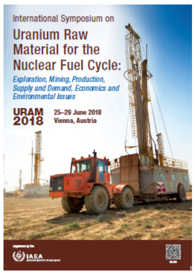

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RARE EARTH ELEMENTS IN URANINITE: BRECCIA PIPE URANIUM DISTRICT, NORTHERN ARIZONA, USA

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INRODUCTION

Interest in rare earth minerals (REE) originated in 1883 with the development of incandescent gas mantles containing rare earth and zirconium oxides. The knowledge that the supply of REE will not be able to keep up with new and ever-growing demands has been no secret in the geological community for years. However, it was not until it was presented to congress as a "potential shortage that could impact US renewable energy sources, communications and defense industries"that politicians and the public tumbled to how critical these metals are and just how vulnerable the US currently is to supply disruption. In 2008, China produced 97% of the worlds REE (primarily from Bayan Obo), India 2.2%, Brazil 0.5%, and Malaysia 0.3%. Up until 2002, the Mountain Pass REE Mine in California produced about 5% of the world's REE supply. China's lock on the world's supply will be difficult to break. Starting in 2005, China put export taxes on REE of 15-20% and put on export restrictions. Forecasts predicted a critical shortage for the rest of the world outside of China by as early as 2012. So, REE prices went up. Just as the Mountain Pass Mine was getting ready to go into production in 2012, China eased their export restrictions and the price of most of the REE plummeted downward. Three years later in 2015, Mountain Pass mine went into bankruptcy.

REE were extracted as a by-product of uranium mining in Canada during 1966-1970 and 1973-1977 at the Blind River and Elliott Lake deposits. The ore mineral uraninite contained sufficient REE to make extraction of REE profitable from the raffinate fluids. From 1966 to 1970, uranium mines in the Elliot Lake district were the world's major source of yttrium concentrate. All rare earths except promethium have been detected in these ores. The Elliot Lake ores also contain about 0.11% uranium oxide (U3O8), and 0.028% rare-earth oxides [1]. The economic appeal of this occurrence is that the REE are concentrated in the uraninite, which was already being concentrated from the ore, so the REE are a bonus. "For a short period of time, HREE were extracted from the raffinate fluids that emanated from the chemical processing of uraninite at Blind River, Ontario."[2]. Since REE are significantly concentrated within the uraninite from breccia pipes in northern Arizona, they likewise could be extracted from northern Arizona uraninite.

POLYMETALLIC NORTHERN ARIZONA BRECCIA PIPE DISTRICT

A unique polymetallic-rich uranium, solution-collapse breccia-pipe district lies beneath the plateaus and in the canyons of northwestern Arizona. It is known for its large reserves of high-grade uranium (average grade of 0.65% U3O8 [3]) that were estimated by the US Geological Survey to comprise over 40% of the US's domestic uranium resources [4]. The breccia-pipe uraninite contains REE enrichment similar to that of the Canadian Athabasca Basin's uranium deposits.

From late1980's until about 2004, the price of most metals had been sufficiently depressed such that little was done to explore or study these polymetallic ores, particularly the REE, that are rich in the district's uranium deposits. Since 2008, the price of most REE has increased over 10-fold. This is true of all energy critical elements, including Co and Cu, also heavily enriched in the breccia pipe ore. These important elements commonly comprise over 1% of the breccia pipe ore.

The northern Arizona metallic district can be thought of as a paleo-karst terrain pock-marked with sink holes, where in this case most "holes"represent a collapse feature that has bottomed out over 3000 ft below the surface in the underlying Mississippian Redwall Limestone. These breccia pipes are vertical pipes of breccia formed when the Paleozoic layers of sandstone, shale, and limestone collapsed downward into underlying caverns. A typical pipe is only approximately 300 ft (91 m) in diameter and extends upward as high in the section as the Triassic Chinle Formation. Although each breccia pipe in itself is not a huge ore deposit –up to 10 million pounds (lbs) (4500 tU) of uranium per pipe –in total the resources in the district are enormous. Many of the various small, mineralized pipes are clustered together providing somewhat contiguous mineralization, which reduces the mining costs. The water table is deep below the orebodies, which lie 500-1600 ft below the surface, sufficiently above the water table to minimize potential contamination of the aquifer.

Mining activity in the Grand Canyon breccia pipes began during the nineteenth century, 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. 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 was proposed for genesis of these ores as members of the class of Mississippi Valley Type (MVT) deposits, but with late-stage uranium mineralization [3]. U-Pb ages on uraninite of 200 and 260 Ma [5] link the mineralization with Pangean time, events, and mid-continent MVT ores; chemistry and fluid-inclusion temperatures on sphalerite and dolomite of 80°-173° also link them with MVT deposits [3]. Mixing of oxidizing groundwaters from overlying sandstones with reducing brines that had entered the pipes due to dewatering of the Mississippian limestone 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 [3].

RARE-EARTH ELEMENTS IN BRECCIA PIPE URANINITE

REE are significantly enriched in much of the breccia pipe ore. Whole-rock analyses of uranium ore-bearing rock from across the district show REE enrichment that is not uncommonly 20 times average crustal abundance. A study of REE within uraninite was undertaken at the facilities of CREGU-GeoRessources, Nancy, France, using Laser Ablation ICP-MS in conjunction with electron microprobe analyses of the uraninite [6]. This research has confirmed that a significant percentage of the bulk rock REE content is tied up in the uraninite crystal structure. Although the breccia-pipe bulk-rock REE content is not as enriched as in the carbonatites at Mountain Pass, California (CA), the breccia-pipe uraninite contains concentrations of Nd, for example, that are between 15-20% of the Nd concentrations in the bastnaesite of Mountain Pass. Considering that at Mountain Pass the bastnaesite (REE ore mineral) has to be mined strictly for REE, the uraninite in the breccia pipes is already processed for the uranium. Hence, the Nd and other REE collected from the raffinate fluids are an added value to the profit. Additionally, the more valuable heavy REE (HREE) are enriched in the uraninite, whereas the Mountain Pass, CA and Bayan Obo, China ore deposits contain essentially little significant HREE.

REE PRIMARY & REMOBILIZED ORE-DEPOSIT SIGNATURES

Distinctive REE signature in uranium oxides is directly related to the variability of the mineralizing processes and geological setting between uranium deposit types [9]. All the uranium oxides from unconformity related deposits, such as from the Eastern Alligator district in Australia and Athabasca Basin district in Canada, are characterized by a bell-shaped REE pattern centered on dysprosium. This type of pattern seems to be characteristic of uranium oxide primary ore deposited from high-salinity basinal brines. The Sage and Pinenut breccia pipes of northern Arizona have bell-shaped chondrite-normalized distributions that are remarkably similar to the Athabasca Basin's McArthur River (currently produces 25% of the world's uranium) and Shea Creek uraninites [8], with a normalized maximum centered on Sm-Eu-Gd. Interestingly, the Pinenut breccia pipe, with its bell-shaped REE pattern, has the oldest age, 260 Ma [5] of those that were part of this study, suggesting it is primary ore (no age determination was completed on the Sage orebody by Ludwig & Simmons).

The REE element patterns of uraninite samples from three of the breccia-pipe uranium mines (Pigeon, Kanab N, and Hack 2) have chondrite-normalized distributions that show some fractionation and a negative Eu anomaly. They distinctly resemble chondrite-normalized plots of uraninite samples [7] from the Athabasca Basin Eagle Point deposit, but with overall lower REE content. The rocks from both the three breccia pipe orebodies and Eagle Point show striking oxidation-reduction fronts within some of the ore. Such samples correspond to uranium oxides that are remobilized by oxidized meteoric fluids. These fluids mobilized the LREE preferentially over the HREE. Therefore, the uranium oxides from the redox front are characterized by LREE enrichment, which differs from the primary ores, and clearly demonstrate their distinct conditions of formation from the primary ore [9]. The HREE part of the chondrite-normalized distribution is preserved. The negative Eu anomaly of these samples could possibly be a result of oxidizing meteoric fluids albitizing the detrital feldspars in the clastic host rocks, permitting preferential incorporation of Eu over the other REE into the albite structure (similar to magmatic plagioclase creating a negative Eu anomaly).

The three more-fractionated uraninite orebodies (Pigeon, Kanab N, and Hack 2) have younger ages of 200 Ma [5] as contrasted with the Pinenut 260Ma ore with a bell-shaped REE pattern. All of the breccia-pipe orebodies are believed to have formed due to a mixing of high-salinity basinal brines (based on fluid inclusion results) and oxidizing groundwaters [3]. Hence, the primary ore, breccia pipe uraninite samples fit the same REE chondrite-normalized pattern as do uraninites from the primary uranium deposits of McArthur River and Shea Creek. Interestingly, the Pigeon, Kanab N, and Hack 2 mines all lie along a N45°E trend that is parallel to one of the two major fracture directions in northern Arizona. So, they may have been more open to oxidizing groundwaters than the Pinenut and Sage orebodies. More samples from each mine and from other uraninite deposits within the district will provide insight into the fluids containing the REE. However, the pipe in pipe structure in many breccia pipes proves secondary dissolution. It is quite possible that all of the breccia-pipe orebodies have an older primary ore preserved and a later secondary oxidation/reduction front ore. The primary ore would be a higher U and REE grade.

BRECCIA PIPE URANIUM & REE RESOURCE ESTIMATES

The northern Arizona breccia-pipe district contains the highest-grade uranium in the U.S., with the potential for reserves that greatly exceed any other province in the U.S. With an average grade of 0.65% U3O8, and an environment conducive to relatively low cost conventional mining, these deposits are still economic in the 45/*lbpricerange*[10].*Unfortunately*, *in*2011, *PresidentObamachosetoissueanexecutiveorderwithdrawingthemillionacreso*
resourcecalculationsontheselandsbyseparateresearchershaveshownremarkablysimilarresults :

1. A uranium-resource estimate (referred to as resource endowment [11]) based on industry drilling for the 1050 mi2 (2719 km2) "mineralized corridor"of the breccia-pipe district have been made by [11]. Spiering and Hillard defined a "mineralized corridor"within the Breccia Pipe uranium district where they believe most of the mineralized pipes lie. It provides a smaller focused area to work with where more data are available. However, these authors still believe that considerable mineralized rock abounds beyond this corridor on private and public lands (the NE quadrant of the Hualapai Reservation is an example). Spiering Hillard calculated the uranium resources [11] by (a) using VTEM Airborne Geophysics results and concluded that the mineralized corridor had 270 million lbs (122,500 tU) of U3O8 and (b) using known pipe density they concluded the corridor has 269 million lbs (122,000 tU) U3O8.

2. In 1987, the USGS [4] calculated the uranium endowment of the entire breccia pipe district. Spiering and Hillard [11] show that these calculations when applied to the "mineralized corridor" result in 375 million lbs (170,000 tU) of U3O8.

3. Using a control area of detailed surface mapping of solution-collapse features and mineralized rock [12] on the NE portion of the Hualapai Reservation, the current authors calculated that the "mineralized corridor"contains 260 million lbs (118,000 tU) of U3O8 (table 2) and the entire withdrawal area contains 385 million lbs (175,000 tU) U3O8.(table 2)

These 3 independent resource estimates average to 302 million lbs (137,000 tU) of U3O8. The estimate by Spiering and Hillard and that by Wenrich et al. using completely different types of data within different geographic parts of the district (industry drilling vs. detailed surface mapping) have come to remarkably similar resource endowment estimates—270 vs. 260 million lbs (122,000 vs. 122,500 tU) of U3O8.

Yetin 2011, the USGS, within the Final Environmental Impact Statement (EIS) for the breccia-pipe land withdrawal, arrived at a paltry 79 million lbs (36,000 tU) for their resource estimate. To arrive at this number, they did not use industry drilling [11], or previous USGS maps [12] or extensive resource calculations [4], but rather a non-peer reviewed elementary article written for the general public by Wenrich in 1988 where a simple statement was made that about 8

4. A 4th approach is also applicable, which results in an estimate closer to the IAEA reasonably assured resources (RAR) 4 rather than a resource endowment. Prior to 1989 over 110 breccia pipes were drilled; 71 of these were identified to have ore-grade mineralization [13]. At an average of 2.9 million lbs (1300 tU) of uranium/pipe, the RAR (IAEA) or "indicated reserves"(USGS definition) total 206 million lbs (93,400 tU) of resources in the part of the district covered by Sutphin and Wenrich' s map [13]. Of these 71 mineralized pipes, 9 became uranium mines, 27 are known to contain an orebody, and 46 were mineralized, but with insufficient drilling to identify an orebody. Because the district is known to have very little low grade mineralization, if a pipe is mineralized with ore-grade mineralization, the odds are great that it contains an orebody. Since 1989, there has been significant exploration for uranium in the northern Arizona breccia-pipe district and more pipes have been located that are known to be mineralized. Hence, this Reasonably Assured Resource number of 206 million lbs (93,400 tU) is probably not an unreasonable estimate based on the historic drilling in the district.

U.S. Energy Information Administration (EIA, U.S. Uranium Reserves Estimates, 2008) estimates

that at 50/lburanium, theUSreservesare539millionlbs(244, 000tU)ofU3O8.Theystatethatthedefinitionof"'reserv
pipedistrictcontains38%oftheUSuraniumreserves.

Using the minimum reserve calculation of 206 million lbs (93,400 tU) of U3O8 and the maximum endowment of 375 million lbs (170,000 tU), the "mineralized corridor"contains between 10 and 18 billion dollars at 50/lburaniumpriceand21and38billiondollarsat100/lb uranium price. REE analyses of breccia-pipe uraninite ore (this study) in France showed the total REE content of the uraninite to be around 0.43%. Hence, between 471,000 and 860,000 lbs (214 and 390 tU) of LREE and 405,000 and 737,000 lbs (184 and 334 tU) of HREE could be produced from the breccia-pipe district. The more valuable HREE have a greater presence in uraninite ores than in bastnaesite ores from the Bayan Obo and Mountain Pass Districts. The value added by REE to the uranium ore at 3.10/lbofU3O8wouldbebetween639milliondollarsand1.2billiondollar

CONCLUSIONS

Rare earth elements are significantly enriched in much of the breccia-pipe ores. A study of REE within uraninite has confirmed that a significant percentage of the whole rock REE content is tied up in the uraninite crystal structure.

All the uranium oxides from unconformity related primary ore deposits from the Eastern Alligator district in Australia and the Athabasca Basin district in Canada are characterized by a bell-shaped pattern centered on dysprosium. The Sage and Pinenut breccia pipes have bell-shaped chondrite-normalized plots that are remarkably similar to the Athabasca Basin's McArthur River and Shea Creek uraninites). The Pinenut breccia pipe, with its bell-shaped REE pattern, has the oldest age, 260 Ma [5] in the district, suggesting it is primary ore. The REE patterns of uraninite from Pigeon, Kanab N, and Hack 2 breccia pipes (age of 200 Ma) have chondrite-normalized distributions that show some fractionation and a negative Eu anomaly, similar to the Athabasca Basin's Eagle Point uranium deposit. The rocks from both these 3 breccia pipe orebodies and Eagle Point show oxidation-reduction fronts within some of the ore suggesting remobilization by oxidized meteoric fluids.

Multiple approaches to uranium resource calculations have been made by separate scientists: (1) Uranium resource estimates based on industry drilling for the 1050 mi2 (2720 km2) "mineralized corridor" have been made by Spiering and Hillard [11], to be 270 million lbs (122,000 tU) of U3O8. (2) In 1987, the USGS [4] calculated the uranium endowment of the entire breccia pipe district. Spiering and Hillard [11], show that these calculations, when applied to the "mineralized corridor,"result in 375 million lbs (170,000 tU) of U3O8. (3) A resource estimate (part of this study) using detailed surface mapping of breccia pipes and mineralized rock [12], on the NE portion of the Hualapai Indian Reservation, showed that the "mineralized corridor"contains 260 million lbs (118,000 tU) of U3O8 and the entire withdrawal area contains 385 million lbs (175,000 tU). Uraninite analyses (this study) show the total REE content of the uraninite to be 0.43

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Country or International Organization

United States of America

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