

JT # 47631
QA: NA

Isotope-geochemical evidence for uranium retardation in zeolitized tuffs at Yucca Mountain, Nevada, USA

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Introduction

Retardation of radionuclides by sorption on minerals in the rocks along downgradient groundwater flow paths is a positive attribute of the natural barrier at Yucca Mountain, Nevada, the site of a proposed high-level nuclear waste repository. Alteration of volcanic glass in nonwelded tuffs beneath the proposed repository horizon produced thick, widespread zones of zeolite- and clay-rich rocks with high sorptive capacities. The high sorptive capacity of these rocks is enhanced by the large surface area of tabular to fibrous mineral forms, which is about 10 times larger in zeolitic tuffs than in devitrified tuffs and about 30 times larger than in vitric tuffs. The alteration of glass to zeolites, however, was accompanied by expansion that reduced the matrix porosity and permeability. Because water would then flow mainly through fractures, the overall effectiveness of radionuclide retardation in the zeolitized matrix actually may be decreased relative to unaltered vitric tuff.

Isotope ratios in the decay chain of ^{238}U are sensitive indicators of long-term water-rock interaction. In systems older than about 1 m.y. that remain closed to mass transfer, decay products of ^{238}U are in secular radioactive equilibrium where $^{234}\text{U}/^{238}\text{U}$ activity ratios (AR) are unity. However, water-rock interaction along flow paths may result in radioactive disequilibrium in both

the water and the rock, the degree of which depends on water flux, rock dissolution rates, α -recoil processes, adsorption and desorption, and the precipitation of secondary minerals.

The effects of long-term water-rock interaction that may cause radionuclide retardation were measured in samples of Miocene-age subrepository zeolitized tuffs of the Calico Hills Formation (Tac) and the Prow Pass Tuff (Tcp) from borehole USW SD-9 near the northern part of the proposed repository area (sampled depth interval from 451.1 to 633.7 m; Engstrom and Rautman, 1996). Mineral abundances and whole-rock chemical and U-series isotopic compositions were measured in unfractured core samples representing rock matrix, in rubble (about 1 cm) rock fragments representing zones of higher permeability (assuming that the rubble core indicates a broken zone in the rock mass rather than an artifact of drilling), and in samples from surfaces of natural fractures representing potential fracture pathways. U concentrations and isotopic compositions also were measured in samples of pore water obtained by ultracentrifugation or by leaching rock samples with deionized H₂O. The concentrations and isotopic compositions of loosely bound U adsorbed on reactive mineral surfaces were obtained by analyzing 1 M sodium acetate (NaOAc) leachates of whole-rock samples.

Experimental Methods

Mineral abundances were measured by X-ray powder diffraction methods using the full-pattern quantitative analysis program FULLPAT. Chemical compositions of major and trace elements were determined by several techniques including standard X-ray fluorescence spectroscopy (XRF) and inductively coupled plasma-mass spectrometry (ICP-MS) techniques. Uranium concentrations and isotopic compositions were measured using a thermal ionization mass spectrometer (TIMS). Reproducibility of TIMS analyses was about 1% (2σ) for elemental concentrations and 0.2% for U isotope ratios. Atomic isotope ratios were converted to activity ratios using known decay constants.

Results and Discussion

The most common secondary minerals in 35 samples of the zeolitized tuff are clinoptilolite (0.5 to 76.3 %), opal-CT (6.5 to 21.8 %), mordenite (1.2 to 22.4 %), and smectite (0.1 to 44 %). Fracture surfaces have more smectite (median value of 6.1%) than unfractured and rubble core (median value of 3.2%).

Trends of concentrations with depth for whole-rock samples from the upper 50 m of the Tac document accumulation of Ca accommodated by loss of Na as a result of downward water movement and cation exchange within the zeolitized rock sequence, consistent with published results (Vaniman et al., 2001). However, systematic variations with depth and zeolite abundance are not observed for U concentrations over this same depth interval.

Uranium contents in NaOAc leachates (0.012 to 0.071 $\mu\text{g/g}$ rock) represent a mobile U component adsorbed on mineral surfaces or in readily acid-soluble secondary minerals. Compared with whole-rock analyses, these data indicate that the adsorbed U comprises 0.3 to 1.7 percent of total rock ^{238}U . These data allow estimates of the time-integrated *in situ* U partition coefficient ($K_d=C_s/C_w$, where C_s and C_w are concentrations in the solid and water, respectively) under natural flow conditions. Use of median U concentrations in pore water (5 ng/mL) and NaOAc leachates (0.035 $\mu\text{g/g}$ rock) yields an estimate of the ^{238}U K_d value of about 7 mL/g. This value is larger than the value of 0.5 mL/g obtained for crushed tuffs from laboratory batch experiments that currently is used for zeolitized units at Yucca Mountain (BSC, 2004, Table 5-1).

Whole-rock samples of unfractured core, rubble core, and fracture surfaces have similar $^{234}\text{U}/^{238}\text{U}$ AR ranging from 0.92 to 1.16 indicating both enrichments ($^{234}\text{U}/^{238}\text{U}$ AR>1) and depletions ($^{234}\text{U}/^{238}\text{U}$ AR<1) in the daughter ^{234}U relative to the parent ^{238}U . In contrast to the rock samples, all pore water and rock leachate samples have elevated $^{234}\text{U}/^{238}\text{U}$ AR ranging from 1.1 to 5.2. Whole-rock $^{234}\text{U}/^{238}\text{U}$ AR greater than 1 for these zeolitized rocks contrast with data from samples of the welded part of the Topopah Spring Tuff (Tpt), the proposed repository horizon, that

invariably have $^{234}\text{U}/^{238}\text{U}$ AR <1. The depletion in ^{234}U in Tpt rocks is caused by preferential removal of ^{234}U by the percolating water as a result of α -recoil processes. Therefore, the large $^{234}\text{U}/^{238}\text{U}$ AR in pore water and in U sorbed on mineral surfaces indicate that ^{234}U removed from overlying units is transported in percolating water and retained in underlying zeolitized units. U-series isotope data for whole-rock samples from subrepository units having $^{234}\text{U}/^{238}\text{U}$ AR > 1 also strongly support the potential for retention of U from percolating water by zeolitized rocks and indicate that amounts of retardation of radionuclides may be greater than currently credited to zeolitized rocks at Yucca Mountain.

References

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