GEOLOGICAL SURVEY CIRCULAR 224

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

By Aaron C. Waters and Harry C. Granger

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ABSTRACT

The relationships between uranium-vanadium ore deposits on the Colorado Plateaus and volcanic material that, in part, make up the host rocks suggest that the uranium and vanadium have a complex origin and history, and that they were emplaced during the structural deformation and igneous intrusion of Tertiary time.

Volcanic debris, now altered to clay minerals, has been recognized in the Salt Wash sandstone and Brushy Basin shale 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 deposited as overgrowths on the quartz grains was probably released by devitrification of the glassy volcanic material. At a later date the quartz grains were dissolved and vanadium hydromica and uranium-bearing minerals were formed. Deposition of the ore minerals was 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, however, implies either (1) reactivated 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

In 1951 the writers visited many of the uranium-bearing localities on the Colorado Plateaus (fig. 1) and collected samples of the ores, sedimentary rocks associated with the ore, and Tertiary igneous rocks that occur as intrusive masses in the sedimentary rocks at some localities. These samples were, in part, analyzed and studied.

Early in the work it was recognized that some of the Mesozoic sedimentary formations on the Colorado Plateaus 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 Plateaus occur chiefly in the upper part of the Salt Wash sandstone member of the Morrison formation, and in the Shinarump conglomerate, although they are by no means confined to these units. Each of these stratigraphic units contains appreciable amounts of volcanic debris, although their major constituents are nonvolcanic. Each is also overlain by a so-called "mudstone" stratigraphic unit that contains a high proportion of altered volcanic ash--the Chinle formation above the Shinarump, and the Brushy Basin shale member above the Salt Wash sandstone member.

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 preliminary report.

The evidence indicates that volcanism took place during, and immediately following the time when the host rocks for the "Plateau type" uranium deposits were accumulating but that later igneous activity, particularly the intrusion of the laccolithic mountain groups, was of primary importance in the origin of the ore deposits.

VOLCANIC MATERIAL INCLUDED IN THE STRATIGRAPHIC SECTION

General field characteristics

The Brushy Basin shale member of the Morrison formation of upper Jurassic age is a sequence of thin-bedded argillaceous sediments with interbedded sandstone lenses. The volcanic origin of much of the
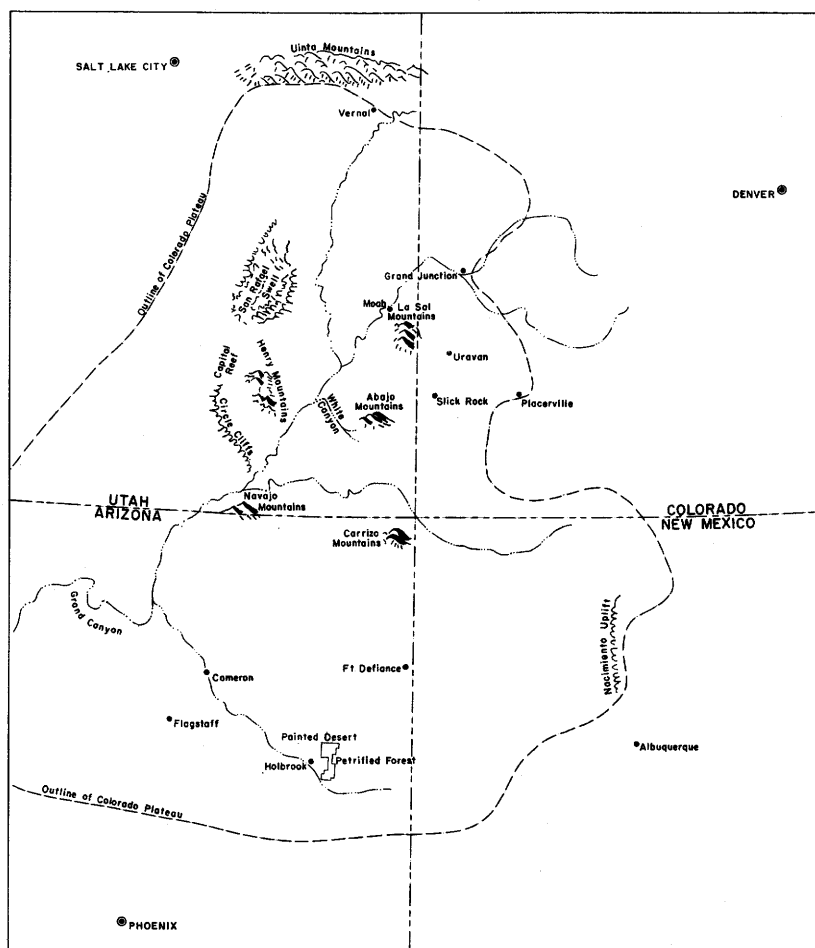
Figure 1.--Index map, Colorado Plateaus.

argillaceous material (Hess, 1933, pp. 463-464; Stokes, 1944)[1] is suggested by two features: (1) the fluffy, popcorn-like 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--each layer is commonly a different color. The chief colors are pastel shades of olive green, blue green, smoky white, pale pink, creamy yellow, blackish purple, and maroon.

In the Chinle formation of Triassic age, especially in its lower part, are many argillaceous beds with characteristics similar to those of the Brushy Basin (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 nonswelling clays.

Both the Salt Wash sandstone member and the Triassic Shinarump conglomerate contain typically cross-bedded quartz with thin conglomeratic lenses

and layers. Clay is generally present as a prominent constituent between the sand grains, and as tiny rounded pellets 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-like surfaces and typical variegated colors; most are maroon or green beds of nonswelling clay.

Fossil wood is abundant in the Shinarump conglomerate, and is also found at many places in the Salt Wash sandstone member. 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. If charcoal is present, then 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 large 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 these 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 conglomerate are highly lenticular, and in places lie in definite scour channels eroded into the underlying Moenkopi formation, 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 conglomerate was deposited by a system of braided streams. These dropped their heterogeneous loads in the stream channels, filling them, and later 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 an interfingering of coarse and fine pebbly sandstone lenses, channel unconformities, clay seams, and "trash piles."

The Salt Wash sandstone member of the Morrison 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, and other characteristics indicative of swift-flowing over-loaded streams. These characteristics are in general more common in the upper part of the Salt Wash, where it grades into or interfingers with the overlying Brushy Basin. The upper, more heterogeneous portion of the Salt Wash is the favored place for uranium deposits.

The stratigraphic work of L. C. Craig and coworkers (1951) shows that the Salt Wash sandstone member was deposited as a broad, gently-sloping alluvial fan which spreads northeastward from a 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 and Chinle sequence had its source in highlands to the south and southeast, and that the sediments were graded toward the Late Triassic California sea in broad fans and deltas.

A question often asked concerning the Shinarump conglomerate 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 generally less than 100 feet of coarse pebbly sediments that seemingly indicate a flood type of deposition from swiftly flowing torrents.

In the writers' opinion the heterogeneous character of the sandstones of the Shinarump, and of those comprising parts of the Salt Wash sandstone member, 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 destroyed 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 particles 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 water-laid tuffs of the Tertiary and Pleistocene just east of the Cascade Mountains in Oregon, and the deposits on the alluvial plains surrounding the Javanese volcanoes are similar to 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 in the course of the field work. In the method used a saturated water solution of benzidine was dropped 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 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 may 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 of tentative value only.

Chinle formation

The widespread light-colored (green, light-blue, smoky-white, pale-gray) clays with the popcorn-like surfaces that are 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 Plateaus from Cameron, Arizona, on the

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

[Based on X-ray studies by Alice Weeks]

Locality	Sample no.	Minerals
Woodside anticline, Utah----------	L537	Montmorillonite, hydromica, quartz, and calcite.
	L535	Do.
South of Floy, Utah---------------	L442	Montmorillonite, quartz, and kaolinite.
	L443	Do.
	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	Do.
Dry Creek anticline, Colorado------	L464	Hydromica(?) and quartz.
Dolores group of mines, Colorado---	L468	Kaolinite, hydromica, and quartz.
	L469	Do.
	L470	Montmorillonite and quartz.
	L539	Montmorillonite.
Unaweep, Colo.---------------------	L455	Montmorillonite and quartz.
Escalante Forks, Colo.-------------	L460	Kaolinite and quartz.

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

[Based on X-ray studies by Alice Weeks]

Locality	Sample no.	Minerals
Woodside anticline, Utah----------	L534	Hydromica, quartz, and calcite.
	L533	Do.
South of Floy, Utah---------------	L448	Hydromica and quartz.
	L449	Do.
	L450	Hydromica, montmorillonite, kaolinite, quartz, and calcite.
	L451	Hydromica, quartz, and calcite.
Kane Springs, Utah----------------	L480	Do.
La Sal Creek, Utah----------------	L475	Do.
Dolores group of mines, Colorado---	L471	Hydromica, kaolinite, quartz, and calcite.
Unaweep, Colo.---------------------	L456	Hydromica, quartz, and calcite.
Escalante Forks, Colo.-------------	L461	Hydromica, kaolinite, and quartz.

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. Generally these either do not react to benzidine, or give faint indefinite colors. The nonreactive beds greatly predominate in some areas.

Brushy Basin shale member of the Morrison formation

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 nonreactive clays. Many of the red and purple beds interstratified with the lighter colored clay also react, although the blue is partly masked by the iron oxides.

Shinarump conglomerate

The conglomerate and sandstone of the Shinarump generally contain thin clay seams, small clay pellets, and, in places, clusters of 1/2- to 2-inch clay galls and in places large angular fragments of clay. 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 within the same outcrop. In general, the matrix clay and the small pellets less than 1/4 inch in diameter react, although many exceptions were noted. In some outcrops two or more kinds of clay galls may be clustered together in the same lens of sandstone. One clay may react to benzidine, another not at all, and a third one may react slightly, or may contain small highly reactive pellets in a nonreactive matrix. In places it can be established that the nonreactive 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 sandstone member of the Morrison formation

The sandstones and interbedded shales and mudstones of the Salt Wash have been systematically tested with benzidine only in the area directly south of the Four Corners and in a few parts of the "Uravan mineral belt" (Fischer and Hilpert, 1952).

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 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, clays that are reactive to benzidine 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 incorporated in sandstone lenses are commonly reactive, although, as at many localities in the Shinarump, nonreactive fragments are common.

To summarize and generalize from these admittedly inadequate data, it appears that both the Shinarump and Salt Wash were derived chiefly from a sedimentary landmass (Craig and others, 1951, p. 42) that 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 apparently began, 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 a greater extent 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 in part confirmed by X-ray and petrographic evidence, as discussed in the following paragraphs.

X-ray investigations

X-ray studies of clay samples from the formations of the Jurassic and Cretaceous systems 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 shale and Salt Wash sandstone 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 clays from the Brushy Basin shale member contain montmorillonite. Some 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.

In a general way these results confirm the benzidine tests, which indicated that the clays of the Brushy Basin shale member are largely bentonitic, whereas the thick beds of red and green clay interstratified with the sandstones of the Salt Wash are nonreactive. Benzidine tests showed, however, that many of the thin clay seams, and some of the clay galls in "trash piles" of the Salt Wash sandstone 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 in some of the clays of the Brushy Basin shale member.

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 the samples of the Shinarump, Chinle, Salt Wash, and Brushy Basin stratigraphic units. In addition, through the kindness of R. 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 sandstone 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 nonvolcanic 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 remain. The textures are beautifully preserved in some specimens (figs. 2 and 3), indistinctly in others. Small particles of porphyritic lava and less commonly pieces of devitrified spherulitic obsidian are better preserved. Even in fragments whose feldspar phenocrysts are completely altered to clay, their textures are unmistakable (fig. 3). Particles 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 too greatly altered for precise identification. 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 is necessary, but the available evidence indicates that the lavas were chiefly biotite latites and biotite keratophyres, with perhaps some admixture of andesitic and dacitic materials.

The source of the volcanics cannot be determined with the meager 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 particles 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 units

Thin sections of clayey sandstones from the Shinarump conglomerate and from the ore-bearing layers of the Salt Wash sandstone member also show volcanic debris, but it is not as easy to recognize as in the Chinle and Brushy Basin units. 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, Ariz., 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 with particles of lava still sticking to them (fig. 4), contrast sharply with the nonvolcanic constituents of the sandstones.

The main nonvolcanic 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 contrast strikingly with the easily destroyed euhedral books of partially chloritized biotite (fig. 4), the half kaolinized sanidines and plagioclases, and the fragile particles 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 sandstones of the Shinarump and upper Salt Wash 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

A. From the Brushy Basin member
   of the Morrison formation

B. From the Chinle formation

0   0.1 mm
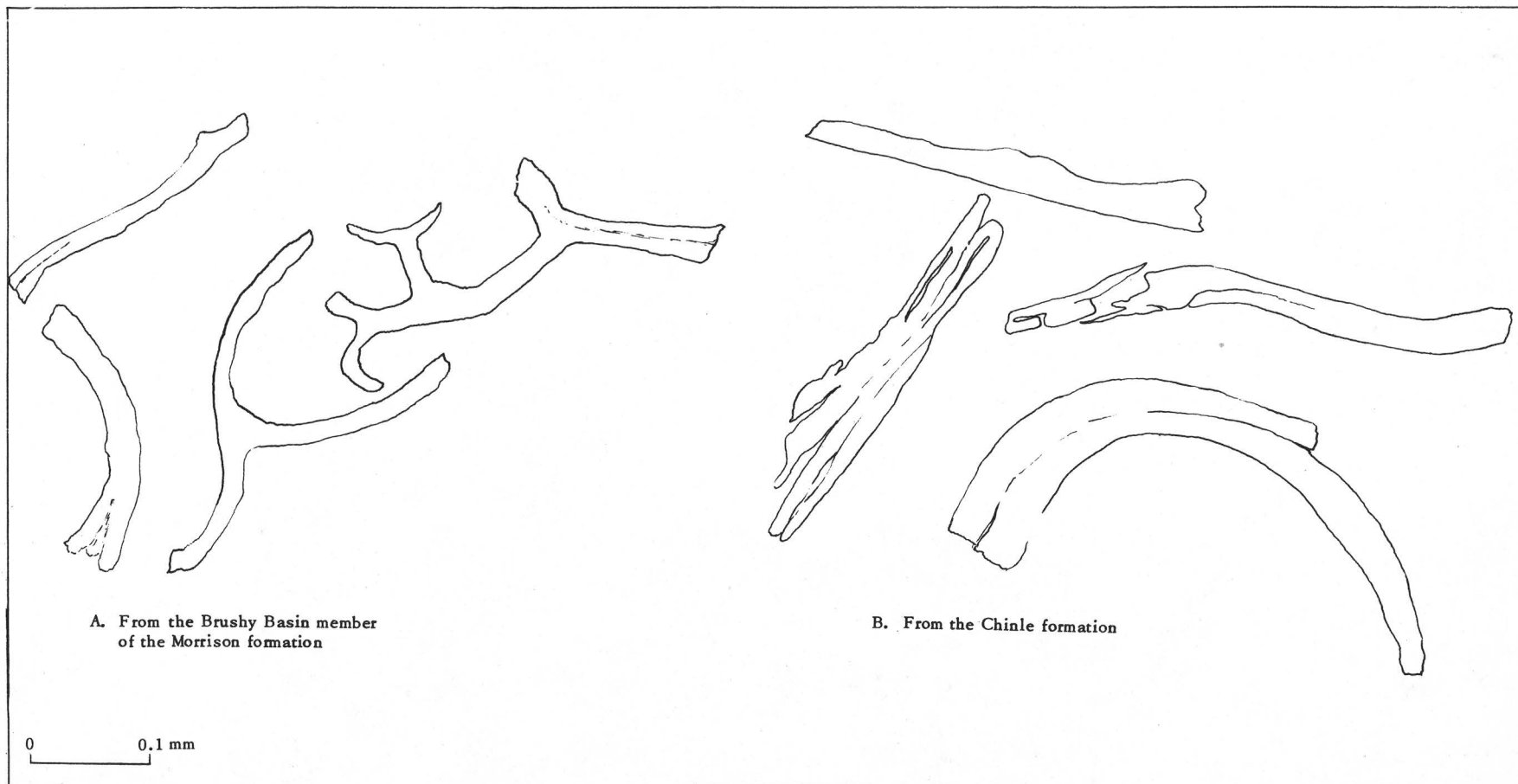
Figure 2.--Glass shards altered to clay minerals.

Tuff fragment

Lava fragment

Fragment of tuff containing
particles of distorted pumice

Pumice, altered to
montmorillonite

0   0.25 mm

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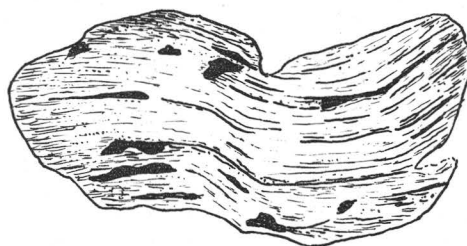
A. - Note slight rounding

0   0.25 mm
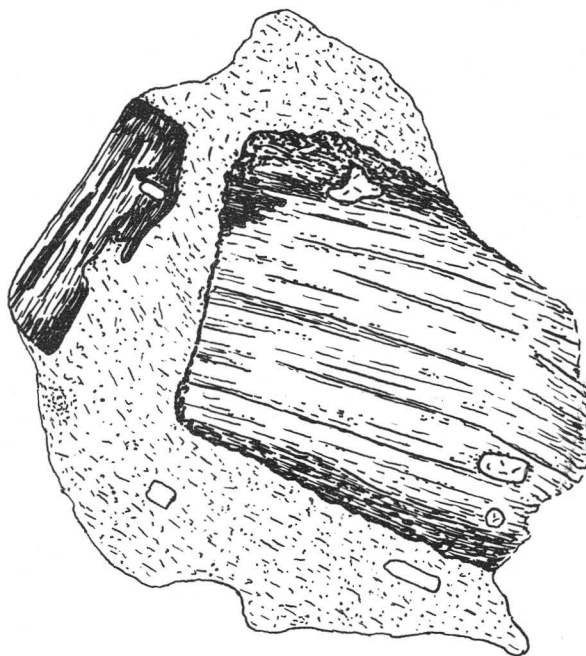
B. Biotite phenocryst partly enclosed in devitrified glass matrix

0   0.25 mm

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

of the sandstone, but, at least near the ore deposits, the common interstitial clay appears to be montmorillonite.

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 also 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 con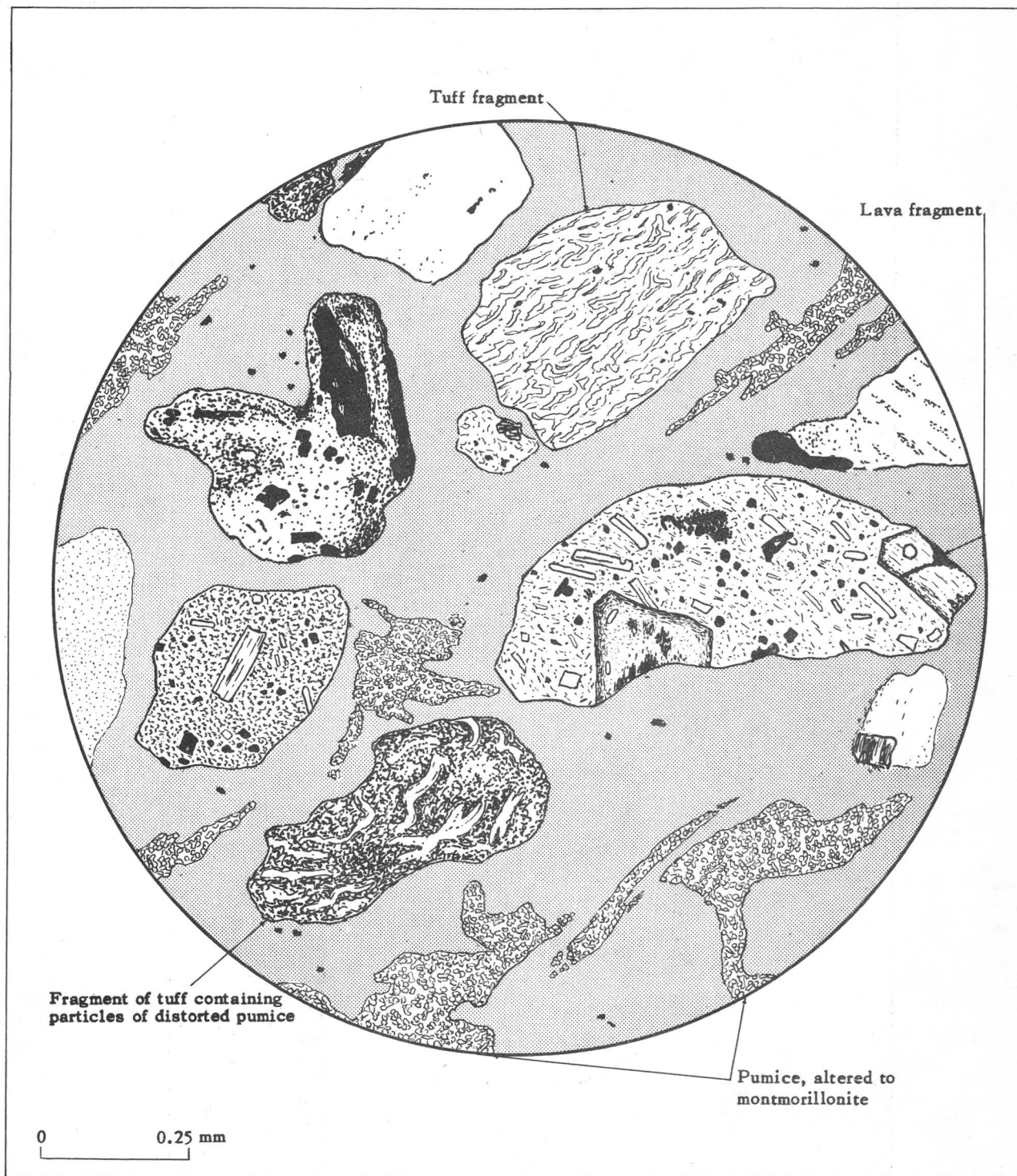tent than along an adjoining bed with less clay--the ore gradually plays out in the less favorable bed. In rolls, however, the ore boundary is generally sharp, and transects the bedding in a smooth curve. A conspicuous banding of the ore minerals may be developed along the edges of the curve.

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 and others, 1952), and on a much smaller scale by the occurrence of features such as those sketched in figure 5 from the Dolores group of mines.

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 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 well-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,(the Happy Jack mine at White Canyon, and the Sevenmile Canyon deposits northwest of Moab, for example) the wood is replaced by clearly visible masses of pitchblende, or by associated sulfides such as pyrite, chalcocite, or galena, but more commonly the woody tissues are impregnated, replaced,and partially destroyed by cryptocrystalline black grains of uranium and vanadium-bearing substances. Commonly the mineralization extends 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 from a few inches to 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 particles 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 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 must be done before we understand how uranium minerals are accumulated and held by organic materials. (McKelvey and Nelson, 1950; Battelle Mem. Inst., 1948-49.)

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 this mechanism seems inadequate because of the vast volume of solution that would be needed to precipitate the uranium found in even a single richly fossiliferous log. More promising leads, perhaps, are 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., 1948-49.)
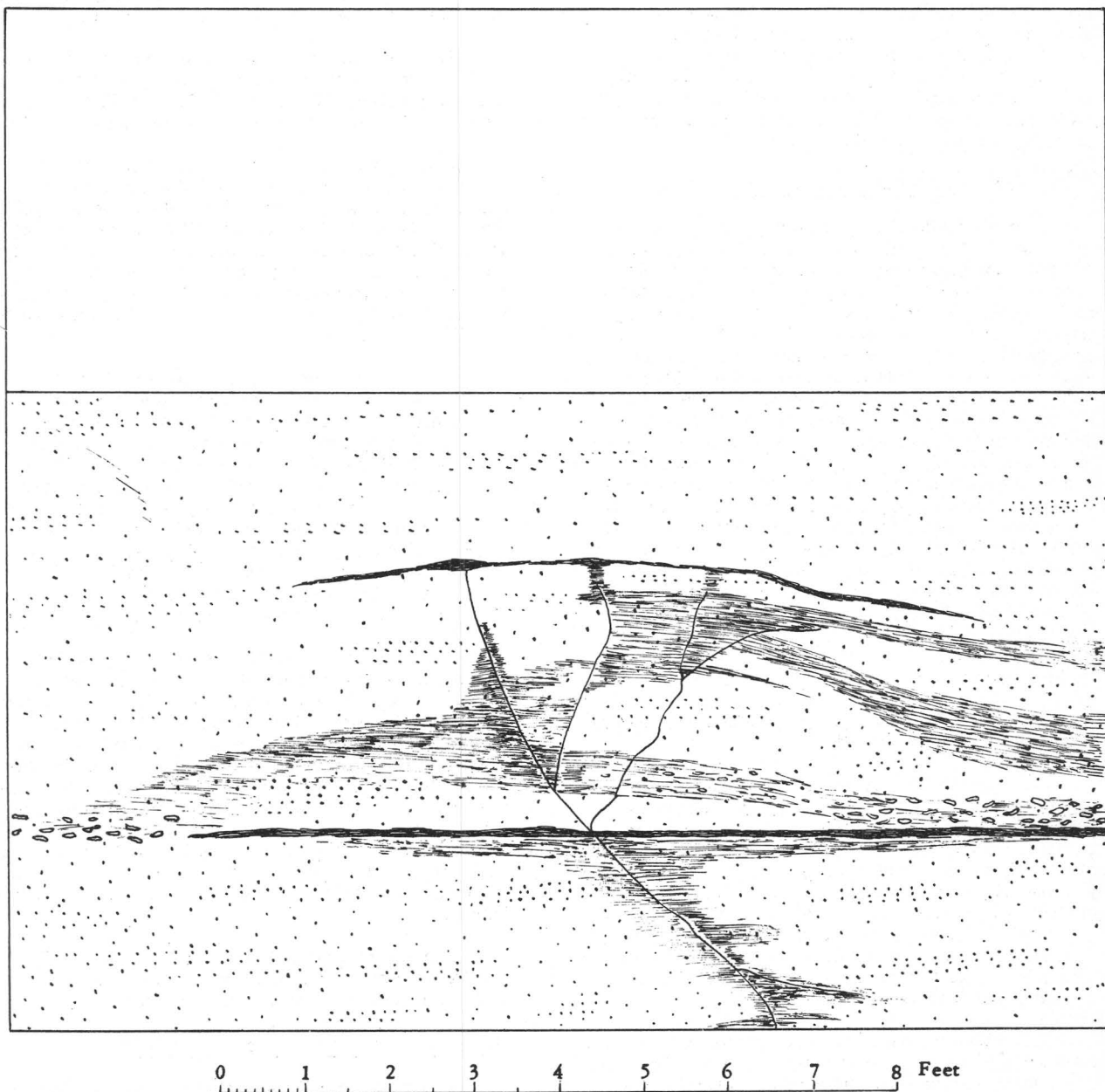
Figure 5.--Sketch showing local fracture control of ore, Dolores group of mines, Uravan, Colo.

In the Shinarump and upper Salt Wash units there would be excellent opportunity for the abundant particles 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 may 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 (oxidation-reduction) 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, apparently were able to trap and cause precipitation of uranium and vanadium minerals from solution. Characteristically the ore minerals occur as impregnations 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 so-called 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 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 determine just what effect both fossil wood and clays of different kinds have had on the precipitation of uranium. It is obvious from the field relations that they have clearly had some effect.

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 see them individually. 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 R. 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 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, Colorado and the White Canyon area in Utah.

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

Montmorillonite-vanadium clay transition

At a group of claims east of the Carrizo Mountains of northeast Arizona, thin seams of clay interstratified
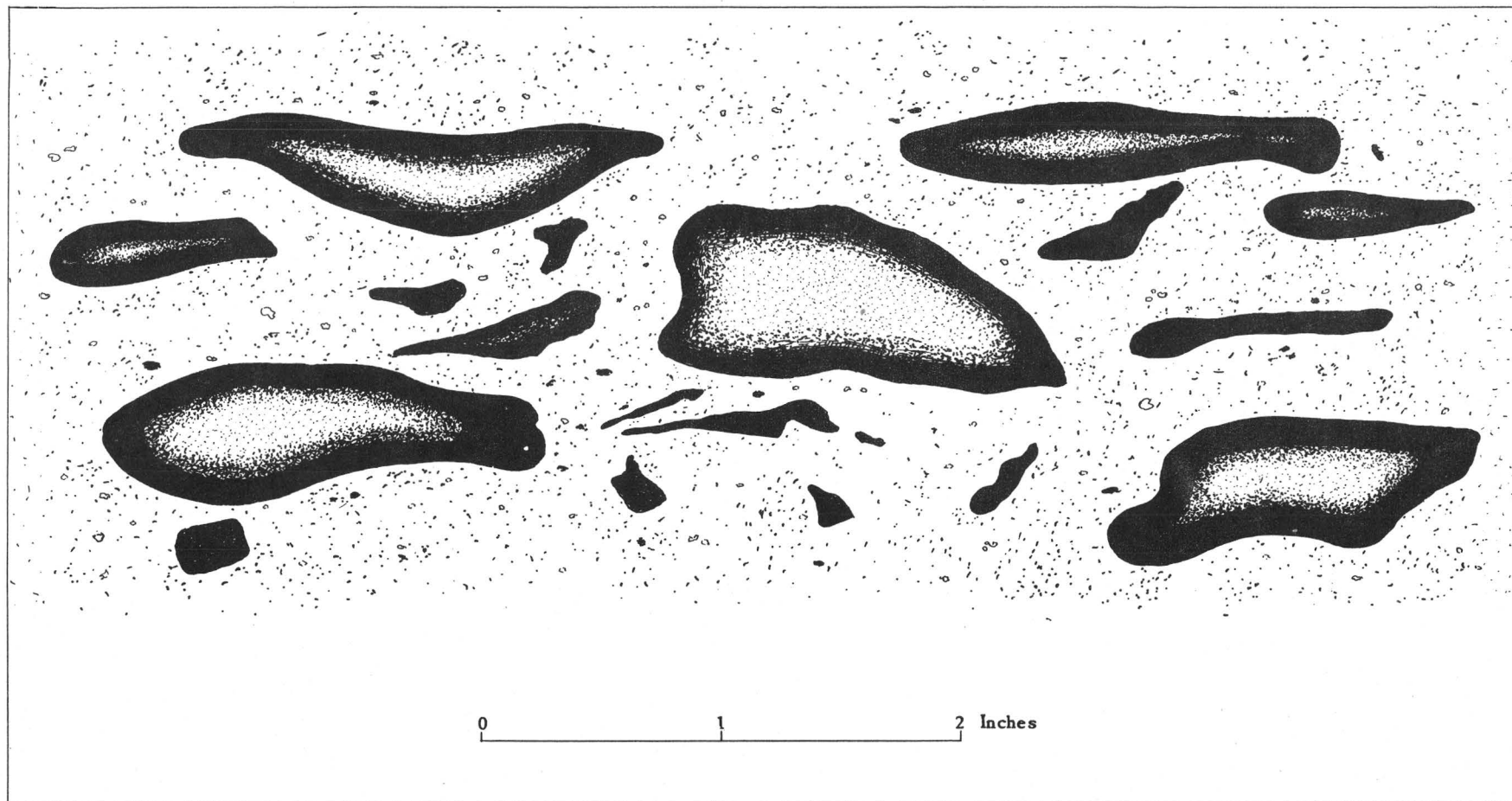
Figure 6.--Clay galls in sandy matrix, Georgetown group of mines, Slick Rock, Colo.
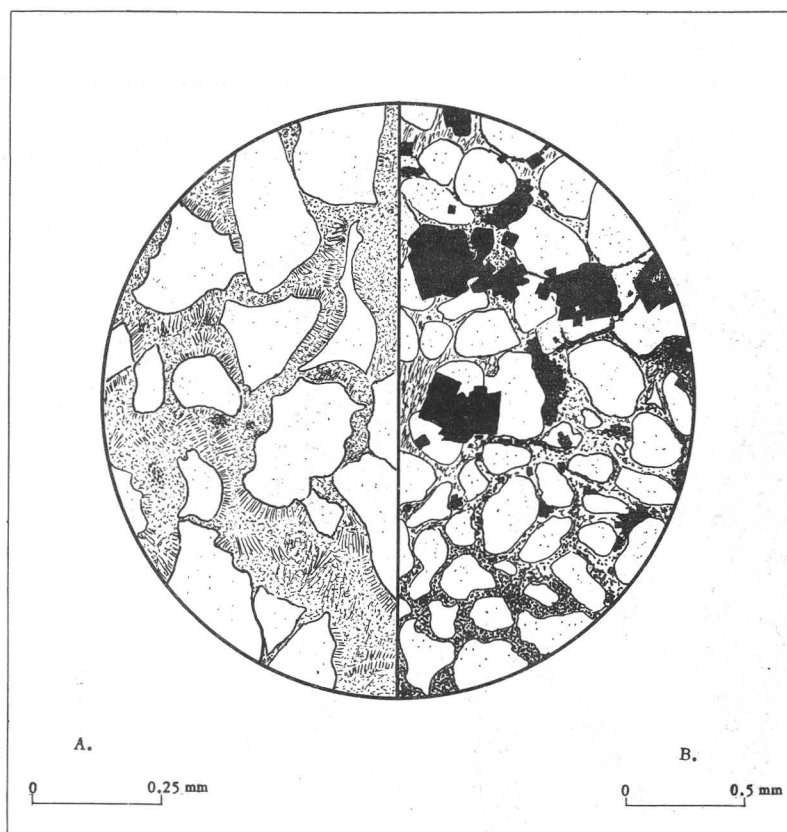
Figure 7.--Ore, Salt Wash sandstone member of the Morrison formation near Uravan, Colo.

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 (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. This is an expectable transition, inasmuch as 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. In this area 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 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 particles 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 ?) acquires 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 more individualized, until ultimately the galls consist of a homogeneous mat of micaceous flakes of a deep brown, 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, although 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 (unfortunately, separated before the petrographic work was done and hence containing variable amounts of shale and volcanic pellets in each sample) showed the following changes in vanadium, uranium, silver, and cobalt contents:

Thin sections from the Waterfall group of mines northeast of Monticello, Utah and from other places on the Colorado Plateaus 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 is necessary, especially 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, although meagre, indicate that silicification is more common 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 clays of the Brushy Basin shale member 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.

The silicification appears to be earlier than the deposition of the vanadium-uranium ore minerals, as shown by the following relations.

Solution of quartz grains

Many thin sections of the ores show 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 dissolved, 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 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 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 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

15

0   0.1 mm

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

0   0.5 mm

A. - Note solution features on quartz grains
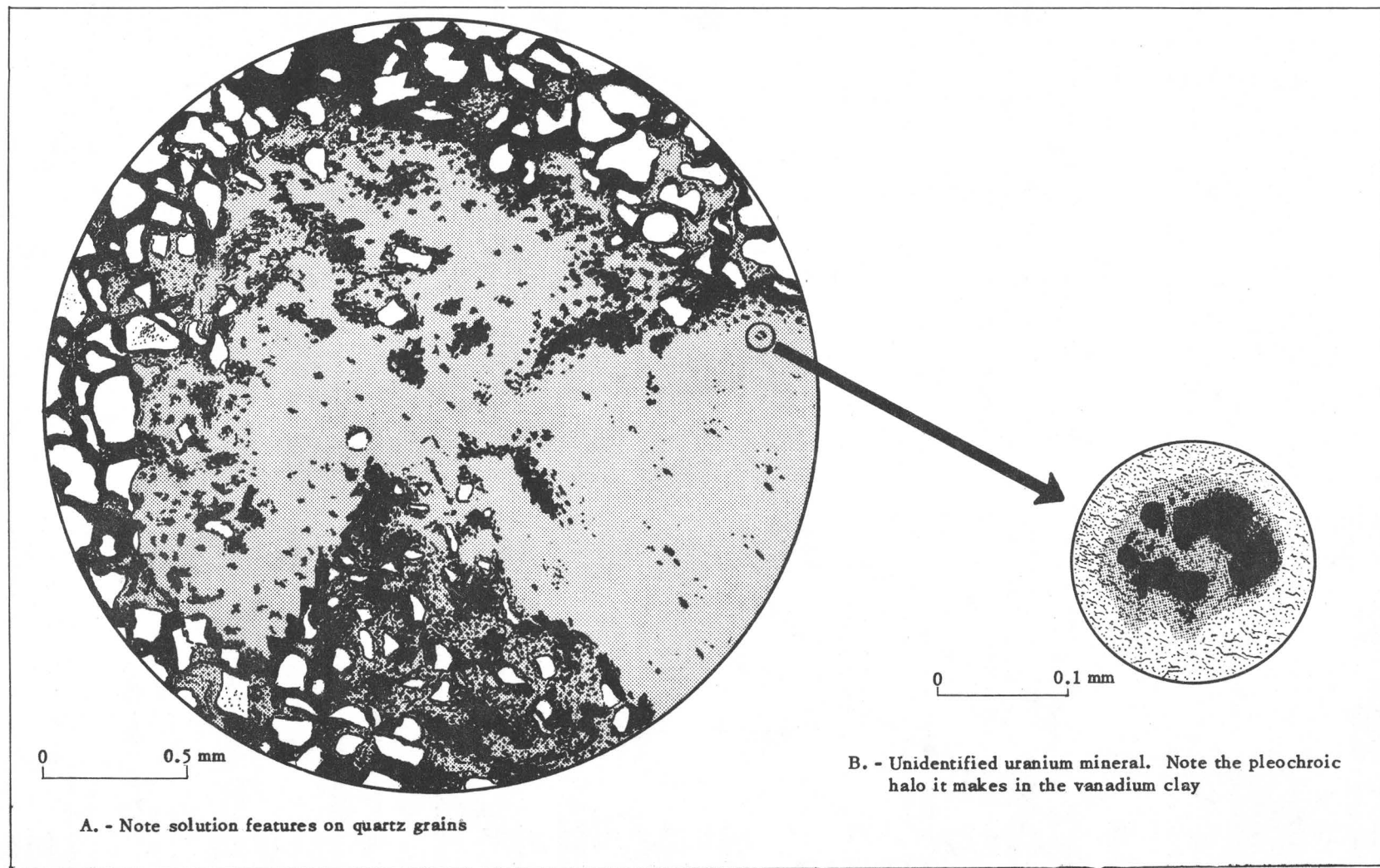
Figure 8.--Vanadium clay pellet derived from a gall of montmorillonite. Section cut from a "trash pile" lens at the Dolores group of mines, Uravan, Colo.
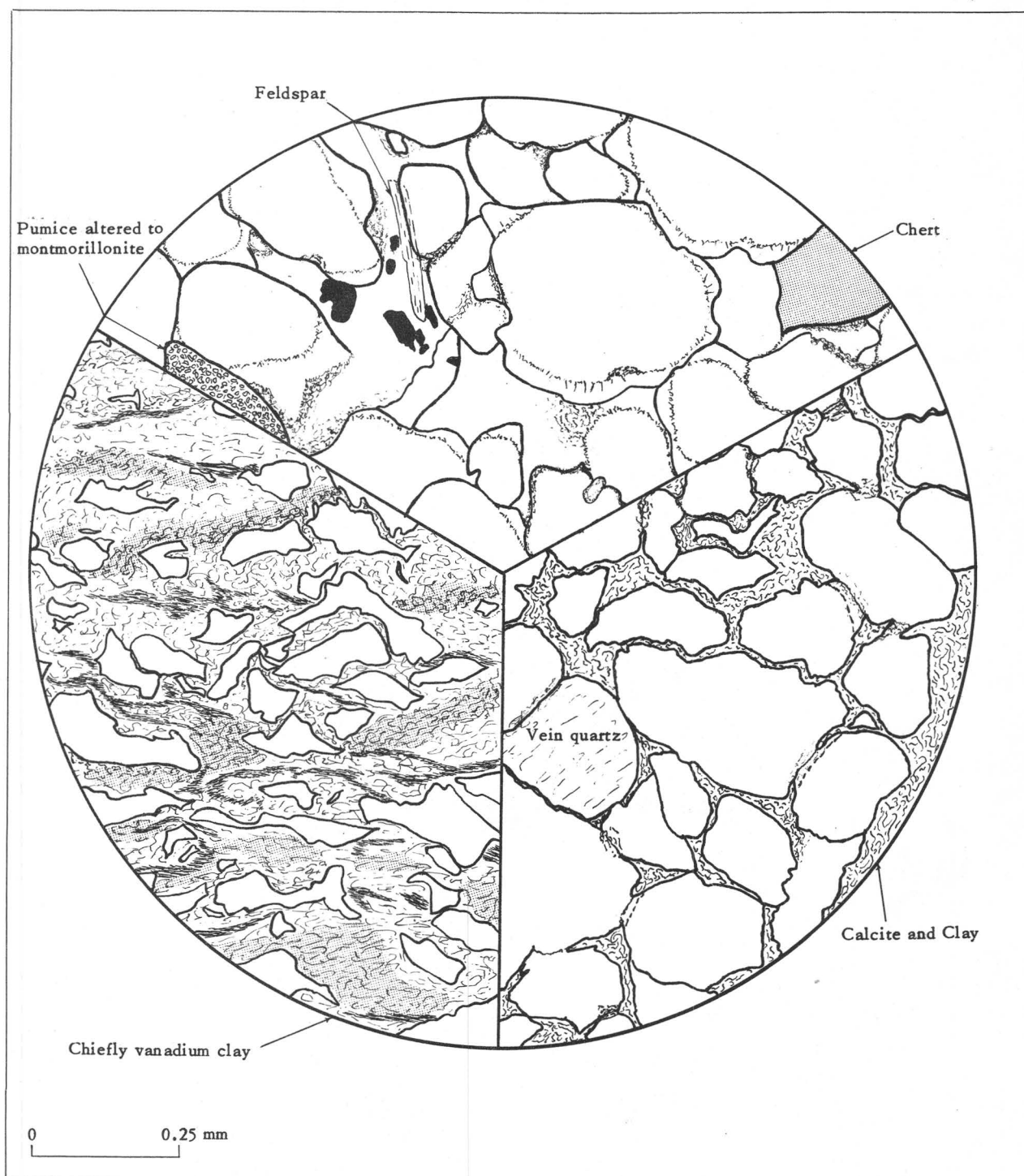
Figure 9.--Authigenic overgrowths and solution features on quartz grains shown in different parts of a single thin section of ore. Salt Wash sandstone member of the Morrison formation.
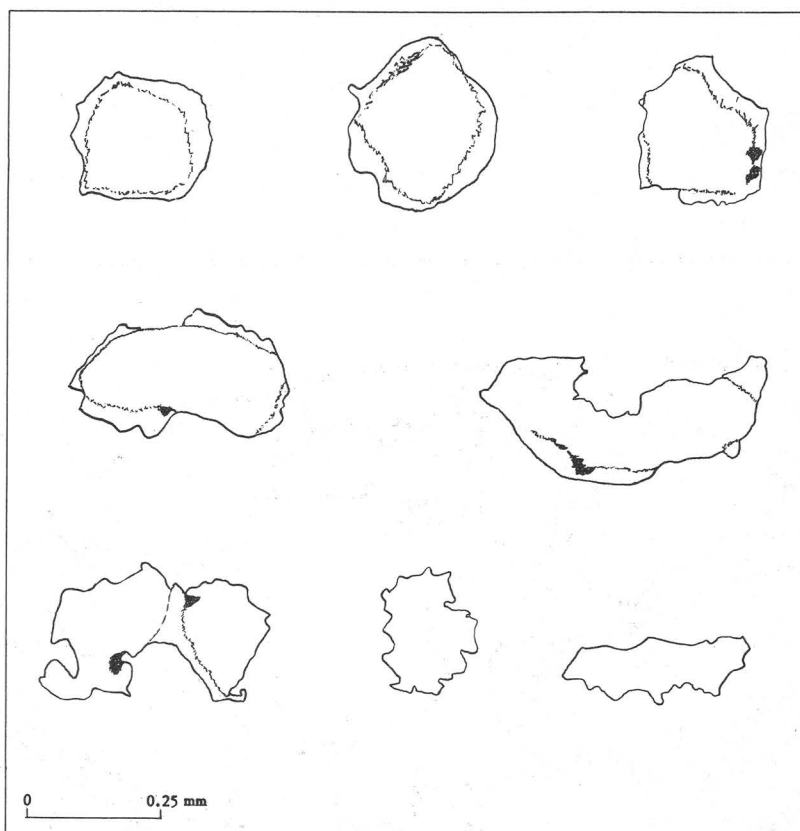
Figure 10. --Stages in the solution of secondarily enlarged quartz grains in an ore body in the Salt Wash sandstone member of the Morrison formation.
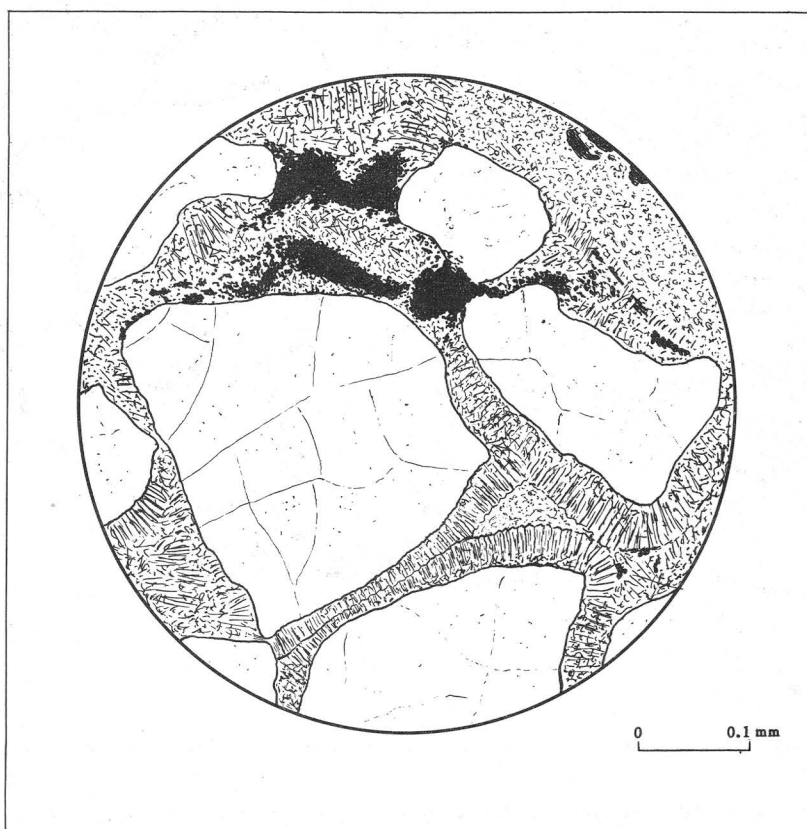
Figure 11. --Clear quartz grains surrounded by vanadium clay dusted with unidentified uranium-bearing(?) mineral.

18
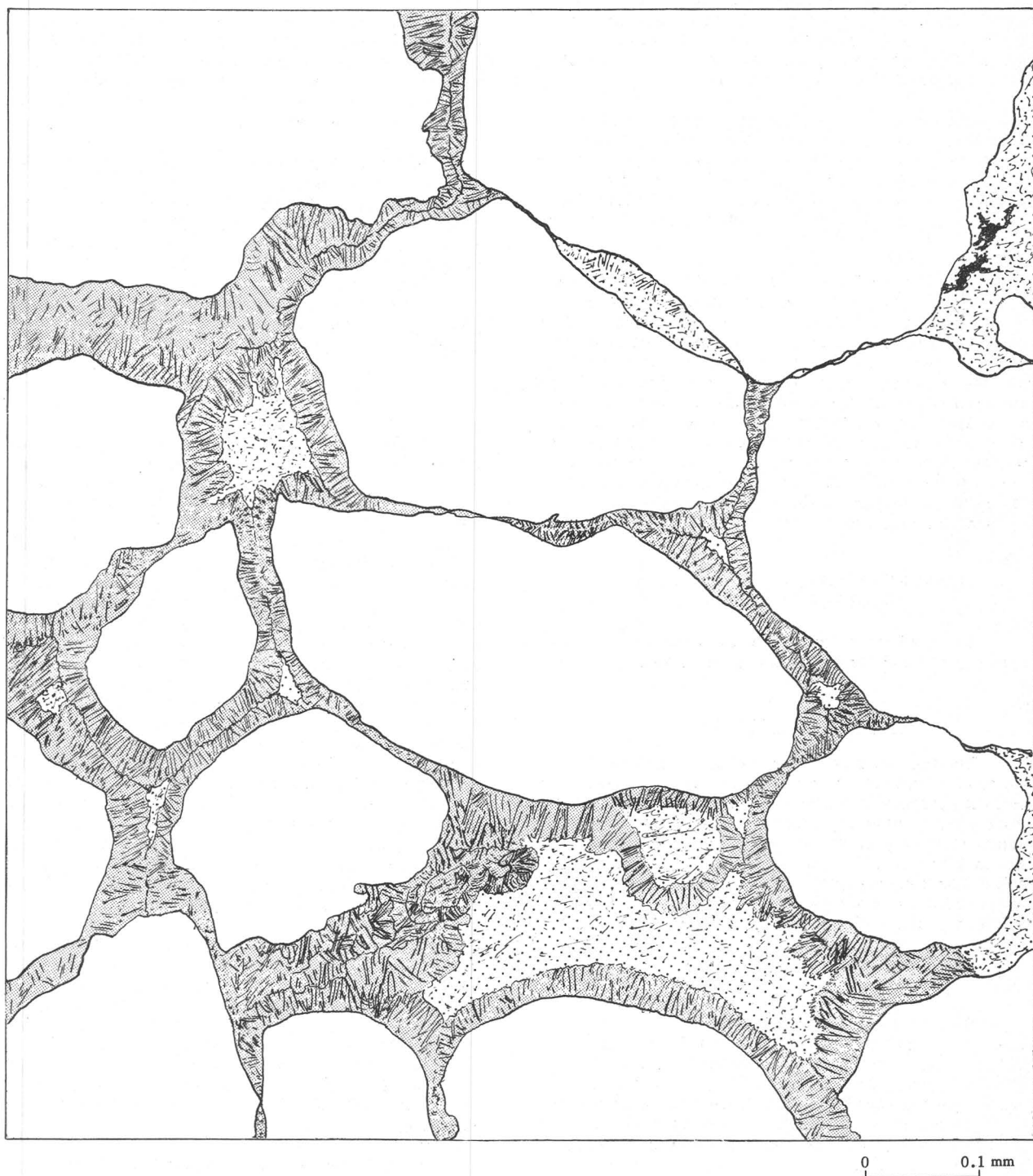
Figure 12.--Partly dissolved quartz grains surrounded by "ropes" of oriented vanadium clay.

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 more distant. In a few places these mats of tiny ropes apparently preserve the rounded outlines that a quartz grain possessed prior to solution.

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 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.

Deposition of sediments

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

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 nonvolcanic origin.

Cementation

Deposition and burial was followed by cementation of the rock, chiefly by calcite and clay. The cemen-

tation, however, seems to have been somewhat patchy and irregular, leaving many places where the voids between the grains were unfilled or only partially filled.

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, forms 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, glassy pyroclastics of early Tertiary time 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 Plateaus did not occur until after burial-- probably to depths of 1,000 feet or more--and after at least partial cementation.

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 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 remains 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 nearby 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 sections indicate that silicification occurred simultaneously with devitrification. The authigenic overgrowths enclose the calcite cement of the rock, and show a strong tendency to fill spaces that were not previously filled by calcite, and clay. Pieces of carbonatized wood with the carbonate par-

tially replaced by silica were noted on the east side of the Henry Mountains and at the Georgetown claims, Slick Rock, Colo. Thin beds of sandstone interstratified with bentonites have been silicified to hard quartzite at many localities.

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Chemical changes in the
connate water of the sandstones
during devitrification

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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 sandstones of the Shinarump and Salt Wash were probably filled with connate water which could not circulate freely because of impermeable formations above and below. Certain changes may 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. Magnesium is an essential constituent of montmorillonite, and it is doubtful if the original biotite latite and biotite keratophyre contain enough magnesium for complete 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 nonmetallic elements that would be expected to be partially leached and removed are sulfur, selenium, tellurium, arsenic, boron, chlorine, and fluorine. Theoretically, therefore, all 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 tuff of Tertiary age near Lysite, Wyo. (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 pyroclastics of the Brushy Basin 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.

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Fixation of uranium and
vanadium by organic matter

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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 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, and 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. (Battelle Memorial Institute reports under Contract no. A. T. 30-1-Gen-202, especially BMI-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 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 in the ores have been leached from the overlying ash beds, and precipitated in the manner outlined?

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 ores of the Colorado Plateaus 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 hydromica 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 Colorado Plateaus, 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 volcanic sediments of the Brushy Basin and Chinle 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.

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 Colorado Plateaus 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 hydro-static 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 sandstones of the Shinarump conglomerate and Salt Wash.

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 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 ash beds of the Mesozoic 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 one, circulating within the sandstone would enable this 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 ores of the Colorado Plateaus may indicate a double source, part of the uranium coming from devitrified ash of the Mesozoic, and part from hydrothermal solutions of the Tertiary.

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 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 Colorado Plateaus 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 hydrothermal solutions of Tertiary age, or even if the principal source is from the leaching of ash of Mesozoic age 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 exploration. The following studies, or lines of approach for studies already begun, are suggested for guidance in further investigation of the origin of the ores of the Colorado Plateaus.

Geologic

Carry out a detailed program of mine mapping closely tied to petrographic work, X-ray studies, and other laboratory techniques. The mapping and lab-

oratory 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.

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

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, Colo., and in other areas.

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.

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.

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

Chemical

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.

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.

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

Physical

Continue work in an attempt to obtain reliable age determinations of the carnotite ores of the Colorado Plateaus. Investigate the possible reasons why many specimens investigated are out of equilibrium, and determine the nature of the leaching (or enrichment) that has occurred.

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."

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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