

Uranium exploration for northern Arizona (USA) breccia pipes in the 21st century and consideration of genetic models

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ABSTRACT

Changes in metal prices, together with renewed interest in nuclear energy based in part on concerns of global warming, have resulted in elevated activity in the search for uranium ores. The solution-collapse breccia pipes of northwestern Arizona include sites of high-grade uranium ore. The intrinsic geology of these pipes, together with growing understanding of the nature of telethermal ores, (a classification category to which the base-metal deposits of the pipes belong), are important components of the model of their genesis. The metallized pipes are base-metal bearing and, regionally, bear a slightly later metal overprint of uraninite. A model is proposed here for genesis of these ores as members of the class of Mississippi Valley Type (MVT) deposits, but with a uranium overprint. U-Pb ages on uraninite of 200 and 260 Ma link the mineralization with Pangean time, events, and mid-continent MVT ores; chemistry and fluid inclusion temperatures on sphalerite and dolomite of 80°-173° link them with MVT deposits. Mixing of oxidizing groundwaters from overlying sandstones with reducing brines that had entered the pipes due to dewatering of the Mississippian limestones created the uranium deposits. Proximity to the west of the Cordilleran miogeocline and various uplifts to the east allow consideration of a basin-dewatering mechanism as the genetic mechanism. Successful discoveries of buried ore minerals during the past year through the use of airborne geophysical methods such as time-domain electromagnetics (VTEM) have opened the door to a broader exploration for these orebodies. Search of the miogeocline shelf margin through the Southwest merits consideration as a prospecting tool for MVT deposits as well as uranium ore.

INTRODUCTION

The uranium industry has made a dramatic turnaround in the first decade of the 21st century that even the most optimistic economist was not willing to predict during the uranium downswing of the 1990s. Uranium reached a 30-year low in February 2001 of \$6.50/lb. By the end of June 2007 it had soared to \$135/pound. This nearly 2000 percent increase in

the uranium spot price within 4 years dwarfed the increase in gold price. The initial slow rise from \$6.50 in February 2001 to \$10.75 in April 2003 (Fig. 1) was primarily driven by the decrease in the value of the dollar. Since then several factors have contributed to the extreme price increase: (1) the recognition by many of the simple fact that uranium supply has not met demand for several years and that the world's stockpiles are being drawn down, (2) realization of how sharply

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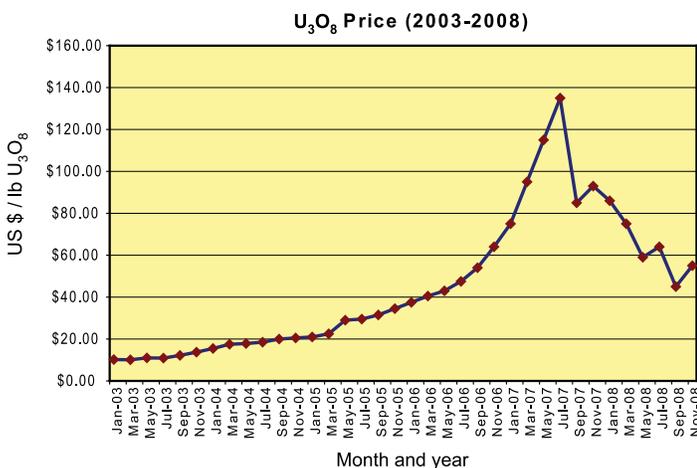


Figure 1. Graph of uranium price, in dollars per pound of U₃O₈, from January 2003 to July 2008. Data from the Ux Consulting Co., LLC. (2008).

this fragile supply can be impacted by disasters at the world's major uranium production facilities, such as (a) the flooding of the McArthur River mine in the spring of 2003, (b) fires at Olympic Dam, (c) the potential that Rossing, with an annual capacity of 4000 tonnes uranium, might close by 2007, (3) the withdrawal of Tenex from the HEU (highly enriched uranium) feed agreement, and (4) the 2005 announcement by the Chinese of their intent to build 30 new nuclear reactors.

The escalating uranium price brought about a flurry of mineral exploration activity that has not been witnessed in the US since the 1849 gold rush. The first uranium boom in the early to late 1950s was also intensive, but the 21st century boom benefited from the knowledge gained during the 1950s and 1970s booms, resulting in more claims staked across the Colorado Plateau within a much shorter time interval. Uranium economics have a significant impact on the state of Arizona. The highest-grade uranium deposits in the United States (average grade of 0.65% U₃O₈) occur in solution-collapse breccia pipes in northwestern Arizona. These deposits are higher grade than most uranium deposits elsewhere in the world, with the exception of the Canadian Athabasca Basin deposits (with an average grade around 20% uranium for the McArthur River and Cigar Lake mines, but an overall lower basin average of around 4%). The flooding of yet another of the Canadian high-grade uranium mines, Cigar Lake in October 2006, has once again emphasized the fragility of the uranium supply. This crisis resulted in an increase in uranium price from \$54/lb to \$60/lb (Fig. 1). The Athabasca Basin mines, located amongst abundant lakes, are exceptionally vulnerable to flooding as has been aptly demonstrated by flooding in both the two highest-grade mines within a 3.5-year period (2003-2006). The Arizona breccia pipes are well above the water table and, although lower grade and smaller size, provide a stable, small-footprint, uranium supply. Presented here is a brief history of breccia pipe mining, some fundamentals of mineralogy and chemical composition, and concepts of origin.

MINING HISTORY

Mining activity in the Grand Canyon breccia pipes began during the nineteenth century (Figs. 10 and 12), although at that time mining was primarily for copper with minor production of silver, lead, and zinc. It was not until 1951 that uranium was first recognized in the breccia pipes. At this time the pipes were still thought to be volcanic in origin; it was not until 1965 that C.G. Bowles (1965) recognized the pipes as originating from solution collapse. Despite periods of depressed uranium prices, the breccia pipes commanded considerable exploration activity in the 1980s and early 1990s because of the high-grade nature of their uranium ore. During the period 1956-69, the Orphan mine produced 4.26 million lb of U₃O₈ with an average grade of 0.42% U₃O₈ (Chenoweth, 1986). In addition to uranium, 6.68 million lb of copper, 107,000 oz of silver, and 3400 lb of V₂O₅ (vanadium oxide) were recovered from the ore (Chenoweth, 1986).

The Orphan mine is located within Grand Canyon National Park where the headframe, which projects above Powell Point, commemorates US heritage of mining history. This history includes one of Teddy Roosevelt's Rough Riders packing his burro down the trails of the Grand Canyon to his Orphan mine where he began to dig for copper and silver in 1893 when he discovered copper on the south wall of the Grand Canyon, 1100 feet below the rim. After serving as a Rough Rider during the Spanish American War, Dan Hogan returned to prospecting. In 1906 he filed for a mining claim patent on the Orphan mine and his old commander, Theodore Roosevelt, signed it himself. From this it might be construed that Teddy Roosevelt believed in multiple land use and that the beauties of the Grand Canyon could coexist with mining.

Uranium mining raises many concerns among those who live in uranium-bearing regions and have seen the results of mid-20th century mining practices, 55-70 years ago that were driven by the race for military supremacy. Yet, not only are those days gone, replaced with modern, strict reclamation and safety regulations, but these breccia-pipe mines are different from the shallow, sandstone-hosted uranium ores of the Colorado Plateau's Four Corners area. The uranium in the pipes is deep beneath the plateau surface and must be extracted by underground mining; nothing extraneous remains on the surface after mine closure. The breccia pipe deposits were so successfully mined (Table 1) and reclaimed in the 1980s and early 1990s that few people even realize that there were eight producing mines in the Arizona Strip (thap portion of Arizona north of the Grand Canyon) near the end of the 20th century. Today even uranium geologists can no longer find the location of the three former producing uranium mines that are located in Hack Canyon or the Pigeon mine, north of a designated Wilderness area in Snake Gulch.

Table 1. Breccia pipe production data for all eight previously producing mines.

Mine*	Average Grade (% U ₃ O ₈)	Production (Pounds U ₃ O ₈)
Hack 1, 2, & 3	0.643	9,542,000
Pigeon	0.695	5,652,000
Kanab North	0.582	2,728,000
Pinenut	1.020	526,350
Hermit	0.760	552,500
Orphan	0.420	4,200,000
Total		23,200,850

*All mines except the Orphan mine produced between 1980 and 1994—production figures for those 7 mines are from Donn Pillmore of Energy Fuels Nuclear (written commun., 2008).

Production

Between 1980 and 1994 seven breccia pipes (Hack 1, 2, and 3, Pigeon, Kanab North, Pinenut, and Hermit) were mined for uranium in northern Arizona with grades averaging 0.65% U₃O₈ (Mathisen, 1987). Two others, the Arizona 1 (Fig. 11) and Canyon mines, have headframes but no production as of 2008. Denison Mines Corp. expects to have the Arizona 1 mine in production in 2009.

Although the uranium grades and size of the breccia pipes are dwarfed by those of the Athabasca Basin unconformity deposits in Canada, it is significant that (1) breccia-pipe mining costs are significantly less for the Arizona deposits, (2) Other than some of the Athabasca Basin deposits these ore grades of 0.4-1% are as high or higher than any other global uranium-deposit type, (3) the breccia-pipe uranium supply is stable, not subject to catastrophic flooding, such as in the Athabasca Basin, (4) they leave a small temporary (5-year mine life) footprint with a mine using less than 10 acres, and (5) they are well above the water table, removing most possibilities of contamination to the regional aquifer system.

Modern exploration – 21st Century

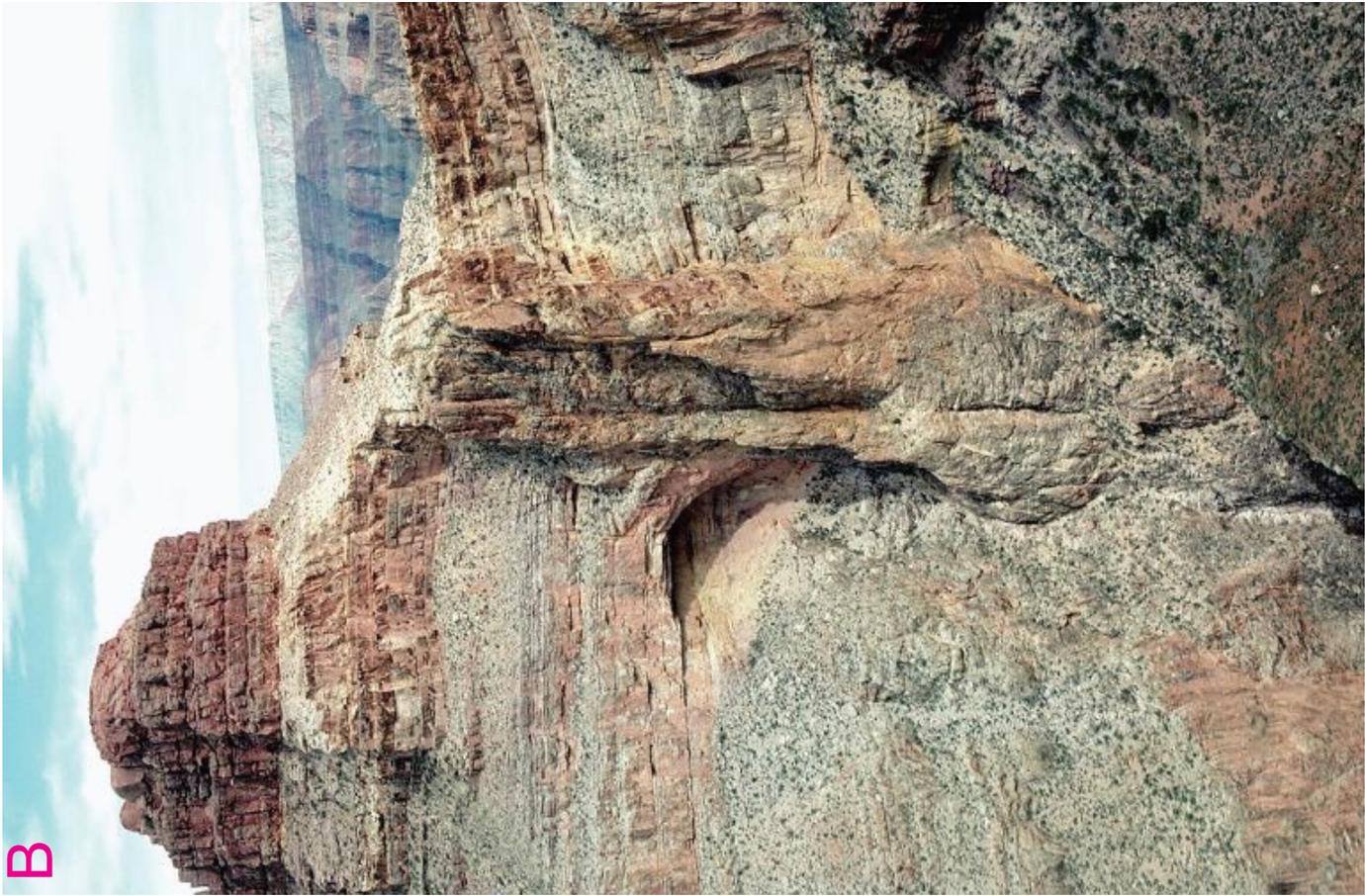
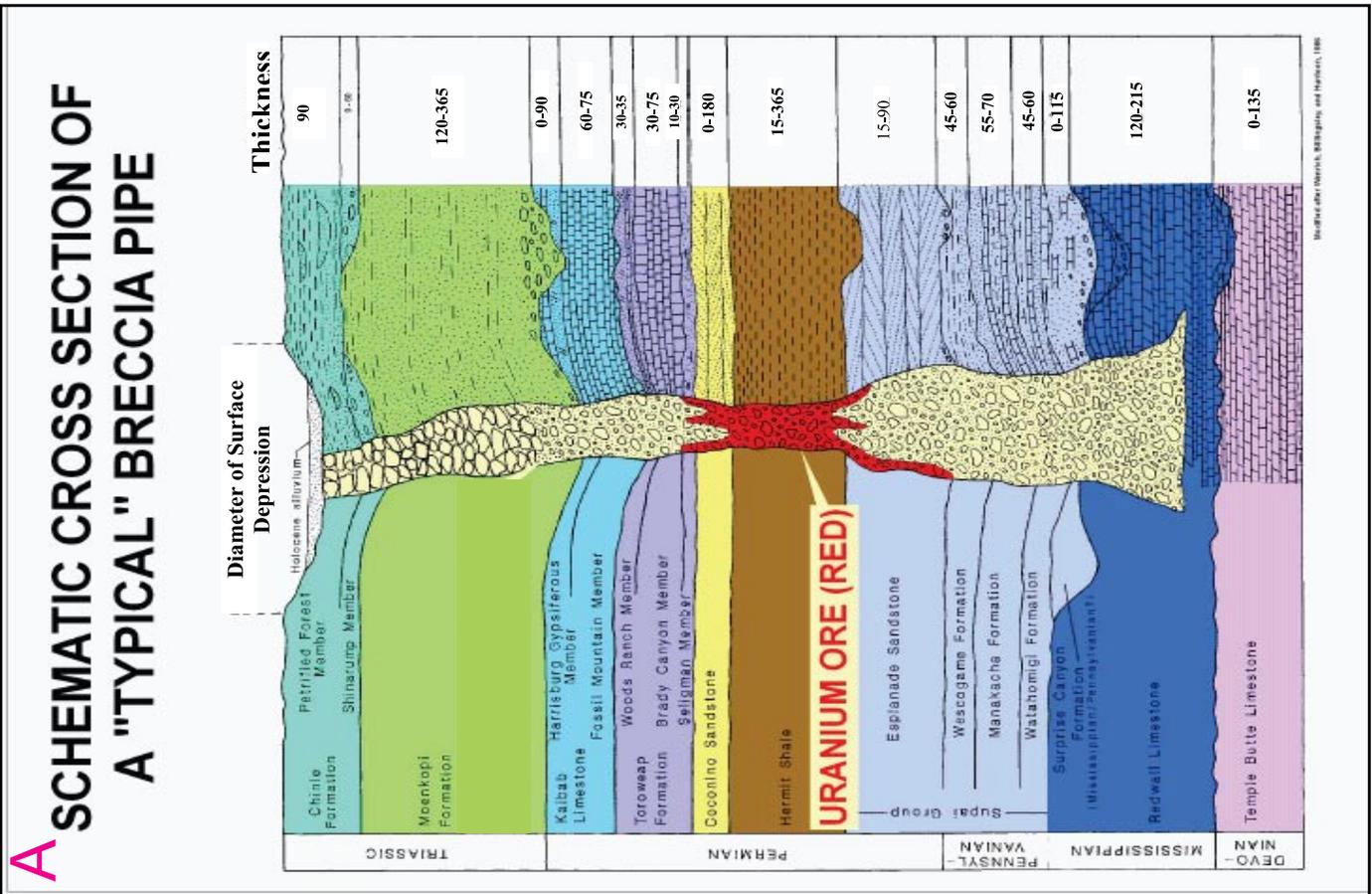
As a result of the third uranium boom – the greatest uranium rush in history, more than 8000 claims have been staked on the Arizona Strip alone; this does not include the land to the south of the Grand Canyon (Fig. 3). The first drilling on the Arizona Strip, following the successes of the 1980s and 1990s exploration flurry when eight orebodies were discovered and mined, began in November 2005. The amount of drilling since then was minimal until early 2007 when three junior companies began drilling on the Arizona Strip. However, no announcements of ore-grade mineralization had been forthcoming until April 2008 when a press release by Quaterra Resources indicated several holes with significant footage of ore-grade mineralization (averaging between 0.33-0.58% U₃O₈). This announcement had particular significance because it represents, for the first time, a discovery of a hid-

den pipe by using airborne time-domain electromagnetic system (VTEM) surveys. Their VTEM surveys conducted since 2006 identified more than 200 geophysical anomalies, and this was the first one to be tested by drilling. The success of this method was underscored one month later when Quaterra announced a second ore-mineralized pipe discovery on their first drill hole with grades of ore intercepts ranging from 0.37-0.63% U₃O₈ (this pipe had geomorphic expression on the surface). The use of airborne VTEM may have opened the door to confirmation of a statement made by I.W. Mathisen that the breccia-pipe district may hold uranium resources that exceed all uranium mined to date in Wyoming, Colorado, and Utah (1989, verbal commun.).

BRECCIA-PIPE OCCURRENCE AND COMPOSITION

Neither intrusive nor volcanic rocks are associated with these breccia pipes. The pipes are vertical columns of broken rock (Fig. 2). Breccia (Fig. 4) formed when upper Paleozoic and Triassic sandstone, shale and limestone collapsed into underlying caverns in the Mississippian Redwall Limestone (Figs. 7-9). Breccia pipes consist of two interrelated parts: the throat and the collapse cone – the cone surrounds the throat above the level of the Permian Coconino Sandstone and was caused by dissolution within the Kaibab and Toroweap formations (Krewedl and Carisey, 1986). The massive Redwall Limestone, which forms many of the 500-ft high sheer walls of the Grand Canyon, is one of the most extensive karst-forming limestones in the U.S. (Wenrich and Sutphin, 1994). Karst development was so extensive that brecciation of overlying sedimentary strata resulted in thousands of breccia columns (Fig 2). The breccia pipes appear to form only where thick sections of Redwall were present. A Redwall isopach map (McKee and Gutschick, 1969) makes a good initial exploration guide for pipe locations (Fig 6). Stopping up through upper Paleozoic and lower Mesozoic strata, as high in the section as the Triassic Chinle Formation, produced vertical, rubble-filled, pipe-like structures approximately 300 ft in

Figure 2 (next page). **Figure 2A:** Schematic cross section of a breccia pipe. The unit thickness shown for the Triassic Chinle and Moenkopi Formations represent their thickness range throughout the Grand Canyon region. Thicknesses for the upper Paleozoic strata correspond to the average unit thickness within the Coconino Plateau of the eastern Hualapai Indian Reservation. Uranium ore in red. From Wenrich et al. (1989). **Figure 2B:** The Bat Cave breccia pipe is eroded and well-exposed along the canyon wall. It is about 200 feet in diameter and extends over 600 feet in elevation from the Redwall Limestone to the Esplanade Sandstone before its top is truncated by erosion. The pipe was formed by solution collapse of overlying sandstone, shale, and limestone into a cavern within the Redwall Limestone. This collapse process left a cylindrical column of broken rock above the cavern. Photo by Karen Wenrich.



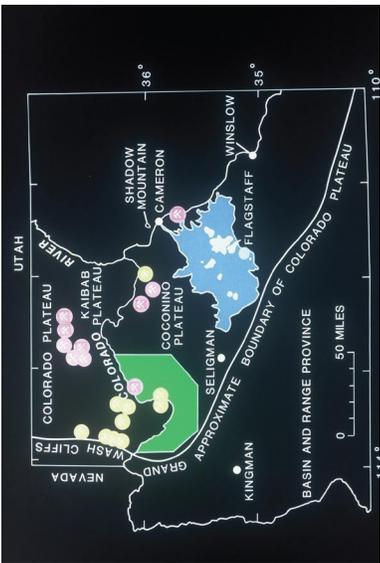


Figure 3. Breccia Pipe District Map; Cu-production (yellow); U+Cu production (pink).

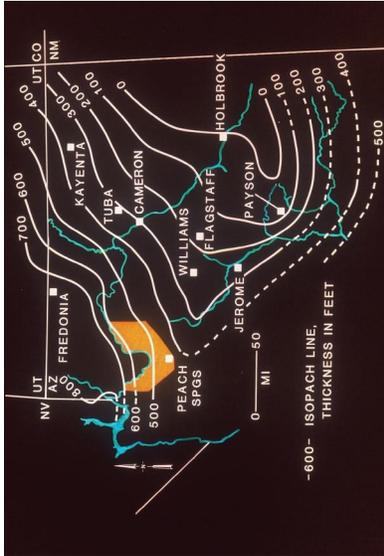


Figure 6. Redwall Limestone Isopach Map (McKee and Gutschick, 1969)



Figure 9. Surprise Canyon Channel in a Thunder Springs Cave



Figure 4. Core from Hack 2 breccia pipe. Sandstone, limestone, & shale clasts in a polymetallic uraninite matrix.



Figure 7. Redwall Limestone cave stalactites reflect the extensive karst development of this limestone

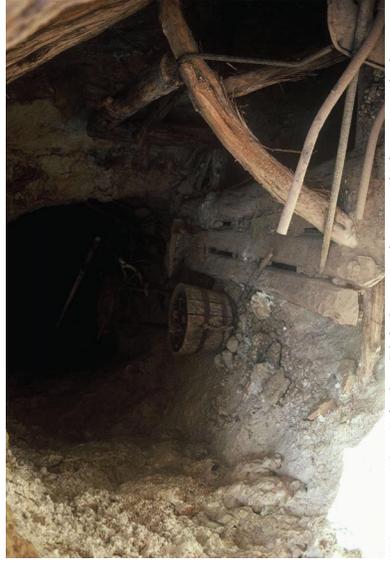


Figure 10. Little Chicken Mine, Mining Activity in the Grand Canyon began in the 1800's, but at that time all mining was for Cu, Ag, Pb, Zn.



Figure 5. Rock Core from MacArthur River U Mine. Note similar clast morphology & matrix to Fig. 4.



Figure 8. View through Redwall Limestone cave to Redwall on North Rim of the Grand Canyon



Figure 11. Arizona 1 Mine



Figure 12. The Ridenour mine, located on the Hualapai Reservation, has been mined intermittently for copper since the 1870's. All that remains of this pipe at the level of the Esplanade Sandstone is one-third of the ring-fracture zone. Samples with uranium concentrations of 3,000 ppm and vanadium concentrations of 4% are present on the outcrop surface where the bleached Esplanade Sandstone has been dissected by the canyon.



Figure 13. Pipes are often preferentially eroded around the ring fracture, and occasionally the core of the pipe is represented as a central hill. At pipe #267, located on the Hualapai Indian Reservation, the core of the hill is composed of a limonite-stained, silicified breccia, which rendered it more resistant to erosion than the surrounding country rock or ring fracture.



Figure 14. Many pipes are expressed at the surface as a concentric series of gently dipping beds that form a closed, or nearly closed basin. Here in the EZ-1 ore-bearing pipe, beds of the Triassic Moenkopi Formation form a rim around the basin. An old copper prospect pit lies along the rim in the far side of the photograph.



Figure 17. Oxidized/reduced breccia with uraninite and hematite. FOV=4in. Pinenut Mine



Figure 16. Bleached Hermit Shale around Pipe 243. The Oxidation/Reduction that controls Uranium behavior can be seen in this breccia pipe.

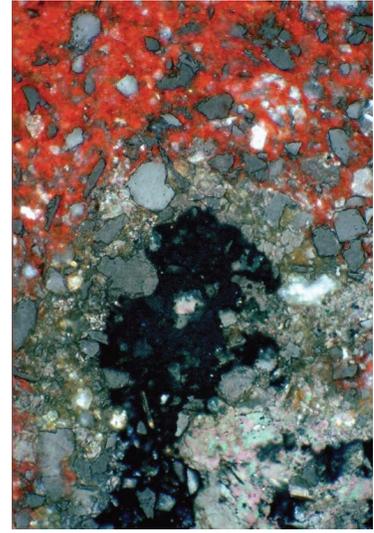


Figure 18. Transmitted light photomicrograph of Hematite + Uraninite, Pigeon Mine

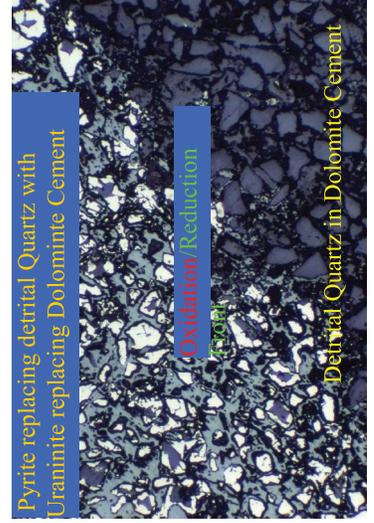


Figure 19. Reflected light photomicrograph with an oxidation/reduction front. Pigeon Mine

Figure 15. Pipes exposed from the canyon wall upward to the overlying plateau are rare. Here at pipe #226 (location shown in Wenrich and others, 1996), the pipe exposure in the canyon wall is overlain by a shallow structural basin with concentrically inward-dipping beds.

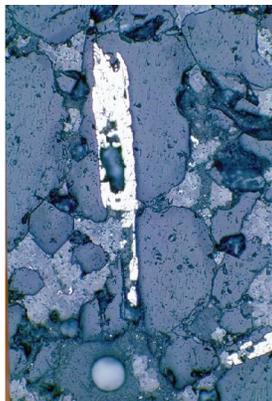


Figure 20. Pyrite after barite, Orphan Mine, Field of View = 0.25 mm

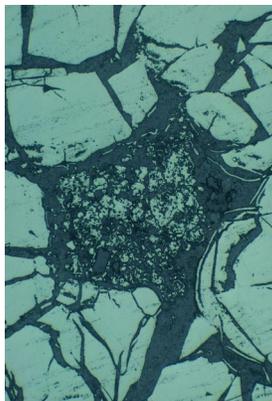


Figure 24. Uraninite-2 Stages: early stage later fractured and later wispy stage. Hack 2 Mine, FOV = 1.34mm



Figure 28. Cyanotrichillite – $\text{Cu}_4\text{Al}_2(\text{SO}_4)_4(\text{OH})_{12}\cdot 2\text{H}_2\text{O}$ from the Grandview mine. Specimen photographed from the collection of the Denver Museum of Natural History

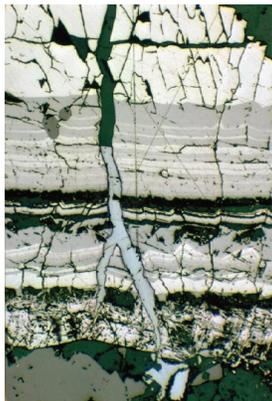


Figure 21. Alternating bands of siegenite, pyrite, & bravoite cut by a later vein of galena. Pigeon Mine. Field of View = 0.9mm

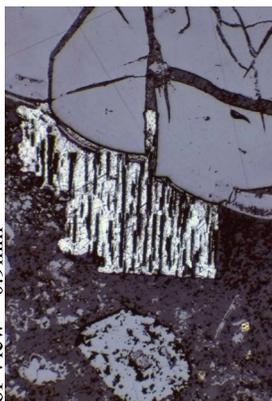


Figure 25. Later galena filling crack in uraninite, sphalerite to left of galena, Hack 2 Mine, Field of view = 1.0mm



Figure 29. Vanadinite – $\text{Pb}_5(\text{VO})_4\text{Cl}$

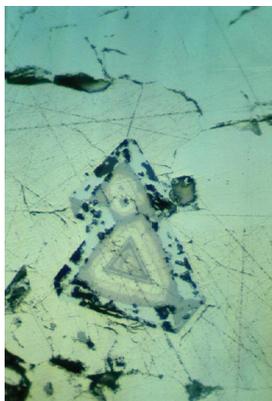


Figure 22. Zoned pyrite-siegenite-bravoite surrounded by galena. Hack 2 Mine, Field of view = 0.11 mm

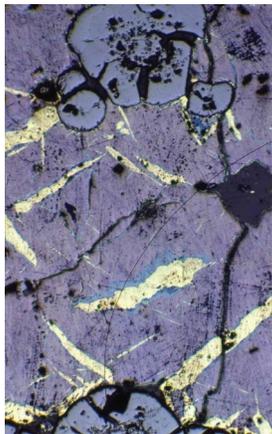


Figure 26. Uraninite with bornite, digenite, covellite, and chalcopyrite. Orphan Mine.



Figure 30. Goethite concretions that replaced early pyrite.

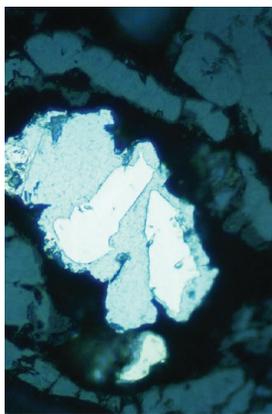


Figure 23. Gersdorffite in galena surrounded by uraninite, Hack 2 Mine, Field of view = 0.09mm

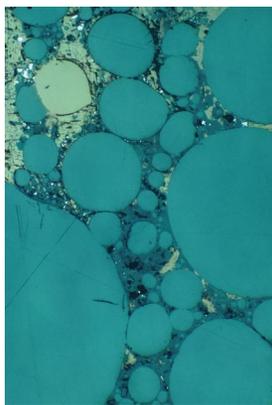


Figure 27. Bitumen Balls, Pigeon Mine, Field of view = 1.29mm



Figure 31. Bitumen formed after most stages of mineralization and fracturing. Note the fractured pyrite, but unfractured bitumen. The bitumen is only known to occur in significant concentrations in 2 of the mineralized breccia pipes

diameter that extend vertically through as much as 3000 ft of strata. Pipes are often preferentially eroded around the ring fracture, and occasionally the core of the pipe is represented as a central hill (Figs. 13 and 16). Other pipes, depending on the stratigraphic level of exposure, are expressed at the surface as a concentric series of gently dipping beds that form a closed, or nearly closed basin (Figs. 14 and 15). Because of the porous nature of these breccia pipes, large volumes of mineralizing fluids were able to pass through many pipes and deposit a large suite of metallic minerals (Figs. 20-31).

These uranium-rich breccia pipes have a Mississippi-Valley Type (MVT) mineral assemblage with a uranium overprint. The breccia-pipe MVT mineral assemblage is similar to that found in the Viburnum Trend, rich in the elements Ag, Co, Cu, Mo, Ni, Pb, V, and Zn (Table 2) and a pyrobitumen that was altered by sulfur-rich mineralizing fluids. According to Leach et al. (2005) "The Viburnum Trend has one of the most complex mineralogies, consisting of a variety of Cu, Co, Ni, Fe, Ag, [Pb, Zn,] and Sb sulfides and sulfosalts (e.g., Heyl, 1983)... Studies of organic material from the Viburnum Trend district (e.g., Leventhal, 1990) show that organic matter in the ore was thermally and compositionally altered by the ore fluids...the Viburnum Trend contains breccia-hosted ores that occur in narrow breccia trends (less than several hundred meters wide...)." Although breccia pipes are not stratabound as are most MVTs, breccia-pipe base-metal mineralization exhibits all but one of the 14 most important characteristics of MVT deposits listed by Leach et al. (2005). The complex mineral assemblage within the breccia pipes appears to have developed during at least four separate mineralizing events, or pulses. The most extensive country rock alteration caused intense bleaching of the normally red sandstones, suggesting extensive reduction of Fe^{3+} to Fe^{2+} .

The following excerpts from Wenrich and Sutphin (1989), who provide more details on the mineralogy, outlines the four stages of mineralization:

(1) "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 early stage. The sulfates, barite and anhydrite, were deposited contemporaneously with, and/or following, the carbonates." (Wenrich and Sutphin, 1989)

(2) "The second major episode of pipe mineralization is characterized by minerals rich in Ni, Co, As, Fe, and S (Figs. 20-23). 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." Although concentric zoning within a single crystal commonly includes up to ten alternating or repeating minerals, the overall outward zoning is usually Ni-Co rich, Ni-Fe rich, and Fe rich; the characteristic minerals are siegenite, bravoite, and 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." (Wenrich and Sutphin, 1989). The zoned crystal shown in Figure 22 is identical to some that were observed by Pignolet and Hagni (1983) from samples collected at the Buick mine, a Mississippi Valley type deposit. A black, glassy pyrobitumen, abundant in some pipes but absent in most, similarly encloses fractured pyrite (Fig. 31). The pyrobitumen has been extensively altered, probably by sulfur stabilization of the mineralizing fluids (Lisa Pratt, written commun., 1985).

(3) "The third major pulse or episode of pipe mineralization is characterized by formation of Cu-Fe-Zn-Pb sulfides (Fig. 23). 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 both cases it typically surrounds the earlier formed pyrite, as do enargite, lautite, and

Table 2. Chemical analyses (in ppm) of breccia-pipe uranium-ore-bearing whole-rock samples* (data from Wenrich et al., 1989; Wenrich and Sutphin, 1989; Wenrich et al., 1990).

Mine	Sample #	Ag	Co	Cu	Mo	Ni	Pb	U	V	Zn
Pigeon	(455OC85)	13	510	8,200	88	2,300	540	7,130	99	330
Hack 2	(643W2C84)	12	120	5,800	50	740	3,200	36,300	63	8,700
Orphan	(991FC85)	58	15	89,000	26	36	130	3,140	11	72
Pigeon	(455NC85)	49	310	2,600	820	1,300	1700	9,500	130	5,600
Ridenour	(223AC82)	20	210	5,500	21	520	4,200	3,100	40,000	150

*Sample mineral assemblages: **455OC85**--Disaggregated sandstone pipe-fill with kaolinite, gypsum, blue anhydrite, barite, pyrite crystals with bravoite cores, marcasite inclusions in sphalerite, chalcopyrite, galena and uraninite; **643W2C84**--Calcareous sandstone with matrix containing calcite, barite, gypsum, uraninite, chalcopyrite, marcasite, galena, and sphalerite; **991FC85**--Sulfide-impregnated calcareous sandstone (310' mine level) with 53% matrix comprised of dolomite, calcite, kaolinite, pyrite, chalcopyrite, digenite, bornite, covellite, and chalcocite; **455NC85**--Severely altered sandstone containing fractured pyrobitumen, massive pyrite with bravoite and siegenite crystals, uraninite, galena, enargite, luzonite, sphalerite, and chalcopyrite; **223AC82**--Very fine grained oxidized quartz sandstone (Esplanade Sandstone) comprised of 11% matrix that is 10% roscoelite with abundant metatyuyamunite in micro-fractures and malachite-rimming quartz grains.

Zn-bearing tennantite. Fluorite occurs in minimal amounts within the growth rings of sphalerite. Galena and sphalerite tend to be coarsely crystalline and megascopic in size, and occur intergrown with each other with mutually interpenetrating grain boundaries. Both minerals occasionally contain oriented exsolution blebs of chalcopyrite.” (Wenrich and Sutphin, 1989). As in the Viburnum Trend MVT deposits, breccia pipe sphalerite contains high concentrations of Co, Ni, Cu, and Fe in its structure (Table 3).

(4) “The mineral assemblages found in these first three pulses of mineralization are similar to those in Viburnum Trend Mississippi Valley type deposits, except that for the most part the breccia pipe ore minerals tend to be finer grained. This fourth assemblage though, is unique to the breccia pipes; that is, there are no known uranium occurrences in MVT deposits. 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 crusts to thin ‘wisps’ and irregular matrix replacement (figs 24-26). Uraninite, especially the ‘wispy’ type occasionally contains wormy intergrowths of associated galena, some of which may have formed from radiogenic lead.” (Wenrich and Sutphin, 1989) The oxidation/reduction necessary for uranium precipitation can be seen in the series of photos (figs 17-19) showing a uraninite/hematite hand specimen, a transmitted-light photomicrograph, and a polished-section photomicrograph.

(5) “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 Ma of canyon dissection, an extensive suite of supergene alteration minerals developed; malachite, azurite, brochantite, cyanotrichite, chrysocolla, hemimorphite, smithsonite, goethite, zippeite, and metazeunite are only a few (figs 28-30). The pyrite cap over the orebody may have been instrumental in retarding the oxidation of the orebody; once the pyrite cap (and/or other base metal sulfides overlying the uranium mineralization) was stripped away by erosion, the orebody oxidized.” (Wenrich and Sutphin, 1989)

Some zoning of the mineral assemblages is present in the pipes. There commonly is a pyrite cap at the top of the ore-bearing rock. This pyrite cap, and the subjacent mineralized rock, contains most of the Ni-Co sulfides of stage 2. The uraninite generally lies beneath these sulfides, although the uraninite is intergrown with such sulfides as galena, sphaler-

ite, and various copper sulfides. This rough zoning, particularly the higher-level pyrite and Ni-Co sulfides, are necessarily significant considerations in any models of ore genesis.

Quaternary and Pliocene erosion and oxidation (stage 5 above) has removed the uranium, and oxidized the base-metal mineralization for pipes exposed within the depths of canyons dissecting the interior of the Colorado Plateau, and along the western margin of the Colorado Plateau where the Toroweap and Hurricane faults have stepped down the Paleozoic rocks in a sequence of normal faults, westward from the Kanab Plateau down to the Esplanade and Shivwits Plateaus. Mineralization on these plateaus is generally restricted to minerals described in Stage 5 above, particularly the copper minerals.

PROPOSED GENETIC MODELS OF THE URANIUM PIPES

Genetic and working models of pipe genesis require consideration of isotopic, chemical, mineralogical and regional-scale geological measurements. At the outset, it is worth noting that whereas the base metals of these ores have an analog for their hypotheses of origin in MVT mineralization, the genesis of the uranium mineralization needs fresh considerations.

The breccia pipe fluid-inclusion filling temperatures and salinities in sphalerite and dolomite are likewise similar to those measured for MVT deposits: Temperatures range from 80-173°C (Fig. 32) and salinities are commonly >19-wt % NaCl equivalent (Fig. 33). Fluid-inclusion temperatures in the upper Mississippi Valley deposits range from 90°-150°C and the MVT ores of central Tennessee range from 100°-125°C (Leach et al., 2005). Central Tennessee salinities are 21-24 wt % NaCl equivalent (Leach et al., 2005). Similar mineral assemblages and fluid-inclusion temperatures (120-140°C) and salinities occur in metallic sulfide deposits in Gulf Coast salt dome cap rocks (Price and Kyle, 1983). Sulfur-rich solid bitumen is present in the Arizona pipes and also present in the MVT deposits.

A large set of U-Pb isotopic analyses by Ludwig and Simmons (1992) show two mineralization events: 260 Ma and 200 Ma. These dates concur well with geologic events in the area. The 260 Ma date coincides with the close of the Harrisburg Member of the upper Permian Kaibab Limestone (Figs. 2a, 34). Some breccia pipes, such as the Sage pipe, contain thicker Harrisburg in the form of coarse sand to

Table 3. Comparison of electron microprobe analyses of sphalerite for the Buick mine, Viburnum Trend (Rogers & Davis, 1977), and the Hermit mine breccia pipe (Wenrich, K.J., unpublished data, 1995).

Sample	Zn (%)	Co (ppm)	Ni (ppm)	Fe (ppm)	Cu (ppm)
Hermit mine - 1227-A1-E01	61.61	330	2,390	8,900	850
Hermit mine - 1227-A1-C06	67.30	<50	<50	420	1,370
Buick mine - Yellow - Central	66.26	130	100	3,040	100
Buick mine - Upper E flank	60.60	1,440	1,500	13,600	6,700

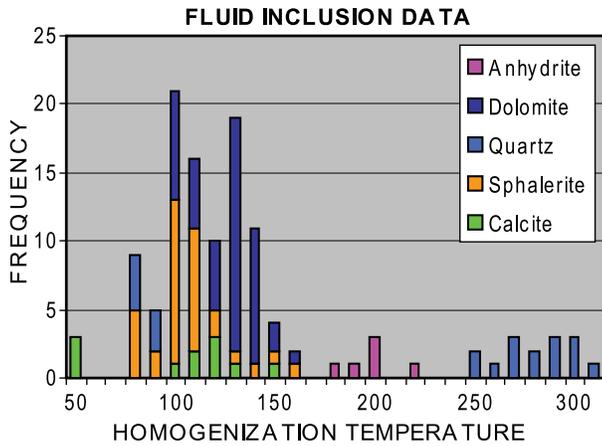


Figure 32. Homogenization temperatures for mineral phases associated with breccia-pipe ore. Each frequency represents a separate fluid inclusion. Temperatures below 80°C are from non-pipe calcite shown as a contrast. The high temperature quartz is believed to be from a late stage of silicification. Minerals related to ore forming processes precipitated from fluids with temperature between 80° and 173°C.

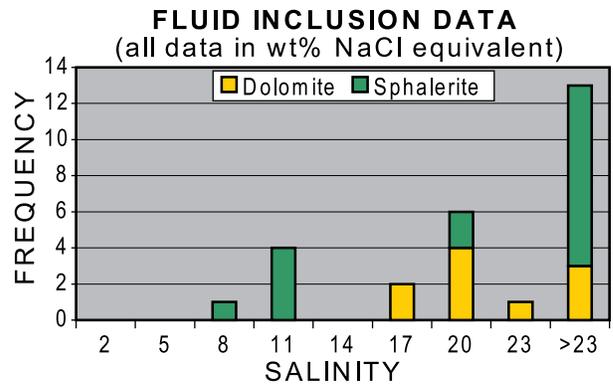


Figure 33. Salinities for dolomite, sphalerite, and calcite fluid inclusions. Primary inclusions in dolomite and secondary (with a few primary) inclusions in sphalerite and calcite are considered to be the most significant and reliable for ore- genesis temperatures.

conglomerate in contrast to the area surrounding the pipe. This suggests activation of the underlying karst system, and increased fluid flow, at the close of the Harrisburg. The 200 Ma date falls approximately during deposition of the Shinarump Conglomerate Member of the Chinle Formation – again during continental sedimentation. At this beginning and end of crustal stasis it is possible that the Redwall Limestone lay within the vadose zone with water table fluctuations that would have reactivated the Mississippian karst, where the solution-collapse breccia pipes are rooted. In the time between 260 and 200 Ma the Grand Canyon area was in a marine/tidal flat environment, as evidenced by the fine sandstones and mudstones of the Triassic Moenkopi Formation, allowing the Mississippian limestone to lie deeper into the phreatic zone where karst development is not as rapid.

The dates of 260 and 200 Ma span the range of times from the beginning to the end of stability in Pangea (Fig. 36), a time that allowed many MVT deposits to form throughout the world (Figs. 37, 38). If intrinsic heat from the earth found no outlet by magmatism or tectonic extension during the time of continental stasis (Pangea) it may have driven the basinal brine waters from strata (Redwall Limestone) deep in the basin up dip to the platform strata of northwestern Arizona (basin dewatering). The uranium mineralization of the pipes occurred during the time span of the Wilson Cycle stasis stage, and is not younger, nor older than other documented mid-Phanerozoic MVT base-metal ores of stable continents. The association of the pipes within carbonate strata and the geological implications of karst development are characteristics proposed for these ores of other regions, for example, Pine Point. We consider our proposition here, and the association of these ores with basin margins, as proposed for the mid-continent ores, as strong if not compelling evidence for our hypothesis and the MVT analog.

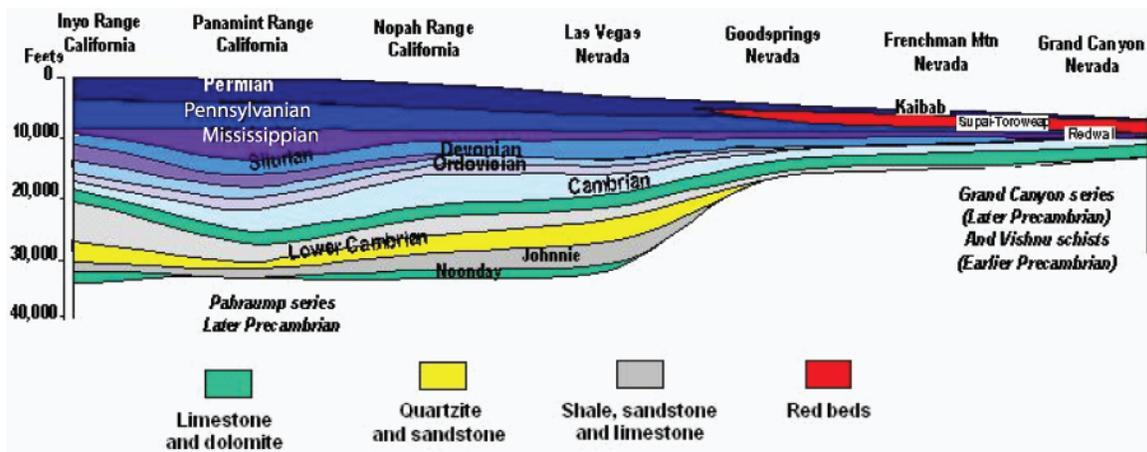
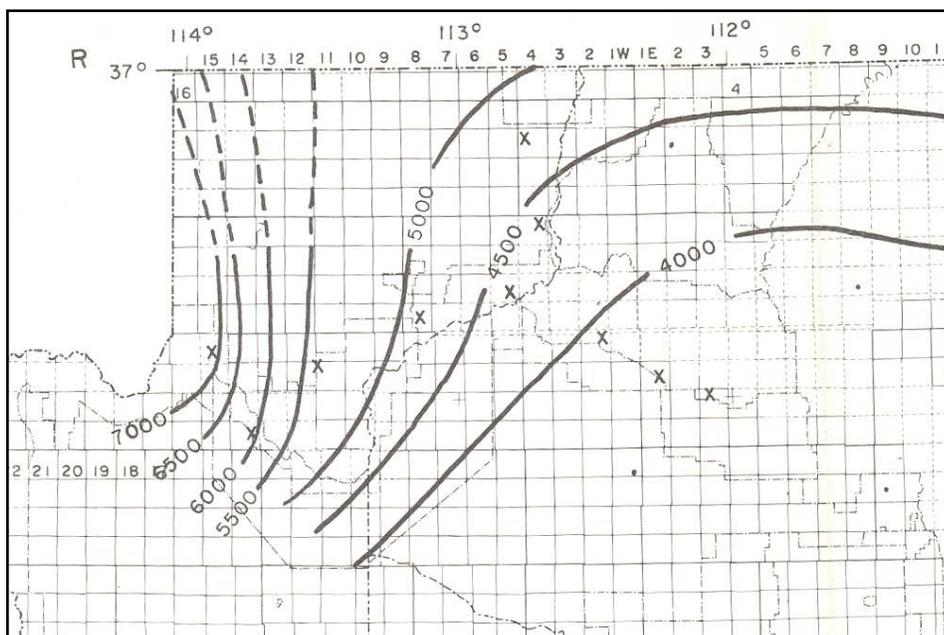


Figure 34. Cross section of Paleozoic miogeosyncline from the Grand Canyon to the Inyo Mountains, California. From P.B. King (1959; Fig. 77, p. 135).

Figure 35 (right). Isopach map, in feet, of all Paleozoic strata in northwestern Arizona. Westward thickening toward the miogeocline is apparent, as is the Paleozoic shelf environment of the breccia pipe regions (from McKee, 1951).



Tectonic loading of the western margin of the miogeocline by overthrusting during the Permian-Triassic Sonoma orogeny could also have caused miogeocline sediment dewatering and expulsion of basin brines eastward through the areas of the Goodsprings and Pioche districts and into the Grand Canyon area. We propose as a hypothesis that the Cordilleran miogeocline (Beus, 1989, Fig. 4) is a significant geological component of the origin of the pipe complex and that basin dewatering (Anderson and MacQueen 1982; Cathles and Smith, 1983) was a principal source of reactive waters and metals. There are significant occurrences of lead-zinc (silver) ores in adjacent western Nevada (Goodsprings District) and Pioche where James and Knight (1979) proposed an MVT origin for ores in the deeper strata. By Pangea time a megabasin, the Cordilleran miogeocline, had formed across eastern Nevada and western Utah, just west of the region of today's Grand Canyon (Figs. 34, 35) as depicted by King (1959). At the same time to the east, northeast, and southeast of the Grand Canyon region the Emery positive area, Kaibab Arch, Defiance Zuni positive area, and the Sedona Arch had formed (Blakey and Knepp, 1989, Fig. 4). These uplifts would have created large hydraulic heads in the Grand Canyon region aquifers (Figs. 39-41). The uranium pipes occur within the platform strata adjacent to the Paleozoic miogeocline. Once the pipes catastrophically formed at the close of Kaibab deposition, as discussed above, due to the fluctuating water table, they had the potential for trapping and mixing of basin dewatered fluids. Not only could they trap upwelling waters and metals of deeper derivation from the reduced strata of the miogeoclinal shelf, but essentially provided conduits for "artesian" movement (created by the regional uplifts around the basin) of these brine waters upward cutting through sandstone aquifers where they would have readily mixed with oxidizing waters from redbed sandstones (Fig. 41). The hydraulic

head dictated the extent of upward fluid movement in the pipe and the stratigraphic location of the ore mineralization. The North Rim pipes would have been slightly deeper toward the basin than the South Rim pipes (Figs. 6, 34) and the ore bodies would be expected to be slightly higher stratigraphically. This appears to be the case with the ore in the Orphan mine extending downward to the Wescogame Formation, which has not been observed in the North Rim pipes. This catastrophic collapse occurred again at the close of Pangea in the Triassic once again permitting mixing of fluids.

Upward stopping connected various aquifers and may have resulted in significant subterranean fluid flow. The mixing of fluids may well have brought uranium and copper out of redbed sandstones of the Colorado Plateaus, such as the Supai Group, into the pipe environment where they mixed with the organic-rich, basal brines that had moved upward into the pipes during basin dewatering, creating the reducing environment necessary for precipitation of uranium (Fig. 41). Redbed sandstones of the Supai Group are known to have contained enough uranium to form small stratiform uranium occurrences associated with coalified plant fossils elsewhere on the Plateau, such as at Promontory Butte (Wenrich and others, 1989). Even if the Supai sandstones only contained an average crustal abundance of uranium, oxidizing waters trapped in this group during the 50-75 million years between its deposition and the probable pipe formation at the close of the Permian would have permitted substantial leaching of uranium into the oxidizing waters. Calculations can be made to show that even assuming minimal leaching into the Supai waters to a concentration of 10 mg/l (ppm), and with significant fluid flow as might be expected in such a basin environment, that a 5 million pound deposit of uranium can be created in about 600,000 years (see Table 4 for calculation parameters) by flushing the large volumes of uranium-bearing

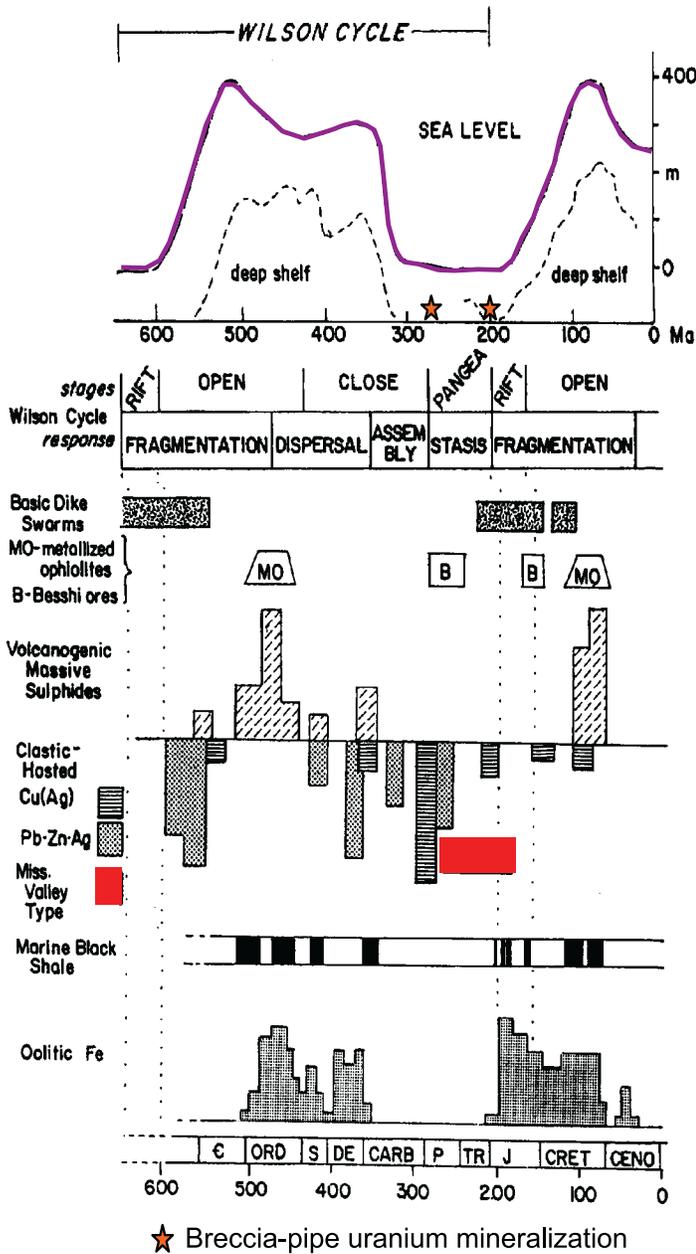


Figure 36. Wilson cycle stratabound ore relationships. MVT ore in red and breccia-pipe uranium mineralization shown with red stars. Modified from Tittley (1993).



Figure 37. Pangea ca. 290 Ma.

waters through a massive reductant, such as the MVT deposits that were formed prior to the uranium mineralization.

The geology of the breccia-pipe uranium deposits have much in common with the ultra high-grade (20% U_3O_8) deposits in the Athabasca Basin: (1) breccia (Fig. 5), (2) desilicification, (3) MVT metals, (4) bitumen, (5) high salinities of the mineralizing fluids, (6) structures that connect aquifer layers, (7) a dynamic fluid-flow system circulating through the aquifers, probably for a sustained period of time, and (8) a period of cratonic stability that continued after ore deposition until the present, preventing later dissection and oxidation of the ground waters

EXPLORATION PARAMETERS

The model of basin dewatering and occurrence of MVT ores along margins of cratonic basins of the mid-continent (Anderson and MacQueen, 1982; Cathles and Smith, 1983) allow proposals that the miogeocline - platform break

Table 4. Parameters used in calculation of ore-deposit formation

Concentration of uranium in Supai aquifer	10 mg/l (ppm)
Flow rate of water through the aquifer*	50 ft/year
Average diameter of a breccia pipe	300 ft
Average thickness of Supai Group in region (McKee, 1982)	1100 ft
Average size of a breccia pipe uranium deposit	5 million lbs U_3O_8

*Fifty feet per year in the Carrizo Sandstone in Texas is listed as typical of many aquifers (Gilluly et al., 1959). Ten meters per year were assumed in MVT calculations (D.L. Leach, verbal commun., 2008).

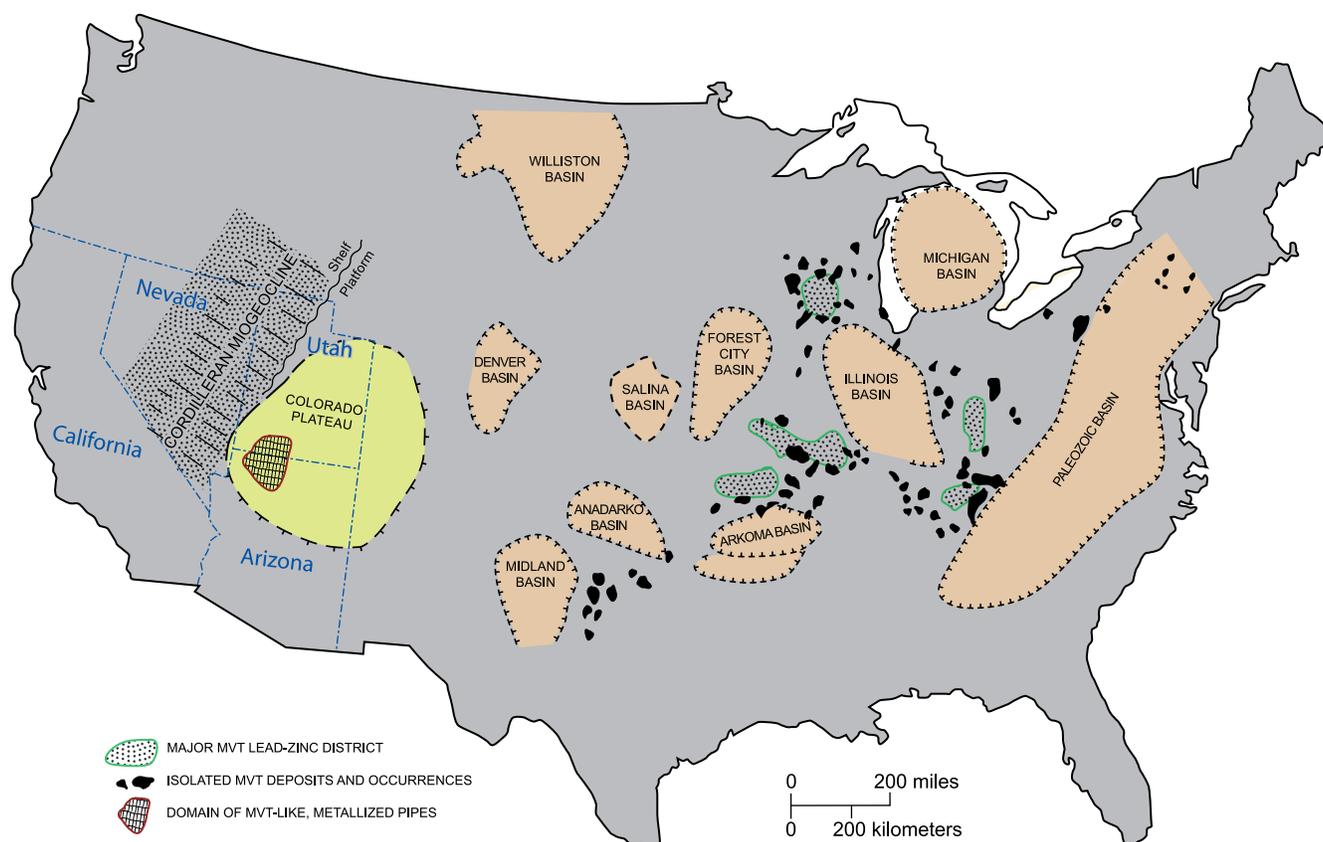


Figure 38. Mid-continent MVT districts and basins, modified from Cathles and Smith (1983).

in Arizona, Utah, and Nevada is a locus of potential MVT ore deposits with a uranium overprint. That suggests areas into Utah that extend from the breccia pipe province along a northeast trend parallel to the platform break, such as the San Rafael Swell, might represent a continuation of the breccia pipe MVT and uranium deposits. Within the northwestern Arizona terrane of pipe occurrence, outcrops of strata above the Redwall Limestone are dominated by Pennsylvanian and Permian rocks, mostly sandstones with carbonate cement. To the northwest the entire package of Paleozoic strata thickens (Fig. 35). However, the Pennsylvanian and Permian rocks of the Supai Group undergo significant facies change westward from sandstone to limestone in most of the Group, and although the upper Esplanade remains a sandstone, it appears to be progressively finer westward (Blakey and Knepp, 1989), which would affect the aquifer porosity. If our hypothesis of ore formation is correct, the potential for MVT deposits within breccia pipes should increase further into the basin where the hydraulic head was even larger and the thickness of the Mississippian limestones is greater. That would suggest that northwest into Nevada would be excellent terrane for future MVT deposit exploration. However, the westward facies change of the Supai Group to limestone and finer non-redbed sandstone would have a profound affect on the uranium content of the aquifer and the volume of fluid flow. That coupled with the tectonic instability of the areas off of the

Colorado Plateau during the past 200 Ma makes the occurrence and preservation of uranium deposits to the northwest of the Plateau tenuous.

The recent success in the past year of airborne VTEM on the Colorado Plateau at locating buried breccia pipes might open new frontiers for exploration into breccia pipes off of the Colorado Plateau to the northwest. The Apex mine (a Tsumeb mine analogue of oxidized base metals + Ge and Ga), located in the Beaver Dam Mountains of Utah in the southern Basin and Range near the Colorado Plateau's western edge, is a known breccia pipe, proving that the province does not end at the boundary of the Colorado Plateau (Wenrich and Sutphin, 1989). The only significant differences in the element concentrations between the Apex Mine and Colorado Plateau breccia pipes is that the Apex base metal minerals have been oxidized, the uranium has been depleted, and Fe, Ga, and Ge have been enriched.

With the placement of these pipes into the tectonic cycle of worldwide MVT deposits, and the elevated prices of most metals, a fresh exploration approach in the 21st century to the mining of these breccia pipes should include some of the MVT metals as a byproduct to uranium (only vanadium was previously recovered as a byproduct during the late 20th century). This is particularly true if exploration following our suggestion of increased probability for MVT deposits along margins of cratonic basins comes to fruition.

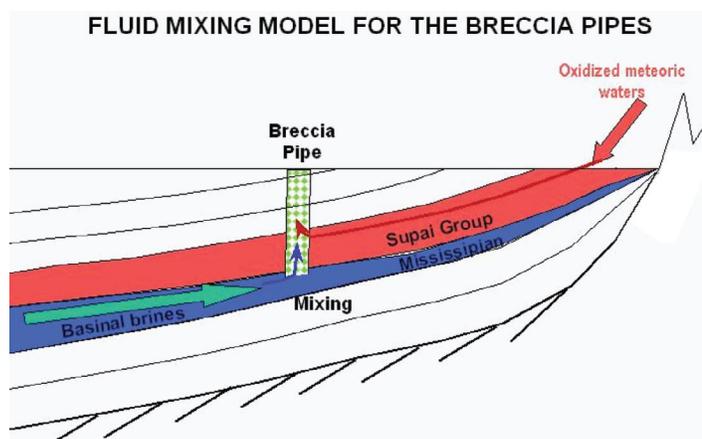


Figure 41. Fluid-mixing model for the breccia pipe ore genesis.

REFERENCES CITED

- Anderson, G.M., and MacQueen, R.U., 1982, Ore deposit models - 6, Mississippi Valley type lead-zinc deposits: *Geoscience Canada*, v. 9, p. 108-117.
- Blakey, R.C., and Knepp, R., 1989, Pennsylvanian and Permian geology of Arizona, in Jenney, J.P., and Reynolds, S.J., eds., *Geologic evolution of Arizona: Arizona Geological Society Digest 17*, p. 313-347.
- Bues, S.S., 1989, Devonian and Mississippian geology of Arizona, in Jenney, J.P., and Reynolds, S.J., eds., *Geologic evolution of Arizona: Arizona Geological Society Digest 17*, p. 287-311.
- Bowles, C.G., 1965, Uranium-bearing breccia pipes formed by solution and collapse of limestone, in *Geological Survey Research, 1965: U.S. Geological Survey Professional Paper 525-A*, p. A12.
- Cathles, L.M., and Smith, A.T., 1983, Thermal constraints on the formation of Mississippi Valley-type lead-zinc deposits and their implications for episodic basin dewatering and deposits genesis: *Economic Geology*, v. 78, p. 983-1002.
- 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.
- Heyl, A.V., 1983, Geologic characteristics of three Mississippi Valley-type districts, in Kisvarsanyi, G., et al., eds., *Proceedings of International Conference on Mississippi Valley-type lead-zinc deposits: Rolla, Missouri, University of Missouri Press*, p. 27-30.
- James, L.P., and Knight, L.H., 1979, Stratabound lead-zinc-silver ores of the Pioche district, Nevada - Unusual "Mississippi Valley" deposits, in Newman, G.W., and Goode, H.D., eds., *Basin and Range symposium and great basin field conference: Rocky Mountain Association of Geologists and Utah Geological Association Basin and Range Symposium, 1979, Proceedings*, p. 389-395.
- King, P.B., 1959, *The Evolution of North America: Princeton, New Jersey, Princeton University Press*, 189 p.
- Krewedl, D.A., and Carisey, J.C., 1986, Contributions to the geology of uranium mineralized breccia pipes in northern Arizona, in Beatty, B., and Wilkinson, P.A.K., eds., *Frontiers in geology and ore deposits of Arizona and the Southwest: Arizona Geological Society Digest*, v. 16, p. 179-186.
- Leach, D.L., Sangster, D.F., Kelly, K.D. Large, R.R., Garven, G., Allen, C.R., Gutmer, J., and Walters, S., 2005, Sediment-hosted lead-zinc deposits: A global perspective, in Hedenquist, J.W., Thompson, J.F.H., Goldfarb, R.J., and Richards, J.P., eds.: *Economic Geology and the Bulletin of the Society of Economic Geologists*, One Hundredth Anniversary Volume, p. 561-608.
- Leventhal, J.S., 1990, Organic matter and thermochemical sulfate reduction in the Viburnum Trend, Southeast Missouri: *Economic Geology*, v. 85, p. 622-632.
- Ludwig, K.R., and Simmons, K.R., 1992, U-Pb dating of uranium deposits in collapse breccia pipes of the Grand Canyon region: *Economic Geology*, v. 87, p. 1747-1765.
- Mathisen, I.W., Jr., 1987, Arizona Strip breccia pipe program: Exploration, development, and production [abs.]: *American Association of Petroleum Geologists Bulletin*, v. 71/5, p. 590.
- McKee, E.D., 1951, Sedimentary basins of Arizona and adjoining areas: *Geological Society of America Bulletin*, v. 62, p. 481-506.
- McKee, E.D. and Gutschick, R.C., 1969, History of the Redwall Limestone of northern Arizona: *Geological Society of America Memoir 114*, 762 p.
- Pignolet, S. and Hagni, R.D., 1984, Cobalt-nickel mineralization associated with lead-zinc-copper mineralization in the Mississippi Valley-Type deposits at Fredericktown, Missouri, in Kisvarsanyi, G., et al., eds., *Proceedings of International Conference on Mississippi Valley-type lead-zinc deposits: Rolla, Missouri, University of Missouri Press*, p. 187-194.
- Price, P.E., and Kyle, J.R., 1983, Metallic sulfide deposits in Gulf Coast salt dome cap rocks: *Transactions, Gulf Coast Association of Geological Societies*, v. 33, p. 189-193.
- Titley, S.R., 1993, Relationship of stratabound ores with tectonic cycles of the Phanerozoic and Proterozoic., in Nagy, B., Leventhal, J.S., and Grauch, R.I., eds., *Metalliferous black shales and related ore deposits: Precambrian Research*, v. 61, p. 295-322.
- Ux Consulting Co., 2008, U₃O₈ prices: Rosewell, Georgia, accessed 2008 at <http://www.uxc.com>.
- Wenrich, K.J. and Sutphin, H.B., 1989, Lithotectonic setting necessary for formation of a uranium-rich solution collapse breccia pipe province, Grand Canyon region, Arizona, in *Metallogenesis of uranium deposits: International Atomic Energy Agency Technical Committee Meeting, Vienna, Austria, March 9-12, 1987, Proceedings*, p. 307-344.
- Wenrich, K.J. and Sutphin, H.B., 1994, Grand Canyon caves, breccia pipes and mineral deposits: *Geology Today*, v. 10, n. 3, p. 97-104.
- Wenrich, K.J., Billingsley, G.H., and Van Gosen, B.S., 1989, The potential of breccia pipes in the Mohawk Canyon Area, Hualapai Indian Reservation, Arizona: *U.S. Geological Survey Bulletin 1683-D*, 39 p.
- Wenrich, K.J., Chenoweth, W.L., Finch, W.I., and Scarborough, R.B., 1989, Uranium in Arizona, in Jenney, J.P., and Reynolds, S.J., eds., *Geologic evolution of Arizona: Arizona Geological Society Digest 17*, p. 759-794.
- Wenrich, K.J., Verbeek, E.R., Sutphin, H.B., Modreski, P.J., Van Gosen, B.S., and Detra, D.E., 1990, Geology, geochemistry, and mineralogy of the Ridenour mine breccia pipe, Arizona: *U.S. Geological Survey Open-File Report 90-0504*, 66 p.
- Wenrich, K.J., Billingsley, G.H., and Huntoon, P.W., 1996, Breccia pipe and geologic map of the northwestern part of the Hualapai Indian Reservation and vicinity, Arizona: *U.S. Geological Survey Miscellaneous Investigations Series Map I-2552*, 16 p., 2 plates (includes fifteen 7.5' quadrangles), scale 1:48,000.

