Uranium-Series Constraints on Subrepository Water Flow at Yucca Mountain, Nevada

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U.S. Department of Energy Science and Technology Program on Natural Barriers—II

Presented to:
2006 International High-Level Radioactive Waste Management Conference

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TUESDAY, MAY 2, 2006
Las Vegas, NV
Yucca Mountain: Proposed U.S. Geologic Repository for High-Level Radioactive Waste

- Located in the Western U.S. within the Basin and Range Province at the Nevada Test Site
- Semi-arid climate
  - ~170 mm/year precipitation minimizes amounts of percolating water
- Thick (500-700 m) unsaturated zone (UZ) composed of ~12.8 Ma felsic tuffs
  - underground storage is well isolated from the water table
  - radionuclide retardation by natural system
Natural Systems of Yucca Mountain

Tpc- 12.7 Ma Tiva Canyon Welded
Tpt- 12.8 Ma Topopah Spring Welded
GDF- Ghost Dance Fault
SCF- Solitario Canyon Fault
PTn- Paintbrush Nonwelded
Tac- 12.9 Ma Calico Hills Nonwelded
Tcp- Prow Pass Tuff

Desert Environment
Unsaturated Overburden
Welded Host Tuff
Partly to Fully Zeolitized Rock
Thick Unsaturated Zone
(Water Table at depth of ~500 m)

Conceptual Drawing - Not to Scale
**Subrepository Flow Study Background**

- Sorption of radionuclides in rocks along downgradient flow paths contributes to the natural barrier at Yucca Mountain
- Altered tuffs beneath the proposed repository horizon form zones of zeolitized rocks with high sorptive capacities
- Alteration reduced primary void space and matrix permeability
- **Current UZ Flow and Transport Model**
  - Fracture flow is dominant in zeolitized rocks
  - Contaminants enter zeolitized zones through molecular diffusion
  - Fractures allow fluids and radionuclides to bypass rock matrix
  - Zeolitized tuffs may not effectively retard radionuclides
- However, if matrix flow is present in zeolitized units, repository performance will be enhanced through sorption processes
Subrepository Flow Study Objectives

- Evaluate long-term water-rock interaction in samples of unfractured and fractured zeolitic tuffs using several indicators of water flow
  > Mineralogy
  > Chemistry
  > U-series isotopes
- Compare results between fractured and unfractured tuffs
- Assess whether water percolates through the rock matrix in zeolitized tuffs beneath the proposed repository horizon
- Assess potential of zeolitized tuffs to retard U under natural flow conditions
Methods

- Mineral abundances by quantitative X-ray diffraction methods (LANL, Los Alamos)
  - "Full-Pattern Quantitative Analysis Program for X-Ray Powder Diffraction Using Measured and Calculated Patterns FULLPAT" (Chipera and Bish, 2002)
- Scanning electron microscope imaging (USGS, Denver)
- Major and trace elements (USGS, Denver)
  - X-ray fluorescence spectroscopy (XRF)
  - Inductively coupled plasma-mass spectrometry (ICP-MS)
- U and Th isotope analyses (USGS, Denver)
  - Isotope dilution thermal ionization mass spectrometry (TIMS, precision 0.2-0.5 %)
238U decays through a series of radioactive isotopes to yield 234U and 230Th.

U and Th isotopes fractionate in water-rock systems that are not closed to mass transfer.

- Alpha-recoil: fractionation of 234U relative to 238U
- Different solubilities: fractionation of 230Th from 238U and 234U

U-series isotope ratios in rocks and waters are indicators of water-rock interactions over 10^5 to 10^6 y.
After a disturbance episode with preferential $^{234}\text{U}$ loss, rock returns to secular equilibrium ($^{234}\text{U}/^{238}\text{U}$ AR = 1) in ~ 1.5 m.y.

Continuous process with $^{234}\text{U}$ loss results in steady state $^{234}\text{U}/^{238}\text{U}$ AR < 1

$f_a$ – fraction of $^{238}\text{U}$ decays resulting in $^{234}\text{U}$ ejection

$^{234}\text{U}/^{238}\text{U}$ AR = 
\[(1 - f_a) - f_a \times \exp(-\lambda_{234}t)\]

Maher et al., GCA, 2004
Zeolite Distribution at Yucca Mountain

- Lateral and vertical variations in zeolite abundances
  - Vitric tuffs most susceptible to alteration:
    - Calico Hills Formation (Tac)
    - Prow Pass Tuff (Tcp)
  - Transition to non-zeolitic, vitric units in the southwest region of Yucca Mountain (Bish et al., 2003)
- Study uses core from borehole USW SD-9
  - Located near the northern part of the proposed repository area, west of the main drift of the Exploratory Studies Facility (ESF)
  - Total depth of 677.8 m
  - Regional water table at 572.3 m
Geologic Units in USW SD-9 and Previous U-series Data

- Subrepository geologic units in USW SD-9
  - Calico Hills Formation (Tac): extensively zeolitized tuffs below 451.0 m
  - Prow Pass Tuff (Tcp): partially zeolitized rocks below 554.9 m

- Previous geochemical and U-series isotope data are available for shallower UZ in this borehole
  - $^{234}\text{U}/^{238}\text{U}$ AR <1 in rocks
  - $^{234}\text{U}/^{238}\text{U}$ AR >1 in waters
Comparison of Tac and Tcp with other UZ tuffs

- Porosity
- Water saturation

- Pore water may be held tightly within zeolites and small pores

- Matrix flow velocity decreases in Tac

- More time for water-rock interaction and sorption in the matrix

(Data from Engstrom and Rautman, 1996)
Zeolites, clays, and opal-CT affect pore-size distribution and affect moisture retention characteristics and permeability.

Permeability of zeolitized rocks is reduced (10^{-7} to 10^{-9} darcies in zeolitized tuff compared to >10^{-2} darcies in unaltered vitric tuff).

Low permeability Tac rocks inhibit downward flow.

Perched water bodies.

(Data from Engstrom and Rautman, 1996)
Samples collected between 451.1 to 633.7 m from Tac and Tcp units

Rock powders from natural fracture surfaces represent potential fracture pathways (n=13)

Rubble core (1-3 cm fragments) assumed to represent zones of higher permeability (n=7) rather than an artifact of drilling

Unfractured core samples represent rock matrix (n=16)
SEM Images of Zeolites on Fracture Surfaces

- Zeolites have large surface/volume ratios

A. tabular clinoptilolite from 451.1 m depth (Tac)

B. fibrous mordenite from 474.8 m (Tac)

C. fibrous mordenite from 481.7 m (Tac)

D. fibrous mordenite from 544.6 m (bedded tuff below Tac)
Volcanic glass reacted in the presence of water to form zeolites, opal-CT, and clays.

Zeolites (high ion-exchange and sorption capacities)
- Clinoptilolite (0 to 73.0 %)
- Mordenite (0 to 22.4 %)
- Opal-CT (6.6 to 20.8 %)
- Smectite (0.1 to 40.2 %)
  - Swelling clay with a high cation-exchange capacity
  - Effectively sorbs cations in bicarbonate water
  - Important for radionuclide retardation (Vaniman et al., 1996)

Mineral Abundance (%)
- Clinoptilolite
- Mordenite
- Smectite

Depth below Surface (m)
- Unfractured and Rubble Core
- Fracture Surface
Variations in Na and Ca in Tac

- Accumulation of Ca is complemented by Na loss in the upper 50 m of zeolitized Tac
  - Downward water movement and cation exchange within the zeolite sequence
  - Similar magnitude of cation exchange in unfractured core, rubble core, and fracture surface samples
    - Evidence for matrix flow
    - No evidence of more ion exchange in fractures
  - Results are consistent with previous studies (Vaniman et al., 2001)
Variations of $^{234}\text{U}/^{238}\text{U}$ AR with Depth in USW SD-9

- Whole-rock $^{234}\text{U}/^{238}\text{U}$ AR vary from 0.92 to 1.18
- Ranges for unfractured core, rubble core, and fracture surfaces overlap
  - Evidence for matrix flow
  - No evidence for greater water-rock interaction on fractures
- $^{234}\text{U}/^{238}\text{U}$ AR > 1 in some samples of zeolitized tuff
  - Different from welded tuffs from the proposed repository horizon with $^{234}\text{U}/^{238}\text{U}$ AR < 1
  - Interpreted as U sorption from $^{234}\text{U}$-enriched water percolated through the UZ

[Graph showing data points and markers for unfractured core, rubble core, and fracture surface]
Time Scale of U Mobility

- Similar $^{234}\text{U}/^{238}\text{U}$ and $^{230}\text{Th}/^{238}\text{U}$ ARs in unfractured and rubble core
  - No recent preferential U mobility relative to less mobile Th

- Episodic process
  - $\sim 300$ k.y. is required for $^{230}\text{Th}$ to reach radioactive equilibrium with its parent $^{234}\text{U}$
  - $>1$ m.y. is required for $^{234}\text{U}$ to reach equilibrium with its parent $^{238}\text{U}$

- Continuous process (steady state)
  - Rates of $^{238}\text{U}$ mobility are slow
  - U dissolution rate constant $\sim 10^{-8}$ y$^{-1}$ (Latham and Schwarcz, 1988)
Mineral Abundances versus $^{234}\text{U}/^{238}\text{U}$ AR in Tac

- $^{234}\text{U}/^{238}\text{U}$ AR > 1 in rocks indicates presence of sorbed U component
- $^{234}\text{U}/^{238}\text{U}$ ARs in samples from fracture surfaces correlate with smectite abundance in upper 50 m of Tac
  - U sorption by smectite
  - Potential for U retardation in fractures
U concentrations and 234U/238U AR in rock, waters, and rock leachates with depth in USW SD-9

Depth below Surface (m)

U Concentration (μg/g)

234U/238U Activity Ratio
$^{234}\text{U} / ^{238}\text{U}$ AR in Water-Rock System

- $[\text{U}]_{\text{Rock}} > [\text{U}]_{\text{NaAc Leach}} > [\text{U}]_{\text{Water}}$
- $^{234}\text{U} / ^{238}\text{U}$ AR NaAc Leach $\approx ^{234}\text{U} / ^{238}\text{U}$ AR Water (pore water and DI water leach)
- U in NaAc leach is easily extractable adsorbed component

Three-pool model for uranium

1. U in rock and in "old" hydrogenic secondary minerals
   $\rightarrow (^{234}\text{U} / ^{238}\text{U} \text{ AR} < 1)$
2. Sorbed U
   $\rightarrow (^{234}\text{U} / ^{238}\text{U} \text{ AR} > 1, \approx \text{water value})$
3. U in water
   $\rightarrow (^{234}\text{U} / ^{238}\text{U} \text{ AR} > 1)$
**In situ Retardation Factor** $R_f$ for Uranium

$R_f = (\text{water velocity})/(\text{transport rate of radionuclide})$

$$R_f = 1 + K_d \left[ \rho_s (1-\phi)/\phi \right]$$

$$K_d = C_{\text{sorbed}} / C_{\text{water}} \text{ (mL/g)}$$

$C_{\text{sorbed}} (\mu g/g); C_{\text{water}} (\mu g/mL); \rho_s$ – rock density (g/cm$^3$); $\phi$ – porosity

- U concentrations in pore water (dissolved pool) and NaAc rock leachates (sorbed pool) allowed estimation of long-term *in situ* distribution coefficient $K_d$ of $\sim 7$ mL/g

- *In situ* retardation factor for U in samples of zeolitized rocks ($\phi \sim 0.25$ and $\rho_s \sim 1.7$ g/cm$^3$) $R_f$ of $\sim 36$
Future Reactive Transport Modeling

\[
\frac{\partial}{\partial t} (\theta C + C_e) = \frac{\partial}{\partial z} \left( D_e \frac{\partial \theta C}{\partial z} \right) - v \frac{\partial \theta C}{\partial z} + \theta \left( R_o + R_d - R_p \right) + \lambda_{238} (\theta C_{238} + C_{e,238}) - \lambda_{234} (\theta C + C_e)
\]

- Reported U isotope data in rocks, rock leachates, and pore water can be used for reactive transport modeling (Maher et al., 2004), which may allow estimates of \((\text{water flux}) / (\text{rock dissolution rate})\) ratios

- Combining reported new U isotope data and available Sr isotope data for USW SD-9 may allow estimates of water flux and dissolution/sorption rates
CONCLUSIONS (I)

- U-series isotope data record a complex history of U mobility in zeolitized tuffs beneath the proposed repository at Yucca Mountain.

- Geochemical and isotopic data for unfractured rock samples show that solute transport through matrix of altered tuff occurs despite decreased permeability caused by zeolitization.

- Similar $^{234}\text{U}/^{238}\text{U}$ and $^{230}\text{Th}/^{238}\text{U}$ AR in samples of unfractured core, rubble core, and fracture surfaces indicate that zones of higher permeability and fractures in zeolitized tuffs did not have significantly larger amounts of water-rock interaction than the rock matrix.
CONCLUSIONS (II)

- Elevated $^{234}\text{U}/^{238}\text{U}$ ARs in rock samples show that zeolitized tuff can adsorb U from percolating water \((in situ \ K_d \sim 7; \ R_f \sim 36)\)

- Matrix flow through the subrepository units remains a viable process that may enhance the proposed repository performance

- U-series results can be used in reactive transport modeling to estimate percolation flux and weathering rates in subrepository units at Yucca Mountain
References Cited


