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Geology - Mineralogy

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GEOLOGICAL SURVEY

VOLCANIC DEBRIS IN URANIFEROUS SANDSTONES, AND ITS POSSIBLE
BEARING ON THE ORIGIN AND PRECIPITATION OF URANIUM*

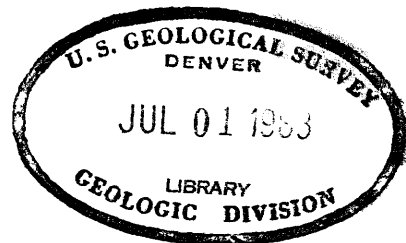
By

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August 1952

Trace Elements Investigations Report 170

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VOLCANIC DEBRIS IN URANIFEROUS SANDSTONES, AND ITS POSSIBLE
BEARING ON THE ORIGIN AND PRECIPITATION OF URANIUM

By Aaron C. Waters and Harry C. Granger

ABSTRACT

The possible relationships between uranium and vanadium ore deposits on the Colorado Plateau and the volcanic material which, in part, makes up the host rocks were investigated in 1951. It is suggested that the uranium and vanadium ore deposits have a complex origin and history, and that they were emplaced during the structural deformation and igneous intrusion of early Tertiary time.

Volcanic debris, now altered to clay minerals, has been recognized in the Salt Wash and Brushy Basin members of the Morrison formation and in the Shinarump conglomerate and Chinle formation. Field studies and microscopic examination of the ores indicate a relationship between the ore minerals and montmorillonite clay formed by devitrification of volcanic glass. The vanadium hydromica formerly called "roscoelite" is believed to be derived from montmorillonite.

A paragenetic sequence of events, shown by examination of thin sections of the ore-bearing sandstones, begins with cementation of the sand by calcite, followed by secondary enlargement of quartz grains. The new silica formed as overgrowths on the quartz grains was probably released by devitrification of the glassy volcanic material. At a later date solution of quartz grains and formation of vanadium hydromica and uranium bearing minerals occurred. Deposition of the ore minerals is probably related to a change in ground water conditions brought about by igneous intrusion.

During devitrification of volcanic ash, ground waters may have leached alkalis, uranium, vanadium, and other substances from the ash. The absence of blanket deposits of uranium and vanadium minerals implies either 1) re-activated circulation of metal-bearing ground water, or, more probably, 2) introduction of metal-bearing juvenile waters into the ground water system. Several additional problems must be investigated before final conclusions can be reached.

INTRODUCTION

From July to the end of November 1951, the writers visited many of the uranium-bearing localities on the Colorado Plateau (fig. 1) and collected samples of the ores, the sedimentary rocks associated with the ore, and the Tertiary igneous rocks that occur as intrusive masses in the sedimentary rocks at some localities. These samples are now being analyzed and studied.

Early in the work it was recognized that some of the Mesozoic sedimentary formations on the Colorado Plateau contain large amounts of volcanic debris; they thus record episodes of volcanism that were contemporaneous with the deposition of the sediments.

The uranium deposits of the Colorado Plateau occur chiefly in the upper part of the Salt Wash member of the Morrison formation, and in the Shinarump conglomerate, though they are by no means confined to these units. Each of these stratigraphic units contains appreciable amounts of volcanic debris, though their major constituents are non-volcanic. Each of them is also overlain by a so-called "mudstone" stratigraphic unit--the Chinle shale above the Shinarump, and the Brushy Basin clays above the Salt Wash--that contains a high proportion of altered volcanic ash.

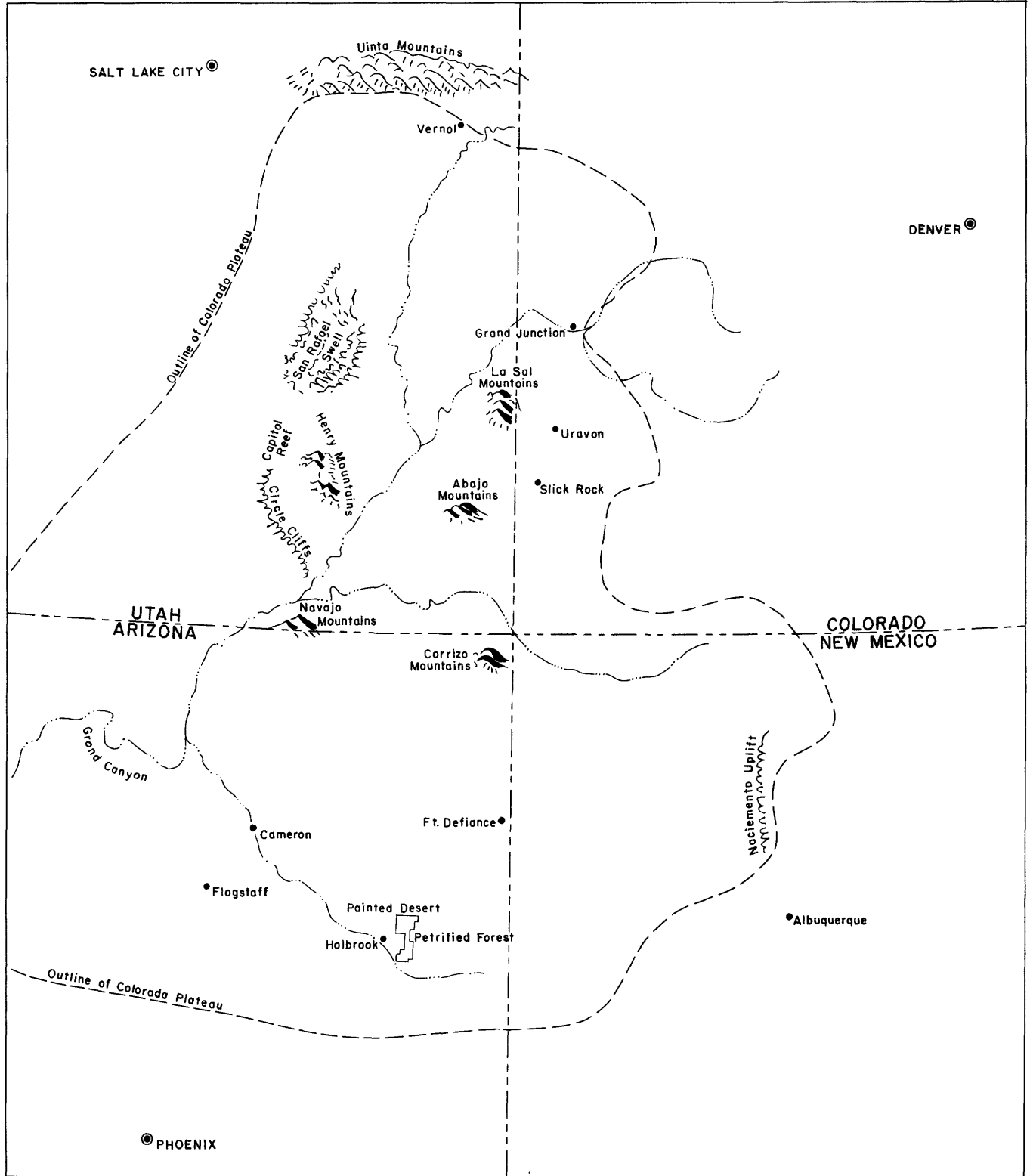


FIGURE 1- INDEX MAP, COLORADO PLATEAU.

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It was decided to investigate the beds containing volcanic debris in order to ascertain, if possible, whether the presence of altered volcanic ash had been of any importance in the concentration of the uranium. The work is unfinished, but some promising leads are outlined in this progress report.

Evidence indicating that volcanism took place during the periods when the host rocks for the "Plateau type" uranium deposits were accumulating is first assembled. The writers then show the possible bearing this volcanic activity and later igneous activity, particularly the intrusion of the laccolithic mountain groups, may have had on the origin of the ore deposits.

ACKNOWLEDGMENTS

The writers' knowledge of the geology of the Colorado Plateau was greatly augmented by two field excursions with C. B. Hunt and L. C. Craig, respectively. Mrs. Alice Weeks kindly supplied results of her studies of the clay mineral constituents of the ore-bearing rocks. An excellent suite of thin sections cut from ore-bearing rocks was kindly loaned by R. P. Fischer. To these people, and the many others who supplied helpful suggestions, the writers are indebted. This report concerns work done on behalf of the Division of Raw Materials of the U. S. Atomic Energy Commission.

VOLCANIC MATERIAL INCLUDED IN THE STRATIGRAPHIC SECTION

General field characteristics

The Brushy Basin clays are a thin-bedded series of argillaceous sediments with interbedded sandstone lenses. The volcanic origin of much of the argillaceous material (Hess, 1933, pp. 463-464; Stokes, 1944) is immediately suggested by two striking features: (1) the "popcorn" surfaces developed by the swelling of the clay where it is exposed to weathering at the surface, and (2) the variegated color of the clay, which is generally thinly layered in pastel shades of olive green, blue-green, smoky white, pale pink, creamy yellow, blackish purple, and maroon.

In the Chinle formation, too, especially in its lower part, are many argillaceous beds with the same characteristics (Camp, 1929; Allen, 1930). Among the most striking examples are the variegated beds of the Painted Desert and the Petrified Forest National Monument in northeastern Arizona. In some areas, however, the Chinle formation consists almost entirely of maroon, light red, or yellow beds of sandstone, siltstone, and shale whose constituents are chiefly quartz sand, silt, and non-swelling clays.

Although there is local and regional variation, both the Salt Wash sandstone and the Shinarump formation contain typically cross-bedded quartz sandstone with thin conglomeratic lenses and layers. Clay is generally present as a prominent constituent between the sand grains, and as tiny rounded pellets which are generally 2 to 5 times as large as the associated sand grains. Locally clay forms abundant galls, patches, and angular fragments distributed along the bedding of the sandstone. Interstratified with the sandstone, especially in the Salt Wash, are thicker layers and irregular lenses of argillaceous sediment ("mudstone"). These generally increase in

number toward the top of the unit. A few of the clay beds have the "popcorn" surfaces and variegated colors typical of the Brushy Basin clays; others are maroon or green beds of non-swelling clay.

Fossil wood is abundant in the Shinarump, and is also found at many places in the Salt Wash. In general it has been altered to coaly material, but in places it is silicified or replaced by carbonates. Some pieces of wood show black powdery edges that, in contrast to the coaly material, give off little or no volatile material when heated in a closed tube. Apparently the material is charcoal, though this identification has not yet been tested by X-ray methods. The presence of charcoal shows that some of the wood was partially burned prior to deposition. Locally the coaly material, and particularly the associated charcoal, are impregnated or replaced with uranium-bearing minerals.

In many places fossil logs, bits of charred wood, abundant 1/2- to 3-inch clay galls, and larger angular fragments of clay are mixed with the normal sand and quartz pebbles in heterogeneous beds that are locally called "trash piles". In some of the trash piles large and small fragments of fossil bone are found. Many of the ore deposits are associated with the trash piles. The uranium and vanadium minerals have impregnated or preferentially replaced the charred wood, certain kinds of clay galls, and bone.

The individual sandstone beds of the Shinarump formation are highly lenticular, and in places lie in definite scour channels eroded into the underlying Moenkopi sandstone, or into beds of the Shinarump itself. These scour channels are generally only a few feet, or at most, a few tens of feet deep.

Most authors agree that the Shinarump formation was deposited by a system of braiding streams. These dropped their heterogeneous loads in

the stream channels, filling them, and then breaking out to scour and fill new ones. Thus the streams spread widely over the depositional plain in intricate anastomosing courses, laying down a thin deposit of dominantly coarse debris which shows a bewildering interfingering of coarse and fine pebbly sandstone lenses, channel unconformities, clay seams, and trash piles.

By contrast the Salt Wash is a much thicker stratigraphic unit, and consists in large part of normally bedded fluviatile sandstones, siltstones and clays. Nevertheless individual beds within it may show the rapidly developed scour and fill features, the trash piles, and other characteristics indicative of swift-flowing overloaded streams. These characteristics are in general more common in the upper part of the Salt Wash, where it grades into or inter-fingers with the overlying Brushy Basin clays. The upper, more "trashy" portion of the Salt Wash is also the favored locale for uranium deposits.

The stratigraphic work of L. C. Craig and co-workers (1951) shows that the Salt Wash member was deposited as a broad, gently-sloping alluvial fan which spread northeastward from a general source in southern Utah and adjacent Arizona. Craig also shows that the sand and pebbles were derived chiefly from reworked sedimentary rocks.

Longwell (1928, p. 56), Allen (1930, p. 288) and others think that the Shinarump-Chinle sequence had its source in highlands to the south and southeast, and that the sediments were graded toward the Upper Triassic California sea in broad fans and deltas.

A striking and oft mentioned question regarding the Shinarump formation is how a stratigraphic unit of such wide areal extent--over 100,000 square miles (Gilluly and Reeside, 1928, p. 67)--can be composed of such a small thickness--generally less than 100 feet--of coarse pebbly and "trashy" sediments that seemingly indicate a flood type of deposition from swiftly flowing torrents.

In the writers' opinion the heterogeneous character of the Shinarump sandstones, and of those comprising parts of the Salt Wash, recall the kind of debris carried by streams whose headwaters have been showered with fine pyroclastics during an episode of explosive volcanic activity. After an explosive eruption of ash and pumice the rivers draining a volcanic area are commonly choked with a slurry of shards, pumice lapilli, and fragments of trees killed by the ash shower, all intermixed with the normal sand and gravel constituents that the stream was carrying prior to the eruption (Segerstrom, 1950; Anderson, 1933; Wolfe, 1878). Such streams, armed with abundant cutting tools in the form of floating and suspended bits of pumice, glass shards, and lava fragments, erode the upper part of their courses rapidly (Segerstrom, 1950, p. 128), but on emerging onto a plain they quickly deposit their load, spreading it widely as channel fills in braided courses. These interfinger with finer deposits formed by bank overflow, and in places with thin seams of ash deposited directly from the air.

The alluvial deposits on the intermontane plateaus of the Andes, the Tertiary and Pleistocene water-laid tuffs just east of the Cascade Mountains in Oregon, and the deposits on the alluvial plains surrounding the Javanese volcanoes have much in common with parts of the Shinarump and Salt Wash stratigraphic units as far as details of bedding, heterogeneous sizing of particles, and intermixture of old detrital material with new volcanic debris and fragments of wood and bone are concerned. In rocks as old as the Salt Wash and Shinarump, however, these features are much more difficult to recognize because volcanic glass in the form of shards and pumice has not survived. It has long since been devitrified, mostly to montmorillonite clay.

Colorimetric tests for montmorillonite

Colorimetric tests for montmorillonite with benzidine solution (Hendricks and Alexander, 1940; Mielenz and King, 1951) were made constantly in the course of the field work. The method used was to squirt a saturated water solution of benzidine on the outcrop. If montmorillonite is present the wetted area should turn bright blue. However, the benzidine test is subject to considerable error in interpretation (Page, 1941), chiefly because of the interference of certain oxidizing or reducing elements present as impurities in the clay, the occurrence of "mixed lattice" clay minerals, and the lack of control of acidity of the sample (Mielenz and King, 1951, pp. 17-21).

Nevertheless, because of the ease with which large numbers of samples can be tested in the field, the method merits attention, and from a statistical point of view the results of many tests can lead to worthwhile generalizations, although the accuracy of any individual test is open to question. We were able to make many hundreds of tests in widely spaced localities but because of the difficulties inherent in the method, the following generalizations should be interpreted as only of tentative value.

Chinle formation

The widespread light-colored (green, light blue, smoky white, pale gray) clays with "popcorn" surfaces that are so characteristic of the lower part of the Chinle formation in northeastern Arizona and southeastern Utah almost invariably react strongly to benzidine. They were tested in many widely separated parts of the Plateau from Cameron, Arizona, on the southwest to the foothills of the Uinta Mountains on the northeast, and from Capitol Reef National Monument, Utah, on the west to the Nacimiento uplift of

northern New Mexico on the southeast. In places, however, the Chinle also contains many beds of red or green clay that weather to small platy chips instead of developing swelling surfaces. These generally do not react to benzidine, or else give faint indefinite colors. The non-reactive beds greatly predominate in some areas.

Brushy Basin member

Light-colored clays of the Brushy Basin sequence reacted strongly to benzidine at nearly every locality where they were tested. Some beds appear to be nearly pure bentonites, others are mixed with varying amounts of silt, sand, and non-reactive clays. Many of the red and purple beds interstratified with the lighter colored clay also react, although the blue color is partly masked by the iron oxides.

Shinarump formation

The conglomerate and sandstone of the Shinarump formation generally contains thin clay seams, small clay pellets, and, in places, clusters of 1/2- to 2-inch clay galls and even much larger angular fragments of clay. Much of the formation also contains clay as a matrix between the sand grains, but some sandstone beds are free of interstitial clay. Marked differences in the reaction of these clays to benzidine occur from place to place, and even within the same outcrop. In general, the matrix clay and the small pellets less than 1/4 inch in diameter react, though many exceptions were noted. In some outcrops two or more kinds of clay galls may be clustered together in the same lens of "trashy" sandstone. One may react to benzidine, another not at all, and a third one may react slightly, or may contain small

highly reactive pellets in a non-reactive matrix. In places it can be established that the non-reactive fragments are pieces of shale and siltstone torn up and incorporated from the underlying Moenkopi formation.

With only a few exceptions the thin clay seams, 1/4 to 2 inches thick, that locally separate the beds of sandstone are strongly reactive.

Salt Wash member

The Salt Wash sandstones and interbedded shales and "mudstones" have been systematically tested with benzidine only in the area directly south of the "Four Corners" and in a few parts of the "Uraivan Mineral Belt" (Fischer, 1950).

In general the prominent beds of red and green shale or "mudstone" interstratified with the prevailing light-colored sandstones do not react to benzidine, or else they show only faint indefinite bluish-gray colors. In places pellets and small fragments of material within the clay are strongly reactive. In the "Four Corners" area the sandstone contains numerous thin seams and partings of light green clay, generally less than 2 inches thick, that react strongly to benzidine. One such parting composed the upper half-inch of a 7-foot bed of green shale, the remainder of which was not reactive. In the areas studied, benzidine-reactive clays are both thicker and more numerous in the upper part of the Salt Wash than they are in the lower part.

In most places that were tested the matrix clay between the sand grains is strongly reactive, but exceptions occur. Fragments of clay in trash piles are commonly reactive, although, as at many localities in the Shinarump, non-reactive fragments are not rare.

To summarize and generalize from this admittedly inadequate data, it appears that both the Shinarump and Salt Wash were derived chiefly from a sedimentary landmass (See Craig, et al., 1951, p. 42.) which contributed quartz pebbles, sand, and silt, and also clays that do not react to benzidine. In the source areas for both formations, however, volcanic activity appears to have broken out, and the sands, gravels, and clays derived from the erosion of the old sediments were diluted and mixed with new accessions of shards, pumice lapilli, and fragments of glassy lava which have since altered to montmorillonite.

As pyroclastics covered more and more of the source area the type of sedimentation gradually changed to the bentonitic clays and siltstones characteristic of the lower Chinle and Brushy Basin sequences.

This sequence of events, suggested by field characters and the benzidine test, is amply confirmed by X-ray and petrographic evidence, as will now be shown.

X-ray investigations

X-ray studies of clay samples from the Jurassic and Cretaceous formations at several localities in southwest Colorado and Utah have been made by Alice Weeks of the U. S. Geological Survey. Mrs. Weeks' preliminary results with respect to the mineralogy of the clays from the Brushy Basin and Salt Wash members of the Morrison formation are tabulated below (tables 1 and 2).

As can be seen from these tabulations, all but 4 of the 17 samples of Brushy Basin clays contain montmorillonite. Some of them appear to be bentonites, in others the montmorillonite is mixed with hydromicas and kaolinite.

On the other hand the chief clay mineral in the Salt Wash samples tested was hydromica. Montmorillonite is reported in only one sample.

Table 1.--Mineralogy of clay samples from the Brushy Basin member
of the Morrison formation

(Based on X-ray studies by Alice Weeks)

<u>Locality</u>	<u>Sample number</u>	<u>Minerals</u>
Woodside anti- cline, Utah	(L537	Montmorillonite, hydromica, quartz, and calcite
	(
	(L535	Montmorillonite, hydromica, quartz, and calcite
	(
South of Floy, Utah	(L442	Montmorillonite, quartz, and kaolinite
	(
	(L443	Montmorillonite, quartz, and kaolinite
	(
	(L444	Montmorillonite, hydromica, and quartz
	(
	(L445	Montmorillonite, quartz, and calcite
	(
	(L446	Montmorillonite and calcite
	(
	(L447	Montmorillonite, hydromica, quartz, and calcite
Kane Springs, Utah	L479	Montmorillonite and quartz
La Sal Creek, Utah	L474	Montmorillonite and quartz
Dry Creek anti- cline, Colorado	L464	Hydromica (?) and quartz
	(L468	Kaolinite, hydromica, and quartz
	(
	(L469	Kaolinite, hydromica, and quartz
	(
Dolores Group mines, Colorado	(L470	Montmorillonite and quartz
	(
	(L539	Montmorillonite
Unawep, Colorado	L455	Montmorillonite and quartz
Escalante Forks, Colorado	L460	Kaolinite and quartz

Table 2.--Mineralogy of clay samples from the Salt Wash member
of the Morrison formation

(Based on X-ray studies by Alice Weeks)

<u>Locality</u>	<u>Sample number</u>	<u>Minerals</u>
Woodside anti- cline, Utah	{ L534	Hydromica, quartz, and calcite
	{ L533	Hydromica, quartz, and calcite
	{ L448	Hydromica and quartz
South of Floy, Utah	{ L449	Hydromica and quartz
	{ L450	Hydromica, montmorillonite kaolinite, quartz, and calcite
	{ L451	Hydromica, quartz, and calcite
	L480	Hydromica, quartz, and calcite
Kane Springs, Utah	L475	Hydromica, quartz, and calcite
Dolores Group mines, Colorado	L471	Hydromica, kaolinite, quartz, and calcite
Unaweep, Colorado	L456	Hydromica, quartz, and calcite
Escalante Forks, Colorado	L461	Hydromica, kaolinite, and quartz

In a general way these results confirm the benzidine tests, which indicated that the Brushy Basin clays are largely bentonitic, whereas the thick beds of red and green clay interstratified with the Salt Wash sandstones are non-reactive. Benzidine tests showed, however, that many of the thin clay seams and some clay galls in "trash piles" of the Salt Wash are strongly reactive. It will be interesting to obtain X-ray data on these highly reactive materials.

Mrs. Weeks' results definitely establish the presence of montmorillonite as a prominent constituent of Brushy Basin clays. It remains to show that the montmorillonite is the product of devitrification of volcanic glass. This has been done by examination of the clays in thin sections.

Petrographic evidence

A few thin sections, ground in oils so that no water could touch them, have been cut from samples of the Shinarump, Chinle, Salt Wash, and Brushy Basin stratigraphic units. In addition, through the kindness of Richard P. Fischer, the writers had the opportunity to examine a large number of thin sections of uranium-vanadium ores from the Salt Wash. These were prepared with water in the usual way.

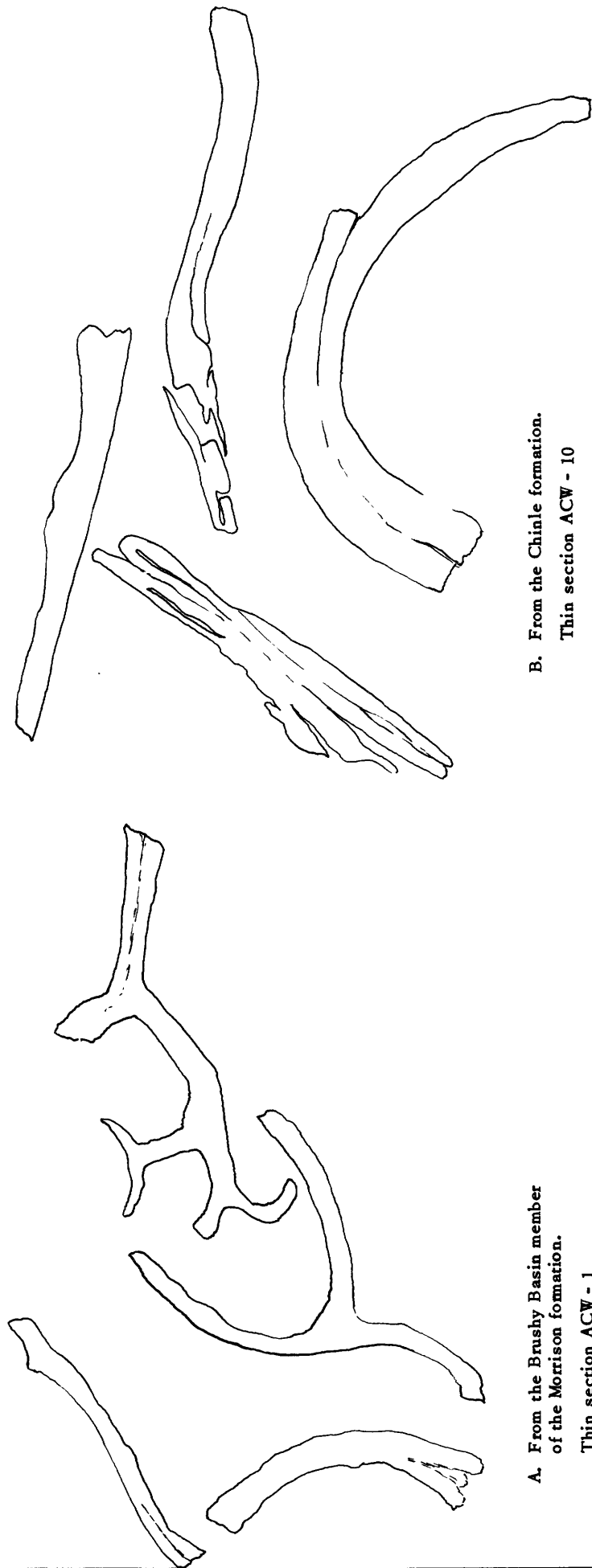
The thin sections give clear evidence of the presence of abundant volcanic debris in each of the four stratigraphic units investigated. However, except for thin clay seams, and some interstitial clay between the sand grains, volcanic material is not abundant in the Salt Wash member except near its top.

Chinle and Brushy Basin units

Fragments of altered volcanic glass, and bits of microlite-filled lava, intermixed with varying amounts of non-volcanic constituents appear in every section cut in oils and more sparingly in the sections cut in water.

The volcanic glass is completely altered, chiefly to rather coarse plates of a clay mineral of moderate birefringence, and with indices of refraction within the range given for montmorillonite (Ross and Hendricks, 1945). Despite complete devitrification, the characteristic shapes of shards, and the bubbly texture of pumice remains. The textures are beautifully preserved in some specimens (figs. 2 and 3), indistinctly in others. Small bits of porphyritic lava and less commonly pieces of devitrified spherulitic obsidian are even better preserved. Their textures are unmistakable even in fragments whose feldspar phenocrysts are completely altered to clay (fig. 3). Bits of welded tuff are present in some specimens (fig. 3), and fragments of trachytic textured lava that were reheated sufficiently during transport in the eruption cloud to cause decomposition of the ferromagnesian minerals to powdery black aggregates (Williams, 1929, pp. 193-198) are seen in a few specimens.

The magmas that produced these pyroclastics were apparently highly feldspathic, quartz-free or quartz-poor types. Sanidine, andesine, albite, and biotite are the chief phenocrysts, but in most rocks the feldspars are so badly altered that precise identification, using the inadequate equipment available in Denver, is impossible. Hypersthene and basaltic hornblende have been identified in one rock. Quartz occurs as phenocrysts in a few bits of spherulitic lava. The most common texture is a mat of tiny feldspar microlites in either a hyalopilitic or very fine-grained trachytic arrangement. About half of the feldspar microlites show the nearly square cross sections characteristic of sanidine, the rest are sodic plagioclase. More work needs to be done, but the available evidence indicates that the lavas were chiefly biotite latites and biotite keratophyres, with perhaps some admixture of andesitic and dacitic materials.



A. From the Brushy Basin member
of the Morrison formation.

Thin section ACW - 1

B. From the Chinle formation.

Thin section ACW - 10

Figure 2 -- Glass shards altered to clay minerals.

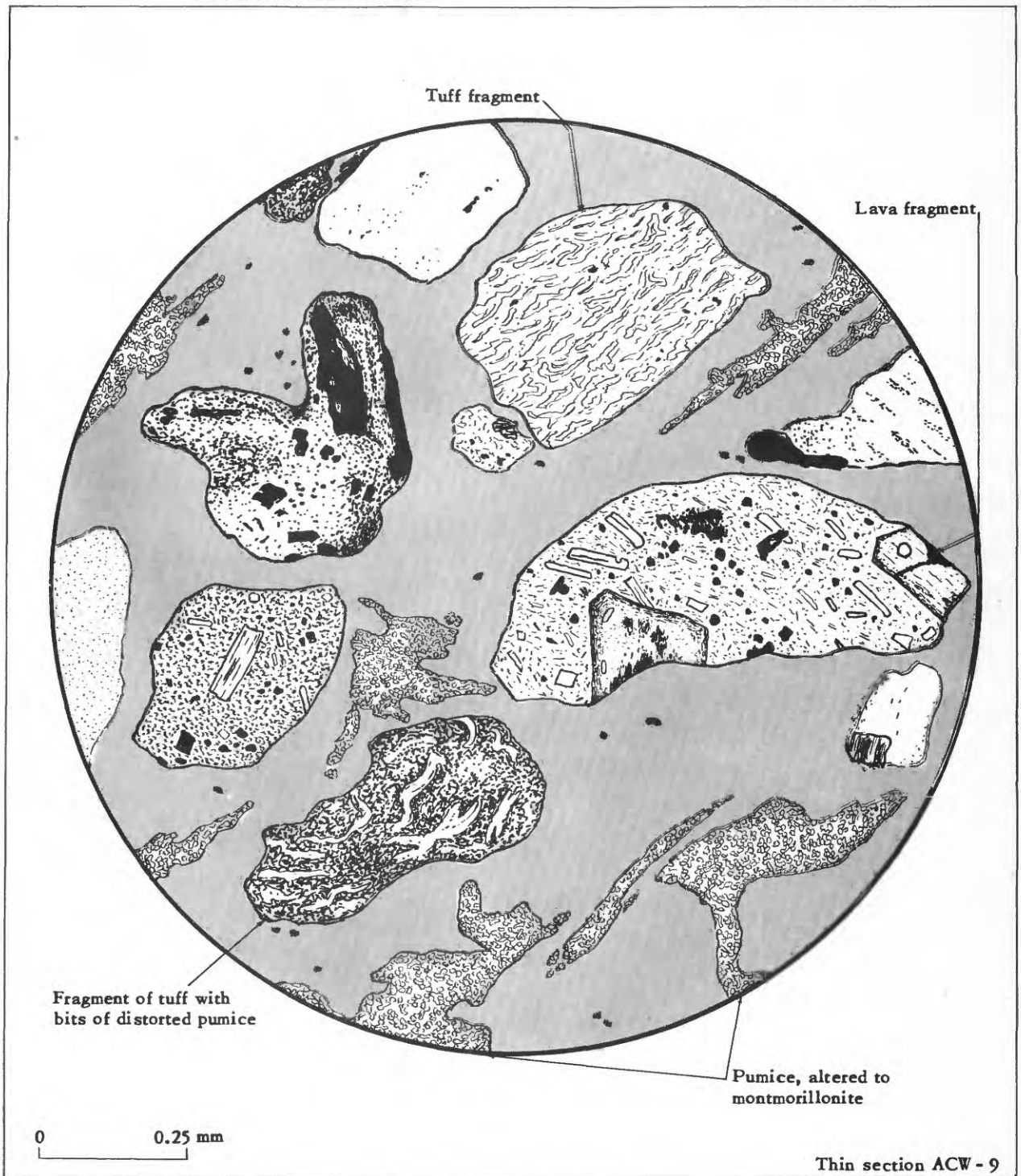


Figure 3 -- Devitrified pumice lapilli tuff from the Chinle formation, Petrified Forest National Monument.

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The source of the volcanics cannot be determined with the meagre data at hand, but the proportion of volcanic material in the Chinle appears to increase toward the south and southwest. At the Petrified Forest National Monument the Chinle formation consists in part of moderately coarse pumice lapilli tuffs containing abundant fragments of "burned" lava and welded tuff, mixed with bits of pumice as much as 1 centimeter in size. It seems unlikely that these coarse but fragile constituents could have been transported far.

A few scattered observations suggest that the volcanic material of the Brushy Basin sequence thickens and coarsens to the west and southwest.

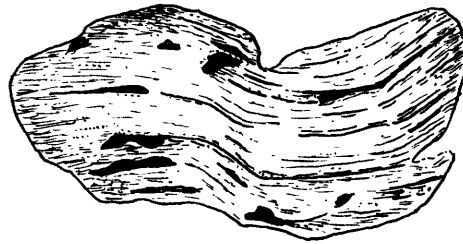
Shinarump and Salt Wash sandstones

Thin sections of clayey sandstones from the Shinarump formation and from the ore-bearing layers of the Salt Wash member also show volcanic debris, but it is not as easy to recognize as in the Chinle and Brushy Basin clays. The clayey matrix between the sand grains generally shows few if any structures characteristic of shards and pumice, though in some rocks, for example, the basal beds of the Shinarump at Fort Defiance, Arizona, small clay pellets in the sandstone show well preserved pumice structure. In a permeable rock like sandstone, it is not surprising that the fragile glass textures would be largely destroyed. They are obliterated in bentonites which have fluffed up by wetting at the ground surface, and in a permeable sandstone with interstitial ash there would be every opportunity for water to enter and destroy the structure after devitrification.

Although the textures characteristic of pumice and shards may be destroyed, fragments of altered lava can nearly always be found in the clayey sandstones. Furthermore euhedral phenocrysts of biotite, sanidine, and plagioclase, some of them with bits of lava still sticking to them

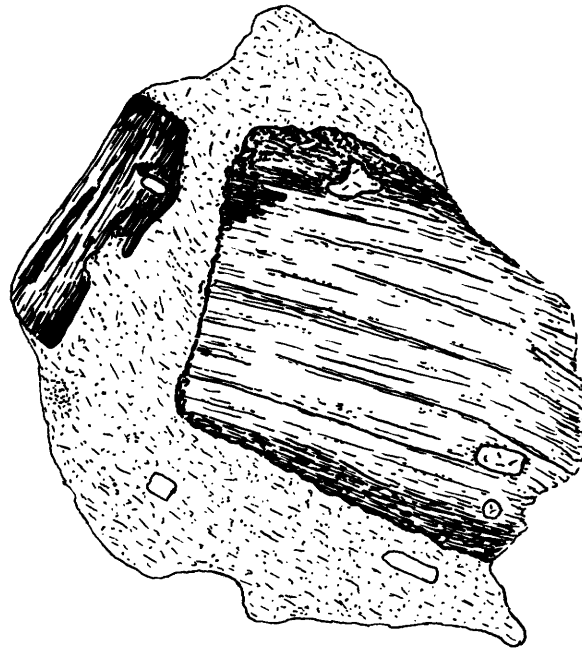
(fig. 4), contrast sharply with the non-volcanic constituents of the sandstones. The main non-volcanic constituent is quartz in well rounded or subrounded grains. It generally makes up 85 to 90 percent of the sandstone. Chert and microcline are abundant locally, and are present in small amounts in nearly every slide. Minor accessories include zircon, staurolite, tourmaline, and garnet. Sillimanite and apatite are commonly present as inclusions in quartz grains. This assemblage of well rounded, weathering resistant minerals contrasts strikingly with the easily destroyed euhedral books of partially chloritized biotite (fig. 4), the half kaolinized sanidines and plagioclases, and the fragile bits of pumice. Obviously reworked sedimentary materials prepared by repeated weathering and long continued wear have been adulterated with easily destroyed new materials of volcanic origin.

Nevertheless, not all of the fine-grained constituents of the Shinarump and Upper Salt Wash sandstones are volcanic. The Salt Wash, particularly, contains abundant beds of clay and silt, most of which do not react to benzidine. From the little petrographic work that has been done these appear to be composed chiefly of a clay mineral of higher refringence and birefringence than the montmorillonite formed from shards and pumice. Alice Weeks' studies indicate that this mineral is hydromica. It was probably derived from the reworking of older marine shales. Hydromica is sometimes present in pellets and flakes, and as a filler between the quartz grains of the sandstone, but, at least near the ore deposits, the common interstitial clay appears to be montmorillonite.



A. - Note slight rounding.

0 0.25 mm



B. - Biotite phenocryst partly enclosed in devitrified glass matrix.

0 0.25 mm

Thin section ACW - 9

Figure 4 -- Altered biotite of volcanic origin in sandstone of the Salt Wash member of the Morrison formation.

DESCRIPTION OF THE ORES

Features visible in the field

Most ore bodies are small--a few feet thick, and a few tens (rarely hundreds) of feet long and wide. The larger ore shoots show a rough control determined by the bedding, and they tend to cluster in certain favorable beds. Although the ore is commonly described as lying in "channels", those deposits for which stope maps or geologic maps are available (Fischer, 1950A, p. 8), rarely show any resemblance to the undulating, more-or-less continuous "shoestring" type of ore body generally visualized by the word channel. Instead, minable ore is generally concentrated in flat ore shoots whose long dimension is seldom much greater than their width.

The small but rich ore bodies that occur in and around fossil logs, the small ore bodies called "rolls" (Webber, 1947, fig. 63), and the ore bodies which occur in deep channels in Monument Valley (Witkind, 1951) are exceptions. These may be many times as long as they are wide.

In detail the ore cuts across the bedding despite the fact that stratification appears to be the dominant structural control. In places this cross cutting relation is a gradational one; a common case is where ore penetrates farther along a sandstone bed with a high clay content than along an adjoining bed with less clay--the ore gradually plays out in the less favorable bed. In "rolls", however, the ore boundary is generally sharp, and it transects the bedding in a smooth curve. A conspicuous banding of the ore minerals may be developed along the edges of the curve.

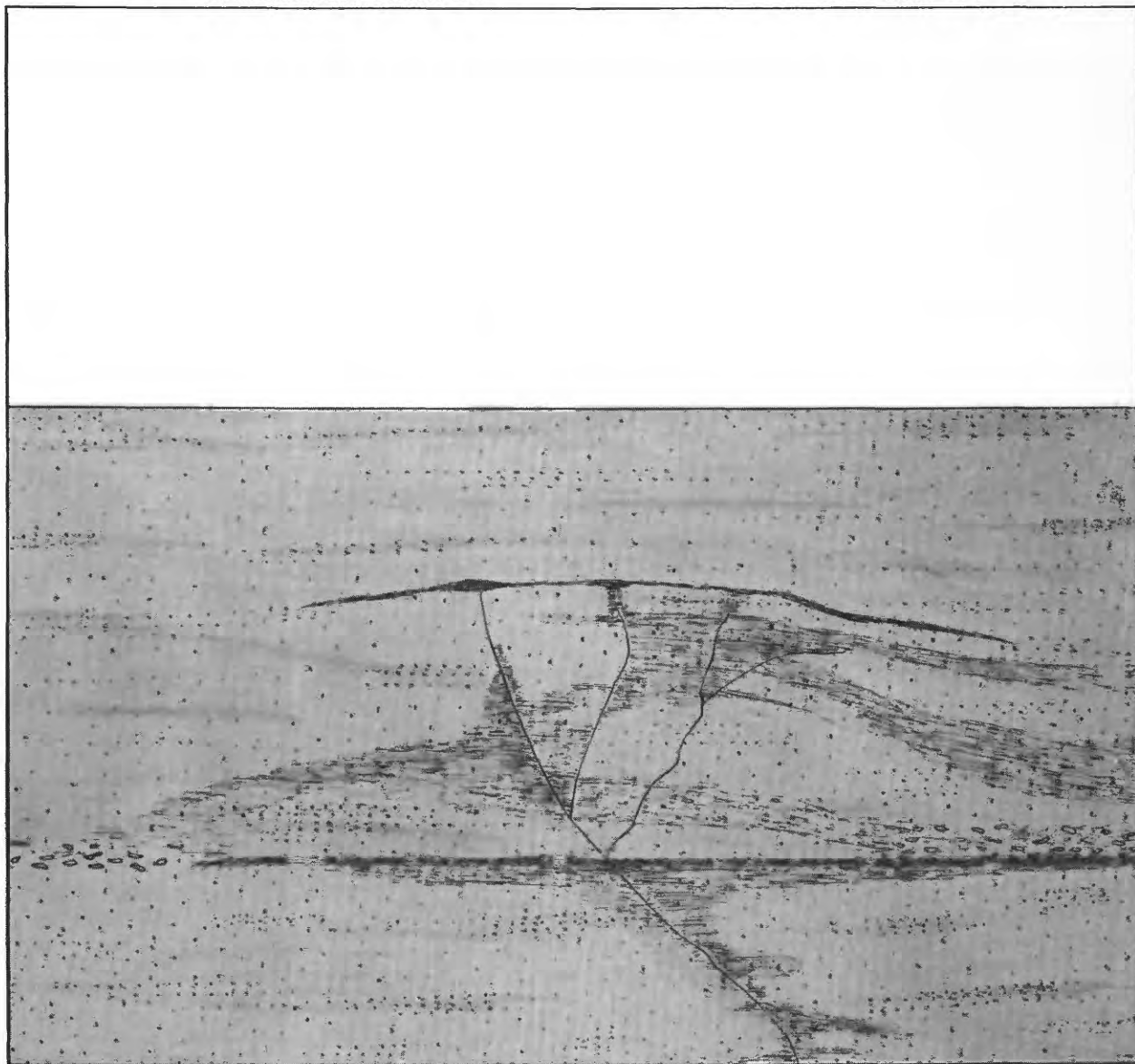
In most mines fracture control is not evident, but, as it is easily overlooked it may be more common than has been recognized. That fractures have, in places, served as feeding channels for the ore solutions is

demonstrated by the mineralization so well displayed along fault gouges in the Rajah mine, by the group of closely spaced mineralized joints in the White Canyon area (Benson et al., 1951), and on a much smaller scale by the occurrence of features such as those sketched in figure 5 from the Dolores group.

In several rolls that the writers have examined, a prominent joint, or series of joints, lined with a thin film of white mineral which resembles dickite or alunite, lies along the axis of the roll. The sandstone adjacent to these joints is commonly bleached and softened. In places the shale floor beneath the ore body is also cut by a plexus of small fractures that show bleaching, films of dickite(?) or alunite(?), staining by copper or vanadium minerals, and other evidences of mineralization. These features suggest that, at least locally, the ore-bearing solutions travelled across the beds, emerging from tight fracture channels into permeable beds where the solutions could spread out and deposit their ore, and then left by another series of small fractures on the other side of the bed. It should be emphasized, however, that the walls of many ore deposits have been magnificently exposed by mining operations, but there is no trace of fracture channels in either floor or roof. For these it appears that ore-bearing solutions must have travelled along the bed.

Relation of ore to fossil wood

Some of the richest ore is closely associated with organic matter. Fossil wood enclosed in ore is generally richly mineralized except where the wood has been strongly silicified or replaced by carbonate prior to mineralization. In places, (Happy Jack mine at White Canyon and Seven-mile Canyon deposits near Moab, for example) the wood is replaced by easily visible masses of pitchblende; or by associated sulfides such as pyrite, chalcocite,



0 1 2 3 4 5 6 7 8 Feet

Figure 5 -- Sketch showing local fracture control of ore, Dolores group, Uravan, Colorado.
Dark areas indicate ore minerals.

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or galena, but more commonly the woody tissues are impregnated, replaced and partially destroyed by microscopic black grains or even by ultramicroscopic uranium and vanadium-bearing substances. Commonly the mineralization extends out some distance from the fragments of wood as impregnations in the surrounding sandstone. Ore-bearing fossil logs commonly have mineralized hulls of this kind extending a few inches or even a few feet into the sandstone.

At many places, however, the woody material seems to have largely rotted out and its place is now filled with clay and calcite mixed with carnotite and other ore minerals. Some of the richest ore bodies are "logs" of this kind.

A close relationship between small bits of organic material and ore is visible in many deposits that do not contain logs or large wood fragments. It is possible that all of the ore-bearing sandstones contain at least a little carbonaceous material.

Observations at several widely spaced localities (for example, Scenic Claims at White Canyon, Petrified Forest National Monument, Uinta Basin, and others) indicate that charcoal and the charred edges of pieces of fossil wood are much more strongly mineralized than the coaly pieces of wood in the same deposit. This relation supports Frederickson's (1948) idea that substances with sheet structures such as charcoal and montmorillonite are able to extract uranium from solution because of the ease with which the large uranyl ions can penetrate between the layers of montmorillonite or charcoal. Here they are supposedly trapped and held by weak electrical charges. This theory may have considerable merit, but much work needs to be done before we understand how uranium minerals are accumulated and held by organic materials. (See McKelvey and Nelson, 1950; Battelle Mem. Inst., 1948-1949.)

It has been assumed by many that decay of organic material causes a change in the pH of the surrounding solution, thus inducing precipitation of uranium in and around the wood, but when one considers the vast volume of solution that is probably involved in precipitating the uranium found in a richly fossiliferous log, this mechanism seems inadequate. A more promising lead, perhaps, would be to appeal to humic colloids and geochemical sorption phenomena. It is well known experimentally that a number of organic compounds and sols have the power of removing uranium almost completely from solution (Batt. Mem. Inst., 1948-1949).

In the Shinarump and upper Salt Wash units there would be excellent opportunity for the abundant bits of wood and other organic materials to slowly decay and produce various kinds of humic colloids, resins, and soluble organic compounds that might then be distributed widely through the sandstone in ground water. Such potential adsorbants of uranium might have been held in these sandstones until the igneous intrusion, structural deformation, and erosion of Tertiary time, for there probably was little opportunity for free circulation of ground water through the highly impermeable formations above and below these units. In addition to its potentialities of precipitating uranium through sorption phenomena and straight chemical reaction, the organic-rich connate water would also be of strongly reducing nature. Perhaps the change of redox potential in a body of ore-bearing solution that might enter and mix with such a body of connate water would be enough to induce precipitation.

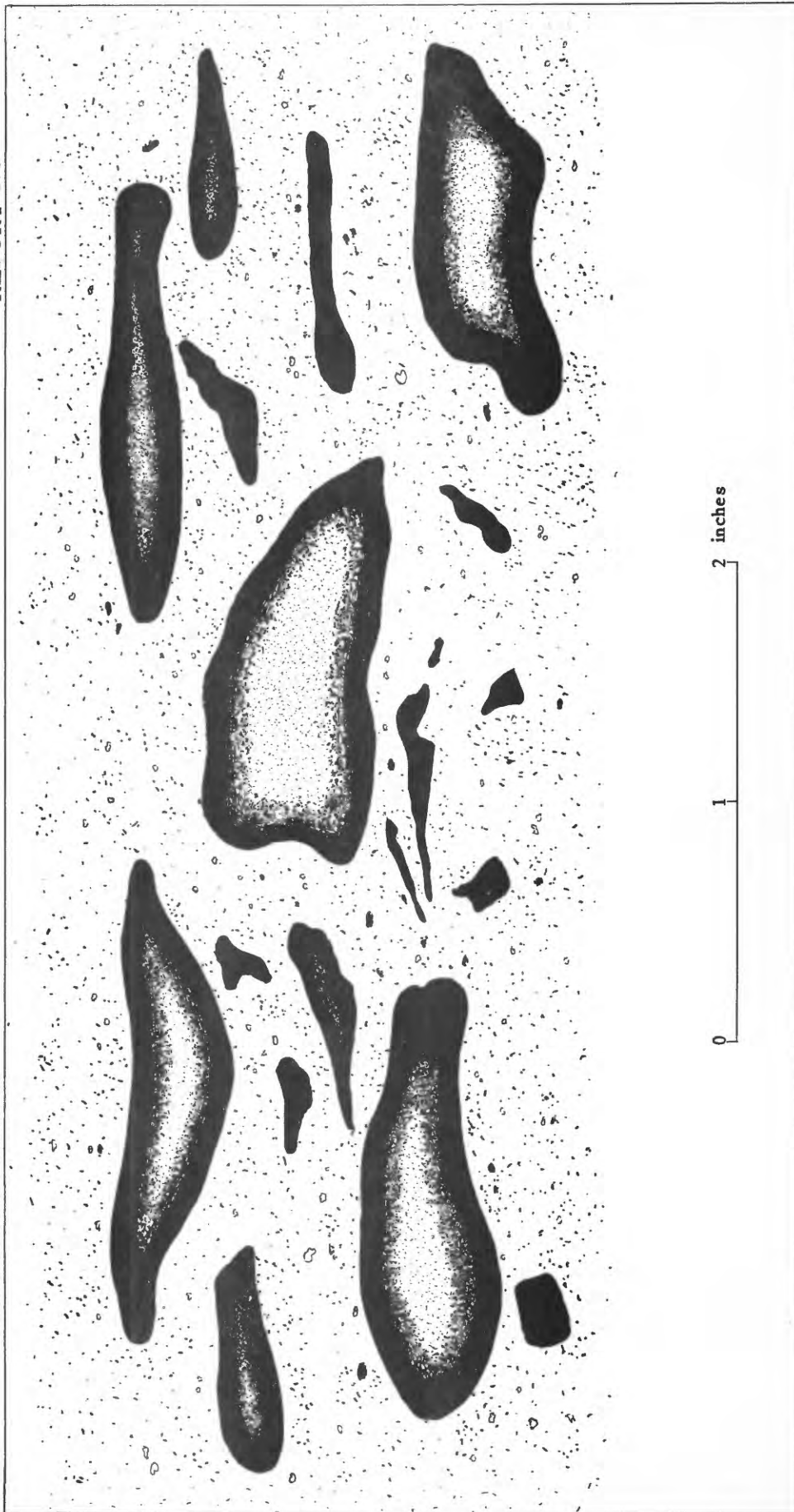
Relation of ore to clay

Certain kinds of clay minerals, as well as the fossil wood, appear to have been able to trap and cause precipitation of uranium and vanadium minerals from solution. Characteristically the ore minerals occur as impregna-

tions or replacements of the clayey matrix of impure sandstones. The preferential impregnation or replacement of clay by both uranium and vanadium minerals is obvious in the field. Not only is the clay matrix of a sandstone mineralized, but thin clay seams, and certain kinds of clay pellets and clay galls that abound in the "trash piles" have been strongly mineralized (fig. 6). Not all clay beds are thus favored, however. The original composition of the clay appears to be a major factor. In many ore deposits a thin clay seam, 1/2 to 2 inches thick, will be a high-grade ore, whereas another clay bed of less favorable composition separated from the first by only a few inches of mineralized sandstone, is almost completely barren. The clay galls in a single sandstone bed are differentially mineralized also. At many deposits one clay gall may be altered to dull, brownish-black, slickensided pellets richly impregnated with vanadium and uranium minerals, whereas an adjacent clay gall of different composition is only slightly mineralized.

The ore-bearing solutions, however, apparently were unable to penetrate deeply into the relatively pure clay beds and galls even when these were of favorable composition. Seams of clay more than 2 inches thick are rarely mineralized throughout, unless their permeability has been heightened by an appreciable content of sand and silt. The edges of clay galls are commonly mineralized to depths of only 1/4 to 1/2 inch, leaving pale colored unmineralized centers that contrast strikingly with the strongly mineralized brownish-black rims (fig. 6).

Chemical experimentation combined with detailed field work is needed to find out just what effect both fossil wood and clays of different kinds have had on the precipitation of uranium. That they have clearly had some effect is obvious from the field relations.



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Figure 6 -- Clay galls in sandy matrix, Georgetown Group, Slick Rock, Colorado.
Note impregnation of margins of clay galls by vanadium minerals.

Microscopic features of the ores

Most of the ore minerals deposited in the clay and fossil wood are of microscopic dimensions; many are tiny opaque specks so small that an oil immersion lens is needed to individualize them. Hence they are too small to identify readily by petrographic methods alone. Perhaps a promising method of making progress in the identification of these minerals would be a study of the ores in thin and polished sections, followed by mechanical separation of the finer-grained minerals by crushing and centrifuging in heavy liquids, and study of the concentrates by X-ray and petrographic methods.

None of this kind of work has been done for this report, and only about 40 thin sections have been studied in detail, though a fairly large collection loaned by Richard P. Fischer has been looked over superficially.

Although the ores are commonly described as "carnotite ores", it is the writers' experience that carnotite is not a prominent mineral except in deposits that have been altered. In these it occurs chiefly as joint fillings, and as haloes and impregnations around other minerals. In many examples it is clearly derived from the fine-grained "blue-black" ores by secondary processes as was pointed out by Frank L. Hess (1913, p. 148) in 1913:

"Faces along many joints of the vanadiferous sandstone are covered with canary-yellow, minutely crystalline carnotite which is clearly secondary and has evidently been leached from the ore-bearing rock Here (on Fall Creek) all joints, even those that are closely spaced, are brightly coated with carnotite. The vanadium ore is peculiarly black on these claims The carnotite seems to be closely connected with the dark or black ores. The original mineral from which the carnotite was derived is unknown."

Mineralogic work to date seems to show that the original fine-grained blue-black ores are made up chiefly of a vanadium clay (the roscoelite or vanadium mica of early workers) plus several other minerals, chiefly hydrous vanadium and uranium oxides. Pyrite (fig. 7) is fairly common in most of the unoxidized deposits, and its former presence is suggested by limonite

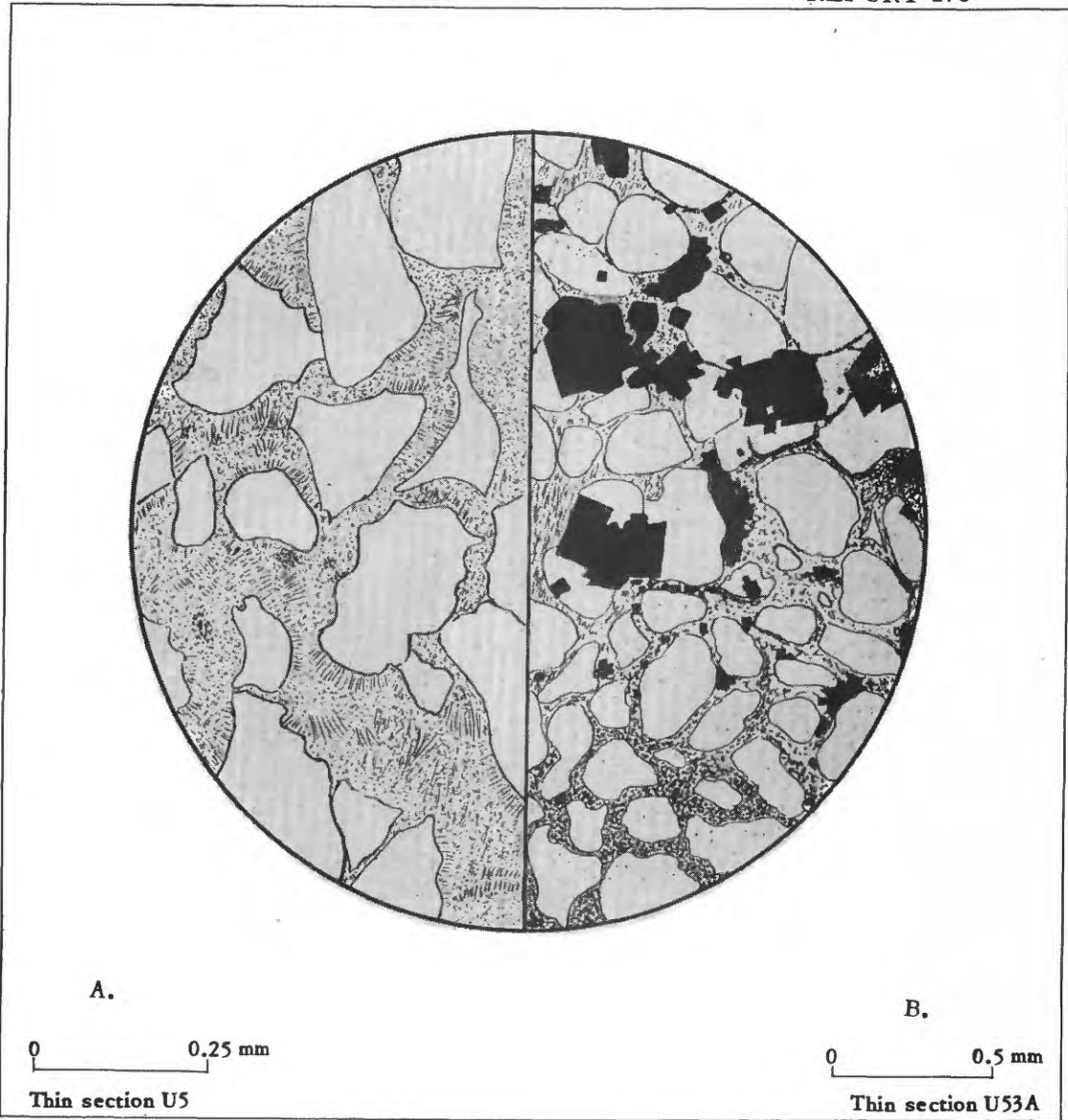


Figure 7 -- Ore, Salt Wash member of the Morrison formation near Uravan, Colorado.
A. Partly dissolved quartz grains surrounded by oriented vanadium clay.
B. Large black grains with square outlines are pyrite. Fine black material is an unidentified uranium (?) mineral in vanadium clay matrix.

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spots in many of the oxidized ores. Other accessory sulfides that appear in places are chalcocite, bornite, chalcopyrite, arsenopyrite, covellite, galena, and their oxidation products. The copper sulfides are especially common in the Slick Rock district and White Canyon area.

Certain textural and paragenetic features of possible genetic significance were noted during study of the thin sections, and will now be summarized:

Montmorillonite-vanadium clay transition

At a group of claims east of the Carrizo Mountains of northeast Arizona, thin seams of clay interstratified with the ore-bearing sandstone are composed mainly of the dark-colored vanadium clay so common in Colorado plateau ores. X-ray studies by Sterling Hendricks (reported in Fischer, 1942, p. 378) indicate that this mineral is a vanadium hydromica.

A notable feature of the eastern Carrizo occurrence is that although the thin clay seams are highly mineralized, they are separated by only a few inches of mineralized sandstone from much thicker beds of red and green clay that are almost entirely barren. Exposures of the Salt Wash sandstone that occupy an equivalent stratigraphic position 1/4 mile to 2 miles from the area of mineralization show that the thicker clay beds do not react to benzidine, whereas the thin clay seams are strongly reactive. The thin clays probably represent ash falls that have devitrified to montmorillonite, whereas the thicker clays are apparently of a different origin and composition.

The suggestion immediately arises that the ore-bearing solutions have converted the montmorillonite to vanadium hydromica. From the standpoint of crystal chemistry this is an expectable transition, since the space lattices of the two minerals are nearly identical (Grim, 1942; Nagelschmidt, 1938; Ross and Hendricks, 1945). The transformation may be similar to the conversion of montmorillonite to the ordinary potassium hydromica ("illite") which Dietz (1941) considers to explain the abundance of illite in marine shales.

In the field an attempt was made to trace one of the clay seams rich in vanadium outward from the eastern Carrizo ore into an unaltered montmorillonite seam, but because of the discontinuity of the seams, the lack of exposures at critical points, and a raging snowstorm, this was not successful. Such a field transition has been found, however, in a thin mineralized layer of clay galls at the Dolores mines near Uravan. Here thickly spaced clay pellets and clay galls ranging from 1/100 inch to 2 inches in diameter, change from green, unmineralized benzidine-reactive clay to dull, black highly mineralized hard masses in a distance of 12 feet along the strike of the sandstone that encloses them. The sandstone also shows increasing mineralization of the clay matrix.

Unfortunately thin sections disclose that at least two and possibly three kinds of clay galls of different origin are all mixed together in this sandstone layer. Thin sections in the unmineralized portion show that many galls are chips of a previously deposited shale. They show bedding, and the clay minerals are oriented in minute flakes parallel with the bedding. This clay has a high birefringence, and X-ray tests made by Alice Weeks indicate that it is hydromica. Another kind of clay gall, generally smaller than the shale chips, shows tiny but unmistakable altered fragments of a glassy trachytic textured lava, and bits of material preserving shard structures. Both the glass and the feldspar microlites are completely altered to clay, probably the montmorillonite detected by X-ray.

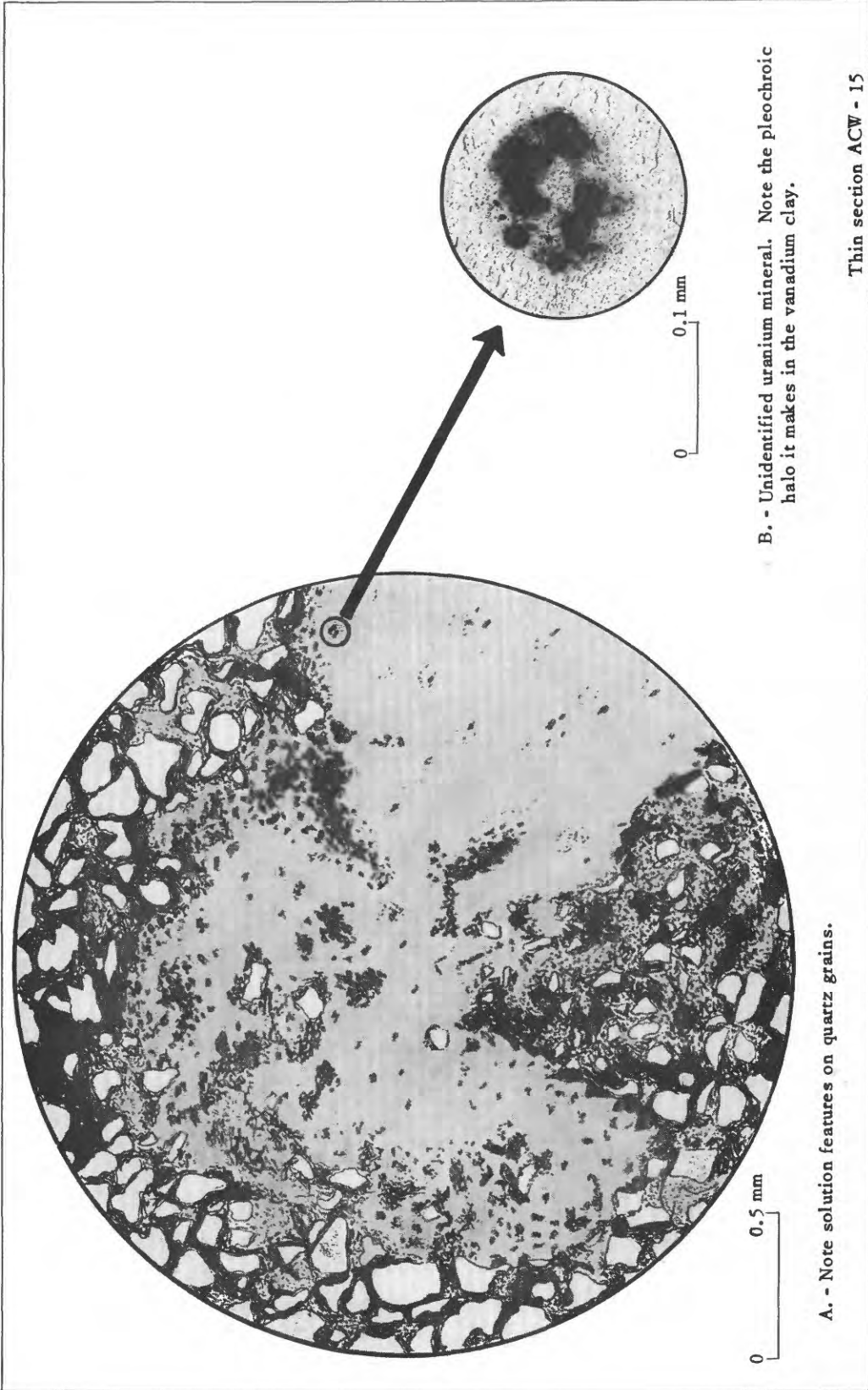
Successive thin sections taken at 5 points to show the increase in mineralization indicate the following changes in the clay galls within the sandstone bed. The colorless clay (montmorillonite ?) begins to acquire a faint sepia color. At the same time shard and other structures fade out, and the gall becomes a homogeneous mat of cryptocrystalline flakes. With increasing mineralization the flakes become better and better individualized,

until ultimately the galls consist of a homogeneous mat of micaceous flakes of a deep brown color, composed of a clay mineral with high birefringence. In a still higher stage of mineralization these galls are impregnated, particularly along their edges and between the cleavages of the clay mineral, by a black, apparently uraniferous mineral in tiny rounded grains surrounded by pleochroic haloes (fig. 8).

Changes in the shale galls formed of original hydromica are different. Little change is noted at first, but ultimately the hydromica darkens in a rather splotchy manner, apparently because of impregnation by the black uranium-bearing (?) mineral. The petrographic work, though not completely definitive, indicates that the original hydromica of the shale has not been recrystallized or changed in composition, whereas the montmorillonite has been converted to a vanadium clay mineral with high birefringence.

An attempt to study the change from montmorillonite to vanadium clay by X-ray methods was only partly successful because the galls used for X-raying were picked from the rock before the petrographic work had disclosed that there were chips of shale as well as galls derived from volcanic debris in the sample. As a result the X-ray results cannot be interpreted in terms of a possible montmorillonite-vanadium hydromica transition, because hydromica is present in all samples. A new attempt will be made on more carefully selected materials. It is hoped that the change can also be demonstrated in the laboratory by experimental methods.

Spectrographic analyses of four samples involved in the transition (again, unfortunately, separated before the petrographic work and hence containing variable amounts of shale and volcanic pellets in each sample) showed the following changes in vanadium, uranium, silver, and cobalt contents:



A. - Note solution features on quartz grains.

B. - Unidentified uranium mineral. Note the pleochroic halo it makes in the vanadium clay.

Thin section ACW - 15

Figure 8 -- Vanadium clay pellet derived from a gall of montmorillonite. Section cut from a "trash pile" lens at the Dolores group, Uravan, Colorado.

Sample number	V (percent)	U (percent)	Co (percent)	Ag (percent)
11	0.09	0.002	0.0006	0.0001-2
12	0.2	0.003	0.0007	0.0003
13	2.2	0.005	0.0040	0.0010
14	3.8	0.064	0.0100	0.0010

Thin sections from the Waterfall group, and from various other places on the Plateau show various stages in the disappearance of shard textures and the conversion of the original clay to a uniform dark-brown micaceous-appearing clay of high birefringence.

More work needs to be done, especially some chemical experimentation, but these preliminary observations suggest that the widespread occurrence of the vanadium clay in the ores is because montmorillonite transforms to a vanadium hydromica in the presence of vanadium-bearing solutions.

Secondary enlargement of quartz grains

In many thin sections of ore-bearing sandstone the quartz grains show authigenic overgrowths in optical continuity with the original quartz grains (figs. 9 and 10). The amount of silica added in this way appears to vary from place to place, and is difficult to estimate accurately because, as will be shown, the quartz grains in many of the ores have later been partially dissolved. In some sections, however, from 10 to 20 percent of the total bulk of the rock consists of secondary silica. In these rocks, overgrowths have filled nearly all the spaces between the grains, cementing the sandstone into a hard quartzite.

The silicification, however, seems to be patchy and irregular. Our field observations, though meagre, indicate that silicification is more common

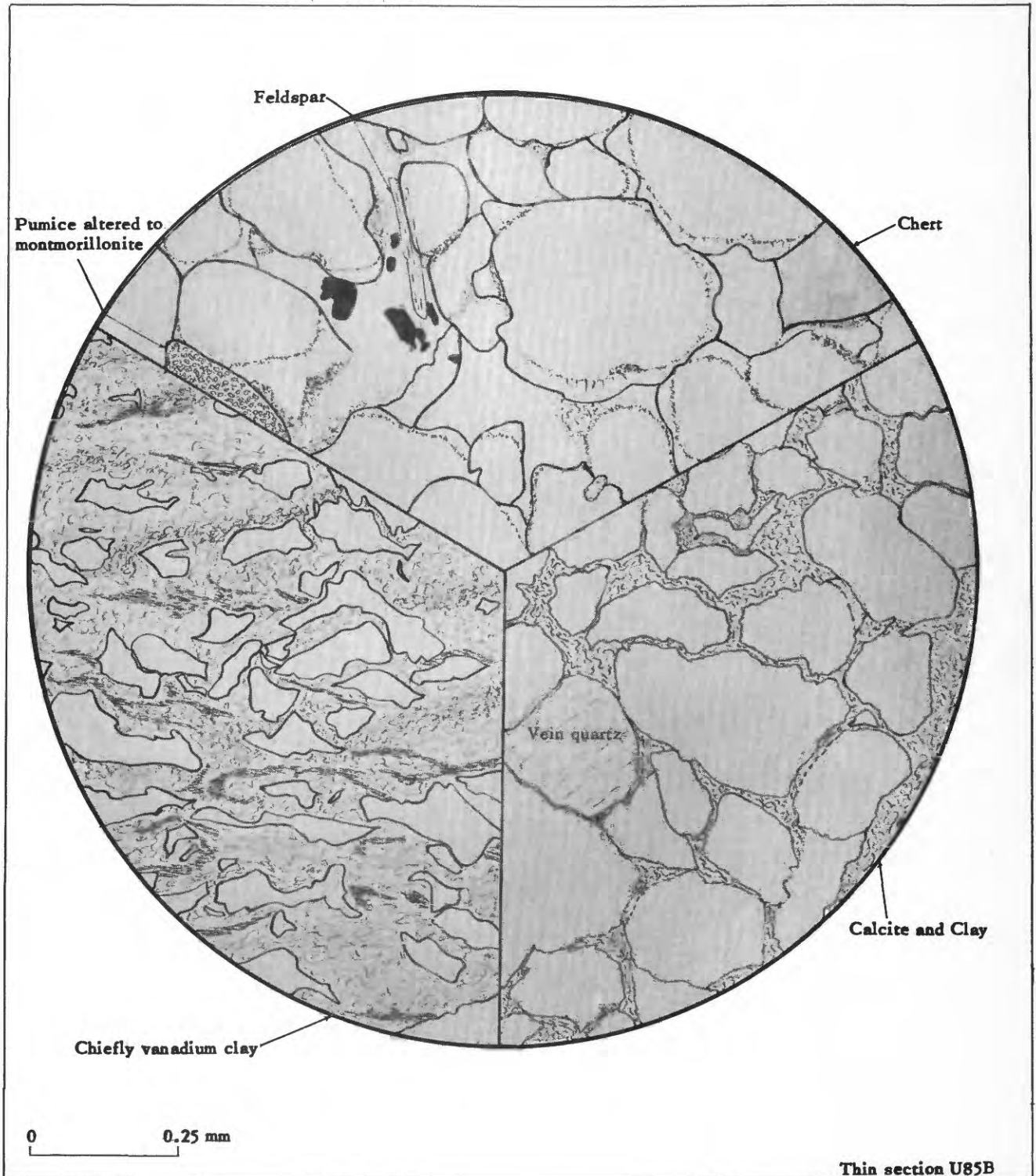


Figure 9 — Authigenic overgrowths and solution features on quartz grains shown in different parts of a single thin section of ore. Salt Wash member of the Morrison formation.

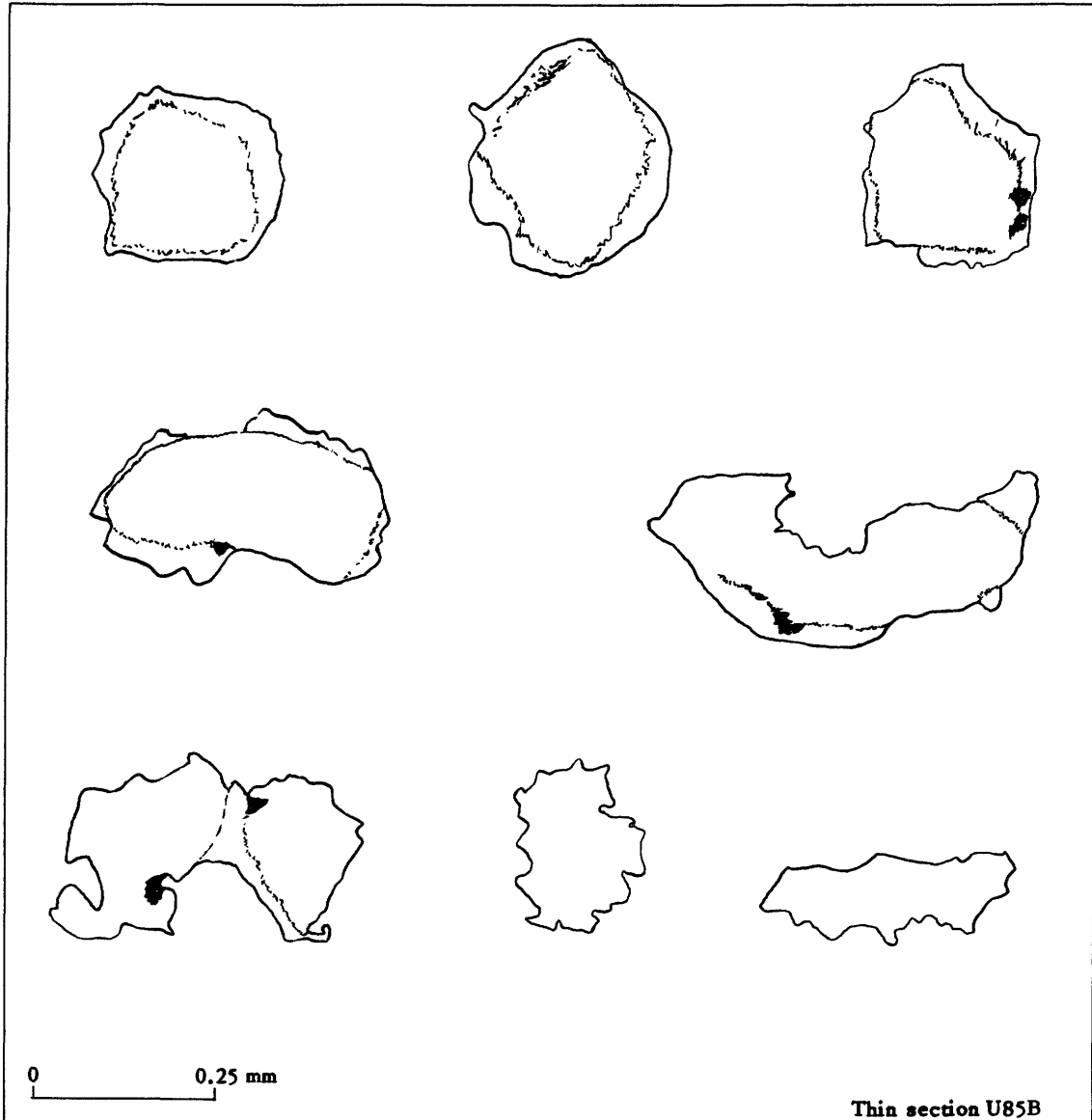


Figure 10 -- Stages in the solution of secondarily enlarged quartz grains in an ore body in the Salt Wash member of the Morrison formation.

along the edges of the ore bodies and in the wall rocks away from the deposits than in the ore itself. It is also more common in thin sandstones interbedded with Brushy Basin clays than it is in the Salt Wash, and seems to be best developed in the Salt Wash near the Brushy Basin contact. The silicification may follow beds, or it may occur in irregular patches that cut across beds. In some unmineralized rocks that have a clay and calcite cement it is entirely absent. In others only a little clay and calcite are left in the interstices between the mutually interfering overgrowths. In places small patches of the clay-rich groundmass have been completely surrounded and appear as tiny islands in the authigenic hull of a single grain.

These relations show that the silicification was later than at least an early stage of cementation by calcite and clay. The patchy distribution of the areas with enlarged grains, however, suggests that the rock was only partially cemented prior to silicification, and that deposition of silica occurred chiefly in the more permeable areas where there was only a little clay and calcite.

That the silicification was definitely earlier than the deposition of the vanadium-uranium ore minerals is shown by the following relations.

Solution of quartz grains

Many thin sections of the ores show clear evidence of solution of the quartz grains of the sandstone. The solution took place at some stage after the overgrowths had formed. Many grains have had the secondary overgrowths partially eaten off, others have had both overgrowths and core deeply indented, and still others have been reduced to ragged elongate remnants (fig. 10).

The solution of quartz has clearly taken place after cementation of the rock, and has obviously been influenced by differences in permeability and by fractures. This is shown by the variable effects that may be seen even

in a single thin section. All of the drawings in figure 10 are from a large thin section, about 1-1/2 inches square, No. U85B in R. P. Fischer's collection. Patches within the section that are tightly cemented by authigenic overgrowths show only a little solution along the edges; in areas where there is a little calcite and clay as cement mild solution has produced stylolitic indentations between adjacent quartz grains; in areas where there was considerable calcite and clay, solution has completely removed most of the authigenic hulls. In a few seams that contain a large amount of interstitial vanadium clay the quartz grains appear to have lost at least half of their volume by solution.

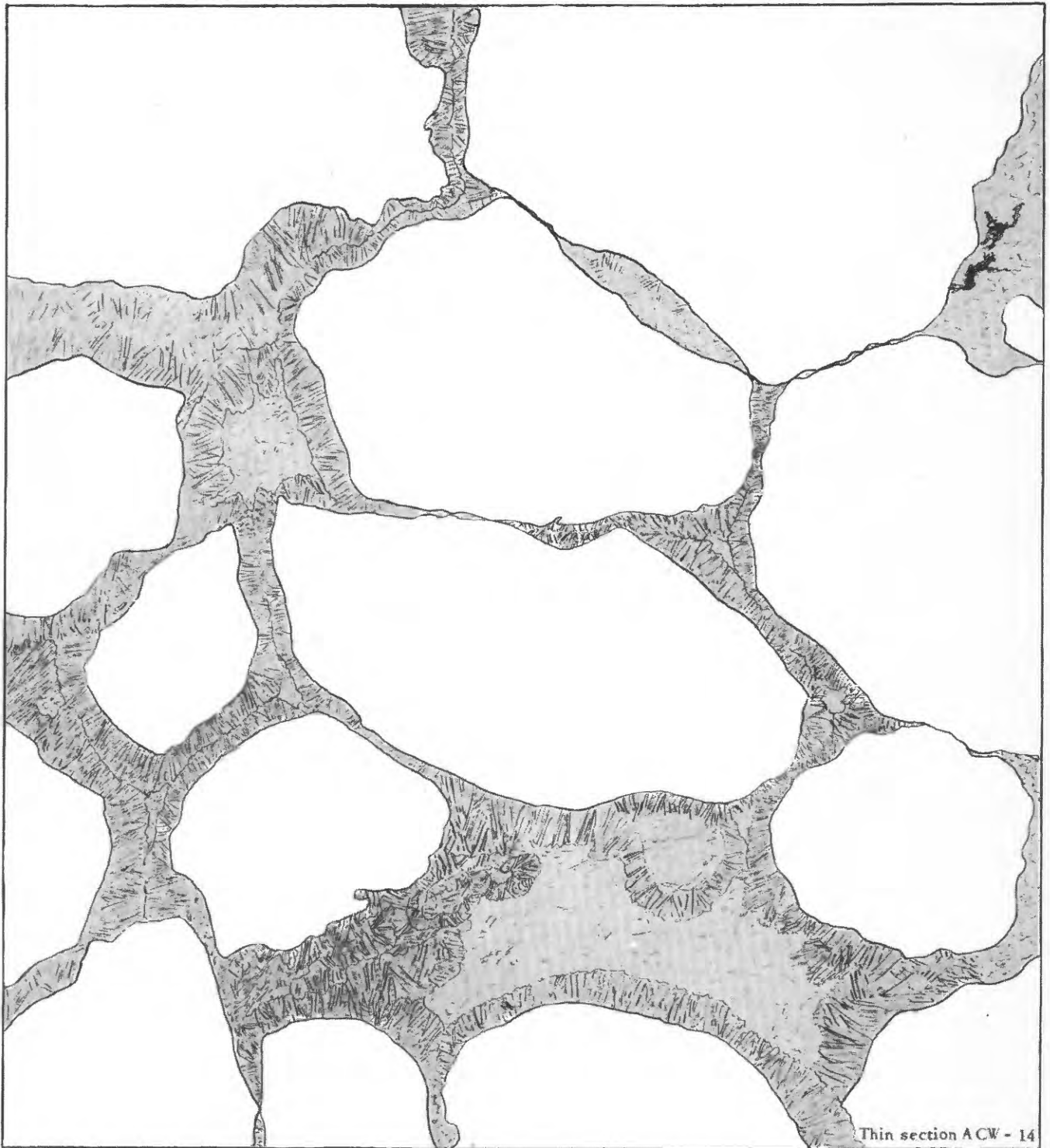
Relation of vanadium clay to partially dissolved quartz grains

In many places where quartz grains show extensive evidence of solution the interstitial vanadium clay between the grains occurs as a nest of small rope-like veinlets that wrap around the quartz grains (figs. 11 and 12). The plates of the clay stand at right angles to the walls of the veinlet-- thus at right angles to the edges of the quartz grain. This kind of crystallization is typical of minerals that grow in open spaces--gypsum plates in small veinlets, comb quartz in veins, ice in cracks within frozen ground. Similar groups of oriented clay plates can be seen to lie at right angles to the walls of minute fractures in the minerals or in the matrix of the sandstone, and to surround the edges of open cavities between the grains.

Where more than one "rope" or veinlet appears around a quartz grain, the veinlet nearest the grain was the last one to be deposited, as indicated by the way it cuts across or merges into "ropes" that are farther out. In a few places these mats of tiny ropes apparently preserve the rounded outlines that a quartz grain possessed prior to solution.



Figure 11 -- Clear quartz grains surrounded by vanadium clay dusted with unidentified uranium-bearing (?) mineral. Note how vanadium clay has crystallized in oriented plates surrounding partly dissolved quartz grains.



0 0.1 mm

Figure 12 -- Partly dissolved quartz grains surrounded by "ropes" of oriented vanadium clay.

The relations show that the solution and filling took place in recurring steps, each one giving rise to a separate veinlet developed between its predecessor and the retreating quartz wall, and indicate that solution of quartz grains was followed almost immediately by filling of the openings by oriented plates of vanadium clay.

This is rather good evidence that solution of the quartz was accomplished by the same solutions that brought in the vanadium. It shows that the ore-bearing solutions did not enter the rock until after cementation by calcite and montmorillonite, and until after the quartz grains had been enlarged by secondary silica. The widespread unidentified uranium (?) mineral that occurs in minute black specks seems to have crystallized simultaneously with the vanadium clay, but to have continued its crystallization even a little later, for it occurs along the cleavages of the vanadium clay and is commonly present as thick clusters on the edges of pellets composed of vanadium clay (figs. 8 and 11).

HISTORY OF DEVELOPMENT, AND ORIGIN OF THE ORES

The field and petrographic evidence may now be summarized and certain implications drawn from it.

1. Deposition of sediments

The two principal ore-bearing formations of the Colorado Plateau (Shinarump and upper Salt Wash) contain appreciable amounts of volcanic debris, intermixed with weathering-resistant detrital material of non-volcanic origin. Some beds are "trashy" sandstones containing abundant pumice and lava fragments, fossil wood, charcoal, clay galls, and in places fossil bone. This kind of material is typical of the pumice-slurry floods produced where volcanic eruption clouds fall into rivers.

2. Burial

Each of the two ore-bearing formations grades upward into a thick stratigraphic unit (Lower Chinle above the Shinarump, Brushy Basin above the Salt Wash) composed in large part of stratified volcanic debris. As originally deposited these formations were chiefly ash and pumice lapilli, mixed with varying amounts of sand, silt and clay of non-volcanic origin.

3. Cementation

Deposition and burial was followed by cementation of the rock, chiefly by calcite and clay. The cementation, however, seems to have been somewhat patchy and irregular, leaving many places where the voids between the grains were unfilled or only partially filled.

4. Devitrification

Devitrification of the glassy volcanic debris changed the water laid tuffs in the lower Chinle and Brushy Basin to bentonitic shales, siltstones, and mudstones. The interstitial ash in the sandstones also devitrified, forming a clay matrix of montmorillonite in some sandstone beds.

Pleistocene and Recent deposits of volcanic ash show little or no devitrification, except adjacent to hot springs or fumaroles. On the other hand, early Tertiary glassy pyroclastics generally are almost completely devitrified. It can reasonably be assumed, therefore, that devitrification of the glassy materials in the Triassic and Jurassic sediments of the Colorado Plateau did not occur until after burial--probably to depths of 1,000 feet or more--and until after at least partial cementation.

5. Silicification

Probably as a result of the devitrification, widespread, but patchy and irregular silicification occurred. Bentonite typically contains less silica than the ash from which it was derived. Bramlette (1946, p. 28) and Ross, Miser, and Stephenson (1929, p. 186) have published analyses of unaltered igneous material and of the bentonites derived from them that show very considerable losses in silica. Ross, Miser, and Stephenson (1929, p. 186) calculate that about half of the original silica was lost during the transformation of an Arkansas trachyte ash to a bentonite. As previously noted, silicification of the sandstones is demonstrated by the widespread occurrence of authigenic overgrowths on quartz grains, by the abundant petrified wood, by jaspery and cherty cementation of some conglomerates and mudstones, and by abundant thin beds of silicified sandstone and shale in the bentonitic sediments. Much work needs to be done, but scattered field observations suggest that silicification has been most extensive in thin, formerly permeable beds of sandstone interstratified in the Brushy Basin sequence, in the basal conglomerates of the Brushy Basin (for example, the jaspery conglomerate of Calamity Mesa), and in the sandstones of the upper Salt Wash.

The obvious source of the silica is from devitrification of the near-by ash beds. Silicification of adjacent permeable rocks during the devitrification of ash beds has been described by many authors (Rubey, 1929, p. 160; Ross and Shannon, 1926, p. 79; Bramlette, 1946, p. 26). Murata (1940) points out the common association of silicified wood with devitrified volcanic ash, and shows that altered pyroclastics are a rich source of readily available silica for geochemical purposes.

The thin section evidence indicates that silicification came at the right time to be associated with devitrification. The authigenic overgrowths en-

close the calcite cement of the rock, and show a strong tendency to fill spaces that were not already filled by calcite, and clay. Pieces of carbonatized wood with the carbonate partially replaced by silica were noted on the east side of the Henry Mountains and at the Georgetown claims. Thin beds of sandstone interstratified with bentonites have been silicified to hard quartzite at many localities.

6. Chemical changes in the connate water of the sandstones during devitrification

The migration of silica during devitrification of volcanic ash is shown by the silification of adjacent rocks, and by chemical analyses. Certain other chemical changes accompanying devitrification are deducible, but are much less susceptible of proof. We have assumed that the rocks were buried deeply during devitrification. Therefore the Shinarump and Salt Wash sandstones were probably filled with connate water which could not circulate freely because of impermeable formations above and below. What changes can be expected in the chemistry of this connate water body and in the enclosing rocks as a result of devitrification?

Addition of alkalis

One obviously deducible fact is that the connate waters would be enriched in the alkalis. Chemical analyses of bentonites from many areas show that potassium and sodium are leached during devitrification; in many rocks they are almost completely removed (Ross, Miser, and Stephenson, 1929, p. 186). Alkalis and alkaline salts are associated with bentonites in many areas (Ross and Shannon, 1926, p. 80; Davis, 1929, p. 335).

Base exchange would still further increase the alkali content of the connate water, and would decrease its content of Ca^{++} ions. Bentonitic clays

tend to extract Ca^{++} ions from waters passing over them, and release Na^+ ions (Renick, 1925). Original Mg^{++} ions are similarly removed by base exchange, and also magnesium is an essential constituent of montmorillonite, and it is doubtful if enough magnesium is present in the original biotite latite and biotite keratophyre to supply the magnesium needed for bentonitization.

By such reactions we may expect the original content of calcium and magnesium in the water to be almost completely removed, and the content of the alkali metals to be greatly increased.

Addition of uranium, vanadium, and other trace elements

Devitrification of the ash may also be expected to result in the redistribution of several other elements besides silica and the alkalis. The metallic elements ordinarily concentrated in pegmatites and hydrothermal veins (Rankama and Sahama, 1950, pp. 178-184) would presumably not have crystallized during eruption of the volcanic materials, and hence would be locked up in the glass shards and pumice. On devitrification any of these elements that ionize readily, or that form soluble ionic complexes may be expected to be partially leached from the ash, and to be concentrated in the connate water of the adjacent sandstones.

Two such elements are uranium and vanadium. Others are the soluble members of the rare earth group, titanium, molybdenum, tungsten, copper, bismuth, zinc, lead, antimony, mercury, and others. Corresponding non-metallic elements that would be expected to be partially leached and removed are sulfur, selenium, tellurium, arsenic, boron, chlorine, and fluorine. Theoretically, therefore, all of these elements might be expected to move into the connate water of the adjacent sandstones. However, even if they had thus migrated and concentrated,

reactivated circulation of the ground water following the Tertiary uplift and erosion would have flushed out most of those elements that had remained in a soluble form.

It is noteworthy, however, that the Salt Wash sandstones still contain appreciable amounts of several of these elements. The only known rock that exceeds the Salt Wash in selenate content is a Tertiary tuff near Lysite, Wyoming (Trelease and Beath, 1949, p. 69). Because of the toxic qualities of certain plants rooted in seleniferous soils, the distribution of selenium in rocks has been widely investigated by agricultural agronomists. One such study of the Salt Wash by Beath (1943) has given us some extraordinarily interesting data. His work, chiefly in the Yellow Cat district, Utah, shows the presence of vanadium, uranium, chromium, zinc, tellurium, copper, molybdenum, and titanium, as well as large amounts of selenium, in rocks from the Salt Wash and in the soils derived from them. He states (p. 704) that doubtless this list would be increased by further investigation. In general the highest concentrations were found in carbonaceous vanadium ores, though barren sandy shales also contain high amounts. He reports that vanadium and uranium tend to cluster in zones, whereas selenium and other metals are more widely, though not uniformly, distributed.

In view of the fact that the Salt Wash sandstones were not known to contain volcanic matter at the time Beath wrote, and that the volcanic origin of the Brushy Basin shales had also been overlooked, his conclusions as to the origin of these metals is interesting (Beath, 1943, p. 609):

"The writer finds it difficult to visualize clearly how so many different minerals were concentrated in the sediments which comprise these poison strips, especially if volcanic activity is not believed to have been an immediate contributing factor."

Beath also reports the presence of selenium in the rocks overlying the Salt Wash, but the plants growing on these formations are generally not dangerously toxic. His results, therefore, are in accord with, but do not necessarily confirm, the hypothesis that many of these metals were leached from the overlying Brushy Basin pyroclastics and concentrated in the connate water of the Salt Wash. Here, of course, there would be opportunity for some of the leached elements to precipitate in the rock by reactions with one another and with the minerals of the sandstone. Let us look into this possibility a little farther with regard to uranium and vanadium.

7. Fixation of uranium and vanadium by organic matter

Assuming that uranium and vanadium were leached from the ash and concentrated in the connate water of the sandstone as outlined above, perhaps there is a possibility that the uranium was extracted from solution by organic material present in the sandstones.

The organic material consists chiefly of fossil wood and small amounts of fossil bone. As previously noted some of the fossil wood is in the form of charcoal. In the space of time that elapsed between sedimentation and devitrification considerable decomposition and change in the original plant tissues of the wood are to be expected. Humic colloids, organic resins and acids, various hydrocarbon gases such as methane, and many other complex organic compounds and sols would be released into the ground water. Such materials might migrate some distance from their point of generation. These substances would, of course, change the redox potential of the ground water.

The remaining parts of the wood would be converted to peat or coal. Charcoal would be expected to remain unchanged. Some leaching of the phosphatic material in fossil bone would be expected.

Several of these organic substances may have served to extract and "fix" uranyl ions present in solution. The possible role of charcoal as a "fixing agent" is emphasized by Frederickson (1948):

"It is here suggested that the wide distribution of uranium throughout the sedimentary crust of the earth is due principally to its tendency to form large UO_2^{++} ions
. . . much of the uranium in shales may be in the form of adsorbed ions and not of discrete minerals."

"A world-wide association of certain types of carbonaceous material with vanadium and uranium materials has been observed. . . . All forms of so-called amorphous carbon, from lampblack and coke to charcoal, are graphitic in character. They are composed of portions of the graphite structure without, however, the regular 3-dimensional periodicity characteristic of crystalline graphite. Because of its structure, with its extensive internal surfaces and unsatisfied valencies, charcoal (and similar forms of carbon) possesses the property of adsorbing ions to a remarkable extent."

As previously noted, field tests with a Geiger counter show that charcoal is more highly radioactive than coaly material when the two occur together in the same ore deposit.

Another group of "fixing agents" are the humic colloids and various other kinds of hydrosols. The possible role of geochemical adsorption in removing uranyl ion from solution apparently has not been fully investigated. On theoretical grounds, however, the large, positively charged uranyl ion with its two attached oxygens located on opposite sides of the uranium atom, should be attracted and held by the following negatively charged sols (Rankama and Sahama, 1950, p. 255) all of which were probably present, at least in small amounts, in pore fluids of the sandstone: humic colloids, hydrate of vanadium pentoxide, metal hydrosols, sulfide hydrosols.

Finally, certain organic compounds such as the long-chain amines, the ion-exchange resins, and various organic compounds of phosphorus and of arsenic are known to be remarkably effective precipitants of uranium. (See Battelle Memorial Institute reports under Contract No. A.T. 30-1-Gen-202, especially

EMI-JDS-127, 146, and 163.) Whether or not any of the particular organic compounds used in the Battelle Institute experiments were actually present in these natural solutions can only be conjectured, but a source for the materials is available in the fossil wood and bone of the sediments, and in arsenic ions which could have been leached from the ash.

To summarize these admittedly theoretical deductions on the possible results of devitrification: We assume that alkalis, uranium, vanadium, and other substances were leached from the ash and added to the ground water in the adjacent sandstones. Calcium and magnesium were simultaneously removed from the water by base exchange and chemical reaction. Humic colloids, hydrocarbon gases, and various other organic compounds were generated by decomposition of the fossil wood and bone, and became widely dispersed in the pore fluids. These, plus the residual coal, charcoal, and fragments of fossil bone may have largely removed the uranium and vanadium from solution.

Does this mechanism explain the origin of the present ore deposits? Could all the uranium of the plateau ores have been leached from the overlying ash beds, and precipitated in the manner outlined?

8. Inadequacy of ash leaching

Some difficulties appear. As Frederickson (1948) points out montmorillonite has a sheet-lattice structure and hence should be as remarkably effective in adsorbing and "fixing" uranyl ions as is charcoal. Evidence that montmorillonite has played a role in the fixation of both vanadium and uranium in the Plateau ores has already been presented under the heading "montmorillonite-vanadium clay transition". There it was also noted that montmorillonite seams in the ore deposits have been converted to vanadium clay and are richly impregnated with uranium minerals, whereas beds of hydro-mica clay are generally almost unmineralized.

Recalling these relations it may justifiably be asked: Would uranyl ions ever escape from the ash during devitrification? Would they not be immediately adsorbed on the newly formed montmorillonite clay and thus remain locked in the bentonite? This possibility, plus the overall distribution of the ore deposits themselves convinces the writers that simple leaching of ash and precipitation of the leached uranium and vanadium by organic matter is inadequate to explain the genesis of the sandstone-type ores of the Plateau, though it may be the answer for the North Dakota (Denson, 1950) and New Mexico (Bachman, 1951) uraniferous lignites. The sandstone-type ores do not occur in a relatively uniform, low grade sheet, as might be expected on this hypothesis. Instead ore shoots are clustered in groups of small relatively high grade deposits. Over wide areas the Brushy Basin and Chinle volcanic sediments are thoroughly devitrified, but there are no ore deposits in the sandstones beneath.

Thus, although leaching of volcanic ash may have been a contributing factor, at least one additional step seems to be required to explain the concentration of the metals in the known ore deposits.

9. Reactivation of ground water circulation by igneous invasion, hydrothermal activity, and uplift

In Tertiary time widespread igneous activity produced the laccolithic complexes, and other igneous bodies of the Plateau area. At approximately the same time considerable structural deformation of the sedimentary rocks also occurred.

A spatial grouping of the uranium-vanadium ore deposits in arcs around the edges of the laccolithic centers is apparent, and strongly suggests that perhaps the ores are of hypogene origin, derived from fluids given off during the crystallization of large deep seated magmatic masses that underlie the laccolithic complexes.

The igneous activity and structural deformation of the sediments would certainly reactivate the ground water circulation in the Shinarump and Salt Wash units. Three factors may be considered: (1) tectonic changes in elevation of different areas would supply a hydrostatic head, (2) tectonic movements and igneous intrusion would open joints and faults in the formerly impermeable formations above and below the ore-bearing sandstones, and (3) accession of steam and of hydrothermal solutions into the sandstones from the crystallizing magmas would reactivate circulation of the ground water. The effects produced by the first two are obvious. Here we restrict the discussion to the possible effects of introducing steam and metal-bearing hypogene solutions into the ground water that filled the Shinarump and Salt Wash sandstones.

If, as a result of devitrification and leaching, the ground water had evolved to the rather unusual composition indicated above, mixing of new magmatic water with this material could not help but produce a number of effects which should be recorded in the rocks themselves. Among the immediate changes that may be expected are:

- (1) The temperature of the magmatic water would immediately drop.
- (2) The redox potential would be likely to change because of the strongly reducing character of the connate water.
- (3) The magmatic waters would be brought into contact with coal, charcoal, fossil bone, humic colloids, and other organic materials which might act as precipitants or adsorbants of their metals.
- (4) The magmatic waters would come in contact with montmorillonite in thin clay seams, clay galls, and as interstitial material between the sand grains. The montmorillonite might selectively adsorb or precipitate some of the metals.

If the magmatic water contained uranium and vanadium any of the four factors mentioned above would be likely to induce their precipitation; the four of them operating together produces a geochemical environment in which abundant precipitation would be almost certain. Thus we can explain why the Shinarump and upper Salt Wash were especially favored by the ore deposits; they have several factors operating to cause precipitation, whereas other stratigraphic units generally lack the combination of organic matter and montmorillonite in a permeable rock filled with ground water.

The structural, mineralogic, and zonal relations of the ores favor, or at least are compatible with the idea of hypogene origin, as has been brought out by Cater, Shoemaker, Benson, and others (unpublished data, and personal communication). Our studies of thin sections bring out still another point. As previously noted, the quartz grains of the ore-bearing sandstone were being dissolved at the same time as the vanadium clay and other vanadium-uranium minerals characteristic of the "blue-black" ores were being deposited. What change ensued in the rock to cause solution of quartz grains, when these same grains had previously been enlarged by addition of silica?

As indicated above, the cause of the original silicification was apparently devitrification of the ash. Devitrification also caused the connate water to be enriched in the alkalis. If hot magmatic water then entered this environment, mixed with the ground water, and induced a dynamic system of active circulation instead of the essentially static condition of water movement that had formerly prevailed, solution of quartz would be an almost certain result. Quartz dissolves in an alkaline solution. Any acidity that the magmatic waters may have had would be neutralized by passing through calcite-rich rocks below the ore-bearing sandstone, or by reacting with the carbonate cement of the sandstone itself. In the Uravan area the solutions may also have picked up salines in passing along the edges of the salt intrusions. The widespread bentonitization of the Mesozoic ash beds supplied

an abundance of soluble alkalis to be leached and incorporated into the magmatic water. The change from a static water body to a hotter, moving one within the sandstone would enable the circulating alkaline solution to attack the quartz and carry away the dissolved silica.

Was all of the uranium and vanadium supplied from the magmatic source or was some, possibly most of it, supplied by devitrification of volcanic ash, and then merely rearranged and reconcentrated into the present ore deposits by the reactivated ground water circulation set up by igneous invasion, hydrothermal activity, and uplift? No completely satisfactory answer can be given to this problem as yet. Possibly the anomalous lead isotope relations that Lorin Stieff (1949) has found to be characteristic of the Plateau ores may indicate a double source, part of the uranium coming from devitrified Mesozoic ash, part from Tertiary hydrothermal solutions.

10. Supergene changes

In some deposits weathering and recent circulation of ground water appears to have changed the mineralogy of the ores considerably since they were originally deposited. Other deposits appear to be fresh and unmodified. As noted earlier carnotite appears to be a supergene mineral developed at the expense of the "blue-black" ores. It is found chiefly as haloes around earlier uranium minerals, as coatings of fractures, as fillings or replacements of fossil wood, and as impregnations in sandstones. Many other secondary uranium and vanadium minerals appear. Because of the bright colors of the secondary minerals they are much more conspicuous than the original uranium-vanadium constituents of the "blue-black" ores. This is probably responsible for the plateau deposits being called "carnotite ores".

Hess (1933, p. 471), states:

"Pintadoite, pascoite and carnotite form on the walls of canyons and carnotite or a similar yellow mineral is inclosed in gypsum filling recent cracks. There can be no doubt of the present day migration of the minerals of the deposits, and this movement is, in general, away from fossilized vegetal matter, which means that plant material was the nucleus of original deposition."

Some of the secondary minerals develop very rapidly. Fossil wood replaced by pitchblende occurs at the Happy Jack mine. Within a few months after it is exposed on the moist walls of the drifts by mining operations it acquires a coat of bright yellow secondary products.

SUGGESTIONS FOR FUTURE WORK

The prevailing view that has guided most of the exploration on the Plateau is that the ore deposits are of syngenetic or of penecontemporaneous origin. The concepts and ideas presented in this report are at variance with this conclusion, but they are only in preliminary form and are based on inadequate data. Much work remains to be done. The true answer to the origin of the ores, however, is of much economic significance.

If the source of the uranium is really in Tertiary hydrothermal solutions, or even if the principal source is from the leaching of Mesozoic ash followed by redistribution of the uranium due to reactivation of the ground water by Tertiary igneous activity and orogeny, the problem of finding ore is rather different than if the ores are assumed to be of penecontemporaneous origin.

A concerted attack on the origin of the ores, including field work closely tied to mineralogic studies and experimentation along chemical and physical lines should be made to solve the problem and thus open the way to the development and application of new concepts in ore finding and explora-

tion. The following studies, or lines of approach for studies already begun, are suggested for guidance in further investigation of the origin of the Plateau ores.

Geologic

1. Carry out a detailed program of mine mapping closely tied to petrographic work, X-ray studies and other laboratory techniques. The mapping and laboratory work should be directed to definitely ascertaining the space and time relations of the ore to fractures, silicification, quartz leaching, mixing of ground water bodies, cementation, and other features. Only a little mine mapping has been done and this has not been closely tied to laboratory studies.

2. Continue and expand the investigation of zoning and mineral ratio relations within the metallic deposits surrounding laccolithic centers on the Colorado Plateau.

3. Make a detailed geologic map, and a thorough spectrographic and mineralogic investigation of the stocks of the La Sal laccolithic complex with special reference to the content of uranium in (1) the igneous rock of the stock, (2) the deep seated inclusions that occur in the igneous rock, (3) the base metal and other ore deposits found as veins in the stocks and in the immediately adjacent wall rocks, and (4) the portions of the stocks that have been altered by hydrothermal solutions.

Similar studies should be made of the igneous bodies near Placerville, and in other areas.

4. Make a detailed stratigraphic, mineralogic, and spectrographic investigation of the bentonitic clays of the lower Chinle and Brushy Basin with special reference to ascertaining the original volume of volcanic material, and determining its uranium content. In particular determine, if

possible, the uranium content of any of the igneous components that have not been devitrified, and compare with the uranium content of the derived bentonite, with that of weathered and "fluffed" material on bentonite outcrops, and with that of ground water in contact with the bentonite. Also determine whether the uranium in these samples is in equilibrium.

5. Determine by petrographic studies, stripping film, and other laboratory techniques the manner in which uranium is distributed in radioactive clays and carbonaceous materials in the sandstones. In particular, attempt to determine its relation to the kind of clay, and to the composition and history of the carbonaceous material.

6. By pyrite decrepitation, studies of clay alteration, and other methods attempt to establish the temperature at which the ore minerals were deposited.

Chemical

1. Investigate the relation of organic material to the precipitation of UO_2^{++} ion. Controlled experiments should be made with wood, rotten wood, humic colloids, peat, coal, charcoal, and asphaltic materials.

2. Investigate the effect of montmorillonitic clays in adsorbing and precipitating uranium and vanadium from solution at various temperatures as much as 200° C. This should be coupled with a detailed study of the base exchange relations between both vanadium and uranyl ions with K^+ , Na^+ , Mg^{++} , and Ca^{++} ions in montmorillonite and related clays.

3. Similar investigations with silica gel, humic colloids, and sulfide hydrosol should be tried.

Physical

1. Continue work in an attempt to obtain reliable age determinations of the carnotite ores of the Plateau. Investigate the possible causes of

why many specimens investigated are out of equilibrium, and determine the nature of the leaching (or enrichment) that has occurred.

2. By scale model experiments simulate the penetration of a hydrothermal water body of different density and chemical properties into an essentially static body of water, the "static" body being the pore-filler in a permeable "sandstone".

3. Investigate the physical changes in wood, charcoal, and related substances when immersed in solutions approximating hydrothermal conditions, and when subjected to radioactive bombardment.

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