

## HLWYM HEmails

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**From:** Miriam Juckett  
**Sent:** Friday, June 30, 2006 4:46 PM  
**To:** Roberto Pabalan; James Myers; English Pearcy  
**Subject:** FW: USGS dust sample request  
**Attachments:** Peterman\_2006 IHLRWM \_DOE Review Draft\_03-29-06.doc

Just got this report from Zell. He's very helpful!

Miriam Juckett, Research Scientist  
Southwest Research Institute  
Center for Nuclear Waste Regulatory Analyses 6220 Culebra Road, San Antonio, TX 78238  
Email: mjuckett@swri.org  
Office: (210)522-3266

-----Original Message-----

From: Zell Peterman/YM/RWDOE [mailto:Zell\_Peterman@ymp.gov]  
Sent: Friday, June 30, 2006 3:42 PM  
To: mjuckett@cnwra.swri.edu  
Subject: RE: USGS dust sample request

Hi Miriam: Nice to hear from you again. The numbers are the locations given in an engineering notation of distance along the tunnel. In this designation, the first number indicates hundreds of meters and the second indicates meters less than a hundred meters. So the designation 8+61 indicates a location 861 meters along the tunnel from a reference point at the north portal. Virtually all of our samples from the tunnel (dust, rock, fractures minerals) are located using this designation.

BSC has a cyclone running at the south portal to collect dust samples (usually less than a gram per month). We have analyzed the soluble components from a couple so far, and they contain much more salts than the surface samples that we sent you. If you are interested in doing analyses of any of these, I'm sure that you could request samples through the proper channels.

I had prepared a report on the geochemistry of natural materials in the near field environment for the International High-Level Radioactive Waste Symposium, but it did not receive approval by the DOE in time for the presentation in April. I've attached a copy as it summarizes the geochemistry of the various dust collections. I hope to present it at the Materials Research Symposium in Boston in November.

(See attached file: Peterman\_2006 IHLRWM \_DOE Review Draft\_03-29-06.doc)

Miriam Juckett <mjuckett@cnwra.swri.edu> on 06/30/2006 11:22:16 AM

Please respond to mjuckett@cnwra.swri.edu

To: "'Zell Peterman/YM/RWDOE'" <Zell\_Peterman@ymp.gov>  
cc:  
Subject: RE: USGS dust sample request

Hi Zell-

This is Miriam from the CNWRA. It's been a while since you sent me these samples, but I am still doing work on them. I was wondering if you could clarify what the numbers listed below by the ESF samples indicate (8+61 to 8+62.7) etc.

Hope all is well with you. Thanks for your time!

Miriam Juckett, Research Scientist  
Southwest Research Institute  
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Email: mjuckett@swri.org  
Office: (210)522-3266

-----Original Message-----

From: Zell Peterman/YM/RWDOE [mailto:Zell\_Peterman@ymp.gov]  
Sent: Friday, December 17, 2004 4:32 PM  
To: mjuckett@cnwra.swri.edu  
Cc: Carol Hanlon/YD/RWDOE; Cliff Howard/YM/RWDOE  
Subject: RE: USGS dust sample request

Hi Miriam: We just completed analyses of some of our surface dust samples and was very surprised to see that the soluble salt contents are unusually low. The two surface samples that we sent you have soluble salt contents (wt percent) of 0.024 and 0.026 percent, respectively. The estimated salt contents that I mentioned to you were based on reported values for dust from pan collectors that also collect precipitation. We can only conclude that when the dust accumulates on rock surfaces or soil, the soluble salts are leached out. BSC will be installing units that will collect only dryfall so we will then be able to measure the actual soluble salt contents excluding rainwater salts. If you need more subsurface samples, just let us know.

----- Forwarded by Zell Peterman/YM/RWDOE on 12/17/2004  
03:23 PM -----

Miriam Juckett <mjuckett@cnwra.swri.edu> on 12/02/2004 01:21:16 PM

Please respond to mjuckett@cnwra.swri.edu

To: "Connie Sorell/YM/RWDOE" <Connie\_Sorell@notes.ymp.gov>  
cc: "Carol Hanlon/YD/RWDOE" <Carol\_Hanlon@notes.ymp.gov>, "Zell Peterman/YM/RWDOE" <Zell\_Peterman@ymp.gov>  
Subject: RE: USGS dust sample request

User Filed as: Not Categorized in ERMS

I received the samples today.  
Thank you very much.

Miriam Juckett, Scientist  
Southwest Research Institute  
Center for Nuclear Waste Regulatory Analyses 6220 Culebra Road, San Antonio, TX 78238  
Email: mjuckett@swri.org  
Office: (210)522-3266

-----Original Message-----

From: Connie Sorell/YM/RWDOE [mailto:Connie\_Sorell@notes.ymp.gov]  
Sent: Wednesday, December 01, 2004 3:26 PM  
To: miriam.juckett@swri.org  
Cc: Carol Hanlon/YD/RWDOE; Zell Peterman/YM/RWDOE  
Subject: USGS dust sample request

Dear Ms. Juckett,  
Per Zell Peterman's request, 4 bulk dust samples were shipped to you via FedEx.

Samples sent on 12/01/2004:

SPC00574982	10.5 grams, unsized, ESF 8+61 to 8+62.7
SPC00574983	10.5 grams, unsized, ESF 12+63.2 to 12.65A
SPC01030803	11.0 grams, unsized, surface sample
SPC01030805	10.3 grams, unsized, surface sample

No bulk dust samples are available from the Cross Drift.

Please acknowledge receipt of these samples upon delivery.

Regards,  
Connie Sorell  
PST, Environmental Science Team  
EST/USGS

**Hearing Identifier:** HLW\_YuccaMountain\_Hold\_EX  
**Email Number:** 1494

**Mail Envelope Properties** (02e201c69c86\$3f612680\$12c8a281)

**Subject:** FW: USGS dust sample request  
**Sent Date:** 6/30/2006 4:46:22 PM  
**Received Date:** 6/30/2006 4:46:34 PM  
**From:** Miriam Juckett

**Created By:** mjuckett@cnwra.swri.edu

**Recipients:**

"Roberto Pabalan" <rpabalan@cnwra.swri.edu>  
Tracking Status: None  
"James Myers" <jmyers@cnwra.swri.edu>  
Tracking Status: None  
"English Percy" <epearcy@cnwra.swri.edu>  
Tracking Status: None

**Post Office:** cnwra.swri.edu

<b>Files</b>	<b>Size</b>	<b>Date &amp; Time</b>
MESSAGE	5335	6/30/2006 4:46:34 PM
Peterman_2006 IHLRWM_DOE Review Draft_03-29-06.doc		696384

**Options**

**Priority:** Standard  
**Return Notification:** No  
**Reply Requested:** No  
**Sensitivity:** Normal  
**Expiration Date:**  
**Recipients Received:**

## Geochemistry of Natural Components of the Near-Field Environment, Yucca Mountain, Nevada

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**Abstract** – *The chemical compositions of the host rock, pore water, seepage water, dust, and accumulated? brown water have been determined to assess possible reactions that may occur among the natural components, waste ~~canisters~~packages, and other materials introduced into the near-field environment of the proposed nuclear waste repository at Yucca Mountain, Nevada. The rock unit hosting the potential repository has a relatively uniform chemical composition as shown by a mean coefficient of variation (CV) of 8.6 percent for major elements. In contrast, the variabilities in the compositions of underground dust (bulk and water-soluble fractions), pore water, and seepage water are large with mean CVs ranging from 28 to 62 percent. High-chloride brown water that has accumulated in a sealed part of an underground tunnel indicates reaction between seepage or condensate and introduced materials, such as rubber in the conveyor belt and galvanized iron in ventilation ducts. The composition of brown water is highly variable with a mean CV of 83 percent. Except for the composition of the host rock, the geochemistry of the natural components of the near-field environment likely will change with time because of changes in precipitation and percolation.*

## I. INTRODUCTION

Construction of and emplacement of waste at the proposed high-level nuclear waste repository at Yucca Mountain, Nevada, could change the natural environment through reactions that may occur among the natural components and other materials introduced into the waste emplacement drifts during the operation of the proposed repository. The purpose of this paper is to summarize the geochemistry of the natural components of the near-field environment in the proposed nuclear waste repository at Yucca Mountain. The near-field environment is the area within the repository where the natural hydrogeologic system will be affected by the excavation of the repository and emplacement of waste, including the waste emplacement drifts, any introduced materials in the drifts (e.g., waste packages, rails, inverters, ground support, drip shields, ~~rubber conveyor belts~~), and the rock immediately surrounding the drifts. The Enhanced Characterization of the Repository Block (ECRB) Cross Drift and the Exploratory Studies Facility (ESF) allow access to the underground at Yucca Mountain, Nevada, for conducting a variety of studies, including collection of water, rock, and dust samples for geochemical analyses (Fig. 1). Because of the variety of natural and introduced materials and the elevated temperatures associated with the repository, complex reactions of these materials may occur (BSC, 2003). During emplacement of waste ~~canisters~~~~packages~~, temperature and humidity will be controlled by ventilation. After the drifts are sealed, temperature will increase to above boiling (greater than 96 degrees Celsius [ $>96^{\circ}\text{C}$ ]), producing a dry-out zone in the adjacent rock mass. As the temperature decreases with cooling of the waste, humidity will increase to nearly 100 percent over  $10^4$  to  $10^6$  years (e.g., Apted et al., 2005) to a condition similar to that currently observed in the sealed part of the ECRB Cross Drift (Salve and Kneafsey, 2005).

The geochemistry of the natural components of the near-field environment is presented in the context of the hydrogeologic framework of Yucca Mountain. The mountain is composed of stratified welded and nonwelded felsic volcanic rocks (Spengler and Fox, 1989). The rock units of interest compose the Paintbrush Group of Miocene age. In descending stratigraphic order (Buesch et al., 1996), the Paintbrush Group is composed of (1) the Tiva Canyon Tuff (Tpc), which crops out over much of Yucca Mountain; (2) a sequence of named and unnamed nonwelded tuffs including the Yucca Mountain Tuff and the Pah Canyon Tuff; and (3) the Topopah Spring Tuff (Tpt), which will host the repository. The Tpc and Tpt are mostly densely welded units that are compositionally zoned, with the lower two-thirds to three-quarters being composed of phenocryst-poor (crystal-

poor) rhyolite (Tpcp and Tptp) and the upper parts transitioning from rhyolite to phenocryst-rich (crystal-rich) trachyte (Tpcr and Tptr) (Peterman and Cloke, 2002).

The lithostratigraphic (rock) units have been grouped into hydrostratigraphic units based on degree of welding and other physical properties (DOE, 1988). The densely welded part of the Tiva Canyon Tuff is called TCw. The nonwelded tuffs between the welded portions of Tpc and Tpt are called Paintbrush Tuff nonwelded or PTn. The densely welded part of the Topopah Spring Tuff is called TSw (the repository host rock). The compositional variability of these units is shown by concentrations of titanium (Ti) relative to depth in cuttings from borehole USW SD-6 (Fig. 2). The intervals of near-constant concentrations of Ti are the rhyolitic parts of TCw and TSw. The inflection points where Ti concentration starts to increase mark the contacts between the crystal-poor and crystal-rich members of both units, and the compositions of the intervals in which Ti increases are transitional between rhyolite and trachyte. The PTn is compositionally transitional between the uppermost TSw trachyte and the lowermost TCw rhyolite (Fig. 2).

## II. WORK DESCRIPTION

The U.S. Geological Survey is conducting ongoing geochemical studies of (1) the host rock and its contained pore water, (2) underground and surface dust, (3) seepage into the shallow south ramp of the ESF, and (4) brown water that accumulates in a sealed part of the ECRB Cross Drift. The brown water is not a natural component of the near-field environment but rather a reaction product of seepage or condensate with materials introduced into the ECRB Cross Drift.<sup>1</sup>

The volcanic rocks and underground dust are similar in chemical composition because most of the dust was produced by comminution of the rock during construction of the ESF. The chemical composition of the rock units within which the repository will be constructed has been determined by Peterman and Cloke (2002) using 300- to 500-gram pieces of core from the ECRB Cross Drift. Dust from the ESF has been collected and analyzed for major and trace elements in both bulk samples and in water leachates (Peterman et al., 2003; U.S. Geological Survey, unpub. data). The leachates were obtained using deionized water in a water-to-rock ratio of 20:1 (by weight), agitating for one minute, and allowing to stand for one hour before separating the leachates from the

<sup>1</sup> Brown water is not expected to form in the near-field environment during post-closure because potentially reactive materials will be excluded from the emplacement drifts (C. Newbury, U.S. Department of Energy, written commun., March 28, 2006).

<sup>2</sup> Peterman\_2006 IHLRWM Conference DOE Review Draft\_03/29/06

solids. In addition, four samples of dust were heated to 150°C and leached to evaluate compositional changes that ~~might occur as the dust ages in the high temperature environment of the waste package surface~~ may indicate the nature of the ammonium salts in the dust.

Pore water has been analyzed from many samples of drill core from the unsaturated zone, with recent emphasis on the repository units (Peterman and Marshall, 2002). The brown water that accumulates in the sealed part of the ECRB Cross Drift is of special interest because of the large chloride-to-nitrate ratios that may facilitate ~~an~~ an ~~ister~~ localized corrosion (Etien et al., 2004). During each re-entry of the ECRB Cross Drift, samples were collected from puddles of water that have accumulated on plastic sheets and on the conveyor belt. The final collection was made on December 1, 2005, after which the sealed part of the ECRB Cross Drift will remain open.

The opportunity for chemical and isotopic characterization of seepage occurred when water seeped into the south ramp of the ESF following an unusually wet winter in 2004-2005 (BSC, 2005a). Precipitation measured on the east side of Yucca Mountain between October 2004 and February 2005 was 12.75 inches or 3.5 times the 9-year average- (1996-2005) for this time interval (BSC, 2005a). Seepage was first noted on February 2, 2005, at ESF station 75+73.6, located 7,573.6 meters from the north portal of the ESF. Water samples were collected between March 1, 2005, and May 5, 2005, and analyzed for major and trace element concentrations as well as oxygen (O), hydrogen (H), strontium(Sr), and uranium(U) isotopic compositions (BSC, 2005a).

### III. RESULTS AND DISCUSSION

Normal distributions are approximated by many of the analyte concentrations in the data sets for samples of repository-host rhyolite, ESF dust, pore water, brown water, and south ramp seepage, whereas others are moderately to highly right-skewed for which the means exceed the medians. For purposes of characterization and comparison of these distributions, the arithmetic means and standard deviations are used. Arithmetic means represent the integrated composition of any population regardless of the nature of the distribution (if the numbers of samples are sufficiently large). Standard deviations are symmetrical about the mean even for highly skewed distributions. Nonetheless, the standard deviations are a useful measure of the dispersion of the distributions for purposes of comparing compositions in this paper.

Mean compositions of samples of the TSw rhyolite and of finer fractions of dust from the Yucca Mountain area are given in Table I. Much of the major and trace element variability in samples of TSw rock is within or  
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only slightly exceeds analytical precision as determined by duplicate analyses of 20 samples (Peterman and Cloke, 2002).

Five suites or collections of dust samples have been obtained and analyzed (Table I). Two suites were collected in the ESF (Peterman et al., 2003). The first suite consisted of 26 multi-gram samples for which the fractions less than 60 mesh size were analyzed (these data are not summarized here.) A suite of 10 larger samples (200-400 grams) were collected later so that particle-size distributions could be measured and a range of size fractions could be analyzed (Peterman et al., 2003). Dust samples also were collected from the ECRB Cross Drift and at the surface from natural accumulations such as in rock cavities and small dust deposits on the leeward side of rocks and bushes along the crest of Yucca Mountain (U.S. Geological Survey, unpub. data). Finally, four samples of dust were collected from sites where the dust was protected from precipitation (“protected [surface dust](#)” in Table I, U.S. Geological Survey, unpub. data~~-~~). Sample 1034504 was collected from an unused concrete missile silo liner that is lying horizontally in southern Jackass Flats, southeast of the ESF. Samples 1034506 and 1034512 were collected from the attics of the Sample Management Facility (SMF) and the SMF warehouse. Sample 1034510 was collected from an accumulation of wind-blown dust below an open window in a house trailer about 100 meters east of the SMF.

Preliminary differences between compositions of the ESF dust samples and the repository host rock (Table 1) are lower silica ( $\text{SiO}_2$ ) and higher ferrous iron oxide ( $\text{FeO}$ ), magnesium oxide ( $\text{MgO}$ ), calcium oxide ( $\text{CaO}$ ), chlorine ( $\text{Cl}$ ), fluorine ( $\text{F}$ ), and carbon dioxide ( $\text{CO}_2$ ) in the dust samples. Further, the dust contains measurable amounts of organic carbon, which is not detected in the host rock. Some of these differences are related to the fact that these tunnels were constructed through rock types other than rhyolite. The ESF intersects trachyte in both Tpc and Tpt and in nonwelded units all of which are lower in  $\text{SiO}_2$  (67 to 68 percent, U.S. Geological Survey, unpub. data) than the rhyolitic members of these units (76 percent  $\text{SiO}_2$ , Peterman and Cloke, 2002). The ECRB Cross Drift is constructed largely in Tpt rhyolite, and ECRB dust compositionally is similar to the rhyolite (Table 1). Some other chemical differences between rock and dust samples are due to non-rock components in the dust. For example, the elevated  $\text{FeO}$  contents in dust samples likely are due to Fe particulates (reported as ferrous iron in the analyses) from abrasion of various metal components of introduced materials, including rails and train wheels. The larger  $\text{CaO}$  and  $\text{CO}_2$  contents of dust probably result from the preferential comminution of calcite in fractures and cavities relative to the tuff, and the larger  $\text{F}$  contents of the dust may relate to the

incorporation of fluorite, which occurs in many fractures. The organic carbon is probably from a variety of sources, but much of it is likely rubber from abrasion of the conveyor belt by muck haulage.

~~Although Soluble-soluble salts in dust that may accumulate and deliquesce on waste canisters/packages, the deliquescent salts are not expected to lead to localized corrosion-may deliquesce and facilitate corrosion~~ (BSC, 2005b), ~~although~~ Apted et al. (2005), ~~persuasively argue that this is an unlikely scenario~~. The mean solute compositions of water leachates of the soluble fractions of the dust samples in Table I are given in Table II in mass of solute per mass of rock (milligrams/kilogram [mg/kg]). The mean soluble fraction of ESF dust samples is 0.47 weight percent (Table II), whereas atmospheric dust contains considerably more, with a mean of 13± 8 percent based on analyses given by Reheis (2003, Table 3B). ECRB Cross Drift dust samples contain smaller amounts of soluble salts (mean 0.13 percent), probably because there was less sustained construction activity there than in the ESF. Samples of surface dust (Table II) have the lowest mean soluble salt content of 0.08 percent. Apparently, the salts in the surface dust are dissolved by precipitation and washed into the subjacent soil or rock depressions where they can be eventually carried downward by infiltrating water. Two of these samples were collected from bowl-shaped depressions in bedrock surfaces where the salts in the dust could only have been lost by dissolution and infiltration into the bedrock. In contrast, the much larger value of 13± 8 percent for atmospheric dust (Reheis, 2003, Table 3B) is for samples from collectors that also trap precipitation that evaporates, leaving salts. The mean soluble salt content of the four protected surface dust samples (Table II) ranges widely from 0.21 to 6.99 percent. Time-integrated samples of atmospheric dust that have not been leached of salts by precipitation and do not include salts from evaporated precipitation would be of value for characterizing the dust that may be introduced into the repository over the long term. ~~Such samples are not yet available.~~

An experiment of heating three dust samples before leaching yielded surprising results (U.S. Geological Survey, unpub. data). For each sample, one split was leached and analyzed as previously described. The second split was heated to 150°C for 72 hours, cooled to room temperature, and then leached. It was expected that ammonium and one or more of the anions would be lost upon heating, thus indicating the type of ammonium salts present. The results are displayed on a spider diagram (Fig. 3) where the leachate composition of the heated dust sample splits is divided by the leachate composition of the unheated splits. If no change had occurred from heating, the results would plot within analytical error around a ratio of one. One of the ESF samples (574984)

and the sample of protected [surface dust](#) (1034512) lost ammonium and corresponding nitrate but not in a stoichiometric proportion. The duplicate samples (57991) did not lose ammonium, although they lost about 20 percent of their nitrate. More surprisingly, the soluble chloride in both ESF samples increased about 250 percent, and fluoride in one sample (57001) increased by about 170 percent. The soluble fraction of this sample also showed a substantial increase in sodium (Na) and potassium (K), whereas ESF sample 574984 showed an increase in calcium (Ca) and magnesium (Mg). These relations clearly reflect the presence of thermally unstable materials in the dust that break down to water-soluble fractions at a temperature of 150°C. ~~The source of Cl and possibly of F likely is particulates of rubber from the conveyor belt.~~

Mean solute compositions (U.S. Geological Survey, unpub. data) of samples of south ramp seepage, PTn pore water (core from borehole USW SD-9), TSw pore water from the ESF and ECRB, and brown water collected from the sealed part of the ECRB Cross Drift are in Table III. Detailed discussions of the solute compositions of south ramp seepage (Oliver and Whelan, this volume) and of brown (puddle) water (Marshall et al., this volume) are given elsewhere in this volume. The concentrations of solutes in the PTn pore water samples range widely, and some vary systematically as a function of depth, such as in USW SD-9 (Scofield and Oliver, 2003). For example, Cl concentrations decrease approximately linearly from 233 milligrams per liter (mg/L) in the stratigraphically highest sample from the PTn to 27 mg/L in the lowest sample (data not shown), with a mean of 128 mg/L. In contrast, the mean Cl concentration for the south ramp seepage is 60 mg/L and the mean for TSw pore water is 47 mg/L, which are indistinguishable within respective uncertainties (Table III). The systematic decrease in Cl through the PTn may be due to decreasing evaporation with depth or may represent temporal changes in the Cl content in infiltration water.

Ion concentrations in the brown water range widely as shown by the large standard deviations (Table III). From a data set for 21 samples collected from puddles in the sealed ECRB cross drift (U.S. Geological Survey, unpub. data), analyses of three samples were excluded from the statistical evaluation because their solute concentrations are ~~much smaller than the other samples~~[outliers to the main distribution](#). Most of the brown water samples are highly saline, with a mean Cl content of 4,950 mg/L—two orders of magnitude greater than TSw pore water. The dissolved ion composition is the result of the reaction of condensate or seepage with introduced materials, such as the conveyor belt, electrical cables, or gaskets in the ventilation ducts, to produce its chloride-rich composition. The large concentrations of dissolved ions may reflect evaporative concentration, which also is

indicated by oxygen and hydrogen isotopic compositions (Oliver and Whelan, this volume). Microbial activity is suspected to be the cause of the low nitrate concentrations relative to those of sulfate, bicarbonate, and chloride.

~~Because the brown water potentially could be corrosive, environmental conditions that lead to its formation should be avoided or mitigated in the emplacement drifts.~~

The mean solute concentrations of brown water and south ramp seepage water are compared to the mean concentrations of TSw pore water in Figure 4. Typically, mean solute concentrations of TSw pore water and south ramp seepage are within a factor of two. In contrast, the brown water is highly enriched in cations and chloride and sulfate relative to mean values for TSw pore water. The highly variable enrichment of cations and anions in the brown water relative to pore water and seepage indicates that evaporative processes alone cannot account for the brown water composition. The three-thousand-fold enrichment of zinc (Zn) in the brown water is the result of interaction with the galvanized steel ventilation duct. The enrichment in manganese may be due to interaction with rock bolts, which are probably high-manganese steel. The lithium enrichment likely reflects the presence of salts derived from construction water that was tagged with lithium bromide. Mean silica concentrations in samples of brown water and south ramp seepage are similar to mean concentrations in samples of TSw pore water, which probably are saturation values.

The ratio of nitrate-to-chloride concentrations of near-field materials is a critical parameter in assessing the potential for ~~anister-localized~~ corrosion (Etien et al., 2004). Figure 5 shows the chloride and nitrate concentrations in samples of the ESF dust leachates, brown water, and TSw pore water. The ~~one-to-one line for~~  $\text{NO}_3^-$  ~~and to~~  $\text{Cl}^-$  ~~ratios is are~~ shown for reference. ~~Because of the lower nitrate ( $\text{NO}_3^-$ ) to chloride ( $\text{Cl}^-$ ) ratios in the pore water and brown water samples, they potentially may be more corrosive than the soluble fractions of dust.~~

Except for the uniform composition of the host-rock rhyolite, the other materials discussed here show substantial variability in composition, as indicated by relatively large standard deviations for many of the analyte distributions. This variability among materials can be compared using the coefficient of variation (CV), which is the standard deviation divided by the respective mean analyte concentration (this quotient is expressed in percent). The CVs for many of the analytes are normally distributed so their means and standard deviations can be compared (Table IV). The distributions that show the smallest average variabilities in major elements are the analyses of host-rock rhyolite samples (mean CV of 8.6 percent) and the analyses of surface dust samples (mean CV of 9.2 percent). The largest mean CVs are for the samples of brown water (mean CV of 83 percent) and the

soluble fraction of surface dust (mean CV of 81 percent). The mean CVs for the other distributions ranging from 28 to 62 percent are indistinguishable from one another.

In considering the geochemistry of the near-field environment, time is an important parameter. The uniform composition of the host rock will not change with time, but the compositions of dust, seepage, and pore water likely will change over the next million years (Zhu et al., 2003) because their compositions, in part, are controlled by long-term climate change, including amount of precipitation and infiltration. Considering perched water compositions at Yucca Mountain, Zhu et al. (2003) estimate mean recharge for the Holocene and Pleistocene to be 5 and 15 millimeters per year (mm/yr), respectively, using chloride mass balance calculations. Using the mean Cl concentration of 47 mg/L for TSw (Table III) pore water samples, a flux of 1.3 mm/yr for the Holocene is calculated using the same parameters as Zhu et al. (2003). Climate change also may affect the composition of atmospheric dust that will infiltrate the proposed repository. Fabryka-Martin et al. (1997) noted that the filling of playas by water during wetter climates might reduce the salt content of atmospheric dust in the region.

#### IV. CONCLUSIONS

Reliable characterization of the chemical compositions of the natural components in the near-field environment is essential for understanding the conditions that will develop at elevated temperatures in and around the emplacement drifts. Key questions for evaluating repository performance are how the natural materials (Tables I and II) will respond to higher temperatures following emplacement of waste, and how they will react with one another and with introduced materials, including the waste [canisters/packages](#), during the heating and cooling phases (BSC, 2003).

A major challenge in using the geochemical properties of the near-field materials in predicting the long-term near-field environment is dealing with the large compositional variability of pore water, potential seepage, and dust. The host rock for the proposed repository is an exception because it is remarkably uniform at the lithostratigraphic zonal scale as shown by Peterman and Cloke (2002). With increased infiltration resulting from increased precipitation, pore water and seepage will become more dilute in dissolved solids, but how key parameters, such as nitrate-to-chloride ratios may change, is unknown. Climate change will affect the composition of atmospheric dust that will infiltrate the repository. Local sources of salts may be reduced if the playas become wet, and it might be expected that the soluble salt content of dust will be reduced.

## ACKNOWLEDGMENTS

The authors acknowledge the analytical support from Kevin Scofield and Loretta Kwak. Reviews by Mel Gascoyne (Gascoyne Geoprojects) and Charles Bryan (Sandia National Laboratories) substantially improved the manuscript. We also thank Charles Bryan for suggesting the experiment to heat dust samples prior to leaching. The study was done by the U.S. Geological Survey, in cooperation with the U.S. Department of Energy, under Interagency Agreement DE-AI28-02RW12167.

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TABLE I. Mean compositions and standard deviations for repository host rock (Tpt rhyolite) and underground and surface dust samples, Yucca Mountain, Nevada. [Data for Tpt rhyolite are from Peterman and Cloke, 2002), Data for ESF dust are from Peterman et al (2003), Data for ECRB dust, surface dust, and protected surface dust are from U.S. Geological Survey (unpub. data). Protected surface dust refers to dust that was protected from leaching by precipitation as described in the text. Dashes (---) mean that this constituent was not analyzed. The low sums for samples 1034506 and 1034512 indicate the presence of one or more additional components that were not analyzed.]

Element	TSw (n=20)		ESF Dust (n=11)		ECRB Dust (n=6)		Surface Dust (n=12)		Protected Surface Dust			
	Mean	Stdev	Mean	Stdev	Mean	Stdev	Mean	Stdev	1034504	1034506	1034510	1034512
	Weight Percent											
SiO <sub>2</sub>	76.29	0.320	67.92	2.19	70.62	3.24	60.36	0.85	53.0	45.4	62.2	45.7
Al <sub>2</sub> O <sub>3</sub>	12.55	0.140	12.22	0.59	12.05	0.87	15.05	0.38	11.8	9.90	13.4	10.1
FeO	0.13	0.050	2.52	0.85	1.42	0.87	0.84	0.18	0.49	1.13	1.12	2.09
Fe <sub>2</sub> O <sub>3</sub>	0.97	0.070	0.93	0.44	1.11	0.52	4.20	0.37	7.26	2.96	3.56	1.57
MgO	0.12	0.020	0.38	0.21	0.31	0.09	2.19	0.17	2.19	2.20	1.67	2.18
CaO	0.50	0.027	2.26	0.65	1.83	1.43	2.69	0.60	6.92	7.41	3.70	7.19
Na <sub>2</sub> O	3.52	0.109	3.18	0.38	3.43	0.27	2.12	0.15	2.30	3.09	2.69	2.53
K <sub>2</sub> O	4.83	0.062	4.34	0.29	4.41	0.36	3.20	0.20	2.95	2.46	3.39	2.52
TiO <sub>2</sub>	0.109	0.004	0.19	0.06	0.113	0.015	0.84	0.04	0.48	0.57	0.91	0.72
P <sub>2</sub> O <sub>5</sub>	<0.05	---	0.16	0.30	0.015	0.004	0.24	0.12	0.16	0.24	0.14	0.23
MnO	0.068	0.008	0.10	0.01	0.092	0.020	0.09	0.01	0.09	0.07	0.10	0.07
Cl	0.017	0.004	0.15	0.06	0.10	0.13	0.013	0.002	0.086	0.369	0.060	0.298
F	0.038	0.008	0.12	0.08	0.055	0.018	0.078	0.009	0.082	0.130	0.074	0.212
CO <sub>2</sub>	0.011	0.003	0.91	0.36	0.84	0.98	0.19	0.44	3.78	3.65	1.09	2.93
C (organic)	---	---	1.36	0.64	0.86	0.83	0.88	0.26	1.16	6.13	1.67	8.01
H <sub>2</sub> O-	0.24	0.072	0.55	0.28	0.46	0.20	2.51	0.42	2.19	1.88	0.87	1.79
H <sub>2</sub> O+	0.40	0.090	2.69	0.78	1.83	1.06	4.31	0.48	3.51	8.17	3.66	2.83
SUM	99.81	---	99.98	---	99.6	---	99.79	---	98.4	95.8	100.3	91.0

TABLE II. Mean compositions and standard deviations of salts in water leachates of underground and surface dust samples, Yucca Mountain, Nevada. [U.S. Geological Survey, unpub. data.]

Ion	ESF Dust (n=10)		ECRB Dust (n=5)		Surface Dust (n=10)		Protected Surface Dust			
	Mean	Stdev	Mean	Stdev	Mean	Stdev	1034504	1034506	1034510	1034512
<b>milligrams/kilogram</b>										
Ca <sup>2+</sup>	879	418	324	169	85	53	1740	7360	258	8260
Mg <sup>2+</sup>	68	51	30	10	12	7	123	954	29.6	842
K <sup>+</sup>	239	61	51	25	111	89	276	1080	166	1080
Na <sup>+</sup>	405	217	133	32	54	59	1980	8820	141	4660
NH <sub>4</sub> <sup>+</sup>	124	78	24	17	10	12	12.2	69	25	154
SiO <sub>2</sub>	250	122	52	47	167	62	98	100	92	196
Cl <sup>-</sup>	202	122	62	15	24	31	636	2500	282	2320
Br <sup>-</sup>	28	17	5.4	2.4	<12	---	<0.12	<2.4	12	34
F <sup>-</sup>	20	9	8.5	6.1	4.2	1.2	19.4	184	19	248
HCO <sub>3</sub> <sup>-</sup>	2270	1490	541	117	347	272	1680	22600	1004	15800
NO <sub>3</sub> <sup>-</sup>	442	314	66	24	75	65	2720	19200	148	7640
SO <sub>4</sub> <sup>2-</sup>	914	426	256	187	42	43	5260	16800	378	14300
PO <sub>4</sub> <sup>3-</sup>	4.4	2.5	2.7	0.5	20	13	24	259	48	132
Total Salts	4692		1281		775		13700	69900	2090	50100
<b>Weight Percent</b>										
Total Salts	0.47		0.13		0.08		1.37	6.99	0.21	5.01

Note: Total salts for samples 1034506 and 1034512 include 1,540 and 2,520 mg/kg of Zn, respectively. These samples were collected from the tops of galvanized steel heating ducts. Other samples do not contain much Zn.

TABLE III. Mean Concentrations and Standard Deviations of South Ramp Seepage, USW SD-9 PTn Pore Water, TSw Pore Water, and Brown Water Samples, Yucca Mountain, Nevada. [Data are from U.S. Geological Survey, unpub. data. Dashes (---) mean that analyses were not done for these constituents.]

PARAMETER	South Ramp Seepage			USW SD-9 PTn Pore Water			TSw Pore Water			Brown Water		
	mg/L		n	mg/L		n	mg/L		n	mg/L		n
	Mean	Stdev		Mean	Stdev		Mean	Stdev		Mean	Stdev	
pH	8.1	0.04	30	7.1	0.2	10	7.6	0.1	42	6.7	1.4	17
Na <sup>+</sup>	31	8	35	52	18	11	83	32	60	2270	1490	19
K <sup>+</sup>	5.4	2.0	30	8	4	5	11	5	60	462	272	19
Mg <sup>2+</sup>	13.7	14.2	30	19	10	11	15	12	59	521	800	19
Ca <sup>2+</sup>	84	14	30	99	15	11	108	68	60	718	442	19
Cl <sup>-</sup>	60	11	30	128	69	11	47	30	58	4950	2340	19
SO <sub>4</sub> <sup>2-</sup>	125	19	30	183	99	11	56	36	58	1060	506	19
HCO <sub>3</sub> <sup>-</sup>	119	32	30	65	37	8	323	176	51	1670	1910	19
NO <sub>3</sub> <sup>-</sup>	37	7	30	11	5	11	13	15	57	23	22	19
F <sup>-</sup>	3.3	0.7	35	1.2	0.7	5	2.5	2.0	58	3.7	4.4	16
SiO <sub>2</sub>	56	12	30	68	11	11	52	7	60	89	62	19
Li <sup>+</sup>	0.036	0.010	30	---	---	---	0.09	0.05	16	14	12	19
Mn <sup>2+</sup>	0.057	0.075	25	---	---	---	0.13	0.16	56	14	13	19
TDS	474.3			601.2			546.8			10946		

TABLE IV. Means and standard deviations of coefficients of variation for major cations and anions in samples of near-field materials, Yucca Mountain, Nevada

Near-Field Material	Coefficients of Variation	
	Mean	Stdev
	Percent	
Tptp rhyolite	8.6	12.3
Surface dust	9.2	7.6
ECRB dust	28	27
South Ramp seepage	31	27
ESF dust	25	19
USW SD-9 PTn pore water	44	16
ECRB dust soluble fractions	50	24
ESF dust soluble fractions	55	14
TSw pore water	62	28
Surface dust soluble fractions	81	33
Brown water	83	36

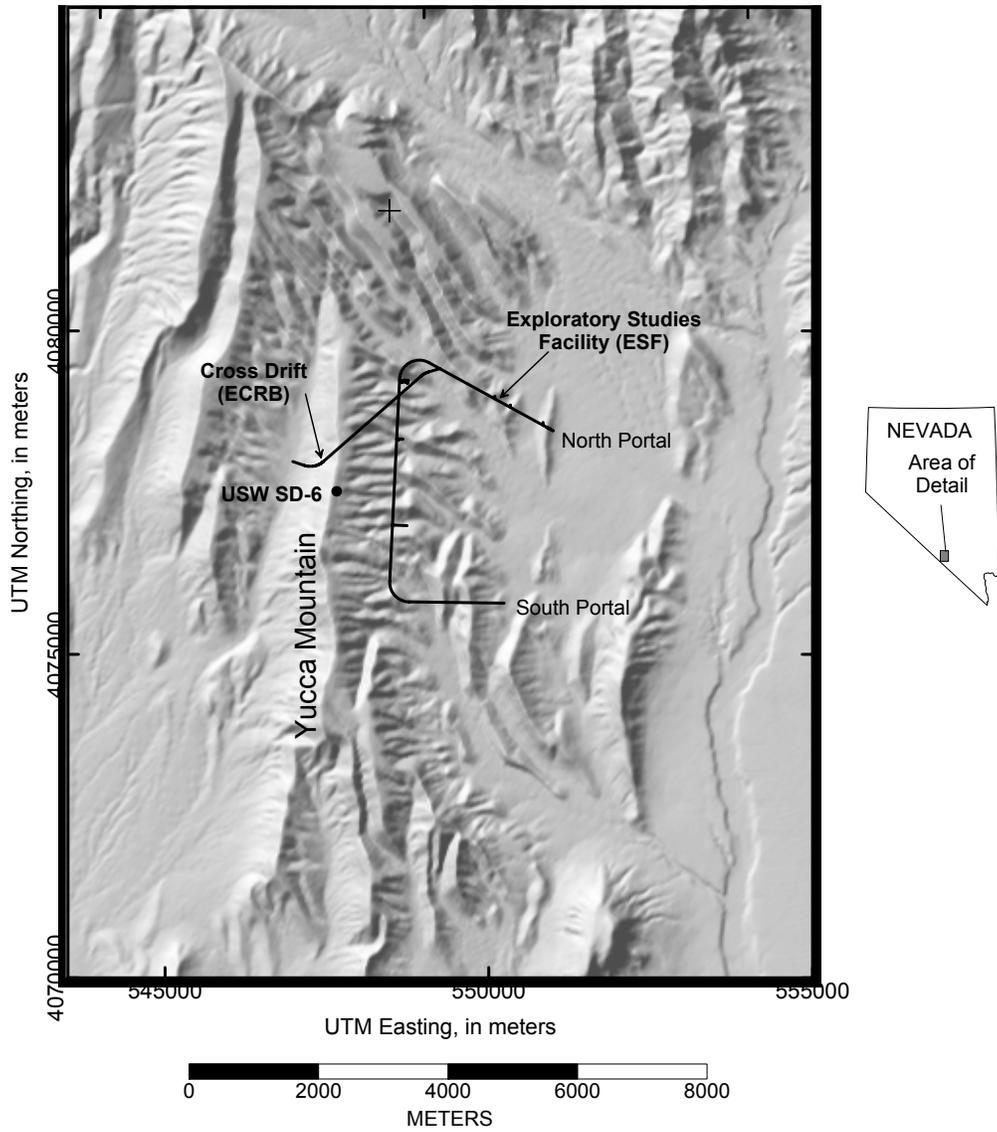


Fig. 1. Shaded relief map showing the location of Yucca Mountain, Nevada, the Exploratory Studies Facility (ESF), and the Enhanced Characterization of the Repository Block (ECRB) Cross Drift. [Shaded relief base from 1:24,000 Digital Elevation Model.]

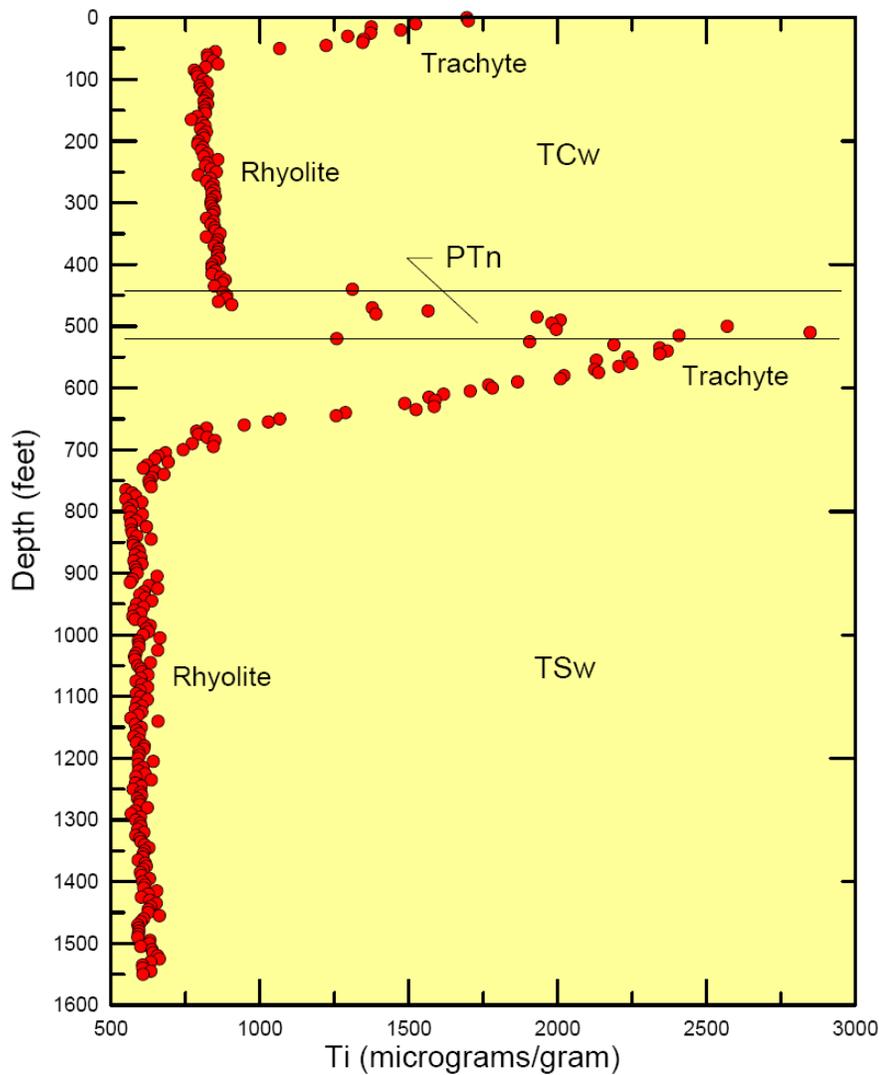


Fig. 2. Distribution of titanium (Ti) in Miocene-age Paintbrush Group rocks intersected in borehole USW SD-6. The energy dispersive X-ray fluorescence analyses are for drill cuttings collected over 5-foot intervals, Yucca Mountain, Nevada, analyzed in the U.S. Geological Survey Environmental Science Team laboratory. [U.S. Geological Survey, unpub. data.]

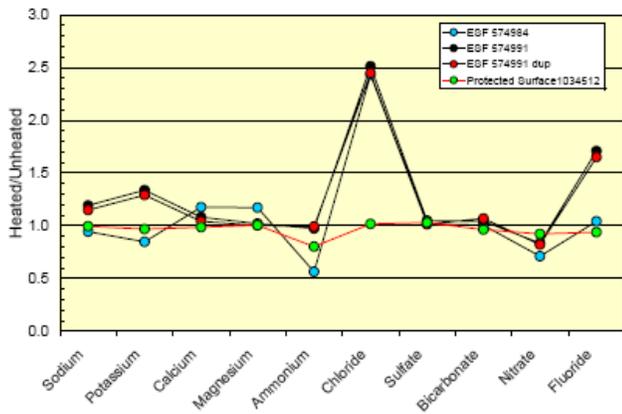


Fig. 3. Spider diagram showing the effects of heating dust prior to leaching. The plot shows the quotient of the compositions of the leachates of the heated dust sample splits and leachates of the unheated dust sample splits, Yucca Mountain, Nevada. [U.S. Geological Survey, unpub. data.]

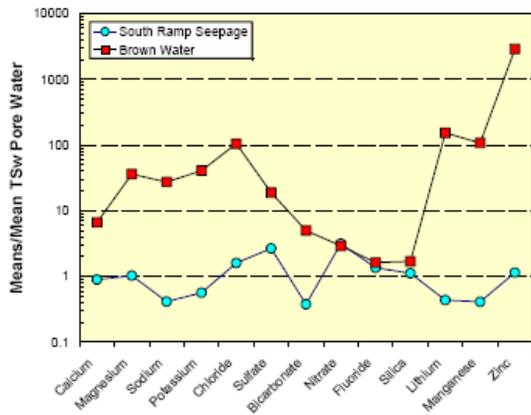


Fig. 4. Spider diagram comparing the mean compositions of samples of south ramp seepage and brown water with the mean composition of samples of TSw pore water, Yucca Mountain, Nevada. [U.S. Geological Survey, unpub. data.] Graph y-axis label should be what? Fig. 3 defines in terms of a quotient, be consistent with that here?

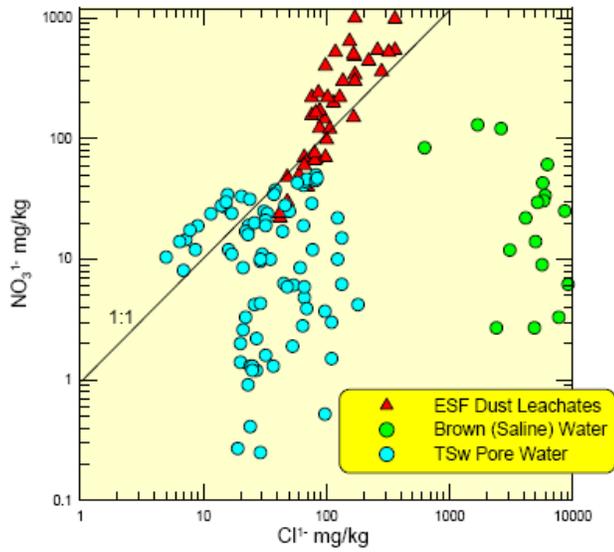


Fig. 5. Plot of chloride ( $\text{Cl}^{-}$ )-versus nitrate ( $\text{NO}_3^{-}$ ) for samples of pore water from the welded Topopah Spring Tuff (TSw), brown water, and the soluble fraction of ESF dust, Yucca Mountain, Nevada. [U.S. Geological Survey, unpub. data.]