OST&I
OCRWM Office of Science and Technology and International

USGS
science for a changing world

Los Alamos
NATIONAL LABORATORY

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

Authors:

L.A. Neymark (U.S. Geological Survey)
J.B. Paces (U.S. Geological Survey)
S.J. Chipera (Los Alamos National Laboratory)
D.T. Vaniman (Los Alamos National Laboratory)

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

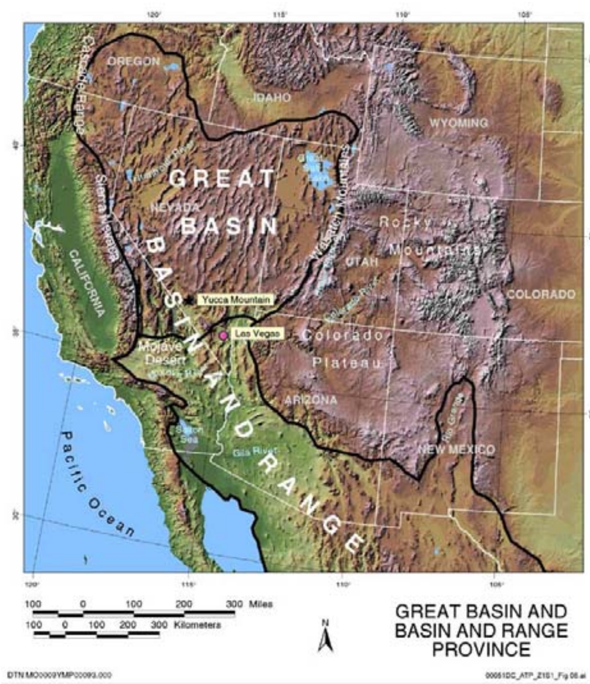
Presented to:
2006 International High-Level Radioactive Waste Management Conference

Presented by:
Leonid A. Neymark, USGS

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

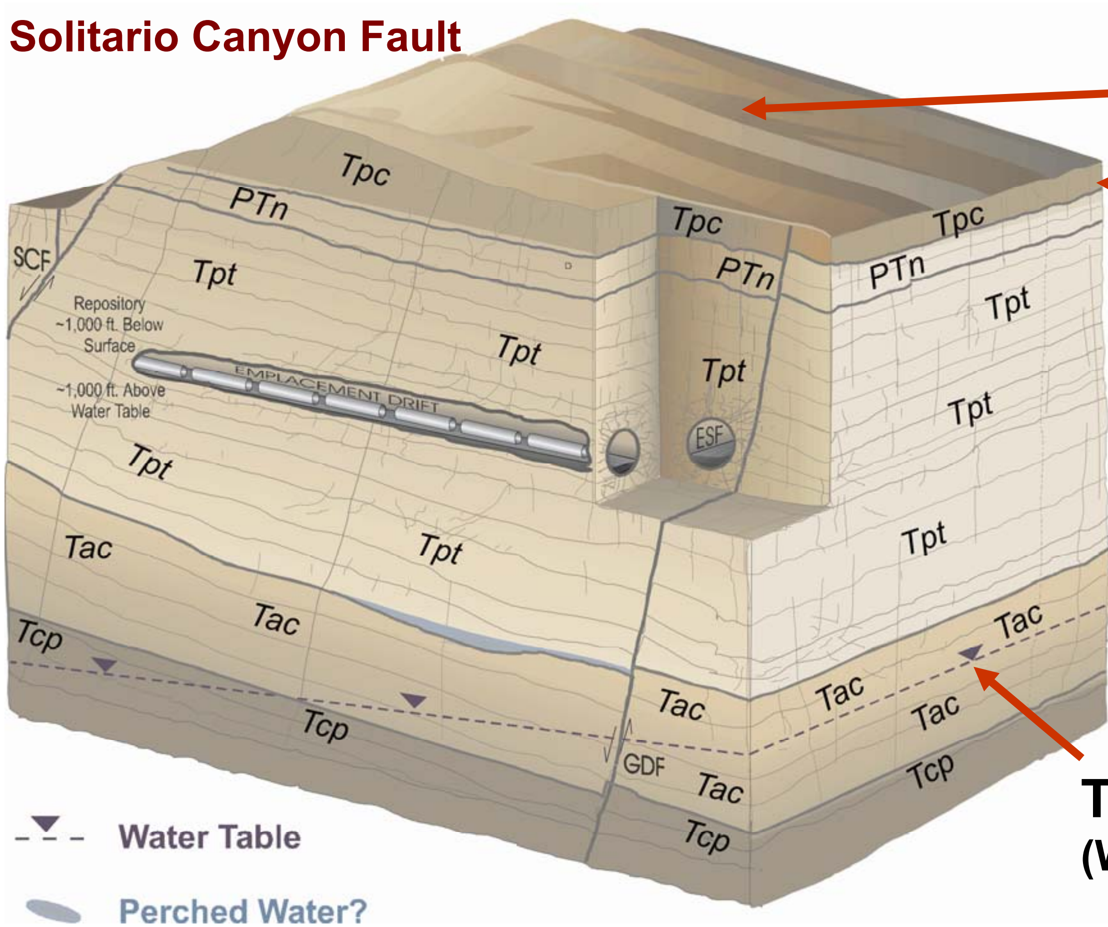
GDF- Ghost Dance Fault

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

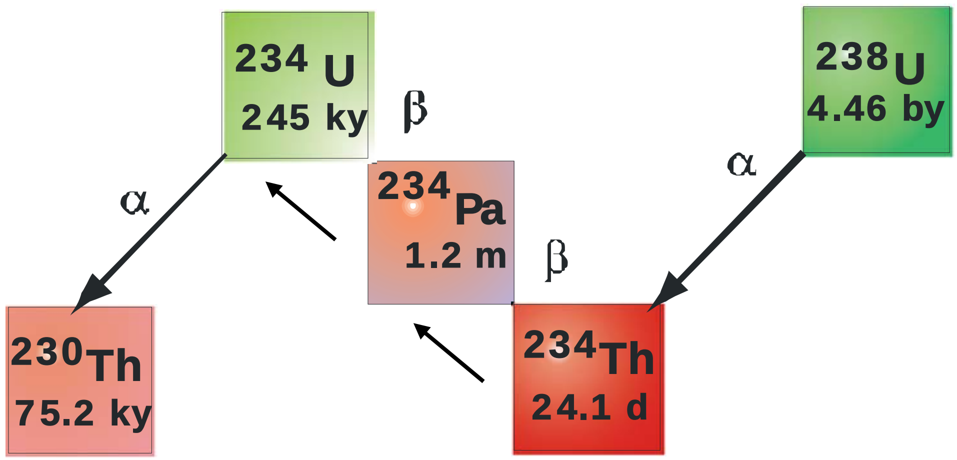
Subrepository Flow Study Objectives

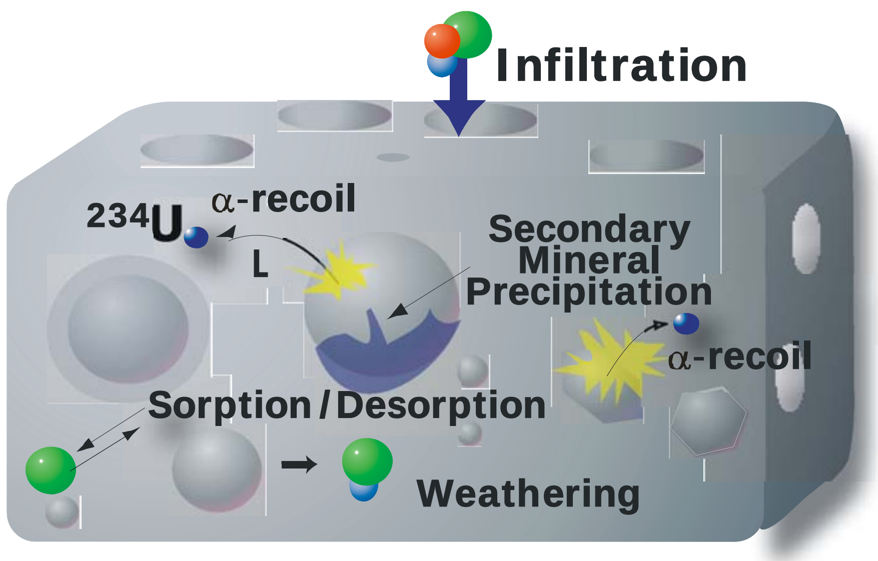
- Evaluate long-term water-rock interaction in samples of unfractured and fractured zeolitic tuffs using several indicators of water flow
  - Mineralogy
  - Chemistry
  - U-series isotopes
- Compare results between fractured and unfractured tuffs
- Assess whether water percolates through the rock matrix 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 %)

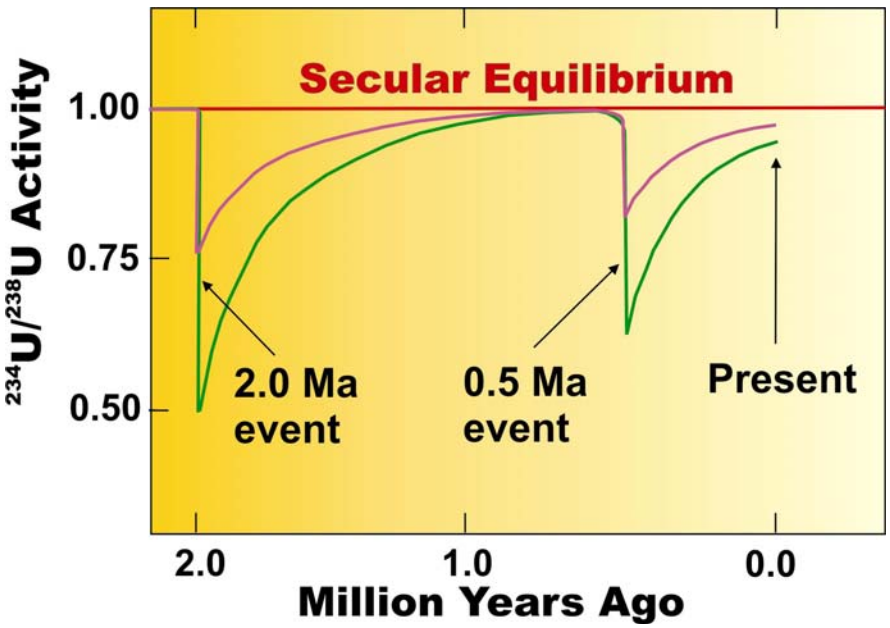
U-series Radioactive Disequilibrium

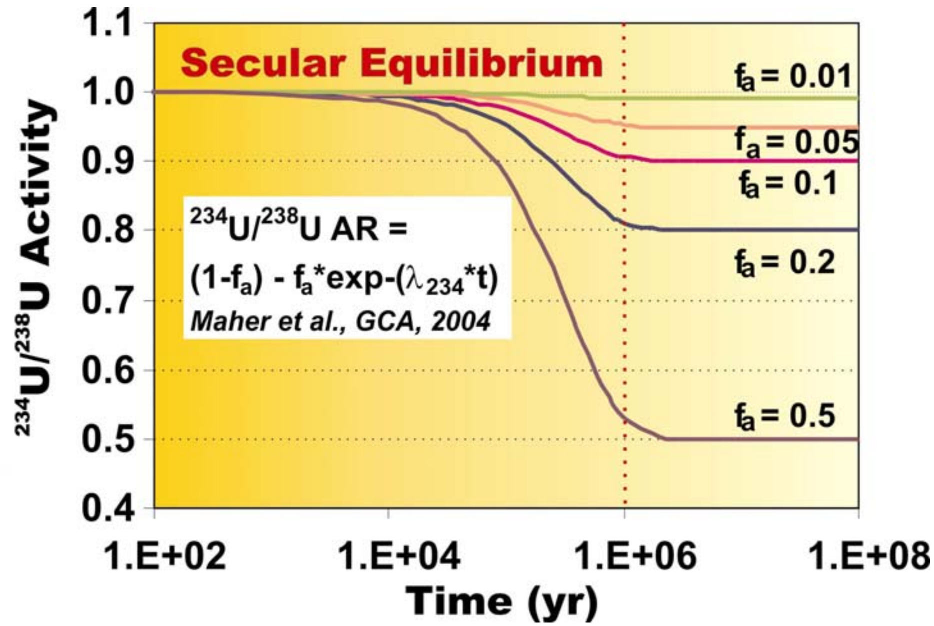




- ^{238}U decays through a series of radioactive isotopes to yield ^{234}U and ^{230}Th
- U and Th isotopes fractionate in water-rock systems that are not closed to mass transfer
  - Alpha-recoil: fractionation of ^{234}U relative to ^{238}U
  - Different solubilities: fractionation of ^{230}Th from ^{238}U and ^{234}U
- U-series isotope ratios in rocks and waters are indicators of water-rock interactions over 10^5 to 10^6 y

Episodic vs Continuous Uranium Leaching





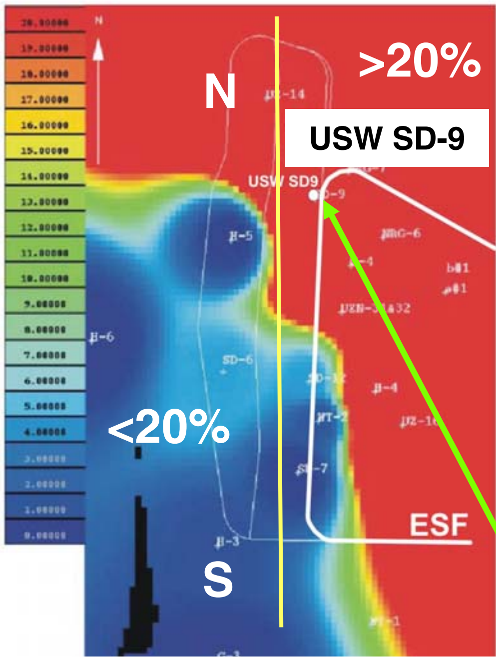
After a disturbance episode with preferential ^{234}U loss rock returns to secular equilibrium ($^{234}U/^{238}U$ AR =1) in ~ 1.5 m.y.

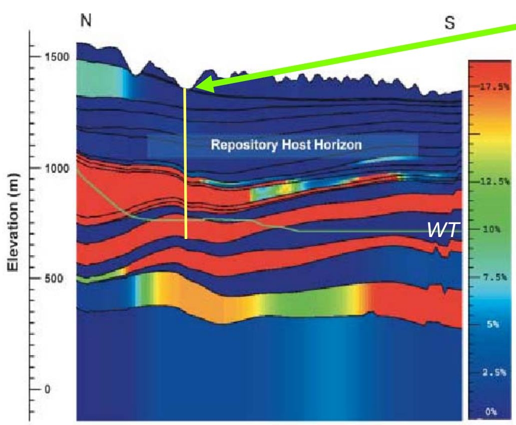
Continuous process with ^{234}U loss results in steady state $^{234}U/^{238}U$ AR <1

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

OST&I
OCRWM Office of Science and Technology and International

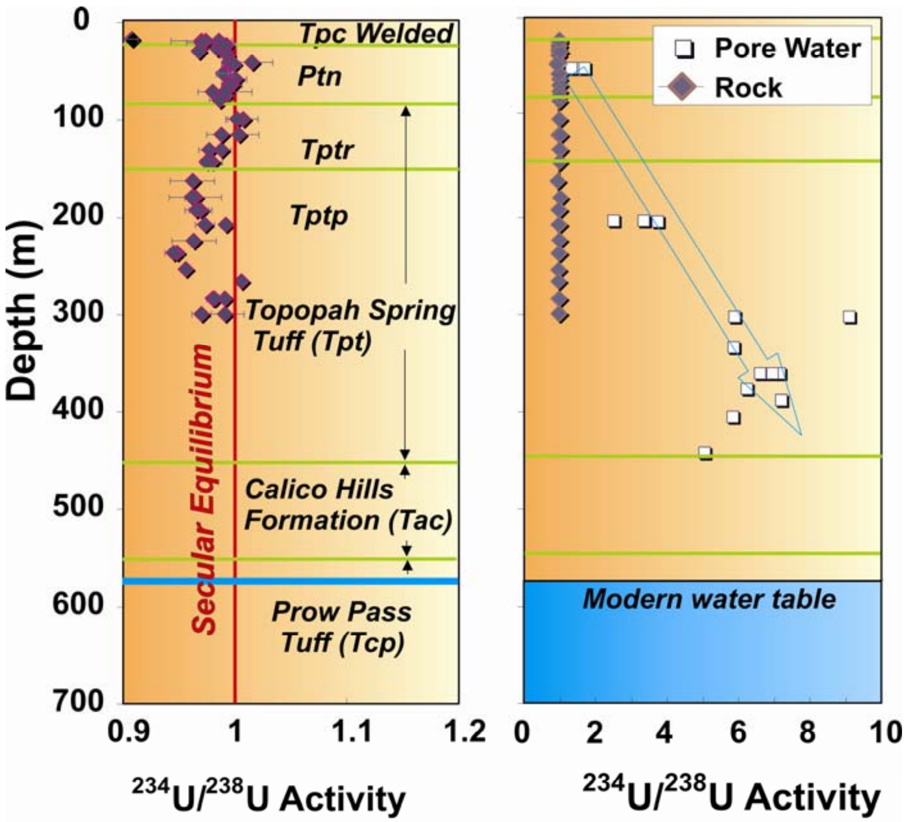
Zeolite Distribution at Yucca Mountain





- **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**

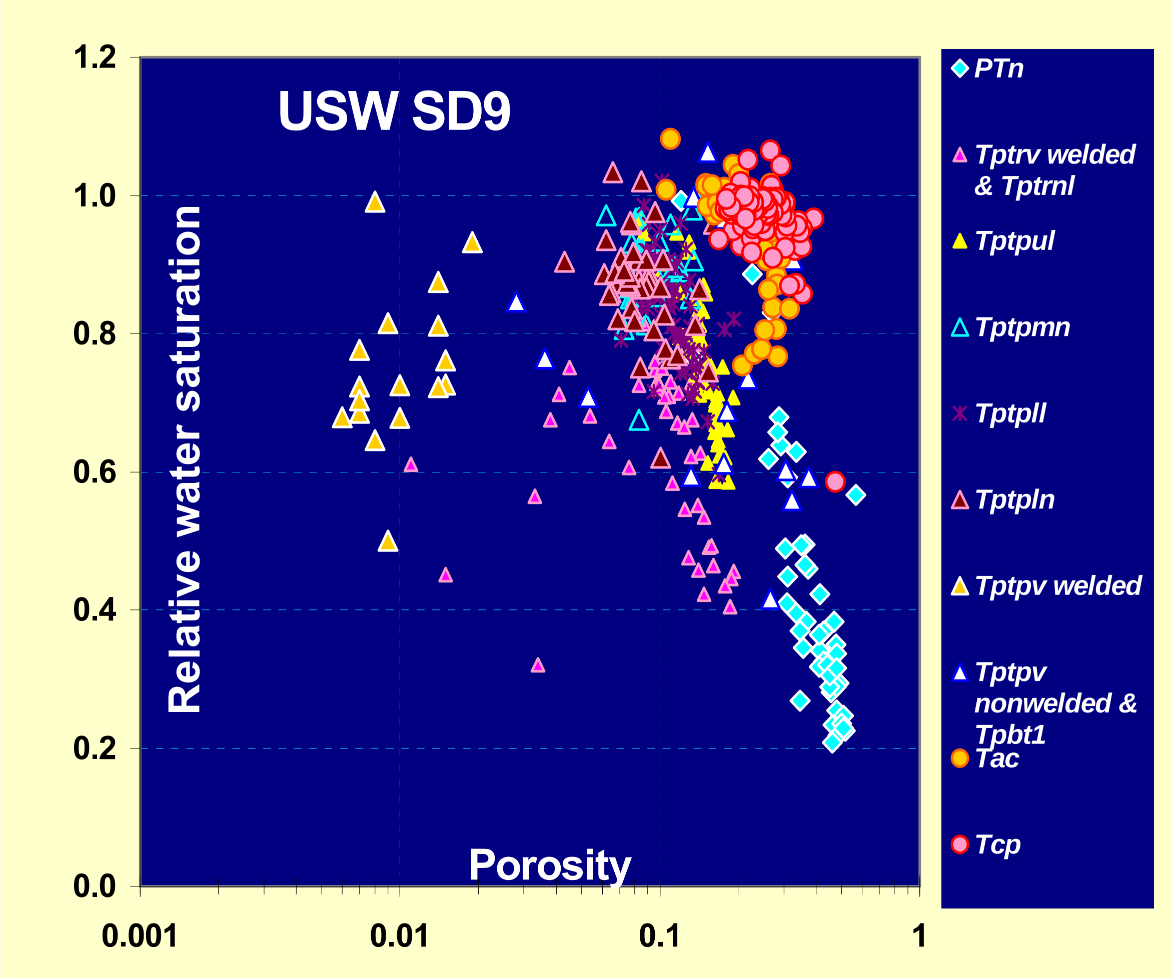
Geologic Units in USW SD-9 and Previous U-series Data



- **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**
  - **$^{234}U/^{238}U$ AR <1 in rocks**
  - **$^{234}U/^{238}U$ AR >1 in waters**

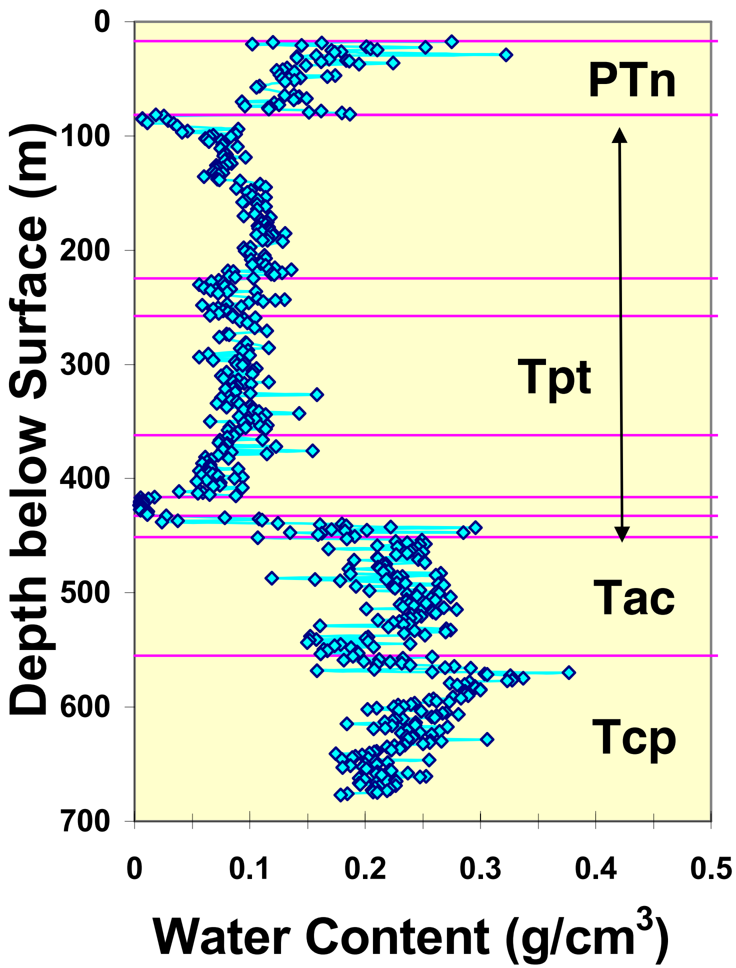
Water Saturation and Porosity in USW SD-9

- 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)

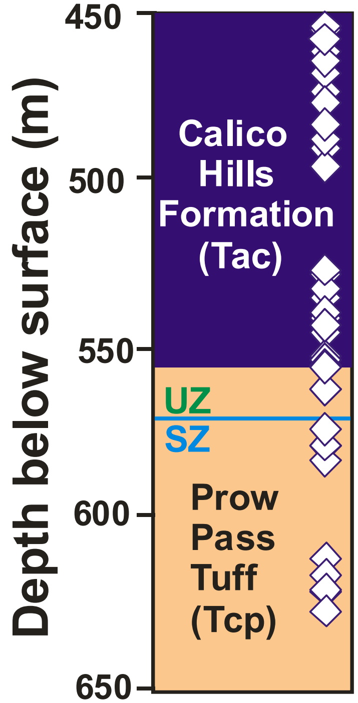
Water Content in USW SD9



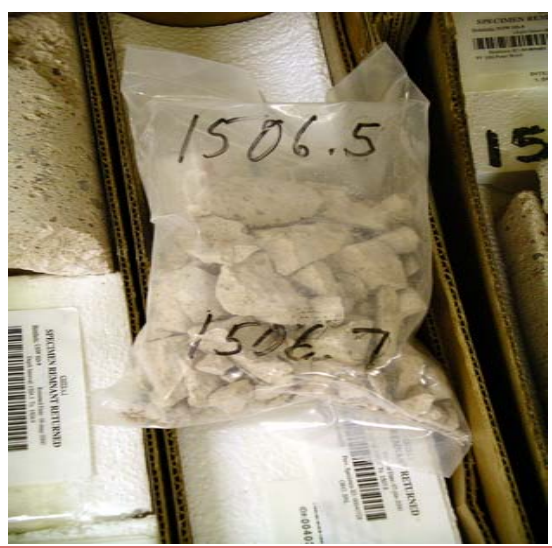
(Data from Engstrom and Rautman, 1996)

- **Zeolites, clays, and opal-CT**
  - **affect pore-size distribution**
  - **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**

Samples from USW SD-9 Core

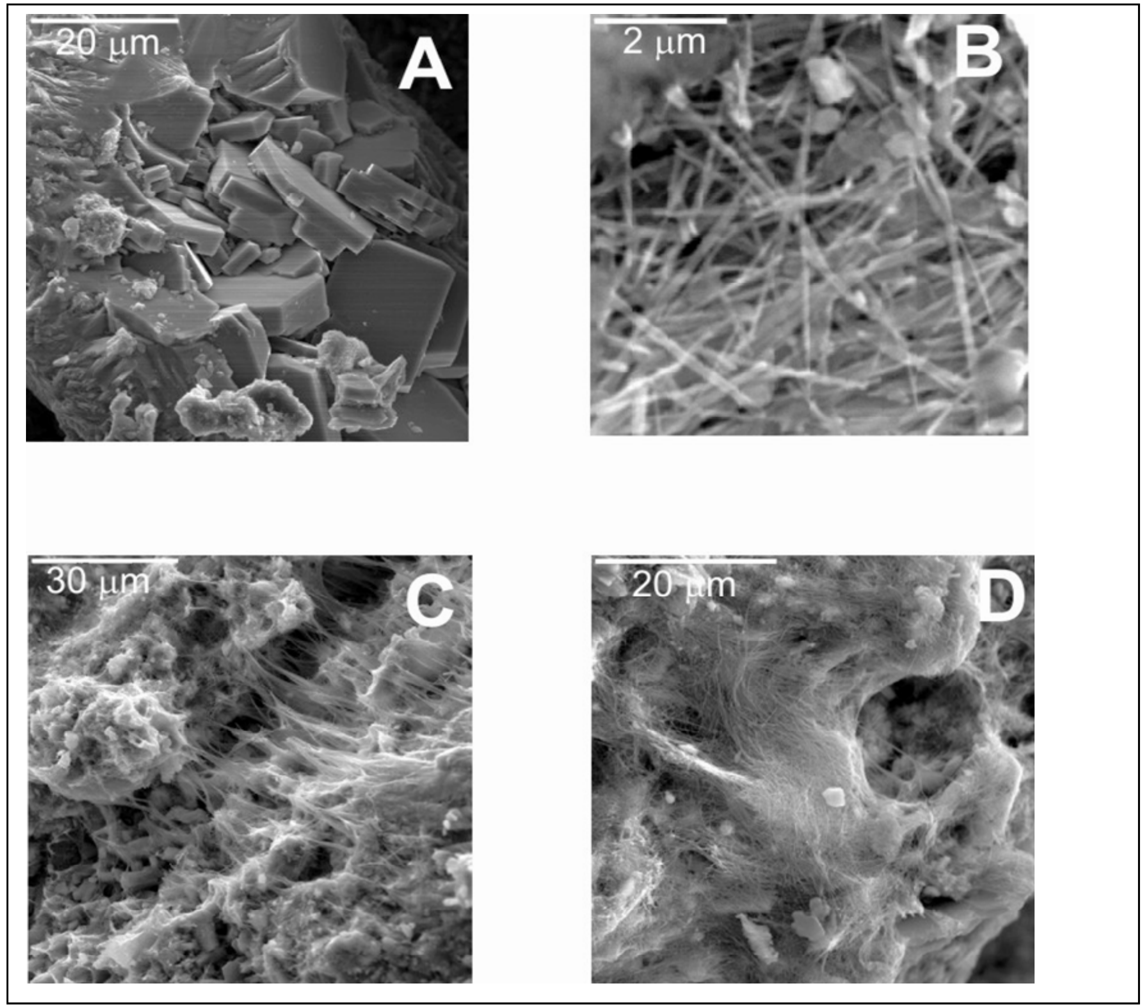


- Samples collected between 451.1 to 633.7 m from Tac and Tcp units
- Rock powders from natural fracture surfaces represent potential fracture pathways (n=13)
- Rubble core (1-3 cm fragments) assumed to represent zones of higher permeability (n=7) rather than an artifact of drilling
- Unfractured core samples represent rock matrix (n=16)



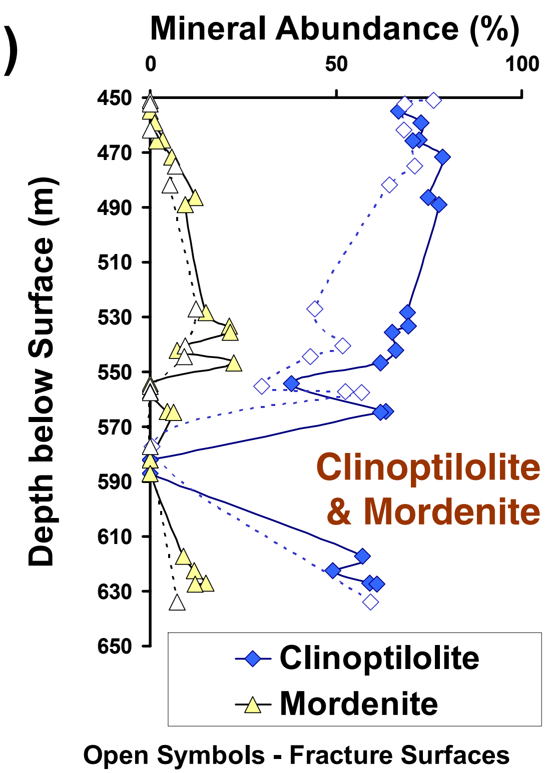
SEM Images of Zeolites on Fracture Surfaces

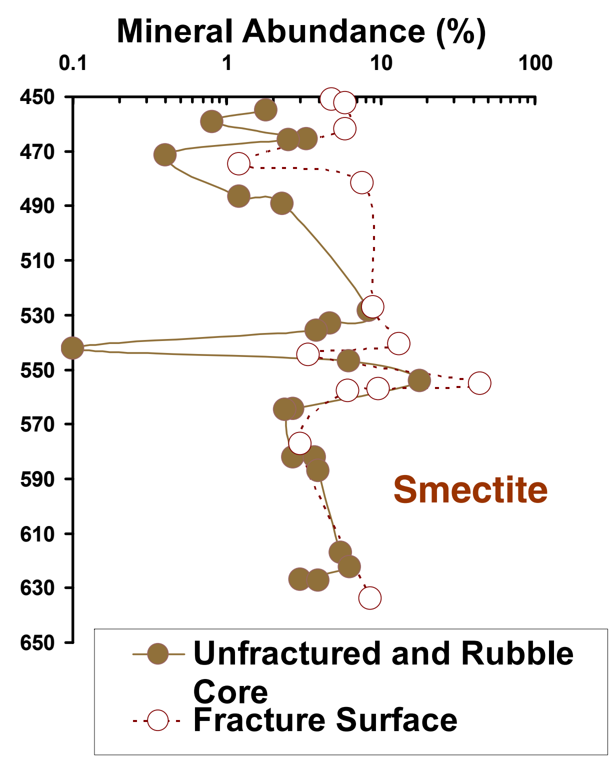
- Zeolites have large surface/volume ratios
  A. tabular clinoptilolite from 451.1 m depth (Tac)
  B. fibrous mordenite from 474.8 m (Tac)
  C. fibrous mordenite from 481.7 m (Tac)
  D. fibrous mordenite from 544.6 m (bedded tuff below Tac)



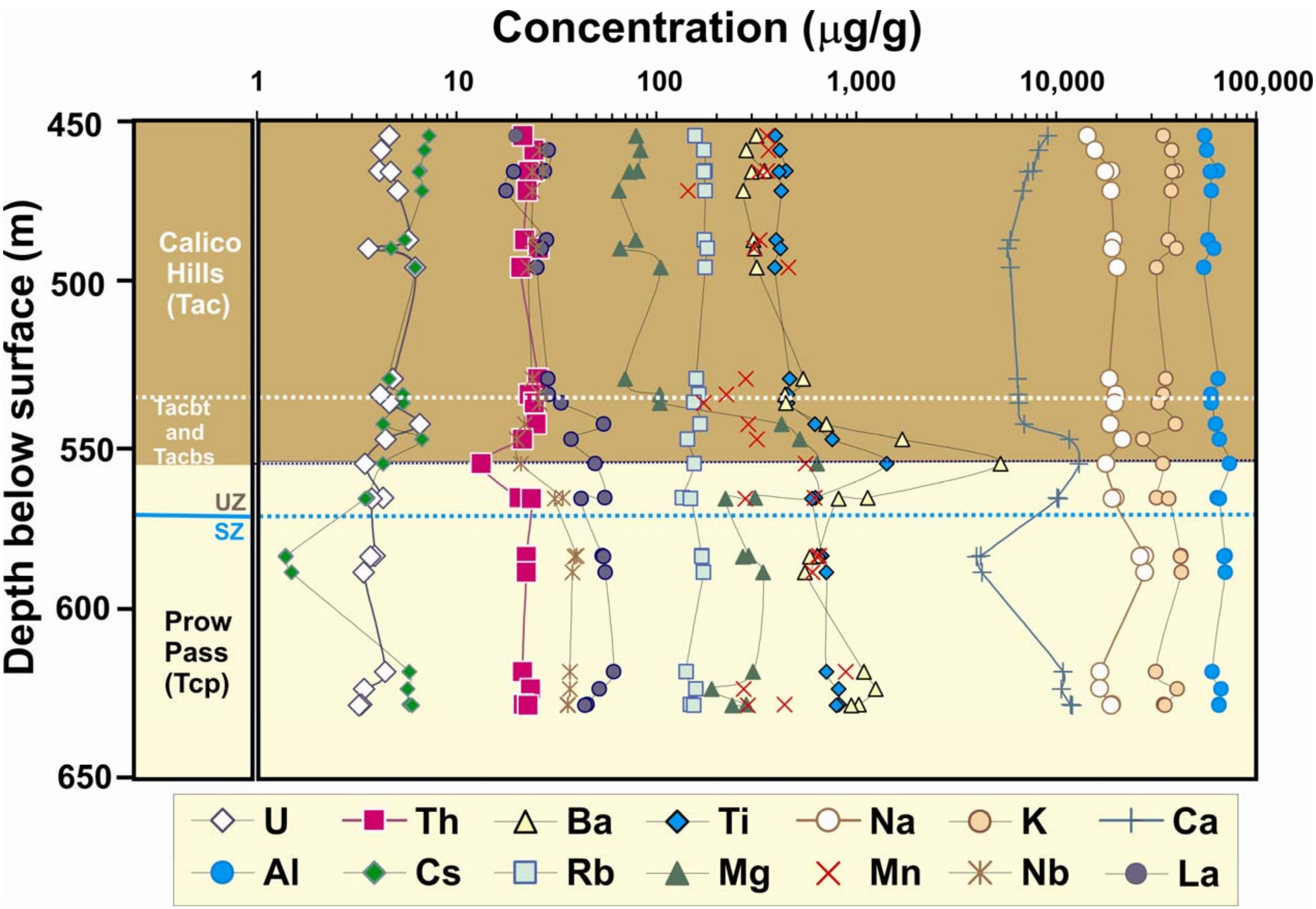
Secondary Minerals in Subrepository Units

- 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)

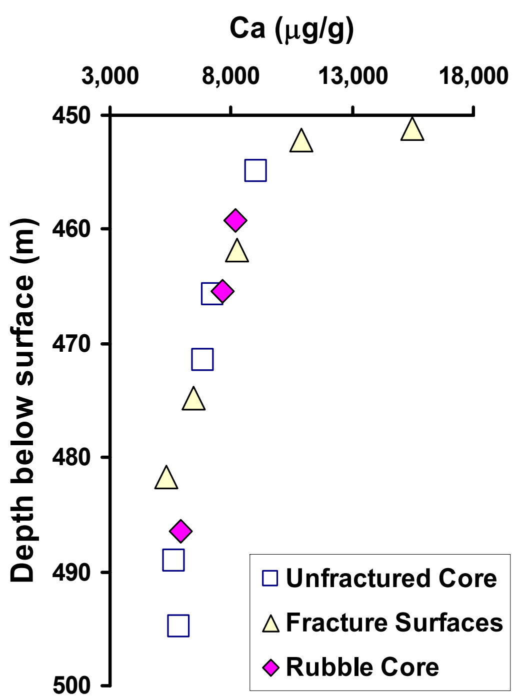


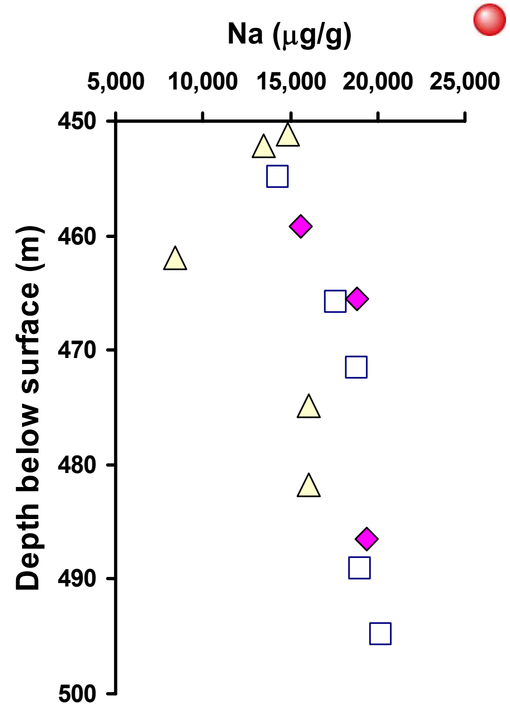


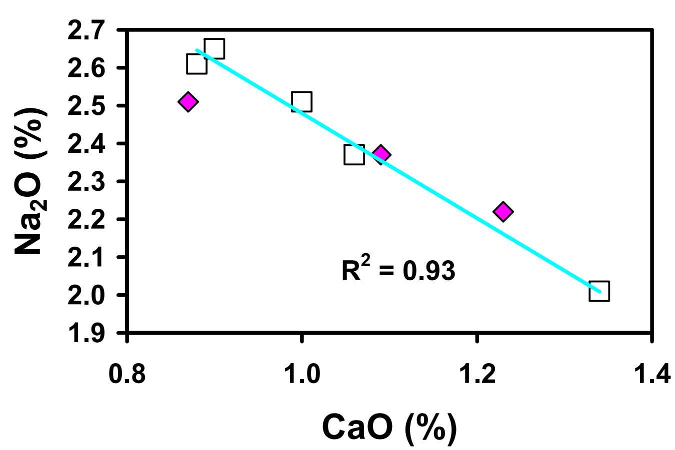
Chemical Composition vs Depth in USW SD-9



Variations in Na and Ca in Tac



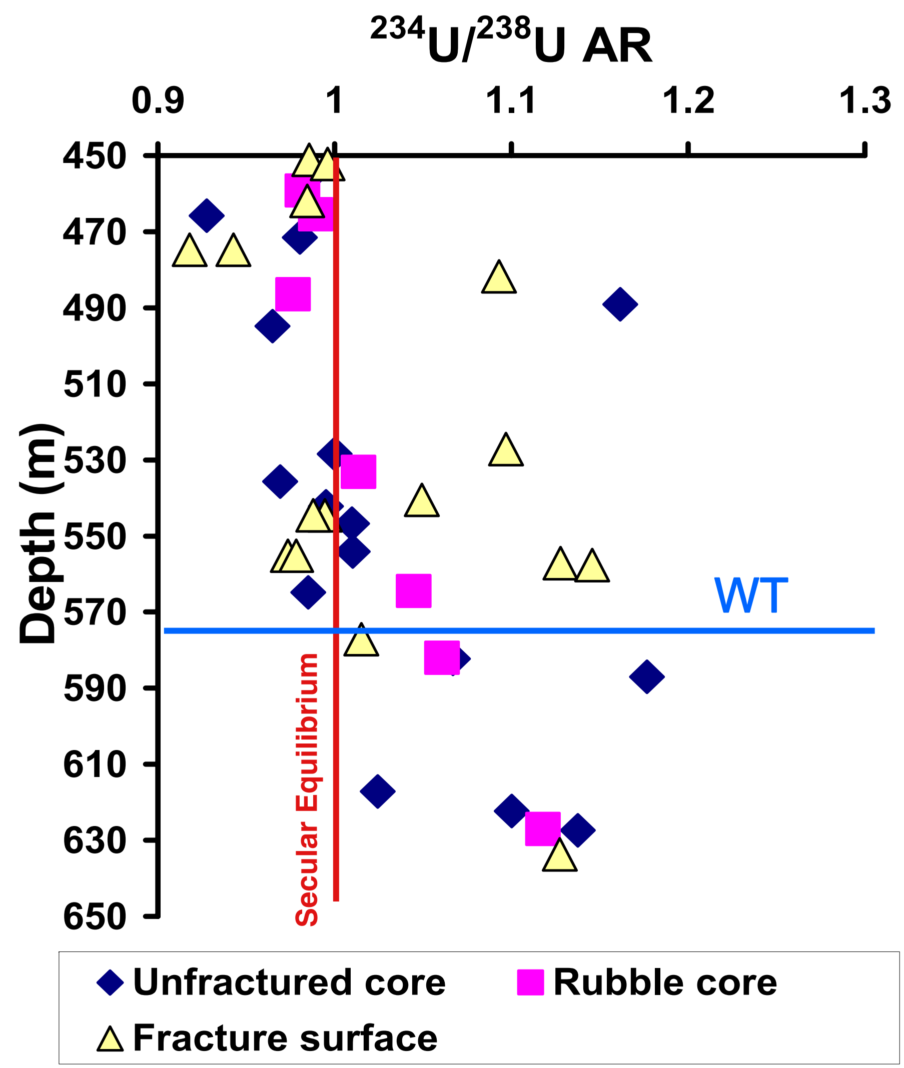




- **Accumulation of Ca is complemented by Na loss in the upper 50 m of zeolitized Tac**
  - **Downward water movement and cation exchange within the zeolite sequence**
  - **Similar magnitude of cation exchange in unfractured core, rubble core, and fracture surface samples**
    - **Evidence for matrix flow**
    - **No evidence of more ion exchange in fractures**
  - **Results are consistent with previous studies (Vaniman et al., 2001)**

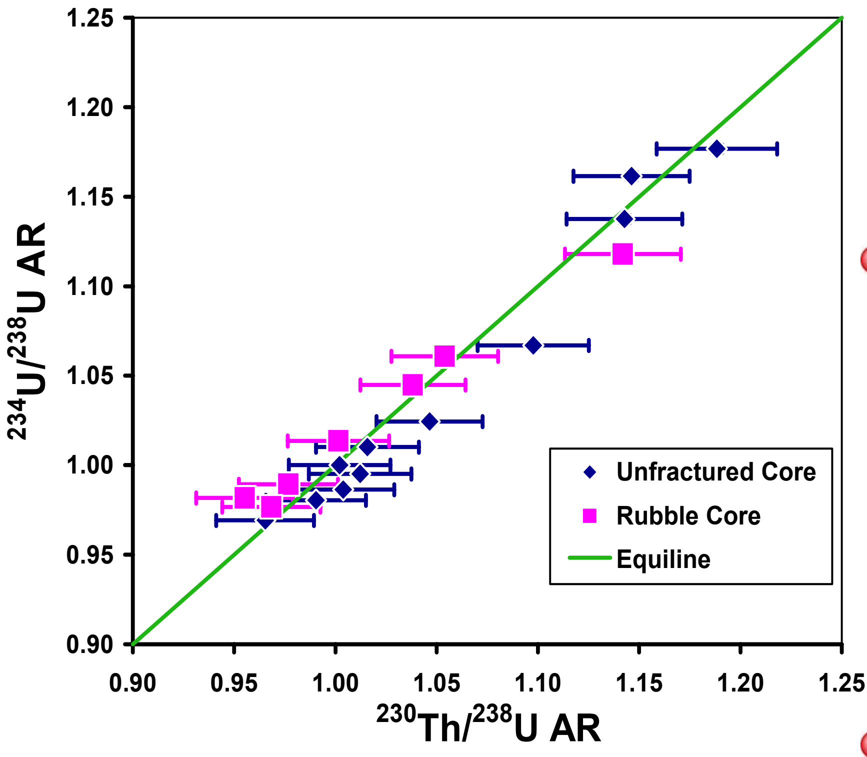
Variations of $^{234}U/^{238}U$ AR with Depth in USW SD-9

- Whole-rock $^{234}U/^{238}U$ 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
- $^{234}U/^{238}U$ AR > 1 in some samples of zeolitized tuff
  - Different from welded tuffs from the proposed repository horizon with $^{234}U/^{238}U$ AR < 1
  - Interpreted as U sorption from ^{234}U-enriched water percolated through the UZ



OST&I
OCRWM Office of Science and Technology and International

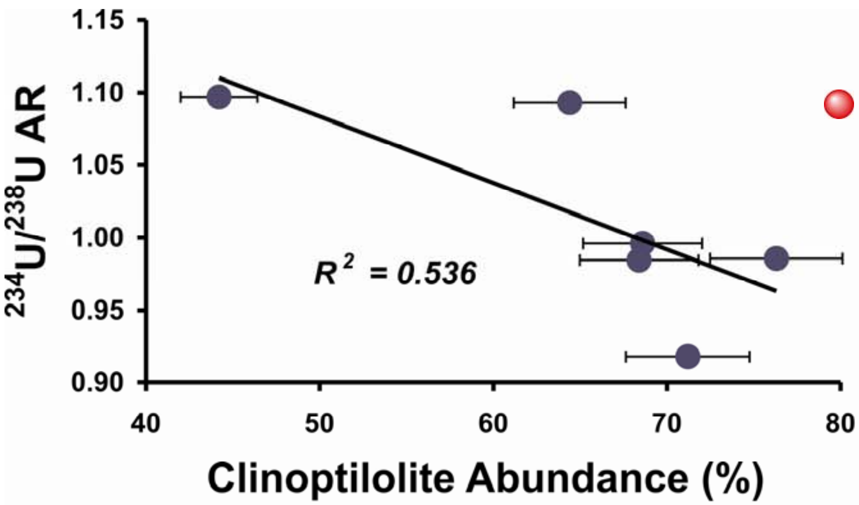
Time Scale of U Mobility

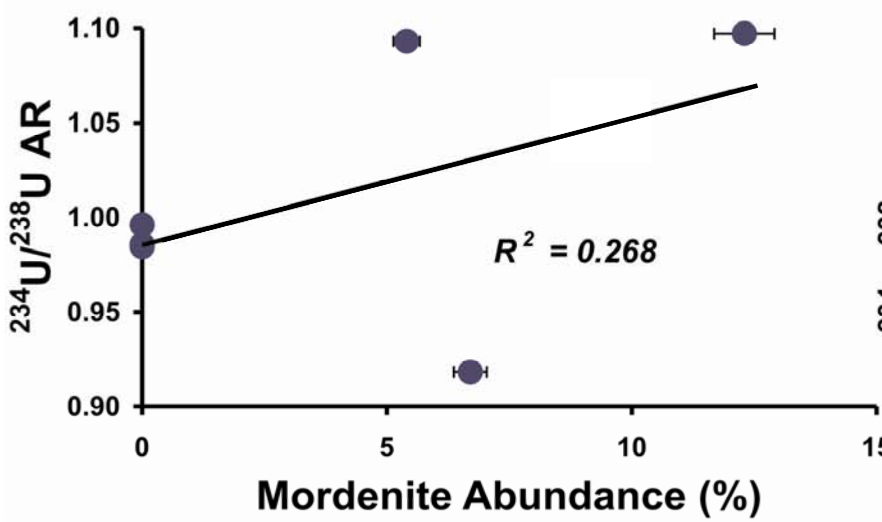


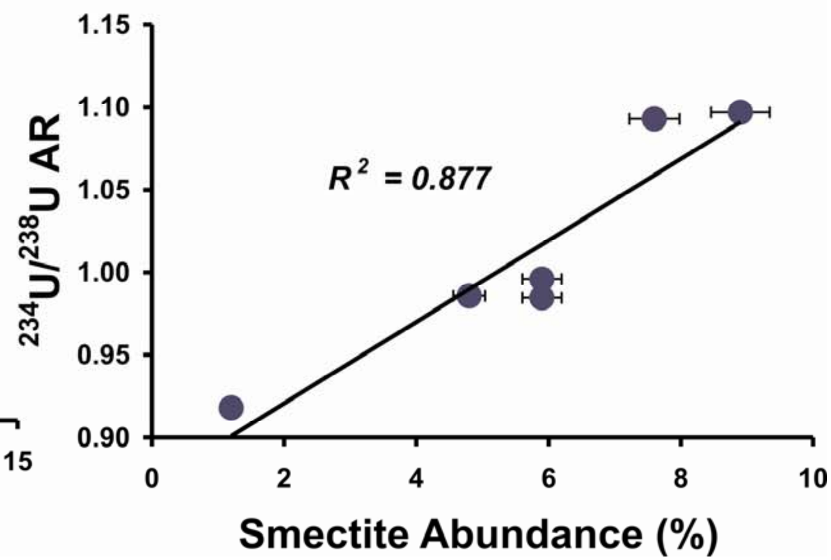
- Similar $^{234}U/^{238}U$ and $^{230}Th/^{238}U$ ARs in unfractured and rubble core
  - No recent preferential U mobility relative to less mobile Th
- Episodic process
  - ~300 k.y. is required for ^{230}Th to reach radioactive equilibrium with its parent ^{234}U
  - >1 m.y. is required for ^{234}U to reach equilibrium with its parent ^{238}U
- Continuous process (steady state)
  - Rates of ^{238}U mobility are slow
  - U dissolution rate constant ~10^{-8} y^{-1} (Latham and Schwarcz, 1988)

Mineral Abundances versus $^{234}U/^{238}U$ AR in Tac

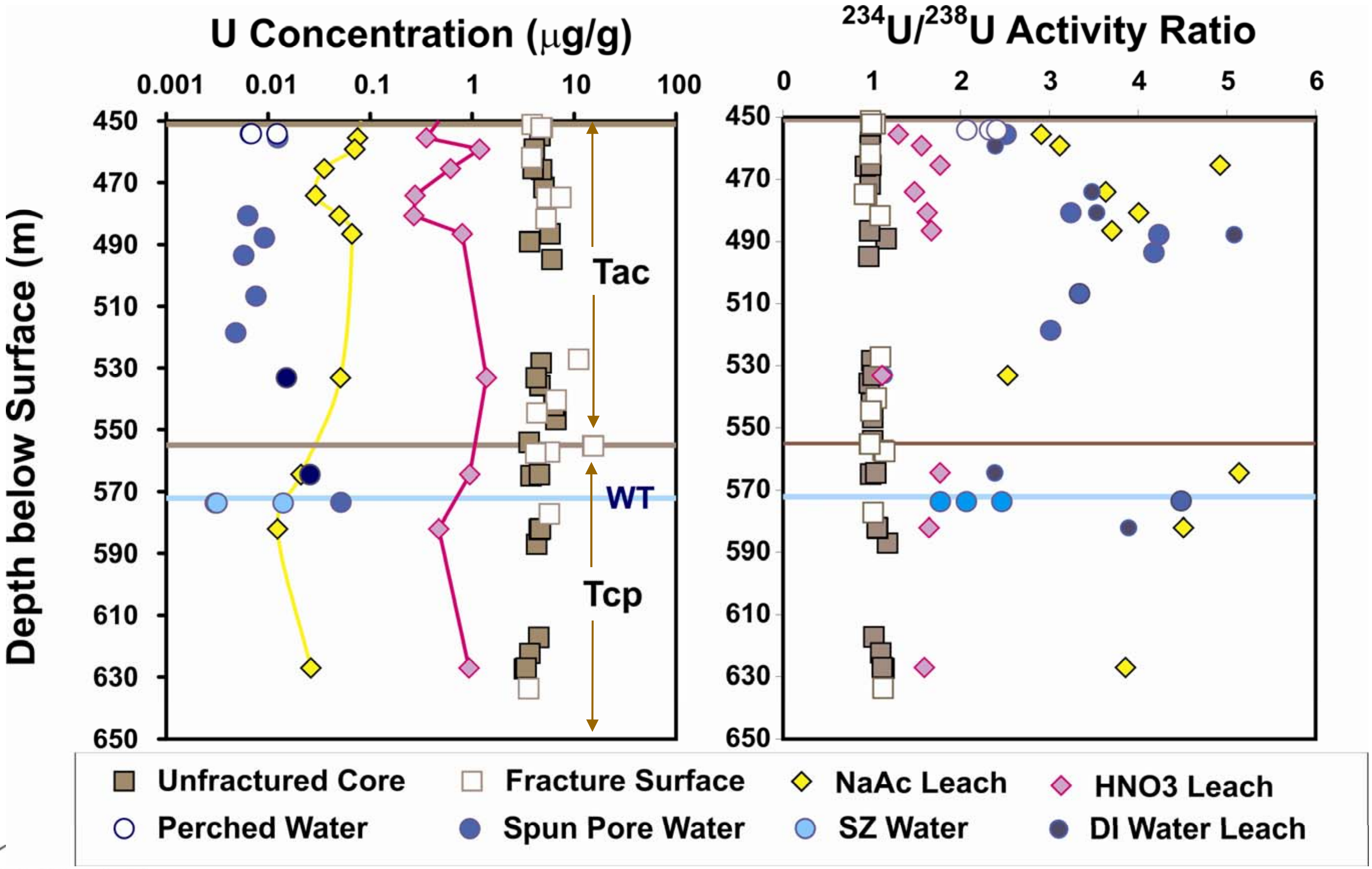
- $^{234}U/^{238}U$ AR > 1 in rocks indicates presence of sorbed U component
- $^{234}U/^{238}U$ ARs in samples from fracture surfaces correlate with smectite abundance in upper 50 m of Tac
  - U sorption by smectite
  - Potential for U retardation in fractures





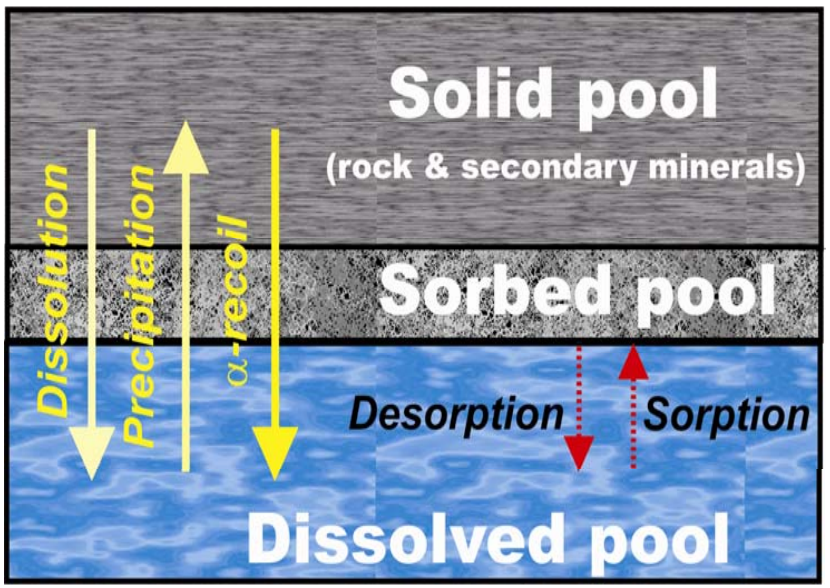


U concentrations and $^{234}U/^{238}U$ AR in rock, waters, and rock leachates with depth in USW SD-9



$^{234}U/^{238}U$ AR in Water-Rock System

- $[U]_{Rock} > [U]_{NaAc\ Leach} > [U]_{Water}$
- $^{234}U/^{238}U$ AR NaAc Leach ≈ $^{234}U/^{238}U$ 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
     - ($^{234}U/^{238}U$ AR<1)
  2. Sorbed U
     - ($^{234}U/^{238}U$ AR>1, ≈ water value)
  3. U in water
     - ($^{234}U/^{238}U$ AR>1)

In situ Retardation Factor R_f for Uranium

R_f = (water velocity)/(transport rate of radionuclide)

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

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

C_{sorbed} (µg/g); C_{water} (µg/mL); ρ_s – rock density (g/cm^3); ϕ – 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 ~7 mL/g**
- ***In situ* retardation factor for U in samples of zeolitized rocks (ϕ ~ 0.25 and ρ_s ~ 1.7 g/cm^3) R_f of ~ 36**

Future Reactive Transport Modeling

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

- **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 (water flux) / (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 $^{234}U/^{238}U$ and $^{230}Th/^{238}U$ 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 $^{234}U/^{238}U$ ARs in rock samples show that zeolitized tuff can adsorb U from percolating water (*in situ* K_d~7; R_f~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

D. L. Bish, D.T. Vaniman, S. J. Chipera, and J. W. Carey (2003) The distribution of zeolites and their effects on the performance of a nuclear waste repository at Yucca Mountain, Nevada, U.S.A. *American Mineralogist, 88, 1889–1902.*

S.J. Chipera and D.L. Bish (2002) FULLPAT: A Full-Pattern Quantitative Analysis Program for X-Ray Powder Diffraction Using Measured and Calculated Patterns," *J. Appl. Crystallography 35, 744-749.*

D.A. Engstrom and C.A. Rautman (1996) Geology of the USW SD-9 Drill Hole, Yucca Mountain, Nevada, SAND96-2030, ACC: MOL.19970508.0288, 128 p., Sandia National Laboratories, Albuquerque, New Mexico (1996). Accessed January 31, 2006, at http://www.lsnnet.gov (LSN# DEN000707221).

A.G. Latham and H.P. Schwarcz (1987) On the Possibility of Determining Rates of Removal of Uranium from Crystalline Igneous Rocks Using U-Series Disequilibria—1: A U-Leach Model and its Applicability to Whole-Rock Data. *Appl. Geochem. 2, 55-65.*

K. Maher, D. J. Depaolo, and Jo Chiu-Fang Lin (2004) Rates of silicate dissolution in deep-sea sediment: In situ measurement using $^{234}U/^{238}U$ of pore fluids. *Geochim. Cosmochim. Acta, 68, 4629-4648.*

D.T. Vaniman, S.J. Chipera, D.L. Bish, J.W. Carey, and S.S. Levy (2001) Quantification of Unsaturated-Zone Alteration and Cation Exchange in Zeolitized Tuffs at Yucca Mountain, Nevada, USA. *Geochim. Cosmochim. Acta 65, 3409*

D.T. Vaniman, A. Furlano, S. Chipera, J. Thompson, and I. Triay (1996) Micro-autoradiography in studies of Pu(V) sorption by trace and fracture minerals in tuff. *Materials Research Society Symposium Proceedings, 412, 639–646.*