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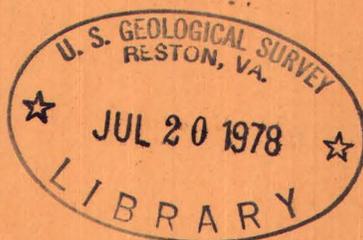
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Detailed mineral and chemical relations in two uranium-vanadium ores

By R. M. Garrels, E. S. Larsen, 3d, A. M. Pommer, and
R. G. Coleman



Trace Elements Investigations Report 635

UNITED STATES DEPARTMENT OF THE INTERIOR
GEOLOGICAL SURVEY

Geology and Mineralogy

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DETAILED MINERAL AND CHEMICAL RELATIONS
IN TWO URANIUM-VANADIUM ORES*

By

R. M. Garrels, E. S. Larsen 3d, A. M. Pommer,
and R. G. Coleman

August 1956

Trace Elements Investigations Report 635

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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 layered 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 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 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, Colo., 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, 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.

THE 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 1, and a sketch of the ore occurrence, together with the sampling pattern, in figure 2. 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 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 very low in vanadium and uranium; 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

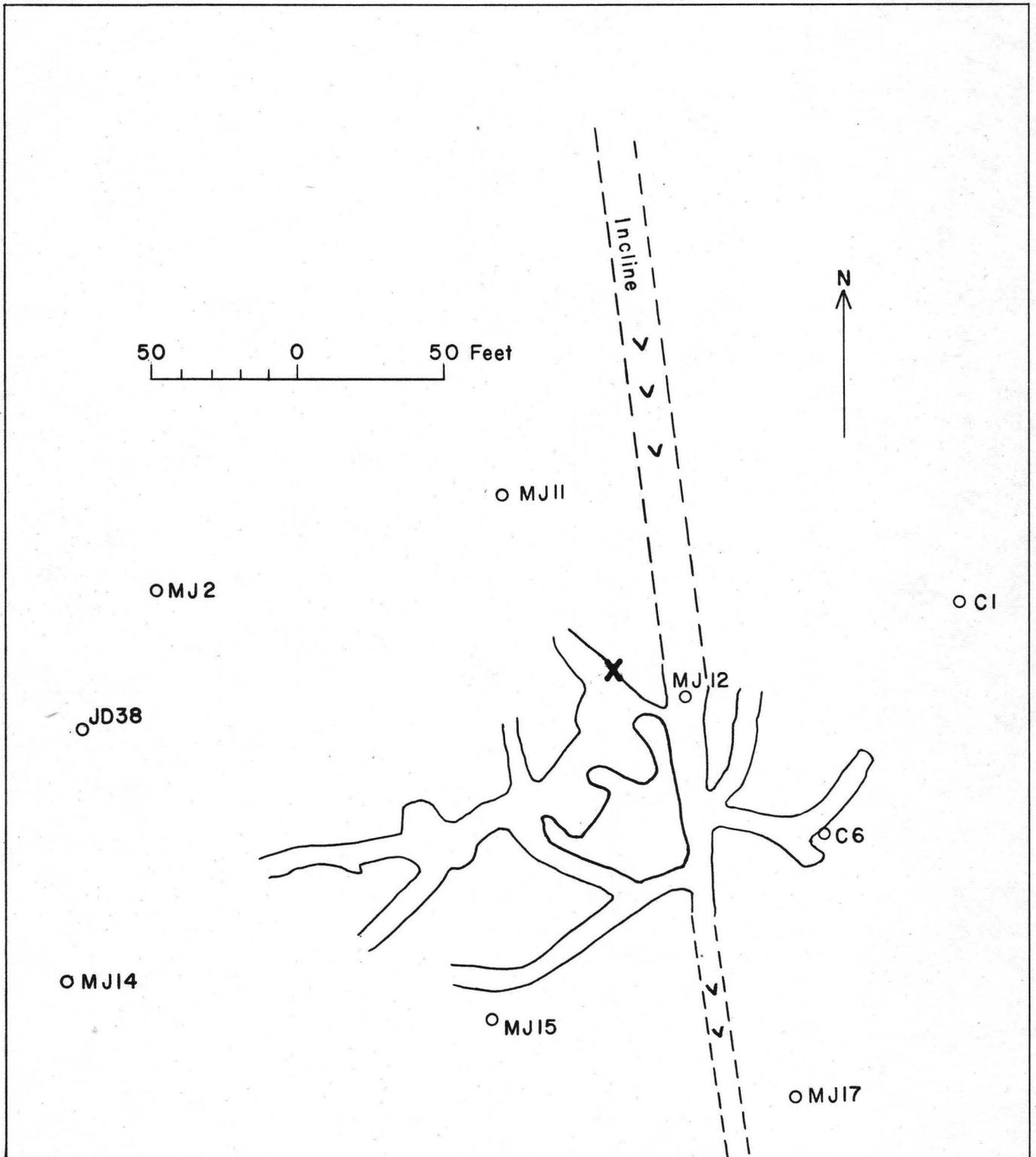


Figure 1.--Sketch of the upper stopes of the Mineral Joe No. 1 mine; X indicates the site of the channel sample taken.

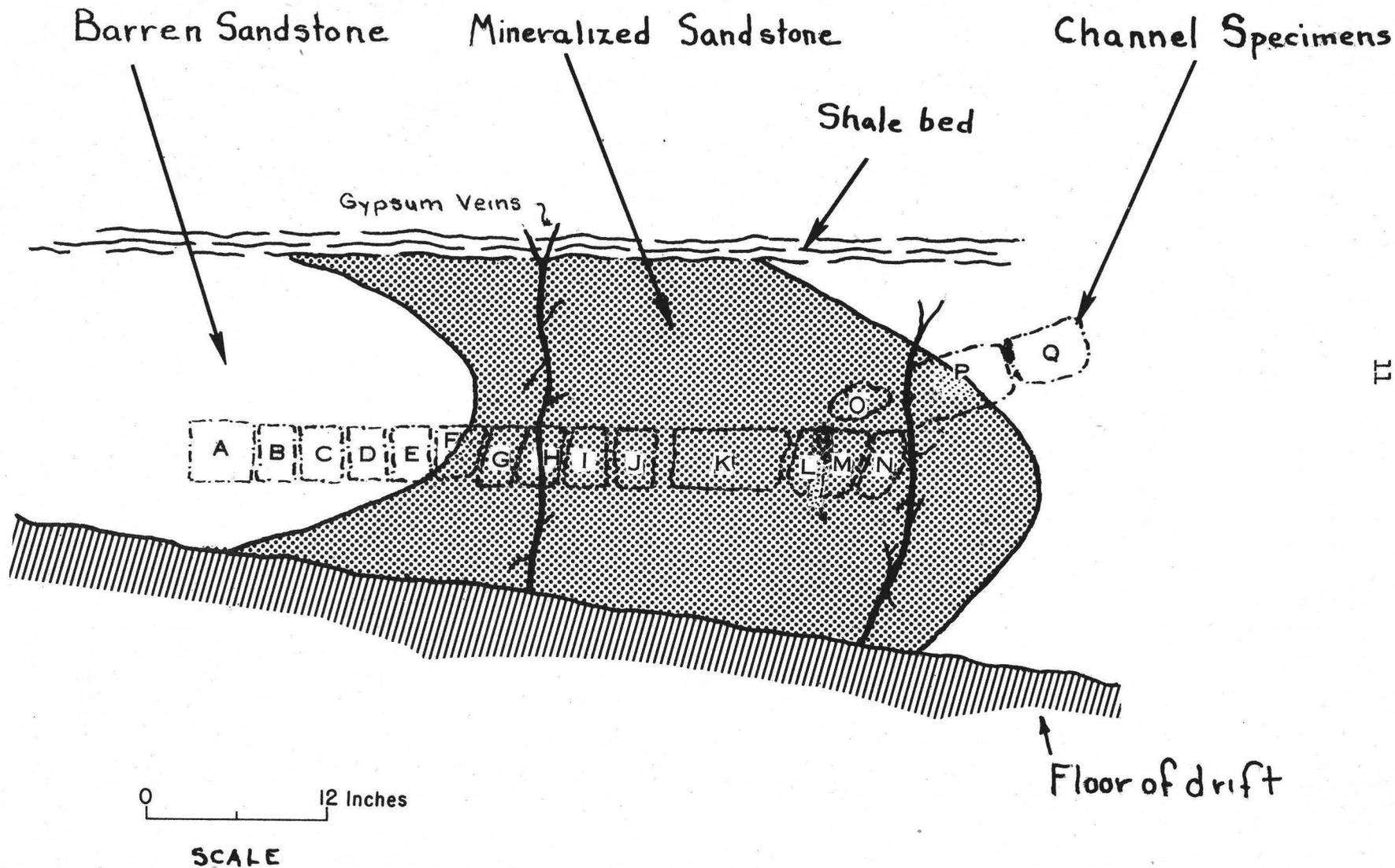


Figure 2.—Sketch of the Mineral Joe No. 1 mine wall showing relation of channel sample to ore. The letters refer to the separate specimens that made up the channel sample. 9165

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 sawed in two along a horizontal plane parallel to the line of the channel. One half of each specimen 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 No. 1 mine is in the Jo Dandy group, which has been described briefly in an unpublished report by E. M. Shoemaker, 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 formation, 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. 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 2 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; one 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	Do.; 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.

Specimen	Description
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. (See figure 2.) 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 birefringence 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 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 the interstitial gypsum, and to a much lesser extent has corroded 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 very 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 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 metahebettite 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 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 colloiddally 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 carnotite-like 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 1/ have been studied by Hathaway (1955). 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

1/ Specimens M and P are coded by Hathaway as P-1-M-53 and P-1-P-53, respectively.

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. (See 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 corvusite-like 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 due to discarded material contaminated during the labeling of the samples. For most of the chemical work 1/2-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 3. In figure 3, 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.

The data clearly reflect the mineralogy. The plots for Ca and S coincide, within the limit of determinative error, except in sample 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 3) 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

analyses of specimens of the Mineral Joe No. 1 mine channel sample (in percent by weight).

	Acid insol. U <u>1/</u>	Total Fe <u>3/</u>	Acid sol. Fe <u>4/</u>	Acid insol. Fe <u>4/</u>	Total V <u>3/</u>	Total S <u>4/</u>	Acid insol. S <u>4/</u>	Sulfate S <u>4/</u>	Ca <u>4/</u>	Al <u>5/</u>
3	0.0005	0.22	0.17		0.11	3.57		3.50	4.37	2.2
3	0.0002	0.12	0.13		0.13	4.16		4.20	4.97	1.1
6	0.0004	0.11	0.08		0.08	4.00		4.02	4.72	1.9
5	0.0004	0.10	0.08		0.10	3.90		3.90	4.37	2.2
4	0.0006	0.11	0.12		0.10	3.90		3.83	4.55	1.2
7	0.0005	0.81	0.76		1.09	2.62		2.57	3.27	4.3
5	0.0010	0.64	0.64		1.41	2.46		2.21	2.91	5.9
	0.0014	0.66	0.40		1.19	5.44		5.38	6.55	2.8
	0.0020	0.93	0.84		1.88	1.53		1.50	2.00	4.1
	0.0022	0.91	0.99		2.06	2.50		2.43	3.27	2.7
	0.0095	0.56	0.51		1.64	2.38		2.30	2.88	4.1
	0.0027	1.18	1.07		2.10	1.41		1.38	1.97	4.7
	0.0050	1.60	1.55	0.011	3.14	1.93		1.95	2.69	5.0
	0.0112	4.40	2.45	1.78	4.15	6.31	3.43	2.23	2.36	2.0
	0.0113	0.68	0.68	0.018	4.82	1.84		1.68	2.36	3.3
	0.0042	0.83	0.76		2.19	1.20		1.09	1.65	8.9
2	0.0015	0.38	0.35		0.47	2.47		2.43	3.17	8.1

Johnson, U. S. Geological Survey. Acid insoluble U determined after leaching sample 24 hours in cold 1N H₂SO₄.

McCall, U. S. Geological Survey.

Tucker, U. S. Geological Survey.

Jenkins, U. S. Geological Survey. Acid soluble and acid insoluble values determined after leaching sample 5 days
0₄.

Annell, U. S. Geological Survey. Quantitative spectrographic determinations.

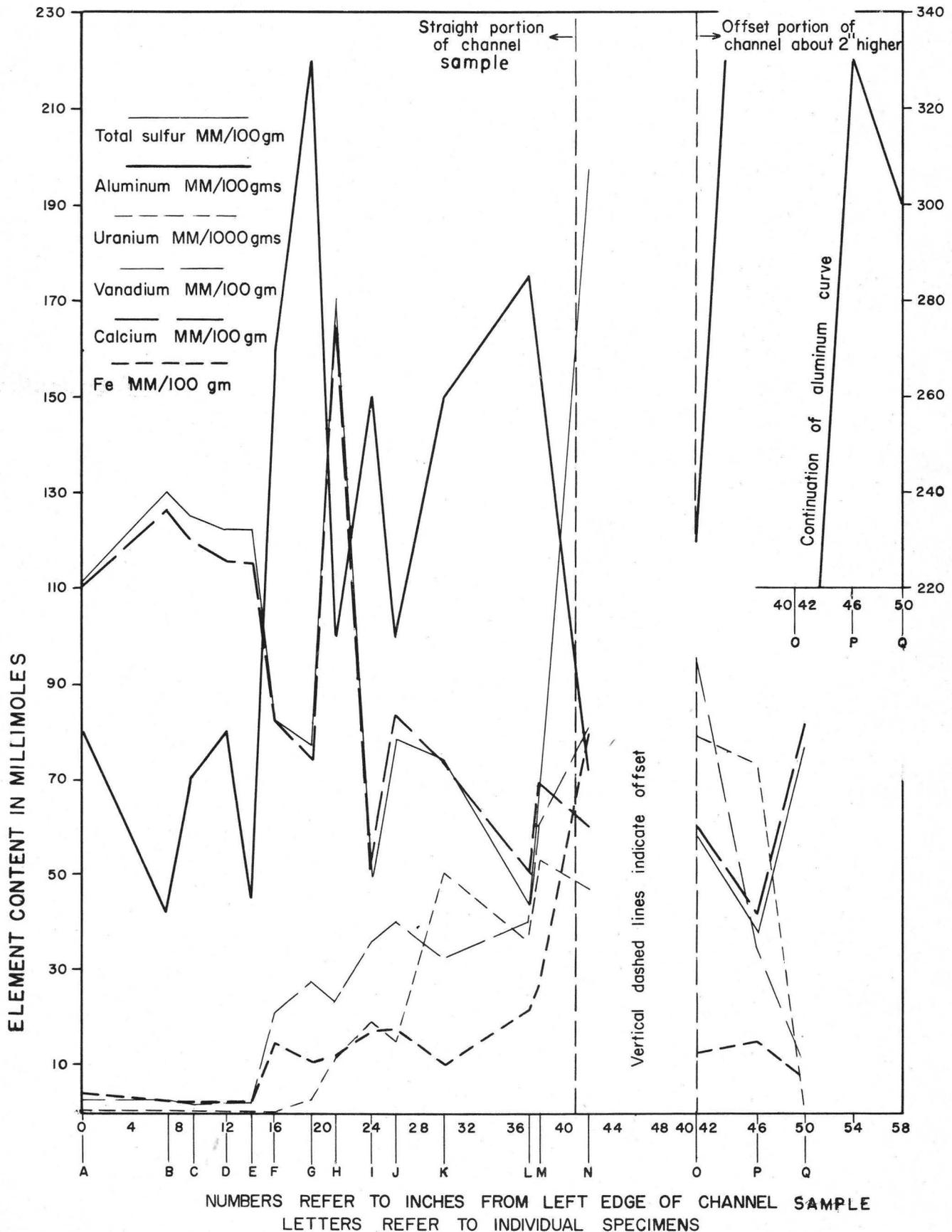


Figure 3.—Graph showing distribution of several elements across the Mineral Joe No. 1 mine channel sample. Values are in millimoles per 100 grams of sample, except uranium which is in millimoles per 1,000 grams of sample. Data derived from table 1.

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 4; 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 5. 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 (Stern and Stieff, 1956). 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.

Trace element relations

Semiquantitative spectrographic analyses of the specimens were obtained, and the results are plotted in figure 6. These data plus the

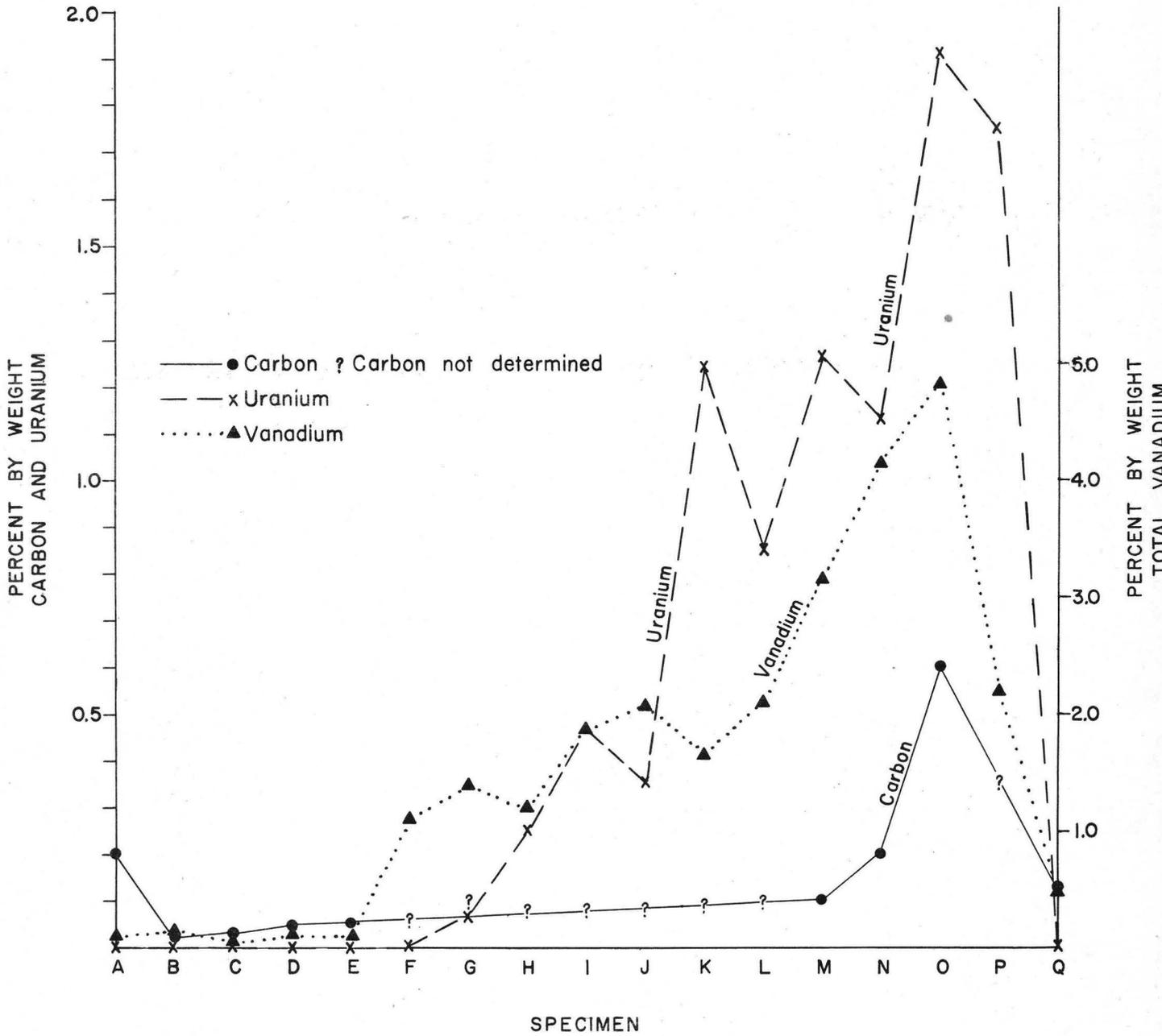


Figure 4.--Distribution of uranium, vanadium, and organic carbon in specimens across the Mineral Joe No. 1 mine channel.

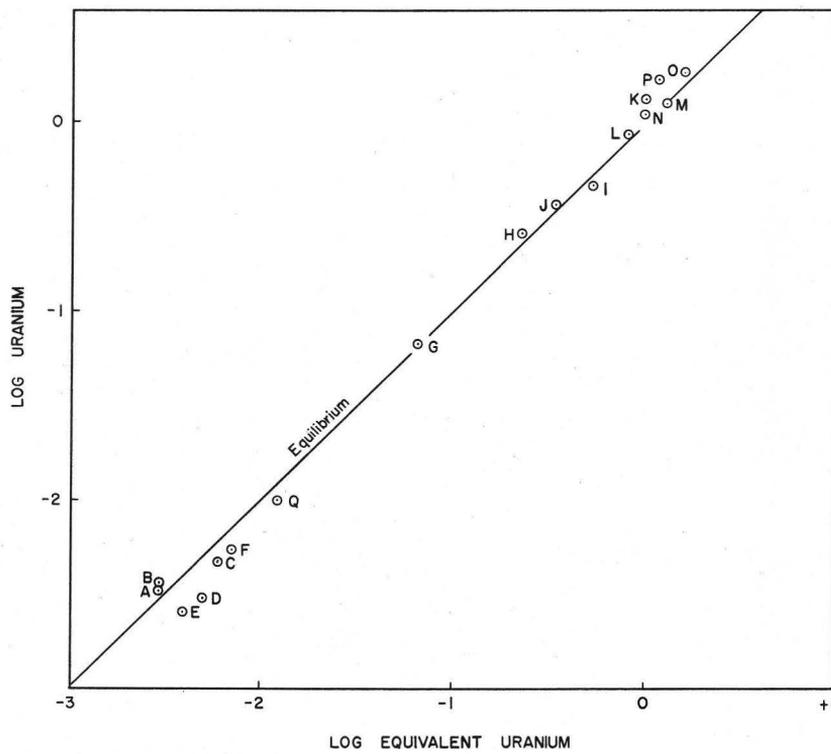


Figure 5.--Plot of log uranium against log equivalent uranium of specimens from the Mineral Joe No. 1 mine channel sample.

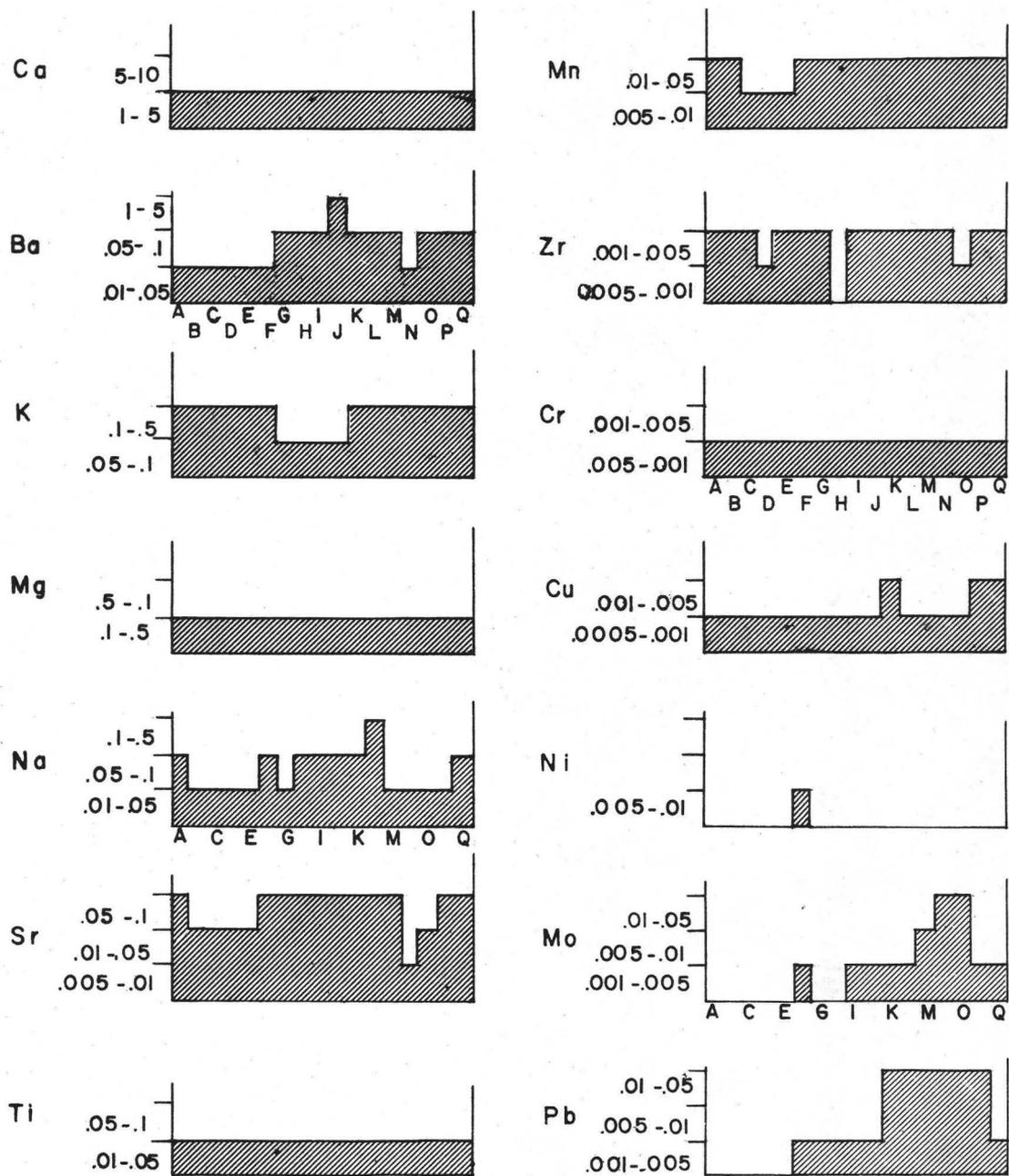


Figure 6.--Semiquantitative spectrographic analyses of specimens from the Mineral Joe No. 1 mine channel sample. Ranges are in percent. Horizontal letters designate specimens. C. A. Annell, analyst.

data in table 1, show definite strong anomalies for uranium, lead, vanadium, and iron; probably 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 (Shoemaker and others, 1955). 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 (Shoemaker and others, 1955). The most remarkable features of the mineralization 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 very 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 insoluble in cold 1N H₂SO₄, but coffinite is appreciably soluble. In the channel sample specimens practically all of the uranium is readily soluble (table 1). Neither coffinite nor uraninite could be 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 2/ 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

2/ Redox-active elements are those that change their valence state with natural changes in reducing or oxidizing environment.

present. Thus, the valences of the metals in solution need not be the same 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 milliliters of a 1N 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 1N 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 ferrous 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 (Garrels and Pommer, 1956);

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) <u>2/</u>	Iron (acid soluble) <u>2/</u>	Reducing capacity <u>3/</u> (acid soluble)
A	2.2	3.0	1.9
B	2.6	2.2	1.9
C	1.5	1.5	2.1
D	2.0	1.5	1.8
E	2.0	1.6	1.6
F	21.4	14.5	19.5
G	27.7	11.4	29.1
H	23.5	11.0	17.6
I	36.9	15.0	21.1
J	40.4	17.6	19.9
K	32.5	8.8	20.2
L	39.5	21.2	26.3
M	61.6	28.0	29.6
N	81.4	33.8	102.0
O	94.6	11.8	59.4
P	34.3	14.5	30.1
Q	9.2	6.7	15.4

1/ Extracted in 33.3 percent H₂SO₄.

2/ All the vanadium present is acid soluble; figures given were recalculated from table 1.

3/ Determined by L. B. Jenkins.

we have no measure of the amount of such reduction, but we feel it was not great enough to distort the conclusions appreciably.

In the unmineralized portion of the channel (specimens A through E), the reducing capacity is low but ranges between about $1/3$ and $2/3$ of the sum of vanadium plus iron; this is the amount of vanadium or iron, or both, which is in a reduced state, i.e., 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 M. D. Foster, written communication. 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, meta-hewettite, 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 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 of the Morrison formation.

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.

THE 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 7. 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.

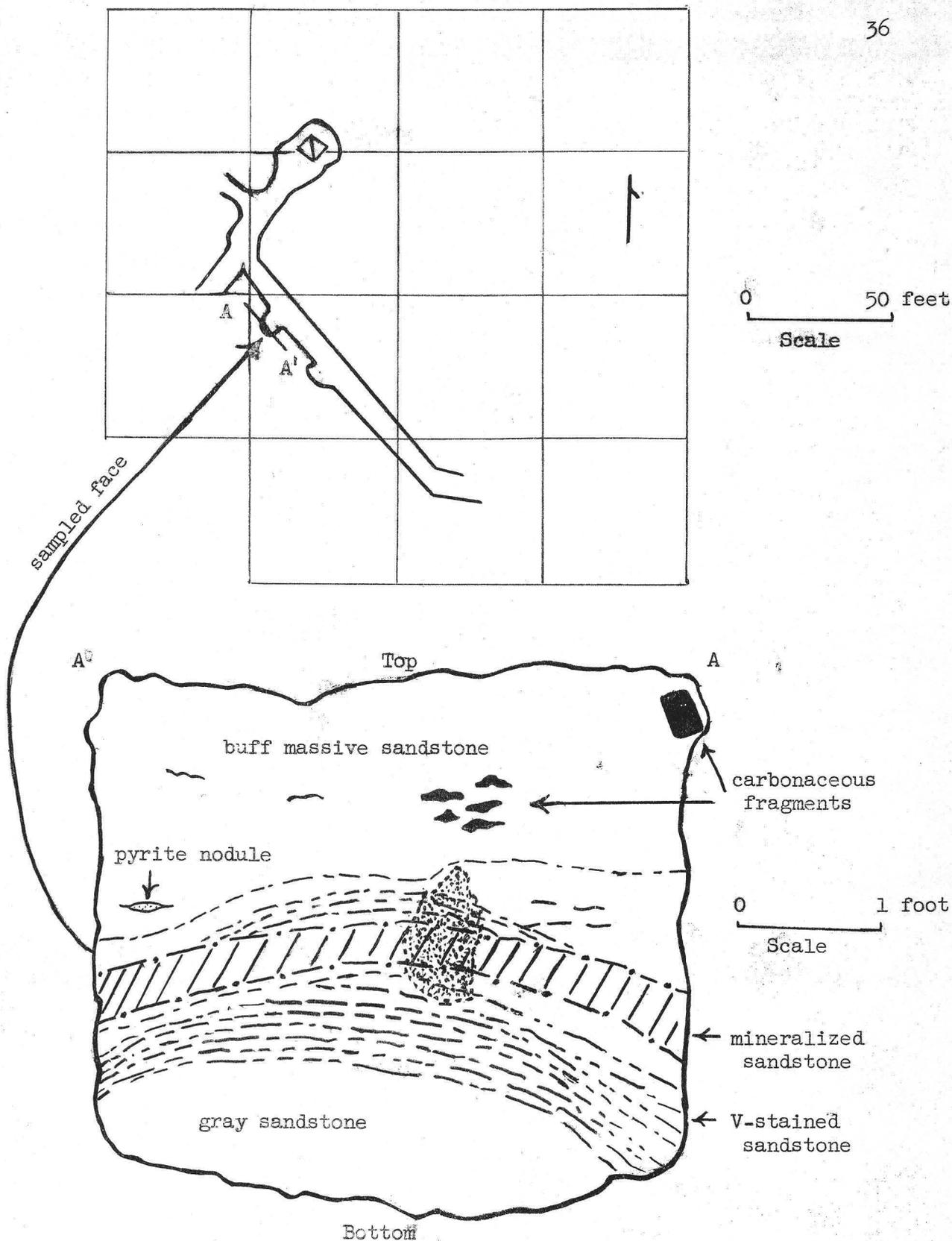


Figure 7.--Sketch of the workings of the Virgin No. 3 mine showing location of sampling site, and sketch of sampled face showing relation of channel sample to mineralized sandstone and sedimentary features. Channel sample is the shaded area.

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 figure 8. The sample was cut in half vertically as marked and divided into ten parts based on the lithologic variations. The ten segments 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, one inch thick, was cut from the right-hand portion of the channel sample and also divided into ten 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 used henceforth refer to those shown in figure 8.

Mineralogy of the channel sample

The discussion of the mineralogy is divided into two parts: weakly mineralized rock and strongly mineralized rock. This division is based on the chemical and mineralogical results. A point-count analysis was made

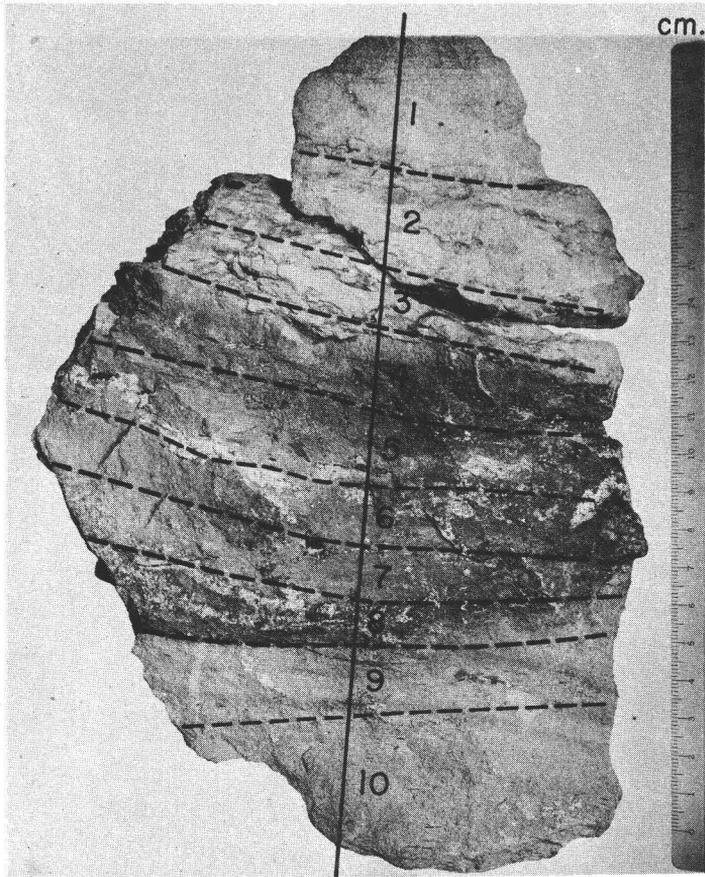


Figure 8.--Photograph of channel sample from Virgin No. 3 mine showing division of sample into specimens referred to in text.

on each thin section to determine the relative abundance of the constituent minerals, and the results were plotted in figure 9. An abrupt change is noted between specimens 3 and 4 and a lesser one between specimens 9 and 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 figure 8. 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

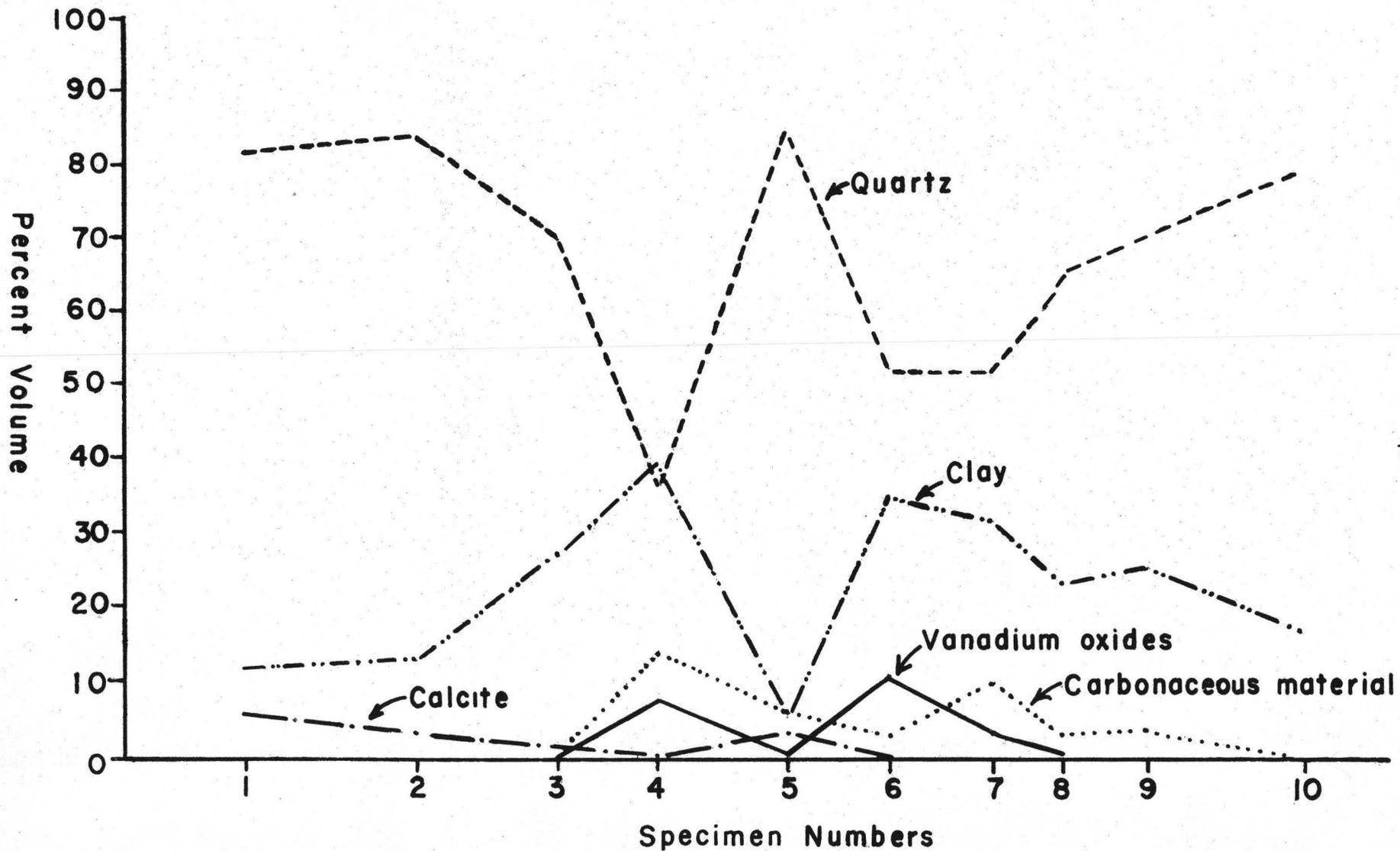


Figure 9.--Mineralogical composition, based on point-count analysis, of specimens from Virgin No. 3 mine channel sample. The specimen numbers are distributed along the horizontal base in proportion to the thickness of each segment in the channel sample.

fragments are commonly 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 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 9; 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 cusped forms. The corrosion

appears to have been greatest normal to the bedding, and the cusped 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 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 gridiron 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 ($\beta = 1.63 \pm 0.01$) is common in specimen 5 in the recrystallized quartz lenses. The irregularity in the quartz content (fig. 9), 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, evidence of strong corrosion was observed on zircon. The negative anomalies in some of the minor elements (fig. 10) 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. 9) 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

Table 3.--Analyses of specimens from the Virgin No. 3 mine channel sample (in weight percent).

Specimen	U <u>1</u> / total	eU <u>2</u> / total	U <u>1</u> / insol.	Fe <u>3</u> / total	V <u>4</u> / total
1	0.003	0.005	< 0.001	0.38	0.10
2	0.003	0.02	< 0.001	0.54	0.30
3	0.095	0.2	0.001	1.31	1.08
4	1.0	1.0	0.003	1.75	6.65
5	5.0	2.9	0.003	1.30	5.98
6	4.0	2.8	0.004	1.42	6.80
7	4.8	2.8	0.004	1.29	4.16
8	4.2	2.9	0.004	1.75	1.24
9	1.2	0.98	0.002	1.57	1.24
10	0.13	0.16	< 0.001	0.74	0.33

1/ Analyst: Roosevelt Moore, U. S. Geological Survey. Acid insoluble U determined after leaching sample 24 hours in cold 1N H₂SO₄.

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.

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.

Semiquantitative spectrographic analyses of minor and trace elements were made, and the results are shown in figure 10. 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. Barium shows no ordered trend across the channel sample and appears to concentrate in the areas of strong quartz overgrowths. Calcium maintains a constant level across the channel. Negative anomalies coinciding with the mineralized zone are apparent for K, Na, Mn, Cu, and Ni. Tin 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 sandstone (Shoemaker and others, 1955). 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.

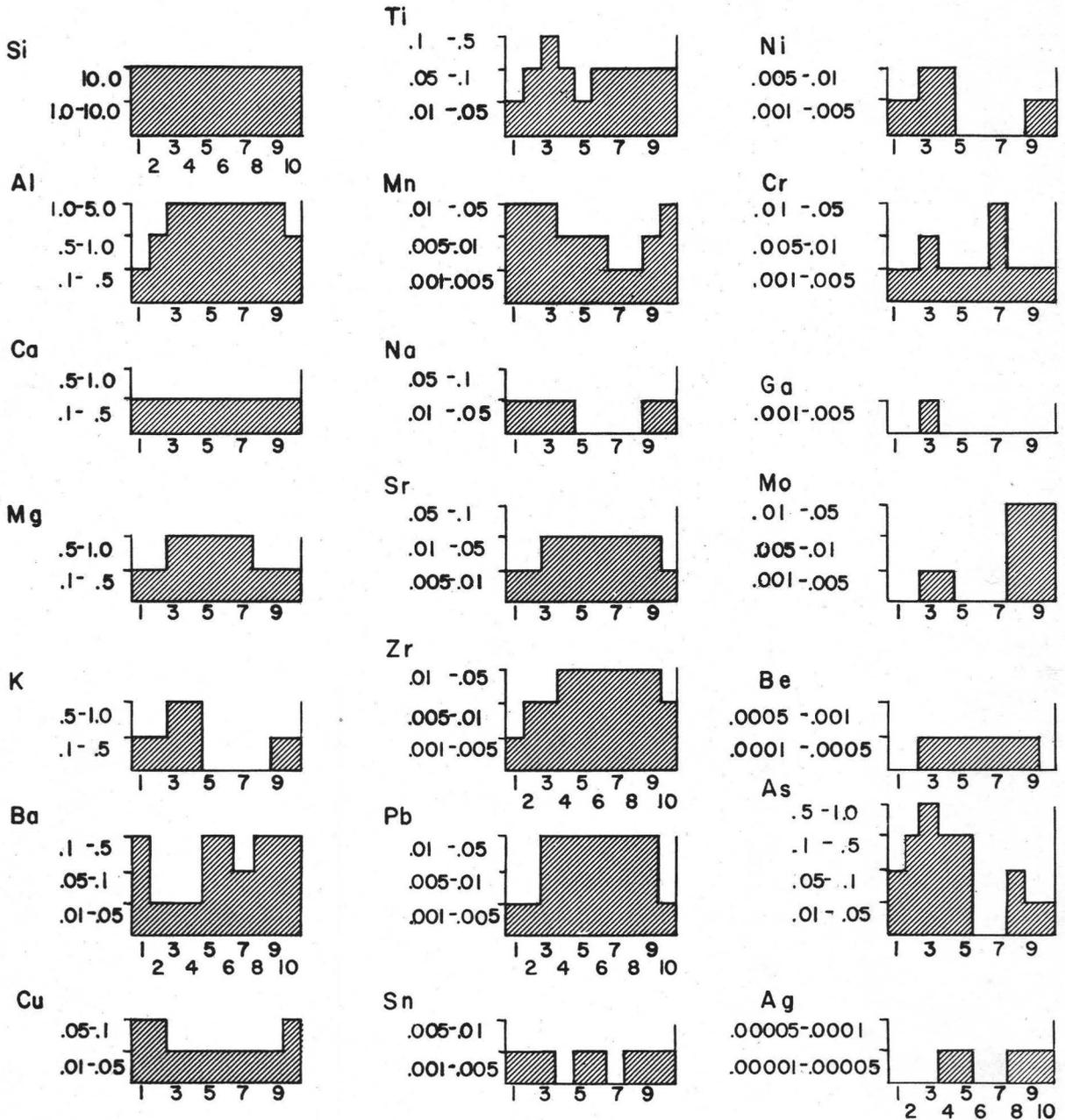


Figure 10.--Semiquantitative spectrographic analyses of specimens from the Virgin No. 3 mine channel sample. Ranges are in percent. Horizontal figures designate specimens. Joseph Haffty, analyst.

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 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 non-sulfide 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).

From the mineralogy, it is known that vanadium 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, and 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

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 100 grams of sample.)

Specimen	Vanadium <u>2/</u>	Iron <u>3/</u> (acid soluble)	Uranium <u>2/</u>	(V + Fe + U)	Reducing capacity <u>4/</u> (acid soluble)
1	1.96	6.6	0.03	8.6	3.4
2	5.97	8.8	0.03	14.8	9.6
3	19.6	17.4	0.78	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 33 1/3 percent H₂SO₄.

2/ Essentially all V and U were soluble in the extraction; values given are total V and total U recalculated from table 3.

3/ Analyst: M. H. Delevaux, U. S. Geological Survey.

4/ Analyst: L. B. Jenkins, U. S. Geological Survey.

near that of uraninite. The stability relations of the vanadium-bearing clays are not known, but work by M. D. Foster (written communication) suggests that in this 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 to 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 (Garrels and Christ, 1956). 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, and 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 lithology. 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; Evans, 1956) 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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