

## LETTER REPORT

5/22/87

TITLE: Review of LA-9328-MS, "Summary Report on the Geochemistry of Yucca Mountain and Environs"

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PROJECT TITLE: Technical Assistance in Geochemistry

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## SUMMARY

The report is composed of two sections: one describing the current state of geochemical information concerning the Yucca Mountain site and one describing future plans for information acquisition. The results of our general review can be summarized as follows:

1. A large amount of sorption data was presented, but it was not organized and correlated in a manner that would allow for comparisons to be made and trends to become evident. Thus, the sorption presentation is little more than a "dump" of available information.
2. Very little information was given concerning solubility and speciation considerations and what was given was based solely on unverified calculations. Clearly, NNWSI efforts in this area are just beginning and have a long way to go.
3. Very little information was given concerning geochemical conditions at the reference location and the reference groundwater compositions employed were from outside the Yucca Mountain block and in the saturated zone.
4. The plans presented indicated that the NNWSI staff has a reasonable understanding of the geochemical information needs, but beyond this the plans were very vague.
5. The effect of water vapor pressure and temperature changes on the mineralogy could be substantial, thus introducing more complexity and uncertainty in the already-complicated geochemical situation at Yucca Mountain.

Overall, it appears that the NNWSI staff is aware of what is needed and is headed in the right direction, but they have a lot of work ahead of them.

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## INTRODUCTION

This letter report contains a review and assessment of geochemical commentary and data presented in the LANL report LA-9328-MS, "Summary Report on the Geochemistry of Yucca Mountain and Environs."

## GENERAL COMMENTS

1. Report Organization - The report is organized into two major sections. The first, Chapter 1, discusses the geochemical information available for Yucca Mountain and adjacent areas of the Nevada Test Site (NTS), while the second, Chapter 2, describes planned studies of various geochemical aspects. This is a useful organization which presumably will be maintained in the Site Characterization Plan to be submitted for the Yucca Mountain repository site by the Nevada Nuclear Waste Storage Investigations (NNWSI) project.
2. Information Emphasis - Considerable emphasis, i.e., many tables, figures, and discussion, are devoted to some geochemical aspects, while other aspects receive scant attention. Presumably, this reflects the importance being assigned by NNWSI to various features of the Yucca Mountain site for repository site selection and construction, and as radionuclide migration barriers. Emphasis in the report is given to: (i) groundwater chemistry, (ii) geochemical retardation, including sorption, storage capacity (permeability, diffusion, and porosity), and fracture and porous flow, and (iii) calculational aspects including modeling groundwater/rock interactions. Only limited attention is given to: (i) near-field conditions, (ii) radionuclide solubility, and (iii) radionuclide transport modeling. Absent from the draft report is any discussion of: (i) radionuclide hazards ranking, (ii) waste form and/or canister or backfill effects on geochemistry, (iii) identification of a reference repository location and the ambient and/or expected geochemical parameters for that location, and (iv) identification of the release pathway(s) to be expected or modeled. The report also contains very few data on the chemistries of minerals in NTS tuffs, and this fact suggests that only scanty information was available at the time the report was assembled. We believe that this aspect of geochemical research should receive greater attention in the future. For example, it would be very worthwhile to determine the limits of crystalline solution that zeolite minerals exhibit in the NTS tuffs. Obviously, in order to properly account for measured sorption characteristics and solubilities of radionuclide elements, it is absolutely essential to know the major-element and trace-element characteristics of the most abundant tuff minerals. It is encouraging to see (pp. 247-248) a recognition that isotope geochemistry is potentially an important aspect of geochemical investigations of NTS tuffs and groundwaters. This is a legitimate and sorely-neglected area of geochemical research pertaining to isolation of radioactive waste in mined repositories, and it is past due time for Los Alamos researchers to get an isotope geochemistry program under way. It is most logical to begin work where (evidently) USGS studies left off; viz., by measuring  $^{14}\text{C}$  contents and  $^{18}\text{O}/^{16}\text{O}$  ratios of NTS groundwaters to learn more about their flow rates and paths of flow in the NTS tuffs.

3. Assessment of the Report - In our opinion, in order to treat the geochemistry of the NTS rocks and groundwaters in a comprehensive way, it is necessary to address the following broad geochemical topics: (i) the sorptive properties and solubilities of radionuclides in tuff-groundwater systems that are expected to exist in the vicinity of a mined repository, (ii) the physicochemical properties of groundwaters in the various tuffs at the NTS, (iii) the geochemical characteristics of minerals in the NTS tuffs, (iv) the isotopic properties of NTS groundwaters  $\pm$  certain solutes that they contain, and (v) matrix diffusion of radionuclides in NTS groundwaters. As noted above (see general comment #2), in our examination of the draft report we have found that topic (i) is discussed in great detail (with sorption receiving the lion's share of attention), the discussion of topic (ii) is focused mainly on the compositions of NTS groundwaters (little information is available on values of Eh and Ph for uncontaminated groundwaters at the NTS), while topics (iii), (iv), and (v) are treated only superficially. Consequently, the bulk of this letter report deals with sorption and solubility of radionuclides in "model" tuff-water systems, and somewhat arbitrarily we have chosen to treat these subjects separately in the discussion that follows.

## RADIONUCLIDE SORPTION

### Overview

Great emphasis has been given for several years at LANL to measuring radionuclide sorption on various tuff samples from the Nevada Test Site and the report contains a great deal of sorption information; 71 pages of text, tables and figures in Chapter 1, and 32 tables covering 66 pages in Appendix A. Sorption behavior, reported primarily as sorption ratios, appears to be very highly dependent upon the specific tuff sample tested. The draft report does not collate or summarize the mass of sorption ratio information for use in the selection of a reference repository location or for release pathway analysis calculations; this may result from the highly complex mineralogy and petrology of the NTS area coupled with the lack of project definition of a reference repository location and a release pathway.

Simplified assumptions and generalizations about radionuclide sorption behavior on tuffs may be of limited accuracy or usefulness. For example, Table XXI, p. 78, gives average sorption ratios for various tuff samples and several radionuclides. To further summarize these and illustrate the complexities involved, the sorption ratio extreme values were listed and mean  $\pm$  standard deviation values were calculated from the data in the table. These are:

Element	R <sub>d</sub> (mL/g)				
	Extremes		Mean +/- Std. Dev.		
Sr	22	- 60,000	7,956	+/-	15,587
Cs	180	- 37,000	6,265	+/-	9,155
Ba	182	- 250,000	28,098	+/-	52,864
Ce	66	- 450,000	54,788	+/-	118,748
Eu	90	- 307,000	32,544	+/-	75,340
Am	130	- 28,000	5,408	+/-	8,756
Pu	64	- 400	153	+/-	106
U	1.3	- 5.3	3.0	+/-	1.5
Tc	0.15	- 4.2	1.2	+/-	1.7
Np	6.4	- 28	12	+/-	8.0

The great range of  $R_d$  values obtained (up to 4 orders of magnitude) for a given element for different tuff samples may significantly complicate release calculations without careful consideration of the release pathway and the specific tuff beds involved. Perhaps the best that can be said in terms of generalization may be that tuffs exhibit good to high sorption ratios for cations, and poor to very poor sorption ratios for anions.

Discussion of needed additional sorption work is included in Chapter 2, pp. 252-255, but potential approaches for collating the mass of data are not discussed.

Normalization of the sorption ratio vs sorptive mineral content was discussed in the report and useful, if not highly accurate, correlations were shown (pp. 92-118) for elements such as Sr, Cs, and Ba. Poor to no correlation of sorption ratio with sorptive mineral content was shown for Tc, Ce, Eu, Am, Np, U, and Pu. It seems possible, where sorption is due to ion-exchange of alkali or alkaline earth elements on zeolites or clays, that the sorptive mineral content correlation may be useful, but where other sorption reactions and/or other minerals are involved, that poor or no correlation results. Strontium and barium showed reasonable correlation to the zeolite (clinoptilolite) content of the tuff samples, while cesium sorption was more related to the clay (smectite) content. All the other elements tested showed poor or no correlation with any mineral constituent of the tuff samples, the sample particle size, or the test temperature. At the present time, the cause of the wide variation in the sorption ratios measured for these other elements remains unknown and means of applying the sorption ratios for these elements in retardation calculations must be uncertain.

It is not at all obvious how LANL or NNWSI plans to use the mass of sorption ratio values accumulated in selecting a reference repository location or in calculational activities to model radionuclide release to the accessible environment.

### Specific Technical Comments

1. Groundwater Composition in the Unsaturated Zone - All of the radionuclide sorption work reported in this draft report was carried out with J-13 well water. This well is located adjacent to, but outside, the Yucca Mountain block and the water is drawn from the saturated zone. At the NRC workshop held at LANL, it was indicated that the reference repository location would be in the unsaturated zone in welded tuff in Yucca Mountain. Thus groundwater intruding into emplaced waste could be of considerably different composition than the J-13 well water. Groundwater in the unsaturated zone probably would be much more concentrated in dissolved salts, perhaps being more like brine. This raises serious questions as to whether the extensive radionuclide sorption measurements and very limited solubility calculations based on J-13 well water are relevant or applicable to the unsaturated zone and, therefore, to the reference repository location and near-field migration/retardation modeling. NNSWI might chose to simplify radionuclide migration modeling calculations by taking the conservative assumption that radionuclides are completely soluble and are not adsorbed in the unsaturated zone or near-field, and base their migration modeling on behavior in the saturated zone or far-field where considerable sorption data has been developed. (Such a simplifying approach assumes that all groundwater flow in the unsaturated zone is downward to the saturated zone.) If this approach is taken, then lack of information on groundwater composition in the unsaturated zone may not be a significant problem. Conversely, if NNWSI decides to stress radionuclide retardation in the near-field, then additional data on groundwater chemistry and radionuclide sorption and solubility behavior will be needed.
2. Temperature Effects on Radionuclide Sorption, Mineral Stability, and the Reference Repository Location - In reviewing this and other reports from LANL, it has become apparent that temperature and its effects on the repository tuff horizon minerals may be a very important aspect of tuff site characterization. A recent summary (BISH 1982) describes the mineralogy of the Yucca Mountain tuffs and their stability with temperature. It appears that the zeolites and clays may be at or near equilibrium with the water vapor pressure and temperature in the tuff beds, and as water vapor pressure is decreased and/or temperature is increased these minerals undergo dehydration and then restructure to more stable silicates. These reactions involve a decrease in the cation sorption capacity and physical deformation with a significant decrease in volume. It can be visualized that simply excavating the engineered facility could lead to dehydration in the near-field due to dry air introduction, and that during the thermal pulse after waste emplacement considerable additional changes could occur in the zeolite and clay minerals in the thermally disturbed zone. Thermal dehydration of minerals also could release liquid water (or steam) in the unsaturated zone after waste emplacement. Thus, during repository development and operation, the near-field tuff mineral composition and the tuff sorption capacity and physical properties could be considerably different from those existing in the undisturbed tuff beds. All of these tuff properties, in addition, could be somewhat different than properties measured in the laboratory on retrieved drill core samples which were flooded with drilling fluid and detergent during recovery and then stored in Nevada desert air.

Evaluation of this potential problem is hindered by the lack of thermal information available on the Yucca Mountain block. Neither the most recent LANL progress report (WOLFSBERG 1982) nor the latest NNWSI progress report (NNWSI 1982) discuss the geothermal gradient or give temperature profiles for Yucca Mountain. Some work on thermomechanics and on heat transfer from the canister to the tunnel walls prior to back-filling and closure is discussed (NNWSI 1982), but the ambient repository temperature is not identified. In this report, the effect of temperature on radionuclide sorption is dispatched in six lines on p. 110 in Chapter 1; no conclusions were drawn except that sorption is generally higher at higher temperatures. (Almost all of the radionuclide sorption ratios were measured under laboratory ambient temperature conditions.) In Chapter 2, p. 254, one sentence discusses experiments at higher temperatures. It appears the consideration being given to temperature effects may be somewhat deficient for careful site analysis and development of a repository in tuff.

Considerable attention was given to temperature effects on radionuclide sorption in an earlier LANL report (WOLFSBERG 1979). Sorption ratios were measured for various radionuclides with various tuff samples at 22 and 70°C. No clear or consistent trend with temperature was established.  $R_d$  values generally were somewhat higher at the higher temperature, although they were lower for some tuff samples or radionuclides. The mineralogic complexity of the tuff samples may partially account for this variable behavior.

3. Radionuclide Multiple Speciation - Many radionuclides, particularly actinides and some fission products, which can exist in multiple valences and/or in several complex forms may exhibit multiple speciation in rock-groundwater systems. Once-through chromatographic column methods are usually used to identify multiple species and to measure separate retardation factors for each species. LANL has done considerable work with both once-through columns (TREHER 1982) and recirculating columns (WOLFSBERG 1981) to compare sorption ratios obtained by batch contact methods with those measured by column methods, and concluded in this draft report (p. 9) that "the results from the two methods fall within the spread of individual experimental values." However, multiple speciation and interpretation of column radionuclide elution patterns in terms of multiple species were never mentioned in any of the reports, including this summary report. This would seem to be a serious technical omission. The analysis in TREHER 1982 may be adequate for the tests reported therein since elution of only Sr, Ba, and Cs was studied and these elements would not be expected to exhibit multiple speciation. It would seem desirable to extend the once-through column chromatographic tests to include actinides and other elements likely to have multiple species. In Chapter 2 of the draft report, the need for additional column tests of an unspecified nature was alluded to only peripherally.

## Conclusions

In our reading of the report, we considered the information provided therein in the context of the multiple retardation barriers usually identified: (i) waste form, (ii) canister, (iii) overpack, (iv) backfill, (v) groundwater flux, (vi) waste/radionuclide dissolution rate, (vii) radionuclide solubility, (viii) geologic storage capacity/fracture flow, (ix) radionuclide sorption, and (x) radionuclide half life/release rate. Very little or essentially no treatment of barriers related to the waste package or the engineered facility is included. This may reflect the fractured organization of the NNWSI in that these items are covered by other contractors. Nonetheless, these repository aspects can have major impacts on and interactions with the geochemical parameters and migration barriers. The processes in and conditions of the waste package and engineered barrier system define the radionuclide source term which must be dealt with in the repository far-field. Accurate modeling of release rates to the accessible environment, or even assertion that the important far-field parameters and conditions have been identified and quantified, cannot be achieved without treating the source term.

Emphasis in the report is given to geologic storage capacity and radionuclide sorption, and presumably these are considered major migration barriers. As discussed above, the report does not make clear how the wealth of sorption data collected is to be used. Presumably other reviewers will deal with the storage capacity argument.

Transport modeling is covered in 1.5 pages of text in Chapter 1 and in 1 page in Chapter 2. The information presented in the report seems inadequate to permit assessment of the geochemical data in terms of application to the transport modeling needs.

The report gives no indication where the reference repository might be located (presumably in Yucca Mountain) or what either the ambient or expected geochemical parameters would be at that location or in the repository far-field along the release pathway. Also, a possible repository design and expected heat load from emplaced waste are not established or even mentioned. Thus, the following questions cannot be evaluated: (i) importance of the issue to repository performance, (ii) additional information needed to resolve the issue, (iii) summary of planned approaches to provide the information needed, and (iv) analysis of completeness, practicality, and likelihood of success. This would seem to be a major deficiency in the report for the NRC analysis needs.

## RADIONUCLIDE SOLUBILITY

### Overview

The report deals with many aspects of the long-range plan to construct a mined repository for high-level radioactive waste in tuff at the NTS. As noted above, subjects treated in some detail include groundwater geochemistry, mechanisms of geochemical retardation of radionuclides (e.g., sorption and solubility), and radionuclide transport modeling. However, while sorption is viewed as a principal deterrent to radionuclide migration from the proposed repository, comparatively little attention has been paid to the possibility

that low solubilities of radionuclides in NTS groundwaters may also contribute significantly to retention of these elements in the near-field repository environment.

For the most part, treatment of radionuclide solubilities in the report is restricted to a discussion of U and Pu solubilities. On the assumption that well J-13 water is representative of groundwater that might ultimately interact with radioactive waste emplaced in tuff at Yucca Mountain, solubilities of U and Pu in this "model" groundwater were calculated using the EQ3 computer code. The principal goal of these calculations was to identify the constituents of well J-13 water that may affect most strongly the solubilities of U and Pu. Assuming a pH of 6.9 for the water, calculations were performed for a variety of Eh values (+700, +400, +100, and -200 mV) because it is not certain what specific value of Eh is most representative of groundwaters in the tuff strata at Yucca Mountain.

According to the report, U complexes most often with carbonate, phosphate, and hydroxyl, whereas plutonium complexes mainly with carbonate. Also, U exists in the IV oxidation state at Eh's less than 0 mV. Therefore, at a given temperature, significant physicochemical variables include the carbonate content, phosphate content, Eh, and pH of the "model" groundwater. For the purpose of estimating U and Pu solubilities in well J-13 water, it was also assumed in the computer calculations that this water was in equilibrium with a single U or Pu crystalline phase (the so-called limiting solid phase). However, this U or Pu phase was not permitted to precipitate in the computer simulations.

The computer calculations were subdivided into three hypothetical cases: well J-13 water containing (1) U, (2) Pu, and (3) both U and Pu.

1. Well J-13 Water Plus U - The calculations suggest that uranium behavior is complex in well J-13 water. The total uranium concentration was found to be high at Eh = +700 and +400 mV ( $3.0 \times 10^{-4}$  molal), but very low at Eh = -200 mV ( $1.5 \times 10^{-11}$  molal). Moreover, the types of uranium complexes, and the particular U mineral in equilibrium with well J-13 water, are also dependent on Eh.
2. Well J-13 Water Plus Pu - In contrast to case 1 above, the calculations suggest that plutonium behavior is rather simple (i.e., independent of Eh). The concentration of Pu in well J-13 water was uniformly high ( $2.9 \times 10^{-3}$  molal). The calculations also suggested that Pu is dissolved predominantly as  $\text{PuCO}_3^{2-}$  ions, and that  $\text{PuO}_2$  is the single Pu crystalline phase in equilibrium with the groundwater.
3. Well J-13 Water Plus U and Pu - The computer calculations suggest that Pu ties up most of the available  $\text{CO}_3^{2-}$  as  $\text{PuCO}_3^{2+}$ , so little carbonate remains to complex with U in the range Eh = +100 to Eh = +700 mV where dissolved U exists predominantly in the VI oxidation state. Therefore, the presence of Pu diminishes the solubility of U in this Eh range. By contrast, U is mainly in the IV oxidation state at Eh = -200 mV, and

since the EQ3 computer code does not contain any data for U(IV) carbonates, the calculations indicate that U solubility is unaffected by the presence of Pu at this Eh.

Finally, a caveat was attached to the commentary describing the computer calculations; viz., that the available thermodynamic data for  $\text{PuCO}_3^{2+}$  may be significantly in error and, therefore, the solubilities of Pu in cases 2 and 3 may have been overestimated. The report states that this possibility is being investigated further.

Chapter 2 of the summary report describes various studies that are planned to increase knowledge of the geochemistry of the rocks and groundwater in the vicinity of Yucca Mountain. Regarding groundwater geochemistry, it is stressed that oxidation-reduction plays a very significant role; for example, it is estimated that differences in oxidation state can cause the solubilities of actinides to vary by up to a factor of 10. It is further recognized that the compositions of vadose zone waters may be significantly different from "normal" groundwater; consequently, in the future it will be necessary to investigate the differences between the Ehs, pHs, and compositions of the various groundwaters at the NTS.

Chapter 2 also alludes to experiments that will be performed to verify radionuclide solubilities estimated by different computer codes. It is stated that experiments will be performed to measure solubilities at a typical far-field temperature ( $\approx 25^\circ\text{C}$ ), as well as at higher temperatures ( $25\text{--}300^\circ\text{C}$ ) which would be expected in the near-field environment. Initially, attention will be focused on the solubilities of  $\text{PuO}_2$  and related hydrous oxides as a function of Eh, pH, and the presence or absence of appropriate complexing anions ( $\text{HCO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{F}_4^-$ , etc.). At a later time, similar work will commence on the solubilities of other radionuclides.

#### Specific Technical Comments

1. In discussing the computer calculations of U and Pu solubilities in well J-13 water, the report states (p. 231):

"Another aspect of a waste repository's geochemistry that must be understood can be inferred from these calculations. Both carbonate and phosphate complexes are important to the solubility of uranium and plutonium. If sources of these anions are available in the local minerals, the total quantity of available carbonate and phosphate could be greater than is indicated by an analysis of the water alone. A similar situation exists in calculations involving the Eh of the groundwater. It is important to consider not only the Eh of the water but also the oxidation-reduction capacity of the mineralogy. Although the calculations did not consider the local mineralogy, a comprehensive analysis of the solubility of actinides in natural waters must take the local minerals into account."

In effect, this dialogue is describing a new NNWSI standard for calculations of radionuclide solubilities using computer codes. It is clear that minerals can supply chemical constituents to groundwater as species reactions take place and, therefore, such rock-water interaction must be properly taken into account in computer calculations of radionuclide solubilities. Furthermore, for the near-field environment the effects of elevated temperature must be considered, because it is to be expected that the Eh's, pH's, and compositions of groundwaters in contact with tuff will change significantly as temperature is increased above 25°C.

2. The report discusses various computer codes (e.g., EQ3) which can predict (i) the solubilities of pure minerals, and (ii) solubility limits for radionuclides in equilibrium with one or more "limiting" radionuclide solid phases. [For (ii), a tacit assumption is that a "limiting" radionuclide solid phase precipitates from groundwater which has come into contact with radioactive waste material. This solid phase would not be expected to exist in the host rocks prior to the time that groundwater interacts with the radioactive waste.] However, to our knowledge, none of the available "solubility" computer codes has been written to account for equilibrium (or near equilibrium) ion-exchange between groundwater and minerals in the host rocks. In some instances such ion-exchange might involve only nonradioactive elements (e.g., Na, K, Ca, etc.), but more often it will be found that certain minerals (e.g., zeolites and clay minerals) possess the capacity to incorporate radionuclides into their crystal structures. Therefore, we believe that the solubility calculations described in the report are unrealistic; it is more likely that, in a "real" repository environment in tuff at the NTS, a groundwater such as well J-13 water would be in contact with zeolites and clay minerals which would incorporate radionuclides in crystalline solution. If so, it may be these zeolites and clay minerals, not one or more radionuclide solid phases, which would effectively control the solubilities of radionuclides in the groundwater(s).
3. It is clear from discussions in the report that tuff-groundwater assemblages at the NTS exhibit significantly different chemical characteristics. This revelation is really not surprising because, given the fact that the mineralogies and petrologies of the tuffs at the NTS are quite variable, it almost necessarily follows that the chemistries of the tuffs will be different. The different geochemistries of the tuffs are matched by variable Eh's, pH's, and compositions of local groundwaters. Active chemical communication between NTS groundwaters and tuffaceous host strata explains why well J-13 water changes composition (amounts of dissolved Na, K, Ca, and Mg decrease) upon prolonged contact with different tuffs from the NTS. A recognition of the variable geochemistries of tuff-groundwater assemblages at the NTS logically prompts the question: Is well J-13 groundwater really representative of the groundwater that is expected to interact with the waste package in the proposed repository in tuff at the NTS? This question becomes even more poignant when it is recognized that the proposed repository may actually be constructed above the local

water table — i.e., in a zone of aeration (vadose zone) where groundwaters are liable to be more heterogeneous in composition and solute-laden than subjacent groundwaters that are below the water table. It seems to us that NNWSI researchers should promptly devote considerable attention to accurately determining the ranges of physicochemical properties exhibited by all of the various types of NTS groundwaters.

4. Near the top of p. 226 in the report it is stated that "Equilibrium calculations often indicate that natural waters are supersaturated because of kinetic effects." However, it is also true that mineral saturation calculations can be in error due to inaccurate data bases in computer codes.

### Conclusions

This summary report contains only a very limited amount of information and discussion on the solubilities of radionuclides in tuff-water systems. Evidently, there are no experimental data on radionuclide solubilities in these systems, and only limited pertinent experimental work is planned for the near future. In lieu of experimentation, emphasis has been placed on calculations of radionuclide solubilities via computer codes; moreover, it appears that in the future great reliance will continue to be placed on such calculations.

The report describes in detail computer calculations of U and Pu solubilities in "model" (well J-13) groundwater under various redox conditions at representative far-field conditions for tuffs at the NTS (P = 1 atm, T = 25°C, pH = 6.9). It follows, therefore, that similar calculations should be performed for radionuclides other than U and Pu. Eventually it will also be important to employ suitable computer codes to estimate the effects of temperature on radionuclide solubilities in tuff-water systems. Calculations performed for temperatures in the range 20-300°C should provide some information on radionuclide solubilities in the near-field environment of a repository in tuff.

It is an appropriate time now for LANL and NNWSI researchers to properly account for the following additional significant aspects of radionuclide solubility in tuff-groundwater systems: (1) that the minerals in tuffs can contribute chemical constituents, mainly material that dissolves in groundwater — i.e., solutes, which can either increase or diminish the solubilities of individual radionuclides; and (2) that mineral-groundwater ion-exchange can have profound effects on radionuclide solubilities. On the other hand, it is evident that LANL researchers already have a good appreciation of another important aspect of radionuclide solubility in groundwater; viz., that there can be chemical interactions among radionuclides (e.g., competition for complexing ligands in the groundwater) which may significantly affect the solubilities of these elements.

Finally, there must eventually be some thorough experimental testing of calculated radionuclide solubilities in tuff-water systems. Whether such testing should be principally laboratory experiments, or field tests, is an open question at this time. It is likely that time constraints stemming from deadlines established by a rigid repository licensing procedure will ultimately determine the specific directions that future research must follow.

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NNWSI 1982. Nevada Nuclear Waste Storage Investigations: Quarterly Report for April-June 1982, NVD-196-31, September 1982.

TREHER 1982. E. N. Treher and N. A. Raybold, The Elution of Radionuclides Through Columns of Crushed Rock from the Nevada Test Site, LA-9329-MS, October 1982.

WOLFSBERG 1979. K. Wolfsberg et al., Sorption-Desorption Studies on Tuff: I. Initial Studies with Samples from the J-13 Drill Site, Jackass Flats, Nevada, LA-7480-MS, April 1979.

WOLFSBERG 1981. K. Wolfsberg et al., Sorption-Desorption Studies on Tuff: III. A Continuation of Studies with Samples from Jackass Flats and Yucca Mountain, Nevada, LA-8747-MS, May 1981.

WOLFSBERG 1982. K. Wolfsberg et al., Research and Development Related to the Nevada Nuclear Waste Storage Investigations: April 1-June 30, 1982, LA-9484-PR, October 1982.

APPENDIX A. SOURCES OF INFORMATION ON RADIONUCLIDE  
SOLUBILITY IN THE REPORT

In contrast to discussions of radionuclide sorption, which are consolidated into a small number of subsections in the summary report, discussions of radionuclide solubility are widely scattered throughout the document. Therefore, for the convenience of the reader, we have listed below all pages of the draft report on which we were able to find any substantial commentary/data that pertain directly or indirectly to radionuclide solubility. (By "substantial" we generally mean at least a sentence or two of commentary, and/or at least one numerical value for a solubility.) Asterisks are used to indicate commentary/data that were found to be particularly useful. In effect, this listing serves as a "list of references" for the review and analysis of radionuclide solubility presented in this letter report.

- |                               |                         |
|-------------------------------|-------------------------|
| 1. p. 2, lines 10-12          | *11. pp. 225-231        |
| 2. p. 2, lines 16-19          | 12. p. 241, lines 9-10  |
| 3. p. 3, paragraph 1          | 13. p. 242, lines 13-16 |
| 4. p. 3, lines 28-33          | 14. p. 245, lines 29-31 |
| 5. p. 14, paragraph 2         | *15. p. 246, lines 1-25 |
| 6. p. 17, lines 25-28         | 16. p. 246, lines 35-36 |
| 7. p. 17 (to 18), paragraph 5 | 17. p. 247, lines 1-8   |
| 8. p. 62, lines 7ff           | 18. p. 251, lines 21-25 |
| 9. p. 63, lines 1-28          | 19. p. 253, lines 1-8   |
| 10. p. 205, lines 8-10        | 20. p. 265, lines 24-30 |

02/02/87

## LETTER REPORT

Title: Review and Evaluation of Chemistry of Diagenetically Altered Tuffs at a Potential Nuclear Waste Repository, Yucca Mountain, Nye County, Nevada, LA-10802-MS, Oct., 1986, by David E. Broxton, Richard G. Warren, Roland C. Hagan, and Gary Luedemann.

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ACTIVITY NUMBER: ORNL #41 88 54 92 4 (FIN No. B0287)  
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## OVERVIEW

This report discusses the geochemical characteristics of diagenetically altered tuffs at Yucca Mountain, Nevada. Diagenetic alteration in Yucca Mountain tuffs is best developed in (1) lithologies that are nonwelded throughout and (2) the nonwelded tops and bottoms of ash-flow cooling units that possess densely welded, devitrified interiors. Geochemical data for these tuffs reveal that whole-rock compositions vary systematically across the repository exploration block and along potential pathways to the accessible environment. Moreover, the geochemical trends of whole-rock compositions are mirrored by variations in the compositions of clinoptilolites in the tuffs. Broxton et al. believe that data obtained on the geochemistries of Yucca Mountain tuffs

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and their constituent minerals can be combined with experimental data to elucidate the effects of zeolite chemistry on the physical and sorptive properties of zeolites and their host tuffs.

## REVIEW

### Introduction

In this report Broxton et al. emphasize that an improved knowledge of the geochemical characteristics of diagenetically altered tuffs at Yucca Mountain, Nevada, would be useful in assessing the performance of a possible tuff-hosted HLW repository at Yucca Mountain. Specifically, Broxton et al. believe that data obtained on the geochemistries of Yucca Mountain tuffs and their constituent minerals can be combined with experimental data to elucidate the effects of zeolite chemistry on the physical and sorptive properties of zeolites and their host tuffs. In this regard, clinoptilolite is receiving special attention because the clinoptilolites in altered Yucca Mountain tuffs have exchangeable-cation compositions that span the entire compositional range between sodium, potassium, and calcium end members. Because of these compositional variations, the thermal expansion/contraction behavior, hydration/dehydration behavior, and ion-exchange properties of these zeolites and their host tuffs may be variable.

The clinoptilolite-rich zone at the top of the basal vitrophyre of the Topopah Spring Member is the first major zeolite barrier that radionuclide-bearing groundwaters would encounter as they move downward through the unsaturated zone. The proximity of the zeolites in this zone to the potential repository makes them susceptible to contraction and dehydration during the thermal pulse expected after repository closure.

In sorption experiments it is observed that sodium and calcium in clinoptilolite exchange readily with a wide range of potential

radionuclides, including cesium, rubidium, strontium, and barium (Ames, 1960; Breck, 1974). Consequently, Broxton et al. believe that the thick, clinoptilolite-bearing tuffs beneath the Topopah Spring Member would be important sorptive barriers to radionuclide migration at the Yucca Mountain Site.

#### Zones of Diagenetic Minerals in Yucca Mountain Tuffs

Broxton et al. claim that authigenic minerals in the tuffaceous lithologies of Yucca Mountain form four diagenetic mineral zones (designated Zones I, II, III, and IV) that become progressively less hydrous with depth. Zone I is the shallowest zone, and is characterized by tuffs that contain large quantities of unaltered volcanic glass. Smectite, opal, heulandite, and calcic clinoptilolite are minor alteration phases that occur principally in fractures and in thin discontinuous zones parallel to bedding. Zone I includes the thin but extensive layers of smectites, calcic clinoptilolites, and heulandite located at the top of the basal vitrophyre of the Topopah Spring Member.

The tuffs in Zone II occur in well-defined layers between the base of the Topopah Spring Member and the top of the Tram Member. Individual layers range in thickness from 10 to 150 m. The tuffs in Zone II typically exhibit complete replacement of volcanic glass by clinoptilolite ± subordinate mordenite. (Many of the tuffs contain 50-75 volume % clinoptilolite.) Zone II tuffs also contain minor opal, quartz, potassium feldspar, and smectite. There are no significant mineralogic or chemical changes in authigenic minerals across stratigraphic contacts within Zone II tuffs. Zone II tuffs are potentially important sorptive barriers for radionuclide migration because they occur along groundwater pathways beneath the reference repository horizon.

Zones III and IV are the deepest diagenetic zones beneath Yucca Mountain. With increasing depth in Zone III, clinoptilolite and

mordenite are progressively replaced by analcime, potassium feldspar, quartz, and minor calcite and smectite. In Zone IV, the deepest diagenetic zone, analcime is partially to completely replaced by authigenic albite.

#### Origin of Altered Tuffs at Yucca Mountain

Broxton et al. claim that all of the altered tuffs at Yucca Mountain were originally high-silica vitric tuffs with similar major-element chemistries. Despite similar starting compositions, however, the tuffs beneath Yucca Mountain now exhibit extremely variable major-element chemistries. Broxton et al. attribute this variability to widespread mobilization and redistribution of chemical constituents within the tuffs during or after diagenesis. It is further hypothesized that groundwater was the medium through which chemical transport occurred. This conclusion is supported indirectly by the experimental observation that alkalis and alkaline earth metals are readily exchanged between zeolites and groundwater. Therefore, systematic variations in the compositions of the zeolitic tuffs at Yucca Mountain are plausibly attributed to variable groundwater compositions during diagenesis. However, it is also possible that all or part of the hydrothermal alteration occurred after diagenetic crystallization.

Diagenetic alteration in Yucca Mountain tuffs is best developed in (1) lithologies that are nonwelded throughout and (2) the nonwelded tops and bottoms of ash-flow cooling units that possess densely welded, devitrified interiors. The nonwelded tuffs remained largely vitric after emplacement and thus were highly susceptible to hydrothermal alteration. Glass in nonwelded tuffs was replaced primarily by clinoptilolite, heulandite, and mordenite. However, in the deeper parts of the volcanic sequence, analcime and authigenic feldspars are observed replacing clinoptilolite and mordenite.

## Chemical Compositions of the Rocks and Minerals in Yucca Mountain

### Whole-Rock Compositions

Broxton et al. calculated the changes in chemical composition of altered Yucca Mountain tuffs by comparing unaltered and altered tuff compositions on a constant-aluminum basis. This approach is based on the assumption that aluminum is relatively insoluble and thus does not migrate significantly during low-temperature hydrothermal alteration. The general validity of this assumption is supported by the observation that groundwaters in volcanic rocks of the arid southwest typically contain only trace amounts of dissolved aluminum.

The calculations performed by Broxton et al. indicate that alkalis and alkaline earths were most strongly affected by hydrothermal alteration. The sodium, potassium, calcium, and magnesium contents of altered tuffs deviate from those of unaltered tuffs by as much as a factor of 10. In general, it is observed that sodium and potassium are strongly depleted in zeolitized tuffs, whereas calcium is strongly enriched. Also, magnesium is strongly enriched in the altered tuffs in Zone I, but the magnesium contents of altered tuffs in Zone II are highly variable. Finally, compared to unaltered tuffs, zeolitized tuffs are depleted in silicon and enriched in oxidized iron.

Data on the alkali and alkaline earth contents of altered Yucca Mountain tuffs reveal that whole-rock compositions change systematically across Yucca Mountain. Based upon mode of occurrence and compositional characteristics, zeolitic tuffs at Yucca Mountain can be divided into three compositional groups: (1) calcium- and magnesium-rich tuffs associated with relatively thin zones of alteration in diagenetic Zone I; (2) zeolitized tuffs of extremely variable composition in thick zones of alteration in diagenetic Zones II, III, and IV; and (3) highly potassic, zeolitic tuffs in Zone II at the northern end of Yucca Mountain.

The altered tuffs in diagenetic Zones II, III, and IV are chemically more diverse than those of Zone I. Alkalies and alkaline earths in these tuffs vary systematically across Yucca Mountain. Tuffs on the eastern side of Yucca Mountain are characterized by calcium-rich compositions, whereas altered tuffs on the western side of Yucca Mountain are more alkali rich. A transition zone separates the two compositional suites.

The calcium-rich tuffs on the eastern side of Yucca Mountain deviate most from original tuff compositions, being strongly enriched in calcium and magnesium and depleted in sodium and potassium. Analcime-bearing tuffs in Zone III and authigenic albite-bearing tuffs in Zone IV exhibit compositional variations similar to those observed in Zone II. However, excess calcium in Zones III and IV occurs in the form of abundant calcite rather than primary Ca-bearing authigenic minerals such as analcime and authigenic feldspar.

Finally, potassium-rich tuffs crop out at Prow Pass near the extreme northern end of Yucca Mountain. These unusual tuffs appear to be confined to this locale.

#### Compositions of Volcanic Glasses and Diagenetic Minerals

Broxton et al. measured the compositions of glass in tuff samples from (1) every stratigraphic member of the Paintbrush Tuff, (2) the tuff of Calico Hills, and (3) the Prow Pass Member of the Crater Flat Tuff. In all cases the glasses were observed to be "high-silica rhyolites" containing subequal amounts of potassium and sodium. It was also discovered that the Si/Al ratios of the glasses are relatively high (5.2 to 5.6) compared with the Si/Al ratios of the clinoptilolites that replaced them (2.6 to 5.4).

The chemical trends of whole-rock compositions are mirrored by variations in the compositions of clinoptilolites in the tuffs. Clinoptilolites in diagenetic Zone I are invariably calcium rich and have Si/Al ratios between 4.0 and 5.0. Magnesium contents of these zeolites are relatively high, ranging from 0.6 to 1.5% MgO by weight.

Clinoptilolite compositions in Zone II vary systematically both vertically and laterally. On the eastern side of Yucca Mountain, clinoptilolite compositions are enriched in calcium and potassium and show strong calcium enrichment with depth. Clinoptilolites on the western side of Yucca Mountain are enriched in sodium and potassium and become more sodic with depth. A transition zone overlaps these two suites of rocks. Finally, clinoptilolites in the potassic tuffs at the northern end of Yucca Mountain exhibit potassium-rich compositions.

All analcimes have nearly pure end-member compositions with only trace amounts of calcium and potassium substituting for sodium. Authigenic potassium feldspars and albites in altered Yucca Mountain tuffs consistently exhibit nearly pure end-member compositions.

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## EVALUATION

This report discusses the geochemical characteristics of diagenetically altered tuffs at Yucca Mountain, Nevada. Diagenetic alteration in Yucca Mountain tuffs is best developed in (1) lithologies that are nonwelded throughout and (2) the nonwelded tops and bottoms of ash-flow cooling units that possess densely welded, devitrified interiors. Geochemical data for these tuffs reveal that whole-rock compositions vary systematically across the repository exploration block and along potential pathways to the accessible environment. Moreover, the geochemical trends of whole-rock compositions are mirrored by variations in the compositions of clinoptilolites in the tuffs. Broxton et al. believe that data obtained on the geochemistries of Yucca Mountain tuffs and their constituent minerals can be combined with experimental data to elucidate the effects of zeolite chemistry on the physical and sorptive properties of zeolites and their host tuffs.

While this report provides valuable new information about the chemical compositions of the rocks and minerals in altered tuffs at Yucca Mountain, numerous questions remain unanswered. First, it is unclear why the altered tuffs at Yucca Mountain display such diverse chemistries. Broxton et al. speculate that the variations in chemical composition are attributable to rock-groundwater interactions (principally ion exchange), but the timing and details of these interactions are obscure. Additionally, the implications of the observed variations in composition are difficult to ascertain. For example, while Broxton et al. have established that several of the tuffaceous lithologies in Yucca Mountain are rich in Ca and Mg, it is uncertain what this discovery implies regarding the geochemical behavior of the tuffs. Does the enrichment in Ca and Mg indicate that these tuffs are saturated with these cations, or is the "affinity" of these rocks for Ca and Mg only partially satisfied? A similar question can be posed with respect to tuffs enriched in alkalis. Until these and related questions are answered, it will be difficult to achieve a key

goal of performance assessments for a tuff-hosted HLW repository: namely, to accurately predict the nature of tuff-groundwater geochemical interactions during the postclosure period.

Finally, Broxton et al. state their belief that cations are rapidly exchanged between Yucca Mountain tuffs and their enclosed groundwaters. Unfortunately, however, the implications of this important claim are not explored. If it is generally true that cations are exchanged rapidly between tuff and groundwater, then it follows that the effects of this ion exchange will be most pronounced in the unsaturated zone at Yucca Mountain where rock/groundwater ratios are very high. This conclusion stems from the fact that the masses of exchangeable alkali and alkaline earth cations in unsaturated Yucca Mountain tuffs are much greater than the corresponding masses of these cations in associated groundwaters. Therefore, rapid cation exchange between unsaturated tuff and contiguous groundwater could induce rapid and major changes in the ratios of dissolved alkali and alkaline earth cations in some Yucca Mountain groundwaters during slow flow down toward the water table. If this is true, then it is legitimate to question the use of a single groundwater (e.g., J-13 well water) as a model for all of the groundwaters in the unsaturated zone at Yucca Mountain.

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## LETTER REPORT

Title: Review and Evaluation of Mineralogic Summary of Yucca Mountain, Nevada, LA-10543-MS, Oct., 1985, by D. L. Bish and D. T. Vaniman

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ACTIVITY NUMBER: ORNL #41 88 54 92 4 (FIN No. B0287)  
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## OVERVIEW

This report offers preliminary observations on the patterns of distribution of primary and secondary minerals in the tuffaceous rocks at the Yucca Mountain, candidate, HLW repository site. Most of the authors' conclusions are based on data obtained from semi-quantitative X-ray powder diffraction analyses of Yucca Mountain tuffs. These data indicate that there are six mappable "mineral types" at Yucca Mountain: primary glass plus tridymite, primary and secondary quartz, secondary smectite, clinoptilolite plus mordenite, secondary analcime, and secondary albite. Two additional primary minerals, cristobalite and K-bearing alkali feldspar, are nearly ubiquitous in Yucca Mountain rocks.

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## REVIEW

### Introduction

DOE-NNWSI is currently conducting detailed petrologic and mineralogic studies of the rocks in and adjacent to Yucca Mountain, Nevada (e.g., Bish et al., 1981; Caporuscio et al., 1982; Levy, 1984; and Vaniman et al., 1984). The ultimate goal of these investigations is to obtain a three-dimensional petrologic-mineralogic model of the Yucca Mountain area. Toward this end, tuffs from Yucca Mountain are being subjected to systematic X-ray powder diffraction (XRD) analysis. This analytical method is being employed extensively because Yucca Mountain tuffs have very fine-grained groundmasses that are not amenable to quantitative mineral analysis by optical techniques and electron probe microanalysis.

The DOE-NNWSI mineralogic studies have three immediate objectives. First, DOE-NNWSI wishes to obtain an improved understanding of the relationship between retardation of radionuclides and the minerals present in Yucca Mountain tuffs. This effort has prompted studies to investigate the correlation between mineralogy and sorption for numerous radionuclides (Bish et al., 1984b). The sorption data obtained to date indicate that the minerals clinoptilolite, mordenite, and smectite are effective sorbents for many cationic radionuclides.

A second objective of DOE-NNWSI mineralogic studies is to determine the thermal stability of hydrous minerals - particularly clinoptilolite and smectite - under temperature conditions similar to those that are expected to develop near the Yucca Mountain engineered facility after repository closure. Bish et al. (1981) and Smyth (1982) have discussed the potential for clinoptilolite and smectite to react to form other minerals (e.g., analcime and albite) if a repository is constructed at Yucca Mountain. These reactions would occur primarily in response to increased temperature, and two important consequences of these reactions would be release of water and decreases in rock volume.

Finally, Lappin (1982) and Lappin et al. (1982) note that the thermal properties of tuff (both matrix thermal conductivity and thermal expansion) are partly a function of mineralogy. These investigators also describe the relationship between the mechanical properties of tuff and mineralogy, emphasizing that data on rock fabric are required to accurately predict bulk mechanical properties.

In view of the potential effects of mineralogy and dehydration reactions on the thermal and mechanical properties of tuff, DOE-NNWSI has concluded that it is desirable to determine the distributions of minerals (and particularly hydrous minerals) in the reference repository horizon.

The discussions presented by Bish and Vaniman summarize current mineralogic investigations of Yucca Mountain rocks. Much of the text is devoted to explaining the methods used to obtain XRD data and the limitations of the data. The report also lists XRD data for samples of core, cuttings, and sidewall material obtained from various drill holes at Yucca Mountain.

#### Spatial Distributions of Minerals at Yucca Mountain

The semi-quantitative XRD data obtained by Bish and Vaniman indicate that there are six mappable "mineral types" at Yucca Mountain: primary glass plus tridymite, primary and secondary quartz, secondary smectite, clinoptilolite plus mordenite, secondary analcime, and secondary albite. Also, the XRD data reveal that primary K-bearing alkali feldspars and cristobalite are nearly ubiquitous in Yucca Mountain tuffs.

#### Glass

Glass-rich rocks (vitric zones) occur both above and below the reference repository horizon at Yucca Mountain (the Topopah Spring Member). The

glasses in vitric zones can be divided into two categories: vitrophyre and nonwelded glass. Vitrophyre is composed predominantly of dense (low-porosity) welded glass. A prominent zone of vitrophyre occurs at the base of the Topopah Spring Member.

In contrast to dense vitrophyre, nonwelded glass consists of open shards and pumice and, for this reason, contains much more pore space than vitrophyre. Nonwelded glass occurs both above and below the Topopah Spring Member, and is more abundant than vitrophyre in Yucca Mountain.

#### Silica polymorphs

The silica polymorphs tridymite, quartz, and cristobalite are abundant in Yucca Mountain tuffs. Tridymite occurs in surficial rocks and persists in subsurface rocks down to the Topopah Spring Member (i.e., to a depth of approximately 300 m). The disappearance of tridymite with increasing depth is marked by the initial appearance of abundant groundmass quartz. Bish and Vaniman hypothesize that this tridymite/quartz transition in part reflects the passage from zones of high-temperature vapor-phase crystallization (tridymite) to zones of lower-temperature devitrification (quartz) within the Topopah Spring Member. The third abundant silica polymorph at Yucca Mountain, cristobalite, is widespread above the water table and persists to depths greater than 500 m above sea level.

#### Smectite

Smectite is a common accessory mineral in Yucca Mountain tuffs. However, in addition to its widespread presence as a minor secondary mineral, smectite also occurs as a major mineral in restricted locales. For example, there are mappable layers of abundant smectite situated at the top of the vitric, nonwelded base of the Tiva Canyon Member and at the top of the basal vitrophyre of the Topopah Spring Member. The smectite-rich layer in the Tiva Canyon Member contains 7 to 35%

smectite, while the layer near the base of the Topopah Spring Member contains 5 to 45% smectite. These smectite layers are generally less than 1 m thick but are notably thicker in several areas (e.g., in the rocks transected by drill holes USW G-1, USW G-2 and UE-25a#1). In addition to these laterally continuous smectite-bearing intervals, smectites are abundant in subsurface rocks near several "major structures" which are believed to be major strike-slip faults (Scott and Bonk, 1984). Abundant smectite in these rocks is accompanied by interstratified illite that becomes more abundant with increasing depth (Caporuscio et al., 1982).

#### Clinoptilolite and Mordenite

Bish et al. (1984a) and Vaniman et al. (1984) claim that there are at least four mappable zones of clinoptilolite (or heulandite) plus mordenite in the rocks beneath Yucca Mountain. These zeolite-rich zones occur principally in the nonwelded tops, bottoms, and distal edges of ash flows. Zeolites are also observed in fractures crossing devitrified layers (Carlos, 1985). The various occurrences of zeolites at Yucca Mountain underscore the complexities of zeolite formation at the site and suggest multiple origins for these minerals (Moncure et al., 1981).

#### Analcite and Albite

Secondary analcite and albite are only observed in the deepest tuffaceous rocks beneath Yucca Mountain. Analcite typically first occurs at a depth of approximately 250 m above sea level, but it is observed in the rocks transected by drill hole USW G-2 at a depth of 600 m above sea level. The occurrence of authigenic albite is restricted to depths below 500 m above sea level. Like analcite, the shallowest occurrence of authigenic albite is in drill hole USW G-2; in this borehole, secondary albite is first observed at a depth of 1080 m.

### Conclusions

Semi-quantitative X-ray powder diffraction data for Yucca Mountain tuffs indicate that there are six mappable "mineral types" at Yucca Mountain: primary glass plus tridymite, primary and secondary quartz, secondary smectite, clinoptilolite plus mordenite, secondary analcime, and secondary albite. These mineralogic zones have the following broad characteristics.

- Glass-rich rocks (vitric zones) occur both above and below the reference repository horizon at Yucca Mountain (the Topopah Spring Member). The glasses in vitric zones can be divided into two categories: vitrophyre and nonwelded glass.
- Tridymite, quartz, and cristobalite are abundant in Yucca Mountain tuffs. Tridymite occurs in surficial rocks and persists in subsurface rocks down to the Topopah Spring Member. The disappearance of tridymite with increasing depth is marked by the initial appearance of abundant groundmass quartz. Cristobalite is widespread above the water table and persists to depths greater than 500 m above sea level.
- Smectite is a common accessory mineral in Yucca Mountain tuffs, but it also occurs as a major mineral in (1) two thin, laterally extensive layers and (2) near several major structural features.
- Clinoptilolite and mordenite occur principally in the nonwelded tops, bottoms, and distal edges of ash flows. These zeolites are also observed in fractures crossing devitrified layers.
- Secondary analcime and albite are only observed in the deepest tuffaceous rocks beneath Yucca Mountain.

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## EVALUATION

This report offers preliminary observations on the patterns of distribution of primary and secondary minerals in the tuffaceous rocks at the Yucca Mountain, candidate, HLW repository site. Most of the authors' conclusions are based on data obtained from semi-quantitative X-ray powder diffraction analyses of Yucca Mountain tuffs. These data indicate that there are six mappable "mineral types" at Yucca Mountain: primary glass plus tridymite, primary and secondary quartz, secondary smectite, clinoptilolite plus mordenite, secondary analcime, and secondary albite. Two additional primary minerals, cristobalite and K-bearing alkali feldspar, are nearly ubiquitous in Yucca Mountain rocks.

Despite fairly clear-cut patterns of zonation (or stratigraphic control) of minerals such as smectite, clinoptilolite, and mordenite in the rocks beneath Yucca Mountain, this report reveals that it is not yet possible to accurately predict the proportions of minerals in the rocks at a given subsurface location beneath the mountain. Furthermore, even when zonation permits crude predictions of the relative abundances of minerals, XRD analysis affords only semi-quantitative checks on these predictions. For these reasons, it is evident that much progress remains to be made in the DOE-NNWSI effort to determine the abundances of minerals in rocks along potential radionuclide-release pathways beneath the Yucca Mountain Site.

It would seem that one potentially useful avenue of future DOE-NNWSI mineralogic research would be to make additional correlations between CIPW norm mineralogy and measured mineralogy (the latter determined by XRD analyses and any other appropriate analytical techniques). These correlations could be made not only for many more whole-rock samples of Yucca Mountain tuff, but also for mineral separates obtained from these rocks. Due to the fine-grained textures of the groundmasses of Yucca Mountain tuffs, complete separation of the minerals in these tuffs is impossible at present. However, this restriction should not deter

attempts to obtain partial mineral separates and to identify the proportions of minerals in these materials. This recommendation is based on the assumption that classical methods of mineral separation would, at the very least, yield rock materials in which the proportions of minerals are significantly different from the original rock sample. These materials could be analyzed compositionally and mineralogically in a fashion similar to the way whole-rock samples are analyzed, thereby permitting validation of XRD analyses over wider ranges of composition and mineralogy. This approach would foster greater confidence in the ability of XRD to accurately predict the proportions of minerals in a suite of tuffaceous rocks in which individual rock samples contain significantly different proportions of minerals.

Finally, the accuracy of XRD analyses of Yucca Mountain tuffs would also be improved by obtaining additional data on the compositions of the glasses in these rocks.

EVALUATION OF: Walter G. R., 1982, Theoretical and Experimental Determination of Matrix Diffusion and Related Solute Transport Properties of Fractured Tuffs From the Nevada Test Site. LANL Report LA-9741-MS, 132 pp.

This is a key NNWSI report on matrix diffusion in tuffaceous rocks from the NTS. It appears to be the only report published to date (3/85) that deals with both experimental and theoretical aspects of matrix diffusion in NTS tuffs. The experimental and SEM data that Walter obtained on the tortuosity and constrictivity of pore space in NTS tuffs are particularly noteworthy because they are the only data of that kind that have been published. (By contrast, there are copious data available on the porosities of NTS tuffs.) The principal shortcomings of the report are that: (1) it is not very well written, and, therefore, some of the text is rather difficult to understand; and (2) the theoretical treatment of matrix diffusion is underdeveloped. The latter shortcoming refers to the fact that the theory presented in the report is not applied to any "real" matrix diffusion problems (e.g., predicting the nature and extent of matrix diffusion of a conservative solute in a representative elementary volume of NTS tuff), so it has not yet been demonstrated that the theory can be used in practical applications. The report states that refinements of the theory are proceeding, and efforts are underway to develop a computer code that will permit the theory to be tested. However, there is no evidence from more recent NNWSI reports that work has progressed very far. In light of the work completed by Walter, development of a versatile matrix-diffusion computer code, followed by satisfactory verification and benchmarking, would seem to be an appropriate future DOE research activity.

EVALUATION OF: Weeks, E. P., and Wilson, W. E., 1984, Preliminary Evaluation of Hydrologic Properties of Cores of Unsaturated Tuff, Test Well USW H-1, Yucca Mountain, Nevada. U.S. Geological Survey Water-Resources Investigations Report 84-4193, 30 pp.

This is an important report because: (1) it presents new and (apparently) high-quality hydrologic data that can be used to ascertain the nature of groundwater movement in the unsaturated zone beneath Yucca Mountain, and (2) it is one of the documents that is cited repeatedly by DOE (1984) as a source of data that lend support to the DOE "matrix flow" hydrologic model for the unsaturated zone at Yucca Mountain. However, the hydrologic data presented in this report apply only to unfractured tuff.

Various comments on the more significant data/conclusions presented in the report are given below.

- ◆ Ambient moisture tension in the unfractured tuffs was found to range from 1 to 2 bars. Unfortunately, however, Weeks and Wilson do not indicate whether this finding was expected or surprising, and they do not explain how their data on moisture tension are related to the matric ("suction") potentials of the tuffaceous rocks. It would be useful to know whether the data on moisture tension are consistent with the DOE (1984) assertion that unsaturated, porous, tuffaceous rocks beneath Yucca Mountain have matric potentials that range from -5 to -20 bars.
- ◆ It is stated on p. 2 of the report that "In unsaturated zones that are hundreds of meters thick, the large near-surface fluctuations in soil-moisture tension that result from episodic infiltration events followed by evapotranspiration become totally dampened at depth, and deep percolation becomes nearly constant with time." This is a very significant conclusion that does not appear in the abstract of the report. The conclusion is important because it forms the basis for estimating an average vertical groundwater flux in the unsaturated zone using information on hydraulic-head gradient and effective hydraulic conductivity.
- ◆ From their data, Weeks and Wilson estimate that vertical flux of groundwater through the unsaturated, porous, tuffaceous rocks beneath Yucca Mountain ranges from 0.003 to 0.2 mm/yr. This estimate suggests that, in the unsaturated, porous, and unfractured tuffaceous rocks beneath Yucca Mountain, groundwater movement is extremely slow.

It is emphasized above that the Weeks and Wilson data apply strictly to unfractured tuffaceous rocks. This point was stressed because it should be kept in mind that the Weeks and Wilson data do not appear to preclude (or even contradict) the suggestion that groundwater movement in the unsaturated, porous, tuffaceous rocks beneath Yucca Mountain may occur

principally by fracture flow. Thus, it is legitimate to cite the Weeks and Wilson data as evidence supporting slow movement of groundwater in the unsaturated zone beneath Yucca Mountain if it is assumed a priori that groundwater flow occurs predominantly by matrix flow, but it is not legitimate to use these data as evidence supporting a "matrix flow" hydrologic model vis-a-vis a "fracture flow" model because the Weeks and Wilson data indicate nothing about the likelihood or unlikelihood of fracture flow of groundwater in the unsaturated zone at Yucca Mountain.

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DOE, 1984, Draft Environmental Assessment, Yucca Mountain Site, Nevada Research and Development Area, Nevada. DOE/RW-0012.

EVALUATION OF: Montazer, F., and Wilson, W. E., 1984, Conceptual Hydrologic Model of Flow in the Unsaturated Zone, Yucca Mountain, Nevada. U.S. Geological Survey Water-Resources Investigations Report 84-4345, 55 pp.

This very important report describes a detailed conceptual model of groundwater flow in the unsaturated zone beneath the candidate repository site (the "primary repository area") at Yucca Mountain, Nevada. This report is the most important of its kind published to date because: (1) it describes and evaluates most of the important information that is currently available concerning the groundwater hydrology of the unsaturated zone at Yucca Mountain; (2) it presents a model of groundwater flow that is sufficiently integrated and detailed to allow important tentative conclusions to be drawn concerning groundwater travel times and the geochemistry of groundwaters beneath the Site; and (3) it appears to be the document that the DOE relied upon most heavily in developing the conceptual hydrologic model for the unsaturated zone at Yucca Mountain described in the Draft Environmental Assessment for the Yucca Mountain Site (DOE, 1984).

The key elements of the model developed by Montazer and Wilson are:

- ◆ The average annual rate of groundwater infiltration into Yucca Mountain (= average annual recharge rate to the water table beneath the mountain) is probably no greater than 4.5 mm/yr. Also, the rate of groundwater infiltration into the mountain is variable both spatially and temporally, and probably occurs as periodic, moderately intense pulses.
- ◆ A combination of dipping beds, permeability layering, and capillary-barrier effects results in significant lateral flow of groundwater within the Paintbrush nonwelded unit toward bounding "structural features." This lateral flow diverts a substantial fraction of downward percolating groundwater away from the underlying Topopah Spring unit, the current reference repository horizon. An important result of this hypothesized pattern of groundwater flow is that rates of percolation through the Topopah Spring unit are decreased to 1 mm/yr or less.
- ◆ Limited fracture flow of groundwater may occur in the higher levels of the Topopah Spring unit; however, diffusion into the matrix probably diminishes the extent of fracture flow in the deeper parts of this unit.
- ◆ It is likely that a substantial fraction of the groundwater that flows into the Calico Hills unit from the overlying Topopah Spring unit is diverted laterally (down-dip) until "structural features" are encountered which permit subsequent flow down to the water table. Vertical flux of groundwater through the Calico Hills unit is

estimated to be less than 0.006 mm/yr.

- ♦ "Structural features" probably transmit the major fraction of percolating groundwaters at Yucca Mountain.

Three major shortcomings of the Montazer and Wilson model are evident. First, the patterns of groundwater flow through the unsaturated zone beneath Yucca Mountain that are inferred from the conceptual model developed by Montazer and Wilson are profoundly influenced by the conclusion that a large fraction of the groundwater that reaches the base of the Tiva Canyon welded unit is diverted down-dip along the contact between this unit and the underlying Paintbrush nonwelded unit. This is an extremely important aspect of the model, because if this lateral flow does indeed occur to the extent envisioned by Montazer and Wilson, then it is virtually certain that very little groundwater flows through the subjacent Topopah Spring unit. However, the assumption of lateral flow in the Paintbrush nonwelded unit is largely based on theory of capillary barriers that may strictly apply only to solid materials of uniform porosity and fracture density that are in contact along a planar surface. The rocks in the Tiva Canyon welded unit and the Paintbrush nonwelded unit certainly do not have either uniform porosities or uniform fracture densities, and the boundary between these units may also be very hummocky rather than planar. Thus the scenario of lateral (down-dip) flow of groundwater in the Paintbrush nonwelded unit described by Montazer and Wilson is probably oversimplified and may be misleading regarding the amount of lateral flow that can reasonably be expected to occur in this unit.

Second, it is implicitly assumed (from surface geologic mapping?) that "structural features" (major faults) are scarce in the central portion of the primary repository area. Evidently, the Ghost Dance fault is the only known major "structural feature" that outcrops in this area. However, on the southeastern boundary of the primary repository area where the Topopah Spring unit is at a shallower depth than it is to the north where the proposed engineered facility is to be located, major faults are in abundance; therefore, the question arises whether it is possible that additional "major" faults in the central portion of the primary repository area remain to be discovered. (Perhaps there are "major" faults in this area that do not have obvious outcrop features or do not outcrop at all.) If it is shown eventually that the Paintbrush nonwelded unit beneath the central section of the primary repository area is in fact transected by a significant number of "major" faults, then it might be difficult to deny the possibility of significant and rapid fracture flow of groundwater through this unit and the underlying Topopah Spring unit.

Finally, as noted above, Montazer and Wilson apparently use the expression "structural feature" to mean "major fault." However, they do not explain what they mean by "major fault," and, therefore, it is uncertain how much deformation would have to be associated with a

fracture before it would be "major fault" according to Montazer and Wilson. The distinction is important, because Montzer and Wilson state that flow of groundwater through "fractures" is very unlikely in both the Paintbrush and Calico Hills nonwelded units, but that flow through "structural features" in these units is the predominant mechanism of groundwater movement toward the water table beneath Yucca Mountain.

#### References

DOE, 1984, Draft Environmental Assessment, Yucca Mountain Site, Nevada Research and Development Area, Nevada. DOE/RW-0012.

EVALUATION OF: Thordarson, W., 1965, Perched Ground Water in Zeolitized-Bedded Tuff, Rainier Mesa and Vicinity, Nevada Test Site, Nevada. U.S. Geological Survey Trace Elements Investigative Report TEI-862, 90 p.

This important report describes the occurrence, movement, and discharge of perched groundwater in tuffaceous rocks that cap and underlie Rainier Mesa. According to Thordarson (p. 10): "The interpretations presented in this report are based primarily on observations of ground-water occurrence in several miles of underground workings and on hydraulic data obtained from six deep test holes. Also utilized were laboratory determinations of the porosity, permeability, and water content of cores and chunk samples of the tuffaceous strata." The tuffaceous strata referred to by Thordarson are (1) 2,000 to 5,000 feet thick, (2) comprise both welded and bedded tuffs, and (3) lie well above the regional water table. These geohydrologic conditions are similar to those at the Yucca Mountain Site to the southwest; therefore, it is widely believed that observations of geohydrologic conditions at Rainier Mesa can provide valuable insights into the nature of groundwater flow in the unsaturated zone beneath Yucca Mountain.

The key points made in this report are as follows:

- ◆ Groundwater movement beneath Rainier Mesa occurs principally by flow along steeply dipping open fractures. Significantly, these fractures are not "major" faults; that is, extensive movement and deformation have not occurred along these fractures, nor do they extend to the surface of the Mesa. Rates of groundwater flow in these fractures are highly variable and depend mainly on the degree of local fracture connectivity.
- ◆ A fraction of the groundwater beneath Rainier Mesa accumulates and remains perched for significant periods of time in poorly connected fractures in a zeolitic-bedded tuff that lies hundreds of feet above the regional water table. (Because of its low permeability, no appreciable volume of water moves through the interstices of this tuff.) Three factors, all highly variable, seem to determine the water-bearing ability and potential storage capacity of individual fractures, namely: (1) the extent of the fracture, (2) the width of the fracture opening (fracture aperture), and (3) the degree to which the fracture is sealed along its strike and in its lower extremities. The apertures of fractures (faults and joints) are highly variable. Some faults are open as much as 6 inches, whereas others are nearly sealed with fault gouge. Furthermore, some fractures, open several inches at one point, are tightly closed within just a few feet along their strike. (These variations in fracture aperture are attributed to local pinching and swelling that accompanied the creation and development of the faults.) Other faults are observed to be completely closed by clayey gouge or are filled with silt and clay

particles, the latter possibly carried downward by percolating groundwater. Most joints are closed, but some have apertures as wide as several inches.

- ◆ Most of the groundwater-bearing fractures intersected by tunnels constructed in Rainier Mesa were observed to drain completely within a few weeks or months, but water continued to drip from some of the fractures for 2 years or more (Clebsch, 1960). It was also observed that numerous open but completely dry fractures were interspersed among the water-bearing fractures.
- ◆ Evidently, lateral movement of interstitial water along bedding planes in the low-permeability zeolitic-bedded tuff beneath Rainier Mesa is negligible compared with movement of water along fractures.
- ◆ The age of perched groundwater beneath Rainier Mesa has been estimated to be between 0.8 and 6.0 years (Clebsch, 1961). This range of ages implies that groundwater flows downward at a rate ranging from 80 to 500 feet per year.
- ◆ Specific conductance data (Keller, 1960, 1962) indicate that groundwater in the interstices (matrix) of the zeolitic-bedded tuff beneath Rainier Mesa is significantly more saline than the groundwater that is perched near fractures. The salinity of interstitial water probably ranges from 3,700 to 5,100 ppm. This salinity is roughly 18 to 30 times that of the perched water. Thordarson believes that these differences in salinity can be explained by: (1) addition of ions to the pore water by "ionization of clay particles," (2) differences in the residence time of the interstitial and fracture water, and/or (3) greater salinity of the interstitial water at the time of its introduction into the bedded tuff. The first hypothesis was suggested by Keller (1962), who surmised that the apparent differences in salinity are due to "release" of ions by clay particles in the tuffs. Keller further speculated that these ions are weakly bound to the clay, and that they would remain in the rock if the groundwater was purged from it.

#### References

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EVALUATION OF: Henne, M. S., 1982, The Dissolution of Rainier Mesa Volcanic Tuffs, and its Application to the Analysis of the Groundwater Environment. M.S. Thesis, University of Nevada, Reno, 113 p.

This poorly written thesis describes research that was conducted to ascertain groundwater travel times in the unsaturated zone beneath Rainier Mesa (NTS). The research included both laboratory investigations and field studies. The principal objective of the laboratory work was to establish experimentally the effects of pH, temperature, and surface area on the dissolution of glass-rich tuff from Rainier Mesa. Also, the experiments were designed to elucidate the quantitative relationship between: (1) reaction time, (2) tuff surface area to water volume ratio, and (3) the concentration of  $\text{SiO}_2$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{++}$ , and  $\text{Mg}^{++}$  in Rainier Mesa groundwaters. This quantitative relationship (eventually cast in the form of a rate equation for dissolution of silica from Rainier Mesa tuff) was employed to estimate the retention times of Rainier Mesa groundwaters. The field studies consisted mainly of collecting samples of (1) soil waters from the surface of Rainier Mesa, and (2) groundwaters from various tunnel excavations beneath the Mesa. Groundwaters in the tunnels were collected with lysimeters and at the sites of natural seeps. The most noteworthy findings of the laboratory and field studies are described below.

#### Results of Laboratory Studies

- ◆ The results of tuff dissolution experiments performed at 25, 30, 50, and 70°C for up to 20 days are in fairly good agreement with results obtained previously by White and Claassen (1980). It was found that pH did not affect the dissolution of  $\text{SiO}_2$ , had only a slight effect on the dissolution of  $\text{Na}^+$ , but had a major effect on the dissolution of  $\text{Ca}^{++}$  and  $\text{Mg}^{++}$ . (The amounts of dissolved Ca and Mg were greater at the lower values of pH.) By contrast, potassium exhibited irregular behavior: at low values of pH the concentration of  $\text{K}^+$  increased at first but subsequently began to decline. However, at values of pH above approximately 6.4, the quantities of dissolved potassium increased steadily during experimentation.
- ◆ It was observed that the rates of mass transfer of  $\text{SiO}_2$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{++}$ , and  $\text{Mg}^{++}$  from Rainier Mesa tuff to contiguous water were greater for the experiments with higher tuff surface area to water volume ratio. Therefore, Henne concluded that, in using dissolution kinetics to estimate the retention time of a groundwater in tuffaceous rocks, it is essential to have an accurate value for the reactive surface area of the rocks.
- ◆ Experiments performed at 25, 50, and 70°C indicate collectively that, for a given tuff surface area to water volume ratio and reaction time, silica solubility increases sharply with increasing

temperature.

- ♦ At 70°C, steady state concentrations of Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>++</sup>, and Mg<sup>++</sup> were achieved in 40 hrs, but the concentration of dissolved SiO<sub>2</sub> continued to rise steadily for up to 284 hrs. Similar behavior of silica solubility was observed at 25 and 50°C.
- ♦ The results of all experiments indicate that silica concentrations provide the most reliable means of estimating groundwater retention time.

#### Results of Field Studies

- ♦ Meteoric waters that flow from the soils on Rainier Mesa into the subjacent rocks experience an increase in pH.
- ♦ The chemistries of groundwaters in Rainier Mesa tunnels vary with geochemical environment, but show only slight variation with time.
- ♦ Retention times of Rainier Mesa groundwaters were estimated in two ways. The first method utilized a long term trend in the cation to silica ratio observed in lysimeter 2 and showed that the maximum in this ratio was observed in June. This observation implies groundwater infiltration six weeks to three months prior to this time (i.e., during the annual spring thaw on the surface of Rainier Mesa when infiltrating meltwaters dissolve "extra" cations from the thin soils on the Mesa). The second method employed silica-dissolution kinetics to estimate the retention time of the groundwaters. Assuming that the tuff surface area to water volume ratio is approximately 100 square meters per liter, and using the minimum silica concentration of the groundwaters collected in the tunnels--33 mg/l--the retention time of groundwater in the Mesa was calculated to be as short as 3 months. The values obtained by the two methods agree closely but "are approximations made with unproven estimates" (Henne, 1982, p. 80).

There are three apparent deficiencies of the research described in this thesis:

1. The silica-dissolution rate equation developed by Henne is of uncertain accuracy. There is no discussion of potential sources of error in the data used to derive the rate equation. Also, Henne fails to describe his regression methods in sufficient detail to permit an assessment of his methodology, and appropriate statistical data concerning the "goodness of fit" of his equation are not presented.
2. Henne's calculation of a minimum three-month travel time for groundwater sampled using lysimeter 2 is based on an assumed value of 100 square meters per liter for the tuff surface area to

groundwater volume ratio. However, no justification is provided for the use of this particular number. Therefore (and for reasons presented in discussion item 1 above), the accuracy of the calculated three-month travel time is very uncertain.

3. Henne does not state what fraction of percolating groundwaters reach the tunnels beneath Rainier Mesa in just three months. It is almost certain that Henne does not believe that all groundwaters in Rainier Mesa percolate downward that rapidly, but he doesn't address this important subject at all in his thesis.

Despite the criticisms above, the research performed by Henne remains noteworthy. The finding that some groundwaters in tunnels beneath Rainier Mesa contain very little dissolved silica is interesting and possibly very significant. Likewise the discovery that the ratio of cations to silica in these groundwaters exhibits an annual maximum in June, an observation that is explained nicely by the hypothesis that "extra" cations released from the thin soils on Rainier Mesa during the annual spring thaw reach the tunnels beneath Rainier Mesa in just a few weeks. Collectively, the data obtained by Henne should be viewed as permissive evidence that some of the groundwaters that infiltrate Rainier Mesa are capable of percolating downward very rapidly through the underlying unsaturated tuffaceous rocks.

#### References

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EVALUATION OF: Knauss, K. G., 1984, Petrologic and Geochemical Characterization of the Topopah Spring Member of the Paintbrush Tuff: Outcrop Samples Used in Waste Package Experiments. Report UCRL-53558, 36 pp.

This well-written and informative report summarizes the general geology of the Topopah Spring Tuff (Tpt) and presents a detailed description of the petrographic, mineralogic, and geochemical characteristics of samples of this tuff obtained from the southern end of Fran Ridge. The recounting of the general geology of the Tpt, originally described by Lipman et al. (1966), is useful because it serves to remind the reader that this rock is not a single homogeneous layer, but rather a multiple-flow, compound cooling unit. This fact is manifested by the observation that there is considerable textural variability--and even some notable mineralogical variability--in the direction perpendicular to layering. However, more useful still are the very detailed descriptions of the petrographic properties and mineralogic characteristics of the Tpt samples obtained from Fran Ridge. These descriptions include numerous photomicrographs and analyses of individual minerals, and thus, collectively, they constitute an important data base for use in predicting and assessing the performance of this rock in various laboratory and field tests relative to the siting of an HLW repository at Yucca Mountain. To cite one example, it is noteworthy that Knauss has found that many of the microfractures observed in thin sections of the Tpt are nearly completely filled with iron-rich and/or manganese-rich materials (it is likely that these materials are hydrated oxides of iron and manganese). This observation is potentially significant for interpreting the results of radionuclide sorption tests, because iron-rich materials (and perhaps the manganese-rich materials as well) are potentially important radionuclide sorbents.

The numerous admirable qualities of this report notwithstanding, two apparent shortcomings are evident. First, the report is somewhat limited in scope. *Sensu stricto*, detailed descriptions of the mineralogic and geochemical characteristics of the Tpt presented by Knauss pertain only to a narrow interval of this unit--namely, the densely welded section of the Tpt which has been identified as the leading candidate host rock for an engineered facility. Therefore, in specific instances, the data obtained by Knauss may not apply to the partly welded and unwelded layers of the Tpt that underlie the densely welded zone. Second, the mineralogic characterization of the samples from Fran Ridge is unsatisfactory for some applications. In particular, the characterization of clay mineralogy is unsatisfactory for interpreting the performance of Tpt in radionuclide sorption experiments. Knauss notes that clay minerals are present in the Fran Ridge samples, occurring most commonly in the altered rims of pumice fragments in the rock, but the quantity of these minerals is insufficient to be detected by XRD methods, and no additional effort was expended to determine the kinds and amounts of these minerals that occur in the rock. Clearly, some follow-up work is called for because, despite their meager amounts, clay minerals may be the dominant sorbing

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minerals in the Tpt.