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Elemental Mobility in Uranium Deposits of the Sierra Peña Blanca as a Natural Analog of Radionuclide Migration in a High-Level Nuclear Waste Repository

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Introduction

For many years research interest in uranium ore deposits was mainly directed toward understanding the mechanisms and processes of formation of the deposits. Motivation for these studies derived from the economic value of the uranium as fuel for nuclear reactors. More recently, concern with disposal of the spent nuclear fuel has prompted research on uranium deposits because they can provide information on the behavior of nuclear waste in geologic repositories.

Because high-level nuclear waste (HLW) will constitute a threat to public safety for many thousands of years, it is necessary to attempt to predict the performance of a HLW repository far into the future. Although such times are short on a geologic scale, they are far in excess of experimental capabilities. In addition, the size of a geologic HLW repository will greatly exceed that of laboratory facilities. One approach to these problems of large time and space scales is to study natural systems. For example, natural materials which approximate components of a repository may be studied to gain a better understanding of the behavior to be expected from the repository material. Similarly, a process which occurs (or has occurred) in nature and which may be significant to the performance of a repository may be investigated to learn of possible effects on a repository system. By studying such natural analogs, which have existed for time spans comparable to radionuclide isolation requirements and which are of comparable scale to a repository, the uncertainty inherent in projecting such large scale processes far into the future can be reduced.

In 1987 the Congress of the United States of America specified Yucca Mountain, Nevada, as the national candidate site for geologic disposal of high-level nuclear waste. The Nopal I uranium ore deposit at Peña Blanca, Chihuahua, Mexico, has been identified as a site for natural analog studies relevant to a repository at Yucca Mountain (e.g. Murphy et al., 1990; Ildefonse et al., 1990a). This paper describes the geologic environment at Yucca Mountain and compares it to that of Peña Blanca. Characteristics of the Nopal I system which are analogous to aspects of a Yucca Mountain HLW repository are discussed and studies of the Nopal ore system which could provide information about radionuclide migration are described.

Yucca Mountain, Nevada

Yucca Mountain is 150 km northwest of Las Vegas, Nevada, on federal land including part of the Nevada Test Site (NTS). Geologic investigations at Yucca Mountain were initially directed toward mineral and energy resource exploration; more recently, studies have been connected with government activities at the NTS. Since 1977, the U.S.

Department of Energy (DOE) has gathered a large amount of data on Yucca Mountain, and the information presented below is drawn largely from that collection (e.g. DOE, 1988).

Yucca Mountain is in the southern part of the Great Basin physiographic province, which is bounded to the east by the Colorado Plateau and to the west by the Sierra Nevada Range. The Great Basin is a product of continental extension over the last 20 Ma and is characterized by north-south trending horsts and grabens which are offset in southern Nevada by widely-spaced regional strike slip faults. The southern part of the basin is composed of heavily eroded tilted-block ranges and sediment filled valleys. Tectonic features near Yucca Mountain are dominated by normal faults and other extensional structures. Yucca Mountain consists of a series of north-trending structural blocks which have been tilted eastward by west-dipping, high-angle normal faults related to Basin and Range tectonism over the last 7 Ma.

At Yucca Mountain, a series of silicic volcanic units with a thickness ranging from 1 to 3 km rests on Silurian dolomite. Erupted from calderas north of Yucca Mountain, these volcanic rocks are variably welded, devitrified and altered ash flow and air fall tuffs with minor volcanic flows and breccias. The oldest of the silicic volcanic units at Yucca Mountain was deposited about 14 Ma ago and the youngest is about 12 Ma old. Subsequent small scale basaltic volcanism has occurred near Yucca Mountain episodically into the Pleistocene epoch.

The proposed repository horizon is in a devitrified rhyolite ash-flow tuff unit in the Topopah Spring Member of the Paintbrush Tuff, which was deposited 12 - 13 Ma ago and is about 300 m thick at Yucca Mountain. The basal welded vitrophyre of the Topopah Spring Member grades upward into a densely welded, devitrified, nonlithophysal zone from 27 to 56 m thick which is the proposed location of the repository. This zone is phenocryst poor (2 - 22%); the phenocrysts include sanidine, plagioclase (andesine to oligoclase), and minor quartz, biotite, amphibole, iron-titanium oxides, allanite, and zircon. The primary groundmass of the Topopah Spring Member is glass and/or devitrification products comprised of alkali feldspar and silica minerals. Smectite and the silica-rich zeolite minerals clinoptilolite and mordenite are dominant alteration products. In some areas primary glass is completely converted to zeolites. Overall, the Topopah Spring Member averages about 70-80% SiO_2, 10-15% Al_2O_3, and 5-8% K_2O (Byers, 1985). Approximately 10 m beneath the Topopah Spring Member is a layer 30 - 300 m thick which is locally rich in zeolites (60 - 80 % clinoptilolite and mordenite).

The saturated zone groundwaters from tuffaceous aquifers at Yucca Mountain are dilute ($<10^{-2}$ molal), oxidizing, sodium bicarbonate solutions, rich in silica, with lesser calcium, potassium, magnesium, chloride, sulfate, nitrate, and fluoride (Kerrisk, 1987). Information about the pore waters in the unsaturated zone is limited at this time. The proposed repository horizon is about 200 m above the water table in rocks thought to be 40 to 70% saturated with water. At these saturation levels, it is believed that the fluid pressure would be low enough to allow the water to vaporize readily as temperatures increase in the repository near-field environment due to radionuclide decay. If dominated by matrix flow, water movement in the unsaturated zone is thought to be slow (e.g. 0.5 mm/yr). The chemistry, distribution and behavior of water in unsaturated, fractured tuffs is incompletely understood, particularly under conditions of thermal perturbations, and is currently a subject of investigation.

Yucca Mountain is in a mid-latitude desert climate with average annual precipitation less than 15 cm and an average temperature of about 13°C. Only about 0.3% of the local precipitation is thought to penetrate to the deeper portions of the unsaturated zone. A variety of evidence (e.g. pack rat middens, palynology, stable isotopes) suggests that the climate has been arid to semi-arid for the last 2 Ma. The aridity of the region results in little groundwater recharge and hence a low rate of groundwater movement. The groundwater in southern Nevada does not discharge into rivers or large bodies of surface water; rather, it discharges by evapotranspiration (e.g. at Alkali Flats, California) and at springs (e.g. at Death Valley, California).

Peña Blanca Uranium District

The Peña Blanca district is in northern Mexico about 50 km north of Chihuahua City and is part of the Chihuahua City uranium province. Uranium deposits in the district have been drilled and/or developed by underground or open pit mining over a period of 20 years (Goodell, 1981); however, there has been no mining activity at Peña Blanca since 1983, except in the extreme northwest part of the area where an exploration adit was completed in 1987 (J. Altamirano, personal communication). Many geologic and hydrologic aspects of the Peña Blanca district are similar to those of Yucca Mountain (e.g. Goodell, 1981, 1985; Cardenas-Flores, 1985; George-Aniel et al., 1985, 1991).

Peña Blanca is part of the northern Mexico basin and range system and lies near the boundary between a stable craton to the west and a more mobile belt to the east (Goodell, 1985). The regional structural province is bounded to the east by the Trans-Pecos Range and to the west by the Sierra Madre Occidental (George-Aniel et al., 1985). The Sierra Peña Blanca is a west-dipping horst block with a superimposed set of parallel northwest-striking normal (extensional) faults. Peña Blanca stratigraphy consists of a sequence of Cretaceous limestones and mudstones on which a series of Tertiary silicic volcanics has been deposited. Host rocks for most of the uranium deposits are the Escuadra and Nopal Formations which are composed of variably welded tuffs with air-fall, ignimbrite, vitrophyre, lahar, and water-worked units. The total preserved thickness of the volcanic units varies over the Sierra Peña Blanca area from 106 to 538 m, and rock ages range from 44 Ma to 35 Ma (Goodell, 1981).

The Peña Blanca tuffs are generally rhyolitic ignimbrites consisting largely of glass devitrification products with quartz, sanidine and minor biotite phenocrysts. Uranium in the ores was likely derived from the host tuffs. It is possible that the uranium was introduced from outside the district, but long-distance mobility is not required given the relatively high background uranium concentrations present in the silicic volcanic rocks (about 10 ppm in the Nopal Formation, George-Aniel et al., 1991). Uranium deposits at Peña Blanca are associated with hydrothermal alteration at faults, fractures, and breccias. There is also evidence of a district-wide alteration event which produced bleached zones along fractures; this alteration is present even kilometers away from known uranium mineralization. The present uranium mineralization is predominantly uranyl silicates (mostly uranophane, nominally $Ca(UO_2)_2Si_2O_7 \cdot 6H_2O$), however, small quantities of uraninite (UO_{2+x}) occur at the Nopal I deposit. The uraninite occurs as irregularly shaped masses of fine-grained crystals and is best described as pitchblende. It appears that pitchblende was the original form of the uranium mineralization and that it has been oxidized and altered to form the uranium silicates.

The distribution of uranium indicates that mineralizing hydrothermal fluids circulated primarily in faults and fractures, with brecciated zones, and small fissures controlling detailed ore distribution. Matrix flow may have been important locally; some samples show pervasive penetration of mineralizing fluids through the matrix of the tuffs (e.g. samples from the Puerto I mine in which feldspar phenocrysts are replaced by weeksite, $K_2(UO_2)_2Si_6O_{15} \cdot 4H_2O$). All of the Peña Blanca uranium deposits are presently located above the water table in the unsaturated zone. At present, it appears likely that uranium is being remobilized by oxidizing meteoric groundwaters which episodically penetrate the deposits through fractures in the unsaturated tuffs. The climate in the Peña Blanca area is arid, with annual precipitation of about 24 cm and average annual temperature of 19° C.

The Nopal I deposit at Peña Blanca has been the subject of earlier research (e.g. Goodell, 1981; Cardenas-Flores, 1985; George-Aniel et al., 1985; Leroy et al., 1987; Ildefonse et al., 1990a, b, c; George-Aniel et al., 1991). The deposit consists of a near vertical breccia pipe about 20 by 40 m in horizontal dimension which extends across the boundary of the Nopal and Coloradas formations, and is known to cover a vertical interval of at least 100 m. The host formations are silicic tuffs and are separated by a basal vitrophyre. The breccia pipe contains high grade uranium mineralization in the form of pitchblende and uranyl silicates. The lowest level of the deposit is significantly above the water table (perhaps 100 to 200 m), as indicated by water levels in nearby wells.

Uraninite at Nopal I is interpreted to have been precipitated along with pyrite and kaolinite (Ildefonse et al., 1990a; George-Aniel et al., 1991). Fluid inclusion studies suggest that this uraninite-pyrite-kaolinite assemblage formed at about 190 to 250°C from solutions with a median salinity of 2.5 equivalent wt. % NaCl (George-Aniel et al., 1991). Subsequent oxidizing hydrothermal alteration has produced rims of soddyite $(UO_2)_2SiO_4 \cdot 2H_2O$, uranophane $Ca(UO_2)_2Si_2O_7 \cdot 6H_2O)$, and bequerellite-group minerals, $(UO_2)_7 \cdot 11H_2O$, around the uraninite (Ildefonse et al., 1990a). There may also have been supergene alteration of the mineralization (George-Aniel et al., 1991). There is some spatial zoning within the breccia pipe, with K-phases (e.g. weeksite $K_2(UO_2)_2Si_6O_{15} \cdot 4H_2O$, boltwoodite $K(UO_2)(SiO_4)(H_3O)$, carnotite $K_2(UO_2)_2V_2O_8 \cdot 3H_2O$) concentrated in the center of the pipe and Ca-phases (e.g. uranophane $Ca(UO_2)_2Si_2O_7 \cdot 6H_2O$) toward the margins of the pipe (Ildefonse et al., 1990a). Paragenetically, uraniferous opal was deposited after the uranophane, which was itself deposited upon the earlier uranium mineralization (Ildefonse et al., 1990a).

Peña Blanca Natural Analog

Release and transport of radionuclides in a Yucca Mountain HLW repository will be affected by the gas, groundwater and mineral chemistry and by the hydrologic properties of the medium. The exceptional geologic, hydrologic, and geochemical similarities between the sites suggest that mass transfer and transport processes at Peña Blanca are likely to be comparable to those which would occur at Yucca Mountain. Specifically, alteration of the uranium ores at Peña Blanca by hydrothermal and supergene processes resulted in elemental remobilization and development of phase assemblages analogous to those that would also characterize the Yucca Mountain repository. The geologic record at Peña Blanca permits recognition and detailed evaluation of these processes. Furthermore, it offers the opportunity to test models that will be used to predict the evolution of geologic nuclear waste disposal systems.

Uraninite (UO_{2+x}) is structurally and compositionally similar to spent nuclear fuel (largely UO_2; Johnson and Shoesmith, 1988), which is the predominant waste form proposed for Yucca Mountain. Therefore, the geochemical processes which controlled elemental redistribution during alteration of the primary uraninite mineralization at Nopal I may be considered to be analogous to alteration of spent fuel in a HLW repository and the resulting radionuclide mobilization. The primary and secondary ore and host rock minerals can provide information on the composition and evolution of the remobilizing fluids. Detailed studies of the secondary mineral assemblages and the paragenetic relations among the phases may indicate the relative stabilities and sequence of alteration minerals to expect

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during hydrothermal degradation of spent nuclear fuel. The distributions and compositions of these secondary minerals may indicate the relative mobilities of elemental species. Such secondary uranium minerals may effectively control the release of spent fuel radionuclides to the broader environment. Analysis of uranium-series radionuclides may allow absolute time constraints to be placed on the remobilization of the ore components at Peña Blanca under varying conditions, and hence provide information on the rate and controls of elemental transport. Secondary localization of uranium, thorium, and other trace elements in or on specific minerals may reveal which phases are important to retardation of radionuclide migration.

Among the several uranium deposits in the Peña Blanca district, the Nopal I deposit has been identified as the most promising site for a geochemical analog study relevant to a HLW repository at Yucca Mountain. The suite of uranium minerals of varying oxidation states, including pitchblende and the assemblage of uranyl silicate minerals, is a good analog of the alteration of spent nuclear fuel in a silicic oxidizing environment. Mining operations at Nopal I have left excellent exposure for field research and sampling, and several recent and detailed petrographic studies of this deposit provide valuable background information.

Conclusions

The Peña Blanca district appears to provide an excellent analog to the proposed Yucca Mountain HLW repository system. Analogous aspects of the district are the silicic, tuffaceous rock types (primary and secondary mineralogy), the semi-arid climate, the unsaturated hydrologic regime, and the uranium mineralization. Specifically, the Nopal I deposit has been identified as a potential site for further work because the deposit has a relatively small scale and simple geometry; both primary pitchblende and secondary uranyl silicate alteration minerals occur in the ore, and information is available from previous research at the deposit. A variety of present and past processes at Nopal I are analogous to those that could affect radionuclide migration at Yucca Mountain. Processes governing the oxidation of Peña Blanca uraninite, the resulting dispersion of uranium from the sites of original mineralization, and the formation of secondary uranyl silicates are analogous to processes that may affect spent nuclear fuel and elemental migration at the proposed repository.

Acknowledgements

This project is supported by the US Nuclear Regulatory Commission. Field work at Peña Blanca was accomplished with the help of J. Altamirano, I. Reyes, and the cooperation of the *Consejo Recursos Minerales* and the *Fideicomiso de Fomento Minero*. Clarity of the manuscript benefitted from reviews by D. Turner and W. Patrick.

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