58) and modified by Foster (1951, p. 728). The calculations involved in deriving a formula for G–29M–53 are shown in detail in table 4. The gram-equivalents of cationic constituents in the structure are obtained by dividing the percent of each constituent present by a factor obtained by dividing the molecular weight of that constituent by the number of cationic valencies in its formula. Thus for SiO_2 the factor to be used is the molecular weight of SiO_2, 60.06, divided by 4, which is 15.015; for Al_2O_3 it is 101.96, divided by 6, or 16.993.

In the idealized unit of 2:1 layer structures there are 20 oxygen ions and 4 hydroxyl ions, which together carry 44 anionic or negative charges, and which are neutralized by the same number of cationic or positive charges. In order to convert the gram-equivalents of the cationic constituents to cationic valencies present in the unit cell, they are, therefore, divided by a factor obtained by dividing the sum of the gram-equivalents by 44. The resulting value is divided by the valence of each cation to obtain the number of cations of that constituent in the unit cell.

TABLE 4.—*Calculation of structural formula of G–29M–53*

	Percent	Calculation	Gram equivalent of cationic constituents	Calculation	Cationic value per total of 44	Calculation	Cations per unit cell	Charge
SiO_2	49.12	÷(60.06÷4)=	3.271	[1] ÷0.1183=	27.650	÷4=	6.912 1.088	−1.088
							8.000	
Al_2O_3	17.62	÷(101.96÷6)=	1.037	÷ .1183=	8.766	÷3=	[2] 2.922 1.834	−.476
FeO	3.54	÷(71.85÷2)=	.099	÷ .1183=	.837	÷2=	.418	
V_2O_4	8.52	÷(165.90÷8)=	.411	÷ .1183=	3.474	÷4=	.869	
MgO	4.16	÷(40.32÷2)=	.206	÷ .1183=	1.741	÷2=	.870	
							3.991	
MgO	.50	÷(40.32÷2)=	.025	÷ .1183=	.211	÷2=	.106	
CaO	.50	÷(56.08÷2)=	.018	÷ .1183=	.152	÷2=	.076	
Na_2O	.28	÷(62.00÷2)=	.009	÷ .1183=	.076	÷1=	.076	
K_2O	6.16	÷(94.20÷2)=	.131	÷ .1183=	1.107	÷1=	1.107	
			5.207		44.014		1.365	−1.564

[1] 5.207+44=0.1183.

[2] 2.922=1.088+1.834.

Note:—Structural formula (half-cell):

$$\underbrace{\overset{-.24}{(Al_{.92}Fe^{+2}_{.21}V^{+4}_{.44}Mg_{.44})}}_{2.01}\ \overset{-.54}{(Si_{3.46}Al_{.54})}O_{10}(OH)_2X_{.78}$$

The aluminum cations are divided between the tetrahedral and octahedral layers, allotting enough to the tetrahedral layer to bring, with silicon, the total cations in that layer to 8.00, and assigning the remainder to the octahedral group. The sum of the cations in the octahedral group should be close to the theoretical 4.00. A total of less than 4.00 may indicate (1) excess silica, (2) unoccupied octahedral positions, or (3) a faulty analysis. A total in excess of 4.00 commonly indicates that some of the magnesium is present as an interlayer exchangeable cation (Foster, 1951). Sufficient magnesium is then withdrawn from the octahedral group to bring the sum of the octahedral ions to 4.00±.04, and is added to the interlayer cations.

The charge on the tetrahedral group is equivalent to the aluminum assigned to that group because aluminum, being trivalent, carries one less charge than an equivalent amount of silicon, which is quadrivalent, and leaves unsatisfied anionic charges equivalent to the amount of aluminum added. The charge on the octahedral group is equivalent to the sum of the cations in that group multiplied by their respective valencies subtracted from 12.00, the number of octahedral anionic valencies. The sum of the tetrahedral and octahedral charges represents the total charge on the structural layers and should agree closely with the sum of the external cations. In the vanadium clays studied the sum of the external cations was usually somewhat higher than the total charge, probably owing to the small amount of chlorite in most of them.

Formulas for 2:1 layer minerals are usually stated in terms of the half-cell; the values for ions per unit cell of the constituents in each group are therefore divided by 2 to obtain the amounts of each ion to be used in writing the formula.

Structural formulas for the vanadium clays studied, calculated as described above from the adjusted analyses (table 2) are given in table 5. Seven of the eight clays form a suite in which the sum of the positions occupied by Al and V, and the number of positions occupied by Fe and Mg is remarkably constant—ranging from 1.37 to 1.43 positions for Al plus V, from 0.18 to 0.21 for Fe and from 0.39 to 0.44 for Mg. In table 5 the formulas for these seven clays are arranged in order of increasing vanadium content, with the formula for the odd clay (AW–144–52) at the end of the table. In general, the formulas show that increase in vanadium is accompanied by (1) decrease in octahedral aluminum, (2) increase in tetrahedral aluminum, (3) decrease in total aluminum, and (4) decrease in silicon. The proxying of increasing amounts of quadrivalent vanadium for trivalent aluminum causes an equivalent decrease in octahedral charge, which is, in most of the samples, compensated by increase in tetrahedral charge, due to increased proxying of aluminum for silicon. Thus, introduction of V^{+4} into the octahedral layer of the clay structure, and consequent decrease in octahedral charge necessitates readjustment in the tetrahedral layers to maintain a relatively constant total charge. Throughout these adjustments, however, the sum of the octahedral aluminum and vanadium and the sum of the iron and magnesium remain essentially constant. These relationships support the conclusions drawn from the analyses; that increase in vanadium content is accompanied by decrease in aluminum and silicon content, but does not affect the content of any of the other constituents—iron, magnesium, calcium, sodium, and potassium.

TABLE 5.—*Structural formulas for vanadium clays*

Sample No.	*Formula*	*External cations*	
		K	*Others*
G-27UM-53	$\overset{-.47}{(\underbrace{\mathrm{Al}_{1.34}\mathrm{V}^{+4}_{.03}}_{1.37}\underbrace{\mathrm{Fe}^{+3}_{.11}\mathrm{Fe}^{+2}_{.10}\mathrm{Mg}_{.43}}_{.64})}\ \overset{-.34}{(\mathrm{Si}_{3.66}\mathrm{Al}_{.34})}\mathrm{O}_{10}(\mathrm{OH})_2\mathrm{X}_{.81}$	0.58	0.23
G-43UM-53	$\overset{-.44}{(\underbrace{\mathrm{Al}_{1.38}\mathrm{V}^{+4}_{.05}}_{1.43}\underbrace{\mathrm{Fe}^{+3}_{.06}\mathrm{Fe}^{+2}_{.12}\mathrm{Mg}_{.39}}_{.57})}\ \overset{-.37}{(\mathrm{Si}_{3.63}\mathrm{Al}_{.37})}\mathrm{O}_{10}(\mathrm{OH})_2\mathrm{X}_{.81}$	.57	.24
G-29UM-53	$\overset{-.46}{(\underbrace{\mathrm{Al}_{1.32}\mathrm{V}^{+4}_{.05}}_{1.37}\underbrace{\mathrm{Fe}^{+3}_{.10}\mathrm{Fe}^{+2}_{.11}\mathrm{Mg}_{.42}}_{.63})}\ \overset{-.39}{(\mathrm{Si}_{3.61}\mathrm{Al}_{.39})}\mathrm{O}_{10}(\mathrm{OH})_2\mathrm{X}_{.85}$	.55	.30
G-29M-53	$\overset{-.24}{(\underbrace{\mathrm{Al}_{.92}\mathrm{V}^{+4}_{.44}}_{1.36}\underbrace{\mathrm{Fe}^{+2}_{.21}\mathrm{Mg}_{.44}}_{.65})}\ \overset{-.54}{(\mathrm{Si}_{3.46}\mathrm{Al}_{.54})}\mathrm{O}_{10}(\mathrm{OH})_2\mathrm{X}_{.78}$	.55	.13
G-43M-53	$\overset{-.19}{(\underbrace{\mathrm{Al}_{.96}\mathrm{V}^{+3}_{.08}\mathrm{V}^{+4}_{.38}}_{1.42}\underbrace{\mathrm{Fe}^{+2}_{.19}\mathrm{Mg}_{.40}}_{.59})}\ \overset{-.69}{(\mathrm{Si}_{3.31}\mathrm{Al}_{.69})}\mathrm{O}_{10}(\mathrm{OH})_2\mathrm{X}_{.88}$	.51	.37
AW-146-52	$\overset{+.13}{(\underbrace{\mathrm{Al}_{.80}\mathrm{V}^{+4}_{.59}}_{1.39}\underbrace{\mathrm{Fe}^{+3}_{.13}\mathrm{Fe}^{+2}_{.05}\mathrm{Mg}_{.43}}_{.61})}\ \overset{-.71}{(\mathrm{Si}_{3.29}\mathrm{Al}_{.71})}\mathrm{O}_{10}(\mathrm{OH})_2\mathrm{X}_{.58}$	.47	.13
AW-22-52	$\overset{+.04}{(\underbrace{\mathrm{Al}_{.57}\mathrm{V}^{+4}_{.82}}_{1.39}\underbrace{\mathrm{Fe}^{+3}_{.14}\mathrm{Fe}^{+2}_{.06}\mathrm{Mg}_{.25}}_{.45})}\ \overset{-.83}{(\mathrm{Si}_{3.17}\mathrm{Al}_{.83})}\mathrm{O}_{10}(\mathrm{OH})_2\mathrm{X}_{.79}$	.65	.14
AW-144-52	$\overset{-.16}{(\underbrace{\mathrm{Al}_{.61}\mathrm{V}^{+4}_{.53}}_{1.14}\underbrace{\mathrm{Fe}^{+3}_{.32}\mathrm{Mg}_{.47}}_{.79})}\ \overset{-.70}{(\mathrm{Si}_{3.30}\mathrm{Al}_{.70})}\mathrm{O}_{10}(\mathrm{OH})_2\mathrm{X}_{.86}$	.50	.36

The amount of V^{+4} that can be admitted into the clay structure without producing a positive charge on the octahedral layer is determined by the bivalent ion content. In the formulas for the clays separated from sandstone (the "G" samples), bivalent ions, or ions like Fe^{+3}, which probably were present originally as bivalent ions, occupy from 0.57 to 0.65 octahedral positions. None of these samples contain more than 0.44 V ions, and in their formulas the octahedral groups all have a negative charge.

In the formula for AW-146-52 the octahedral group has a positive charge of 0.13, exactly equivalent to the Fe^{+3} present. If it is assumed that all the iron was originally present as Fe^{+2}, the V^{+4} present would have been almost exactly equivalent to the sum of the Fe^{+2} plus Mg (0.59 and 0.61 respectively), and would represent the maximum amount of V^{+4} that could be accepted into the structure without inducing a positive charge on the octahedral layer.

The V^{+4} content of these six samples does not exceed the original bivalent ion content, assuming Fe to have been present originally as Fe^{+2}. In AW-22-52, however, V^{+4} is greatly in excess of Fe and Mg, occupying 0.82 positions, whereas Fe and Mg occupy only 0.45 positions. This excess of V^{+4} over bivalent ions does not lead to a positive charge on the group, as would be expected, because of the deficiency of octahedral positions occupied—1.84 of the theoretical 2.00.

It has been pointed out that in the formulas for this suite of seven samples the sum of the positions occupied by octahedral Al and V^{+4} is remarkably constant, as is also the number of positions occupied by Fe and by Mg. In the formula for AW-22-52 the number of positions occupied by Al plus V^{+4} and by total Fe fall within the range of the number of positions occupied by these ions in the other members of the suite, but the number of positions occupied by Mg is lower by approximately the same number of positions (0.16) as the octahedral group is deficient of the theoretical 2.00. This deficiency in Mg and in octahedral positions suggests that if V^{+4} in excess of the bivalent ion content enters the structure of a clay similar to G-29UM-52, electrical balance is achieved and a positive octahedral charge is avoided by vacating bivalent positions, Mg in this case, equivalent to the excess of V^{+4}.

AW-144-52 differs from the other clays studied in having a lower Al plus V^{+4} content (1.14 positions) and a higher Fe (0.32 positions) content. The Mg content (0.47 positions) is only slightly higher than the highest number of positions occupied by Mg in the other clays (0.44). At the time of analysis oxidation had proceeded farther in this sample than in any of the others, and all the iron was present as ferric iron. In the unadjusted analysis of this sample some vanadium was found to be present as V_2O_5 (2.39 percent). As this V_2O_5 was found to be free of the clay structure, it was not included in the adjusted analysis. However, it may have been present originally in the clay structure as V^{+4} and have been expelled from the structure on oxidation to V (V), with perhaps some Fe (III), thus accounting for the deficiency of octahedral positions occupied. The ease with which this sample is broken down by acid treatment suggests that the structure is under considerable strain and perhaps disorganization. If iron is considered to have once been present as Fe^{+2}, the original bivalent ion content of this sample was considerably higher than that of the samples that have been considered—0.75 as compared with an average of 0.61. It had, consequently, a correspondingly greater capacity for the acceptance of V^{+4} into the structure without inducing a positive charge on the octahedral group. The V^{+4} content of the sample is, however, considerably lower (0.54) than the maximum that could have been accepted by neutralization of the bivalent ion content (0.75).

X-ray diffraction studies showed that the vanadium clays studied are composed predominantly of mica (roscoelite) and mixed-layered mica (roscoelite) and montmorillonite. As vanadium is present in roscoelite as V^{+3}, it might be postulated that vanadium was originally present in these clays as V^{+3}. Three of the formulas shown in table 6 are rewritten below on this assumption, with the further necessary assumption that Fe was present originally as Fe^{+2}.

Sample No.	*Formula*	*K*	*Ex*
G–29UM–53	$\overset{-.62}{(\underbrace{Al_{1.32}V^{+3}_{.05}}_{1.37}\underbrace{Fe^{+2}_{.21}Mg_{.42}}_{.63})}\ \overset{-.39}{(Si_{3.61}Al_{.39})}O_{10}(OH)_2X_{1.01}$	0. 55	0. 56
G–29M–53	$\overset{-.62}{(\underbrace{Al_{.92}V^{+3}_{.44}}_{1.36}\underbrace{Fe^{+2}_{.21}Mg_{.44}}_{.65})}\ \overset{-.54}{(Si_{3.46}Al_{.54})}O_{10}(OH)_2X_{1.14}$	. 55	. 59
AW–146–52	$\overset{-.59}{(\underbrace{Al_{.80}V^{+3}_{.59}}_{1.39}\underbrace{Fe^{+2}_{.18}Mg_{.43}}_{.61})}\ \overset{-.71}{(Si_{3.29}Al_{.71})}O_{10}(OH)_2X_{1.30}$	. 47	. 83

Most significant in these formulas is the high charge or external cation value (X value), especially in the formulas of the mineralized clays. In clays like these, made up predominantly of mica and interlayered mica and montmorillonite, the X-value or charge would be expected to be less than that of a mica (1.00) but more than that of a montmorillonite (0.30 to 0.50). The K equivalent (average 0.55) indicates that they are made up of approximately 55 percent mica (including interlayered mica), and 45 percent montmorillonite (interlayered with mica), and consequently, should have a charge or X value of 0.70 to 0.80. In these formulas, however, the charge increases from 1.01 to 1.30, as V^{+3} increases from 0.05 to 0.59.

When V^{+4} proxies for Al^{+3} in a 2:1 layer structure the charge on the octahedral layer decreases with increase in V^{+4} content, and becomes zero when V^{+4} is equivalent to the bivalent ions (Fe^{+2} and Mg) present. To maintain a constant charge on the structure, such decrease in octahedral charge must be accompanied by increase in tetrahedral charge—that is, increased proxying of Al for Si. On the other hand, when V^{+3} proxies for octahedral Al, it causes no change in the octahedral charge and there is no need for adjustment and increase in charge on the tetrahedral layers with increase in vanadium content. In the formulas for Colorado roscoelites shown in table 6, in which the numbers of octahedral positions occupied by V^{+3} ranges from 0.73 to 1.16, there is no correlation between V^{+3} content and tetrahedral charge.

TABLE 6.—*Formulas for Colorado roscoelites*

Sample No. and Location	*Formula*
1. Paradox Valley	$\overset{-.08}{(\underbrace{Al_{.88}V^{+3}_{.99}}_{1.87}\underbrace{Fe^{+2}_{.10}Mg_{.04}}_{.14})}\ \overset{-.95}{(Si_{3.05}Al_{.95})}O_{10}(OH)_2X_{1.03}$ $K_{.90}$
2. Placerville	$\overset{-.18}{(\underbrace{Al_{1.12}V^{+3}_{.73}}_{1.85}\underbrace{Fe^{+2}_{.04}Mg_{.10}}_{.14})}\ \overset{-.75}{(Si_{3.25}Al_{.75})}O_{10}(OH)_2X_{.93}$ $K_{.79}$
3. Placerville	$\overset{-.10}{(\underbrace{Al_{.69}V^{+3}_{1.07}V^{+4}_{.09}}_{1.85}\underbrace{Fe^{+2}_{.04}Mg_{.09}}_{.13})}\ \overset{-.94}{(Si_{3.06}Al_{.94})}O_{10}(OH)_2X_{1.04}$ $K_{1.09}$
4. Placerville	$\overset{-.04}{(\underbrace{Al_{.73}V^{+3}_{1.16}}_{1.89}\underbrace{Fe^{+2}_{.09}Mg_{.04}}_{.13})}\ \overset{-.81}{(Si_{3.19}Al_{.81})}O_{10}(OH)_2X_{.85},$ $K_{.80}$

1. Wells, R. C., and Brannock, W. W., 1945, Composition of roscoelite: U. S. Geol. Survey Bull. 950, p. 123.
2. Hillebrand, W. F., and Ransome, F. L., 1900, On carnotite and associated vanadiferous minerals in western Colorado: Am. Jour. Sci., 4th ser., v. 10, p. 133.
3. A. L. Bush, analyst; calculated from an unpublished analysis, U.S. Geological Survey.
4. V. North, analyst; calculated from an unpublished analysis, U. S. Geological Survey.

As (1) the analyses of the clays show that increase in vanadium content is accompanied by decrease in silica and alumina content, (2) formulas derived from the analyses show increase in V^{+4} content and decrease in octahedral charge and maintainance of a relatively constant total charge, that is, (X) value, and (3) substitution of V^{+3} for V^{+4} in the formulas leads to abnormal X values (see table 7), whereas the X values obtained with V^{+4} are reasonable and in accord with the mineralogy of the clays, it may be concluded that vanadium entered the clays as V^{+4} and not as V^{+3}.

TABLE 7.—*V^{+3} substituted for V^{+4} in formulas for vanadium clays*

Sample No.	*Formula*	*K*	*Ex*
G-27UM-53	$\overset{-.60}{(\underbrace{\mathrm{Al}_{1.34}\mathrm{V}^{+3}_{.03}}_{1.37}\underbrace{\mathrm{Fe}^{+2}_{.21}\mathrm{Mg}_{.43}}_{.64})}\overset{-.34}{(\mathrm{Si}_{3.66}\mathrm{Al}_{.34})}\mathrm{O}_{10}(\mathrm{OH})_2\mathrm{X}_{.94}$	0.58	0.36
G-43UM-53	$\overset{-.54}{(\underbrace{\mathrm{Al}_{1.38}\mathrm{V}^{+3}_{.05}}_{1.43}\underbrace{\mathrm{Fe}^{+2}_{.18}\mathrm{Mg}_{.39}}_{.57})}\overset{-.37}{(\mathrm{Si}_{3.63}\mathrm{Al}_{.37})}\mathrm{O}_{10}(\mathrm{OH})_2\mathrm{X}_{.01}$	.57	.34
G-29UM-53	$\overset{-.62}{(\underbrace{\mathrm{Al}_{1.32}\mathrm{V}^{+3}_{.05}}_{1.37}\underbrace{\mathrm{Fe}^{+2}_{.21}\mathrm{Mg}_{.42}}_{.63})}\overset{-.39}{(\mathrm{Si}_{3.61}\mathrm{Al}_{.39})}\mathrm{O}_{10}(\mathrm{OH})_2\mathrm{X}_{1.01}$	.55	.56
G-29M-53	$\overset{-.62}{(\underbrace{\mathrm{Al}_{.92}\mathrm{V}^{+3}_{.44}}_{1.37}\underbrace{\mathrm{Fe}^{+2}_{.21}\mathrm{Mg}_{.44}}_{.65})}\overset{-.54}{(\mathrm{Si}_{3.46}\mathrm{Al}_{.54})}\mathrm{O}_{10}(\mathrm{OH})_2\mathrm{X}_{1.14}$	.55	.68
G-43M-53	$\overset{-.57}{(\underbrace{\mathrm{Al}_{.96}\mathrm{V}^{+3}_{.46}}_{1.42}\underbrace{\mathrm{Fe}^{+2}_{.19}\mathrm{Mg}_{.40}}_{.59})}\overset{-.69}{(\mathrm{Si}_{3.31}\mathrm{Al}_{.69})}\mathrm{O}_{10}(\mathrm{OH})_2\mathrm{X}_{1.36}$	.51	.85
AW-146-52	$\overset{-.59}{(\underbrace{\mathrm{Al}_{.80}\mathrm{V}^{+3}_{.59}}_{1.39}\underbrace{\mathrm{Fe}^{+2}_{.18}\mathrm{Mg}_{.43}}_{.61})}\overset{-.71}{(\mathrm{Si}_{3.29}\mathrm{Al}_{.71})}\mathrm{O}_{10}(\mathrm{OH})_2\mathrm{X}_{1.30}$	.47	.83
*AW-22-52	$\overset{-.92}{(\underbrace{\mathrm{Al}_{.57}\mathrm{V}^{+3}_{.82}}_{1.39}\underbrace{\mathrm{Fe}^{+2}_{.20}\mathrm{Mg}_{.25}}_{.45})}\overset{-.83}{(\mathrm{Si}_{3.17}\mathrm{Al}_{.83})}\mathrm{O}_{10}(\mathrm{OH})_2\mathrm{X}_{1.75}$	.65	1.15
AW-144-52	$\overset{-.79}{(\underbrace{\mathrm{Al}_{.61}\mathrm{V}^{+3}_{.53}}_{1.14}\underbrace{\mathrm{Fe}^{+2}_{.32}\mathrm{Mg}_{.47}}_{.79})}\overset{-.70}{(\mathrm{Si}_{3.30}\mathrm{Al}_{.70})}\mathrm{O}_{10}(\mathrm{OH})_2\mathrm{X}_{1.49}$	.50	.99

*The discrepancy between the charge (0.92) on the octahedral group and the charge resulting from divalent-ion substitution (0.45) is due to 0.16 unoccupied position, which leaves 0.48 anionic charge unneutralized, and which adds that much to the charge induced by divalent ions.

DISCUSSION AND CONCLUSIONS

The eight clays from the Salt Wash member of the Morrison formation in the Colorado Plateau that have been studied are mineralogical mixtures, consisting predominantly of mica and interlayered mica and montmorillonite, with minor amounts of chlorite and quartz. There is little difference, mineralogically, between the mineralized and unmineralized clays. Their potassium content indicates that mica (including the mica interlayered with montmorillonite) makes up about 50 percent of the clays. Vanadium is present, in the tetravalent state, in all the mineralogical phases making up the mineralized clays.

In chemical composition the mineralized and unmineralized clays are also very similar. The most significant feature of difference is the progressive decrease in SiO_2 and Al_2O_3 with increase in V_2O_4 content, the other constituents remaining relatively the same. Vanadium is present in the structure of the mineralized clays as an octahedral cation, replacing aluminum ion for ion. Substitution of tetravalent vanadium for trivalent aluminum causes an equivalent decrease in the octahedral charge. This is compensated for by increased replacement of silicon by aluminum, with consequent increased tetrahedral charge, so that the total charge remains relatively constant. In the unmineralized clays the octahedral charge is slightly greater than the tetrahedral charge. With increase in V^{+4} content the octahedral charge progressively increases, until in the most highly mineralized there is no negative charge on the octahedral layer—all negative charge is on the tetrahedral layer. These relationships are reflected in the chemical composition as decrease in SiO_2 and Al_2O_3 content with increase in V_2O_4 content.

The increase in tetrahedral charge with decrease in octahedral charge which accompanies increase in V_2O_4 content suggests that vanadium entered the structures of the mineralogical phases making up the clays in the tetravalent state, and not in the trivalent state as in roscoelite. If vanadium had originally entered these structures in the trivalent state, substituting for aluminum, it would have caused no change in the octahedral charge and there would have been no need for adjustment and increase in charge in the tetrahedral layers with increase in V content, as is observed.

It is worthy of note that the vanadium clays studied, in which vanadium is present in the tetravalent state, occur in clay-bearing sands (the Salt Wash member of the Morrison formation), whereas roscoelite, a mica containing trivalent vanadium, is found in the Colorado Plateau in sand formations with low clay content. This difference in environment suggests that the minerals deposited, and the state of valence of the vanadium in them, is in some way related to the presence or absence of clay in the sands. In the absence of clay, roscoelite containing trivalent vanadium was deposited by the invading solutions; in the presence of clay, there was interaction between the clay and the invading solutions, which resulted in (tetravalent) vanadium-bearing clays similar to the non-vanadium-bearing clays in mineralogy and in chemical composition except for greater or less replacement of octahedral (trivalent) aluminum by tetravalent vanadium and additional replacement of silicon by aluminum sufficient to maintain the total charge at a relatively constant value. On the other hand, cases are known (for instance, at the Mineral Joe mine, see Part 15) where vanadium hydromicas have been introduced as part of the mineralization process.

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Part 11. MIXED-LAYERED STRUCTURES IN VANADIUM CLAYS

By John C. Hathaway

CONTENTS

ILLUSTRATIONS

ABSTRACT

A group of claylike silicates containing vanadium have been examined by X-ray diffraction methods to determine their mineralogic composition. The results indicate that mica and chlorite are the principal minerals. The micas resemble roscoelite but depart from it in two different ways, by interstratification with montmorillonitic layers and by variation in octahedral substitution. Some of the chlorites also exhibit mixed-layered expanding structures, but no interstratification of mica and chlorite layers has yet been noted. The chlorites show some variation in the temperature of decomposition, presumably because of differences in composition and degree of crystallinity.

INTRODUCTION

Identification of the claylike materials occurring in zones of vanadium mineralization in the sandstone type deposits of the Colorado Plateau is often hampered by the fine particle size and poor crystallinity of these materials, although mica-type minerals have been recognized through usual X-ray diffraction methods and have been variously reported as roscoelite or vanadium hydromica. In this investigation, X-ray diffraction procedures commonly used in the study of clay minerals have been applied to the problem of differentiating these poorly crystalline materials. The chemistry of some of these samples used is discussed in Part 10 of this volume.

MATERIALS

[The American Museum of Natural History supplied sample AMNH–13565]

The samples studied were as follows:

AMNH–13565	Roscoelite, Coloma, Calif.
ALB–34–54	Roscoelite, Fall Creek mine, Placerville, San Miguel County, Colo.
AW–207–54A	Vanadium silicate from oxidized ore, Rifle, Garfield County, Colo.
AW–207–54B	Vanadium silicate from unoxidized ore, Rifle, Garfield County, Colo.
AW–146–52	Vanadium silicate from Cougar mine, San Miguel County, Colo.
AW–144–52	Vanadium silicate from Sunnyside mine, east of Carrizo Mountains, San Juan County, N. Mex.
AW–67–51	Vanadium silicate, Little Pittsburg No. 5 mine, Thompson district, Grand County, Utah.

G-53-53	Vanadium silicate, Bitter Creek mine, Montrose County, Colo.
P-1-M-53	Mineral Joe mine, Jo Dandy group, Montrose County, Colo.
P-1-P-53	Mineral Joe mine, Jo Dandy group, Montrose County, Colo.

PROCEDURE

All of the samples except AMNH 13565, P-1-M-53, and P-1-P-53 were purified by water elutriation, bromoform separation, or both. Sample AMNH 13565 consisted of a group of fairly pure roscoelite crystals and therefore did not require further separation. A portion of these crystals was crushed in a mullite mortar to pass a 230-mesh sieve. This material as well as a portion of each of the other purified samples were placed in plastic test tubes and dispersed in distilled water using a motor-driven brush. A small amount of sodium metaphosphate was added to each sample as a dispersing agent. Oriented aggregates were prepared by pipetting portions of each suspension onto each of three glass slides. The suspension remaining in the test tube was allowed to stand about four hours and the material still in suspension at the end of this time was pipetted on three additional slides. The material placed on these two groups of slides will hereinafter be referred to as coarse and fine, respectively.

Samples P-1-M-53 and P-1-P-53 [8] were dispersed in distilled water, wet sieved to remove particles larger than 62μ, further dispersed using an end-over-end shaker, and centrifuged repeatedly to separate the silt (2-62μ) and clay ($<2\mu$) fraction. Excess water was removed from the clay fraction using porcelain filter candles under vacuum and portions of the resulting concentrated suspensions were pipetted onto glass slides. The remaining suspensions were dried at room temperature and the clay removed and crushed.

X-ray diffractometer patterns were made for each sample as follows:

Oriented aggregates:
1. Untreated.
2. Treated with ethylene glycol.
3. Heated to 400° C.
4. Heated to 500° C.
5. Treated with hot concentrated MCl (samples AMNH 13565, AW-67-51, G-53-53, P-1-M-53, and P-1-P-53 only).

Randomly oriented powder (samples AMNH 13565, ALB-34-54, P-1-M-53, and P-1-P-53, only).

RESULTS

In figure 35 a comparison is shown between the X-ray diffractometer patterns of minerals which have been identified by chemical and optical methods as roscoelite. Most of the apparent differences in the randomly oriented powder patterns are the result of the much higher degree of preferred orientation that occurred in the preparation of the mount for sample AMNH 13565. Otherwise both samples exhibit similar patterns except that the peak marked "A" at 33.4° 2θ in the randomly oriented powder pattern for sample AMNH 13565 is not evident in ALB-34-54 and calcite is present in ALB-34-54. Inasmuch as the spacing of peak "A" is not part of the integral series of higher orders for the 001 spacing, its presence is probably not due to the preferred orientation of the roscoelite flakes but more probably represents a separate unidentified phase. Further evidence for this suggestion is the appearance of a peak with a spacing of 6.9A in the pattern for an oriented aggregate of sample AMNH 13565 heated to

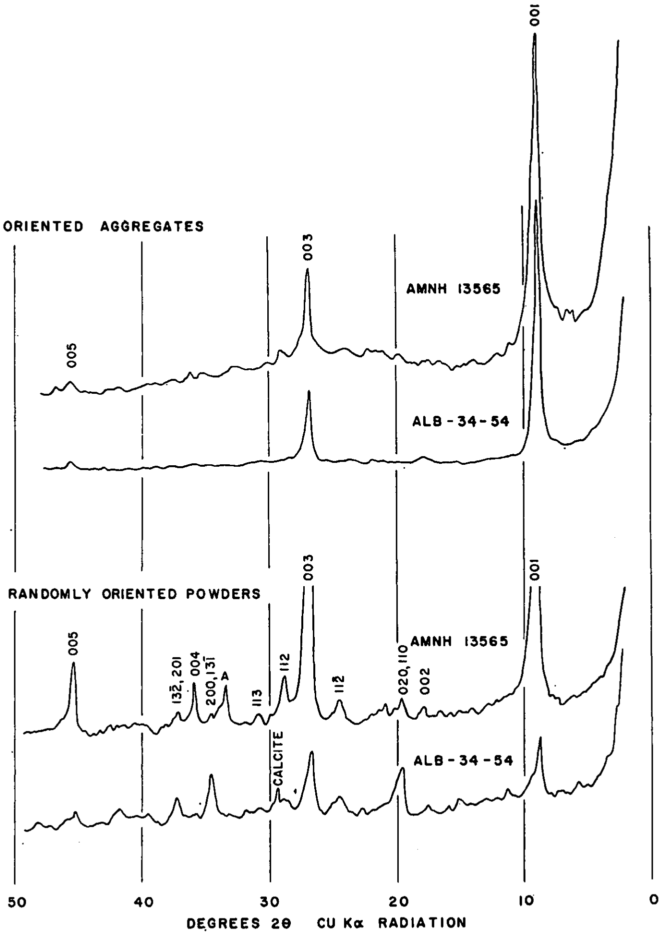

FIGURE 35.—X-ray diffraction patterns of two roscoelite samples.

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[8] These two samples are further considered in Part 15 of this volume, and there are identified as samples M and P, respectively.

500° C. The same peak appears with considerable intensity at the same temperature in the acid-treated sample suggesting that this separate phase is acid insoluble. Elimination of lines apparently due to separate phases leaves a pattern with a distribution of *hkl* lines that closely resembles a one-layer monoclinic muscovite. This is in agreement with the proposal of Heinrich and coworkers (1953) that roscoelite is characterized by a one-layer monoclinic structure. An important departure from the muscovite pattern may be seen in the distribution of intensities of the 00*l* lines shown in the oriented aggregate patterns in figure 35. Whereas the 001 and 003 reflections show strong and medium intensities, respectively, the 002 and 004 reflections are almost absent. Muscovites, on the other hand, show a second-order reflection of considerably greater intensity relative to the first- and third-order reflection. A weak second-order basal reflection is usually, but not always, a characteristic of the biotites. The spacings of the 060 reflections (not shown in fig. 35) for samples AMNH 13565 and ALB-34-54 are 1.525A and 1.515A, respectively, which places them within the overlap of the ranges usually associated with the dioctahedral and trioctahedral micas. It does not seem likely, however, that a trioctahedral mica would form with vanadium occupying the octahedral positions. Calculations of the octahedral layer population by the Marshall method (1949, p. 58) for ALB-34-54 and for a roscoelite from Placerville, Colo., from the analysis quoted in Weeks and Thompson (1954, p. 55) give sums of 1.969 and 2.069 atoms per half-unit cell, respectively. It seems probable then that these micas are dioctahedral and that the moderately large b_0 dimensions shown by the 060 spacings are due to the replacement of aluminum by vanadium in the octahedral layer. Such substitutions would also account for the low intensities of the second order 00*l* reflections. G. Brown (1951, p. 162) has calculated the effect on 00*l* intensities of substitution of Fe^{+3} for Al^{+3} in the dioctahedral mica structure and has demonstrated that a high-iron mica should exhibit an extremely weak 002 reflection. As the atomic scattering curve for vanadium closely follows that of iron (Klug and Alexander, 1954, p. 138), a similar distribution of 00*l* intensities should occur for both a roscoelite and a high-iron dioctahedral mica such as a glauconite, and figure 36 shows the similarity of the X-ray patterns for oriented aggregates of the two minerals. Conversely a lesser amount of vanadium substitution should be revealed by an increase in intensity of the 002 reflection relative to the 001 and 003 reflections.

Figure 37 shows the X-ray patterns given by oriented aggregates for five Colorado Plateau samples in which mica is the principal constituent. All show a weak 002 reflection although in samples AW-207-54A and AW-146-52 this line is relatively stronger than in the other samples suggesting a lesser amount of octahedral vanadium in these two samples. The patterns are arranged in order of decreasing degree of crystal perfection toward the bottom of the diagram, although the first three patterns show approximately equal crystallinity. Accompanying this decrease is an increase in the 001 spacing as tabulated below:

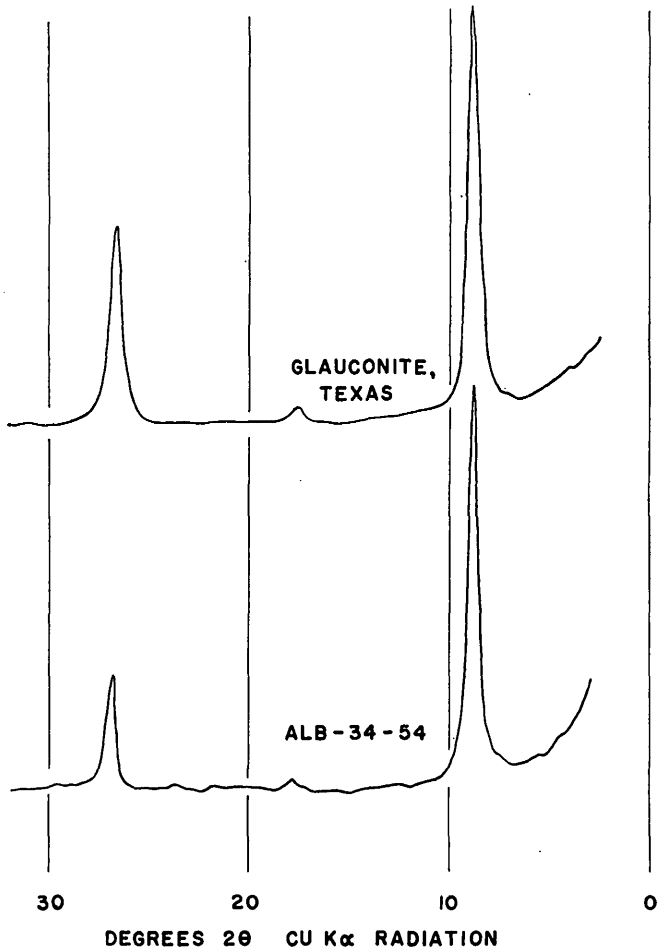

FIGURE 36.—Comparison of X-ray diffraction patterns of oriented aggregates of roscoelite and glauconite.

Sample No.	*001 spacing in A*
ALB-34-54	10.1
AW-207-54B	10.1
AW-207-54A	10.1
AW-146-52	10.3
AW-144-52	10.5

All the samples in figure 37 except ALB-34-54 contain impurities as indicated on the diagram by *C* for chlorite and *T* for metatyuyamunite. Ethylene glycol treatment had little effect on samples ALB-34-54, AW-207-54B, and AW-207-54A, but some expansion took place in samples AW-146-52 and AW-144-52 as is shown in figure 38. The extreme loss in intensity suf-

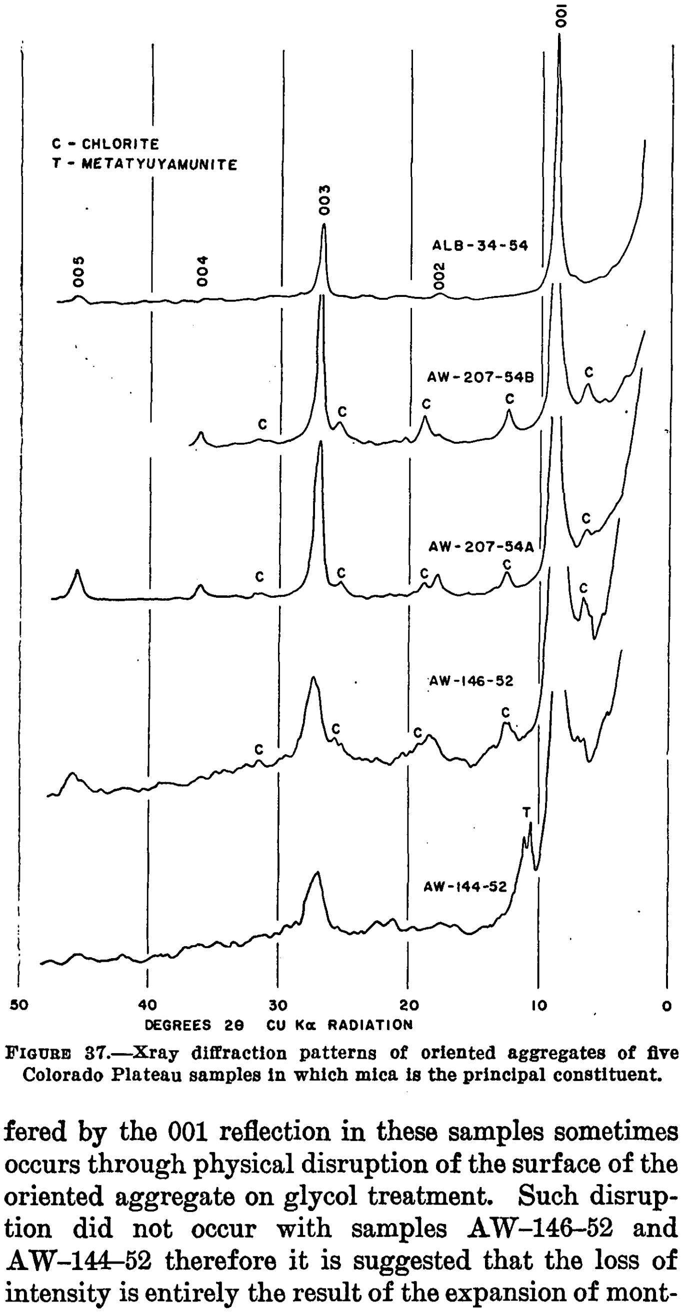

FIGURE 37.—Xray diffraction patterns of oriented aggregates of five Colorado Plateau samples in which mica is the principal constituent.

fered by the 001 reflection in these samples sometimes occurs through physical disruption of the surface of the oriented aggregate on glycol treatment. Such disruption did not occur with samples AW–146–52 and AW–144–52 therefore it is suggested that the loss of intensity is entirely the result of the expansion of montmorillonitic layers randomly interstratified with layers of roscoelite. These two samples might justifiably be called vanadium hydromicas in the sense that they are micaceous and contain vanadium and would show a high proportion of water in a chemical analysis; however, they might better be identified as mixed-layered mica-montmorillonite minerals which would acknowledge their expandable properties.

A slightly different type of material is shown in figure 39 by sample AW–67–51. This sample is a mixture of at least two minerals, both of which expand slightly on ethylene glycol treatment. The shift of a peak at 12.9 A to 13.8 A is suggestive of a vermiculitic mineral, whereas the behavior of the other major component with a reflection at 10.6 A suggests a mixed-layered mineral similar to samples AW–144–52 and AW–146–52. Heat treatment however indicates that both of these minerals are less durable than either vermiculite or the mixed-layered minerals discussed above. At 400° C both AW–144–52 and AW–146–52 collapsed to structures closely resembling roscoelite and at 500° C still give lines of strong intensity. AW–67–51, on the other hand, gives evidence of destruction of the crystal lattice at 400° C, and at 500° C a new unidentified phase has appeared. Treatment of this sample with hot concentrated HCl leaves a residue which gives an X-ray pattern similar to that of roscoelite except that its structure is apparently destroyed between 400° and 500° C.

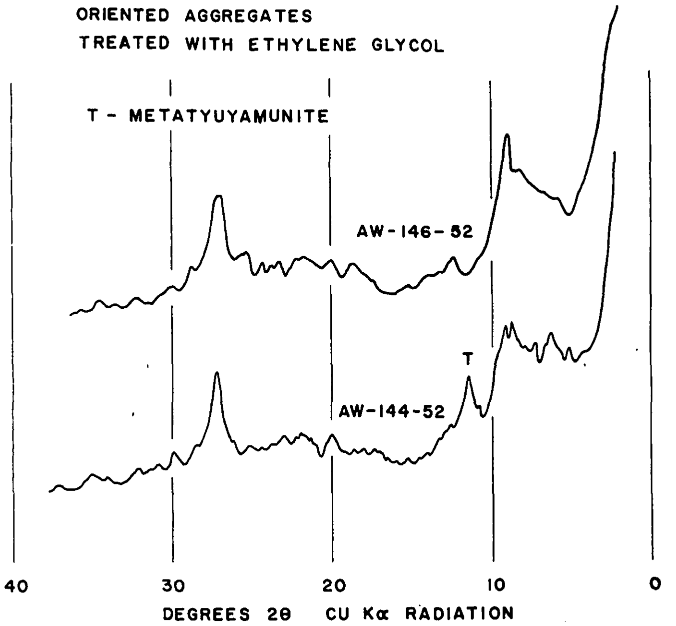

FIGURE 38.—X-ray diffraction patterns showing expansion of vanadium silicates treated with ethylene glycol.

Sample G–53–53 (fig. 40) is an example of a mixture of chlorite and a mica which shows only a minor amount of interstratification with more highly hydrated layers as ethylene glycol and heat treatment affect the shape and position of the mica 00*l* reflection only slightly. The intensity of the 002 reflection after heat treatment at 500°C suggests that the mica is roscoelite with less substitution of vanadium for aluminum than in sample ALB–34–54. The chlorite in sample G–53–53 is characterized by the almost equal intensity of the first four 00*l* reflections and by the accentuation of the first order reflection with loss of the higher orders after heat treatment at 500°C, a reaction that occurs in most well-crystalized chlorites. It should be noted that the chlo-

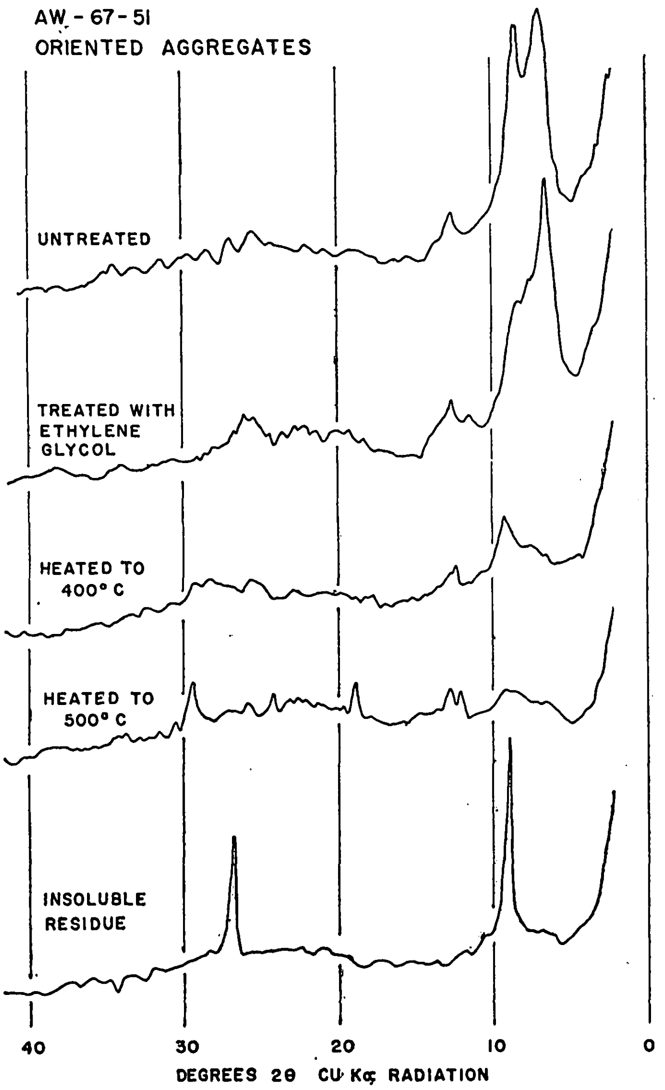

FIGURE 39.—X-ray diffraction patterns of AW-67-51 (a mixture of 2 or more minerals) showing shift in peaks caused by treating with ethylene glycol and by heating.

rites in samples AW-207-54A and AW-146-52 behave similarly, whereas in AW-207-54B the increase in intensity of the 001 line fails to take place at elevated temperature, the chlorite lines disappearing and the lines of an unidentified new phase appearing at 400°C instead. At 500°C still another unidentified phase appears replacing the one occurring at 400°C. No experiments have been carried out as yet to determine if these phases are at equilibrium at the given temperatures. Inasmuch as sample AW-207-54B comes from unoxidized ore whereas AW-207-54A represents an oxidized zone, it seems possible that the oxidation state of the vanadium in the chlorite affects the stability of the mineral. The relationship, however, may be difficult to visualize when it is considered that the normal chlorite usually contains bivalent elements in both the octahedral layer and the interlayer brucite sheet. The manner in which vanadium (III), (IV), or (V) atoms are contained in a chlorite structure remains as a further problem of investigation.

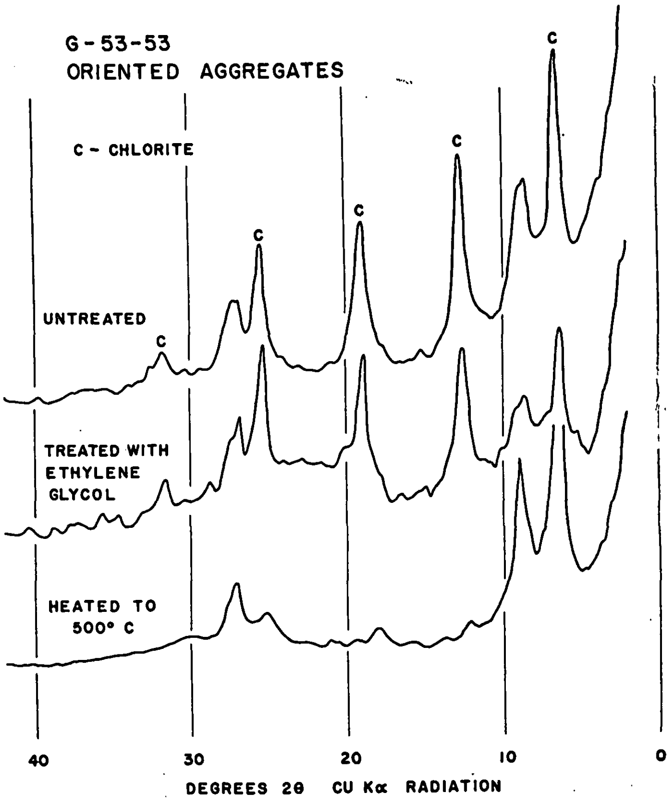

FIGURE 40.—X-ray diffraction patterns of sample G-53-53 untreated, after ethylene glycol treatment, and after heating.

Samples P-1-M-53 and P-1-P-53 from a channel sample taken at the Mineral Joe mine, Montrose County, Colo. (Part 15), were examined without purification other than size fractionation to concentrate the clay size particles. The X-ray patterns for oriented aggregates of the $< 2\mu$ fraction of these samples are given in figure 41. Mica, chlorite, and carnotite are the principal constituents of the clay fraction of sample P-1-M-53. The mica and chlorite 001 reflections show slight shifts on treatment with ethylene glycol suggesting that they have montmorillonitic layers interstratified with them. Their behavior on heat treatment lends support to the supposition that the mica and chlorite are mixed-layered minerals, as a distinct shift toward lower spacings occurs after heating of the sample to 400°C. The characteristics of the first-order chlorite reflection after heating is suggestive of a vermiculitic mineral except that the higher order $00l$ reflections of the untreated material show intensities greater than those expected from a vermiculite.

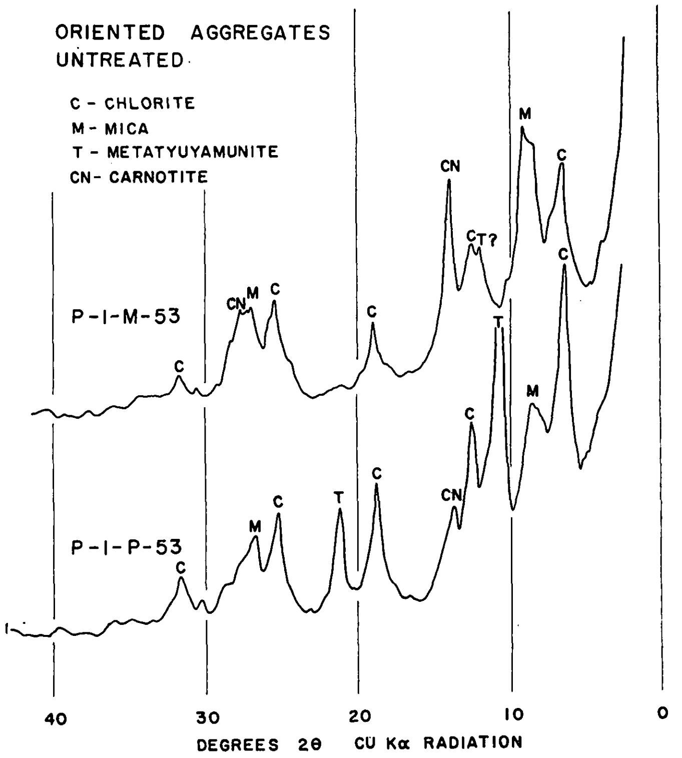

FIGURE 41.—X-ray diffraction patterns of oriented aggregates of two samples from the Mineral Joe mine, Montrose County, Colo.

Sample P-1-P-53 differs from the previous sample in that metatyuyamunite is present as a major constituent. Further differences are a higher degree of mixed layering in the mica and a chlorite which shows greater thermal stability closely resembling the chlorite of sample G-53-53. The mica in turn shows characteristics on ethylene glycol treatment similar to the mica of sample AW-144-52.

CONCLUSIONS

The vanadium silicates examined contain mica that varies from roscoelite (AMNH 13565) to highly mixed layered mica-montmorillonite (AW-144-52) in which the mica layers are probably roscoelite-like in octahedral composition but of very poor crystallinity. Chlorites are present in most of the samples and vary from types of high thermal stability and good crystallinity (G-53-53) to mixed-layered chlorite-montmorillonite aggregates (P-1-M-53) and chlorites of poor thermal stability (AW-207-54B).

The samples might be grouped according to the character of each of their mineral components as follows:

Mica:
Roscoelite ⟶ Increasing mixed layering
AMHN 13565
ALB-34-54
AW-207-54A
AW-207-54B
G-53-53
P-1-M-53
AW-146-52
AW-67-51
P-1-P-53
AW-144-52

Roscoelite: ⟶ Decreasing octahedral substitution of V for Al (based on relative 002 intensity)
AMNH-13565
ALB-34-54
AW-207-54B
AW-144-52
AW-67-51
AW-207-54A
AW-146-52
G-53-53
P-1-M-53
P-1-P-53

Chlorite ⟶ Increasing mixed layering
G-53-53
P-1-P-53
AW-207-54A
AW-207-54B
AW-146-52
P-1-M-53
AW-67-51 (vermiculite?)

Chlorite ⟶ Decreasing thermal stability
G-53-53
P-1-P-53
AW-207-54A
AW-146-52A
P-1-M-53
AW-67-51 (vermiculite?)
AW-207-54B

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Part 12. ASSOCIATION OF URANIUM WITH CARBONACEOUS MATERIALS, WITH SPECIAL REFERENCE TO TEMPLE MOUNTAIN REGION

By Irving A. Breger and Maurice Deul

CONTENTS

ILLUSTRATIONS

TABLES

ABSTRACT

On the Colorado Plateau uranium is associated with coalified wood, crude oil, carbonaceous shale, and carbonaceous matter of unknown origin. Investigations have shown that crude oil plays no role in the emplacement of uranium, although its ability to pick up small quantities of uranium while migrating through uraniferous zones may make oils an aid to general **prospecting. Carbonaceous matter with no cellular structure occurs as impregnations in sandstones or as pellets, and has been chemically related to coal. Tar acid yields, infrared spectra, and differential thermal analyses, as well as ultimate analyses, all indicate that these substances are derived from coal** or coal extracts. The reduction to U(IV) of uranium asso**ciated with coalified wood may take place after absorption of the uranyl ion. Study of a terrestrial shale shows that the uranium is associated with carbonaceous material similar to lignite in chemical composition. From these studies it is concluded that the fundamental association of uranium with carbonaceous material on the Colorado Plateau is with coalified** wood and allied chemical substances.

INTRODUCTION

Coalified plant debris is the most common type of carbonaceous material occurring on the Colorado Plateau. Coal beds are absent in uraniferous zones, but ore-bearing rocks may contain several kinds of carbonaceous matter. Some of these carbonaceous materials are comparable to coals and as such vary in rank from lignite to bituminous. Replacements and impregnations of fossil wood by uranium minerals and by sulfide minerals, as well as by silica and calcium carbonate, are common, and it is not at all surprising that we have found evidence for the migration of extracts of organic material.

An unusual and perhaps unique situation exists in the Temple Mountain area, Emery County, Utah. There, in addition to an association with coalified wood, uranium is associated with crude oil and with carbonaceous substances apparently derived as extracts from coaly material. Because these various kinds of organic matter occur within the same or neighboring mines in the same formation, samples were collected from this area for detailed study to determine the relationship of the uranium to the different carbonaceous materials.

Uranium-bearing carbonaceous shale occurs within the Colorado Plateau near Gallup, New Mexico, and a sample of this shale, which occurs in the Dakota sandstone of Cretaceous age in the Zuni uplift area, was studied in detail.

The carbonaceous substances studied have at various times been known by different names. Some of these names, although applied to substances of then unknown origins, have genetic connotations. "Asphalt" and "asphaltite" are two such terms that have been used to describe hard black impregnations in sandstone, rounded black pellets, viscous crude oil, and even coalified fragments of wood. Use of these terms to describe materials from the Colorado Plateau is misleading, hence this nomenclature has not been applied to such substances in this paper.

Soluble or extractable organic substances are amenable to study by standard physical and chemical techniques such as chromatography, fractional distillation, infrared and ultraviolet absorption analysis, and functional group (—OH, hydroxyl; —CHO, aldehyde; etc.) analysis. When organic material is found to be insoluble in any common solvent, physical and chemical methods of analysis become less effective and interpretation of results less reliable. Furthermore, fine-grained mineral matter is often intimately associated with insoluble carbonaceous material and a problem arises in attempting to separate the organic material by mechanical techniques that result in only minor changes, if any, to its chemical structure and composition.

Of the various carbonaceous materials collected, only the crude oils, occurring as seeps or as impregnations in sandstone, are readily soluble. Because of the relative ease of working with oils they were studied first to determine the relationship of uranium to them and the manner by which uranium is retained by them.

CRUDE OILS

EXPERIMENTAL AND ANALYTICAL DATA

Samples containing crude oil were collected from four operating uranium mines in the Temple Mountain area (table 1). One sample was an oil-impregnated sandstone exposed during mining operations. The other samples were collected from seeps by scraping the oils from mine walls or by chipping portions of the rock through which they were flowing. The viscosity of these oils varied greatly, the most viscous having a taffylike consistency.

TABLE 1.—*Oils collected from mines in the Temple Mountain region, Emery County, Utah*

Source	Description	Collectors
AEC No. 8 mine	Seep through uraniferous zone. Consistency of taffy.	L. R. Stieff and T. W. Stern.
Marsh Bank Canyon mine	Seep through uraniferous zone	A. D. Weeks.
AEC No. 5 mine	Oil seep on mine wall	I. A. Breger and M. Deul.
AEC No. 4 mine	Oil-impregnated sandstone	I. A. Breger and M. Deul.

In the laboratory each oil was first dissolved in benzene to free it from mineral matter. Multiple filtrations of the benzene solution were carried out to make certain that suspended mineral matter was removed from the oil. Benzene was removed from filtered oils by distillation at room temperature and then by freeze-drying. Small samples (approximately 5 g) of the oils were redissolved in 25 to 30 ml of benzene and pure pentane was added to the solutions in the ratio of 40 volumes of pentane per volume of benzene. This mixture was stored overnight at approximately 5° C to precipitate asphaltenes. The chilled solutions were filtered, and the asphaltenes were thoroughly washed with pentane. The filtrate and washings from the asphaltenes were mixed and diluted with pentane to assure complete precipitation of asphaltenes from the oil.

The asphaltenes were vacuum dried for two hours at room temperature and then analyzed for carbon and hydrogen by standard microcombustion techniques. Ash from each analysis was weighed and analyzed for uranium (Grimaldi and others, 1954). Nitrogen and sulfur were determined by combustion analysis. Analytical data for the asphaltenes are shown in table 2. Table 3 summarizes data showing the distribution of uranium in the oils.

TABLE 2.—*Analysis, in percent, of asphaltenes from oils of the Temple Mountain area*

[Analysts: R. T. Moore and E. B. Brittin, U. S. Geological Survey. Asphaltenes isolated by H. M. Ezekiel, U. S. Geological Survey]

	AEC No. 4 mine	AEC No. 5 mine	Marsh Bank Canyon mine	AEC No. 8 mine
Ash	0.34	0.28	1.83	1.07
Uranium	.000147	.0221	.0386	.0922
Carbon	82.21	82.84	82.71	83.31
Hydrogen	7.92	8.44	8.24	9.44
Nitrogen	.98	1.07	.40	1.0
Sulfur	5.7	5.1	5.7	6.3
Oxygen, by difference	3.2	2.5	3.0	-----------

TABLE 3.—*Distribution of uranium in the oils from the Temple Mountain area*

[All data are in percent]

	AEC No. 4 mine	AEC No. 5 mine	Marsh Bank Canyon mine	AEC No. 8 mine
Original oil:				
Uranium	0.0000438	0.00445	0.0137	0.0310
Asphaltenes	22.7	16.2	22.5	27.8
Asphaltenes:				
Uranium	.000147	.0221	.0386	.0922
Ash	.34	.28	1.83	1.07
Uranium in ash	.0432	7.89	2.11	8.62
Uranium in original oil held by asphaltenes	76.2	80.5	63.4	82.6
Uranium in extracted sandstone	.00020	-----------	-----------	-----------

OILS AS TRANSPORTING AGENTS FOR URANIUM

The uranium content of crude oils from nonuraniferous provinces is known to be low. Unkovskaya (1940) has reported from 0.0001 to 0.001 ppm of uranium in naphthenic base oils from Russia and, although these results may be low, an increase by one or even by two orders of magnitude will not make them geochemically significant. Erickson, Myers, and Horr (1954) have also shown that oils from nonuraniferous provinces contain very small quantities of uranium—0.00001 to 0.064 ppm. Because crude oils normally contain extremely small percentages of uranium, it is reasonable to surmise that the oils collected from operating uranium mines on the Colorado Plateau have absorbed uranium during their migration through uraniferous zones.

Variations of from 45 to 310 ppm of uranium in the three oils collected from seeps probably reflect the migratory history of each oil. The uranium content of the oil extracted from impregnated sandstone from the AEC No. 4 mine is somewhat lower than might be anticipated considering the proximity of the oil to the uranium. Here the oil-impregnated sandstone occurs below the ore horizon, and the uranium in the oil (0.44 ppm) may represent only that which came into contact with it through a medium such as ground water. It is possible that the oil in this sandstone was already in place before the introduction of the uranium in the region and has remained static. If this is so, then oil in this sandstone might represent oil that migrated into the Temple Mountain area before the introduction of uranium into the region. Oil collected from seeps would then represent the same oil that had migrated by various paths within the area following introduction of the uranium.

Asphaltenes from crude oils range in sulfur content from 0 to as much as 11 percent (Sachanen, 1945; Mariani, 1951); the asphaltenes isolated from the oils that have been studied in this work contain from 5.1 to 6.3 percent sulfur. This narrow range of variation in sulfur contents suggests that these oils are from the same source.

In the oils that have been studied, 63.4 to 82.6 percent of the uranium is retained in the asphaltenes. Infrared studies of the asphaltenes indicate the existence of functional oxygen-containing groups that may be responsible for the retention of the uranium.

From these results, it is suggested that reconnaissance for uranium might be carried out in uraniferous provinces, such as the Colorado Plateau, by analyzing oils that may occur. Oils found to contain appreciable percentages of uranium might then be used as guides to uranium ore. A factor that must be considered is the unknown migratory course a crude oil may take. Use of an oil as an ore guide would, therefore, be based on the assumption of very limited movement of the oil or other geologic evidence that would indicate the course of migration.

CARBONACEOUS SANDSTONE

EXPERIMENTAL AND ANALYTICAL DATA

The ore-grade sample of carbonaceous sandstone used in this study was collected from the AEC No. 9 mine, Temple Mountain area, Emery County, Utah, by L. R. Stieff and T. W. Stern of the U. S. Geological Survey. The sample was taken from the Moss Back member of the Chinle formation (Triassic). By means of lead-uranium isotope analysis, Stieff and Stern (oral communication) have shown the age of the uranium in an equivalent sample to be not older than 60 million years. In hand specimen the material is black and very dense and yields a faint X-ray powder pattern for uraninite; on being struck, the material emits a petroliferous odor which may have led to its being called an "asphaltite." In thin section the sandstone consists of clean rounded quartz grains. Voids between the grains are filled with black, carbonaceous material. Abraham (1945) describes similar material that, on the basis of physical tests, has been classified as glance pitch.

Soxhlet extraction of 80-mesh carbonaceous sandstone with 1:1 benzene-alcohol dissolved 0.09 percent by weight of the sample. Further treatment of the sample with pyridine, aniline, 6N hydrochloric acid, 5 percent sodium hydroxide, or a pyridine-acetic acid mixture resulted in no further extraction.

Because of the difficulty in performing accurate organic microanalyses on a sample containing 72 percent ash (table 4), it was first necessary to concentrate the organic material. This separation was accomplished by using a technique (Deul, 1956) developed during studies of carbonaceous shales, namely, by ball-mill grinding with a mixture of kerosene and water. Under these conditions organic substances concentrate in the kerosene phase. As shown in table 4, an organic separate containing only 18.01 percent ash was isolated from the carbonaceous sandstone. Each separate was analyzed for ash, carbon, hydrogen, and uranium. Semiquantitative spectrographic analyses of the ashes obtained from the samples are given in table 5 (Waring and Annell, 1953).

TABLE 4.—*Analysis of fractions from carbonaceous sandstone ore*

[Analysts: C. Johnson, A. Sweeney, and E. Brittin, U. S. Geological Survey]

	Ash (percent)	Carbon (percent)	Hydrogen (percent)	Uranium (percent)
Original sample	72.46	20.49	1.53	2.4
Organic separate	18.01	62.63	4.01	1.1
Inorganic separate	95.35	1.92	.35	.63
Organic middlings	83.16	12.69	1.24	1.1
Inorganic middlings	88.38	9.05	1.22	4.9

TABLE 5.—*Semiquantitative spectrographic analyses of ashes from carbonaceous sandstone ore and separates*

[Analyst: C. S. Annell, U. S. Geological Survey]

	Original sandstone	Organic separate	Mineral separate	Organic middlings	Mineral middlings
Ash [1] (percent)	72.46	18.01	95.35	83.16	88.38
U in ash [2] (percent)	3.2	6.1	.66	1.3	5.5
Range (percent):					
>10	Si	Si	Si	Si	Si
5–10					
1–5	U, Al, Fe, V	U, Fe, Al, V	Fe, Al, V	Fe, Al, U, V	Al, U, Ca, Fe, V
0.5–1		Ca	U		
0.1–0.5	Ca, As	As, Na, Mg	Zr, Ca	Ca, As, Mg, Na, Zr	Mg, Na
0.05–0.1	Ba, Mg	Sn, Ba, Zn	Mg, As, Ba	Ba	Ba, As
0.01–0.05	Mn, B, Pb, Ti, Zn	Pb, Mn, B, Ti, Ni, Zr, Cu	Na, Ti, Mn, B, Pb, Zn	Zn, Pb, Mn, Ti, B	Zr, Mn, B, Pb, Ti, Zn, Ni
0.005–0.01	Ni		Ni	Ni, Sn	Sn
0.001–0.005	Sr, Cu, Zr, Y, Sn	Sr, Y	Sn, Y, Sr, Cu	Sr, Cu, Y	Sr, Cu, Y
0.0005–0.001					
0.0001–0.0005	Cr, Ag, Be	Ag, Cr, Be	Cr, Ag	Ag, Cr, Be	Cr, Ag, Be

[1] Data from table 4.

[2] Calculated from data of table 4. Ratio of percent U in each fraction to percent ash in corresponding fraction.

ORIGIN OF CARBONACEOUS MATERIAL IN SANDSTONE ORES

The black, carbonaceous ore bodies of the Temple Mountain region have been known by several names since their discovery, and the terms used have implied genesis from crude oils. Because of the conclusions reached with regard to the association of uranium with crude oil, it was necessary to establish the composition and structure of these carbonaceous materials and their relationship to the oils.

From autoradiographic studies (Stieff and Stern, 1952) to investigate the relationship of uranium to the mineral and organic constituents of the sandstone, the following observations were made:

1. There is no concentration of alpha-particle tracks at boundaries between the carbonaceous material and mineral fragments indicating that uranium is not present in the ore as a coating on the mineral grains.
2. Alpha-particle tracks are dispersed throughout the carbonaceous material with some areas containing greater or lesser concentrations of tracks.
3. Quartz and pyrite grains are practically devoid of tracks. Vanadium minerals show some tracks but not nearly as many as appear in the carbonaceous material.

Because permeable sandstones permit the flow of aqueous solutions, gases, petroleum, or other fluids, it is possible that uranium entered the interstices of the sandstone before the introduction of the organic matter. If this were true, there should be a concentration of uranium on the surfaces of the quartz and other mineral particles. Such evidence is lacking. On the contrary, the dispersion of uranium throughout the organic matter and the fact that the quartz grains are practically devoid of alpha-particle tracks suggest that the uranium and carbonaceous matter entered the sandstone in solution or as a nearly homogeneous suspension. The separation of uranium from the organic matter by fine grinding (table 4) indicates that most of the uranium is not now chemically associated with the organic matter. Had a chemical combination existed, separation has since taken place, perhaps as a result of bond cleavage by the alpha particles.

Recalculation to a moisture- and ash-free basis of the composition of the organic matter isolated by ball-mill grinding shows that the organic matter contains 76.5 percent carbon, 4.9 percent hydrogen, and, by difference, 18.6 percent oxygen, nitrogen, and sulfur. This composition is indistinguishable from that of lignite and suggests that the organic impregnation in the sandstone is derived from a low-rank coal.

The data of table 5 show that the organic separate from the carbonaceous sandstone, as compared to the mineral separate, has been enriched in uranium, tin, copper, beryllium, and possibly arsenic. The same elements are also enriched in the ashes of organic separates from coal as compared to ash of minerals separated from coal (Deul, 1955). The organic separate from the sandstone contains a higher percentage of uranium than does the mineral separate, but both are lower in uranium content than the original sandstone ore.

Vacuum differential thermal analysis (Whitehead and Breger, 1950) provides further evidence that the impregnating organic material is related to coal. Carbonaceous material separated from the sandstone gives a decomposition curve similar to those obtained for low-rank coals (fig. 42) but different from those for such substances as gilsonite, wurtzilite, etc. (fig. 43). As can be seen from figure 42, the shape of the exothermic curves for carbonaceous material from the pellet and from the ore are similar to the shape of the curve for coals between 300° and 500° C (Breger and Whitehead, 1951). The small exothermic peaks at 300° C are superimposed on the general curve and are of unknown origin. The small endothermic peak on the curve for the carbonaceous material from the ore at about 425° C is similarly superimposed on the general curve and is of unknown origin. It is possible that mineral matter may be the source of these small peaks.

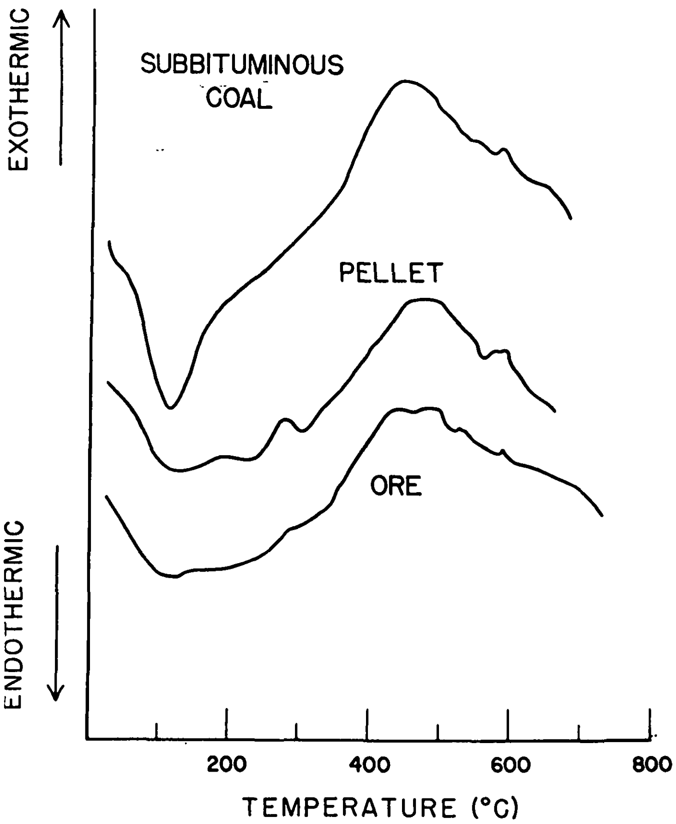

FIGURE 42.—Vacuum differential thermal analysis of carbonaceous material from Utah pellets and ore. The curve for a subbituminous coal is shown for comparison. Small peaks at 575° C are caused by quartz used as an internal standard.

The curves of figure 43 for wurtzilite, gilsonite, and other asphaltites are quite different from the curves for coal.

In figure 44 infrared absorption curves, obtained by R. G. Milkey, are shown for the asphaltenes isolated from an oil of the Temple Mountain region (curve A), for the residual oil following removal of the asphaltenes (curve B), and for the extract isolated from the carbonaceous sandstone by means of Soxhlet extraction (curve C).

In curves A and B the large absorption indicative of saturated carbon-hydrogen bonding (3.4, 6.9, and 7.3 μ) with respect to absorption from aromatic structures (6.3 μ) is important. Curve C, in contrast, shows practically no saturated carbon-hydrogen bonding; the extract has strong absorption in the −OH region (2.9 μ) and is practically wholly aromatic in structure. From this evidence it can only be concluded that the extract from the carbonaceous sandstone cannot be related to petroleum.

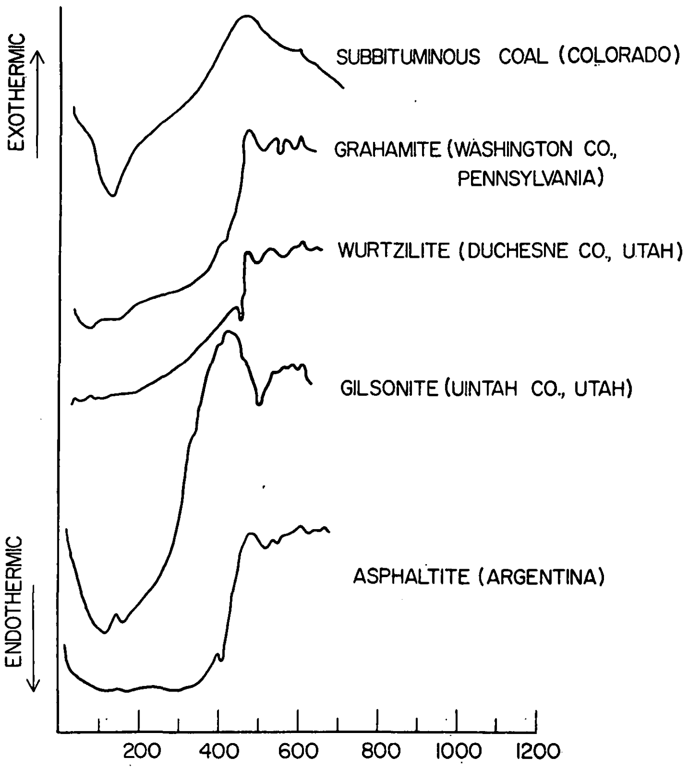

FIGURE 43.—Vacuum differential thermal analysis of asphaltites and related substances. The curve for a subbituminous coal is shown for comparison. Small peaks at 575° C are caused by quartz used as an internal standard. Curves by S. Rubinstein, U. S. Geological Survey.

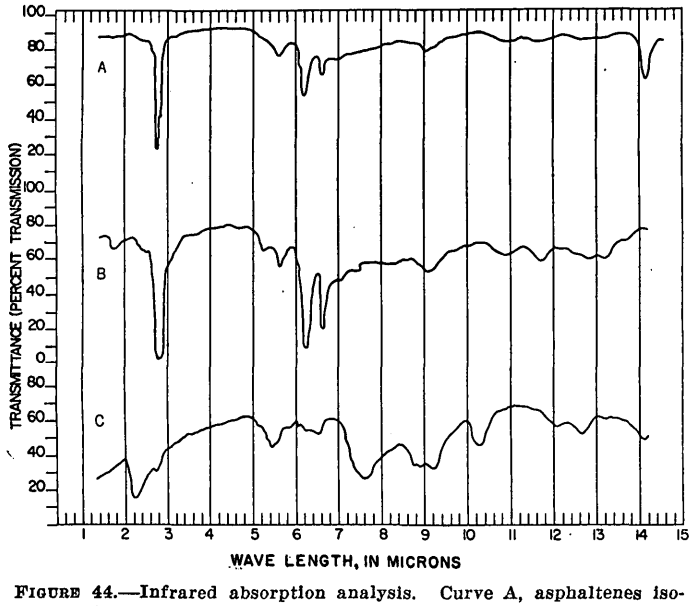

FIGURE 44.—Infrared absorption analysis. Curve A, asphaltenes isolated from a crude oil; curve B, crude oil after removal of asphaltenes; curve C, extract from carbonaceous sandstone. All spectra obtained with material compressed in potassium bromide pellets.

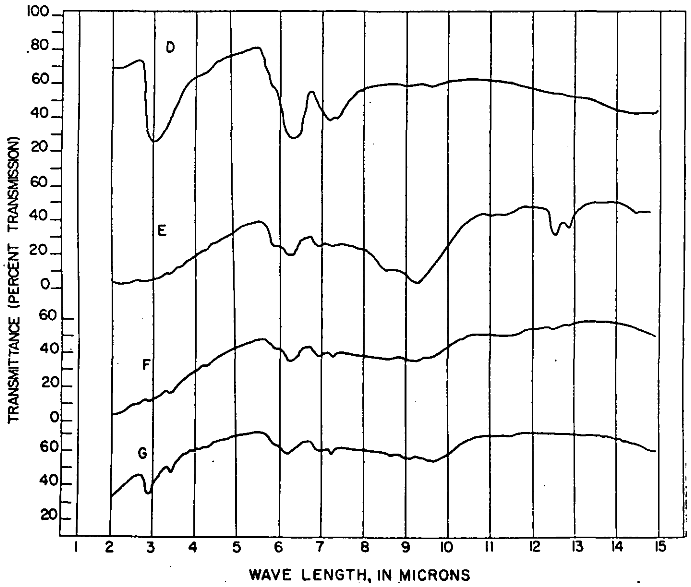

FIGURE 45.—Infrared absorption analysis. Curve D, extract from lignite from South Dakota; curve E, organic separate from carbonaceous sandstone; curves F and G, pellets from Temple Mountain area, Emery County, Utah. All spectra obtained with sample compressed in potassium bromide pellets.

Curve D of figure 45 is the infrared absorption curve for an organic extract obtained from a uranium-bearing lignite (Breger, Deul, and Rubinstein, 1955). The strong —OH absorption, strong aromatic absorption, and absence of appreciable saturated carbon-hydrogen structure are all significant features. Curve E of figure 45 was obtained for the organic isolate from the carbonaceous sandstone. Absorptions in the —OH and aromatic regions, and absence of appreciable absorption in the saturated carbon-hydrogen region provide further strong evidence that the isolate is not related to crude oil but, rather, to coal.

Attempts have been made to establish the origin of the carbonaceous impregnation in the sandstone by other techniques. It has long been known that coals derived from vascular plants have aromatic and phenolic structures that lead to the formation of relatively high percentages of phenolic products (tar acids) on distillation. Other types of coal, such as boghead coal which is mainly derived from algae, have long-chain fatty acid skeletal structures that lead to the formation of much tar but not of much tar acid. The great bulk of carbonaceous substances is derived either from higher plants or from algae, and it is possible to use the composition of tar produced as a clue to the origin of such materials. The technique followed consisted of retorting 3-g samples—using a modification of the technique described by Cuttitta (1953)—collecting the total distillate, and extracting, purifying, and weighing the tar acids. Because tar formation is dependent on rank, the criterion for evaluation is not the total tar acid produced but the percentage of tar acids in the tar. Data obtained are tabulated below:

Sample	*Tar (percent)*	*Tar acids (percent)*
Lignite	2. 33	17. 33
	2. 35	16. 15
	3. 80	20. 50
Average	2. 83	17. 99
Boghead coal	25. 76	2. 87
	26. 58	1. 57
	24. 77	1. 85
Average	25. 70	2. 10
Organic isolate from ore from AEC No. 9 mine	0. 41	86. 10
	. 34	42. 60

Stadnikoff (1930) suggested that coals such as lignite should yield 15 to 50 percent of tar acids, while bogheads and other substances mainly of algal origin should yield less than 5 percent of tar acids. The experimental data for the lignite and boghead coal fit the pattern suggested by Stadnikoff. The yields of tar acids from the isolate from the carbonaceous sandstone are high, indicating that this material was derived from vascular plants. Considering the small amounts of sample available for this work and the low yields of tar, better check data for tar acids are not to be expected.

Based on the analytical data, a possible explanation for the accumulation of uranium in the carbonaceous sandstones of the Temple Mountain region is that aqueous solutions carrying organic material extracted from low-rank coals in the region, along with uranium and vanadium, may have saturated the pores of the sandstone. Eventually the organic matter was devolatilized and converted to its present insoluble state, perhaps radiochemically.

CARBONACEOUS PELLETS

EXPERIMENTAL AND ANALYTICAL DATA

Pellets of black carbonaceous material, ranging from several millimeters to several centimeters in diameter, occur in certain strata of a sandstone unit (the Moss Back member) of the Chinle formation at Temple Mountain. In places these rounded masses merge with the carbonaceous material that impregnates sandstone. Gruner (oral communication) and Stieff and Stern (oral communication) have reported that some of the carbonaceous material replaces clay balls imbedded in sandstone. The carbonaceous material of the pellets also corrodes some of the quartz grains with which it comes into contact.

Pellets for this study were collected at three sites: the Rex No. 2 mine, the AEC No. 4 mine, and the AEC No. 8 mine, all in the Temple Mountain region, Emery County, Utah. Because many of the pellets were extremely small and weighed less than 100 mg each, detailed work on individual pellets has been limited.

Six pellets from a suite collected in the AEC No. 4 mine were selected on the basis of their specific gravities, which ranged from 1.29 to 1.56. One pellet from the AEC No. 8 mine was chosen because of its rather large size and its relatively high specific gravity. The specific gravity of the pellet from the Rex No. 2 mine was determined to be 1.38±0.02. Analyses of these pellets are given in table 6.

Spectrographic analysis of ash (6.94 percent) from the pellet from the Rex No. 2 mine is shown in table 7.

TABLE 6.—*Analytical data, in percent, for carbonaceous pellets from the Temple Mountain region, Emery County, Utah*

[Carbon, hydrogen, oxygen, nitrogen, and sulfur determined on a moisture- and ash-free basis]

Mine	Specific gravity	Ash	Carbon	Hydrogen	Oxygen, nitrogen, and sulfur	Uranium in original pellet
AEC No. 4	1. 29	6. 61	80. 2	7. 54	12. 26	0. 038
	1. 34	9. 13	80. 8	6. 52	12. 68	2. 54
	1. 38	10. 77	81. 4	5. 18	13. 42	2. 96
	1. 43	15. 88	79. 7	6. 12	14. 20	2. 44
	1. 57	19. 15	78. 7	6. 08	15. 22	2. 51
	1. 56	8. 26	77. 7	6. 20	16. 10	1. 67
Rex No. 2 [1]	1. 38	6. 94	76. 1	4. 93	18. 97	2. 77
AEC No. 8 [2]	1. 63	9. 72	76. 3	5. 53	18. 17	1. 68

[1] Collected by L. R. Stieff and T. W. Stern, U. S. Geological Survey.
[2] Collected by T. Botinelly, U. S. Geological Survey.

TABLE 7.—*Semiquantitative spectrographic analysis of ash from carbonaceous pellet from Rex No. 2 mine*

[Analyst: Helen Worthing, U. S. Geological Survey]

Percent	*Elements*
>10	U
5–10	Si
1–5	Al, Fe, V, Ca
0.5–1	As, Pb
0.1–0.5	P, Mg, Y, Ba, Ti
0.05–0.1	B, Ce, Sr, Nd
0.01–0.05	Zn, Mn, Ni, Pr, Dy, Er, Yb, Gd, Cr, Co
0.005–0.01	Zr, La, Cu, Sn
0.001–0.005	Sc, Ho, Lu
0.0005–0.001	Be

ORIGIN OF CARBONACEOUS PELLETS

The origin of carbonaceous pellets occurring in the Temple Mountain region has been a subject for speculation for some time. Abraham (1945) states, "The asphaltite is characterized by the fact that it carries uranium and vanadium, which are assumed to have been incorporated in it during its migration from the underlying strata, thereby hardening the asphaltite and "fixing" it in the present associated rocks." Others have since extended the hypothesis that the material has been derived from petroleum.

With obvious exceptions, examination of the data of table 7 reveals certain trends: (1) ash rises with specific gravity; (2) carbon and hydrogen both decrease with specific gravity; and (3) the total of oxygen, nitrogen, and sulfur rises regularly with specific gravity. There does not appear to be any specific relationship between uranium and any of the other components or properties of the pellets.

In figure 46 data have been plotted for a number of carbonaceous pellets and other substances collected from the Colorado Plateau. Represented are analyses of pellets (table 6), analysis of the carbonaceous material isolated from the carbonaceous sandstone (table 4), analysis of vitrain (table 10), and analyses of four samples of vitrain from the Corvusite mine, Grand County, Utah (tables 12 and 13). The dashed lines enclose an area in which most normal mined coals occur (Lowry, 1945). The deviation from this area for a coal that has been subjected to mineralization is clearly shown. Analyses for the pellets all fall close to or within the normal coal curve strongly suggesting that these materials are related to coal in origin. This conclusion has been confirmed by the differential thermal analysis of one pellet from the region (fig. 42). Infrared curves F and G of figure 45, moreover, show the material to be related structurally to coal and not to have the characteristics generally found in crude petroleum or its fractions. The evidence points to the materials as being coaly in nature.

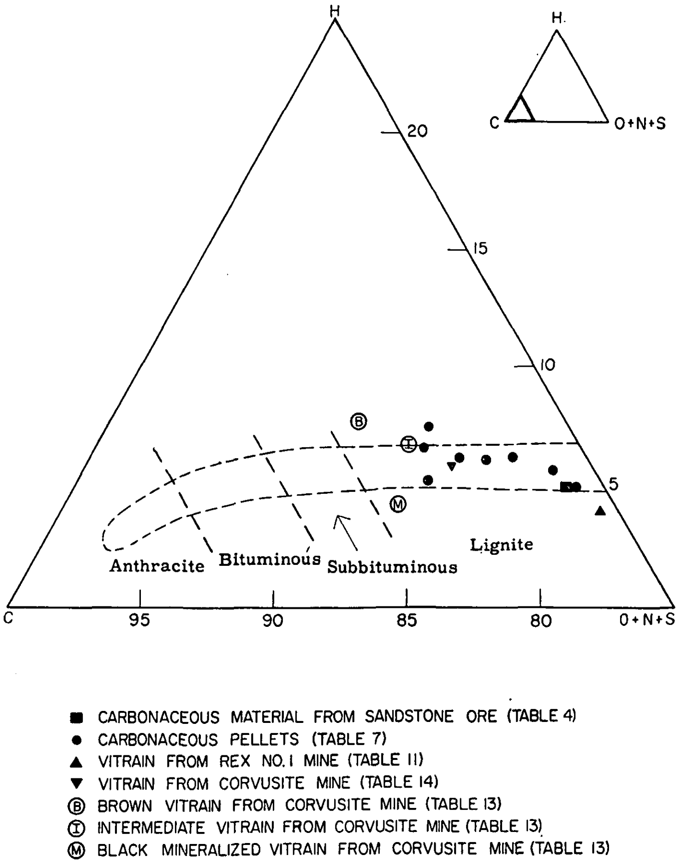

FIGURE 46.—Plot of analyses of carbonaceous materials from the Colorado Plateau on a standard coal curve. All analyses on moisture- and ash-free basis. Dashed lines enclose average analyses of most mined coals.

The occurrence of pyrite in the pellets indicates that they have not been subjected to appreciable oxidation. In view of this fact, it is not believed that the relatively high oxygen content of the pellets can be explained as resulting from oxidation of carbonaceous material of petroliferous origin.

Spectrographic analysis of the ash from the pellet from the Rex No. 2 mine (table 7) has shown the presence of 10 of the 15 rare earths. This is in contrast to analyses of petroleum ash (Erickson, Myers, and Horr, 1954) which normally show the presence of only the more abundant and more easily detectable rare earths. Sodium, on the other hand, should appear in the analysis of the ash if the pellet were derived from petroleum (Erickson, Myers, and Horr, 1954). These data may be interpreted as signifying a nonmarine and therefore, a nonpetroliferous origin for the pellets.

CARBONACEOUS SHALE

EXPERIMENTAL AND ANALYTICAL DATA

Although uranium-bearing carbonaceous shales are quantitatively unimportant on the Colorado Plateau, a shale from the Zuni uplift area of New Mexico was studied to determine the relationship of the uranium to the carbonaceous material. The section of the Dakota sandstone containing the carbonaceous shale is reported to have been deposited marginal to the sea. In contrast to marine shales, these stream and lagunal sediments are essentially terrestrial, exhibiting braided stream deposits and paleostream channels (Mirsky, 1953). Shale for this study was collected by T. W. Stern. Mineral and organic fractions were separated and concentrated by the ball-mill technique that has already been mentioned.

Table 8 gives the analytical data for carbon, hydrogen, ash, and uranium for the original shale and for

TABLE 8.—*Analysis, in percent, of carbonaceous shale collected from Dakota sandstone in Zuni uplift area, New Mexico, and of separates from shale*

[Analysts: H. Levine and R. T. Moore, U. S. Geological Survey]

	Ash	Carbon	Hydrogen	Uranium
Original sample	76.22	12.97	1.62	0.091
Organic separate	30.21	48.47	[1] 2.98	.41
Mineral separate	89.68	.81	[1] 1.60	.0051
Middlings	67.85	13.90	[1] 2.25	.12

[1] High hydrogen values caused by hydration of shales during milling.

the separates. The results of the spectrographic analyses of the ashes of the same samples are shown in table 9.

TABLE 9.—*Semiquantitative spectrographic analyses of ash of orignial shale sample from Dakota sandstone and of ash of separates*

[Analysts: Mona Franck and K. Valentine, U. S. Geological Survey]

Sample	Original sample	Organic concentrate	Mineral concentrate	Middlings
Ash [1]	76.22	30.21	89.68	67.85
U in ash [2]	.12	1.35	.0057	.18
Range:				
>10	Al, Si	Al, Si	Al, Si	Al, Si
5-10	---	---	---	---
1-5	Ti, K	Ca	---	Ca, K, Fe
0.5-1	Fe, Ca, Mg	Fe, K, Ti, Mg	K	Mg
0.1-0.5	---	Ba, Na	Ca, Fe, Mg, Ti, Na	Ti, Na
0.05-0.1	Na, Ba, V	Cu, Sr, Ce, Pb	Ba, Zr	Zr, Ba, Sr
0.01-0.05	B, Pb, Zr, Co, Sr	Zr, V, Zn, B, Co, Mn, Cr, La, Ni, Y	Sr, B, Zn	Pb, B, Cu, Cr, Mn
0.005-0.01	Cu, Ni, Cr, La, Y	Ga	Cr, Ni, V	Ga, Ni, V, Y, Co, Mo
0.001-0.005	Ga, Mn, Mo	Sc, Sn, Yb, Ag, Mo	Y, Ga, Pb, Cu, Mn, Mo, Co, Sc	La, Sn, Sc
0.0005-0.001	Sc, Be, Yb	Be	---	Yb
0.0001-0.0005	---	---	Yb, Ag, Be	Be, Ag
0.00005-0.0001	---	---	---	---
0.00001-0.00005	Ag	---	---	---

[1] Data from table 8.

[2] Calculated from data of table 8. (Ratio of percent U in each fraction to percent ash in corresponding fraction.)

SIGNIFICANCE OF URANIUM-ORGANIC ASSOCIATION IN CARBONACEOUS SHALE

The shale from the Dakota sandstone yielded a mineral fraction which contained only about 1 percent organic matter, whereas the organic concentrate showed a fourfold enrichment of carbonaceaus material (table 8). The direct association of uranium with organic material is shown in the analyses for uranium where the organic concentrate has a fourfold enrichment of uranium over that in the original sample and an eightyfold enrichment of uranium over that in the mineral concentrate. It is not at all unlikely that most of the uranium in the mineral fraction is associated with organic matter remaining with the mineral matter.

Spectrographic analyses of the fractions (table 9) show that the organic concentrate, with respect to the original shale, is enriched in uranium, cerium, tin, copper, manganese, silver, and ytterbium. In addition, the organic concentrate, as compared with the mineral separate, is enriched in lanthanum, cobalt, lead, and calcium. With the exceptions of calcium and silver, it has been shown that the minor and trace elements concentrated in the organic fraction are similar to the elements concentrated in organic separates from coal (Deul, 1955).

The analysis of this sample for carbon and hydrogen, when calculated on an ash-free basis (carbon, 69.5 percent; hydrogen, 4.3 percent), shows that, although too low in carbon content to fall on the coal curve as plotted in figure 46, the composition of the material is in the proper range for a lignite. The data, when considered in the light of the geologic interpretation for this deposit as given by Mirsky (1953), provide strong evidence that the uranium in the shale is associated with carbonaceous material similar to coal in composition. Observation of plant casts in the shale during recent field studies has confirmed this conclusion.

COALIFIED WOOD

EXPERIMENTAL AND ANALYTICAL DATA

The association of uranium with coalified wood on the Colorado Plateau is universally recognized. Extensive studies conducted on uraniferous coals from other regions (Breger, Deul, and Rubinstein, 1955) have demonstrated the nature of the association of uranium with the coal substance. It was felt that our present studies could best be directed toward carbonaceous substances about which little was known, hence only few samples of coalified wood have been studied.

Although coalified wood from the Colorado Plateau has not yet been investigated in detail, hand-picked vitrain from a coalified log taken from the Rex No. 1 mine, Temple Mountain region, Emery County, Utah, was submitted to the U. S. Bureau of Mines for standard coal analysis. On the basis of data shown in table 10, the equivalent rank of this coal is subbituminous C. The uranium content of the coal is 7.54 percent, and X-ray diffraction patterns have weak lines indicating the presence of uraninite. Table 11 gives the semiquantitative spectrographic analysis of the ash from the vitrain. The radioactivity of fusain in contact with the vitrain is extremely low.

A small sample of coalified wood was collected in 1952 from the Corvusite mine, Grand County, Utah, by Alice D. Weeks of the U. S. Geological Survey.

TABLE 10.—*Analysis of coalified wood from Rex No. 1 mine*

[Analyses by U. S. Bureau of Mines, Lab. No. E-61765, Jan. 26, 1955]

	As received	Moisture free	Moisture and ash free
Proximate analysis (percent):			
Moisture	2.6	---	---
Volatile matter	24.2	24.8	32.2
Fixed carbon	50.9	52.3	67.8
Ash	22.3	22.9	---
Ultimate analysis (percent):			
Hydrogen	3.3	3.1	4.0
Carbon	56.8	58.3	75.6
Nitrogen	.1	.1	.2
Oxygen	8.9	6.8	8.8
Sulfur	8.6	8.8	11.4
Ash	22.3	22.9	---
Forms of sulfur (percent):			
Sulfate	.07	.07	.09
Pyritic	1.04	1.07	1.39
Organic	7.45	7.65	9.92
British thermal units	10,210	10,480	13,600

TABLE 11.—*Semiquantitative spectrographic analysis of ash from vitrain from the Rex No. 1 mine*

[Analyst: Mona Franck, U. S. Geological Survey]

Percent	*Elements*
>10	U, V
5–10	------
1–5	Si, Pb, Ca
0.5–1	Al, Fe
0.1–0.5	Zn
0.05–0.1	Ba, Nd, La, Cu
0.01–0.05	B, Ti, Y, Mg, Mn
0.005–0.01	Sr, Co, Dy
0.001–0.005	Cr, Ag, Sc, Zr
0.0005–0.001	------
0.0001–0.0005	Be

Note.—Na obscured by high Zn; K obscured by high U; Yb obscured by high V.

This sample of vitrain, about 2 inches long, graded longitudinally from brown at one end to black at the other end. The black end was highly mineralized. Analytical data for this sample are given in table 12.

TABLE 12.—*Analysis, in percent, of coalified wood fragment from Corvusite mine, Grand County, Utah.*

[Analysis on dry basis. Analysts: Jesse J. Warr, Jr., and Robert Meyrowitz, U. S. Geological Survey]

Description	Ash	Carbon [1]	Hydrogen [1]	Uranium	Atomic ratio (C:H)
Brown vitrain	3.01	82.7	7.7	0.057	0.90
Intermediate vitrain	.64	81.3	6.7	.0018	1.00
Black, highly mineralized vitrain	22.46	83.0	4.2	6.63	1.64

[1] Ash-free basis.

Another sample of coalified wood from the Corvusite mine consisted of vitrain and fusain, analyses for which are given in table 13.

TABLE 13.—*Analysis, in percent, of coalified wood from Corvusite mine, Grand County, Utah*

[Analysis on dry basis. Analysts: Jesse J. Warr, Jr., and Robert Meyrowitz, U. S. Geological Survey]

Description	Ash	Carbon [1]	Hydrogen [1]	Uranium
Vitrain	13.06	80.1	5.8	2.28
Fusain	2.04	94.4	2.8	.0038

[1] Ash-free basis.

ROLE OF COALIFIED WOOD IN URANIUM FIXATION

The samples studied probably represent in rank most of the coalified wood in the region. The hand-picked vitrain from the Rex No. 1 mine has an extremely high content of organic sulfur for which no explanation can as yet be made. The presence of a very high concentration of zinc, of high copper, of cobalt in concentrations greater than nickel (table 11), and the unusually high sulfur content of the coal are undoubtedly related to the mineralization of the sample.

Examination of the analytical data shows that where vitrain is in contact with fusain, the vitrain contains the uranium. Fusain—mineral charcoal—is chemically inert and would not, therefore, be expected to contain chemically bound uranium. Vitrain, on the other hand, is chemically reactive because it contains functional groups which are capable of combining with uranium. The data of table 12 illustrate variations in carbon-hydrogen ratios that exist within a single specimen of vitrain. When the data for vitrain shown in tables 10, 11, and 12 are plotted in figure 46, only one of the points falls within the normal coal range as defined on the graph. This coal range is based on analyses of coals composed of vitrain, fusain, and other coal ingredients. Vitrain normally contains more hydrogen than do other major coal ingredients, while fusain contains less. It is not possible to determine from the few data available whether there is a direct relationship between increasing uranium content and decreasing hydrogen content in vitrains, but we suspect that this is so.

A hypothesis has been proposed that ground-water solutions bearing alkaline or alkaline-earth uranyl carbonates introduced uranium into coals; in acid environment below a pH of 4.5 such complex compounds decompose and release uranyl ions (UO_2^{++}) which are made available for the formation of ionic uranyl organic compounds, insoluble above a pH of about 2.2 (Breger, Deul, and Meyrowitz, 1955).

It is not known whether the uranium associated with coalified wood on the Colorado Plateau was introduced as the uranous ion, which was directly absorbed, or whether the uranyl ion was reduced by the carbonaceous material upon or subsequent to absorption. Both degraded wood and subbituminous coal can reduce the uranyl ion to uraninite under laboratory conditions (Breger and Moore, written communication, 1955). Mechanisms are known that would permit the retention of uranium by coal, coalified wood, or related substances regardless of the state of oxidation of the uranium in the ore solution.

SUMMARY AND CONCLUSIONS

Studies of the carbonaceous materials from the Colorado Plateau lead to several conclusions:

1. The crude oil that occurs in seeps in the operating mines seems to have no effective role in the emplacement of uranium. The association of uranium with oil results from the ability of oil to pick up and carry small quantities of the element. The association of crude oil with the other carbonaceous substances in the Temple Mountain region is fortuitous—the result of geological conditions which permit the flow of crude oil through strata containing uranium and vanadium. The ability of crude petroleum to pick up small quantities of uranium may make oils an aid to geochemical prospecting.

2. The carbonaceous material associated with the sandstone ore that we have studied is apparently derived from plant material that has been coalified, or from the low-rank coals of the region. It is possible that uranium- and vanadium-bearing solutions extracted organic matter from degraded plant debris in the sediments and that the mixture of carbonaceous material, uranium, and vanadium was subsequently deposited in porous sandstones. The present insolubility of the carbonaceous matter may be the result of cross-linkage of coal molecules caused by irradiation by the alpha particles from the uranium and its daughter products.
3. The carbonaceous pellets are believed to have much the same origin as the carbonaceous material that is impregnating the sandstone ore. Some samples of sandstone ore show impregnations of carbonaceous material that appear to coalesce into peletal groups replacing sandstone, and the rank of the materials, as reflected by their composition, is similar. Discussion of the mechanics of such replacements is beyond the scope of this paper.

   The carbonaceous pellets are by no means uniform and it is not at all surprising that this is so. Plant materials and coals vary in composition and type, and migrating solutions or dispersions of colloidal material derived from coal could not be expected to be uniform in composition. Analyses have shown that coals from the Colorado Plateau can deviate more from the normal coal curve than do the carbonaceous pellets. This is illustrated in figure 46.
4. The direct association of uranium with carbonaceous material separated from the shale from the Dakota sandstone is further evidence of the potency of certain kinds of carbonaceous material for the fixation of uranium. That this particular shale is of terrestrial rather than of marine origin supports the conclusion that the organic material separated from the shale is related to lignite.
5. Coalified fragments of wood and coalified logs are the most abundant carbonaceous materials on the Colorado Plateau. We have shown that many of the carbonaceous materials that are of unknown origin or that have been considered to be of petroliferous origin have probably been derived from woody or coaly material. Insofar as carbonaceous materials are concerned, on the Colorado Plateau as well as in the Dakotas, in the Red Desert area of Wyoming, and in the Fall Creek area of Idaho (Vine and Moore, 1952), coal and humic materials related to coal are the major controls for the fixation of uranium.

Based on available evidence, it appears that the fundamental association of uranium with carbonaceous materials on the Colorado Plateau is with coalified plant debris and allied chemical substances.

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Part 13. RADIUM-URANIUM EQUILIBRIUM AND RADIUM-URANIUM AGES OF SOME SECONDARY MINERALS

By T. W. STERN and L. R. STIEFF

CONTENTS

ILLUSTRATION

TABLES

ABSTRACT

Ten samples of carnotite and metatyuyamunite ore that contain more than 0.1 percent lead have been analyzed for uranium, Ra^{226}, and lead. Seven contain less than the equilibrium amount of Ra^{226} for the uranium present, and three are in radioactive equilibrium within the limits of experimental error. Radioactive equilibrium between U^{238} and Th^{230} is effectively established in 500,000 years, therefore the seven radium-deficient minerals have been altered within that time span. The remaining three samples have not lost Th^{230} by alteration within the last 500,000 years or Ra^{226} within the last 15,000 years. An approximate lead-uranium age can be determined from these lead-bearing minerals if they have not been significantly leached of lead or uranium.

Carnotite and metatyuyamunite that have formed on joints and fractures are low in lead (less than 0.01 percent) and appear from field relations to be of recent origin. These coatings are local concentrations formed after the water table was lowered and the deposits were oxidized. If these minerals are not now in radium-uranium equilibrium, did not contain Th^{230} and Ra^{226} at the time of their deposition, and have not been further altered by selective leaching or enrichment of radium, Th^{230}, or uranium, their time of formation can be established. Radium-uranium ages determined on five Colorado Plateau secondary minerals range from approximately 10,000 to 120,000 years.

Radiocolloids, local concentrations of radium and its daughter products, which persist for only about 15,000 years, are present in some oxidized ores.

INTRODUCTION

The primary vanadiferous uranium ores of the Colorado Plateau are characterized by their black color. Low-valence vanadium and uranium minerals as well as iron, copper, lead, and zinc sulfides, arsenides and selenides are present. Uraninite and coffinite are associated with carbonaceous materials; vanadium is present in montroseite and in vanadium silicates. Pyrite and marcasite are abundant.

Oxidation of the uranium deposits probably took place when the water table was lowered. Ores exposed to the air oxidize rapidly and a highly variable and complex mineral suite results (Part 5 of this volume). Vanadium minerals oxidize from vanadium (III) to vanadium (IV) and (V) minerals and uranium minerals oxidize from uranium (IV) to (VI). When the uranium is in the sexivalent form it is relatively soluble and free to migrate unless precipitated by complexing with vanadium. Many samples of ore containing carnotite and tyuyamunite (or metatyuyamunite) which were formed in place give Pb^{206}/U^{238} ages comparable to the unoxidized ores because there was no opportunity for the uranium or the elements derived from the decay of the uranium to become separated. Some deposits, however, have been leached both during and after oxidation, the uranium and vanadium having migrated relative to Th^{230}, Ra^{226}, and radiogenic lead. A criterion of such movement of uranium and vanadium would be the redeposition of carnotite or metatyuyamunite on joints and fractures containing essentially no radiogenic lead. In other cases, daughter products may be moved and the uranium and the radiogenic lead remain in place. Presence of radium-uranium disequilibrium in ores oxidized in place is another measure of migration of radioactive daughter products during the past 500,000 years.

A. M. Sherwood and R. G. Milkey of the U. S. Geological Survey made the chemical analyses for uranium and lead. R. G. Rice and W. A. Peavy, Jr., of the National Bureau of Standards, and John Rosholt of the Geological Survey measured the radium content of our samples.

OCCURRENCE OF CARNOTITE, TYUYAMUNITE, AND METATYUYAMUNITE

Several distinct occurrences of carnotite, tyuyamunite, and metatyuyamunite can be observed in the field and laboratory. These occurrences are:

1. Secondary uranyl vanadates locally replace woody material such as branches and trunks of trees and "trash piles" of organic material. Some of these occurrences are very rich in uranium and samples with as much as 35 percent uranium may be obtained with little purification. Cellular structure of these woody materials is no longer visible in thin sections although in the field the general treelike shape is still evident. Age determinations by the lead-uranium method of this type of occurrence of carnotite, tyuyamunite, and metatyuyamunite as a rule give Tertiary ages but not Quaternary ages.
2. Some of the secondary uranium minerals from the Colorado Plateau impregnate clay pebbles of various sizes and shapes. These clay pebbles are of varying uranium content and some are very high grade. These occurrences, in general, give lead-uranium ages no older than Late Cretaceous but not as young as Quaternary.
3. A large portion of the secondary ore is disseminated in sandstone. These ores are believed to be the result of oxidation essentially in place accompanied or followed by some leaching. The lead-uranium ages of these samples are variable.
4. Coatings of carnotite and tyuyamunite or metatyuyamunite on joints and fractures are relatively rare and make up a very minor amount of the secondary uranium ores of the Plateau. The geologic evidence indicates they are of Quaternary age.

RADIUM-URANIUM EQUILIBRIUM

CONDITIONS FOR EQUILIBRIUM

Radium-uranium equilibrium is established when the rates of radium formation and decay are equal. Ninety-nine percent of radium-uranium equilibrium is attained in approximately 500,000 years (Knopf, 1931, p. 110) assuming Th^{230} was not present at the time of deposition. The isotopes of uranium, U^{235} and U^{238}, decay through two series of radioactive nuclides to the radium isotopes, Ra^{223} and Ra^{226}, respectively, which in turn decay through a number of radioactive nuclides to the stable end products Pb^{207} and Pb^{206}, respectively. The contribution of the actinium series (U^{235}) to the radium content in the samples is negligible and therefore, this series will not be considered in the discussion that follows. Figure 1 is a curve of the age in years plotted against percent Ra^{226} and U^{238} equilibrium for the range 10,000 to 500,000 years.

If a uranium mineral contains less radium than required by the equilibrium ratio 3.32×10^{-7} g Ra^{226}/g U^{238}, two explanations are possible:

1. The mineral has been unaltered since deposition, and its age is less than 500,000 years.
2. The mineral has been influenced by selective leaching of Ra^{226}, Th^{290}, or enrichment of uranium, or all three, and the radium-uranium age of the mineral is indeterminate but the leaching or enrichment has taken place within 500,000 years.

Only those samples with essentially no radiogenic lead can be given meaningful radium-uranium ages, for the absence of such lead is the clue that uranium in these samples has migrated away from its former location. In addition it must be assumed that all the Th^{230} and Ra^{226} present has been produced since the redeposition of the uranium. Finally, the geologic evidence for lack of post-mineral leaching must be established.

In pyritic environments uranium ores can also depart from equilibrium in the direction of a large excess of radium caused by preferential leaching of uranium (Phair and Levine, 1953, p. 358). However, to the authors' knowledge large excesses of radium are uncommon in the various occurrences of secondary minerals from the Plateau, suggesting that this type of alteration is unusual.

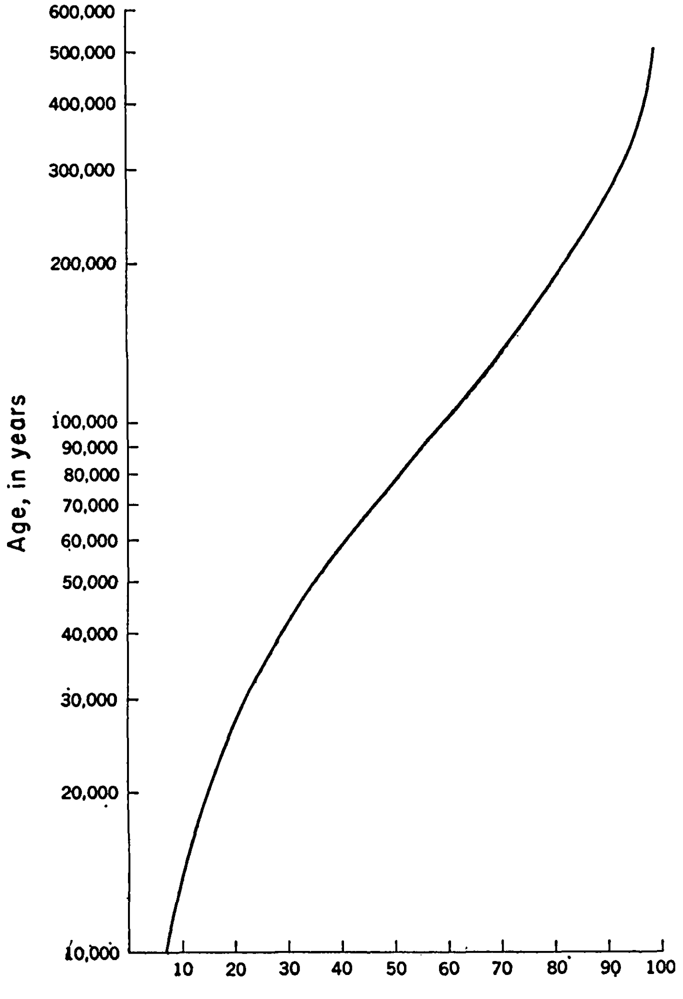

FIGURE 47.—Age in years as a function of percent radium-uranium equilibrium.

PREVIOUS WORK

In the study of the variation of the radium-uranium ratio in minerals other than pitchblende, Boltwood (1904, 1908) and McCoy (1904, 1905) found that carnotite did not show any abnormalities. Mlle. Gleditsch (1911) and Marckwald and Russell (1911a, p. 771; 1911b) found, however, that small samples of carnotite were appreciably deficient in radium.

Lind and Whittemore (1915) have published the only detailed study of the radium-uranium ratio in Colorado Plateau carnotite. They found that in samples of a few hundred pounds to several tons the ratio was in agreement with that of pitchblende, whereas small samples of a few pounds or less exhibited abnormal ratios. In one small sample the ratio was 25 percent deficient and in another 39 percent in excess of the normal ratio for pitchblende. The fact that abnormal radium-uranium ratios, both high and low, occurred in samples representative of small quantities of ores, and that all samples from bulk specimens of ores showed normal radium-uranium ratios, was interpreted as an indication of local reconcentration of radium within the ore body rather than removal of the radium by leaching.

RADIUM CONTENT OF UNOXIDIZED URANIUM ORES

It is reasonable to expect that samples of massive, unleached uraninite would be essentially in radium-uranium equilibrium. At the present time, however, only two samples of unoxidized Colorado Plateau uraninite have been examined indirectly for their radium-uranium ratio. Senftle, Stieff, Cuttitta, and Kuroda (1957) have determined that the Ra^{223}/Ra^{226} activity ratio for samples of uraninite from the Happy Jack mine and Mi Vida mines, San Juan Co., Utah to be 0.048. This agrees with the value of 0.048 for the Ra^{223}/Ra^{226} activity ratio determined by Kuroda for Great Bear Lake uraninite which is in radioactive equilibrium. For samples of secondary minerals from the Colorado Plateau, Kuroda (1954, p. 10) determined Ra^{223}/Ra^{226} activity ratios of from 0.0441 to 0.131. He interpreted this variation as a variation in the U^{235}/U^{238} ratio. However, mass spectrometric analyses of the uranium present in a selected group of secondary Colorado Plateau samples do not show any variation greater than 0.8 percent in the U^{235}/U^{238} ratio (Senftle, Stieff, Cuttitta, and Kuroda, 1957). The variation in the Ra^{223}/Ra^{226} activity ratio is here interpreted to be the result of recent preferential leaching of daughter elements during oxidation and is a consequence of the relatively shorter time required for Ra^{223} compared to Ra^{226} to return to radioactive equilibrium.

RADIUM CONTENT OF OXIDIZED URANIUM ORE

Of the 10 samples of oxidized uranium ore tabulated in table 1 containing more than 0.1 percent lead, 7 are deficient in radium when compared with the equilibrium amount. Three of the samples are in equilibrium within experimental error. As these 10 samples contain radiogenic lead they should not be dated by the radium-uranium method. These radium analyses are consistent with those reported for small samples by Lind and Whittemore (1915) and those reported by Gleditsch (1911).

As a rule, the near-surface occurrences of metatyuyamunite and carnotite have the greatest radium deficiencies. However, even samples collected from underground occurrences may show large radium deficiencies. For example, samples from the Club mine (Nos. 61, 62, and 63) were collected within 30 feet of each other and have essentially the same Pb^{206}/U^{238} age of about 70

TABLE 1.—*Radium-uranium content of some high-grade lead-bearing carnotite and metatyuyamunite samples*

Sample No.	Type of occurrence [1]	Locality	Mineral	Average U (percent)	Theoretical g Ra/g sample [2] $(\times 10^{-8})$	Experimental g Ra/g sample [3] $(\times 10^{-8})$	Percent radium-uranium equilibrium
9	2, 3, 4	Monument No. 2 mine, Apache County, Ariz	Metatyuyamunite	37.9	12.6	7.62	60
13	2	Jo Dandy mine, Montrose County, Colo	Carnotite	31.1	10.3	8.53	83
19	2, 3	Radium No. 6 mine, San Miguel County, Colo	Metatyuyamunite	21.7	7.20	7.36	2 excess
20	2, 3	do	Carnotite	32.6	10.8	11.3	5 excess
25	2	Calamity No. 13 mine, Mesa County, Colo	do	32.5	10.8	10.6	98
28	2	do	do	36.0	12.0	11.1	92
61	2	Club mine, Montrose County, Colo	do	32.2	10.7	8.64	81
62	1	do	do	14.8	4.91	1.78	36
63	2	do	do	25.4	8.43	7.19	85
64	2, 3	Bob Tail mine, Montrose County, Colo	do	34.6	11.5	8.45	73

[1] These numbers refer to the numbers given under the heading "Occurrence of carnotite, tyuyamunite, and metatyuyamunite" on p. 152.

[2] Computed from g Ra/g U in equilibrium$=3.32\times 10^{-7}$ g Ra/g U.

[3] Prepared for analysis by R. G. Rice and counted under direction of L. S, Stockman, National Bureau of Standards.

Sample 9.—Shinarump member of the Chinle formation. The sample was collected from a freshly blasted face of the open cut. The tyuyamunite and metatyuyamunite are found as coatings on the joints and fractures, as disseminated material in the sandstone and conglomerate, in thin veins of very pure material, and as tyuyamunite and metatyuyamunite replacements of clay pebbles. The sample was covered by a minimum of 6 to 10 feet of sandstone and probably was protected from extreme weathering.

Sample 13.—Salt Wash sandstone member of the Morrison formation. Sample 13 was taken from a small pocket of very high grade carnotite with corvusite approximately 140 feet inside the portal of the lower haulage adit. The field relations of sample 13 strongly suggest that the mineralizing solutions were controlled by a small joint. In comparison to the Jo Dandy mine sample given in table 2, this sample is well protected from the effects of weathering.

Samples 19 and 20.—Salt Wash sandstone member of the Morrison formation. Sample 19 was collected from a pillar at the mine portal and should be representative of the effects of moderate weathering. The metatyuyamunite occurs as a clayey seam as much as 1 inch thick and also as disseminated material. The carnotite in sample 20 was taken from a pillar approximately 100 feet inside the portal where the carnotite occurs both in small pockets and as disseminated material. This sample was overlain by approximately 30 feet of sandstone.

Samples 25 and 28.—Salt Wash sandstone member of the Morrison formation. The deposit is reached by an incline. Sample 25 was collected from a clayey seam of carnotite in the back of a small drift approximately 25 feet from the foot of the incline. Sample 28 was taken from another clayey seam in the back of a stope approximately 160 feet from sample 25.

Samples 61, 62, and 63.—Salt Wash sandstone member of the Morrison formation. All three samples were collected from a small stope approximately 200 feet from the entrance to the upper workings of the mine. Samples 61 and 63 were collected from a clayey seam near the back and on the opposite sides of the stope. Sample 61 was collected slightly lower in the formation than sample 63. Sample 62 was collected from the back near the middle of the stope. This sample seemed to be a carnotite replacement of a crushed log.

Sample 64.—Salt Wash sandstone member of the Morrison formation. The deposit has been developed by an incline. The sample was obtained from the first drift to the left down the incline. Close to the sample location, the deposit was overlain by about 10 to 15 feet of sandstone. The sample was taken from a rich pocket of clayey carnotite and corvusite. The carnotite is disseminated or occurs in thin clayey seams.

million years. Their radium-uranium equilibrium ranges from 36 to 85 percent. Such deficiencies are believed to be the result of preferential leaching processes which have removed either radium or its longer half-lived radioactive parent, Th^{230}. The differences in radium deficiency may reflect relative accessibility of the samples to the leaching solutions.

In summary, the radium-uranium equilibrium of carnotite and metatyuyamunite, which occur as replacements of woody material or as impregnations of clay or as disseminations in sandstone, is variable and is probably related to the habit and to local geologic factors such as distance from the surface of the ground and porosity and permeability of the surrounding rock. On the other hand, the deposition of crystalline carnotite and metatyuyamunite on joints and fractures is recent and the lack of radioactive equilibrium may be a result of the short time that has elapsed since the formation of the minerals.

In recent work Garrels and others (Part 15 of this volume) give a comparison of the uranium and equivalent uranium determinations for specimens from a channel sample from the Mineral Joe mine. These measurements show general agreement for each sample indicating that the channel sample is in radioactive equilibrium in spite of marked differences in extent of oxidation from sample to sample. This is evidence supporting the conclusion that uranium or radium has not been leached from the channel sample.

RADIOCOLLOIDS

If recent movement of radium within the ore body has occurred, the Plateau deposits might be expected to contain radium-bearing barite, $(Ba,Ra)SO_4$, and, in fact, they do. This highly radioactive mineral is formed by the coprecipitation of radium and barium sulfate. It is possible that the radium would exchange with the barium in barite as it moved through the sandstone in the ground waters so that these radiocolloids might actually be formed more or less continuously. Unless continuously deposited, radiocolloids—local concentrations of radium—would be apparent for only about 15,000 years after formation because of the relatively short half-life of $radium^{226}$ (1,620 years). These radiocolloids are additional evidence, therefore, of a recent alteration of the radioactive equilibrium.

RADIUM CONTENT AND RADIUM-URANIUM AGES OF SECONDARY URANIUM MINERALS

The calculated radium-uranium ages for four samples of carnotite and metatyuyamunite from the Colorado Plateau containing less than 0.01 percent Pb determined by the Geological Survey together with the earlier result of Hess and Foshag are given in table 2. These samples are carnotite or metatyuyamunite. Their ages range from 10,000 to 120,000 years. The spread in ages from 10,000 to 120,000 years is real providing that there has been no postmineralization leaching and no Th^{230} or Ra^{226} was deposited with the sam-

TABLE 2.—*Radium-uranium content and radium-uranium ages of some high-grade carnotite and metatyuyamunite containing less than 0.01 percent lead*

Locality	Mineral	U (percent)	Theoretical, g Ra/g sample ($\times 10^{-8}$)	Experimental, g Ra/g sample ($\times 10^{-8}$)	Percent radium-uranium equilibrium	Ra/U age
Parco mine, Yellow Cat group, Grand County, Utah	Carnotite	[1] 27.2	9.03	[2] 2.60	29	40,000
Jo Dandy mine, Montrose County, Colo	Metatyuyamunite	[1] 20.0	6.64	[2] .461	7	10,000
May Day mine, Mesa County, Colo	do	[3] 52.0	0.173	[4] .108	62	105,000
Small Spot mine, Mesa County, Colo	do	[3] 56.6	0.184	[4] .0333	18	24,000
Bridger Jack Flat, Cane Springs Pass, Utah [5]	Carnotite	54.6	0.186	.1244 .1269	67	120,000

[1] Average of four determinations: two by L. R. Stieff, M. N. Girhard, and T. W. Stern, U. S. Geological Survey, and two by W. A. Peavey, Jr., National Bureau of Standards.

[2] Analyst: R. G. Rice, National Bureau of Standards.

[3] Analyst: A. M. Sherwood, U. S. Geological Survey.

[4] Analyst: John Rosholt, U. S. Geological Survey.

[5] Hess, F. L., and Foshag, W. F., 1927, Crystalline carnotite from Utah: U. S. Nat. Mus. Proc., v. 72, art. 12, p. 1–6.

Parco mine.—Salt Wash sandstone member of the Morrison formation. The sample was collected from coatings of carnotite found on the surface of joint blocks at the entrance to the mine and from blocks of sandstone found on the mine dump.

Jo Dandy mine.—Salt Wash sandstone member of the Morrison formation. This sample was taken from a completely unprotected outcrop of very friable mineralized sandstone in an open cut leading to the lower haulage adit of the mine.

May Day mine.—Salt Wash member of the Morrison formation. The sample was *taken from a joint surface at the portal of the mine. This metatyuyamunite formed* on gypsum and was coarsely crystalline.

Small Spot mine.—Salt Wash sandstone member of the Morrison formation. This sample of coarsely crystalline metatyuyamunite had formed on gypsum which filled a fracture in the sandstone. The sample was found in the ore bin and no information concerning its exact location within the mine is available.

Bridger Jack Flat.—Salt Wash sandstone member of the Morrison formation. Hess and Foshag (1927) describe this sample, thus: "The mineral formed compact crusts one to two millimeters thick and 15 to 20 centimeters broad on the walls of narrow cracks. Where the crusts did not entirely fill the cracks the exposed surface had a dull greenish color and showed indistinct crystal terminations."

ples. If uranium has been leached from these carnotite and metatyuyamunite samples, the measured radium-uranium age would be older than the actual age of the mineral. Hess and Foshag (1927) found that crystalline carnotite from the Bridger Jack Flat, Cane Springs Pass, Utah, is 32 percent deficient in radium. The radium-uranium age of this material, using the currently accepted time required to reach radium-uranium equilibrium is approximately 120,000 years. The young ages are apparently a result of Quaternary deposition of carnotite and metatyuyamunite after the water table was lowered and the deposits oxidized. The field relations also strongly indicate that these joint and fracture coatings have been recently deposited and are related to the present erosion surface. The source of the metals in those secondary coatings was the unoxidized vanadium and uranium ores whose age is thought to be not greater than 75 million years (Stieff, Stern and Milkey, 1953, p. 1; Stieff and Stern, 1952). These Quaternary ages give the approximate time for the oxidation of the particular deposits.

These Quaternary ages were determined on local reconcentrations of carnotite and metatyuyamunite which formed after the water table was lowered and the deposits were oxidized; the ages give a minimum time for oxidation of the particular deposits.

SUMMARY

Methods of determining the time of Quaternary alteration of the oxidized Colorado Plateau uranium ores are here suggested. First, there is a group of uranium ores which appear to have been oxidized in place. These ore samples contain significant amounts of radiogenic lead yet they are not in radium-uranium equilibrium. It is assumed that these samples were in radium-uranium equilibrium until oxidation and Quaternary leaching selectively removed some of the radium or thorium^{230} present. The time at which the selective leaching took place cannot be calculated from the radium deficiency. However, the fact that radium-uranium equilibrium has not been reestablished sets an upper limit of approximately 500,000 years for this leaching process. This disequilibrium can also be explained by the recent addition of uranium but this explanation in the case of the Plateau ores is not believed likely.

Secondly, uranium essentially stripped of its daughter products has been redeposited on joints and fractures as coatings of metatyuyamunite and carnotite. These coatings contain only trace amounts of lead and are not in radium-uranium equilibrium. Assuming that the Th^{230} and Ra^{226} present have been produced since the formation of the minerals, the radium-uranium ages calculated from their disequilibrium range from 10,000 to 120,000 years. These ages indicate that some Quaternary redistribution of the uranium in the Colorado Plateau deposits has occurred after their oxidation. Finally, local concentrations of radium sulfate coprecipitated with barium sulfate are present in some oxidized deposits. These concentrations of radium are apparent for only about 15,000 years after their formation because of the relatively short half-life, 1,620 years, of radium^{226} and are another indication of Quaternary alteration of the uranium deposits.

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PART 14. SOME QUANTITATIVE ASPECTS OF THE OXIDATION AND REDUCTION OF THE ORES

By R. M. Garrels and A. M. Pommer

CONTENTS

Oxidation of uranium ores—Continued

TABLES

ABSTRACT

Equations illustrating the oxidation of many minerals of the ores are presented, and the "oxygen demand" for complete oxidation of a representative uraninite-montroseite-pyrite-vanadium clay ore is calculated. Approximately 100 to 150 pounds of oxygen are required per ton of ore. From considerations of the rate at which oxygen can be supplied by ground water as opposed to that from air circulation in unsaturated rocks, it is concluded that significant oxidation below the water table is not likely.

Experiments on the reduction of quinquevalent vanadium solutions by fresh Norway spruce and a North Dakota lignite at 120° to 150° C show that both materials are effective reducing agents. Their experimentally determined reducing capacity in runs lasting a few days is approximately half the theoretical reducing capacity calculated on the assumption of complete oxidation to CO_2 and H_2O. The conclusion is reached that about 0.5 weight percent of lignite is sufficient to form a typical uranium-vanadium ore by reduction of uranium (VI) and vanadium (V) or (IV) in solution to uraninite and montroseite, respectively. Subbituminous or higher rank coals may be expected to behave in a similar fashion.

INTRODUCTION

The mineralogic and chemical changes during oxidation of the Colorado Plateau uranium deposits are now known in considerable detail. The primary ore minerals are chiefly low-valence uranium, vanadium, iron and copper compounds. In the first part of this paper the probable chemical reactions that occur during oxidation are assembled, and estimates are made of the quantitative oxygen requirements for maximum alteration of a typical ore. The latter part is devoted to study of a process that may have been important in ore deposition, namely, the reducing effect of woody materials.

We are grateful to G. J. Jansen who worked with us on the high-temperature experiments; to C. A. Kinser for his help with the glass blowing; to I. A. Breger who gave us samples of wood and lignite as well as chemical advice; to R. G. Milkey for infrared spectroscopy; and to J. C. Chandler for his capable assistance in the laboratory.

OXIDATION OF URANIUM ORES

Oxidation of uranium ores involves chiefly the oxidation of pitchblende (UO_2), montroseite (VOOH), vanadiferous chlorite, vanadiferous hydromica, pyrite (FeS_2), and chalcopyrite ($CuFeS_2$). Many other minerals are present in small amounts from mine to mine, but oxidation of the six chosen probably constitutes more than 90 percent of the oxygen demand. They serve also as examples for the other compounds. The oxidation equations, plus some of the subsequent reactions with wall-rock constituents, are given in sequence for the individual minerals. A few notes on the environment of oxidation are included.

PYRITE

Pyrite usually oxidizes to produce ferric oxide or hydrated ferric oxide. Jarosite is important locally. From the reaction:

$$2FeS_2+15/2\ O_2+4H_2O \longrightarrow Fe_2O_3\downarrow+8H^++4SO_4^=$$

it is evident that every mol of pyrite produces 4 mols of hydrogen ion. If calcite is present, as is common, it is dissolved to give bicarbonate ion and calcium ion in solution:

$$8H^++8CaCO_3 \longrightarrow 8HCO_3^-+8Ca^{++}.$$

Some of the Ca^{++} commonly reacts with $SO_4^=$ to give gypsum:

$$4Ca^{++}+4SO_4^=+8H_2O \longrightarrow 4(CaSO_4\cdot 2H_2O).$$

Reaction with calcite tends, then, to give gypsum and a neutral or slightly alkaline solution with residual dissolved Ca^{++}. If calcite is absent or sparse, the hydrogen ions may attack clay or feldspar. Little is known of the process in Plateau deposits, although it may be an important reaction.

The reaction to form jarosite requires K^+ from the environment:

$$2K^++6FeS_2+45/2O_2+15H_2O \longrightarrow 2KFe_3(OH)_6(SO_4)_2+ 8SO_4^=+18H^+.$$

Free acid is formed, as in the oxidation of pyrite to Fe_2O_3, but each mol of pyrite produces 3 mols of hydrogen ion. It is probably necessary to use up most of the acid produced by reaction with minerals such as calcite, if jarosite is formed as a stable solid.

CHALCOPYRITE

In the oxidation of chalcopyrite, iron and copper are released when sulfide goes to sulfate. Iron is usually precipitated as ferric oxide or hydrated ferric oxide, whereas copper reacts with carbonate and hydroxyl ions to form malachite or azurite. For chalcopyrite:

$$CuFeS_2+4O_2 \longrightarrow Cu^{++}+Fe^{++}+2SO_4^=.$$

The Fe^{++} oxidizes to Fe^{+++} and hydrolyzes to ferric oxide:

$$2Fe^{++}+1/2O_2+2H_2O \longrightarrow Fe_2O_3+4H^+.$$

Cupric ion reacts with water and carbonate ion in solution to form malachite:

$$2Cu^{++}+CO_3^=+2H_2O \longrightarrow Cu_2(OH)_2CO_3+2H^+.$$

The overall reaction is:

$$2CuFeS_2+17/2O_2+CO_3^=+4H_2O \longrightarrow Fe_2O_3+ Cu_2(OH)_2CO_3+4SO_4^=+6H^+.$$

MONTROSEITE

Montroseite oxidizes in a complex manner. Figure 26, page 101, shows the minerals formed and some of the possible pathways. Here many of the individual reactions are given. They then can be used for calculation of oxygen demand for a given stage of oxidation along a desired pathway.

Montroseite to paramontroseite.—As shown by Evans and Mrose (1955, p. 872), montroseite alters pseudomorphously to paramontroseite by loss of hydrogen from the structure:

$$2VOOH+1/2\ O_2 \longrightarrow 2VO_2+H_2O.$$

Montroseite to simplotite.—Under slightly alkaline conditions montroseite may oxidize to the calcium vanadite simplotite, for at a pH of about 8 vanadium (IV) behaves as an anion. Direct oxidation is not likely; paramontroseite probably precedes formation of other vanadium (IV) species.

Paramontroseite may dissolve under slightly alkaline conditions and reconstitute to simplotite by combining with Ca^{++}:

$$4VOOH+O_2 \longrightarrow 4VO_2+2H_2O$$

$$4VO_2+2OH^-+Ca^{++} \longrightarrow CaV_4O_9+H_2O.$$

Montroseite to duttonite.—Duttonite, a vanadium (IV) hydroxide, has been recognized. It may form by solution of paramontroseite under either alkaline or acid conditions, with reprecipitation by neutralization. Paramontroseite may dissolve under the influence of acid from pyrite:

$$VO_2+2H^+ \longrightarrow VO^{++}+H_2O.$$

Then reprecipitation by increase in pH would give:

$$VO^{++}+2OH^- \longrightarrow VO(OH)_2 \text{ (duttonite).}$$

Alternatively, simplotite might be converted to duttonite by decrease in pH:

$$CaV_4O_9+2H^++3H_2O \longrightarrow 4VO(OH)_2+Ca^{++}.$$

Paramontroseite to mixed vanadium (IV) and (V) oxides.—It appears that paramontroseite is the most common first oxidation product of montroseite and that further oxidation reactions probably involve paramontroseite more frequently than duttonite or simplotite. Under neutral or acid conditions part of the vanadium (IV) apparently oxidizes to vanadium (V) containing anions, which react with the vanadyl ion (VO^{++}) to form vanadyl vanadates. The formation of many compounds is possible, and many actually do form as indicated by the complex corvusite group of mixed vanadium (IV) and (V) oxides. The summary equation of a typical reaction might be:

$$12VO_2+H_2O+5/2\ O_2\longrightarrow V_2O_4\cdot 5V_2O_5\cdot H_2O.$$

According to the postulated mechanism the reaction takes place in two steps. First, some of the paramontroseite is oxidized to a vanadate ion:

$$10VO_2+3H_2O+5/2\ O_2\longrightarrow H_2V_{10}O_{28}^{-4}+4H^+.$$

The reaction of some of the remaining paramontroseite with water produces some vanadyl ions:

$$2VO_2+2H_2O\longrightarrow 2VO^{++}+4OH^-.$$

Then the vanadyl ion combines with the vanadate ion to form vanadyl vanadate (a member of the corvusite group):

$$2VO^{++}+H_2V_{10}O_{28}^{-4}\longrightarrow (VO)_2(H_2V_{10}O_{28})\text{ or } V_2O_4\cdot 5V_2O_5\cdot H_2O.$$

The great variety of species possible becomes evident when it is considered that VO^{++} ion might react with $H_2V_{10}O_{28}^{-4}$ as indicated, or with $H_3V_{10}O_{28}^{-2}$, as well as with such vanadate ions as $V_4O_{12}^{-4}$, $HV_4O_{12}^{-3}$, or $H_2V_4O_{12}^{-2}$, to mention but a few (see Part 7 for discussion of vanadate ion relations). However, most combinations in the neutral or acid range would be expected to produce compounds with a V_2O_5/V_2O_4 ratio of 3 or higher, the ratio increasing with decreasing pH.

Paramontroseite to metal vanadite-vanadates.—The reactions to form mixed vanadium (IV) and (V) compounds so far discussed involve reaction between V^{+4} as a cation (VO^{++}) and vanadate ions. Inasmuch as vanadium (IV) also occurs as anions in such minerals as simplotite (CaV_4O_9), there is a possibility of forming compounds by reaction among metal ions, vanadite ions ($V_4O_9^{-2}$ or $HV_4O_9^{-1}$), and vanadate ions. Again the probable complexity is apparent. However, a typical reaction might be described in steps. First, paramontroseite could react with hydroxyl ions to form vanadite ions:

$$4VO_2+OH^-\rightarrow V_4O_9^{-2}+H^+.$$

Also, paramontroseite could be oxidized to a vanadate ion:

$$6VO_2+3/2\ O_2+3H_2O\rightarrow 2H_2V_3O_9^{-1}+2H^+.$$

The metal ions, such as calcium, could combine with the vanadite and vanadate ions to form a mineral such as melanovanadite:

$$2Ca^{++}+V_4O_9^{-2}+2H_2V_3O_9^{-1}\rightarrow Ca_2(V_4O_9)(H_2V_3O_9)_2.$$

This also can be written as

$$2CaO\cdot 2V_2O_4\cdot 3V_2O_5\cdot 2H_2O.$$

In general, such metal vanadite-vanadates have a lower ratio of V_2O_5/V_2O_4 than the vanadyl vanadates and probably form at higher pH (Part 7).

Paramontroseite to metal vanadates.—With sufficient oxygen available, the complex of mixed vanadium (IV) and (V) compounds is oxidized completely to metal vanadates, such as hewettite, hummerite, pascoite, and rossite. Overall reactions are presented for the oxidation of paramontroseite to some of the chief metal vanadates.

For paramontroseite to hewettite:

$$6VO_2+Ca^{++}+3/2\ O_2+10H_2O\rightarrow CaV_6O_{16}\cdot 9H_2O+2H^+.$$

For paramontroseite to hummerite:

$$10VO_2+2K^++2Mg^{++}+5/2\ O_2+19H_2O\rightarrow K_2Mg_2V_{10}O_{28}\cdot 16H_2O+6H^+.$$

Montroseite to metal vanadates.—The overall reaction from montroseite to metal vanadates shows the total oxygen demand. The change to hewettite is typical:

$$6VOOH+3O_2+7H_2O+Ca^{++}\rightarrow CaV_6O_{16}\cdot 9H_2O+2H^+.$$

Pitchblende and montroseite to carnotite.—The overall reaction from original pitchblende and montroseite to carnotite is:

$$K^++UO_2+VOOH+O_2+(1\text{ to }3)H_2O\rightarrow K(UO_2)(VO_4)\cdot(1\text{ to }3)H_2O+H^+.$$

One mol of pitchblende and one mol of montroseite thus require one mol of oxygen to form one mol of carnotite.

Uraninite to uranyl carbonate, sulfate, or silicate.—In the presence of excess vanadium, oxidation of pitchblende yields only carnotite or tyuyamunite. If vanadium is absent, uranyl carbonates, silicates, or sulfates may form. For all such uranyl compounds, the oxygen demand is ½ Mol O_2 for each mol of pitchblende. A typical reaction is the oxidation of pitchblende to form bayleyite:

$$UO_2+1/2\ O_2+2Mg^{++}+3CO_3^{=}+19H_2O \rightarrow Mg_2(UO_2)(CO_3)_3 \cdot 18H_2O+2OH^-.$$

VANADIUM MICA, VANADIUM HYDROMICA, AND VANADIUM CHLORITE

Details of oxidation of the vanadium silicates are not known, but some inferences can be drawn from the chemical analyses (Part 10). Vanadium mica (roscoelite) contains vanadium (III) and apparently is not altered at a finite rate by ordinary oxidation processes. Vanadium chlorite and vanadium hydrous mica are found by analysis to contain vanadium (IV) and a mixture of iron (III) and iron (II). According to Foster's interpretation (Part 10), the vanadium entered the structure as V (IV), in which case only enough oxygen would be used to change iron from Fe (II) to Fe (III). If, on the other hand, the iron and vanadium originally were Fe (II) and V (III), the maximum oxygen demand would be that necessary to change the vanadium to V (IV) and the iron to Fe (III).

The chemical formulas of the vanadium hydrous micas are complex, but the analyses (Part 10) can be approximated by:

$$[Al,Mg)_{1.4}(V^{+3}Fe^{+2})_{0.6}\cdot][Si_{3.5}Al_{0.5}]O_{10}(OH)_2.$$

Thus the maximum oxygen requirement would be that necessary to change the $(V^{+3}, Fe^{+2})_{0.6}$ to $(V^{+4}, Fe^{+3})_{0.6}$ or about 0.15 mols O_2. Therefore, the oxygen demand ranges somewhere between zero and 0.15 mols per mol of vanadium hydromicas. That for the vanadium chlorites is presumably about the same.

SUMMARY OF OXYGEN REQUIREMENTS

The amount of oxygen required for maximum oxidation of the various primary minerals of the Plateau ores is given in table 1.

Table 1.—Summary of maximum oxygen demand for oxidation of some typical Plateau minerals.

Mineral	Oxidation products	Mols O_2/per mol mineral
Pyrite	Fe_2O_3 and $SO_4^=$	3¾
Chalcopyrite	$Cu_2(OH)_2CO_3$, Fe_2O_3 and $SO_4^=$	4¼
Montroseite	Hewettite	½
Montroseite+pitchblende	Carnotite	1 (per 1 mol each o reactants).
Uraninite	Uranyl silicate, sulfate, or carbonate.	½
Vanadium chlorite	Oxidized vanadium chlorite	¼ (approximately).
Vanadium hydrous mica	Oxidized vanadium mica	
Vanadium mica	Does not oxidize	0

OXIDATION OF A TYPICAL URANIUM-VANADIUM ORE

Consider the oxidation of an ore containing pitchblende 0.5 percent, montroseite 4 percent, vanadium hydromica 6 percent, and pyrite 6 percent by weight, with the remainder chiefly quartz and other unreactive detrital minerals. Each ton of ore contains 16.8 mols of pitchblende, 433 mols of montroseite, 456 mols of pyrite, and 146 mols of vanadium silicate. This figure must be considered a rough approximation because of the variability of the vanadium and iron content of the silicates.

The final result of natural oxidation might convert the iron of pyrite to ferric oxide, and the sulfide to sulfate; montroseite and pitchblende would oxidize to carnotite and the excess montroseite to hewettite. Assuming original V^{+3} and Fe^{+2} in the structure of the hydrous mica, the vanadium would be changed from trivalent to quadrivalent, and the iron from bivalent to trivalent.

The oxygen requirements can be determined from table 1.

	Mols O_2 required
17 mols pitchblende+17 mols montroseite	17
416 (433–17) mols montroseite	208
456 mols pyrite	1710
146 mols vanadium hydromica	21
Total mols O_2 per ton of ore	1956
Total pounds O_2 per ton of ore	137

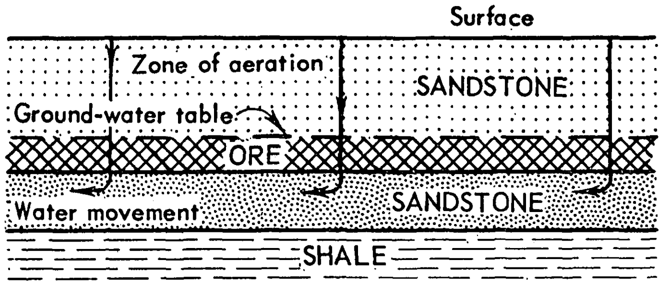
It is of interest to assess the two chief mechanisms by which oxidation can occur in terms of this oxygen requirement. Oxidation can be accomplished either by air moving in and out of damp rock or by oxygenated ground waters flowing through the ore. In the former case, oxidation would take place in a thin film of adsorbed water on the rock grains. In the latter, oxidation would take place below the water table, in the former above it.

Air is 21 percent by weight oxygen; thus it would require about 137/0.21=650 pounds of air for complete oxidation by a "breathing" or "moist air" process. At earth-surface conditions, 650 pounds of air occupy about 250,000 liters, or about 8,800 cubic feet. A ton of ore occupies about 15 cubic feet; with 10 percent porosity it could accommodate about 1.5 cubic feet of air. Thus, for final oxidation the air in a given volume of ore would have to be changed 8800/1.5=5850, or about 6,000 times.

On the other hand, if oxidation occurs below the water table through the agency of air-saturated water, about 8,000,000 liters of water would be required per ton of ore, for the solubility of air in water is only about 20 milliliters per liter, and its oxygen content is about 6 milliliters per liter.

In other words, about 280,000 cubic feet of water would have to pass through each ton of ore. Assuming 10 percent porosity and ideal permeability, this would mean refilling of the volume occupied by 1 ton 185,000 times.

From these considerations it appears that "moist air" oxidation above the water table could be far more rapid than oxidation by air-saturated water below it. For example, if an ore layer 3 feet thick, of the composition assumed, occurred just below the water table, so that oxidation had to take place by air dissolved in the ground water draining downward through the ore, 56,000 cubic feet of water would have to drain through each square foot of surface to oxidize the ore completely (as illustrated below). The source of water, under the condition shown, would be rain.



Inasmuch as the amount of water now being added to the zone of saturation by rain is probably negligible because of loss by evaporation and transpiration, oxidation by such a mechanism is undoubtedly much slower than by circulating air.

Large volumes of water and long time intervals are involved if it is assumed that oxidation is by aerated water moving laterally through an ore-bearing layer. Under these circumstances the ore would have to be oxidized sequentially in the direction of water movement. Each linear foot of ore oxidized would require about 185,000 linear feet of water flow. At common rates of ground-water movement of a few feet per year in moderately permeable media, several million years would be required to oxidize an ore body a hundred feet long, even if the entering water were fully aerated.

Inasmuch as the reducing capacity of rocks is such that the oxygen content of ground water disappears at or near the water table, and as a result conditions below the water table are reducing, oxidation of ores beneath the water table must be extremely slow or lacking under all but unusual conditions of very rapid circulation.

In summary, oxidation of the Colorado Plateau uranium ores probably has taken place after the water table dropped below the ore zones.

Important, perhaps, is the demonstration of the difficulty of moving deposits by lateral migration of ground water during the geologic past, when the rocks were saturated with water. If uranium and vanadium were moved, it appears unlikely that the process involved was an oxidation-transportation-reduction and deposition cycle, where laterally moving phreatic waters act as both oxidizing and transporting agents. The oxygen (or equivalent) demand for large-scale oxidation in water-saturated rocks is large, and ground waters are characteristically anaerobic.

The conclusion drawn is not new; long ago Spencer (1917) deduced that oxidation of copper ores under semiarid conditions takes place above the water table in a film of moisture on the mineral grains. Describing the copper deposits at Ely, Nevada, he says (p. 80–81):

> By considering the amount of oxygen that water can absorb by contact with the air under atmospheric pressure at 7,000 feet elevation and at the present mean annual temperature of the region, it is found that, even if precipitation in the past has been 25 percent greater than at present, and that as much as 60 percent of the rainfall could have penetrated to the ore body, the oxygen required to oxidize 500 feet of ore like that now existing would require the contributions of rainfall during a period longer than physicists and geologists are willing to allow for the age of the earth. [Spencer assumed 60 million years at that time.] Although all the assumptions made tend to a minimum, the time required, as calculated in this way, is still so immoderately great as to demand a different hypothesis in regard to the manner in which oxygen has been delivered to the place of sulfide decomposition. It is thought, therefore, that a large part of the oxygen must have been derived from air that circulated through the oxidizing capping. * * * It would seem, then, that the greater part of the oxidization must take place when the sulfides are moist rather than when they are flooded. * * *

REDUCING EFFECT OF WOODY MATERIALS[9]

It is well known that many reduced uranium ores are associated with woody material; impregnation and replacement of woody material by pitchblende, coffinite, montroseite, and pyrite in ore-bearing material are quite common. Is it possible that such ores were deposited by the reducing action of woody material upon oxidized mineralizing solutions carrying vanadium (V) and uranium (VI) ions?

Because interest here is in a quantitative appraisal of the reduction requirement, it becomes necessary to determine the reducing capacity of woody material, so that the amount of woody material necessary to produce a typical ore can be calculated. To do this it is first necessary to consider some aspects of the chemistry of woody material; as no experimental values of reducing capacity of woody material in solutions containing uranium (VI) and (or) vanadium (V) have been found in the literature, it was necessary to determine this factor experimentally, using conditions approach-

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[9] Extracted from a dissertation presented by A. M. Pommer to Georgetown University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

ing the geological environment within the limits of the laboratory.

SOME ASPECTS OF WOOD CHEMISTRY

Wood usually contains moisture ranging up to 10 percent and a fraction of a percent ash (Lange, 1949). The dry matter contains 40–50 percent cellulose, 10–30 percent hemicellulose, and 20–30 percent lignin. Cellulose and hemicellulose are polymers of glucose or its isomers. Some sugars of slightly different composition, such as xylose, are present, but they do not change the calculated results significantly and may be treated as glucose.

In the presence of a strong oxidizing agent glucose is decomposed according to the following reaction:

$$C_6H_{12}O_6+6O_2\rightarrow 6CO_2+6H_2O$$

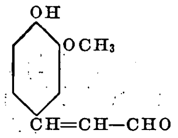
One mol (180 g) of glucose then requires 24 equivalents to oxidize it completely; it has an equivalent weight of 7.5.

The cellulose monomer is $C_6H_{10}O_5$ with a molecular weight of 162. For complete oxidation:

$$C_6H_{10}O_5+6O_2\rightarrow 6CO_2+5H_2O$$

Thus cellulose or its monomer, assuming complete oxidation to CO_2 and H_2O, also requires 24 equivalents and its equivalent weight is 6.75. In other words 100 grams of cellulose has a theoretical reducing capacity of 14.8 equivalents, or 14,800 milliequivalents.

The oxidation of lignin is much more complicated. Klason (1920) postulated lignin to be a polymer of coniferyl alcohol or coniferyl aldehyde



and this belief is currently accepted by many (Gortner, 1949). Assuming complete oxidation of the coniferyl aldehyde monomer to CO_2 and H_2O gives an equivalent weight of 4.05 and a reducing capacity of 24,700 milliequivalents per 100 g, almost twice that of cellulose, according to the reaction:

$$C_{10}H_{10}O_3+23/2O_2\rightarrow 10CO_2+6H_2O$$

If a formula for lignin proposed by Russell (1948) is used, the summary equation is:

$$C_{10}H_8O_3+21/2O_2\rightarrow 10CO_2+4H_2O$$

The equivalent weight is 4.03 and the reducing capacity of 24,900 meq/100 g. These two examples illustrate that different proposed lignin structures do not differ greatly in reducing capacity.

We have no assurance, of course, that cellulose or lignin are completely oxidized.

EXPERIMENTAL DETERMINATION OF REDUCING CAPACITIES

A series of experiments was carried out to determine the reducing capacity of wood. When wood is placed in an acidified solution of ammonium vanadate at room temperature and pressure, a green color is observed after a few days, indicating partial reduction of V(V) to V(IV). It also was possible to reduce V(IV) solutions to V(III) with wood at elevated temperatures. However, to simulate conditions in nature, experiments were run at 150° C, a temperature representing a consensus of several of our coworkers of the temperature of formation of the ores. Determinations of reducing capacity were carried out according to the following procedure: a 10-mg sample was placed together with 10 ml 0.1 formal $(VO_2)_2SO_4$ solution containing an excess of free sulfuric acid and some Na_2SO_4 in a Pyrex tube, sealed, and heated at 150° C at an estimated pressure of 70 psi (ignoring the boiling-point elevation of the solution by the added electrolytes) for three days; at the end of the run the reduced vanadium was titrated potentiometrically. Any remaining sample was recovered, washed, dried, and weighed. (See table 2.) From the data two sets of reducing capacity values were obtained. The first set is the milliequivalents of vanadium reduced per 100 grams of original sample, the second set is the milliequivalents of vanadium reduced per 100 grams of wood or lignite decomposed (wood decomposed equals original sample minus solid residue).

TABLE 2.—*Reducing capacity of wood and lignite*

	Wood [1] (*meq/100 g*)	*Lignite* [2] (*meq/100 g*)
Calculated reducing capacity [3]	15800	14600
Experimental reducing capacity [4]	10300	5600
	5100	6800
	9700	8200
Average experimental reducing capacity	8400	6900
Experimental reducing capacity corrected for insoluble constituents [5]	11300	8600
	7100	8400
Average corrected reducing capacity [6]	9200	8500
Average corrected reducing capacity expressed as percentage of calculated reducing capacity	58	58

[1] Fresh spruce (*Picea excelsa* Lk) containing 58 percent cellulose and 29 percent lignin (Varossieau and Breger, 1951).

[2] Lignite from the Beulah-Zap bed, Dakota Star mine, Mercer County, N. Dak., containing 41.2 percent moisture and ash (Analyst, R. T. Moore, U. S. Geological Survey).

[3] For details of calculation see text.

[4] All reducing capacities were determined by potentiometric titration of the product obtained by heating a 10-mg sample with 10 ml of a 0.1-formal vanadium (V) solution acidified to a pH of 0.7 in a sealed Pyrex tube for 3 days at 150° C. All values were corrected for a blank (0.15 ml).

[5] The undecomposed residue was isolated, washed, dried, and weighed, and the reducing capacity of the decomposed portion calculated. This was done on duplicate samples only owing to experimental difficulties on the triplicate run.

[6] This value was rounded off to 9000 in both samples for use in table 3.

As the experimental results were 58 percent of the calculated results, an attempt was made to obtain reducing capacities closer to the calculated value by extending the time of the run to 12 days. This attempt was not successful. Although it was possible to increase the reducing capacity of glucose under parallel conditions from 8900 meq per 100 g to an apparent 10,000 meq per 100 g by increasing the heating time from 3 to 12 days, the reducing capacities of wood and lignite samples were of the same order of magnitude in the 3 day runs and in the 12 to 13 day runs, with some of the long runs giving slightly lower reducing capacities. There are two possible explanations for this phenomenon, both probably contributing simultaneously: it was noted in the blank runs that the vanadate solution on heating gave a brown precipitate, which gave an X-ray pattern of $V_2O_5 \cdot H_2O$. If we consider that we have two competing reactions, one the precipitation of the vanadium (V) oxide which removes it from the reaction, and the other the reduction of the VO_2^+ ion by the slowly decomposing polymers of the woody material, it can be seen that relatively soon a point is reached where the concentration of vanadium (V) ions in the solution is so low that reduction becomes very slow and in effect ceases. The other reaction is the formation of high-carbon polycyclic compounds by partial degradation of the wood which loses hydrogen and oxygen atoms during oxidation and results in reaction products becoming increasingly more resistant to attack. In the case of glucose this phenomenon does not take place.

The calculated reducing capacities used in table 2 were obtained as follows: The theoretical reducing capacity of a fresh spruce of the given composition is computed, assuming complete oxidation to CO_2 and H_2O and using the Russell formula for lignin. A 100-g sample contains 58 g cellulose with a reducing capacity of (0.58 x 14,800) 8600 milliequivalent (meq) per 100 g; it also contains 29 g lignin with a reducing capacity of (0.29 x 24,800) 6700 meq per 100 g, giving a total reducing capacity of 15,300 meq per 100 g. The experimental value at pH 0.7 corrected for undecomposed matter is 9200 meq per 100 g, or 58 percent of the theoretical maximum value.

The reducing capacity of the lignite used is substantially that of wood; this was an unexpected result. The chemistry of lignite is little known, but Breger (1951) has presented evidence based on infrared spectra that the skeletal structures of humic acid and lignin are related and has suggested that they may even be identical. Let us now assume that the reducing capacities of lignin and humic acid are the same. Let us next assume that lignite consists of moisture, ash, and humic acid only; we know that this is not quite correct, but this assumption would leave us with the same carbon content for lignite as for lignin. The carbon content of Russell lignin is 66 percent and its carbon-hydrogen ratio is 100: 7.4; both values are not markedly different from typical lignite values and our assumption may not be far off. Because our lignite has a moisture and ash content of 41.2 percent, it now is assumed to contain 58.8 percent humic acid (reducing capacity 24,800 meq per 100 g) and its reducing capacity assuming total oxidation is (0.588 x 24,800) 14,600 meq per 100 g. The experimental value of 8500 meq per 100 g then indicates either incomplete oxidation or the transition of some of the humic acid to fixed carbon, which is not too unlikely in a lignite. To investigate whether the oxidation of cellulose, lignin, wood, and lignite by vanadium (V) solutions proceeds to CO_2 and H_2O at least in part or whether it does not proceed at all beyond some intermediate state, the reaction products of these substances with vanadium (V) solutions were examined by infrared spectroscopy; carbon dioxide was identified in all samples (R. G. Milkey, analyst, written communication).

AMOUNT OF REDUCING AGENT REQUIRED

If primary ore was deposited by the reduction of solutions carrying quinquevalent vanadium and sexivalent uranium ions, it may now be possible to make rough estimates of the concentration of wood or lignite necessary for precipitation of a typical ore. Unfortunately, the requirement in terms of equivalents of reducing agent is not necessarily the same as equivalents of oxygen necessary to oxidize low-valent ore minerals as shown in table 1.

For oxidation the primary mineral assemblage is reasonably well known as are the oxidation products. It is not necessary to distinguish between minerals already present in the rock before ore deposition and those superimposed during mineralization. Any pyrite present in an ore body becomes oxidized eventually, whether it is syngenetic, diagenetic, or epigenetic.

Therefore, it may be instructive to calculate the weight percent of fresh spruce or lignite necessary to precipitate each ore mineral from aqueous solution by reduction from a specified ion.

In this connection it must be noted that it is impossible to make an intelligent allowance for pyrite. In the first place, it is impossible to make a valid correction for syngenetic or diagenetic pyrite, which must be deducted from the total pyrite in the ore. Also no accurate correction can be made for other sulfides or sulfur compounds in the organic matter available for the reduction of possible ferric iron carried in a mineralizing solution. Finally, in the absence of sulfide made available by the woody material and free hydrogen sulfide fortuitously present in the system—which of course also would reduce vanadium and uranium ions—any pyrite sulfur must be produced by reduction of sulfate ions. Under 200° C, reduction of sulfate ions to sulfide or polysulfide in nature is known only in the presence of certain microorganisms—for example, *Sporovibrio.*

Table 3 is a compilation of data which, it is hoped, will enable its user to compute the amount of woody material required to precipitate an ore containing a given amount of montroseite, pitchblende, and vanadium clay. He can then judge whether the amount of carbonaceous material expected in the formation under consideration is sufficient to make this process probable. It can be seen from the calculations that woody material can easily be present in sufficient amounts to deposit typical ore concentrations from oxidized solutions by reduction, but, of course, this does not hold in every case. Subbituminous and higher rank coals may be expected to behave like lignite.

SOME TYPICAL REDUCTION EQUATIONS

Finally, it may be of interest to demonstrate some possible reducing reactions by writing down some speculative equations showing the reduction of uranyl and vanadate ions by cellulose (represented by $C_6H_{10}O_5$, its monomer). Of course, it is also possible to write similar reactions for lignin.

TABLE 3.—*Amount of reducing material required for the deposition of some reduced minerals from oxidized solutions*

Mineral species formed	Formula	Oxidized species in solution	Concentration of mineral species in sediment	Fresh spruce or lignite required					
				Theoretical			Experimental		
				Wt percent	Lb/ton	Percent C	Wt percent	Lb/ton	Percent C
Pitchblende	UO_2	UO_2^{++}	1 wt percent of mineral	0.048	0.96	0.022	0.082	1.6	0.037
			1 lb-ton of mineral	.002	.048	.001	.004	.082	.002
			1 wt percent of U	.055	1.10	.025	.092	1.8	.040
			1 lb/ton of U	.002	.055	.001	.005	.092	.002
Montroseite	VOOH	VO_2^+	1 wt percent of mineral	.15	3.1	.69	.26	5.3	.12
			1 lb/ton of mineral	.008	.15	.004	.013	.26	.006
			1 wt percent of V	.25	5.1	.11	.44	8.8	.20
			1 lb/ton of V	.013	.25	.006	.022	.44	.010
V-silicates V-mica V-hydromica V-chlorite	(1)	VO_2^+	1 wt percent of mineral	.034	.68	.015	.060	1.2	.027
			1 lb/ton of mineral	.002	.034	.003	.003	.060	.005
			1 wt percent of V	.25	5.1	.11	.44	8.8	.20
			1 lb/ton of V	.013	.25	.006	.022	.44	.010

[1] Molecular weight, 373.

NOTES.—Values used in construction of table: "Theoretical" equivalent weight of wood or lignite, 6.5: this weight was obtained by averaging the equivalent weight for wood (6.3) and lignite (6.8) obtained from the calculated reducing capacities given in the text by the conversion formula; equivalent weight (in g)=100000:reducing capacity (in meq/100 g). The "experimental" value was obtained from the rounded off reducing capacity of 9000 meq/100 g. Both the wood and the lignite contained about 45 percent C (actual values: wood 46 percent, lignite 42 percent). 1 percent V_2O_5=0.56 percent V; 1 percent U_3O_8=0.85 percent U.

Sample calculation:

1. An ore contains 50 lb/ton montroseite, and 100 lb/ton pitchblende. What is the theoretical amount of lignite required for deposition? Answer: 50×0.15+100×0.048=12.3 lb/ton or about 0.6 wt percent lignite.

2. Ore content: 2 percent V_2O_5 and 0.5 percent U_3O_8. Lignite required: 2×0.56×0.25+0.5×0.85×0.055=0.5 wt percent.

Reduction of vanadium (V) ion to montroseite—

$$12\ VO_2^+ + C_6H_{10}O_5 + 7\ H_2O \longrightarrow 12\ VOOH + 12\ H^+ + 6\ CO_2$$

Reduction of vanadium (V) ion to duttonite—

$$24\ VO_2^+ + 31\ H_2O + C_6H_{10}O_5 \longrightarrow 6\ CO_2 + 24\ H^+ + 24\ VO(OH)_2.$$

Reduction of uranyl ion to pitchblende—

$$12\ UO_2^{++} + C_6H_{10}O_5 + 7\ H_2O \longrightarrow 12\ UO_2 + 6\ CO_2 + 24\ H^+.$$

SUMMARY AND GEOLOGIC APPLICATION

It has been assumed that uranium and vanadium ores of the Colorado Plateau originally were in a reduced form and have been oxidized subsequently. This oxidation was carried on by moist air above the water table. The reduced ore may have been deposited either from reduced or oxidized solutions. In the latter case woody materials are a likely precipitating agent, and it is possible to appraise their sufficiency in a given environment from reducing capacities.

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Part 15. DETAILED CHEMICAL AND MINERALOGICAL RELATIONS IN TWO VANADIUM-URANIUM ORES[10]

By R. M. GARRELS, ESPER S. LARSEN 3D, A. M. POMMER, AND R. G. COLEMAN

CONTENTS

ILLUSTRATIONS

TABLES

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[10] Based in part on a dissertation presented by A. M. Pommer to Georgetown University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

ABSTRACT

Channel samples from two mines on the Colorado Plateau have been studied in detail both mineralogically and chemically.

A channel sample from the Mineral Joe No. 1 mine, Montrose County, Colo., extends from unmineralized rock on one side, through a zone of variable mineralization, into only weakly mineralized rock. The unmineralized rock is a fairly clean quartz sand cemented with gypsum, and contains only minor amounts of clay minerals. One boundary between unmineralized and mineralized rock is quite sharp and is nearly at right angles to the bedding. Vanadium clay minerals, chiefly mixed layer mica-montmorillonite and chlorite-montmorillonite, are abundant throughout the mineralized zone. Except in the dark "eye" of the channel sample, the vanadium clay minerals are accompanied by hewettite, carnotite, tyuyamunite, and probably unidentified vanadates. In the dark "eye," paramontroseite, pyrite, and marcasite are abundant, and are bordered on each side by a zone containing abundant corvusite. No recognizable uranium minerals were seen in the paramontroseite zone although uranium is abundant there. Coaly material is recognizable throughout all of the channel, but is most abundant in and near the dark "eye." Detailed chemical studies show a general increase in Fe, Al, U, and V, and a decrease in $SO_4^{=}$ toward the "eye" of the channel. Reducing-capacity studies indicate that V(IV) and Fe(II) are present in the clay minerals throughout the channel, but only in and near the "eye" are other V(IV) minerals present (paramontroseite and corvusite). The uranium is everywhere sexivalent, although its state of combination is conjectural where it is associated with paramontroseite. Where the ore boundary is sharp, the boundary of introduced trace elements is equally sharp. Textural and chemical relations leave no doubt that the "eye" is a partially oxidized remnant of a former lower-valence ore, and the remainder of the channel is a much more fully oxidized remnant.

A channel sample from the Virgin No. 3 mine, Montrose County, Colorado, extends from weakly mineralized sandstone on both sides through a strongly mineralized central zone. The weakly mineralized zone is a poorly sorted sandstone with common detrital clay partings; chlorite and mixed layer mica-montmorillonite are abundant interstitial to the quartz grains. No distinct vanadium or uranium minerals are recognizable, although the clay minerals are vanadium-bearing. Euhedral pyrite grains and selenian galena are present but rare. The strongly mineralized rock is separated from the weakly mineralized rock by a narrow transition zone which only approximates the bedding planes. It contains abundant vanadium-bearing clay minerals (predominantly chlorite) interstitial to the quartz grains, and apparently replacing them. Paramontroseite is common and is intergrown with the clay minerals. Pyrite and marcasite are present, chiefly in or near the abundant blebs and fragments of carbonaceous material. Selenian galena is rarely present, and generally in or near carbonaceous material. Coffinite is the only uranium mineral identified; it is extremely fine-grained and was identified only in X-ray diffraction patterns of heavy separates. Distribution of trace elements is not clear; some are consistently high in the strongly mineralized rock, and some are consistently low. The trace element composition of the unmineralized rock is not known. Chemical studies show a very abrupt rise in the total U, V, and Fe from the weakly mineralized to strongly mineralized rock. Reducing capacity studies indicate that most of the vanadium is present as V(IV), but some is present as V(V); that iron is present as both Fe(II) and Fe(III), the latter believed to have been present in the primary clays of the unmineralized rock; and that some of the uranium is present as U(VI) in addition to the U(IV) in the coffinite. All evidence points to weak oxidation of an ore once having a somewhat lower valence state.

The channel samples from both the Mineral Joe No. 1 mine and the Virgin No. 3 mine are believed to have been essentially identical in mineralogy prior to oxidation by weathering: vanadium was present as V(III) in montroseite and V(IV) in the vanadium clays; uranium was present largely as U(IV) in coffinite and/or uraninite. The Mineral Joe No. 1 mine channel sample is now more fully oxidized.

Vanadium clays are unquestionably formed abundantly during the primary mineralization, and they persist with a minimum of alteration during much of the weathering. They suggest that the vanadium is carried as V(IV) in the ore-forming fluids; it seems likely too that the uranium is carried as a U(VI) ion.

INTRODUCTION

Until the last few years the uranium-vanadium ores in the developed "sandstone type" deposits of the Colorado Plateau contained chiefly carnotite (or tyuyamunite) and vanadium clays together with a host of minor uranium and vanadium minerals. Except in the clays, the uranium and vanadium were usually present in their highest oxidation state—U(VI) and V(V). For lack of reason to think otherwise, these were commonly considered "primary" ores and ideas of their genesis were based on this concept. Recently, many so-called "black ore" deposits, both large and small, have been discovered and developed; these share many common geologic characteristics with the carnotite-bearing ores and differ primarily in the oxidation state of the contained uranium, iron, and vanadium. In some deposits, the carnotite ores grade at depth into the "black ores," and in others the two occur together. In the "black ores" U(IV) is common as uraninite and coffinite, and V(IV) and V(III) are common in hydrated oxides and hydroxides as well as clays.

These deposits containing lower-valence metals are now thought to be the "primary" ore from which the carnotite deposits were derived by oxidation during weathering (Garrels, 1955). Since some single deposits commonly contain high-valence ores that grade into low-valence ores, we felt it would be fruitful to study in detail the nature of the changes in the mineralogy, element distribution, valence state, and relation of host rock to mineralization in a channel sample crossing from one type of ore to the other. Moreover, since much less is known about the low-valence ores and their relation to host rock, we felt it desirable to study these in the same way, but less intensively. It was hoped that these studies might lead to a more specific knowledge of the nature of the alteration of the ores, at least for the deposits studied. Results of the study of two channel samples are reported below.

We are indebted to John C. Hathaway, Jr., and Margaret D. Foster, for discussions on the character of the vanadium-bearing clay minerals. Howard T. Evans, Jr., and A. E. Flint assisted Garrels in selecting and collecting the channel sample from the Mineral Joe No. 1 mine. John C. Chandler assisted with the chemical laboratory work. Lillie B. Jenkins was of great help in selecting a consistent and reliable method for the determination of reducing capacity.

MINERAL JOE NO. 1 MINE CHANNEL SAMPLE

SAMPLING

After a reconnaissance of a number of mines an ore occurrence at the Mineral Joe No. 1 mine, Jo Dandy group, Montrose County, Colo., was selected for detailed work. The location of the sampling site is shown in figure 48, and a sketch of the ore occurrence, together with the sampling pattern, in figure 49. The site was chosen because it appeared possible to collect a continuous channel sample from unmineralized sandstone through a heavily mineralized zone that exhibited a variety of brown, yellow, and black colors presumably

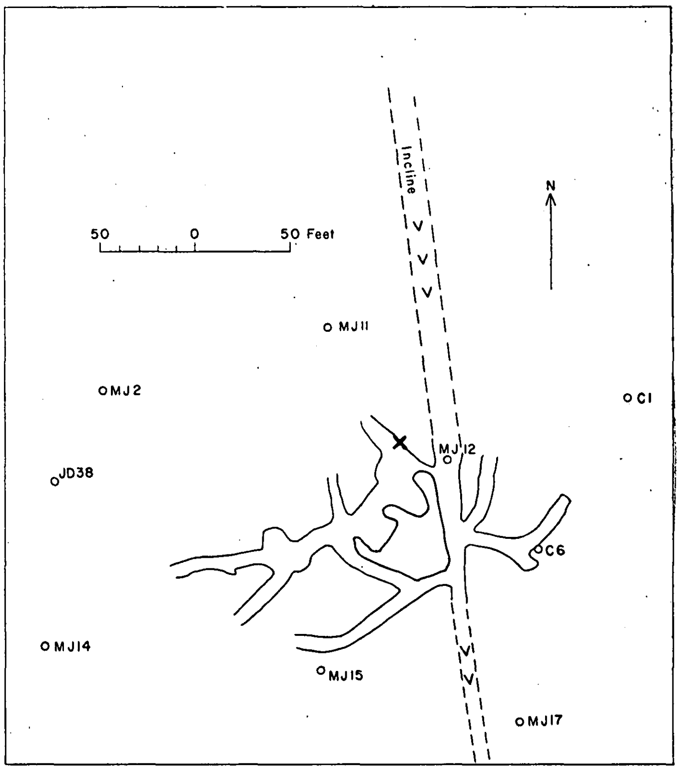

FIGURE 48.—Sketch of the upper stopes of the Mineral Joe No. 1 mine; x indicates the site of the channel sample taken.

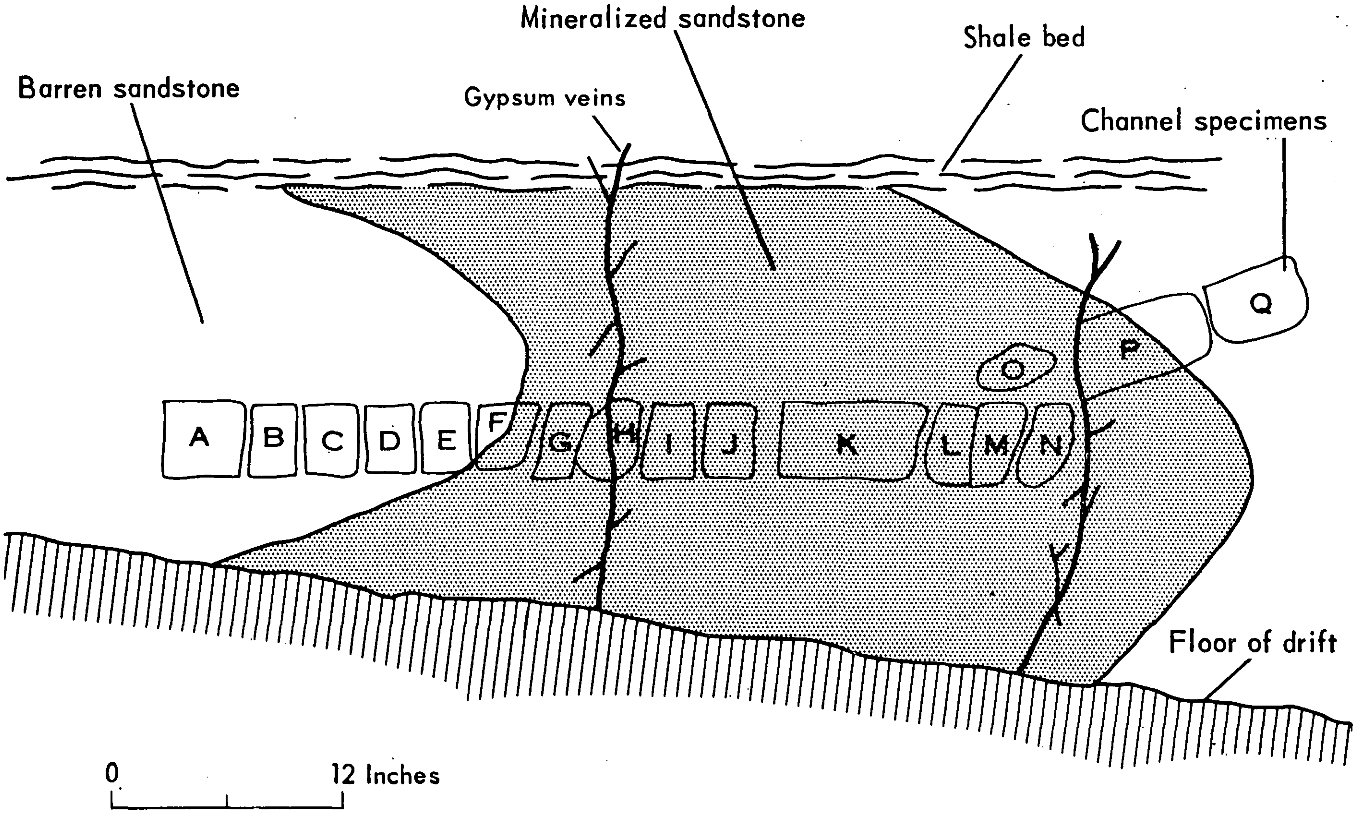

FIGURE 49.—Sketch of Mineral Joe mine wall showing relation of channel sample to ore. The letters refer to the separate specimens which made up the channel sample.

representing differences in oxidation state. It was not possible to get a continuous set of samples that crossed from unmineralized rock on one side of the mineralized zone to unmineralized rock on the other side, but field observation suggested that one end of the channel sample was in unmineralized rock, and the other end of the channel was in weakly mineralized ground probably low in vanadium and uranium, but that all of the more highly mineralized zone was included in the channel. It was hoped that detailed study of the mineralogy, oxidation state, and distribution of major and minor elements all in relation to the host rock, would provide more concrete data with which to consider the geochemical history of the ore. Before collecting the specimens, the entire working face was cleaned with a wire brush. No marked difference was seen between the exposed surface of the sample area after wire brushing and the face freshly exposed by channeling. Most of the specimens were obtained as unbroken rock units; a few were broken into several pieces during sampling. Only specimen I had to be collected as an incoherent mass. It is estimated that the specimens are essentially as satisfactory as a single unbroken piece of rock.

In the laboratory, the individual specimens were sawn in two along a horizontal plane parallel to the line of the channel. One half of each sepcimen was retained for mineralogic work, the other for chemical tests. No water was used in any of the processing steps such as sawing, grinding, or polishing.

GEOLOGY AND GROSS APPEARANCE OF THE ORE

The Mineral Joe mine is in the Jo Dandy group, which has been described briefly in an unpublished report by E. M. Shoemaker in 1950. The Jo Dandy group lies on the south side of Paradox Valley, a structural valley developed in the crest of a salt anticline. Narrow fault blocks, caused by the solution or subsidence of salt and gypsum of the underlying Paradox member of the Hermosa formation of Pennsylvanian age, form the south side of the Valley; many of the deposits are faulted, but the beds remain essentially flat-lying. The deposits occupy the uppermost sandstone lenses of the Salt Wash member of the Morrison formation of Jurassic age. Thin lenses of mudstone are interbedded with the sandstone, and mudstone pebbles and pockets of plant remains are scattered through it. Certain unusual features characterize the deposits in the Jo Dandy area, particularly the abundance of gypsum which impregnates the sandstone and fills fractures; the almost continuous extent of the deposit along 3,000 feet of outcrop; and the relatively great abundance of pyrite and lower-valence vanadium minerals.

At the sampling site in the Mineral Joe No. 1 mine a mineralized zone cuts across the flat-lying sandstone at a steep angle. The sandstone is overlain by a greenish shale bed which is irregularly mineralized. Figure 49 shows the general appearance of the ore in relation to the channel taken. The following is a description of the specimens along the channel:

Specimen	*Description*
A	White sandstone; fairly well cemented; unmineralized.
B	Weakly cemented sandstone; tan with brownish speckles; unmineralized.
C	Same as B, but with thin carbonaceous seams at base of specimen.
D	Similar to B; speckles less prominent.
E	Do.
F	Edge of mineralized zone; half of specimen is light-buff sandstone; other half is dark yellowish brown; boundary is quite sharp.
G	Yellowish-brown sandstone; heavily mineralized; contains reddish-brown patches, probably hewettite.
H	Same as specimen G; cut by 8-mm seam of coarsely crystalline gypsum.
I	Soft, largely incoherent yellow-brown sand.
J	Mottled yellowish to reddish brown coherent ore.
K	Strongly fractured zone; mottled yellow and brown; surrounded and impregnated by gypsum.
L	Friable yellow ore; considerable organic matter along bedding planes; few seams of hewettite.
M	Mottled ore; brown, yellow, with small nodular black masses.
N	Black dense ore forming coarse irregular masses in brownish matrix.
O	Black ore, apparently corvusite, forming small irregular masses in bleached-looking sandstone. Bounded sharply by narrow gypsum seam.
P	Friable bleached carbonaceous sandstone; carries some yellow minerals near gypsum band. Numerous coaly seams.
Q	Light colored, friable, carbonaceous sandstone; not evidently mineralized.

MINERALOGY OF THE CHANNEL SAMPLE

Essentially unmineralized sandstone is represented in the channel sample by specimens A through E (fig. 49). The rock is made up of subangular to poorly rounded quartz grains, very minor amounts of microcline, and rare green tourmaline; varying but small amounts of clay aggregates both as tiny pellets and as stringers are common. The quartz carries euhedral overgrowths in small patches. Limonitic grains probably representing the oxidation remnants of authigenic pyrite crystals appear as widely scattered dark spots on some of the specimens. Gypsum occupies almost the entire interstitial space between the granular minerals; it also occupies small veinlets where it is later than the matrix gypsum. Calcite is present only as very rare grains and not at all as matrix. Patches and seams of coalified wood can be seen in some sections. Evidence of extremely weak mineralization is in flakes of "vanadium clay" which can be seen wrapping around quartz grains; this material has a variable reddish brown color, mean index of refraction near 1.61, and high birefrigence typical of the clays in the mineralized portion of the channel. Evidence of weak mineralization is also shown by the faint yellowish stain which developed on the surface of the samples after they were originally collected and air dried. A few tiny patches of carnotite are present on some of the specimens.

Evidence of mineralization begins abruptly in the channel in specimen F. Part of this sample is typical of the unmineralized rock, made up largely of detrital quartz and interstitial gypsum, with a very minor amount of reddish brown clay forming coatings around some of the quartz grains. Very abruptly, along a line nearly at right angles to the general bedding, reddish-brown vanadium clay becomes abundant as an interstitial component. In one thin section cut across this boundary, the gradational zone between essentially unmineralized rock and that more or less typically mineralized rock is only 0.2 to 0.3 mm across. The vanadium clay forms rims on many of the quartz grains and has clearly replaced and encroached on the interstitial gypsum, and to a much lesser extent corrodes the quartz grains. The clay is erratically distributed, being absent in parts of some slides, forming thin films around quartz grains, or occupying the entire interstitial volume between the detrital grains. Isolated ragged plates of the clay are commonly scattered through the gypsum. The sedimentary clay aggregates are only slightly replaced by shreds of the vanadium clay. Limonitic aggregates (presumably goethite) are considerably more abundant in the clay-mineralized portions; they are highly irregular in outline and it can be only a guess that they are derived from oxidation of pyrite.

This generally typifies the channel sample between specimens F and J. Carnotite first is seen as more than traces in specimen H. It is erratically distributed as small patches or very fine grained aggregates apparently replacing the clays and gypsum.

An unidentified mineral, perhaps a vanadate, is common, but not abundant, in most of the mineralized section of the channel; it is in tiny lath-shaped grains, light yellowish brown across the length and dark brown to nearly opaque parallel to the length; it has a relatively high index of refraction and a strong birefringence. It appears to replace both interstitial gypsum and the vanadium clays. We have so far been unable to isolate the mineral for further study.

Carnotite becomes abundant in specimen K. It is quite erratically distributed, some parts of the rock being essentially unmineralized and showing strong development of quartz overgrowths and others showing marked corrosion of the quartz grains accompanied by carnotite. The carnotite commonly hugs the quartz grains, and appears to replace the clay irregularly; it also spreads into areas of sandstone where clays are absent. It forms small haloes around many of the isolated grains of coaly material present. The irregularly mineralized patches are in places bounded by a thin band of a very fine grained opaque mineral, which seems to be largely replaced by carnotite; the mineral is unknown. Gypsum, abundant in the unmineralized areas, continues as an important interstitial component in the strongly mineralized patches. Hewettite and metahewettite form a few thin seams in narrow fractures across the rock; they appear to be definitely later than all of the other minerals.

Specimen L is basically similar, but has carnotite more uniformly distributed through the matrix.

Corvusite and small amounts of pyrite, marcasite, and paramontroseite appear in specimen M. The corvusite is in irregular patches, in places completely filling the matrix between the quartz grains. Elsewhere it irregularly replaces vanadium clay minerals and penetrates along gypsum cleavages as long fingers. Carnotite is abundant in areas bordering corvusite, and in one place a microscopic veinlet of carnotite cuts corvusite. Hewettite and metahewettite are rare as fillings in late fractures, in one place bordering a late gypsum veinlet. Pyrite and marcasite grains, mostly small and anhedral but including a few larger euhedral crystals, are locally rather abundant and are limited to areas where corvusite is absent. A few of the pyrite grains are corroded remnants of larger grains, and are surrounded by goethite (?), but most show no evidence of corrosion. The pyrite and marcasite clearly were introduced at the time of mineralization. Paramontroseite is very sparingly present as prisms radiating from quartz grains and as minute rosettes; it is present in areas near pyrite and away from corvusite.

Specimen N comprises the black heavily mineralized "eye" of the ore zone. Parts of the sample contain abundant corvusite, similar to specimen M. Most of the sample has abundant euhedral pyrite and marcasite crystals, mostly in the interstitial space between quartz grains, and commonly replacing parts of quartz grains. The two sulfides occur side by side, with pyrite somewhat in excess of marcasite. Where they occur near corvusite the crystals show evidence of corrosion and limonitic material is present. Associated with the pyrite and marcasite is abundant paramontroseite; it forms prisms and massive areas between the quartz grains, growing into both clay and gypsum; paramontroseite too is absent near corvusite areas. Carnotite is abundant where pyrite and paramontroseite are absent. No uraninite or coffinite have been found. Carnotite does not seem sufficiently abundant to account for the amount of uranium in the sample, and it seems likely that uranium is distributed colloidally in the matrix material containing the pyrite and paramontroseite. It seems likely, also, by comparison with occurrences in other mines, that uraninite was originally present.

Specimen O is heavily mineralized with corvusite and carnotite, and in this way is similar to specimen M on the opposite side of the "eye" of the channel. In irregular areas, corvusite forms nearly all of the matrix between the quartz grains, and the quartz grains are rounded and corroded. Elsewhere the corvusite clearly replaces parts of the gypsum and vanadium clay matrix. Some areas show only minor mineralization and strong euhedral overgrowths of quartz so that little interstitial volume remains. A small amount of pyrite, in what appears to be remnants of larger grains, and very small marcasite grains, are present in the protected quartz areas, and only rarely are near corvusite. Carnotite and metatyuyamunite (the latter predominating) are abundant and widespread; they replace corvusite, and commonly form a band between the corvusite areas and the less mineralized areas.

Carnotite, metatyuyamunite, and vanadium clay are abundant in specimen P. Mineralized clay is abundant, replacing gypsum. In addition, primary clay is common as pellets and less so as thin clay seams and stringers; this clay has a much lower index of refraction and low absorption as compared to the vanadium clay, and is of sedimentary origin. The carnotitelike minerals are spottily distributed, and are abundant in large patches; they appear to replace chiefly the clay minerals. The quartz grains are largely embayed and corroded. Coalified organic remains are abundant and form thin streaks that emphasize the bedding. The mineralization does not seem to have been influenced in detail by the organic material. An unidentified reddish brown mineral, perhaps goethite, appears as irregular streaks and bands associated with strong carnotite mineralization.

Evidence of mineralization is weak in specimen Q. Carnotite is limited to a few small specks seen in hand specimen. Gypsum comprises most of the matrix material. Vanadium clays form thin films around many of the quartz grains, and in patches fill the interstices. Fairly large sedimentary clay pellets are present but not abundant. Microscopic clay seams of sedimentary origin are present and commonly accompany microscopic seams of coalified organic material. The quartz grains show little corrosion.

A small amount of organic matter (coalified wood) is present in nearly all of the specimens. Most of it forms microscopic rounded or worm-shaped grains; under crossed nicols in polished section the material ranges from isotropic to that showing a grating structure similar to microcline; no cellular woody structures were seen. Only in specimens P and Q are continuous seams of coaly material common; these were not studied in polished section.

The clay fractions from specimens M and P have been studied by John C. Hathaway and are considered in detail in Part 11.[11] These clays appear to have been introduced during mineralization. Briefly, the clays in each sample are chiefly mixed layered mica-montmorillonite and chlorite-montmorillonite, and are similar to vanadium clays in other deposits.

Summary of the mineral sequence.—The rock prior to mineralization was a fairly clean quartz sand with relatively little clay, a very small amount of coaly material, and was cemented with gypsum; specimens P and Q contained more abundant clay and organic material. Prior to mineralization, euhedral overgrowths developed on a portion of the quartz grains. Mineralization commenced with the introduction of vanadiferous clays, which replaced gypsum and in part quartz. Perhaps simultaneous with the clay, but probably later, was the deposition of pyrite, marcasite, and montroseite; the relative ages of these latter three minerals are not clear, but they appear to be nearly contemporaneous. The montroseite has since oxidized pseudomorphously to paramontroseite (Evans and Mrose, 1955). The clay minerals were widespread in the channel sample, but the others were largely limited to the areas in the vicinity of the dark eye of the channel sample.

The corvusitelike minerals are distinctly later; they replace clays, gypsum and the other matrix minerals and apparently were simultaneous with or later than the oxidation of pyrite and marcasite. Widespread development of carnotite and metatyuyamunite followed corvusite. Even later was the formation of hewettite and metahewettite, with gypsum, in open cracks.

CHEMISTRY OF THE CHANNEL SAMPLE

Preparation of samples.—The specimens were hand crushed to −40 mesh, with special care taken to avoid loss of material and contamination. About 1 percent of each specimen was lost during crushing, most of this

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[11] Specimens M and P are coded by Hathaway as P-1-M-53 and P-1-P-53, respectively.

due to discarded material contaminated during the labeling of the samples. For most of the chemical work ½-gram samples were prepared by careful hand splitting. Duplicate samples checked well during various determinations, indicating that the sampling procedure and sample size apparently were satisfactory.

Major constituents.—A sample of each specimen in the channel was analyzed for Ca, Al, Fe, V, U, total S, and SO_4; the results are shown in table 1 and plotted in figure 50. In figure 50, instead of showing values as percent by weight of each element in the specimen they are shown as millimoles of each element per 100 grams (except U, which is shown as millimoles per 1,000 grams). Thus, each plotted value is proportional to the number of atoms of each element present, rather than to the weight of each element.

TABLE 1.—*Chemical analyses of specimens of the Mineral Joe mine channe sample*

[In percent by weight]

Specimen	U [1]	eU [2]	Acid [1] insoluble U	Total [3] Fe	Acid [4] soluble Fe	Acid [4] insoluble Fe	Total [3] V	Total [4] S	Acid [4] insoluble S	Sulfate [4] S	Ca [4]	Al [5]
A	0.003	0.003	0.00005	0.22	0.17	------------	0.11	3.57	------------	3.50	4.37	2.2
B	.003	.003	.00002	.12	.13	------------	.13	4.16	------------	4.20	4.97	1.1
C	.005	.006	.00004	.11	.08	------------	.08	4.00	------------	4.02	4.72	1.9
D	.003	.005	.00004	.10	.08	------------	.10	3.90	------------	3.90	4.37	2.2
E	.003	.004	.00006	.11	.12	------------	.10	3.90	------------	3.83	4.55	1.2
F	.005	.007	.00005	.81	.76	------------	1.09	2.62	------------	2.57	3.27	4.3
G	.066	.065	.0010	.64	.64	------------	1.41	2.46	------------	2.21	2.91	5.9
H	.25	.23	.0014	.66	.40	------------	1.19	5.44	------------	5.38	6.55	2.8
I	.47	.53	.0020	.93	.84	------------	1.88	1.53	------------	1.50	2.00	4.1
J	.36	.34	.0022	.91	.99	------------	2.06	2.50	------------	2.43	3.27	2.7
K	1.22	1.0	.0095	.56	.51	------------	1.64	2.38	------------	2.30	2.88	4.1
L	.85	.82	.0027	1.18	1.07	------------	2.10	1.41	------------	1.38	1.97	4.7
M	1.26	1.3	.0050	1.60	1.55	.011	3.14	1.93	------------	1.95	2.69	5.0
N	1.13	1.0	.0112	4.40	2.45	1.78	4.15	6.31	3.43	2.23	2.36	2.0
O	1.90	1.6	.0113	.68	.68	.018	4.82	1.84	------------	1.68	2.36	3.3
P	1.74	1.2	.0042	.83	.76	------------	2.19	1.20	------------	1.09	1.65	8.9
Q	.009	.012	.0015	.38	.35	------------	.47	2.47	------------	2.43	3.17	8.1

[1] Analyst: Carmen Johnson, U. S. Geological Survey. Acid insoluble U determined after leaching sample 24 hours in cold 1 *N* H_2SO_4.

[2] Analyst: B. A. McCall, U. S. Geological Survey.

[3] Analyst: W. B. Tucker, U. S. Geological Survey.

[4] Analyst: L. B. Jenkins, U. S. Geological Survey. Acid-soluble and acid-insoluble values determined after leaching sample 5 days in hot 33⅓ percent H_2SO_4.

[5] Analyst: C. S. Annell, U. S. Geological Survey. Quantitative spectographic determinations.

The data clearly reflect the mineralogy. The plots for Ca and S coincide, within the limit of determinative error, except in samples M and N, and represent gypsum; in specimen N the excess sulfur is present as pyrite and marcasite and is accompanied by an appropriate increase in total Fe. The values for SO_4, as distinct from total S, were not plotted because they so nearly coincide with Ca throughout. The unusually high Ca and S values for specimen H reflect an 8 mm thick gypsum seam in the specimen; this depresses the values of most of the other elements for that specimen. The Al value is a proportionate measure of the "clay" minerals present; it is roughly complementary to the Ca values, representing gypsum. The unusually high Al content in specimens P and Q reflects abundant sedimentary clay.

Clay and gypsum comprise the bulk of the material interstitial to the detrital grains except in specimens M, N, and O, where pyrite, marcasite, and vanadium oxides bulk large. Uranium (which is exaggerated by a factor of 10 in figure 50) is everywhere far subordinate to V, with which it combines in a 1:1 ratio to form carnotite or metatyuyamunite or both. The excess of V above that combined with uranium in carnotite largely follows the Al in the clay minerals, but in samples M, N, and O it occurs also as separate vanadium oxide minerals (corvusite and paramontroseite). The iron in small part forms limonitic material and in larger part is combined in the clays; in specimen N, and to a much lesser extent to M, it is abundant as pyrite and marcasite.

Organic carbon, a measure of the coalified wood present, is plotted for some of the specimens in weight percent in figure 51; total uranium and vanadium are also shown for comparison. Uranium and vanadium are highest in and near the organic-rich part of the channel.

The analytical data reflect the sharp boundaries of mineralization. Clearly U, V, Fe, and Al have been introduced, and Ca and S (as SO_4) have been removed.

Uranium and equivalent-uranium relations.—The analytical results for U and equivalent U are plotted in figure 52. Inspection shows differences only of the order of magnitude of the expected determinative error. The ore is essentially in radioactive equilibrium, and it can be concluded that there has been no appreciable migration of the uranium for many thousands of years; in all probability none during Quaternary weathering. (See Stieff and Stern, Part 13, p. 152.) The only explanation of the observed relations, if recent migration had taken place, would be that the transporting medium had exactly the same solvent capacity both for uranium and for its daughter products—a most unlikely coincidence.

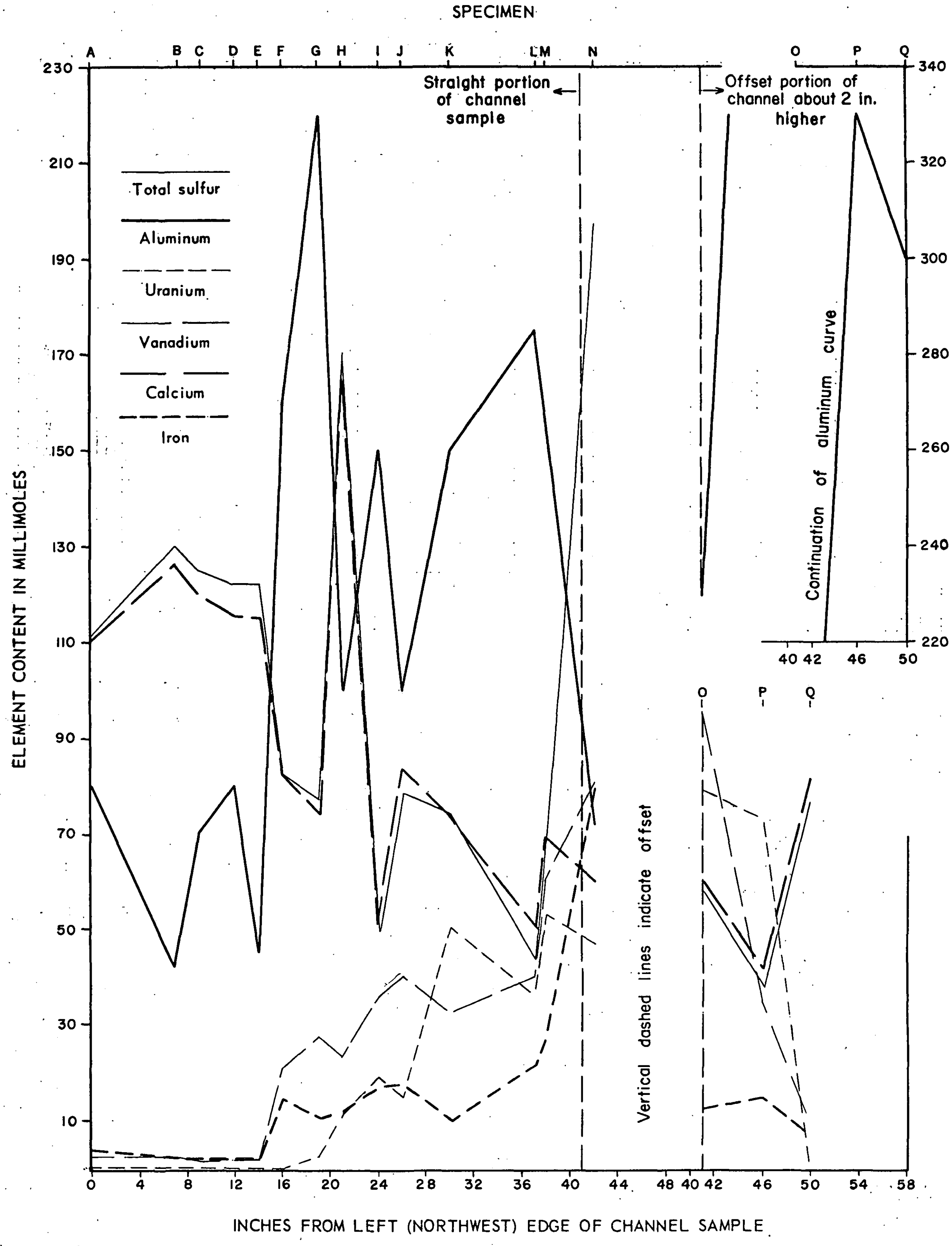

FIGURE 50.—Graph showing distribution of several elements across the Mineral Joe No. 1 mine channel sample. Values are in millimoles per 100 grams of sample, except uranium which is in millimoles per 1,000 grams of sample. Data derived from table 1.

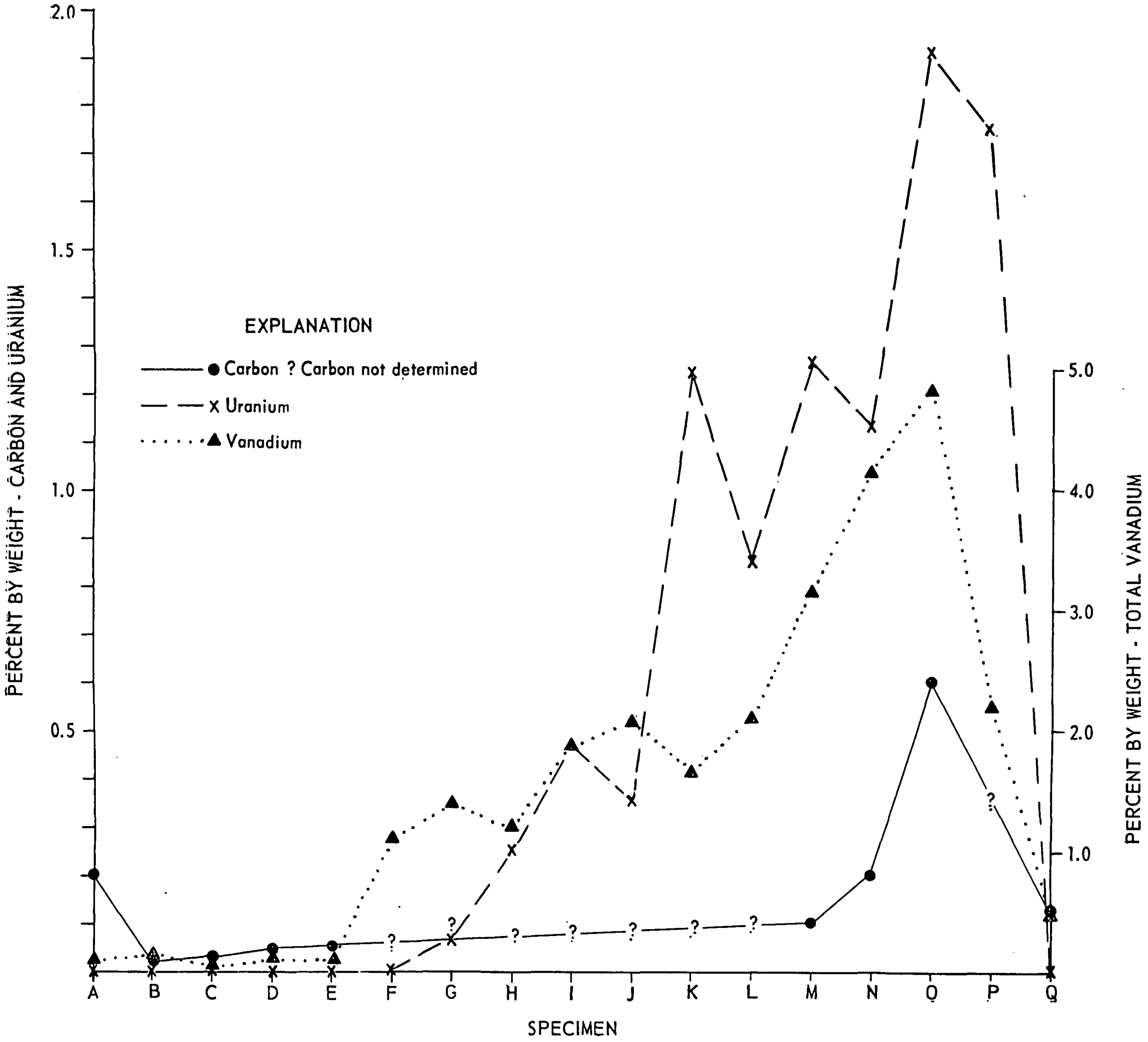

FIGURE 51.—Distribution of uranium, vanadium, and organic carbon in specimens across the Mineral Joe No. 1 mine channel.

Trace-element relations.—Semiquantitative spectrographic analyses of the specimens were obtained, and the results are plotted in figure 53. These data, plus the data in table 1, show definite strong anomalies for uranium, lead, vanadium, and iron; probable anomalies for barium, strontium, aluminum, and molybdenum; and a doubtful anomaly for copper. The definite and probable anomalies, with the exception of that for barium, appear initially in specimen F and are maintained across the profile; that for barium occurs initially in specimen G. The first five specimens, classified as "unmineralized" in the field, are remarkably uniform in trace-element content, and they approach closely the barren sandstone of the Salt Wash member of the Morrison formation except for small uranium and vanadium anomalies (see Part 3, p. 32). Furthermore, the anomalies are all positive; there is no indication of removal of any minor element during the mineralization process.

The channel sample selected is a representative one in its minor element content; the unmineralized sandstone is uniform, and typical of barren sandstone of the Salt Wash member; the mineralized zone contains additions of the elements that are enriched in "average ore," as determined from many ore pulps (see Part 3, p. 32). The most remarkable features of the minerali-

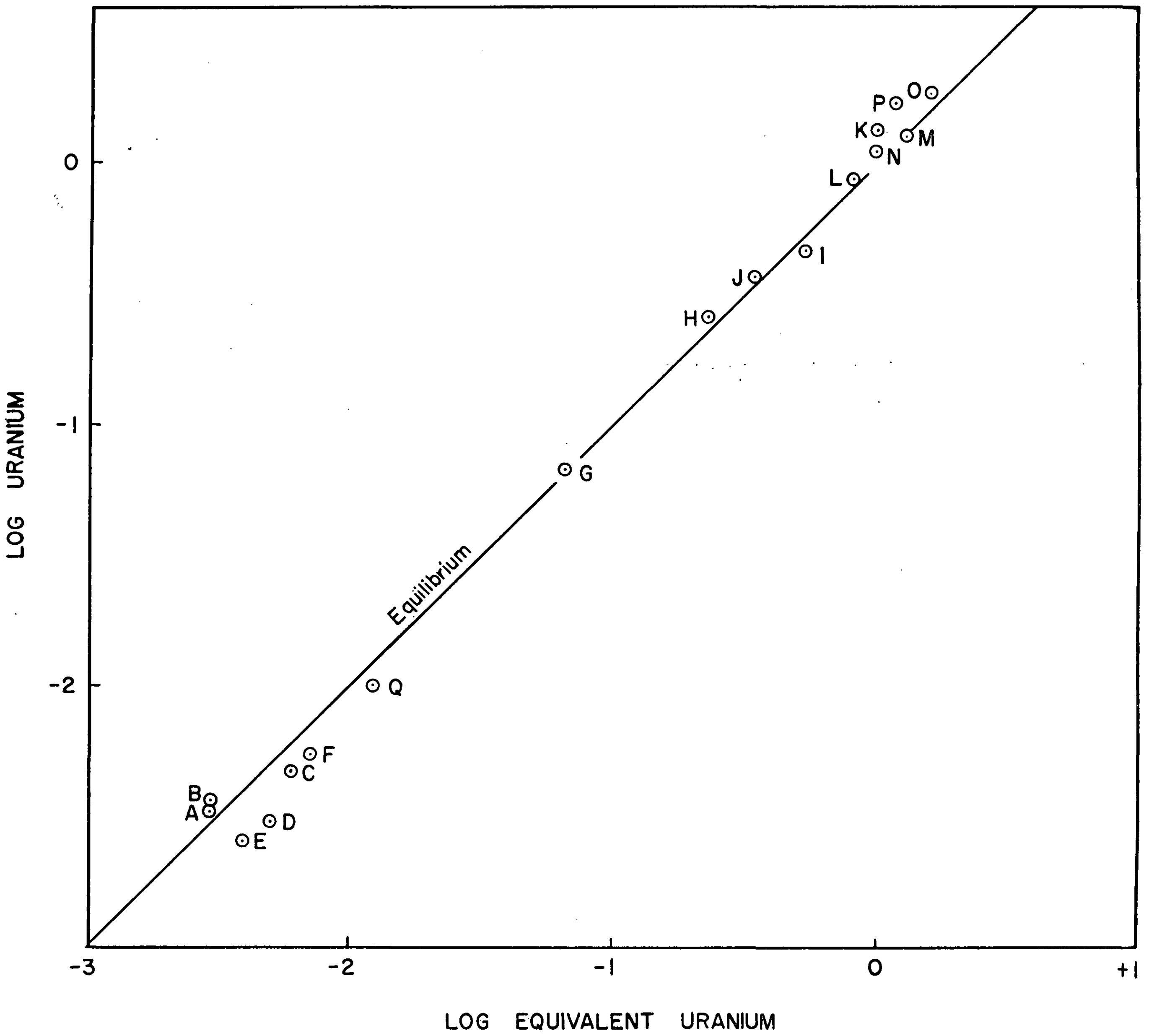

FIGURE 52.—Plot of log U against log equivalent U of specimens from the Mineral Joe No. 1 mine channel sample.

zation are: (1) the abrupt cut-off of all introduced elements at a zone no more than a few inches wide, and perhaps only a few tenths of an inch wide if the mineralized clay is an indicator; and (2) the lack of any negative trace element anomalies in the mineralized zone, suggesting that no minor constituents have been removed during or after mineralization.

STATES OF OXIDATION OF THE SPECIMENS

It is desirable to know the proportion of each element present in each of its oxidation (valence) states. Of the elements likely to be present in unknown valence states, spectrographic and chemical data show that only iron, uranium, vanadium, and sulfur are present in any sample in amounts exceeding 0.05 percent. Sulfur is present as sulfide and as sulfate; these can be readily separated by their relative solubilities, and are reported separately in table 1. Gypsum, and probably a minor amount of barite, represent the sulfate; pyrite and marcasite, the sulfide.

Uranium can be present both as U(IV) and as U(VI). Of the U(IV) minerals, uraninite is essentially insoluable in cold 1*N* H_2SO_4, but coffinite is appreciably soluble. In the channel sample specimens practically all of the uranium is readily soluble (see table 1). Neither coffinite nor uraninite could be

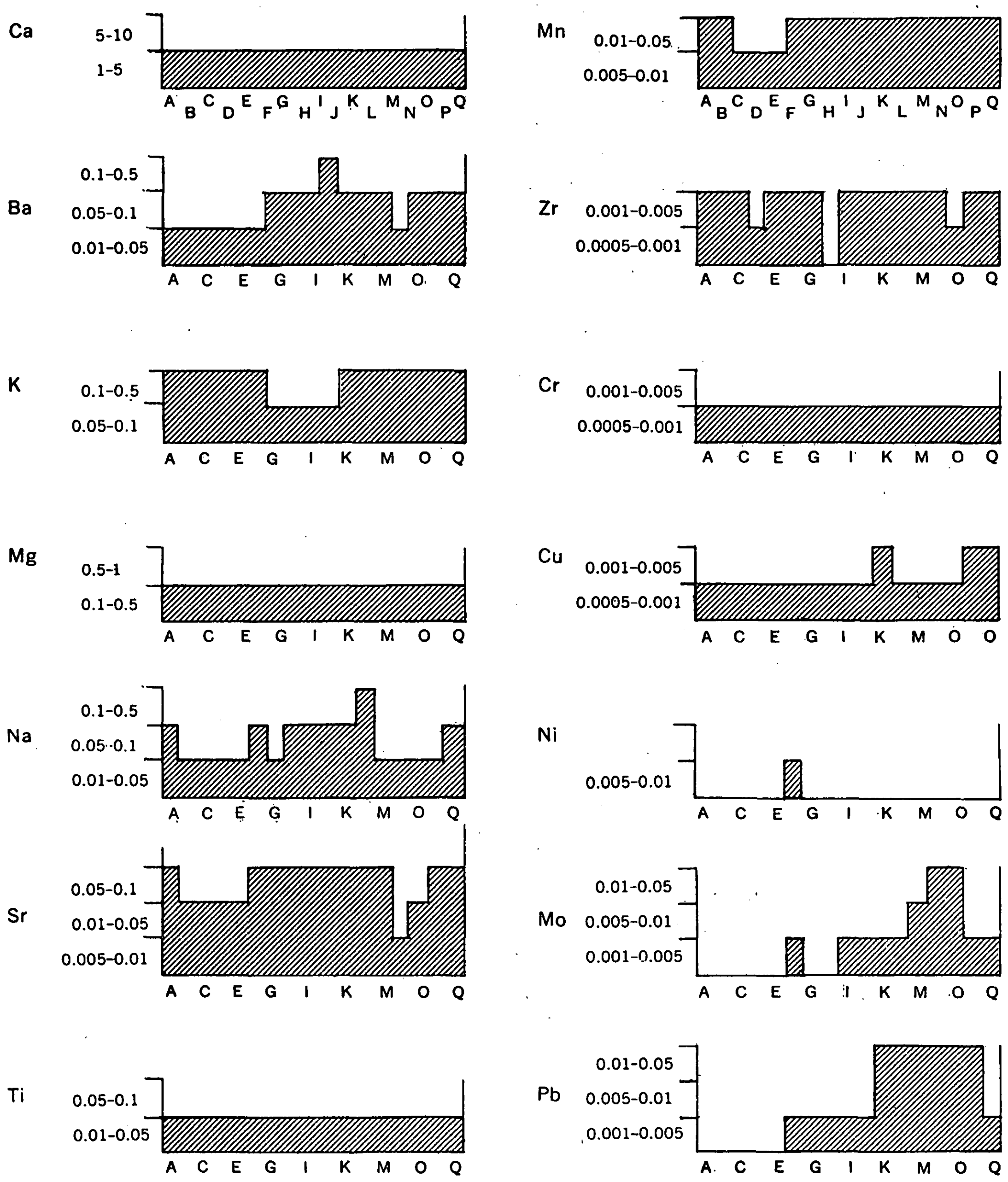

FIGURE 53.—Semiquantitative spectrographic analyses of specimens from the Mineral Joe mine channel sample. Ranges are in percent. Horizontal letters deisgnate specimens. Analyst, C. A. Annell.

found mineralogically, and the abundance of oxidized mineral species in all samples suggests (by analogy with other deposits) that any U(IV) minerals would not have persisted. It is therefore assumed that the uranium is present entirely as U(VI).

The valence states in which vanadium and iron are present cannot be directly determined, and yet these largely control the variable oxidation state of the ore. From the mineralogy, it is known that vanadium is present as V(IV) and V(V), and that the iron is present as both Fe (II) and Fe (III), at least in some parts of the channel sample. If such an assemblage of redox-active[12] elements is taken into solution in air-free sulfuric acid (where no over-all oxidation or reduction will take place), the vanadium and iron ions formed will promptly reach an equilibrium state in which the valences of the ions are a function of both the pH of the solution and the cumulative interactions of all the redox-active elements present. Thus, the valences of the metals in solution need not be the same

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[12] Redox-active elements are those that change their valence state with natural changes in reducing or oxidizing environment.

as they were in the minerals dissolved. However, the reducing capacity of the solution should be the same.

The reducing capacity of a sample refers to the amount of oxidant the sample can reduce, and can be expressed in milliequivalents per 100-gram sample. The reducing capacity expressed in this unit is given by the number of ml of a 1 *N* solution of oxidant ($KMnO_4$ in this case) reduced by a 100-gram sample. For direct comparison, it is convenient to state composition of the sample in milliequivalents per 100 grams. If the equivalent weight of the oxidant is defined as the amount necessary to oxidize one mole of any ion by removal of a single electron, one milliequivalent of an element is equal to one millimole of that element.

To determine the reducing capacity of each part of the channel sample, about 100 mg of each was digested for five days in hot 33.3 percent H_2SO_4 in a carbon dioxide atmosphere. Quantitative tests showed that essentially all of the redox-active elements, except iron in the sulfides, were taken into solution. The solution was then titrated with 1 *N* $KMnO_4$. The reducing capacity of each specimen, together with the concentration of vanadium and iron in solution, expressed in milliequivalents as defined above, are given in table 2.

Pyrite and marcasite are insoluble under the treatment noted above. Therefore, the sulfur present as sulfide and the iron combined with the sulfide are not reflected in the value of the reducing capacity obtained. Sulfides were present in chemically significant amounts only in sample N.

The coaly material contained in the specimens may have reduced some of the redox-active elements during digestion (see Part 14, p. 162); we have no measure of the amount of such reduction, but we feel it was not great enough to distort the conclusions appreciably.

TABLE 2.—*Reducing capacities and vanadium and iron content of acid extracts*[1] *of specimens from the Mineral Joe No. 1 mine channel sample.*

[All values are in milliequivalents per 100 grams of sample]

Specimen	Vanadium, acid soluble[2] (meq/100g)	Iron, acid soluble[2] (meq/100g)	Reducing capacity,[3] acid soluble (meq/100g)
A	2.2	3.0	1.9
B	2.6	2.3	1.9
C	1.5	1.4	2.1
D	2.0	1.4	1.8
E	2.0	2.1	1.6
F	21.4	13.6	19.5
G	27.7	11.4	29.1
H	23.5	7.1	17.6
I	36.9	15.0	21.1
J	40.4	17.7	19.9
K	32.5	9.1	20.2
L	39.5	19.1	26.3
M	61.6	27.7	29.6
N	81.4	43.8	102.0
O	94.6	12.1	59.4
P	34.3	13.6	30.1
Q	9.2	6.3	15.4

[1] Extracted in 33.3 percent H_2SO_4.

[2] All the vanadium present is acid soluble; figures given were recalculated from table 1.

[3] Determined by L. B. Jenkins.

In the unmineralized portion of the channel (specimens A through E), the reducing capacity is low but ranges between about ⅓ and ⅔ of the sum of vanadium plus iron; this is the amount of vanadium or iron, or both, which is in a reduced state—that is, V(IV) or Fe(II); the remainder must be V(V) or Fe(III) or both. It has been shown mineralogically that small amounts of carnotite (or tyuyamunite) and ferric hydroxides are present, accounting for part of the V(V) and the Fe(III). The reduced vanadium and iron must be present in the clays.

The reducing capacity rises abruptly at the boundary of mineralization (specimen F) and continues at roughly the same level through specimen L. Basing interpretation on the mineralogy, the bulk of the reducing capacity is due to the vanadium (IV) and the ferrous iron contained in the clay minerals; this conforms to the chemical study of vanadium clays by Foster, reported in Part 10 of this volume. The clays may also contain a small amount of vanadium (V) and considerable iron (III). The iron staining observable in the samples may account for some iron (III). It seems likely that more vanadium (V) is present than can be accounted for by the carnotite and hewettite reported mineralogically; probably other vanadates not identified under the microscope are dispersed through the fine-grained matrix.

The reducing capacity of specimen M, which contains a small amount of lower-valence oxides, appears to result largely from the vanadium (IV) and iron (II) in the clays and to a much smaller degree to the paramontroseite and corvusite. The increase in acid soluble iron probably reflects the oxidation products of pyrite and marcasite. The large amount of vanadium (V) is present chiefly in hewettite, metahewettite, carnotite, and perhaps other unidentified vanadate minerals, as well as corvusite.

In specimen N, the black "eye" of the channel sample, the reducing capacity is very high and approaches the sum of the vanadium plus iron in milliequivalents, so that most of both the iron and vanadium must be present in reduced minerals as V(IV) and Fe(II). This conforms with the mineralogy, in that vanadium clays and paramontroseite are the dominant vanadium minerals, with smaller amounts of corvusite. The fully oxidized elements present in minor amounts, make up carnotite, perhaps unidentified vanadates, and corvusite; iron (III) is present in oxidation products of pyrite and marcasite.

Specimen O is nearly as heavily mineralized as specimen N, but has only half the latter's reducing capacity. Here paramontroseite is lacking, but considerable vanadium (IV) is present in the corvusite as well as in the clays. Carnotite, corvusite, and perhaps unidentified vanadates account for the abundant vanadium (V). A small amount of iron (III) may be present as a result of alteration of pyrite and marcasite; the remaining iron, mostly as iron (II), is in the clays.

Specimen P is comparable to specimens on the opposite side of the black "eye" of the channel sample. The reducing capacity appears to result wholly from the abundant vanadium clays present. Some iron (III) may be present as goethite; vanadium (V) is present in uranyl vanadates, and probably in other unidentified vanadates.

The reducing capacity of specimen Q nearly equals the sum of iron plus vanadium (in milliequivalents per 100 g), so that most of these metals must be present as vanadium (IV) and iron (II); they are doubtless contained in the clay structures. Judging from the petrographic study of this sample, these elements were likely introduced into existing sedimentary clays.

To summarize, the entire reducing capacity, except in the very highly mineralized "eye" of the channel sample, can be accounted for by the vanadium (IV) and iron (II) held structurally in the clay minerals. The remaining iron taken into solution as Fe(III), can be accounted for by the clays in part and the rest by hydrated ferric oxides. The remaining vanadium, as V(V), is present in the form of vanadates, some of them probably unidentified mineralogically. Only in specimen N, and to a much smaller extent in the adjacent specimens M and O, does the reducing capacity result from the presence of vanadium oxides containing vanadium (IV) (chiefly paramontroseite). In these same samples, the low-valence iron sulfides (pyrite and marcasite) are also present, but these are insoluble and do not affect the measured reducing capacity. There is no evidence, either from the reducing capacities or from the mineralogy, that vanadium (III) or uranium (IV) are present in any part of the channel sample.

SALIENT FEATURES OF THE MINERAL JOE NO. 1 MINE CHANNEL SAMPLE

1. One boundary between mineralized and unmineralized rock is nearly pencil-sharp, and cuts across the bedding at right angles. The boundary bears no relation to sedimentary or other structures, or to changes in lithology. The unmineralized rock contains appreciably more uranium and vanadium than typical unmineralized sandstone of the Salt Wash member.
2. Vanadium-bearing clay minerals are abundant throughout the mineralized part of the channel sample. A large part of the vanadium in the clays has a valence of 4. The vanadium clays are mostly newly constituted minerals, and are not simply "vanadated" sedimentary clays.
3. Except in the dark "eye" of the channel sample (specimen N and parts of M and O), the vanadium clays are associated with vanadates, uranyl vanadates, and traces of ferric oxides, and represent an assemblage largely in equilibrium under oxidizing conditions.
4. In the dark central "eye" of the channel sample (specimen N and parts of M and O) the vanadium clays are associated in part with vanadates, uranyl vanadates, and traces of ferric oxides; and in addition, grading inward to the center of the dark "eye," with vanadyl vanadates, and ultimately with iron sulfides and a vanadium (IV) oxide (paramontroseite). This gradational zone represents a mineral assemblage out of equilibrium; part of the assemblage is in equilibrium under oxidizing conditions, and part is in equilibrium under mildly reducing conditions.
5. The relatively high percentage of vanadium and uranium in the dark core of the channel coincides with the relatively high organic content of the rock in that part of the channel. The presence of iron sulfides and of vanadium (IV) oxides also coincides with this high organic content.

VIRGIN NO. 3. MINE CHANNEL SAMPLE

LOCATION AND GEOLOGY

The Virgin No. 3 mine is in the Long Park area, Montrose County, Colo. The channel sample used for this study was collected by T. W. Stern. The site of the sampling and a sketch of the ore occurrence is shown in figure 54. The sample was removed as one large piece as shown by the shaded area in the sketch. No precautions were taken to prevent air oxidation after sampling.

The locality sampled in the Virgin No. 3 mine is approximately 300 feet below the surface. The mineralized zone occurs in the Salt Wash member of the Morrison formation. The mine generally shows little megascopic evidence of oxidation and the gross appearance of the mineralized sandstone at the sampling site suggests no alteration of the primary features. It can be assumed that the position of the mineralized lens is essentially the same as it was just after mineralization and that the sample is fairly representative of rich primary ore in the Salt Wash member in that area.

PREPARATION OF THE SAMPLE

The general shape and appearance of the channel sample is shown in plate 3. The sample was cut in half vertically as marked and divided into ten parts based on the lithologic variations. The ten segments

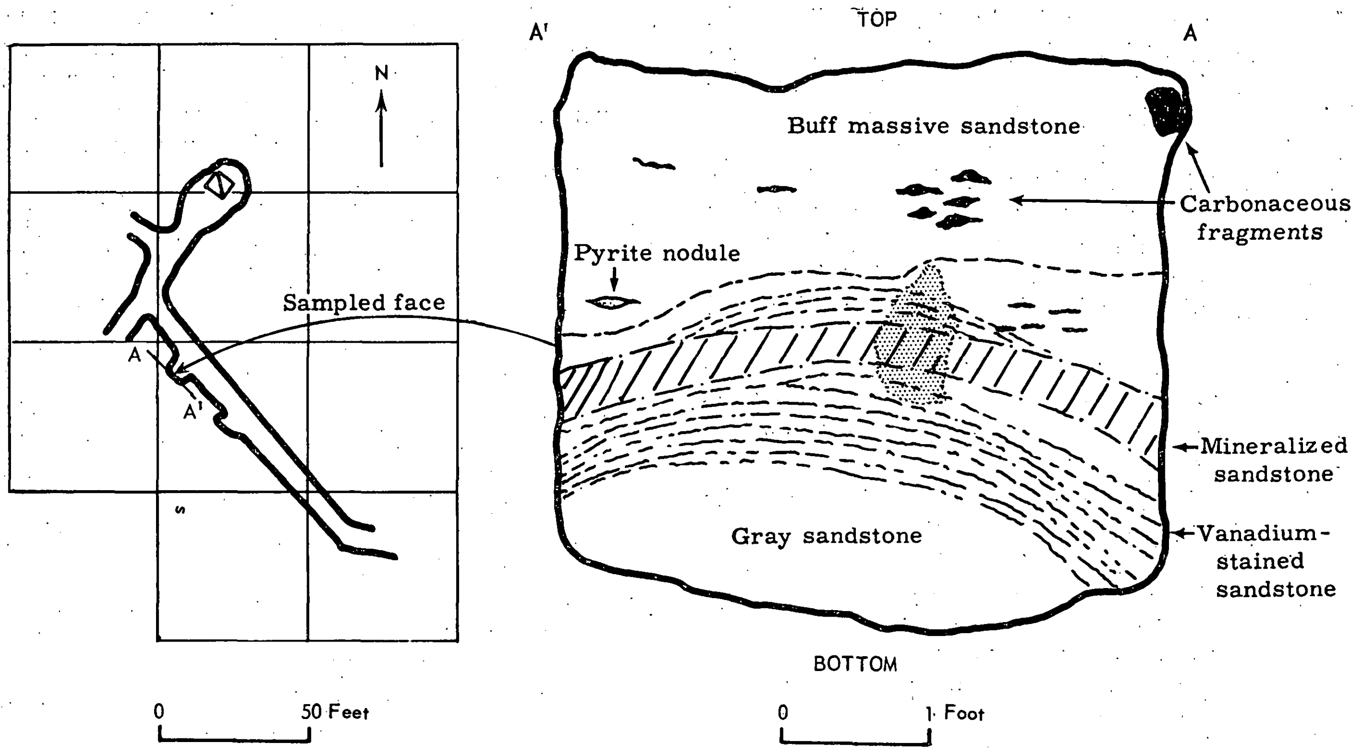


FIGURE 54.—Sketch of the workings of the Virgin No. 3 mine showing location of sampling site, and sketch of sampling site showing relation of channel sample to ore and sedimentary features. Channel sample is the shaded area.

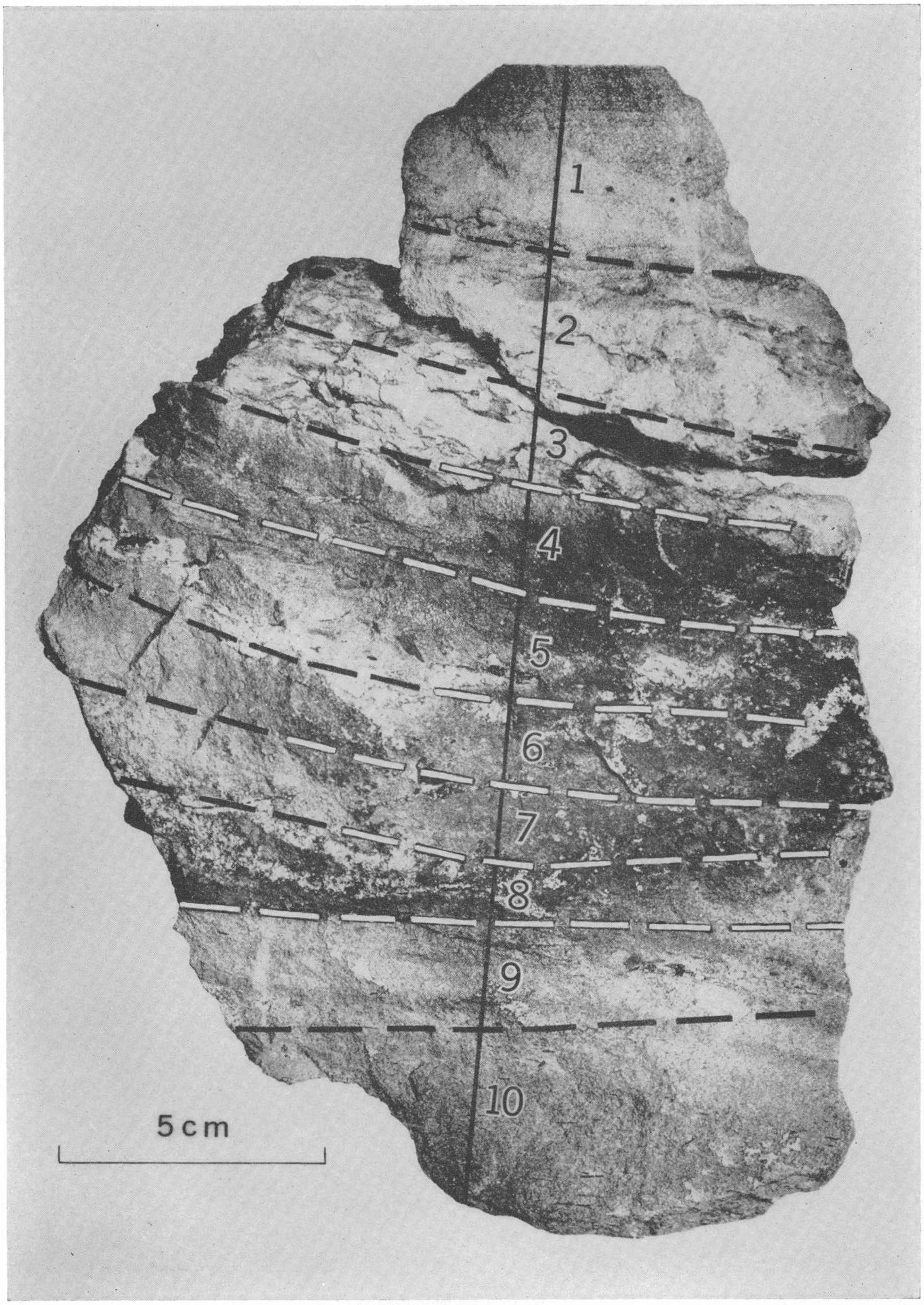
on the left side of the channel sample were ground to pass through an 80-mesh sieve. These pulverized portions were used for chemical and spectrographic analysis. A second slab, 1 inch thick, was cut from the right-hand portion of the channel sample and also divided into 10 parts equivalent to the left-hand portion. These parts in turn were cut in half and a thin section and polished section were made of each along the mutually cut planes. The sections were ground and polished without using water to retain any water-soluble minerals that might be present. The specimen numbers henceforth refer to those shown in plate 3.

MINERALOGY OF THE CHANNEL SAMPLE

The discussion of the mineralogy is divided into two parts: weakly mineralized and strongly mineralized rock. This division is based on the chemical and mineralogical results. A point-count analysis was made on each thin section to determine the relative abundance of the constituent minerals, and the results were plotted in figure 55. A sharp change is noted between specimens 3 and 4 and a lesser one at specimen 10; specimens 1, 2, 3, and 10 are here considered as weakly mineralized rock and specimens 4 through 9 as strongly mineralized rock. The strongly mineralized zone is highly irregular and mineralogical continuity is lacking because of discontinuous horizontal zones. The channel sample exhibits marked color changes from weakly mineralized rock into strongly mineralized rock. The weakly mineralized portion is dark gray with a banding derived from minor mineralization by vanadium clay minerals. The strongly mineralized zone is dark green to black and contains many irregular patches of light-gray recrystallized quartz; small black carbonaceous fragments are randomly distributed throughout the zone.

WEAKLY MINERALIZED ROCK

The weakly mineralized rock contains no recognizable uranium or vanadium minerals, although minor amounts of vanadium are present within the clay minerals shown in plate 3. The detrital quartz is poorly sorted and authigenic overgrowths produce a mosaic texture. Clastic feldspar, both microcline and plagioclase, is present but never in excess of 2 percent. Clastic mudstone partings that roughly parallel the bedding are common in specimens 2 and 3. These partings have been contorted by compaction, and along the upper and lower surfaces strong pressure solution of the quartz is apparent from the corroded grains and development of microstylolites. The mudstone partings retain their original particle orientation and contain mostly mixed layer mica-montmorillonite, sericite, and quartz with minor pyrite and marcasite showing framboidal textures. Wisps of carbonaceous fragments are commonly



PHOTOGRAPH OF CHANNEL SAMPLE FROM VIRGIN NO. 3 MINE, SHOWING DIVISION OF SAMPLE INTO SPECIMENS REFERRED TO IN TEXT

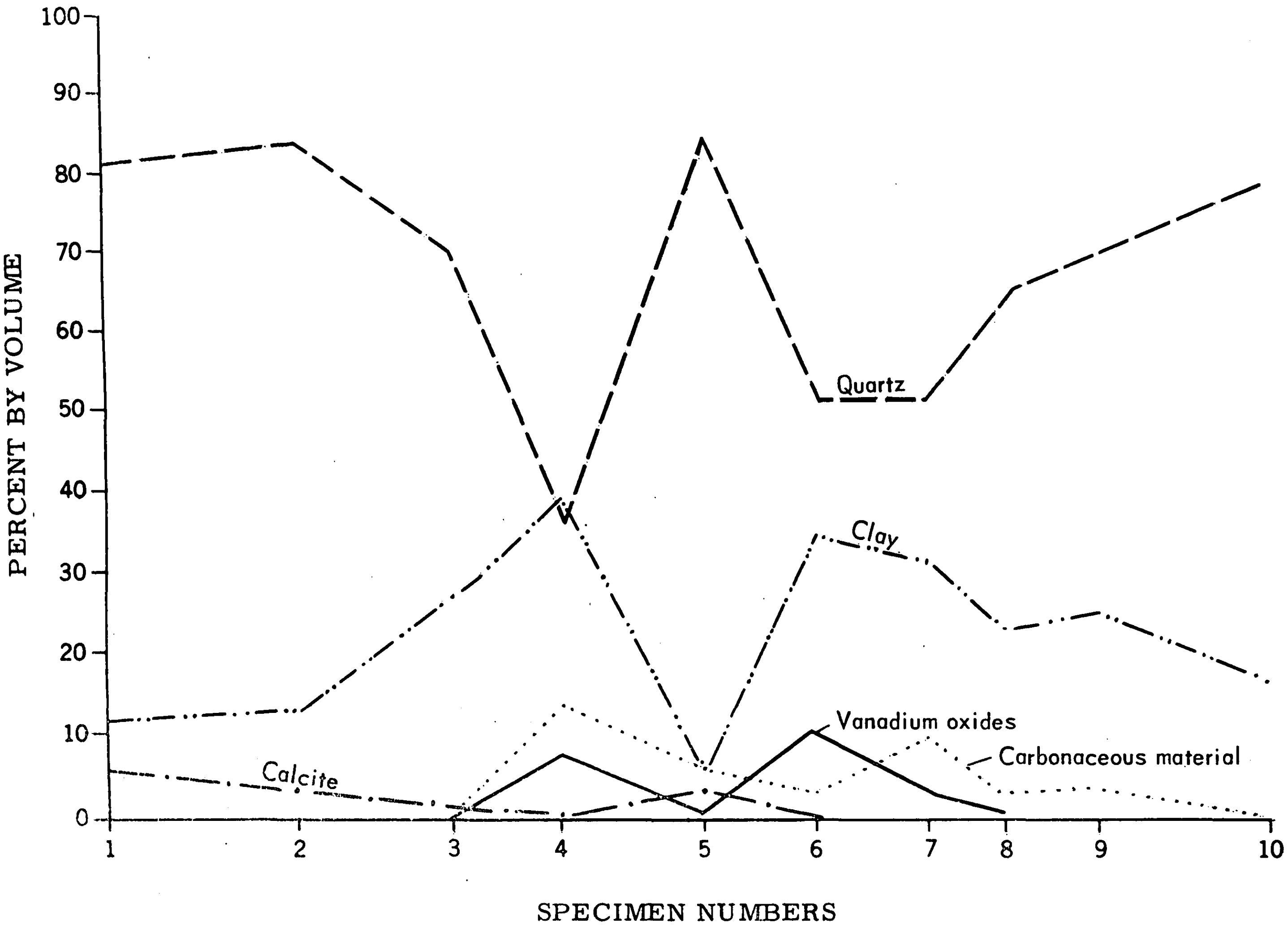


FIGURE 55.—Mineralogical composition, based on point-count analysis, of specimens from the Virgin No. 3 mine channel sample. Specimen Nos. are distributed along the horizontal base in proportion to the thickness of each segment in the channel sample.

present in the clastic mudstone partings. The intergranular areas of the sandstone contain mixed layer mica-montmorillonite, chlorite, and kaolinite accompanied by calcite and minor barite. Clear calcite forms anhedral patches replacing the quartz and it appears to truncate the quartz overgrowth boundaries. Honey-yellow barite with weak pleochroism also forms anhedral patches which usually show a prominent inclusion band near the outer boundary. In specimen 10, euhedral pyrite forms inclusion bands in the barite. Possible evidence of weak oxidation of the sulfides is observed in the polished sections along with limonitic stains around the outer boundaries of the clastic mudstone partings. Several anhedral grains of galena-clausthalite were identified in specimen 3. The X-ray patterns of this mineral suggest that there is more selenium present than sulfur. Heavy mineral separations of the weakly mineralized rock samples contain tourmaline, zircon, and apatite in decreasing order of abundance.

STRONGLY MINERALIZED ROCK

The boundary of strong mineralization is reflected by an abrupt change in gross mineralogy of the rock. The upper boundary is marked visually by a dark-greenish coloration which cuts across the bedding planes and in the lower boundary there is a narrow transition zone from black to gray. Within the mineralized zone the coloration is variegated and roughly follows the trend of the bedding. Quartz, clay minerals, vanadium oxides, and carbonaceous material comprise the bulk of the rock. The relative abundance of these is shown in figure 55; the color banding is due only to different proportions of minerals.

The quartz no longer maintains its detrital outline within the mineralized zone and is strongly corroded into cuspate forms. The corrosion appears to have been greatest normal to the bedding and the cuspate quartz grains show elongation in the directions of the bedding planes. Microstylolites are commonly developed where the quartz grains are in juxtaposition. Isolated elongate patches of quartz grains within the mineralized zone, particularly in specimen 5, have not been corroded but rather show strong secondary overgrowths on the detrital quartz grains. Clastic feldspar grains are also scarce in the mineralized zone, although the feldspar appears to be much more stable than the quartz and little or no corrosion of the feldspars was noted. Most of the feldspars are orthoclase and microcline.

Associated with the corroded quartz are green to brown vanadium clay minerals that fill the matrix around the quartz. It appears that the clay minerals have replaced the quartz and may have derived their silica from the breakdown of the quartz. The vanadium clay minerals form extremely fine aggregates with moderate birefringence and marked pleochroism. In areas rich in vanadium clays, the clays have an aggregate structure with a strong preferred orientation parallel to the bedding producing a "pseudo-flow structure."

The fine clay aggregates have a mean index of refraction near 1.61; it was not possible to identify the clay minerals optically. X-ray diffraction studies, carried out by John C. Hathaway, indicate that chlorite is the most abundant vanadium silicate and it is assumed from previous chemical work that the chlorite contains appreciable amounts of vanadium. Accompanying the chlorite is a mixed-layered vanadium mica-montmorillonite. Kaolinite also has been identified although it apparently does not contain vanadium.

Chlorite increases from the barren rock into the mineralized zone with concomitant decrease in the mixed layer mica-montmorillonite; kaolinite does not present any definite trend from barren to mineralized rock. As indicated above, it is not possible to distinguish the clay minerals optically, although strong color variations were noted. The clay matrix is a reddish brown near carbonaceous fragments and a strong greenish color where associated with vanadium oxides. The greatest corrosion of the detrital quartz takes place in the vanadium clay rich layers, but in those isolated stringers carrying quartz overgrowths, vanadium clay is absent.

Paramontroseite is intimately interleaved with the vanadium clay minerals and forms opaque elongate crystals in minute rosettes. The abundance of paramontroseite roughly parallels that of vanadium clay. X-ray determinations have indicated only paramontroseite, but the poor quality of the X-ray patterns was such that montroseite could be present in small amounts and not be identified. No other vanadium-bearing minerals were found in the channel sample.

Carbonaceous material is common within the mineralized zone and forms elongate stringers characterized by a pitchy luster and subconchoidal fracture. Two distinct types of carbonaceous material can be distinguished in thin and polished sections: (1) fragments showing well preserved cell structure of woody material. These particles conform to, or wrap around contiguous detrital quartz grains and are translucent in thin section. (2) Kidney-shaped, opaque, carbonaceous blebs that cross-cut the bedding and replace the detrital and recrystallized quartz overgrowths. There is no recognizable wood structure present within these blebs, although in polished section under polarized light, strong anisotropy is observed. This anisotropy is similar to the grid-iron twinning observed in microcline.

These kidney-shaped blebs appear to have formed from the detrital coalified wood of the first type, although as yet the relationship is not clear. Autoradiographs show that these carbonaceous fragments contain a large part of the uranium, although no distinct uranium minerals have been identified within the carbonaceous material.

Coffinite is the only uranium mineral identified from the channel sample. Coffinite could not be identified in polished section and was determined only by X-ray analysis of a heavy residue. Coffinite was also identified in the clay-size fraction during the study of the clay minerals. From the autoradiograph and X-ray analysis the coffinite is probably dispersed as colloidal size particles. Uraninite may be present also as colloidal size particles but neither X-ray nor polished section studies revealed its presence. The chemical studies show that there is little or no acid insoluble uranium (in $1N$ H_2SO_4) and since uraninite is considered insoluble (Phair and Levine, 1953) it can be concluded from the chemistry that most of the crystallized uranium is contained within the coffinite which is appreciably soluble in $1N$ H_2SO_4.

Calcite is common in the barren sandstone and also in the mineralized zone within the recrystallized quartz lenses. No calcite was found in the mineralized zone associated with vanadium clays and corroded detrital quartz. Honey yellow barite (beta$=1.63\pm.01$) is common in specimen 5 in the recrystallized quartz lenses. The irregularity shown in the quartz content, figure 55, results from the fact that specimen 5 has more quartz overgrowths than the other specimens.

Pyrite and marcasite are irregularly distributed in the mineralized zone and are closely associated with the carbonaceous fragments. The iron sulfides form near the fragments and in some cases impregnate the wood cell cavities. The iron sulfides in specimen 7 form a marked stringer parallel to the bedding and coincide with a high concentration of uranium. Marcasite and pyrite are commonly intergrown in framboidal clots. Euhedral cubes of pyrite are common particularly in specimen 7. Sphalerite was identified in the recrystallized quartz lenses and appears to be a late mineral; it truncates the quartz overgrowths. Patches of a solid solution mixture of galena-clausthalite are common in and around the carbonaceous fragments and in one isolated spot sphalerite was seen to have replaced this lead selenium mineral. The scattered nature of the sulfide minerals precludes the establishment of a complete paragenetic sequence.

The heavy detrital minerals remain the same in the strongly mineralized zone except for apatite. The absence of apatite suggests the possibility of leaching by the ore solutions. In polished sections, strong corrosion was observed on zircon. The negative anomalies in some of the minor elements (fig. 56) suggest the possibility of differential leaching of heavy detrital minerals during mineralization.

CHEMISTRY OF THE CHANNEL SAMPLE

A portion of each specimen of the channel sample was analyzed for uranium, vanadium, and total iron. The results are given in table 3 in percent by weight. The relatively sharp boundaries of mineralization types are apparent. The high vanadium content of specimen 5 suggests that the percent of paramontroseite, and perhaps vanadium clays (fig. 55), was not representative in the thin section studied. Abundant carbonaceous material coincides with the strong mineralization.

Chemical uranium and equivalent uranium shown in table 3 appear to be close to radioactive equilibrium, although there is some suggestion of differential movement of daughter products. Equivalent uranium determinations at values as high as most of these are not usually considered accurate. There is no other evidence of movement of elements after mineralization.

TABLE 3.—*Analyses of specimens from the Virgin No. 3 mine channel sample*

[In weight percent]

Specimen	Percent U Total [1]	Percent Equiv. U Total [2]	Percent U Insol. [1]	Percent Fe Total [3]	Percent V Total [4]
1	0.003	0.005	<0.001	0.38	0.10
2	.003	.02	<.001	.54	.30
3	.095	.2	.001	1.31	1.08
4	1.0	1.0	.003	1.75	6.65
5	5.0	2.9	.003	1.30	5.98
6	4.0	2.8	.004	1.42	6.80
7	4.8	2.8	.004	1.29	4.16
8	4.2	2.9	.004	1.75	1.24
9	1.2	.98	.002	1.57	1.24
10	.13	.16	<.001	.74	.33

[1] Analyst: Roosevelt Moore, U. S. Geological Survey. Acid-insoluble U determined after leaching sample 24 hours in cold 1 *N* H_2SO_4.
[2] Analyst: B. A. McCall, U. S. Geological Survey.
[3] Analysts: L. B. Jenkins and M. H. Delevaux, U. S. Geological Survey.
[4] Analyst: L. B. Jenkins, U. S. Geological Survey.

Semiquantitative spectrographic analyses of minor and trace elements were made, and the results are shown in figure 56. Al, Sr, Zr, Be, Pb, and Mg show a slight to marked increase from weakly mineralized rock into strongly mineralized rock. These anomalies for the most part maintain a remarkably uniform level across the strongly mineralized zone. Ba shows no ordered trend across the channel sample and appears to concentrate in the areas of strong quartz overgrowths. Ca maintains a constant level across the channel. Negative anomalies coinciding with the mineralized zone are apparent for K, Na, Mn, Cu, and Ni. Sn and Cr show no trend. The potassium anomaly in specimens 3 and 4 and the lack of alkali metals in the strongly mineralized zone suggests a selective removal during mineralization. Truly unmineralized rock was not available for analysis.

The positive anomalies for Fe, U, V, and Pb can be construed as definite additions. Although there is evidence of extensive movement of silica in the strongly mineralized zone, and we have no adequate data on the silica balance, it is not likely that sufficient silica was removed to account for the other positive anomalies by residual enrichment. Some of the anomalies, however, may be due in part to irregular placer concentrations of heavy minerals and not related to mineralization.

The minor element composition of the weakly mineralized portion of the channel sample is not similar to typical unmineralized Salt Wash sandstone (see Part 3 of this volume). The most striking feature of the minor element distribution is the sharp boundary, coinciding with the boundary of strong mineralization, of the positive and negative anomalies.

STATE OF OXIDATION OF THE CHANNEL SAMPLE

The valence states of the specimens from the channel sample were studied as in the Mineral Joe No. 1 mine channel sample, described previously. The reducing capacity of the acid-soluble fraction of each sample, and the acid-soluble Fe, V, and U (the only soluble redox-active species present in significant amounts), all expressed in milliequivalents per 100 grams, is given in table 4. Essentially all of the V, U, and nonsulfide Fe are acid soluble.

Milliequivalents of vanadium and iron are used in the sense that one milliequivalent equals one millimole; for uranium, two milliequivalents equal one millimole, because two electrons must be removed to oxidize uranium from U(IV) to U(VI).

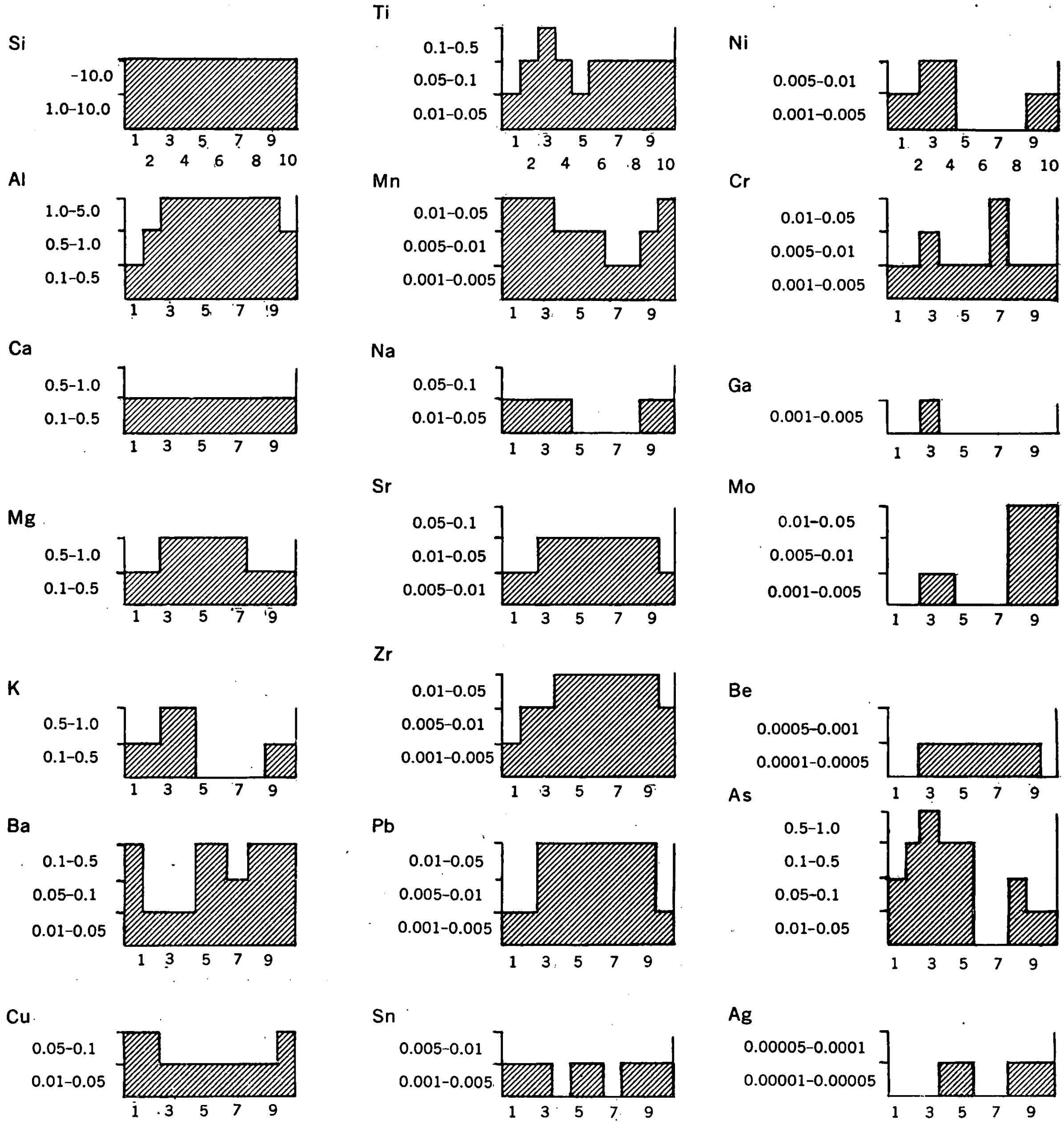


FIGURE 56.—Semiquantitative spectrographic analyses of specimens from the Virgin No. 3 mine channel sample. Ranges are in percent. Horizontal figures designate specimens. Joseph Haffty, analyst.

From the mineralogical character of vanadium, it is known that it occurs in the clay minerals, probably as vanadium (IV), and in paramontroseite as vanadium (IV); it is not certain that montroseite is absent, so that some vanadium (III) may be present. The acid soluble iron is believed to be entirely present in the clay minerals, and in this assemblage of low valences is probably present as Fe(II). At least part of the uranium is present in coffinite, as uranium (IV); the valence state of any additional uranium may be (IV) or (VI).

Garrels (1955, p. 1014–1019, particularly his figure 7) discusses the theoretical (and partly hypothetical) pH-Eh stability fields of some major minerals and mineral assemblages from the Colorado Plateau. The strongly mineralized portion of the channel sample corresponds mineralogically to his "Field 2" in that it contains paramontroseite, pyrite, and sphalerite; coffinite is also present and probably has a stability field near that of uraninite. The stability relations of the vanadium-bearing clays are not known, but work by Foster (Part 10 of this volume) suggests that in this

TABLE 4.—*Reducing capacities and vanadium, iron and uranium content of acid extracts*[1] *of specimens from the Virgin No. 3 mine channel sample*

[All values are in milliequivalents per 100g of sample]

Specimen	Vanadium[2] (meq/100g)	Iron,[3] acid soluble (meq/100g)	Uranium[2] (meq/100g)	V+Fe+U (meq/100g)	Reducing capacity,[4] acid soluble (meq/100g)
1	1.96	6.6	0.03	8.6	3.4
2	5.97	8.8	.03	14.8	9.6
3	19.6	17.4	.78	37.8	37.6
4	130.5	27.0	8.4	165.9	168.4
5	117.0	22.9	42.0	181.9	149.6
6	133.5	25.1	33.6	192.2	158.7
7	81.6	22.0	40.2	143.8	117.8
8	24.3	15.4	35.2	74.9	65.0
9	24.3	12.3	10.1	46.7	46.2
10	6.47	10.0	1.10	17.6	16.6

[1] Extracted for 5 days on steam bath in 33⅓ percent H_2SO_4.

[2] Essentially all V and U were soluble in the extraction; values given are total V and total U recalculated from table 3, in this paper.

[3] Analyst: M. H. Delevaux, U. S. Geological Survey.

[4] Analyst: L. B. Jenkins, U. S. Geological Survey.

mineral association, the vanadium contained in the clays should all be V(IV) and the iron largely Fe(II). If it is assumed that all of the uranium is U(IV), all of the vanadium is V(IV), and all of the acid-soluble iron is Fe (II), then the measured reducing capacities should equal the sum of (U+V+Fe), all expressed in milliequivalents.

The measured reducing capacities of the specimens from the channel sample are significantly less than the sum of (U+V+Fe), with the exception of samples 3, 4, and 9. These latter samples appear to fall ideally in Garrels' "Field 2". In the remaining samples, the deficiency in reducing capacity is believed to be due to the presence of Fe (III) (and possibly some V(V)) in the clays and to some U(VI). Specimens 1 and 2, the weakly mineralized part of the channel sample, must contain a considerable amount of Fe(III), probably in the sedimentary clays of the original unmineralized rock; such sedimentary clays probably persist to some extent throughout the channel sample. A considerable part of the uranium is believed to be present as U(VI); this assumption is based on analogy with uraninite, which invariably contains considerable amounts of U(VI). Although analyses of coffinite do not show any appreciable U(VI) (Stieff and others, 1956), coffinite is believed to oxidize early and through much the same course as uraninite (Part 6 of this volume). The belief that much of the uranium is present as U(VI) is consistent with the mineralogy of the channel sample in that coffinite was identified only in a few concentrates, and yet uranium values are relatively high. The uranium is probably dispersed as amorphous UO_3.

SALIENT FEATURES OF THE VIRGIN NO. 3 MINE CHANNEL SAMPLE

1. The boundary between weakly mineralized and strongly mineralized rock is sharp. This boundary roughly follows a sedimentary boundary.
2. The zone of intense mineralization coincides with the presence of abundant organic matter in the rock.
3. Vanadium - bearing clay minerals are present throughout the channel sample. In the more strongly mineralized portions, the vanadium-bearing clays clearly replace clastic quartz grains.
4. Paramontroseite, coffinite, pyrite, marcasite, and vanadium clay minerals characterize the strongly mineralized portion of the channel sample. Much of the uranium is probably present as amorphous UO_3. These minerals constitute an assemblage in equilibrium under mildly reducing conditions.

SUMMARY AND CONCLUSIONS

The two channel samples reported on support a number of generalizations concerning the nature of the primary ore and its course of alteration. Most of the generalizations have been recognized previously by other workers.

1. The boundary between mineralized rock and unmineralized rock can be sharp and independent of any observable sedimentary or other structures and of any changes in original lithologic character. The Mineral Joe No. 1 mine channel sample demonstrates this clearly.
2. The mineralized rock is enriched by a somewhat variable suite of minor and trace elements. The most important added elements are U, V, Fe, Pb, Ba, and Sr. Most of the trace elements originally present in the unmineralized rock have not been removed by the mineralizing process.
3. Vanadium-bearing clay minerals have been introduced in the mineralized portions of the Mineral Joe No. 1 mine channel sample. Sedimentary clay minerals in the Virgin No. 3 mine channel sample have been recrystallized, and vanadium introduced into their structures; additional vanadium-bearing clay minerals have been introduced.
4. The principal vanadium clays are mixed-layered mica-montmorillonite and chlorite-montmorillonite. The vanadium is present largely in a valence of (IV). The vanadium clays persist without evident alteration during weathering.
5. The Mineral Joe No. 1 mine channel sample represents a section through an ore ranging from dominantly vanadates, uranyl vanadates, and vanadium clays to a dark core of paramontroseite, pyrite and marcasite, and vanadium clays; the state of combination of much of the uranium is not known. This dark core is actively oxidizing, with destruction of the sulfide and the formation of vanadium (IV)-(V) minerals, vanadates, and

uranyl vanadates. The paramontroseite indicates that montroseite was originally present (Evans and Mrose, 1955, and Part 7 of this volume) and that much of the vanadium must have been present previously as vanadium (III). The present assemblage is markedly out of chemical equilibrium and must be moving toward a higher state of oxidation. The primary assemblage, assuming equilibrium, must have contained montroseite, vanadium clays, a uranium (IV) mineral (uraninite or coffinite), and pyrite and marcasite.

6. The Virgin No. 3 mine channel sample is in a lower state of oxidation than the Mineral Joe No. 1 mine channel sample. It comprises an equilibrium assemblage of paramontroseite, coffinite (and additional uranium as amorphous UO_3), pyrite and marcasite, and vanadium clays in which the vanadium is present largely as vanadium (IV). Montroseite must have been the precursor of paramontroseite. Thus the original ore must have been a more reduced assemblage consisting of montroseite, coffinite (and perhaps uraninite), pyrite and marcasite, and vanadium clays. This is essentially identical to the original assemblage proposed for the Mineral Joe No. 1 mine channel sample.
7. Both channels studied show unequivocal evidence of partial oxidation of an original low-valence assemblage.

The vanadium clay minerals are not yet completely defined and the role in them of vanadium in its various valence states is still somewhat uncertain. Little is known of their fields of stability under varying Eh-pH conditions, except that they are resistant to oxidation. And yet they are the dominant carrier of vanadium in many of the so-called "primary" ores on the Colorado Plateau. The Mineral Joe No. 1 mine channel sample typifies many such deposits. In the "primary" ore, the great bulk of vanadium was in the clays, with the vanadium at valence (IV); accompanying it was a small but commercially important content of uranium, probably present as uraninite or coffinite, or both, and probably predominantly located in or near scattered coalified wood fragments. Actually, montroseite (or paramontroseite) is rare in most ore of this type. Only where the organic matter is abnormally abundant do the rich patches of montroseite ore develop, but even here the vanadium clay minerals are abundant. It seems probable that the nature of the ore-bearing fluids may be better defined by the vanadium clays than by the vanadium oxides. Speculation at this stage leads to the guess that the vanadium was originally carried as a V(IV) ion and precipitated with the clays without the need of a markedly reducing environment; the uranium may well have been carried as a U(VI) ion (probably complexed) and precipitated locally where reducing conditions were adequate—such as near coaly remains.

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Part 16. MINERALOGY OF THE URANIUM DEPOSIT AT THE HAPPY JACK MINE, SAN JUAN COUNTY, UTAH

By Albert F. Trites, Jr., Randall T. Chew III, and Tom G. Lovering

CONTENTS

ILLUSTRATIONS

TABLES

ABSTRACT

The large uranium deposit at the Happy Jack mine occurs in beds of the Shinarump member of the Chinle formation of Triassic age that fill a channel cut into the underlying Moenkopi formation of Triassic age. The deposit has been divided on the basis of mineralogy into a sulfide zone, a transition zone, and an oxidized zone. Three types of ore are recognized in all these zones: replacements of woody "trash" accumulations, replacements of larger wood fragments, and bedded ores.

Ores of the sulfide zone consist of uraninite associated with pyrite, chalcopyrite, sphalerite, bornite, and galena. These primary sulfide ores appear to have been localized in the more permeable beds containing concentrations of coalified vegetal material and siltstone. Uranium and copper show evidence of secondary enrichment in the sulfide zone and the inner part of the transition zone.

Ores of the transition zone contain relict concentrations of uraninite and sulfide minerals and large amounts of goethite and jarosite. The ores of the oxidized zone contain abundant iron oxides but no sulfide minerals. Some uranium, copper, and iron have been retained during the weathering process, but most of the manganese, zinc, and lead are believed to have been removed by oxidation.

INTRODUCTION

The Happy Jack is the largest uranium mine in the White Canyon district, San Juan County, Utah. It is about 75 miles west of Blanding, Utah, in a deep reentrant in the southwest rim above White Canyon. Uranium ore was first shipped from the mine in 1948, and constant production has been maintained since 1951.

This study, begun in 1952, was to determine the mode of occurrence of the uranium minerals, to find structural and lithologic features that may be used as ore guides, and to obtain information on the geochemistry of the emplacement and oxidation of the ore deposit.

The walls of approximately 900 feet of drifts in the northeast part of the mine have been mapped on a scale of 1 inch equals 5 feet. About 750 feet of these drifts were mapped by Trites and Chew between August 7 and October 2, 1952; the remainder was mapped by Trites, assisted by E. J. Ostling, on August 19 and 20, 1954. The mineralogical study was made by Trites who examined about 30 polished sections and 50 thin sections of rock specimens from the mine. X-ray identification of some of the minerals was made by W. F. Outerbridge of the U. S. Geological Survey. Statistical analyses of assays from 103 chip samples from the mine have been made by Lovering and Chew.

Four main adits, connected by crosscuts, have been driven into the Shinarump. The main workings were all on one level and consisted of slightly more than 3,000 feet of drifts and crosscuts when the study was made.

The writers wish to thank W. P. Walker, of the photographic laboratory of the Geological Survey, for his careful preparation of the photomicrographs used in this paper.

GENERAL GEOLOGY

The rocks exposed in the area are sedimentary beds of continental origin that range in age from Permian to Jurassic. They have a total thickness of more than 4,000 feet and are predominantly sandstone and siltstone. The nearest exposures of igneous rocks are in the Henry Mountains about 17 miles west of the Happy Jack mine.

The uranium deposit at the Happy Jack mine is in the Shinarump member of Late Triassic age. The member is from 16 to 40 feet thick at the Happy Jack mine; it pinches out half a mile northwest and 1¼ miles southeast of the mine. The lower part of the formation fills a discontinuous channel cut into siltstone and sandstone of the underlying Moenkopi formation of Early and Middle(?) Triassic age. The channel trends about due east and is more than 750 feet wide and 10 feet deep in the area of the mine workings. Diamond drilling by the U. S. Atomic Energy Commission has suggested that the channel bends rather abruptly toward the southwest near the southwestern limit of the mine workings.

The Shinarump is overlain conformably by the Chinle formation of Late Triassic age. This younger formation is composed principally of beds of siltstone and sandstone, and is gradational with the Shinarump member. A prominent sandstone member of the Chinle formation is about 175 feet above the top of the Shinarump, from which it is separated by siltstone and small lenses of sandstone.

The Shinarump member is composed of about 80 percent coarse- to fine-grained sandstone, 15 percent conglomerate, 8 percent siltstone, and 2 percent claystone. Gradation is common between beds of coarse-grained sandstone and conglomerate and between beds of fine-grained sandstone and siltstone. The sandstone beds are lenticular in shape and range from 1 to 100 feet in length and from a few inches to 4 feet in thickness. Cross-stratification is common in the sandstone beds; the cross-strata dip from less than 10° to more than 20° toward the northwest. Planar cross-stratification (McKee and Weir, 1953) is common in fine-grained sandstone and in coarse-grained conglomeratic sandstone containing abundant interstitial clay and silt. Small-scale slump features and current lineation also have been noted in the Shinarump conglomerate.

The sandstone is composed predominantly of colorless, angular to subangular, quartz grains; it also contains from a trace to 5 percent of microcline, and a trace of tourmaline and zircon(?). Authigenic quartz overgrowths have been added to many of the quartz grains before the deposition of the metallic minerals. Granules and pebbles of quartz, quartzite, siltstone, and claystone comprise from 1 to more than 10 percent of many of the sandstone beds; siltstone and claystone pebbles are especially abundant in the lower parts of the sandstone beds. In general, conglomerate beds grade laterally into beds of coarse-grained sandstone.

Siltstone and claystone are present throughout the Shinarump conglomerate at the Happy Jack mine. They occur in beds ranging from 10 to 100 feet in length and from 1 to 4 feet in thickness; they also occur in thin layers ranging from 1 to 6 feet in length and from one-eighth to one-half inch in thickness.

Most of the beds contain carbonaceous matter which ranges in size from finely comminuted organic material to logs as much as 3 feet long and 6 inches in diameter. Accumulations of smaller fragments have been termed "trash deposits" (Trites and Chew, 1955), a term that is in general use on the Colorado Plateau. These trash accumulations are commonly present near the bottom of the sandstone beds and at the contacts between sandstone beds.

STRUCTURE

The White Canyon district is on the west flank of the Monument upwarp, a broad south-plunging anticline that extends northward from 30 miles south of the San Juan River to Elk Ridge, 30 miles north of the river (Gregory, 1938, p. 85–88). The Monument upwarp has a steeply dipping east flank in which dips exceed 50°; and a gently dipping west flank in which dips range from half a degree to 3°.

The rocks in the White Canyon district strike regionally from north to northwest and dip 2° to 3° west to southwest. Small folds occur locally and their axes are generally parallel to subparallel to the axis of the Monument upwarp. Normal faults with displacements as much as 100 feet cut the beds in the northwestern and southwestern part of the area.

The rocks at the Happy Jack mine strike about N. 20° W. and dip 3° SW. These rocks have been cut by four sets of steeply dipping fractures that have the following strikes listed in order of decreasing prominence: N. 65° W., N. 60° E., N. 85° E., and due north. Only one small fault was noted in the mine, about 30 feet from the portal. This fault strikes N. 69° W., dips almost vertically, and has had horizontal movement of less than 2 feet but no vertical movement. Minor bedding-plane movement is suggested by clay seams that have been thickened by movement along lithologic contacts.

Although uraninite and sulfide minerals have filled local microscopic fractures in the rocks, no relationship could be found between the uranium deposits and the larger fractures that were mapped.

MINERALOGY

The minerals listed below have been observed at the Happy Jack mine by J. W. Gruner, Lynn Gardiner, and D. K. Smith, Jr. (written communication), who reported them officially to the Atomic Energy Commission. They have not been observed by the present writers and are not discussed in this paper.

Mineral	*Formula*
Cyanotrichite	$Cu_4Al_2(SO_4)(OH)_{12}\cdot 2H_2O$
Gersdorffite	$NiAsS$
Sabugalite (Al-autunite)	$HAl(UO_2)_4(PO_4)_4\cdot 16H_2O$
Schoepite	$UO_3\cdot 2H_2O$ (approximately)
Siderotil	$FeSO_4\cdot 5H_2O$(?)
Sulfur	S
Not described before	$(Co,Fe)SO_4\cdot 4H_2O$
Not described before	$MgSO_4\cdot 6H_2O$
Bright-yellow	Unknown uranium mineral
Waxy yellow	Unknown uranium mineral
Yellow	Unknown uranium mineral

The alphabetical list of minerals given below includes those observed by the senior author at the Happy Jack mine; many of these minerals are discussed in this paper. The formulas are from Dana's Textbook of Mineralogy (1932) unless otherwise stated.

Mineral	*Formula*
Allophane (silicate)	$Al_2SiO_5\cdot nH_2O$
Antlerite (sulfate)	$Cu_3(SO_4)(OH)_4$ [1]
Azurite (carbonate)	$Cu_3(OH)_2(CO_3)_2$ [1]
Barite (sulfate)	$BaSO_4$ [1]
Bieberite (sulfate)	$CoSO_4\cdot 7H_2O$
Bornite (sulfide)	Cu_5FeS_4 [2]
Brochantite (sulfate)	$Cu_4(SO_4)(OH)_6$ [1]
Chalcanthite (sulfate)	$CuSO_4\cdot 5H_2O$ [1]
Chalcedony (oxide)	SiO_2 [2]
Chalcocite (sulfide)	Cu_2S [2]
Chalcopyrite (sulfide)	$CuFeS_2$ [2]
Covellite (sulfide)	CuS [2]
Erythrite (arsenate)	$(Co,Ni)_3(AsO_4)_2\cdot 8H_2O$ [1]
Galena (sulfide)	PbS [2]
Goethite (oxide)	$HFeO_2$ [2]
Gypsum (sulfate)	$CaSO_4\cdot 2H_2O$ [1]
Hematite (oxide)	Fe_2O_3 [2]
Hydrous mica (silicate)	$K_2O\cdot 3Al_2O_3\cdot 6SiO_2\cdot 2H_2O$
Ilsemannite (sulfate)?	$MoO_3\cdot SO_3\cdot 5H_2O$ [1]
Jarosite (sulfate)	$KFe_3(SO_4)_2(OH)_6$ [1]
Johannite (sulfate)	$Cu(UO_2)_2(SO_4)_2(OH)_2\cdot 6H_2O$ [3]
Magnetite (oxide)	$FeFe_2O_4$ [2]
Malachite (carbonate)	$Cu_2(OH)_2(CO_3)$ [1]
Marcasite (sulfide)	FeS_2 [2]
Metatorbernite (phosphate)	$Cu(UO_2)_2(PO_4)_2\cdot nH_2O$ $n=4$ to 8 [3]
Metazeunerite (arsenate)	$Cu(UO_2)_2(AsO_4)_2\cdot 8H_2O$ [3]
Microcline (silicate)	$K_2O\cdot Al_2O_3\cdot 6SiO_2$
Psilomelane(?) (oxide)	$BaMn^{2}Mn^{4}_{8}O_{16}(OH)_4$ [2]
Pyrite (sulfide)	FeS_2 [2]
Quartz (oxide)	SiO_2 [2]
Sepiolite (silicate)	$2MgO\cdot 3SiO_2\cdot 2H_2O$
Sphalerite (sulfide)	ZnS [2]
Tourmaline	$H_9Al_3(B\cdot OH)_2Si_4O_{19}$
Uraninite	Ideally UO_2 [3]
Uranopilite (sulfate)	$(UO_2)_6(SO_4)(OH)_{10}\cdot 12H_2O$ [3]
Uranophane (silicate)	$Ca(UO_2)_2(SiO_3)_2(OH)_2\cdot 5H_2O$ [3]
Zippeitelike mineral	$(UO_2)_2(SO_4)(OH)_2\cdot 4H_2O$ [4]

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[1] (Palache, and others, 1951).

[2] (Palache, and others, 1944).

[3] (Frondel and Fleischer, 1955).

[4] (Weeks and Thompson, 1954).

NOTE.—Pitchblende has been omitted from the above list as being a variety of uraninite. However, the term "sooty pitchblende" is retained as a generic term.

ORE DEPOSIT

The ore deposit at the Happy Jack mine may be divided on the basis of mineralogy into a sulfide zone, a transition zone, and an oxidized zone. The sulfide zone is exposed in those parts of the mine farthest from the surface; the outer edge of this zone is about 200 feet horizontally from the outcrop of the Shinarump member and is roughly parallel to the outcrop. The transition zone extends from the sulfide zone to within 10 to 60 feet of the Shinarump rim in the part of the mine studied. The oxidized zone extends outward from the transition zone and includes the leached outcrop. The contacts between these zones are gradational.

The sulfide zone contains uraninite and sulfide minerals with no appreciable amounts of goethite. The transition zone contains abundant goethite and jarosite and locally it contains relict concentrations of uraninite and sulfide minerals. The oxidized zone contains abundant goethite, little jarosite, and insignificant amounts of sulfides.

ORES OF THE SULFIDE ZONE

About 15 percent (approximately 325 feet) of the mine workings in the sulfide zone were mapped and studied in detail in 1952. Most of the workings examined extend in a line across the Shinarump channel. The farthest part of the mine studied is about 475 feet from the rim. The uranium ore in the sulfide zone occurs mainly in sandstone and conglomerate. Three types of ores are recognized: replacements of "trash" accumulations, bedded deposits, and replacements of larger wood fragments.

Replacements of "trash" accumulations constitute most of the high-grade uranium deposits and, although the rock has not been mined selectively, these probably have yielded the greatest tonnages of ore from this zone. Ore bodies of this type are widely distributed in the mine in sandstone beds containing carbonaceous material. They range from 50 to 150 feet in length, from 25 to 50 feet in width, and from a fraction of an inch to 3 feet in thickness in the part of the mine studied.

Bedded ore bodies contain less carbonaceous material, are much smaller, and of slightly lower grade than the ores resulting from the replacements of "trash" accumulations; they have supplied less than 10 percent of the ore produced from the sulfide zone. Bedded ore bodies range from 1 to 25 feet in length, from 6 inches to 10 feet in width, and from a knife-edge to slightly more than 1 foot in thickness. They are localized at contacts between two sandstone beds and commonly replace siltstone seams at the contacts.

Large wood fragments, sparsely disseminated in the mine, are commonly replaced by ore minerals in or near the two other types of uraniferous ores. These replacement ores are extremely variable in grade and contribute only a small part of the ore.

Local concentrations of uraninite, pyrite, chalcopyrite, sphalerite, and galena have been noted, but no definite zoning of these minerals has been found in the sulfide zone. Most of the uraninite apparently has been localized by sedimentary features; localization by faults and fractures has not been shown. The most highly mineralized beds appear to be semipermeable sandstone and conglomerate, in the lower part of the Shinarump, which commonly overlie siltstone. They contain from 1 to 5 percent carbonized wood, from 5 to 25 percent siltstone or claystone seams, and from 10 to 20 percent siltstone or claystone matrix.

A microscopic study was made of 13 polished sections from the sulfide zone. The modes of occurrence of the uraninite and the primary sulfide minerals are discussed below; the sulfides are given in descending order of abundance.

URANINITE

Uraninite (ideally UO_2) is the principal uranium mineral in the sulfide zone. The term "uraninite" is here reserved for the massive, nearly metallic variety and "sooty pitchblende" is reserved for the finely divided nonmetallic variety. Coffinite, the newly described uranous silicate (Stieff, Stern, and Sherwood, 1955), which has been identified in more than 15 uranium mines in the Colorado Plateau, has not been found at the Happy Jack mine.

The uraninite replaces carbonized wood, is disseminated in sandstone where it replaces quartz grains and microcline grains along cleavage planes, and fills microscopic veinlets cutting sandstone adjacent to fossil wood fragments. The suites of sulfide minerals, with which the uraninite is associated, appear to vary with the mode of occurrence of the uraninite. In wood and other organic matter the uraninite is most commonly associated with pyrite, chalcopyrite, sphalerite, bornite, galena covellite, and marcasite; in sandstone containing no appreciable amounts of organic debris, uraninite is associated mainly with pyrite and sphalerite.

The uraninite is of two distinct colors in polished section: most of the uraninite is gray but some of that which occurs with chalcopyrite and covellite in wood is brownish gray. The reason for this color difference is not known. The variation in color may reflect a difference in age of the uraninite or may be caused by admixed copper minerals. Uraninite with crystal outlines has not been observed except where the uraninite is intergrown with pyrite by replacement of organic material.

Many wood fragments have been replaced by chalcopyrite and uraninite; a few have been replaced by uraninite and sphalerite. In general, the uraninite has replaced the cell walls and chalcopyrite has either replaced or filled the cell cores (pl. 4*A*). Even in wood containing little or no chalcopyrite the uraninite shows a preference toward cell wall replacement as shown in plate 4*A*. Nearly complete replacement of wood by uraninite is not uncommon, but sufficient unreplaced cell core material commonly remains to preserve the woody structure.

Uraninite is more concentrated in the centers of the wood fragments and is commonly surrounded by chalcopyrite which has in part replaced the edge of the wood and in part nearly completely impregnated the sandstone adjacent to the wood. Uraninite extends outward into the sandstone surrounding the wood fragments, partly filling interstices between the grains of the sandstone, coating some of the quartz grains, and filling cavities in chalcopyrite. The uraninite seems to be especially abundant in the sandstone at the ends of wood fragments, suggesting a "streaming out" of the uraninite from the wood which was the locus of deposition. Further study of the relative amounts of uraninite deposited in the sandstone at each of the ends of the pieces of uraninite-replaced wood may suggest a direction of flow of the uranium-bearing solutions.

Some of the uraninite in the sandstone near wood seems to have a cell structure suggesting that smaller bits of organic matter have been replaced. Three specimens of sandstone containing uraninite without recognizable organic material were studied. In each of these specimens the uraninite was gray in color and was associated either with pyrite or with pyrite and sphalerite. Uraninite has embayed and replaced quartz grains, has replaced feldspar grains along the cleavages, has formed a thin rim around many grains of quartz, and has lined cavities. Some of the uraninite appears to be intergrown with the pyrite, and has crystal outlines (pl. 4*B*). The uraninite is believed to be younger than the pyrite and to have replaced either organic material or a gangue mineral which was not completely replaced by the pyrite.

Locally uraninite has partly filled microscopic veinlets cutting individual quartz grains in the sandstone (pl. 4*C*).

PYRITE

Pyrite is a widespread mineral at the Happy Jack mine; it is the most abundant sulfide mineral in the sulfide zone although it was subordinate to chalcopyrite in the polished sections studied. It occurs as a partial to nearly complete wood replacement, as a replacement of finely divided organic material, as disseminations in sandstone, and as partial fillings in fractures cutting the quartz grains in the sandstone. The pyrite is commonly associated with chalcopyrite, uraninite, sphalerite, marcasite, galena, and bornite in many places in the sulfide zone.

A few pieces of wood have been replaced mainly by pyrite with subordinate sphalerite or chalcopyrite. In the pieces of wood replaced by pyrite and sphalerite, the pyrite has replaced both the cell cores and walls, retaining a large part of the cell structure. Stringers of sphalerite grains cut the pyrite-replaced wood and replace the pyrite. In pieces of wood replaced by pyrite and chalcopyrite the cell structure has been destroyed and the pyrite is in the form of irregular masses that have been embayed and replaced by chalcopyrite.

Pyrite replaces wood which apparently acted as a nucleus of deposition. Both individual cells, and entire fragments of wood as much as 5 inches long and 3 inches wide have been replaced. Pyrite that has been deposited in larger areas in the wood commonly occupies the centers of cells whose walls remain unmineralized or have been replaced by pyrite or uraninite. Most of the pyrite in the center of the cells is separated from the pyrite or uraninite in the cell walls by unreplaced organic material.

Some of the pyrite in the sandstone has replaced small bits of disseminated organic material. Study of this occurrence of pyrite under high magnification has shown that the pyrite has surrounded the organic material in thin crenulated subround bands and has formed small blebs within the organic mass.

Pyrite has been deposited between the grains of the sandstone, especially near pieces of wood that contain abundant pyrite. Some of the pyrite has been concentrated along the edges of the quartz grains, incompletely filling the interstices between the grains (pl. 5*A*) and embaying and replacing the edges of the grains.

A small amount of the pyrite is in microscopic crystals; both cubes and pyritohedrons have been observed under the microscope. Four different types of pyrite crystals have been observed: simple homogeneous crystals; crystals with a core of unreplaced coalified wood; crystals with a core of pyrite separated from a rim of pyrite by a layer of unreplaced coalified wood or uraninite; and zoned crystals of alternating pink and yellow layers.

The simple homogeneous pyrite crystals are the most widespread and abundant. These simple crystals have been deposited in the sandstone as well as in the wood, and have mainly cubic forms.

Some pyrite crystals that have grown around plant cells have a core of organic material. The skeletal crystal of pyrite in plate *4D* is believed to have been formed in this manner. A more complex type of selective replacement of the cell by pyrite has produced the crystals with cores and rims of pyrite separated by unreplaced organic material. Later replacement of the unaffected part of the cell by uraninite has produced zonal intergrowths made up of pyrite and uraninite (pl. *4B*). Both cubic and pyritohedral forms are found in pyrite crystals of these types.

The zoned pyrite crystals are of many types. The most simple type of zoned pyrite crystal is that of normal yellow pyritohedral pyrite crystals having pinkish cores. More complex zoned crystals have many alternating zones as shown in plate *4D*. Square, pentagonal, and triangular outlines have been noted on these crystals, suggesting that the crystals have cubic and pyritohedral forms. In general, the inner zones have crystal forms similar to the outer boundaries of the pyrite crystals. Many of the inner zones are rotated with respect to the outer faces of the crystals so that the edges of the inner zones are not parallel to the outer edges of the crystals.

The reason for the pyrite zoning has not been determined, but the difference in color may be differences in the trace amounts of cobalt, nickel, or selenium in the layers.

CHALCOPYRITE

Although chalcopyrite is overwhelmingly the most abundant sulfide in specimens studied from the sulfide zone, the gross aspects of the deposit suggest that it is less abundant than pyrite. The chalcopyrite has formed disseminations in the sandstone, conglomerate, and siltstone; it has replaced fragments of wood and stringers of carbonaceous siltstone; and it has filled small fractures cutting the sandstone. In most places the chalcopyrite is associated with pyrite and locally it is associated with uraninite, sphalerite, bornite, and galena in the sulfide zone.

The amount of chalcopyrite in the beds varies from a few scattered masses to complete fillings between grains. Chalcopyrite is most abundant in sandstone and conglomerate that contain coalified wood. Rims of concentrated chalcopyrite as much as one centimeter wide surround many wood fragments that have been replaced by uraninite and sulfide minerals. The concentrated chalcopyrite grades outward from the rims into more widely scattered masses in the sandstone. The chalcopyrite has embayed and apparently has replaced many of the quartz grains; complete replacement of quartz grains is uncommon in specimens studied from the mine. Most of the chalcopyrite in the sandstone is massive, although many small crystals have been observed.

Many fragments of coalified wood have been partly replaced by chalcopyrite. The amount of chalcopyrite in these wood fragments ranges from an occasional "eye" or lens of chalcopyrite in the center of the cells (pl. *4A*) to nearly complete replacement of both cell cores and walls. The initial deposition of chalcopyrite in the wood seems to have been a filling or replacement of the core of the cells. Subsequent replacement of the cell walls took place only where there was a superabundance of chalcopyrite. In its preference to fill cavities, the chalcopyrite is similar to that in the porphyry copper deposit at Ajo, Ariz. (Gilluly, 1946, p. 87.)

Small subround masses of chalcopyrite in the sandstone have a pattern that suggests the replacement of seeds, pollen, or finely divided organic material with a very small cell structure. Chalcopyrite in carbonaceous siltstone has also been concentrated in fragments of wood and in finely divided organic matter.

Megascopic veins and fracture fillings of chalcopyrite have been observed at several places in the Happy Jack mine. Veinlets of chalcopyrite, less than 6 inches long and one-fourth inch across, cut siltstone lenses southwest of the part of the mine mapped, and small concentrations of chalcopyrite were observed in the sandstone adjacent to a vertical fracture in the eastern part of the mine workings.

OTHER SULFIDE MINERALS

Sphalerite is the third most abundant sulfide mineral in the sulfide zone; it is about one-tenth as abundant as chalcopyrite. Most of the sphalerite occurs as minute fracture fillings and linings of cavities; as replacements in wood that was previously replaced by pyrite, chalcopyrite, and uraninite and as disseminations in sandstone. The sphalerite is light gray in polished section and nearly free of iron; it forms crystals and anhedral masses that display yellow internal reflections.

Bornite is found in trace quantities replacing wood and chalcopyrite in the sulfide and transition zones. Some of the bornite forms a eutectoid intergrowth with rods of chalcopyrite. Bornite has also been deposited as rims between chalcopyrite and grains of sphalerite; locally the bornite has been deposited in veinlets cutting chalcopyrite. All of the bornite is of microscopic size and most patches of it are less than 0.05 mm across.

Galena occurs in trace quantities as microscopic crystals and irregular masses that have been deposited locally in the wood and sandstone. The galena is surrounded and veined by chalcopyrite and covellite.

Covellite and chalcocite are present in the sulfide zone and the inner part of the transition zone. Covellite occurs as bladed crystals cutting chalcopyrite and chalcocite and as rims surrounding many grains of chalcopyrite, pyrite, and galena; the covellite is the youngest of the sulfide minerals. The chalcocite occurs as feathery masses along fractures cutting chalcopyrite and as replacement rims around grains of chalcopyrite and bornite. The covellite and chalcocite are believed to be of supergene origin because they appear to be localized near the boundary between the sulfide and transition zones.

Marcasite is present locally in microscopic veinlets cutting and replacing the uraninite, pyrite, and chalcopyrite (pl. 5*B*) in fragments of replaced wood. A small amount of wood cell texture has been preserved by marcasite but most of the woody texture has been destroyed. The marcasite occurs in the sulfide zone and in the inner part of the transition zone and is associated with either covellite or chalcocite in all but one of the specimens examined. Most marcasite found in nature is in surface or near-surface deposits where it is considered to have been formed at low temperatures and from acid solutions (Palache and others, 1944, p. 313). The origin of the marcasite at the Happy Jack mine is not clearly shown, but its association with covellite and chalcocite suggests that it also may be a supergene mineral.

NONMETALLIC GANGUE MINERALS

The nonmetallic gangue minerals in the sulfide zone are mainly quartz, microcline, and clay minerals (mostly hydrous mica and kaolinite) typical of the Shinarump conglomerate. Quartz is present as grains and locally as authigenic overgrowths on quartz grains. The most abundant quartz overgrowths appear to be in areas surrounding abundant uraninite and sulfide minerals; although microscopically, a few overgrowths occur with the uraninite and sulfides and have been embayed by these minerals. The association of minor amounts of quartz overgrowths with uraninite and sulfide minerals and the embayment of the authigenic quartz by these minerals suggests that silica was leached from the quartz grains of the sandstone by the mineralizing solutions and redeposited in the beds nearby. Silica was thereby moved, as a front, ahead of the ore-bearing solution; and as deposition of sulfide minerals advanced, the authigenic quartz previously deposited was moved further outward from the deposit. The more intense silicification that Waters and Granger (1953, p. 15) observed surrounding ore bodies on the Colorado Plateau could possibly be explained by this process.

Barite has been introduced locally into the sulfide zone and is particularly associated with sphalerite. The barite rims cavities that are filled with sphalerite, and is believed to be older than the sphalerite. Its age, relative to the other sulfide minerals, has not been determined.

Jarosite, apparently one of the earliest secondary minerals formed by the oxidation of sulfide minerals in the mine, is common throughout the part of the sulfide zone studied.

STATISTICAL INTERPRETATION OF ASSAY DATA

Preliminary studies suggest an approximately log-normal distribution of certain elements in the samples (figs. 57 and 58). No histogram is shown for the oxidized zone because of the low number of samples. A statistical study based on the assumption of log-normal distribution of these elements in the deposit was made of chemical analyses of 68 samples from the sulfide zone,

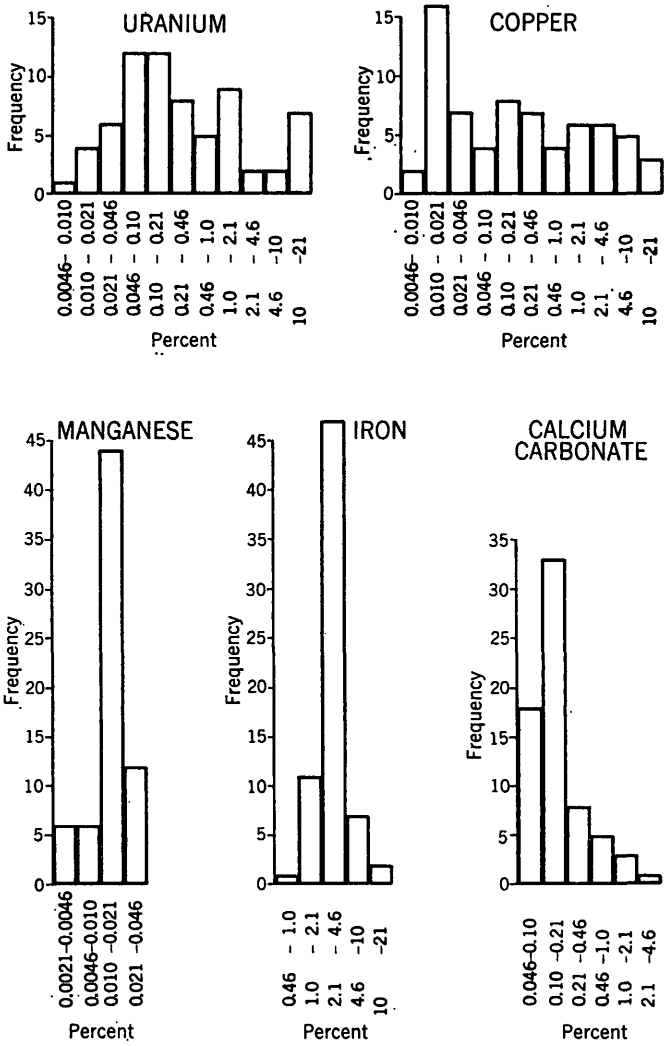

FIGURE 57.—Frequency-distribution histograms of uranium, copper, iron, manganese, and calcium carbonate, sulfide zone, Happy Jack mine, San Juan County, Utah (logarithmic class intervals; 68 samples).

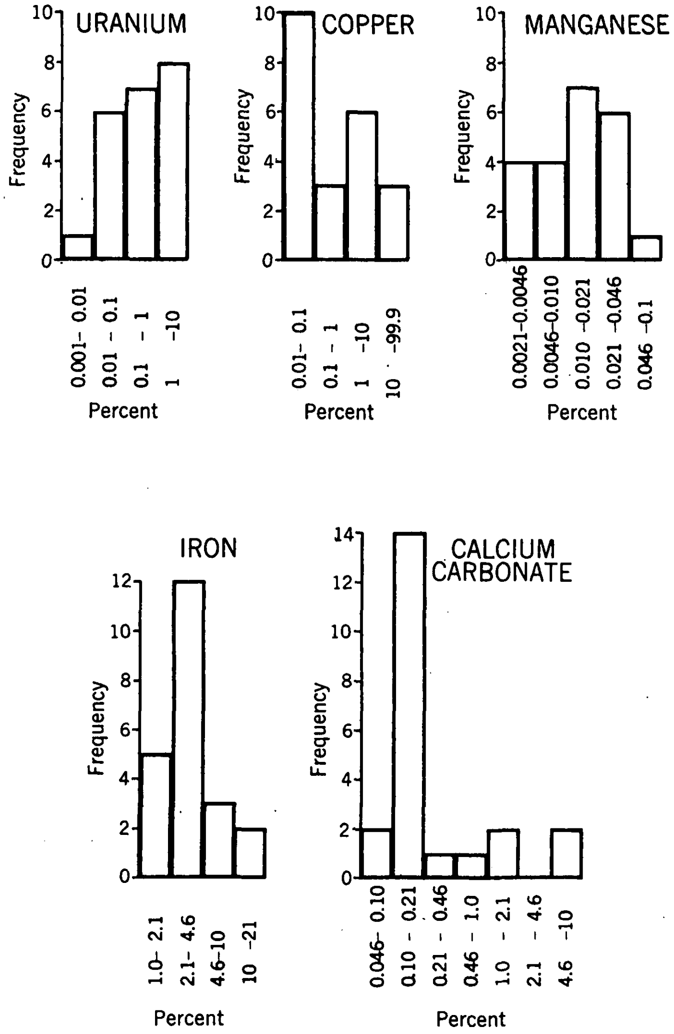

FIGURE 58.—Frequency-distribution histograms of uranium, copper, manganese, iron, and calcium carbonate, transition zone, Happy Jack mine, San Juan County, Utah (logarithmic class intervals; 22 samples).

22 samples from the transition zone, and 10 samples from the oxidized zone. The results of this study are shown in tables 1 and 2. The geometric means (M) and the geometric deviations (GD) of samples from each of the three zones are shown in table 1; the correlation coefficients of copper, manganese, iron, and calcium carbonate[13] with respect to uranium in each of the three zones are shown in table 2.

The geometric deviations (GD) suggest that copper (GD=10.02) and uranium (GD=7.62) have the greatest deviation, and therefore, the greatest dispersion in the sulfide zone. Dispersion means the amount of scatter of the values about a mean. This high dispersion of uranium and copper assays is in accordance with the observed non-uniform high-grade concentrations of uraninite and chalcopyrite in the mine. The dispersion of calcium carbonate (GD=2.25), manganese (GD=1.83) and iron (GD=1.67) is lower than that of copper and uranium suggesting that distribution of these elements is more uniform in the part of the sulfide zone studied.

TABLE 1.—*Geometric means and geometric deviations of various elements and calcium carbonate at the Happy Jack mine, San Juan County, Utah*

Element	Geometric mean (M), in percent; geometric deviation (GD)	Zones		
		Sulfide (68 samples)	Transition (22 samples)	Oxidized (10 samples)
Uranium	M	0.31 $\frac{\times}{\div}$ 1.43	0.28 $\frac{\times}{\div}$ 2.42	0.021 $\frac{\times}{\div}$ 2.72
	GD	7.62	7.10	3.85
Copper	M	0.20 $\frac{\times}{\div}$ 1.76	0.39 $\frac{\times}{\div}$ 5.35	0.54 $\frac{\times}{+}$ 4.38
	GD	10.02	41.12	7.30
Manganese	M	0.014 $\frac{\times}{\div}$ 1.16	0.013 $\frac{\times}{\div}$ 1.50	0.0018 $\frac{\times}{+}$ 3.95
	GD	1.83	2.47	6.35
Iron	M	3.09 $\frac{\times}{\div}$ 1.15	3.39 $\frac{\times}{\div}$ 1.35	2.51 $\frac{\times}{+}$ 1.60
	GD	1.67	1.95	1.88
Calcium carbonate	M	0.17 $\frac{\times}{\div}$ 1.22	0.26 $\frac{\times}{\div}$ 1.82	0.16 $\frac{\times}{\div}$ 2.72
	GD	2.25	3.79	3.84

TABLE 2.—*Correlation coefficients between uranium and various other elements and calcium carbonate at the Happy Jack mine, San Juan County, Utah*

Elements correlated with uranium	Correlation coefficient (r)	Zones[1]		
		Sulfide (68 samples) $r_s=0.23$	Transition (22 samples) $r_s=0.42$	Oxidized (10 samples) $r_s=0.63$
Copper	r	+0.12	+0.25	+0.45
Manganese	r	−.07	−.12	+.52
Iron	r	+.59	+.22	+.44
Calcium carbonate	r	+.09	−.38	+.11

[1] r_s=significant value of correlation coefficient—that is, that value, which if exceeded, yields a 95-percent probability that the two variables being correlated are not independent.

The arithmetic mean of iron was calculated to be 3.43 percent in samples in the sulfide zone. This indicates that considerably more iron is present than that which is chemically combined with copper (arithmetic mean Cu 1.51 percent) in chalcopyrite. Most of this iron is contained in pyrite.

The uranium appears to correlate significantly with iron, but does not show significant correlation with copper, manganese, or calcium carbonate in the sulfide zone (table 2). The relatively high correlation of uranium with respect to iron suggests that sites in the sulfide zone which favored the deposition of pyrite also favored the deposition of uraninite. Since the principal mode of occurrence of both uraninite and pyrite is the replacement of coalified wood, it is believed

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[13] This refers to the determination as made for metallurgical purposes. Although this is an empirical method that measures calcium taken into solution by an acetic acid leach, it generally gives a good approximation of the calcium carbonate actually present in most sandstone-type ores. The weakness of this method is that it measures any acetic acid soluble calcium salt including some, but not necessarily all, of calcium carbonate. All the calcium found in the leach is expressed as calcium carbonate.

that these sites of deposition consisted of wood and other organic matter in sandstone, conglomerate, and siltstone. The pyrite was both earlier and more abundant than the uraninite, consequently its distribution is more uniform than the uraninite.

PARAGENESIS AND ORIGIN

The general paragenetic sequence of the formation of the uraninite and sulfide minerals in the sulfide zone is shown in figure 59. Secondary silica was added to the sandstones prior to the deposition of these metallic minerals which have embayed and replaced the authigenic quartz. Significant wall-rock alteration apparently did not accompany the deposition of the metallic minerals. The solutions which deposited the minerals in the sulfide zones are believed to have contained large amounts of iron and abnormal amounts of zinc, lead, and other metallic ions.

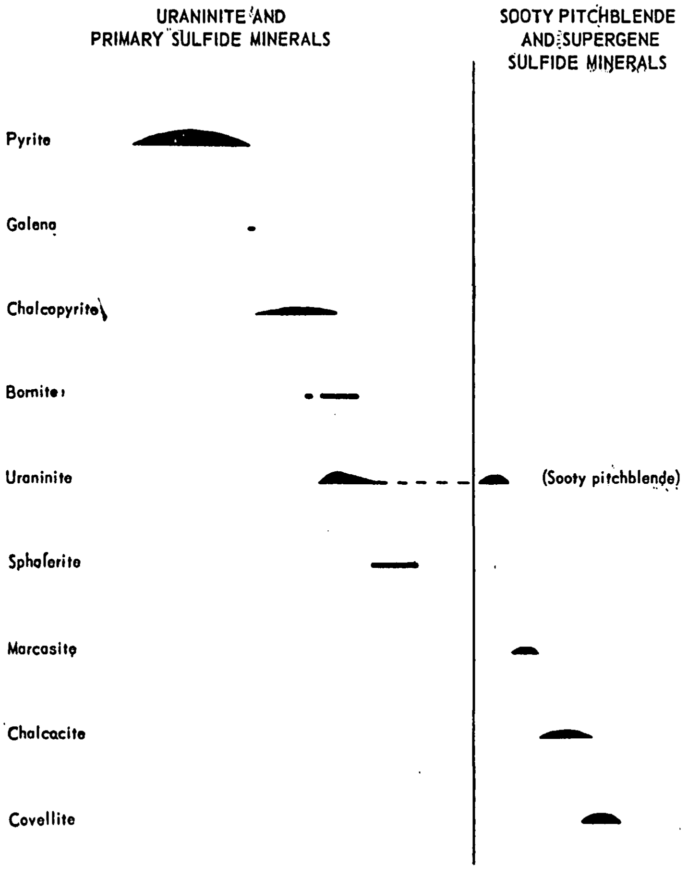


FIGURE 59.—Chart showing paragenesis of uraninite and sulfide minerals, Happy Jack mine, San Juan County, Utah.

Lovering (1949, p. 56) believed that the abundance of barite and the absence of alunite suggested precipitation from bicarbonate solution in late barren stage alteration of East Tintic, Utah. Iron and zinc are known to be soluble in a bicarbonate solution under pressure (Lovering, T. S., oral communication, 1955). With a release of pressure and in the presence of available hydrogen sulfide the sulfides of iron and zinc are precipitated. Copper and lead are considerably less soluble than iron or zinc in bicarbonate solution and may not have been carried in such a solution. Both iron sulfide and zinc sulfide will be reacted on by such solutions as that of lead chloride to precipitate lead sulfide, the iron and zinc ions returning to solution during the process. Such processes as these may have taken place during the deposition of the uranium deposits. Pyrite was apparently the earliest of the sulfide minerals formed and could have been derived from iron carried in bicarbonate solution under pressure and precipitated in the presence of hydrogen sulfide, extracted perhaps from organic matter. If solutions carrying copper and lead were passed over the pyrite, the sulfur could have been removed from combination with the iron to recombine with these cations. Sulfur could unite with the lead to form the galena, and sulfur and iron could combine with the copper to form chalcopyrite and bornite. The role of uranium and zinc in this sequence of reactions is not known. Uranium apparently has a greater affinity for oxygen than for sulfur and has been deposited as the oxide instead of the sulfide. Sphalerite was apparently deposited later than the pyrite, galena, and uraninite; its replacement of pyrite suggests that it may have been deposited similarly to the manner suggested for the galena, by solution of the pyrite and combining of the zinc with sulfur. Much of the pyrite has been etched by the later sulfide minerals, suggesting that solution of the pyrite took place as these minerals were being deposited.

The average ratio of equivalent uranium to uranium (eU percent/U percent) is less than 1.0 in samples from the sulfide zone, greater than 1.0 in samples from the transition zone, and considerably greater than 1.0 in samples from the oxidized zone. Dodd (1950) has previously described these differences between radiometric count and percent uranium and attributed them to leaching (see also Part 13 of this volume). These data suggest that uranium has been leached from the oxidized and transition zones and some of it redeposited in the sulfide zone. Uranium is thus apparently being secondarily enriched in the sulfide zone. An alternative, believed to be less likely, is that daughter products of uranium have been enriched by deposition in the oxidized and transition zones.

ORES OF THE TRANSITION ZONE

The transition zone has been defined as a zone containing abundant geothite and relict concentrations of primary sulfide minerals. The three types of uranium ores (replacements of "trash" accumulations, bedded ores, and replacements of large wood fragments) found in the sulfide zone are also recognized in the transition zone. In general, the grade of the ores of each type is lower in the transition zone than in the sulfide zone. The relict concentrations of uraninite and sulfide minerals are believed to remain in the transition zone because the oxidizing solutions did not penetrate the rock everywhere and local concentrations of carbonaceous matter may have retained reducing conditions.

MINERALOGY

The uranium ore in the transition zone consists of relict uraninite and primary sulfide minerals, secondary uranium and copper minerals, and possibly uraniferous iron oxides. Secondary uranium minerals include the oxide sooty pitchblende (Kerr, 1951, p. 91–92), the sulfates, uranopilite and a zippeite-like mineral, and the silicate uranophane. The secondary copper minerals are the sulfates chalcanthite, brochantite, and antlerite(?) and the carbonates malachite and azurite. Secondary uranium-copper minerals include the sulfate, johannite; the phosphate, metatorbernite; and the arsenate, metazeunerite. Most of these secondary minerals have formed disseminations in the sandstone, conglomerate, and siltstone, and are associated with gypsum, goethite, and hematite as fracture coatings. Some of the sulfates, especially the zippeite-like mineral, johannite, uranopilite, siderotil, bieberite, and chalcanthite, and the arsenate erythrite have formed efflorescent coatings on the walls in moist parts of the mine.

Goethite, hematite, jarosite, and gypsum are abundant in the transition zone. The goethite has impregnated sandstone and conglomerate, coated fractures, and replaced pieces of wood that were formerly replaced by sulfide minerals. Locally the goethite appears to be an alteration product of hematite and jarosite, and some of the goethite is colored red by hematite.

Jarosite is believed to be the first product formed during the oxidation of the deposit. It is present in greatest amounts in the inner part of the transition zone and in the sulfide zone. Only small amounts of the mineral are found in the oxide zone and in the outer part of the transition zone. Oxidation in arid rather than humid climate is believed to favor the deposition of jarosite (Locke, 1926, p. 107).

Gypsum is common throughout the transition zone. It has formed disseminations in the sandstone and conglomerate and has coated the surfaces of fractures.

STATISTICAL INTERPRETATION OF ASSAY DATA

A statistical study was made of 22 samples from the transition zone. The results (table 1) suggest that the only statistical values which are significantly different from the values of the sulfide zone are the geometric deviations of copper, manganese, and calcium carbonate. The geometric deviation of copper (GD=41.12) in the transition zone is much higher than that of copper (GD=10.42) in the sulfide zone. Large amounts of secondary copper minerals, mainly the sulfates, have formed local concentrations in the transition zone and probably account for the greater dispersion of copper assays. Secondary copper minerals are present in local concentrations similar to those found in zones of secondary enrichment in many porphyry copper deposits and vein copper deposits elsewhere. Chalcocite and covellite have been deposited in some of the relict sulfide bodies in the transition zone where they commonly replace chalcopyrite and bornite.

Manganese is present in about the same amount in the transition zone (M=0.013) as in the sulfide zone (M=0.014), although the manganese assays show a greater dispersion in the transition zone (GD=2.47). Some of the manganese apparently has been moved about in the transition zone, but apparently no significant amounts have been removed from or added to the zone.

The distribution of calcium carbonate is also more variable in the transition zone (GD=3.79) than in the sulfide zone (GD=2.76). The calcium carbonate may be more variable in the transition zone because it is being removed near the oxidizing sulfides. Calcium carbonate is present in such extremely small amounts that it cannot be recognized in the mine.

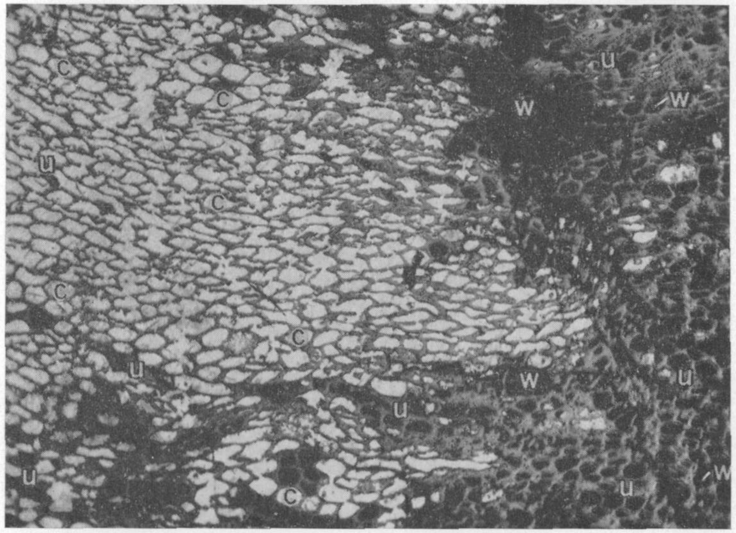
Uranium shows no significant correlation with copper, iron, manganese, or calcium carbonate in the transition zone.

ORES OF THE OXIDIZED ZONE

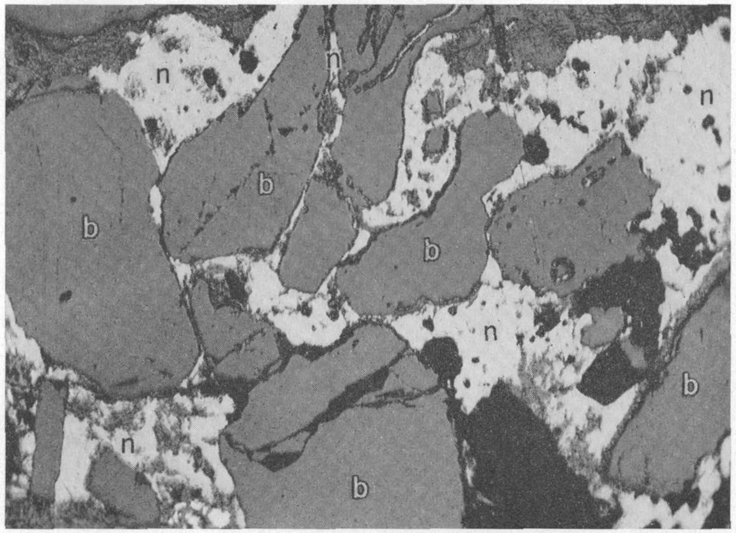
The uranium ores in the oxidized zone are similar in type to those in the transition zone but the average grade of the deposits in the oxidized zone is only about one-tenth of those in the transition zone. Copper, however, shows a slight increase in the oxidized zone over the transition zone. All the uraninite has been leached from the oxidized zone and nearly all of the sulfide minerals have been removed by oxidation. In general, the secondary uranium and copper minerals are similar to those in the transition zone, although efflorescent deposits of secondary uranium minerals are not common on the mine walls and jarosite is sparse in the oxidized zone.

STATISTICAL INTERPRETATION OF ASSAY DATA

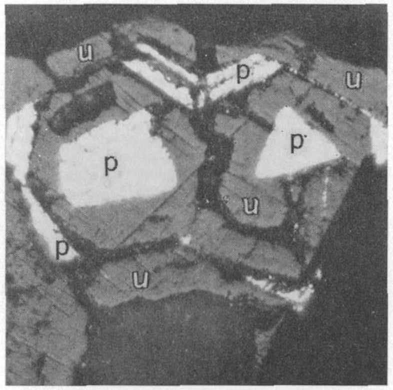
A statistical analysis was made on 10 samples from the oxidized zone (table 1). The number of samples is admittedly small and may be insufficient for the



A.



B.



C.

A. PHOTOMICROGRAPH OF A CROSS SECTION OF A WOOD FRAGMENT PARTLY REPLACED BY URANINITE AND CHALCOPYRITE.

Uraninite has replaced the cell walls, and chalcopyrite has filled or replaced part of the cell cores: *u*, uraninite; *c*, chalcopyrite; *w*, unreplaced wood. x 145.

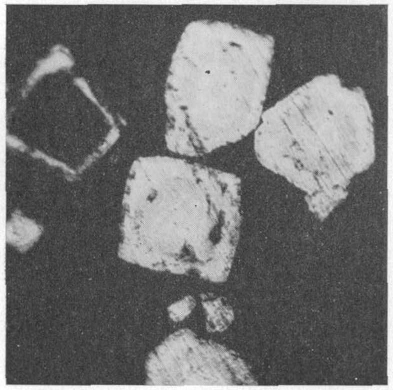
B. PHOTOMICROGRAPH OF URANINITE INTERGROWN WITH PYRITE, REPLACING FINE-GRAINED ORGANIC MATERIAL IN SANDSTONE.

u, Uraninite; *p*, pyrite. x 710.

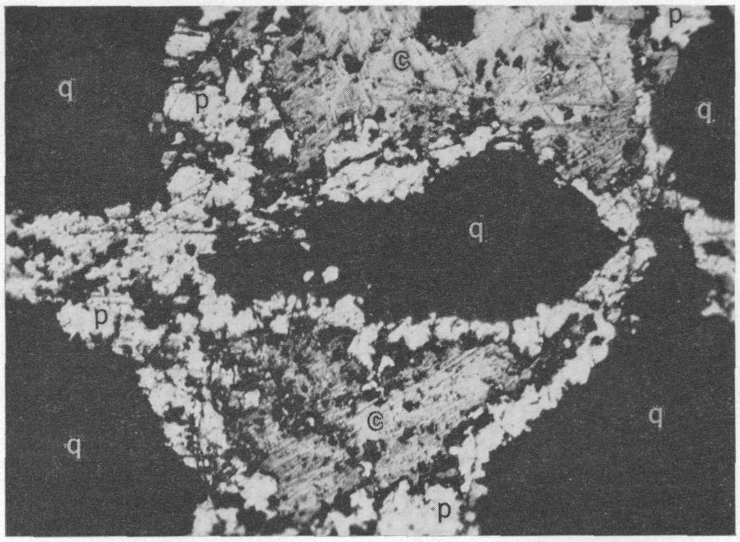
C. PHOTOMICROGRAPH OF URANINITE PARTLY FILLING THE SPACES BETWEEN QUARTZ GRAINS AND FILLING FRACTURES CUTTING THE GRAINS.

u, Uraninite; *q*, quartz grains. x 145.

D. PHOTOMICROGRAPH OF COMPLEX ZONED PYRITE CRYSTALS AND A SKELETAL PYRITE CRYSTAL. x 710.

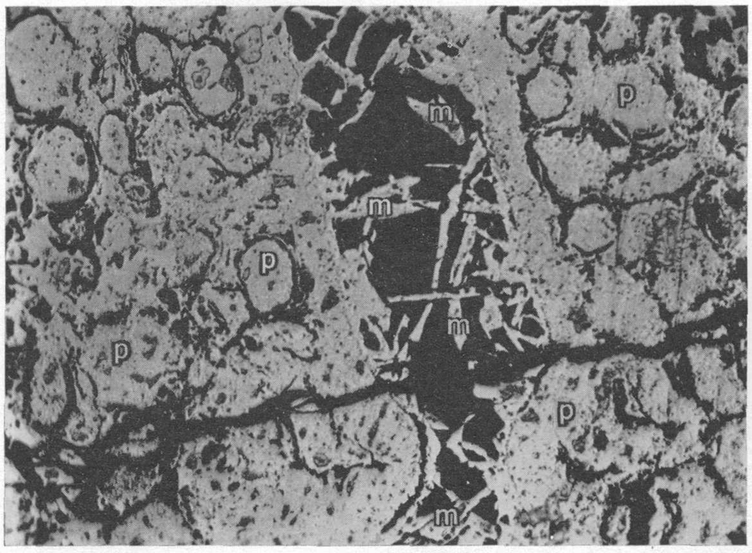


D.



A. PHOTOMICROGRAPH OF PYRITE RIMMING QUARTZ GRAINS AND CHALCOPYRITE FILLING THE SPACES BETWEEN THE GRAINS OF THE SANDSTONE.

p, Pyrite; *c,* chalcopyrite; *q,* quartz grains. Blue filter, x 145.



B. PHOTOMICROGRAPH OF MARCASITE RIMMING A CAVITY IN WOOD THAT HAS BEEN REPLACED BY PYRITE.

m, Marcasite; *p,* pyrite. x 145.

drawing of valid conclusions. The data suggest, however, that the amount of uranium is significantly less in the oxidized zone (M=0.021) than in the transition zone (M=0.28) or the sulfide zone (M=0.34) although its distribution is more uniform in the oxidized zone (GD=3.85) than in the transition (GD=7.10) and sulfide zones (GD=8.40). Complete oxidation of concentrations of uraninite with the formation of dispersed secondary minerals probably accounts for the greater uniformity of uranium distribution.

The amount of manganese is considerably smaller and the assay values show more dispersion in the oxidized zone (M=0.0018; GD=6.35) relative to both the transition (M=0.013; GD=2.47) and the sulfide zones (M=0.014; GD=1.80). Manganese has apparently been leached from the deposit near the outcrop and a large part of it is believed to have migrated along fractures. The deposition of manganese oxide along many of the fractures is believed to account for part of its variability in the oxidized zones. The correlation of uranium with copper, manganese, iron, and calcium carbonate is not significant in the oxidized zone.

SUMMARY

The uranium deposits at the Happy Jack mine are in the Shinarump member of the Chinle formation which have filled a channel cut into the underlying Moenkopi formation. The deposits are believed to have been localized principally in the more permeable beds containing large amounts of coalified wood and claystone or siltstone seams. Secondary silica was added to the quartz grains prior to the deposition of the uraninite and sulfide minerals. Iron, copper, uranium, zinc, lead, barium, manganese, and other metallic elements apparently were deposited by solutions which removed a large part of the secondary quartz. The acidity of the solution is not known, but it is believed that bicarbonate solution could have removed part of the quartz and deposited some of the metallic minerals. Pyrite, galena, chalcopyrite, bornite, uraninite, and sphalerite were deposited from the solution by replacement of wood and of portions of sandstone and deposition in the pores of the sandstone.

Oxidation of the sulfide ore body by oxygen-bearing acid sulfate waters has penetrated to about 200 feet behind the cliff face. With oxidation of the sulfide ore body, movement of metallic ions has been both, outward to be lost to surface waters, and inward to increase the concentration of elements. Although large amounts of copper and uranium have been lost by oxidation and removed at the surface, small amounts of uranium and significant amounts of copper have migrated inward from the rim and have been redeposited as supergene minerals. The uranium apparently has migrated farther than the copper to form sooty pitchblende in the outer part of the primary sulfide zone. Copper has been enriched as chalcocite and covellite principally in the transition zone and as sulfates in the transition and oxidized zone. Some of the iron has been redeposited as jarosite and possibly as marcasite in the transition zones and the outer part of the sulfide zone; a large part of the iron has been deposited as goethite and hematite in the transition and oxidized zones. Most of the manganese, zinc, and lead, are believed to have been removed by oxidation. In general, the oxidation and supergene enrichment has tended to decrease the size of the ore body, although slightly enriching it.

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Part 17. SEDIMENTARY STRUCTURES AND LOCALIZATION AND OXIDATION OF ORE AT THE PEANUT MINE, MONTROSE COUNTY, COLORADO

By Carl H. Roach and Mary E. Thompson

CONTENTS

ILLUSTRATIONS

ABSTRACT

At the Peanut mine in the Bull Canyon mining district, Montrose County, Colo., vanadium-uranium ore is mined from the Salt Wash member of the Morrison formation of Late Jurassic age. All of the ore bodies occur in the upper ore-bearing sandstone zone of the Salt Wash member. Ore bodies are relatively small and occur in clusters on the flanks of channels cut into a mudstone zone below. Most ore bodies conform in shape to the outlines of festoon "solids"; smaller ore bodies are restricted to the upper parts of festoon "solids." The upper parts of individual ore bodies are more oxidized than lower parts. The festoon surfaces are relatively impermeable to ground water; many of the ore bodies are saturated with water perched above the basal surfaces of festoons.

The principal ore minerals are uraninite, coffinite, montroseite, and vanadiferous clays. Four unidentified and probably new vanadium minerals occur in the ore. Molybdenite, digenite, and native selenium are present in addition to the normal suite of metallic minerals.

The hypothesis is offered that the less permeable festoon surfaces "trap" the ore and inhibit draining of ground water, thus protecting the lower parts of ore bodies from oxidation.

INTRODUCTION AND ACKNOWLEDGMENTS

The Peanut mine is in the Bull Canyon mining district, Montrose County, Colo., about 15 miles west of Naturita, Colo.

A detailed study of the geology of the Peanut mine was begun in February 1954, for the primary purpose of determining the trace element composition of the ore deposit. Secondary objectives were to determine (1) if trace element dispersion patterns are present that might be used as guides to ore, (2) possible structural controls of the ore bodies, and (3) the paragenesis of the ore minerals.

The study of the mine included detailed mapping and extensive sampling of the ore and adjacent rock, as mining progressed. The mine was visited almost every day during the first year of the study. Thin sections and polished sections were obtained for many of the samples. Preliminary results of the study reported in this paper indicate a definite relation between sedimentary structures of the host rock and the localization and oxidation of the ore bodies.

Mining on the Peanut claims was begun early in 1954 by the J. R. Simplot Mining Co. of Boise, Idaho. In September 1954, the mine was sold to the Camoose Mines of America, Incorporated, of New York. The managements of both these companies were very cooperative in permitting the extensive studies of the mine.

Thanks are due to the chemists and spectrographers at the Denver and the Washington laboratories of the U. S. Geological Survey, who analyzed samples from the Peanut mine, and to D. A. Jobin, U. S. Geological Survey, who made permeability measurements of a number of samples.

STRUCTURE AND STRATIGRAPHY

The Peanut mine is located along the axis of the Dry Creek Basin syncline which lies between the Paradox Valley and the Gypsum Valley salt anticlines (Cater, 1954). The rock strata are essentially horizontal in the vicinity of the mine.

The dissection of Bull Canyon has caused the regional water table to lower to a position several hundred feet below the ore horizon. This dissection, according to Fenneman (1931, p. 325), began at, or soon after, the beginning of the Pleistocene. Water now present in the Peanut mine is in small perched water tables.

Sedimentary rocks exposed in the vicinity of the mine range in age from Late Jurassic to Late Cretaceous. The formations in ascending order of age are the Entrada sandstone, the Summerville formation, and Morrison formation of Jurassic age and the Burro Canyon formation and Dakota sandstone of Cretaceous age. The Morrison formation of Late Jurassic age is composed of two members, the lower, the Salt Wash member, and the upper, the Brushy Basin member.

The Brushy Basin member consists of varicolored mudstones with a few interstratified layers of sandstone and conglomerate. It is about 400 feet thick in the vicinity of the Peanut mine, and has an indistinct contact with the underlying Salt Wash member.

The Salt Wash member is about 350 feet thick near the Peanut mine. It consists of a series of sandstone layers separated by red and green mudstone beds. Regionally, the sandstone layers pinch out or coalesce with other sandstone units. The top 40 to 60 feet of the Salt Wash member consists of a series of broad discontinuous sandstone lenses and thin discontinuous layers of red and green mudstone. All of the ore bodies at the Peanut mine occur in this stratigraphic zone, which is commonly referred to as the ore-bearing sandstone. The ore-bearing sandstone is underlain by a mudstone layer from 20 to 40 feet in thickness. Throughout most of the area the ore-bearing sandstone has a nearly uniform thickness of about 40 feet. Locally, it thickens abruptly to 60 feet or more where channels are cut into the underlying mudstone. Much of the ore-bearing sandstone is flat bedded or gently crossbedded, but in the vicinity of a channel the crossbedding is more complex. On the flanks of the channels a particular type of crossbedding, known as festoon cross-lamination, is especially well developed.

According to Knight (1929; 1930), festoons are the results of (1) the erosion of plunging troughs having the shape of a quadrant, or segment,[14] of an elongate ellipsoid; (2) the filling of the troughs by clastic sediments, commonly in thin laminae which generally conform to the shape of the trough floors; and (3) the partial destruction, in differing degrees, of the filling laminae by subsequent erosion, producing younger troughs which intersect the older troughs.

Knight believes the force that created the festoons to have been oscillating currents in comparatively shallow water. Probably the same stream that cut the channel into the mudstone layer, at a later stage in its history and after some aggradation, created the festoon cross-laminations.

The geometric features produced by the intersections of groups of festoons are many and complex. The feature shown diagrammatically on figure 60 is produced by the intersection of three festoons and is more common than any other. Festoon 1 has been intersected by the later formation of festoon 2 and both have been intersected and partially destroyed by the formation of festoon 3.

For convenience in discussion, this physical feature as shown in figure 60, will be referred to as a festoon solid, i. e., a solid bounded by three festoon surfaces. The lower erosion surface, or trough floor, of the festoon solid will be called a basal festoon surface, and the mass of sandstone above the basal festoon surface and terminated by the upper festoon surfaces will be called the festoon fill. Less prominent cross-lamina-

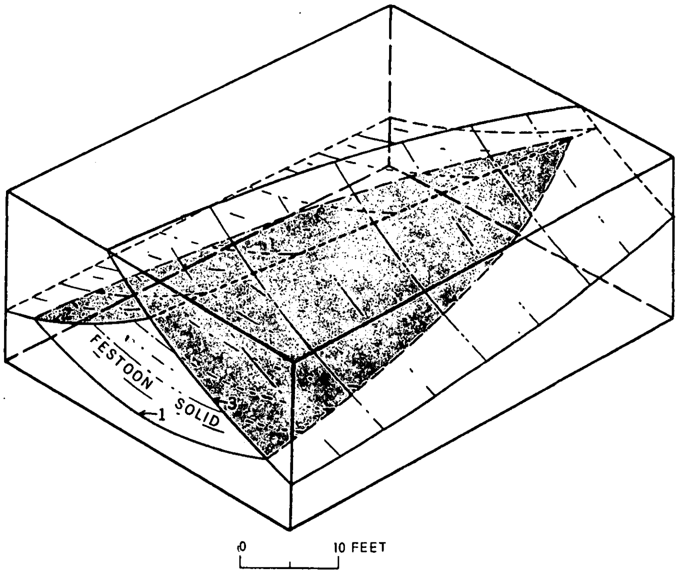

FIGURE 60.—Diagrammatic sketch of a festoon solid, showing festoon surfaces under which ore occurs. Numbers indicate order of formation of surfaces. Shaded areas represent roof of festoon solid under which ore occurs.

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[14] The word "segment" was added by the authors.

tions occur in the festoon fill. They are related to the basal festoon surface, and will be referred to as second-order festoon surfaces.

The festoon surfaces are relatively impermeable. Water perched above a basal festoon surface will drain only after the festoon surface is punctured by mining activities. A number of permeability measurements were made on samples taken from an unmineralized festoon solid. Samples from the center of the festoon solid showed relatively small differences in permeability measured parallel to and normal to the bedding planes. Samples taken from close to the festoon surface showed marked differences in permeability in the two directions; some samples were more than 100 times more permeable parallel to the bedding than normal to it. A thin clay seam is commonly present along the festoon surface; this clay is seldom retained when the core is prepared for the permeability measurement; therefore, the relative impermeability may actually be much greater through the festoon surface than measurements indicate on available samples.

ORE BODIES

Most of the ore bodies at the Peanut mine occur as clusters in the lower part of the ore-bearing sandstone zone, but small bodies of mineralized rock also occur in a zone 5 to 15 feet above the principal ore-bearing zone.

The ore bodies are lenticular in shape and tend to pinch out rapidly. Some closely spaced lenticular masses of ore coalesce into a single ore body. The average ore body is about 50 feet long, 20 feet wide, and varies in thickness from a few inches at the edges to 6 or more feet at the thickest part. Contacts between mineralized rock and barren rock are very sharp, and in general correspond to the major changes of direction of bedding, i. e., the cross-laminated festoon surfaces.

A few ore bodies in the mine have the shape of rolls (Fischer, 1942); the contact between mineralized and barren rock curves across the bedding. The contact is well defined and may be mapped as a continuous surface for a distance of 20 feet or more. Rolls trend about S. 70° to 80° E., and conform to the trend of rolls mapped in other mines in the district.

The average vanadium-uranium ratio of the ore bodies is about 9 to 1. Assays of a number of drill cores of ore bodies show an average grade of 0.5 percent U and 4.5 percent V. The average vanadium-uranium ratio of the smaller bodies of mineralized rock that occupy a stratigraphically higher position is about 4 to 1. Assays of a few drill cores of these bodies show about 1 percent U and about 4 percent V. The grade of ore within one ore body does not appear to vary significantly, except where oxidation along fractures may have leached the ore. Local concentrations of higher grade uranium-bearing material are associated with organic matter. Sulfide minerals accompanying the ore tend to concentrate at the base of ore bodies.

The shapes of all ore bodies, except those few that make rolls, conform to the shapes of festoon solids whose surfaces mark the boundaries of the ore. Larger ore bodies nearly fill a festoon solid, but most of the ore bodies are smaller and are restricted to the upper parts of the structure.

The upper contacts of ore with barren rock almost invariably correspond to festoon surfaces—the few exceptions are the ore bodies in the shape of rolls. Ore bodies are restricted to those festoon solids, or parts of festoon solids, whose upper surfaces have structural closure. The lenticular shape of the ore body is determined by the shape of the festoon solid in which it occurs and the amount of structural closure formed by the upper surfaces of the festoon solid. The simple lenticular shape of an ore body may be complicated by the presence of "splits" of barren rock penetrating the ore body. These "splits" correspond to second-order festoon surfaces.

Many variations of the symmetrical festoon solid are present in the mine. Some of the most common of these are shown in figure 61. Figure 61A shows a cross section of a symmetrical festoon solid, with mineralized rock in the upper part. Figure 61B shows a longitudinal section of the same festoon solid. The mineralized rock extends downward no further than the structural closure of the upper festoon surfaces. Figure 61B also shows the festoon solid as completely closed to the right, whereas to the left the festoon surfaces gradually flatten in dip, and either lose definition, or are truncated by other festoon surfaces.

Smaller bodies of mineralized rock that occur stratigraphically 5 to 15 feet above the ore zone commonly show a "satellite" relation to larger bodies of ore that are enclosed (in part) under the same through-going festoon surface. Such a relation is shown in figure 61C.

Some festoon solids are skewed rather than symmetrical, but in those too, the ore extends downward only as far as the festoon solid has closure, as shown in figure 61D.

Figure 61E shows a generalized cross section of a cluster of closely spaced or coalescing ore bodies contained in a complex group of interpenetrating festoon solids. It can be seen from this figure that prediction of the location and extent of ore bodies is difficult or impossible without recognition of the relation of ore bodies to the festoon surfaces. A positive result of this study has been the adaptation of mining methods to the

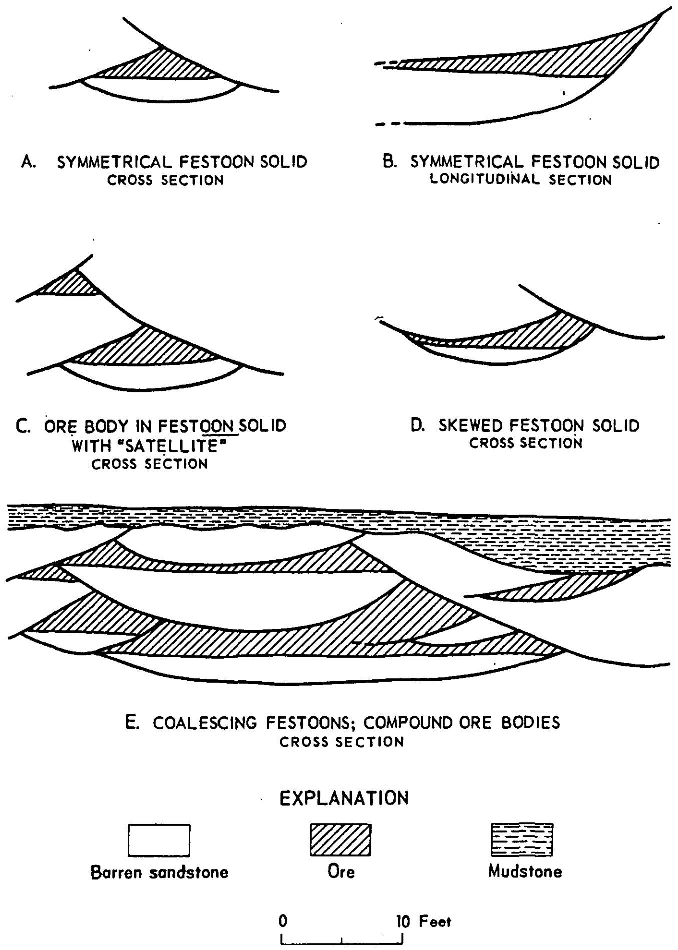

FIGURE 61.—Various types of festoon solids and their relation to ore bodies.

controlling influences of the festoon surfaces, and a number of ore bodies have been discovered that might otherwise have been missed.

The position of ore bodies under relatively impermeable surfaces is similar to petroleum occurrences in anticlinal reservoirs under impermeable cap rocks, and also resembles certain types of hydrothermal mineral deposits where the ascending ore solutions are considered to have been impounded by an overlying impervious cover. A density stratification of the ore solutions with the ground water may have been responsible for this relation, or perhaps a hydrostatic head forced the solutions up into areas where under the influence of gravity alone they would not travel.

It is difficult to understand how the parts of festoons having closure, which would have been areas of relative stagnation, should have become loci of deposition. Presumably the solutions were dilute, though perhaps not far from saturation, and a large body of solution passing through the incipient ore body would seemingly be required. It is probably important that the festoon surfaces were only relatively impermeable.

It has been suggested, with certain types of hydrothermal ore deposits (Mackay, 1946), that the impounding rocks were not entirely impermeable to the ore solutions, and by a process of "hypofiltration" permitted the water to pass through, leaving the minerals behind.

Much of Mackay's theory seems applicable to localization of vanadium-uranium ore. One of the physical features of ore deposits which he cites as evidence for his argument is the frequently observed presence of smaller ore bodies or weakly mineralized areas above the major ore body and localized under another "impermeable" layer. But the ore solutions must have passed through the lower "impermeable" rock! The "satellite" ore bodies observed in the Peanut mine are very similar in physical arrangement to the secondary ore bodies discussed by Mackay. The particular suite of metals that compose these vanadium-uranium deposits may be explained by a careful investigation into the penetrative power of the ions involved.

This discussion of the localization and method of deposition of the ore does not lead one inevitably to the conclusion that the ore solutions were hydrothermal. Circulating ground waters would most likely have been subjected to the same controls as low-temperature hydrothermal solutions.

Most of the ore bodies at the Peanut mine are unoxidized. Some oxidation has taken place, but is commonly restricted to zones along fractures, or to the upper parts of ore bodies. One partly oxidized ore body was sampled in detail. The pattern of oxidation is shown in figure 62. The lower part of the ore is unoxidized, and contains montroseite, vanadiferous clays,

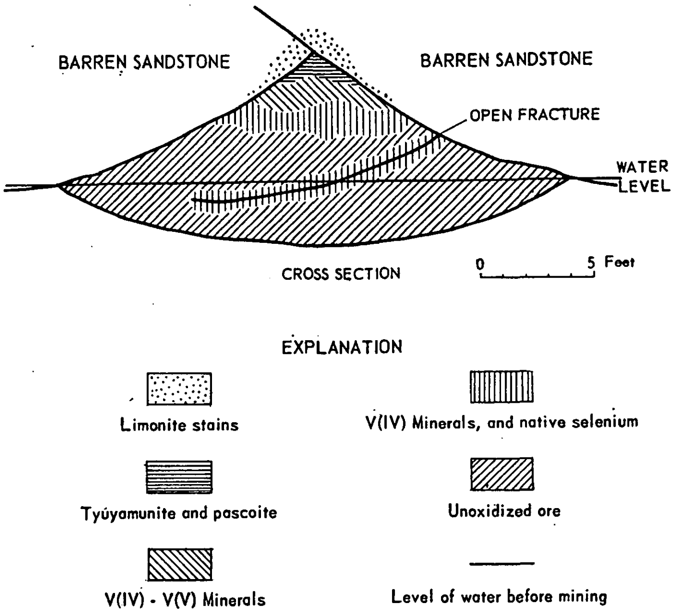

FIGURE 62.—Pattern of oxidation of a typical ore body in the Peanut mine, Montrose County, Colo.

uraninite, and coffinite. Doloresite and other vanadium (IV) minerals occur as fracture coatings in the montroseite-bearing sandstone and at the top of the unoxidized ore. Abundant crystals of native selenium are also present in the fractures. Melanovanadite and other vanadyl vanadates occur slightly higher in the ore body than the vanadium (IV) minerals. At the top of the ore body are tyuyamunite and pascoite. The unmineralized sandstone around the most oxidized part of the ore body is stained by limonite.

The approximate level of the water perched above the basal festoon surface is indicated in figure 62. Montroseite containing essentially all vanadium (III) was collected from beneath the water level in one ore body, and after a few months in the laboratory, the material had oxidized almost completely to vanadium (IV), indicating that the presence of standing water in the festoon solid prevented oxidation of the montroseite in place.

The controlling influence of the festoon cross-laminations on the oxidation of the ore is indirect. After the lowering of the regional water table, the relative impermeability of the basal festoon surfaces caused the formation of perched water tables. The standing water saturating the ore bodies prevented their oxidation or restricted the oxidation that took place to the upper parts of the ore bodies.

MINERALOGY AND PARAGENESIS

Ore minerals impregnate sandstone and replace coalified wood. The highest grade uranium-bearing samples are associated with coalified wood. The chief uranium minerals are uraninite and coffinite; the most abundant vanadium minerals are montroseite and vanadium silicates.

Vanadiferous silicates occur as ill-defined masses interstitial to the quartz grains in the sandstone, and montroseite occurs as euhedral, lath-shaped crystals radiating from quartz grains. Commonly, the montroseite crystals are partly or completely surrounded by secondary quartz overgrowths. Montroseite associated with wood occurs both as masses of loosely coherent lath-shaped crystals and as more solid botryoidal aggregates. In sandstone ore, uraninite and coffinite are finely divided and are not generally visible as discrete minerals. Polished section studies show that uraninite and coffinite in coalified wood replace cell walls and cell interiors selectively.

Montroseite in coalified wood is commonly associated with pyrite and yellow barite. Sulfide minerals found in small amounts with the unoxidized ore are pyrite, marcasite, chalcopyrite, chalcocite, molybdenite, galena, and sphalerite. Studies of polished sections show that a small amount of digenite is associated with the chalcocite. Molybdenite and chalcocite commonly occur as thin layers along bedding planes at the base of an ore body, or at the base of a festoon solid whose upper part contains an ore body.

Doloresite is found intermixed with paramontroseite, but occurs more commonly as thin massive coatings on fractures. Thin coatings of doloresite are velvety black. In polished section extremely small terminated crystals are seen along the outer edges of the doloresite coating. In immersion the doloresite is brown and anisotropic. Simplotite (Thompson, Roach, and Meyrowitz, 1956a), a new calcium tetravanadite, and duttonite (Thompson, Roach, and Meyrowitz, 1956b), a new oxide of tetravalent vanadium, form on the coatings of doloresite. Associated with the new minerals are felted masses of native selenium crystals.

Simplotite, $CaV_4O_9 \cdot 5H_2O$, occurs as hemispherical aggregates of dark-green platy crystals. Duttonite, $VO(OH)_2$, occurs as crusts of randomly oriented platy crystals, light brown in color. Although simplotite, duttonite, and native selenium typically occur together on the earlier coating of doloresite, they are not intermixed, but instead each mineral occupies a separate though generally contiguous area.

The best samples of duttonite are associated with thicker layers of doloresite, which appears gray and submetallic. In these samples the doloresite partly or completely recements the fractures. Crusts of duttonite crystals are found in open spaces in the fractures, apparently altering from the doloresite.

Melanovanadite is the next formed vanadium mineral. It is abundant at the Peanut mine and a number of excellent specimens have been collected. It is found associated with duttonite and simplotite, as well as alone, and with two undescribed vanadium minerals that are considered to be vanadyl vanadates. On samples of coalified wood that has been replaced in part by uraninite and coffinite, melanovanadite occurs with the two undescribed vanadyl vanadates and tyuyamunite. In this type of occurrence, however, it apparently forms earlier than the other secondary minerals, because, while they occur as surface coatings, the crystals of melanovanadite penetrate the wood.

There is little oxidized ore as such at the Peanut mine although minerals typical of oxidized ore are present in small amounts—that is, tyuyamunite, corvusite, and efflorescences of pascoite. Oxidation of the ore apparently results in the movement of some ions because limonite typically stains the unmineralized sandstone around the oxidized parts of ore bodies. Small amounts of malachite are found with the limonite. There is some indication that during oxidation vanadium moves out into previously unmineralized sandstone and combines with silicates in place to form the light-gray low-grade "vanadium clay" typical of oxidized ore.

No selenides have been found at the Peanut mine although clausthallite is present in a mine not far away. Detailed studies of the selenium content and association of pyrite and marcasite at the Peanut mine have not been made, but there is probably enough selenium in pyrite and marcasite to account for all of the native selenium found. Native selenium occurs relatively early in the oxidation sequence, with the last formed quadrivalent vanadium minerals, duttonite and simplotite, but pyrite occurs with more oxidized vanadium minerals. It is probable that marcasite alters before pyrite and yields the first formed native selenium.

In summary, the primary ore minerals are uraninite, coffinite, montroseite, and vanadiferous silicates. Associated with the primary minerals are small amounts of a number of sulfides and barite.

Montroseite alters in place to paramontroseite, but doloresite most commonly forms secondary coatings. Two new quadrivalent vanadium minerals form in the doloresite and are associated with native selenium. Melanovanadite forms next, then two undescribed vanadyl vanadates, and lastly corvusite, tyuyamunite, pascoite, and probably "vanadium clay." Limonite and malachite are associated with the last formed vanadium minerals.

CONCLUSIONS

Ore bodies are concentrated on the flanks of channels, where festoon cross-laminations are best developed. Contacts between mineralized and barren rock are sharp, and in all ore bodies, except rolls, they correspond to festoon surfaces. Ore bodies are contained within festoon solids and are found only in the part of the festoon solid having structural closure. This fact is verified by observation of many separate ore bodies in the Peanut mine, and the same relationship has been observed in other mines in the area. Permeability measurements and the presence of perched water tables indicate that the festoon surfaces are relatively impermeable. Oxidation of the ore bodies has been inhibited by the presence of the perched water tables and most of the ore at the Peanut mine is unoxidized even though the regional water table is several hundred feet below the ore-bearing sandstone.

The sedimentary structures of the host rock, in particular the festoon cross-laminations, have exerted a controlling influence on the localization of the ore, and have determined the pattern of oxidation of individual ore bodies.

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Part 18. GEOLOGY AND MINERALOGY OF THE J. J. MINE, MONTROSE COUNTY, COLORADO

By Donald P. Elston and Theodore Botinelly

CONTENTS

ILLUSTRATIONS

TABLES

ABSTRACT

Vanadium-uranium ore is mined at the J. J. mine in the Jo Dandy area, Montrose County, Colo. The ore is in the upper sandstone layer of the Salt Wash member of the Morrison formation of Jurassic age. Permeability and variations in permeability in cross-stratified sandstone units within the sandstone layer have influenced the gross distribution and, in many places, controlled the detailed configuration of ore. Carbonized wood apparently has been influential in localization of ore minerals where sedimentary structures have allowed ore solutions access to the wood. The J. J. mine intersects the ground water table; above the water table the ore and enclosing sandstone are oxidized, and carnotite and "vanadium clay" are the major ore minerals. Below the water table the ore is unoxidized, and montroseite, uraninite, and coffinite are the major ore minerals. An intermediate oxidized zone composed of hydrous vanadium oxides with intermediate valences is thin and poorly defined. The configuration and distribution of ore are little changed by oxidation. The ore minerals were emplaced by mineralizing fluids which moved laterally through the sandstone and which deposited low-valent minerals.

INTRODUCTION

Detailed geologic mine mapping and sampling of the J. J. mine in the Jo Dandy area, Montrose County, Colo., were undertaken to study a vanadium-uranium ore body in terms of the physical relationships of ore to host rock, the paragenetic sequence of ore minerals, and the sequential development of an oxidized suite of ore minerals from unoxidized ore.

The J. J. mine is in the southwest part of the Jo Dandy area in the Bull Canyon mining district, and is about 8 miles due west of Naturita, Montrose County, Colo. The Jo Dandy area is an elongate strip of land, about 4 miles in length, bounded on the northeast by the floor of Paradox Valley (elevation 5,600 feet) and on the southwest by the rim of Monogram Mesa (elevation 7,100 feet).

Early in 1955, eight mines were active in the Jo Dandy area; in addition many mines and prospects were abandoned or inactive. The J. J. mine is the easternmost mine in the area. Production from the mine since 1949 has been in excess of 10,000 short tons.

Detailed mine mapping was begun in December 1953 and completed by March 1954. Since that time periodic mapping has kept the outline of workings and geology up to date.

Permission to map and sample the J. J. mine was given by Mr. Everett M. Paris of the U. S. Vanadium Co. X-ray analyses were made by M. E. Thompson, U. S. Geological Survey.

GENERAL GEOLOGY

STRATIGRAPHY

Rocks exposed in the area range from Pennsylvanian to Early Cretaceous in age (table 1). All the Mesozoic strata present in the area are exposed in faulted blocks along the south margin of Paradox Valley. Triassic and Lower Jurassic sedimentary rocks thin and pinch out toward the axis of the Paradox Valley anticline to the north; the Morrison formation of Jurassic age and the Cretaceous formations were deposited across the anticline (Cater, 1954).

The mines are in the upper sandstone layer of the Salt Wash member of the Morrison formation of Jurassic age. Locally this sandstone is called the "ore-bearing sandstone." In the vicinity of the J. J. mine, the ore-bearing sandstone is subdivided into two sandstone strata separated by green or green and red mudstone (fig. 63, section *A*). At the mine the ore-bearing sandstone is about 50 feet thick; the upper sandstone stratum ranges from 20 to 30 feet in thickness and contains the principal reserves of the area. The ore body in the J. J. mine is in the lower and middle parts of the upper sandstone stratum.

The ore-bearing sandstone is generally light to dark brown, medium to fine grained, and may be stained or speckled by limonite derived from the oxidation of pyrite. Light- to bright-red hematite staining has been observed locally. In areas where the pyrite has not been oxidized the sandstone is light gray. The sandstone is composed largely of subangular, clear and frosted grains of quartz and, in places, contains, apparently reworked, rounded to subrounded grains of quartz. Minor amounts of feldspar, biotite, red and green chert, and opaque minerals are present. Silica and calcite are the most common cementing agents. Where the rock is highly fractured and the pyrite well oxidized, little cementing material remains and the sandstone is friable. Seams of gypsum occur along many fractures above the water table, and in many places within the J. J. mine gypsum is currently being

TABLE 1.—*Generalized description of Paleozoic and Mesozoic strata, southwest side of Paradox Valley, Jo Dandy area, Montrose County, Colo.*

[Data are in part from an unpublished report on the Jo Dandy area by E. M. Shoemaker, 1950]

Era	System	Group	Formation	Thickness (feet)	Character
Mesozoic	Cretaceous		Burro Canyon formation	175–250	Conglomeratic sandstone with interbedded green mudstone; minor red mudstone near top. Vanadium-uranium bearing locally.
		Unconformity			
	Jurassic		Morrison formation	375–425	Brushy Basin member; red and green mudstone; some sandstone lenses; locally conglomeratic. Vanadium-uranium bearing locally.
				205–400	Salt Wash member; red and green mudstone, light-colored sandstone layers persistent near top and base; lenticular strata between. Locally rests on Paradox member of Hermosa formation. Vanadium-uranium bearing.
		San Rafael group	Summerville formation	50–70	Red with minor green mudstone; light-brown sandstone bed with ripple marks near top.
			Entrada sandstone	0–95	Yellow to light-red very fine-grained to fine-grained sandstone with subordinate medium-fine rounded quartz grains; locally large-scale crossbedding; red silt in basal part equivalent to the Carmel (?) formation.
		Unconformity			
	Jurassic(?)	Glen Canyon group	Kayenta formation	0–200	Lavender micaceous sandstone, light brown locally; thin maroon mudstone beds.
	Triassic		Wingate sandstone	0–300	Red massive sandstone, white locally; irregularly bedded.
			Chinle formation	0–80+	Dark- to light-red mudstone and sandstone; thin bedded; micaceous locally.
		Unconformity			
Paleozoic	Pennsylvanian		Hermosa formation	10,000+ locally	Paradox member; gypsum and black to dark-gray contorted shale and limestone; dark colored where overlain by Morrison formation, light colored where overlain by landslide debris.

precipitated as hairlike coverings on the mine walls. Soft, white subangular grains, resembling chert fragments altered to clay, occur both in barren and mineralized rock. X-ray patterns of samples of this material collected in the Jo Dandy area from the Salt Wash sandstone member of the Morrison formation and Burro Canyon formation show quartz (Outerbridge, William F., written communication).

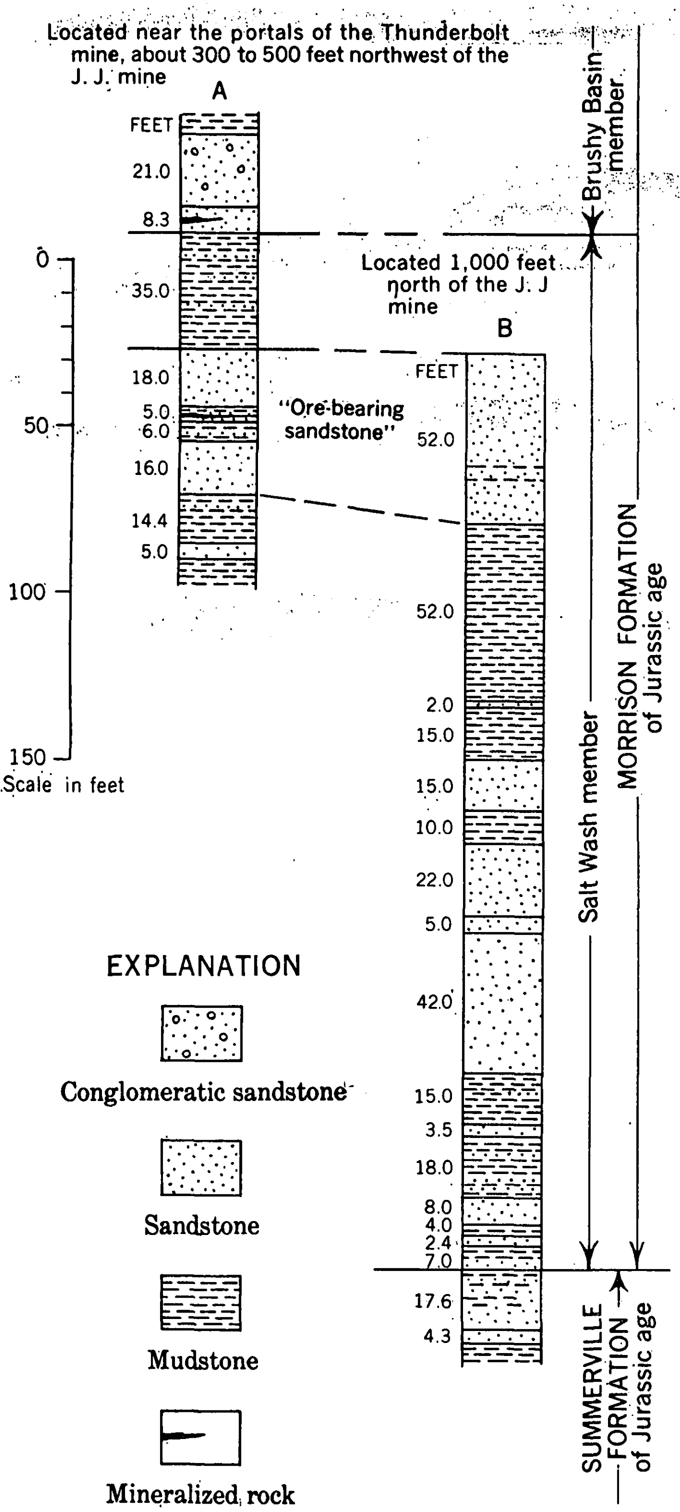


FIGURE 63.—Measured sections near the J. J. mine, Jo Dandy area, Montrose County, Colo.

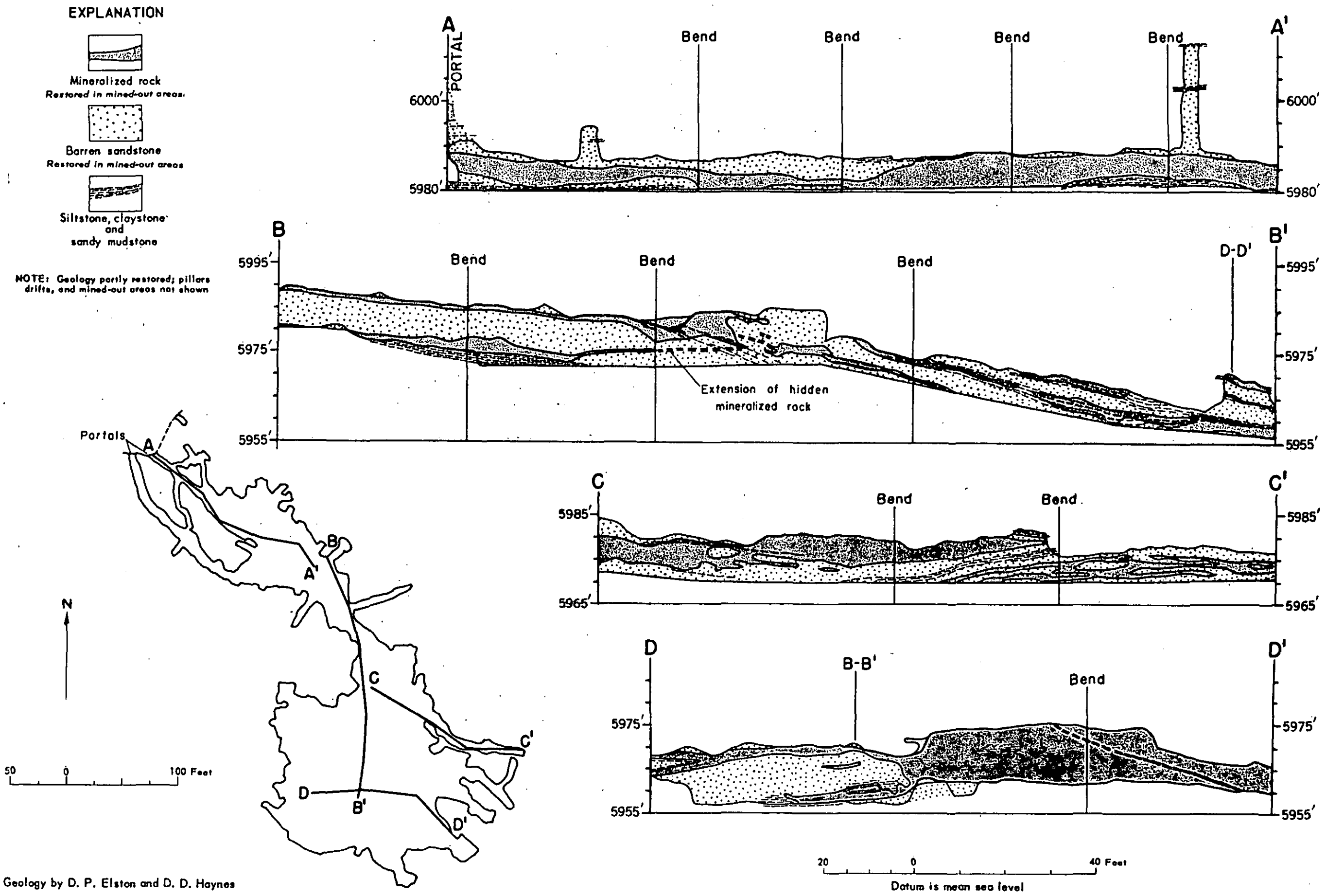
The ore-bearing sandstone is composed of an interbedded sequence of cross-stratified units similar to the simple, planar, and trough cross-stratified units described by McKee and Weir (1952). Discontinuous, interbedded seams of gray-green mudstone, scattered mudpebble layers and carbonaceous zones and trash pockets are common. Cross-stratification ranges from laminations a few inches in length, within an individual bed, to trough cross-stratified beds tens of feet in length which crosscut earlier sediments. The trough cross-stratified beds are similar to "festoons" as described by Knight (1929), Stokes (1953), and Roach and Thompson (Part 17, p. 198).

STRUCTURE

The J. J. mine is adjacent to faulted strata on the southwest flank of the Paradox Valley anticline. In general the beds strike N. 64° W. and dip 10° to 14° SW. Fractures in the mine generally parallel the long axis of Paradox Valley. The dominant fracture set in the J. J. mine strikes N. 30° to 70° W. and has an average dip of 85° NE. A minor fracture set strikes about N. 30° E. and dips either southeast or northwest. Most fractures show no displacement; a few show displacements of a few inches. In the Jo Dandy area faults displace both the ore and the enclosing sandstone and no fault or fracture set has been found that clearly predates the ore.

DESCRIPTION OF ORE BODY

The ore body is composed of interconnecting and overlapping layers of mineralized rock which coalesce locally to form minable rock as much as 19 feet thick. Ore minerals are distributed as mineralized spots, streaks, and disseminations, and in many places follow bedding laminae within larger sandstone units. Ore is distributed irregularly through cross-stratified sandstone units and generally is bounded top and bottom by less permeable mudstones and sandstones. In places the lower edge of mineralized rock may be 2 to 5 feet above the gray-green mudstone that separates the upper stratum of the ore-bearing sandstone from the lower. In other places the ore is in contact with or penetrates the upper few inches of this mudstone. The upper edge of mineralized rock coincides in places with mudstone seams and mudstone pebble layers (fig. 64, sections *A–A′* and *B–B′*). Individual ore layers are more persistent and continuous along rather than across the trend of the sedimentary structures (compare figs. 64 and 65). The trend of the main part of the ore body



Geology by D. P. Elston and D. D. Haynes

FIGURE 64.—Geologic sections and outline map of the J. J. mine, Jo Dandy area, Montrose County, Colo.

follows these sedimentary structures and crosscuts, at a low angle, the dominant fracture set of the area.

HABITS OF THE ORE

Although the boundaries of mineralized rock in many places cut across sedimentary structures, the sedimentary structures seem to control the location of ore both on a broad scale and in detail.

On outcrop at the portal of the J. J. mine (fig. 64, section *A–A′*) two layers of sandstone, that are less massive and more intensely cross-stratified than overlying and underlying beds, are mineralized. The lower mineralized layer is more prominently crossbedded and this layer is extensively mineralized throughout the mine. Near the portal of the mine a flat-layered thin-bedded mineralized sandstone contains a single tabular layer of ore. The upper and lower limits of ore are gently undulating; in detail they cross the bedding at a low angle, but in general parallel the bedding. Ore minerals follow minor cross-laminae within the sandstone layer.

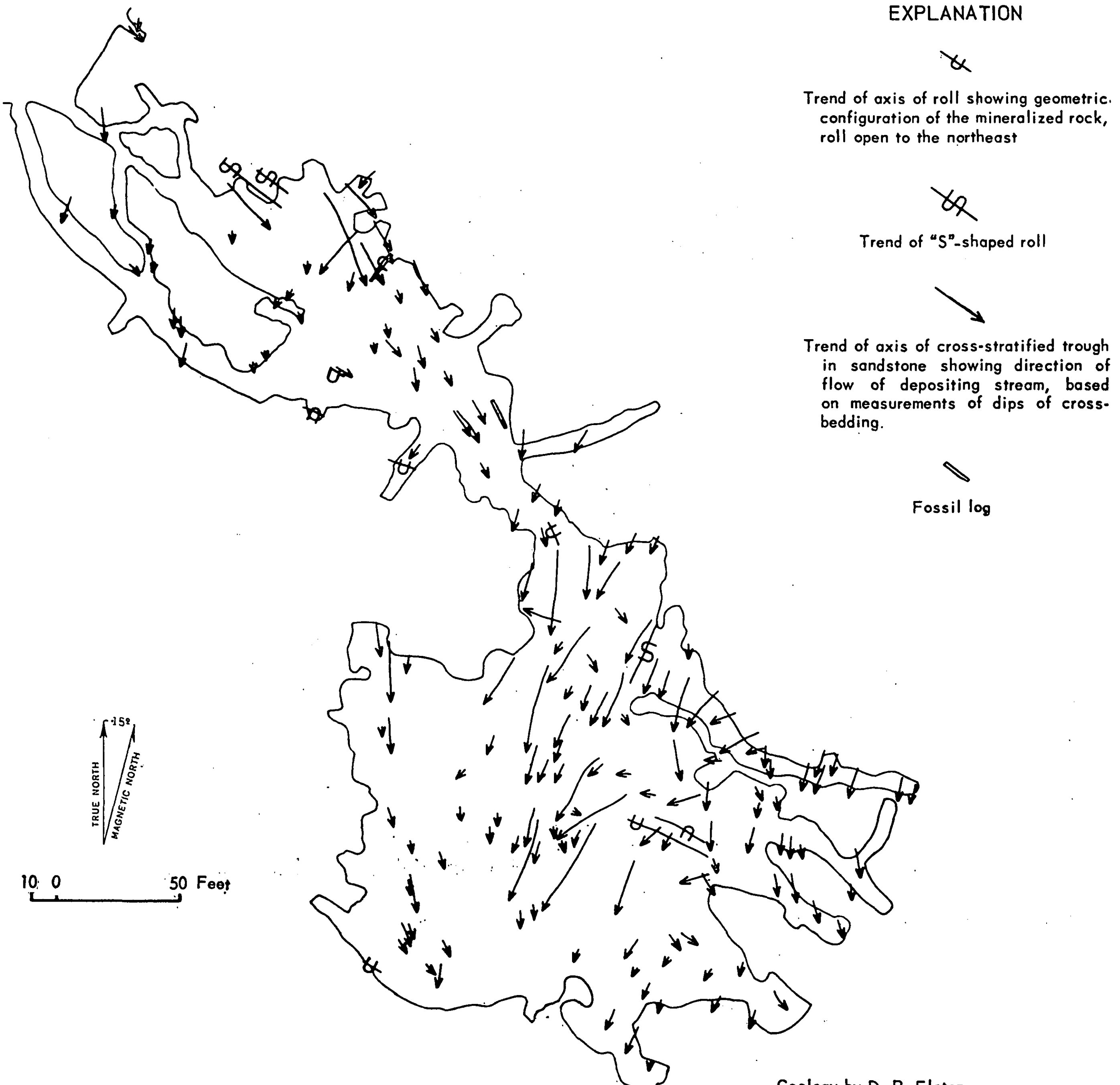
In places in the J. J. mine the distribution of mineralized layers is erratic, and abrupt variations in thickness and sharp crosscutting relationships are prominent (fig. 64, secs. *A–A′*, *B–B′*, *D–D′*). These configurations are associated in part with trough cross-stratification. The ore minerals follow bedding laminations in detail, but the ore minerals may pinch out against intersecting structures.

In mineralized zones, pods of very rich ore are found associated with carbonaceous material. Essentially similar carbonaceous material in barren zones is barren.

ORE CONTROLS

The relations described above indicate that the varying permeability of the different sedimentary structures controls the detailed shape of the ore body. The permeability is high, but irregular in sandstones that show trough crossbedding, and in these beds the ore layers and mineralized zones are very irregular. In the sandstones where simple and planar crossbedding is dominant, and where the permeability is less variable, the ore layers are tabular and less irregular in shape.

Carbonaceous material has caused, probably by chem-



Geology by D. P. Elston

FIGURE 65.—Outline map showing trends of paleostreams as mapped from trough cross-stratified sandstone beds, J. J. mine, Jo Dandy area, Montrose County, Colo.

ical rather than physical means, the precipitation of rich pods of ore where permeable layers have allowed access of solutions to this material.

The gross control for the localization of mineralized ground is not evident. Although the ore body is elongate in the general direction of the dominant fracture set, which in turn parallels the Paradox Valley anticline, the trend of the thicker or main parts of the ore body crosscuts the fractures. The southward and southeastward extension of the ore body, as known from drilling, supports the mapped and observed data in the mine. The trend of the best ore is parallel to the stream trends as determined by mapping of the sedimentary structures (fig. 65). Lateral separation of the ore body, from a single mineralized layer, into two or more thinner mineralized layers is more abrupt and more pronounced across rather than along the trend of the sedimentary structures. The trend of the best ore is southeastward in the northern part of the mine and swings to a more southerly direction in the southern part of the mine. The sedimentary structures do not represent a clearly defined channel in the ore-bearing sandstone, but they seem to define a composite channel trend developed at the time of deposition of the sediments. As such they would present a zone of greater permeability to laterally moving mineralizing solutions.

ROLLS

The term roll (Fischer, 1942, p. 380–384) is applied to mineralized rock where the edges of mineralized rock, or the configurations of leaner and richer material with mineralized rock, cut across bedding and usually described a geometric figure (e. g. C-shaped, S-shaped). The formation of some rolls in the J. J. mine can be attributed to primary sedimentary structures (pl. 6*A*, *B*). Some may be the result of localization of ore minerals around fossil trees (C-roll around fossil tree, fig. 65). Plate 6*C* and *D* show views of C-rolls in the J. J. mine. Other rolls may be the result of local redistribution of vanadium (pl. 6*B*). Still others are unexplained.

The axes of the roll surfaces in the J. J. mine (fig. 65) parallel the regional structure, are normal to the "Uravan mineral belt" (Fischer and Hilpert, 1952), and parallel the long axis of the trend of mineralized ground in the mine which in turn generally parallels the trend of the sedimentary structures. One roll, which has an anomalous strike, contains a thin, mineralized tree along its axis. The tree seems to have been trapped and buried in sandstone at an angle to the stream flow of that time.

A set of S-shaped roll surfaces in oxidized sandstone (pl. 6*A*, *B*) has diffuse bands of gray "vanadium clay" which in part crosscuts the bedding and obscures the remants of primary spotted and streaked disseminations similar to those in unoxidized ore. No similar S-rolls have been found in unoxidized parts of the mine. Several modes of formation can be postulated for the S-shaped rolls: (1) the rolls are primary and represent periods of pulsation and temporary stagnation of an edge of a mineralizing solution; (2) the rolls represent a pulsating movement of the mineralizing solutions which caused a partial redistribution of the ore minerals into the poorly defined S-shaped bands with a partial depletion of the ore minerals from the intervening areas; or (3) the roll surfaces are the result of a partial redistribution of ore minerals during oxidation and were superimposed on original spotted and streaked mineralized rock. In any event, the field relations indicate that the configuration of these S-rolls is the result of a deflection of solutions by an overlying partly intersecting, trough crossbedded sandstone structure.

MINERALOGY

The ore in the J. J. mine ranges from oxidized ore in the upper part of the mine to unoxidized ore below the water table (fig. 66). The major uranium minerals are carnotite, tyuyamunite, uraninite, and coffinite. The major vanadium minerals are montroseite, vanadium silicates,[15] and corvusite. Accessory vanadium minerals are melanovanadite, hewettite, and several unnamed vanadate minerals. Nonmetallic gangue minerals are quartz, gypsum, calcite, barite, clay minerals, and limonite. Carbonaceous material is widely distributed through the mine in small quantities. Metallic gangue minerals include pyrite, marcasite, galena, sphalerite, and native selenium.

The black unoxidized ore containing montroseite, coffinite, and uraninite occurs below the water table. Immediately above the water table is a thin discontinuous zone of partly oxidized ore. Above this zone is the zone of oxidized ore containing carnotite, tyuyamunite, and vanadium silicates. Minor exceptions to this distribution occur. In black ore, high-valent minerals occur close to some through-going fractures. In oxidized ore, pods of unoxidized or partly oxidized ore occur where carbonaceous material has reduced oxidizing solutions or, more likely, an impermeable area has prevented oxygen from reaching the ore.

UNOXIDIZED ORE

Ore minerals of the black unoxidized ores are montroseite, uraninite, coffinite, and vanadium silicates. Quartz, calcite, gypsum, clay minerals, and barite are the major gangue minerals. Pyrite and marcasite are prominent locally. Galena and sphalerite occur sparsely distributed through the ore.

Characteristic microtextures of unoxidized ore show montroseite in intergranular areas either by filling or by replacement of the clay mineral matrix. A few specimens show corrosion of the quartz grains (pl. 7*A*) and some show montroseite crystals penetrating silica overgrowths on the quartz grains (pl. 7*B*).

Montroseite occurs typically as bladed crystals in radial arrangement. A few crystals show terminal faces; typically the ends are ragged or fibrous.

Uraninite and coffinite were studied in polished sections of organic material; uraninite with montroseite fills cell interiors and coffinite replaces cell walls. Where cell textures are obscure, coffinite occurs as fine dark

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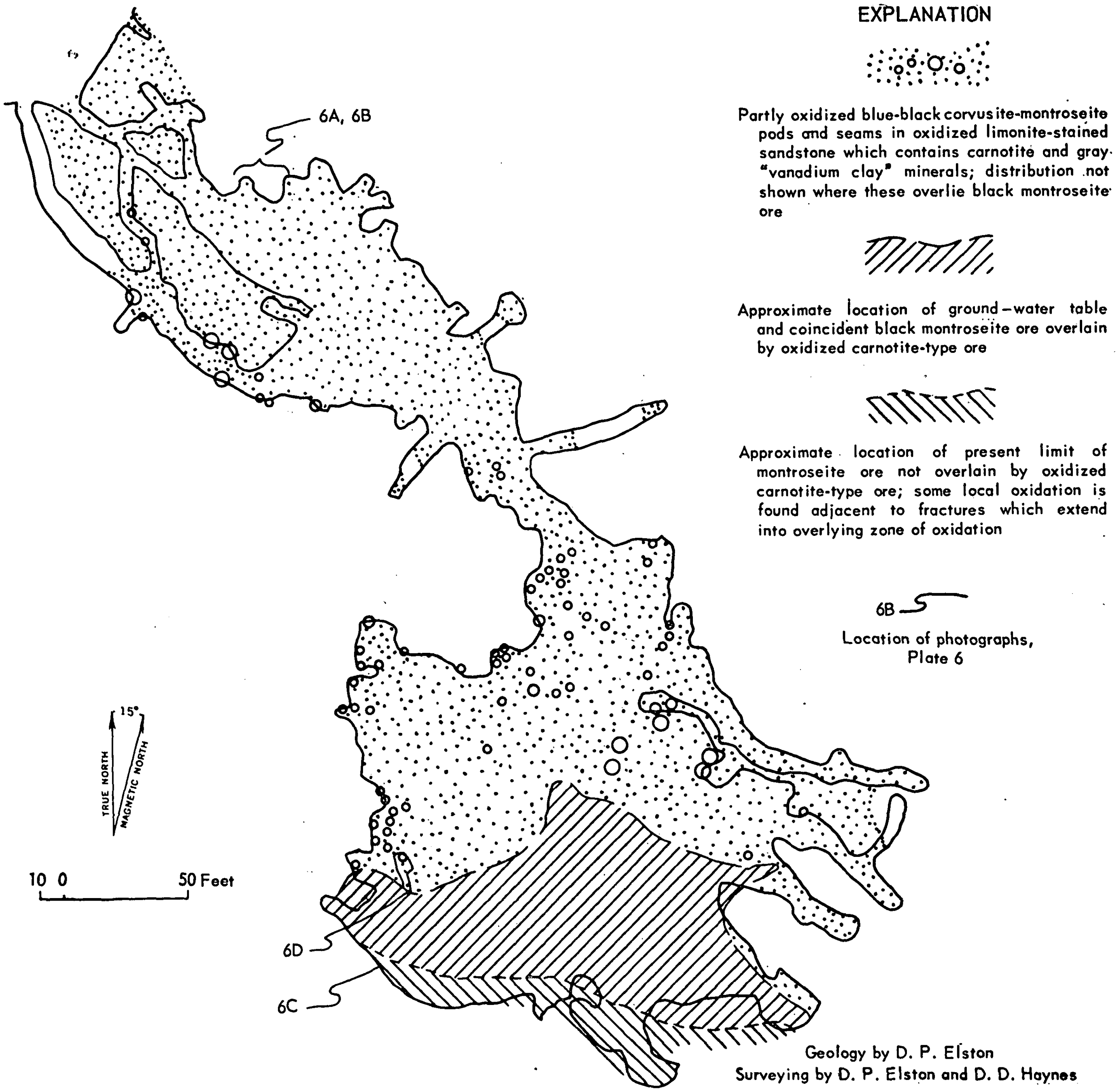
[15] Vanadium silicates here denote the fine-grained nonmetallic vanadium-bearing matrix material of the sandstone and include one or more of the following: vanadium mica, vanadium-bearing chlorite and clay minerals, and clay minerals with adsorbed vanadium.



Geology by D. P. Elston
Surveying by D. P. Elston and D. D. Haynes

FIGURE 66.—Outline map showing location of ore types and water table, J. J. mine, Jo Dandy area, Montrose County, Colo. Numbered locations: 1, figure 4; 2, figure 5; 3, figure 6.

shreds in a lighter-colored matrix (pl. 7*C*). A few minute grains tentatively identified as uraninite were seen in sandstone.

All the organic material examined shows some indication of woody texture. Samples of organic material with low radioactivity are brownish black in color and contain small amounts of metallic minerals. Samples of organic material with high radioactivity are black, and contain a larger amount of metallic minerals. Under the reflecting microscope, the brownish-black material is gray and isotropic; the black material is olive tan and strongly anisotropic.

Overgrowths on quartz grains are common, and in areas a few millimeters across, the rock type approaches a quartzite. Partial crystal outlines are common.

PARTLY OXIDIZED ORE

Partly oxidized ore as it occurs in the mine is a mixture of low-, intermediate-, and high-valent minerals. The chief vanadium mineral of this stage is corvusite which gives the ore a blue-black color. Uranium occurs in uraninite and coffinite as relicts of unoxidized ore, and in carnotite and tyuyamunite where oxidation has occurred. Accessory vanadium minerals are melanovanadite and other vanadate minerals. Gangue minerals are limonite, native selenium (rare), and gypsum. Some sulfides, such as pyrite, may remain from the primary ore.

Many of the textures of unoxidized ore are retained in the partly oxidized ore. Shreds and corroded fragments of montroseite remain in the clay matrix; carbonized wood is apparently not changed by oxidation. Carnotite and tyuyamunite occur in sandstone as disseminations and seams.

OXIDIZED ORE

Carnotite and tyuyamunite are the major uranium minerals in oxidized ore; the major vanadium minerals are vanadium silicates. Common gangue minerals are gypsum and limonite. A small amount of hewettite occurs disseminated in seams.

Oxidized ore is primarily an intergranular filling. Seams of the bright yellow uranyl vanadates are conspicuous, but most of the ore minerals are disseminated through the sandstone.

PARAGENESIS

Paragenesis of the ore and gangue minerals is shown in outline form in table 2. The minerals of each stage are approximately contemporaneous; minerals of an early stage may persist into a later stage. No textural evidence was found to indicate any separation in time of emplacement of the low-valent uranium and vanadium minerals. Some minerals such as pyrite and gypsum may have formed in several stages.

TABLE 2.—*Paragenesis of the ore and gangue minerals in the J. J. mine, Jo Dandy area, Montrose County, Colo.*

Paragenetic stage	*Mineral*	*Mode of occurrence*
1. Sedimentary	Quartz	Detrital minerals, sand grains, and intergranular material.
	Feldspar	
	Clay minerals	
	Carbonaceous material	
2. Diagenetic	Gypsum	As cements and intergranular material.
	Calcite	
	Quartz	Overgrowths on quartz grains.
	Pyrite	As disseminated grains, replacing wood.
3. Mineralization	Montroseite	As crystals in intergranular material, in cells in wood, in quartz overgrowths.
	Vanadium silicates	In intergranular area.
	Uraninite	In carbonaceous (woody) material, in wood cells.
	Coffinite	In carbonaceous (woody) material, in cell walls.
	Sulfides	Disseminated and massive, replacing wood, quartz, and in intergranular space.
4. Partly oxidized	Corvusite	Disseminated, in seams, massive.
	Melanovanadite	Rosettes in veins (rare).
	New vanadate minerals	Surrounding quartz and other vanadium minerals, in fine-grained irregular masses (rare).
	Native selenium	Disseminated, banding (rare).
	Limonite	Disseminated, replacing pyrite or marcasite.
5. Oxidized	Carnotite	Coatings on fractures, veins, disseminated in sandstone.
	Tyuyamunite	
	Gypsum	Efflorescences, veins, disseminated in sandstone.
	Hewettite	

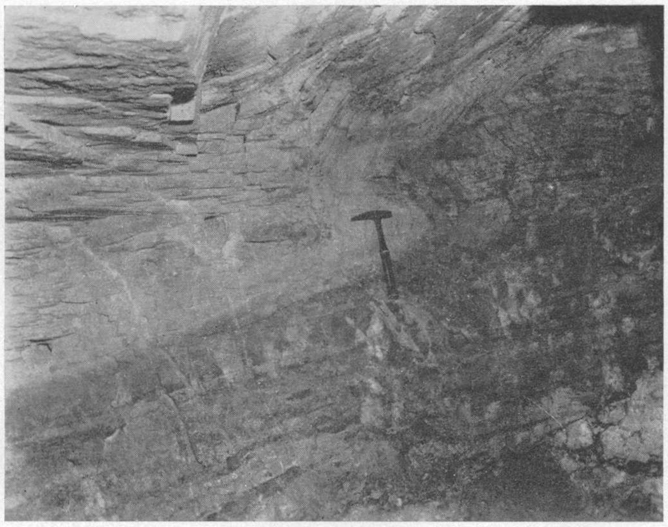
OXIDATION OF ORE

The ore minerals were originally distributed as spotted and streaked disseminations in sandstone, as local high-grade zones or bands in sandstone, and as pods or irregular masses of high-grade ore associated with carbonaceous material.

Spotted and streaked montroseite-type ore oxidizes from black through varying stages of gray, to a light- and dark-gray ore faintly speckled with carnotite. This sequence can be observed in a vertical space of about 10 feet at places in the mine where stoping has intersected the ground water table. The gross physical appearance of such spotted and streaked disseminations is not changed by oxidation.

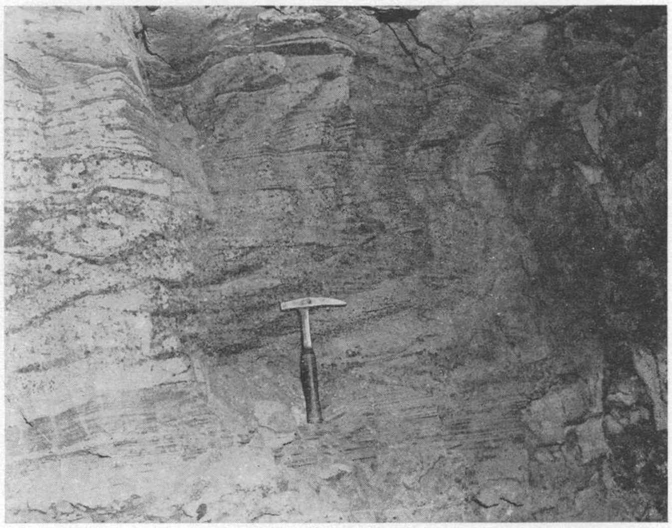
Blue-black corvusite ore is not megascopically apparent where disseminated ore minerals have been oxidized. If a corvusite stage does form during oxidation of all montroseite-type ore, it may be short lived and megascopically inconspicuous in places where the ore minerals are disseminated in sandstone.

Blue-black corvusite pods, masses, and seams are distributed through the oxidized light-gray carnotite-vanadium clay part of the mine (fig. 66). The pods contain corvusite, montroseite, pyrite, marcasite, and carbonaceous material. These are the little or partly oxidized equivalents of black high-grade montroseite pods and seams of ore which have been protected from

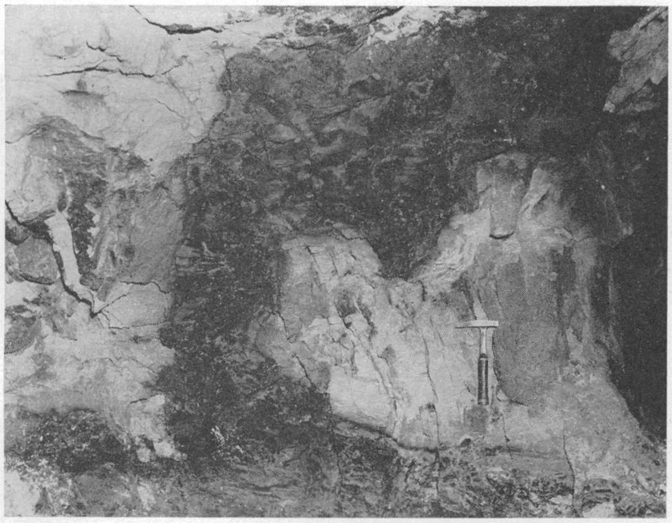


A. ORE MINERALS DEFLECTED INTO A DIFFUSE S-ROLL AT THE BASE OF AN OVERLYING TROUGH CROSS-STRATIFIED SANDSTONE BED.

Bed strikes into picture.

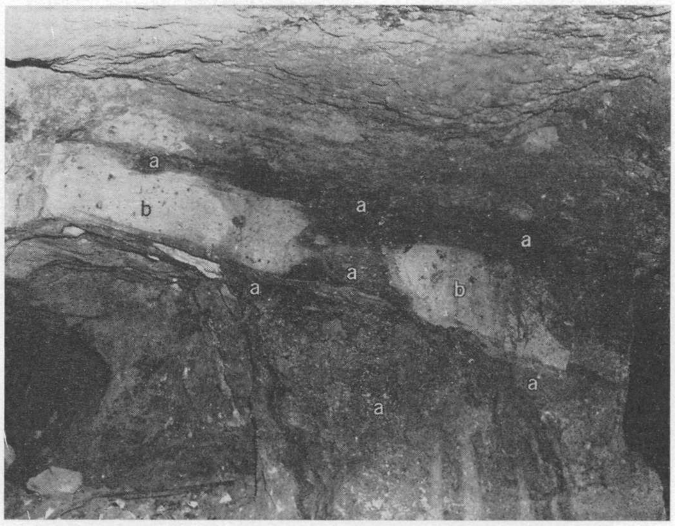


B. DIFFUSE S-ROLLS, WHICH REFLECT THE S-ROLL CONFIGURATION OF FIGURE *6A*.



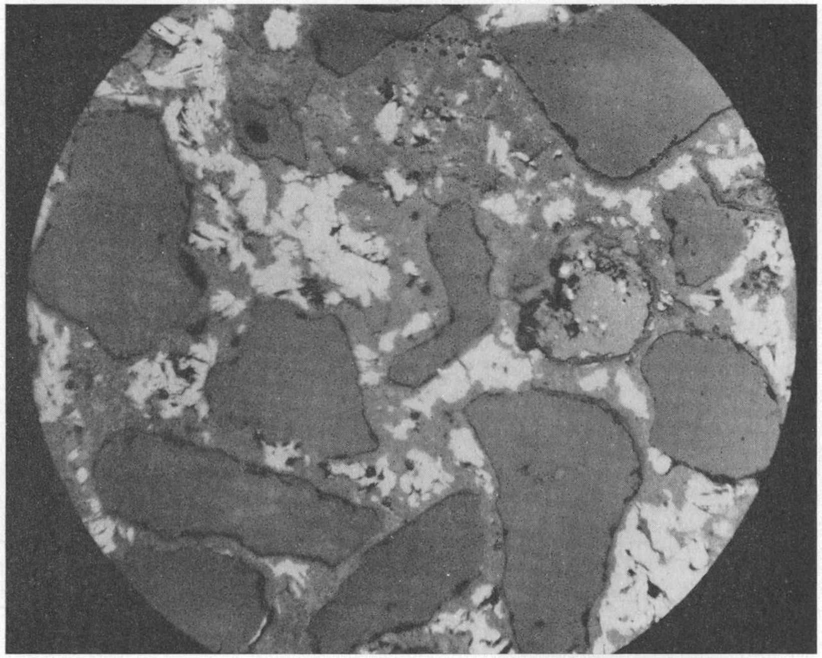
C. C-ROLL IN BLACK ORE.

Ore minerals are partly oxidized in upper part of roll.

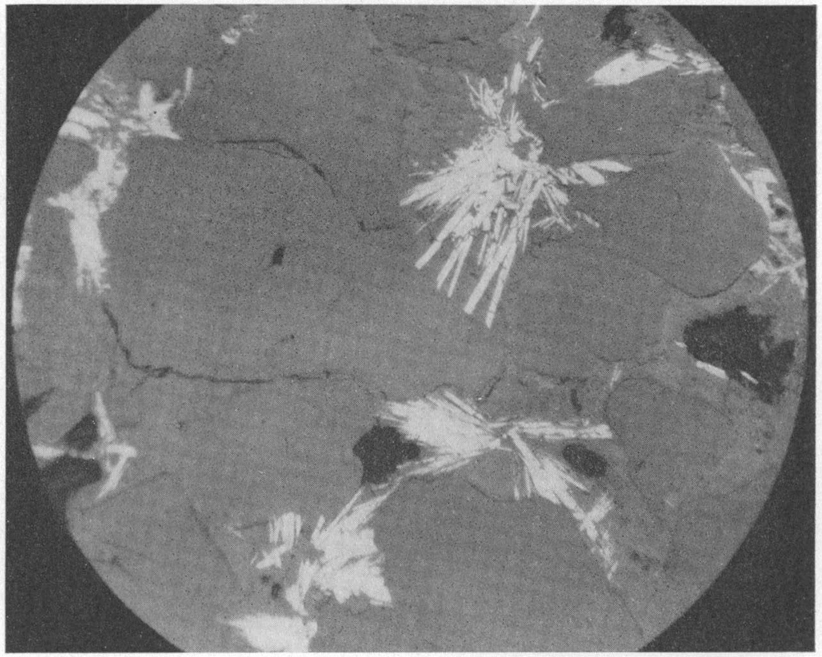


D. ORE MINERALS WITH A DOUBLE C-ROLL CONFIGURATION CONNECTING TWO MINERALIZED LAYERS.

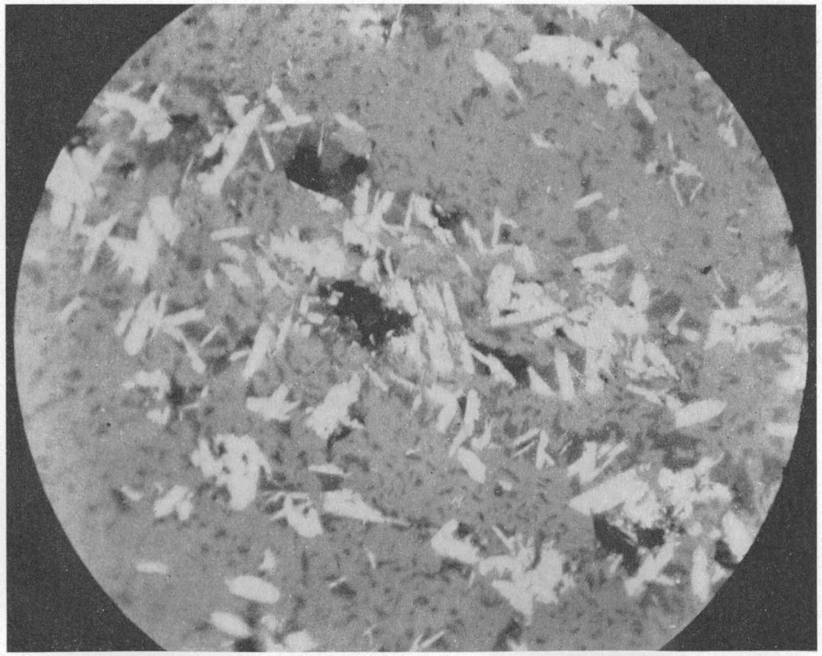
Ore is partly oxidized.



A.



B.



C.

A. CORRODED QUARTZ GRAINS (DARK GRAY) SURROUNDED BY CLAY (GRAY) WITH MONTROSEITE CRYSTALS (WHITE).

Black dots are pits in section. Polished section, x 470, plain light, green filter.

B. MONTROSEITE CRYSTALS (WHITE) PENETRATING QUARTZ OVERGROWTHS (GRAY).

Clay and quartz are same shade of gray. Black dots are pits in section. Polished section, x 165, plain light, green filter.

C. MONTROSEITE (WHITE) IN ORGANIC MATERIAL (GRAY) WITH COFFINITE (DARK GRAY).

Black dots are pits in section. Polished section, x 470, plain light, green filter.

rapid oxidation by a combination of physical and chemical means. Oxidation proceeds more slowly within these pods and the change from a black to a blue black is coupled with a decrease of montroseite and an increase of corvusite. A thin disseminated red to red-brown band is formed adjacent to the main mass of the montroseite; outside of this is a thin diffuse band of native selenium and outside of this a yellow zone. Further oxidation causes removal of the native selenium and the unidentified red band. Vestiges of these pods are represented by high-grade pods of carnotite developed when the uranium and vanadium are oxidized to U (VI) and V (V).

CONCLUSIONS

In the J. J. mine sedimentary structures have, in many places, influenced the detailed configuration of the ore and are probably the cause of the gross localization of the ore. The permeability and the variation in permeability are the major controlling features of the sedimentary structures. Fractures show no controlling relation to ore. Carbonized wood has caused deposition of rich ore where mineralizing solutions have had access to it.

The ore was deposited as low-valence oxides and silicates of uranium and vanadium. Oxidation above the ground water table has modified the original distribution of minerals. The carnotite assemblage is in the oxidized zone and the montroseite-uraninite assemblage is in the unoxidized zone. Oxidation has caused no important change in either the gross or the detailed configuration of the ore; however, some minor redistribution of vanadium and uranium occurs during oxidation.

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Part 19. MINERALOGY AND GEOLOGY OF THE RIFLE AND GARFIELD MINES, GARFIELD COUNTY, COLORADO

By THEODORE BOTINELLY and R. P. FISCHER

CONTENTS

ILLUSTRATIONS

ABSTRACT

The vanadium-uranium deposit at the Rifle and Garfield mines is in the Navajo(?) sandstone of Jurassic and Jurassic(?) age and the overlying Entrada sandstone of Jurassic age. Both formations are composed of clean, light-colored, fine-grained, massive, and crossbedded sandstone.

The ore, which consists of vanadium with only a small uranium content, occurs in fine-grained minerals that impregnate the sandstone. It forms three partly overlapping layers, each of which is tabular and lies generally parallel to the major bedding. Each vanadium layer is bordered on one side by a very thin band of finely disseminated galena and clausthalite, beyond which is a thin greenish layer containing a chromium-bearing mineral. The galena band and the chromium-bearing layer lie above the lower and upper vanadium layers but below the middle vanadium layer.

Primary ore minerals of the vanadium layer are roscoelite, vanadium-bearing hydromica, and small amounts of vanadium-bearing chlorite and montroseite. Base-metal sulfides are sparse in the ore but abundant in the galena band. The chromium-bearing layer is similar in appearance to that at Placerville, Colo., where mariposite has been described. Oxidation has not appreciably affected the roscoelite; montroseite and perhaps vanadium-bearing chlorite and hydromica have oxidized to form minor secondary vanadium minerals. A little carnotite is present in the oxidized parts of the deposits, but the primary uranium minerals have not been recognized.

The deposit is similar to vanadium-uranium deposits of the Plateau but is unique in the high ratio of vanadium to uranium, the lack of carbonaceous material, and the abundance of roscoelite.

INTRODUCTION

The vanadium-uranium deposit at the Rifle and Garfield mines is partly in the Entrada sandstone of Jurassic age and partly in an underlying sandstone that has been questionably correlated with the Navajo sandstone of Jurassic and Jurassic(?) age. Both formations are composed entirely of clean, fine-grained, massive sandstone. This deposit, like those in the Entrada near Placerville, Rico, and Durango, Colo., has been worked mainly for vanadium; the uranium content of the ore is so low that it has had only byproduct value. In addition to the low uranium content, these deposits in the Navajo(?) and Entrada sandstones differ from most of the vanadium-uranium deposits in other formations on the Colorado Plateau in that abundant shaly and carbonaceous material is lacking. Otherwise these deposits are quite alike, and all are of the same general type.

The Rifle and Garfield mines are on East Rifle Creek about 13 miles northeast of Rifle, Garfield County, Colo. The Rifle mine, on the east side of the creek, was worked from 1925 to 1932, during World War II, and again in the late forties and early fifties. Mine workings extend for more than 7,000 feet eastward from the outcrop along the creek. The Garfield mine, on the west side of the creek, was worked mainly during World War II, though a small amount of mining was done before then and some development has been done since the war. The workings extend several hundred feet westward from the outcrop.

The deposit at the Rifle and Garfield mines presents an unusually good opportunity to study and interpret some geochemical relations that are more confusing elsewhere. Not only is this deposit well exposed in the mines and at the outcrop, so the character of the ore and the habits of the ore bodies can be readily observed, but also these features are more consistent than in many of the Plateau deposits. Even so, in spite of these advantages, the geologic factors that influenced localization of the deposit have not been recognized, and the genesis cannot yet be explained.

The mines and surrounding area were studied and mapped by the junior author, assisted by W. L. Stokes and L. E. Smith, in the summer of 1944. The area was revisited by the junior author in 1954, to bring the geologic map of the mine workings up to date, during which time he was assisted for intervals of several days each by D. C. Hedlund, E. B. Ekren, R. T. Chew III, H. S. Johnson, and D. D. Haynes. The present report is based on this field work and the samples collected at that time; these samples and thin sections from them were studied by the senior author. A more detailed report on the geology and ore deposits of the area, which will include an areal geologic map as well as detailed geologic maps of the mines, is being prepared.

GEOLOGY

The area lies on part of the Grand Hogback monocline, a fold that flanks the White River Plateau uplift to the north and east, and which exposes rocks ranging from Precambrian to Tertiary in age. Rocks in the immediate vicinity of the Rifle and Garfield mines consist of sedimentary formations of Triassic, Jurassic, and Cretaceous ages. Only the Navajo(?) sandstone (Jurassic and Jurassic(?)) and the Entrada sandstone (Jurassic), which contain the ore deposit in these mines, will be described in detail.

STRATIGRAPHY

The oldest rocks in the vicinity of the Rifle and Garfield mines consist of a thick sequence of red beds, and the upper few hundred feet of which have been correlated by Thomas, McCann, and Raman (1945) with the Chinle formation of Triassic age. The Chinle is composed of shale, siltstone, and fine-grained sandstone. These beds are dominantly red, but in the vicinity of the Rifle and Garfield mines the upper few feet of the formation is altered to gray.

The sandstone unit immediately above the Chinle and beneath the Entrada sandstone is host to much of the ore in the Rifle mine. Several formational names have been applied to this unit, but on the basis of recent work, which is not yet published, N. Wood Bass and John R. Donnell (written communication, 1957) consider this unit to be equivalent to the Navajo sandstone. This name, with a query, will be used in this report.

The Navajo(?) is a light-brown fine-grained sandstone with large-scale crossbedding inclined southward. It crops out in a rough, nearly vertical cliff. As it is hard and brittle, it is fractured by many vertical joints, both at the outcrop and underground. This formation ranges from 30 to 70 feet in thickness in the vicinity of the mines, and it pinches out a few miles east of the mines. The Navajo(?) contains the principal ore body (No. 1 vein) in the Rifle mine.

The Entrada sandstone is white to light gray and predominantly fine grained but with large, well-rounded grains scattered through it. Crossbedding is prominent; the planes are curved, but, in contrast to the Navajo(?), they are not inclined in a common direction. The formation is soft and friable and weathers to rounded cliffs and steep slopes; jointing is not as conspicuous as in the Navajo(?). The Entrada ranges from 75 to 125 feet in thickness. It contains the ore bodies (No. 2 and No. 3 veins) in the Garfield mine and several small masses of ore in the Rifle mine.

The Entrada sandstone is overlain by the Morrison formation of Jurassic age. The Morrison is about 500 feet thick. The lower 150 feet consists of several lenticular sandstone strata that are gray to greenish gray, medium grained, and interbedded with red, green, and gray mudstone. The sandstone beds contain a few small deposits of uranium-vanadium ore, which will not be described in the report. The upper part of the Morrison consists of mudstone that is predominantly green or gray but in part varicolored, with a few thin and lenticular beds of sandstone, siltstone, and limestone.

The Dakota(?) sandstone of Cretaceous age overlies the Morrison and consists of gray and brown sandstone and shale. It is about 80 feet thick.

The Mancos shale, also of Cretaceous age, lies on the Dakota(?). It consists of several thousand feet of gray shale.

STRUCTURE

The rocks in the vicinity of the Rifle and Garfield mines generally dip southward at moderately low angles, but this attitude is modified locally by faults and minor flexures. Within the mines, beds dip southward at angles ranging from about 15° to 30°.

Three sets of faults are present; two sets dip nearly vertical and the third dips at low angles. Of the two high-angle sets, one trends generally eastward and is the stronger and apparently the older. One fault has been traced for several miles and has a maximum displacement of a few hundred feet; most faults of this set, however, are shorter and have displacements of less than 100 feet. The other set of high-angle faults trends northwestward, rarely exceeds a few tens of feet in displacement, and has not been traced for more than a few thousand feet. Faults of both sets are exposed in the mines but none of these have displacements exceeding 10 feet.

The low-angle faults are reverse faults with displacements ranging from a small fraction of an inch to as much as a foot. All dip southward and for the most part follow the bedding planes or cut across the beds at small angles. They are conspicuous in massive sandstone and probably resulted from bedding plane sliding at the time of folding. They appear to be younger than the high-angle fractures.

Joints are common, especially in the hard sandstone units, such as the Navajo(?). All the joints dip at high angles, and most strike easterly and northwesterly, parallel to the two sets of nearly vertical faults.

Below the zone of oxidation, some of the joints and a few of the high-angle faults contain thin, discontinuous veinlets of calcite and marcasite; where oxidized these fractures are iron stained. In the Chinle formation, some of the joints and faults are bordered by a narrow band of alteration, which has changed the color of the rock from red to gray, and which is similar in appearance to the zone of alteration that is present at the top of the Chinle in the vicinity of the ore deposit.

ORE DEPOSITS

The ore is sandstone impregnated with fine-grained vanadium and uranium minerals. These minerals color the rock gray, and, in general, the color darkens as vanadium increases in content. Most of the ore that has been mined contains between 1 and 3 percent V_2O_5. No plant fossils or other carbonaceous material has been recognized in the ore-bearing sandstone, except for small pellets of asphaltic material that occur sparsely along a few joints.

The ore occurs in three layers, which the miners call the No. 1, No. 2, and No. 3 "veins" in ascending order. These layers are tabular, and they range in thickness from a few inches to as much as 30 feet. They lie generally parallel to the major bedding or formational contacts, but in detail they cross the bedding and in a few places even the formational contacts. The No. 1 vein is the principal ore layer in the Rifle mine. It lies mostly in the Navajo(?) sandstone, but in at least two places it thickens sufficiently to extend up into the lower part of the Entrada sandstone, and in a few places it crosses into the upper foot of the underlying Chinle formation. The No. 2 vein is discontinuous. It forms the principal ore body in the Garfield mine and a few small- to moderate-sized ore bodies in the Rifle mine. The No. 2 vein is in the Navajo(?) sandstone at the east end of the Rifle mine, where it connects with the No. 1 vein. All of the other known ore bodies in the No. 2 vein are in the Entrada and do not obviously connect with the No. 1 vein. The No. 3 vein is known only in the Garfield mine, where it forms two ore bodies in the Entrada. One small body has been mined at the outcrop, and it is about 20 feet above the No. 2 vein. The second ore body in the No. 3 vein lies several feet above the ore layer of the No. 2 vein in the main workings of the mine and the two layers join along the northwest edge of the mine.

Each of the layers is strikingly asymmetric vertically across the layer. Each shows the same asymmetry, but the middle layer (No. 2 vein) is a mirror image (or upside down) with respect to the lower and upper layers (No. 1 and No. 3 veins, respectively). The asymmetric characteristics of the No. 3 vein are shown and described in plate 8*A*. The No. 1 vein shows exactly the same characteristics, and the same vertical sequence; the No. 2 vein shows exactly the same characteristics but in a reverse vertical sequence.

The No. 1 vein in the Rifle mine forms an elongate ore body that has been followed by mining for about 7,000 feet in a northeasterly direction from its outcrop on East Rifle Creek. The ore is generally thicker and lower grade on the north side of the body, and the limit of minable ore to the north is mainly an assay wall. On the south side, on the other hand, the layer thins gradually until it is too narrow to mine profitably, but the grade of the thin ore is generally higher than average for the deposit. In a few places along the south edge of the deposit, the layer passes from the Navajo(?) sandstone into the top foot of the altered zone of the underlying Chinle formation. The No. 1 vein also is in the altered zone at the top of the Chinle on the west side of East Rifle Creek.

Where the ore in the Rifle mine is thick, the upper and lower limits of the layer usually are not well defined, and the asymmetric character of the ore layer is not obvious; similarly, the associated galena-clausthalite band and chromium-bearing layer are not recognizable or are poorly developed.

Although none of the ore bodies in the No. 2 vein in the Rifle mine have been completely explored by mining or drilling, they appear to be moderately small bodies that are not connected with one another by mineralized material. Those known to contain material of approximate commercial grade and thickness all lie satellitic to or fringe the ore body in the No. 1 vein in plan projection; none have yet been found that directly overlie minable ore in the lower layer. Only one of the ore bodies in the No. 2 vein is known to be connected with the No. 1 vein.

The altered zone at the top of the Chinle formation ranges from a feather edge to 8 feet in thickness. The contact with the unaltered rock beneath is well defined but uneven and crosses the bedding. Where fresh, the altered rock is greenish gray and contains finely disseminated cubic crystals of pyrite; at the outcrop the color of the altered zone is buff.

Beneath the ore body in the Rifle mine the altered zone ranges from 2 to 8 feet in thickness, and there is no obvious systematic relationship between the thickness of this zone and the thickness or grade of ore. Nevertheless, generally speaking, the altered zone is thicker beneath and near the ore body, and it decreases in thickness away from the deposit. On the west side of East Rifle Creek the altered zone thins to a vanishing point about 2,000 feet from the deposit and is absent beyond that point. Its character and habit are similar to the zone of altered mudstone near uranium-vanadium deposits in the Morrison formation elsewhere on the Plateau.

MINERALOGY

The vanadium ores at the Rifle and Garfield mines consist of sandstone with the interstitial volume occupied by micaceous vanadium-bearing silicates, a few other vanadium minerals, a few common base metal sulfides, and a solid-solution mixture of galena and clausthalite. The Navajo (?) and Entrada sandstones, in which the ore occurs, are fine-grained moderately sorted sandstones, mainly quartz with a little feldspar and clay minerals.

Where mineralization was strong, the ore minerals uniformly impregnate the sandstone, coloring it dark gray, and the bedding is almost completely obscured. Where mineralization was weaker, the ore minerals accumulated mostly along favorable bedding planes and laminae, yielding a banded ore that makes bedding conspicuous. These two types of ore grade into one another.

The galena-clausthalite band, like the vanadium layer, also may cut across bedding. In detail it is made up of thin laminae of abundant sulfide grains parallel to the bedding.

VANADIUM ORE

The vanadium-bearing silicates in the ore have been identified by X-ray analyses as mixed-layered mica-montmorillonite, chlorite, and roscoelite, according to John Hathaway (written communication, 1955). Samples from different locations in the mine show variations in mineral composition, some samples having a large proportion of vanadium-bearing mixed-layered mica-montmorillonite (hydromica) and chlorite and others showing principally roscoelite with only traces of chlorite.

The roscoelite and vanadium-bearing clays occur as extremely fine grained irregular masses surrounding the quartz grains, and no determination of the relative amounts could be made in thin section. Roscoelite, according to Heinrich and Levinson (1955) is a vanadium mica with vanadium substituting for aluminum in the tetrahedral layer. It may contain as much as 17 percent V_2O_3 (Wells and Brannock, 1946). Roscoelite in thin section is brown with a faint tinge of green and has weak pleochroism and a high birefringence.

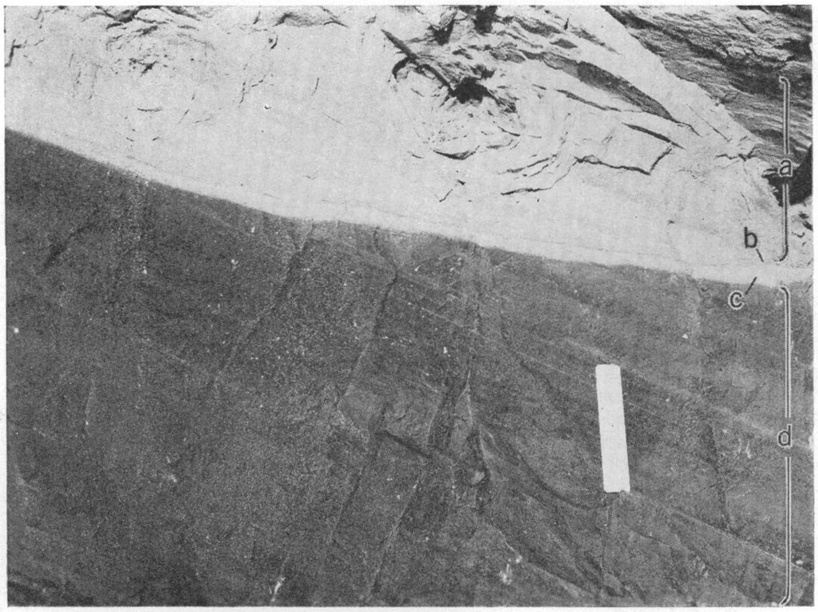
Montroseite occurs as very small opaque black bladed crystals with high luster, in radial aggregates and in individual crystals in the spaces between the sand grains (pl. 8*B*). It is a trivalent vanadium oxide, ideally $VO(OH)$; iron may substitute for vanadium, requiring some quadrivalent vanadium to balance the ionic charges. Specimens of montroseite oxidize readily to paramontroseite (VO_2) in air.

Pyrite, marcasite, galena, sphalerite, and chalcopyrite are sparsely distributed throughout the ore. They occur as small discrete grains disseminated among the ore minerals in the space between the sand grains.

No low-valence uranium minerals were found, but it is speculated that uranium may occur in fine-grained uraninite. Uranium in the unoxidized ore of other deposits of this type on the Plateau occurs in uraninite and coffinite. Uraninite may occur with or without organic material, whereas coffinite is known to occur only with organic material. As practically no organic material has been recognized at Rifle, it seems most likely that uranium occurs as uraninite rather than coffinite.

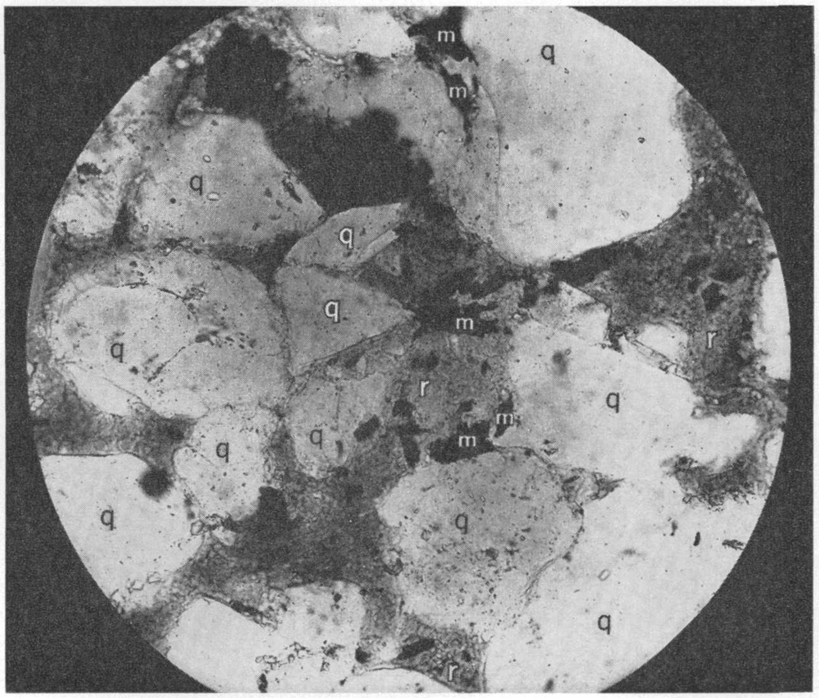
OXIDATION OF THE VANADIUM ORE

Oxidation apparently does not affect the vanadium-bearing silicates and produces little change in this type of ore. Montroseite oxidizes to melanovanadite, corvusite, and pascoite. Carnotite is present in small amounts coating fractures and impregnating sandstone. Other vanadate minerals are present in small amounts but could not be definitely identified. Traces of bayleyite, water-soluble magnesium uranyl carbonate, occurring as a pale-greenish-yellow efflorescence on the walls not far inside the portals of the Garfield and Rifle mines, indicate leaching of uranium near the surface of the ground. The sulfide minerals in the ore are destroyed by oxidation and the usual evidence of their former presence is a brown limonitic stain.



A. PHOTOGRAPH OF NO. 3 VEIN, GARFIELD MINE, SHOWING THE MINERAL LAYERS.

The scale of the photograph is indicated by the 6-inch scale on the right side of the picture. Note that the galena-clausthalite band and the vanadium layer cross the laminae with little regard for the bedding. Chromium-bearing layer (*a*), galena-clausthalite layer (*b*), barren or weakly mineralized layer (*c*), and vanadium ore (*d*).



B. PHOTOMICROGRAPH OF THIN SECTION OF TYPICAL UNOXIDIZED HIGH-GRADE VANADIUM ORE OF THE NAVAJO(?) SANDSTONE.

Black is montroseite (m); gray is roscoelite (r); white is quartz (q). Plane-polarized light, x 250.

MINERALOGY OF THE GALENA-CLAUSTHALITE BAND

Each of the three vanadium layers is bounded on one side by a thin layer of disseminated sulfides, called the galena-clausthalite band (see p. 215 and pl. 8A). This band consists mostly of galena-clausthalite with minor amounts of marcasite, pyrite, chalcopyrite, and sphalerite. These sulfides form small discrete grains up to 0.2 mm in diameter, filling pore spaces in the sandstone rather than replacing the sandstone grains. Calcite and dolomite occupy some of the pore spaces in the band but are also present in the barren rock away from the ore.

Tables 1 and 2 (R. G. Coleman, written communication, December 1955) show the results of analyzing concentrates of galena-clausthalite, which contain only minor amounts of impurities (pyrite, marcasite, and other heavy minerals). Selenium was determined by chemical analysis, and all other elements by spectrographic analysis.

X-ray studies of the galena-clausthalite concentrates show that the lead mineral in these concentrates is a solid-solution mixture of galena and clausthalite. The amount of clausthalite in solid solution as determined by X-ray in the concentrates varies from 25 to 74 weight percent; the chemical analyses for Se in the concentrates verify the order of magnitude of these figures (table 1).

TABLE 1.—*X-ray and chemical analyses of galena-clausthalite from the Rifle and Garfield mines, Garfield County, Colo.*[1]

[X-ray measurements by J. R. Houston]

Sample No.	Vein No.	Unit cell (in A)	PbS [1]	PbSe [1]	Se [2]
			Percent		
Garfield mine					
66-RGC-55	3	5.996	69	31	8.10
68-RGC-55	2	5.981	75	25	7.09
65-RGC-55	2	5.996	69	31	8.66
Rifle mine					
69-RGC-55	1	6.044	49	51	14.2
74-RGC-55-C	1	6.048	47	53	15.1
72-RGC-55	2	6.033	53	47	11.8
74-RGC-55	1	6.099	26	74	17.0
73-RGC-55	2	6.048	47	53	18.0

[1] Determined from unit-cell measurements using 5.92 A for galena and 6.162 A for clausthalite.

[2] Quantitative chemical analyses of concentrates estimated to be at least 95 percent pure galena-clausthalite. Analyst, Maryse Delevaux.

Although no physical variation in the galena-clausthalite band is apparent along the strike of the ore body, some of the elements in the concentrates show a spatial variation. The selenium content increases from west to east along the strike of the ore-bearing horizon. Silver is consistently present in amounts from 0.001 to 0.01 percent and no spatial variation is apparent. Nickel and cobalt are erratic in their distribution showing no correlation with position or mineralogy. Copper is consistently present and seems to show a slight increase from east to west along the strike of the beds. Cr and V are present in all the concentrates and in general an increase in one is reflected by a concomitant increase in the other. Since the galena-clausthalite concentrates have heavy detrital minerals as impurities, as well as vanadium and chromium minerals introduced as part of the ore deposition, it is not possible to determine if the Cr and V are camouflaged in the sulfide structure or contained in these other impurities. The Zn detected in three of these samples probably comes from sphalerite, which has been identified in polished sections. Cd, Bi, Th, and Te commonly reported as trace and minor elements in galenas from hydrothermal deposits were not detected in any of these concentrates.

Marcasite associated with calcite from a vertical joint within the vanadium layer and pyrite from the altered zone at the top of the Chinle were purified and analyzed in the same fashion as the galena-clausthalite concentrates (table 2). The selenium content in marcasite and pyrite, although much less than that of the galena-clausthalite, was above average for Se normally present in iron sulfides. Mo and Zn were not detected in the iron sulfides although Ni, Co, Ag, V, Cr, As, and Sr are present in the same relative amounts as found in the galena-clausthalite concentrates. Cu shows a 10-fold increase in the pyrite from the altered red beds of the Chinle compared to the galena-clausthalite.

OXIDATION OF THE GALENA-CLAUSTHALITE BAND

The galena-clausthalite band shows more rapid oxidation than does the vanadium layer. Where it is exposed near the surface, the sulfides are completely destroyed by oxidation. The galena-clausthalite alters to cerussite from the outer rim inward, and relict galena grains are present within the cerussite. During oxidation selenium forms monoclinic native selenium, the unstable polymorph of hexagonal native selenium, rather than selenates or selenites. The monoclinic native selenium remains stable underground and produces a characteristic pink bloom along the band. A limonitic stain is also present due to the oxidation of iron sulfides associated with the galena-clausthalite.

MINERALOGY OF THE GREEN (CHROMIUM-BEARING) LAYER

Overlying the galena band in the number 1 and 3 veins and underlying it in the number 2 vein is a 2- to 3-foot layer that is similar in habit to the vanadium layer. This layer is usually green, ranging from a pale to an intense light green. Hess (1913, p. 148, 154) has

TABLE 2.—*Semiquantitative spectrographic and chemical analyses of sulfides from the Rifle and Garfield mines, Garfield County, Colo.*

[Analyst, Joseph Haffty]

Element	Garfield mine				Rifle mine						Sensitivity
	66-RGC-55 galena-clausthalite	67-RGC-55 marcasite in fracture	68-RGC-55 galena-clausthalite	65-RGC-55 galena-clausthalite	69-RGC-55 galena-clausthalite	74-RGC-55-C galena-clausthalite	72-RGC-55 galena-clausthalite	70-RGC-55 pyrite altered zone	74-RGC-55 galena-clausthalite	73-RGC-55 galena-clausthalite	
Se [2]	8.1	0.02	7.09	8.66	14.2	15.1	11.8	0.14	17.0	18.0	0.0003
Ni	.01-.05	.001-.005	.001-.005	.001-.005	.01-.05	.01-.05	.005-.01	.01-.05	.001-.005	---	.005
Co	.01-.05	.005-.01	---	---	.01-.05	.01-.05	.001-.005	.01-.05	.001-.005	.001-.005	.008
Ag	.01-.05	.01-.05	.001-.005	.001-.005	.01-.05	.01-.05	.01-.05	---	.001-.005	.001-.005	.00001
Cu	.01-.05	.01-.05	.01-.05	.01-.05	.01-.05	.01-.05	.005-.01	.1-.5	.001-.005	.001-.005	.00005
Mo	.01-.05	---	.001-.005	.0005-.001	.001-.005	.01-.05	.01-.05	---	.001-.005	.001-.005	.0005
V	.01-.05	.01-.05	.01-.05	.01-.05	.1-.5	.01-.05	.01-.05	.01-.05	.05-.1	.001-.005	.001
Cr	.01-.05	.001-.005	.005-.05	.01-.05	.05-.1	.001-.005	.01-.05	.01-.05	.01-.05	.001-.005	.0006
Zn	---	---	---	---	.01-.05	.01-.05	.01-.05	---	---	---	.008
As	.01-.05	.01-.05	---	---	.01-.05	.01-.05	---	.05-.1	---	---	.11
Sr	.001-.005	.001-.005	.005-.01	.005-.01	.001-.005	.001-.005	---	.001-.005	.005-.01	---	.001

[1] Samples taken along the strike of the ore; columns arranged progressively from west (at left) to east (at right).

[2] Quantitative chemical analyses; analyst, Maryse Delevaux.

described a green layer in the geologically similar vanadium deposits at Placerville, Colo., and ascribes the green color to the chromium-bearing mica, mariposite; the green layer both at Placerville and Rifle contains as much as 0.X percent chromium. However, X-ray analyses of the clay-size material from this layer at Rifle show that the dominant mineral is mixed layered mica-montmorillonite with a small amount of chlorite. No mariposite has yet been identified.

Thin sections of samples of this layer show a small amount of fine-grained material surrounding the quartz grains that is pleochroic in shades of green; polished sections show no sulfides except close to the galena-clausthalite band.

Exposure of this green layer to oxidation produces no apparent changes.

CONCLUSIONS

From the standpoint of ore textures, ore habits, and the assemblage of metals, the ore at Rifle shows certain similarities to the uranium-vanadium deposits of other parts of the Colorado Plateau. Certain differences are also obvious—the ratio of vanadium to uranium is very high, organic material is practically absent, vanadium-bearing silicates are the predominant vanadium minerals, and secondary vanadium minerals are rare. The cause of the difference in primary minerals is not known but this difference results in only rare secondary minerals and general resistance to oxidation of these deposits.

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Part 20. VANADIUM AND URANIUM IN ROCKS AND ORE DEPOSITS

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CONTENTS

ILLUSTRATIONS

TABLES

ABSTRACT

Trace amounts of vanadium and uranium are common in both igneous and sedimentary rocks. Vanadium is more abundant in mafic igneous rocks, uranium in silicic ones. Both metals tend to concentrate in some sedimentary rocks containing organic material.

Uranium accumulates in some igneous rocks, pegmatites, veins, sandstones, limestones, conglomerates, coals, black shales, and phosphorites, but the more productive deposits are those in veins, sandstones, and conglomerates. Uranium minerals have been recognized in many types of hydrothermal veins.

Productive sources of vanadium include deposits with uranium in sedimentary rocks, iron ores (both magmatic and sedimentary), vanadates of base metals, asphaltic deposits, phosphate rock, and the soot or ash of some natural carbonaceous material. None of these deposits are clearly of hydrothermal origin. Accessory vanadium minerals are not generally recognized in hydrothermal deposits except titanium-bearing veins and gold-telluride deposits.

The average vanadium content of 775 samples of ores and mill products is less than 100 parts per million (ppm), which is less than the average reported for igneous rocks and shales. A group of 296 samples from uranium-bearing veins also shows less than 100 ppm vanadium.

These data suggest that vanadium does not tend to concentrate in the common hydrothermal environment, and specifically that it does not concentrate in most veins containing uranium ore. If this is true, unusual processes and conditions might be required to explain the origin and source of vanadium and uranium in deposits containing commercial amounts of both metals.

INTRODUCTION

Vanadium and uranium are intimately associated in many productive uranium deposits in sedimentary rocks, especially in those of the type found in sandstone. The genesis of these deposits is an unsolved problem and the source of the metal is also unknown. This study of vanadium and uranium in rocks and ore deposits was undertaken to see if the geochemical habits of these metals might focus attention on certain aspects of the problems of genesis and source of metals that need special study.

It has long been known that vanadium and uranium are disseminated in igneous rocks but are not closely associated in this environment, whereas, these two metals do get together in the sedimentary environment, especially in rocks containing organic material. On these aspects of the subject, this report merely summarizes information available in published literature. It has also long been recognized that vanadium and uranium do not commonly concentrate together in normal hydrothermal deposits, but heretofore, this picture has been based largely on negative information—the lack of known occurrences. Some quantitative information on the amount of vanadium in ore deposits is contributed in this report.

GEOCHEMICAL CHARACTERISTICS OF VANADIUM AND URANIUM

The information in this section is summarized mainly from the comprehensive studies on geochemistry by Rankama and Sahama (1950) and by Goldschmidt (1954). The reader interested in more detailed information should refer to these works and the references cited in them.

IN IGNEOUS ROCKS

Vanadium is relatively abundant among the "trace elements" in igneous rocks. It averages 150 grams per metric ton (parts per million), is slightly more abundant than zinc, about twice as abundant as copper, and about 10 times more abundant than lead. Uranium averages 4 parts per million (ppm) in igneous rocks (Rankama and Sahama, 1950, table 2.3, p. 39 and 40).

Both vanadium and uranium are classed among the "lithophile" elements, those that are enriched in the silicate crust. Within this environment, however, the two metals are not intimately associated.

Vanadium is more abundant in the mafic igneous rocks than in the silicic ones. Vanadium does not form a constituent part of any common rock-forming mineral; rather its ions replace those of iron and aluminum in the common ferromagnesian minerals and those of titanium and iron in titanium minerals and titaniferous iron ores.

Uranium, on the other hand, concentrates more abundantly in the later or more silicic part of igneous differentiates. In these rocks some uranium is held in accessory minerals, such as zircon, monazite, allanite, and some is in a loosely bound form in mineral interstices (McKelvey, Everhart, and Garrels, 1955). Uranium is common in pegmatites and hydrothermal veins; many uranium minerals are found in pegmatites and veins, but uraninite is the most important of these.

DURING WEATHERING

During weathering of igneous rocks, much of the vanadium goes into clay minerals. Some of it, and perhaps a large part of it, must remain with these minerals as they are transported to places where they accumulate as sedimentary rocks, for argillaceous sediments are generally richer in vanadium than sandstone or limestone. Some vanadium, however, goes into solution, from which it can enter the geologically temporary states of combination with heavy metals to form vanadates or be taken up by plants and animals. Rankama and Sahama (1950, table 6.19, p. 295) show that 90 ppm of vanadium is supplied to sea water but that only 0.0003 ppm is present. Either much of the vanadium precipitates rapidly from sea water, or more likely, most of that supplied is associated with clay particles suspended in river waters rather than being in solution.

The habits of uranium during weathering are more varied. Some of the uranium-bearing minerals in rocks and veins are refractory, and they mainly weather mechanically and are distributed to clastic sediments. Other minerals oxidize readily to form complex secondary minerals and soluble salts; these salts are carried seaward, either in solution or adsorbed on hydroxide gels—Rankama and Sahama (1950, table 6.19, p. 295) report that 0.0016 ppm U is present in sea water whereas 0.6 ppm is supplied to sea water.

IN SEDIMENTARY ROCKS

The average content of vanadium is <10 ppm in carbonate rocks, 20 ppm in sandstone, and 120 ppm in clays and shales (Rankama and Sahama, 1950, table 5.52,

p. 226). Shaw (1954, table 4, p. 1170) also shows a 120 ppm vanadium content in shales, schists, and gneisses. As a general rule, vanadium increases with the increase in argillaceous material, and especially with an increase in organic matter; it is richly concentrated in some coal, petroleum, and asphalt (Jost, 1932). Uranium is more dispersed and of uniform grade in the three principal types of sedimentary rocks. Rankama and Sahama (1950, table 5.52, p. 226) give 1.2 ppm U in sandstones, 1.2 ppm in shales, and 1.3 ppm in limestones. These authors show (p. 637), however, that uranium is significantly concentrated in some carbonaceous shales of marine origin, in certain coals, and in some petroleum, as is vanadium. Erickson, Myers, and Horr (1954) give more specific information regarding uranium and vanadium, as well as other metals, in crude oil, asphalt, and petroliferous rock.

URANIUM DEPOSITS

Uranium is widely distributed and its types of occurrences much varied; it is enriched in some igneous rocks, pegmatites, veins, sandstones, limestones, conglomerates, coals, black shales, and phosphorites (McKelvey, Everhart, and Garrels, 1955). Representatives of many of these types have yielded production, either for uranium itself or as a byproduct, but the deposits in veins, sandstones, and conglomerates have been the more productive.

VEINS

As Everhart and Wright (1953) have recently summarized the geologic character of typical uranium-bearing (pitchblende) veins, including the more productive deposits, only the general features of these deposits will be mentioned here. They recognize two major types of deposits. One, a nickel-cobalt-native silver type, has a complex mineralogy, a gangue dominantly of carbonates with lesser silica, and occurs in metasediments and volcanic host rocks. The second, a siliceous-pyrite-galena type, has a simple mineralogy, a gangue of silica and fluorite with lesser carbonate, and occurs in felsic intrusives. McKelvey, Everhart, and Garrels (1955) have added a third type, iron-titanium veins, in which uranium occurs as the mineral davidite, with a silica gangue, in granitic intrusives.

Intensive exploration for radioactive material during recent years has revealed the presence of uranium in many vein deposits of varied metal and mineral assemblages. Many of these deposits, however, have not yielded significant production, either because the uranium content is low or restricted to small ore shoots.

Generally speaking, all of these deposits have characteristics of typical veins, to which an origin of hydrothermal mineralization from a hypogene source is normally ascribed.

SANDSTONE DEPOSITS OF THE COLORADO PLATEAU

The so-called "carnotite" deposits of the Colorado Plateau form a group of deposits with wide distribution and many common characteristics. They have yielded important amounts of vanadium, uranium, and radium.

Although these deposits are found in many formations, ranging from late Paleozoic to middle Tertiary in age, the more productive deposits are restricted to a few stratigraphic units of Mesozoic age. Most of the deposits are in sandstone beds of continental origin, though some are in limestone and a few in shale. The host rocks in nearly all deposits contain carbonaceous material, mostly fossil wood.

The early minerals in the ore consist of low-valent oxides and silicates of vanadium and uranium, small amounts of copper and iron sulfides, and traces of galena and sphalerite. The ore minerals alter to higher valent oxides of vanadium and to vanadates and other secondary uranium minerals. They mainly occupy pore spaces in the sandstone, though in part they replace sand grains and associated argillaceous and carbonaceous material. The ore bodies are tabular layers that lie nearly parallel to bedding but do not follow beds in detail. Most ore bodies are small, and they range from masses only a few feet across to those several hundred feet across.

It is generally agreed that the ore minerals were introduced into their present position by solutions, but the nature of these solutions and the source of the metals are not known. Some students believe the solutions were hypogene and that the metals were introduced from deep-seated sources; others favor the idea that the metals were originally disseminated in the ore-bearing and associated rocks and were transported and concentrated at favorable site by aqueous solutions or perhaps even petroleum. It is also generally agreed that sedimentary structures, such as lenses, had some influence on the migration of the ore-bearing solutions and the localization of many ore deposits. In addition, the regional distribution of deposits suggests to some geologists that regional deformation also influenced localization by providing pathways for the vertical movement of solutions to ore-bearing beds, and a few deposits show a close association with such vertical pathways. Igneous activity and mineralization of definite hydrothermal origin are not closely associated with carnotite deposits, except in a few places.

McKelvey, Everhart, and Garrels (1955) give a fairly complete list of references to reports on these deposits.

Deposits similar to these on the Colorado Plateau are also present elsewhere; some in Wyoming and South Dakota have yielded significant production.

LIMESTONE DEPOSITS OF TYUYA MUYAN, RUSSIA

At Tyuya Muyan, Fergana, in central Asia, oxidized uranium, vanadium, and copper minerals, associated with barite, calcite, and quartz, occur in limestone. The ore bodies are peculiar pipelike structures that partly fill cavities and perhaps partly replace the host rock. The area is one of complex structure and geologic history, with considerable faulting and igneous activity.

The origin of these deposits also is in doubt. Pavlenko (1933) believes the ore formed from thermal solutions derived from diabase intrusives. According to Bain (1950, p. 295), Fersman considers the uranium and vanadium to have been leached from nearby black shales, which, according to Rankama and Sahama (1950, p. 638) contain "approximately 400 g/ton U and 850 g/ton V."

WITWATERSRAND CONGLOMERATE

Conglomerate beds of the Witwatersrand, South Africa, are yielding large quantities of uranium as well as gold. In addition to native gold, the ore minerals consist of uraninite and thucholite, a uraninite-hydrocarbon aggregate. These minerals, along with minor amounts of common sulfides, are mainly disseminated in pore spaces in lenses of coarse sandstone and conglomerate. Some gold and uranium, but apparently only minor amounts, occur in quartz and thucholite veinlets where these cross ore-bearing beds. Although the rocks are fractured and also invaded by igneous dikes, the ore bodies are not clearly localized by these features. A "placer" versus "hydrothermal" origin for the gold ores has long been debated among geologists and the same discussion continues since the discovery of uranium in these deposits. Readers interested in more detail regarding these deposits and the problem of their origin are referred to McKelvey, Everhart, and Garrels (1955) and the reports they list.

VANADIUM IN ORE DEPOSITS

There are but few deposits in which vanadium alone is sufficiently concentrated to support a profitable operation, though there are several types of deposits that have yielded byproduct vanadium or from which production might be economic under reasonably favorable conditions. These are described below under "Productive vanadium deposits." Vanadium shows little or no tendency to concentrate in most types of ore deposits; available information regarding the vanadium content of these deposits is presented below.

PRODUCTIVE VANADIUM DEPOSITS

VANADIUM-URANIUM DEPOSITS IN SANDSTONE AND LIMESTONE

A description of the vanadium-uranium deposits in sandstone on the Colorado Plateau and in limestone at Tyuya Muyan, Russia, has been given previously.

IRON ORES

Many iron ores contain small amounts of vanadium, and some have yielded byproduct vanadium. Commonly the titaniferous magnetite deposits are the most vanadiferous (Singewald, 1913); the vanadium content ranges from about 0.2 percent V_2O_5 to more than 1 percent and probably averages between 0.4 and 0.6 percent. In these deposits, vanadium is reported to be in the magnetite rather than in the titanium minerals (Balsley, 1943), a seemingly peculiar relation considering that most nontitaniferous magnetites contain less vanadium.

Many sedimentary iron ores contain 0.02 to 0.2 percent V_2O_5. During World War II Germany produced considerable vanadium from iron ores containing about 0.2 percent V_2O_5 (Fischer, 1946). Vanadium is also concentrated in laterites and bauxites, especially those derived from mafic igneous rocks.

VANADATE ORES

Vanadates of lead, zinc, and copper are found in many base metal deposits in southwestern United States, Mexico, South America, Spain, Africa, and Australia; some vanadium has been produced from a number of these deposits, but most productive are those at Broken Hill, Northern Rhodesia, and in the Otavi district, Southwest Africa. Most, though not all, of these deposits are in carbonate country rock. Typically they are in areas of moderately arid climate and deep oxidation; the vanadate ores are described as being in the oxidized parts of the deposits.

Evidence and opinions differ as to the source of the vanadium in these deposits. Skerl (1934) reports that the unoxidized ore at Broken Hill was tested chemically and spectrographically, but no trace of vanadium was found; Clark (1931) states that the primary ores in Southwest Africa contain little or no vanadium and believes that no reasonable amount of concentration from the weathering of eroded lead-zinc ore bodies could account for the vanadium ore. In both areas the vanadium is thought to have come from that originally disseminated in the surrounding rock. The same explanation has been offered for other deposits.

In contrast to the evidence and opinions mentioned above, Peterson (1938) finds that the vanadate minerals at the Mammoth-St. Anthony area, Arizona, were introduced during the last stage of hypogene mineralization and later than the base-metal sulfides.

In addition, Newhouse (1934), aided by spectroscopic work of Claussen (1934), tested specimens of pyrite, galena, and sphalerite for vanadium, and concluded that at least some of the vanadium in the vanadates of the oxidized base-metal deposits was derived from the trace amounts in the sulfides. Five selected samples each of pyrite, galena, and sphalerite were tested; 1 sample of pyrite and 5 of galena showed 0.0X—0.00X percent V spectrographically, and the vanadium content of the other samples was below the limit of detection. One pyrite sample showed 0.01 percent V by chemical analysis and the rest much less; the sphalerite samples showed less vanadium than the pyrite samples; and the chemical tests on the galena samples showed a few thousandths percent, confirming the spectroscopic results (Newhouse, 1934).

Moritz (1933) reported about 0.001 percent vanadium in the sulfide ore (tenantite, enargite, sphalerite, and other sulfides), as well as in calcite and dolomite, and as much as 0.01 percent vanadium in pyrite in the Tsumeb mine, Otavi district, Southwest Africa.

The problem of the origin of the vanadate ore in oxidized base-metal deposits, per se, is not of immediate concern. The source of vanadium may be the country rock, as some believe; or it may be the trace amounts disseminated in sulfides, as suggested by Newhouse; or it may be a separate hypogene stage, as reported by Peterson at the Mammoth-St. Anthony deposit. But two points are of immediate interest: (1) all available evidence shows only a very low concentration of vanadium in the primary sulfides and (2) even if the vanadate ore at the Mammoth-St. Anthony area is hypogene, as Peterson suggests, it is a phase separate from the normal sulfide mineralization.

MINASRAGRA, PERU

The vanadium sulfide ("patronite") deposit at Minasragra, Peru (Hewett, 1909), has been the most productive single deposit of vanadium. The ore consists of quisqueite (a hydrocarbon), coke, and patronite; bravoite, an iron-nickel sulfide, is present in small amounts in the patronite. These materials occupy a fracture and permeate the adjoining shale, forming a lens-shaped body up to 30 feet wide and a few hundred feet long. The fracture dips steeply and crosses bedding at a moderate angle. Country rock consists of shales and thin-bedded limestones of Cretaceous age. These rocks are invaded by several igneous dikes and cut by numerous faults near the deposit.

Similar vanadiferous asphaltic veins are common in this part of Peru; though none are nearly as rich in vanadium as the Minasragra deposit, they do contain about 1 percent vanadic oxide. All the asphaltic deposits apparently are in the same group of sedimentary beds, which also contain vanadiferous black shales.

Although the origin of the Minasragra deposit certainly is not known, most authorities (Hewett, 1909; Jost, 1932; and Rankama and Sahama, 1950) relate the formation of this deposit to the process responsible for forming asphaltite and its common contamination by vanadium. Thermal solutions, however, may have played a part in transporting or altering the asphaltite and enriching this deposit.

MISCELLANEOUS DEPOSITS

Under peculiarly favorable conditions, vanadium has been, or can be, recovered as a byproduct from several other sources. Among these are ash or soot from crude oil or petroleum refinery products or from other carbonaceous material such as natural asphalt and vanadiferous coals. Byproduct vanadium has also been obtained from phosphate rock at Conda, Idaho (Argall, 1943, p. 47 and 48); uranium is also present (McKelvey and Nelson, 1950, p. 41). Lovering and Goddard (1950, p. 234) report that in 1910 some gold-telluride ore was shipped for its vanadium content from the Kekionga claim, Boulder County, Colo. A brief discussion of vanadium in gold-telluride veins is given on page 225.

VANADIUM IN OTHER DEPOSITS

Not much information is available regarding the distribution and amount of many elements that occur in ore deposits in quantities below levels of economic value, especially if the elements do not form constituent parts of readily recognized minerals. Vanadium is one of these. The failure of observers and analysts to detect, or mention, the presence of vanadium in many hydrothermal ore deposits can be used, in a negative manner, to suggest a low vanadium content, as well as to indicate that its geochemical habits do not favor concentration in this particular environment. Even so, conclusions based on such negative information are unsatisfactory. In recent years, however, some quantitative information has become available, and perhaps this information can support broad generalizations.

VANADIUM IN ROCKS, ORES, AND MILL AND SMELTER PRODUCTS

In 1942, at the request of the War Production Board, the Geological Survey began a search for certain strategic and minor elements in domestic rocks, ores, concentrates, tailings, smelter slags, and flue dusts. Several hundred samples of these materials were collected by geologists or furnished by mining and smelting companies and were tested for 22 elements, including vanadium, by semiquantitative spectrographic analyses. The analytical results are published in a report by Kaiser, Herring, and Rabbitt (1954).

Although these samples are not completely representative of any single deposit or type of deposit, they do give a coverage of most types of ore deposits in the United States—the samples are from deposits that yielded 85 percent or more of the 1942 domestic production of copper, lead, zinc, manganese, mercury, tin, tungsten, and chromium, and lesser percentages of production of aluminum, gold, silver, iron, and pegmatite minerals. As such, these samples have some value on which to base generalizations. Information regarding vanadium in these deposits is summarized below. Similar information regarding vanadium in veins that have been studied and sampled because they are uranium-bearing (or might be), is summarized in the section "Vanadium in uranium-bearing veins."

The semiquantitative spectrographic results for vanadium in rocks, ores, and mill and smelter products (Kaiser, Herring, and Rabbitt, 1954) are mostly expressed in numerical percentages and as V_2O_5. For this study, these values were converted to percent V, and then grouped into the grade classes shown on figures 67, 68, and 69, and table 1 so the values would be more nearly comparable to the manner in which semiquantitative spectrographic results are now being reported by the U. S. Geological Survey laboratories. To convert the numerical values of V_2O_5 to V, the figures were multiplied by 0.5 rather than by the true conversion factor of 0.56. Obviously this introduced a consistent error, though one so small as to be of little import, and the error is lost in most cases in conversion to the X categories.

A few values of V_2O_5 are reported by Kaiser, Herring and Rabbitt (1954) as "X" to the proper decimal place. These were assumed to have a medial value of 5 to the same decimal place, and they were converted in the manner described above. Values reported as 0.001 percent V_2O_5, and those shown as "trace" V_2O_5, are grouped in the category of "trace" V in table 1.

The distribution by grade classes of the 775 samples tested for vanadium is shown in the left side of table 1. The samples were divided into two groups: one group (column 1) includes mill heads, tailings, and ore (including grab samples), as it was thought these might be more representative of ore deposits; the other group (column 2) includes concentrates, slag, and flue dust. There appears to be no significant difference between the two groups. The combined total of these two groups is shown in column 3. The graphic plot below each column shows the distribution of samples in each grade class by percent of the total number of samples.

By inspection of the subcolumns "percent of total," it is obvious that at least half of the total samples in columns 1, 2, and 3 fall in the grade classes containing .00X or less (0.0046 percent, or 46 ppm, V or less). At least half of the samples, therefore, contain considerably less vanadium than the figures given by Rankama and Sahama (1950, table 5.52, p. 226) as V content of igneous rock (150 ppm) or shale (120 ppm); on the other hand, more than half of the samples contain more than the average amount of vanadium in sandstone (20 ppm) and limestone (<10 ppm).

Thus, if these 775 samples should be considered representative of ore deposits in general, it appears that vanadium does not tend to concentrate in most deposits; rather, the vanadium content of most samples possibly represents the vanadium content of the host rock.

For those readers who may be interested in seeing the character and source of the higher grade vanadium samples reported by Kaiser, Herring, and Rabbitt (1954), this information is listed in table 2 for all samples reported to contain 0.1 percent V_2O_5 or more (about 0.056 percent V, in the $.0X^+$ class or higher).

Table 2 shows moderate amounts of vanadium in iron, chromium, and manganese ores, as might be expected. It also shows moderate amounts of vanadium in samples of some ores of titanium and gold, a relation that seemed to the writer to be worthy of a sideline investigation and to justify a brief mention here.

The habit of vanadium to accumulate in magmatic titaniferous-magnetite deposits is well known. The relatively high vanadium content in brookite and rutile samples (see table 2, samples ARK–26–1, ARK–26–2, and ARK–26–3; more data regarding vanadium and titanium at Magnet Cove, Ark., are given by Fryklund, Harner, and Kaiser, 1954) suggests that the association of vanadium with titanium may even extend into other types of titanium deposits, including titanium-bearing hydrothermal veins. If this is true, it may explain the presence of vanadium in the deposit of davidite (uranium-bearing iron-titanium oxide) at Radium Hill, South Australia (Parkin and Glasson, 1954), as well as the vanadium in the lower levels of the Ace mine, Saskatchewan, Canada, where ilmenite also is reported to be abundant (Robinson, 1955, p. 22–23). Only field study will establish whether the vanadium in these two deposits is more intimately associated with uranium or titanium, or largely independent of each.

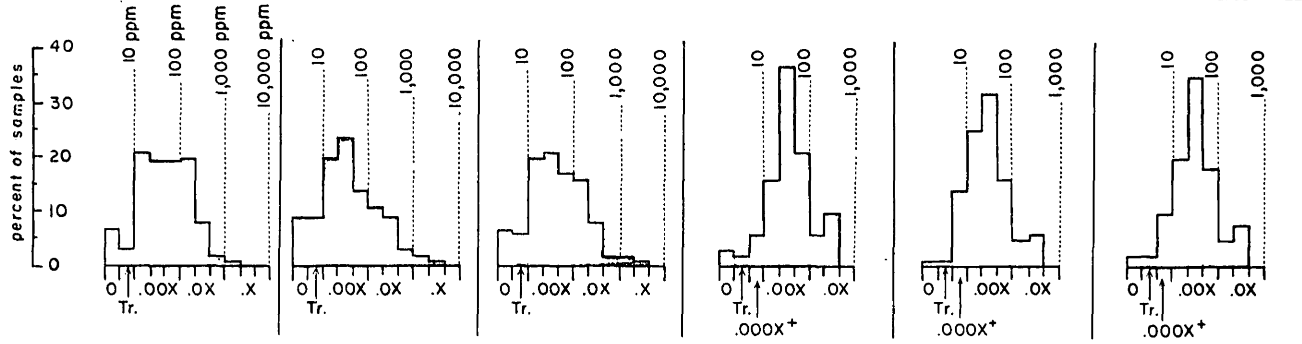
More information regarding the association of vanadium and titanium in uranium-bearing veins is given on page 228.

The presence of roscoelite, the vanadium mica, in gold-telluride veins is not infrequent and suggests a

TABLE 1.—DISTRIBUTION OF VANADIUM SAMPLES BY GRADE CLASSES

[The limits of the grade classes are generated by integral powers of the cube root of 10 (2.154); for example, $0.0X^-$ = 0.01 to 0.0215 percent, 0.0X = 0.0215 to 0.0464 percent, and $0.0X^+$ = 0.0464 to 0.1 percent]

	Vanadium in some rocks, ores, and mill and smelter products						Vanadium in uranium-bearing veins					
	Column 1 Samples of ore, mill heads, and tails		Column 2 Samples of concentrates, flue dust, and slag		Column 3 Combined total		Column 4 Samples containing 0.01 percent or more U		Column 5 Samples containing <0.01 percent U		Column 6 Combined total	
Grade class, percent V	Number of samples	Percent of total	Number of samples	Percent of total	Number of samples	Percent of total	Number of samples	Percent of total	Number of samples	Percent of total	Number of samples	Percent of total
0	28	7	30	9	58	7	4	3	2	1	6	2
Tr.	15	3	33	9	48	6	3	2	2	1	5	2
$0.000X^+$	....	....	....	....	....	....	9	6	21	14	30	10
$.00X^-$	87	21	69	20	156	20	23	16	38	25	61	20
.00X	79	19	84	24	163	21	53	37	49	32	102	35
$.00X^+$	80	19	48	14	128	17	30	21	24	16	54	18
$.0X^-$	86	20	38	11	124	16	8	6	7	5	15	5
.0X	33	8	31	9	64	8	14	10	9	6	23	8
$.0X^+$	8	2	9	3	17	2	....	....	....	....	....	....
$.X^-$	6	1	7	2	13	2	....	....	....	....	....	....
.X	2	0	2	1	4	1	....	....	....	....	....	....
Totals	424	100	351	102	775	100	144	101	152	100	296	100



second type of hydrothermal deposit in which vanadium tends to concentrate.

Eckel (1949, p. 74) emphasizes the association of roscoelite with gold-telluride veins in the La Plata district, Colorado. Lovering and Goddard (1950) mention the presence of roscoelite in several veins in the Colorado Front Range, all but one of which are classified as gold-telluride veins. Roscoelite is also mentioned in other reports in districts where gold-telluride deposits are known, but the literature available to the writer is not sufficiently specific to determine whether or not roscoelite and the telluride minerals are closely associated.

The specific association of vanadium with gold tellurides was noted by de Launay (1911), whereas Lindgren (1933, p. 873) generalized, stating "Roscoelite is found in many gold-quartz veins." This subject is introduced here merely to call this problem to the attention of geologists, in the hope that others may furnish a better understanding of relations.

VANADIUM IN URANIUM-BEARING VEINS

Uranium-bearing (pitchblende or uraninite) veins have been the source of much of the world's radium and uranium. The geologic characteristics of the typical and more productive deposits of the class have been summarized by Everhart and Wright (1953). This summary makes no mention of vanadium in any of the 13 deposits described, and both Everhart and Wright have told the writer personally that they watched for but failed to find mention of vanadium in these de-

TABLE 2.—*Character and source of samples reported by Kaiser, Herring, and Rabbitt (1954) to contain 0.1 percent* V_2O_5 *or more*

V_2O_5 (percent)	Sample No.	Character and source of sample
0.1	ARI-7-14	Copper tails, Oracle, Pima County, Ariz.
0.1	ARI-13-13	Molbydenum-vanadium-lead-zinc tailings, Mammoth-St. Anthony mill, Pinal County, Ariz.
0.2	ARK-15-1	Manganese ore, grab sample from high-grade stockpile, Batesville district, Arkansas.
0.1	ARK-15-2	Manganese ore, grab samples from MRC stockpile, Batesville district, Arkansas.
0.1	ARK-15-3	Manganese ore, grab sample from high-grade stockpile, Batesville district, Arkansas.
0.1	ARK-15-4	Manganese ore, grab sample from low-grade stockpile, Batesville district, Arkansas.
0.58	ARK-26-1	Brookite crystals, composite sample, Magnet Cove, Ark.
0.54	ARK-26-2	Rutile crystals, composite sample, Magnet Cove, Ark.
0.2	ARK-26-3	Rutile concentrate, high grade, Magnet Cove, Ark.
0.1	COL-10-8	Gold concentrates, ore chiefly from Cripple Creek district, Colorado.
0.1	COL-10-9	Gold mill heads, ore chiefly from Cripple Creek district, Colorado.
0.6	COL-10-12	Gold refinery byproduct from treated slag, ore chiefly from Cripple Creek district, Colorado.
0.6	COL-10-13	Gold refinery slag from roaster, ore chiefly from Cripple Creek district, Colorado.
0.X	MIC-7-1	Copper concentrates, Kearsarge Amygdaloid mine, Houghton County, Mich. (0.X TiO_2).
0.X	MIC-7-2	Copper concentrates, Iroquois mine, Houghton County, Mich. (0.X TiO_2).
0.X	MIC-7-3	Copper concentrates, Allouez No. 3 mine, Houghton County, Mich. (0.X TiO_2).
0.X	MIC-7-11	Copper concentrates, White Pine mine, Ontonagon County, Mich. (3.6 TiO_2).
0.X	MIC-7-12	Copper concentrates, White Pine mine, Ontonagon County, Mich. (0.X TiO_2).
0.2	MON-10-25	Gold tailings from tailings dump, Little Ben mine, Phillips County, Mont.
0.1	NEV-27-12	Tungsten tailings, Rawhide, Nev.
0.2	ORE-5-1	Chromite heads, mill sample, ore from Lagoons gold tailings deposits, Coos County, Ore.
0.4	ORE-5-2	Chromite concentrate, ore from Lagoons gold tailings deposit, Coos County, Ore.
0.1	ORE-5-5	Chromite heads, mill sample, Seven Devils mine, Coos County, Ore.
0.2	ORE-5-6	Chromite concentrate, Seven Devils mine, Coos County, Ore.
0.2	ORE-5-8	Chromite mill heads, Coos County, Ore.
0.2	ORE-5-9	Chromite flotation concentrate, Coos County, Ore.
0.2	ORE-5-10	Primary chromite concentrate, Coos County, Ore.
0.1	SD-10-6	Gold heads, Maitland mine, Lawrence County, S. Dak.
0.3	UT-12-2	Grab samples, magnetite iron ore, Iron Mountain mine, Iron County, Utah.
0.2	UT-12-3	Magnetite iron ore, Great Western ore body, Iron County, Utah.
0.3	UT-12-5	Flue dust from steel plant, Provo, Utah; ore from Iron Mountain mine, Iron County, Utah.
0.1	VA-10-1	Gold tailings, ore from Red Bank Gold mine, Virgilina district, Virginia.
0.1	VA-15-1	Manganese concentrates, Appalachian district, Virginia.
0.1	VA-15-2	Manganese concentrates, Appalachian district, Virginia.
0.2	VA-70-1	Kyanite concentrate, Pamplin, Va.
0.1	WAS-5-1	Heavy sand concentrate (chromite), Cle Elum district, Kittitas County, Wash.

posits in the geologic reports to which they referred during their study.

In a similar study, Bain (1950) summarized the geologic characteristics of all types of uranium deposits that have been or might be productive. He classifies the deposits as primary or hypogene, sedimentary or bedded, and oxidized. In the primary or hypogene class Bain mentions most of the deposits described by Everhart and Wright, as well as a few other deposits of this type. Again no mention is made of vanadium in these deposits, though vanadium is frequently mentioned in connection with the descriptions of sedimentary and oxidized deposits.

To obtain quantitative data on vanadium in uranium-bearing veins, the writer has made a search of published and unpublished material in the files of the Atomic Energy Commission and the Geological Survey. These data are presented below, grouped in two categories—geologic samples and ore samples—because of differences in the character of the samples and in the methods of assay.

The assay results of the group of "geologic samples" are plotted on the right side of table 1 and on figure 67.

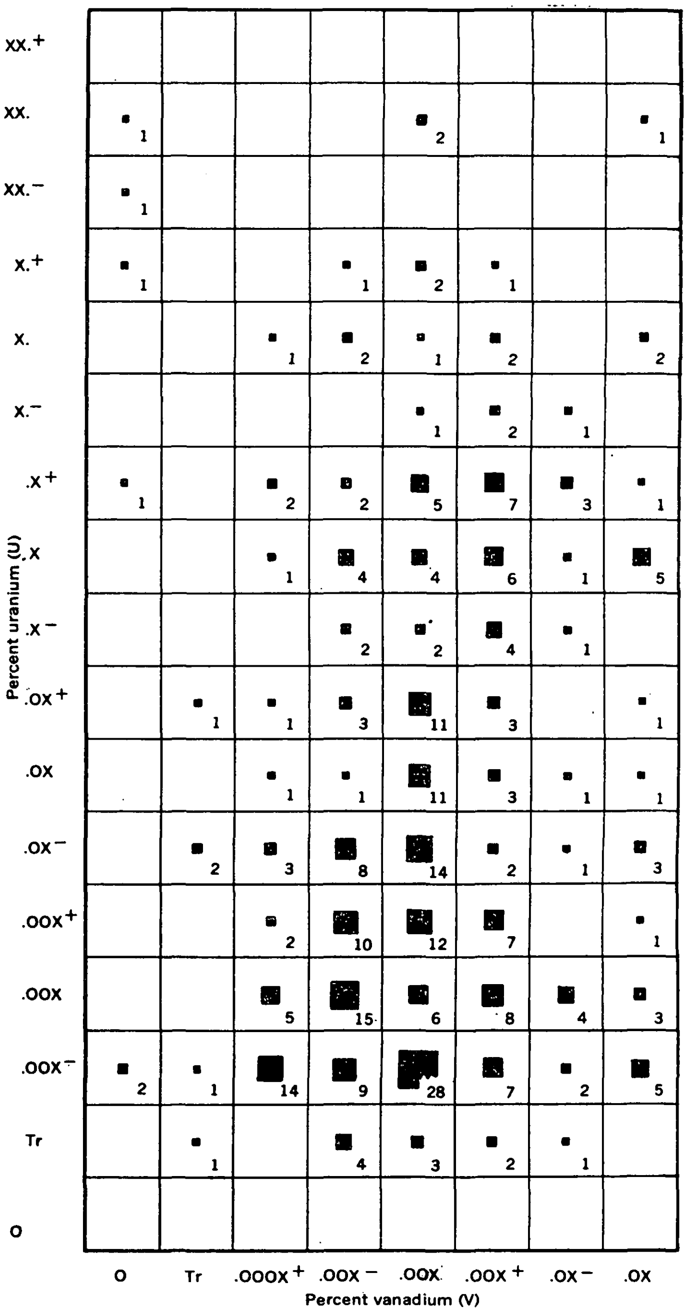


FIGURE 67.—Scatter diagram of geologic samples from uranium-bearing veins, showing the vanadium content plotted against uranium. The number of samples in each grade class is shown by the figure in the lower right corner of each square. The solid blocks, which are plotted as equivalent squares of the number of samples, also indicate visually the quantitative distribution of samples.

They consist of 296 samples taken by geologists of the Atomic Energy Commission and the Geological Survey during geologic study of uranium-bearing vein deposits. The samples are from 84 localities in 9 western states; some localities are represented by a single sample, others by a dozen or more samples. The localities represented were screened with care to include only those deposits that would be classed as hydrothermal veins; deposits for which there might be some reasonable doubt or argument regarding the hypogene source of the uranium are not represented in this group of samples. All available assay reports from these deposits were used. This group contains a few samples representing ore shipments or mill heads, but mostly they consist of grab or channel samples. As such, most individual samples cannot be considered as good samples of ore bodies, but collectively they may be broadly representative of this type of ore deposit—uranium-bearing vein deposits of hydrothermal origin.

All assays were made in the Denver laboratory of the Geological Survey; only equivalent uranium determinations were made on samples having low radioactivity (a few thousandths percent eU), but chemical determinations for U were available for all other samples; all vanadium determinations were made by semiquantitative spectrographic analysis. For purposes of plotting on figure 67, the uranium assays (either eU or chemical U) were converted from the numerical figure to the grade classes used in reporting spectrographic results.

The frequency distribution of vanadium determinations in the several grade classes is tabulated on the right side of table 1. The samples are divided into two groups: one group consists of samples containing 0.01 percent or more U (column 4), as it was thought that this group might be more representative of uranium-bearing ore bodies or ore shoots; the other group consists of samples containing less than 0.01 percent U (column 5). The combined totals for the two groups are shown in column 6. The graphic plot below each column shows the distribution of samples in each grade class by percent of the total number of samples.

The geometric means for the combined total of samples (column 6, table 1) is 31 ppm V, that for the samples containing 0.01 percent or more U (column 4) is 36 ppm V, and that for the samples containing less than 0.01 percent U (column 5) is 27 ppm V. These figures suggest a slight tendency for vanadium to increase with an increase in uranium content of these samples, but the differences in the mean figures are so small that they might result from chance or random variation in the sampling. The correlation coefficient between vanadium and uranium for all samples (fig. 67) is +0.12, which is below the normal level of significance.

The assay results of the group of 74 "ore samples" are plotted on figure 68. This group includes samples taken for settlements on ore shipments, samples of material used for metallurgical or pilot-plant tests, and a few samples submitted by miners and prospectors. These samples are from 36 localities (deposits) in 10 western states and 4 foreign countries; some localities are represented by single samples, others by several samples; a few samples represent average assays calculated for numerous shipments of ore from a single mine. As such, most of the samples are presumably well representative of ore and the parent ore bodies, and from this standpoint they are better than those classed as geologic samples. All assays were made by chemical methods, mostly of the routine "commercial" type, and by several laboratories. With these methods the threshold of determination for vanadium is in the low hundredths percent V_2O_5, and assay accuracy at this level is admittedly poor. Discrepancies ranging from 0.01 to 0.04 percent V_2O_5 have been noted between different laboratories and different standards of analyses. At this low level of vanadium content, such discrepancies, of course, are of no practical concern to the ore vendor, buyer, or metallurgist, but they do present problems in a study of this kind. Furthermore, many of the vanadium determinations in this group of samples are reported as "0.00 per-

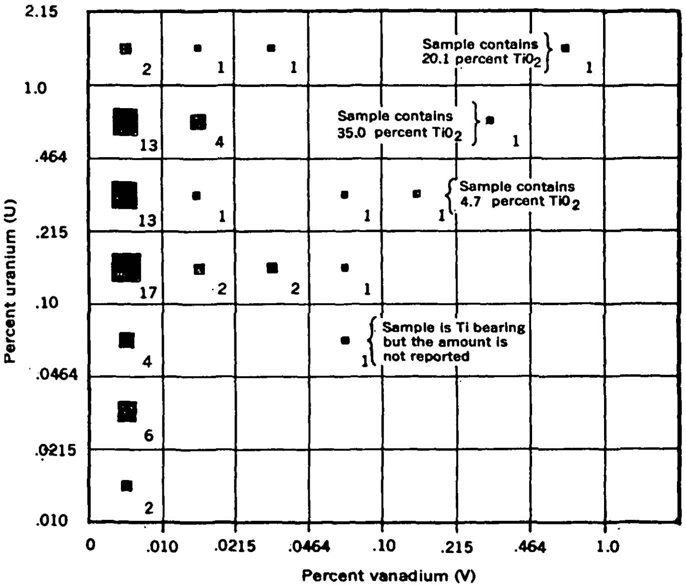


FIGURE 68.—Scatter diagram of uranium ore samples, showing the vanadium content plotted against uranium. The number of samples in each grade class is shown by the figure in the lower right corner of each square. The solid blocks, which are plotted as equivalent squares of the number of samples, also indicate visually the quantitative distribution of samples.

cent V_2O_5" or as "<0.01 percent V_2O_5." When converted to V for plotting on figure 68, these values are all plotted in the vanadium grade class of "less than 0.01."

Because the accuracy of the vanadium assays for these ore samples is subject to question, it is difficult to determine whether or not the relations shown by figure 68 have any true significance. The illustration is presented, however, so the reader can see these data and arrive at his own conclusions. It is obvious that the higher grade vanadium samples occur with some of the higher grade uranium samples and none of the low-grade uranium samples contain much vanadium. Even so, the vanadium content of all these samples is quite low, except those containing abundant titanium.

Because of the vanadium-titanium relations shown on figure 68 and the association suggested by the study of the ores and mill-products samples (p. 224), a record was made of the spectrographic determinations of titanium for 172 of the 296 samples of uranium-bearing veins. Figure 69 is a scatter diagram showing the vanadium content of these 172 samples plotted against titanium. The correlation coefficient between vanadium and uranium in these samples is +0.36, which is low but significantly different from zero. Presumably none of these samples are from deposits in which titanium is much enriched, for the titanium content of most samples, as well as their vanadium content, is that common among rocks. Likely the titanium and vanadium in these samples is essentially the same as the content of these metals in the host rocks of these deposits.

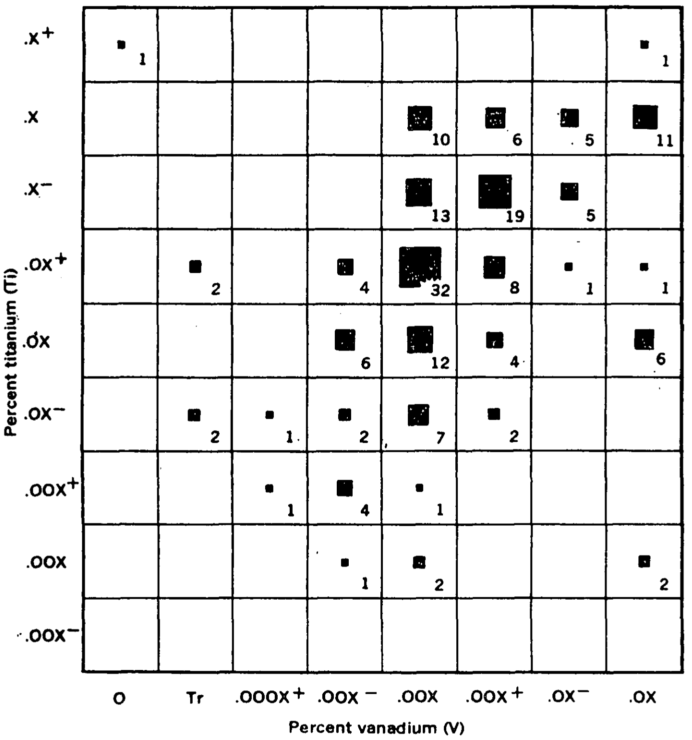


FIGURE 69.—Scatter diagram of samples from uranium-bearing veins, showing the vanadium content plotted against titanium. The number of samples in each grade class is shown by the figure in the lower right corner of each square. The solid blocks, which are plotted as equivalent squares of the number of samples, also indicate visually the quantitative distribution of samples.

Wright (1954) arrived at a similar conclusion regarding vanadium and titanium in his study of a uraninite deposit at Caribou, Colo. He tested the vein at three places with sets of samples from the host rock through the altered zones on both sides of the vein; spectrographic determinations showed the titanium content to be constant at 0.1 to 1.0 percent and the vanadium content at 0.01 to 0.1 percent (Wright, 1954, figs. 3, 4, and 5). In an unpublished report to the Atomic Energy Commission he states, "this distribution indicates that the titanium and vanadium present in the altered wall rock were original constituents of the monzonite and were not supplied by the vein; and that leaching of these elements by vein solutions was negligible."

The information plotted on figures 67 and 68, and tabulated on the right side of table 1, permit a few broad generalizations. For the deposits represented by the samples used in this study it appears that vanadium is concentrated in large amounts only in uranium-bearing veins containing abundant titanium. The average vanadium content in the other deposits is probably no more, and perhaps is somewhat less, than the average vanadium content of most rocks at the earth's crust, as reported by Rankama and Sahama (1950) and by others. This suggests that there is little or no tendency for vanadium to concentrate with uranium in most hydrothermal uranium-bearing veins. Nevertheless, the tabulated sample assays do show a slight tendency for vanadium to increase in amount with an increase in uranium.

In addition to the generalizations made above, a few more detailed observations made during the compilation of these data seem worthy of record.

The assays of several uraninite or pitchblende specimens or concentrates were found; these, however, were not included with the other samples, because of the peculiar character of the sample or the manner in which the assay was reported. The vanadium content of these samples was reported to range from zero to a few tenths percent V_2O_5. Among these several samples there is a slight suggestion that the vanadium content may be higher in "sooty pitchblende" than in crystalline uraninite. Geologists working on uranium-bearing veins may be interested in checking this suggestion.

Among groups of samples from most uranium-bearing veins there is no obvious tendency for the vanadium content to increase with the uranium content. Exceptions to this generalization were noted in samples from the Schwartzwalder mine, Jefferson County, Colo., and the Miracle mine, Kern County, Calif. In both deposits the vanadium content is moderately high (perhaps averaging 0.1 to 0.2 percent V_2O_5)[16], and in the available samples from both deposits there is an obvious, though not invariable, tendency for vanadium to increase with uranium. The writer has no idea why these two deposits have a moderately abnormal vanadium content. Titanium is not obviously concentrated in the Schwartzwalder deposit; the writer has no data regarding the titanium content of the ore from the Miracle mine.

VANADIUM IN HOT SPRINGS

Like the geologic descriptions of most ore deposits, reports on hot springs and hot-spring sediments usually fail to mention vanadium. The assumption can be made that vanadium is not abundant in these thermal solutions and that it does not precipitate from them in recognizable minerals—but this is negative evidence and weak.

Based on his studies of hot-spring waters and sediments at Steamboat Springs, Nev., and Morgan Springs and Wilbur Springs, Calif., D. E. White (written communication) states:

> Vanadium is not present in amounts detectable by spectrographic methods in the dissolved solids of water samples from Steamboat Springs, Nev., and Morgan Springs and Wilbur Springs, Calif. Its content in the water at Steamboat Springs is less than 0.2 ppm and less than 2 ppm in the highly saline water of Wilbur Springs.
>
> On the other hand, several samples of sediments from these three springs showed 0.0X percent V by spectrographic analysis, and two from Steamboat Springs showed 0.01 percent V_2O_3 by gravimetric analysis.
>
> Vanadium is not being deposited within the explored depths of the Steamboat Springs system, and there is even some evidence pointing toward a slight leaching of vanadium from the wall rock by the hydrothermal solutions.
>
> Hot springs have not yet thrown light on the origin of hypogene uranium deposits. Hot spring waters are lower in uranium content than many other types of waters.

SUMMARY AND CONCLUSIONS

Vanadium and uranium are both dispersed in igneous rocks, but the two metals are not intimately associated in this environment—vanadium is more abundant in the mafic rocks, uranium in the silicic ones.

Both metals tend to concentrate in some sedimentary rocks, especially those containing organic material; in these rocks either metal alone may be enriched, or both together.

Uranium obviously enters the hydrothermal environment, and in places it concentrates sufficiently in veins to form commercially valuable deposits. Prospecting in recent years has shown that uranium is rather widely distributed in hydrothermal veins.

None of the productive vanadium deposits, on the other hand, are of undoubted hydrothermal origin, although the vanadate ores and the deposit at Minasragra do have some characteristics of hydrothermal deposits. Furthermore, except in some titanium-bearing veins and some gold or gold-telluride deposits, vanadium-bearing minerals have not been generally recognized in hydrothermal deposits, suggesting a low-vanadium content in most hydrothermal deposits, a suggestion that seems to be confirmed by recently available spectrographic data. A group of 775 analyses of samples of ores and mill products from numerous deposits in the United States shows an average of less than 100 ppm V, a content somewhat less than that commonly reported for igneous rocks and shale. A second group of 296 samples from uranium-bearing veins also shows an average of less than 100 ppm V. Perhaps the vanadium in many of these samples is that of the wall rock rather than introduced vanadium.

Although these samples certainly do not give a complete coverage of ore deposits, and many individual samples certainly are not representative of their parent ore bodies, as a group they probably represent the best available sample of vanadium in ore deposits in general and in uranium-bearing veins in particular. They suggest that vanadium does not tend to concentrate in the common hydrothermal environment, and specifically that it does not concentrate in most veins containing uranium ore. If this is true, it appears that deposits containing commercial amounts of both vanadium and uranium, such as deposits of the sandstone type, are not common hydrothermal deposits.

The fact that both vanadium and uranium do accumulate in some sedimentary rocks containing organic material suggests that a thorough study be made of the geochemical processes that influence this accumulation, to see if in any way these processes are compatible with the geologic habits of the productive vanadium-uranium deposits of the sandstone type, most of which do contain plant fossils.

The lack of evidence that vanadium and uranium are enriched together in common hydrothermal deposits does not eliminate the possibility of a hydrothermal origin and a hypogene source of these metals in the sandstone deposits, but it would seem to require field evidence that unusual processes or conditions were extant in order to support the idea of a hydrothermal origin and a hypogene source.

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[16] A composite of sample pulps representing more than 400 tons of ore shipped from the Schwartzwalder mine shows only 0.0X− percent V, spectrographically. This analysis was received after the tabulation of all the other data used in this report.

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Part 21. THE KNOWN AND THE UNKNOWN

CONTENTS

SUMMARY AND CONCLUSIONS

The problem around which this volume has been compiled, as discussed in Part 1, is the deciphering of oxidation relations in the Colorado Plateau ores. Most of the workers soon became convinced of the validity of the postulate that all ores were at one time reduced mineral suites, and most of their effort has gone into documenting the case. In fact, the postulate was so readily accepted, and fitted so well when deposits were examined, that it is almost a tacit assumption of many of the papers presented. This perhaps questionable scientific act of faith has been justified; the abundant data now available fit without difficulty into the theory. There are still areas of ignorance, to be sure, but no contradictory relations are known, which is rare in the explanation of a geologic phenomenon. This chapter is devoted to those areas of ignorance. In exposing them a framework is provided for summarizing the known. Whereas it is not the intent of this report to speculate on the origin of the ores, definition of the character of the various low-valent preoxidation suites necessarily precedes any speculation on origin.

The major conclusion derived from the preceding papers is that the ores are made up of an equilibrium low-valence assemblage if they occur in rocks saturated with water. In unsaturated rocks oxidation alteration has taken place, ranging from barely recognizable changes to nearly complete reconstitution of the mineral suites. The degree of oxidation depends upon many factors, such as time since exposure, proximity to the land surface, permeability of the blanketing rocks, structural attitude of the enclosing rocks, local rainfall, and the specific mineralogy and occurrence of the unweathered ore.

Unoxidized ore is commonly referred to as primary; at the moment there seems to be little reason to suspect that it is not. Whereas it would be extremely difficult to prove that the ores now found beneath the water table have resided there unchanged since original emplacement, in the absence of evidence to the contrary the view can be entertained with appropriate reservation concerning the possibility of new data.

Thus the picture has emerged that the unweathered ores have resulted from addition of a suite of elements to the enclosing rocks. The elements were emplaced in a reducing environment (whether they brought it with them or encountered it) in Late Cretaceous or early Tertiary time before regional deformation or during its early stages, so that movement of the transporting agent and the locus of deposition were chiefly controlled by sedimentary structures in essentially undeformed rocks. The major added elements, which differ markedly in their absolute amounts and proportions from place to place, are vanadium, copper, and iron, in addition to the essential uranium. Minor added elements which vary similarly include selenium, arsenic, phosphorus, lead, zinc, cobalt, nickel, molybdenum, and chromium. The entire suite is one generally characterized in its geologic behavior as being strongly affected by biochemical processes.

In terms of compounds formed, the ore is a mixture of oxides, silicates, and sulfides, with oxides and silicates predominating in vanadium-rich material, and oxides and sulfides in copper-rich deposits. Unoxidized ores have a relatively simple mineralogy, in that few phases are added to the enclosing rocks. The ore forming process appears chiefly to have been an additive one, in that the ores are to a large extent pore fillings.

Hematite, calcite, and gypsum are the chief minerals reconstituted during ore formation. Quartz is attacked locally.

The host rock is typically nonmarine sandstone lying in the range between pure quartz sand and greywacke. In the vicinity of ore the host is almost invariably light colored, with traces to large amounts of disseminated pyrite, and with traces to large amounts of carbonaceous matter of woody origin. Also, the host is usually a sandstone that has developed from the deposits of streams moving back and forth across an aggrading plain, so that it is lenticular, with interbedded lenses of shale, and is generally characterized by lithologic units of small lateral extent, abundant cross bedding, and complex channeling of higher units into lower ones. The chief clay mineral of the sandstones and of the associated shales is mixed-layer mica-montmorillonite, or so-called hydrous mica.

Texturally, the ore is characterized by fineness of grain, controlled in part by its restricted development in the rock pores, but also apparently resulting from the conditions of deposition. The development of several ore minerals within a given interstice suggests that the ore might well have been fine grained, even if large open spaces were available to accommodate it.

In gross configuration the ore bodies are generally tabular, with their long dimensions parallel to the formational boundaries. However, in many places ore boundaries transgress bedding at both low and high angles. Where transgression is abrupt, the ore boundary tends to be smoothly curved, producing lobate or crescentic forms known as rolls. There is a tendency for ore to occupy the lower or upper parts of the containing sandstone layer, as in the deposits in the Shinarump member of the Chinle formation where it lies in channels in the Moenkopi formation or where it is formed adjacent to roof shales in the Morrison formation.

Oxidation of the ores has occurred almost entirely above the zone of saturation. Because over most of the Plateau the general water table is at an unknown depth at present, but certainly many hundreds of feet below the surface, oxidation is prevented locally by perched water tables, and is prevented elsewhere simply by the distance air must penetrate to reach ore. If, for example, an ore body is above the zone of saturation but is 500 feet from the nearest land surface, oxidation might take place at an infinitely slow rate. The result of the gradual encroachment of oxidation as the land surface approaches the ore bodies is a markedly erratic pattern, as air infiltrates slowly along fractures and along zones of bulk rock permeability. In a humid climate, with the water table near the surface, abrupt mineralogic transitions parallel to the water table occur; in the Plateau where the oxidation is a slowly accelerating process, air has ample opportunity to seek out and employ the most delicate differences in permeability, resulting in complex oxidation patterns, and marked disequilibrium from one part of an ore body to another.

Consequently oxidation has resulted in a remarkably complex mineral assemblage as a given body passes from the relatively simple low-valence mineral assemblage to the simple high-valence assemblage developed at or near the surface. On the other hand, the slowly progressive nature of the process has produced essentially all possible intermediate stages, and has permitted detailed documentation of the process.

The mineralogical behavior of uranium and vanadium during the oxidation stages is clearly summarized in figure 13 of Part 6 (page 82) and figure 26 of Part 7 (page 101).

AREAS OF IGNORANCE

QUALITATIVE ELEMENTAL AND MINERAL COMPOSITION OF UNWEATHERED ORE

In general the elemental and mineral composition of unweathered ores are now known. The kinds and amounts of extrinsic elements have been established and the major minerals identified. As pointed out in Part 2, the added elements show marked regional and stratigraphic differences, but the major added elements of a "composite" ore are uranium, vanadium, iron, aluminum, copper, and sulfur and the prominent minor elements are lead, zinc, molybdenum, cobalt, arsenic, nickel, and selenium. The major minerals are pitchblende, coffinite, montroseite, vanadium silicates, pyrite, marcasite, bornite, and chalcopyrite. Of these pitchblende, coffinite, and pyrite are ubiquitous whereas the vanadium, aluminum, and copper minerals vary regionally.

There are two major areas of ignorance apparent at the moment: the nature of some of the carbonaceous materials associated with ores, and the detailed mineralogy of the vanadiferous silicates. A great deal of uranium is clearly associated with coalified wood. Chemical and physical studies have demonstrated that where uranium occurs in intimate association with material from the Temple Mountain region that is not obviously of woody origin, the carbonaceous material is, nevertheless, derived from wood or coalified wood. Early work emphasized an apparent relationship between uranium and carbonaceous substances derived from petroleum, but investigations to date have shown no such relationship to exist. The final answer to this problem must await further study of carbonaceous substances of all types from various parts of the Colorado Plateau.

The vanadiferous silicates have been among the most vexing mineralogic problems of the Plateau. First of all, as pointed out by R. P. Fischer (oral communication), there are two distinct geologic occurrences of such silicates. In the first the silicate is developed by entry of vanadium into the structure of a pre-existing detrital clay; in this instance vanadium apparently is added and silica and alumina ejected, while the cationic constituents and the original structures are maintained; even if recrystallization occurs, the structure apparently is duplicated (Part 10). In the second, the vanadiferous silicate is formed where no clay or mica mineral previously existed. In this second case, although evidence is far from complete, the tendency seems to be to form roscoelite, a true vanadium mica. At Rifle (Part 19) and at Placerville, in particular, where vanadium silicates are developed in reasonably clean sandstones, the major silicate is known to be roscoelite. The vanadium in roscoelite is trivalent, even in those occurrences where the mineral has been exposed at the surface for many years.

On the other hand the superimposition of vanadium on preexisting hydrous micas yields a vanadiferous variety of that mineral, and it is fairly well established that the original valence of the vanadium is four (Part 10). It is not known to what extent vanadiferous chlorite is the result of addition of vanadium to preexisting chlorite, or whether it is developed as a transformation of preexisting hydrous mica, or whether it is a new species in the rock. Analyzed chlorites contain tetravalent vanadium, and the question as to original valence is not settled.

There is still uncertainty concerning the possibility of the development of vanadiferous silicates during the oxidation stages of primary montroseite. Much vanadium silicate is clearly primary, but because the fate of primary nonsilicate vanadium is not known, it has been suggested that new vanadium silicates are developed during weathering.

QUANTITATIVE ASPECTS OF UNWEATHERED-ORE MINERALOGY

Not enough is yet known of the quantitative aspects of Plateau mineralogy, although the work presented in Part 3 (p. 32) on average elemental composition of unmineralized rocks versus ore has gone far toward making accurate reconstructions possible. The elements, unfortunately, do not tell the whole story, for only in a few occurrences is it known accurately how uranium is divided between uraninite and coffinite, or how much of the vanadium is distributed among montroseite, roscoelite, chlorite, and hydrous mica. Until more data are accumulated it will not be possible to determine with confidence to what extent montroseite has a genetic relation to carbonaceous matter; if coffinite is more abundant in vanadiferous ores; or if the roscoelite-bearing rocks are characteristically relatively clean sandstones, to mention but a few relations that have been suggested.

The nature and amount of carbonaceous material in and near ore is another question that needs quantitative study. Carbonaceous material has been suggested as a requirement for precipitation of uranium, and perhaps for vanadium as well. Pommer, in Part 14 (p. 162), has established some approximate values for the reducing capacity of wood and lignite; now studies of the actual content of such materials in ore and adjacent rocks are needed to establish fully its sufficiency for one or both reductions.

Another study would be the silica balance in a given deposit. In some ore samples quartz is strongly corroded; in others grain growth has taken place. Both features have been observed within a given ore body. It should be possible to determine whether the total silica remains the same, with a balance reached, for example, between quartz solution and development of new silicates, or whether there is gross silica loss during mineralization. The devitrification of volcanic ash in horizons close to ore-bearing sandstones probably furnished silica for overgrowth on quartz sand grains and silicification of fossil wood (Murata, 1940; and Waters and Granger, 1953). In some samples ore minerals are outside the silica overgrowth; in others ore minerals rim the detrital quartz grains and the silica overgrowth apparently formed after the ore minerals or in a late stage of the ore process. More work is needed to document the history of silica deposition and solution. Such studies would provide further background for hypotheses of origin. Also such studies would help to assess the degree to which the ores are simply additions to the preexisting rocks and the extent to which rock constituents have been leached. Certainly calcite and gypsum have been removed in large quantities in some cases; otherwise the ore-forming process appears to have been an additive one. In Part 15 (p. 171, 173), for example, element anomalies reported chemically and spectrographically are positive except for calcium and sulfur, indicating removal only of interstitial gypsum.

Also of interest in the genesis of the ores is the "bleaching" that accompanies ore bodies. Unweathered ores are found surrounded by light-colored sandstones or green mudstone, particularly the large ore bodies in the Uravan belt—almost never by reddish sandstone or mudstone. The extent and nature of this "envelope" and its relation to ore has received much attention, but it deserves still more attention. In a stratigraphic section composed of alternations of "reduced" and "oxidized" rocks—that is, light-colored pyritic sandstones with carbonaceous material, and green shales, as opposed to hematite-stained sandstones and shales—it is extremely difficult to distinguish between primary features and subsequent changes. Although some of the red and gray coloration is undoubtedly primary, some alteration was probably effected by one or more of the following: diagenetic processes; alteration due to sulfur-bearing waters from the salt anticlines or oil and gas fields; bleaching accompanying ore formation; postore-preweathering bleaching; and the results of Quaternary weathering.

In some areas a strong positive correlation has been established between the thickness of ore and the thickness of green mudstone directly beneath. Furthermore, the boundary between green and adjacent red mudstone transgresses bedding. Under these circumstances it appears that the change from red to green has accompanied the emplacement of ore. Studies to date of chemical changes accompanying the alteration from red to green have shown little but disappearance of calcite and hematite as mineral species, plus a slight decrease in the ferric-ferrous ratio. Huff (1955) found a higher base-metal content (Pb+Zn+Cu) in bleached clays than in adjacent unbleached clays in one deposit. Clearly much more work is needed.

CHEMICAL AND MINERALOGIC CHANGES DURING OXIDATION OF ORE

The preceding papers show that the gross changes that occur during weathering have been worked out out theoretically, experimentally, and from field observation.

Uraninite and coffinite oxidize rapidly when exposed to air above the zone of saturation. In the presence of excess vanadium the resultant uranyl ion is fixed as difficultly soluble carnotite or tyuyamunite. If vanadium is deficient a host of uranyl compounds is possible, ranging through phosphates, arsenates, silicates, carbonates, sulphates, and hydrated hydroxides. In general these compounds are not so stable as the vanadates. Thus in a semiarid climate where little or no vanadium is washed out by circulating water vanadium fixes uranium; without vanadium, migration occurs.

Although the gross changes are known, much remains to be done to permit satisfactory prediction of the behavior of a given ore in a given matrix under a stipulated geologic environment. Among the problems is isolation of enough coffinite for satisfactory chemical analysis. It is so extremely fine grained and so intimately intermixed with other materials that there is still uncertainty concerning its nature. Coffinite has recently been synthesized (Hoekstra and Fuchs, 1956), so that material for analysis should soon be available. More needs to be learned about the mechanism of oxidation of uraninite and coffinite, as well as about their relative rates. Both alter early to dark-colored materials containing uranium (VI), but there appears to be a considerable proportion of the time involved in the weathering process during which the uranium-bearing material is not further characterized. The evidence for this is analyses of samples of "black ores" that show abundant V(IV) mineral species, or mixed V(III)-V(IV) species, but have no trace of carnotite or tyuyamunite. They may contain several percent uranium, present in the six-valent state, but there is no uranium mineral species identifiable. Presumably the uranium is present chiefly as amorphous anhydrous UO_3. The considerable duration of this oxidation stage is attested by the frequency of its occurrence.

Also, there must be a difference in oxidation rate between uraninite and coffinite, but so far the absence of free energy data on coffinite has prevented calculation of an oxidation potential stability boundary for it; the obscurity of its mineralogy and the complexity of the oxidation process have prevented conclusions from study of natural material, and the inability to synthesize it, until recently, has prevented laboratory studies.

The successive stages of oxidation of the primary vanadium hydroxy-oxide montroseite have been worked out in considerable detail theoretically, experimentally, and from natural materials. The relations are summarized well in figures 15 (p. 92) and 26 (p. 101). Because of the number of ionic species in solution that contain vanadium, a long list of possible or probable compounds can be drawn up, many of which perhaps will be found eventually as minerals. Among these "possible" mineral groups are metal vanadites, analogous to the recently discovered calcium vanadite simplotite. Combinations of vanadite ions with the other cations present in the system should be looked for in partly oxidized ores in alkaline environments. Two other obvious groups are corvusite and rauvite. So-called corvusite, the abundant "blue-black" material in so many ores that have been oxidized in place by damp-air oxidation, is poorly characterized. Two analyses of apparently pure phases of "corvusite" gave

$$V_2O_4 \cdot 6V_2O_5(+H_2O) \text{ and } V_2O_4 \cdot 5V_2O_5(+H_2O)$$

These combinations can be regarded as vanadyl analogues of the calcium vanadates, hewettite, and pascoite. If so, there may be as many species in the corvusite groups as have been recognized among the calcium vanadates. The same possibility of uranyl analogues of calcium vanadates exists in the material currently called rauvite—"a uranyl vanadate of uncertain composition."

Still other vanadiferous species could be postulated, but these three perhaps suffice to show that mineralogic study of vanadium species has not been completed.

Oxidation studies of copper minerals have not been emphasized, for in general they behave as in nonuraniferous copper ores, which have been much studied, with the obvious exception of the development of small amounts of oxidized copper uranium compounds such as johannite.

OXIDATION RATES

The small amount of information available through measurements of radioactivity and radium-uranium equilibrium (Part 13) indicates oxidation has taken place during the past 100,000 years at least. The data, although fragmentary, agree well with the conclusion from geologic data (Part 5, p. 78) that oxidation has taken place since the ores emerged above the water table during the Quaternary cycle of canyon cutting. Further indirect evidence comes from the fact that minerals out of chemical equilibrium occur side by side in many ores—minerals that alter rapidly in the laboratory under simulated natural conditions.

Unweathered ores, when dumped at the surface, alter markedly during a few months exposure. In fact, the uranium ores are such sensitive indicators of oxygen availability that they could be used to map in detail the controls of air movement underground. No trace of oxygen can move far through an ore containing uranium and nonsilicate vanadium before being used to produce a new mineral species.

A remarkable aspect of ore oxidation is the apparent uniformity of the oxidation reaction rates. The number of oxidation stages that can be discerned shows that each species in the sequence has a "half-life" of the same order of magnitude as that of the next higher stage. Indeed, it is almost as if the oxidation process has been carried on at near-equilibrium with a continuously rising oxidation potential, which is not the case, for the merest trace of oxygen produces an environment of high potential. The oxidation process, in the beginning, is the reaction between two extremes—the high potential of aerated water versus the low potential of unweathered ore. If reaction to equilibrium between entering air and the ore minerals took place instantaneously, there would be no intermediate phases—instead, but two sharply delimited facies: unweathered ore and fully oxidized material.

Specifically, uraninite is usually the first mineral to oxidize completely, followed by montroseite. Both of these react much more rapidly than the sulfides. If the vanadium hydrous micas and chlorites originally contained trivalent vanadium, which is doubtful, it oxidized very rapidly to valence four, inasmuch as all specimens analyzed so far contain tetravalent vanadium. The oxidation of paramontroseite to corvusite group minerals is slower than that of montroseite to paramontroseite, and that of corvusite to vanadates still slower. Inasmuch as each is the precursor of the other, the total vanadium involved in each stage is the same, so that the relative abundance of each species throughout the Plateau is a rough index of its lifetime. More quantitative studies are needed, but the relative rates given probably will not be changed.

NEAR-SURFACE EFFECTS

When ore is exposed to air above the water table, but below the reach of surface processes, oxidation takes place in an essentially closed system. That is, oxygen comes in and combines with minerals, but nothing moves out. Also, under these conditions, oxidation apparently takes place in place, with but minor diffusional movements over distances measured in inches, or perhaps, in extreme cases, a few feet. Maintenance of radioactive equilibrium within such ores, the presence of abundant water-soluble materials, the clear superposition of oxidation on an unaltered primary element distribution—these and other criteria have been advanced to document the case. From the economic standpoint, this conclusion is important, for it means that the weathered ore drilling target is the same as that for unweathered ore.

But when the descending erosion surface approaches ore, a series of changes set in about which little information is available. The effects of the zone of capillary water movement must be drastic, especially in a semiarid area, where water sinks in after each rain, and then evaporates back to the surface. As pointed out by Weeks (Part 5, p. 77) the effect must be especially great in host rocks with calcareous cement, where alkaline bicarbonate waters would be expected to complex and thus solubilize uranium. We can be sure the effects are marked, for all the "free" vanadium—that is, not in silicates and much of the carnotite—disappears somewhere between oxidized ore underground and oxidized ore at the surface.

How much vanadium is simply dissolved and moved away, and how much (if any) is fixed in hydrous micas and chlorites is at present a matter of conjecture. For vanadium at least it is known that a major change takes place near the surface; information concerning uranium is much less concrete. Study of the Happy Jack Mine (Part 16, p. 194) is the only one that has traced such changes. Nothing comparable has been done on a high vanadium occurrence. Furthermore, the magnitude of the changes in uranium content brought about by weathering near the surface at Happy Jack shows how misleading many outcrops may be. The persistence of vanadium silicates and of copper "stains" at the outcrop has led to the discovery of many ore properties that would otherwise have been missed; the relatively late development of low copper-low vanadium deposits in northwest New Mexico can be blamed on the absence, in part, of persistent indicator minerals.

VALEDICTORY

In concluding this report that has resulted from the concentrated effort of many scientists using the field and laboratory equipment of the atomic age, respect and praise are asked, not for the writers of this volume, but for the geologists who learned so much about the Colorado Plateau uranium ores and reasoned and speculated so well in the period from 1900 to 1920—Hillebrand, Ransome, Hess, Butler, and Coffin.

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