UNITED STATES DEPARTMENT OF THE INTERIOR

GEOLOGICAL SURVEY

Lithotectonic Setting Necessary for Formation of a Uranium-Rich, Solution-Collapse Breccia-Pipe Province, Grand Canyon Region, Arizona

by

Karen J. Wenrich[1] & Hoyt B. Sutphin[1]

Open-File Report 89-0173

This report is preliminary and has not been reviewed for conformity with U.S. Geological Survey editorial standards and stratigraphic nomenclature.

U.S. Geological Survey
Box 25046, MS 905
Denver Federal Center
Denver, CO 80225

1989

CONTENTS

ILLUSTRATIONS

TABLE

LITHOTECTONIC SETTING NECESSARY FOR FORMATION OF A URANIUM-RICH, SOLUTION-COLLAPSE BRECCIA-PIPE PROVINCE, GRAND CANYON REGION, ARIZONA

Karen J. Wenrich & Hoyt B. Sutphin
U.S. Geological Survey, Federal Center, MS 905
Denver, CO. 80225, U.S.A.

ABSTRACT

Thousands of solution-collapse breccia pipes crop out in the canyons and on the plateaus of northwestern Arizona; some are host to high grade, uranium-rich deposits. Mining activity in breccia pipes of the Grand Canyon region of northern Arizona began during the nineteenth century, although at that time production was primarily for Cu. Later, during the period 1956-1969, the Orphan mine yielded 1.64 million kg of uranium (4.26 million lb of U_3O_8) with an average grade of 0.36% uranium (0.41% U_3O_8). During the period of 1982-1987 five additional breccia pipes were mined for uranium.

Distinct alignments of breccia pipes in N45W and N50E trends occur in northern Arizona. In addition, the pipes within some of these alignments tend to be equally spaced. A study of joints on the Redwall Limestone-capped Hualapai Plateau showed that N45W- and N50E-trending fracture sets were imposed upon the Mississippian Redwall Limestone prior to the deposition of the overlying Pennsylvanian and Permian Supai Group. The ring fracture, encasing each breccia pipe, and the mineralization apparently predated any jointing in the Pennsylvanian or younger host rocks. Thus, the pipe locations were probably controlled by NW- and NE-trending fracture sets, and the pipes appear to have been both formed and mineralized prior to any other significant jointing in the rock.

The breccia pipes contain an extensive mineral suite. The paragenetic sequence begins with the deposition of calcite, dolomite, barite, siderite, and kaolinite. The second stage of mineralization is characterized by minerals rich in Ni, Co, As, Fe, and S, such as siegenite, bravoite, pyrite, millerite, gersdorffite, rammelsbergite, niccolite, arsenopyrite, and marcasite. The third stage of mineralization was characterized by the formation of Cu-Fe-Zn-Pb sulfides. Uraninite was later deposited in the coarsely crystalline calcite matrix, in minor vugs, and as rims around detrital quartz grains. In some pipes, supergene alteration has resulted in the formation of bornite, chalcocite, djurleite, digenite, and covellite, along with an assemblage of nonopaque supergene minerals.

Uranium mineralization occurred in most breccia pipes roughly around 200 Ma. Ore-forming fluids that deposited the sphalerite, calcite, and dolomite had minimum ranging between 80°C and 173°C with salinities always >9 wt. % NaCl equivalent, although most commonly >18 wt. % NaCl equivalent.

Mineralized breccia pipes are enriched in a large suite of elements. In addition to the metals U, Cu, Pb, Zn, and Ag that have been mined in the past from various breccia pipes, mineralized rock is also enriched in As, Ba, Cd, Co, Mo, Ni, Se, and V.

The breccia pipes were excellent conduits for the movement of any fluids present within the Grand Canyon region since the pipes began to form in the Mississippian. Because this is a region of flat lying strata the breccia pipes provided very permeable vertical conduits for fluid movement. So, the opportunity existed for the movement into the breccia pipes of (1) brines dewatered from marine sediments, (2) ground water, and (3) trapped

hydrocarbons. Most of this fluid movement probably occurred during the Triassic after the development of the Mogollon highlands. This produced a steepened hydraulic gradient that permitted fluid movement toward the breccia pipes in the Grand Canyon region.

To date no other large uranium-rich breccia pipes province has been recognized elsewhere in the world. There are several other mineral deposits in solution-collapse breccia pipes elsewhere in the world, such as the Apex mine in the Basin and Range province of the U.S.A. and Tsumeb mine in Namibia, but none of these contain significant uranium minerals.

The Colorado Plateau uranium-rich breccia pipes represent a unique province for several reasons. Combinations of several geochemical, mineralogic, and geologic conditions were necessary to form the numerous breccia pipes and such uranium-rich deposits. If such a province of U-rich pipes is to be located elsewhere in the world it would most likely occur in a region of (1) flat-lying strata, (2) long cratonic stability, and (3) a thick sequence of limestones with overlying sand-bearing units.

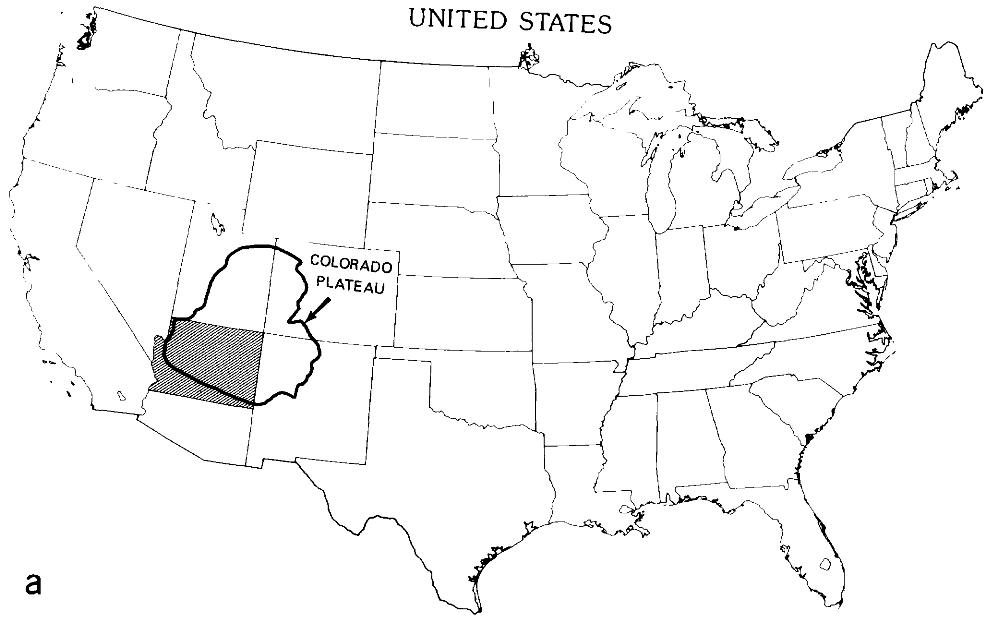
INTRODUCTION

Thousands of solution-collapse breccia pipes crop out in the canyons and on the plateaus of northwestern Arizona, Colorado Plateau physiographic province, USA (Fig. 1). The Colorado Plateau is underlain by a 40-50 km thick crust that has been stable since the end of the Precambrian. The thick sequence (over 1500 m in parts of the plateau) of flat-lying Paleozoic and Mesozoic strata covering most of the Colorado Plateau contains more than 55% of United States uranium resources (W.I. Finch, personal communication, 1987).

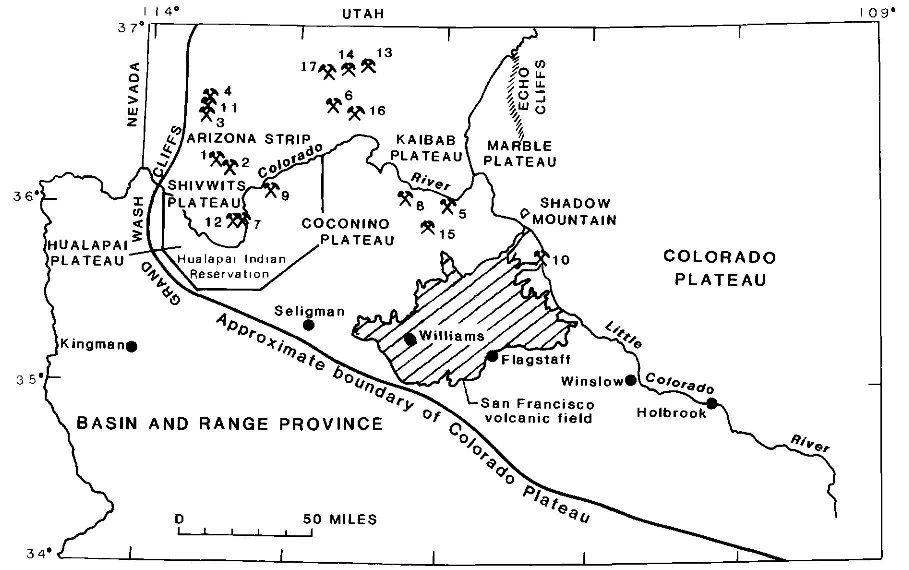
The breccia pipes were formed as sedimentary strata collapsed into dissolution caverns in the underlying Redwall Limestone. Continued, gradual, upward stoping through to the Triassic Chinle Formation (Wenrich, 1985) a vertical distance on the order of 1300 m, resulted in the vertical, rubble-filled pipe-like structures (Fig. 2) approximately 100 m in diameter. Few pipes have been observed to occur in rock below the base of the Redwall Limestone, attesting to their origin within this unit; the two (located on the western edge of the Colorado Plateau) that have been observed to extend lower, go less than 75 m into the Devonian limestone. The stoping process produced extensive brecciation of the rock between the steep walls of the pipe. At no level in any pipe have breccia clasts been observed from lower units; all material has been dropped into the pipes from stratigraphically higher units. As a result of collapse, brecciated rock within each pipe abuts against generally well-stratified, undeformed country rock; the plane demarking this contact is obviously one along which the breccia dropped downward and is therefore, by definition, a fracture. This nearly vertical, and roughly circular fracture is referred to here as the ring fracture.

Collapse began shortly after deposition of the Redwall Limestone, about 300 Ma ago, with infilling of karst depressions by the Upper Mississippian and Early Pennsylvanian Surprise Canyon Formation. The dissolution of the Redwall Limestone and upward stoping of the overlying strata either continued throughout the Late Paleozoic and Early Mesozoic, or ceased after Mississippian time and was reactivated again during Late Triassic time. No pipes have been observed in strata younger than Triassic, although such strata have been removed by erosion across most of northwestern Arizona.

The breccia pipes tend to occur in clusters; as many as six have been mapped per square kilometer, while other regions have tens of square



a



b

Figure 1. a. Index map of the U.S.A. showing the location of figure 1b (stipled pattern), and the approximate outline of the Colorado Plateau. **b.** Index map of northern Arizona, U.S.A. showing the locations of plateaus, breccia pipes developed into mines, and the San Francisco volcanic field that buries terrane with high potential for breccia pipes. Numbers refer to the following mines: (1) Copper House, (2) Copper Mountain, (3) Cunningham, (4) Grand Gulch, (5) Grandview, (6) Hack Canyon, (7) Old Bonnie Tunnel, (8) Orphan, (9) Ridenour, (10) Riverview, (11) Savannic, (12) Snyder, (13) Pigeon, (14) Kanab North, (15) Canyon, (16) Pinenut, and (17) Hermit.

Figure 2. Breccia pipe exposed in the Redwall Limestone and Lower Supai Group. The vertical column of breccia from pipe #338, located in the northwestern corner of the Hualapai Indian Reservation, is enhanced by preferential erosion around the more resistant breccia pipe.

kilometers with no surface expression of any breccia pipes (Wenrich, and others, 1986; Billingsley, and others, 1986). Likewise, pipes which contain mineralized rock are also clustered. This is especially obvious in the area of Hack Canyon, where the Hack 1, 2, 3, and old Hack Canyon mines (4 separate pipes) all occur within a square kilometer.

The actual breccia pipes commonly outcrop along the cliffs of the Grand Canyon, but are rarely exposed on the high plateaus. Thus, pipes are mapped on the plateau surfaces through the recognition of circular features, particularly those with concentrically, inward-dipping beds. Shallow circular depressions and vegetation anomalies are also suggestive of underlying breccia pipes.

Mapping of breccia pipes on these high plateaus of northern Arizona is complicated by the occurrence of gypsum collapses within the Permian Toroweap and Kaibab Formations. Although the dissolution of gypsum in both of these formations produces surface collapse features which are similar in morphology to those associated with breccia pipes, they are shallow seated, and consequently not mineralized. However, gypsum dissolution apparently enhances the surface expression of those features that are indeed breccia pipes. For example, at the Pigeon mine (Fig. 3), the actual pipe is less than 100 m (330 ft) in diameter, but the collapsed surface expression over the pipe on the Kaibab Plateau is 0.9 km (0.5 mi).

Figure 3. Aerial view of the Pigeon mine. Note the inward dip of the Kaibab Limestone strata from the upper right into the center of the feature. The collapse feature is 0.9 km (0.5 mi) in diameter, while the underlying pipe is <100 m (300 ft) in diameter.

A significant number of the total pipes mapped in northern Arizona contain uranium-mineralized rock, as well as anomalous concentrations of Ag, Co, Cu, Mo, Ni, Pb, and Zn. On the 4000 km^2 Hualapai Indian Reservation, 886 confirmed and suspected breccia pipes have been mapped. Of these, approximately 8% exhibit surface expression of mineralized rock--either recognizable copper minerals, most notably malachite, azurite, chrysocolla, or brochantite, or gamma radiation in excess of 2.5 times background. Despite periods of depressed uranium prices, the breccia pipes have commanded considerable exploration activity because of their high-grade uranium deposits.

Mining activity in breccia pipes of the Grand Canyon region of northern Arizona began during the nineteenth century, although at that time production was primarily for Cu with minor production of Ag, Pb, and Zn. It was not until 1951 that uranium was first recognized in the Orphan breccia pipe

(Chenoweth, 1986). During the period 1956-1969, the Orphan mine yielded 1.64 million kg of uranium (4.26 million lb of U_3O_8) with an average grade of 0.36% uranium (0.42% U_3O_8) (Chenoweth, 1986). In addition to uranium, 3.03 million kg (6.68 million lb) of copper, 3,000 kg (107,000 oz) of silver, and 870 kg of vanadium (3,400 lb of V_2O_5) (Chenoweth, 1986) were recovered from the ore. Because of the location of the Orphan mine in Grand Canyon National Park and the associated environmental restrictions, the unmined portions of this orebody will probably never be recovered. The Hack 1, Hack 2, Hack 3, and Pigeon pipes (Fig. 1) were brought into production during the early 1980's, and the Kanab North, Canyon, and Pinenut pipes (Fig. 1) will probably go into production during the late 1980's. All of the Hack pipes and the Pigeon pipe have been mined solely for uranium.

STRUCTURAL CONTROL OF BRECCIA PIPES

Alignment of breccia pipes

Distinct alignments of breccia pipes occur in some places throughout northern Arizona. Alignments are particularly striking on the Marble Plateau because this area is free of morphologically-similar solution features that are shallow-seated in Permian gypsiferous and limy strata (650 m) 2000 ft above the Redwall Limestone. Further westward, facies changes in the Permian Kaibab and Toroweap Formations yield thick, aerially-extensive layers of gypsum that allow for these younger collapse features, which mask the pipes associated with the Redwall Limestone and thus, complicates the process of identifying breccia pipes on the plateau surfaces capped by Permian and younger strata. Maps of breccia pipe locations on the Marble Plateau show nine distinct linear zones of pipes (Sutphin, 1986; Sutphin and Wenrich, 1988; Wenrich, 1986) (Fig. 4). One of these is a particularly distinct northwest-trending (N45°W) line of 10 pipes extending for 25 km (15 mi), and including 2 pipes containing Cu, Ag, and U-bearing minerals. None of these alignments are in any way governed by the joints or faults expressed in the Kaibab Limestone surface of the Marble Plateau (Sutphin, 1986; Sutphin and Wenrich, 1988; E.R. Verbeek, written communication, 1985). The pipes within these northwest- and northeast-trending alignments tend to be equally spaced. Breccia pipes located within two northeast trends (one at N50°E and the other at N55°E) indicated on the breccia pipe and geologic map of the Marble Plateau (Sutphin, 1986; Sutphin and Wenrich, 1988) can be connected by a straight line drawn through the center of each feature in each trend (Fig. 4). In addition, the distance intervals from collapse features #210 to #209 and from #209 to #203 are almost exactly 2.1 km (1.25 mi). The distance from collapse feature #203 to #175 is 4.01 km (2.5 mi) or twice the distance (Sutphin, 1986). This strongly suggests that there is a buried pipe located midway between #203 and #175. Similar spacings also occur in a northwest direction (approximately N45°W).

Joints in the Mississippian Redwall Limestone

Joint patterns in the Redwall Limestone have been found by Huntoon (1970) to consist of a "system of regularly spaced master joints in a rectilinear network that extends up to five miles on either side of major faults". Thus, the major joints within the Redwall Limestone along the northeast-trending

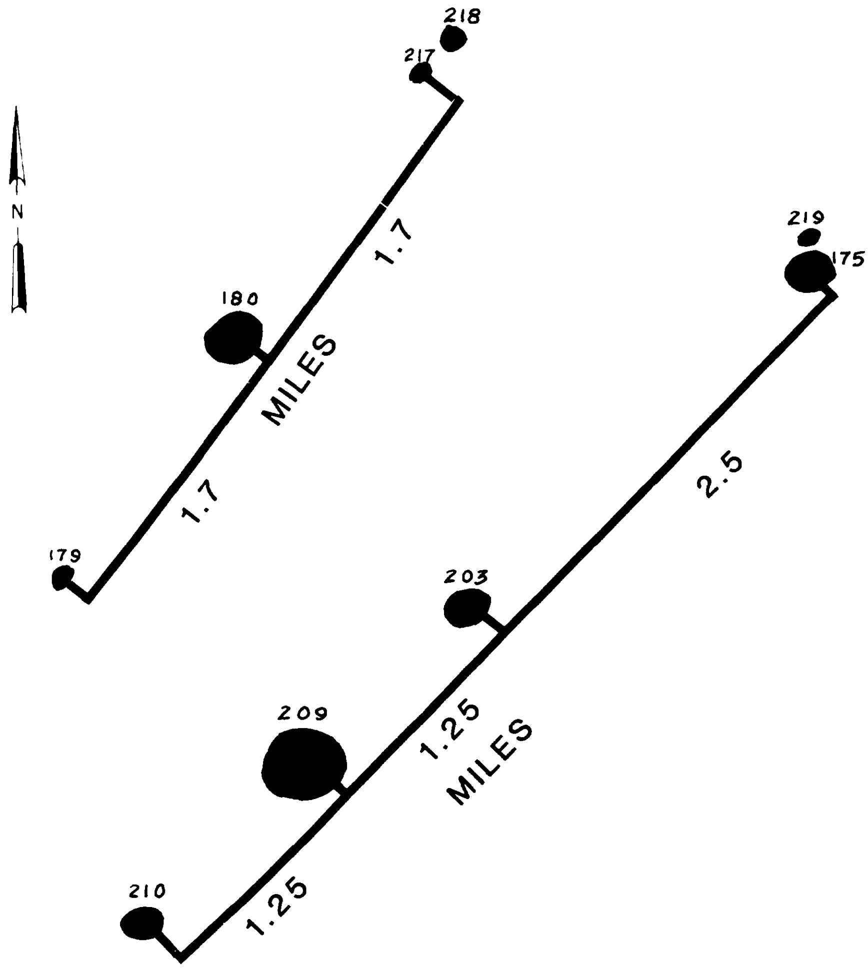


Figure 4. Two northeast-trending alignments of collapse features on the Marble Plateau. The relative distance between the two trends is not to scale. Note the equal spacing between collapse features within each trend.

Bright Angel fault system trend northwest and northeast. Mapping of joints on the Redwall Limestone-capped Hualapai Plateau revealed that northeast- and northwest-trending fracture sets (f1 and f2) were imposed upon the Redwall Limestone prior to the deposition of the overlying Pennsylvanian Supai Group, as these two fracture sets (f1 and f2) do not exist in the basal Supai Limestone (Watahomigi Formation) (Roller, 1987). Joint orientations in the northeast set (f1) average approximately N50°E and those of the northwest set (f2) cluster between N40°W and N50°W (Roller, 1987). These are the exact orientations of the breccia pipe alignments on the Marble Plateau (described above in section). The northwest and northeast fractures apparently localized groundwater movement during Mississippian time and exerted significant control on the development of the Redwall Limestone karst. Major fault zones and lineaments defined by aligned cinder cones and fault traces on the Colorado Plateau show preferred northeast and northwest directional trends (Shoemaker, and others, 1978). These observed fault systems probably extend to deep within the crust and have been episodically active since Precambrian time (Shoemaker, and others, 1978).

Joints in the overlying Permian strata

Although the fabric developed during the Mississippian time appears important to the genesis of the breccia pipes, the fabric developed in later time appears unimportant. The oldest joints in the Lower Permian Esplanade Sandstone are not northeast or northwest trending, but instead strike nearly due north (Roller, 1987; Verbeek, and others, 1988). The Esplanade Sandstone was subjected to five separate episodes of fracturing. Although two of these, episodes 3 and 5 are N60W and N30E respectively (Verbeek, and others, 1988) which is close to the orientation of breccia pipe alignments, they do not appear to have any control on the location of the breccia pipes. Even when the measurement variance is considered for both fracture episodes no fractures from either set appear in the N45°W and N50°E orientations of the mapped breccia pipe alignments. Thus, no fracture set orientations studied thus far in the Permian strata (Roller, 1987; Verbeek, and others, 1988) appear related to any recognized alignments of pipes.

The relationship of the breccia pipe ring fracture to the joints

Mapping of joints within the Ridenour mine (a breccia pipe exposed in the Esplanade Sandstone--Fig. 1) has shown that ring fractures encasing the breccia pipe predate any regional jointing within the Esplanade Sandstone (Verbeek, and others, 1988). In addition, ore mineralization apparently predated the regional jointing also, as essentially all Cu and U minerals were deposited along the ring fractures, or within the breccia matrix (Verbeek, and others, 1988); none were deposited along the regional joints in the Esplanade. Likewise the bleaching of breccia pipes throughout the Grand Canyon area apparently predated the jointing; this is suggested by the circular halo of the bleached rock--if the joints had been present prior to fluid movement and reduction of the oxidized rock, the pattern of bleached rock would have become elongated in the joint direction (Verbeek, and others, 1988). Thus, the breccia pipes apparently formed and were mineralized prior to any regional jointing, other than the N45W and N50E joints that were probably already present at the lower stratigraphic level of the Redwall Limestone.

These data provide a useful exploration method to distinguish the shallow-seated gypsum collapses from the breccia pipes. That is, those collapse features aligned along the above mentioned northwest and northeast trends are probably breccia pipes, whereas those that don't appear to follow such alignments may well be the younger unmineralized collapses that bottom in the Toroweap and Kaibab Formations.

Breccia pipes exposed in Redwall Limestone caves

Thousands of caves lace the Mississippian Redwall Limestone throughout northwestern Arizona. One cave located on the west side of Peach Springs Canyon on the Hualapai Reservation contains at least six breccia pipes that are exposed in the ceilings of the cave passages (Fig. 5). All of the breccia pipes are located in passages that have northwest and northeast trends (Fig. 6), identical to those discussed above. In addition, the four pipes located along the one northeast passage (Fig. 6) are equally spaced; originally only three pipes were located, but after plotting their locations on a map it was decided that according to the "equal-spacing theory" (discussed previously) there should be a pipe located where the vertical-lined symbol is shown on figure 6. Further checking resulted in the discovery of a breccia pipe in the exact location predicted. It is interesting to note that the passages shown in figure 6 that are not northwest- or northeast-trending lack exposed breccia pipes. These passages probably formed subsequent to the later jointing--that is, the joints that postdate the breccia-pipe ring fractures and mineralization, such as at the Ridenour mine.

MINERALIZATION OF THE BRECCIA PIPES

Mineralogy and paragenesis

The collapse-breccia contained within the breccia pipes was an excellent, highly-porous host for mineral deposition. The unaltered pipe material consists of clasts, which vary in size from 1 mm to over 10 m, derived from overlying units, primarily carbonate-cemented sandstones and siltstones. The breccia matrix is composed of individual sedimentary framework grains which were decemented and freed from their host formations during and following collapse. Abundant porosity is present between the individual matrix-framework grains, which are >95% quartz. Vugs not filled by breccia matrix are commonly host sites for coarsely crystalline calcite, barite, and gypsum.

Strong zoning within the breccia pipe orebodies is uncommon. Most minerals, discussed in the following sections, are moderately well distributed throughout most of the orebody. The major exception to this is the development of a "pyrite cap" over the orebody that for the most part consists of pyrite impregnated sandstone to massive pyrite with few associated ore minerals. In some pipes, such as the Orphan and Ridenour mines uranium ore has accumulated in an "annular ring", as well as within the pipe, but in most of the other mines the uraninite is concentrated within the pipe. The highest grade uranium commonly appears to be well below the "pyrite cap" toward the center of the orebody.

Based on mineral associations, the complex mineral assemblage within the breccia pipes appears to have occurred during at least four separate mineralizing events, or pulses. The paragenetic sequence of minerals deposited in collapse-breccia pipes in the region is shown in figure 7.

Deposition of early carbonates and sulfates

The first stage in the mineralization/alteration of the pipe breccia was the addition of carbonate and sulfate along with the simultaneous removal of silica. All of the later-formed opaque minerals were hosted by, and replaced, the coarsely crystalline calcite, dolomite, anhydrite, and barite of this

Figure 5. Breccia exposed within the cavern system shown in figure 6. Note the breccia clasts, with a matrix of red sandstone from the Surprise Canyon Formation, in the cave ceiling.

early stage. The sulfates, barite and anhydrite, were deposited contemporaneously with, and/or following, the carbonates.

The introduction and crystallization of calcite in the matrix was accompanied by recrystallization of the finer unaltered calcite cement within the breccia clasts. Euhedral dolomite rhombs were also crystallized in this manner. The resulting matrix texture is one in which the point-contact, framework-supported, breccia matrix was converted to one containing floating quartz grains that are poikilitically enclosed within large carbonate crystals. The framework quartz grains underwent partial dissolution during this process, as evidenced by the passive-solution-contact with the enclosing carbonate along with their reduced grain size and corroded grain edges, in contrast to similar unreplaced quartz grains that are larger with well-rounded edges. The quartz framework grains contained within dolomite show a greater degree of dissolution than those contained in calcite, which in places appear not to have replaced any quartz at all. The crystallization of these two

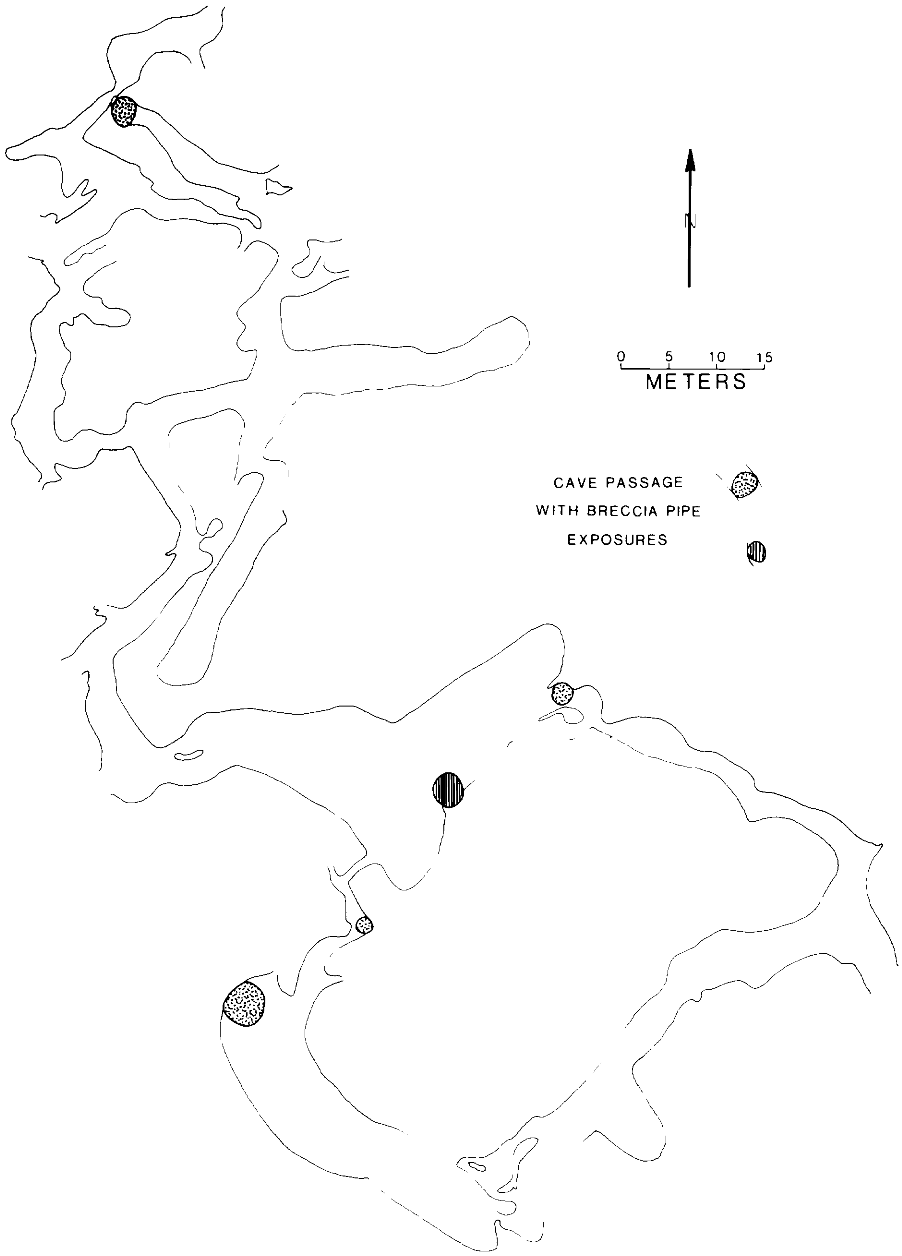


Figure 6. Map of a cavern within the Redwall Limestone located on the west side of Peach Springs Canyon. Note the location of breccia pipes only in the northwest- and northeast-trending passages. The pipe shown with vertical lines was discovered later than the other 3 along the same alignment by using the "equal-spacing theory".

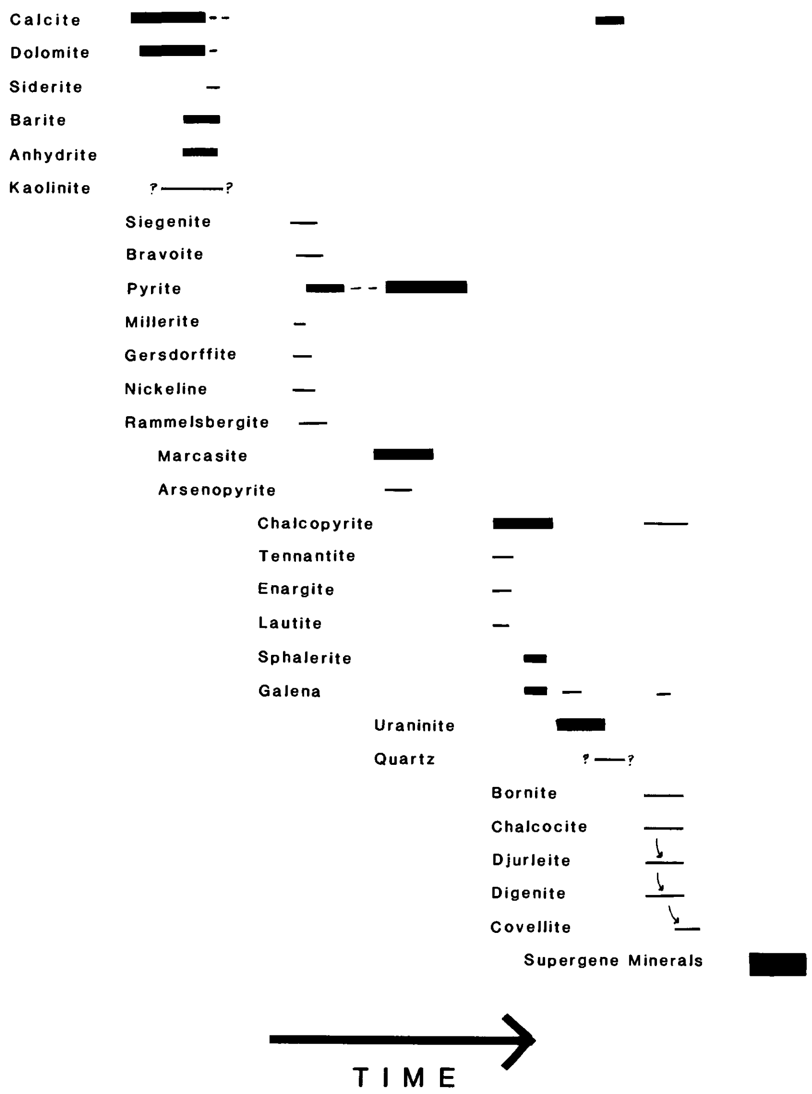


Figure 7. Paragenetic sequence for minerals in collapse breccia pipes.

carbonate minerals is very prevalent and is considered to have occurred early, because all later phases replace them to some degree. These phases are very widespread and are continuous into nonsulfide-bearing portions of the pipe as well. Both the dolomite and calcite probably formed at, or close to, the same time, as their respective grain boundaries are mutually interpenetrating.

Barite was deposited in the form of acicular euhedral prisms and radiating clusters of blades. Barite probably crystallized at this time because: (1) like the carbonates, it too is host to all of the later-formed opaque minerals; and (2) the chemical environment of deposition for barite was similar to calcite and dolomite, as framework quartz grains were dissolved during the deposition of all three minerals. The barite crystals grew with apparent disregard for the confining framework grains, and replaced all quartz within the crystal growth paths.

Anhydrite, which primarily occurs as very coarsely crystalline open-space vug fillings, is associated with gypsum and barite. Commonly, the anhydrite crystals have alteration rinds of gypsum, and in some cases are completely replaced by gypsum. The local abundance of anhydrite in the Toroweap horizon of these pipes suggests that evaporites within the Toroweap are a local source for recrystallized anhydrite and perhaps barite.

Minor amounts of siderite were deposited sequentially after the dolomite and barite. In areas in which the matrix has not been completely filled in by calcite, crystalline masses of siderite surround or form partial rinds or crusts around dolomite rhombs and barite crystals. On this basis and because of the lack of any other relationship, siderite is considered to have formed shortly after barite and dolomite. Siderite does not appear to be associated with any other mineral phases.

Very coarse, undeformed, euhedral plates of kaolinite line and fill pore spaces not previously filled by carbonate. Based on the crystal size and lack of deformation of the clay, the kaolinite is considered to have formed sometime after the pipe breccia, and is not merely an original sandstone matrix component. The absence of any other associated mineral phases precludes an exact paragenetic placement of the kaolinite. It does, however, occur in samples along with barite, dolomite, and calcite, and is thus tentatively placed in this first episode of mineralization.

Deposition of Ni-Co-As-Fe-S-bearing minerals

The second major episode of pipe mineralization is characterized by minerals rich in Ni, Co, As, Fe, and S. The intricately zoned minerals which were the first to crystallize during this stage, are small (<1 mm), disseminated, euhedral, and commonly exhibit zoning of several phases within a single crystal. The minute intricately zoned crystals are hosted by the aforementioned carbonates and preferentially hosted by barite if it is present (Fig. 8). Although the concentric zoning within a single crystal commonly varies in composition, with up to 10 alternating or repeating minerals present, the overall outward zoning is usually NiCo rich-NiFe rich-Fe rich; the characteristic minerals are: siegenite-bravoite-pyrite. There are many variations of this, the simplest and most common of which is a bravoite core with a pyrite rim. More complex and rarer assemblages contain bands of millerite, Fe-siegenite, cobaltian pyrite, and other Ni-Co-Fe sulfides (Fig. 9). The crystal shown in Figure 9 is identical to some that were observed from samples collected at the Buick mine, a Mississippi Valley-type deposit.

A second, less common zonal assemblage is restricted to the Ni arsenides: niccoline, rammelsbergite, and pararammelsbergite. Rammelsbergite is the most abundant of the three minerals and occurs as "annealed" clusters of individual crystals, or as euhedral crystals with cores of pararammelsbergite or niccoline. The sites of crystallization of these arsenides, and the previously mentioned Ni-Co-Fe sulfides, are mutually exclusive. However, both assemblages are enclosed, and in some cases replaced, by later-formed minerals.

Gersdorffite and Co-gersdorffite are occasionally present within the zoned pyrite-rich crystals (Fig. 9), but more commonly occur as disseminated euhedral cubes (Fig. 10). They too, show replacement by later-formed minerals.

The euhedral crystals and aggregates of Ni-Co-Fe sulfides and arsenides,

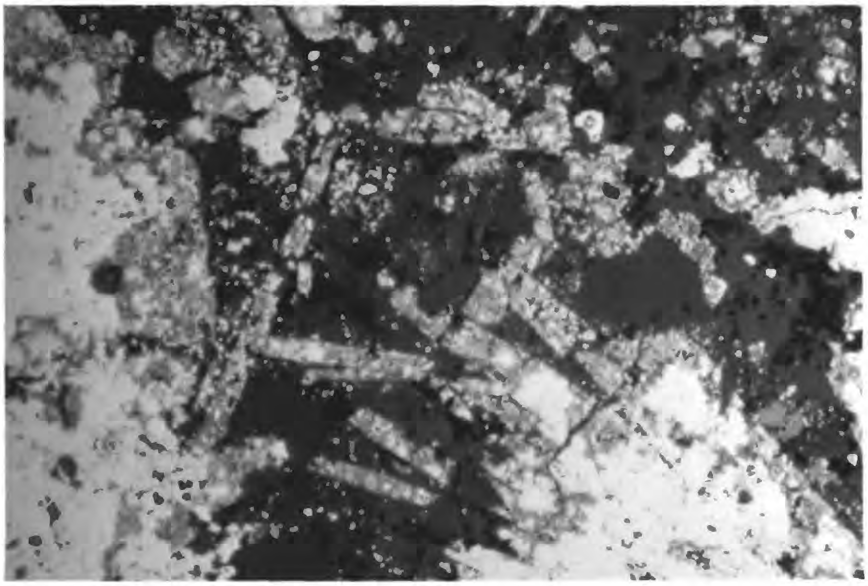


Figure 8. Aggregates of pyrite cubes replacing laths of barite. Background matrix (dark grey) is coarsely crystalline calcite. Width of figure is 0.7 mm.

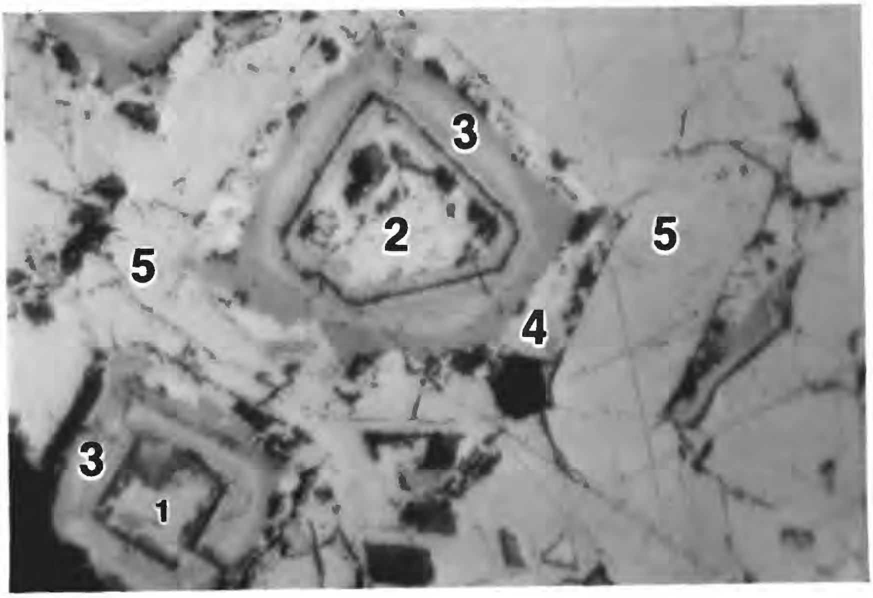


Figure 9. Zoned crystals composed of (1) millerite, (2) gersdorffite, (3) bravoite, (4) siegenite, and (5) pyrite. Width of figure is 0.11 mm.

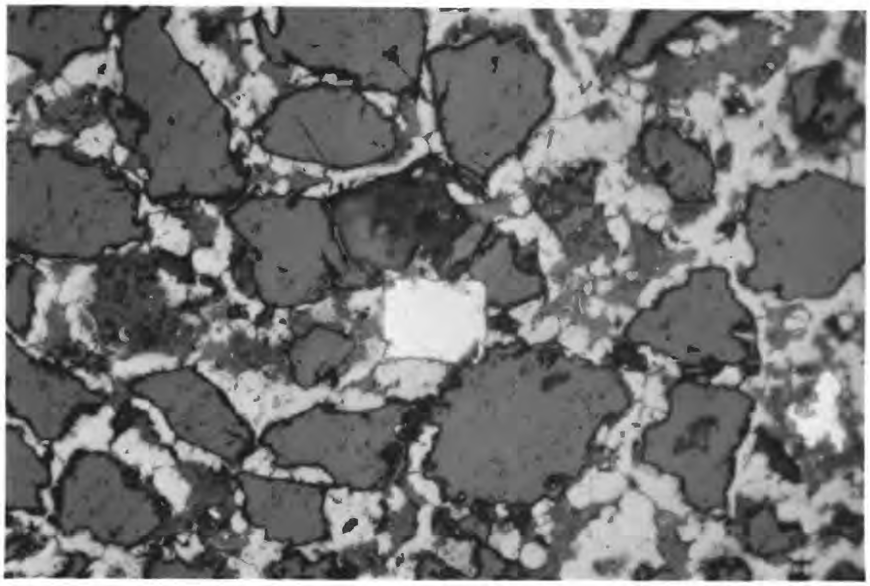


Figure 10. Gersdorffite crystal (bright white - center of figure) is enclosed by later uraninite (light grey). Note the corrosion of detrital quartz grains. Width of figure is 0.7 mm.

especially the more pyrite-rich, may or may not be enclosed by later, massive pyrite. Whether this later pyrite is widely separated in time from the euhedral crystals, or whether the smaller zoned crystals were just a precursor to this later massive pyrite is unknown. The more massive pyrite is anhedral and shows partial to complete replacement of carbonates, barite, and even detrital quartz grains. The pyrite contains trace amounts of associated arsenopyrite, along with much larger quantities of marcasite. The marcasite is present as: (1) disseminated euhedral to anhedral laths; (2) large equant masses commonly present in equal abundance to the pyrite; and (3) as clusters or spheres of radiating crystals with a characteristic cockscomb habit. Originally a large percentage of the massive pyrite may have been marcasite, which subsequently converted to pyrite. The massive pyrite exhibits extensive microfracturing. The fractures are filled with later-formed minerals such as uraninite, chalcocite, and galena. Empty bravoite molds in some of the zoned pyrite crystals are filled in by the same later-formed minerals (Fig. 11). A black, glassy pyrobitumen, locally abundant in some breccia pipes, but absent in most, similarly encloses fractured pyrite (Fig. 12). Paragenetically, the relationship shown in figure 12 clearly shows the pyrobitumen as being deposited after the pyrite. Yet, some samples suggest that the pyrobitumen was present prior to the sphalerite. The lack of samples showing pyrobitumen occurring with other minerals precludes a determination on exactly how soon after the pyrite it was deposited.

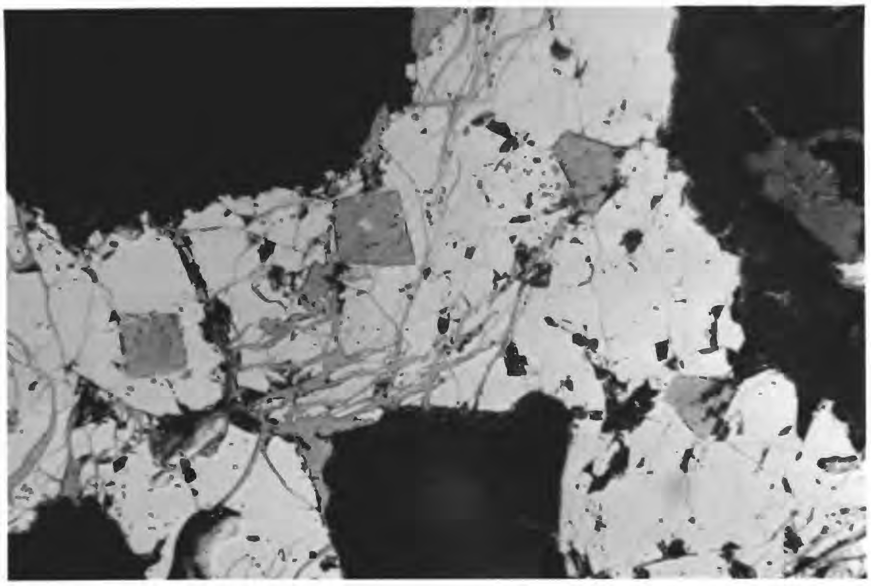


Figure 11. Chalcocite (gray) filling fractures and voids within pyrite (white). Note the similarity in shape between the replaced voids and the crystal outlines shown in figure 9. Width of figure is 0.21 mm.

Deposition of Cu-Pb-Zn sulfides

The third major pulse or episode of pipe mineralization is characterized by formation of Cu-Fe-Zn-Pb sulfides. The most abundant minerals deposited during this episode are chalcopyrite, sphalerite, and galena, with lesser amounts of tennantite, enargite, lautite, and trace amounts of molybdenite and fluorite. Chalcopyrite occurs both as anhedral masses and as euhedral crystals. In either case, it typically surrounds the earlier formed pyrite as do Zn-bearing tennantite, enargite, and lautite. Fluorite occurs in minimal amounts within the growth rings of sphalerite. Galena and sphalerite tend to be coarsely crystalline, megascopic in size, and occur intergrown with each other with mutually interpenetrating grain boundaries (Fig. 13). Both minerals occasionally contain oriented exolution blebs of chalcopyrite.

The mineral assemblages found in these first 3 pulses of mineralization are similar to those in Mississippi Valley-type deposits, except that for the most part the breccia pipe ore minerals tend to be finer grained. The next mineral assemblage though, is unique to the breccia pipes--that is, there are no known uranium occurrences in Mississippi Valley-type deposits.

Deposition of uraninite and Cu-Fe sulfides

Uraninite is the only primary uranium-bearing mineral present in the breccia pipes. It replaces coarsely crystalline calcite matrix, lines or fills vugs, and rims detrital quartz grains. The morphology of uraninite is variable, ranging from distinct spheres and clusters of spheres to botryoidal

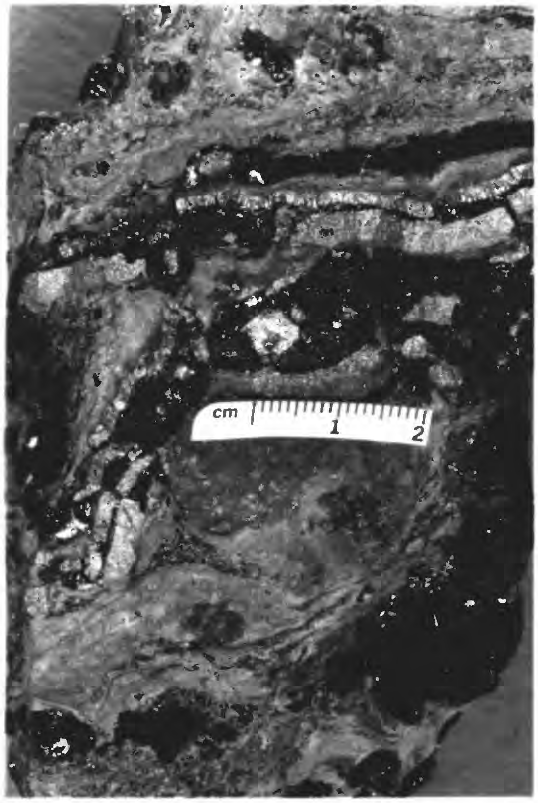


Figure 12. Breccia sample showing black glassy organic matter (pyrobitumen) engulfing fractured pyrite.

crusts (Fig. 14) to thin "wisps" and irregular matrix replacement, such as that shown in figure 10. Uraninite, especially the "wispy" type, occasionally contains wormy intergrowths of associated galena, some of which may have formed from radiogenic lead.

In some pipes a second group of Cu and Cu-Fe sulfides were deposited following uraninite deposition. In places, the CuS and Cu-Fe-S minerals are very abundant, and the assemblage is dominated by digenite, chalcopyrite, and bornite. Also present is chalcocite and minor galena, with accessory amounts of djurleite. All of these minerals are closely related in time, and are post uraninite, as all enclose uraninite spheres and fill shrinkage cracks in the botryoidal uraninite crusts (Fig. 14). Examples can be found of each mineral intergrown with and rimming the others. Small amounts of galena typically occur as tiny unmixing droplets within the more massive bornite. Covellite is locally very abundant, and although some may be primary, it is probably a later supergene alteration mineral, as it is most abundant in oxidized-ore zones, and as lamellae and "flames" replacing chalcopyrite, and digenite. It

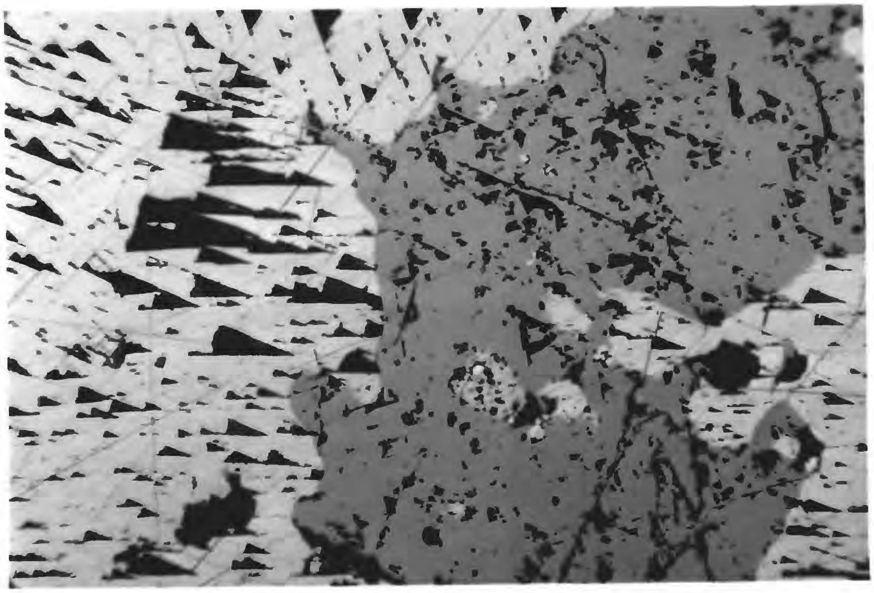


Figure 13. Late stage galena and sphalerite with mutually interpenetrating boundaries. Galena contains triangular cleavage pits. Width of figure is 1.4 mm.

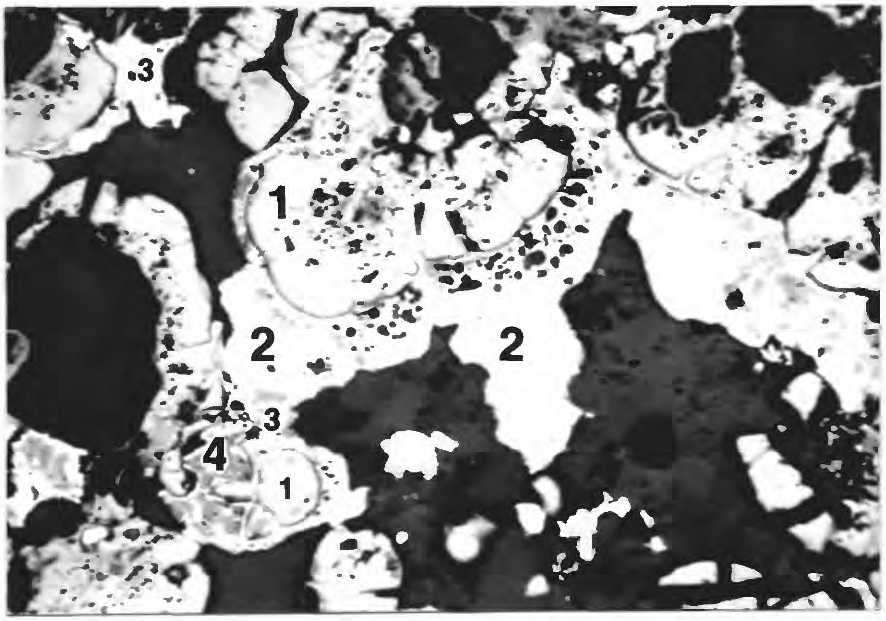


Figure 14. Uraninite (1) (high relief, grey) enclosed and rimmed by bornite (2) (light gray) with associated chalcopyrite (3) (white) and digenite (4). Width of figure is 0.45 mm.

is unclear as to whether these sulfides represent a separate influx of Cu-bearing fluids or are merely a supergene remobilization of the earlier formed Cu minerals. Their restricted occurrence in pipes such as the Orphan mine (Fig. 1), which have been exposed by downcutting of the Grand Canyon, suggest the latter.

Extensive silicification is rare within the breccia pipes orebodies, although some quartz overgrowths formed subsequent to uraninite mineralization. The quartz overgrowths enclose uraninite "dust rims" that rim detrital quartz grains. Some pipes have been silicified sufficiently to form erosional pinnacles, such as the Blue Mountain Pipe located on the Hualapai Indian Reservation, but this silicification is probably younger than the ore mineralization. Perhaps where ore mineralization filled the matrix between the clasts, little silicification occurred, but, for instance, where there was adequate open-space between the detrital quartz grains in the comminuted Coconino Sandstone above the Orphan pipe orebody, the rock became well silicified.

Remobilization and deposition of ore metals above and below the ore zone

As the suite of primary minerals became exposed to a more oxidizing environment through gradual erosion of the breccia pipe columns during the past 5 m.y. of canyon dissection, an extensive suite of supergene alteration minerals developed: Malachite, azurite, brochantite, cyanotrichite, chrysocolla, hemimorphite, smithsonite, goethite, zippeite, and metazeunerite are only a few. The outcrop exposure of these minerals, especially the obvious, colorful Fe- and Cu-bearing ones, within the surface collapse feature above a breccia pipe can be a favorable indicator of ore in the underlying pipe. The "pyrite cap" over the orebody may have been instrumental in retarding the oxidation of the orebody; once the "pyrite cap" was stripped away by erosion the orebody oxidized. This may explain the extensive oxidation of metals in such breccia pipes as the Grand Gulch, Savannic, Cunningham, and Ridenour, which have been eroded down to the level of the Esplanade Sandstone. The "pyrite cap", if it was present, would have been located stratigraphically higher.

One of the breccia pipes exposed within a Redwall Limestone (Mooney Falls Member) cave on the west side of Peach Springs Canyon contains several minerals that are rarely, or have never been, reported from caves. Likewise, these minerals contain elements uncommon to caves, such as As, Cu, Mo, V and U that are all major mineral-forming elements within breccia pipe orebodies. Bright white encrustations of calcite and aragonite with occasional green bands and spotty yellow patches cover the cave walls. These green and yellow colorations are the result of several minerals unique to caves. The yellow color is due to powellite [$CaMoO_4$] and carnotite [$K(UO_2)_2(VO_4)_2 \cdot 3H_2O$], and the green to conichalcite [$CaCu(AsO_4)(OH)$] and talmessite [$(Ca_2Mg(AsO_4)_2 \cdot 2H_2O$]. The apple green color of the talmessite is probably due either to its 790 ppm Cr substituting for Mg in the octahedral site or to its 1190 ppm V substituting for As in the tetrahedral site. The mineral hoernesite [$Mg_3(AsO_4)_2 \cdot 8H_2O$] forms radial white crystals in association with aragonite. This appears to be the first reported occurrence of talmessite and hoernesite in the U.S. In addition to the above minerals, hematite, dolomite and ankerite also occur within this breccia pipe exposed in the cave. These rare speleothem minerals are believed to have been deposited from fluids enriched in the metals As, Cu, Mo, V, and U subsequent to flowing through, and leaching the metals from, either an orebody located higher up in the overlying Permian sandstone units within this breccia pipe that have since been eroded off, or from a nearby mineralized breccia pipe.

Age of the uraninite ore

The breccia pipes have not been observed to stope upward into rocks that are younger than the Triassic Chinle Formation, although this lack of recognized breccia pipes in the Jurassic or younger strata may be a result of (1) the nonpreservation of these younger rocks throughout most of northwestern Arizona, (2) thinning of the Redwall Limestone (to the extent that karst formation may have been hindered) under those areas where Jurassic rock is preserved, or (3) stoping had ceased by the end of the Triassic. "Unfortunately, the U-Pb isotope method of age determination of these ores is hampered by (1) the pervasive and continuous open-system behavior of both Pb and radioactive daughters of ^{238}U and (2) the presence of high amounts of common-Pb whose isotopic ratios are significantly variable" (Ludwig, and others, 1986). A large set of U-Pb isotopic analyses from the Hack 1, Hack 2, Kanab North, EZ-1, EZ-2, and Canyon breccia pipe orebodies (Fig. 1--EZ-1 and EZ-2 are located due west of the Hack mines) show that the main uranium mineralizing event for all but the Canyon pipe occurred roughly around 200 Ma (K.R. Ludwig, personal communication, 1987). The Canyon Pipe has a distinct age of roughly 260 Ma (K.R. Ludwig, personal communication, 1987). Unfortunately, as can be observed from figure 7, there are no primary minerals in the orebody that can be used for K-Ar or Rb-Sr age determinations of the ore. In any event, it appears that the uranium mineralization (formed during the last stage of mineralization) occurred by 200 Ma. Because neither the uraninite, nor the uraninite cemented breccia appear to be fractured, it is probably safe to assume that little or no stoping within the mineralized pipes has occurred since the uraninite was deposited. Consequently, the lack of observed pipes in rock younger than the Triassic Chinle Formation is probably due to their absence rather than an artifact of erosion, or a thinning of the Redwall Limestone. A corollary to this might be that those pipes which stope into younger rocks, such as the Temple Mountain collapse in Utah, probably do not have a preserved "northern Arizona, uranium-rich, Mississippi Valley-type orebody", because any post-uraninite stoping would probably have destroyed the orebody.

Temperatures and salinities of ore-forming fluids

Fluid inclusions studies were made on six mineral species that are, with the possible exception of quartz, related to the ore-forming fluids: Sphalerite, calcite, dolomite, quartz, barite, and anhydrite. Of the six, sphalerite, calcite, and dolomite are thought to be the most reliable. The breccia pipe ore is very fine-grained, making it difficult to locate fluid inclusions. Quartz is rare in the breccia pipes, and where present, it may be related to a late stage silicification event that could be as late as Tertiary, and totally unrelated to the mineralization. In addition, in much of the quartz the fluid inclusions (1) were small, (2) only contained one phase (of unknown composition), and/or (3) had inconsistent liquid to vapor ratios. For barite only salinity measurements could be made because of inconsistent liquid to vapor ratios. The reliability of anhydrite measurements in fluid inclusion studies is uncertain, but measurements have been used successfully in the past, so some were tried here. The anhydrite filling temperatures were higher than those from the other mineral phases (Fig. 15), and thus the results are considered questionable. Sphalerite is the most reliable in terms of its relation to the ore-forming event, but primary inclusions within it are rare, and the fine-grained nature of the sphalerite within breccia pipe orebodies makes studies of even secondary inclusions difficult. Both dolomite and calcite are common within the breccia pipes, and primary inclusions within dolomite are not as rare as they are in sphalerite.

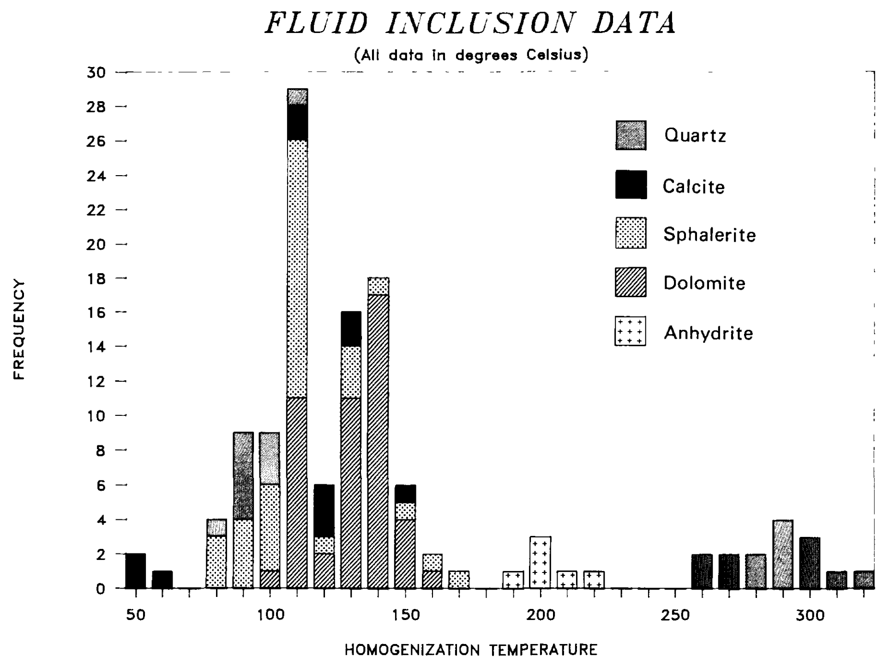


Figure 15. Homogenization temperatures for mineral phases associated with breccia pipe ore. Each frequency represents a separate fluid inclusion. Temperatures below 80°C are from non-pipe calcite shown as a contrast. The high temperature quartz is believed to be from a late stage of silicification. Minerals related to ore-forming processes preciptiated from fluids with temperatures between 80° and 173°C.

Sphalerite

The sphalerite, which began to form (Fig. 7) after deposition of the Ni-Co-As sulfides during the third major pulse of mineralization, contains fluid inclusions with filling temperatures that range from 80°C to 173°C (Fig. 15). Only two measurements on sphalerite are of primary inclusions and they have temperatures of 80°C, and 103°C; the remainder of the measurements (33) are of secondary inclusions, with 27 of them >103°C. The composition of these inclusions is very saline--70% of them have salinities that are >19 wt. % NaCl equivalent (Fig. 16) and the other 30% range from 9 and 12 wt. % NaCl equivalent (forming a somewhat bimodal distribution of data). A few rare secondary fluid inclusions in sphalerite have petroleum that emitted an orange fluorescence when exposed to intense blue light, and these petroleum inclusions may be related to the pyrobitumen found in some pipes.

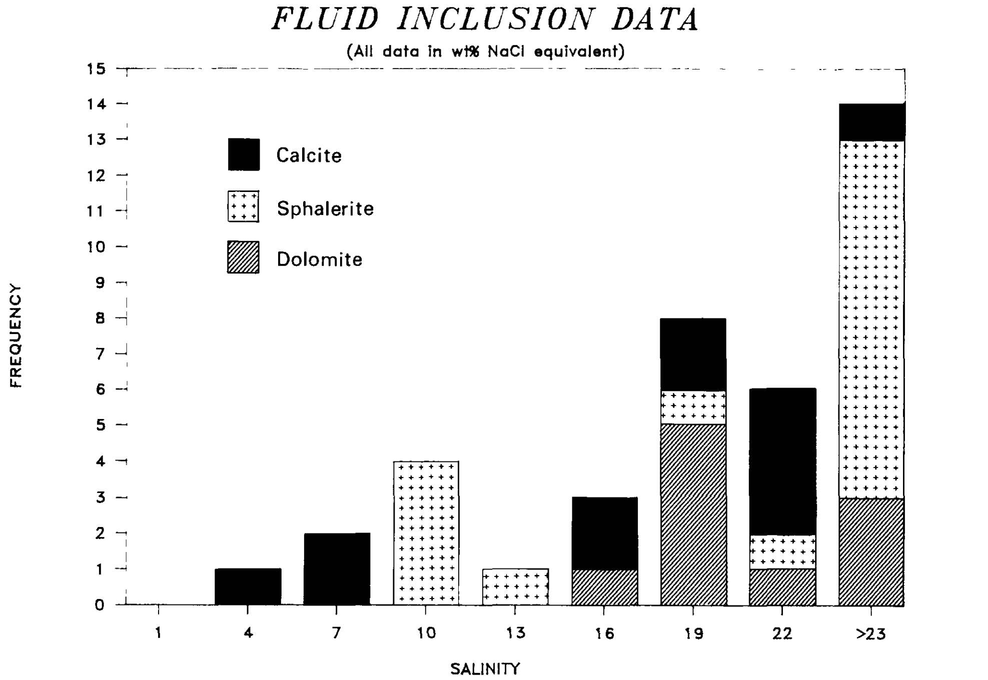


Figure 16. Salinities for dolomite, sphalerite, and calcite fluid inclusions. Primary inclusions in dolomite, and secondary (with a few primary) inclusions in sphalerite, and calcite are considered to be the most significant and reliable for ore genesis temperatures.

Dolomite

The dolomite measurements are the most consistent. Many of them are from breccia pipes not yet known to contain orebodies, yet the temperatures and salinities of primary fluid inclusions are identical to the primary and secondary inclusions in sphalerite. Forty-seven measurements from three different pipes provide filling temperatures ranging from 105°C to 161°C (Fig. 15). Ten melting point measurements provided fluid inclusion compositions all ≥17 wt. % NaCl equivalent (Fig. 16) .

Calcite

Fluid inclusion measurements in calcite were very interesting--

comparisons of those from calcites within orebodies and those from nonore calcite may be useful in exploration for breccia pipes. The filling temperatures of 108°C to 155°C (Fig. 15) for inclusions of unknown origin in calcite contained within breccia pipes are in good agreement with the dolomite and sphalerite results. Measurements were also made on primary inclusions in calcite from drill core (Van Gosen and Wenrich, 1987) of strata in the area of Hack Canyon. No breccia pipes are known to the authors to be located near this drill hole. The calcite formed in vugs within the Harrisburg Member of the Kaibab Limestone. In contrast to the fluid inclusions in minerals that presumably were deposited from the ore-forming fluids, these samples had filling temperatures of 53°C-60°C (Fig. 15), significantly lower than any measurements made from breccia pipe minerals. Although some of the melting point measurements in these non-pipe calcites were similar to ore-related calcite, many were much lower--the salinities ranged from 4.8 to 21 wt. % NaCl equivalent (Fig. 16). These differences between nonpipe-calcite and pipe-calcite fluid inclusions might be used as an exploration tool for distinguishing pipes which have had ore-forming fluids traveling through them from those which have not. That is, a collapse feature on a Kaibab or Moenkopi Formation-capped plateau containing calcite with high fluid-inclusion filling temperatures plus high salinities might be a good target for further exploration as compared to those calcites with low temperatures and low salinities.

Similarily, it appears that calcite found in breccia within (1) the Muav (2) an unnamed Cambrian unit, and (3) non-pipe calcite within caves, can be readily distinguished from calcite within Redwall-rooted breccia pipes. In the area of Horse Flat Canyon several vertical pipes of breccia were found within the Cambrian Muav Limestone, the Devonian Temple Butte Formation, and an unnamed Cambrian unit. The overlying rock has been eroded so it was not possible to determine if these units stoped upward through the Redwall Limestone and hence were "breccia pipes". This obviously has posed the question of "do some of the breccia pipes have deeper roots than the Redwall?"--yet this is the only area where such lower Paleozoic pipes have been observed. The fluid inclusion filling temperatures and salinities found in calcites (some of it optically clear) from these lower Paleozoic pipes are in sharp contrast to those from the Redwall breccia pipes. The temperatures from 5 lower Paleozoic pipes were <60°C, and the salinities were all 0.0 wt. % NaCl equivalent. Identical results were obtained from calcite collected along a non NW- or NE-oriented cave passage within the cave shown in figure 6. This cave calcite is probably much younger than the breccia pipe ore, as are the cave passages which trend in directions other than NW or NE.

Quartz

The fluid inclusion filling temperatures in quartz from the breccia pipes are distinctly bimodal. Quartz filling vugs within the silicified breccia spire at the Blue Mountain pipe have filling temperatures of 91°C to 107°C (6 measurements) and 256°C to 317°C (15 measurements) (Fig. 15). This high temperature silicification may have been associated with Tertiary volcanism such as that of Blue Mountain (14.6 Ma--Damon, 1968) located 10 km (6 mi.) south of the Blue Mountain pipe, and/or several, probably related, Tertiary intrusives located within 5 km (3 mi.) of the pipe. At the Mohawk Canyon pipe all quartz appears to be late stage and perhaps unrelated to the breccia pipe mineralizing event, because (1) it is associated with celadonite and chalcedony on the surface, (2) has low filling temperatures 81°C to 90°C (4 measurements), and (3) low salinities of 1.4 to 5.5 wt % NaCl equivalent (7 measurements).

Summary of the fluid inclusion temperatures and salinities

In summary it can be said that the ore-forming fluids that deposited the sphalerite, calcite, and dolomite had minimum temperatures (the overburden at the time was probably between 700 and 1500 m, such that accompanying pressure corrections on the filling temperatures would yield slightly higher temperatures) ranging between 80°C and 173°C with salinities commonly >18 wt % NaCl equivalent, and probably always >9 wt % NaCl equivalent. These are not necessarily the temperatures and salinities of the fluid that transported and deposited the uranium. Although some of the uraninite deposition may have been contemporaneous with the sphalerite, breccia pipes studied to date suggest that the sphalerite was deposited prior to the uraninite, and the dolomite and calcite much earlier in the paragenetic sequence than the sphalerite (Fig. 7). These fluid inclusion filling temperatures and salinities are similar to those found in Mississippi Valley-type deposits. Like the Mississippi Valley-type deposits, evidence for the presence of some hydrocarbons in the breccia pipes can be observed in fluid inclusions and in the presence of pyrobitumen. It is not clear though, whether these associated hydrocarbons may be post uraninite deposition, as the sparse petroleum hydrocarbons found in sphalerite fluid inclusions have been observed only in secondary inclusions.

Geochemistry

Mineralized breccia pipes are enriched in a large suite of elements. In addition to the metals U, Cu, Pb, Zn, and Ag that have been mined in the past from various breccia pipes, mineralized rock is also enriched in As, Ba, Cd, Co, Mo, Ni, Se, and V. The rare earth elements, Cs, Hg, and Sb appear to be enriched in some samples, but not in most. Other than a somewhat minor stage of silicification, represented primarily by quartz overgrowths, there has been no increase in Si within the breccia pipes. Although dolomitization and calcification of the breccia matrix can be observed petrographically, there is little obvious enrichment of Ca or Mg in the breccia sample compared to the background values in the unaltered rock (same formation). In fact, in areas where traverses have been made from unaltered, unbleached rock laterally into altered, bleached rock of the same unit, a depletion in Mg commonly occurs, along with a decrease in Al, Ti, and K. The common, pronounced bleaching of red sandstones, adjacent to and within breccia pipes, to an almost pure white by fluids associated with pipe mineralization is due to reduction of ferric to ferrous Fe. Studies made across these color zones show few elemental changes between the bleached and unbleached rock.

Geochemistry of rock from breccia pipe mines

Table 1 presents the geochemistry of one sample from each of nine breccia pipe mines. Samples 1, 2, 8, and 9 are examples of primary ore from 4 separate breccia pipes. The samples were either collected from mines, or are samples of drill core from breccia pipes that are ore-bearing and may be going into production in the near future. Sample 7 is from a mineralized reduced zone of Cu-Ni-Co-Pb-Zn sulfides in drill core from a pipe that needs

Table 1--Chemical analyses of breccia pipe samples
All values in parts per million except where indicated otherwise.
Bi, Ho, and Sn were also determined, but all samples were less than the detection limits of 20, 40 and 20 ppm respectively.

Element	Sample Number 1	2	3	4	5	6	7	8	9
Ag	40.0	9.0	3.0	36.0	5.0	20.0	<2.0	49.0	<0.4
Al_2O_3	1.27	1.60	0.36	2.53	0.37	9.26	5.06	5.18	1.4
As	0.44%	0.12 %	250.	460.	1.4%	0.25%	0.14%	0.35%	290.
Au	<8.0	<8.0	--	34.0	0.10	<20.	<8.0	<8.0	<20.0
Ba	360.	140.	.15%	94.0	260.	640.	180.	16.0	0.32%
Be	<1.0	<1.0	<1.0	<1.0	<1.0	14.0	<1.0	7.0	<2.0
Crb C%	0.17	1.29	3.07	7.01	0.21	0.01	0.02	0.01	4.78
Org C%	0.02	3.70	0.19	0.88	0.10	<0.01	0.13	2.76	0.08
Total C%	0.19	4.99	3.26	7.89	0.31	<0.01	0.15	2.77	4.86
CaO%	1.30	15.4	11.2	18.6	0.33	0.36	0.02	0.53	18.2
Cd	40.0	<2.0	950.	420.	49.0	<4.0	<2.0	23.0	<4.0
Ce	325.	12.0	3.8	19.0	9.0	56.	12.6	58.0	32.
Co	8.94	99.0	69.0	333.	0.91%	210.	19.5	310.	13.2
Cr	69.9	14.0	11.0	23.8	18.0	18.3	28.1	170.	63.
Cs	--	--	--	1.53	--	8.0	1.57	--	0.45
Cu	1.2%	2.0%	320.	0.22%	4.6%	0.55%	36.0	0.26%	470.
Eu	1.29	<2.0	0.87	0.91	<2.0	13.4	0.20	4.0	3.06
F%	0.01	0.02	0.02	0.03	0.03	0.06	0.02	0.09	0.04
Fe_2O_3%	3.74	3.96	1.19	1.52	67.7	0.79	5.22	14.5	0.81
Ga	<40.0	14.0	<4.0	5.0	300.	13.0	5.0	27.0	14.
Hf	21.8	--	--	3.42	--	9.53	5.35	--	3.42
Hg	0.5	--	0.58	15.0	--	0.62	0.06	1.1	--
K_2O%	0.64	0.56	0.11	0.78	0.04	3.72	0.90	1.23	0.60
La	312.	6.0	1.03	10.8	3.0	23.1	8.35	25.0	45.3
Li	10.0	11.0	<2.0	7.0	3.0	40.0	11.0	33.0	6.0
LOI	4.05	15.6	--	30.4	15.3	--	5.02	14.6	13.2
Lu	--	--	--	0.18	1.00	1.00	0.13	--	--
MgO%	0.22	5.35	0.22	12.7	0.16	0.86	0.20	0.40	6.88
Mn	21.0	170.	260.	720.	0.10%	21.	<0.06	0.58	360.
Mo	80.0	26.0	4.0	35.0	460.	260.	29.0	820.	5.0
Na_2O%	0.36	0.15	0.01	0.72	0.75	0.10	<0.15	0.46	<0.15
Nb	5.0	--	--	5.0	--	26.0	--	--	--
Nd	140.	11.0	<1.8	13.8	<4.0	100.	5.79	56.0	39.
Ni	60.0	150.	22.0	560.	0.35%	520.	90.0	0.13%	41.
P_2O_5%	0.05	0.05	--	0.08	<0.10	<0.02	<0.05	0.33	0.35
Pb	0.33%	290.	0.55%	0.12%	0.16%	0.42%	110.	0.17%	280.
Rb	--	--	--	21.2	--	120.	24.5	--	12.1
Ttl S%	4.13	2.47	0.03	0.03	0.06	0.01	3.7	12.8	4.45
Sb	15.8	--	3.6	1.84	--	2.89	1.48	--	1.64
Sc	1.53	<2.0	1.39	2.15	<2.0	6.83	1.93	25.0	1.85
Se	29.0	--	0.8	78.0	--	6.8	3.0	9.8	--
SiO_2%	81.4	50.6	--	28.7	3.71	--	83.2	54.0	37.4
Sm	--	--	0.31	3.75	--	39.4	1.12	--	8.46
Sr	110.	46.0	67.	140.	150.	290.	90.0	460.	0.15%
Ta	<0.71	<40.0	1.0	0.24	<40.0	<0.45	0.31	<40.0	<80.
Tb	0.99	--	--	0.48	--	5.70	0.15	--	0.66
Th	1.16	<4.0	0.69	2.09	<4.0	4.84	1.93	<4.0	1.14
TiO_2%	0.09	0.07	--	0.16	<0.04	.20	0.20	0.28	0.08
U	1.28%	1.0%	12.7	29.5	29.4	0.31%	23.9	0.95%	0.33%
V	20.0	7.0	11.0	67.0	21.0	4.0%	21.0	130.	18.
Y	30.0	12.0	<2.0	13.0	5.0	72.0	3.0	110.	51.
Yb	2.04	--	0.41	1.08	<1.0	8.10	0.82	13.0	3.
Zn	0.7%	110.	35.4%	2.87%	2.7%	150.	18.4	0.56%	130.
Zr	--	--	--	--	--	720.	110.	--	--

Crb C%= inorganic carbon
Org C%= organic carbon
LOI= Loss on ignition at 900° C
Ttl S%= total sulfur
"--" not determined

Sample sources:

1--Ore grade breccia pipe
2--Orphan mine
3--Chicken mine
4--Copper Mountain mine
5--Apex mine
6--Ridenour mine
7--Mohawk Canyon Pipe
8--Ore grade breccia pipe
9--Ore grade breccia pipe

additional drilling, but may prove to be ore grade. Samples 3, 4, and 6 are from oxidized rock in three separate breccia pipes that produced Cu during the early 1900's, but do not appear to contain economic concentrations of U; in addition sample 4 is from the only known breccia pipe to have produced Au, or contain any significant Au anomalies. Sample 5 is from a mine that is in a collapse breccia pipe, but is located in the Basin and Range rather than on the Colorado Plateau. It is discussed further in section 5.

There is no consistent depletion or enrichment between samples in the oxidized mineralized rock and the primary ore except that the oxidized ore is depleted in sulfur with values consistently <0.06%, while the primary ore, with one exception, contains >1% sulfur (Table 1). Also, the oxidized rock contains much lower uranium concentrations than the primary ore, as might be expected because its high solubility in the oxidized +6 state.

Two of the primary ore samples, 2 and 8, are very rich in organic carbon; the remainder of the samples contain two orders of magnitude less carbon. Some breccia pipes contain abundant hydrogen-sulfur-rich, black glassy pyrobitumen (described above and shown in Fig. 12). The pyrobitumen is composed of hydrogen, 85.6% carbon (precision of 1%) and 3.74% sulfur. It contains very few other elements in concentrations over a few ppm; the only exceptions are: Ba (50 ppm), Cr (3 ppm), Ni (50 ppm), Pb (50 ppm), V (100 ppm), Zr (15 ppm), and Si (70 ppm). Rock eval measurements by Lisa Pratt suggest that the pyrobitumen was never subjected to temperatures in excess of 150°C, although it has been extensively altered, probably by sulfur stabilization (Lisa Pratt, written communication, 1985). The material is very stable and hence will not dissolve in most solvents (Lisa Pratt, written communication, 1985).

Geochemistry of ore-forming fluids

The bleaching of rock adjacent to and inside of the breccia pipes appears to have occurred prior to precipitation of calcite, the first mineral in the paragenetic sequence. Because only minor organic material has been observed in the breccia pipes, mostly plant fossils from the Hermit Shale and Esplanade Sandstone, reduction of the Fe^{3+} by H_2S is most probable (Gornitz, and others, 1988) The presence of pyrobitumen in some pipes and the strong fetid smell present in the Toroweap, Surprise Canyon, and Temple Butte Formations indicates that H_2S was present in the Paleozoic strata of the Grand Canyon region. Because the paragenesis of the pyrobitumen has not been clearly established and because the pyrobitumen is only present in some ore-bearing breccia pipes, its role in the ore genesis has not been established.

The large assemblage of ore minerals was probably produced by at least two separate mineralizing fluids. Because uranium is mobile only in the oxidized 6+ state and generally travels as a carbonate or bicarbonate complex it is unlikely to have migrated in the same fluid with the Co, Ni, Pb and Zn. The second and third mineralizing pulses, those depositing the Ni, Co, Fe, As, Cu, Pb, and Zn minerals, were probably a result of deposition from brines, similar to those that produced the Mississippi Valley-type deposits, that may well have been trapped in the Paleozoic marine strata. The uraninite followed in the next mineralizing event and was probably precipitated from uranium-rich ground water. The late stage copper mineralization of such minerals as bornite, chalcocite, djurleite, digenite, and covellite may well have formed from copper that was transported in ground water with the uranium, but are more likely to be secondary minerals formed by supergene alteration of the primary Cu-bearing minerals. The uranium may not have required organic material, or H_2S, to precipitate. The presence of the sulfide-rich ores already present within the breccia pipes, may well have reduced the uranium, which precipitated uraninite from the ground water.

The breccia pipes were excellent conduits for the movement of any fluids present within the Grand Canyon region since the pipes formed. Because this is a region of flat lying strata the breccia pipes provided very permeable vertical conduits for fluid movement. So, the opportunity existed for the movement into the breccia pipes of (1) brines dewatered from marine sediments, (2) ground water, and (3) trapped hydrocarbons. All of these fluids probably contributed to the large mineral assemblage present in these breccia pipes.

PALEOGEOGRAPHY AND PALEOTECTONICS

After deposition of the Mississippian Redwall Limestone, northwestern Arizona remained slightly above sea level or was inundated by shallow seas during Pennsylvanian and Permian times (McKee, 1982). The region remained tectonically stable and flat-lying during this period, which probably provided a very low hydraulic gradient and permitted little movement of connate waters within the sediments. Streams flowed approximately northwestward or southwestward across northwestern Arizona during parts of Late Mississippian through Permian time (Fred Peterson, written communication, 1986).

In the Triassic Period, a magmatic arc formed across southwestern Arizona and extended northwestward into southeastern California and western Nevada (Bilodeau, 1986). Large quantities of gravel and sand were transported northwestward across northwestern Arizona by streams that originated in the uplifted flap of Precambrian and Paleozoic rocks (Mogollon highlands) on the back or northeast side of the magmatic arc (Bilodeau, 1986). The uplift of the Mogollon highlands imposed strong hydraulic gradients that (1) may have circulated brines out of the Pennsylvanian and Permian strata trapped there since the beginning of the Pennsylvanian, and (2) facilitated the circulation of uranium-rich groundwater from the volcanic Mogollon Highlands into the Grand Canyon region, through aquifers, such as the Coconino Sandstone, the Supai Group, or the Redwall Limestone (Fig. 17).

The movement of fluids may have also been accelerated by sudden development or enlargement of the breccia pipes during the Triassic. "There was a significant fluvial and deltaic basin in the Cameron area during deposition of the [Triassic] Shinarump and Petrified Forest Members of the Chinle Formation. Significant fluctuations in lake level, and associated ground water level, occurred in response to both seasonal and longer-term climatic fluctuations, in part due to the tropical monsoonal climate and its long-term intensity variations. These hydrologic fluctuations resulted in significant "pumping" in the system" (Russell F. Dubiel, written communication, 1986). This "pumping" of the hydrologic system is known to accentuate karst development today in northern Florida. The monsoonal rains would have increased the water volume entering aquifers in the highlands, providing additional water movement that probably also accentuated karst development. Thus, it is possible that sudden collapse and brecciation of the pipes during the Triassic provided fluids from several sources with highly permeable conduits for upward movement. The steepened hydraulic gradient permitted the fluid movement toward these breccia pipes in the Grand Canyon area around 200 Ma when the uraninite was deposited. The fluid movement is believed to have been upward in the breccia pipes as opposed to downward for two reasons: (1) In a basin environment, particularly toward the center, the

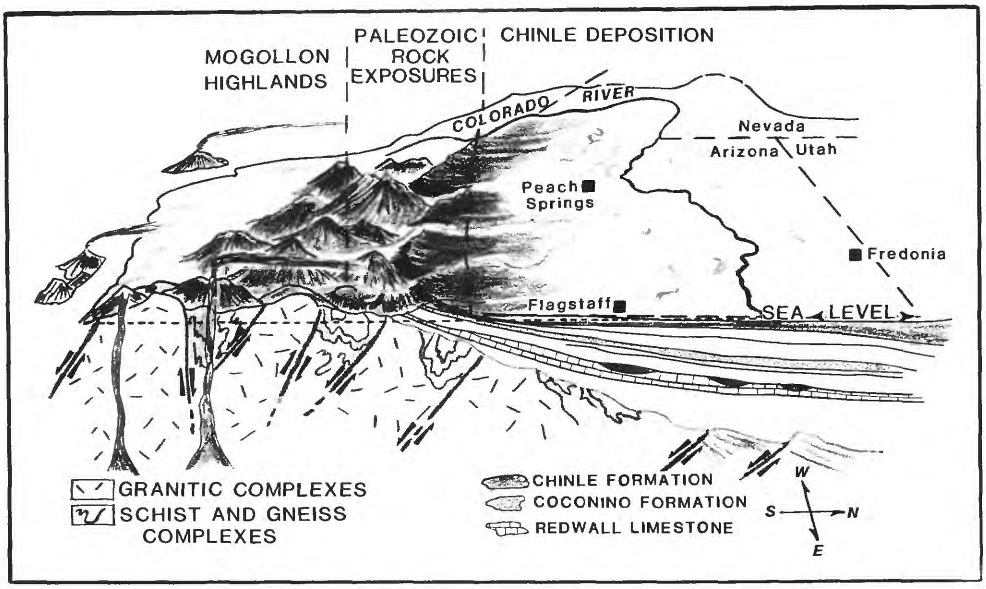


Figure 17. Cartoon of the paleogeography of northern Arizona during uraninite ore deposition in the Triassic. Paleogeography constructed and drawn by G.H. Billingsley.

hydraulic gradient is upward; generally downward fluid movement should have only occurred in northern Arizona during periods of extensive canyon cutting, and (2) If the uranium ore fluids had migrated down the pipe uraninite should have been deposited shortly after encountering the pyrite cap; yet there is little uranium associated with the pyrite cap, and in fact the higher grade ore is commonly located toward the center of the pipe.

The ore horizon in the Orphan mine (Fig. 1) is located (primarily in the Supai Group) at a lower stratigraphic level than that in pipes (primarily in the Hermit Shale) to the north of the Grand Canyon along the Arizona strip (Fig. 1). Perhaps, this suggests that the pipes on the North rim, such as the Hack Canyon pipes or the Pigeon pipe, were located topographically lower in the basin at the time of ore deposition. This assumes that the ore-forming fluids were using the same aquifer, or aquifers, throughout the breccia pipe province.

MINERALIZED BRECCIA PIPES OUTSIDE OF THE COLORADO PLATEAU

No other large uranium-rich breccia pipe province has been recognized elsewhere in the world. There are several other mineral deposits in solution-collapse breccia pipes in other parts of the world, such as the Apex mine in the Basin and Range of the U.S.A., Tsumeb in Namibia, and the Redbank copper deposits in Australia, but none of these contain significant uranium minerals.

The Apex mine is located in the southern Basin and Range near the Colorado Plateau's western edge. In 1985 processing of Ge and Ga ore began at the Apex, making it the world's first primary producer of these two metals. In addition, Ag, Cu, and Zn are being recovered as by-products. The Apex mine is in a Colorado Plateau-type solution-collapse breccia pipe (Wenrich, and others, 1987). The Apex orebody appears to be an oxidized version of the U-rich, Ag-Co-Cu-Ni-Pb-Zn-sulfide-bearing breccia pipe ore present in such mines as the Orphan, Hack 1, 2, and 3, Kanab North and the Pigeon. The only significant differences in element concentrations between the Apex and Colorado Plateau breccia pipe mines are that the Apex base metals have been oxidized, the U has been depleted, and Fe, Ga, and Ge have been enriched probably by supergene enrichment due to downward circulation resulting from dewatering of the pipe. These events were likely related to Basin and Range extensional tectonics. The Ga and Ge are closely associated with abundant jarosite in the Apex breccia pipe. Two samples of jarosite from the mine yielded K-Ar isotopic ages of 4.00 ±0.10 and 6.15 ±0.23 Ma (M. Shafiqullah and P.E. Damon, 1987, written communication). This suggests that the Ga and Ge mineralizing event is related to Miocene Basin and Range extensional tectonics. Depletion of uranium at the Apex, assuming that uranium mineralization occurred there around 200 Ma as it did in the other breccia pipes, would not be surprising as uraninite is rarely preserved in a carbonate-rich oxidizing environment, such as has been present at the Apex for at least the last 6 Ma.

The mineralogy and geochemistry of the Apex mine are exceptionally similar to the Tsumeb deposit in Namibia, which is also believed to be a solution-collapse breccia pipe (Lombaard, and others, 1986) and like the Apex contains no uranium minerals. This deposit has been one of the most productive mines in southern Africa. At various times from 1906 to 1979 the mine produced Cu, Pb, Zn, Cd, Ag, As, and/or Ge (Lombaard, and others, 1986). As at the Apex mine, most ore minerals in the Tsumeb pipe are supergene; whether either pipe originally contained the Mississippi Valley-type reduced Pb-Zn-Ni-Co ores associated with later uraninite as do the Colorado Plateau breccia pipes is unknown.

The Redbank copper deposits in Australia are small occurrences in contrast to Tsumeb, but there are 50 recognized collapse pipes and drilling "has established the presence of chalcopyrite mineralization in nine collapse breccia pipes" (Orridge and Mason, 1975). Orridge and Mason (1975) believed the pipes formed from a combination of processes including magma withdrawal and solution of carbonate beds. The Redbank pipes do not have the diversified mineral assemblage present at Tsumeb and Apex, but they do have several mineralogic similarities to the Colorado Plateau breccia pipes: Chalcopyrite, pyrite, galena, barite, and pyrobitumen (Orridge and Mason, 1975). The Redbank deposits have also been intensely bleached and "reddened" in different locations.

CONCLUSIONS - LITHOTECTONIC CONTROLS

The Colorado Plateau uranium-rich breccia pipes represent a unique province for several reasons. Combinations of several geochemical, mineralogic, and geologic conditions were necessary to form high-grade uranium-rich deposits within such a breccia pipe-rich province; some of these conditions are themselves rare elsewhere in the world:

1. An extensive karst-forming limestone.
2. An overlying thick sequence of sediments containing abundant

sandstones, most of which are cemented by carbonate.

3. A stable cratonic environment with a very low hydrologic gradient, such that the sediments retained their connate waters, which became increasingly saline and metal-rich through concentration over time.
4. A later period (subsequent to deposition of the thick sequence of sandstones) of extensive carbonate dissolution.
5. The formation of a basin, which provided a steepened hydraulic gradient and permitted saline metal-rich connate waters to migrate into the highly permeable conduits formed by the breccia pipes.
6. Deposition of a pyrite-rich Co-Cu-Ni-Pb-Zn sulfide rich-orebody within the pipes--a Mississippi Valley-type deposit. These sulfides later acted as an excellent reductant for later uranium-rich fluids. The "pyrite cap" over the orebody may be instrumental is preventing oxidation of the ore during later periods of dewatering.
7. A volcanic highland that provided a uranium-rich source rock, and one or more good aquifers permitting ground water flow downdip into the basin containing the sulfide-rich breccia pipes.
8. A subsequent period of cratonic stability that continued until the present, which prevented dissection and oxidation of the orebodies. Tilting and folding of the strata would permit downward percolating water to come in contact with the sides of the orebody, which would no longer have its "pyrite cap" on "top".

Perhaps condition #8 is the most important. Because uranium is so soluble in the oxidizing environment, any oxidation of the orebody would cause the removal of uranium and form an oxidized orebody, such as that at the Apex and Tsumeb mines. In addition, because the breccia pipes are so small, they are difficult to recognize even on the plateaus of northern Arizona covered by flat-lying strata. Terrane with highly tilted, faulted, or folded rock is exceptionally difficult in which to locate breccia pipes. Because the ore is buried, commonly beneath as much as 300 meters (1000 ft) of strata, location of the pipes would be almost impossible without some surface expression that is recognizable. If such a province of U-rich breccia pipes is to be located elsewhere in the world it would be best to begin in a region of (1) flat-lying strata, (2) long cratonic stability, and (3) a thick sequence (on the order of 175 m (500 ft)) of limestones with overlying sand-bearing units.

ACKNOWLEDGEMENTS

The authors wish to thank Bradley S. Van Gosen for his continual help, advice, and assistance in assembling this manuscript. Many scientists working on the breccia pipe project have contributed significantly to our ideas presented here - most notably Earl R. Verbeek, Peter W. Huntoon, George H. Billingsley, Kenneth R. Ludwig, Fred Peterson, Russell F. Dubiel, and Julie Roller. James G. Crock completed the geochemical analysis of the tallmessite sample and Larry L. Jackson analyzed the pyrobitumen. William L. Thoen contributed the computer graphics for the fluid inclusion data. Thanks also goes to T. James Reynolds for the many hours spent searching for fluid inclusions in our fine-grained breccia pipe samples and providing us with the fluid inclusion filling temperatures and salinities for the breccia pipes. The age determinations completed by Muhammad Shafiqullah and Paul E. Damon of our jarosite samples from the Apex Mine provided us with the evidence to

support our past assertion that the Ge and Ga mineralization is very recent compared to the breccia pipe uranium mineralization.

REFERENCES CITED

Billingsley, G.H., Wenrich, K.J., and Huntoon, P.W., 1986, Breccia pipe and geologic map of the southeastern Hualapai Indian Reservation and vicinity, Arizona: U.S. Geological Survey Open-File Report 86-458B, 26 p., 2 plates, scale 1:48,000.

Bilodeau, W.L., 1986, The Mesozoic Mogollon highlands, Arizona--an Early Cretaceous rift shoulder: Jour. Geol., v. 94, p. 724-735.

Chenoweth, W.L., 1986, The Orphan Lode Mine, Grand Canyon, Arizona, a case history of a mineralized, collapse-breccia pipe: U.S. Geological Survey Open-File Report 86-510, 126 p.

Damon, P.E., 1968, Correlation and chronology of ore deposits and volcanic rocks: U.S. Atomic Energy Commission Annual Progress Report No. COD-689-100, Contract at (11-1)-689, Research Division, p. 49-50.

Gornitz, Vivien, Wenrich, K.J., Sutphin, H.B., and Vidale-Buden, R., 1988, Origin of the Orphan mine breccia pipe uranium deposit, Grand Canyon, Arizona, in, Vassiliou, A.H., Hausen, D.M., and Carson, D.J., eds., Process Mineralogy VII - As applied to separation technology: The Metallugical Society, Warrendale, Pa., p. 281-301.

Huntoon, P.W., 1970, The hydro-mechanics of the ground water system in the southern portion of the Kaibab Plateau, Arizona: PhD Thesis, University of Arizona, Tucson, Ariz., 251 p.

Lombaard, A.F., Gunzel, A., Innes, J., and Kruger, T.L., 1986, The Tsumeb lead-copper-zinc-silver deposit, South West Africa/Namibia, in, Anhaeusser, C.R., and Maske, S., eds., Mineral Deposits of Southern Africa, I & II: Geol. Soc. of S. Africa, Johannesburg, p. 1761-1787.

Ludwig, K.R., Rasmussen, J.D., and Simmons, K.R., 1986, Age of uranium ores in collapse-breccia pipes in the Grand Canyon area, northern Arizona: Geol. Soc. Am. Bull., v. 18, no. 5, p. 392.

McKee, E.D., 1982, The Supai Group of Grand Canyon: U.S. Geological Survey Professional Paper 1173, 504 p.

Orridge, G.R. and Mason, A.A.C., 1975, Redbank copper deposits, Australasian Inst. of Mining and Metallurgy Monogr. Ser. 5: Economic Geology of Australia, Papua, New Guinea, 1, Metals, p. 334-343.

Roller, J.A., 1987, Fracture history of the Redwall Limestone, western Hualapai Reservation, northwestern Arizona: U.S. Geological Survey Open-File Report 87-359, 33 p.

Shoemaker, E.M., Squires, R.L., and Abrams, M.J., 1978, The Bright Angel and Mesa Butte fault systems of northern Arizona, in, Smith, R.B., and Eaton,G.D., eds., Cenozoic tectonics and regional geophysics of the western Cordillera: Geol. Soc. Amer. Memoir 152, p. 341-368.

Sutphin, H.B., 1986, Occurrence and structural control of collapse features on the southern Marble Plateau, Coconino County, Arizona: MS Thesis, Northern Arizona University, Flagstaff, Ariz., 139 p.

Sutphin, H.B., and Wenrich, K.J., 1988, Map showing structural control of breccia pipes on the southern Marble Plateau, Arizona: U.S. Geological Survey Miscellaneous Investigations Series Map I-1778, 2 plates with text, scale 1:50,000.

Van Gosen, B.S., and Wenrich, K.J., 1987, Lithology and stratigraphy of a drill core from the vicinity of the Hack Canyon mines, Mohave County, northern Arizona: U.S. Geological Survey Open-File Report 87-0144, 11 p.

Verbeek, E.R., Grout, M.A., and Van Gosen, B.S., 1988, Structural evolution of a Grand Canyon breccia pipe: The Ridenour copper-vanadium-uranium mine, Hualapai Indian Reservation, Coconino County, Arizona: U.S. Geological Survey Open-File Report 88-006, 75 p.

Wenrich, K.J., 1985, Mineralization of breccia pipes in northern Arizona: Econ. Geol., v. 80, no. 6, p. 1722-1735.

Wenrich, K.J., 1986, Uranium mineralization of collapse breccia pipes in northern Arizona, Western United States, in, Fuchs, H., ed., Vein-type uranium deposits: IAEA-TECDOC-361, p. 395-414.

Wenrich, K.J., Billingsley, G.H., and Huntoon, P.W., 1986, Breccia pipe and geologic map of the northeastern Hualapai Indian Reservation and vicinity, Arizona: U.S. Geological Survey Open-File Report 86-458A, 29 p., 2 plates, scale 1:48,000.

Wenrich, K.J., Verbeek, E.R., Sutphin, H.B., Van Gosen, B.S., and Modreski, P.J., 1987, The Apex Mine, Utah--A Colorado Plateau-type solution-collapse breccia pipe, in USGS research on mineral resources--1987 program and abstracts: U.S. Geological Survey Circular 995, p. 73-74, 76-77.