

Mifflin & Associates, Inc.
2700 East Sunset Road, Suite C25
Las Vegas, Nevada 89120
702/798-0402 & 3026
FAX: 702/798-6074

PRELIMINARY

YUCCA MOUNTAIN PROJECT

A Summary of Technical Support Activities

January 1987 to June 1988

By:

**Mifflin & Associates, Inc.
Las Vegas, Nevada**

Submitted to:

**State of Nevada
Agency for Nuclear Projects
Nuclear Waste Project Office
Carson City, Nevada**

RECEIVED

MAY 15 1989

NUCLEAR WASTE PROJECT OFFICE

**May 1989
Volume 2**

89 10 10 302 - Part 2

100

Section C

Geochemistry and Mineralogy Program

Geochemistry and Mineralogy Program

Introduction

The activities in the Geochemistry and Mineralogy section of our program support three independent and interrelated subject areas which are:

1. Geochemical retardation/transport of radionuclides to the accessible environment.
2. Site-specific mineralogy and geophysical studies to establish the hydrogeology of the vadose zone.
3. Past climate and related genesis of authigenic desert carbonates and silicates.

Within the classification of these three licensing issues, there are a total of ten intensive review and research activities that have been performed. These activities are distributed in the following manner.

1. **Geochemical Retardation:**
 - a. An assessment of the potential for radionuclide sorption as a function of authigenic mineral stability with respect to thermodynamic properties of zeolites, clays, and associated silicates and oxyhydroxides.
 - b. Determination and characterization of the behavior of authigenic zeolites, clays, and transition metal oxyhydroxides during sorption and desorption of radionuclides (and proxies) under laboratory-imposed repository conditions.
 - c. An assessment of volcanic glass stability with respect to magnetic and paramagnetic primary minerals included in the volcanic glasses of Yucca Mountain.
 - d. An assessment of the geochemical and mineralogical stability of rhyolitic glass at Yucca Mountain with respect to authigenic mineral production and its relation to geochemical retardation of radionuclides.
 - e. An assessment of desert varnish dating to determine its utility with respect to determining the rates of authigenic mineral formation from rhyolitic glass at Yucca Mountain.
2. **Site-Specific Hydrogeology:**
 - a. Utilization of tritium, carbon-14, and iodine concentration exchanged into zeolite supercages to determine the relative age of last vadose waters of exposure, to assess the rate of fracture flow in vadose-zone liquid transport.
 - b. To determine the magnetic stratigraphy for Yucca Mountain for use as a drilling control during sample collection and search for vadose water.
3. **Past climate and desert carbonates:**
 - a. Characterization of diagenetic events at Lake Tecopa for the resolution of hydrostratigraphic events as they relate to past climate in the region of Yucca Mountain.
 - b. An assessment of genesis of desert carbonates with respect to the interpretation of past climate events as they can be resolved from trenches and ground-water discharge deposits.

c. **Characterization of opaline and carbonate deposits with specific reference to Trenches 14, 17, 1, and the sand ramps.**

The basic design and focus of the geochemical retardation/transport section of the program is to address the ability or inability of the natural environment to isolate radioactive waste from the accessible environment after repository closure. In order to accomplish this task, it has been necessary to assess the thermodynamics of the vadose-zone system with respect to vadose-water chemistry, mineralogy, and temperature (see Appendix C: Bowers, T. J. and R. G. Burns, 1988). These information can be utilized to ascertain sorptive mineral stability under repository conditions. However, predictive value is only as good as input data provided. In this particular case, there is a serious void in good vadose-water chemistry and therefore until this void is filled, the thermodynamic calculations must remain tenuous.

In a parallel study, the sorption behavior of single-crystal zeolites are being assessed (see Appendix C: Wood, V. J., et al., 1988). Crystallographic orientation, initial supercage composition among a host of other parameters, affect the sorption capacity of Yucca Mountain type zeolites such as clinoptilolite and heulandite. These studies will provide a predictive baseline of radionuclide behavior with respect to zeolite crystal chemistry and allow us to move into whole-rock studies in the future. This overall base of information will provide an ability to address our ultimate goal which is the retardation capacity of fracture surfaces, the Topopah Springs Member of the Painbrush Tuff and the Calico Hills formation. With respect to the Calico Hills formation, there is concern with regards to glass and authigenic mineral stability. This issue is being addressed with the glass studies that are described in this report (see Appendix C: Blundy, J., et al., 1987, 1988).

Site-specific hydrogeology issues that are being addressed in our studies involve drilling and obtaining fracture and matrix samples that contain zeolites. Utilizing a tandemron in Toronto, we are developing procedures to analyze for gases such as C-14 to determine the age of the water of last exposure. These information will give us a better understanding of the fracture flow mechanism at Yucca Mountain.

Past-climate geochemical studies are primarily support-type studies assisting in the interpretation of stratigraphic events (see Appendix C: O'Hara, P. F., et al., 1988). In addition to these, specific studies regarding authigenic carbonates and opal are aiding interpretation of hydrologic and paleoclimatic events and processes for the Yucca Mountain trenches and surrounding desert region.

Appendix C contains abstracts of papers presented at professional symposia and other technical documents that are offshoots of our efforts.

Geochemical Retardation/Transport of Radionuclides to the Accessible Environment.

The capacity for Yucca Mountain tuffs to provide radionuclide retardation for the limitation of radionuclide transport to the accessible environment is an extremely complex issue. It deals with the identification of: the most likely paths of travel, potentially sorptive mineral availability along those paths, crystal orientation, chemical composition, mineral and glass stability under natural and imposed conditions, colloid formation, precipitation, and diffusion. The following efforts explore various aspects of the issue of the natural retardation barrier at Yucca Mountain to assess the capability of that barrier to provide meaningful retardation.

Geochemistry and Mineralogy

ISSUES:

Can potentially sorptive minerals such as clinoptilolite, mordenite, smectite, and other authigenics provide retardation of radionuclides to the extent that credit can be taken by the DOE for isolation of the radioactive waste from the accessible environment after closure in accordance with the requirements set forth in 40 CFR Part 191, 10 CFR Part 60, and 10 CFR Part 960? Will these potentially sorptive minerals remain actively stable and capable to provide sorption even under near-field and far-field repository conditions?

Characterization Issues:

Can we construct activity diagrams for clinoptilolite to provide sufficient data relative to the susceptibility of this zeolite to further diagenetic reactions?

Can we construct activity diagrams for mordenite?

Can we construct activity diagrams for the smectites?

Can we obtain sufficient in situ chemical data concerning vadose-water chemistry to be able to construct activity diagrams for the authigenic minerals situated in the vadose zone?

Can we obtain sufficient in situ ground-water chemical analysis to be able to construct activity diagrams for authigenic minerals in the saturated zone?

GENERAL OBJECTIVE:

Develop activity diagrams for authigenic mineral stability relating to the geochemistry of the aqueous fluids and temperatures in the near and far fields, so as to be able to predict their stability under repository conditions and thereby assist in understanding the role of these minerals during potential retardation of radionuclides.

Specific Objectives:

Review the DOE water-chemistry literature to obtain basic chemical conditions that might be used for constructing activity diagrams.

Review the open literature for the same purpose, since the DOE literature is incomplete and potentially inaccurate.

Review the open literature for basic thermodynamic properties of clinoptilolite and associated minerals.

Construct multicomponent activity diagrams for clinoptilolite on the basis of aluminosilicate activity and temperature.

ACTIVITY SUMMARY:

The stability limits of clinoptilolite and its vulnerability to changes in ground-water chemistry relative to well J-13 have been assessed, by constructing activity diagrams for clinoptilolite solid solutions in the system Ca-Na-K-Mg-Fe-Al-Si-H₂O employing available thermodynamic data for relevant oxide and aluminosilicate phases (see Appendix C: Bowers, T. J. and R. G. Burns, 1988, and R. G. Burns and T. J. Bowers, 1988).

FINDINGS:

The results of our investigations have been submitted to the American Mineralogist for publication (see Appendix C for a copy of the paper. Significantly, it appears that authigenic minerals such as clinoptilolite modify and are modified by ground-water compositions. We have been unable to acquire vadose-water compositions to date and therefore can make no comments concerning zeolite stability in the vadose zone.

INTERPRETATION OF FINDINGS:

The following observations are made:

The coexistence of clinoptilolite with opal correlates with its calculated wide stability field in aqueous solutions saturated with amorphous silica.

Clinoptilolite-smectite assemblages indicate that the zeolite crystallized from ground water with dissolved Al concentrations lower than saturation values with respect to gibbsite.

Calcic clinoptilolite associated with calcite are consistent with crystallization from fracture-flow ground water containing Ca^{+2} and HCO_3^- derived from incipient dissolution of microcrystalline devitrified tuffs. Alkali-rich clinoptilolites correlate with ground water having elevated Na^+ and K^+ but depleted Ca^{2+} concentrations which are associated with altered vitric tuffs.

The clinoptilolite stability field diminishes appreciably between 25°C and 100°C, correlating with burial diagenetic reactions; but, confirming doubts about the thermal stability of clinoptilolite when exposed to repository conditions.

ADDITIONAL WORK REQUIRED:

Obtain vadose-water chemical data and recalculate clinoptilolite stability using these information.

Calculate stability fields of the other zeolites and clays that might provide sorption retardation for radionuclides.

Previous research into zeolite and clay stability will be utilized more heavily in future analytical efforts.

RECOMMENDED PROGRAM:

To continue the existing program of activities and to collect in situ data using our own drilling technology. These new data could then be utilized to calculate authigenic mineral stability more accurately than the present analytical efforts.

Principal Investigator:

Dr. R. G. Burns (MIT) with Dr. T. Bowers (MIT) are Co-Principal Investigators on the project.

Geochemistry and Mineralogy

ISSUES:

To what extent, if any, can the DOE take credit for radionuclide sorption by zeolites, clays, and oxyhydroxides? Can credit be taken for key radionuclides whose travel time and concentration limits might otherwise exceed the established limits?

Characterization Issues:

How do clays and zeolites behave during sorption/desorption? To what extent do they favor certain radionuclides? How does temperature affect sorption, sorption rates, desorption, and desorption rates? How do radionuclide concentrations affect sorption and desorption? How does zeolite crystal orientation affect sorption and desorption?

How do transition-metal oxyhydroxides respond to actinide transport as colloids? To what extent if any do transition-metal oxyhydroxides provide sorption? If sorption is provided, by what mechanism does this occur?

Review Issue:

Does the sorption/desorption work done by the DOE contractors cover the significant issues and are their methods of analyses sound to the extent that they report conservative values?

GENERAL OBJECTIVE:

Determination and characterization of the behavior of authigenic zeolites, clays, and transition-metal oxyhydroxides during sorption and desorption of radionuclides (and proxies) under repository near-field and far-field conditions.

Specific Objectives:

Review the sorption/desorption literature provided by the DOE contractors and determine the value of those data with respect to providing a comprehensive understanding of the retardation parameters for the Yucca Mountain site. Determine whether these parameters are conservative and are focused towards obtaining realistic in situ approximations.

Provide basic laboratory analyses on single crystal (pure mineral) sorption/desorption studies using a variety of proxies for radionuclides. Utilize co-calibrated equipment to insure reproducibility of the results.

Through the experiments with pure minerals, provide an understanding of the effects of variation in temperature, crystal orientation, time of exposure, crystal size, radionuclide (proxy) concentrations, competing cations, sieving effects and other parameters that may be important with respect to predicting in situ Yucca Mountain sorption/desorption reactions.

Provide an understanding on an atomic/molecular basis on how, where, and why sorption/desorption take place with respect to each mineral and radionuclide in the potential reaction, so that there is a sound theoretical basis for future postclosure predictions of potential retardation.

Provide similar basic information as explained in the previous objectives for minerals in fractures and compare these data to similar information collected for minerals in pores.

ACTIVITY SUMMARY:

Constant temperature bath exchange solutions have been utilized to explore single crystals of known composition (by electron microprobe [EM], scanning electron microprobe [SEM], and ion microprobe analyses [SIMS]). Single crystals of clinoptilolite, mordenite, and analcime have been studied. After experimental exposure, SEM, EM, and SIMS analyses of each crystal with respect to its crystallographic orientation is performed. These experiments are run with variations in both solutions (proxies for radionuclides) and variations in temperatures (see Appendix C: Wood, V. J., M. S. Hubbard, and R. G. Burns, 1988).

Magic angle NMR studies are made on exchanged crystals to determine the sites of sorption by the radionuclide proxies.

Clay minerals and oxyhydroxides have not been utilized as yet during the experiments.

Sorption/desorption data have been reviewed as has been provided by the DOE program.

FINDINGS:

Magic angle studies are beginning to indicate where in the clinoptilolite and heulandite structures various exchanged ions are located. These information are preliminary and more work is needed to resolve this basic issue.

Analcite is not a very good exchanger, primarily because of its tight structure; consequently, it will be insignificant with respect to acting as a sorbing barrier to radionuclide escape from the repository.

Both heulandite and clinoptilolite are relatively good exchangers and both show crystallographic influences for Cs (clinoptilolite shows less of an influence than heulandite). The Cs concentration of the (010) face of heulandite is considerably lower than those of the other two faces, demonstrating that Cs readily enters the heulandite structure along the open channel [100] and [001] direction. The Cs concentrations of the heulandite (100) and (001) faces are comparable or slightly greater than corresponding faces of clinoptilolite which conflicts with older literature which states that the cation exchange properties of heulandite and clinoptilolite are quite dissimilar (see Appendix C).

Since the ground water flowing through Yucca Mountain is likely (chemistry unknown at present) to be dominated by Na, HCO_3 , and Cl ions, these were included in some of the experiments. The results of these analyses indicate a slight enrichment of Na and a depletion of K occurred in the Na-loaded crystals (clinoptilolite). The presence of NaCl, however, decreases the uptake of Cs into clinoptilolite and heulandite (see Appendix C).

Clinoptilolite crystals have been mounted on their (010) faces and reacted with 50 ml aliquots of CsCl solutions ranging in concentration from 1 M to 0.0001 M. The amount of Cs exchanged into clinoptilolite crystals decreases with increasing dilution of the CsCl solutions. The efficiency of removal of Cs uptake by the (010) crystal faces increases from 1 M CsCl to 0.0001 M CsCl. Heulandite shows similar effects of CsCl dilution to clinoptilolite (see Appendix C).

INTERPRETATION OF FINDINGS:

The findings of our experiments indicate that various major sorption issues are not being addressed by the DOE subcontractors. Among these issues are the effects of crystal orientation and crystal size. The mineralogy investigators working for the DOE do not report crystal orientation for minerals described from the fractures, therefore, it is not feasible at present to determine potential sorption in the fracture system.

We have concluded that of the zeolites present clinoptilolite, heulandite, and mordenite have the potential to be good sorbing exchangers. Temperature, crystal size, crystal orientation, vadose-water chemistry, concentrations of competing cations, interactions with competing exchangers, initial cations within the supercage of the exchangers, among other controlling parameters greatly affect the potential sorption ability of the natural environment. Unless these issues are fully addressed, the predictability of natural barrier sorption for Yucca Mountain is virtually impossible.

ADDITIONAL WORK REQUIRED:

Reestablish our program using magic angle NMR.

Continue our standards exchange single-crystal bath studies.

Start oxyhydroxide studies with actinide proxies.

Start clay exchange, ion filtration studies.

Analyze key pore and fracture horizons which may provide the bulk of the potential sorption effort at Yucca Mountain.

Build a predictive model using the field and laboratory data collected.

RECOMMENDED PROGRAM/EXISTING PROGRAM:

Objective:

To respond to our Key and Characterization Issues relative to licensing issues.

Activity:

To continue our efforts as outlined in Additional Work Required.

EXISTING PROGRAM:

The existing program is moving ahead with very satisfactory progress. It will be necessary to obtain in situ samples from Yucca Mountain to bring this research in line with licensing issues.

Principal Investigator:

Dr. R. G. Burns (MIT) is the Principal Investigator of this project.

Geochemistry and Mineralogy

ISSUE:

Will glass instability above and below the proposed high-level nuclear waste repository jeopardize the isolation or assist in the isolation of radionuclides from the accessible environment?

Characterization Issues:

To what extent do iron oxides, titanium oxides, and oxyhydroxides as microphenocrysts provide chemical information regarding geochemical-environmental parameters during the diagenetic hydration of acid volcanic glass.

To what extent do the iron oxides and oxyhydroxides contribute to volcanic-glass stability? Instability? In this respect, do they contribute to elevated hydration rates of the glass, and if so, by what reaction mechanism?

How can these information be used to assess sorption chemistry, colloid formation, and neomineralization of smectites and zeolites?

GENERAL OBJECTIVES:

Determination and identification of magnetic and paramagnetic microphenocrysts in volcanic glass in tuffs at Yucca Mountain.

Specific Objectives:

Identify micromineral phenocrysts in volcanic glass at Yucca Mountain.

Describe their distribution, magnetic properties and crystal structure.

Describe and identify these minerals with respect to their stratigraphic position above and below the proposed repository horizon.

Collect similar data from fresh and altered (hydrated) glasses to acquire data on iron mobility.

ACTIVITY SUMMARY:

Samples have been collected from the Tiva Canyon and upper portions of Topopah Springs Member of the Paintbrush Tuff. Sample collection has been made during magnetic stratigraphy investigations (see Appendix C: Schlinger, C. M., 1989).

Laboratory data using Transmission Electron Microscopy (TEM) and magnetics have been acquired.

FINDINGS:

The iron-oxide phases appear to be mostly magnetite-maghemite microphenocrysts. Euhedral microphenocrysts of silicate phases have been found to be present in the upper Topopah Springs Member. It appears that the upper Topopah Springs Member has undergone remagnetization (CRM) which suggests that the time stratigraphic depositional history may be correct. This period of remagnetization probably has occurred during the emplacement of the Tiva Canyon Member (see Appendix C).

INTERPRETATION OF FINDINGS:

Magnetic and paramagnetic microphenocrysts are subject to diagenetic alteration changing their magnetic properties and therefore the paleomagnetic signature of the host rock. The geochemical interaction of these components with the host glass is not yet understood as changes in funding have not allowed for this line of research.

ADDITIONAL WORK REQUIRED:

Additional TEM and probe data must be acquired to resolve the geochemical interaction of volcanic glass and oxyhydroxide phenocrysts.

RECOMMENDED PROGRAM:**Objective:**

To respond to our Key and Characterization Issues.

Activity:

To continue our efforts by accomplishing the additional work that we stated is required.

EXISTING PROGRAM:**Status of Previous Research:**

Although our preliminary results indicate that significant geochemical reactions have taken place and are probably taking place, we have not followed through to analyze the significance of these reactions with respect to repository performances. Future work is scheduled to accomplish our goals.

Principal Investigator:

Dr. C. M. Schlinger (University of Utah) is the Principal Investigator of the project. After the TEM work is completed, Dr. R. G. Burns will become the Principal Investigator dealing with the mineralogy and geochemistry problems.

Geochemistry and Mineralogy

ISSUES:

Can the stability (chemical and physical) of volcanic glass above and below the repository horizon at Yucca Mountain affect the postclosure performance of the proposed repository?

Can the chemical stability of volcanic glass at the desert surface act as an analog for past and future geochemical reactions within the vadose zone?

Characterization Issues:

To what extent will there be an evolution of heat from hydrating volcanic glass below the proposed repository and to what extent might heat ponding affect repository performance?

To what extent is volcanic glass from Yucca Mountain chemically stable or unstable with respect to forming authigenic minerals in the recent past?

Can rates of volcanic-glass hydration be determined from soil samples?

If volcanic glass is not chemically stable under repository conditions, how might this change water chemistry and thereby affect authigenic-mineral stability and radionuclide retardation?

Might additional authigenic minerals be formed from future volcanic glass hydration?

The potential future hydration of volcanic glass might change the physical properties of the vitrifier below the proposed repository. How might this affect potential future transport of radionuclides, in particular, travel-time estimates?

Review Issue:

The DOE has stated in their EA that they do not expect dissolution and that volcanic glass that could be altered has already been altered. To what extent can their statements be supported by our research into glass stability?

GENERAL OBJECTIVES:

Assess the geochemical and mineralogical stability of rhyolitic volcanic glass at Yucca Mountain under present conditions and under proposed repository conditions, so as to be able to predict the rates of authigenic-mineral formation, the chemistry of fracture flow and pore-water liquids and whole-rock stability.

Specific Objectives:

Obtain geochemical data relative to the hydration reactions of volcanic glass at Yucca Mountain.

Obtain mineralogical data for neomineral formation and authigenic-mineral stability.

Obtain rates of potential reactions that are presently occurring at Yucca Mountain.

Assess statements made by the DOE in the literature, which appear to be unfounded based upon lack of supportive evidence.

Assess authigenic mineral production to assist in resolving issues relative to the genesis of Trench 14 deposits.

Obtain basic information as to the heats of reactions for glass hydration, so as to be able to predict future repository conditions.

ACTIVITY SUMMARY:

Bedded tuff cobbles and pebbles acting as clastics have been studied geochemically and mineralogically. Literature produced by the DOE has been reviewed.

FINDINGS:

Rain-water acting on bedded tuff cobbles at the surface have a tendency to replicate diagenetic and textural features of similar lithologies at depth in Yucca Mountain, such as in the Calico Hills formation. Opal formed as a consequence of glass-hydration reactions appear similar to opal observed from Trench 14 (see Appendix C: Blundy, J., et al., 1987, 1988).

INTERPRETATION OF FINDINGS:

Our findings at present raise fundamental questions concerning future diagenetic reactions within Yucca Mountain. We find that contaminated fluids leaking from the proposed repository may not pass through highly sorptive zeolite-rich tuffs altered 11 million years ago, but along fractures lined with more recently formed authigenic minerals containing nonsorptive calcite and silica assemblages. We find evidence to suggest that volcanic glass at Yucca Mountain is very reactive and that reaction rates are relative to the availability of water and affected dramatically by increasing temperatures. A manuscript with some of our results has been submitted to Earth and Planetary Science Letters for publication (a copy is included in Appendix C).

ADDITIONAL WORK REQUIRED:

Obtain the actual rates of reaction of surface-glass hydration and authigenic-mineral production.

Obtain basic geochemical and mineralogical data from glass at depth at Yucca Mountain.

RECOMMENDED PROGRAM/EXISTING PROGRAM:

As a result of funding cuts, this program has been temporarily suspended until the 1989-1990 funding period. It is recommended that this program be reactivated as soon as possible.

STATUS OF PREVIOUS RESEARCH:

We are presently awaiting the publication of our last manuscript.

Principal Investigator:

Dr. R. G. Burns (MIT) is the Principal Investigator assisted by Dr. M. Morgenstein and Dr. J. Blundy (Oxford).

Geochemistry and Mineralogy

ISSUES:

Can the rates of vadose-zone chemical reactions be determined to the extent that we understand the roles of these reactions in providing retardation of radionuclides, thereby establishing isolation of the radioactive waste from the accessible environment after closure in accordance with the requirements set forth in 40 CFR Part 191, 10 CFR Part 60, and 10 CFR Part 960?

Characterization Issues:

Can desert-varnish dating by cation-ratio techniques be used to determine geologic ages of terraces in the Yucca Mountain area?

Can desert-varnish dating by cation-ratio techniques be used to determine rates of authigenic mineral formation from rhyolitic glass at Yucca Mountain?

Can desert-varnish dating by cation-ratio techniques assist in resolving Trench 14 problems and sandramp problems?

Review Issue:

Can the desert-varnish dating by cation-ratio techniques utilized by the USGS be reproduced with similar results?

OBJECTIVES OF ACTIVITY:

Make an independent assessment of desert-varnish dating cation-ratio technique by doing the following:

Review the cation-ratio dating literature and determine the methods employed.

Reproduce this established methodology and assess the results relative to those data which have been reported in the literature.

If the results do not match, determine the reason(s).

Provide support data for the work completed.

ACTIVITY SUMMARY:

The following techniques have been scrutinized with respect to cation-ratio dating of desert varnish:

Backscatter Electron Microscopy (BSE).

Electron Microprobe (EM).

Scanning Electron Microscope with Energy Dispersive Analyses (SEM/EDX).

PIXE element analysis.

The literature generated by Dorn, Harrington, and Whitney have been reviewed.

Samples of desert varnish have been examined by the various techniques from various locations in Nevada and South Mountain, Arizona.

FINDINGS:

Preliminarily, there appears to be various serious problems with the established methods of investigation. Element concentrations and element/element ratios show extreme variability. Potassium, calcium, K+Ca, and K+Ca/Ti do not consistently decrease with varnish age (depth of the varnish layer) as the cation ratio dating method implies. Using EDX analysis, as was done by Harrington and Whitney (1987), Ba in the varnish interferes with the Ti signal, suggesting that all previously reported cation ratio dating values are effectively K+Ca/Ba+Ti instead of K+Ca/Ti. Since Ba, like K and Ca, is a mobile element, the accuracy of the cation ratio dating technique is compromised. The PIXE method used by Dorn has the same problem as the EDX method used by the USGS. Finally, the oldest varnish on a rock specimen, due to its location in hollows and fractures, makes up only a small percentage of the total varnish and is biased against sampling (PIXE) on analysis (SEM/EDX) (see Appendix C: Krinsley, D. and S. Anderson, 1989).

INTERPRETATION OF FINDINGS:

At present, we do not understand why the established cation-dating method appears to give usable minimum ages. We do not know if the method as is or as possibly modified will provide accurate chronological information. On these basis, we have been unable to respond to our Key Issue or Characterization Issues. With respect to our Review Issue, we find that the results of our investigation to date do not match the USGS data.

ADDITIONAL WORK REQUIRED:

Analyze desert varnish using a variety of techniques including SEM/WDX (wave length dispersive which appears to distinguish between Ba and Ti).

Analyze desert varnishes for two major locations previously analyzed by Dorn.

RECOMMENDED PROGRAM/EXISTING PROGRAM:

Objective:

To respond to our Key and Characterization Issues.

Activity:

To continue our efforts by accomplishing the additional work that we stated above.

STATUS OF PREVIOUS RESEARCH:

Although our preliminary results indicate serious problems with the cation-dating method for desert varnish dating, we must stress that more work is required prior to obtaining reliable conclusions. The information we presently have is not publishable without additional supportive data which needs to be collected.

Principal Investigator:

Dr. D. Krinsley (ASU) is the Principal Investigator on this Project.

Site-Specific Mineralogic and Geophysical Studies to Establish the Hydrogeology of the Vadose Zone.

The complex and essentially unknown hydrologic conditions in the vadose zone and general absence of demonstrated investigative techniques that are powerful enough to characterize this environment with confidence have stimulated several alternative investigative approaches. The following efforts explore possibilities that have been recognized as potentially useful in drilling investigations and in establishing indirect evidence of ephemeral fracture flow.

Geochemistry and Mineralogy

ISSUES:

Is there a method, that complements hydrogeologic observations (water sampling and moisture monitoring), such as utilizing the geochemistry of authigenic zeolites, that will provide an understanding of fracture flow in the vadose zone? If such a method is developed, to what extent does it predict the motion of vadose-zone water? And how would data obtained using such a method affect radioactive waste isolation?

Characterization Issues:

Can the tandemron (accelerator mass spectrometer, or AMS) identify the presence of carbon-14, tritium, and/or iodine in single zeolite crystals? And, if so, can a technique be developed to do this on a routine basis?

Will this technique be able to distinguish between liquid flow and vapor flow?

Can we distinguish between authigenic zeolites in fracture and matrix with respect to their exposure to relatively "young" waters?

GENERAL OBJECTIVES:

Utilize AMS (tandemron) technology to develop a new technique whereby tritium, carbon-14, and iodine can be analyzed in single crystals of zeolites to determine the relative age of last waters of possible exposures within the zeolite supercage. This will make an assessment of the role of fracture flow in vadose-zone liquid transport possible.

Specific Objectives:

Develop an ability to utilize more than one key ion so as to strengthen the dating ability of this technique (such as carbon-14 and tritium).

Once developed, test this technique to insure its utility with respect to licensing issues.

Utilize this technique on a survey of fractures and matrix in situ materials obtained from Yucca Mountain to make a determination of the depth of penetration of "young" water through the vadose zone.

ACTIVITY SUMMARY:

Utilizing the tandemron facility at the University of Toronto, we have been successful in developing a laboratory technique to measure carbon-14 in single crystals of clinoptilolite. These results indicate that ^{14}C (as CO_2) are exchangeable into clinoptilolite. The fractionation factors are being worked out for the exchange reaction. Consequently, we should be able to distinguish the relative activity of vadose fracture flow if and when we are able to obtain Yucca Mountain samples.

We are progressing with iodine and tritium techniques so that we would be able to use these in conjunction with ^{14}C when in situ samples become available.

FINDINGS:

We are optimistic about the relevance of this approach since we now have the capability to obtain the ages of the water of last exposure to zeolites in the vadose zone. If actual liquid samples are not obtained from Yucca Mountain, then whole-rock samples may prove useful in deciphering the relative importance of fracture flow in the vadose zone.

INTERPRETATION OF FINDINGS:

At present, we are unable to make an interpretation of our findings since we have not had the opportunity to obtain Yucca Mountain samples to apply our laboratory results. With an appropriate drilling program, we will be in a position to be able to distinguish the potential flow paths to the accessible environment and the mechanism of that transport.

ADDITIONAL WORK REQUIRED:

Continuation of our laboratory efforts in development of techniques utilizing the Tandetron.

Acquisition of Yucca Mountain whole-rock samples for pore and fracture analyses.

RECOMMENDED PROGRAM:**Objective:**

To respond to our Key and Characterization Issues.

Activity:

To continue our laboratory efforts and to expand our efforts into a field/laboratory program specific to Yucca Mountain materials.

EXISTING PROGRAM:

The existing program is moving ahead very slowly due to constraints with funding, and obtaining in situ samples from Yucca Mountain. The design aspects of the program with respect to the development of new techniques have been extremely satisfying.

Principal Investigator:

The Principal Investigator of the program is Dr. J. C. Rucklidge (University of Toronto, Canada). Dr. R. G. Burns (MIT) is assisting with respect to issues in mineralogy.

Geochemistry and Mineralogy

ISSUE:

Will the geologic barriers isolate the radioactive waste from the accessible environment after closure in accordance with the requirements set forth in 40 CFR Part 191, 10 CFR Part 60, and 10 CFR Part 960?

Characterization Issue:

Can magnetic stratigraphy of the volcanic units at Yucca Mountain be used to fingerprint time stratigraphic units, thereby aiding the control of depth of drilling stratigraphy?

GENERAL OBJECTIVE:

Determination of magnetic stratigraphy for Yucca Mountain for use as a drilling control tool.

Specific Objectives:

Establish the feasibility for using magnetics to determine stratigraphic position during drilling.

Establish the similarities and variabilities of magnetic properties in a lateral extent per unit.

Establish the similarities and differences of magnetic properties in stratigraphic profiles.

ACTIVITY SUMMARY:

Field-data collection of samples and magnetic data from outcrop samples from Tiva Canyon to the upper beds of Topopah Springs Member have been carefully made. The sampling areas have been carefully mapped and susceptibility and NRM data have been collected. Magnetic-background data have been collected also. Data have been collected from the west side of Yucca Mountain (see Appendix C: Schlinger, C. M., 1989).

Transmission-electron microscopy (TEM) has been used to characterize the size, distribution, and mineralogy of the magnetic minerals.

FINDINGS:

Magnetic-field data collected suggest that there is good lateral continuity and stratigraphic susceptibility anomalies to utilize magnetics as a "fingerprinting" indication of drilling depth (formation stratigraphy).

There appears to be a time stratigraphic problem in the upper Topopah Springs Member of the Paintbrush Tuff where this portion of the unit has NMR characteristics similar to the overlapping unit (Tiva Canyon) and is dissimilar with the Topopah Springs Member below. This may suggest that the emplacement and cooling history of the stratigraphic framework is not well understood or that the top of the Topopah Springs Member has a CRM component (see Appendix C).

INTERPRETATION OF FINDINGS:

The findings thus far suggest that magnetics appears to be a good tool to use to obtain stratigraphic control during drilling. Nevertheless, more field data are required to obtain detailed information not presently exposed. In order to accomplish this, drilling samples must be obtained. It appears that magnetic data can assist in refining time-stratigraphic cooling history of the tuff units and that our present understanding of the parameters are limited and potentially inaccurate.

ADDITIONAL WORK REQUIRED:

Obtain closely-spaced detailed magnetic data from core samples and boreholes.

Compare the magnetic data with petrographic data so that magnetic profiles can be constructed.

RECOMMENDED PROGRAM:

A field-sampling program is recommended to obtain detailed magnetic information.

Objective:

The objective of this program is to establish detailed magnetic stratigraphy of Yucca Mountain to be used in drilling control and to refine our understanding of the time stratigraphic units.

EXISTING PROGRAM:

The existing program has been held on standby due to budget constraints.

Principal Investigator:

The Principal Investigator for this project is Dr. C. M. Schlinger (University of Utah).

Past Climate and Related Genesis of Authigenic Desert Carbonates and Silicates.

There are analytical support activities of a geochemical and mineralogic nature that have been called upon to aid climate-change investigations. These generally seek to establish paleohydrologic conditions of formations based on textures, mineralogy, geochemistry, and other parameters that can only be established by indepth laboratory analyses.

Geochemistry and Mineralogy

ISSUE:

Can authigenic reactions within volcanic ash be sufficiently understood so that these ashes can be correlated across the Tecopa Basin, and be used in obtaining accurate stratigraphic data which then can be utilized for interpretation of past climate and paleohydrologic issues?

Characterization Issues:

Can the history of diagenesis in volcanic ashes in the Tecopa region be of assistance in studying authigenic reactions in volcanic tuffs at Yucca Mountain?

Can the history of diagenesis in volcanic ashes in the Tecopa region be of assistance in understanding the paleohydrology of Lake Tecopa with respect to the last 100,000 years?

GENERAL OBJECTIVE:

Characterize the diagenetic geochemical activities that have taken place in volcanic ashes in Lake Tecopa, to assist in resolving stratigraphic correlation of units and thereby resolving the interpretive hydrogeologic activity of the area, as it may relate to past climate in the region of Yucca Mountain.

Specific Objectives:

Develop an understanding of the variation of volcanic-glass diagenesis and authigenic-mineral production in the Lake Tecopa Basin and margins, with respect to key ash horizons.

Provide geochemical data, which can be utilized to quantify the diagenetic changes across the Tecopa Basin.

Provide these data to the senior Field Stratigrapher, so that he may utilize these information in mapping the sediments of the Tecopa Basin.

ACTIVITY SUMMARY:

Field data and samples have been collected from Lake Tecopa and geochemically analyzed.

Laboratory and field data have been provided to Dr. R. Morrison, senior Field Stratigrapher, to assist him in his efforts.

FINDINGS:

A paper containing our findings has been presented at the Denver GSA meeting in 1988. Tuff B (Bishop Ash) has been found to alter differently depending upon its geographic location. As a consequence, it is assumed at present that there are three fluid sources reacting with the ash:

- a. hot springs;
- b. hydrothermal fluids (alkali enriched); and
- c. carbonate-enriched ground water venting into the lake as cold springs.

The details of these information will assist in the mapping of the Tecopa Beds (see Appendix C: O'Hara, P. F., et al., 1988).

INTERPRETATION OF FINDINGS:

At present, the stratigraphic units in Tecopa are being mapped and each bed is being classified as to the environment of deposition. When this process is completed, a better history of the hydrogeology of the Tecopa Basin will be available. This information will then be utilized to understand the regional past climate and paleohydrology of the southern Great Basin near Yucca Mountain (see Appendix C).

ADDITIONAL WORK REQUIRED:

Additional work required in this program will primarily be in resolving various ages of the ashes located by the principal investigator. Most of the program is designed to support Dr. R. Morrison's work on Lake Tecopa stratigraphy and thus, until more field work is completed, it is difficult to predict the geochemical and mineralogic requirements for the future.

RECOMMENDED PROGRAM:**Objective:**

To respond to our Key and Characterization Issues and to assist Dr. Morrison with geochemical and mineralogic sample studies.

STATUS OF PREVIOUS RESEARCH:

The research is progressing at a satisfactory pace.

Principal Investigator:

Dr. D. Krinsley (ASU) is assisting Dr. R. B. Morrison in obtaining basic geochemical and mineralogic data.

Geochemistry and Mineralogy

ISSUES:

Carbonates, as sedimentary precipitates forming on the desert surface, in fracture fillings, and as K horizons in desert soils, have distinguishing characteristics with respect to the environment of deposition (geochemical and biogeochemical precipitation). If the environment of deposition is affected by the past climate and paleohydrology, desert carbonates could prove of importance with respect to resolving licensing issues. Can sufficient paleohydrological information be acquired from desert carbonates to assist in interpreting the past climate for the past 100,000 years?

Characterization Issues:

Can desert carbonates be distinguished on the basis of petrological and geochemical evidence to the extent that these information impart information concerning the environment of genesis?

To what extent does biological activity such as algal growth promote carbonate precipitation in desert marsh lands, desert lakes, and temporary desert ponds?

To what extent are these deposits different/similar to inorganic-carbonate precipitation? To what extent do biocarbonate deposits inform us of past climate conditions?

How do Trench 1 carbonate sediments compare with modern-day desert-pond sediments?

How do marshland sediments differ from desert-lake sediments?

How variable is the aerosol-carbonate depositional contribution to desert soils in the immediate area of Yucca Mountain? What is the relative contribution between aerosol and in situ biotic transfer carbonate precipitation in the immediate area of Yucca Mountain.

GENERAL OBJECTIVE:

Obtain sufficient baseline information concerning the petrographic, geochemical, and biogeochemical composition of desert carbonates to be able to understand their genesis from the standpoint of environmental parameters.

Specific Objectives:

Be able to distinguish the mechanism and environment of deposition of carbonate sediments including clastic deposition and reprecipitation, biocarbonate precipitation, and evaporite precipitation.

Develop petrological tools for distinguishing varieties of carbonate deposition.

Develop geochemical tools for distinguishing varieties of carbonate deposition.

Utilize these information in interpreting the environments of deposition and thereby the paleohydrology and past climate of the area of deposition.

Utilize these information in interpreting the conditions which promoted sedimentation in Trenches 14, 17, and 1.

ACTIVITY SUMMARY:

Utilizing the SEM, TEM, and electron microprobes determine the fabric and geochemical compositions of desert carbonates from various known and unknown environments of deposition.

Determine whether the information collected are significant in distinguishing various environments and mechanisms of carbonate precipitation from each other. Utilize these information to assist in interpreting past climate conditions and genesis of opal-carbonate deposits.

FINDINGS:

Petrographic and mineral analyses of carbonate sediments from known environments of desert-marsh lands have been completed. Backscatter SEM data have been obtained from Trench 1 samples indicating cool fresh-water environment for carbonate deposition. These information, along with geochemical data which are yet to be collected, will provide the startup data accumulation for this program. Trench 14 and sandramp samples have been collected and are planned for future laboratory analysis. Carbonates from Tecopa have been studied to ascertain the contribution of detrital volcanic glass and these information have been provided to the Tecopa project personnel.

INTERPRETATION OF FINDINGS:

At present, our findings are insufficient to obtain firm conclusions. More samples and more analyses are necessary prior to obtaining usable conclusions.

ADDITIONAL WORK REQUIRED:

Continuation of laboratory efforts in the acquisition of petrographic and geochemical data on carbonate sediments from Yucca Mountain and surrounding areas.

Start comprehensive analyses of Trench 14 samples as soon as we have completed Trench 1 samples.

RECOMMENDED PROGRAM:

Objective:

To respond to our Key and Characterization Issues.

Activity:

To continue our laboratory and field data collection efforts.

EXISTING PROGRAM:

The existing program will expand its efforts as soon as we have completed working on desert-varnish studies.

Principal Investigator:

The Principal Investigator for this effort is Dr. D. Krinsley (ASU) assisted by Mr. J. Quade (University of Utah) and paleontologists (from Columbia University, Lamont-Doherty Geological Observatory).

Geochemistry and Mineralogy

ISSUES:

Silica and carbonate fracture-filling deposits located in Trench 14 are geochemical precipitates from aqueous solutions. To what extent do the aqueous solutions responsible for these authigenic mineral precipitates jeopardize the postclosure performance of the proposed repository at Yucca Mountain, if the conditions responsible for their formation were to reoccur?

Characterization Issues:

What is the genesis of fracture-filling opal in Trench 14?

What is the genesis of fracture-filling carbonates in Trench 14?

What is the immediate source for ash and bioclastic(?) debris in the fracture filling of Trench 14?

Is there geochemical evidence, such as might be obtained from isotope analyses, that might suggest the origin and timing of these deposits?

Are there analog deposits that have known origins that might assist in interpreting the genesis of deposits in Trench 14?

GENERAL OBJECTIVES:

Provide a comprehensive understanding of the genesis of the carbonate and silicate deposits and features within Trench 14 and similar and potentially related structures (such as sandramps and Trench 17), to be able to assess their significance on the postclosure performance of the proposed repository at Yucca Mountain.

Specific Objectives:

Study carbonate and opal deposits of known origin for comparison to Trench 14 deposits.

Analyze Trench 1 deposits from the carbonate characterization study to assess the significance of biological-carbonate production (in situ) in desert fractures and faults.

Obtain field and laboratory data utilizing paleontological, geochemical, and mineralogical techniques so that a reasonable understanding is obtained for the genesis of Trench 14 deposits.

ACTIVITY SUMMARY:

Soil-opal genesis from diagenetic reactions of volcanic glass at Yucca Mountain have been investigated both geochemically and mineralogically. These information indicate that CT opal is presently or relatively recently being formed in the desert soils juxtaposed to Yucca Mountain.

Trench 1 studies indicate that biocarbonate precipitate may be more important than previously recognized and that not all of the desert carbonates are a function of aerosol accumulation.

Field evidence of fracture boundaries indicate that host rocks do not appear to be hydrothermally altered; consequently, the liquids responsible for the deposition of the opal and carbonates may have been ambient in temperature.

SEM backscatter analysis has been determined as a usable tool to distinguish textural carbonate data important to the project.

FINDINGS:

Desert-soil opal formed from the diagenesis of volcanic glass can be partially and possibly wholly responsible for the opal deposits as observed in Trench 14. Additionally, other mechanisms of opal genesis for Trench 14 are certainly possible (see Appendix C: Blundy, J., et al., 1987, 1988).

Blotic-carbonate genesis in desert environments such as ponding water in fractures, may be a fairly significant mode of carbonate production (see Appendix C).

Calcium is released from volcanic-glass hydration reactions at the desert surface. This release of calcium may be partially responsible for carbonate precipitation in desert soils. All of the calcium is not necessarily supplied through aeolian transport and deposition (see Appendix C).

INTERPRETATION OF FINDINGS:

At present, there is insufficient data to resolve the Key and Characterization Issues. Diagenetic reactions in the soil zone and on outcrops may in part provide sufficient source materials to form opaline and carbonate deposits. In addition, aeolian transport may contribute to the supply. Since the timing of these reactions and the relative importance of other variables such as biological precipitation of authigenic minerals are essentially unknown, it is presently too early to establish the genesis of these deposits (see Appendix C).

ADDITIONAL WORK REQUIRED:

To analyze Trench 14 material recently collected during the USGS field trip to Yucca Mountain.

To complete analyses of Trench 1 samples.

To reestablish the volcanic-glass alteration studies and obtain rates of chemical reactions for the desert-surface authigenics.

RECOMMENDED PROGRAM:

Objective:

To respond to our Key and Characterization Issues.

Activity:

To continue our efforts as stated in Additional Work Required.

EXISTING PROGRAM:

Status of Previous Research:

As a consequence of funding cuts, we have been unable to continue our glass-hydration research and have had to slowly schedule Trench 1, 14, 17 and sandramp samples into our laboratory. Consequently, although our research is progressing, it is fairly slow.

Principal Investigator:

Dr. D. Krinsley (ASU) is the Principal Investigator for carbonate research and Dr. R. G. Burns (MIT) is the Principal Investigator for opal research.

Appendix C

Geochemistry and Mineralogy

List of Published Papers, Abstracts, and Manuscripts Included in the appendix.

- Blundy, J. D., R. G. Burns, and M. E. Morgenstein, 1987, Authigenic minerals in rhyolite tuff at Yucca Mt., Nevada; diagenesis in a proposed nuclear waste repository: Geological Society of America Annual Meeting, Poster Session, Abstract.
- Blundy, J. D., R. G. Burns, M. E. Morgenstein, 1988, Non-sorptive minerals forming in rhyolite tuff at Yucca Mountain, Nevada: diagenesis in a proposed nuclear waste repository: submitted to Earth and Planetary Science Letters, 39 p.
- Bowers, T. J. and R. G. Burns, 1988, Activity diagrams for clinoptilolite: susceptibility of this zeolite to further diagenetic reactions: manuscript submitted to the American Mineralogist, 41 p.
- Burns, R. G. and T. J. Bowers, 1988, Activity diagrams for clinoptilolite: relevance of zeolitized vitric tuffs at Yucca Mountain, Nevada: Geological Society of America, Abstracts with Program, vol. 20, no. 7, p. A359.
- Krinsley, D. and S. Anderson, 1989, Desert varnish: a new look at chemical and textural variations: Geological Society of America Annual Meeting, Poster Session, Abstract.
- O'Hara, P. F., Manley, C. R., and Krinsley, D., 1988, Chemical zonation within Bishop Ash, Pleistocene Lake Tecopa, Inyo County, California: Geological Society of America, Annual Meeting, Poster Session, Abstract and manuscript, Poster Session, 22 p.
- Schlinger, C. M., 1989, Magnetic Stratigraphy of Ash-flow Sheets at Yucca Mountain, Nevada, Eng. Geol. and Geotech. Eng., Watters (ed.), Balkema, Rotterdam, p. 19 to 24.
- Wood, V. J., Hubbard, M. S., and Burns, R. G., 1988, Cesium uptake by clinoptilolite crystals: implications to the immobilization of radionuclides stored at Yucca Mountain, Nevada, Geological Society of America, Abstracts with Program, vol. 20, no. 7, p. A359.
- Wood, V. J., Hubbard, M. S., and Burns, R. G., to be published, Cesium uptake by clinoptilolite crystals, manuscript, 19 p.

1987 GSA ABSTRACT FORM

USE THIS FORM FOR ALL 1987 GSA MEETINGS (SECTION & ANNUAL MEETINGS)

YOU MUST COMPLETE ALL SECTIONS BELOW, [1] THROUGH [7]

[1] TYPE YOUR ABSTRACT IN THE SPACE BELOW, using fresh black carbon ribbon. Follow the format shown on the attached instructions. Blue lines below show absolute limits. Do not fold abstract; mail flat with reinforcement to avoid retying charge.

AUTHIGENIC MINERALS IN RHYOLITE TUFF AT YUCCA MT, NEVADA;
DIAGENESIS IN A PROPOSED NUCLEAR WASTE REPOSITORY

No 136950

BLUNDY, Jonathan D.^{1,2}, BURNS, Roger G.¹, and MORGENSTEIN, Maury E.³

¹Dept. of Earth, Atmos. & Planet. Sci., MIT, Cambridge MA 02139;

²Dept. of Earth Sciences, Cambridge University, Cambridge, England CB2 3ED;

³Mifflin & Assoc. Inc., 2700 E.Sunset Rd, Las Vegas NV 89120.

Cobbles in desert pavement at the base of Yucca Mt derived from bedded tuff above the Topopah Springs Member display prominent geopetal textures in which a leached rind (zone A, 2-4 mm) is separated from core (zone C) by brown vitreous zone B (3-6 mm). This weathering profile is also displayed on outcrop surfaces. Concentration profiles by EMP and SIMS analyses across individual glass shards in the tuffs show uniform Al; losses near margins of Na, Ca, Li, Mn, Fe, and Zr; and gains of K, Rb, and Si. Shards from zones A and B show greater Si and Al relative to zone C, while water (measured by difference) decreases from ~3 wt% (zone C) to ~1% (zone A). Comparisons of zone C glass shards in outcrop surfaces and pavement cobbles reveal that total (mole %) alkali contents remain approximately constant, with higher K and Rb and lower Na, Li, and Ca concentrations in outcrop samples. This indicates a coupled diffusion transport mechanism for these cations in hydrated rhyolite glasses. Subtle variations in Si and Al concentrations correlate with changes of shard surface textures and mineralogy from zone A to C revealed by SEM and XRD. Thus, zone C shards are associated with authigenic smectite and minor clinoptilolite and silica. Shards at the B-C boundary are coated with lepispheres of opal CT and dendritic clinoptilolite, whereas shards at the B-A boundary have crusts of botryoidal opal CT associated with sparry calcite. Therefore, the prominent geopetal zone B corresponds to the boundary between Zones I and II of diagenetic zeolites defined by Iijima (1975). Zone A shards, as well as feldspar phenocrysts, show pitted surfaces indicating the onset of dissolution. They are associated with calcite rhombs, Ca-Mg zeolite, Mn-Fe oxides and evaporite minerals.

The clinoptilolite + opal CT + calcite + smectite phases recorded here resemble mineral assemblages lining fractures throughout the proposed repository and in underlying bedded tuff horizons at Yucca Mt. Thus, diagenetic reactions similar to those between aerated rainwater and rhyolite tuff in desert pavement may be occurring (or have occurred) at depth in the vadose zone throughout the proposed repository.

[2] ALL ABSTRACTS—INCLUDING SYMPOSIA ABSTRACTS—MUST be categorized into ONLY ONE of the 35 disciplines below. Do not add to the list. Choose the ONE discipline in which peer reviewers would be best qualified to evaluate your abstract. This does not necessarily determine the final technical session assigned.

- 1 archaeological geology
- 2 coal geology
- 3 economic geology
- 4 engineering geology
- 5 environmental geology
- 6 general geology
- 7 geochemistry
- 8 geology education
- 9 geomorphology
- 10 geophysics
- 11 geoscience information
- 12 glacial geology
- 13 history of geology
- 14 hydrogeology
- 15 marine geology
- 16 micropaleontology
- 17 mineralogy/crystallography
- 18 oceanography
- 19 paleontology/paleobotany
- 20 petroleum geology
- 21 petrology, experimental
- 22 petrology, igneous
- 23 petrology, metamorphic
- 24 petrology, sedimentary
- 25 planetary geology
- 26 Precambrian geology
- 27 Quaternary geology
- 28 remote sensing
- 29 sedimentology
- 30 stratigraphy
- 31 structural geology
- 32 tectonics
- 33 tectonics/geophysics
- 34 vertebrate paleontology
- 35 volcanology

DETAILS FOR MAILING

[3] SESSION TYPE:

This abstract was invited for the symposium titled _____

If you checked "symposium" above, skip the rest of this item and go on to item (4).

Oral session Poster session Either type

If you checked "Oral" or "Poster" above, the Program Committee may have to change the type of presentation due to time/space limits; therefore, check one of the following:

- I will accept a change of session type if necessary.
- Withdraw my abstract rather than change session type.

[4] % OF THIS PAPER PREVIOUSLY PRESENTED _____
WHERE AND WHEN _____

[5] CAN YOU BE A SESSION CHAIRMAN? Yes
Topic _____
Your name _____
Telephone (late June/early July) _____

[6] SPEAKER'S IDENTITY AND MAILING ADDRESS:

Speaker's status (check one):
1 GSA Mem or Fel 2 GSA Student Assoc
3 Professional geologist, but not GSA Mem 4 Student, but not GSA Assoc

Speaker's name R. G. Burns
Address 54-816 MIT
Address Cambridge
City State Zip MA 02139
Country
Office Telephone: (617) 253-1906
Home Telephone: () _____
Dates we can reach you: June 11-July 18, 1987

[7] SEND ORIGINAL + FIVE COPIES OF ABSTRACT TO APPROPRIATE ADDRESS SHOWN ON INSTRUCTION SHEET AND ON BACK OF THIS FORM. ALL ABSTRACTS MUST ARRIVE ON OR BEFORE DEADLINE SHOWN FOR EACH MEETING.



**Non-sorptive minerals forming in rhyolite tuff at Yucca
Mountain, Nevada: Diagenesis in a proposed nuclear
waste repository**

**Jonathan D. Blundy^{1,2}, Roger G. Burns¹, and
Maury E. Morgenstein³**

¹ *Department of Earth, Atmospheric, and Planetary Sciences,
Massachusetts Institute of Technology, Cambridge, MA 02139, U.S.A.*

² *Department of Earth Sciences, Cambridge University, Cambridge CB2 3EQ,
UK.*

³ *Mifflin and Associates Inc., Ste C-25, 2700 E. Sunset Rd., Las Vegas, NV
89120, U.S.A.*

[Submitted to *Earth and Planetary Science Letters*, December 9, 1988]

Cobbles of desert pavement at the base of Yucca Mt. derived from bedded tuffs above the Topopah Springs Member display prominent geopedal textures in which a leached rind (zone A, 1-2 mm) is separated from core (zone C) by brown vitreous zone B (3-6 mm). This weathering profile is also displayed on outcrop surfaces. Concentration profiles by EMP and SIMS analyses across individual glass shards in the tuffs show uniform Al and Mg; losses near margins of Na, Ca, Li, Mn, Fe, and Zr; and gains of K, Rb, Ba, and La. Shards from zone A have highest Si contents, and water (measured by difference) decreases from ~ 4 wt.% (zone C) to <3% (zone A). Comparisons of zone C glass shards in outcrop surfaces and pavement cobbles reveal that total (mole %) alkali contents remain approximately constant, with higher K and Rb and lower Na, Li, and Ca in outcrop samples. This indicates a coupled diffusion transport mechanism for these cations in hydrated rhyolite glasses. Subtle variations in Si and Al concentrations correlate with changes of shard surface textures and mineralogy from zone A to zone C revealed by SEM and XRD measurements. Thus, zone C shards are associated with authigenic smectite and minor clinoptilolite and silica. Shards at the zone B-C boundary are coated with lepispheres of opal CT and dendritic clinoptilolite, whereas shards at the zone B-A boundary have crusts of botryoidal opal CT associated with sparry calcite. Therefore, the authigenic minerals in geopedal zone B correspond to assemblages occurring in diagenetic Zone II of buried pyroclastic deposits (Iijima, 1975). Zone A shards, as well as feldspar phenocrysts, show pitted surfaces indicating the onset of dissolution. They are associated with calcite rhombs, palygorskite, Mn-Fe oxides, and evaporite minerals. The clinoptilolite + opal CT + calcite + smectite assemblages recorded here resemble mineral deposits lining fractures throughout the proposed repository for underground storage of high-level nuclear waste and in underlying bedded tuff horizons at

Yucca Mt. Thus, diagenetic reactions similar to those between aerated meteoric water and rhyolite tuff in desert pavement may be occurring, or have occurred, in the vadose zone throughout the proposed repository, producing non-sorptive calcite and opal coatings which may retard cation exchange reactions of clinoptilolite and clay silicates.

1. Introduction

Located on the southwest border of the Nevada Test Site, 120 km northwest of Las Vegas, Yucca Mountain consists of a sequence of rhyolitic lavas, ash-flow tuffs and bedded tuffs which exceeds a thickness of 1800 m and ranges in age from 16 to 11 million years [1,2]. Yucca Mountain is the site of a proposed repository for the underground storage of high-level nuclear waste materials [3]. The candidate repository horizon is located approximately 400 m below the surface in the vadose zone some 170 m above the present-day water-table in densely welded tuff of the Topopah Springs Member of the Miocene Paintbrush Tuff unit [4-7]. Numerous drill-core samples taken from widespread locations through Yucca Mountain indicate that secondary minerals, including clay silicates, zeolites, opal and carbonate, have formed by alteration of rhyolitic glasses in certain tuffaceous horizons [8,9]. Zones of zeolitization occur in tuffs now located both above and below the present-day water table. Such zones are commonly discordant with bedding and thicken to the northeast. These observations led to the proposition [9] that extensive zeolitization occurred during elevated heat-flow associated with caldera development approximately 11 Ma ago and pre-dates tectonic tilting of the Yucca Mountain sequence. However, detailed studies of authigenic mineral chemistry through the Yucca Mountain section [9,10] have revealed that significant modifications to zeolite compositions have occurred through interaction of zeolitized tuff with groundwater subsequent to 11 Ma.

Furthermore, zeolites occur along fractures throughout the compacted tuff units, including the level immediately underlying the proposed repository horizon, where glass is partially altered to smectite and calcic clinoptilolite-group minerals [11]. Opal and calcite coatings on fractures have also been observed in the vadose zone [7,11,12] yielding radiometric ages between 300,000 and 30,000 years [13,14]. This evidence, that post-Miocene groundwater interactions have modified pre-existing zeolite compositions and locally precipitated non-sorptive silica and carbonate phases raises questions about future diagenetic trends at Yucca Mountain and the long-term sorptive capacity of the repository host-rocks. In order to assess the nature of vitric tuff/water interactions at Yucca Mountain under present-day conditions, and their influence on ancient tuff-water interactions, a suite of clastic pebbles and outcrop surface samples of tuff from Solitario Canyon adjacent to Yucca Mountain were selected for detailed geochemical and scanning-electron microscope (SEM) studies. The results summarized here suggest that zeolitized vitric tuffs adjacent to the proposed repository are vulnerable to continuing diagenetic reactions.

2. Samples

Solitario Canyon is a prominent fault-bounded depression west of Yucca Mountain developed subsequent to fault movement about 30,000 years ago [15]. The canyon floor is littered with clastic detritus derived from erosion of the Yucca Mountain fault scarp. Particularly prominent amongst this detritus are pebbles of non-welded bedded tuffs derived from horizons between the Tiva Canyon and Topopah Springs Members of the Paintbrush Tuff unit, including vitric tuffs from the Pah Canyon Member, which crop out near the crest of Yucca Mountain above the proposed repository horizon [15,16]. These non-welded bedded vitric tuff units have a characteristic orange-brown coloration and abundant yellow-gray

pumice clasts defining a weak bedding fabric [4,5]. In petrographic and compositional characteristics, portions of the Pah Canyon Member resemble the tuffaceous beds of Calico Hills unit which underlies the Topopah Springs Member throughout Yucca Mountain [4,5]. These tuffaceous beds were deposited on 13.6 Ma-old Crater Flat Tuff units as a sequence of sixteen non-welded vitric ash-flows, with thin air-fall and reworked tuffs separating each of the ash flows [15,16]. The interlayered nature of the Calico Hills unit indicates that successive surface layers were exposed to atmospheric weathering between each eruptive event over a 500,000 year interval before they were covered by ash-flow tuffs of the Topopah Springs Member 13.1 Ma ago [2]. Resemblances to the tuffaceous beds of Calico Hills unit make non-welded bedded tuffs below the Tiva Canyon Member a suitable analogue material for the study of progressive diagenetic processes affecting vitric tuffs at Yucca Mountain.

Cobbles of the bedded tuff unit occurring in desert pavement at the base of Solitario Canyon and in outcrop on the west flank of Yucca Mountain display conspicuous weathering rinds resulting from interaction of the tuff with rainwater since pavement and outcrop formation. In pavement cobbles these alteration rinds have a geopedal configuration relative to the desert surface (Figure 1), confirming their origin by *in situ* diagenesis. The alteration rinds are designated as zones A, B, C, and D. The cobble surface develops a vinar of red-brown desert varnish characteristic of arid-climate weathering. The outermost alteration zone A, 1-2 mm thick, effervesces and is readily leached when treated with dilute HCl, indicating the presence of calcite. The conspicuous zone B, 3-6 mm wide, is darker in color, has a vitreous luster, and is only affected by acid in its outer portion. Zone C, representing the bulk interior of the sample, is unaffected by acid and resembles fresh samples of the bedded tuff unit collected at outcrop on Yucca Mountain. Zone D is similar to zone C, but lies below the sediment surface. Two

such clastic tuff specimens, designated as samples PC1 and PC4, were among cobbles and pebbles collected in Solitario Canyon from a stable desert pavement (PC4) and an active erosion scarp (PC1) at the foot of Yucca Mountain. In addition, two specimens of bedded tuff were collected at outcrop on the western flank of Yucca Mountain adjacent to the location of drill-core USW G-3 [7]. Sample PC5 was taken close to the base of the bedded tuff horizon, while sample PC6 was collected some 20 cm below the basal vitrophyre of the Tiva Canyon Member. Both outcrop samples have developed alteration rinds on their exposed surfaces resembling the geopedal zones in clasts described above.

3. Analytical Procedures

3.1. Petrology

Thin-section petrographic examination revealed a similarity between the interior portions of outcrop samples PC5 and PC6 and central zone C of the clastic samples PC1 and PC4. Both comprise non-welded vitric tuff in which fresh glass shards (0.15-1 mm long) and welded vitric clasts (1-3 mm) are set in a matrix of argillaceous glass fragments, disseminated fine-grained iron oxides and scarce 5-10 μm plates of a yellow-brown clay silicate. The shards are commonly yellow in color although the vitric clasts and larger shards may have a brown core. Some glasses show perlitic fractures. Phenocrysts (up to 2 mm long) comprise sanidine, plagioclase, biotite, and quartz, and constitute less than 10 volume % of the samples. Pumice clasts up to 1 cm in diameter are invariably altered to fine-grained aggregates of zeolite, clay, and opaque oxide. There is a weakly transitional contact towards zone B marked by the local coalescence of the clay silicate platelets to form irregular lathe-like patches of zeolite, identified as clinoptilolite by X-ray diffraction (XRD) and scanning electron microscopy (SEM)

measurements described later, having diameters of up to 50 μm and partially enclosing the glass shards. Within zone B these zeolitic masses increase in abundance but disappear suddenly at the contact with zone A. The interstices in zone A are filled instead by a cryptocrystalline isotropic colorless phase identified as opal CT by XRD and SEM measurements.

3.2. *Electron Microprobe*

Concentrations of major elements were obtained from electron microprobe (EMP) analyses of individual mineral and glass shards in polished thin sections using a four-spectrometer JEOL 733 Superprobe with full on-line computerized matrix correction and data reduction procedures [17]. In measurements of rhyolitic glasses, a 15 kV accelerating voltage and 10 nA beam current were used with counting times of 20 seconds for all elements except Na, which was analysed first and counted for only 10 seconds in order to minimize loss through volatilization. Loss of volatiles was further reduced by using a defocussed beam of approximately 10 microns diameter to analyse the glass shards. However, a more finely-focussed beam was necessary to analyse the thin zeolite coatings on shards in zone B. To improve precision of elements present in low concentration (e.g. Fe), counting times were increased to 40 seconds. Calibrations were made against analysed standards, such as diopside(65%)-jadeite(35%) glass (providing Ca, Mg, Na, Al, and Si), aenigmatite (Fe, Ti, Na, Si), orthoclase glass (K), and rhodonite (Mn). Precision values to one standard deviation (1σ) in the EMP analyses of glasses, which are limited by counting statistics, were as follows: SiO_2 0.3%; Al_2O_3 0.5%; CaO 0.5%; K_2O 1.4%; Na_2O 1.1%; FeO 4.8%. Overall accuracy of the EMP-determined concentrations was assessed by analysing the standards as unknowns during and after an analytical session.

3.3. Ion Microprobe

Trace element concentrations were determined by secondary ion mass spectrometry (SIMS) on a Cameca IMS 3F ion microprobe using a primary beam of O^- ions with a net energy of 12.61 KeV and ion current of about 0.1 nA. Spot size was 5-8 microns in diameter. An energy filtering technique [18] was used to reduce molecular ion interferences. Representative isotopes measured relative to ^{28}Si included 7Li , ^{23}Na , ^{39}K , ^{40}Ca , ^{47}Ti , ^{55}Mn , ^{56}Fe , ^{85}Rb , ^{89}Y , ^{90}Zr , ^{93}Nb , ^{138}Ba , and ^{139}La . Element ratios against ^{28}Si were calculated from the background and deadtime corrected intensities, and an individual correction was made for isotopic abundances. Calibration was made by establishing empirical working curves [19] relating relative intensities and absolute concentrations for fused pellets of USGS granite standards G-2 and GSP-1. Precision limits (to 1σ) based on counting statistics were as follows: Li 2.3%; Na_2O 0.5%; MgO 4%; K_2O 0.4%; CaO 1.4%; TiO_2 2.5%; FeO 1.3%; Rb 2.5%; Y 3.3%; Zr 2.9%; Nb 4.2%; Ba 6.2%; La 10%. Overall accuracy of the SIMS analyses were evaluated by measuring element concentrations in G-2 and GSP-1 run as unknowns at the end of an analytical session. Comparison of SIMS and EMP analyses for K_2O on glass shards revealed a relative discrepancy of only 2%. H_2O contents were obtained by subtracting total oxides (including major elements analysed by EMP and trace elements obtained from SIMS analyses) from 100% [20,21].

3.4 Scanning Electron Microscope Measurements.

The JEOL 733 Superprobe used to obtain EMP data was employed as a scanning electron microscope with a reduced condenser aperture and accelerating voltages of 15-25 kV. Typical beam currents were of the order of 150 pA. Semi-quantitative analyses were made by energy dispersive analysis (EDS) with counting times of 20 to 40 seconds.

4. Results

4.1. EMP and SIMS Data

Electron- and ion- microprobe profiles were made across several glass shards in each of the clastic and outcrop specimens, including the different weathering zones A through C of PC1 and PC4. Analyzed shards were generally vesicle- and fracture-free. Table 1 lists representative average compositions of analysed centers of glass shards in different samples, which resemble published analyses of volcanic glasses in drill-core samples from vitric tuffs at Yucca Mountain [9,10], including specimens from the tuffaceous beds of Calico Hills unit. The close resemblance of glass compositions between vitric tuffs from surface deposits and drill-core samples vindicates the importance of studying present-day surface alteration processes in order to understand diagenetic reactions currently, or historically, operating at depth. Average trace element concentrations of a glass shard analysed by SIMS are also given in Table 1. Note the excellent correspondence between EMP and SIMS values for K_2O , CaO , TiO_2 , and MgO , testifying to the mutual consistency of these two analytical methods. The relatively high H_2O contents (~4 wt.%) of the glass shards listed in Table 1, which are significantly higher near perlitic fractures, are comparable to values reported for other naturally-occurring [20,21] and experimentally-hydrated [22,23] rhyolitic glasses. Such high H_2O contents largely represent post-erruption water of hydration, since fresh volcanic glasses in pyroclastic rocks rarely exceed 1 wt.% [24] but undergo hydration rapidly [25,26]. The high water contents of glasses in drill-core samples [9,10], inferred from differences of total oxides from 100%, suggests that post-erruption hydration of vitric tuffs has been pervasive throughout Yucca Mountain.

Typical concentration profiles of major and minor elements across a glass shard are shown in Figures 2 and 3. These analytical data illustrate major and minor element variations generally observed across glass shards from zone C interiors of clastic and outcrop vitric tuff samples, which include: roughly constant Al, Mg and Si; losses near margins of Na, Ca, Li, Zr, Mn and Fe; and gains near margins of K, Rb, Ba and La. Compositional variations between glass shards from outcrop and clast samples are illustrated in Figure 4. While all analyzed glasses contain approximately constant molar proportions of K_2O plus Na_2O , K_2O concentrations tend to be higher and Na_2O concentrations lower in outcrop samples PC5 and PC6. Furthermore, glasses in stable pavement PC4 cobbles have higher K_2O and lower Na_2O contents than glasses from the active erosion slope PC1 sample. Contours of equal molar alkali concentration in Figure 4 confirm the strongly coupled alkali-exchange trend associated with glass hydration [20,27,28]. The correlation between the extent to which this exchange has proceeded and the sample provenance (pavement or outcrop) suggests that, although initial glass hydration may have been a relatively early event accompanying tuff emplacement [19], alkali-exchange through interaction of glass with vadose water is still actively occurring at the desert surface. Such exchange reaches its greatest extent in PC6 and least in PC1.

4.2. SEM Observations.

Textural features and secondary mineralization associated with glass shards in zones A-C of freshly fractured rock chips of clastic samples are demonstrated by the SEM photographs in Figures 5-8. Glasses in zone A, as well as feldspar phenocrysts, were observed to show extensive pitting indicative of dissolution, in contrast to zone C in which both phases have smooth fresh surfaces. Calcic smectite accompanies glass in zone C, occurring both as interstitial platy

aggregates and as honeycomb texture [29] surface coatings (Figure 5). Similar textural features were reported [30] in vitric tuff sequences above zones of clinoptilolite crystallization at Rainier Mesa 50 km north-northeast of Yucca Mountain. Towards the zone C-B contact, shard surfaces develop mammiform protruberances (Figure 6A), which become increasingly spherical and develop into lepispheres of silica (identified by XRD as opal-CT and shown in Figures 6B and C) in inner zone B (designated later as zones B₃ and B₂). The same silica phase takes the form of botryoidal crusts in outer zone B (zone B₁). Compositionally, the botryoidal crusts are nearly pure SiO₂, whereas the opal-CT lepispheres contain appreciable Al, K and Na. The opal lepispheres in inner zone B (zone B₂) are associated with sheaf-like aggregates of dendritic clinoptilolite (Figures 6D and 7). Electron microprobe analyses of the zeolite phase in zone B summarized in Table 2 show that the clinoptilolite crystallites contain higher atomic proportions of (Ca+Mg) than K and Na, with Si/Al ratios of 4.5-5. Such compositions resemble those reported for clinoptilolites associated with opal in tuffaceous beds of the Calico Hills unit and along fractures adjacent to the proposed repository horizon in the Topopah Springs Member [9-12], particularly to the northeast of the exploration block at Yucca Mountain [9]. Calcite is associated with opal-CT in outer zone B (zone B₁), where clinoptilolite is absent. Two textural associations of calcite and opal are observed: calcite rhombs with opal lepispheres near the zone B₁-B₂ contact (Figure 8C and D); and sparry "dog-tooth" calcite with the botryoidal silica crusts near the zone B₁-A contact (Figure 8A and B). Similar calcite + silica assemblages have been recorded as fracture-coatings from borehole [11,12] and trench [13,31] samples at Yucca Mountain. Calcite also occurs in zone A, where opal-CT is absent, in association with a magnesian clay silicate identified by XRD as palygorskite, which occurs as ovoid concretions up to 10 microns in length. Palygorskite + calcite assemblages are common in desert calcretes [32,33], where

they often display a concretionary habit [34,35]. Some concretion surfaces are coated with Cl-bearing salts. Manganese and iron oxides occur in the outermost portions of zone A.

The authigenic mineralogy of the geopedal alteration rinds on clastic pebbles of the bedded tuff unit summarized in Figure 9. The mineral zonation sequence resembles portion of that observed in burial diagenesis of thick pyroclastic deposits [36-38], in which Zone I is zeolite-free and is characterized by glass shards altering to smectite and opal. Diagenetic Zone II is defined by the appearance of clinoptilolite in zeolitized rhyolitic tuffs, which is replaced by analcime in Zone III and by albite in Zone IV. Drill-core samples indicate that each of these diagenetic zones occurs at progressive depths beneath Yucca Mountain [9]. Therefore, the glass alteration and mineral sequences observed in zones C and B of clastic and outcrop samples are analogous to those documented in diagenetic Zones I and II, respectively.

5. Discussion

The microprobe analyses demonstrate that glasses in vitric tuffs have interacted with aqueous solutions, during which dissolution, leaching, cation exchange and hydration reactions have occurred. Some of the water involved in these reactions may have been derived from volatiles originally present in the volcanic debris [38], although the variation in the extent of alkali-exchange with sample provenance (pavement versus outcrop) shown in Figure 4 indicates that glass hydration is still occurring at the desert surface. Hence it is inferred that a significant component of meteoric water is involved in these reactions.

The geopedal configuration of the alteration rinds in clastic pebbles suggests that reactions involved a radial movement of solutions between clast core and surface. Evaporation is an important process in arid-climate weathering [33].

Hence, reactions in clasts are likely to have involved both the influx and efflux of water, and to be accelerated by day-time high temperatures in desert environments. The zonal mineralogy appears to be determined by the relative solubility of the dissolved species, which is typical of low-temperature, kinetically-controlled glass-water reactions [39]. Evaporation-driven efflux of variably saturated pore fluids towards the clast surfaces caused progressive outward migration of the more soluble species (e.g. Ca) while less soluble species (notably Al) are retained in the sample core. Consequently aluminous phases such as Ca-bearing smectite and clinoptilolite occur in zones C, B₃, and B₂, while calcite and palygorskite prevail in zones B₁ and A. The clinoptilolite-opal-calcite assemblage delineating the zone B₁-B₂ boundary in geopedal alteration rinds (Figure 9) is also consistent with equilibrium activity diagrams calculated for clinoptilolite solid-solutions [40]. The Na⁺ and K⁺ ions are also mobile but are occupied principally in cation-exchange reactions within silicate glass. Nonetheless the salty taste of clast outer surfaces testifies to some precipitation of sodium chloride at the sample surface.

The chemistry of the solutions from which the authigenic phases precipitate during evaporation is made up of rainwater and windblown aerosols together with solutes derived from tuff dissolution. Studies of chemical weathering of the 1980 Mount St. Helens ash-fall deposits [41] have demonstrated the importance of dissolved CO₂, derived from the atmosphere and from plant respiration, in chemical weathering reactions of silicates, during which Na⁺, Ca²⁺ and HCO₃⁻ ions are released. Silica-rich glasses are particularly vulnerable to chemical attack [30]. These solutions percolate into clasts and surface exposures during periods of precipitation. Dissolution may be both congruent (c.f. surface pitting of glass shards and feldspar phenocrysts in zone A) and incongruent (e.g., the losses near shard margins of Na, Ca, Fe, Zr, Li, and Mn; Figures 2 and 3). The aqueous phase as

it penetrates the bedded vitric tuff, deposits sequentially calcite, opal, calcic clinoptilolite and smectite phases in a zonal front onto glass shards and transports soluble ions to greater depths in downward-percolating surface waters. Similar glass dissolution, ion migration and mineral deposition might occur deeper in pyroclastic tuff terranes if the aqueous solutions were to migrate along fractures. Therefore, continued diagenetic alteration of buried vitric tuffs induced by meteoric water is possible.

Presumably similar surface weathering reactions occurred when vitric tuffs in the Calico Hills unit were exposed to the atmosphere between 13.6 and 13.1 Ma ago. The numerous ash-fall and reworked tuff sequences constituting the tuffaceous beds of Calico Hills probably represent periods during which hydration of the vitric tuffs and diagenetic alteration to clay silicate-clinoptilolite-opal-calcite assemblages occurred between successive volcanic eruptive episodes within the 500,000 year period prior to burial by the Topopah Spring Member the ash-flow deposits 13.1 Ma ago. Although extensive zeolitization of the vitric tuffs in the Calico Hills unit may have taken place during caldera development to the north of Yucca Mountain 11 Ma ago [2,9], further diagenetic reactions producing mineral zonations of calcic clinoptilolite-opal-calcite assemblages could occur in the presence of bicarbonate-rich fracture-flow groundwater with a high meteoric water component. On the other hand, calcic clinoptilolite and calcite-lined fractures occurring throughout Yucca Mountain probably formed by precipitation from descending surface water rather than from upwelling groundwater from underlying Paleozoic carbonate aquitards [42].

6. Conclusions

The tendency of present-day reactions between surface rainwater and bedded tuff to replicate diagenetic and textural features of similar lithologies at depth

(e.g., tuffaceous beds of Calico Hills [10,11]), as well as fracture-coatings within the Yucca Mountain sequence [12,13], raises fundamental questions about the agents and mechanisms of future diagenetic reactions within Yucca Mountain. Rainwater under desert conditions is a powerful agent of diagenetic alteration of tuff deposits. Notwithstanding the low precipitation at Yucca Mountain, the presence of such water at depth raise doubts about the long-term sorptive capacity of the host-rock adjacent to the proposed repository for nuclear waste. Contaminated fluids leaking from the repository may pass ~~not~~ through highly sorptive zeolite-rich tuffs altered 11 million years ago, but along fractures lined with more recently formed authigenic minerals containing non-sorptive calcite and silica assemblages which prevent zeolites and clay silicates from immobilizing radiogenic elements in the groundwater.

Acknowledgments

This study was funded by the State of Nevada, Nuclear Waste Project Office, under the Department of Energy grant from the Nuclear Waste Fund. We gratefully acknowledge the assistance of Dr. N. Shimizu in carrying out the ion-microprobe measurements and the helpful comments made by Dr. J. A. Apps who read an early draft of the manuscript.

References

- 1 Lipman, P. W., R. L. Christiansen and J. T. O'Connor, A compositionally zoned ash-flow sheet in southern Nevada, *USGS Prof. Pap.* 524-F (1966) 47pp.
- 2 Byers Jr, F. M., W. J. Carr, P. P. Orkild, Q. D. Quinlivan and K. A. Sargent, Volcanic suites and related cauldrons of Timber Mountain-Oasis Valley caldera complex, southern Nevada, *USGS Prof. Pap.* 919 (1976) 70pp. (1976).
- 3 U. S. Department of Energy, Site characterization plan, Yucca Mountain Site, Nevada, research and development area, Nevada. *Report DOE/RW-0160* (1988) 8 vols.
- 4 Spengler, R.W., D. C. Muller and R. B. Livermore, Preliminary report on the geology and geophysics of drill hole UE25a-1, Yucca Mountain, Nevada, *USGS Open-File Rep.* 79-1244 (1979) 43pp.
- 5 Spengler, R. W., F. M. Byers Jr. and J. B. Warner, Stratigraphy and structure of volcanic rocks in drill hole USW G1, Yucca Mountain, Nye County, Nevada, *USGS Open-File Rep.* 81-1349 (1981) 50pp.
- 6 Maldonado, F. and S. L. Koether, Stratigraphy, structure and some petrographic features of Tertiary volcanic rocks at the USW G-2 drill hole, Yucca Mountain, Nye County, Nevada, *USGS Open-File Rep.* 83-732 (1983) 53pp.
- 7 Scott, R. and M. Castellanos, Preliminary report on the geologic character of drill holes USW GU-3 and USW G-3, *USGS Open-File Rep.* 84-491 (1984) 121pp.
- 8 Bish, D. L. and D. T. Vaniman, Mineralogic summary of Yucca Mountain, Nevada, *U.S. Nat. Tech. Inform. Service* LA-10543-MS (1983) 55pp.
- 9 Broxton, D. E., D. L. Bish and R. G. Warren, Distribution and chemistry of diagenetic minerals at Yucca Mountain, Nye County, Nevada, *Clays & Clay Min.* 35 (1987) 89-110.
- 10 Broxton, D. E., R. G. Warren, R. C. Hagan and G. Leudenmann, Chemistry of diagenetically altered tuffs at a potential nuclear waste repository, Yucca Mountain, Nye County, Nevada, *U.S. Nat. Tech. Inform. Service* LA-10802-MS (1982) 47pp.
- 11 Levy, S. S., Studies of altered vitrophyre for the prediction of nuclear waste repository-induced thermal alteration at Yucca Mountain, Nevada, *Mat. Res. Soc. Symp. Proc.* 26 (1984) 959-974.
- 12 Carlos, B. A., Minerals in fractures of the unsaturated zone from drill core USW G-4, Yucca Mountain, Nye County, Nevada, *U.S. Nat. Tech. Inform. Service* LA-10415-MS (1985) 55pp.
- 13 Szabo, B. J. and T. K. Kyser, Uranium, thorium isotopic analyses and uranium-series ages of calcite and opal, and stable isotopic compositions of calcite from drill cores UE25a#1, USW G-2 and USW G-3/GU-3, Yucca Mountain, Nevada, *USGS Open-File Rep.* 85-224 (1985) 25pp.

- 14 Rosholt, J. N., D. A. Bush, W. J. Carr, D. L. Hoover, W. C. Swadley and J. R. Dooley Jr., Uranium-trend dating of quaternary deposits in the Nevada Test Site area, Nevada and California, *USGS Open-File Rep.* 85-540 (1985) 72pp.
- 15 Caporuscio, F., D. T. Vaniman, D. L. Bish, D. E. Broxton, B. Arney, G. Heiken, F. M. Byers Jr., R. Gooley and E. Semarge, Petrologic studies of drill cores USW G-2 and UE25B-1H, Yucca Mountain, Nevada, *U.S. Nat. Tech. Inform. Service LA-9255-MS* (1982) 111pp.
- 16 Bish, D. L., D. T. Vaniman, F. M. Byers Jr. and D. E. Broxton, Summary of the mineralogy-petrology of tuffs of Yucca Mountain and the secondary phase thermal stability in tuffs, *U.S. Nat. Tech. Inform. Service LA-9321-MS* (1982) 47pp.
- 17 Albee, A. L. and L. Ray, Correlation factors for electron probe microanalysis of silicates, oxides, carbonates, phosphates and sulfates, *Anal. Chem.* 42 (1970) 1408-1414.
- 18 Shimizu, N. and A. P. LeRoux, The chemical zoning of augite phenocrysts in alkaline basalts from Gough Island, South Atlantic, *J. Volc. Geotherm. Res.* 29 (1986) 159-188.
- 19 Shimizu, N. and S. R. Hart, Applications of the ion microprobe to geochemistry and cosmochemistry, *Ann. Rev. Earth Planet. Sci.* 10 (1982) 483-526 (1982).
- 20 Jezek, P. A. and D. C. Noble, Natural hydration and ion exchange of obsidian: an electron microprobe study, *Amer. Mineral.* 63 (1978) 266-273.
- 21 Froggatt, P. C., Toward a comprehensive Upper Quaternary tephra and ignimbrite stratigraphy in New Zealand using electron microprobe analysis of glass shards, *Quatern. Res.* 19 (1983) 188-200.
- 22 Colella, C., R. Aiello and C. Forcellì, Hydration as an early stage in the zeolitization of natural glass, In: *Natural Zeolites Occurrence, Properties, Use.* (F. A. Mumpton and L. B. Sands, eds; Pergamon Press, 1978) p.345-350.
- 23 Delaney, J. R. and J. L. Karsten, Ion microprobe studies of water in silicate melts: concentration-dependent water diffusion in obsidian, *Earth Planet. Sci. Lett.* 52 (1981) 191-202.
- 24 Newman, S., E. M. Stolper and S. Epstein, Measurement of water in rhyolitic glasses: Calibration of an infrared spectroscopic technique, *Amer. Mineral.* 71 (1986) 1527-1541.
- 25 Frieman, I. and W. Long, Hydration rate of obsidian, *Science* 191 (1976) 105-121.
- 26 Michels, J. W., I. S. T. Tsong and C. M. Nelson, Obsidian dating and East African archeology, *Science* 219 (1983) 361-366.
- 27 Noble, D. C., Sodium, potassium, and ferrous iron contents of some secondarily hydrated natural silicic glasses, *Amer. Mineral.* 52 (1967) 280-286.

- 28 Lipman, P. W., R. L. Christiannsen and R. E. Van Alstine, Retention of alkalis by calc-alkaline rhyolites during crystallization and hydration, *Amer. Mineral.* 34 (1969) 286-291.
- 29 Odom, I. E., Smectite clay minerals: properties and uses, *Phil. Trans. Royal Soc. London* 311A (1984) 391-409.
- 30 White, A. F., H. C. Claassen and L. V. Benson, The effect of dissolution of volcanic glass on the water chemistry in a tuffaceous aquifer, Rainier Mesa, Nevada, *USGS Water-Supply Paper* 1535-G (1980) 34pp.
- 31 Vaniman, D. T., D. L. Bish and S. Chipera, A preliminary comparison of mineral deposits in faults near Yucca Mountain, Nevada, with possible analogs, *U.S. Nat. Tech. Inform. Service* LA-10901-MS (1988) 31 pp.
- 32 Velde, B. and A. Meunier, Petrogic phase equilibria in natural clay systems, Ch.9 in: *Chemistry of Clays and Clay Minerals* (A. C. D. Newman, ed.) *Min. Soc. Monogr.* 6 (1987) 423-458.
- 33 Vanden Heuvel, R. C. The occurrence of sepiolite and attapulgite in the calcareous zone of a soil near Las Cruces, New Mexico, *Clays & Clay Min.* 13 (1966) 193-200.
- 34 Yaalon, D. H. and M. Weider, Pedogenic palygorskite in some arid brown (calciorthid) soils of Israel, *Clay Min.* 11 (1976) 73-80.
- 35 Hay, R. L. and B. Wiggins, Pellets, ooids, sepiolite and silica in three calcretes of the southwestern United States, *Sedimentology* 27 (1980) 559-576.
- 36 Iijima, A., Effect of pore water in clinoptilolite-analcime-albite reaction series, *Journ. Fac. Soc. Univ. Tokyo, Sec. II* 19 (1975) 133-147.
- 37 Iijima, A., Geology of natural zeolites and zeolitic rocks, *Proc. Ffth Intern. Conf. Zeolltes* (L. V. C. Rees, ed; Heyden & Co, London, 1980) p. 103-118.
- 38 Smyth, J. R., Zeolite stability constraints on radioactive waste isolation in zeolite-bearing volcanic rocks, *Journ. Geol.* 90 (1982) 195-202.
- 39 Dibble Jr, W. E. and W. A. Tiller, Kinetics of glass dissolution and zeolite formation under hydrothermal conditions, *Clays & Clay Min.* 29 (1981) 323-339.
- 40 Bowers, T. S. and R. G. Burns, Activity diagrams for clinoptilolite: susceptibility of this zeolite to further diagenetic reactions, *Amer. Mineral.* (in press).
- 41 White, A. F., L. V. Benson and A. Yee, Chemical weathering of the May 18, 1980, Mount St. Helens ash fall and the effect on the Iron Creek watershed, Washington. Ch. 14 in: *Rates of Chemical Weathering of Rocks and Minerals* (Academic Press, Inc., 1986), 351-375.
- 42 Snyder, D. B. and W. J. Carr, Preliminary results of gravity investigations at Yucca Mountain and vicinity, southern Nye County, Nevada, *USGS Open File Rep.* (1982) 82-701 36pp.

Table 1. Average compositions of analysed glasses

Oxide Wt. %	PC1.G1 [C] (4)	PC4.G1 [C] (15)	PC4.G2 [B] (8)	PC4.G3 [B] (7)	PC4.G4 [B] (1)	PC4.G5 [A] (11)	PC4.G2* [B] (13)
SiO ₂	74.00	73.95	73.72	73.92	73.05	75.10	
Al ₂ O ₃	12.03	12.01	11.89	11.98	12.00	11.86	
TiO ₂	0.13	0.13	0.12	0.12	0.12	0.12	0.13
FeO	0.75	0.77	0.81	0.73	0.76	0.71	
MgO	0.05	0.03	0.04	0.03	0.05	0.03	0.033
CaO	0.20	0.14	0.13	0.18	0.09	0.03	0.124
Na ₂ O	3.92	3.72	3.68	3.19	3.04	3.66	
K ₂ O	4.67	5.25	5.25	5.50	5.46	5.40	5.36
MnO	0.11	0.10	0.11	0.09	0.08	0.07	
H ₂ O**	4.15	3.90	4.34	4.33	5.35	2.99	

* Analysis by SIMS. Other minor elements analysed (in ppm) included: Li, 30.6; Rb, 232; Zr, 410; Ba, 27; La, 42

** Determined by difference

[C], etc.: center of glass shard from zone C, etc.
 (4), etc.: number of analyses used in the average
 PC1.G1: 1.70 mm, pertilic glass shard from zone C
 PC4.G1: 0.43 mm. vesicular shard 9 mm from zone B
 PC4.G2: 0.84 mm, glass shard at zone C-B contact
 PC4.G3: 2.09 mm. pertitic shard at zone B-C contact
 PC4.G4: 0.23 mm. glass shard within zone B
 PC4.G5: 0.22 and 0.14 mm. adjacent shards in zone A.

Table 2. Microprobe analyses of zeolites on glass shard surfaces

Oxide Wt. %	PC1 Z1 [B] (3)	PC4.Z2 [B] (4)	PC5.Z3 [B] (1)
SiO ₂	55.8	58.9	64.0
Al ₂ O ₃	10.4	9.1	11.9
TiO ₂	0.1	0.1	0.1
FeO	0.9	0.7	1.4
MgO	1.5	1.9	4.0
CaO	3.4	1.3	1.5
Na ₂ O	1.5	2.5	2.2
K ₂ O	2.6	2.4	1.9
Total*	76.2	76.9	86.8

* Low totals reflect the difficulty of analysing thin surface coatings of clinoptilolite on glass shards (see Figure 7).

Captions to Figures

Figure 1. Photograph of a sectioned slab through a clastic cobble of the non-welded bedded tuff unit showing the surficial alteration rind. The top outermost weathered zone A is separated from the interior zone C by the conspicuous dark vitreous band designated as zone B.

Figure 2. Compositional profiles measured by electron microprobe across a glass shard in zone B of a clastic cobble of non-welded bedded tuff. Water estimated by difference is ~3-4 wt.%.

Figure 3. Compositional profiles measured by ion microprobe across the same glass shard used in Figure 2. The two figures together illustrate the general trends: uniform Si, Al and Mg; losses of Na, Ca, Li, Zr and Fe; and gains of K, Rb, Ba and La towards the margins of the glass shard.

Figure 4. Correlations of K_2O versus Na_2O in interiors of glass shards from zone C of clastic and outcrop samples of the non-welded bedded tuff unit. Contours of constant molar concentration suggest a strongly coupled alkali exchange trend during glass hydration.

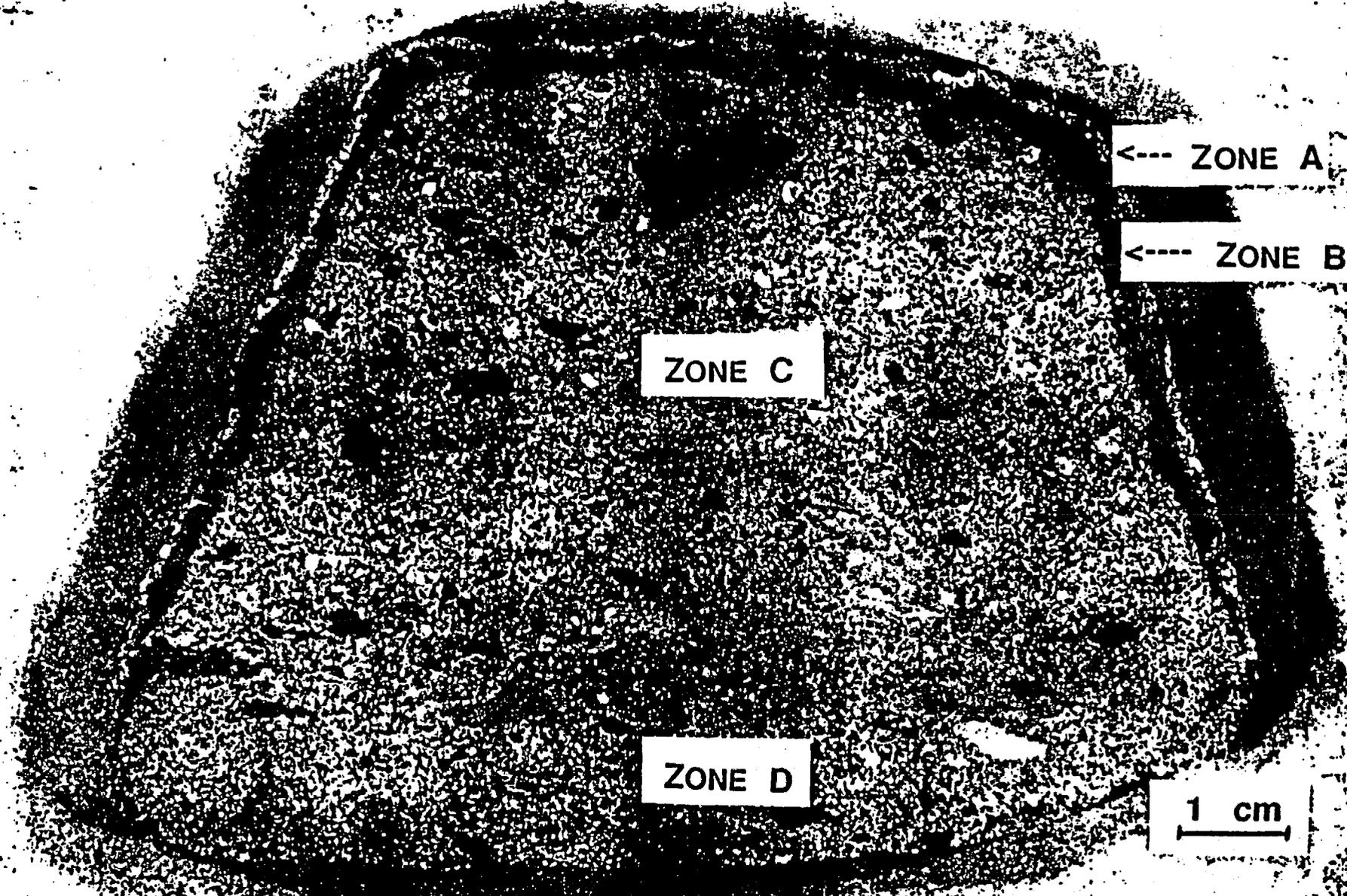
Figure 5. Scanning electron microscope photographs of smectite in Zone C (A,B) coating glass shards; and (C,D) associated with glass in the groundmass. The vertical bar at bottom left of each photograph represents 10 microns.

Figure 6. Scanning electron microscope photographs of surfaces of glass shards near the Zone B-C contact (A) with mammiform protuberances of silica, which become increasingly spherical (B,C) and associated with acicular zeolite crystallites (D).

Figure 7. Scanning electron microscope photographs showing dendritic clinoptilolite crystallites associated with lepispheres of opal CT in Zone B.

Figure 8. Scanning electron microscope photographs of calcite in Zone B. (A,B) as sparry dog-tooth crystallites with botryoidal silica near the zone B-A contact; and (C,D) as rhombs associated with lepispheres of opal CY near the Zone B-C contact.

Figure 9. Zonal mineralogy patterns observed in alteration rinds on non-welded vitric bedded tuffs. The visual zone B of Figure 1 is subdivided into three subzones B_1 , B_2 and B_3 , based on mineral assemblages identified by SEM and XRD measurements.



<--- ZONE A

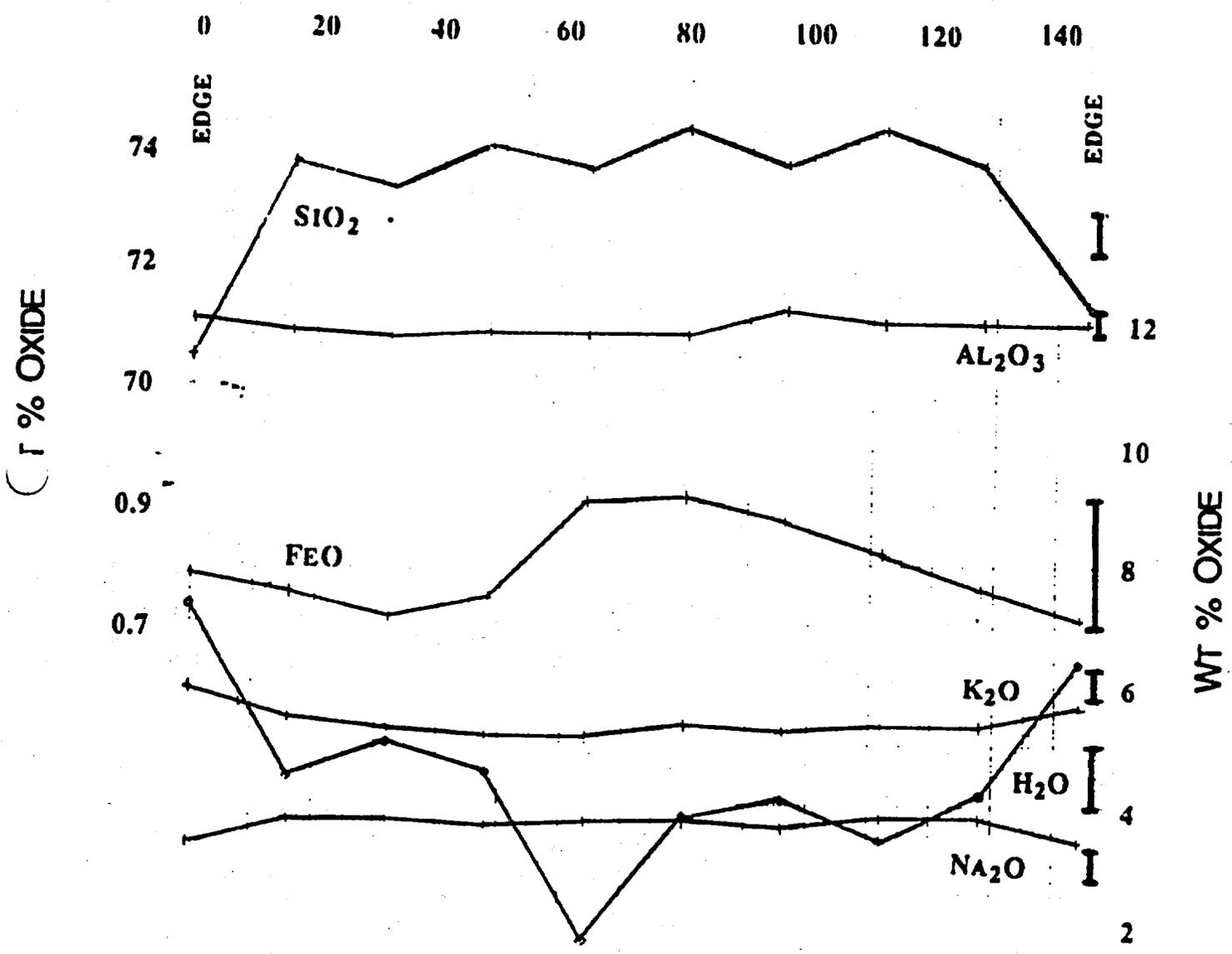
<--- ZONE B

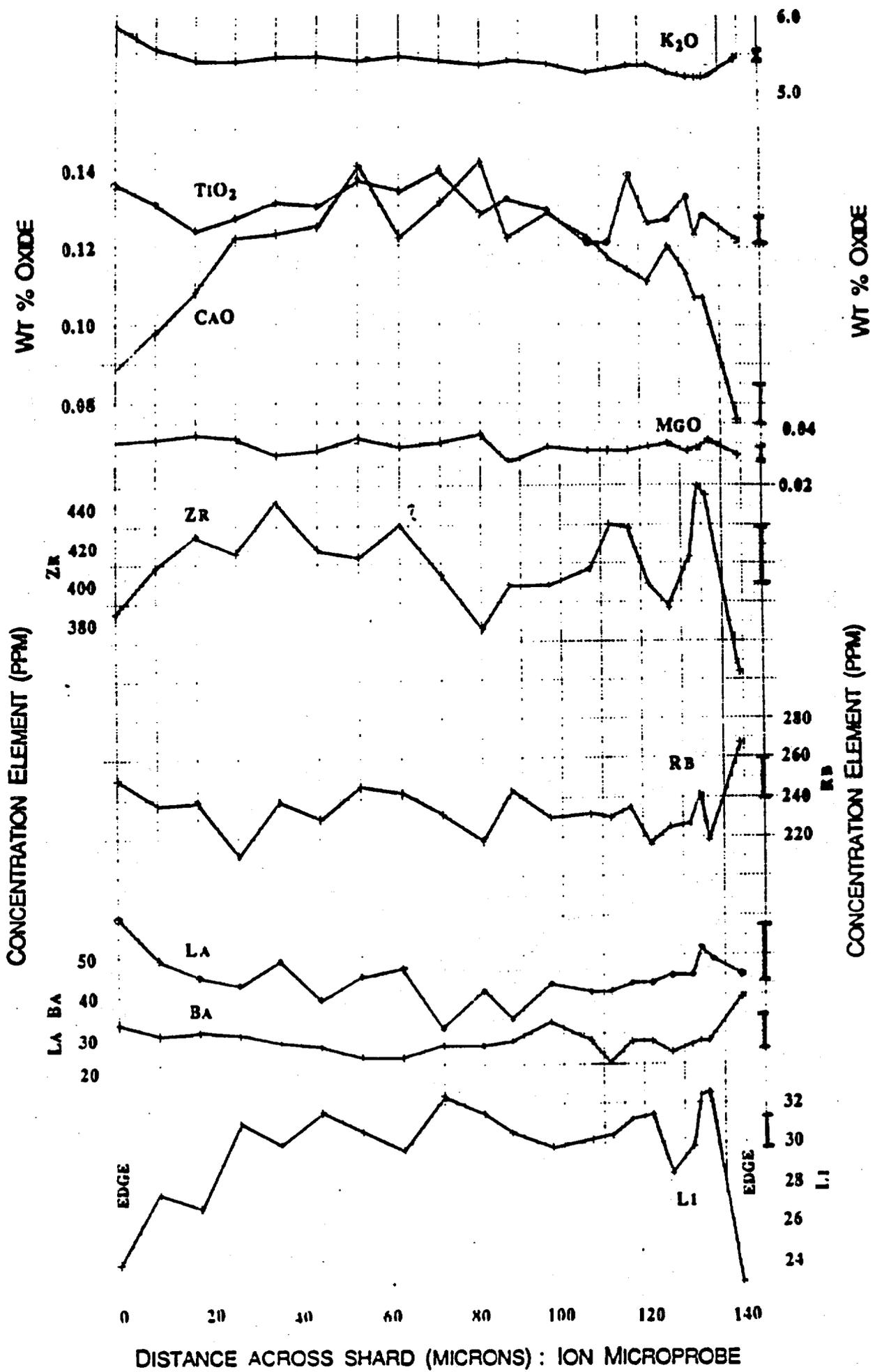
ZONE C

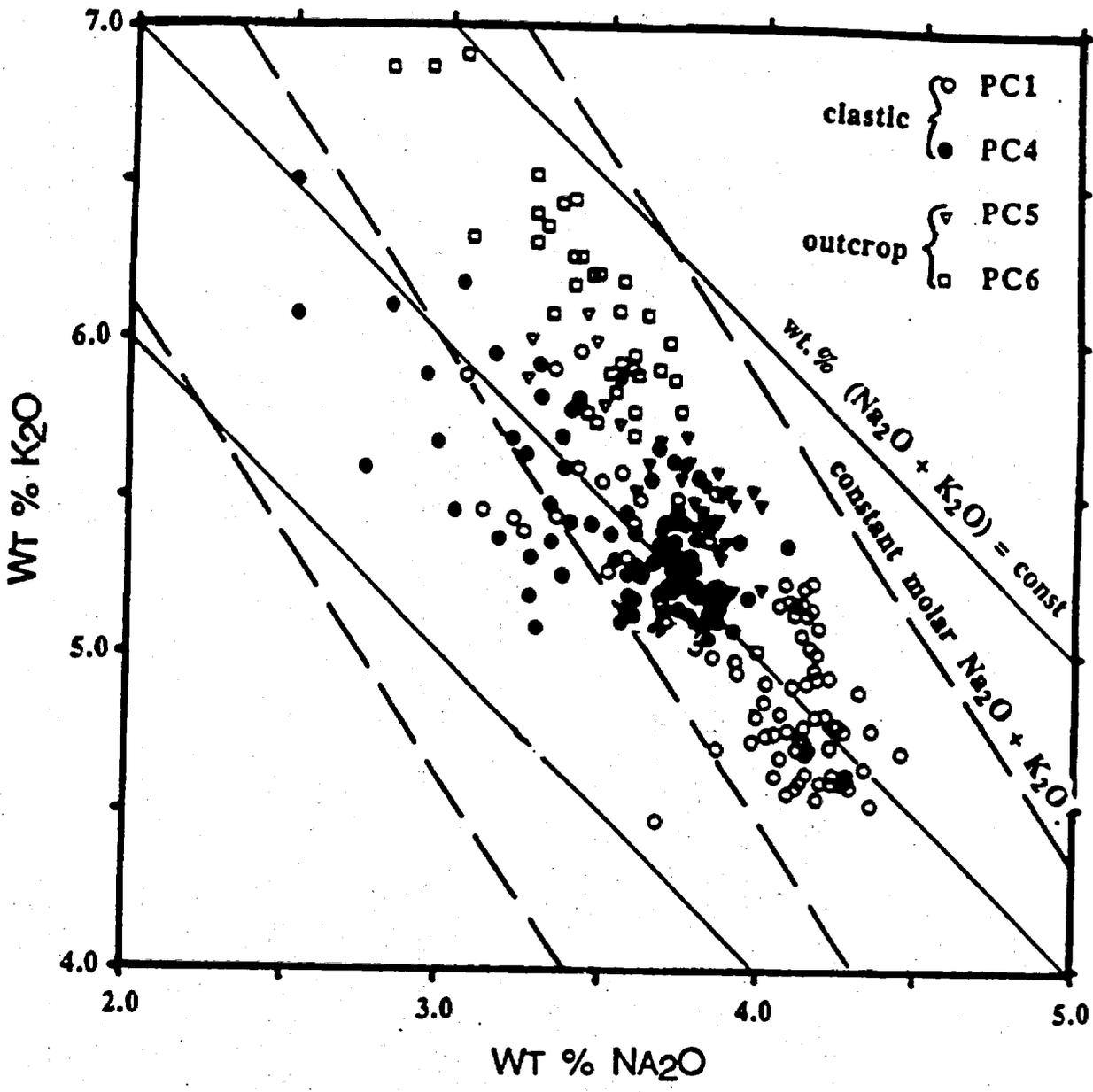
ZONE D

1 cm

DISTANCE ACROSS SHARD (MICRONS) : ELECTRON MICROPROBE

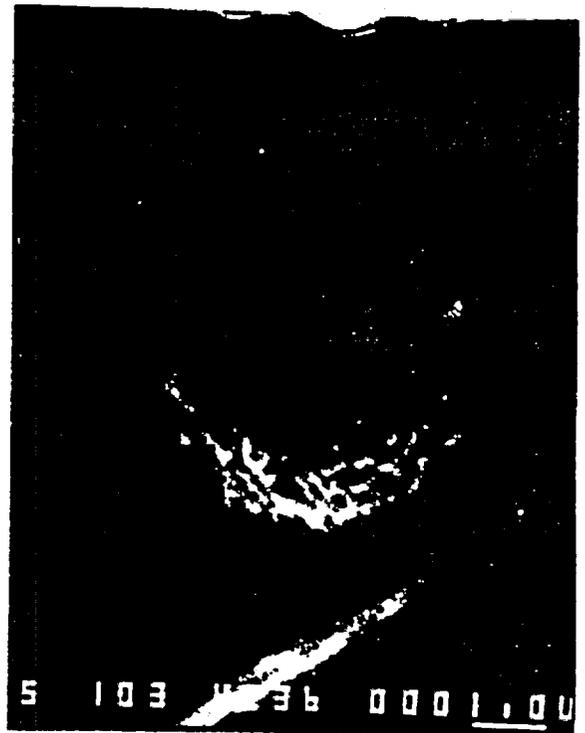


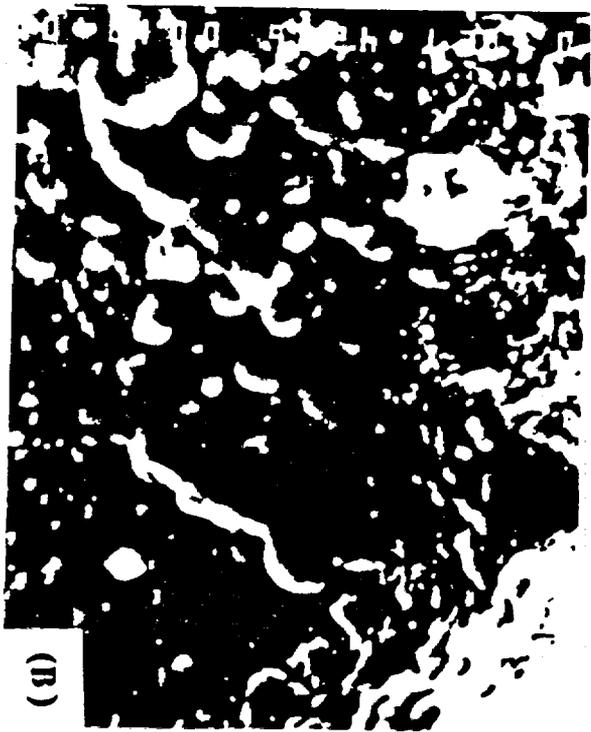


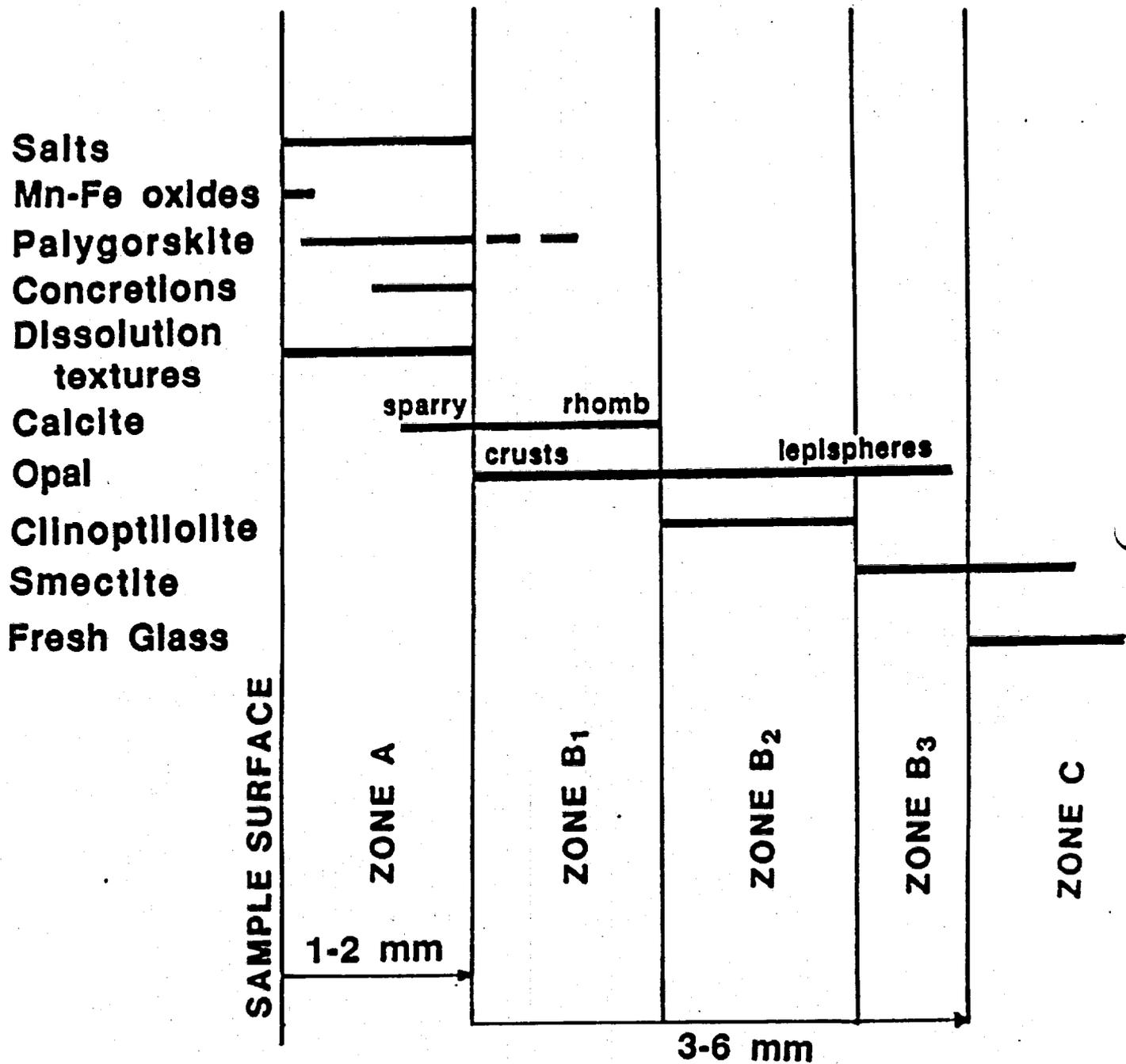












**ACTIVITY DIAGRAMS FOR CLINOPTILOLITE: SUSCEPTIBILITY OF
THIS ZEOLITE TO FURTHER DIAGENETIC REACTIONS**

TERESA S. BOWERS AND ROGER G. BURNS

**Department of Earth, Atmospheric and Planetary Sciences
Massachusetts Institute of Technology,
Cambridge, Massachusetts 02139.**

[Manuscript submitted to the American Mineralogist]

November 28, 1988.

ABSTRACT

Clinoptilolite is the predominant zeolite in diagenetically altered volcanic rocks at Yucca Mountain, Nevada, having formed by post-eruptive reactions of groundwater with vitric tuffs in the pyroclastic deposits there. The zeolite, which lines fractures adjacent to the proposed repository for high-level nuclear waste in a densely welded, devitrified tuff unit located in the vadose zone well above the present-day water table, is particularly abundant in underlying vitric to zeolitized non-welded tuffs. Compositional variations of clinoptilolites in the fractures and zeolitized tuffs not presently in contact with groundwater raise questions about the long-term stability of this zeolite to further diagenetic reactions. Equilibrium activity diagrams were calculated for clinoptilolite solid-solutions in the seven-component system Ca-Na-K-Mg-Fe-Al-Si plus H₂O employing available thermodynamic data for related minerals, aqueous species and water. Stability fields are portrayed graphically on plots of $\log(a_{\text{Na}^+}/a_{\text{H}^+})$ versus $\log(a_{\text{Ca}^{2+}}/(a_{\text{H}^+})^2)$, assuming the presence of K-feldspar, saponite and hematite and using ranges of activities for SiO₂ and Al³⁺ defined by the saturation limits for quartz, amorphous silica, gibbsite, kaolinite and pyrophyllite. Formation of clinoptilolite is favored by higher SiO₂ activities than allowed for by the presence of quartz, thus accounting for the coexistence of clinoptilolite with opal CT in zeolitized vitric tuffs. The clinoptilolite stability field broadens with increasing atomic substitution of Ca for Na, K for Ca, and Mg for Ca, reaches a maximum for intermediate activities of dissolved Al, and decreases at elevated temperatures. The thermodynamic calculations show that sodium bicarbonate-type groundwater, such as reference J-13 well-water collected from fractured devitrified tuffs at the adjacent Nuclear Test Site in Nevada, is approximately in equilibrium at 25 °C with calcite and several zeolites including Ca-bearing clinoptilolite. Sodic clinoptilolites are stabilized in groundwater depleted in Ca²⁺ and enriched in Na⁺ derived from

altered vitric tuffs. Decreasing Al^{3+} activities results in the association of clinoptilolite with calcite and opal CT observed in weathered zeolitized vitric tuffs at Yucca Mt. The activity diagrams indicate that prolonged diagenetic reactions with groundwater depleted in Al, enriched in Na and heated by the thermal envelope surrounding the nuclear waste repository may eliminate sorptive clinoptilolite.

INTRODUCTION.

Clinoptilolite, ideally $(\text{Na,K,Ca})_{5-6}\text{Si}_{30}\text{Al}_6\text{O}_{72}\cdot 24\text{H}_2\text{O}$, is an abundant natural zeolite that is common in diagenetically altered volcanic rocks where it forms by post-eruptive reactions of saline groundwater with rhyolitic glass shards in tuffaceous ash-fall and ash-flow deposits (Hay, 1966; Hay and Sheppard, 1977; Iijima, 1975, 1980). Such silicic ash-flow tuffs are the predominant lithology at Yucca Mountain, Nevada, the site of the proposed repository for burial of high-level nuclear waste (U.S. Dept. Energy, 1988). The repository horizon there is a densely welded and devitrified tuff unit underlain by vitric to zeolitized non-welded tuffs containing high proportions of clinoptilolite (Broxton et al., 1987). Because of its favorable cation exchange reactions, clinoptilolite is assumed to serve as an agent for immobilizing several of the soluble cations and to be an effective barrier to radionuclide migration should groundwater flowing through the repository cause leakage of fission products in the future.

Clinoptilolites analysed in drill-core samples throughout Yucca Mountain and its immediate vicinity display wide compositional variations, particularly in fractures adjacent to the repository horizon in the Topopah Spring Member of the Paintbrush Tuff unit (Levy, 1984) and in the underlying zeolitized tuffaceous beds of Calico Hills unit (Broxton et al., 1987). In the vadose zone beneath Yucca Mountain, clinoptilolites with high Ca and Mg contents line fractures in the Topopah Spring Member (Carlos, 1985; Broxton et al., 1986, 1987). However, in the underlying tuffaceous beds of Calico Hills unit and deeper zeolitized tuff members, the clinoptilolites display regional and depth variations (Broxton et al., 1986, 1987). On the western side of Yucca Mountain the clinoptilolites are Na-K-bearing and become Na-rich with depth. To the east, the clinoptilolites are Ca-K-bearing and become Ca-rich with depth. Such compositional variations of

clinoptilolites not presently in contact with groundwater raise questions about the long-term stability of this zeolite to further diagenetic reactions.

Although the Topopah Springs Member and tuffaceous beds of Calico Hills unit both lie in the undersaturated zone well above the present-day water table beneath Yucca Mountain, the two formations dip to the east so that at the location of the nearest water-supply well, designated J-13 and located 6 km to the east at Jackass Flat on the Nevada Test site, the Topopah Springs Member lies beneath the water table. As a result, the major producing horizon for J-13 well-water is a highly fractured interval within the Topopah Springs Member (Delany, 1985). The chemical composition of the sodium bicarbonate-type groundwater obtained from well J-13 has been monitored for several years (Daniels et al., 1982; Bish et al., 1984; Kerrisk, 1987) and serves as a reference standard in laboratory experiments and geochemical modelling studies for characterizing the Yucca Mountain exploration block (e.g. Oversby, 1985; Delany, 1985; Knauss et al., 1985a,b; Moore et al., 1986). Whether or not J-13 water is of an appropriate composition for prediction of authigenic mineral reactions in the undersaturated zone beneath Yucca Mountain requires critical evaluation.

In order to assess the stability limits of clinoptilolite and its vulnerability to changes of groundwater chemistry relative to the composition of J-13 well-water, equilibrium activity diagrams have been calculated for clinoptilolite solid-solutions in the system Ca-Na-K-Mg-Fe-Al-Si-H₂O employing available thermodynamic data for relevant oxide and aluminosilicate phases. Results reported here indicate that authigenic minerals such as clinoptilolite modify, and are modified by, groundwater compositions.

CALCULATIONS OF ACTIVITY DIAGRAMS

Sources of Thermodynamic Data.

The method for calculating activity diagrams is described in Bowers et al. (1984), who also tabulated thermodynamic data for many of the phases considered here (Table 1). Additional thermodynamic data for zeolites are provided by calorimetric measurements made by Johnson et al. (1982, 1983, 1985) and Hemingway and Robie (1984).

The clinoptilolite measured by Hemingway and Robie (1984) from altered tuffs of the Big Sandy Formation, Mohave County, Arizona (Sheppard and Gude, 1973) was formulated by them as



and, as indicated in Table 2, resembles some of the (Ca + Mg)-rich clinoptilolites lining fractures in the Topopah Spring Member and present in the zeolitized tuff of Calico Hills unit, particularly beneath the north-eastern block of Yucca Mountain (Broxton et al., 1987). However, since Hemingway and Robie (1984) provided only increments to the free energy and enthalpy with no reference points, it was necessary to estimate the standard free energy of formation (ΔG°_f) and enthalpy of formation (ΔH°_f) for clinoptilolite at 25 °C by a component-summation method, using thermodynamic data for water and related minerals listed in Table 1 (Helgeson et al., 1978; Robie et al., 1978). Thus, the ΔG°_f and ΔH°_f values of clinoptilolite that are listed in Table 3 were estimated from data for natrolite, scolecite, K-feldspar, brucite, hematite, gibbsite, quartz, and water. Similarly, the ΔG°_f for the Ca end-member heulandite was estimated from the value given by Johnson et al. (1985) after correcting for minor Ba, Sr, K and Na components. The ΔG°_f of Na-phillipsite was estimated from the experimental value for natrolite (Johnson et al., 1983) and data for quartz and water. Values of ΔG°_f for Ca-

phillipsite and epistilbite were estimated in a similar manner from published data for scolecite (Johnson et al., 1983), while the free energy of formation of K-phillipsite was estimated from those of Na-phillipsite, albite and K-feldspar. All estimated data used in this study are listed in Table 3.

Table 4 contains estimated free energies of formation for compositionally variable clinoptilolites. Independent substitutions are allowed of Na for Ca, K for Ca and Ca for Mg, where charge balance is maintained. ΔG^0_f is estimated from the value given for clinoptilolite in Table 3 by a component-summation method using natrolite, scolecite and H₂O for Na-Ca substitution; K-feldspar, anorthite and quartz for K-Ca substitution; and CaO and MgO for Ca-Mg substitution. These correction mechanisms result in lower free energies for Ca over Na, K over Ca and Ca over Mg-rich clinoptilolites.

Composition of Groundwater.

Because the Topopah Spring Member tuff is the major producing horizon for water pumped from J-13 well, it is generally assumed (Oversby, 1985) that the composition of J-13 well-water approximates the prevailing groundwater chemistry of the proposed repository horizon in the same formation at Yucca Mountain even though the Topopah Spring Member there is in the undersaturated zone. As a result, J-13 well-water has been widely used as the reference aqueous phase for calibrating numerous environmental parameters relevant to the Yucca Mountain repository horizon (Oversby, 1985; Delany, 1985; Knauss et al., 1985a,b; Moore et al., 1986). The chemical composition of J-13 well-water has been monitored for several years (Daniels et al., 1982; Kerrisk, 1987) and typical concentrations of dissolved species in it are summarized in Table 5. Small fluctuations of concentrations with time have been recorded, but the variations are minor compared with other variables in experiments in which J-13 well-water

was used (Daniels et al., 1982). However, during experiments in which J-13 well-water was contacted with tuff samples of the Topopah Spring Member taken from a drill core at the appropriate region of main water production of the J-13 well, concentrations of many constituents changed slightly (Table 5), particularly Mg and Al which decreased after 3 weeks at room-temperature (Daniels et al., 1982). Moreover, filtration affected the composition of some elements, particularly Fe, Al and Mg, which were drastically reduced in samples passed through 0.05 micron Nuclepore membranes compared to those obtained from 0.45 micron Millipore filters (Daniels et al., 1982). The Al concentration, for example, decreased from ~40 mg/l (0.45 μm filter) to <0.01 mg/l (0.05 μm filter) (Daniels et al., 1982). Cation concentrations in solutions contacted with vitrophyre samples from the Topopah Springs Member at 152 °C showed significant increases of dissolved Si, Fe, Al, K and Na and a decrease of dissolved Mg, which were attributed to dissolution of glass and precipitation of clays. A specimen of zeolitized tuff from the tuffaceous beds of Calico Hills unit reacted with J-13 water at the same temperature showed marked dissolution of clinoptilolite and disappearance of mordenite and cristobalite (Daniels et al., 1982). In later experiments, Knauss et al. (1985a,b) studied compositional changes of J-13 well-water after reacting it with crushed tuff and polished wafer samples of the densely-welded, devitrified ash-flow tuff in a drill core taken from the repository level in the Topopah Spring Member. The modal mineralogy of this horizon consists of a ~98% microcrystalline feldspar-cristobalite-quartz and accessory (<2%) biotite-montmorillonite assemblage (Bish et al., 1984). Reactions were performed for 2-3 month intervals at temperatures of 90, 150 and 250 °C and pressures of 90-100 bars. Results from the 150 °C experiments are summarized in Table 5, where it can be seen that dissolved SiO_2 concentrations increase and are close to the cristobalite saturation value (Knauss et al., 1985a). Sodium also increased during the

experiments, Ca and Mg decreased, and Al and K both increased rapidly and then decreased. These effects were attributed to dissolution of montmorillonite and precipitation of calcite and smectite. The experiments at 90 °C and 250 °C produced similar trends. Phases identified by scanning electron microscopy included illite, Mg-Ca or Fe-rich clays, gibbsite, calcite and a pure SiO₂ phase considered to be cristobalite (Knauss et al., 1985 a,b).

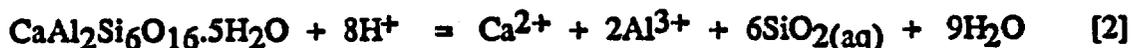
Studies to determine compositional changes of groundwater as it passes through the undersaturated zone in tuffaceous deposits have been conducted at Rainier Mesa located 50 km to the north-northeast of Yucca Mountain (Benson, 1976; White et al., 1980). At Rainier Mesa welded and vitric tuffs overlie zeolitized tuffs, resembling the sequence of ash-flow deposits at Yucca Mountain. Concentrations of Ca and Mg in interstitial waters decreased as a function of depth and were generally lower than in J-13 well-water, whereas opposite effects were observed for Na (Benson, 1976; White et al., 1980). The concentration of dissolved K was lower at depth, and SiO₂ higher, than J-13 water compositions, while Cl⁻ decreased and HCO₃⁻ increased with depth. The maximum compositional variations of the interstitial water occurred in alteration zones containing clinoptilolite and montmorillonite (Benson, 1976; White et al., 1980). Water seeping through fractures in tunnels beneath the zeolitized tuffs was HCO₃⁻-rich, and had lower Ca, Mg and SiO₂ contents, variable K and higher Na concentrations than J-13 well-water (Benson, 1976; White et al., 1980). The clinoptilolites along fractures were Ca-Mg-K-rich, correlating with the depletion of these cations in the groundwater, while the fracture-flow water was enriched in HCO₃⁻ relative to the more Cl⁻-rich interstitial water. Comparisons made with dissolution experiments on vitric and crystalline tuffs demonstrated the rapid dissolution of Na and SiO₂ but retention of K in glass-bearing tuffs, whereas dissolution of crystalline tuffs containing sanidine, quartz, biotite and clinopyroxene phenocrysts and sanidine-

cristobalite groundmass resulted in solutions rich in Ca, Mg and HCO_3^- (White et al., 1980). White et al (1980) thus concluded that fracture-water compositions, such as J-13 well-water, are dominated by dissolution of vitric tuffs, but are modified by infiltration through zeolitized tuffs.

These results clearly show that zeolitized tuffs affect groundwater chemistry and suggest that compositional variability of clinoptilolites influence, and are influenced by, groundwater compositions.

Representation of Activity Diagrams.

Three- and four-component plus H_2O systems can be readily represented in two dimensions. For example, in the system Ca-Al-Si- H_2O , two components are selected for the x and y axes, a third component is balanced upon, leaving the activity of H_2O to be assigned, commonly equal to unity. A reaction between amorphous silica and epistilbite can be represented by writing a hydrolysis reaction for each mineral:



Combining reactions [1] and [2] such that no $\text{SiO}_2(\text{aq})$ remains gives:



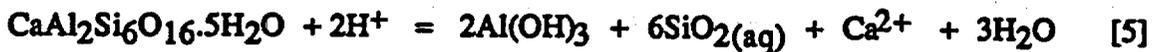
A $\log k$ as a function of pressure and temperature can be calculated from thermodynamic data for this reaction and is expressed as:

$$\log k = 2\log(a_{\text{Al}^{3+}}/(a_{\text{H}^+})^3) + \log(a_{\text{Ca}^{2+}}/(a_{\text{H}^+})^2) \quad [4]$$

If the x and y axes are chosen as $\log(a_{\text{Al}^{3+}}/(a_{\text{H}^+})^3)$ and $\log(a_{\text{Ca}^{2+}}/(a_{\text{H}^+})^2)$, respectively, reaction [4] is the equation of a line with a slope of -2 and a y intercept of $\log k$ that forms the boundary on an activity diagram between amorphous silica and epistilbite (see Figure 2a discussed later). Similar calculations are performed for all mineral pairs and the resulting intersecting lines

form the boundaries of the phases that appear on the stability diagrams presented here.

Four- (or more) component systems plus H₂O are calculated in a similar manner, but with the inclusion of an additional mineral assumed to be at saturation to constrain the fourth component. For example, the system Ca-Na-Al-Si-H₂O might have Ca and Na on the axes, be balanced on Al, and have coexisting amorphous silica, as in reaction [3]. Alternatively, this four-component system could be balanced on SiO₂ and have the Al component constrained by a saturation phase such as gibbsite:



Gibbsite, however, provides a maximum activity of the Al³⁺ component that may not be desirable in all circumstances. Saturation with respect to any Al-bearing mineral in the four-component system can be assumed, although if the chosen saturation phase includes the components plotted on the axes of the diagram it will change the topology of the other fields. At Yucca Mountain, drill core samples in the vadose zone have established the presence of opal and smectite as coexisting authigenic SiO₂ and Al³⁺-bearing phases, respectively, with some authigenic K-feldspar and minor amounts of cristobalite, quartz, kaolinite, and calcite (Broxton et al., 1987). These phases, together with the composition of J-13 well-water summarized in Table 5, serve to define the ranges of silica and Al³⁺ activities shown in Figure 1 which were used to construct the activity diagrams presented here. Thus, lines labelled D and H on Figure 1 represent the extremes of dissolved silica saturation limits corresponding to quartz and amorphous silica, respectively; cristobalite, a constituent of the welded devitrified tuffs at Yucca Mountain, has an intermediate saturation level approximated by line E; line F corresponds to coexisting kaolinite and pyrophyllite; and line G is the activity of dissolved SiO₂ in J-13 well-water. Similarly, for dissolved Al³⁺, lines A,

B, and C correspond to saturation values for coexisting amorphous silica plus pyrophyllite, coexisting pyrophyllite plus kaolinite, and gibbsite, respectively, while line I represents an arbitrary low value of dissolved Al which, as shown later is consistent with the coexistence of opal, calcite and clinoptilolite. The reported analysis of Al in J-13 well-water (0.012 mg/l) is too high to be equilibrium controlled. The fluid speciation program used to calculate cation activities (EQ3NR of Wolery, 1983) indicates that at the pH of J-13 water (~7.5), dissolved Al occurs predominantly as $\text{Al}(\text{OH})_4^-$, with a calculated equilibrium value for $[\text{Al}^{3+}]$ of $\sim 2 \times 10^{-11} \text{M}$. Using an activity coefficient of ~ 0.6 gives a value for $\log(a_{\text{Al}^{3+}}/(a_{\text{H}^+})^3)$ of 9.6, in excess of the gibbsite saturation value of ~ 7.9 (Figure 1). A possible interpretation of this result is that the Al in J-13 well-water includes unfiltered particulate matter passing through membrane filters. In calculating the activity diagrams, the activity of H_2O is taken to be unity, and the calcite boundary is added to appropriate diagrams by assuming a dissolved HCO_3^- content equivalent to that of J-13 well-water (Table 5) and using the 90 °C analytical data in the activity diagrams calculated at 100 °C.

RESULTS

Three-Component plus H_2O Diagrams

A series of three-component plus H_2O diagrams are shown in Figures 2 to 4 for the systems Ca-Al-Si, Na-Al-Si, and K-Al-Si, respectively. All of these diagrams are balanced on SiO_2 . Quartz has been suppressed throughout the calculations described here in favor of amorphous silica because opal is reported to be the commonly observed authigenic SiO_2 phase in zeolitized ash-flow tuffs at Yucca Mountain (Broxton et al., 1986, 1987). As a result, all of the three-component diagrams in Figures 2-4 have amorphous silica as the stable phase in the bottom left-hand corner. Amorphous silica occupies a relatively smaller stability field

than would quartz had quartz not been suppressed. Figures 2a-c illustrate the changes in mineral phase relations for the system Ca-Al-Si with increasing temperature at 25, 100, and 200 °C with pressures corresponding to the steam saturation curve. Note that the epistilbite field at 25 °C is replaced by Ca-phillipsite at higher temperatures. The scolecite field decreases in size with increasing temperature and this zeolite is no longer stable at 200 °C (Fig. 2c). The Ca-beidellite field apparent at 200 °C may exist at lower temperatures as well, but does not appear in Figs. 2a and b possibly because of inaccuracies in the thermodynamic data for Ca-beidellite or adjacent phases. The stable limits of these and other activity diagrams described later are delineated by the dashed lines labelled gibbsite (or diaspore at 200 °C) and calcite. Higher Al or Ca activities can only result from supersaturation of the fluid with respect to these phases. As noted earlier, J-13 well-water is unconstrained on the Al axis. It is apparent from Figs 2a and b that in the simple Ca-Al-Si system, J-13 well-water is somewhat undersaturated with respect to calcite at 25 °C and slightly oversaturated at 100 °C.

Activity diagrams for the system Na-Al-Si illustrated in Figures 3a and b show that Na-beidellite becomes stable at 100 °C. Figs. 4a and b show similar diagrams for the system K-Al-Si at 25 and 100 °C. J-13 well water plots below any of the Na- or K-rich zeolites in Figs. 3 and 4 and is consistent with equilibrium with respect to feldspar: albite in Fig. 3 and K-feldspar in Fig. 4.

These diagrams indicate that although the activity of Al is unconstrained, calculated cation activities for J-13 well-water are consistent with the formation of Ca-rich zeolites and smectite observed in experimental studies of tuff samples contacted with water at ambient and elevated temperatures (Knauss et al., 1985a,b; White et al., 1980).

Multicomponent Diagrams

The three-component diagrams in Figures 2 to 4 provided simplified reference activity diagrams for comparison with the more complex four- and five-component plus H₂O systems necessary for plotting the stability field of clinoptilolite. Figures 5-8 are activity diagrams for the system Ca-Na-K-Al-Si. Values of $\log(a_{\text{Na}}+a_{\text{H}^+})$ and $\log(a_{\text{Ca}^{2+}}/(a_{\text{H}^+})^2)$ are plotted on the x- and y-axes, respectively, in each diagram. Either Al (Figs. 5 and 6) or Si (Figs. 7 and 8) has been used as the balancing component. In each case, two additional components need to be specified. The component K⁺ is constrained by assuming the presence of K-feldspar, since it occurs as an authigenic mineral (Broxton et al., 1987) and as a phenocryst and groundmass mineral in the rhyolite tuffs at Yucca Mountain. The other component, Al³⁺ or SiO₂, is assigned the series of values shown in the plot of $\log(a_{\text{Al}^{3+}}/(a_{\text{H}^+})^3)$ versus $\log a_{\text{SiO}_2}$ at 25 °C in Figure 1. The activity diagrams in Figures 5a-d are balanced on Al at 25 °C and have $\log a_{\text{SiO}_2}$ specified by the lines labelled D, E, F, G and H in Figure 1. The activity diagrams in Figures 6a and b are balanced on Al with amorphous silica and quartz saturations, respectively, at 100 °C. Figures 7a-d are balanced on Si at 25 °C and have Al³⁺ concentrations constrained by values corresponding to lines labelled I, A, B, and C, respectively, on Figure 1. The 100 °C diagrams shown in Figures 8a-c are balanced on Si with Al constrained by pyrophyllite-amorphous silica, kaolinite-pyrophyllite, and gibbsite saturations, respectively. Clinoptilolite is included in these diagrams, where stable, by considering it to be in equilibrium with Ca-saponite (smectite) and hematite to constrain the small amounts of Mg and Fe in the clinoptilolite specimen measured by Hemingway and Robie (1984). On all of the activity diagrams shown in Figures 5 to 8, calcite is plotted with a dashed line by assuming a bicarbonate ion content comparable to J-13 well-water, and the

circular symbol labelled J-13 corresponds to Ca and Na activities of this reference groundwater.

By comparing the activity diagrams shown in Figures 5-8 through changing temperature, or for different activities of Al or Si, trends in the relative stability of various zeolite phases may be easily recognized. For example, Figure 5 shows that: mesolite is a stable zeolite at low activities of silica; the mesolite field narrows and then disappears with increasing silica activity; and, clinoptilolite is stable at high activities of silica and increases in size the higher the silica activity.

The effects of temperature can be seen by comparing Figure 5a with Figure 6a (corresponding to amorphous silica saturation) and Figure 5d with Figure 6b (quartz saturation), where it is apparent that both clinoptilolite and mesolite have smaller regions of stability at 100 °C than at 25 °C.

The effects of variable Al activity at 25 °C can be observed in Figure 7. Mesolite has the largest stability field at gibbsite saturation (Figure 7d). Clinoptilolite is not stable at high Al activities corresponding to gibbsite saturation, but appears with decreasing Al activity (Figures 7a-c). Its stability field maximizes in size at an intermediate Al activity constrained by the coexistence of amorphous silica and pyrophyllite (Figure 7b), and then becomes smaller with further decrease in Al activity (Figure 7a). Note that circles representing Ca and Na concentrations of J-13 well-water plot close to the join of mesolite, epistilbite and clinoptilolite in Figures 7b and c. Again, effects of increasing the temperature to 100 °C may be seen in Figure 8 which shows that the clinoptilolite stability field decreases with increasing temperature and appears only at low $A^{\beta+}$ activities.

In Figures 9a and b, the system Ca-Na-K-Al-Si is represented with $\log(a_{K^+})/(a_{H^+})$ replacing $\log(a_{Na^+})/(a_{H^+})$ on the x-axis and albite replacing K-feldspar as the saturation phase. Figure 9a is balanced on Al and amorphous

silica is the saturation phase, whereas Figure 9b is balanced on Si with Al^{3+} activity controlled by coexisting amorphous silica plus pyrophyllite. These two representative activity diagrams based on K^+ activities are very similar to their Na-counterparts except that K-silicate phases replace Na-silicate minerals. The stability field of clinoptilolite is again largest at high silica activities, intermediate Al^{3+} activities, and low temperatures.

Activity Diagrams for Clinoptilolites of Variable Compositions.

Since clinoptilolites at Yucca Mountain occurring in the zeolitized tuffaceous beds of Calico Hills unit vary from Ca-rich compositions in the east to (Na + K)-rich compositions in the west (Broxton et al., 1986, 1987), and are (Ca + Mg)-rich in fractures in the Topopah Spring Member tuff (Levy, 1984; Carlos, 1985; Broxton et al., 1987), activity diagrams were calculated for variable Na-Ca, K-Ca and Ca-Mg contents of the zeolite. The results are shown in Figures 10a-c, respectively. Each activity diagram is related to that shown in Figure 7b in which Si is balanced and Al activities are constrained by the pyrophyllite-amorphous silica (plus K-feldspar) assemblage.

Figure 10a shows that with increasing atomic substitution of Na in clinoptilolite, the clinoptilolite stability field narrows and is displaced to lower calcium activities. Conversely, the clinoptilolite stability field widens for clinoptilolites with higher Ca contents. Clinoptilolites more sodic than $Na_{1.56}Ca_{1.0}$ are no longer in equilibrium with J-13 well-water, suggesting that groundwater with higher Na concentrations, perhaps derived from altered vitric tuffs (White et al., 1980), is necessary to stabilize sodic clinoptilolites.

Potassium has the opposite effect on the clinoptilolite stability field (Figure 10b), which widens considerably with increasing atomic substitution of K for Ca in clinoptilolite. Clinoptilolites less potassic than $K_{0.5}Ca_{1.74}$ would no longer be in

equilibrium with J-13 well-water. Magnesium, too, replacing Ca in clinoptilolite widens its stability field (Figure 10c). Clinoptilolites less magnesian than $\text{Ca}_{1.7}\text{Mg}_{1.03}$ would not be in equilibrium with J-13 well-water, but this effect could be compensated by increased atomic substitution of K into the zeolite. Clinoptilolites less magnesian than $\text{Ca}_{2.5}\text{Mg}_{0.23}$ do not coexist stably with Ca-saponite under the conditions of the activity diagram shown in Figure 10c.

DISCUSSION

The activity diagrams demonstrate that the formation of clinoptilolite is favored by higher SiO_2 activities than allowed for by the presence of quartz. This is clearly demonstrated by Figure 5 and is achieved, for example, when clinoptilolite coexists with opal in diagenetically altered volcanic glasses. Such assemblages are commonly observed in vitric tuff samples from drill cores at Yucca Mountain (Benson, 1976; White et al., 1980; Broxton et al., 1987) and from surface desert pavement and outcrop locations (Blundy et al., 1988).

Clinoptilolite has a maximum stability field at some intermediate aluminium activity value, but shrinks with either increasing or decreasing activities of aluminum. This is indicated by Figure 7 in which the clinoptilolite stability field is largest when aluminium activities are controlled by the amorphous silica-pyrophyllite assemblage (Figure 7b). Furthermore, since the composition of J-13 well-water appears to be approximately in equilibrium with respect to calcite, the J-13 $\text{Ca}^{2+}/\text{Na}^+$ points plotted in Figures 5a, 7b and 7c suggest that the aluminum activities lie between the values for kaolinite-pyrophyllite and pyrophyllite-amorphous silica. Such aluminum activities also indicate that J-13 well-water could be in equilibrium with other zeolites represented on the activity diagrams,

including epistilbite (Figure 5b) and mesolite (Figure 5c, 7b and 9b), particularly when the stability field of Na-rich clinoptilolites is diminished (Figure 10a).

The clinoptilolite stability field decreases in size with increasing temperature between 25 °C and 100 °C (Figures 6 and 8), and has disappeared by 200 °C. This correlates with hydrothermal experiments (Boles, 1971; Knauss et al., 1985a,b; Hawkins et al., 1978) and observed geological occurrences of clinoptilolite (Hay, 1966; Hay and Sheppard, 1977). Zeolite diagenetic zones have been suggested for alteration of vitric tuffs based on the appearance and disappearance of clinoptilolite in buried pyroclastic deposits (Iijima, 1975, 1980; Smyth, 1982). Zone I, for example, is characterized by large-scale preservation of glass in vitric tuffs above the water table, and incipient alteration of glass shards, particularly in groundmass, to smectite and opal. The Topopah Spring Member at Yucca Mountain, lying well above the water table, falls into Zone I. However, Ca-rich clinoptilolites occur in fractures through lower welded tuff and vitrophyre horizons and may be indicative of groundwater interactions, perhaps with microcrystalline devitrified tuffs which produce relatively high concentrations of dissolved Ca^{2+} , Na^+ and HCO_3^- in fracture-flow water (White et al., 1980). The 25 °C activity diagrams consistently show that calcic clinoptilolites are stable in the presence of fracture-flow J-13 well-water originating from microcrystalline devitrified Topopah Spring Member tuffs, even though such zeolites have not been observed as fracture-lining minerals at this level in J-13 drill cores (Carlos, 1988). The abundance of drusy quartz coating fractures there (Carlos, 1988) may depress the silica activity below that necessary to crystallize clinoptilolite.

Diagenetic zone II, which characterizes the tuffaceous beds of Calico Hills unit, represents extensive zeolitization of vitric tuffs to clinoptilolite-bearing assemblages, and is promoted by saline groundwater and slightly elevated temperatures (Smyth, 1982). Progressive hydration and dissolution reactions of

the rhyolitic vitric tuffs increase the concentrations of SiO_2 , Na^+ , and ultimately K^+ in groundwater (White et al., 1980) from which clinoptilolite-clay silicate-opal assemblages are derived. The presence of Ca-poor, K-Na-rich clinoptilolites in diagenetic zone II conforms with the activity diagrams which consistently show the clinoptilolite stability field moving away from J-13 well-water compositions at elevated temperatures and for increased Na, but depleted Ca, concentrations in groundwater.

Deeper drill-cores through Yucca Mountain have yielded analcime instead of clinoptilolite which is indicative of diagenetic Zone III, while Zone IV is represented by the breakdown of analcime to albite at greater depths. The Zone II - Zone III boundary appears to be between 100 °C and 150 °C (Smyth, 1982), which again is consistent with the absence or decreased stability field of clinoptilolite in activity diagrams calculated at elevated temperatures. Adverse effects of temperature on the clinoptilolite stability field also indicate the vulnerability of calcic clinoptilolites to thermal decomposition in the vicinity of the heat envelope surrounding stored radioactive waste at Yucca Mountain, particularly if concentrations of dissolved Na were to increase, and Ca decrease, in heated groundwater.

Several observed reactions suggested by phase assemblages in weathered vitric tuffs (Benson, 1976; White et al., 1980; Blundy et al., 1988) can be demonstrated on the activity diagrams. For example the reaction of glass + clay silicates to clinoptilolite plus opal plots at the intersection of amorphous silica + pyrophyllite, albite and clinoptilolite in Figures 5a and 7b, but requires lower calcium activities in the coexisting fluid than that of J-13 well-water. Low Ca and slightly reduced K activities would account for the assemblage glass-opal-clay silicates-authigenic K-feldspar forming on weathered vitric tuffs and outcrop and in detritus forming desert pavement (Blundy et al., 1988). The assemblage of

clinoptilolite-calcite-opal also found in weathered vitric tuffs is represented on Figure 7a requiring, however, very low activities of Al.

CONCLUSIONS

The calculated activity diagrams presented here quantify observed field occurrences and verify deductions made about the stability of clinoptilolite in diagenetically altered tuffs. The coexistence of clinoptilolite with opal correlates with its calculated wide stability field in aqueous solutions saturated with amorphous silica. Clinoptilolite-smectite assemblages indicate that the zeolite crystallized from groundwater with dissolved Al concentrations lower than saturation values with respect to gibbsite. Calcic clinoptilolites associated with calcite are consistent with crystallization from fracture-flow groundwater containing Ca^{2+} and HCO_3^- derived from incipient dissolution of microcrystalline devitrified tuffs. Alkali-rich clinoptilolites, on the other hand, correlate with groundwater having elevated Na^+ and K^+ but depleted Ca^{2+} concentrations which are associated with altered vitric tuffs. Although the crystallization of clinoptilolite may be promoted by saline groundwater, the clinoptilolite stability field diminishes appreciably between 25 °C and 100 °C, correlating with burial diagenetic reactions but confirming doubts about the thermal stability of clinoptilolite when it is in close proximity to buried radioactive waste.

ACKNOWLEDGMENTS

We gratefully acknowledge the assistance of Drs. M. E. Morgenstein, C. L. Johnson and D. L. Shettel who reviewed early drafts of the manuscript and provided information about groundwater chemistry at Yucca Mountain. The study was funded by the State of Nevada, Nuclear Waste Project Office, under a Department of Energy grant from the Nuclear Waste Fund.

REFERENCES CITED

- Benson, L. V. (1976) Mass transport in vitric tuffs of Rainier Mesa, Nye County, Nevada. U. S. Energy Research and Development Administration, Nevada, Report NVO-1253-10.
- Bish, D. L., Ogard, A. L., and Vaniman, D. T. (1984) Mineralogy-petrology and groundwater chemistry of Yucca Mountain Tuffs, Materials Research Society Symposium Research Proceedings, 26, 283-291.
- Blundy, J. D., Burns, R. G., and Morgenstein, M. E. (1988) Non-sorptive minerals forming in rhyolite tuff at Yucca Mountain, Nevada: Diagenesis in a proposed nuclear waste repository. *Earth Planet. Sci. Lett.*, submitted.
- Bowers, T. S., Jackson, K. J., and Helgeson, H. C. (1984) *Equilibrium Activity Diagrams for Coexisting Minerals and Aqueous Solutions at Pressures and Temperatures to 5 kb and 600°C.* Springer-Verlag.
- Broxton, D. E., Bish, D. L., and Warren, R. G. (1987) Distribution and chemistry of diagenetic minerals at Yucca Mountain, Nye County, Nevada. *Clays and Clay Minerals*, 35, 89-110.
- Broxton, D. E., Warren, R. G., Hagan, R. C., and Luedemann, G. (1986) Chemistry of diagenetically altered tuffs at a potential nuclear waste repository, Yucca Mountain, Nye County, Nevada. U.S. National Technical Information Service, Report LA-10802, 160 pp.

Carlos, B. A. (1985) Minerals in fractures of the unsaturated zone from drill core USW G-4, Yucca Mountain, Nye County, Nevada. U.S. National Technical Information Service, Report LA-10415, 55pp.

Carlos, B. A. (1988) Fracture coating minerals in the Paintbrush Tuff below the static water level in drill hole J-13, near Yucca Mountain, Nevada. Geological Society of America, Annual Meetings, Denver, Abstract with Programs, 20, A359-360.

Daniels, W. R., et al. (29 coauthors) (1982) Summary report on the geochemistry of Yucca Mountain and environs, U.S. National Technical Information Service, Report LA-9328.

Delany, J. M. (1985) Reaction of Topopah Spring tuff with J-13 water: a geochemical modeling approach using the EQ3/6 reaction path code. U.S. National Technical Information Service, Report UCRL-53631.

Hawkins, D. B., Sheppard, R. A., and Gude, A.J., 3rd (1978) Hydrothermal synthesis of clinoptilolite and comments on the assemblage philipsite-clinoptilolite-mordenite. In: *Natural Zeolites*. (L. B. Sands and F. A. Mumpton, eds.; Pergamon Press, New York), p. 337-349.

Hay, R. L. (1966) Zeolites and zeolite reactions in sedimentary rocks. Geological Society of America, Special Paper 85, p. 130-146.

Hay, R. L. and Sheppard, R. A. (1977) Zeolites in open hydrologic systems. Chapter 5 in: *Mineralogy and Geology of Natural Zeolites*. (F. A. Mumpton, ed., Mineralogical Society of America) *Reviews in Mineralogy*, 4, 92-102.

Helgeson, H. C., Delany, J. M., Nesbitt, H. W., and Bird, D. K. (1978) Summary and critique of the thermodynamic properties of rock-forming minerals. *American Journal of Science*, 274, 1089-1198.

Hemingway, B. S. and Robie, R. A. (1984) Thermodynamic properties of zeolites: low temperature heat capacities and thermodynamic functions of phillipsite and clinoptilolite. Estimates of the thermochemical properties of zeolitic water at low temperatures. *American Mineralogist*, 69, 692-700.

Iijima, A. (1975) Effect of pore water in clinoptilolite-analcime-albite reaction series. *Journal of the Faculty of Science, University of Tokyo, Series II*, 19, 133-147.

Iijima, A. (1980) Geology of natural zeolites and zeolitic rocks, *Proceedings of the Fifth International Conference on Zeolites* (L. V. C. Rees, ed., Heyden & Co., London), p. 103-118.

Johnson, G. K., Flotow, H. E., O'Hare, P. A. G., and Wise, W. S. (1982) Thermodynamic studies of zeolites: analcime and dehydrated analcime. *American Mineralogist*, 67, 736-748.

Johnson, G. K., Flotow, H. E., O'Hare, P. A. G., and Wise, W. S. (1983) Thermodynamic studies of zeolites: natrolite, mesolite, and scolecite. *American Mineralogist*, 68, 1134-1145.

Johnson, G. K., Flotow, H. E., O'Hare, P. A. G., and Wise, W. S. (1985) Thermodynamic studies of zeolites: heulandite. *American Mineralogist*, 70, 1065-1071.

Kerrisk, J. F. (1987) Groundwater chemistry at Yucca Mountain, Nevada, and vicinity. U.S. National Technical Information Service, Report LA-10929, 113 pp.

Knauss, K. G., Beiringer, W. J., and Peifer, D. W. (1985a) Hydrothermal interaction of crushed Topopah Spring tuff and J-13 water at 90, 150, and 250 °C using Dickson-type, gold-bag rocking autoclaves. U.S. National Technical Information Service, UCRL-53630, 27pp.

Knauss, K. G., Delany, J. M., Beiringer, W. J., and Peifer, D. W. (1985b) Hydrothermal interaction of Topopah Spring Tuff with J-13 water as a function of temperature, Materials Research Society Symposium Proceedings, 27, 539-546.

Levy, S. S. (1984) Studies of altered vitrophyre for the prediction of nuclear waste repository-induced thermal alteration at Yucca Mountain, Nevada. Materials Research Society Symposium Proceedings, 26, 959-966.

Moore, D. E., Morrow, C. A., and Byerlee, J. D. (1986) High-temperature permeability and groundwater chemistry of some Nevada Test Site tuffs, Journal of Geophysical Research, 82, 2163-2171.

Oversby, V. M. (1985) The reaction of Topopah Spring tuff with J-13 water at 90 °C and 150 °C - samples from drill cores USW G-1, USW GU-3, USW G-4, and UE-25h#1. U.S. National Technical Information Service, Report UCRL-53629, 26pp.

Robie, R. A., Hemingway, B. S., and Fisher, J. R. (1978) Thermodynamic properties of minerals and related substances at 298.15K and 1 bar (10^5 Pascals) pressure and at higher temperatures. U.S. Geological Survey, Bulletin 1452.

Sheppard, R. A. and Gude, A. J., 3rd (1973) Zeolites and associated authigenic silicate minerals in tuffaceous rocks of the Big Sandy formation, Mohave County, Arizona. U.S. Geological Survey Professional Paper 830.

Smyth, J. R. (1982) Zeolite stability constraints on radioactive waste isolation in zeolite-bearing volcanic rocks. *Journal of Geology*, 90, 195-201.

U. S. Department of Energy (1988) Site characterization plan, Yucca Mountain Site, Nevada, research and development area, Nevada, Report DOE/RW-0160, 8 vols.

White, A. F., Claassen, H. C., and Benson, L. V. (1980) The effect of dissolution of volcanic glass on the water chemistry in a tuffaceous aquifer, Rainier Mesa, Nevada. USGS Water-Supply Paper 1535-Q, 33pp.

Wolery, T. J. (1983) EQ3NR, geochemical program for geochemical aqueous speciation-solubility calculations. U.S. National Technical Information Service, UCRL-5, Distribution Category UC-70.

TABLE 1: MINERALS AND FORMULAS

Quartz	SiO_2
Amorphous silica	SiO_2
Gibbsite	$\text{Al}(\text{OH})_3$
Diaspore	$\text{AlO}(\text{OH})$
Kaolinite	$\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$
Pyrophyllite	$\text{Al}_2\text{Si}_4\text{O}_{10}(\text{OH})_2$
Wollastonite	CaSiO_3
Grossular	$\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$
Prehnite	$\text{Ca}_2\text{Al}_2\text{Si}_3\text{O}_{10}(\text{OH})_2$
Margarite	$\text{CaAl}_4\text{Si}_2\text{O}_{10}(\text{OH})_2$
Ca-beidellite	$\text{Ca}_{.165}\text{Al}_2(\text{Al}_{.33}\text{Si}_{3.67}\text{O}_{10})(\text{OH})_2$
Lawsonite	$\text{CaAl}_2\text{Si}_2\text{O}_7(\text{OH})_2 \cdot \text{H}_2\text{O}$
Ca-phillipsite	$\text{CaAl}_2\text{Si}_5\text{O}_{14} \cdot 5\text{H}_2\text{O}$
Scolecite	$\text{CaAl}_2\text{Si}_3\text{O}_{10} \cdot 3\text{H}_2\text{O}$
Epistilbite	$\text{CaAl}_2\text{Si}_6\text{O}_{16} \cdot 5\text{H}_2\text{O}$
Heulandite	$\text{CaAl}_2\text{Si}_7\text{O}_{18} \cdot 6\text{H}_2\text{O}$
Albite	$\text{NaAlSi}_3\text{O}_8$
Nepheline	NaAlSiO_4
Paragonite	$\text{NaAl}_2(\text{AlSi}_3\text{O}_{10})(\text{OH})_2$
Na-beidellite	$\text{Na}_{.33}\text{Al}_2(\text{Al}_{.33}\text{Si}_{3.67}\text{O}_{10})(\text{OH})_2$
Analcime	$\text{NaAlSi}_2\text{O}_6 \cdot \text{H}_2\text{O}$
Natrolite	$\text{Na}_2\text{Al}_2\text{Si}_3\text{O}_{10} \cdot 2\text{H}_2\text{O}$
K-feldspar	KAlSi_3O_8
Kalsilite	KAlSiO_4
Muscovite	$\text{KAl}_2(\text{AlSi}_3\text{O}_{10})(\text{OH})_2$
K-phillipsite	$\text{K}_2\text{Al}_2\text{Si}_5\text{O}_{14} \cdot 5\text{H}_2\text{O}$
Mesolite	$\text{Na}_{.675}\text{Ca}_{.657}\text{Al}_{1.99}\text{Si}_{3.01}\text{O}_{10} \cdot 2.647\text{H}_2\text{O}$
Clinoptilolite	$(\text{Na}_{.56}\text{K}_{.98}\text{Ca}_{1.5}\text{Mg}_{1.23})(\text{Al}_{6.7}\text{Fe}_{.3})\text{Si}_{29}\text{O}_{72} \cdot 22\text{H}_2\text{O}$
Ca-saponite	$\text{Ca}_{.165}\text{Mg}_3(\text{Al}_{.33}\text{Si}_{3.67}\text{O}_{10})(\text{OH})_2$
Hematite	Fe_2O_3

**TABLE 2: REPRESENTATIVE CHEMICAL
COMPOSITIONS AND FORMULAE
OF CLINOPTILOLITE**

	[1]	[2]	[3]	[4]
SiO ₂	62.78	65.5	68.6	68.1
TiO ₂	0.28	0.02	0	0
Al ₂ O ₃	12.33	13.3	12.4	12.2
Fe ₂ O ₃	1.41	0	0	0
MgO	1.99	0.86	0.07	0.09
CaO	3.10	5.19	3.59	1.11
BaO	0.13			0.03
Na ₂ O	0.63	0.17	1.13	2.84
K ₂ O	1.67	0.21	3.00	4.20
Total	84.32	85.2	88.8	88.5
Formulae calculated for 72 oxygens				
Si	29	29.2	29.7	29.8
Ti		0.01	0	0
Al	6.7	6.98	6.35	6.28
Fe	0.3	0	0	0
Mg	1.23	0.57	0.04	0.06
Ca	1.50	2.48	1.67	0.52
Ba	0.02	0.00	0.01	0.01
Na	0.56	0.15	0.95	2.41
K	0.98	0.12	1.66	2.35
%K	23	4	16	44
%Na	13	4	31	45
Si/Al	4.33	4.18	4.68	4.75
[1] Hemingway and Robie (1984): Thermodynamic data				
[2] Topopah Spring Member fractures; Broxton <i>et al.</i> (1987)				
[3] Tuff of Calico Hills, eastern YM; Broxton <i>et al.</i> (1987)				
[4] Tuff of Calico Hills, western YM; Broxton <i>et al.</i> (1987)				

TABLE 3:		
ESTIMATED FREE ENERGIES AND ENTHALPIES		
	$\Delta G_f^\circ(298)(cal.)$	$\Delta H_f^\circ(298)(cal.)$
Na-phillipsite	-1,850,051.	-2,002,144.
K-phillipsite	-1,868,183.	-2,022,272.
Ca-phillipsite	-1,860,596.	-2,010,073.
Epistilbite	-2,065,242.	-2,234,763.
Heulandite	-2,321,459.	-2,514,766.
Clinoptilolite	-9,055,456.	-9,809,599.

**TABLE 4: ESTIMATED FREE ENERGIES
FOR COMPOSITIONALLY VARIABLE
CLINOPTILOLITE**

	$\Delta G_f^\circ(298)(cal.)$
$(Na_{.56}K_{.98}Ca_{1.5}Mg_{1.23})$	
$(Al_{6.7}Fe_3)Si_{29}O_{72} \cdot 22H_2O$	-9,055,456.
Na-Ca substitution	
$Na_{1.56}Ca_{1.0}$	-9,028,215.
$Na_{2.56}Ca_{0.5}$	-9,000,973.
$Na_{3.56}$	-8,973,732.
$Na_{0.28}Ca_{1.64}$	-9,063,084.
$Ca_{1.67}$	-9,070,711.
K-Ca substitution	
$K_{1.98}Ca_{1.0}$	-9,064,389.
$K_{2.98}Ca_{0.5}$	-9,073,322.
$K_{3.78}Ca_{0.1}$	-9,080,468.
$K_{0.5}Ca_{1.74}$	-9,051,168.
$Ca_{1.99}$	-9,046,702.
Ca-Mg substitution	
$Ca_{0.73}Mg_{2.0}$	-9,049,080.
$Ca_{1.7}Mg_{1.03}$	-9,057,112.
$Ca_{2.0}Mg_{0.73}$	-9,059,596.
$Ca_{2.5}Mg_{0.23}$	-9,063,736.
$Ca_{2.73}$	-9,065,640.

**TABLE 5: CHEMICAL COMPOSITION
OF J-13 WELL WATER (mg/l)**

	[1]	[2]	[3]	[4]	[5]	[6]	[7]
Li	0.042				0.06	0.05	0.05
Na	43.9	55	58.5	44	45	51	54.1
K	5.11	7.5	5.58	4.4	5.3	4.9	6.4
Ca	12.5	11.5	6.46	13	11.5	14	11
Mg	1.92	1.1	0.315	2.0	1.76	2.1	0.95
Sr	0.035					0.05	0.002
Al	0.012	0.999	1.64		0.02	0.03	0.01
Fe	0.006				0.01	0.04	0.004
SiO ₂	57.9	53	148	59	31.87	66	71.6
NO ₃	9.6	9.0	9.5	8.7	10.1	5.6	
F	2.2	2.3	2.4	2.2	2.1	2.2	
Cl	6.9	7.2	7.4		6.4	7.5	
HCO ₃	125.3	178.8	61.0	120	143	120	
SO ₄	18.7	18.3	18.5	19	18.1	22	
pH	7.6	7.27	6.97	7.5	6.9	7.1	

[1] Delany (1985)

[2] J-13 reacted with TS tuff at 90°C;
Knauss *et al.* (1985)

[3] J-13 reacted with TS tuff at 150°C;
Knauss *et al.* (1985)

[4] Moore *et al.* (1986)

[5] Bish *et al.* (1984)

[6] Daniels *et al.* (1982)

[7] Daniels *et al.* (1982), after J-13 water reacted with
TS tuff at 25°C

FIGURE CAPTIONS.

Figure 1. Ranges of dissolved silica and aluminum activities used in the calculations of activity diagrams. Silica activities correspond to amorphous silica (H), J-13 well-water (G), coexisting pyrophyllite-kaolinite (F), cristobalite (E) and quartz (D) saturated solutions. Aluminum activities are those for solutions saturated by pyrophyllite-amorphous silica (A), pyrophyllite-kaolinite (B), and gibbsite (C) assemblages and an arbitrary low value (I).

Figure 2. Activity diagrams for the three-component Ca-Al-Si plus H₂O system balanced on Si (a) at 25 °C; (b) at 100 °C; and (c) at 200 °C and 15.5 bars.

Figure 3. Activity diagrams for the three-component Na-Al-Si plus H₂O system balanced on Si (a) at 25 °C; and (b) at 100 °C.

Figure 4. Activity diagrams for the three-component K-Al-Si plus H₂O system balanced on Si (a) at 25 °C; and (b) at 100 °C.

Figure 5. Activity diagrams for the Ca-Na-K-Al-Si plus H₂O system balanced on Al at 25 °C for different silica activities (a) amorphous silica; (b) J-13 well-water; (c) pyrophyllite-kaolinite; and (d) quartz and cristobalite (inset dashed lines). Saturation phases also include K-feldspar, hematite and Ca-saponite.

Figure 6. Activity diagrams for the Ca-Na-K-Al-Si plus H₂O system balanced on Al at 100 °C for different silica activities (a) amorphous silica; and (b) quartz.

Figure 7. Activity diagrams for the Ca-Na-K-Al-Si plus H₂O system balanced on Si at 25 °C for different aluminum activities (a) low Al activity corresponding to line

I in Figure 1; (b) pyrophyllite-amorphous silica; (c) kaolinite-pyrophyllite; and (d) gibbsite. Saturation phases again include K-feldspar, hematite, and Ca-saponite.

Figure 8. Activity diagrams for the Ca-Na-K-Al-Si plus H₂O system balanced on Si at 100 °C for different aluminum activities (a) pyrophyllite-amorphous silica; (b) kaolinite-pyrophyllite; and (c) gibbsite.

Figure 9. Activity diagrams based on K and Ca activities in the Ca-Na-K-Al-Si plus H₂O system at 25 °C (a) balanced on Al with silica saturation by amorphous silica; and (b) balanced on Si with aluminum saturation by pyrophyllite plus amorphous silica. Saturation phases include albite, hematite and Ca-saponite.

Figure 10. Activity diagrams for clinoptilolites having variable cation compositions (a) Ca-Na; (b) K-Ca; and (c) Ca-Mg. The calculated 25 °C stability fields correspond to aluminum saturation by pyrophyllite plus amorphous silica and are balanced on Si (Fig. 7b).

Figure 1

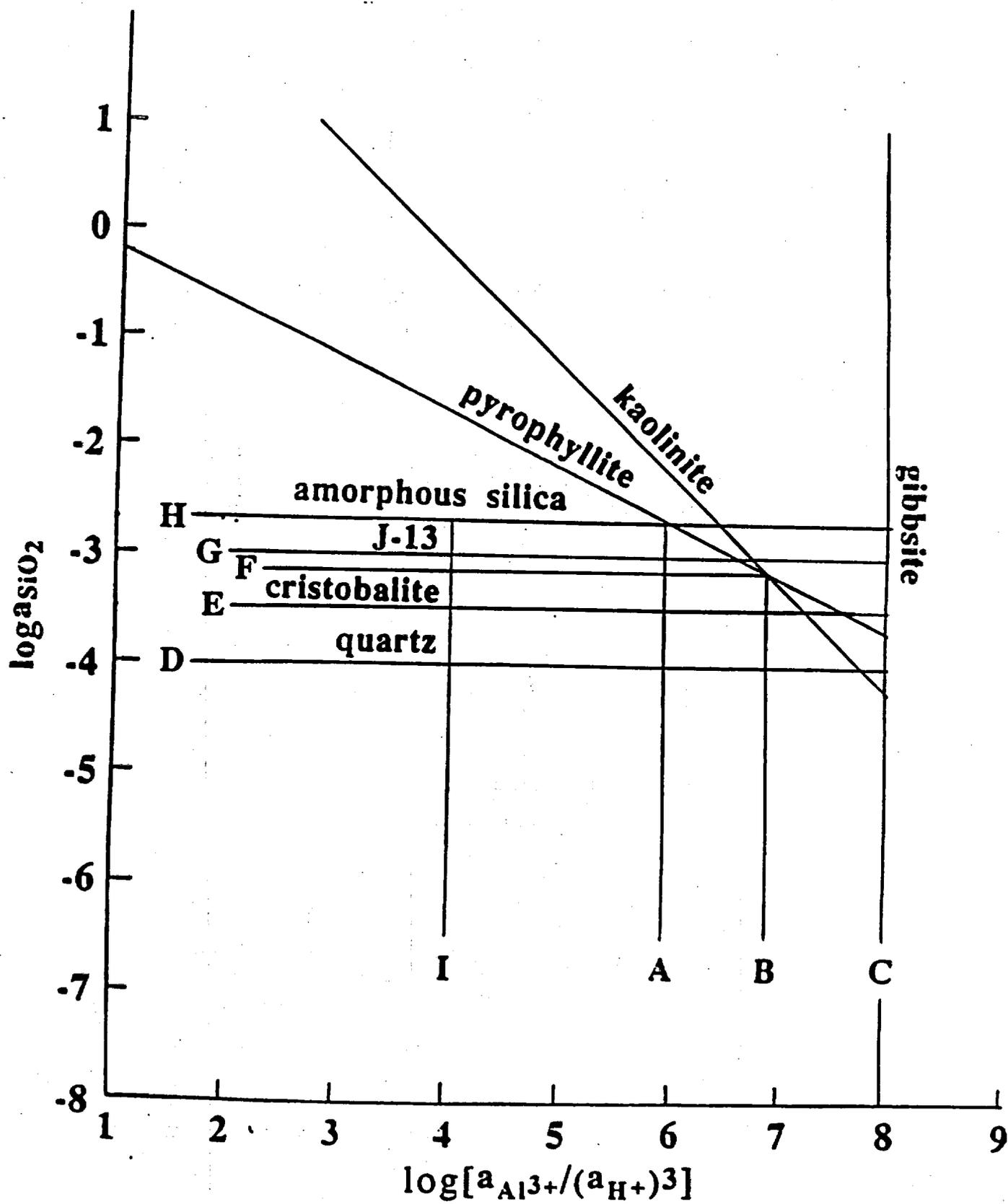


Figure 2

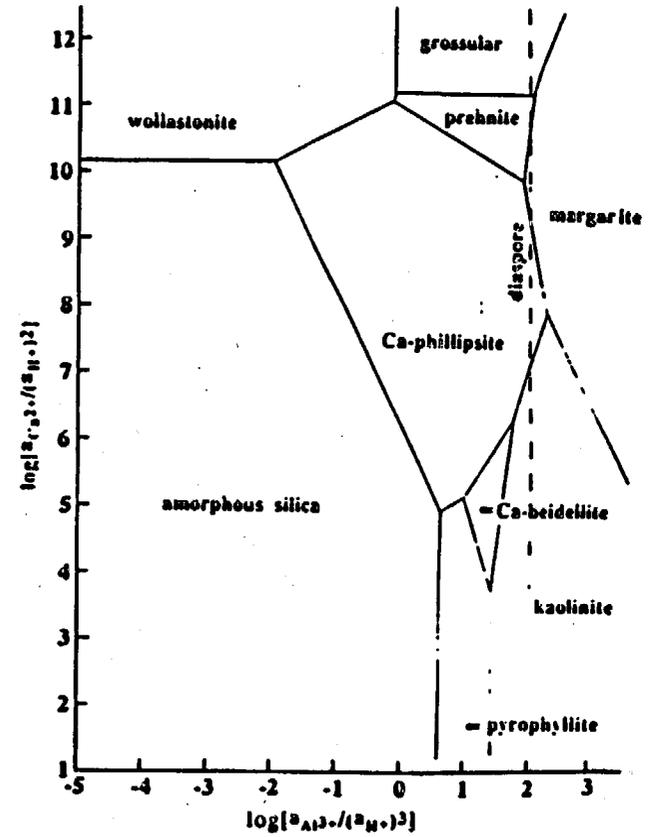
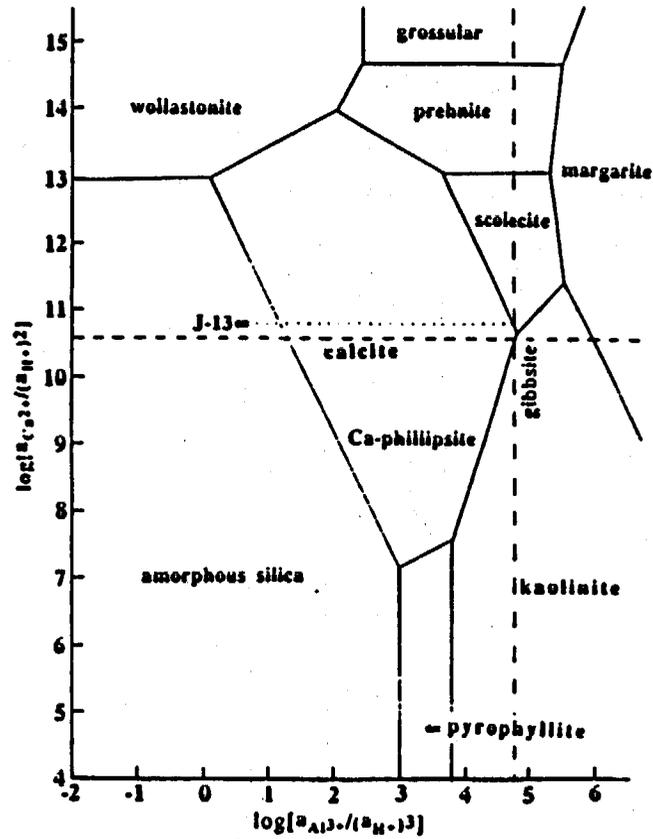
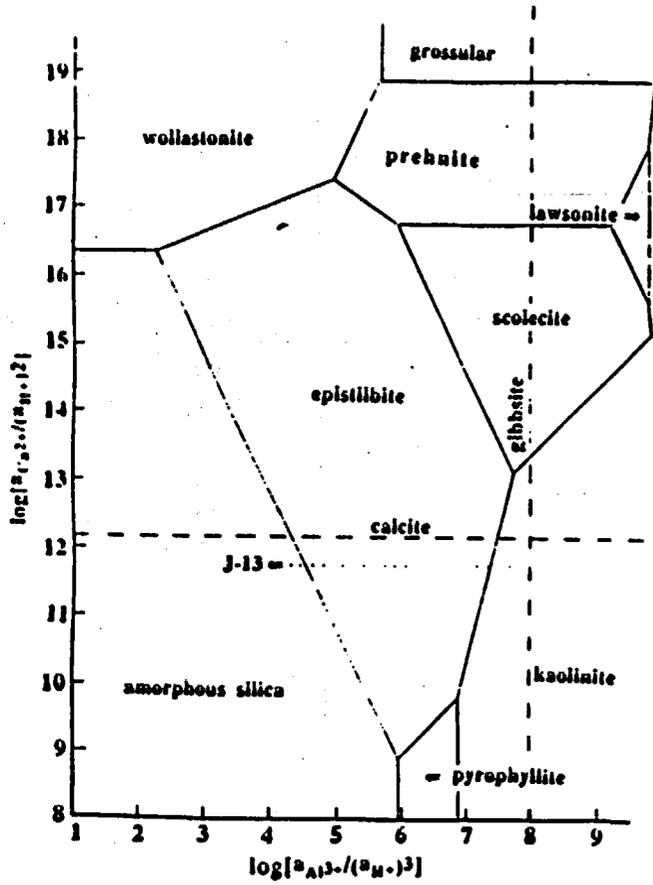


Figure 3

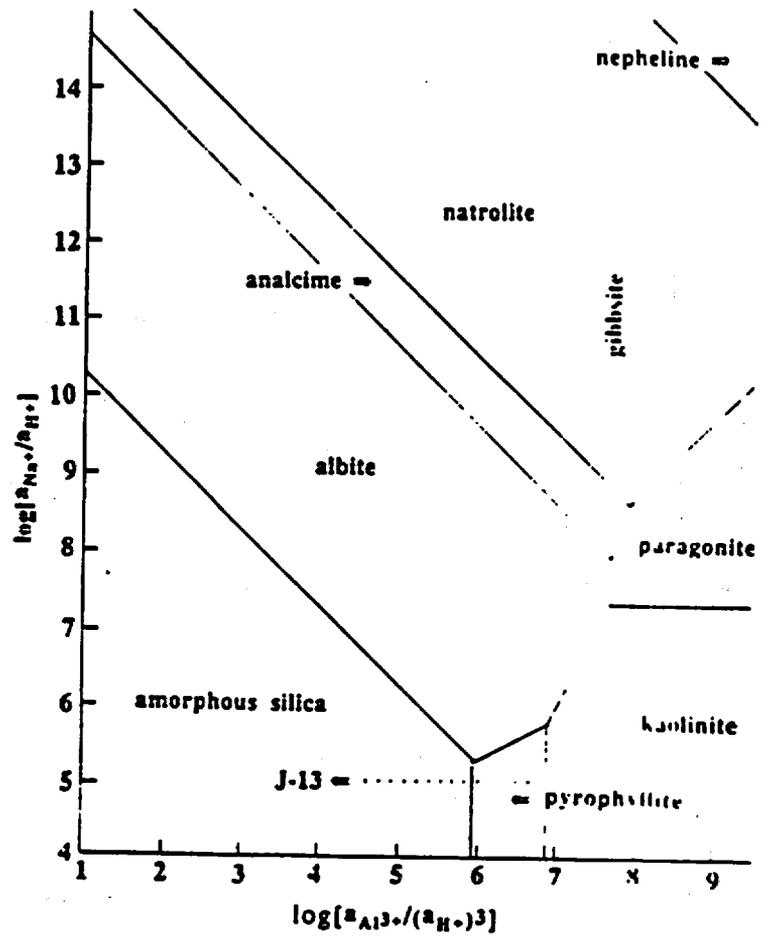
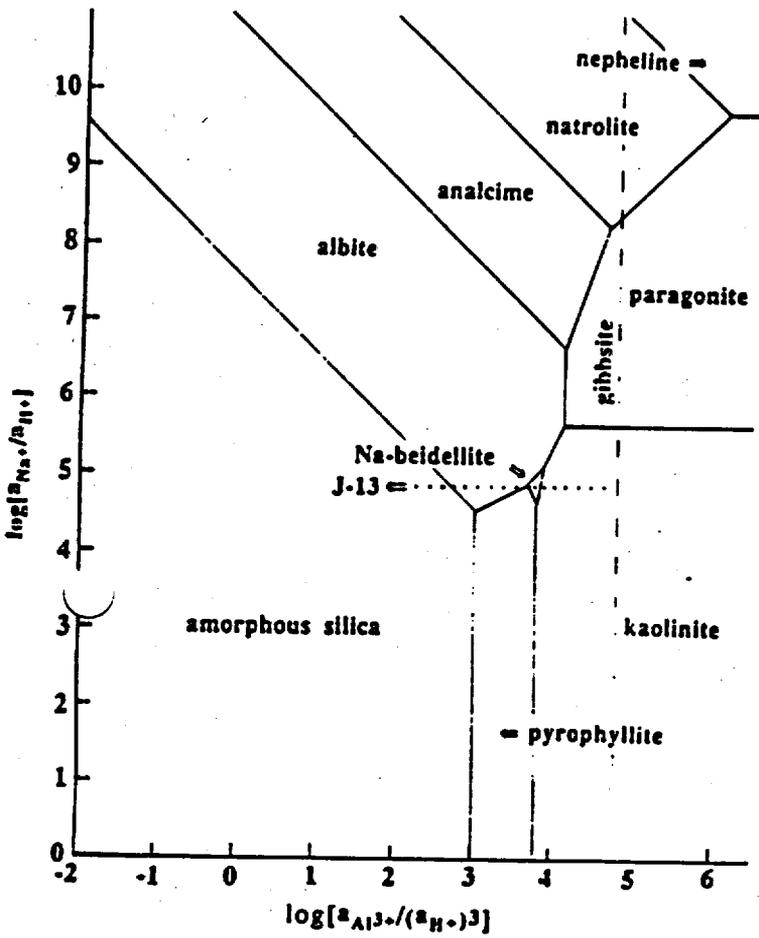
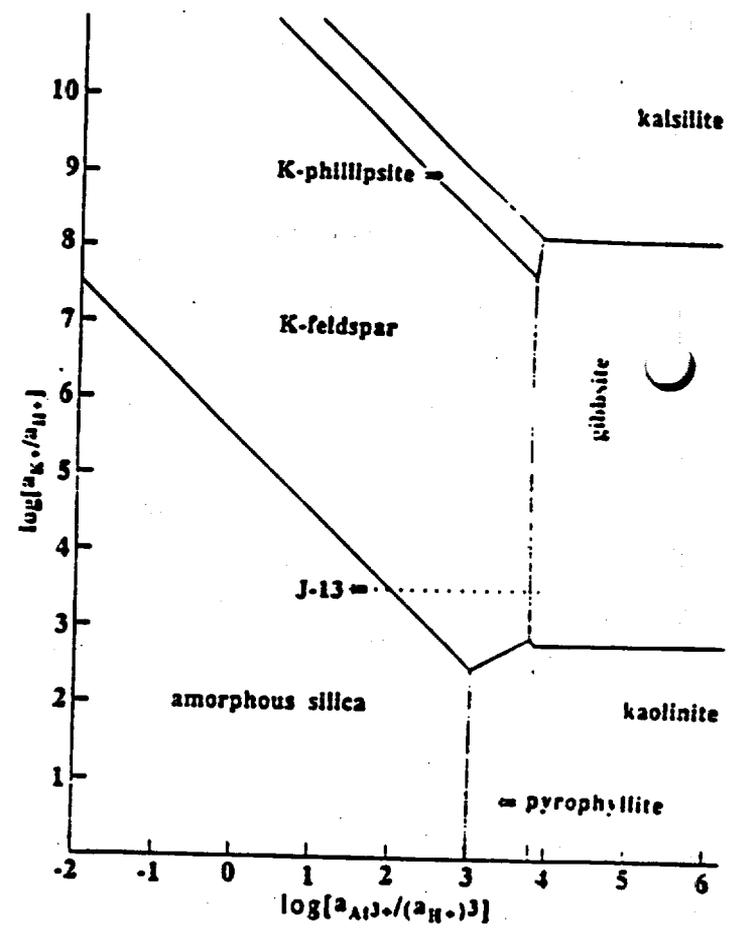
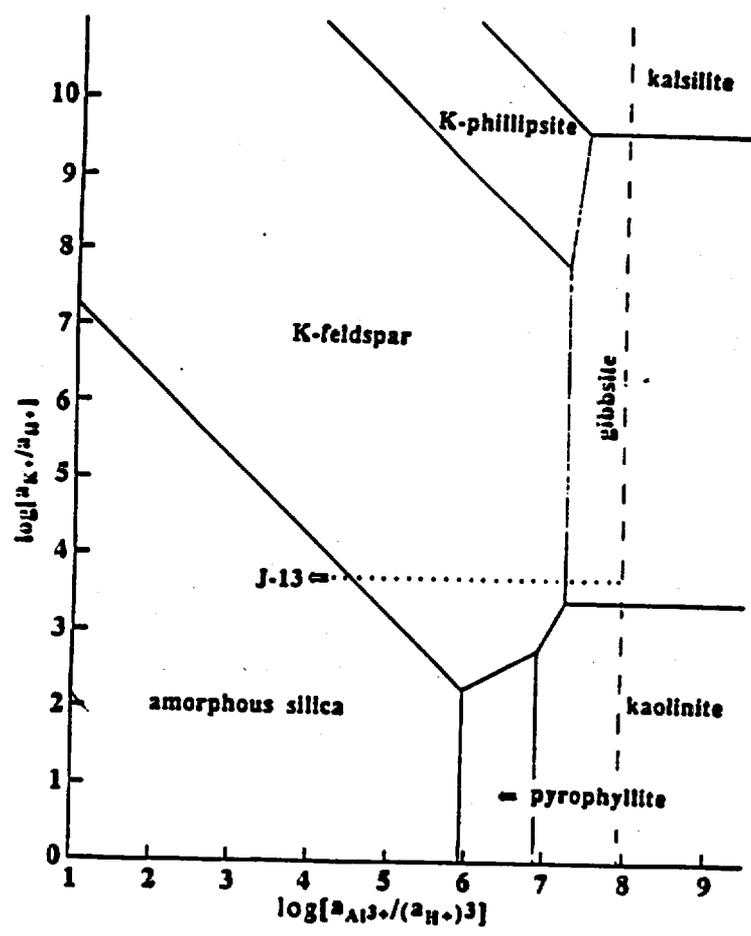


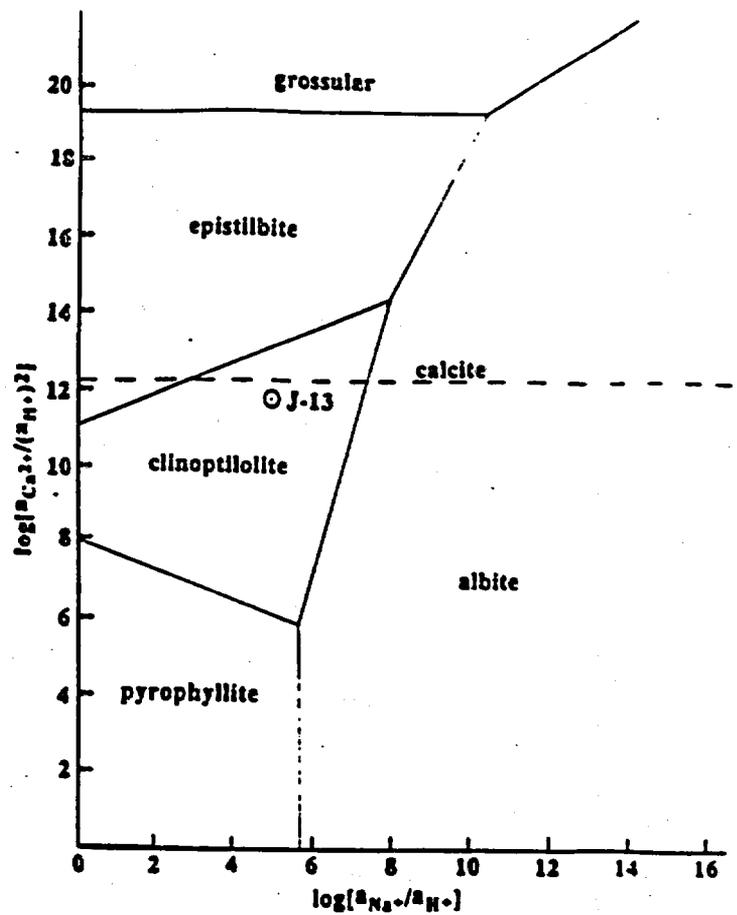
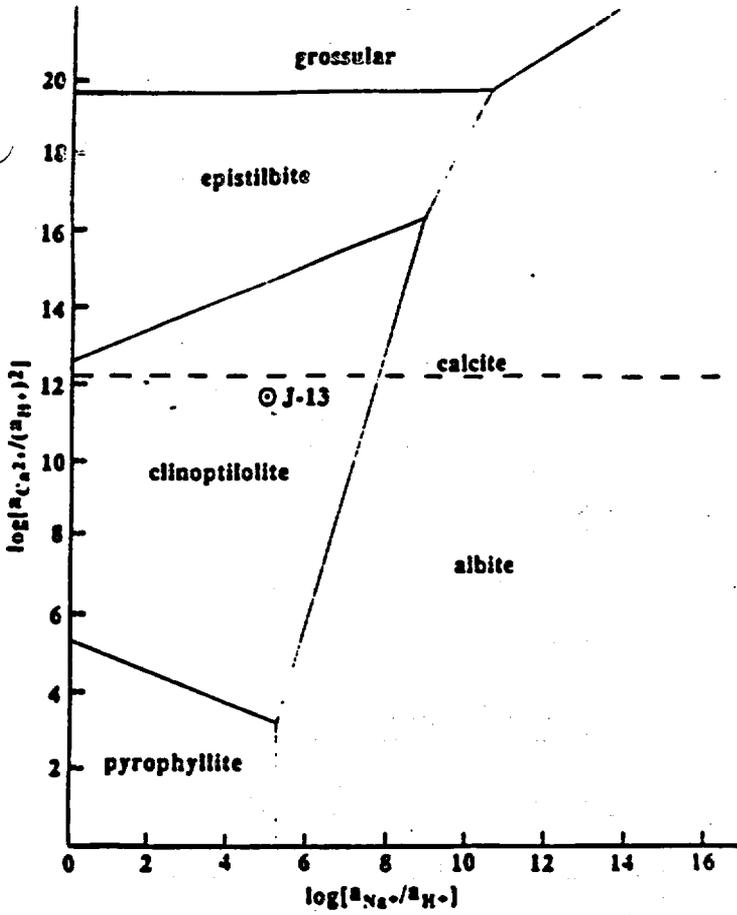
Figure 4



Al balanced; 25°C
 $^{\#}\text{SiO}_2$: amorphous silica

Al balanced; 25°C
 $^{\#}\text{SiO}_2$: J-13 well-water

Figure 5



Al balanced; 25°C
 $^{\#}\text{SiO}_2$: pyrophyllite/kaolinite

Al balanced; 25°C
 — $^{\#}\text{SiO}_2$: quartz
 - - - $^{\#}\text{SiO}_2$: cristobalite

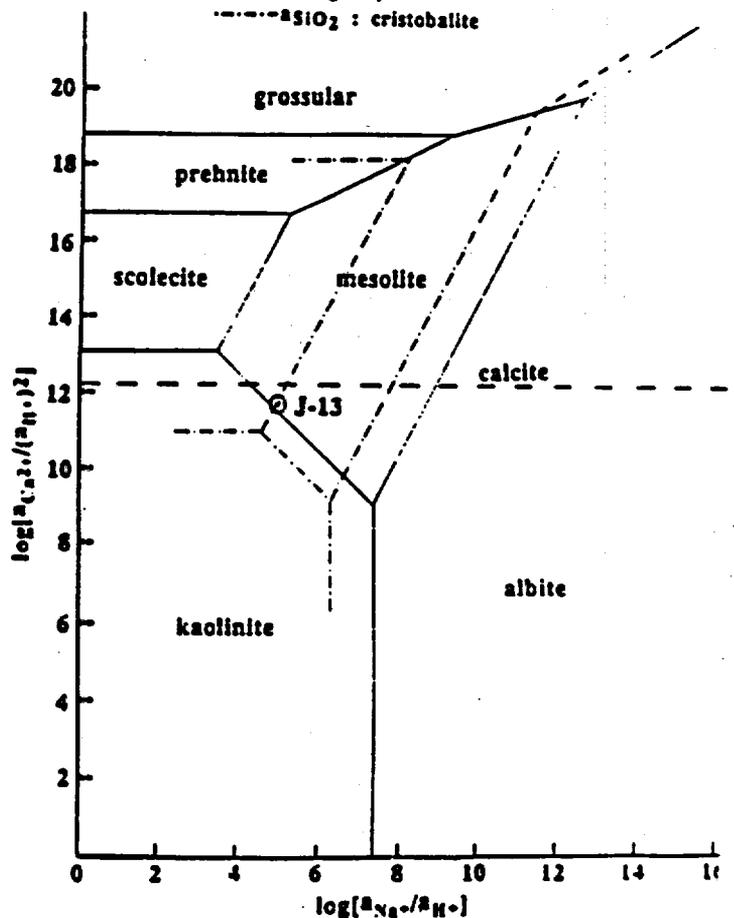
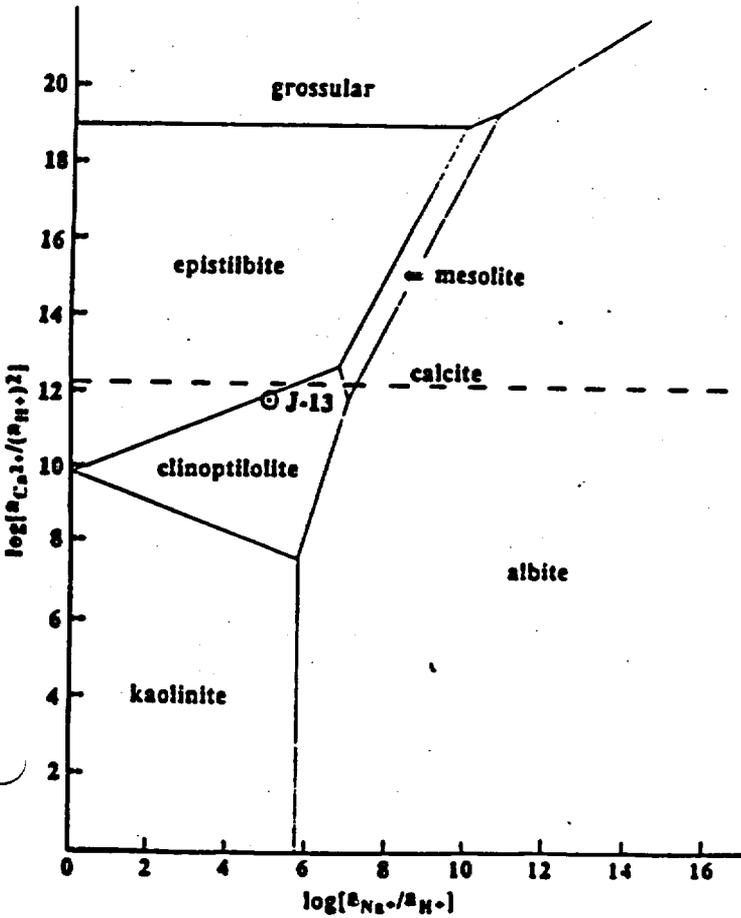
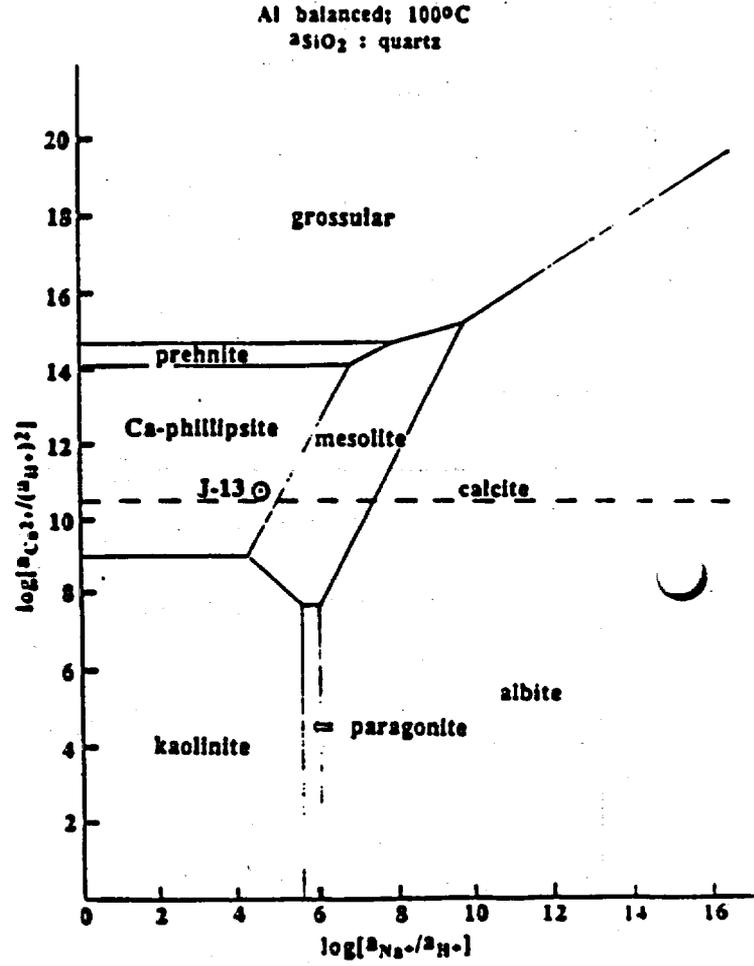
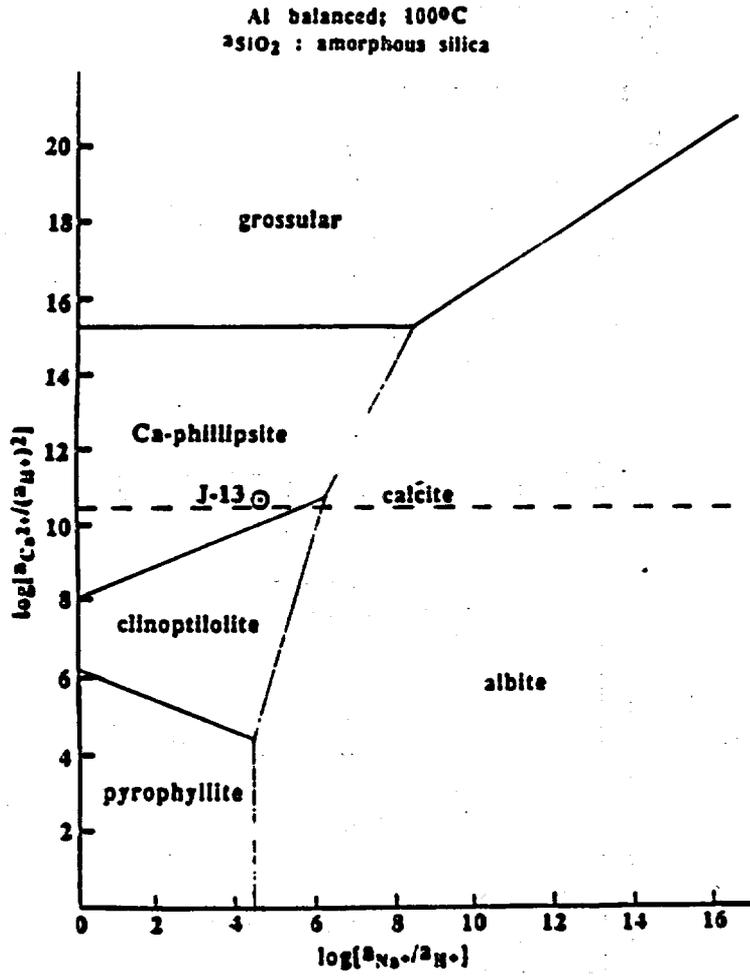
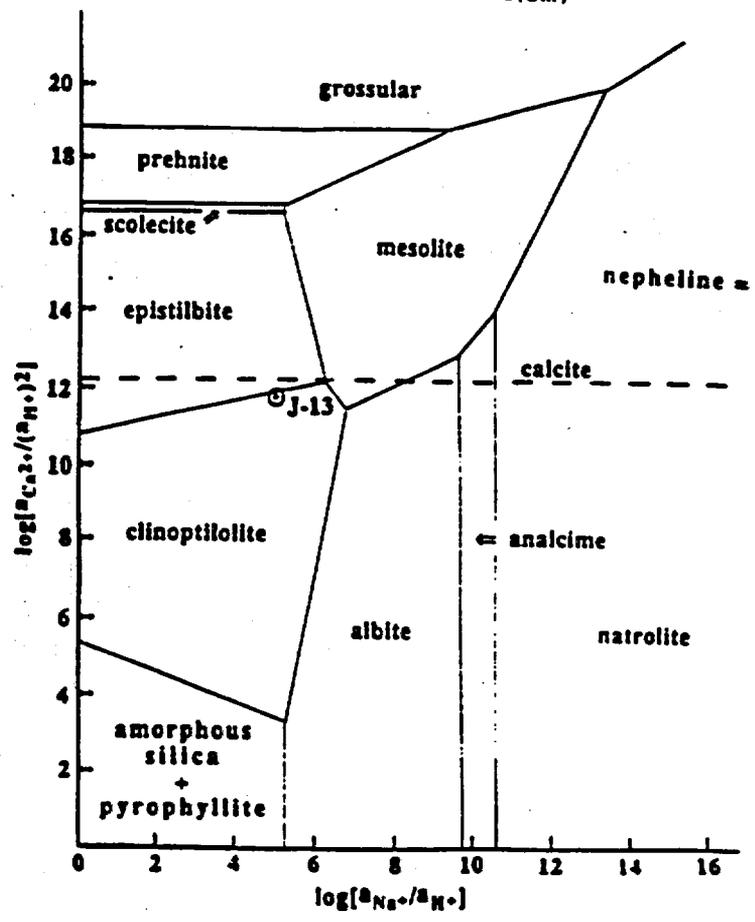
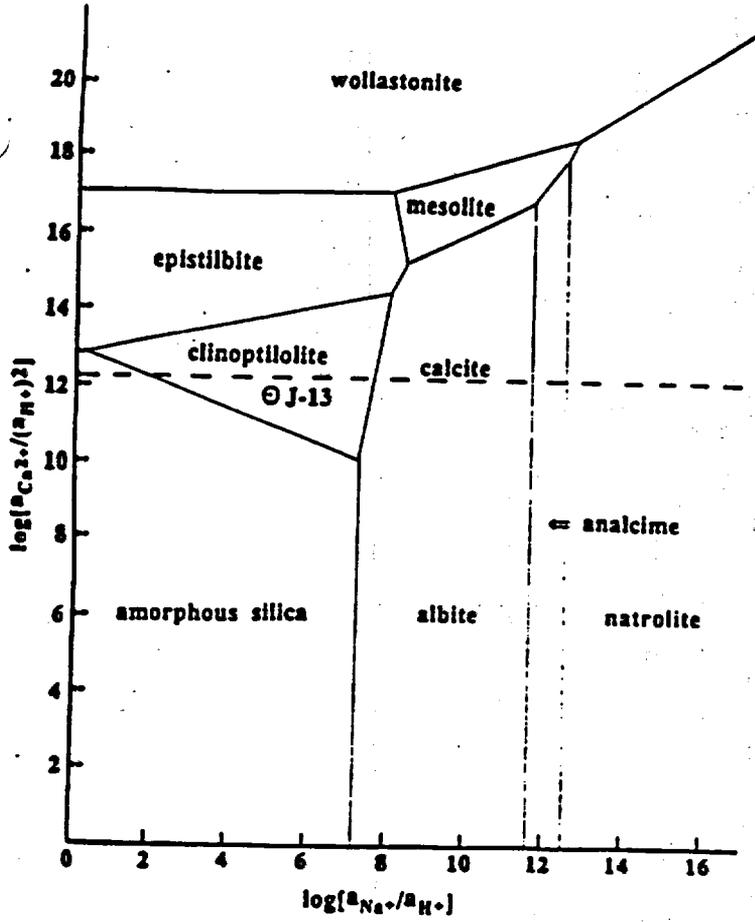


Figure 6



Si balanced; 25°C
 $a_{Al_2O_3} / (a_{H_2O})^3 : 10^4$

Si balanced; 25°C
 $a_{Al_2O_3} / (a_{H_2O})^3 : \text{pyrophyllite} + \text{SiO}_2(\text{am})$



Si balanced; 25°C
 $a_{Al_2O_3} / (a_{H_2O})^3 : \text{kaolinite/pyrophyllite}$

Si balanced; 25°C
 $a_{Al_2O_3} / (a_{H_2O})^3 : \text{gibbsite}$

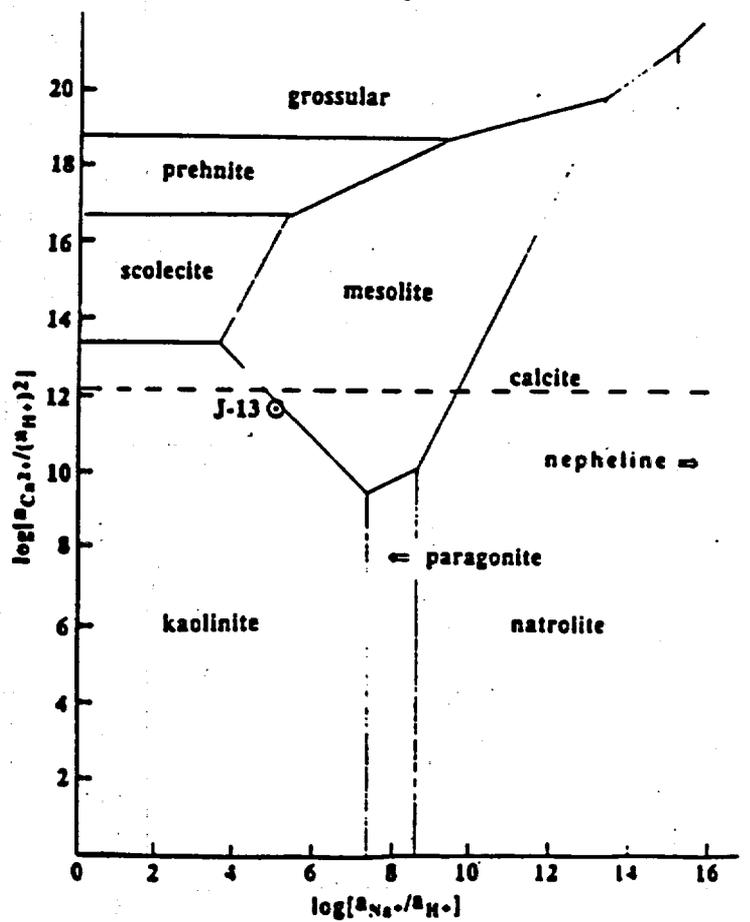
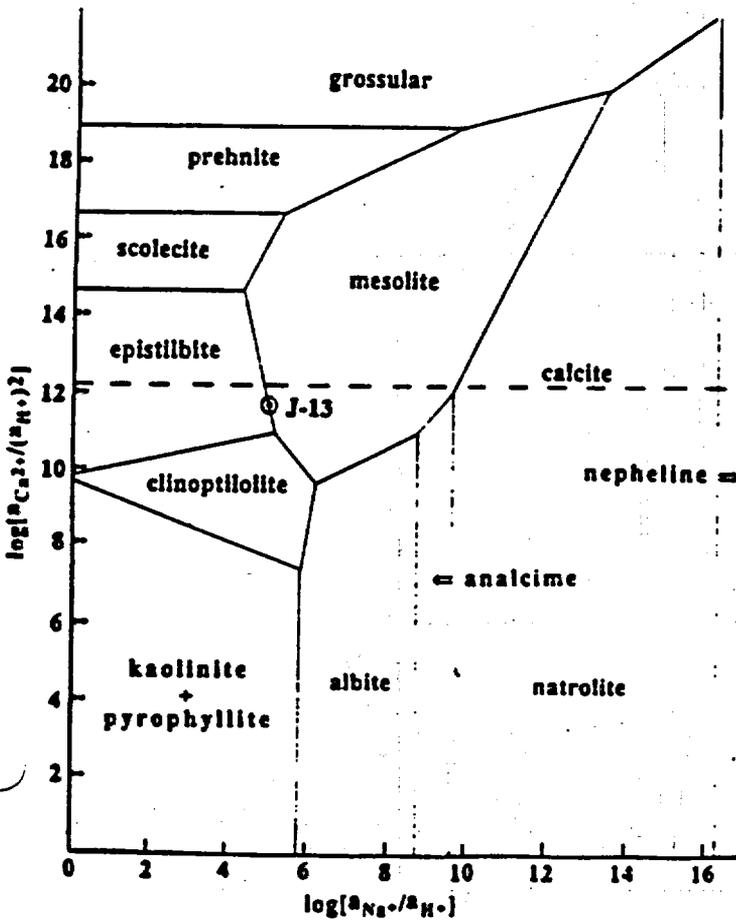


Figure 8

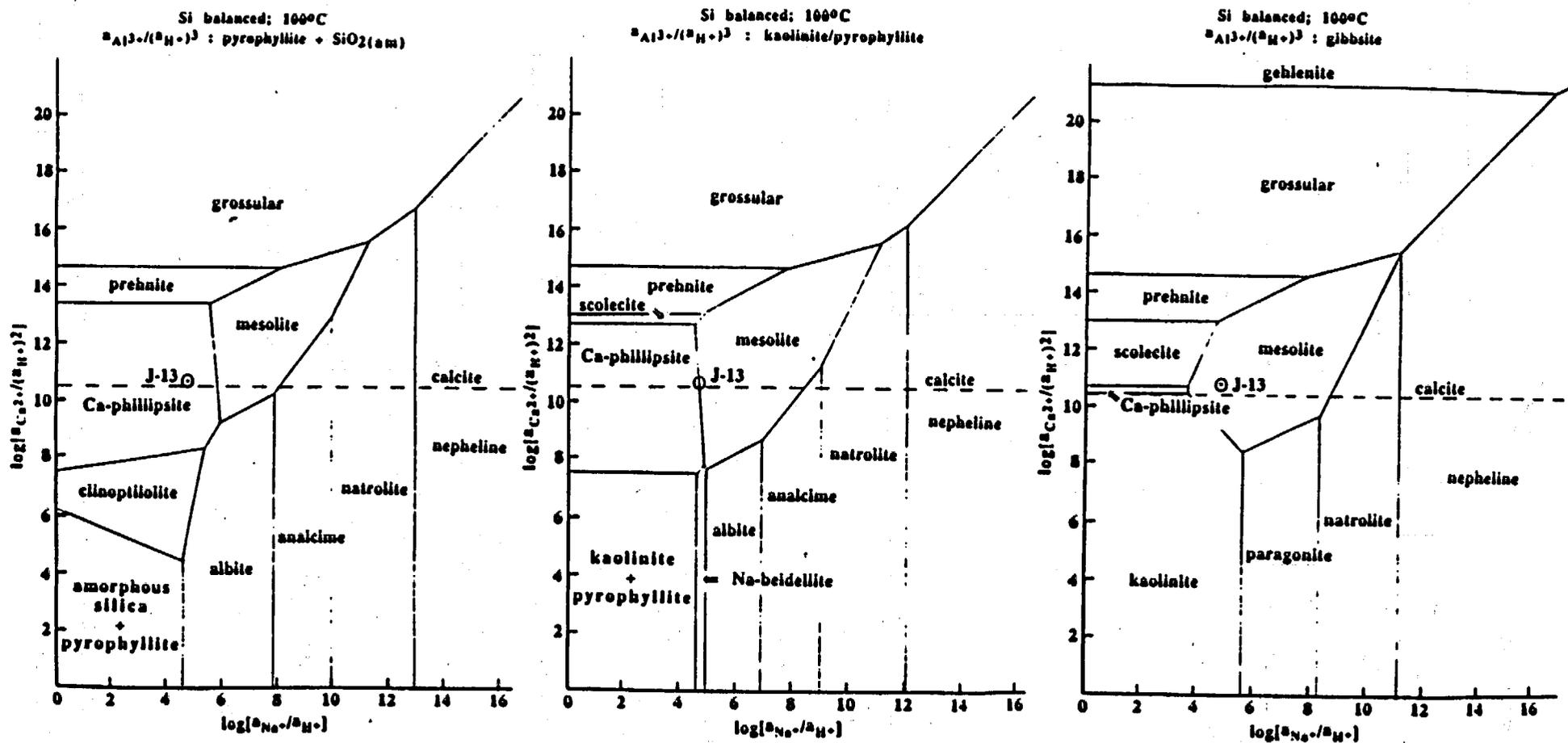


Figure 9

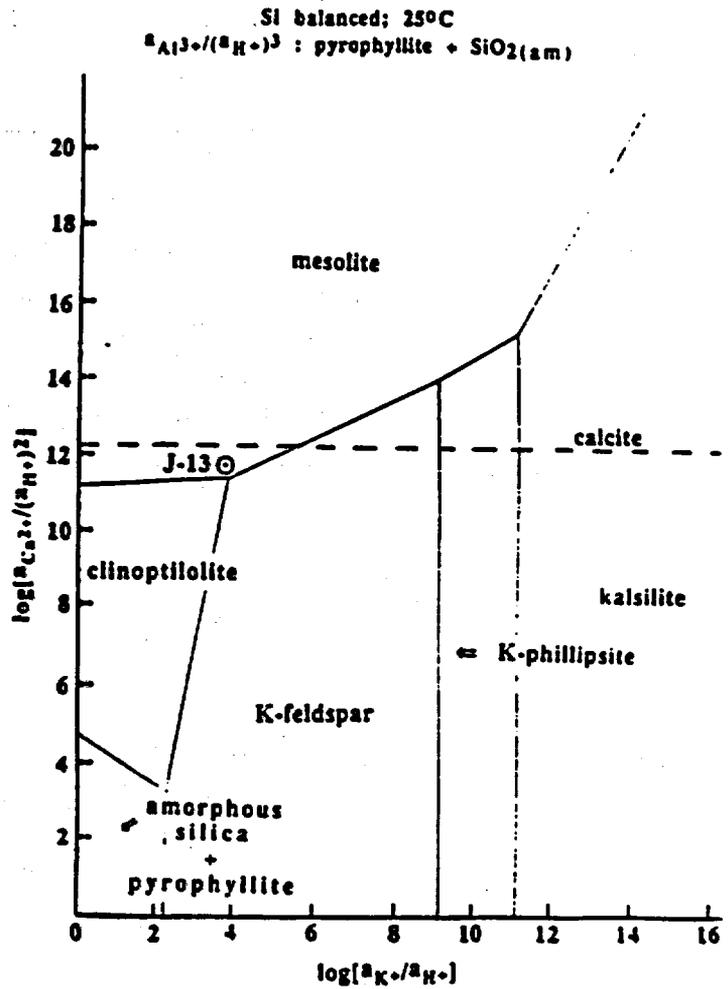
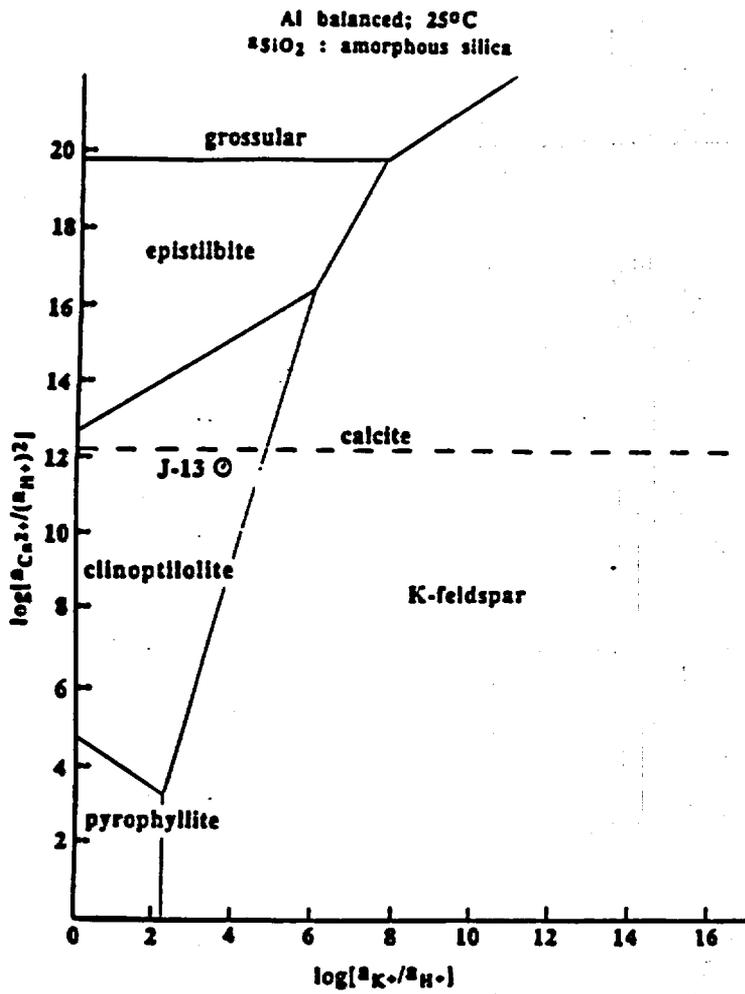
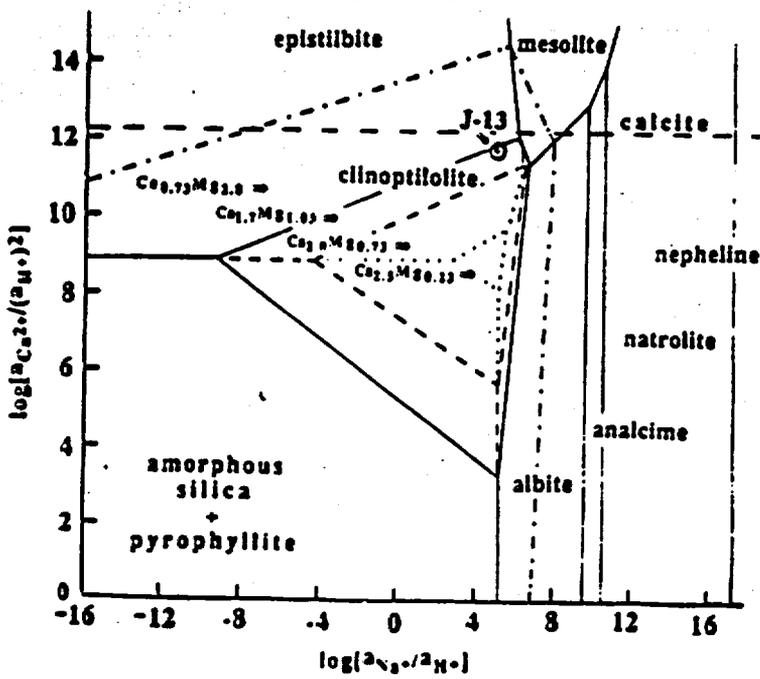
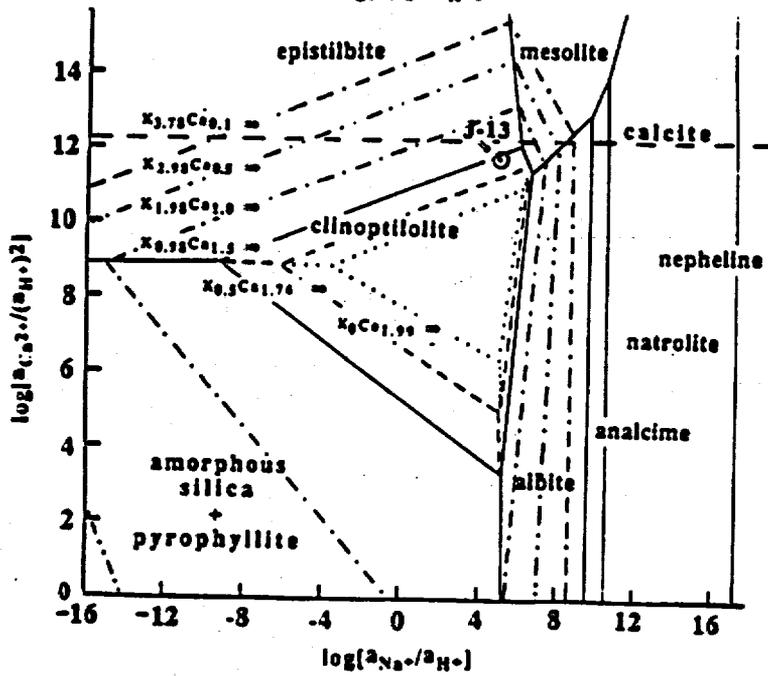
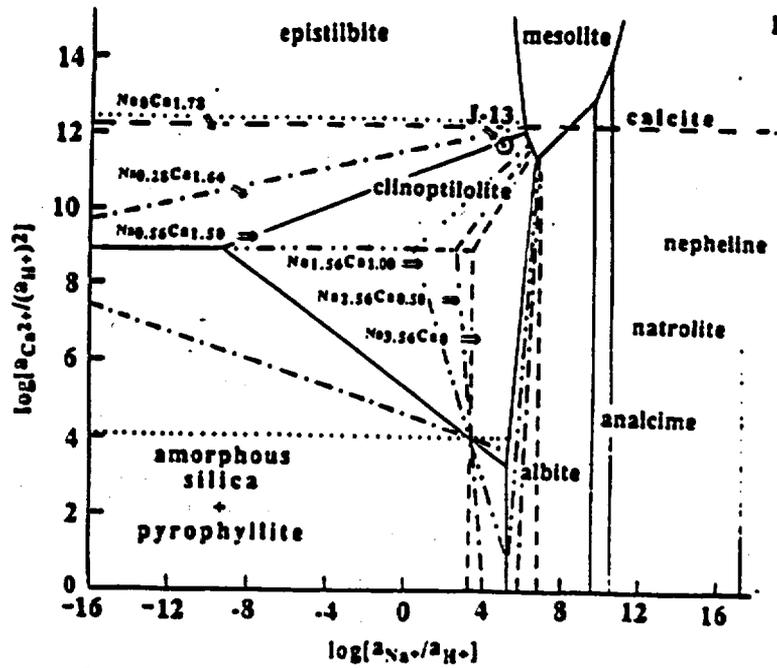
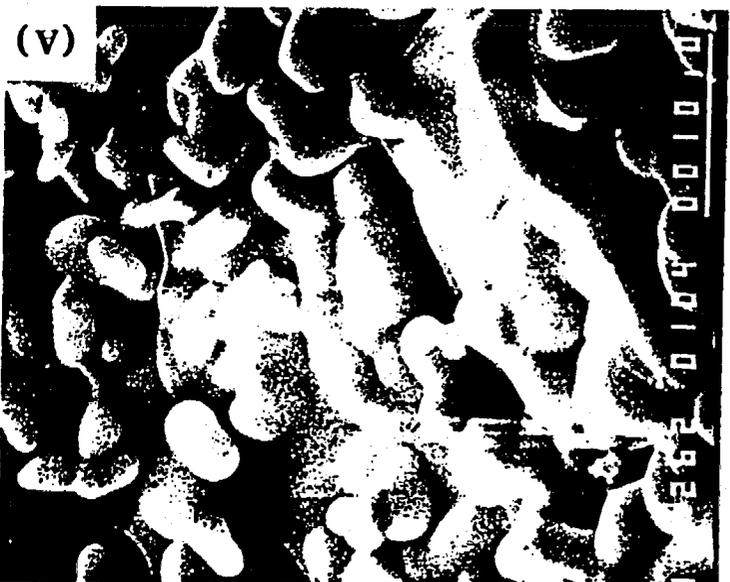
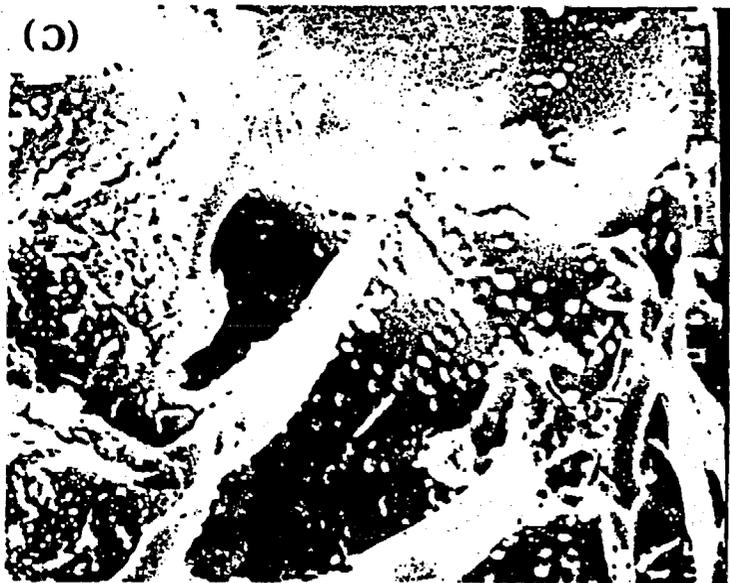
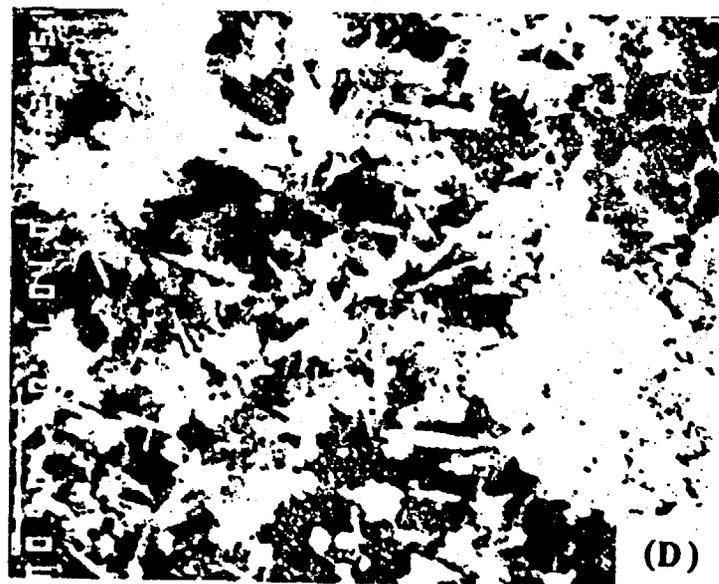
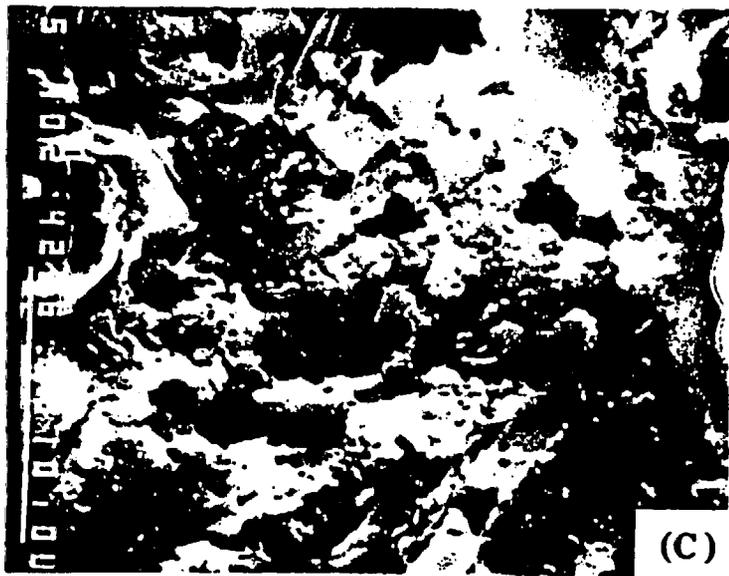
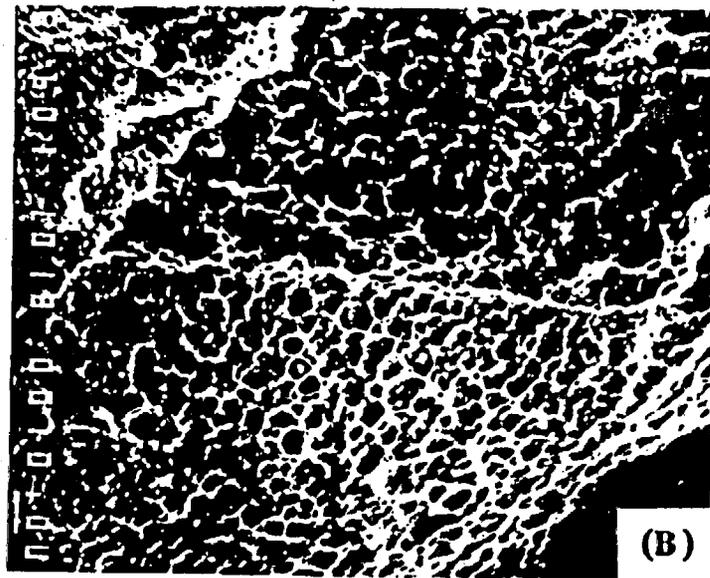


Figure 10



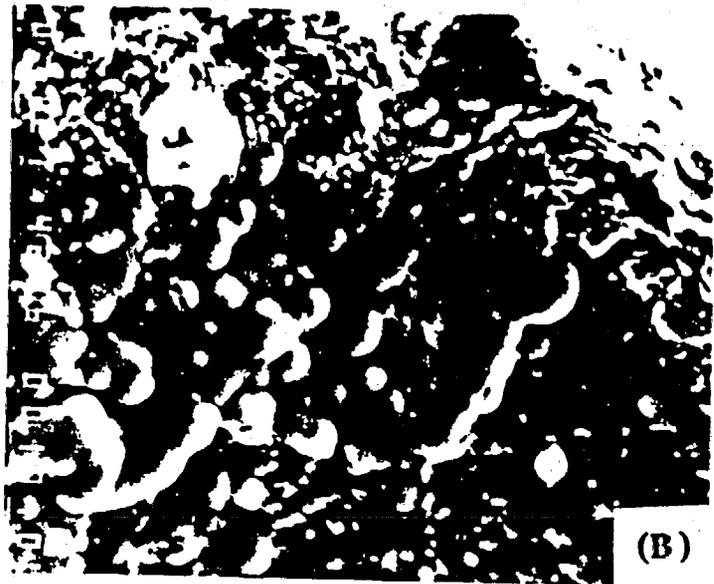








(A)



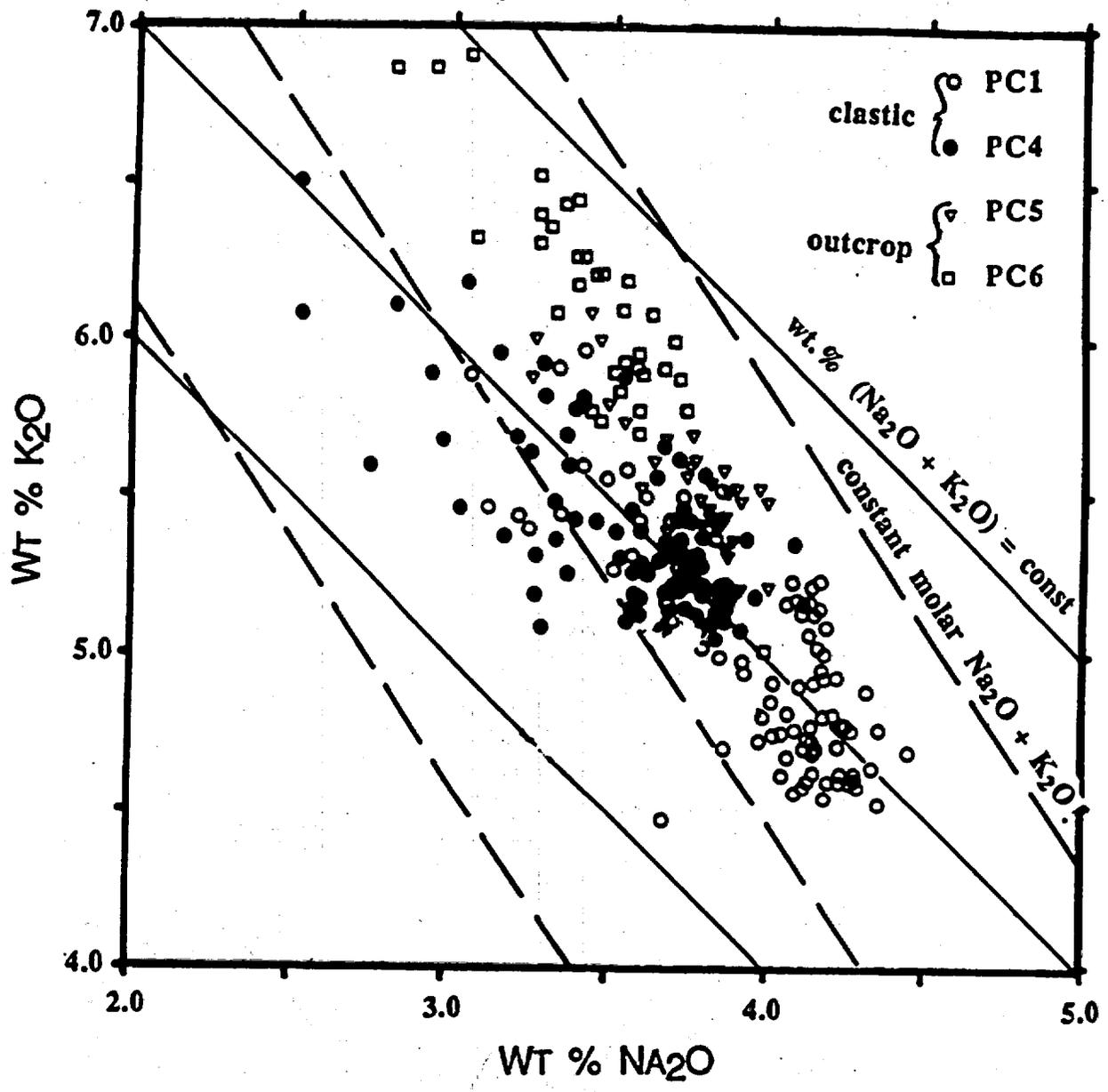
(B)



(C)



(D)



DISTANCE ACROSS SHARD (MICRONS) : ION MICROPROBE

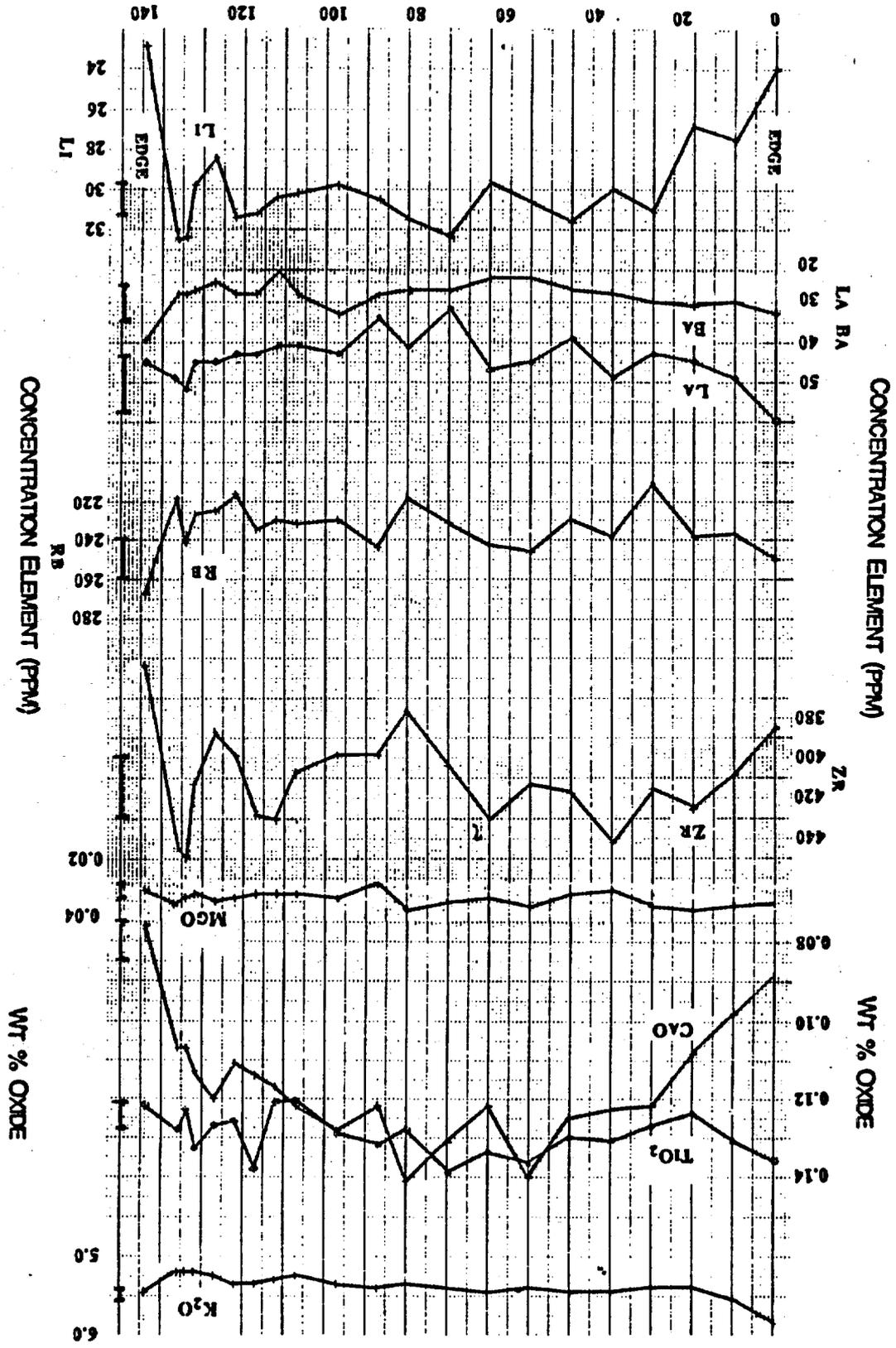
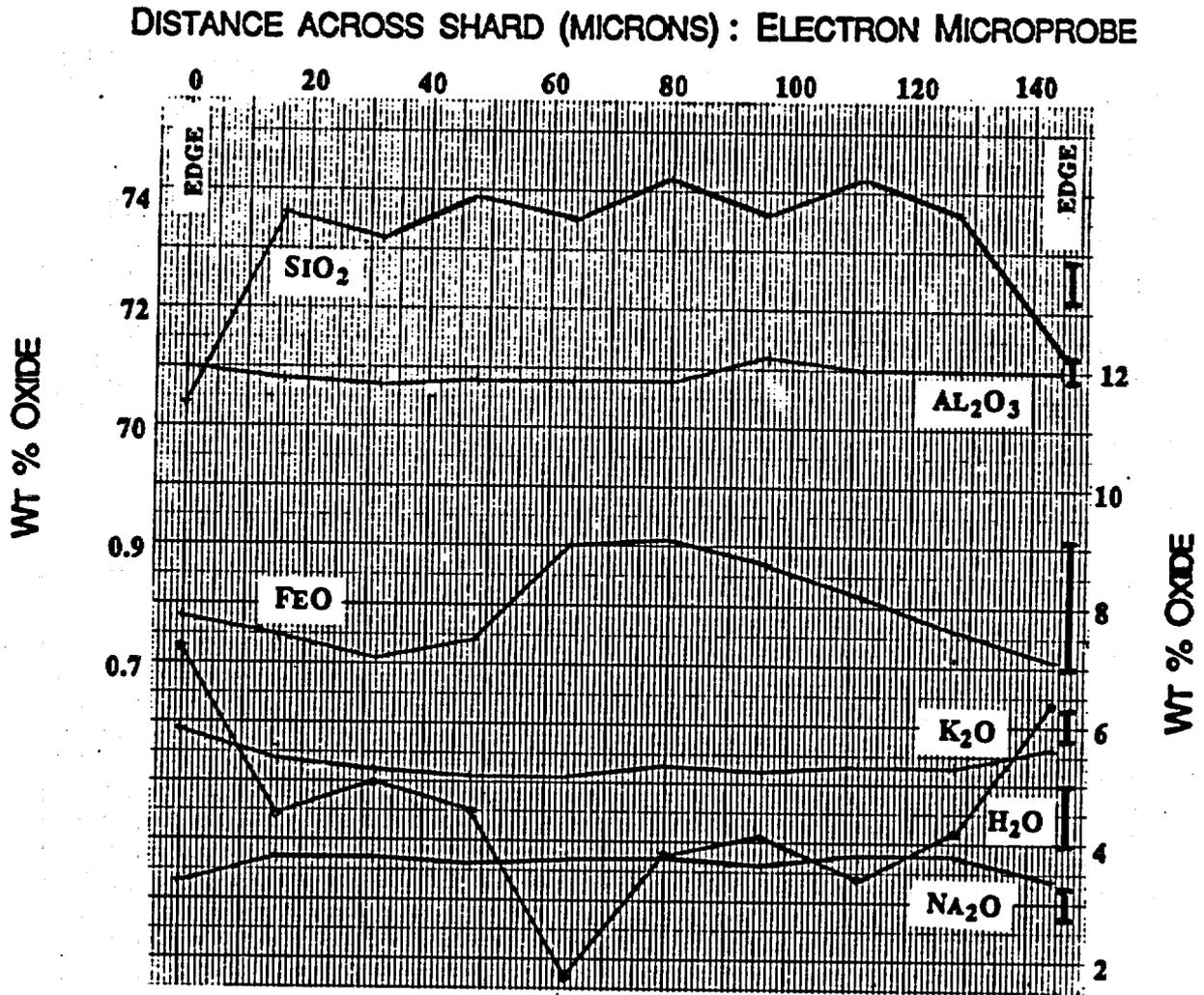


Fig. 1. Missing -
no extra
prints left
R



Geological Society of America, Abstracts with Program,
vol. 20, no. 7, 1988, p. A359.

(Paper presented in session: "Geochemistry VI:
Layered Silicates and Zeolites/Mineralogy/Crystallography II)

No 23742

ACTIVITY DIAGRAMS FOR CLINOPTILOLITE: RELEVANCE TO ZEOLITIZED VITRIC
TUFFS AT YUCCA MOUNTAIN, NEVADA

BURNS, Roger G., and BOWERS, Teresa S.: Department of Earth, Atmospheric and
Planetary Sciences, Massachusetts Institute of Technology, Cambridge, MA 02139.

Clinoptilolite, e.g. $(\text{Na}_{0.56}\text{K}_{0.98}\text{Ca}_{1.50}\text{Mg}_{1.23})(\text{Si}_{29}\text{Al}_{6.7}\text{Fe}_{0.3})\text{O}_{72.22}\text{H}_2\text{O}$, occurs as a secondary mineral in zeolitized vitric tuffs and is considered to be a prime candidate for immobilizing certain soluble radionuclides (e.g. ^{135}Cs , ^{90}Sr) contained in fission products to be stored in the proposed repository for high-level nuclear waste at Yucca Mt. Clinoptilolites, occurring in the undersaturated zone above the water table there, show regional variations of Na and Ca, which raise questions about the vulnerability of the zeolites to further diagenetic reactions with groundwater. Therefore, equilibrium activity diagrams were calculated for clinoptilolite solid-solutions in the seven component system Na-K-Ca-Mg-Fe-Al-Si plus H_2O , employing available thermodynamic data for relevant oxide and aluminosilicate phases. Stability fields were portrayed graphically on plots of $\log(a_{\text{Na}^+}/a_{\text{H}^+})$ versus $\log(a_{\text{Ca}^{2+}}/a_{\text{H}^+})^2$, assuming the presence of K-feldspar, saponite and hematite and using ranges of activities for SiO_2 and Al^{3+} defined by the saturation limits for quartz, amorphous silica, gibbsite, kaolinite and pyrophyllite. Formation of clinoptilolite is favored by higher SiO_2 activities than allowed for by the presence of quartz, thus accounting for coexistence of clinoptilolite with opal CT in zeolitized vitric tuffs. The clinoptilolite stability field broadens with increasing ratio of Ca to Na, reaches a maximum size for intermediate Al^{3+} activities, and decreases at elevated temperatures. In the absence of analytical data for vadose-zone water at Yucca Mt., the water composition of the nearest producing well (J-13 at the adjacent Nuclear Test Site) was used as reference. The thermodynamic calculations show that sodium bicarbonate-type J-13 well-water is approximately in equilibrium with calcite and several zeolites, including clinoptilolite. Decreasing Al^{3+} activities results in the association of clinoptilolite with calcite and opal CT observed in some zeolitized vitric tuffs at Yucca Mt. This suggests that prolonged diagenetic reactions with groundwater depleted in Al and heated by the thermal envelope surrounding the repository may eliminate sorptive clinoptilolite.

ABSTRACT FORM FOR ALL GSA MEETINGS IN 1989

Complete all sections **3** through **7** below

1 TYPE ABSTRACT within blue lines — they're absolute! Mail flat, reinforced.

No 6647

2 CATEGORIZE EVERY ABSTRACT! Check ONE of the following disciplines below in which reviewers would be best qualified to evaluate your abstract. If you check "OTHER", we will choose for you.

- 1 archaeological geology
- 2 coal geology
- 3 economic geology
- 4 engineering geology
- 5 environmental geology
- 6 general geology
- 7 geochemistry
- 8 geology education
- 9 geomorphology
- 10 geophysics
- 11 geoscience information
- 12 glacial geology
- 13 history of geology
- 14 hydrogeology
- 15 marine geology
- 16 micropaleontology
- 17 mineral./crystal.
- 18 oceanography
- 19 paleontology/paleobot.
- 20 petroleum geology
- 21 petrology, experimental
- 22 petrology, igneous
- 23 petrology, metamorphic
- 24 petrology, sedimentary
- 25 planetary geology
- 26 Precambrian geology
- 27 Quaternary geology
- 28 remote sensing
- 29 sedimentology
- 30 stratigraphy
- 31 structural geology
- 32 tectonics
- 33 tectonics/geophysics
- 34 volcanology
- 35 OTHER _____

DESERT VARNISH: A NEW LOOK AT CHEMICAL AND TEXTURAL VARIATIONS
KRINSLEY, David, and ANDERSON, Steven, Geology Department,
Arizona State University, Tempe, AZ 85287

We have combined several analytical techniques and used them to acquire chemical and textural information from rock varnish samples. Polished sections of varnish and underlying rock material were photographed at both low and high magnification (up to 15,000X) using scanning electron microscopy (SEM) in the backscattered electron mode (BSE). Photomosaics show the relations between the varnish and the underlying rock, including textural variations and chemical differences within the varnish layers. Sections were analyzed with the electron microprobe to obtain major element distributions. Water content and trace element data on the same section were then acquired using the ion microprobe. Chemical analyses were related to depth in the varnish layers, overall varnish thickness, and structure within the varnish. The percentage of water at a number of points in cross section was compared to chemical composition and texture.

BSE microphotography has shown that the contact between the varnish and the rock substrate is very sharp and distinct, with no evidence of chemical weathering. This suggests that either the rock to which the varnish adheres is resistant to chemical weathering, or varnish accretion begins soon after the rock has become mechanically stable; the latter is probably more likely. There also does not appear to be chemical exchange between rock and varnish. In addition, porosity decreases with depth, and 1-2 micron lamellae are concentrated at the bottom of the varnish near the rock-varnish interface.

Preliminary analysis of ion and electron microprobe data from South Mountain, Arizona and Coso volcanic field, California varnish samples has revealed a highly varied chemistry. Major elements, trace elements, water contents, and the cation ratios (Ca+K/Ti) do not show any clear trends with depth.

3 TYPES OF SESSIONS AVAILABLE

A. INVITED ABSTRACTS:

ONLY if your abstract has been formally invited by a Symposium Convener, write the name of the symposium on the blank line then skip to item **4**. When your abstract is ready, send original + 5 photocopies direct to your Convener to arrive on or before July 19, 1989.

B. VOLUNTEERED ABSTRACTS:

If this is a volunteered abstract, complete item (1) or item (2) below—but not both.

(1) ALL VOLUNTEERED ABSTRACTS for Section Meetings & GSA Annual Meeting

(Check below)

ORAL: Check here if you want an oral presentation in a regular session, organized by discipline.

POSTER: Check here if you want a presentation by display of graphic materials in a booth which you attend.

I've checked ORAL or POSTER, but I'll accept a change of session type (ORAL — POSTER) if necessary.

I've checked ORAL or POSTER. Please withdraw my abstract rather than change my session type.

Skip directly to item **4** if you have completed this section, or if this abstract is submitted for a section meeting.

(2) THEME SESSIONS or OPEN SYMPOSIA (Annual Meeting only, not applicable to Section meetings): A list of Theme Sessions and Open Symposia for 1989 Annual Meeting will be announced in January 1989, and regularly thereafter in the newsletters of GSA and associated societies, and will accompany abstract forms mailed after February 1989. Write in below the exact name of the Theme Session or Open

Symposium for which this abstract is intended. Send original + 6 copies to GSA to arrive on or before July 19, 1989.

If your abstract is NOT accepted for the special session you indicated above, tell us what to do with it:

- Consider it for a regular ORAL presentation
- Consider it for a regular POSTER presentation
- Consider it for EITHER type
- Withdraw my abstract

4 % OF THIS PAPER PREVIOUSLY PRESENTED 0

Where and when? _____

5 CAN YOU BE A SESSION CHAIRMAN? Yes

Topic (from list above) _____

Your Name _____

Phone number (late June/early July) _____

6 SPEAKER'S IDENTITY AND MAILING ADDRESS:

Speaker's Name: Steven Anderson

Address: Dept. of Geology

Address: Arizona State University

City/State/ZIP Tempe, AZ 85287-1404

Country _____

Office Telephone: (602) 965-6236

Home Telephone: (602) 829-7812

Dates we can reach you: Any time

7 SEND ORIGINAL + 6 COPIES OF ABSTRACT TO APPROPRIATE ADDRESS SHOWN ON INSTRUCTION SHEET AND ON BACK OF THIS FORM. ALL ABSTRACTS MUST ARRIVE ON OR BEFORE DEADLINE SHOWN FOR EACH MEETING. PLEASE MAIL EARLY!

DETACH FOR MAILING

ABSTRACT FORM FOR ALL GSA MEETINGS IN 1988

Denver
Meeting

Complete sections 1 through 7 below

TYPE ABSTRACT within blue lines — they're absolute! Mail flat, reinforced.

No 26427

2

CHEMICAL ZONATION WITHIN BISHOP ASH, PLEISTOCENE LAKE TECOPA, INYO COUNTY, CALIFORNIA

O'HARA, Parick F., Kaaterskill Exploration, 691 Robinson Dr., Prescott, AZ 86303; MANLEY, Curtis R., KRINSLEY, David, Dept. Geology, Arizona State Univ., Tempe, AZ 85287

Tuff B (Bishop Ash) is a LREE enriched, corundum normative calc-alkaline rhyolite, which crops out within the mudstones of the Late Tertiary Lake Tecopa basin, and is present in the fresh glass, zeolite, and K-feldspar diagenetic facies of Sheppard and Gude (1988). Because airfall tuff has a nearly fixed chemical composition during deposition, lateral elemental variation (31 elements) is used to deduce changing geochemical processes and patterns.

Samples of fresh glass are enriched in F, Mo, W and Y, but these elements are depleted in all samples of recrystallized tuff. Two zones enriched in alkalis and depleted in U are present in the altered tuff. An As + B trace element association is found in a six sample zone where the most anomalous samples containing alkali enrichment, U depletion and high Cu + Ba concentrations exist. Anomalous Pb and U flank this zone.

Zones of both As + B and alkali depletion flank corresponding zones of high concentrations, suggesting potential paths of fluid flow. Both fresh glass and recrystallized tuff facies locally contain high calcite + Mn concentrations. Three fluid sources are inferred: 1) hot springs which added high concentrations of B + As and associated elements, 2) alkali enriched fluid, which might be associated with hydrothermal fluids, and 3) carbonate-enriched groundwater venting into the lake as cold springs.

Lack of correlation between these chemical zones and the diagenetic mineral assemblages may preclude a direct relation between the fluid and diagenetic phases. The Bishop Ash could have been open to chemical exchange prior to diagenesis.

CATEGORIZE ALL ABSTRACTS — Check ONE discipline below in which reviewers would be best qualified to evaluate this abstract.

- 1 archaeological geology
- 2 coal geology
- 3 economic geology
- 4 engineering geology
- 5 environmental geology
- 6 general geology
- 7 geochemistry
- 8 geology education
- 9 geomorphology
- 10 geophysics
- 11 geoscience information
- 12 glacial geology
- 13 history of geology
- 14 hydrogeology
- 15 marine geology
- 16 micropaleontology
- 17 mineralogy/crystallography
- 18 oceanography
- 19 paleontology/paleobotany
- 20 petroleum geology
- 21 petrology, experimental
- 22 petrology, igneous
- 23 petrology, metamorphic
- 24 petrology, sedimentary
- 25 planetary geology
- 26 Precambrian geology
- 27 Quaternary geology
- 28 remote sensing
- 29 sedimentology
- 30 stratigraphy
- 31 structural geology
- 32 tectonics
- 33 tectonics/geophysics
- 34 volcanology

3 TYPES OF SESSIONS AVAILABLE

A. SPECIAL — INVITED ABSTRACT FOR A SYMPOSIUM.

- This abstract was invited for the symposium titled _____

If you checked here, skip to item 4.

B. VOLUNTEERED ABSTRACTS

(1) SPECIAL—THEME SESSION, ANNUAL MEETING ONLY.

I would like this abstract considered for oral presentation at the following Theme Session for the Annual Meeting, Denver, 1988.

- 1 Diagenesis of lacustrine rocks
- 2 Geology & Public Policy for the 21st Century
- 3 Geophysical patterns in North America
- 4 Global aspects of sedimentary geology
- 5 Organic compounds in ground water
- 6 Paleontologic constraints on accreted terranes
- 7 Physics and chemistry of mylonites
- 8 Secular variation in the sedimentary record

If not accepted for the Theme Session, do you want it considered for a regular technical session?

- Yes No

(2) ORAL SESSION POSTER SESSION EITHER TYPE

I'll accept a change of session type (ORAL ↔ POSTER) if necessary;

- Withdraw my abstract rather than change session type.

4 % OF THIS PAPER PREVIOUSLY PRESENTED 0

Where and when _____

5 CAN YOU BE A SESSION CHAIRMAN? Yes

Topic _____

Your name _____

Telephone (late June/early July) _____

6 SPEAKER'S IDENTITY AND MAILING ADDRESS

Speaker's name DR. PAT O'HARA

Address 691 Robinson Drive

Address _____

City Prescott State AZ Zip 86303

Country _____

Office Telephone: 602 778-5321

Home Telephone: () _____

Dates we can reach you: Any time

7 SEND ORIGINAL + 5 COPIES OF ABSTRACT TO APPROPRIATE

ADDRESS SHOWN ON INSTRUCTION SHEET AND ON BACK OF THIS FORM. ALL ABSTRACTS MUST ARRIVE ON OR BEFORE DEADLINE SHOWN FOR EACH MEETING.

**CHEMICAL ZONATION WITHIN BISHOP ASH, PLEISTOCENE LAKE TECOPA,
INYO COUNTY, CALIFORNIA**

O'HARA, Patrick F., Kaaterskill Exploration, 691 Robinson
Dr., Prescott, AZ 86303; MANLEY, Curtis R., KRINSLEY,
David, Dept. Geology, Arizona State Univ., Tempe, AZ 85287

Tuff B (Bishop Ash) is a LREE enriched, corundum normative calc-alkaline rhyolite, which crops out within the mudstones of the Late Tertiary lake Tecopa basin, and is present in the fresh glass, zeolite, and K-feldspar diagenetic facies of Sheppard and Gude (1968). Because airfall tuff has a nearly fixed chemical composition during deposition, lateral elemental variation (31 elements) is used to deduce changing geochemical processes and patterns.

Samples of fresh glass are enriched in F, Mo, W and Y, but these elements are depleted in all samples of recrystallized tuff. Two zones enriched in alkalis and depleted in U are present in the altered tuff. An As + B trace element association is found in a six sample zone where the most anomalous samples containing alkali enrichment, U depletion and high Cu + Ba concentrations exist. Anomalous Pb and U flank this zone.

Zones of both As + B and alkali depletion flank corresponding zones of high concentrations, suggesting potential paths of fluid flow. Both fresh glass and recrystallized tuff facies locally contain high calcite + Mn concentrations. Three fluid sources are inferred: 1) hot springs which added high concentrations of B + As and associated elements, 2) alkali enriched

fluid, which might be associated with hydrothermal fluids, and 3) carbonate-enriched groundwater venting into the lake as cold springs.

Lack of correlation between these chemical zones and the diagenetic mineral assemblages may preclude a direct relation between the fluid and diagenetic phases. The Bishop Ash could have been open to chemical exchange prior to diagenesis.

INTRODUCTION

Pleistocene lake beds in Lake Tecopa formed as a result of the damming of the ancestral Amargosa River. Surface flow in the Amargosa River was a direct result of higher groundwater levels and associated increase in groundwater flow. Either at the time of lake sediment distribution or at some later date, rock-fluid reactions have changed the chemistry and mineralogy of the lake deposits. This study is a preliminary attempt to explain the spacial distributions, timing and physiochemical processes associated with these changes.

Lake sediments may have several sources; therefore, they probably have a high degree of chemical variance. For this reason it would be difficult to model chemical variation caused by alteration. However, because felsic volcanic ash of fixed initial chemical composition exists within the basin, these rocks can be used to model chemical and mineralogical changes due to groundwater discharge and alteration, hot spring alteration and diagenetic reactions.

PREVIOUS WORK

Field studies of Lake Tecopa (Map 1) have delineated the areal distribution of lake sediments (Hillhouse, 1987) and the zonation of diagenetic facies using mineral assemblages from felsic ash beds (Sheppard and Gude, 1968; Sheppard, 1985). Currently Roger Morrison, is mapping the distribution of sedimentary rock units and tuffs within the lake beds in order to generate a model of sedimentary facies within Lake Tecopa.

OBJECTIVES

The Bishop Ash is present in all diagenetic facies of Sheppard and Gude (1968) and crops out throughout the Lake Tecopa basin. Textural relationships indicate that the mineral assemblages, which make up the diagenetic facies (Figure 1) change progressively as discontinuous reactions from fresh glass to zeolites and then from zeolites to potassium feldspar (Sheppard and Gude, 1968). Because a felsic ash airfall approximates a fixed composition at the time of deposition, the Bishop Ash can be used to model chemical change caused by rock fluid reactions which occurred after deposition. Therefore, initial hypotheses can be generated which can be tested at a later date with more precise methods.

In order to explain chemical variance within the Bishop Ash, multi-element geochemical analyses and x-ray diffraction data are used in conjunction with multivariate statistical analysis. This data is then used to generate hypotheses concerning the geochemical processes of rock-fluid reactions within alkaline lake deposits. The use of the SEM-EDS system allows petrographic testing of the initial hypotheses and the determination of the timing of each processes (textural analysis). Once all this information is evaluated, an inclusive model can be generated which summarizes rock-fluid reaction processes in alkaline lake deposits.

GEOCHEMISTRY

Fifty-two elements were analysed for thirty-two samples of Bishop Ash. Table I summarizes the elements analysed, detection limits, extraction techniques and method of analysis. Thirty-one of these elements were used in the statistical analyses. The remaining elements were rejected because the samples were mostly below detection limit or had extremely low variance. (Table 1). Each variable was \log_{10} normalized in order to compare skewness between the arithmetic and \log_{10} normalized data. The use of either the arithmetic or \log_{10} normalized variable was based upon the data set that had a skewness value closer to zero.

PRELIMINARY STATISTICAL RESULTS

Initial factors (table 2) derived from the database suggest that seven processes are responsible for changes in chemistry within the Bishop Ash. Fresh samples are enriched in a lithophile element suite containing high concentrations of Mo, W and Rb with depleted concentrations in Ba. This data suggests that during alteration Mo, W and Rb are leached out of the ash and that Ba is added to the ash, preferentially partitioning into the new alteration phases. Locally within the altered rocks alkali addition occurs along with a weak tendency towards U depletion. A strong B, As association is noted and high concentrations of this suite is inferred to be associated with hydrothermal activity. The presence of a "chert" in the Bishop Ash locally within the area of B, As enrichment lends credence to this hypothesis. Because

the "chert" is fairly dirty (contaminated with many components) it is unclear whether it is formed by replacement of ash by SiO_2 (silicification), formed by silicification of sediments immediately above the Bishop Ash, or is an exhalative rock which is contaminated by an ash or sediment component. Further petrographic and geochemical work is needed to test these possibilities. Carbonate addition is present in many samples and is associated with an increase in Mn. Detailed field and petrographic studies will be needed to determine whether these carbonate enriched rocks are formed by a precipitation type chemical reaction within local beds by groundwater, as tuffa mounds or as exhalative zones.

Two sets of associated elements are present within the altered Bishop Ash, which may be related to mineral reactions during alteration or diagenesis.

1. Fe, Ti concentrations
2. MgO , F, Li concentrations

ZONATION WITHIN THE BISHOP ASH (Figures 3 through 9)

Relative zonation of elemental associations is observed by plotting the samples within the highest factor scores for each elemental association on a map. Figure 1 is a map generated by computer use of coordinates arbitrarily devised for this data set. The east-west axis is exaggerated in order to enhance the differences between samples. Figure 2 summarizes the original data set's distribution. Fresh samples are located in the northeast while all other samples are variably altered. Two zones

of alkali addition are present, while the southern zone is associated with hydrothermal (B, As) activity. Comparison with the diagenetic facies map (Figure 1) of Sheppard and Gude (1968) indicates that many of these processes may have occurred before diagenesis, while some may be related to diagenetic reactions. Future petrographic work with SEM-EDS should help unravel the timing of these events.

FACTOR ANALYSIS

Principle component and factor analysis are designed to represent complex relationships between a large number of variables, measured on a set of objects by similar relationships among fewer variables. This reduction should make complex relationships more comprehensible. Various mathematical procedures are performed to describe the objects in terms of a small number of new variables. These new variables are linearly related to the original measured variables by rotation in space and should explain most of the sample variance in far fewer variables than originally measured (Till, 1974).

R-mode factor analysis proceeds in four steps, namely:

1. Correlation matrix is computed
2. Factor extraction
3. Rotation
4. Factor scores computed (optional)

Once the correlation matrix is computed, principle components analysis is used to estimate the initial factors. Principle components analysis is a mathematical procedure which calculates the number of eigenvectors and associated eigenvalues which explain the largest percentage of variance in the database. The first principle component is the combination of variables which accounts for the largest amount of variance in the sample. The second principle component accounts for the next largest amount of variance and is uncorrelated with one another. It is possible to compute as many principle components as there are

variables. If all principle components are used, each variable can be exactly represented by them, but nothing has been gained because there are as many factors (principle components) as variables. When all factors are included in the solution, all the variance of each variable is accounted for, and there is no unique factor in the model. The proportion of variance accounted for by the common factors (communality) is 1.0 for all variables (Norusis, 1984).

In order to determine how many factors are needed to represent the data, the percentage of total variance which is explained by each factor must be examined. The procedure which is used in this report for determining the number of useful factors in the model is the "eigenvalue 1.0" technique. This model suggests that only factors which account for variance greater than 1.0 should be included, because factors with a variance less than 1.0 are no better than a single variable (communality = 1.0 by definition).

Once the number of usable factors is chosen it is important to determine how well the factor model describes the variances of the original variables. First, the total percentage of variance explained by the chosen factors is calculated. Because the factors are uncorrelated the total percentage of variance, which has been determined, is the sum of the variance explained by each factor. Second, the percentage of variance of the original variables, which is explained by the factor model, is calculated and is presented in table form as the communality of the variable. Communalities can range from 0 to 1.0 with 0 indicating that all

the chosen factors explain none of the variance, and 1.0 indicating that all of the variance is explained by the chosen factors.

During state 2 (factor extraction) factor loadings are generated for each of the chosen factors and all the original variables. These loadings are difficult to analyse and interpret because they are generally all quite high. In order to maximize or minimize the loading of each variable within an individual factor, the factors are mathematically rotated (varimax rotation). The goal of rotation is to transform complicated matrices into simpler matrices (stage 3). The rotation matrix is then calculated and new loadings determined. It is in this format that the data is used for interpreting geochemical processes. Factor loadings of each variable are considered significant if their values fall between 0.55 and 1.0. The closeness of the value of the coefficient to 1.0 (positive or negative) indicates the relative degree of influence an element has in the factor.

TABLE 1

CHEMICAL ANALYSIS
by
BONDAR - Clegg; Denver, Colorado

<u>ELEMENT</u>	<u>LOWER DETECTION LIMIT</u>	<u>EXTRACTION</u>	<u>METHOD</u>	
A1203	0.01 PCT	BORATE FUSION	PLASMA EMISSION SPEC	*
CaO	0.01 PCT	BORATE FUSION	PLASMA EMISSION SPEC	*
FE203	0.01 PCT	BORATE FUSION	PLASMA EMISSION SPEC	*
101	0.01 PCT		GRAVIMETRIC	*
K2O	0.01 PCT	BORATE FUSION	PLASMA EMISSION SPEC	*
MgO	0.01 PCT	BORATE FUSION	PLASMA EMISSION SPEC	*
MnO	0.01 PCT	BORATE FUSION	PLASMA EMISSION SPEC	*
Na2O	0.01 PCT	BORATE FUSION	PLASMA EMISSION SPEC	*
P2O5	0.01 PCT	BORATE FUSION	PLASMA EMISSION SPEC	*
S102	0.01 PCT	BORATE FUSION	PLASMA EMISSION SPEC	*
T102	0.01 PCT	BOARTE FUSION	PLASMA EMISSION SPEC	*
Au	5 PPM	NOT APPLICABLE	IND. NEUTRON ACTIV.	
Sb	0.2 PPM	NOT APPLICABLE	IND. NEUTRON ACTIV.	
B	50 PPM	MULT ACID TOT DIG	D.C. PLASMA	*
Ag	1 PPM	NOT APPLICABLE	IND. NEUTRON ACTIV.	*
Ba	100 PPM	NOT APPLICABLE	IND. NEUTRON ACTIV.	*
Br	1 PPM	NOT APPLICABLE	IND. NEUTRON ACTIV.	
Cd	1 PPM	MULT ACID TOT DIG	D.C. PLASMA	
Ce	10 PPM	NOT APPLICABLE	IND. NEUTRON ACTIV.	*
Cs	1 PPM	NOT APPLICABLE	IND. NEUTRON ACTIV.	
Cr	50 PPM	NOT APPLICABLE	IND. NEUTRON ACTIV.	
Cu	1 PPM	MULT ACID TOT DIG	D.C. PLASMA	*
Co	10 PPM	NOT APPLICABLE	IND. NEUTRON ACTIV.	
Eu	2 PPM	NOT APPLICABLE	IND. NEUTRON ACTIV.	
F	20 PPM	101 HYDROXIDE FUSION	SPECIFIC ION	*
Hf	2 PPM	NOT APPLICABLE	IND. NEUTRON ACTIV.	
Lr	100 PPB	NOT APPLICABLE	IND. NEUTRON ACTIV.	
La	5 PPM	NOT APPLICABLE	IND. NEUTRON ACTIV.	*
Lu	0.5 PPM	NOT APPLICABLE	IND. NEUTRON ACTIV.	
Li	1 PPM	MULT ACID TOT DIG	D.C. PLASMA	*
Mo	2 PPM	NOT APPLICABLE	IND. NEUTRON ACTIV.	*
Pb	5 PPM	MULT ACID TOT DIG	D.C. PLASMA	*
NI	1 PPM	MULT ACID TOT DIG	D.C. PLASMA	*
Rb	10 PPM	NOT APPLICABLE	IND. NEUTRON ACTIV.	*
Sm	0.1 PPM	NOT APPLICABLE	IND. NEUTRON ACTIV.	*
Sc	0.5 PPM	NOT APPLICABLE	IND. NEUTRON ACTIV.	
Se	10 PPM	NOT APPLICABLE	IND. NEUTRON ACTIV.	
Ag	0.5 PPM	MULT ACID TOT DIG	D.C. PLASMA	
Ta	1 PPM	NOT APPLICABLE	IND. NEUTRON ACTIV.	
Tb	20 PPM	NOT APPLICABLE	IND. NEUTRON ACTIV.	
Tb	1 PPM	NOT APPLICABLE	IND. NEUTRON ACTIV.	
Th	0.5 PPM	NOT APPLICABLE	IND. NEUTRON ACTIV.	*
Sn	200 PPM	NOT APPLICABLE	IND. NEUTRON ACTIV.	
W	2 PPM	NOT APPLICABLE	IND. NEUTRON ACTIV.	*
U	0.5 PPM	NOT APPLICABLE	IND. NEUTRON ACTIV.	*
Yb	5 PPM	NOT APPLICABLE	IND. NEUTRON ACTIV.	*
Zn	1 PPM	MULT ACID TOT DIG	D.C. PLASMA	*
Zr	500 PPM	NOT APPLICABLE	IND. NEUTRON ACTIV.	
Sr	5 PPM		X-RAY FLOURESCENCE	*
Nb	5 PPM		X-RAY FLOURESCENCE	*

TABLE 2

PRELIMINARY RESULTS OF STATISTICAL ANALYSES OF BISHOP ASH SAMPLES

FACTOR ANALYSIS

<u>FACTOR</u>	<u>EIGENVALUE</u>	<u>PCT OF VAR</u>	<u>CUM PCT</u>
1	8.99753	29.0	29.0
2	5.75474	18.6	47.6
3	3.45885	11.2	58.7
4	3.28152	10.6	69.3
5	2.10266	6.8	76.1
6	1.73358	5.6	81.7
7	1.62365	5.2	86.9
8	1.06045	3.4	90.4

<u>VARIABLE</u>	<u>COMMUNALITY</u>
AL203	.93758
CAO	.95609
FE203	.97706
LOI	.98011
K20	.96308
MGO	.95873
MNO	.90565
NA20	.92039
P205	.84802
ST02	.94326
TT02	.93632
LB	.95217
LAS	.90764
LBA	.85746
LCE	.87833
CU	.85993
LF	.95300
LA	.95259
LLI	.92472
LMO	.90581
PB	.85928
NI	.85065
LRB	.94059
SM	.93140
TH	.76246
LW	.89476
U	.85786
LZN	.86382
SR	.91479
NB	.85710
LY	.87236

ROTATED FACTOR MATRIX:

	<u>FACTOR</u> <u>1</u>	<u>FACTOR</u> <u>2</u>	<u>FACTOR</u> <u>3</u>	<u>FACTOR</u> <u>4</u>	<u>FACTOR</u> <u>5</u>	<u>FACTOR</u> <u>6</u>	<u>FACTOR</u> <u>7</u>	<u>FACTOR</u> <u>8</u>
AL203					-.71			
CAO					.88			
FE203		.81						
LOI	-.77							
K2O						.56		
MGO			.95					
MNO					.74			
NA2O						.69		
P2O5								
SiO2			-.61			-.56		
TiO2		.85						
LB							.84	
LAS							.88	
LBA		.72						
LCE				.91				
CU								.88
LF	.67		.69					
LA				.90				
LLI			.85					
LMO	.80							
PB		-.75						
NI	.88							
SM				.66				
TH								
LW	.70							
U						-.86		
LZN								
SR			.61					
NB		-.67						
LY	.64							

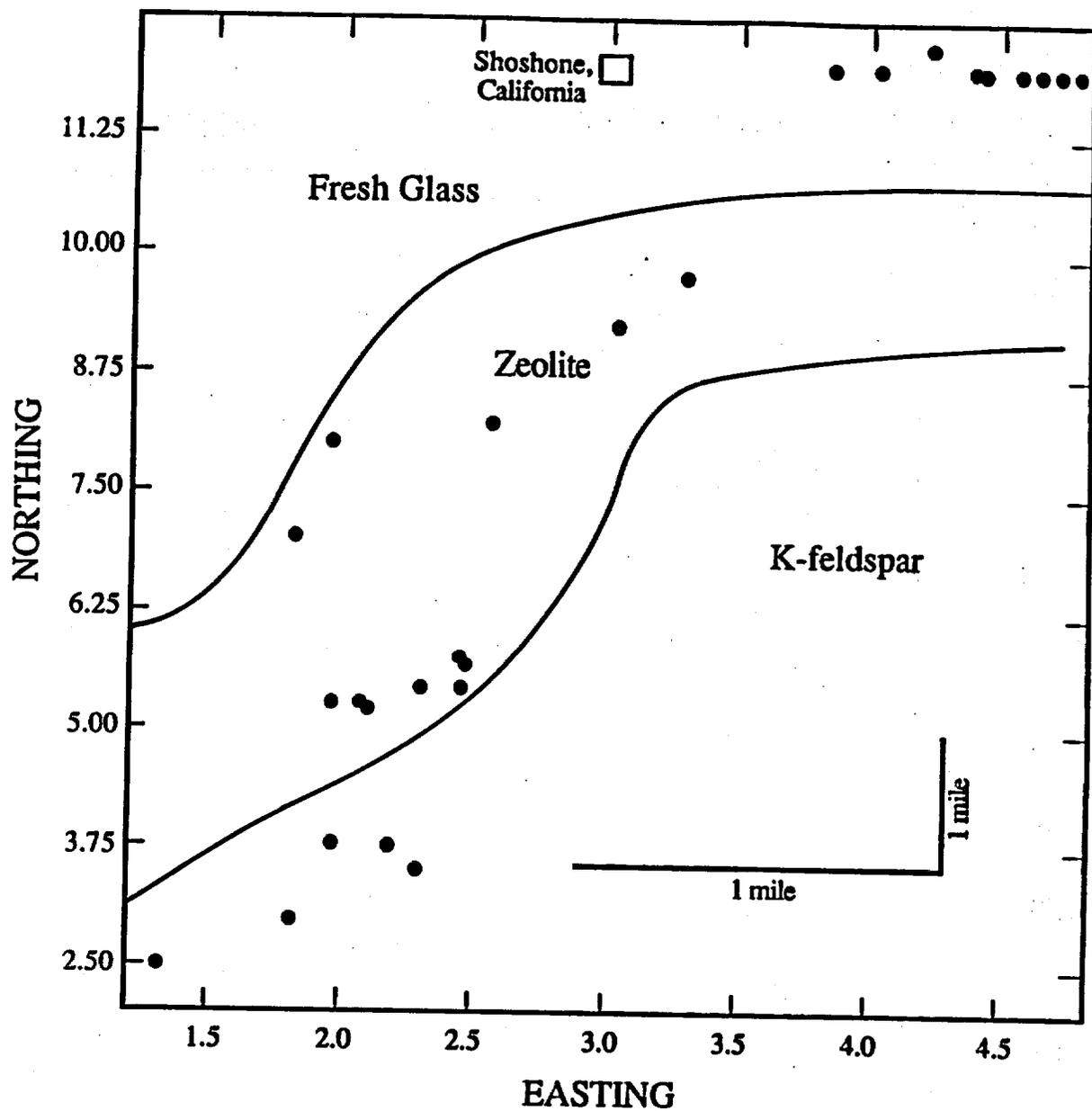


FIGURE 1

Diagenetic facies boundaries for Bishop Ash (Sheppard and Gude, 1968).

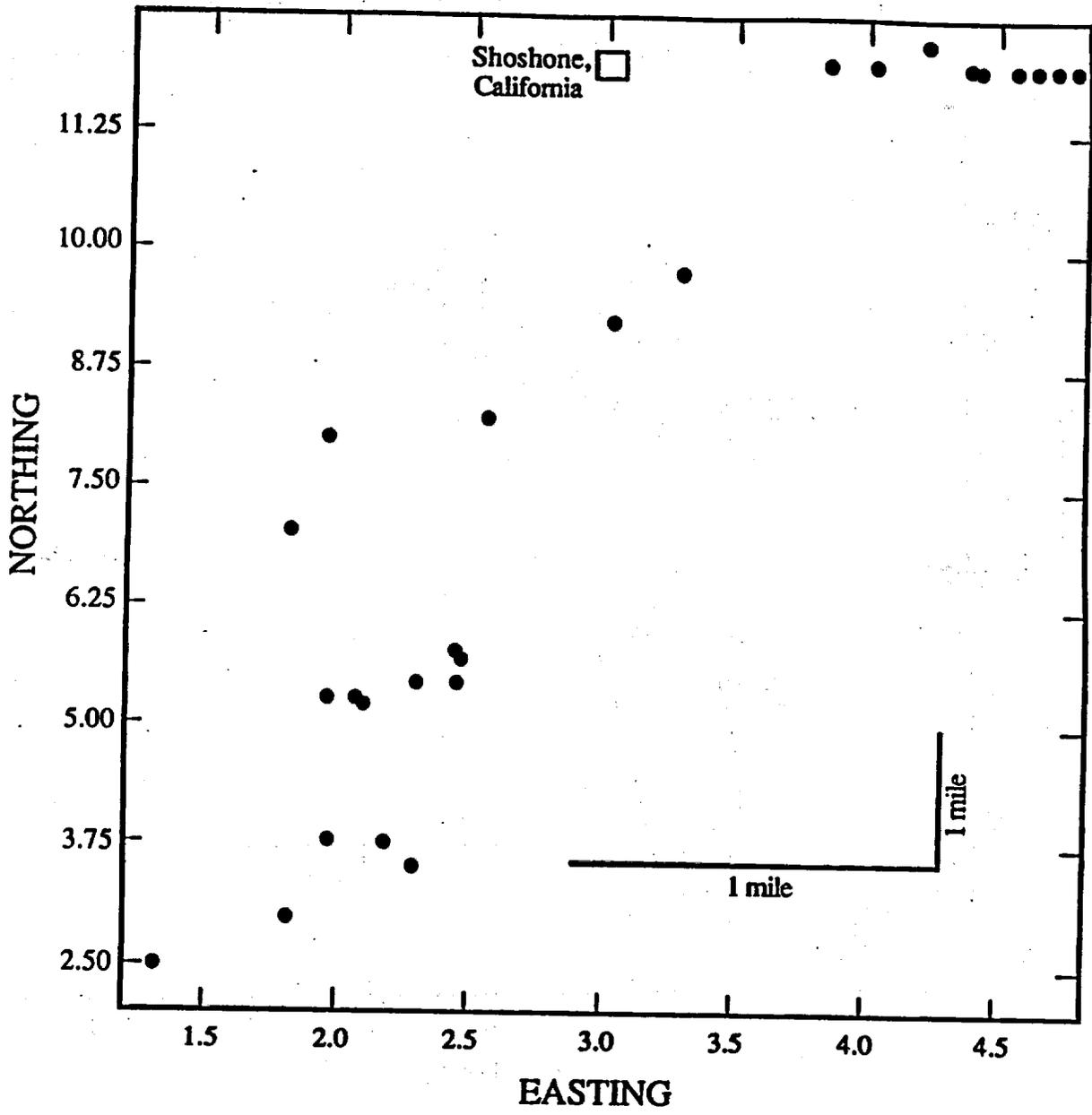


FIGURE 2

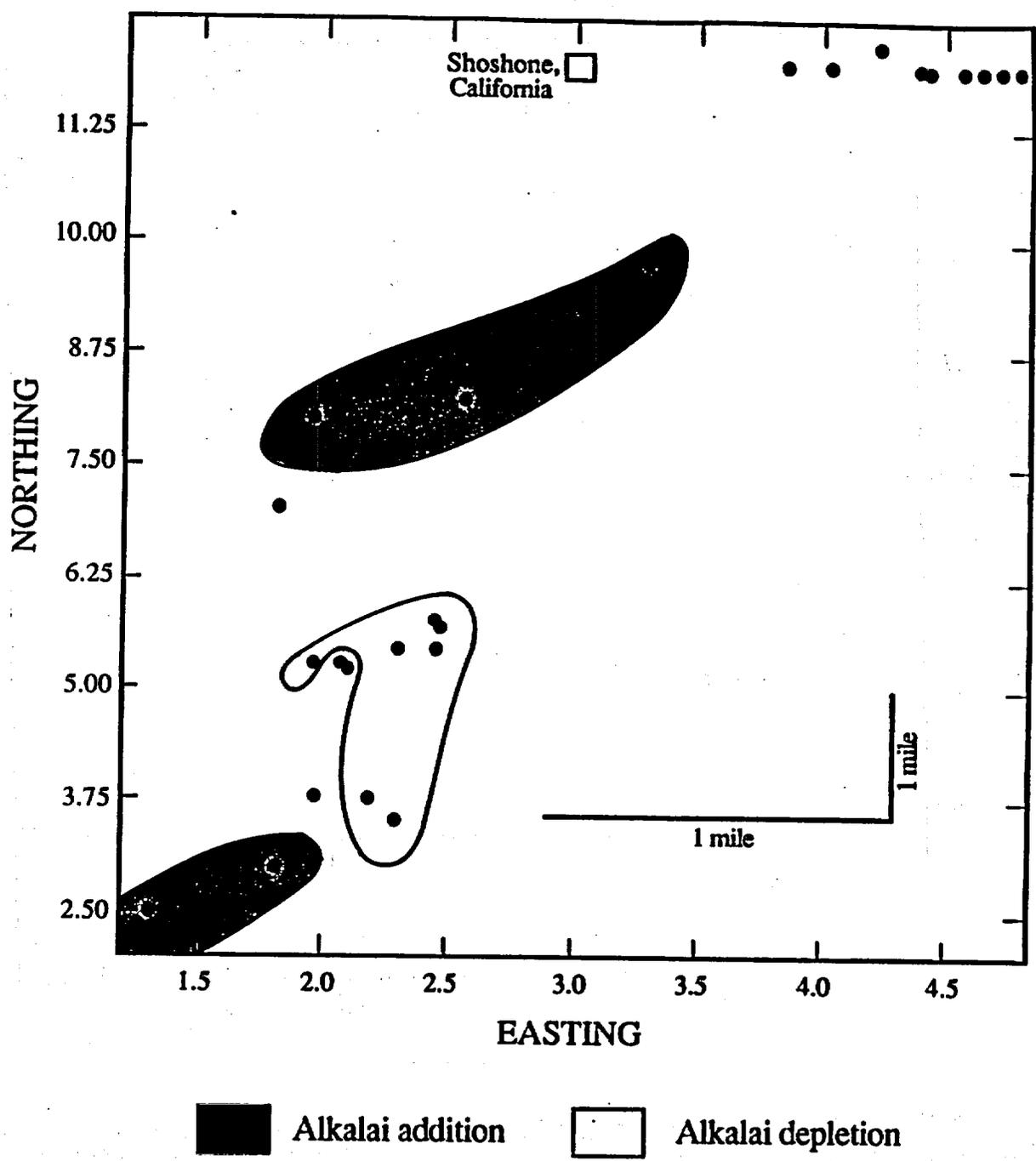


FIGURE 3

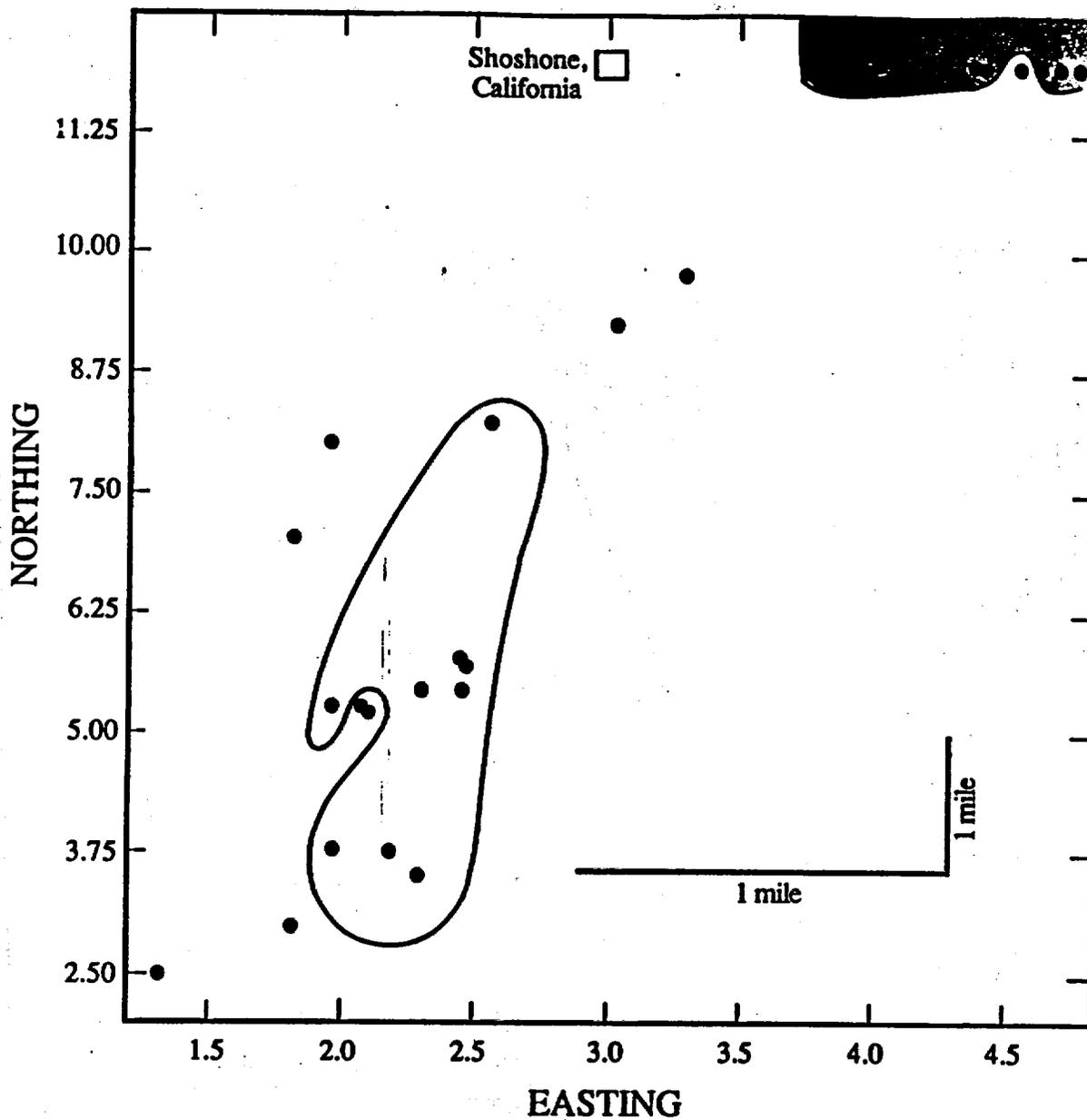
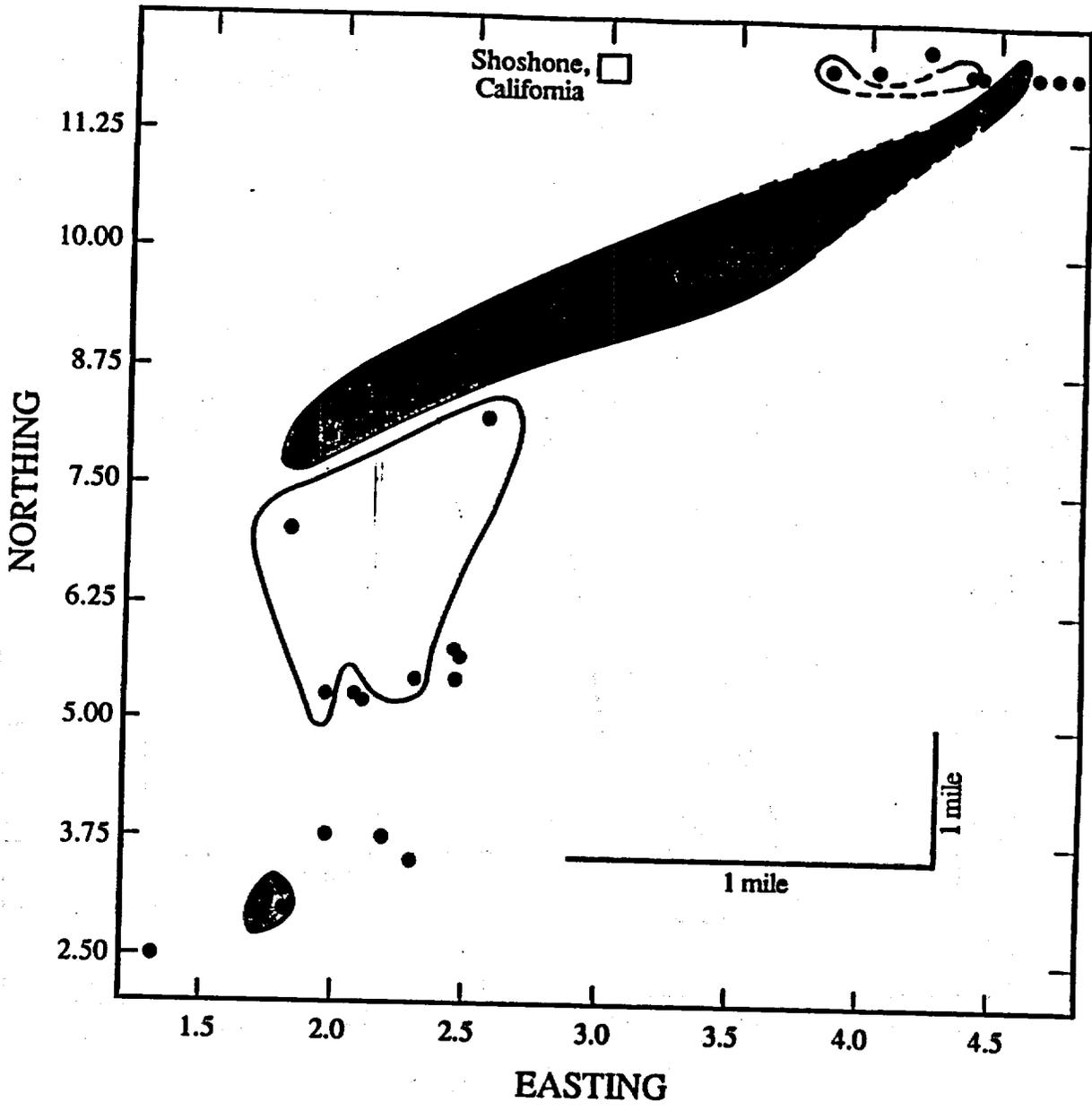


FIGURE 4



MgO, Li, F and Sr addition
 SiO₂ weakly depleted

Weak addition of SiO₂
 MgO, Li, F and Sr depleted

FIGURE 5

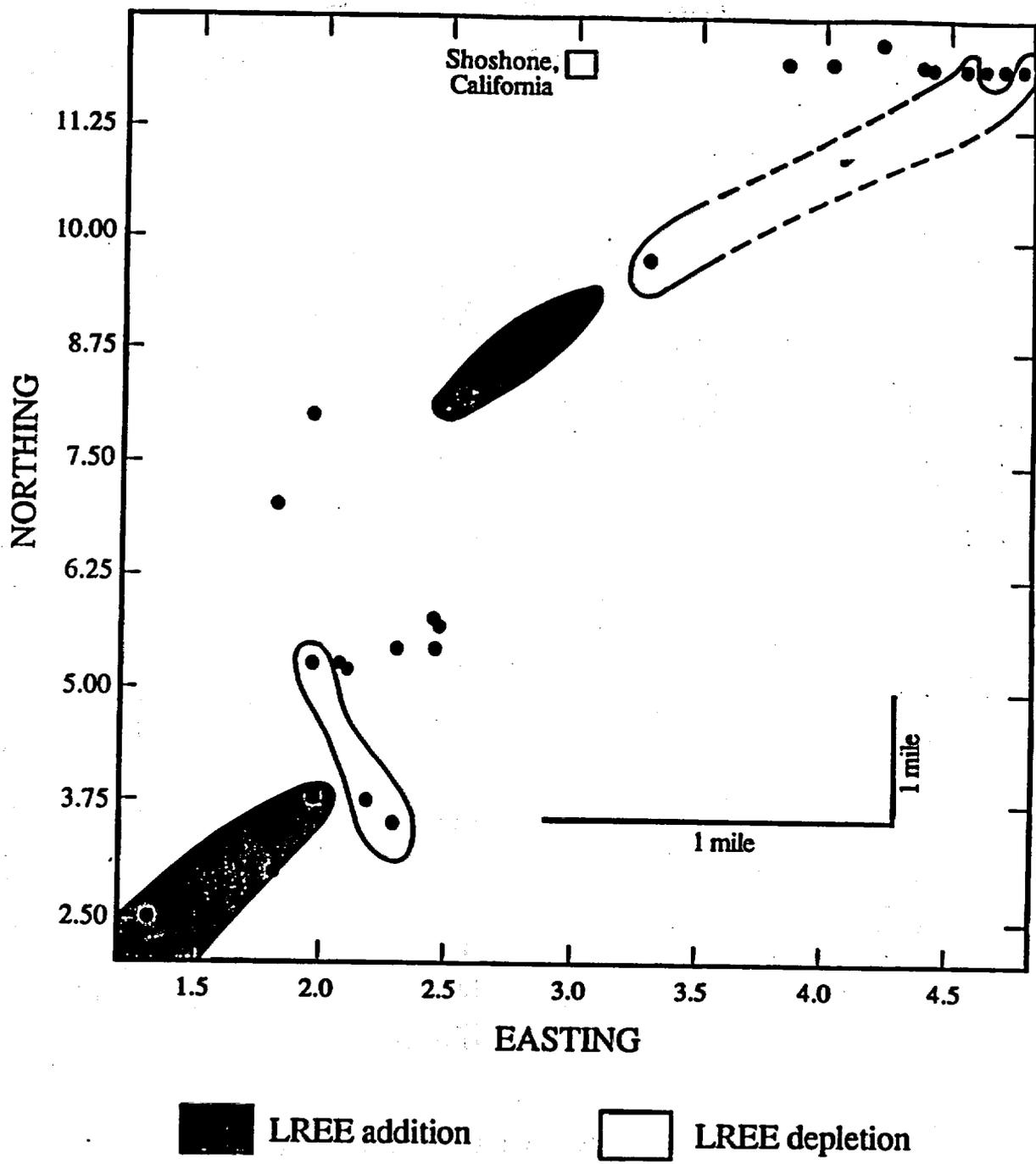
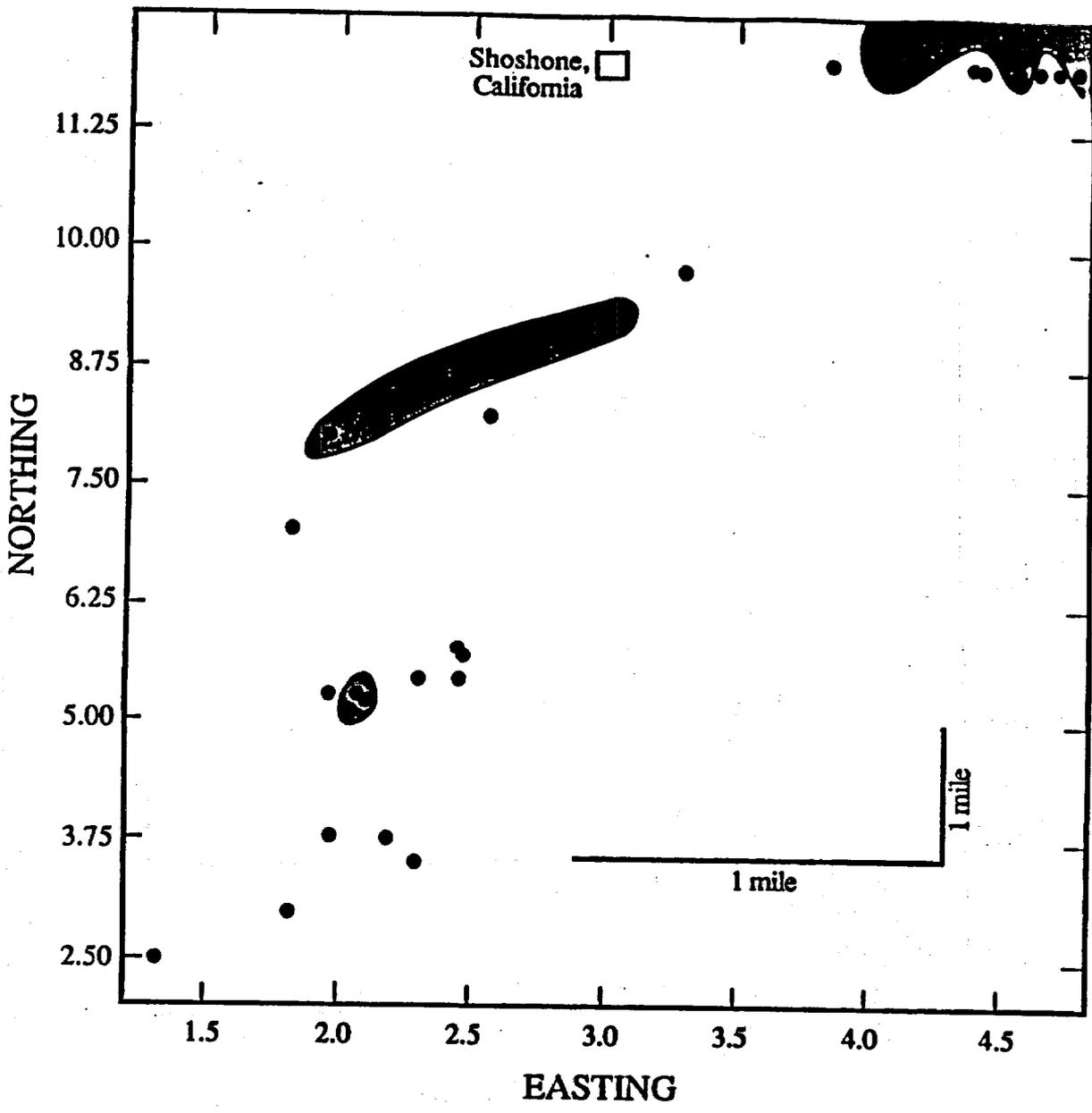


FIGURE 6



■ Moderate to intense calcite addition

FIGURE 7

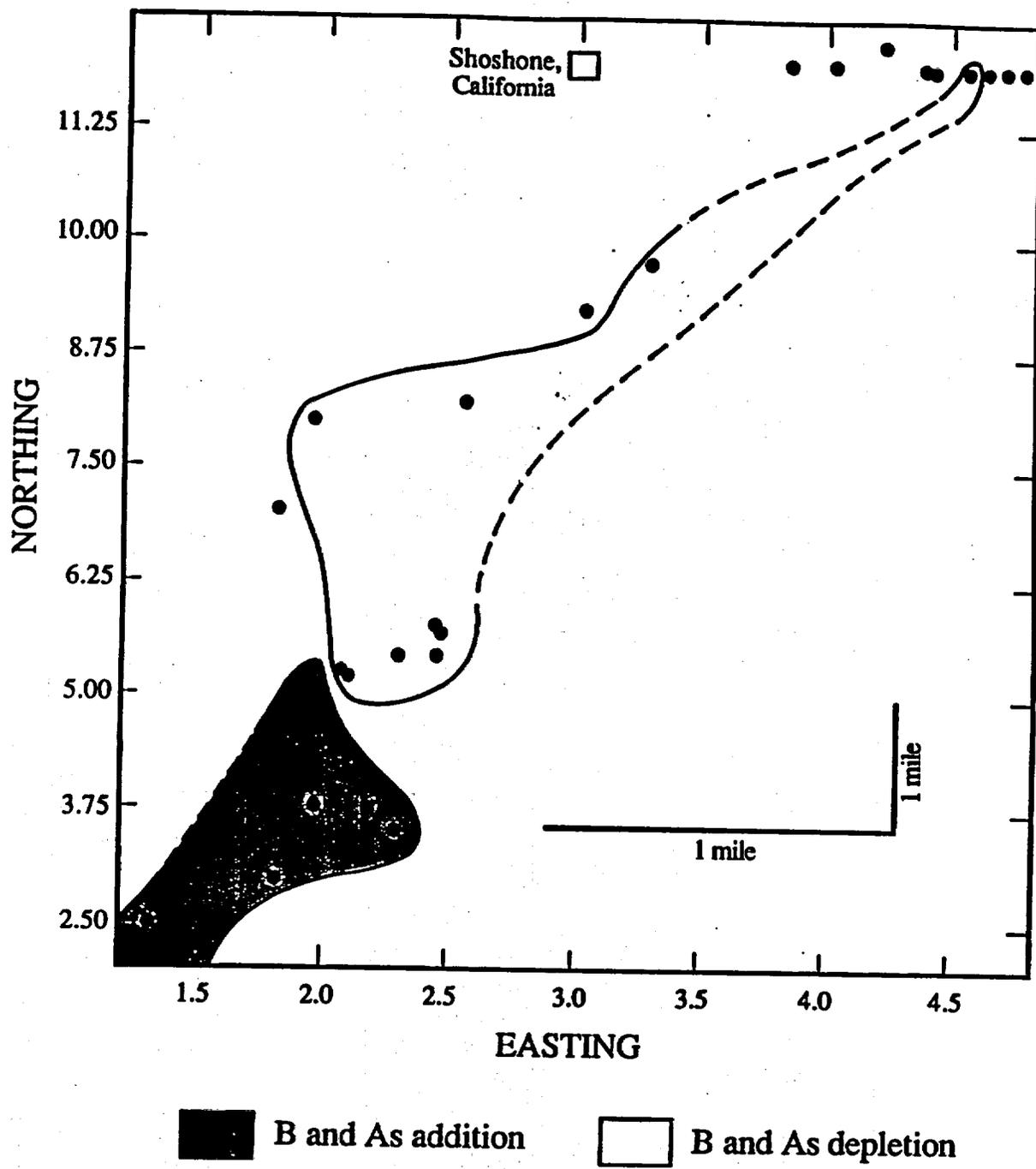


FIGURE 8

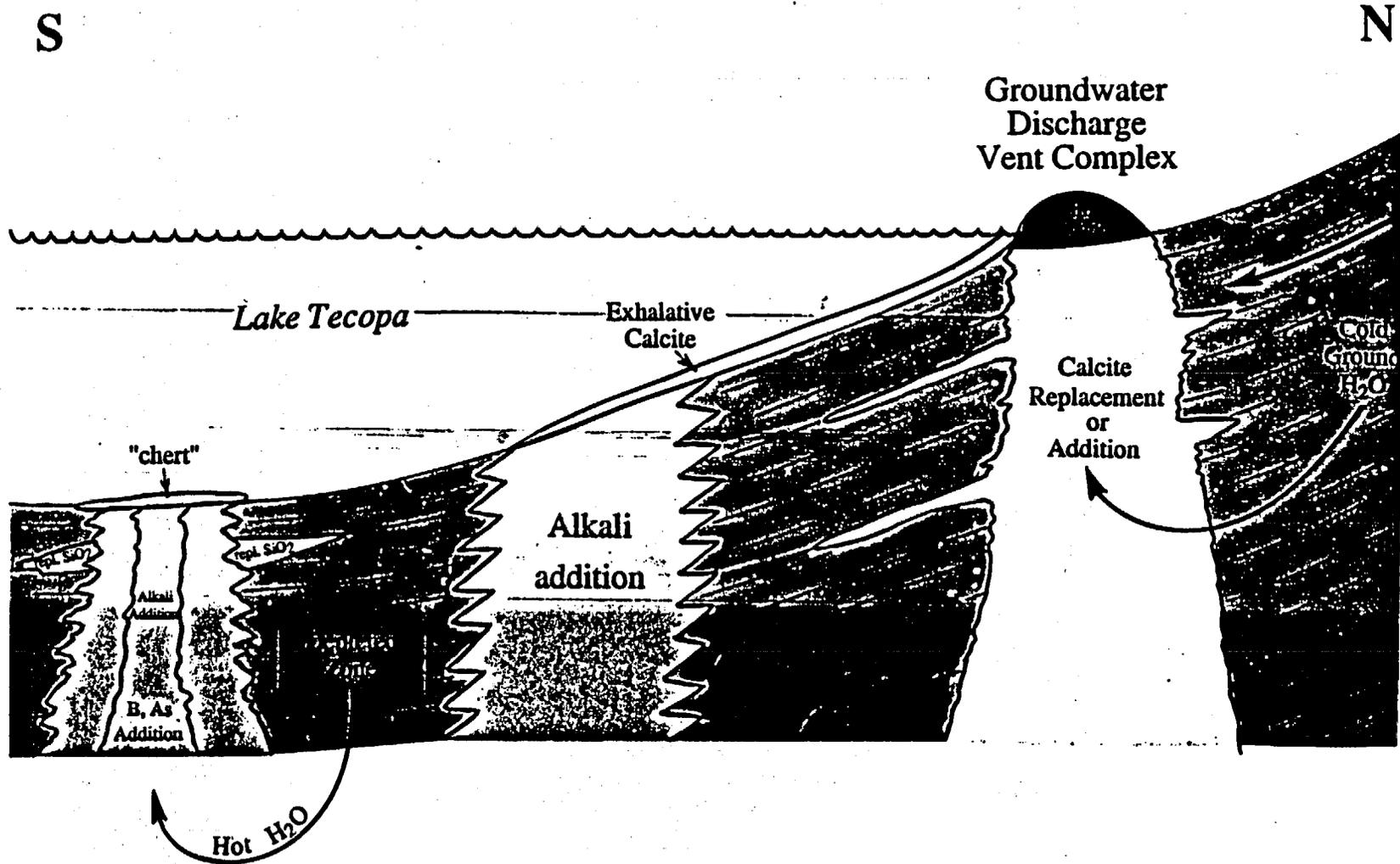


FIGURE 9

Highly schematic N-S cross section through Lake Tecopa at the time of Bishop Ash Emplacement. Potential exhalative processes producing "chert" and or calcite would occur immediately after deposition of the ash. Alternative and diagenetic changes could form any time after deposition.

Magnetic stratigraphy of ash-flow sheets at Yucca Mountain, Nevada

C.M. Schlinger

Department of Geology and Geophysics, University of Utah, Salt Lake City, Utah, USA

ABSTRACT: Ash-flow sheets are widely distributed in the geological record, both spatially and temporally. A variety of engineering studies of these volcanic rocks can take advantage of borehole measurements of magnetic susceptibility for stratigraphic correlation and control in faulted terrain. The magnetic 'stratigraphy' of ash-flow sheets is especially useful because the cooling of ash-flow sheets has a profound impact on rock magnetization, which can be readily observed by measurement of magnetic susceptibility and remanent magnetization. As part of a larger study we have obtained magnetic susceptibility profiles for portions of the Tiva Canyon and Topopah Spring Members of the Paintbrush Tuff using a hand-held susceptibility meter. The results provide a calibration of susceptibility to known geology and underscore the feasibility of the proposed borehole method. The susceptibility measurements were located spatially using an electronic theodolite and electronic distance meter. Maxima and minima in susceptibility measured along the profiles at Yucca Mountain, Nevada, are observed to be reliable stratigraphic markers within the Tiva Canyon and Topopah Spring Members of the Paintbrush tuff. The minima and maxima exist over the 8 km of section examined. Maxima in susceptibility correspond either to magnetic Fe-oxide precipitates that nucleated and grew in volcanic glass subsequent to eruption, or to an abundance of magnetic Fe-Ti oxide phenocrysts. Minima in susceptibility are indicative of: precipitates that grew too large to have high susceptibility; alteration of magnetic Fe-Ti oxide phenocrysts (or precipitates) to weakly magnetic or nonmagnetic phases; or an absence of magnetic minerals altogether. The size and mineralogical variations of precipitated Fe-oxide in volcanic glass of outcrop samples, which have been established using both the transmission electron microscope and the petrographic microscope, are consistent with variations in susceptibility measured at the outcrop. Susceptibility variations in these rocks are readily detectable with borehole instruments, although existing instrumentation could benefit from improvements.

INTRODUCTION

Magnetic susceptibility is a material property that has been used in numerous instances to outline geological variations in outcrop and borehole environments, where petrologic or mineralogic changes can be related to fluctuations in the amount, size and mineralogy of magnetic minerals. Often the applications have been economic (Glenn and Nelson, 1979; Hood et al., 1979), however, a variety of other investigations have taken advantage of susceptibility measurements (e.g., Hearst and Nelson, 1985; Rosenbaum and Snyder, 1985; Thompson and Oldfield, 1986; Balch et al., in press). In addition, engineering and geotechnical problems commonly involve layered soil and rock materials that may be suitable for study and characterization by means of magnetic susceptibility measurements. Examples of such layered media would be ash-flow tuffs at Yucca Mountain, Nevada, in the Basin and Range Province of the western United States.

Yucca Mountain is the proposed site of a national nuclear waste repository; consequently the region has been the subject of numerous engineering and scientific investigations. Past, ongoing and future studies of this site can take advantage of whatever stratigraphic and structural control might be established there. The geology consists of normal-faulted ash-flow tuff layers, or ash-flow sheets as they are known, which have been mapped and sampled at the outcrop and by means of boreholes. For borehole stu-

dies, the identification of units and determining their lateral extent and structural disruption by faulting can possibly be accomplished by means of painstaking geochemical and petrographic studies. However, in lieu of rapid methods for geochemical and petrographic analyses, an easier, less-time-consuming and less-expensive geophysical method is desirable. Even in situations where such a geophysical investigation cannot supplant other studies, the results of such a study may be of use for unequivocal interpretation of data from analytical investigations.

Recent magnetic studies of volcanic glasses, including samples from boreholes at Yucca Mountain (Schlinger et al., 1988a, 1988b), have shown that magnetic susceptibility variations in volcanic glasses are often a consequence of Fe-oxide that nucleated and grew (precipitated) in volcanic glass at high-temperatures, subsequent to eruption. These results suggest that cooling history-dependent variations should exist in most ash-flow sheets. Furthermore, it is known that the phenocryst content of ash-flow sheets varies with stratigraphic position and this variation can also influence susceptibility. Early work on the magnetic properties of U.S. Geological Survey (U.S.G.S.) drill core from Yucca Mountain (Rosenbaum and Snyder, 1983; Rosenbaum and Spengler, 1986; data also presented by Schlinger et al., 1988) provided good evidence for the existence of magnetization (including susceptibility) variations. Typically the spatial sampling interval for these studies was large, on the order of 3 meters, which raised questions about relatively

abrupt variations in susceptibility, which would not have been detected with this relatively large measurement spacing.

A high-spatial-resolution record of susceptibility variations was deemed essential for studies of magnetic precipitates in ash-flow sheets, and as part of ongoing research we measured magnetic susceptibility along 5 profiles through exposed sections of the two most voluminous ash-flow sheets of the Paintbrush Tuff at Yucca Mountain. The profile data give us a good indication that quantitative and qualitative variations in susceptibility, which are observed moving vertically through the section, exist over a large strike distance (Schlinger and Rosenbaum, 1988). At the same time, we have sought to understand the geological origin and significance of these variations with position in the section (Schlinger et al., 1988a, manuscript in preparation).

In this paper the susceptibility data are presented and discussed. The vertical variations and the lateral continuity of these variations, observed at the outcrop, offer convincing evidence in favor of susceptibility measurements for assessments of lateral extent and structure of ash-flow sheets, especially where they are hidden in the subsurface and can be accessed only by means of boreholes.

GEOLOGICAL SETTING

Miocene-aged volcanic rocks of the Paintbrush Tuff are exposed at Yucca Mountain, a volcanic plateau in Nye County, Nevada (Figure 1). The geology of the area has been discussed by Lipman et al. (1966), Byers et al. (1976), and Christiansen et al. (1977). Lithologic descriptions of the outcrop at Yucca Mountain have been given by Scott et al. (1983). Scott and Castellanos (1984) discussed the lithologies as encountered in U.S.G.S. boreholes, and a geological map of the area has been published by Scott and Bonk (1984). The source of the Paintbrush Tuff is believed to have been the Claim Canyon cauldron (outline shown on Figure 1). Two compositionally-zoned compound-cooling ash-flow tuffs, the Tiva Canyon Member and the Topopah

Spring Member, make up the majority of the thickness of the Paintbrush Tuff (about 100 m and 300 m, respectively). In the vicinity of Yucca Mountain the volcanic layers are sub-horizontal in attitude, with dips typically less than 15° (Scott and Castellanos 1984).

SUSCEPTIBILITY MEASUREMENTS

During the Fall of 1987 we gained access to Yucca Mountain through Bureau of Land Management property. Magnetic susceptibility was measured at the outcrop, along profiles that took us up and down the west flank of Yucca Mountain, through the section exposed there. Measurements were obtained along 5 distinct profiles. These profiles were spaced nonuniformly over approximately 8 km (between VABM 'Mile' and VABM 'Iron' on the U.S.G.S. 7.5 minute quadrangle map "Busted Butte, Nevada"). Due to a lack of outcrop exposure, detailed sampling of susceptibility with measurement spacings as small as 10 cm was restricted to the lower part of the Tiva Canyon Member, the top of the Topopah Spring Member, and the intervening Bedded Tuff. We used an EDA K-2 hand-held susceptibility meter for our work. This meter has a resolution of 10^{-3} c.g.s. dimensionless Gaussian units.

In order to spatially locate the susceptibility measurements, selected measurement points along these 5 profiles were periodically surveyed using an electronic theodolite with an electronic distance meter. This surveying effort was designed to maintain both absolute and relative positioning (tied to USGS brass cap bench mark and VABM control points, and surveyed neutron-log and water-table borehole locations). The locations of measurements made between the surveyed points were linearly interpolated. In anticipation of this, efforts were made during the course of the survey to obtain equal spacing of measurements between surveyed measurement points. All measurements points were assigned an x-y-z location in the Nevada State Plane Coordinate system. The 5 profile locations in this coordinate system are given in Figure 2.

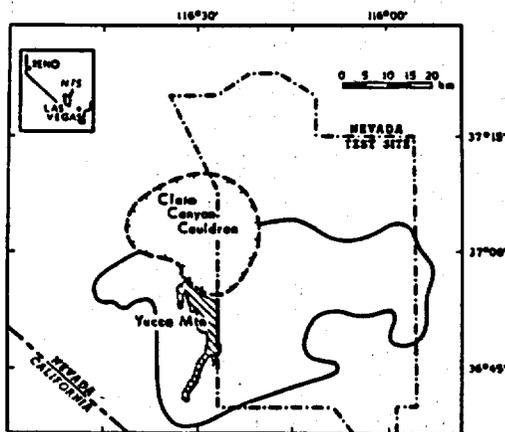


Figure 1. Location map for Yucca Mountain, Nevada. The approximate lateral extent of the Paintbrush Tuff is indicated by the solid line. After Rosenbaum (1986).

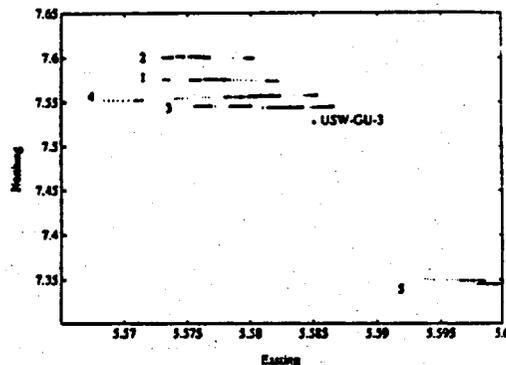


Figure 2. Location map for magnetic susceptibility profiles at Yucca Mountain. The location of U.S.G.S. drill hole USW-GU-3 is indicated. All distances (northings and eastings) are in units of 10^3 feet. The horizontal scale on this map is exaggerated by a factor of 10, relative to the vertical scale.

The magnetic sus...
five profiles is show...
ties correspond to...
the Bedded Tuff...
below the Tiva Ca...
Spring Member. Ne...
on profiles in Figur...
a horizon that has...
member. A similar

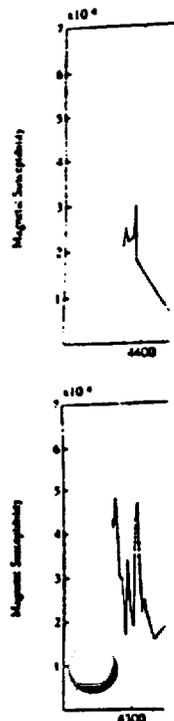


Figure 3. Magnetic susceptibility profiles for the Tiva Canyon Member, converted to SI units.

thickness of
spectively).
: layers are
as than 15'

area Moun-
erty. Mag-
rop, along
k of Yucca
asurements
rofiles were
n (between
7.5 minute
o a lack of
ibility with
restricted to
top of the
dded Tuff.
eter for our
dimension-

y measure-
: 5 profiles
theodolite
effort was
positioning
3M control
le borehole
k between
in anticipa-
of the sur-
tween sur-
oints were
nc Coordin-
inate sys-

ty profiles
drill hole
and east-
le on this
be vertical

The magnetic susceptibility (c.g.s.) of outcrop along these five profiles is shown in Figure 3. The lowest susceptibilities correspond to measurements in the pumice-rich unit of the Bedded Tuff (bt on profiles in Figure 3) which lies below the Tiva Canyon Member and above the Topopah Spring Member. Near the base (labeled bz, for basal zone, on profiles in Figure 3) of the Tiva Canyon Member there is a horizon that has the highest susceptibility within the member. A similar susceptibility maximum is found near

the top of the Topopah Spring Member, within a thin black vitrophyre (i.e., a stratum that is largely glass, formed by high-temperature 'welding' of what was once mostly glass fragments and pumice) that is on the order of a meter or less in thickness. This maximum is labeled c, for caprock, on profiles in Figure 3. Wherever the susceptibility of the columnar zone of the Tiva Canyon Member was measured, it was uniformly about 2×10^{-4} . This zone is a thick basal vitrophyre and is labeled as in Figure 3. Note that the sus-

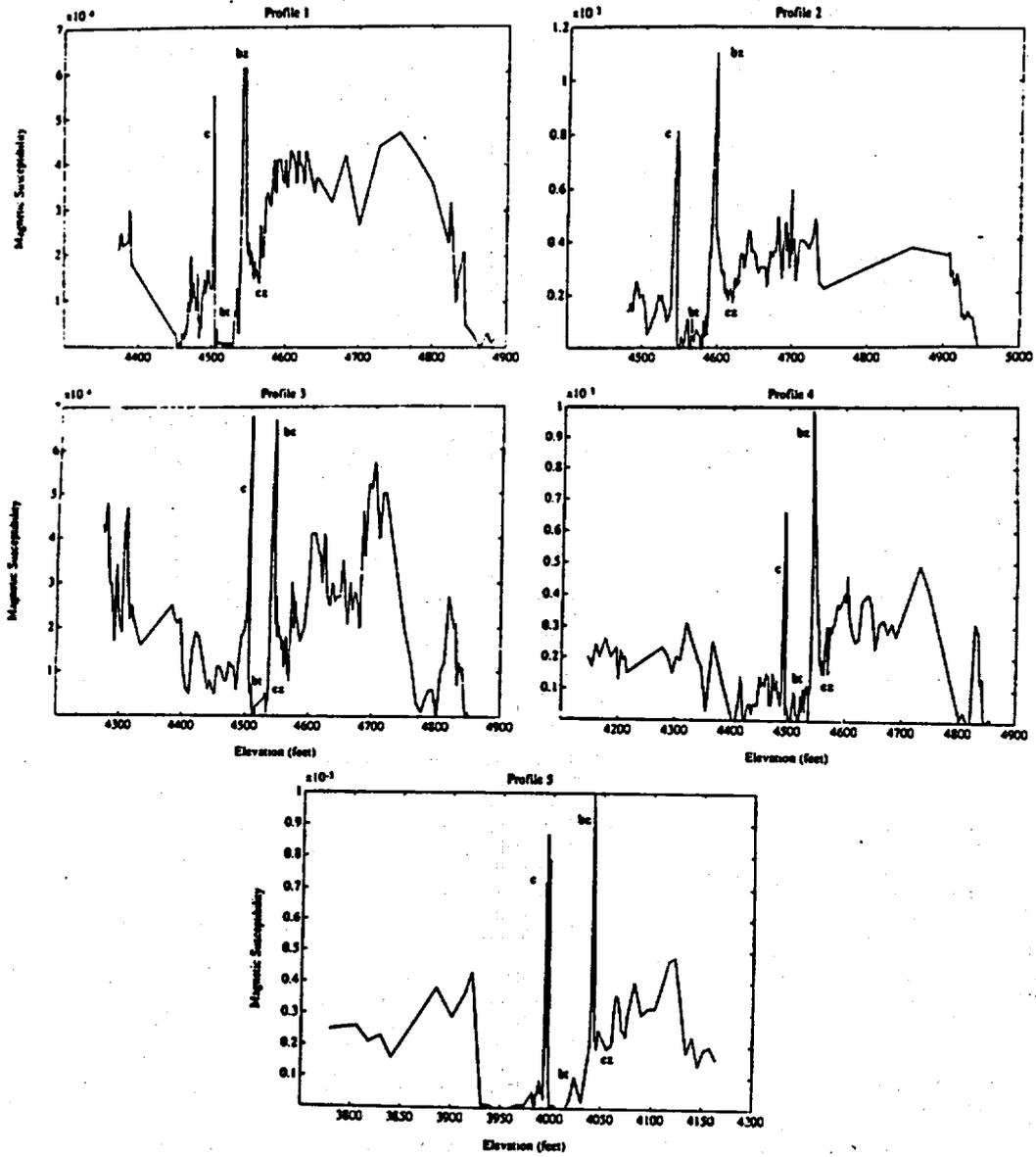


Figure 3. Magnetic susceptibility along profiles 1 to 5. bt is Bedded Tuff, cz is columnar zone and bz is basal zone (Tiva Canyon Member), c is caprock portion of Topopah Spring Member. Susceptibilities are given in c.g.s. dimensionless units; to convert to SI units multiply c.g.s. values by 4π .

ceptibility maxima and minima can be observed, in both a quantitative and qualitative sense, on each of the 5 profiles, which sample the two members of the Paintbrush Tuff over a strike distance of 8 km. There is some structure in the narrow susceptibility peaks on these profiles that needs to be explained. The relatively broad nature of the peak labeled 'c' on Profile 1 is a result of a lateral movement along the side of Yucca Mountain during susceptibility sampling (necessitated by intermittent outcrop exposure). Since the sheets have some tilt we ended up with a duplicate measurement of the high susceptibility horizon at a different elevation after a lateral move. A similar lateral move accounts for the apparent structure in the peak labeled 'c' on Profile 5.

DISCUSSION

Interpretation of susceptibility maxima and minima

The origins of the magnetic susceptibility variations that can be seen in the outcrop profiles shown in Figure 3 deserve some attention. The susceptibility maximum near the top of the Topopah Spring Member ('c' in Figure 3) is indicative of a large modal abundance of what appears to be titanomagnetite phenocrysts (Figure 4). Above and below

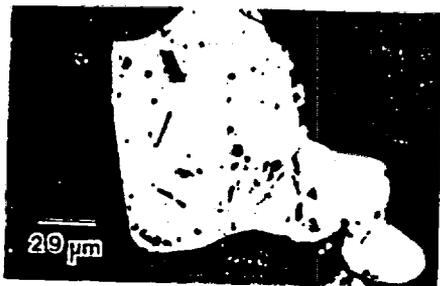


Figure 4. Reflected light photomicrograph of a titanomagnetite phenocryst in a sample with high magnetic susceptibility from near the top of the Topopah Spring Member.

this horizon, which is a thin black vitrophyre, the titanomagnetite has been altered to Fe-Ti oxide intergrowths that are only weakly magnetic. Incipient alteration is evident as light colored regions in this crystal, which presumably are hematite (hematite after magnetite). The susceptibility maximum at the base of the Tiva Canyon Member ('bz' in Figure 3) exists due to the presence of magnetic Fe-oxide precipitates within volcanic glass, which nucleated and grew at high-temperature, subsequent to emplacement of this member (Schlinger et al., 1988a, manuscript in preparation). At the level of this maximum these precipitates are only a few hundred Angstroms long. High susceptibilities at this crystal size are a consequence of superparamagnetic behavior of single domains. Above this horizon the susceptibility drops abruptly, which reflects the fact that the precipitates grew too large to have high susceptibility; instead they carry intense remanent magnetization. A representative transmission electron microscope image of representative remanence-carrying precipitates is shown in Figure 5. In

this particular image, one can see long thin crystals of cubic Fe-oxide (magnetite/maghemite) that nucleated on a yet longer microcrystal of what is probably a pyroxene. The aggregate resides in a matrix of volcanic glass.

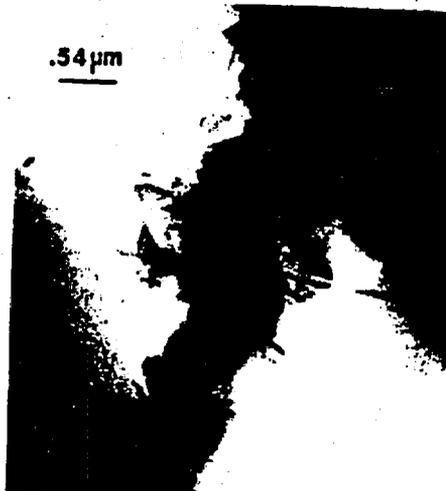


Figure 5. Transmission electron microscope image of precipitated Fe-oxide microcrystals in glass from the basal vitrophyre (columnar zone) of the Tiva Canyon Member.

The low susceptibility of the Bedded Tuff ('bt' in Figure 3) is indicative of an absence of precipitates and an absence of phenocrystic titanomagnetite. We have not had an opportunity to explore other less-pronounced susceptibility variations at other stratigraphic levels that also might prove useful as marker horizons.

Application to borehole susceptibility investigations

From our observations of susceptibility variations with vertical position in ash-flow sheets, it is clear that distinctive and laterally-persistent susceptibility marker horizons exist in ash-flow sheets of the Paintbrush tuff. This is because Fe-oxide mineralogy, amounts, and grain size vary so markedly in ash-flow sheets of this tuff. This is probably true for other ash-flow sheets as well. Since magnetic susceptibility is a physical property that is easily measured in the borehole, it can be useful for assessments of lateral variations in the subsurface, which may come about due to faulting, inhomogeneous deposition, or alteration of these ash-flow sheets. Past geological investigations at Yucca Mountain have in numerous instances focussed on boreholes and drill core. With these new results on susceptibility variations in hand, the application of borehole susceptibility measurements to questions of lateral extent and the subsurface structure of these sheets at this site can be explored.

Assessing the lateral extent of a given ash-flow sheet in a limited geographic area may be relatively straightforward, since one is not especially concerned with the position in space where a unit is found, provided that it exists. This is

a rudimentary form of chooses to consider a lateral position in deposition must tionally, remanent magnetic graphic correlation of ash (1985). However, its a numerous oriented sample remanent magnetic measuring these remanent remanent magnetization interpretation of the relevant assumptions that may be that a given sheet is a throughout). Plastic deformation (baum, 1986) and tectonic the interpretation of remanent Assessing lateral extent prevents most of these ability is a scalar quantity alone.

Determining whether or ash-flow sheets is a much absolute positions of subspace, combined with any dip), must be quantified in units. Furthermore, a pre-existing topography, a fully be constrained by i tion, which might be established. Additionally, other seismic reflection profile, for volcanic lithologies (problem with an elusive as

Finally, from geological known that sheet thickness produces lateral variations will probably be manifest variations in susceptibility netic precipitates, which the interpretation process.

For magnetic susceptibility the Paintbrush Tuff, a meters are commercially of a susceptibility log made the discrete and non-uniform of outcrop). General channel diameter sondes (40 mm vertical distance of 20 cm of -5 to 20×10^{-6} c.g.s. not favor faithful resolution layers of relatively low or the high susceptibility layer Member). To alleviate this shortened, however, with this cannot be done without Hämäläinen, personal communication.

Thus, it seems that bore benefit from some modification response to this layers, Canyon Member, and perhaps turns out to be diagnostic runs the risk of taking amplitude signal and wavelengths and smaller interest may be hidden or less correlatable features in

ng thin crystals of cubic
at nucleated on a yet
ably a pyroxene. The
mic glass.



Microscopic image of precipitates from the basal vitrophyre of the Tiva Canyon Member.

Bedded Tuff ('b' in Figure 3) has precipitates and an absence of pyroxene. Susceptibility variations also might prove useful.

Investigations

Susceptibility variations with vertical distance that distinctive and marker horizons exist in the Paintbrush Tuff. This is because Fe-Ti oxide grain size vary so markedly that this is probably true for the magnetic susceptibility variations measured in the sections of lateral variations come about due to faulting and alteration of these ash-flow sheets at Yucca Mountain. Susceptibility variations on boreholes and on susceptibility variations on borehole susceptibility variations and the subsurface can be explored.

Given an ash-flow sheet in a relatively straightforward manner, the position in the field that it exists. This is

a rudimentary form of stratigraphic correlation. If one chooses to consider a large geographic area, lateral variations in deposition must be taken into consideration. Traditionally, remanent magnetization has been used for stratigraphic correlation of ash-flow tuffs (Hildreth and Mahood, 1985). However, its application requires the use of numerous oriented samples, due to directional dispersion of remanent magnetic moments, and magnetometers for measuring these remanent moments. Additionally, while remanent magnetization may be used for correlation, the interpretation of the relevant data is subject to a number of assumptions that may be difficult to justify (for example, that a given sheet is normally or reversely magnetized throughout). Plastic deformation during cooling (Rosenbaum, 1986) and tectonic rotation(s) can further complicate the interpretation of remanent magnetization directional data. Assessing lateral extent using magnetic susceptibility circumvents most of these problems simply because susceptibility is a scalar quantity that depends on petrologic history alone.

Determining whether or not faulting has occurred in these ash-flow sheets is a much different problem. In this case absolute positions of susceptibility maxima or minima in space, combined with any information on attitude (strike and dip), must be quantified in order to delimit structural discontinuities. Furthermore, since ash-flow sheets drape over pre-existing topography, a structural interpretation will hopefully be constrained by independent stratigraphic information, which might be established with drill cuttings or drill core. Additionally, other geophysical information, such as a seismic reflection profile, acquired in a manner appropriate for volcanic lithologies (which has often proven to be a problem with an elusive answer) may be of use.

Finally, from geological mapping of ash-flow sheets it is known that sheet thicknesses vary laterally, and this will produce lateral variations that reflect cooling history. These will probably be manifested as quantitative and qualitative variations in susceptibility maxima and minima due to magnetic precipitates, which must be taken into account during the interpretation process.

For magnetic susceptibility logging of formations such as the Paintbrush Tuff, a number of borehole susceptibility meters are commercially available. The continuous record of a susceptibility log makes it especially attractive (versus the discrete and non-uniform sampling obtained in this study of outcrop). General characteristics of all are: relatively thin diameter sondes (40 mm to 50 mm); sensing over a distance vertical distance of 20 cm to 40 cm; advertised resolutions of -5 to 20×10^{-6} e.g.s. units. These sonde geometries do not favor faithful resolution of thin -5 to 10 cm-thick layers of relatively low or high susceptibility material (e.g., the high susceptibility layer at the base of the Tiva Canyon Member). To alleviate this problem, sensing coils could be shortened, however, with other parameters remaining fixed this cannot be done without some loss of sensitivity (M.T. Hämäläinen, personal communication, 1988).

Thus, it seems that borehole susceptibility meters could benefit from some modifications that would improve their response to thin layers, which in the case of the Tiva Canyon Member, and possibly other lithologies elsewhere, turn out to be diagnostic marker horizons. Otherwise, one runs the risk of taking a short-spatial-wavelength high-amplitude signal and smearing it out towards longer wavelengths and smaller amplitudes. In this case signals of interest may be hidden amongst less easily interpretable or less correlatable features in the overall borehole susceptibil-

ity record. In other geological environments, including volcanic settings, thin diagnostic horizons might be characterized by low susceptibilities; faithful response to thin layers seems essential. An additional improvement would be thermal stabilization of the sonde, since temperature drift degrades the resolution of the instrument. However, one can make efforts to characterize drift effects, measure temperature in the sonde, and apply a correction (e.g., Balch et al., in press).

Within the Paintbrush Tuff we have found that the susceptibility maxima may be indicative of either relatively coarse-grained Fe-Ti oxide phenocrysts (the thin vitrophyre above the caprock of the Topopah Spring Member) or relatively fine-grained Fe-oxide precipitates in the basal zone of the Tiva Canyon Member. These maxima, similar in appearance to one another ('c' and 'bz' in Figure 3), could in all likelihood be distinguished from one another by measuring susceptibility at two (or more) frequencies. This would take advantage of the fact that the susceptibility of tiny superparamagnetic crystals (the precipitates in glass at the base of the Tiva Canyon Member) probably has a different frequency dependence than that of coarse-grained Fe-Ti oxide phenocrysts (Thompson and Oldfield, 1986). Variable-frequency susceptibility meters are available for laboratory work, however, to my knowledge, this option has not been incorporated into existing borehole instrumentation.

While borehole measurements of magnetic susceptibility at Yucca Mountain remain at this time only a future objective, we find that a geological calibration can be obtained by means of outcrop measurements; were no outcrop available, the calibration could be made using continuous drill core, or possibly with cuttings.

CONCLUSIONS

Over a strike distance of 8 km at Yucca Mountain, the Tiva Canyon and Topopah Spring members and the Bedded Tuff have a marked lateral uniformity in measured values of magnetic susceptibility, even though the thickness and outcrop appearance of the units may vary from place to place. Furthermore, the variations in susceptibility with vertical position in the geologic column persist laterally.

Spatial variations in physical properties, e.g., magnetic properties, can often be understood in terms of the geological history of a given formation. This investigation of outcrop susceptibility has demonstrated the existence of magnetic marker horizons in ash-flow sheets, which can be understood in terms of Fe-Ti oxide mineralogy and grain size. In the case of the ash-flow sheets of the Paintbrush Tuff, grain size and mineralogical variations, acquired mostly subsequent to emplacement, define the marker horizons that we see. A suitable calibration of physical property variations to mineralogy and petrology is essential before measurements of magnetic properties in boreholes can be interpreted in a constrained manner.

ACKNOWLEDGEMENTS

This research was supported by the State of Nevada Nuclear Waste Project Office under a Department of Energy grant from the Nuclear Waste Fund. We thank P. Eick, J.B. Hollis and R.J. Johnson for assistance in the field, and M. Morgenstein for logistical support and advice.

REFERENCES

- Balch, S.J., Morris, W.A., Blohm, D. and Thuma, B. Interpretation of borehole magnetic data for mineral exploration and lithological mapping. Transactions of the Annual Well Logging Symposium. Society of Professional Well Log Analysts, Denver, 1987.
- Byers, F.M., Carr, W.J., Orkild, P.P., Quinlivan, W.D. and Sargent, K.A. 1976. Volcanic suites and related cauldrons of Timber Mountain-Oasis Valley Caldera Complex, southern Nevada. U.S. Geological Survey Professional Paper 919.
- Christiansen, R.L., Lipman, P.W., Carr, W.J., Byers, F.M., Orkild, P.P. and Sargent, K.A. 1977. Timber Mountain-Oasis Valley caldera complex of southern Nevada. Geological Society of America Bulletin 88: 943-959.
- Glenn, W.E. and Nelson, P.H. 1979. Borehole logging techniques applied to base metal ore deposits. in Hood, P.J. (ed.), Geophysics and geochemistry in the search for metallic ores. Geological Survey of Canada Economic Geology Report 31: 273-294.
- Hearst, J.R. and Nelson, P.H. 1985. Well logging for physical properties. New York: McGraw Hill Book Co.
- Hildreth, W., and Mahood, G. 1985. Correlation of ash-flow tuffs. Geological Society of America Bulletin 96: 968-974.
- Hood, P.J., Holroy, M.T. and McGrath, P.H. 1979. Magnetic methods applied to base metal exploration. in Hood, P.J. (ed.), Geophysics and geochemistry in the search for metallic ores, Geological Survey of Canada Economic Geology Report 31: 77-104.
- Lipman, P.W., Christiansen, R.L., and O'Connor, J.T. 1966. A compositionally zoned ash-flow sheet in southern Nevada. U.S. Geological Survey Professional Paper 524-F: F1-F47.
- Rosenbaum, J.G. 1986. Paleomagnetic directional dispersion produced by plastic deformation in a thick Miocene welded tuff, southern Nevada: Implications for welding temperatures. Journal of Geophysical Research 91: 12817-12834.
- Rosenbaum, J.G. and Snyder, D.B. 1985. Preliminary interpretation of paleomagnetic and magnetic property data from drill holes USW G-1, G-2, GU-3, G-3, and VH-1 and surface localities in the vicinity of Yucca Mountain, Nye county, Nevada. U.S. Geological Survey Open-File Report 85-49.
- Rosenbaum, J.G. and Spengler, R.W. 1986. Variation in magnetic properties in thick sections of the Crater Flat tuff, southern Nevada (abs). EOS (Transactions of the American Geophysical Union) 67: 924.
- Schlinger, C.M. and Rosenbaum, J.G., 1988. TEM and magnetic study of ash-flow sheets from Yucca Mountain, Nevada. EOS (Transactions of the American Geophysical Union) 69: 1486-1487.
- Schlinger, C.M., Rosenbaum, J.G. and Veblen, D.R. 1988a. Fe-oxide microcrystals in welded tuff from southern Nevada: Origin of remanence carriers by precipitation in volcanic glass. Geology 16: 556-559.
- Schlinger, C.M., Griscom, D., Papaefthymiou, G., and Veblen, D.R. 1988b. The nature of magnetic single domains in volcanic glasses of the KBS tuff. Journal of Geophysical Research 93: 9137-9156.
- Scott, R.B. and Castellanos, M. 1984. Stratigraphic and structural relations of volcanic rocks in drill holes USW GU-3 and USW G-3, Yucca Mountain, Nye County, Nevada. U.S. Geological Survey Open File Report OFR-84-491.
- Scott, R.B. and Bonk, J. 1984. Preliminary geologic map of Yucca Mountain with geologic sections, Nye County, Nevada. U.S. Geological Survey Open File Report OFR-84-494.
- Scott, R.B., Spengler, R.W., Diehl, S., Lappin, A.R. and Chomack, M.P. 1983. Geologic character of tuffs in the unsaturated zone at Yucca Mountain, Southern Nevada. in Mercer, J.W., Rao, P.S.C. and Marine, L.W. (ed.), Role of the unsaturated zone in radioactive and hazardous waste disposal, Ann Arbor, Michigan: Ann Arbor Science Publishers.
- Thompson, R. and Oldfield, F. 1986. Environmental magnetism. London: Allen and Unwin.

Seismic
assessment
Alvin K.
Brigham

ABSTRACT
geologic
faulting
existing
mapping
located
refractive
more comp
Provo, UT
methods :

1 INTRO

The Wasatch
central
Idaho.
major
valleys
valley by
Wasatch
the fault
magn
the valley
mountain
these fault
future.
associated
major ca
Surface
occur al
(faults)
number o
expressi
subsurface
investig.
geophysic
and refr
electrom
methods
of one o
to incor
subsurface
inherent
an integr
geotechn

Geological Society of America, Abstracts with Program,
vol. 20, no. 7, 1988, p. A359.

(Paper presented in session: "Geochemistry VI:
Layered Silicates and Zeolites/Mineralogy/Crystallography II)

No 23744

**CESIUM UPTAKE BY CLINOPTILOLITE CRYSTALS: IMPLICATIONS TO THE
IMMOBILIZATION OF RADIONUCLIDES STORED AT YUCCA MOUNTAIN, NEVADA**

WOOD, Valerie J., HUBBARD, Mary S., and BURNS, Roger G.: Dept. of Earth, Atmos. and
Planet. Sci., Massachusetts Institute of Technology, Cambridge, MA 02139.

At the proposed repository for high-level nuclear waste at Yucca Mtn, densely welded tuff is overlaid by zeolitized vitric tuffs containing microcrystalline clinoptilolite and mordenite. These zeolites are assumed to be capable of immobilizing dissolved, long-lived radionuclides (e.g. ^{137}Cs and ^{135}Cs) should leakage occur. Euhedral clinoptilolite crystals with habits dominated by coffin-shaped (010) cleavage faces also line fractures throughout the repository, the most probable conduits for groundwater which may be of the sodium bicarbonate-type. To assess the efficiency of clinoptilolite for removing cesium from such groundwater, Cs-exchange experiments were performed on polished mounts of several specimens, using both 1 mm clumps of microcrystalline samples and single crystals oriented parallel to (010), (001), (100) and (101). Reactions at 60°C (simulating groundwater permeating the heat envelope of the repository) with CsCl solutions (1M, 0.01M and 0.001M, with and without NaHCO_3) were performed for 1 to 4 weeks in a shaking water bath. Cesium selectively exchanges with other cations in the order $\text{Na} > \text{K} > \text{Ca} > \text{Mg}$. Electron microprobe analyses of reacted surfaces reveal that microcrystalline clinoptilolite attains higher Cs concentrations in shorter time periods than do mounted single crystals, which are often compositionally zoned possibly due to stacking faults. The Cs is initially least in (010) faces, the one direction (parallel to the *b* axis) along which channels do not exist in the tetrahedral framework of the clinoptilolite structure. However, after a month the Cs contents of all mounted crystals are still inhomogeneous but approach those of microcrystalline samples. The uptake of Cs into all clinoptilolite samples diminishes with CsCl dilution (e.g. ~22 and ~6 wt. % Cs_2O for 1M and 0.001M CsCl, respectively, on (010) faces) and in the presence of dissolved Na^+ particularly when added as NaHCO_3 (e.g. a decrease to ~1.3 % Cs_2O for 0.001M CsCl + NaHCO_3). We conclude that clinoptilolite crystals dominated by large surface areas of (010) faces, either lining fractures or cemented in zeolitized vitric tuff, may be inefficient at mobilizing radiogenic Cs in NaHCO_3 -bearing fracture-flow groundwater when it permeates leaking fission products stored at Yucca Mtn.

(Second Draft)

CESIUM UPTAKE BY CLINOPTILOLITE CRYSTALS

VALERIE J. WOOD, MARY S. HUBBARD, AND ROGER G. BURNS

**Department of Earth, Atmospheric and Planetary Sciences,
Massachusetts Institute of Technology,
Cambridge, Massachusetts 02139.**

INTRODUCTION

Clinoptilolite is renowned for its desirable ion exchange properties, which have been investigated more intensely than those of any other natural zeolite (Vaughan, 1978). This zeolite, ideally $(\text{Na},\text{K},\text{Ca})_5 \cdot 6\text{Si}_{30}\text{Al}_6\text{O}_{72} \cdot 24\text{H}_2\text{O}$ and formed by the alteration of rhyolitic glasses in aqueous environments, is widely used for the treatment and disposal of industrial pollutants and hazardous materials (Mercer and Ames, 1978), including scavenging of ammonium ions from municipal waste streams and removal of radiogenic cesium from high-level nuclear waste. The occurrence of potentially highly sorptive clinoptilolite in zeolitic bedded tuffs at Yucca Mountain is one of the factors influencing the selection of this locality in Nevada adjacent to the Nuclear Test Site as the primary geological repository for the long-term storage and disposal of high-level radioactive waste (Vieth, 1984; U.S. Dept. of Energy, 1986).

The high cation-exchange selectivity of clinoptilolite for cesium, and to a lesser extent strontium, was demonstrated by Ames (1960, 1961, 1962a,b,c, 1963, 1964, 1965) and other investigators (Howery and Thomas, 1965; Chelishchev et al., 1974) in radioactive tracer experiments which involved measurements of radionuclides either absorbed by powdered zeolites in an exchange column or removed from spiked aqueous solutions emerging from the ion-exchange column. Little attention was paid in these experiments to the chemical composition and homogeneity of individual zeolite crystals involved in the cation exchange experiments. Euhedral clinoptilolite crystals occur along joints and fractures in densely welded tuffs throughout Yucca Mountain (Carlos, 1985), particularly in the vicinity of the proposed nuclear waste repository (Levy, 1984). Since these

clinoptilolite-bearing openings are the most likely conduits for groundwater flowing through the repository and may transport leakages of fission product buried there in the future, we undertook an electron microprobe study of the cesium uptake by single crystals of clinoptilolite and related zeolites in order to assess effects of crystallographic orientation on kinetics, cation selectivity, capacity and homogeneity of Cs-exchanged zeolites.

BACKGROUND

Cation Exchange Measurements.

The high selectivity and capacity of clinoptilolite for cesium were discovered by Ames (1959, 1960, 1961, 1962a,b,c; 1963, 1964, 1965). Most of Ames's measurements centered on clinoptilolite in a zeolitized vitric tuff from Hector, California, composed of microcrystalline lamellae (Mumpton and Ormsby, 1978) and 5-15% unaltered glass, quartz and feldspar impurities. He used aqueous salt solutions labelled initially with ^{137}Cs (Ames, 1960, 1961) and later with ^{134}Cs (Ames, 1962a,b,c; 1963, 1964, 1965), and measured concentrations of radiogenic Cs removed in shallow beds of clinoptilolite packed in an exchange column or in the spiked solutions emerging from the columns. Ames (1960) showed that particle sizes of cemented aggregates of the Hector clinoptilolite crystallites affected the Cs capacity, increasing significantly for clumps smaller than 1 mm. In the presence of competing cations, usually involving 1M salt solutions containing 0.01M CsCl, clinoptilolite was shown to have a high selectivity for Cs, leading to the well-known (Vaughan, 1978) replacement series $\text{Cs} > \text{K} > \text{Na} > \text{Li}$ and $\text{Ba} > \text{Sr} > \text{Ca} > \text{Mg}$. Cesium capacities increased with decreasing concentrations of CsCl, but were lowered by increasing

concentrations of NaCl. Changing the sodium salt from chloride to SO_4^{2-} or NO_3^- did not influence the Cs capacity (Ames, 1960), but it was suggested later (Ames, 1964) that dissolved carbonates might influence cation exchange equilibria. Reactions performed at elevated temperatures decreased the Cs capacity, the concentration exchanged into clinoptilolite dropping by about one-third between 25°C and 60°C. Kinetic measurements of diffusion coefficients (Ames, 1962a,b) showed that the efficiency of Cs to exchange into clinoptilolite increased with temperature, decreased with dilution, and varied inversely with particle size. Ames (1963) suggested that zeolitic altered tuffa, being cemented aggregates of crystallites that rarely exceeded a few microns in diameter, would require a much shorter equilibration time than more coarsely crystalline zeolite assemblages. The Cs capacity of clinoptilolite was found (Ames, 1964) to be influenced by composition differences, being smaller in more the more silicic Hector clinoptilolite than in more calcic clinoptilolite from the John Day formation having a lower Si/Al ratio.

Crystal Structure Determinations.

Clinoptilolite and heulandite are isostructural and have the basic zeolite structure consisting of a three-dimensional framework silicate in which all four oxygens of individual $(\text{Si,Al})\text{O}_4$ tetrahedra are mutually shared to form secondary rings of corner-sharing tetrahedra (Gottardi and Galli, 1987). The different linkages of these secondary ring systems define different zeolite groups. The clinoptilolite and heulandite structures (Merkle and Slaughter, 1968; Bartl, 1973; Alberti, 1972,1975; Koyama and Takeuchi, 1977) contain complex 4- and 5-ring systems arranged in a sheet-like array parallel to (010) connected by relatively few oxygen

bridges, with the result that clinoptilolite crystals display characteristic platy or lamellar habits and basal (010) cleavage. Linkages between the tetrahedral ring systems along the b axis, as well as the a axis, define cages which are open and form channels through the clinoptilolite structure. The channel systems in clinoptilolite consist of one set parallel to the a axis formed by 8 tetrahedra rings with free-aperture dimensions $4.0 \times 5.5 \text{ \AA}$ (designated as the C channels by Koyama and Takeuchi, 1977) and two sets parallel to the c axis formed by 10 and 8 rings (the A and B channels, respectively) with corresponding free apertures of $4.4 \times 7.2 \text{ \AA}$ and $4.4 \times 4.4 \text{ \AA}$. It is important to note that no channels exist along the b axis in clinoptilolite and heulandite.

Cations and water molecules are located in specific sites along the channels. In heulandite there are two cation sites, $M(1)$ and $M(2)$, each in one of the two main channels, A and B , respectively, parallel to the c axis. Both are coordinated to water molecules in the channels and to framework oxygens on one side only of the tetrahedral rings. Calcium alone occupies the $M(2)$ site, and monovalent (Na) cations, when present, occur in $M(1)$ sites with Ca (Gottardi and Galli, 1987). The same two sites also occur in clinoptilolite, again with relative enrichments of Na and Ca in the $M(1)$ and $M(2)$ sites, respectively, in specimens from two localities studied by Koyama and Takeuchi, 1977), comprising a clinoptilolite from Agoura, California which contained higher K and lower Ca contents than crystals from the other locality in Kuruma, Japan. The $M(1)$ site located in channel A is coordinated by two framework oxygens and five water molecules, giving for the coordination polyhedron an average $M(1)$ -oxygen distance of 2.69 \AA (range 2.32 - 2.85 \AA) for the Kuruma clinoptilolite and 2.75 \AA for the Agoura specimen. The $M(2)$ site located in channel B has neighbors

consisting of three framework oxygens and five water molecules with average $M(2)$ -oxygen distances of 2.58 Å (Kuruma, range 2.38-2.75 Å; Agoura, average 2.57 Å). The $M(3)$ site is located in the C channels parallel to the a axis and is coordinated by six framework oxygens and three water molecules, giving a mean $M(3)$ -oxygen distance of 3.06 Å (Kuruma, range 2.71-3.20 Å; Agoura, average 3.05 Å). The clinoptilolite $M(3)$ site is occupied preferentially by K, which is believed to be responsible for the increased thermal stability of clinoptilolite relative to heulandite. A fourth site, $M(4)$ located in the A channels, is coordinated by six water molecules, has an average $M(4)$ -oxygen distance of 2.03 Å (Kuruma, range 1.59-2.71 Å; Agoura, average 2.09 Å), and is occupied by Mg. Each of the four cation sites is incompletely filled and generally have <50% cation occupancies (Gottardi, 1978). Some of the paired occupancies are forbidden by the close proximity of the cations to one another or to water molecules located in nearby structural positions (Koyama and Takeuchi, 1977).

Water molecules, which may occupy seven distinct positions in the channels, fall into two categories. The first category consists of those water molecules which have a maximum occupancy regardless of changes of cation composition, and include $W(3)$ and $W(4)$ located in the C channel tightly bonded to cations in $M(2)$ or $M(3)$ positions. The second category comprises water molecules with variable and low occupancies, including $W(5)$ and $W(6)$ associated with cations in $M(1)$ and $M(4)$ positions, $W(2)$ associated with $M(1)$ and $M(3)$ cations, $W(1)$ bonded only to $M(1)$, and a poorly defined $W(7)$ water position associated with $M(4)$ cations. The vulnerability of clinoptilolites to dehydration at moderate temperatures (Bish, 1984) may reflect diminished water occupancies of all but the $W(3)$

and W(4) positions. Conversely, prolonged soaking of clinoptilolites in some aqueous salt solutions could induce high populations of the water positions in the crystal structure.

Geochemical Constraints.

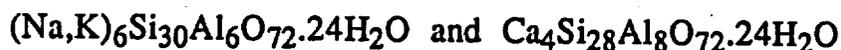
Groundwater flowing through volcanic deposits such as those at Yucca Mountain contains dissolved constituents which have been leached from the bedded vitric, devitrified and welded ash-flow tuffs. Concentrations of Na^+ , HCO_3^- and Cl^- ions and dissolved SiO_2 , reported to lie the range 0.001-0.002 M, are generally an order of magnitude higher than K^+ , Ca^{2+} , Mg^{2+} , SO_4^{2-} , F^- , etc. (White et al., 1980). Groundwater compositions vary with depth and are modified by passage through zeolitized tuffs, with the result that fracture-flow water is generally more HCO_3^- -rich than interstitial water containing higher Cl^- concentrations (White et al., 1980). The widely used reference groundwater used in laboratory experiments and geochemical modelling studies relevant to the repository horizon at Yucca Mountain is from well J-13 in the near-by Nevada Nuclear Test site and is sodium bicarbonate-type fracture-flow groundwater (Bish et al., 1984; Delany, 1985; Moore et al., 1986).. Therefore, our cesium exchange experiments were conducted in NaHCO_3^- or NaCl -bearing solutions.

Heat production during radioactive decay of fission products will elevate the temperature of volcanic rocks surrounding the proposed repository at Yucca Mountain, so that permeating groundwater will be heated perhaps to temperatures exceeding 100°C (Smyth, 1982). To simulate effects of elevated temperatures, we conducted our the majority of our cesium exchange measurements at 60°C but carried out some reactions at 80°C .

EXPERIMENTAL DETAILS.

Zeolite Specimens.

Clinoptilolite and heulandite are isostructural, and a solid-solution series appears to exist (Boles, 1972) between the ideal compositions



clinoptilolite

heulandite

Three criteria have been proposed to distinguish clinoptilolites from heulandites. The zeolite is named clinoptilolite when: (i) $(\text{Na} + \text{K}) > \text{Ca}$ (Mason and Sand, 1960); (ii) the Si/Al ratio exceeds 4 (Boles, 1972); and (iii) the crystal structure survives (i.e. the x-ray pattern is unchanged) after overnight heating at 450 C (Mumpton, 1960). Conversely, heulandites are defined by $(\text{Ca} + \text{Sr} + \text{Ba}) > (\text{Na} + \text{K})$, $\text{Si}/\text{Al} < 4$, and thermal decomposition above 450 C. Since microprobe analyses of clinoptilolites from Yucca Mountain exhibit wide ranges of Na, K, Ca (and Mg) and Si-Al contents (Broxton *et al.*, 1986, 1987), it was deemed desirable to study a variety of clinoptilolite-heulandite specimens. Compositions and sources of the zeolites studied here are summarized in Table 1.

Microcrystalline clinoptilolite from Hector, California, was one of the zeolites used by Ames (1960, 1961, 1962a,b,c, 1963, 1964) in early cation exchange experiments. Later, Ames, (1964, 1965) used samples of clinoptilolite from the John Day Formation, Oregon. The Hector clinoptilolite was reported (Ames *et al.*, 1958) to contain 5-15% impurities consisting of unaltered glass, quartz, feldspar and minor clay silicate and carbonate. Scanning electron microscope photographs of the Hector clinoptilolite (Mumpton and Ormsby, 1978) indicate that it consists of plates of euhedral, coffin-shaped crystals dominated by (010) faces only a

few microns in diameter. A similar morphology and crystallinity is displayed by the clinoptilolite from Castle Creek, Idaho (Mumpton and Ormsby, 1978) which is virtually 100% pure (Sheppard and Gude, 1983) and was the principal zeolite used by Bish (1984) in his thermal studies of cation-exchanged clinoptilolites. The more coarse-grained clinoptilolite from Agoura, California (Wise et al., 1969), also studied by Bish (1984), was used in crystal structure refinements by Alberti (1975) and Koyama and Takeuchi (1977). Unfortunately, only limited amounts of Agoura clinoptilolite crystals were available to us. Therefore, in our detailed investigations of oriented single crystals, we used samples of the clinoptilolite from Succor Creek, Malheur County, Oregon, which consists of euhedral crystals 1-2 mm in diameter. The microprobe data summarized in Table 2 indicate that the Succor Creek clinoptilolite with its rather high Ca content and low Si/Al ratio is close to the (arbitrary) classification boundary between clinoptilolite and heulandite; however, the Succor Creek clinoptilolite resembles compositions of some calcic clinoptilolites occurring in fractures throughout densely welded tuff at Yucca Mountain (Broxton *et al.*, 1986, 1987). Retention of its x-ray pattern after overnight heating at 450 C established the identity of the Succor Creek specimen, *sensu stricto*, as clinoptilolite. In addition to these four clinoptilolites, large single crystals of an Icelandic heulandite were also employed in some cesium exchange experiments, as well as an euhedral analcite from Lake Superior.

Mounted Zeolites.

Polished mounts were prepared of small pieces of the microcrystalline Hector and Castle Creek clinoptilolites and of oriented single crystals of the Agoura and Succor Creek clinoptilolites, Icelandic heulandite and the

analcime. The samples were encapsulated in cold-setting epoxy cement in small brass cylinders. The characteristic euhedral coffin-shaped habit of the Icelandic heulandite, as well as the Succor Creek clinoptilolite, enabled individual crystals to be mounted on their (010), (100), (101), and (001) faces. Once orientation effects in cesium exchange reactions had been established, most of the subsequent experiments were carried out using crystals mounted on (010) faces, since these have the largest surface areas and are more easily manipulated, particularly for the Succor Creek clinoptilolite. The specimens were polished, carbon-coated, and analysed by electron microprobe before carrying out cation-exchange reactions.

Microprobe Analyses

Chemical compositions of the zeolites were determined using a four-spectrometer JEOL Superprobe with full on-line computerized matrix correction and data reduction procedures. Operating beam currents ranged were 10 KeV and 5 and 10 nA, with counting times of 20 seconds for all elements except Na, which was analysed first and counted for only 10 seconds in order to minimize loss through volatilization. Loss of Na and zeolitic H₂O was further reduced by using a defocussed beam of approximately 10 microns diameter. Calibrations were made against analysed standards, such as diopside (65%)-jadeite (35%) glass (providing Ca, Mg, Na, Al and Si), cossyrite (Fe, Ti, Na, Si), and orthoclase glass (K), using the general Bence-Albee standardization procedure. Cesium analyses, using a CsCl crystal as primary standard and a pollucite from Mumford, Maine as a secondary standard, were corrected using the ZAF program of Tracer Northern. Counts were collected for a minimum of 5

seconds to a 60 second maximum or until one standard deviation of the counting statistics was less than 1%.

Cesium Exchange Experiments

After the polished mounts had been analysed, the carbon-coating was removed by gentle polishing with .3 micron corundum powder. The probe mounts were then placed inside individual stoppered flasks and specified volumes of different concentrations of cesium chloride solutions were added. Matching experiments were performed in the presence of CsCl solutions and either 1M NaCl or 1M NaHCO₃. Initially 1M CsCl solutions were used, followed by progressively lower dilutions of 0.01M, 0.001M or 0.0001M CsCl (without or with 1M NaCl or NaHCO₃ being present). In some reactions, unmounted 1-2 mm clumps of the Castle Creek and Hector clinoptilolites, as well as individual crystals of Succor Creek clinoptilolite and Icelandic heulandite, were exchanged first with CsCl solutions before being mounted, polished and microprobed.

The stoppered flasks were placed in a constant-temperature shaking water-bath set at either 60°C or 80°C, and the exchange reactions were carried out for time periods ranging from 5 days to 1 month. After each reaction time interval crystal mounts were removed, washed several times with cold distilled water, dried at ambient temperatures, and re-coated with carbon prior to microprobe analyses. After microprobe analyses, carbon-coated surfaces of the mounts were gently removed, and the Cs-exchange reaction continued.

RESULTS

NaCl or NaHCO₃ Alone.

Since the groundwater flowing through Yucca Mountain is likely to be dominated by Na^+ and HCO_3^- or Cl^- ions, some mounted crystals of the Succor Creek clinoptilolite were reacted first with 1M NaCl or 1M NaHCO_3 . The analyses shown in Table 2 (columns -- and --) indicate that slight enrichment of Na and depletion of K occurred in these Na-loaded crystals.

[VALERIE,

- To Do: (1) Load mounted clumps of Hector clinoptilolite 1M NaCl (60°C)
(2) Analyse by microprobe to find out whether K (and Ca?) are depleted.
(3) Load crystals with Ca by reacting Succor Creek and Hector clinoptilolites with 1M CaCl_2 (60°C).
(4) Measure by microprobe any increases of Ca (and depletion of Na and K?)
(5) Then React the NaCl-loaded and CaCl_2 -loaded Succor Creek and Hector clinoptilolites with 1M CsCl (or 0.01M CsCl?) for 7 days and 30 days at 60°C
(6) Analyse for Cs to see if different capacities exist for Na-loaded and Ca-loaded clinoptilolites.

Rationale At Yucca Mt, there regional differences of Na and Ca contents of the clinoptilolites in the zeolitic tuffs of Calico Hills. And, Ca-rich clinoptilolites are found in fractures through and beneath the repository horizon. Does high Ca affect the Cs capacity of clinoptilolite?]

Oriented Crystals.

Individual crystals of the Succor Creek clinoptilolite were mounted onto (100), (101), (001) and (010) faces. Microprobe analyses of these crystals before cation exchange reactions summarized in Table 2 indicate a slightly higher Na concentration for the (010) face, suggesting that sodium is less

susceptible to volatilization along the [010] axis because open channels do not exist in this direction in the clinoptilolite structure.

Progressive cesium exchange reactions with 1M CsCl were carried out for accumulated time periods of 5, 10, 17 and 30 days and the Cs concentrations of the crystals after each time interval are plotted in Figure 1. The drop-off of Cs after 10 days resulted from accidental condensation in initially unstoppered reaction flask, which decreased the CsCl concentration from 1M to ~0.5M. Thereafter, continued reactions in stoppered flasks with 1M CsCl for 30 days revealed that each crystal face has a different Cs capacity. The Cs concentrations are highest for the (100) and (001) faces, less for the (101) face, and least for (010), demonstrating that Cs selectively exchanges along the [100] and [001] axes which are the two directions in the clinoptilolite structure where open channels exist.

Heulandite shows a much stronger crystallographic influence on Cs-uptake than does clinoptilolite, which is indicated by Figure 2. The Cs concentration of the (010) face of heulandite is again considerably lower than those of the other two faces, demonstrating that Cs readily enters the heulandite structure along the open channel [100] and [001] directions. Furthermore, the Cs concentrations of the heulandite (100) and (001) faces are comparable or slightly greater than corresponding faces of clinoptilolite, which conflicts with conclusions by Ames (1960) who stated that the cation exchange properties of heulandite and clinoptilolite are quite dissimilar.

Effects of Changing CsCl Concentrations

Weighed Succor Creek clinoptilolite crystals with diameters of 1-2 mm were mounted on their (010) faces and reacted for accumulated 30 day

periods with 40 or 50 ml. aliquots of CsCl solutions ranging in concentration from 1M to 0.0001M. The results plotted in Figure 3 show that the amount of Cs exchanged into clinoptilolite crystals decreases with increasing dilution of the CsCl solutions. These results differ from conclusions drawn by Ames (1960) that decreasing concentrations of CsCl increase the Cs capacity of clinoptilolite. However, efficiency of removal of Cs uptake by the (010) crystal faces, as indicated by the ratio

Cs content of clinoptilolite/Cs remaining in solution increases from (%) for 1M CsCl to (%) for 0.0001M CsCl.

A measure of the reproducibility of the Cs-exchange data for different crystals of the Succor Creek clinoptilolite mounted in identical (010) orientations is demonstrated by the data for 1M CsCl reacted for 30 days. Figure 3 shows ~21 wt% Cs₂O compared with ~22 wt% Cs₂O in Figure 1. These Cs concentrations are somewhat lower than microprobe measurements of aggregates of the Hector clinoptilolite, also reacted for 30 days, which accumulated ~27 wt% Cs₂O. This high Cs content is comparable to values obtained by Ames (1960, 1961) for the Hector clinoptilolite reacted at 25°C with 0.2M CsCl alone (23.3 wt% Cs₂O, compared with 18.75 wt% Cs₂O for reactions with 0.01M CsCl) (c.f. ~12.34 wt% Cs₂O for reactions with 0.01M CsCl at 60°C in figure 3). Ames (1960) also noted that the effect of increasing temperature is to reduce Cs capacities by ~1/3 between 25°C and 60°C, so that our data for the Hector clinoptilolite compare favorably with his results.

Heulandite shows similar effects of CsCl dilution to clinoptilolite. Thus, the Cs₂O content shown in Figure 4 decreases from ~13 wt% Cs₂O to 3 wt% Cs₂O in 30 day reactions with 1M CsCl and 0.01M CsCl, respectively.

Presence of NaCl

Cesium-exchange reactions of (010)-mounted clinoptilolite crystals with solutions containing 1M NaCl and different concentrations of CsCl are summarized in Figure 5. Again, the Cs content of the zeolite decreases with CsCl dilution. Moreover, the presence of NaCl also decreases the uptake of Cs into clinoptilolite compared to NaCl-free solutions. Our data for reactions with 1M NaCl plus 0.01M CsCl, for example, provided ~7 wt % Cs₂O in clinoptilolite, whereas ~12 wt% Cs₂O entered the zeolite in the absence of NaCl. Ames (1960, 1961) in his measurements of the Hector clinoptilolite, observed a decrease of the Cs capacity from ~18.75 wt% Cs₂O to ~10.3 wt.% in reactions with 0.01M CsCl in the absence and presence, respectively, of 1M NaCl. He also reported ~7.5 wt% Cs₂O in the Hector clinoptilolite after reactions with 0.01M CsCl (alone) at 60°C, in good agreement with our measurements for single crystals of the Succor Creek clinoptilolite. Ames (1961) also measured comparable Cs concentrations in 25°C reactions of the Hector clinopilotite reacted with 0.2M CsCl and either 1M NaCl or 2M NaCl (~8 wt% Cs₂O relative to ~23 wt% Cs₂O in the absence of NaCl), and concluded that clinoptilolite tends to maintain a given Cs distribution between zeolite and solution despite an increasing Na concentration. A similar conclusion may be drawn from our 60°C reactions of the Succor Creek clinoptilolite with 0.01M CsCl and 0.1M CsCl in the presence of 1M NaCl.

[Reactions of heulandite with 1M NaCl and different CsCl concentrations are confusing? Cs uptake in Figure 6 decreases in the order 0.1M CsCl > 1M CsCl > 0.01M CsCl ?]

Presence of NaHCO₃

The decreased Cs capacity of clinoptilolite in the presence of Na is further demonstrated by exchange reactions with different concentrations of CsCl in the presence of 1M NaHCO₃. Results summarized in Figure 7 show that the Cs₂O concentrations in the Succor Creek clinoptilolite not only decrease appreciably between 1M CsCl and 0.001M CsCl in the presence of NaHCO₃, but also are exchanged into the zeolite in significantly lower concentrations than NaCl-bearing solutions. A similar trends occur for heulandite exchanged with different concentrations of CsCl in the presence of NaHCO₃ (Figure 8). These results suggesting that different anions affect Cs-exchange reactions of clinoptilolite appear to be at variance with observations by Ames (1960) who stated that the use of competing Na cations in solutions with the chloride, nitrate, and sulfate anions made no appreciable difference in their effects on Cs capacity. However, Ames (1964) stated later that if less dissociated carbonate salts were used differences might be expected from chloride salts, but these differences were not specified. Our measurements demonstrate that the presence of HCO₃⁻ anions lowers the exchange capacity clinoptilolite for cesium ions, which has important consequences for the storage of fission products at the proposed repository for nuclear waste at Yucca Mountain..

(to be continued!)

REFERENCES CITED

- Alberti, A. (1972) On the crystal structure of the zeolite heulandite. *Tschermaks Mineralogisches Petrographisches Mitt.*, 18, 129-146.
- Alberti, A. (1975) The crystal structure of two clinoptilolites. *Tschermaks Mineral. Petrogr. Mitt.*, 22, 25-37.
- Ames Jr., L. L. (1959) Zeolitic extraction of cesium from aqueous solutions. U.S. Atomic Energy Commission, Report HW62607, 25pp.
- Ames Jr., L. L. (1960) The cation sieve properties of clinoptilolite. *American Mineralogist*, 45, 689-700.
- Ames Jr., L. L. (1961) Cation sieve properties of the open zeolites chabacite, mordenite, erionite and clinoptilolite. *American Mineralogist*, 46, 1120-1131.
- Ames Jr., L. L. (1962a) Kinetics of cesium reactions with some inorganic cation exchange materials. *American Mineralogist*, 47, 1067-1078.
- Ames Jr., L. L. (1962b) Effect of base cation on the cesium kinetics of clinoptilolite. *American Mineralogist*, 47, 1310-1316
- Ames Jr., L. L. (1962c) Characterization of a strontium-selective zeolite. *American Mineralogist*, 47, 1317-1320.
- Ames Jr., L. L. (1963) Mass action relationships of some zeolites in the region of high competing cation concentrations. *American Mineralogist*, 48, 868-881.
- Ames Jr., L. L. (1964) Some zeolite equilibria with alkali metal cations. *American Mineralogist*, 49, 127-145.
- Ames Jr., L. L. ((1965) Self diffusion of some cations in open zeolites. *American Mineralogist*, 50, 465-478.
- Ames, Jr., L. L., Sand, L. B., and Goldich, S. S. (1958) A contribution on the Hector, California, bentonite deposits. *Economic Geology*, 53, 22-37.

- Bahtl, H. (1973) Neutronenbeugungsuntersuchung des Zeolites Heulandit, $\text{Ca}(\text{Al}_2\text{Si}_7\text{O}_{18}6\text{H}_2\text{O})$. Zeitschrift für Kristallographie, 137, 440-441.
- Bish, D. L. (1984) Effects of exchangeable cation composition on the thermal expansion/contraction of clinoptilolite. Clays and Clay Minerals, 32, 444-452.
- Boles, J. R. (1972) Composition, optical properties, cell dimensions, and thermal stability of some heulandite group zeolites. American Mineralogist, 57, 1453-1493.
- Broxton, D. E., Warren, R. G., Hagen, R. C., and Luedemann, G. (1986) Chemistry and diagenetically altered tuffs at a potential nuclear waste repository, Yucca Mountain, Nye County, Nevada. Los Alamos National Laboratory, Report LA-10802-MS, 160pp.
- Broxton, D. E., Bish, D. L., and Warren, R. G. (1987) Distribution and chemistry of diagenetic minerals at Yucca Mountain, Nye County, Nevada. Clays and Clay Minerals, 35, 89-110.
- Carlos, B. A. (1985) Minerals in fractures of the unsaturated zone from drill core USW G-4, Yucca Mountain, Nye County, Nevada, Los Alamos National Laboratory Report La-10415, 55pp.
- Chelishchev, N. F., Marynova, N. S., Fakina, L. K., and Berenshtein, B. G. (1974) Dokl. Akad. Nauk, SSSR, Chem. Phys., 217, 1140-1141.
- Gottardi, G. (1978) Mineralogy and crystal chemistry of zeolites. In: Natural Zeolites: Occurrence, Properties, Use. (L. B. Sand and F. A. Mumpton, eds.; Pergamon Press), 31-44.
- Gottardi, G. and Galli, E. (1987) Natural Zeolites. Springer-Verlag
- Howery, D. G. and Thomas, H. C. (1965) Ion exchange on the mineral clinoptilolite. Journal of Physical Chemistry, 69, 531-537.

- Koyama, K. and Takeuchi, Y. (1977) Clinoptilolite: the distribution of potassium atoms and its role in thermal stability. *Zeitschrift für Kristallographie*, 145, 216-239.
- Mason, B. and Sand, L. B. (1960) Clinoptilolite from Patagonia. The relationship between clinoptilolite and heulandite. *American Mineralogist*, 45, 341-350.
- Merkle, A. B. and Slaughter, M. (1968) Determination and refinement of the structure of heulandite. *American Mineralogist*, 53, 341-350.
- Mumpton, F. A. (1960) Clinoptilolite redefined. *American Mineralogist*, 45, 351-369.
- Mumpton, F. A. and Ormsby, W. C. (1978) Morphology of zeolites in sedimentary rocks by scanning electron microscopy. In: *Natural Zeolites: Occurrence, Properties, Use* (L. B. Sand and F. A. Mumpton, eds., Pergamon Press), p. 113-132.
- Sheppard, R. A. and Gude, A. J. (1982) Mineralogy, chemistry, gas adsorption, and NH_4^+ -exchange capacity for selected zeolitic tuffs from the Western United States. USGS Open File Rept., 82-969, 16pp.
- U.S. Department of Energy (1986) Environmental Assessment, Yucca Mountain Site, Nevada Research and Development Area, Nevada. Report DOE/RW-0079, 3 vols.
- Vaughan, D. E. W. (1978) Properties of natural zeolites. In: *Natural Zeolites: Occurrence, Properties, Use*. (L. B. Sand and F. A. Mumpton, eds.; Pergamon Press), p. 353-371.
- Vieth, D. L. (1984) Site description and selection process. In: *Scientific Basis for Nuclear Waste Management. VII.* (G. L. McVay, ed.) Materials Research Society Symposium Proceedings, 26, 279-282.

Wise, W. S., Nokleberg, W. J., and Kokinos, M. (1969) Clinoptilolite and
ferrierite from Agoura, California. *American Mineralogist*, 54, 887-895.

Section D

Disturbed Zone Program

Disturbed Zone Program

Introduction

The concept of the disturbed zone is important because the outer boundary of the disturbed zone (away from the repository) is the starting point for the calculation of ground-water travel time to the accessible environment. If this boundary is close in to the mined openings of the repository, more credit can be taken by DOE for travel of the ground water through a larger volume of rock in the vadose zone. Conversely, if the boundary extends a greater distance from the repository, less credit for ground water-travel time can be claimed.

Complicating the concept is the possibility that a generic, fixed-distance boundary might be claimed for the disturbed zone, based only upon the thermo-mechanical effects on the rocks from mining the openings of the repository, such as proposed by the NRC. An alternative is a site specific variable distance boundary that also considers phase changes in the wetting fluid within the vadose zone as well as the pathways these fluids might encounter, such as fractures. Furthermore, dissolution and alteration of the solid phases by water-rock interactions should be taken into account as well because these changes can potentially affect the thermo-mechanical properties of the enclosing rock.

The DOE prefers the first approach, the potentially nonconservative, generic fixed distance boundary from mined repository workings because this approach yields the greater physical distance and thus the greater ground-water travel times. However, this approach may not be completely in keeping with the original definition of the disturbed zone, i.e., that volume of rock adjacent to the repository in which processes resulting from loading nuclear waste canisters into the repository are too complex to be accurately modeled or simulated. If the generic fixed distance boundary is closer to the repository than the site specific boundary the implication is that complex processes occurring in the disturbed zone can be modeled by DOE.

In our review of DOE's Environmental Assessment and the NRC's Draft Generic Technical Position on the Disturbed Zone, we found an incomplete and perhaps even lack of understanding of the complicated processes likely to occur in a disturbed zone within the vadose zone, such as refluxing of aqueous fluids and dissolution/alteration of the rock mass. Thus, the choice of a generic fixed-distance disturbed-zone boundary by DOE and NRC is at best simplification of reality or a nonconservative error in judgment to obtain the greatest possible ground-water travel times for satisfying regulatory requirements (see Appendix D).

Based on this tack by DOE and NRC and our concerns on the reasonableness of this approach to satisfying several key licensing criteria, we have chosen the subject of the disturbed zone for further investigation and evaluation. The issues addressed in this section briefly stated are:

1. Effects of phase changes in the aqueous fluids in the fractures and matrix pores of the host rock on the physical extent of the disturbed zone.
2. Effects of dissolution and alteration of the host rocks on the integrity of the repository with respect to the release of radionuclides to the accessible environment.
3. Should the boundary of the disturbed zone be fixed at some generic distance (presently about 50 meters) from mined openings in the repository host rock or at a site specific variable distance depending upon phase changes in fluids, fluid pathways, and alteration and dissolution of the repository host rock resulting from fluid-rock interaction.

The results of exploratory investigations in this section point to the fact that the integrity of the repository will be affected, and that the boundary of the disturbed zone could be at a greater distance than the currently defined 50 meters from mined openings of the repository because of rapid fluid

movement in fractures and fissures and dissolution/alteration which will be induced by the heat from the entombed high-level nuclear waste canisters.

The appendix of this section contains abstracts of papers presented at professional meetings and other technical documents that are offshoots of our efforts. A list of these papers and technical documents precedes the appendix.

Disturbed Zone

ISSUES:

How is the extent of the disturbed zone affected by phase changes in the aqueous fluids in the fractures and matrix pores of the host rock, Topopah Springs tuff, and possibly other surrounding units? The phrase "phase changes in the aqueous fluids" implies boiling of pore and fracture water within the drying out envelope which is in the immediate vicinity of the nuclear waste canisters, and the condensation of water vapor to liquid water at some greater distance from the canister where the rock is below the boiling point of water (altitude corrected).

OBJECTIVES OF ACTIVITY:

Determine by geochemical computer modeling, using (as realistic as possible) vadose-zone water composition: (1) the chemistry of the aqueous and gaseous phases as boiling of vadose water progresses; (2) the degree of precipitation of minerals in the zone of boiling; and (3) the degree of dissolution/reaction of minerals in the condensation zone.

ACTIVITY SUMMARY:

Preliminary calculations of open and closed system boiling of Rainier Mesa vadose water, condensation of boiled gases, and reaction of boiling water with the Topopah Springs welded tuff were completed. Computer codes (CHILLER and SOLVEQ) were modified to improve calculations involving aluminum, for heat addition to calculate volumes of minerals produced or destroyed, and to compute changes in rock porosity. Documentation of the computer codes was completed as part of the quality assurance guidelines.

FINDINGS:

As boiling of vadose-zone water proceeds, the pH of the residual solution increases due primarily to degassing of CO₂ and concentration of the salts. If gas remains in contact with the water and minerals precipitating due to boiling, the system is referred to as closed; otherwise, if the gas is removed incrementally (Rayleigh fractionation) the system is considered open. Open system boiling calculations in which the gas phase escapes consistently produces higher pH's in the residual solutions. The predominant mineral precipitate is calcite.

INTERPRETATION OF FINDING(S):

Calculated boiling of vadose water produces a highly alkaline, saline solution that precipitates several minerals, dominantly calcite. These precipitated minerals would most likely plug pores and fractures above the canisters in the zone of boiling resulting in the formation of a perched water layer due to the gravity and capillary induced return of condensed water vapor and ongoing infiltration of surface water. Residual pockets of highly alkaline saline water plus any water that may penetrate the zone of plugging as the thermal peak wanes may redissolve previously precipitated salts in the zone of complete drying out (between canister and zone of boiling), and may eventually contact the canisters and accelerate corrosion under oxidizing conditions.

ADDITIONAL WORK REQUIRED:

- Significance of calculations would be greatly improved if actual analyses of the compositions of vadose waters from Yucca Mountain were available.
- Calculations should proceed to dryness (all liquid water converted to vapor).

- Investigation of the reaction of condensed water vapor with repository host rock (Topopah Springs tuff).
- Determine or estimate thermochemical properties of phases needed to complete calculations.

RECOMMENDED PROGRAM:

Ultimately the geochemical calculations must be combined with hydrogeological calculations on heat and fluid transport (to establish temperature gradients and mass fluxes) to compute the geochemical interaction of the entire refluxing system (boiling fluids to condensing vapor and all water-rock interactions). The importance of fracture versus matrix flow must also be independently established (by field studies) for these types of modeling computations to be relevant to the disposal of high-level nuclear waste at Yucca Mountain.

EXISTING PROGRAM:

The computer algorithms for the geochemical calculations involving boiling and condensing aqueous fluids are currently under development by Dr. M. H. Reed and colleagues at the Department of Geological Sciences, University of Oregon. Preliminary calculations thus far have involved Rainier Mesa vadose water and Topopah Springs welded tuff for open and closed systems (see published abstract by Reed and Spycher in Appendix D-I).

Principal Investigator:

Dr. M. H. Reed, Department of Geological Sciences, University of Oregon.

Disturbed Zone

ISSUES:

Will dissolution of the host rock impact the postclosure integrity of the repository with respect to release of radionuclides to the accessible environment?

How significant will dissolution be as a result of the refluxing of aqueous fluids that most likely will occur during the thermal pulse (thermal peak is about 50 to 100 years after emplacement of canisters)?

Will the zone of dissolution significantly extend the disturbed zone as defined by the U.S. Nuclear Regulatory Commission?

OBJECTIVES OF ACTIVITY:

Determine the effectiveness of a thermal gradient in promoting mass transfer, dissolution, and alteration of the host rock mineralogy, including those phases thought to sorb radionuclides efficiently, such as clays and zeolites.

ACTIVITY SUMMARY:

A vertical thermal gradient experiment was designed and tested that simulated conditions anticipated in partially saturated Topopah Springs welded tuff after emplacement of waste canisters. The experiment consists of a vertically-operated reactor (PVC or aluminum pipe, 4" O.D. and 24" long) containing the rock sample and a heater assembly at the bottom and a cooling assembly at the top. The power adjustment of the heater at the bottom produces a zone of boiling while adjustment of water temperature and flow rate in the cooling assembly results in a condensation zone above the boiling zone. These adjustments permit the heat flux, and consequently, the mass flux through the reactor to be controlled.

Additionally, a hydrothermal mixed flow reactor has been designed, constructed, and pressure and flow tested. This reactor operates at a constant temperature and is to measure the rates of reaction of minerals important for sorption of radionuclides and dissolution of the repository host rock.

FINDINGS:

A zone of boiling formed at the bottom and a zone of condensation formed directly above it. Almost all the grains showed evidence of leaching with the most extensive dissolution occurring in the zone of condensation. Iron oxyhydroxides globules and opaline silica coatings precipitated throughout the experimental sample. Alteration mineral phases formed on grains near the bottom of the reactor column, and tuff grains at the very bottom of the reactor were tightly cemented by deposits of opaline silica.

INTERPRETATION OF FINDINGS:

The results strongly support the hypothesis that mass transport, dissolution, and mineral alteration/precipitation are greatly enhanced in temperature gradients versus isothermal pseudo-equilibrium conditions. Temperature gradients exist today at Yucca Mountain in the form of the geothermal gradient and those formed after emplacement of waste canisters will certainly be more extreme than the preexisting natural geothermal gradient. Although isothermal experiments provide baseline information that can be interpreted in terms of existing geochemical computer models, processes and interactions in thermal gradients can not be predicted nor interpreted with the current "equilibrium" geochemical algorithms.

ADDITIONAL WORK REQUIRED:

Past experiments have utilized crushed tuff; future experiments would also employ solid cores of Topopah Springs tuff with and without fractures. Realistic vadose-zone water compositions must eventually be utilized for these experiments to be relevant to Yucca Mountain in particular. Other parameters that need to be varied to determine their effect on the rate of mineral alteration and/or dissolution and the rate of mass transfer include the thermal flux and the degree of filling of the vessel (determines the degree of saturation during the experiment).

Authigenic mineral phases need to be identified, physical properties of products determined (porosity and permeability), and analysis of sampled waters during experiments analyzed.

Kinetic experiments in the hydrothermal mixed-flow reactor would commence as soon as possible. Kinetic information on those mineral phases important to the sorption and dissolution issues is sorely needed.

RECOMMENDED PROGRAM:

The ultimate goal of this program is to determine if the nonequilibrium thermodynamics of the situation being simulated by experiments can be predicted (with a reasonable number of quantified experiments), and if it is predictable, can the results of models be scaled up to the repository scale? To achieve this goal, a sufficient number of experiments is required in which the sample type (crushed tuff versus solid core, with and without fractures), thermal flux, water composition, degree of saturation, and physical size of the reactor vessel are varied. The results must be quantified as well for input to a model that is to be developed.

EXISTING PROGRAM:

To date, the existing program has been preliminary and exploratory with the main purpose of demonstrating that the phenomenon of mass transport and mineral alteration/dissolution in a thermal gradient can be a significant factor in the safety of a repository at Yucca Mountain (see published abstract by Newcomb and Rimstidt in Appendix D-II).

Principal Investigator:

Dr. J. D. Rimstidt, Department of Geological Sciences, Virginia Polytechnic Institute and State University.

Disturbed Zone

ISSUE:

The key issue of the disturbed zone is whether the boundary should be fixed at some distance (presently 50 meters) from mined openings in the repository host rock. This 50 meter distance is purportedly based on changes in intrinsic rock properties and not (as we believe) on any changes in multiphase fluid states in the host rock's pores and fractures. As defined, the disturbed-zone boundary distinguishes between processes that are too complex to be modeled (thermal and mass transport and transfer) within the boundary and those processes that can be modeled outside of the boundary.

Should the disturbed-zone boundary take into account the multiphase fluid effects and accompanying mineral alteration/dissolution effects?

OBJECTIVES OF ACTIVITY:

We are attempting to evaluate the scientific reasonableness of the disturbed zone definition, and thus the boundary, on the basis of published data in the open literature, and by obtaining and utilizing public domain and DOE/contractors hydrogeologic and geochemical modeling software on realistic problems associated with the development of the thermal envelope surrounding the loaded repository.

ACTIVITY SUMMARY:

A review was written of the NRC's draft generic technical position on the disturbed zone (see Appendix D-III). Three draft technical progress reports on the disturbed zone were generated (see Appendix D-IV). A preliminary annotated bibliography of references concerning the disturbed zone was prepared. Many hydrogeologic and geochemical software modeling packages (programs) were requested and a few were obtained and evaluated (see Progress Report, Appendix D-V):

TOUGH (hydrogeological, K. Pruess, LBL): obtained, and tested on mainframe and personal computers.

PHREEQE (geochemical, U.S.G.S., Intera version): obtained, debugged on personal computer.

EQ3/6 (geochemical, DOE-LLNL): requested, but not obtained.

SAGUARO (hydrogeological, DOE-SNL): requested, but not obtained.

NORIA (hydrogeological, DOE-SNL): requested, but not obtained.

PETROS (hydrogeological, DOE-SNL): requested, but not obtained.

Princeton Transport Code (hydrogeological, Princeton University): obtained, but not completely debugged on non-IBM personal computers.

FINDINGS:

The existing working definition of the disturbed zone (NRC) is seriously flawed and unrealistic. The disturbed-zone boundary is an extremely complicated concept and existing hydrogeologic and geochemical computer software modeling algorithms are not capable of realistically modeling the situation simultaneously (no one program exists that performs both hydrogeologic and geochemical modeling) or individually. The hydrogeological models must be capable of handling thermal and mass transport of multiphase fluids in matrix and fractures under saturated and undersaturated conditions; geochemical models must have the ability to model mass transfer under nonequilibrium (irreversible thermodynamics)

conditions (thermal gradients). However, from a more fundamental standpoint, the basic hydrogeologic and geochemical parameters needed to perform modeling have not been determined to a sufficient degree of detail or accuracy by DOE and their contractors.

INTERPRETATION OF FINDINGS:

These findings strongly suggest that if the extent of the disturbed zone is based on that volume of rock in which processes are sufficiently complex that they can not be modeled, the boundary of the disturbed zone could be at a much greater distance than the currently defined 50 meters from mined openings of the repository.

ADDITIONAL WORK NEEDED:

Computer software modeling packages that have been obtained need further evaluation (debugging and testing) within the full gamut of problems: from simple cases to realistically complex ones. Technical literature, as well as NRC and DOE documents, will be reviewed and evaluated as they become available. New software developed by DOE or their contractors needs to be reviewed and tested in terms of assumptions employed, data utilized, and situations modeled.

RECOMMENDED PROGRAM:

The recommended program has three parts and is similar to that described above:

- Review and evaluation of published technical literature, including that by DOE and their contractors, and the U.S. Nuclear Regulatory Commission (NRC).
- Acquisition of public domain, commercial, and DOE/USGS/NRC - contractor computer modeling software and hands-on testing and evaluation of these codes;
- Generation of progress reports, technical position papers, and/or publications for the State's program regarding the disturbed zone.

EXISTING PROGRAM:

The existing program is essentially similar to the recommended program, except that beginning in July, 1987 there were no funds specifically designated for computer work; thus this aspect of the program is suffering.

Principal Investigators:

Drs. D. L. Shettel, Jr. and C. L. Johnson, of MAI.

Appendix D
Disturbed Zone Program

List of Appendices

- D-I Reed, M. H. and Spycher, N. F., 1988, Chemical modeling of boiling, condensation, fluid-fluid mixing and water rock reaction using programs (CHILLER and SOLVEQ: Abstract presented at 196th American Chemical Society Meeting, Los Angeles, California.
- D-II Newcomb, W. D., and Rimstidt, J. D., 1988, An experiment to simulate mass transport near the Yucca Mountain High Level Radioactive Waste Repository: Geological Society of America Annual Meeting, Poster Session, Abstract.
- D-III Review and recommendations: draft generic technical position: interpretation and identification of the extent of the disturbed zone in the high-level waste rule, by M. Gordon, NRC.
- D-IV Draft technical position on determination of dissolution reactions and kinetics for the proposed Yucca Mountain high-level nuclear waste repository.
- Progress report on a technical position on the disturbed zone.
- Draft technical position on the determination of the disturbed zone at Yucca Mountain proposed high-level nuclear waste repository.
- D-V Progress report: computer codes and anticipated modeling during intensive review of the disturbed zone.

Appendix D-1

**Reed, M. H. and Spycher, N. F., 1988, Chemical modeling of boiling, condensation, fluid-fluid mixing and water rock reaction using programs (CHILLER and SOLVEQ
Abstract presented at 196th American Chemical Society Meeting, Los Angeles, California.**

26. CHEMICAL MODELING OF BOILING, CONDENSATION, FLUID-FLUID MIXING AND WATER-ROCK REACTION USING PROGRAMS CHILLER AND SOLVEQ, Mark H. Reed and Nicolas F. Spycher, Department of Geological Sciences, University of Oregon Eugene, OR 97403

In geothermal systems, waters boil at depth, precipitating ore sulfide and carbonate minerals; boiled gases, including H_2 , condense near the surface where they are oxidized, producing sulfuric acid waters that alter host rocks to clays, or back-react with boiled waters to precipitate As, Sb and Au. This example illustrates the type of complex natural chemical system that SOLVEQ and CHILLER model by computing: Phase assemblage; Compositions of the aqueous phase and gas phase, treating CO_2 , H_2O , Cl_2 , and H_2S gases as non-ideal mixtures of real gases; Compositions of solid solutions (ideal or non-ideal); Distribution of heat among phases. Key computational capabilities that make this possible include: An internal enthalpy balance equation that is solved simultaneously with the chemical mass balance and mass action equations; Arbitrary selection of redox couples to provide for calculations over the entire range of natural oxygen fugacities; Re-selection of the phase assemblage during the iterative solution process.

Appendix D-II

**Newcomb, W. D., and Rimstidt, J. D., 1988, An experiment to simulate mass transport near the Yucca Mountain High Level Radioactive Waste Repository
Geological Society of America Annual Meeting, Poster Session, Abstract.**

Complete sections 1 through 7 below

1 TYPE ABSTRACT within blue lines — they're absolute! Mail flat, reinforced.

No 22748

2

AN EXPERIMENT TO SIMULATE MASS-TRANSPORT NEAR THE YUCCA MOUNTAIN HIGH LEVEL RADIOACTIVE WASTE REPOSITORY

NEWCOMB, William D. and RIMSTIDT, J. Donald, Department of Geological Sciences, Virginia Polytechnic Institute and State University, Blacksburg, Virginia 24061

A vertical thermal gradient experiment (VTGE) was designed to subject samples of partially saturated Topopah Springs member of Yucca Mountain tuffs to geochemical conditions that will likely result from the burial of heat producing, high level radioactive waste canisters. The reactor consists of a PVC pipe, 4 inches diameter, 24 inches long filled with crushed tuff and enough water to partly saturate the pore spaces. A heating assembly at the bottom and a cooling assembly at the top of the pipe impose a thermal gradient so that water in the pores of the tuff at the bottom of the reactor boils and travels upward as steam which condenses near the top of the reactor. The condensate dissolves some of the tuff and returns to the bottom of the reactor by gravity flow. The reactor design allows the solution and gas composition, heat flux, percent saturation, and matrix permeability to be varied from experiment to experiment.

Initial experiments of one month duration with 30 and 80% of the pore volume filled with liquid water show significant alteration of the tuff. Scanning electron microscope observation of the run products show leaching and pitting of grains from throughout the entire column, with more extensive damage to samples from the upper 20 cm of the column. Zeolite alteration minerals formed in the middle and bottom of the column. Iron oxyhydroxide formed by the oxidation of ferrous iron leached from the tuff and opaline silica coatings were ubiquitous and extensive throughout the run products. Near the very bottom of the reactor the tuff grains were cemented together by precipitates.

These experiments show that refluxing of water from partly saturated pore spaces in the Yucca Mountain tuffs can result in extensive mineral alteration and transport and that geochemical conditions similar to those found in vapor saturated geothermal systems and epithermal gold deposits may obtain during the early stages of the life of the proposed high level waste repository.

CATEGORIZE ALL ABSTRACTS:
—Check ONE discipline below to which reviewers would be best qualified to evaluate this abstract.

- 1 archaeological geology
- 2 coal geology
- 3 economic geology
- 4 engineering geology
- 5 environmental geology
- 6 general geology
- 7 geochemistry
- 8 geology education
- 9 geomorphology
- 10 geophysics
- 11 geoscience information
- 12 glacial geology
- 13 history of geology
- 14 hydrogeology
- 15 marine geology
- 16 micropaleontology
- 17 mineralogy/crystallography
- 18 oceanography
- 19 paleontology/paleobotany
- 20 petroleum geology
- 21 petrology, experimental
- 22 petrology, igneous
- 23 petrology, metamorphic
- 24 petrology, sedimentary
- 25 planetary geology
- 26 Precambrian geology
- 27 Quaternary geology
- 28 remote sensing
- 29 sedimentology
- 30 stratigraphy
- 31 structural geology
- 32 tectonics
- 33 tectonics/geophysics
- 34 volcanology

3 TYPES OF SESSIONS AVAILABLE

A. SPECIAL — INVITED ABSTRACT FOR A SYMPOSIUM.

This abstract was invited for the symposium titled _____

If you checked here, skip to item 4.

B. VOLUNTEERED ABSTRACTS

(1) SPECIAL—THEME SESSION, ANNUAL MEETING ONLY.

I would like this abstract considered for oral presentation at the following Theme Session for the Annual Meeting, Denver, 1988.

- 1 Diagenesis of lacustrine rocks
- 2 Geology & Public Policy for the 21st Century
- 3 Geophysical patterns in North America
- 4 Global aspects of sedimentary geology
- 5 Organic compounds in ground water
- 6 Paleontologic constraints on accreted terranes
- 7 Physics and chemistry of mylonites
- 8 Secular variation in the sedimentary record

If not accepted for the Theme Session, do you want it considered for a regular technical session?

Yes No

(2) ORAL SESSION POSTER SESSION EITHER TYPE

I'll accept a change of session type (ORAL ↔ POSTER) if necessary.

Withdraw my abstract rather than change session type.

4 % OF THIS PAPER PREVIOUSLY PRESENTED 0%

Where and when _____

5 CAN YOU BE A SESSION CHAIRMAN? Yes

Topic _____

Your name _____

Telephone (late June/early July) _____

6 SPEAKER'S IDENTITY AND MAILING ADDRESS

Speaker's name W. D. Newcomb

Address Dept. of Geological Sciences

Address Virginia Tech

City Blacksburg State VA Zip 24061

Country _____

Office Telephone: (703) 961-6589

Home Telephone: () _____

Dates we can reach you: _____

7 SEND ORIGINAL + 5 COPIES OF ABSTRACT TO APPROPRIATE ADDRESS SHOWN ON INSTRUCTION SHEET AND ON BACK OF THIS FORM. ALL ABSTRACTS MUST ARRIVE ON OR BEFORE DEADLINE SHOWN FOR EACH MEETING.

Appendix D-III

Review and recommendations: draft generic technical position: interpretation and identification of the extent of the disturbed zone in the high-level waste rule, by M. Gordon, NRC.

Mifflin & Associates, Inc.
Review and Recommendations:

DRAFT GENERIC TECHNICAL POSITION:
INTERPRETATION AND IDENTIFICATION OF
THE EXTENT OF THE DISTURBED ZONE IN
THE HIGH-LEVEL WASTE RULE (10CFR60)/
M. Gordon, et al., NRC, 20 June 1986

Reviewed by:

C. L. Johnson
M. D. Mifflin
M. E. Morgenstein
D. L. Shettel, Jr.

Submitted to:

Carl Johnson
AGENCY FOR NUCLEAR PROJECTS
NUCLEAR WASTE PROJECT OFFICE
Capitol Complex
Carson City, Nevada 89710

August 1986

Table of Contents:

	page
1.0 Background	1
2.0 Draft Generic Technical Position	1
3.0 General Review and Comments	3
4.0 Factors Affecting the Complexity of Determining the "Disturbed Zone" Boundary at Yucca Mountain	6
4.1 Zeolite Stability	6
4.2 Smectite Stability	8
4.3 Temperature Rise as a Consequence of Authigenic Reactions	11
4.4 Volcanic Glass Hydration	11
4.5 Temperature Distribution at Vitrophyre	13
4.6 Summary of Concern	14
5.0 Silica Dissolution	15
5.1 Heat Transfer Model	16
5.2 Transport Model	16
6.0 Summary	18
References	21
Figure 1: Temperature distribution for a proposed repository at Yucca Mountain containing 57 KW/acre spent fuel.	5

Authorship Responsibility:

OVERVIEW:

M. D. Mifflin.

SPECIFIC TECHNICAL AREAS:

Mineral and Rock Stability:

M. E. Morgenstein.

Heat Transfer Model:

C. L. Johnson and
M. D. Mifflin.

Transport Model:

C. L. Johnson and
D. L. Shettel, Jr.

1.0 BACKGROUND:

The NRC Draft Generic Technical Position (Gordon, et al., 1986) on the Disturbed Zone Concept (DGTP) is intended to establish a clarified definition of the inner boundary from which ground-water travel times from High-Level Nuclear Waste (HLW) repositories to the accessible environment are determined. The DGTP restricts the definition of the "disturbed zone" to include only that region where the intrinsic properties of the rockmass (i.e., permeability and effective porosity) are changed as a result of HLW emplacement, admitting that a definition which includes completely the zone of increased temperatures and associated fluid buoyancy effects might include portions of the accessible environment. The motivation for this re-definition of the disturbed zone is the recognized difficulty in using pre-waste-emplacment rockmass properties to predict post-waste-emplacment conditions in the region of intrinsic property changes. In contrast, the effects of fluid property changes that are demonstrably not coupled to the intrinsic properties of the rockmass can be modeled using well developed assessment methods.

2.0 DRAFT GENERIC TECHNICAL POSITION:

The revised disturbed zone definition proposed by NRC establishes the inner boundary from which ground-water travel time is determined, thereby simplifying by omission the effects of the creation of the repository and the heat generated by the waste. Credit towards the 1,000 year pre-waste-emplacment travel time is not considered within the disturbed zone, because of the potential difficulty (46FR35280, 35281, July 8, 1981) in assessing the physical and chemical processes contributing towards waste isolation within that region. Consequently, in order to avoid the potential uncertainties of the characterization process, the

disturbed zone was established as the inner boundary from which travel-time calculations are to be made for demonstrating compliance with 10CFR60.113(a)(2).

The DGTP indicates clearly:

"...that the disturbed zone may be considered to be 1) defined by the zone of substantial thermo- hydro-chemical- mechanical changes in intrinsic permeability and effective porosity caused by underground facility construction or by HLW heat generation and 2) should at least include the portion of the host rock directly adjacent to the underground facility in order that a proper measure of the quality of the geologic setting far from the buried waste may be obtained through application of the groundwater travel time criterion."

and:

"...a disturbed zone of 5 diameters for circular openings, 5 opening heights for noncircular openings, or 50 meters, whichever is largest, from any underground opening, excluding surface shafts and boreholes, may be the minimum appropriate distance for use in calculations of compliance with the pre-waste-emplacement groundwater travel time criterion (10 CFR 60.113 (a)(2))." "The disturbed zone at a given site may, however, extend further than this distance depending on the site and design characteristics." "The extent of the disturbed zone should be calculated by DOE on a site-specific basis." (Gordon, et al., 1986, page 17).

Further, Gordon, et al. (1986) state that the site specific analyses should account for: anomalous geologic situations; effects of the heterogeneous geologic system; the magnitude of the likely ground-water flux (implying vadose and saturated zone flux); the magnitude of areal thermal loading of the repository; geochemical and hydrogeochemical characteristics of the site; and changes in the configuration of the facility through time. (Gordon, et al., 1986, page 17).

3.0 GENERAL REVIEW AND COMMENTS:

We find the DGTP on the disturbed zone conceptually valid with respect to its recognition that near-field processes will change intrinsic properties of permeability and porosity in an indeterminate manner. However, the DGTP clearly excludes thermal effects on fluids as part of the definition of the disturbed zone, stating that these will be treated during assessment of compliance with the overall system standard (10CFR60.112). We assume that this exception also includes phase changes in fluids, and these are anticipated to be of significant impact in the Yucca Mountain vadose environment. Phase changes in fluids and associated moisture redistribution as the result of the phase changes should be explicitly addressed within the technical position, because such changes will occur in the vadose zone and will constitute the disturbed zone as originally defined.

We believe, however, that even with the simplifying exclusion of fluid responses to thermal effects, the objective "...establishment of generic and easily evaluated guidance on the disturbed zone is desirable in order to allow for the demonstration of compliance with the groundwater travel time criterion (10CFR60.113(a)(2)) consistent with NRC's intent in the criterion..." (Gordon, page 16) will not be realized without additional guidance and specific (if arbitrary) definitions of the word substantial. Even with such a definition, considerable additional characterization effort will be required to confidently judge the thermochemical impact on the rock properties within the thermal envelope produced by the waste at the Yucca Mountain site.

Before the DGTP definition of the disturbed zone can be applied to the Yucca Mountain site, the thermal history envelopes for the site need to be accurately established.

Figure 1 is a "site-specific" thermal envelope model developed for Yucca Mountain for 14.2 W/m^2 spent fuel (SF) with a repository midplane at 390 m (Braithwaite and Nimick, 1984, page 10).^{*} Commercial high-level waste (CHLW), not considered in this example, would produce even higher peak temperatures in a shorter time frame given identical initial thermal loadings. Based on the EA (DOE, 1986) the average depth to the repository horizon will likely be between 250 and 300 m below land surface (see Figure 6-19, EA 10-6-248), rather than the assumed 390 m.

We have added to Figure 1 (which depicts the maximum overburden scenario) the position of the repository zone and the range in position of the basal vitrophyre of the Topopah Spring Member. Also, the relative ranges in position of the landsurface and water table with respect to the repository horizon have been indicated. It is important to note that the figure at best represents uncertain approximations in terms of accurately determined thermal envelopes and relative positions of the important features such as land surface, water table, and basal vitrophyre. The thermal envelopes neglect the effects of convective transport of heat via vapor and water transport in fractures, as well as the more complex issue of possible heat sinks and sources triggered

* It should be noted that the source document for these thermal envelope studies (Svalstad, 1984) is not referencable, i.e. Sandia National Laboratory (SNL) has not reviewed it for external distribution. Details of parameter estimation, boundary conditions, and key assumptions used in constructing the predicted Yucca Mountain thermal envelopes, all of which constitute baseline information for mineral stability studies, must therefore be considered speculative.

by endothermic and exothermic mineral alteration reactions that may occur due to the thermal envelope and migrating steam and hot water. We emphasize that no site-specific, referencable predictions of convective heat flow are available for Yucca Mountain; a highly preliminary study by Lawrence Berkeley Laboratory (LBL) is being reviewed by Sandia National Laboratory (SNL) at the time of this writing (September, 1986), and is not available for external review or comment.

Our objective in presenting Figure 1 is to lend perspective to the problem of establishing the boundary of the disturbed zone as proposed by the DGTP definition. We anticipate at least a 30° C rise in temperature down to the water table in some areas, and major thermal impact on the basal vitrophyre, with temperatures up to 80° C or more. In some areas, it seems likely that 40 to 50° C temperatures will occur at or near land surface if convective heat transport occurs and CHLW constitutes a supplementary waste-form.

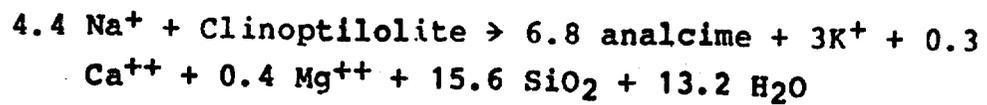
4.0 FACTORS AFFECTING THE COMPLEXITY OF DETERMINING THE "DISTURBED ZONE" BOUNDARY AT YUCCA MOUNTAIN:

4.1 Zeolite Stability:

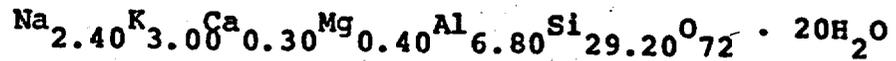
- a. Bish and Semarge (1982) state that clinoptilolite and mordenite are not stable over 80-100° C in Yucca Mountain tuffs. Iijima and Utada (1971) have studied the Niigata Oil Field in Japan which contains buried authigenic facies through zeolite-metamorphic facies mineral associations. Temperatures at the top of the mordenite and clinoptilolite zone are 41-49° C, and at the analcime-albite transition, they are 120-124° C. The alkali clinoptilolite stabil-

ity zone appears to range from 55-91° C and the calcite-clinoptilolite appears to be stable at 8491° C. If for argument's sake, we ignore the aqueous chemistry (not necessarily a conservative approach), zeolite stability for at least clinoptilolite might be safely placed as Bish and Semarge (1982) did, that is between 80-100° C. The term stability, however, needs to be defined as mineral stability does not reflect the loss of adsorbed water.

- b. It has been shown by various students of zeolites that Na and K concentrations in the aqueous media greatly affect the zeolite temperature stability field by reducing the stability of the zeolite below calculated and/or observed zeolite stability temperatures.
- c. Zeolite stability may be viewed as its endothermic reaction temperature, which liberates water; and its exothermic reaction temperature which condenses its structure and causes mineral transformation. In the light of Differential Thermal Analysis (DTA) analyses on clinoptilolite, it is reasonable to presume that temperatures above its formational temperature will yield endothermic water loss. Whether or not this loss of water is accompanied by cation escape (from the super-cage) is unknown, as there is a paucity of data on this subject.
- d. The transformation of clinoptilolite to analcime has been studied by Boles and Wise (1977) and Boles (1977). They report the reaction of deep-sea clinoptilolite to analcime as follows:



where: clinoptilolite composition is:



analcime composition is:



In addition to pressure and temperature controls, the above reaction would be dependent upon sodium and to a lesser extent other cation and water activities. Gieskes (1976, Table 1) cited in Boles (1977) indicates that sediments sharing the clinoptilolite to analcime reaction have pore fluids with molar Na/K ratios of about 160; whereas clinoptilolite-bearing sediments show average molar Na/K ratios of about 60. Consequently, the presence of analcime may be due to high Na/K ratios.

If vadose water evolved from mineral dehydration (such as smectites) were to tend towards relatively high Na/K ratios the transformation of clinoptilolite to analcime might occur even though the temperature regime of the zone(s) of transformation might be below the 120° C Stage 4 (Iijima and Utada, 1971). This reaction would (on the basis of Boles, 1977, calculation above) evolve significant quantities of water and SiO₂ and could also be responsible for a significant change in overall porosity and/or permeability.

4.2 Smectite Stability:

- a. Smectites contain both adsorbed water (as interlayer water between lattice sheets) and high-temperature

water (as OH^-) which is an essential portion of the crystal lattice structure. Dehydration curves for montmorillonite are S-shaped. Variations are dependent upon Na, H, and Ca - montmorillonite structures with Na more stable than Ca. Adsorbed water loss is usually indicated below 150-200° C with a flattening of the curve between this and 300° C where high-temperature water is generally evolved and structural transformation is indicated. Any temperatures above formational ambient temperature should provide adsorbed water loss until curve flattening temperatures are reached at 150-300° C. This water loss may be accompanied by cation-loss where the cations are in exchange interlayer sites. Na-bentonites may swell to 8-10 times their original volume upon hydration; comparable volumetric decreases accompany dehydration. Thus, in fluctuating temperature regimes, smectites may act as water (and cation) pumps adsorbing and releasing these constituents depending upon temperature fluctuations.

Since the smectites can accommodate more adsorbed water than the zeolites, and are apparently more sensitive to temperature changes (under 80° C), loss of adsorbed water and cations can be responsible for producing fluids which may lower the effective zeolite stability temperatures. Additionally, porosity, permeability, and hydrofracturing effects may be greatly enhanced by changes in the hydration-structure of the smectite minerals.

- b. Perry and Hower (1972) have developed a four stage model for dehydration in deeply buried pelitic sediments based upon smectite and mixed-layered clay

associations. Above 80° C (1972, figure 7) they show significant changes in clay stability and mineral associations. These changes may also be somewhat dependent upon aqueous chemistry and burial pressure.

- c. Jackson (1956, page 266, figure 5-3) shows a Differential Thermal Analysis (DTA) curve for montmorillonite from 0 to 1,000° C. There are two major endothermic peaks between 0-240° C and 550-700° C indicating water loss. The first peak has a rapid water loss from 0-25° C, a significant water loss from 25 to 100° C and thereafter a sharper decline to about 160° C which is the maximum of the peak. This indicates that there is a significant water loss immediately upon heating. The rate of water loss upon heating at low temperatures (from 0-100° C) will be partially dependent upon isomorphous substitution in the octahedral layer of the montmorillonite (as indicated by Jackson, 1956, page 295). Consequently, the thermal behavior of the smectites at Yucca Mountain will be in part a function of their composition; therefore, detailed field data are required prior to attempting to determine the implications of dehydration due to repository heating.
- d. Porrenga (1967) has found that for montmorillonites there is a tendency for Ca and Na in montmorillonite to be replaced by Mg. This exchange of Mg for Na and Ca is extremely important with respect to the evolution of vadose water chemistry and therefore on zeolite stability at elevated temperatures.

4.3 Temperature Rise as a Consequence of Authigenic Reactions:

"Surdam and Boles (1977) calculated that the hydration of andesine to laumontite in a sandstone with density of 2.3 g/cc, to 40% andesine, and an initial temperature of 60° C at 1.5 km of burial would raise the temperature of the rock by 40° C if the heat of the reaction is conserved." (Boles, 1977b). Boles (1977(b), page 129), states that "Zeolitization of volcanic glass should also evolve heat."

Consequently, authigenic reactions, which might take place within the disturbed zone as a consequence of repository heating, may also be influenced by the heat-of-reaction produced during diagenetic hydration and this heat evolved may be outside as well as inside the defined disturbed zone boundary.

If this is a factor to be considered, then the temperature distribution envelope for a proposed repository must not only take into account the repository heating, but also, heat evolved due to authigenic reactions which may be beyond the near-field. The heat of reaction temperatures as postulated by Surdam and Boles (1977) are almost as significant as the repository heating itself if those reactions proceed in a demonstrably rapid fashion.

4.4 Volcanic Glass Hydration:

- a. Friedman, et al., (1966) have determined the rate of obsidian (rhyolitic glass) hydration in terrigenous environments exposed to humidity and ground water. Rates determined are not intrinsic and are based upon Fick's Law of Diffusion with experimental evidence derived at 100° C. During the diagenetic

transformation of obsidian to perlite (hydrated glass) the rates are approximately five times faster at 100° C than at 70° C, and about one order of magnitude faster at 70° C than at 30° C. Consequently, the hydration rate has been shown to be temperature dependent. Perlite further hydrates to transition metal oxyhydroxides, zeolites, and smectites. The rates of formation of this phase of authigenics is unknown. Other significant controlling parameters relating to the hydration of glass are the alkalinity of both the glass and surrounding fluids, bonding chemistry of the glass, initial water (HOH and OH) composition of the glass, among other parameters (which are less significant). Although it has been shown that diffusivities of glass are related to its viscosity which is a function of the original state of polymerization of the melt (Scholze, 1966; Stolper, 1982) it has also been documented that hydration rates are dependent upon the activity of dissolved alkali metals in the environment. Consequently, glass hydration becomes an effective and rapid mass transition process during elevated temperatures in the presence of high concentrations of dissolved alkali metals.

Hydration proceeds along any exposed glass surfaces, causing increases in volume. Many of the glasses respond to volume increases by tensile fracturing, geometrically providing additional surfaces for hydration. The resultant configuration of the alteration mass is a reticulate pattern of interconnected fractures with expandable and exchangeable authigenic mineral fracture coatings and fillings. Glass vesicles previously segregated from the expos-

ed environment are either filled with authigenic minerals or are associated with fracture surfaces. The permeability is significantly increased even when total porosity changes are negligible due to the relatively small effective porosity of the fractures.

At Yucca Mountain, a vitrophyre is present between 45 and 113 meters below the repository horizon and partly within the 50 meter minimum disturbed zone. Temperature elevation above geothermal-ambience in the presence of high humidity will provide adequate conditions to promote glass hydration. Under these conditions "significant amounts of water" might be construed as 80-100% humidity (not necessarily a situation of liquid saturation).

- b. The diffusion mechanism of water entering glass and other solids is poorly understood in fractured media. Although, diffusion appears to follow Fick's Law, when single surfaces are present, it appears that it is anomalous in behavior in fractured media (Anacker and Kopelman, 1984). Consequently, rates of diffusion require empirical observations especially when these reactions may affect obtaining accurate disturbed zone boundaries.

4.5 Temperature Distribution at the Vitrophyre:

In accordance with Figure 1 (Braithwaite and Nimick, 1984, figure 2), on which we have superimposed the vitrophyre (from information presented in the EA, DOE/RW-0073) the following temperature distribution for a 57 kW/acre spent fuel loading is anticipated:

<u>Location</u>	<u>250 years</u>	<u>1,000 years</u>	<u>10,000 years</u>
Top of Vitrophyre	67° C	83° C	70° C
Btm. of Vitrophyre	54° C	78° C	67° C

The depth of the Braithwaite and Nimick (1984) repository is 390 m below surface, which is possibly some 70 m deeper than indicated as an average in the EA. Consequently, temperatures shown are possibly a bit higher than they should be for the "average" repository horizon.

4.6 Summary of Concern:

The anticipated temperature distribution over time for a 57 kW/acre loading raises the temperature for the vitrophyre from the ambient 25° C to 83° C in 1,000 years of exposure, an increase of 58° C. This should, on the basis of heat conduction alone, raise the reaction rate of the vitrophyre glass about 25 fold (from about 8 microns squared to 200 microns squared per thousand years for exposed surfaces). If the hydration reaction is seeded by the repository temperature, then it is feasible for the hydration reaction itself to release heat thereby further raising the temperatures in the vitrophyre and surrounding zeolite zones.

We expect that on the basis of repository heating alone, there should be sufficient reactivity to cause significant permeability increases within the vitrophyre. This is especially true when considering only a few fracture flow paths would be required to provide a "most likely pathway" for transit between the repository horizon and the water table. "Most likely" in this sense is defined in a similar manner as Browning (1985) has done.

Of further concern are the elevated temperature effects upon smectites and clinoptilolite with respect to dehydrating these authigenic mineral components and providing sodium-enriched waters to the system. This condition could be responsible for:

1. Elevating the rate of glass hydration.
2. Reducing the effective-temperature for clinoptilolite stability.
3. Thereby providing additional pore and fracture fluids for reactions.

Knauss, et al., (1985, Tables 1 and 2) show a significant increase in dissolved alkali metals in water reacted with crushed tuff during a short term experiment (an increase of sodium of about 25% at 90° C in less than 80 days). At this temperature, which is about 7° C higher than the calculated maximum vitrophyre temperature at 1,000 years (fig. 1) what would the increase be for sodium in 250 to 1,000 years? And how might this contribute towards driving various reactions whose ultimate result would be a significant increase in permeability?

In addition to the dissolved alkali metals, Knauss, et al. (1985) show a decrease in pH which would aid in promoting dissolution of glass and other silicate minerals.

5.0 SILICA DISSOLUTION (Appendix B):

It is stated in the DGTP (Appendix B, page 15, paragraph 2) that generic calculations presented in Appendix B indicate that silica dissolution and resultant porosity increase are not expected to be significant beyond the mechanically "disturbed zone." It is also recognized that the distance to the edge of the thermochemically "disturbed

zone" is strongly dependent on the thermal loading of the repository and the ground-water flux in the host rock. The following paragraphs offer specific comments on the treatment of silica dissolution in the thermochemically "disturbed zone" presented in Appendix B of the DGTP.

5.1 Heat Transfer Model:

Codell's analysis of silica dissolution is intended to address 'typical to conservative' conditions expected near HLW repositories. However, the assumption that convective heat transfer by flowing ground water is negligible (DGTP, 1986, page B2) is certainly not conservative in our opinion, and the basis for this assumption is contained in an unpublished memorandum. The statement that effects of phase changes are expected to be negligible (DGTP, page B2) should be supported by mineralogical data.

Two errors in the thermal data are noted; on page B3 the units for heat capacity of rock, C_p , which should be $J/(m^3\text{°C})$ are incorrectly given as $J(m^3\text{°C})$. On page B8, the geothermal gradient, which is on the order of 20°C to 30°C per 1,000 m (Turcotte and Schubert, 1982), is incorrectly given as "on the order of" 5°C per 1,000 m and neglected on this basis.

5.2 Transport Model:

The transport model is unconvincing, because of: the choice of a conceptual model based on total silica in the rock rather than a surface area to fluid mass ratio; the exclusion of convective heat transport, although convective solute transport is treated explicitly; the exclusion of geothermal gradient from the analysis; and the exclusion of kinetic effects. The rate of silica dissolution is fast on

a geologic time scale, but should be considered on the time scale (1,000 years) of the heating of a repository and vicinity. An important aspect that effects silica kinetics is the solid-surface area to fluid mass ratio. Higher surface areas to fluid mass ratio yield faster dissolution rates, and therefore, a quicker approach to equilibrium. This ratio varies widely for different porosity models.

Dissolution rates of silica are also affected by flow velocity. Faster moving water has less time to equilibrate with rock and less material is dissolved. Thus, marked differences in dissolution rates of silica would be expected between matrix flow and fracture flow, if fracture flow velocities are relatively high.

The inclusion of kinetic effects will result in a smaller amount of silica dissolution than the equilibrium model. However, the distribution of the dissolution sites may be somewhat different. Codell's model indicates "that silica dissolution is greatest where the temperature gradient is steepest." (Codell, 1986, page B9). Areas of the repository with the steepest temperature gradients are likely to have the shortest residence time for aqueous fluids and thus little resulting dissolution. The maximum amount of dissolution may ensue when the thermal envelope around the repository is fully developed and the fluid has the longest residence time to approach equilibrium with the rock. This could be in a halo of saturated fractures beyond the zone of vaporization of water. Dissolution will then be maximized in the hottest areas.

In summary, other porosity models need to be considered, and kinetic affects of silica dissolution need to be considered if flow rates are expected to be significant.

A sign error is present in Table B2; the b-coefficient for quartz should be -2.028×10^{-3} (Rimstidt and Barnes, 1980).

6.0 SUMMARY:

The disturbed zone as defined by NRC is that zone which responds to repository thermal and construction activities by producing substantial (significant) changes in intrinsic permeability and effective porosity. The terms "substantial" and "significant" require clarification as they are subjective.

The DGTP has stated the NRC objective:

"...establishment of generic and easily evaluated guidance on the disturbed zone is desirable in order to allow for the demonstration of compliance with the groundwater travel time criterion (10CFR60.113(a)(2)) consistent with NRC's intent in the criterion..." (Gordon, et al., page 16).

In our opinion, before site characterization, highly complex sites such as Yucca Mountain do not yield to confident determination of the disturbed zone boundary as attested to by our preceding discussions of possible distribution of thermochemical and physical effects. Closely associated with these discussed effects are the fluid phase changes and heat and moisture redistributions, which are more complex than bouyancy effects. These interrelated complexities are reasonable to anticipate considering the strength of the HLW heat source and the associated disruption of the ambient thermal regime. There are at least three alternative approaches in dealing with the determination of the disturbed zone:

1. NRC could stand by the original definition of the disturbed zone.

2. NRC could proceed with the proposed draft generic technical position.
3. NRC could restrict the boundary of the disturbed zone to arbitrary but stated distances.

The ramifications of these alternatives briefly are as follows when viewed from the Yucca Mountain Site perspective:

1. The original NRC definition precludes confident pre-site characterization determination of the disturbed zone and therefore travel time.
2. The proposed draft generic position appears to also preclude confident pre-site-characterization determination of the "disturbed zone" boundary and therefore travel time.
3. The arbitrary distance boundary approach allows for pre-site characterization travel distances to be established. However, the intent of confident determination of the travel-time objective may not be realized due to the other uncertainties with respect to fracture and matrix flow conditions prior to in-depth site characterization.

In our opinion, the Yucca Mountain site provides a useful test of the NRC generic position on the disturbed zone. After careful consideration of site-specific conditions, we have come to the conclusion that the DGTP does not simplify the determination of an inner boundary from which travel-time calculations begin. The complexity of the site and the general absence of experience and data in such fractured rock environments in the vadose zone combine to greatly reduce the general level of confidence in "modeled" conditions. Such are presently based on sparse field data and limited knowledge of physical and chemical processes.

We have also noted that, should the disturbed zone boundary be established through an arbitrary distance criterion, site complexities and processes uncertainties still

do not lend themselves to confident travel-time determinations. In summary, we think that considerably better site characterization results than currently exist will be necessary before a confident pre-waste-emplacment travel-time estimate can be realized.

References:

- Anacker, L. W. and R. Kopelman, 1984. Fractal Chemical Kinetics: Simulations and Experiments, *J. Chem. Phys.*, vol. 81, no. 12, Pages 6402-6403.
- Bish, D. L. and R. E. Semarge, 1982. Mineralogic Variations in a Silic Tuff Sequence: Evidence for Diagenetic and Hydrothermal Reactions. ABSTRACT. 19th Annual Clay Minerals Soc. Mtg., Hilo, Hawaii.
- Boles, J. R., 1977(a). Zeolites in Deep-Sea Sediments, Mineralogy and Geology of Natural Zeolites, Chapter 7 (In: Mineralogical Society of America Short Course Notes, Ed. F. A. Mumpton, vol. 4, Washington, D. C.
- Boles, J. R. 1977(b). Zeolites in Low-Grade Metamorphic Grades, Chapter 6 (In: Mineralogical Society of America Short Course Notes, Ed: F. A. Mumpton, vol. 4, Washington, D. C.
- Boles, J. R. and W. S. Wise, 1977. Nature and Origin of Deep-sea Clinoptilolites (In: Sand, L. G. and Mumpton, F. A., Eds., Natural Zeolites: Occurrence Properties, Use, Pergamom Press, Elmsford, New York.
- Braithwaite, J. W. and F. B. Nimick, 1984. Effect of Host-Rock Dissolution and Precipitation on Permeability in a Nuclear Waste Repository in Tuff, SAND84-0192, (DEA Ref. no. 713).
- Browning, R. E. 1985. Letter from R. E. Browning (NRC) to R. Stein (DOE), 12 June 1985; regarding NRC position on ground-water travel time.
- Friedman, I., R. L. Smith, and W. D. Long, 1966. *Geological Soc. of Amer., Bull.* 77:323.
- Gordon, M., et al., 20 June 1986. Draft Generic Technical Position: Interpretation and Identification of the Extent of the Disturbed Zone in the High-Level Waste Rule (10CFR60), NRC.
- Iijima, A. and M. Utada, 1971. Present-day Zeolitic Diagenesis of the Neogene Geosynclinal Deposits in the Niigata Oil Field, Japan (In: Advances in Chemistry Series 101, Molecular Sieve Zeolites - 1: Amer. Chem. Soc., pages 342-349).

- Jackson, M. L. 1956. Soil Chemical Analysis - Advanced Course, University of Wisconsin, College of Agriculture, Dept. of Soils, Madison, Wisconsin.
- Knauss, K. G., W. J. Beiriger, and D. W. Peifer, 1985. Hydrothermal Interaction of Crushed Topopah Spring Tuff and J-13 Water at 90, 150, and 250° C Using Dickson-Type, Gold-Bay Rock Autoclaves, UCRL-53630.
- Perry, E. A., Jr. and J. Hoer, 1972. Late-Stage Dehydration in Deeply Buried Pelitic Sediments, AAPG Bull., vol. 56, no. 10, pages 2013-2021.
- Porrenga, D. H., 1967. Clay Mineralogy and Geochemistry of Recent Marine Sediments in Tropical Areas. Thesis, University of Amsterdam.
- Rimstidt, J. D. and H. L. Barnes, 1980. "The Kinetics of Silica-water Reactions," Geochimica et Cosmochimica Acta, vol. 44, pages 1683-1699.
- Scholze, H., 1966. Gases and Water in Glass, Part II (In: The Glass Industry, vol. 47, no. 11, pages 622-628. Ashlee Publishing, Co., Inc., NY).
- Stolper, E., 1982. Water in Silicate Glasses : an Infrared Study (In: Contrib. Mineral. Petrol., vol. 18, pages 1-17).
- Surdam, R. C. and J. R. Boles, 1977. Diagenesis of Volcanogenic Sandstones (Abstract), AAPG, Annual Mtg., Denver, Colorado.
- Svalstad, D. K., 1984. Far-Field Thermomechanical Analyses of 57 and 90 kW/Acre Spent Fuel Repositories in the Topopah Spring Member of Yucca Mountain, Nevada Test Site (RE/SPEC Topical Report RSI-0232).
- Turcotte, D. L. and Schubert, G, 1982. Geodynamics: Application of Continuum Physics to Geological Problems, John Wiley and Sons, New York, 450 pages.
- U. S. Department of Energy, 1986. Environmental Assessment - Yucca Mountain Site, Nevada Research and Development Area, Nevada (DOE/RW-0073), May 1986.

Appendix D-IV

Draft technical position on determination of dissolution reactions and kinetics for the proposed Yucca Mountain high-level nuclear waste repository.

Progress report on a technical position on the disturbed zone.

Draft technical position on the determination of the disturbed zone at Yucca Mountain proposed high-level nuclear waste repository.

**Draft Technical Position on Determination of Dissolution
Reactions and Kinetics for the Proposed Yucca Mountain
High-Level Nuclear Waste Repository.**

1.0 Purpose:

This document presents site-specific objectives and approaches for determining the extent of dissolution reactions and kinetic effects in welded and nonwelded tuffs of and adjacent to the repository horizon of Yucca Mountain in support of licensing requirements.

2.0 Regulatory Framework:

The Nuclear Waste Policy Act of 1982 (NWPA, 1983, Public Law 97-425) requires the Department of Energy (DOE) to establish guidelines for the recommendation of sites for nuclear waste repositories (high-level waste and spent fuel) in geologic formations, select sites, perform site-characterization studies, construct and operate approved repositories for the disposal of nuclear waste, and close and decommission such repositories. The Environmental Protection Agency (EPA) has the responsibility for developing standards for offsite release limits of radionuclides to the environment. The Nuclear Regulatory Commission (NRC) is responsible for establishing technical procedures and criteria that will apply in approving or disapproving applications for licenses and authorizations for construction of high-level nuclear waste repositories and for closure and decommissioning of such repositories.

Under the multiple barrier concept for isolation of high-level nuclear waste in a permanently closed repository, the geologic setting of Yucca Mountain, as well as the eng-

ineered barrier system and the shafts, boreholes, and their seals, should have the capacity to retard the transport of long-term and short-lived radionuclides, and thus assure that releases of radioactive material to the accessible environment conform to established EPA standards (NRC: 10 CFR60.112 - Overall system performance objective for the geologic repository after permanent closure).

The postclosure technical guidelines for dissolution (section 960.4-2-6) consist of one qualifying condition, one favorable condition, one potentially adverse condition, and one disqualifying condition.

Section 960.4-2-6 Dissolution.

- (a) Qualifying condition. The site shall be located such that any subsurface rock dissolution will not be likely to lead to radionuclide releases greater than those allowable under the requirements specified in section 960.4-1. In predicting the likelihood of dissolution within the geologic setting at a site, the DOE will consider the evidence of dissolution within that setting during the Quaternary Period, including the locations and characteristics of dissolution fronts or other dissolution features, if identified.
- (b) Favorable Condition. No evidence that the host rock within the site was subject to significant dissolution during the Quaternary Period.
- (c) Potentially Adverse Condition. Evidence of dissolution within the geologic setting--such as breccia pipes, dissolution cavities, significant volumetric reduction of the host rock or surrounding strata, or any structural collapse-- such that a hydraulic interconnection leading to a loss of waste isolation could occur.
- (d) Disqualifying Condition. The site shall be disqualified if it is likely that, during the first 10,000 years after closure, active dissolution, as predicted on the basis of the geologic record, would result in a loss of waste isolation."

Section 960.4-1 referred to above is the qualifying condition for the system guideline:

Section 960.4-1 System Guideline.

- (a) **Qualifying Condition.** The geologic setting at the site shall allow for the physical separation of radioactive waste from the accessible environment after closure in accordance with the requirements of 40CFR Part 191, Subpart B, implemented by the provisions of 10CFR Part 60. The geologic setting at the site will allow for the use of engineered barriers to ensure compliance with the requirements of 40CFR Part 191 and 10CFR Part 60..."

Section 121 of NWPA directs the EPA to "promulgate generally applicable standards for the protection of the general environment from offsite releases from radioactive materials in repositories" and the EPA has published high-level radioactive wastes standards (50CFR38066). Section 121 further specifies that the NRC regulations "shall not be inconsistent with any comparable standards promulgated by [EPA]." Published NRC rules which established procedures and technical criteria for disposal of high-level radioactive waste in a geologic repository by DOE are 10CFR Part 60, 46FR 13980, and 48FR 28204.

The applicable section of the proposed EPA rules (40CFR Part 191, Subpart B - Environmental Standards for Disposal), Section 13, sets forth containment requirements. It specifies that disposal systems for high-level and transuranic wastes shall be designed to provide reasonable expectation that 10,000 years after disposal: (a) "reasonably foreseeable releases of the waste to the accessible environment are projected to be less than quantities calculated according to Table 1 (Appendix A)"[Table 1: Release Limits for Containment Requirements; units: curies/1,000 MTHM for various radionuclides]; (b) "very likely release of waste to the

accessible environment are projected to be less than 10 times the quantities calculated according to Table 1." Applicable definitions are: Accessible environment: includes the atmosphere, land surfaces, surface water, oceans, and parts of the lithosphere that are more than 10 km in any direction from the original location of radioactive waste in the disposal system (NRC has proposed reducing distance to 5 km); reasonably foreseeable releases: releases of radioactive waste to the accessible environment that are estimated to have more than one chance in 100 of occurring within 10,000 years; very unlikely releases: releases of radioactive waste to the accessible environment that are estimated to have between one chance in 100 and one chance in 10,000 of occurring within 10,000 years; disposal: isolation of radioactive waste with no intention of recovery; and disposal system: any combination of engineered and natural barriers that contain radioactive waste after disposal.

3.0 Dissolution Issue:

The Yucca Mountain site has been recommended as one of three sites for characterization in accordance with the Nuclear Waste Policy Act of 1982 (NWPA, 1983) and the Environmental Assessment utilizing the DOE siting guidelines (10CFR Part 960) was the basis for that nomination.

The DOE objective for evaluating dissolution is to ensure that dissolution processes will not adversely affect the nuclear waste isolation capabilities of the Yucca Mountain site. The primary concern is that dissolution of the host rock will compromise the waste isolation capabilities of the site by creating new pathways for radionuclide migration to the accessible environment. However, the evaluation of dissolution processes is based on the evidence of dissol-

ution in the geologic setting of the Yucca Mountain site during the Quaternary Period. The DOE considers the question of dissolution to be of no concern at Yucca Mountain because: (1) no evidence of dissolution (breccia pipes or solution cavities) have been found to date, and (2) rock types present are "considered insoluble."

The manner in which the dissolution guidelines are phrased render them more appropriate for preclosure repository considerations than postclosure. Postclosure dissolution guidelines must consider the effects of repository emplacement on potential dissolution processes. Therefore, the issue of dissolution has been inadequately treated in the Environmental Assessment of Yucca Mountain by DOE due to:

1. uncertainty in the enhancement of existing pathways for radionuclide transport to the accessible environment by dissolution versus the creation of new pathways;
2. the uncertainty of utilizing the geologic past as a basis for evaluating a perturbation to the environment, namely the emplacement of a nuclear waste repository, that apparently has not occurred at any time in the geologic past, including the Quaternary Period;
3. the extremely simplistic and incorrect notion of considering silicate rocks, volcanic glass, and minerals insoluble;
4. a poor understanding of the metastability of volcanic glasses and authigenic minerals;
5. a poor understanding of the kinetics of dissolution of volcanic glass and associated minerals;
6. the uncertainty of future physical and geochemical conditions at the site due to emplacement of nuclear waste; and

7. the uncertainty of applying equilibrium (isothermal) relationships to processes (dissolution reactions and kinetics) that are more likely irreversible (nonequilibrium).

These uncertainties have been ignored in the site-selection process and form a series of basic concerns with respect to licensing issues. These issues are now best addressed during the site-characterization process.

4.0 Statement of Position:

It is the position of the State of Nevada that evaluation of dissolution must be based on a combination of laboratory experiments, in situ field observations, and theoretical modeling which establish the present extent of dissolution and possible range of future dissolution for a given loading of nuclear waste in the repository. Equilibrium and kinetic constants for dissolution reactions, as well as the extent of nonequilibrium processes, can be obtained during site characterization through a site-characterization program strategy which:

1. Characterizes vadose-zone hydrology including climatically induced changes, specifically fluid flux rates in fractures (lateral and depth extent of interconnectivity, aperture width, roughness, and filling mineral distribution) versus matrix;
2. Characterizes vadose-zone hydrogeochemistry: pH, Eh, concentrations of dissolved cations, anions, including organics, colloids, and particulates; and depth variation;
3. Characterizes the chemistries and physicochemical stabilities of the solid phases: volcanic glass, authigenic minerals, and mineral products of devitrification;

as a function of temperature, aqueous fluid pressure, aqueous fluid composition (including organics), pH, and Eh;

4. Characterizes the stabilities of artificial materials (shot-crete, stainless steel, soft steel of roof bolts and meshing, and epoxies used to coat and cement roof bolts, etc.) with respect to the thermal and geochemical regimes expected during the first 10,000 years of repository existence;
5. Characterizes the kinetics of volcanic glass dissolution/hydration/dehydration reactions and dissolution of authigenic minerals, such as clays and zeolites;
6. Characterizes the equilibrium (isothermal) dissolution of natural mineral and artificial phases separately and as a system for the expected variations in temperature, and fluid compositions represented by the range (yet to be determined) of vadose-zone hydrogeochemical analyses to condensed steam under: (a) closed system conditions (static, no flow), and (b) open system conditions with flow rates representative of convective fluid flow rates after repository emplacement;
7. Evaluates uncertainties in thermodynamic data used in equilibrium geochemical modeling of dissolution reactions to obtain conservative estimates of the effects of such processes;
8. Characterizes rocks and minerals for microscopic dissolution features and textures (although large-scale dissolution structures, such as breccia pipes and solution cavities, have not been found to date, megascopic features should be preceded by microscopic dissolution textures);
9. Determines the extent of nonequilibrium (polythermal) dissolution and the rates of reaction of natural minerals present at Yucca Mountain and artificial materials separately and in combination as a system in

experiments scaled to "expected" temperature gradients due to repository emplacement for: (a) closed system (no flow) and (b) open system conditions for representative convective fluid flow rates;

10. Characterizes the post-emplacement concentration gradient of aqueous species in vadose-zone fluids for expected temperature gradients imposed by nuclear waste heating;
11. Determines the importance of thermodiffusion versus convective fluid flow at various stages in the thermal evolution of the repository (Soret coefficients must be known for aqueous species in order to evaluate thermodiffusion);
12. Characterizes effective matrix porosity and permeability changes of volcanic rocks due to equilibrium and nonequilibrium processes;
13. Characterizes effective fracture permeability and transmissivity changes due to equilibrium and nonequilibrium processes affecting volcanic glass, mineral products of devitrification, and authigenic fracture-coating minerals; and
14. Characterizes heat and mass transfer (dissolution/precipitation reactions) expected by convective circulation of aqueous vapor and liquid resulting from nuclear waste emplacement;

Achievement of these objectives may allow bounding estimates to be placed on the extent of dissolution resulting from repository emplacement and its effects on overall repository performance release limits of radionuclides to the accessible environment.

PROGRESS REPORT ON A TECHNICAL POSITION
ON THE DISTURBED ZONE

Background

The potential importance of the hydrothermal effects in the vadose zone of Yucca Mountain due to waste-generated temperatures which exceed the boiling temperature of water is generally unrecognized. * Our analysis indicates marked increases in both vapor and liquid-phase flow should be expected due to the strong thermal envelope generated by the waste. In the fractured-rock environment, the complexity of heat and mass-transfer processes and associated solution-mineral reactions will be greatly increased by the multiphase liquid and vapor-flow environment.

The DOE definition of the disturbed zone to date continues to ignore the presence and importance of multiphase fluid transport. Their current definition is not as defined and intended in 10 CFR 60.2 (46FR35280, 35281, July 8, 1981). Instead of a mechanically disturbed zone of the current DOE definition (measured as extending several meters from the repository horizon) hydrothermal effects may extend many tens of meters downward towards the water table and upward towards the land surface.

The disturbed zone continues to be one important focus of review activities. We find that the zone of difficult-to-understand (and characterize) processes (46FR35280, 35281, July 8, 1981) has been equated conceptually, in a draft technical position by the NRC, to the zone of intrinsic property changes (Gordon, et al., 1986). The central concept of a zone of intrinsic property changes also appears in most, if not all, DOE-sponsored literature that requires a disturbed-zone definition (Langkopf, 1987 and DOE, 1988, Section 8.3.5.12.5, for example). However, even if there were no intrinsic property changes, heat-driven changes in the hydrologic system at Yucca Mountain can reasonably be expected to be profound (and extraordinarily complex from a modeling perspective). The argument that fluid-buoyancy effects can be modeled with "well developed assessment methods" (Gordon, 1986, p. 6) is not applicable to poorly-characterized, subvertical-fracture networks where countercurrent flows of water vapor and liquid water may occur in a partially-saturated environment. These hydrothermal processes can be reasonably expected to occur within 100 years of the beginning of repository loading based on simple calculations using DOE's physical-property values.

Basic Data

Ranges and preferred values for hydrogeologic parameters at Yucca Mountain are summarized by Langkopf (1987, Appendix D). The following data are pertinent to our discussion:

1. Mean and standard deviation of the saturation data for the Topopah Spring welded unit: 65%, $1s = 19\%$
2. Porosity of Topopah Spring matrix: 0.11
3. Residual saturation of Topopah Spring matrix: 0.08
4. Porosity of Topopah Spring fractures: 18×10^{-5} , derived from (1) apertures reported by

* Langkopf (1987) refers to unpublished modeling studies by J. Gauthier and R. R. Peters communicated to Langkopf in a 1986 internal memorandum (SANDIA). In the modeling study, water redistribution was considered from the repository midline to below the repository. Their reported findings support our scenario of total water expulsion in 100 years as vapor. However, their model assumes the matrix would sorb the displaced moisture.

Peters, et al. (1984) and (2) the assumption that 40 fractures/m³ reported by Scott, et al. (1983) are all vertical.

5. Residual saturation of Topopah Spring fractures: 0.0395

The fracture porosity in the rock mass above and below the repository horizon is a very important parameter, yet very uncertain. Fracture porosity is the receiving volume into which water vapor, mobilized during repository heating, will be driven into and condensed. Two approaches have been used to calculate fracture porosity. Sinnock, et al. (1984) used bulk-saturated hydraulic-conductivity values from wells J-13 (Thordarson, 1983) and H-1 (Barr, 1984) to obtain effective hydraulic aperture via the cubic law. Peters, et al. (1984) measured the permeability of a planar fracture in a single piece of core (sample G4-2F) from the Topopah Spring welded unit, and used the cubic law to obtain an estimate of its effective hydraulic aperture. Both groups of authors use a fracture density of 40 fractures per cubic meter in the Topopah Spring welded unit (Scott, et al., 1983) to calculate effective porosity as the product of fracture density and aperture. The field-scale approach yields order-of-magnitude larger estimates of fracture porosity, but both methods suffer from a limited understanding of actual aperture geometry and the degree to which adjoining fracture surfaces are in contact.

Multiplying the porosity of the Topopah Spring welded unit matrix (0.11) by its mean saturation (65%), we obtain 0.0715; seven percent (by volume) of the rockmass is water. Langkopf (1987, p. 68) indicates that, with an initial areal power density (APD) of 57 kw/acre, the 100°C isotherm will reach its maximum extent 10 m below the centerline of the waste package 90 years after waste emplacement. Actually, water will boil at 95°C under the ambient atmospheric pressure of 85 kPa at the repository horizon (Weeks, 1987), so the zone of vaporization will extend beyond 10 m from the centerline. Therefore, the zone of vaporization can be conservatively estimated to be 20 meters (65.6 ft) thick.

The CD-SCP (DOE, 1988, p. 6-227) indicates some uncertainty as to the area available and the area needed for the proposed repository at Yucca Mountain. We have selected an area of 2,000 acres for our calculations. A simple volume calculation yields a conservative estimate of the volume of liquid water within the 95°C isotherm during the first 100 years of repository operation:

$$2,000 \text{ Acres} \times 65.6 \text{ Ft.} \times 0.0715 = 9,381 \text{ Acre-Feet}$$

Possible Worst Case Scenario

The matrix water will entirely vaporize within the 95°C thermal envelope and, as water vapor, migrate away from the 95°C isotherm along the most permeable fracture networks. Most, if not all, of the 9,000 plus acre-feet of matrix water will condense on the walls of the cooler fractures beyond the 95°C isotherm. This condensation could continue until any given fracture is saturated. Perhaps roughly one-half of the vapor would condense to free water above the repository thermal envelope, assuming that fracture permeability is approximately equal above and below the repository thermal envelope. Gravity drainage of condensate in the regions both above and below the repository would occur in the fracture networks on a very large scale. Some condensate trapped above the 95°C thermal envelope could be recycled from vapor to liquid phases many times before draining through the repository horizon. The hot repository zone would likely be continuously penetrated by some returning condensate flow along highly permeable fractures which, in turn, might establish steam explosions and increasingly corrosive fluids in the envelope of hot rock surrounding the repository. An extensive envelope of fracture (and perhaps matrix) saturation totally surrounding the repository horizon seems likely. Recharge flux would also accumulate in the upper zone of saturation as long as the 95°C isotherm existed (assuming that porosity exists to accept the accumulating recharge flux). Upon cooling of the thermal envelope to below 95°C, the repository horizon would eventually be effectively penetrated by the saturation front, and additional fracture flow from the repository horizon to the underlying units would occur.

Significance of Worst-Case Scenario

Licensing criteria would not be met with the above scenario. The disturbed zone could extend upward to near the land surface, which is by definition the accessible environment, and down to the water table. Pre-emplacment ground-water travel time in the saturated zone would be less than the required 1,000 year if the edge of the disturbed zone is at the water table. All travel-time estimates established in the saturated zone are substantially less than 1,000 years.

The presence of extensive fracture saturation above and below the repository from condensing water vapor insures fracture flow and associated rapid travel times to the saturated zone. The invasion of the repository horizon by fracture-flow water during a cool down to below 95°C suggests canister contact with water early in the history of required repository performance. The main attraction of the vadose zone in an arid environment is its presumed dry nature -- the absence of moisture for fracture flow is the postulated waste-isolation attribute. If the thermal envelope changes the environment to one of widespread fracture flow, the postulated waste-isolation attribute of the hydrogeologic environment at Yucca Mountain is lost.

There remains important uncertainties associated with establishing a confident analysis of disturbed-zone behavior. In the preceding scenario, fracture porosity and permeability are key physical properties that are poorly known. In addition, the rate of vapor production/migration in the thermal envelope is uncertain. Configuration of the thermal 95°C envelope, mineral solution, and mineral dissolution rates are also uncertain. Laboratory experiments in conjunction with a much stronger field database would permit a more confident analysis of the extents and rates of development of the hydrothermal effects of the repository.

Progress Summary

Based on a high probability of strong hydrothermal (heat-pipe) effects occurring as the waste heats the surrounding rock matrix to boiling temperature, including a zone of vaporization and upper and lower zones of condensation that could extend upward to land surface and downward to the zone of saturation, we believe that the DOE and NRC have failed to recognize the probable ramifications of the disturbed zone at the Yucca Mountain site. Physical and chemical changes within the zones of vaporization and condensation will be difficult to characterize and accurately predict extents, durations, as well as their effects on intrinsic properties. There is no valid or rational basis for restricting the disturbed-zone definition to some region of intrinsic property changes in the vadose zone.

References

- Barr, G. E., 1984, Preliminary report on the reduction of the well test data for test well USW H-1, adjacent to the Nevada Test Site, Nye County, Nevada (SAND84-0637): Sandia National Laboratories, Albuquerque, New Mexico.
- Gordon, M., et al., 1986, Draft generic technical position: interpretation and identification of the extent of the disturbed zone in the high-level waste rule (10 CFR 60): U.S. Nuclear Regulatory Commission, Washington, D.C.
- Langkopf, B. S., 1987, Proposed preliminary definition of the disturbed-zone boundary appropriate for a repository at Yucca Mountain (SAND86-1955): Sandia National Laboratories, Albuquerque, New Mexico.

- Peters, R. R., et al., 1984, Fracture and matrix hydrologic characteristics of tuffaceous material for Yucca Mountain, Nye County, Nevada (SAND84-1471): Sandia National Laboratories, Albuquerque, New Mexico.
- Scott, R. B., et al., 1983, Geologic character of tuffs in the unsaturated zone at Yucca Mountain, Southern Nevada, in "Role of the unsaturated zone in radioactive and hazardous waste disposal," ed. by J. Mercer, Ann Arbor Science, Ann Arbor, Michigan.
- Sinnock, S., et al., 1984, Preliminary bounds on the expected postclosure performance of the Yucca Mountain repository site, southern Nevada (SAND84-1492): Sandia National Laboratories, Albuquerque, New Mexico.
- Thordarson, W., 1983, Geohydrologic data and test results from well J-13, Nevada Test Site, Nye County, Nevada (USGS Water-Resources Investigation Report 83-4717): U.S. Geological Survey, Denver, Colorado, 57 p.
- U.S. Department of Energy, 1988, Consultation draft site characterization plan, Yucca Mountain site, Nevada research and development area, Nevada (v. VII), Sec. 8.3.5.12.5, "Information Need 1.6.5: Boundary of the Disturbed Zone-Technical Basis for Addressing the Information Need."
- Weeks, E. P., 1987, Effect of topography on gas flow in unsaturated fractured rock - concepts and observations, flow and transport through unsaturated fractured rock, Geophysical Monograph 42, D. D. Evans and T. J. Nicholson, eds., American Geophysical Union, Washington, D.C.

**Draft Technical Position on the Determination of the
Disturbed Zone at Yucca Mountain Proposed High-Level
Nuclear Waste Repository.**

1.0 Purpose:

The technical position of the State of Nevada on the determination of the disturbed zone boundary is presented as an element of site selection and with the cognizance that licensing issues are dependent upon appropriate site-selection procedures. This document interprets and identifies the "disturbed zone" as it applies to Yucca Mountain and NRC regulations (10CFR Part 60).

2.0 Regulatory Framework:

The Nuclear Waste Policy Act of 1982 (Public Law 97-425) confers responsibility to EPA for developing applicable standards for protection of the environment from off site releases of radionuclides (Section 121); to the NRC for issuing technical requirements and criteria that will apply in approving or disapproving applications for licenses and authorization to construct high-level radioactive waste repositories (Section 121), and for closure and decommissioning of such repositories; and to the DOE for issuing general guidelines for site selection and site characterization, and for construction and operation of the waste disposal facility in accordance with NRC regulations (Section 121).

The NRC has established performance objectives for high-level radioactive waste repositories including performance criteria for both the geologic and engineered barrier systems (10CFR Part 60, Subpart E-Technical Criteria). Within this section, the travel time criteria is stated:

"The geologic repository shall be located so that the pre-waste-emplacement groundwater travel time along the fastest path of likely radionuclide travel from the disturbed zone to the accessible environment shall be at least 1000 years or such other travel time as may be approved or specified by the Commission." (10CFR60.113(a)(2)).

The "disturbed zone" cited in (10CFR Part 60.113(a)(2)) within the travel time criterion has been defined as:

"That portion of the controlled area the physical or chemical properties of which have changed as a result of underground facility construction or as a result of heat generated by the emplaced radioactive waste such that the resultant change of properties may have a significant effect on the performance of the geologic repository." (10CFR Part 60.2).

Chu, et al. (1983) have suggested that the "disturbed zone" definition requires additional clarification by NRC; and Gordon, et al (NRC) have developed the Draft Generic Technical Position (DGTP) for the Disturbed Zone (1986). Based on extensive comments received by NRC, a revised NRC Generic Technical Position on the Disturbed Zone is anticipated.

3.0 Disturbed Zone Issue:

The disturbed zone, as defined by NRC (10CFR Part 60) is a concept intended to establish a definition of the inner boundary from which ground-water travel times from High-Level Nuclear Waste (HLW) Repositories to the accessible environment are determined.

Credit towards the 1,000 year pre-waste-emplacment travel time objective is not considered within the "disturbed zone" because of the potential difficulty in assessing the physical and chemical processes contributing towards waste isolation within that region. NRC (Gordon, et al., 1986) state that site-specific analyses for determination of the extent of the "disturbed zone" should account for: anomalous geologic situations; effects of the heterogeneous geologic system; the magnitude of the likely ground-water flux (implying vadose and saturated zone flux); the magnitude of areal thermal loading of the repository; geochemical and hydrogeochemical characteristics of the site; and changes in the configuration of the facility through time. (DGTP, page 17).

However, Gordon, et al. (1986) clearly exclude the thermal effects of bouyancy on fluids as part of the definition of the disturbed zone by stating that this will be treated during assessment of compliance with the overall system performance (10CFR Part 60.112). We assume that this exception also includes phase changes in fluids, and we anticipate these to be of significant impact in the Yucca Mountain vadose environment. Therefore, the State of Nevada's position on the "disturbed zone" explicitly addresses phase changes in fluids and associated moisture redistribution as the result of the fluid-phase changes.

4.0 Statement of Position:

It is the position of the State of Nevada that the existing NRC definition of the disturbed zone is appropriate:

"That portion of the controlled area the physical or chemical properties of which have changed as a result of underground facility construction or as a result

of heat generated by the emplaced radioactive waste such that the resultant change of properties may have a significant effect on the performance of the geologic repository." (10CFR60.2).

Following the above NRC regulation, the "disturbed zone" boundary within the vadose zone of Yucca Mountain may be considered to be:

- 1) Defined by the maximum extent of thermally-induced fluid (gas and liquid) migrations; and
- 2) Defined by that part of the thermal envelope within which, changes in the:
 - a) Abundant* mineral and/or volcanic glass dehydration or hydration states are 10% or greater than the intrinsic values (as non-structural water - determined as water of hydration evolved from ambient temperature to 100°C, inclusive; and
 - b) Mineral and/or volcanic glass volume changes exceed the yield point of any mineral, glass or whole rock so that tensile failure occurs and results in an increase in intrinsic permeability, effective porosity, and/or a loss of structural strength.

The maximum extent of fluid migration is determined as a function of the maximum extent of 100°C isotherm during the first 1,000 years after waste emplacement, effective fracture porosity within the host rock, total quantity of vadose water (including evolved mineral water) and accumula-

* Abundant indicates greater than 5 percent for clays and greater than 10 percent for zeolites and volcanic glass.

ted recharge flux. Thermal effects due to hydration reactions should be added to that heat generated by the radioactive waste.

The disturbed zone calculations require laboratory and in situ data acquisition. They will not be considered valid if solely derived from theoretical model studies unsupported or inadequately supported by site-specific data, including fracture network conductivity and effective porosity, fracture and rock matrix water contents, recharge flux, and distribution and concentrations of minerals and volcanic glass which may be hydrated or dehydrated.

5.0 Discussion:

The concept of the disturbed zone was proposed by NRC (10CFR Part 60) as a volume boundary which constitutes the division of highly disturbed host rock due to waste emplacement that is difficult to characterize from host rock which approaches geothermally ambient temperatures and contains metastable and stable mineral and volcanic glass assemblages whose behavior may be modeled or predicted with reasonable confidence. The determination of the location of the disturbed zone boundary is imperative to the proper calculation of travel times, since travel-time calculations commence at the disturbed zone boundary and continue through to the edge of the accessible environment.

The imposition of the proposed repository at Yucca Mountain upon a regional geothermal gradient in the tuffaceous rock mass superposes a thermal regime and radionuclide inventory which abruptly modifies the natural environmental setting. To date, the boundary between the disturbed zone and the apparently less affected and easier to characterize environment has been determined by arbitrary definitions

promulgated by changes in intrinsic porosity and permeability, suppositions of mineral stability, such as for clinoptilolite, and technological achievements for approximating kinetic and thermodynamic data into idealized and generic models in addition to the 50 m zone of physically disturbed rock caused by mining.

The DOE has viewed the Yucca Mountain mineral associations as being non-reactive quasi-stable phases under the time and temperatures anticipated during the repository life. These information are treated as conservative estimates; yet, due to limitations in laboratory techniques, thermodynamic variables assumed to control mineral equilibria are limited in their ability to predict the real world (in situ) reactions. Gibb's free energy values, as are used in geochemical models for pure mineral end-members, do not normally have the precision or accuracy required to determine mineral association stabilities in the natural environment. Furthermore, to facilitate modeling, only the end-members of minerals that typically form solid-solution series in nature are considered (such as feldspar, clays, and zeolites). This simplification is thus only an approximation of reality. Consequently, the underlying context for creating the concept of the disturbed zone is valid, however, it is problematic due to the inability to treat its boundary on a site-specific, activity-stability basis.

The thermal envelope produced by the repository is dynamic in its geometric configuration, because heating and cooling events are produced by the thermal load decay rates. Since there is apparent debate on the density and size of the canister load, little of significance has been offered with respect to a precise thermal envelope for the Yucca Mountain site and consequently, peak loading temperatures of the host rock are yet to be reported as a function of both convection and conduction. It seems inappropriate then, to

establish a generic distance from the repository center line to the edge of the disturbed zone (50 meters) as a minimum distance requirement. Likewise, it seems premature to establish fixed temperature requirements for the determination of the "disturbed zone" boundary.

There are no radionuclide waste repositories which can offer analog environments for comparison. A presumably reasonable natural analog to the proposed repository system is the hydrothermal alteration of an environment where most of the chemical components can be treated as mobile and reactive variables. In these natural systems, phyllosilicates, aluminosilicates, and tectosilicates tend to be zoned in monomineralogic bands concentric to the zone of hydrothermal fluid introduction. These, attest to systems with very few immobile variables. In the hydrothermal systems, rapidly circulating fluids (as per fracture flow) often increase the temperature locally in prominent paths of fluid transport. Steiner (1968) has observed for Wairakei, New Zealand, that in alteration zones juxtaposed to fissures, a new mineral assemblage is produced adjacent to the pathways of circulating fluids; however, the mineral phases of the general rock series tend to conform to the general trend which is dependent upon the geothermal gradient of the system. In this natural system, a disturbed zone boundary has a strong geometric dependence on fluid phase paths of transport, thermal convection and conduction, and whole-rock petrology (such as mineral associations, grain boundaries, and pore and fracture densities). Although there may be differences in the peak temperatures of hydrothermal analogs and the Yucca Mountain proposed repository, dynamic fluids may produce striking similarities in the dynamic-fractal-thermal envelopes developed in both situations. Thus, a zonation of mineral assemblages is expected for Yucca Mountain as represented by intensive variables of temperature and pressure, and

extensive variables such as the mass of fluid, abundances of aqueous solutes, minerals, and glasses. In this context, the most important pathways extending from the repository toward the accessible environments represent, in part or in whole, the fluid migration perturbations surrounding the more general thermal envelope and hence, the disturbed zone boundary as a consequence of fluid movement. In the Topopah Spring Member of the Paintbrush Tuff, near-field reactions should be similar to reactions expected at the zones of fluid perturbation.

Zones of fluid (gas and liquid phases) transport (most likely by fractures) are uniquely complex in their potential behavior due to:

1. Elevated temperatures above geothermal ambience resulting in faster reaction rates;
2. Neoformation of gels and solid phases;
3. Hydration and dehydration reactions uptaking and yielding water of crystallization, respectively;
4. Exchange of cation and anion species resulting in a change in aqueous geochemistry and aluminosilicate and phyllosilicate exchangeable supercage dimensions;
5. Dissolution of stable and metastable phases providing divalent, monovalent, and complex ions into solution; and
6. Providing thermal-chemical-mechanical stresses on the whole rock, mineral and glass phases resulting in tensile failure aiding transport and reducing whole-rock stability.

The State of Nevada views the fracture and joint systems of Yucca Mountain as potential and likely paths of transport, and as potential perturbations of disturbed zone in areas of fluid phase change, and as zonations which are geochemically and physically too complex to characterize.

These zones of fractures and faults should be considered the prominent paths of transport and have the capability of transporting radionuclide species both in solution and as vapor from the repository to the accessible environment. Important vapor transport is accomplished at 100°C or greater, provides outer zones of condensation and fluid convection above the repository, and zones of condensation and transport towards the accessible environment below the repository. Vapor phase escape to the atmosphere above the repository may be sufficient to be taken seriously with respect to licensing criteria.

5.2 Anticipated Diagenetic Events:

5.2.1 Phyllosilicates:

The dominant clay minerals present in the tuffs of Yucca Mountain are montmorillonite - beidellite (10 to 20 Angstrom spacing) and dioctahedral beidellite interstratified with illite. The beidellites are sodium enriched but may be more calcic high in the Yucca Mountain stratigraphy. Sodium montmorillonites have swelling pressures ranging from 10^5 to 10^7 dyne/cm² which varies with the water to clay ratios, and basal spacing may vary significantly with very minor changes in temperature and humidity. Minor heating of the clay minerals resulting in concomitant collapse of the basal spacing could release significant quantities of water and result in opening of fractures. Additionally, loss of mineral water could be accompanied by a loss in sodium to the aqueous system. Clay minerals are commonly in abundance as fracture lining and fillings and as fillings between volcanic glass shards. Swelling of these minerals could either be responsible for fracturing of the surrounding rock, sealing small fractures or closing the diffusion pathways between the fracture walls and pores in the tuff.

Any sodium-enriched aqueous fluids evolved from the sodium-montmorillonite dehydration could be responsible for a lowering of the stability temperature of clinoptilolite, thereby reducing the sorption capability of that zeolite. Illite interstratification increases with increasing pressure and temperature thereby reducing the base-exchange capacity of the clay and providing water and sodium to the aqueous system.

5.2.2 Aluminosilicates:

The dominant zeolites associated with the repository horizon are clinoptilolite and mordenite. Clinoptilolites are in a continuous solid-solution series with heulandite (A and B), analcite and albite. The introduction of Cs as an exchange ion coming from the nuclear waste will result in a loss in mineral water in clinoptilolite. Similar ion exchange accompanies changes in the hydration state of the zeolite supercage. Temperature elevations smaller than are required to transform clinoptilolite to analcime also result in water loss to the extent that continuous heating to about 350°C results in a continuous water loss until the dehydrated phase is reached. Water loss both from clay and zeolites can be important relative to glass hydration and aqueous geochemistry. As the alkalic ion concentration in the vadose aqueous system is increased, the rates of glass hydration are increased and the stability of clinoptilolite is decreased. Base exchange (sorption) in clinoptilolite as a means for radionuclide retardation depends upon existing ionic activity in the supercage sites and the composition of the aqueous phases. As these parameters are affected by physico-chemical reactions within the disturbed zone the sorption characteristics of the zeolite becomes variable and difficult to determine.

5.2.3. Volcanic Glass:

Obsidian and its intermediate hydration product perlite are unstable, brittle components in abundance above and below the repository horizon. These glasses have the potential to be affected by both autocatalytic hydration (hydration accompanied by base exchange) and dissolution. Boles (1977) states:

"The rise in temperature associated with increasing burial depth may undergo perturbations from hydration reactions involving zeolites. Surdam and Boles (1977) calculated that the hydration of andesine to laumontite in a sandstone with density 1.3 g/cc, 40% andesine, and an initial temperature of 60°C at 1.5 km of burial would raise the temperature of the rock by 40°C if the heat of the reaction is conserved. Zeolitization of volcanic glass should also evolve heat." (Boles, 1977, page 129).

The effects of the loss of heat during the hydration reaction on the repository thermal envelope has not been assessed for Yucca Mountain even though the vitrophyre just below the repository may be subjected to significant hydration effects especially in the light of thermal increases above the geothermal norm. The hydration of glass involves a increase in volume and results in glass fracturing providing additional reactive surface and paths of fracture interconnectivity.

5.2.4 Tectosilicates:

As a consequence of higher rates of dissolution, evolution of mineral water and cations, and increases in environmental temperature, the aqueous system within the vadose zone could potentially contain sufficient components required for opal precipitation. This could be partially responsible for fracture sealing (inhibiting fracture flow). In addition, fracture coatings might be responsible for a red-

uction in diffusion pore space thus inhibiting the circulation of fluids in the rock matrix and increasing the transport of fluids by fracture flow.

5.2.5 Other Reactions:

Pore fluid chemistry is an important control on mineral reactions in volcanic tuff environments. High CO₂ pressures might favor clay-carbonate assemblages over clinoptilolite-mordenite-analcite assemblages. Changes in the pH and Eh values for the aqueous system will also change the activity of mineral and glass species and will promote either the retardation of radionuclides or their transport to the accessible environment. Effective porosity and permeability changes provide for the transfer of ions between reaction sites and provide variations in the mixing of aqueous fluids by matrix diffusion and fracture flow.

The whole rock and vadose aqueous system should be considered as an interrelated suite of minerals, glass and aqueous phase(s) which are subjected to geologically rapid thermal and chemical changes resulting in a dynamic shift in equilibrium (thermodynamically irreversible processes). The "disturbed zone" concept provides a volume within the geologic system where complex interactions and reactions occurring as a consequence of irreversible thermodynamic processes induced by thermal loading, associated fluid migration, and mechanical effects of repository construction, do not require comprehensive and accurate characterization. This is a reasonable and conservative approach as there is compelling evidence that the "disturbed zone" is probably too complex to obtain the required characterization to meet licensing criteria.

References:

- Boles, J. R. Zeolites in Low-Grade Metamorphic Grades (In: Mineralogy and Geology of Natural Zeolites, vol. 4, chapter 6, pages 103 to 135, Mineralogical Society of America, Short Course Notes/ edited by F. A. Mumpton. November 1977.).
- Chu, M. S., N. R. Ortiz, K. K. Wahi, et al. "An Assessment of the Proposed Rule (10CFR60) for Disposal of High-Level Radioactive Wastes in Geologic Repositories," vol. 1 (NUREG/CR-3111). U.S. Nuclear Regulatory Commission, June 1983.
- Gordon, M., N. Tanious, J. Bradbury, et al. "Draft Generic Technical Position: Interpretation and Identification of the Extent of the Disturbed Zone in the High-Level Waste Rule (10CFR60)," Division of Waste Management, Office of Nuclear Material Safety and Safeguards, U.S. Nuclear Regulatory Commission, June 1986.
- Steiner, A. Clay Minerals in Hydrothermally altered rocks at Wairakei, New Zealand (In: Clays and Clay Minerals, vol. 16, pages 183 to 213. 1968.).

Appendix D-V

Progress report: computer codes and anticipated modeling during intensive review of the disturbed zone.

Mifflin & Associates, Inc.
2700 East Sunset Road, Suite B13
Las Vegas, Nevada 89120
(702) 798-0402, (702) 798-3026

Document No. MY870422b

PROGRESS REPORT: Computer Codes and Anticipated Modeling During Intensive Review of the Disturbed Zone.

Computer software that will benefit the disturbed zone intensive review falls into two general categories, i.e. programs that simulate mass and energy transport, and those that simulate geochemical reactions. Geochemical reaction models can be further subdivided into reaction path models and mass transfer models. Coupling of a geochemical reaction simulator with a multiphase flow and energy transport code is clearly beyond the state-of-the-art at present (1987), and is considered unlikely to occur during site characterization. It is therefore necessary to model geochemical and transport phenomena as uncoupled processes, using professional judgement to guide feedback between the necessarily separate modeling activities.

In anticipation of the need for review and recalculation of the thermal envelope and host-rock dissolution effects at Yucca Mountain, a number of numerical simulators were added to Mifflin & Associates' code library. These codes will allow for independent assessment of strongly heat-driven flow in partially saturated fractured porous media, consideration of possible reaction paths and mass transfers, and investigation of the significance of highly uncertain parameters and boundary conditions. To our knowledge, only four computer codes presently in existence might solve the problem of heat-driven

mass and energy transport in partially-saturated porous media. As outlined below, we either have or expect to have "official" versions of all four of these codes during 1987. There is a much greater variety of geochemical codes from which to choose; we have chosen two that are able to perform all necessary aqueous speciation modeling functions and are able to describe quantitatively the effects of ongoing geochemical reactions.

The following codes are expected to form the basis of in-house modeling efforts:

TOUGH, by Karsten Pruess of Lawrence Berkeley Laboratory, is a three-dimensional finite-difference program that takes into account most of the physical effects which are important in multi-phase fluid and heat flow. Based on discussions with Pruess, this program is an appropriate tool for studying an environment characterized by gravity drainage of a mixture of recharge and condensate in discrete vertical fractures. The TOUGH code and user's manual were received on March 30, 1987.

NORIA, a finite element computer program for analyzing water, vapor, air, and energy transport in porous media, is expected to be released by Sandia in the near future. NORIA can solve the same types of problems that are solved by TOUGH, but includes Knudsen diffusion and nonlinear binary diffusion. The present status of NORIA is that Sandia has not forwarded it to Argonne's National Energy Software Center, and a DOE mandate requires this formality prior to release of any code. Based on discussions with NORIA'S author, Nathan Bixler, and his supervisor, Dave Gartling, we expect that NORIA will be available to us within a few weeks of this writing (April 1987). We have arranged for release of PETROS, a one-

dimensional finite-difference code that solves exactly the same set of equations as NORIA, following discussions with G. Ron Hadley of Sandia. To complete the transport code picture, Bryan Travis of Los Alamos has indicated that he will send us a copy of WAFE, although the code is being revised to run "much faster" and the documentation is still incomplete.

PHREEQE, by Parkhurst, Thorstenson, and Plummer of the U.S. Geological Survey, is a mass transfer code capable of simulating a variety of solution-mineral reactions including evaporation and mixing. Johnson and Shettel of MAI both have extensive experience with PHREEQE, and have found it to be relatively efficient and easy to apply compared to other available reaction-path simulators such as EQ3/6. Extreme evaporation will be handled using a modified Pitzer approach that will be set up as a subroutine in PHREEQE. PHREEQE and the Pitzer routine are in our library now (April 1987).

The EQ3/EQ6 software package by Dr. Thomas Wolery of Lawrence Livermore National Laboratory, is a reaction-path model that is presently undergoing extensive revision. Available versions are EQ3.3015U19 of April 9, 1981, and EQ6.3015U93 of March 28, 1981. Since both programs are expected to be superseded in May of 1987 by greatly improved versions, we do not anticipate immediate application of the EQ3/EQ6 package to Yucca Mountain geochemical issues. However, since the new EQ3 will incorporate the Pitzer approach to computing activity coefficients in high-ionic-strength waters, and EQ6 will handle

dissolution and precipitation kinetics, these codes will be incorporated into our review process as soon as they are available.

In summary, our collection of transport and geochemical model codes will be adequate in the immediate future for a rigorous review of the predicted thermal envelope and associated geochemical effects, subject to the major hydrogeologic uncertainties at Yucca Mountain. In addition, some intercode comparisons between functionally similar members of the transport and reaction-code families can be expected during 1987.

REFERENCES:

- Bixler, N. E., 1985, NORIA - A FINITE ELEMENT COMPUTER PROGRAM FOR ANALYZING WATER, VAPOR, AIR, AND ENERGY TRANSPORT IN POROUS MEDIA : Sandia National Laboratories, SAND84-2057.
- Hadley, G. R., 1985, PETROS - A PROGRAM FOR CALCULATING TRANSPORT OF HEAT, WATER, WATER VAPOR, AND AIR THROUGH A POROUS MATERIAL : Sandia National Laboratories, SAND84-0878.
- Parkhurst, D. L., Thorstenson, D. C., and Plummer, L. N., 1980, PHREEQE - A COMPUTER PROGRAM FOR GEOCHEMICAL CALCULATIONS : U. S. Geological Survey Water-Resources Investigations 80-96.
- Pruess, K., 1987, TOUGH USERS GUIDE (DRAFT) : Lawrence Berkeley Laboratory, LBL-20700.
- Wolery, T. J., 1979, CALCULATION OF CHEMICAL EQUILIBRIUM BETWEEN AQUEOUS SOLUTION AND MINERALS: THE EQ3/6 SOFTWARE PACKAGE : Lawrence Livermore Laboratory, UCRL-52658.

Section E

Review of Technical Documents Program

Review of Technical Documents Program

Introduction

The Technical Review activity was review of selected technical documents in hydrogeologic and related topical areas. Documents reviewed were generally by DOE and NRC (or their contractors), and the open scientific literature. The activity also provided for State of Nevada requests for specific document reviews and attendance at meetings where hydrogeologic, climatic change, and geochemical issues or investigations are discussed. In general, the activity provides ongoing technical review for hydrogeologic investigations, including the following topical or issue areas: vadose-zone hydrogeology, saturated-zone hydrogeology, hydrogeochemistry, mineral geochemistry, authigenic mineralogy, climate change, disturbed zone, sorption, and modeling (flow models, transport models, reaction-path models, etc.).

In addition to general technical document review, the most important technical reviews for 1987 and 1988 were DOE Environmental Assessment (EA) and Consultation Draft Site Characterization Plan, Yucca Mountain Site (CD-SCP). The DOE prepared a draft EA (December, 1984) which received public comments and was revised and published as a final EA (May, 1986).

The CD-SCP was released by DOE in January 1988. The CD-SCP is the key document with respect to the manner in which the DOE intends to characterize the proposed Yucca Mountain repository. This document, when considered in the context of existing information and the DOE perspectives established in the EA, made it possible for the State of Nevada to judge the viability of the DOE program with respect to each issue area. Each specific objective of the CD-SCP was judged from the following criteria:

- A. Existing database for Yucca Mountain and region
- B. Issue and licensing requirements
- C. General technical experience/general scientific literature
- D. Technical Position of the State of Nevada

The objective of the review was to establish a State of Nevada response with respect to the credibility and acceptability of the SCP for resolution of key technical issues. In those site characterization aspects where credibility or acceptability is absent, the State of Nevada concerns needed to be established and technically justified.

Reviews of the DEA and EA and several draft technical positions established by the NRC prompted the preparation of Technical Position Papers by MAI on behalf of the State of Nevada on the following:

- 1. Climate change
- 2. Disturbed Zone
- 3. Ground-water Travel Time
- 4. Dissolution
- 5. Vadose/Saturated zones.

The review section deals mainly with two major technical documents - the Environmental Assessment: Yucca Mountain Site, Nevada Research and Development Area, Nevada, vols. I to III [DOE/RW-0073] (EA) and the Consultation Draft of the Site Characterization Plan : Yucca Mountain Site, Nevada Research and Development Area, Nevada, January 1988 [DOE/RW-0160] (CD-SCP), both by the U.S. Department of Energy. As indicated above other technical documents were reviewed. A list of such documents is provided below.

A. In reviewing the EA, MAI efforts focused on:

1. Identifying and documenting major scientific concerns raised by the EA which warrant scrutiny on the basis of:
 - a. Data used;
 - b. Methodology used;
 - c. Results obtained;
 - d. Incompleteness or inaccuracy in reported results; and
 - e. Incompleteness or inaccuracy in methodologies used.
2. Identifying and documenting any inconsistencies between scientific results reported in the EA and the results reported in cited literature or open literature.
3. Identifying, documenting, and assessing the support (or lack thereof) within the EA for the DOE nomination and recommendation decision.
4. Providing our expert judgment with respect to assumptions adopted and with respect to whether or not a conservative analysis has been established.

B. In reviewing the CD-SCP, MAI efforts focused on hydrogeology and related activities in terms of:

1. Conceptual completeness and focus;
2. Appropriateness of methodology to accomplish stated objectives;
3. Availability of supportive technology; and
4. Probability of success and/or feasibility.

C. Other technical documents reviewed in addition to the EA and CD-SCP are:

1. Yucca Mountain USGS water-level data.
2. Proposal for new baseline data format for static and aquifer test water level data/Lehman & Associates.
3. Smectite dehydration and stability: applications to radioactive waste isolation at Yucca Mountain, Nevada (LA-11023-MS)/D. L. Bish, Los Alamos National Laboratory (LANL).
4. Draft generic technical position guidance for determination of anticipated processes and events and unanticipated processes and events/U.S. Nuclear Regulatory Commission (NRC).
5. Performance assessment of radioactive waste repositories/ J. E. Campbell and R. M. Cranwell, in Science, vol. 239, p. 1289 to 1392.
6. A preliminary comparison of mineral deposits in faults near Yucca Mountain, Nevada with possible analogs (LA-11289-MS)/ D. T. Vaniman, D. L. Bish, and S. Chipera, LANL.

Appendix E

Review of Technical Documents Program

List of Appendices

- E-1 Technical review comments on the Environmental Assessment: Yucca Mountain Site, Nevada Research and Development Area, Nevada, vols. I to III (DOE/RW-0073), DOE by MAI.**
- E-2 Review of: Consultation Draft of the Site Characterization Plan : Yucca Mountain Site, Nevada Research and Development Area, Nevada, January 1988 (DOE/RW-0160), DOE by MAI.**
- E-3 Technical Meeting/Symposia Attended.**

Appendix E-I

Technical review comments on the Environmental Assessment: Yucca Mountain site, Nevada Research and Development Area, Nevada, vols. I to III (DOE/RW-0073) by DOE.

Review of Technical Documents

ISSUE:

The technical accuracy of the U. S. Department of Energy Environmental Assessment : Yucca Mountain Site, Nevada Research and Development Area, Nevada : Nuclear Waste Policy Act (Section 112) (DOE/RW-0073), vols. I to III, 1986 (EA).

General Objectives:

Identify and document major scientific concerns raised by the EA which warrant scrutiny on the basis of:

Data used;

Methodology used;

Results obtained;

Incompleteness or inaccuracy in reported results; and

Incompleteness or inaccuracy in methodologies used.

Identify and document any inconsistencies between scientific results reported in the EA and the results reported in cited support literature or open literature.

Identify, document, and assess the support (or lack thereof) within the EA for the DOE nomination and recommendation decision.

Provide our expert judgment with respect to assumptions adopted and with respect to whether or not a conservative analysis has been established.

ACTIVITY SUMMARY:

All of the sections (Vadose Zone, Climate Change, Hydrogeology, Geochemistry, Mineralogy, and the Disturbed Zone) of the final draft of the EA were reviewed taking into consideration certain specific points such as: impact of a pleniuvial climate on repository performance, dissolution, radionuclide retardation by authigenic minerals, the stability of the engineered-barrier system in a chemically reactive ground water in the host rock and Ground-Water Travel Time (GWTT).

FINDINGS:

The following are general conclusions reached after reviewing the preemplacement EA. Excerpts or (where possible) summaries of important sections of our review (important with regard to the postclosure performance of the repository) of the EA are provided immediately after this section and come under "Specific Findings."

We find that there is little scientific evidence available to confidently demonstrate long-term waste isolation at the Yucca Mountain Site.

There is no site-specific data that indicates the lengthy travel times postulated for the vadose zone. Basically the DOE postulates that matrix flow dominates and that recharge is distributed uniformly and is limited by the rock matrix to transmit the flux. We think this is unlikely given the highly fractured

rock environment, the manner in which recharge probably occurs in time and space, and suggestive, but unreported evidence of localized saturation within the vadose zone in the proposed repository area. Therefore, we judge the DOE postulated hydrology of the vadose zone unlikely, and their assessments nonconservative.

There is little evaluation or treatment of vapor-phase radionuclide migration in the vadose zone via fracture networks to the land surface, the accessible environment. A conservative evaluation would assume that gas-phase radionuclides migrate very rapidly to land surface if fracture networks are unsaturated.

There is little appropriately developed evidence that important sorption or retardation of the total inventory of radionuclides will occur in the vadose zone. The DOE has placed heavy weight on the concepts of matrix flow and associated retardation and sorption due to abundant authigenic minerals, low flux rates of recharge, and very long travel times. None of these postulates can be demonstrated as valid based on realistic scenarios of postclosure repository conditions and appropriate data bases. In the absence of an appropriate data base, a conservative analysis should recognize the possibility of important fracture flow, significantly larger flux rates, and the thermal envelope's impact on hydrated authigenic minerals and moisture migration in liquid and vapor phases.

There is little fundamental understanding of most species of radionuclides with respect to migration, sorption, and retardation in the anticipated environments of migration pathways. These migration pathways must include the fracture pathways. We think it nonconservative to take important sorption and retardation credit when an indepth review demonstrates the serious weakness of the laboratory data available, and the absence of comparable radionuclide behaviors in natural hydrologic environments.

We find that the vadose-zone environment is subject to marked changes in the hydrologic regimen when the available paleoclimatic information is considered. If the extremely low modern flux rates postulated by the DOE are in error, and larger flux rates are in fact present, major impact on the hydrologic regimen of the vadose zone should be anticipated during a pluvial climate. The majority of recharged flux would be by fracture flow, and we see no mechanism by which long-term retardation of radionuclides could occur in the vadose zone.

We find that the Yucca Mountain Site has not been selected on the basis of conservative scientific assessments of the environment and site-selection criteria, rather the selection is on postulated, but unproven, conceptual arguments.

A number of conceptual models have been treated as scientifically supported fact. There has not been a consistent effort to conservatively evaluate issues of the site selection in view of no data, sparse data, inappropriate or questionably applicable data, unknown or uncertain physical and chemical processes, highly idealized numerical models, etc.

We recognize no case of an overly conservative treatment of uncertain relationships in the EA. We have recognized (and discussed) many cases of nonconservative treatment of issues in favor of meeting site-selection criteria.

We recognize and discuss cases where the general scientific knowledge base has been selectively visited, or ignored, to further the conceptual models favorable to site selection.

We recognize inconsistent and inappropriate use and interpretation of support document findings to further conceptual models favorable to site selection.

We note that some potentially key site-specific data have been ignored in the preparation of the EA and are as published in support documents.

INTERPRETATION OF FINDINGS WITH RESPECT TO OBJECTIVES AND ISSUES:

The following are conclusions based on the above findings. In the "Specific Findings" section which comes later in this report, findings and our comments or conclusions are treated together.

We believe, on the basis of the above observations, that the EA has fallen short of the scientific objectivity desirable in repository site selection. On the basis of our more conservative evaluations of the available data base and general scientific knowledge pertinent to the site performance issues of Yucca Mountain, we find the site highly complex and unlikely to be demonstrated to meet licensing criteria. We find the required waste isolation at the Yucca Mountain Site unlikely to be confidently demonstrated during characterization of the site.

Specific Findings:

Climate:

The EA theme is that great uncertainty exists in the analyses of effects of a change to pleniuvial climate but that the available data indicate no significant impact on repository performance. We believe climate change to a pleniuvial climate (significantly more effective moisture for runoff and recharge) creates repository performance issues of: 1) water-table position; 2) extent of perched water; 3) ground-water travel time in the vadose zone; 4) recharge rates; and 5) in general the ability of the proposed repository to isolate waste. Indepth treatments of these issues within the context of existing data have been avoided in the EA.

We believe repository performance issues during a pleniuvial climate have not been appropriately addressed in the EA nor resolved with respect to the existing paleohydrologic evidence in the region. Available evidence indicates that recharge rates during a pleniuvial climate may greatly exceed the transmissive capacity of the rock matrix, and hence fracture flow may constitute the majority of the recharge flux in the vadose zone and zones of perched water could become extensive. If fracture flow dominates, the ground-water travel time for majority of flux through the vadose zone would be very rapid. In addition, perched zones of saturation, the site-specific position of regional saturation, and the total flux rate of recharge to the thermal envelope all become serious and unresolved repository performance issues.

Dissolution:

The EA's assessment of compliance with the qualifying condition for the dissolution guideline 10 CFR, Part 960.4-2-6 - ("The site shall be located such that any subsurface rock dissolution will not be likely to lead to radionuclide releases greater than those allowable under the requirements specified in Section 960.4-1." (DOE, 1986, vol. II, p. 6-253).) is based on evidence of dissolution in the geologic setting of the site during the Quaternary Period. As there was no repository in these rocks during this geologic time frame, the potential dissolution effects of placing a thermal source in the vadose zone that is capable of generating steam are unknown.

The EA claims that the "potential host rock at Yucca Mountain has no dissolution features" and that on the basis of the geologic record that "no dissolution is expected during the first 10,000 years after repository closure or thereafter."

We find that the DOE has not provided convincing evidence that: 1) sufficient dissolution would not lead to radionuclide releases greater than those specified in 10 CFR Part 960.4-1, and 2) hydraulic interconnections leading to a loss of waste isolation would not occur because they may in fact already exist.

Further, a thermodynamically unstable mineral assemblage of silica polymorphs is present in the host rock that may be subject to enhanced readjustment (dissolution/precipitation) under expected repository conditions (elevated temperature, convective fluid flux, and above normal geothermal temperature gradients).

Finally, we find that the geologic past at Yucca Mountain is not an adequate basis for evaluating a postclosure technical guideline such as dissolution.

In closing, it appears that the DOE intended the dissolution guideline for those sites containing highly soluble phases, such as halite, and thus treated dissolution in a cursory fashion at Yucca Mountain. However, dissolution/alteration of metastable phases such as volcanic glass and silica polymorphs, zeolites, and clays may be more important to the long-term performance of a nuclear-waste repository at Yucca Mountain than previously thought.

Geochemistry:

The guideline for the Geochemistry Section of the EA contains five favorable conditions, three potentially adverse conditions, and one disqualifying condition. A detailed treatment of each of the conditions of the guideline will not be included in this 18-month report so as to avoid producing a cumbersome volume. What this section contains are therefore excerpts/summaries of points reviewed in the Geochemistry Section of MAI's "Technical Review Comments on the Environmental Assessment: Yucca Mountain Site, Nevada Research and Development Area, Nevada (May 1986, vols. I, II, III [DOE/RW-0073], by DOE, July 1987."

Favorable Conditions:

Favorable Condition 1:

"The nature and rates of the geochemical processes operating within the geologic setting during the Quaternary Period would, if continued into the future, not affect or would favorably affect the ability of the geologic repository to isolate the waste during the next 100,000 years." (DOE, 1986, vol. II, p. 6-174).

The EA indicates that this condition is present at Yucca Mountain because "sorptive minerals (zeolites) were present in the tuff at Yucca Mountain throughout the Quaternary time; they are still present and are expected to contribute to isolation over the next 100,000 years." (DOE, 1986, vol. II, p. 6-169).

We find that the thermal envelope may seriously jeopardize the potential sorptive capacity of the clays and zeolites. In addition, the thermal envelope may promote the evolution of mineral water affecting mineral dissolution, glass hydration, and increasing effective permeability, thereby inhibiting the geologic repository from isolating the waste during the next 100,000 years.

In summary, we find the conceptual arguments presented in the EA are poorly supported by actual field and analytical data. Consequently, we find that a conservative assessment of the evidence indicates that this favorable condition is not present at Yucca Mountain, as there is little evidence to suggest that authigenics are responsible for sorption; and that these minerals will be stable under imposed thermal conditions, within likely paths of transport of the vadose zone.

Favorable Condition 2:

"Geochemical conditions that promote the precipitation, diffusion into the rock matrix, or sorption of radionuclides; inhibit the formation of particulates, colloids, inorganic complexes, or organic complexes that increase the mobility of radionuclides; or inhibit the transport of radionuclides by particulate, colloids, or complexes." (DOE, 1986, vol. II, p. 6-176).

The EA indicates that this condition is present at Yucca Mountain because: geochemical properties are expected to promote matrix diffusion; zeolites along flow paths will sorb radionuclides; organic complexes that would increase radionuclide mobility are not present; particulates and colloids may be filtered by tuffs, thereby inhibiting transport.

Many studies concerning waste-glass radiolysis conclude by exclaiming that acid and hydrogen-peroxide production may radically change the vadose-water chemistry at the proximity of the canisters. These chemically dramatic events, favoring colloid production, may be responsible for more than actinide-colloidal formation to the extent that:

1. Other radionuclides may form colloids.
2. Acid attack on silicates may promote dissolution pathways associated with fracture systems favoring fracture flow over matrix flow.
3. The induced high-oxidation potential may not be adequately reduced considering the paucity of transition-metal complexes present (except for canister material itself).
4. The oxidation of canister stainless steel will provide iron and other transition-metal oxyhydroxides, which tend towards colloidal behavior. These complexes may further the colloidal complexation of radionuclides inhibiting authigenic-mineral sorption, and resulting in a reduction of retardation.

In conclusion we do not find sufficient evidence to demonstrate that this condition is present at Yucca Mountain.

Favorable Condition 3:

"Mineral assemblages that, when subjected to expected repository conditions, would remain unaltered or would alter to mineral assemblages with equal or increased capability to retard radionuclide transport." (DOE, 1986, vol. II, p. 6-192).

The EA indicates that this condition is present at Yucca Mountain because the radionuclide-retardation capacity of tuffs is not expected to degrade due to repository conditions.

We find that retardation capacity as a function of zeolite and clay stability has been inadequately treated in the EA. We find that although volcanic glass likely alters to authigenic minerals with sorption abilities, these minerals may not be stable in the vadose zone to the extent that sorption will have significant capacity for radionuclide retardation. Furthermore, we find that the negative effects of evolution of mineral water may provide increased access for radionuclide escape to the accessible environment. Therefore, we do not find favorable condition 3 present at Yucca Mountain, because when subjected to expected repository conditions, the zeolite/clay assemblage will have a diminished effect in retardation of radionuclide transport, and the presence of these assemblages will likely promote radionuclide escape by providing significant quantities of water of hydration to the system.

Favorable Condition 4:

"A combination of expected geochemical conditions and a volumetric flow rate of water in the host rock that would allow less than 0.001 percent per year of the total radionuclide inventory in the repository at 1,000 years to be dissolved." (DOE, 1986, vol. II, p. 6-193).

The EA indicates that this condition is present at Yucca Mountain, because expected geochemical conditions and vertical flux of less than 0.5 millimeter (0.02 inch) per year are expected to limit release to less than 0.001 percent per year of total radionuclide inventory at 1,000 years after permanent closure.

We note that the EA does not specifically deal with the reactions or release rates of radionuclides which may occur in gaseous states in the vadose-zone repository environment (^{14}C , ^3H , ^{129}I). Gas-phase radionuclides have a potentially short migration path and associated travel time to the accessible

environment (land surface) above the repository through the fracture networks. Release of C-14, as CO₂ may be critical as the sealed canisters fail. This aspect continues to be a serious deficiency of both the DEA and EA.

In conclusion, we find that the geochemical setting of Yucca Mountain is not likely to be benign, but rather reactive with respect to waste glass and stainless steel. We find that the flux of vadose water could, conservatively, be up to two orders of magnitude higher than reported in the EA, and we find, therefore, that the waste glass may release considerably greater than 0.001 percent per year of the total radionuclide inventory 1,000 years after permanent closure. Consequently, we do not find that favorable condition 4 is present at Yucca Mountain.

Favorable Condition 5:

"Any combination of geochemical and physical retardation processes that would decrease the predicted peak cumulative releases of radionuclides to the accessible environment by a factor of 10 as compared to those predicted on the basis of ground-water travel time without such retardation." (DOE, 1986, vol. II, p. 6-198).

The EA indicates that this favorable condition is present at Yucca Mountain because chemical adsorption, low flux, and matrix diffusion are expected to limit radionuclide release by at least a factor 10.

The diffusive retardation factor of 100, which the DOE recognizes, is better attributed to Neretnieks (1980), who has not been offered the opportunity to study Yucca Mountain tuffs. Neretnieks does indicate that for those rocks he studied, accessibility to the rock matrix (pores) is a major determining factor with respect to the magnitude of the potential retardation. There is strong evidence that there are significant differences between diffusion in granites and tuffs. Consequently, until the tuffs at Yucca Mountain are appropriately characterized, it is premature to attribute matrix potential (diffusion) during fracture flow as a mechanism of retardation. Further, if fracture flow is the prime mechanism for radionuclide transport, matrix diffusion will be of minor importance with a diminished capacity in higher velocity flow.

The calculation employed to make the determination that a factor of 11.4 decrease of the cumulative radionuclide release can be attributed to geochemical retardation does not utilize conservative values of flux nor travel times, and consequently does not arrive at conservative site-specific results. The "representative path" from the disturbed zone to the water table which has the mean travel time is not the fastest path and thus is not a conservative numerical evaluation.

As stated in the "Technical Review Comments of the Environmental Assessment: Yucca Mountain Site, ..., July 1987, we find that favorable condition 5 has not been demonstrated to be present at Yucca Mountain, due to nonconservative assumptions made with respect to radionuclide-retardation factors, potential sorptive-barrier behavior, vadose-zone flux, and travel-time calculations. Further, we note that in order to obtain accurate travel-time estimates, there needs to be a reasonably defined disturbed-zone boundary which presently has not been accomplished, and site-specific field data which clearly demonstrates that fracture flow does not dominate.

Potentially Adverse Conditions:

Potentially Adverse Condition 1:

"Ground-water conditions in the host rock that could affect the solubility or the chemical reactivity of the engineered-barrier system to the extent that the expected repository performance could be compromised." (DOE, 1986, vol. II, p. 6-199).

The EA indicates that this condition is not present at Yucca Mountain because "the stainless steel waste disposal container and waste forms are not expected to show detrimental effects due to host-rock water chemistry." (DOE, 1986, vol. II, p. 6-170).

Contrary to DOE assumptions and postulates, there is no site-specific evidence that ground-water conditions in the vadose-zone host rock would not jeopardize the repository performance due to the chemical reactivity of the vadose-zone components. General chemical evidence suggests that undesirable effects with respect to oxidation could significantly limit the lifetime of the engineered-barrier system. The reactivity of vadose-zone water therefore is a paramount issue, but it remains totally unstudied at Yucca Mountain. Consequently, we find that potentially adverse condition 1 could reasonably be present at Yucca Mountain. We therefore disagree with the EA conclusions and find the condition present at Yucca Mountain.

Potentially Adverse Condition 2:

"Geochemical processes or conditions that could reduce the sorption of radionuclides or degrade the rock strength." (DOE, 1986, vol. II, p. 6-202).

The EA indicates that this condition is not present because sorptive zeolites are metastable, but little reaction is expected in the next 100,000 years and because geochemical processes are too slow to affect repository performance through the degradation of rock strength.

Potentially Adverse Condition 2 is directed towards potential changes of the sorption of radionuclides presumably due to a loss or gain of potentially sorbing authigenic minerals and changes in rock strength as a consequence of mineral reactions. The Dibble and Tiller (1981) publication has been inadequately treated in the EA. The kinetic parameters involved in metastable authigenic-mineral transformation towards thermodynamically more stable phases have not been addressed. Reaction rates therefore, on a site-specific basis, given a repository thermal regime and completely uncharacterized vadose-water chemistry, are not determinable. Yet, the EA arrives at certain expectations dealing with reaction rates and related transformation times which appear to be totally unrelated to constructive extrapolation of scientific data.

Consequently, we find that the timing of potential reactions are unknown; and the arguments presented in the EA are totally unsupported.

An underlying assumption in the EA is that the only mode of rock-strength degradation would be the transformation of metastable authigenics to a thermodynamically more stable mineral association; however, we find that reactions such as the hydration of volcanic glass and accompanying volume increases can produce significant changes in structural characteristics (and strength) of the host rock as well as providing significant fracture pathways for radionuclide transport. Dissolution of metastable minerals alters the existing mineral assemblages, rendering them less effective towards sorption. The EA misconception that clinoptilolite must be transformed to an analcime or albite prior to loss of sorption capacity is totally unfounded. Minor changes in the vadose-water chemistry and thermal regime can cause major sorption stability effects.

There are sufficient information available to suggest that both rock strength and sorption capacity could be jeopardized by the thermal load and associated geochemical processes that, in the conservative view, may develop in the host rock of the repository block. Consequently, we find that adverse condition 2 is present at Yucca Mountain.

Potentially Adverse Condition 3:

"Pre-waste-emplacment ground-water conditions in the host-rock that are chemically oxidizing." (DOE, 1986, vol. II, p. 6-204).

The EA indicates that this condition is present at Yucca Mountain because water is expected to contain dissolved oxygen and be chemically oxidizing (DOE, 1986, vol. II, p. 6-170).

The EA recognizes (DOE, 1986, vol. II, p. 6-204 to 6-205) that:

1. The host rock is in the vadose zone and its pores are partially filled with air and water. Consequently, water can have up to 8.1 ppm oxygen at 25°C.
2. The austenitic stainless-steel waste container should develop a protective oxide film that would limit further corrosion. Therefore, the oxidizing conditions may prolong the lifetime of the waste container.
3. Solubility of spent fuel in an oxidizing environment is greater than in a reducing environment. This could result in larger releases of radionuclides.
4. The lifetime of the zircaloy cladding may be adversely affected if uranium dioxide were to become oxidized and cause stress rupture of the cladding.
5. These conditions could be altered after waste emplacement and are not expected to cause serious problems with respect to the solubility or chemical reactivities of the engineered-barrier system.

We agree with the EA that this condition is present at Yucca Mountain, and believe it may be a more serious condition than is alluded to in the EA. We find no mention of radionuclide-colloid formation due to oxidizing conditions which is a reaction that will tend to inhibit sorption retardation. Further, we underline the fact that the vadose water has not been characterized and that the degree to which these waters are oxidizing is unknown. We believe a scenario of the condensation of water vapor in fractures above the repository horizon, and eventual penetration of these waters by fracture flow to the repository horizon as cooling occurs may set the stage for strongly oxidizing conditions.

We, too, conclude that this adverse condition is present at Yucca Mountain.

Hydrogeology:

Ground-water travel time (GWTT) appears to be the most crucial part of the hydrogeology and ground-water sections of the EA with regard to: calculations on the time radionuclides would be released to the accessible environment. Furthermore, the treatment of GWTT involves a discussion of vadose-zone flux, vadose-zone travel time and saturated-zone travel time. This portion of the 18-month report has therefore been devoted to it.

The GWTT analysis in the EA, is a probabilistic approach that attempts to account for variabilities and (uncertainties?) in the key parameters used for calculating ground-water travel time. Unsaturated (vadose) zone flux, unsaturated (vadose) zone travel time, and saturated-zone travel time are considered separately in the EA and the following comments are structured accordingly.

Vadose (Unsaturated) Zone Flux:

A critical and highly uncertain parameter that is of fundamental importance to ground-water travel-time estimation is the flux of water through the vadose zone. Vadose zone flux at Yucca Mountain has been estimated by two general approaches; the first approach uses a variety of indirect local field and laboratory measurements to provide estimates of flux, while the second method involves extrapolation of an empirical regional relationship between elevation, precipitation, and recharge to the local environment at Yucca Mountain. Flux is considered in the EA to be distributed, that is, not locally concentrated in space by structural features, slope, soil cover, etc., or in time by short-term precipitation events leading to pulses of infiltration and percolation.

Using thermal flux, properties of core and in-situ potential gradients, DOE finds that:

- 1) 10-7 to 0.2 mm per year of flux could be occurring in the matrix of the Topopah Spring welded unit.
- 2) All preliminary field and laboratory estimates of moisture flux in the Topopah Spring unit are less than 0.5 mm per year.
- 3) An upper bound of 0.5 mm per year is consistent with the available information.

Direct measurements of infiltration and recharge have not been made at Yucca Mountain (Montazer and Wilson, 1984, pa. 37). Recent moisture profiles (Hammermeister, et al., 1984) indicate that topography exerts a significant influence on localization of recharge; infiltration from summer storms seems to be most pronounced beneath washes, as opposed to higher ground. Generalizations regarding the distribution of infiltration from winter storms, which seldom generate runoff, are not available. It should be clear from the available data, however, that flux is not uniformly distributed in either time or space.

Calculation Based on Geothermal Gradient:

DOE has used measurements of subsurface temperature gradients to estimate moisture flux in the unsaturated zone at Yucca Mountain. Sass and Lachenbruch (1982, p. 24) calculated a downward vertical flux of 9 mm per year in both the saturated and vadose zones. These authors emphasize, however, that results from Yucca Mountain are inconclusive since only one of the 50 wells studied was completed in the manner required of a confident analysis of the thermal effects of natural ground-water flow (Sass and Lachenbruch, 1982, p. 25). The statement in the EA that "...all preliminary field and laboratory estimates are less than 0.5 millimeter" (DOE, 1986, p. 6-151) is, then, a misrepresentation.

In a referenceable letter to D. L. Veith of DOE/Nevada Operations, W. W. Wilson of the USGS (1985) details the rationale for using 0.5 mm/yr. as a "reasonable and conservative" value of flux beneath the repository horizon at the primary repository area. Geothermal data from USW UZ-1 have been used by Montazer, et al., (1985) to estimate the quantity of water in vapor form that is migrating vertically in the Topopah Spring welded unit. The analysis based on an analytical solution for vertical steady flow of ground water and heat through an isotopic, homogeneous, and fully saturated porous medium (Bredenhoeft and Papadopulos, 1965). The interpretation by Montazer, et al. (1985) and Wilson (1985) that temperature profiles are generally convex upward between 91 m and 305 m is open to question; table 1 and figure 12 of Montazer, et al. (1985) reveal that the geothermal gradient can also be interpreted as piecewise linear. The interval from 40 m to 128 m shows a uniform geothermal gradient of 31.45°C per km, and the interval from 128 to 368 m shows a lesser, uniform gradient of 17.50°C/km. Linear regression on temperature-depth data from Montazer, et al. (1985, table 1) results in regression coefficients (r^2) values of 0.99 and 1.00, respectively, for the shallow and deep intervals (Figure 1).

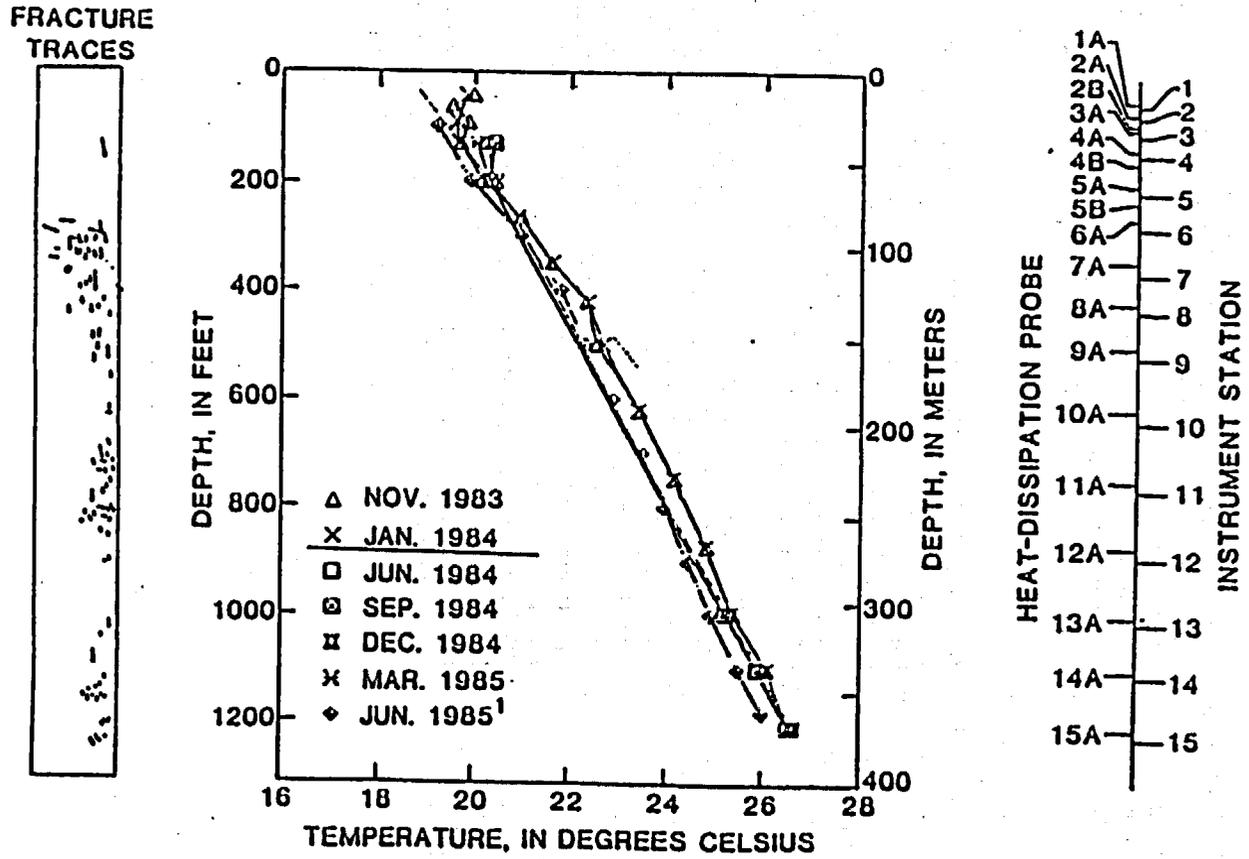
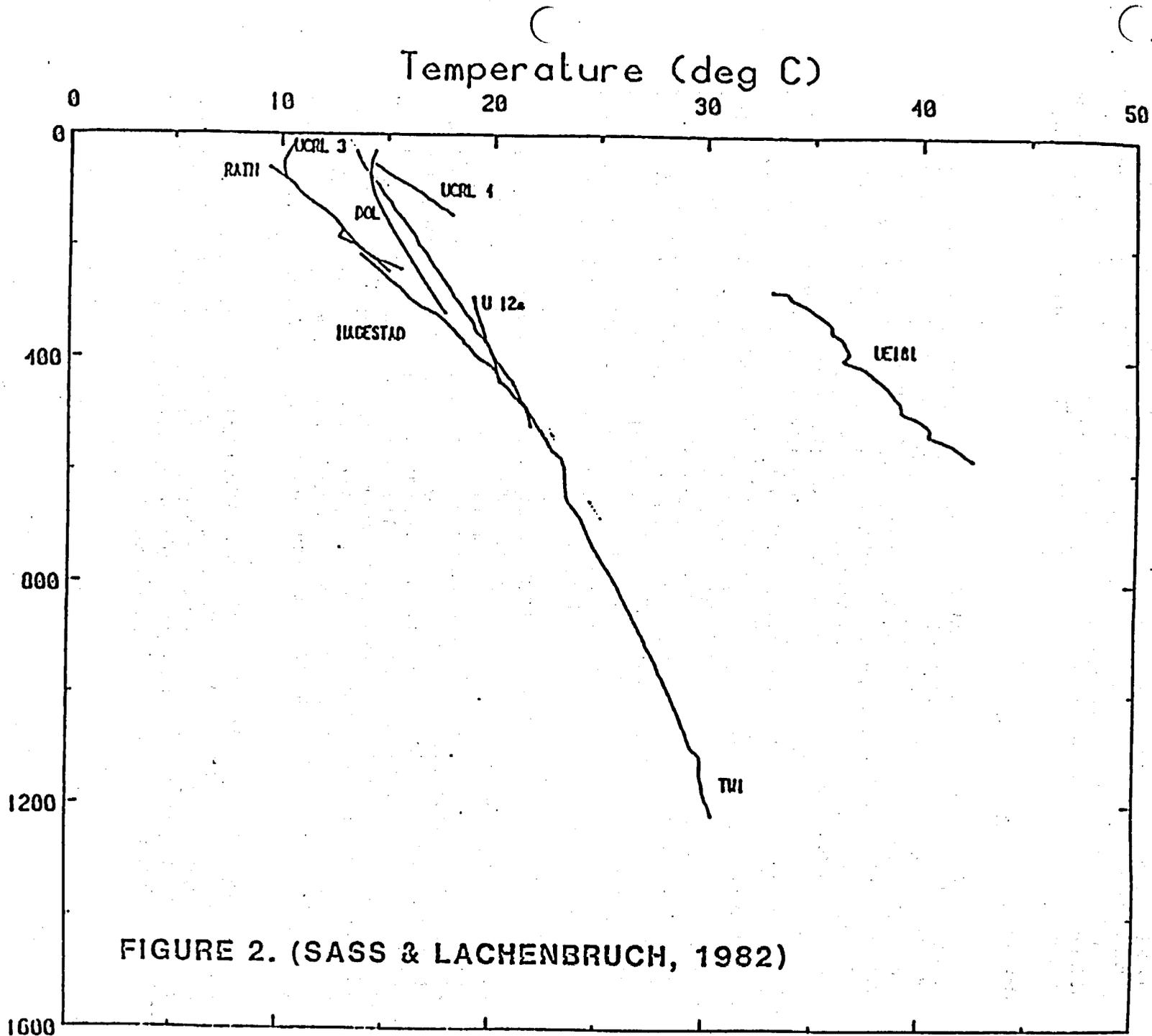


FIGURE 1. (MONTAZER & OTHERS, 1985)

Temperature profiles and distribution of fracture traces at test borehole USW UZ-1. Data for June 1985 from John Sass (U.S. Geological Survey, written commun., 1985).

Depth (meters)



Composite Temperature Profile for Rainier Mesa & Environs.

Sass and Lachenbruch (1982, figure 5) present a geothermal profile from well TW1 at Rainier Mesa that is similar in shape to that presented by Montazer, et al. (1985) for well USW UZ-1 at Yucca Mountain (Figure 2). The fact that the profile at Yucca Mountain resembles that from an area where seasonal flows from fractures into a tunnel network provides direct evidence of active recharge (Henne, 1982) casts doubt on the utility of the geothermal-gradient-convexity approach to unsaturated-zone flux estimation.

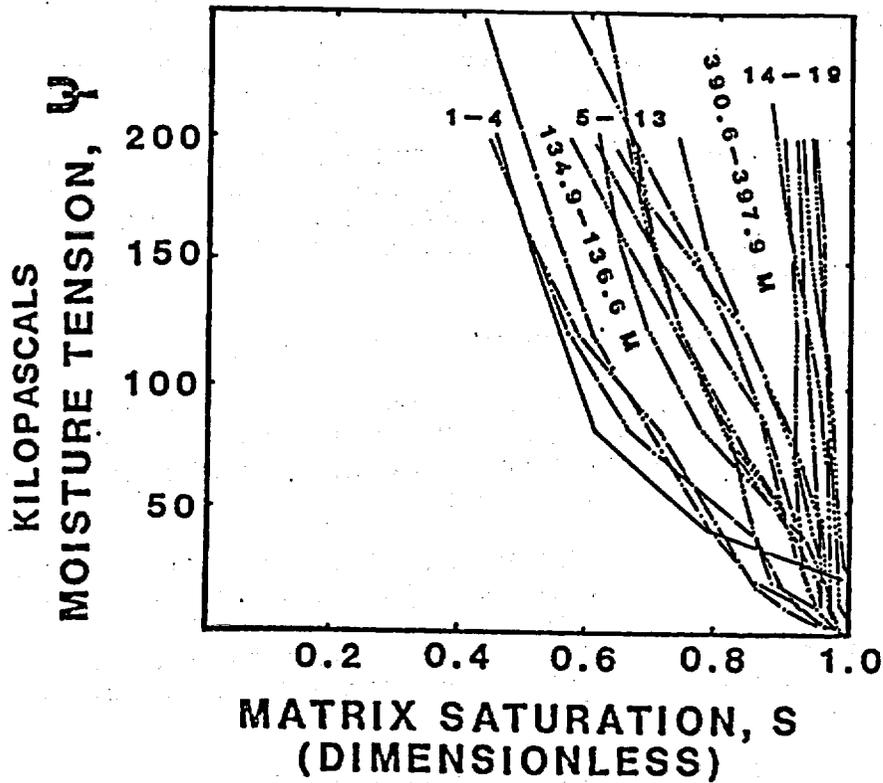
Calculation Based on Properties of Core:

Wilson (1985, p. 2) cites Weeks and Wilson (1984) for an estimated moisture flux of 0.003 to 0.2 mm/yr. in the matrix of the Topopah Spring welded unit. Moisture-characteristic curves relating saturation and moisture tension were developed from results of mercury-injection tests on 19 core samples of unsaturated tuff from test well USW H-1 (Weeks and Wilson, 1984, p. 1). Sixteen of these samples were from the Topopah Spring unit. Relative hydraulic conductivity, defined as the ratio of hydraulic conductivity at a given matrix saturation to that as complete matrix saturation, was estimated from the moisture-characteristic curves (Weeks and Wilson, 1984, p. 12). Only seven of the sixteen samples for the Topopah Spring unit were considered "analyzable", that is, their moisture-characteristic curves could be fit with an analytical expression that can then be integrated to give an equation for relative permeability as a function of matrix saturations or moisture tension. One value of relative permeability (sample 9) was discarded because "...the porosity of the total sample was much larger than that of the small sample used in the porosimeter" (Weeks and Wilson, 1984, p. 13). Ambient unsaturated hydraulic conductivity was obtained from relative hydraulic conductivity (Weeks and Wilson, 1984) and saturated hydraulic conductivity measurements on core from test well UE25a#1 (Anderson, 1982) which is located 2.0 km east of well USW H-1. One of Anderson's (1981) measurements was discarded because of a visible fracture (Weeks and Wilson, 1984, p. 14). The resulting "effective" hydraulic conductivity values were used with an assumed unit hydraulic gradient to obtain the reported 0.003 to 0.012 mm/yr. vertical water flux through the tuff matrix.

The most noteworthy point regarding flux estimation from core analysis is the systematic exclusion of fractured samples from the analysis. In addition, there could be intentional bias in Weeks and Wilson (1984) toward presentation of their data in a way that minimizes the computed vertical flux through the Topopah Spring unit. For example, sample 8 (Weeks and Wilson, 1984, page 8) was excluded from the calculation of geometric mean relative hydraulic conductivity for reasons quoted in the last paragraph, but sample 9, for which the porosity difference between "small" and "total" sample was higher than sample 8 sample was higher than sample 8 by a factor of four, was included! Furthermore, the calculated geometric mean of the seven values of relative hydraulic conductivity that are considered "valid" (Weeks and Wilson, 1984, page 13) include on very low value from the Paintbrush nonwelded unit. Wilson (1985, page 2) is therefore in error when he cites Weeks and Wilson (1984) for a flux estimated in the Topopah Spring welded unit: their treatment combines nonwelded Paintbrush data with selected Topopah Spring data.

A major uncertainty in the Weeks and Wilson (1984) data is the effect of the air-foam method on measured ambient water content on the core samples. If core samples were subjected to variable amounts of drying during collection and analysis, hydraulic conductivities estimated from laboratory studies would show greater scatter and a lesser magnitude than field values. The importance of wetting or drying effects for this sample set are not known quantitatively.

**MOISTURE CHARACTERISTIC CURVES
FROM BOREHOLE USW H-1,**



PAINTBRUSH NON-WELDED UNIT

————— 33.5 m below ground level (BGL)

TOPOPAH SPRING WELDED UNIT

— · — · — 128.0 - 134.9 m BGL

— · · · — 136.6 - 143.3 m BGL

— · · · · — 219.2 - 225.6 m BGL

— · · · · · — 390.4 - 405.8 m BGL

CALICO HILLS NON-WELDED UNIT

— · · · · · — 530.7 - 532.8 m BGL

FIGURE 3.

MODIFIED AFTER WEEKS AND WILSON (1984).

Examination of figures 4 through 22 in Weeks and Wilson (1984, p. 17 to 26) reveals three reasonably distinct sets of moisture-characteristic curves from core samples from borehole USW H-1 (Figure 3). The upper (lithophysal?) portion of the Topopah Spring unit is very similar to the Paintbrush nonwelded unit in terms of percent matrix saturation and the shape and position of the moisture-characteristic curves. Matrix saturation in the upper zone of USW H-1 averages 0.50 ± 0.05 . The middle portion of the Topopah Spring unit also shows an internal consistency, with matrix saturation averaging 0.71 ± 0.10 . Matrix saturation in the lower zone, which includes two samples from the Calico Hills nonwelded unit, is 0.85 ± 0.07 . It appears that a stratigraphic inhomogeneity is present in the Topopah Spring unit; and significantly, there is no evidence of a discontinuity in the character of moisture-characteristic curves across the upper and lower boundaries.

Weeks and Wilson (1984) have used geometric mean saturated hydraulic conductivities from Anderson (1981) as a basis for computing "effective" hydraulic conductivities from the "relative" hydraulic conductivities obtained in their own study. The geometric mean of a data set minimizes the effect of extreme values; utilization of geometric mean hydraulic conductivity data is therefore not a conservative approach in the present application.

Calculation Based on In-Situ Potential Gradients and Properties of Core:

Montazer, et al., (1985) report "relatively constant" matrix potential in the Topopah Spring welded unit in the 400 to 800 foot depth interval of USW UZ-1. Based on an assumed unit hydraulic gradient, Montazer, et al., (1985) use relative matrix hydraulic conductivities calculated by Peters, et al., (1984) to estimate 0.1 to 0.5 mm/yr. flux through this interval.

It is evident from figures 7, 8, 9, of Montazer, et al., (1985) that there has been considerable drift in the output from thermocouple psychrometers and heat-dissipation probes in USW UZ-1 over the two year monitoring period, and several of the instrument stations have failed. Wetting trends, drying trends, and reversals have occurred at individual stations. The interpretation by Montazer, et al., (1985) that these data, when extrapolated, indicate "relatively constant" matrix potential that represent ambient conditions is judged to be premature.

Rush, et al, (1984, p. 54) indicate that a perched saturated zone is "probably" present in USW H-1 in the depth interval 448 to 458 m; this is based on 45 minutes of airlift water production at flow rates of 1.3 to 1.6 liters/second (21 to 25 gpm) while the well was at a depth of 458 m (Rush, et al., 1983, p. 19). This zone is in the lower portion of the Topopah Spring welded unit.

Similarly, drilling of USW UZ-1 was discontinued at 387 m because a "large" volume of water was encountered, and "the water level could not be lowered significantly." This may represent a naturally occurring perched-water zone, although the water is reported to contain polymer identical to that used in drilling USW G-1, 305 m to the southeast (Whitfield, 1985). However, no analyses of either the encountered water in UZ-1 or drilling water used at USW G-1 have been published.

Prior drilling activities in the vicinity of USW UZ-1 is reported to have introduced large quantities of drilling fluids not the subsurface. Approximately 8,700,000 liters (2,300,000 gallons) of water-based polymer drilling fluid were lost during drilling of USW G-1 (Whitfield, 1985) and over 2,200,000 liters (580,000 gallons) were lost during drilling of USW H-1 (Rush, et al., 1983, p. 20). Locating USW UZ-1 in an area that was proximate to areas perturbed by prior drilling activities was an error in judgment in our opinion.

The vadose-zone saturation encountered in H-1 and UZ-1 may be naturally occurring saturation (perched water) or saturation caused by drilling fluid losses. As chemical analyses of fluid samples for UZ-1 and H-1 (448-458 m zone) have yet to be published, we are not able to judge if the water is only drilling fluid, mixtures of perched water and drilling fluid, or perched water. However, to be conservative,

we assume that the fluid encountered is perched water until proven otherwise. The DOE program has, to date, ignored this evidence for perched water in the Topopah Spring Member immediately adjacent to the repository block at approximately the repository-zone depth. Establishing the natural occurrence of perched water is key to site characterization because its presence indicates fracture flow to the depth of occurrence. Instead of following through with an assessment program of the vadose-zone saturation in the area, the water-potential measurement experiment of USW UZ-1 was established. Unfortunately, this effort has yielded so little useful water-potential data that the principal investigators (Montazer, et al., 1985) have treated the widely scattered data as single-valued in terms of fluid-potential gradient! These ambiguous results and the failure to study encountered saturation leaves the vadose-zone flux question totally unresolved at this locality.

The Maxey-Eakin Recharge Method for Flux Estimation:

Another line of "evidence" cited by Wilson (1985) in support of the "conservative" upper-bound flux of 0.5 mm/yr. is a calculation based on the Maxey-Eakin method. In the Maxey-Eakin method, the recharge to a ground-water basin is calculated from specific percentages of the precipitation which is estimated to fall upon several elevation zones on the mountains surrounding that ground-water basin. Without explanation from the original authors, "...the amount of water from the successive zones that reach the ground-water reservoir is estimated as 0, 3, 7, 15, and 25 percent of the precipitation in the respective zones (Maxey and Eakin, 1949, p. 40, cited in Watson, et al., 1976, p. 342).

The Maxey-Eakin method of estimating recharge has not demonstrated validity or utility for determining accurate rates of recharge for localized site-specific hydrogeologic environments such as Yucca Mountain. The basic assumptions necessary for application of the method are: 1) recharge is systematically related to mean annual precipitation, 2) higher percentages of recharge occur from precipitations which falls at the higher altitudes (and usually in greater annual amounts), and 3) the ground-water catchment basins can be delineated. The method also required two other assumptions when originally developed: that the available ground-water discharge estimates were accurate and that the flow systems are in equilibrium (recharge is equal to discharge).

A serious weakness of the Maxey-Eakin method for estimating recharge in a local setting is the general absence of knowledge of the conditions under which recharge occurs, such as the roles varying local hydrogeologic environments and climatic events may play in controlling recharge. It is also undemonstrated that mean annual precipitation is the best parameter of climate from which to estimate recharge. Through trial and error, percentages of mean annual precipitation by zonation have been assumed to equal estimated discharge, and it has been assumed that the higher terrane precipitation is more important and thus more heavily weighted with higher percentages of recharge resulting from the precipitation. There are, however, no studies that have demonstrated unique recharge rates based on percentages of precipitation, and therefore, the Maxey-Eakin recharge estimate derived for a relatively small area like Yucca Mountain has no dependable validity.

In the general absence of knowledge of recharge processes and rates in site-specific environments of the Great Basin, including those at Yucca Mountain, there is little reason to postulate or justify a uniform flux rate in the vadose zone or to believe a method such as the Maxey-Eakin method would accurately characterize the flux rates for travel-time purposes. It is entirely possible, in the climate that prevails at Yucca Mountain, that all recharge is restricted to localized site specific hydrogeologic conditions, such as wash areas underlain by alluvium and fractured rock. It is also possible that in the more arid area, such as Yucca Mountain, much of the recharge may be closely related to "extreme event" precipitation occurrences related to the arid climate. In other words, recharge at Yucca Mountain may be highly localized in both time and space, and travel time estimates for the vadose zone should be so structured to address these possibilities in order to meet the intent of the travel-time objective.

Vadose (Unsaturated) Zone Travel Times:

Vadose-zone travel time estimates in the EA are based on the analysis by Sinnock, et al., (1986). The analysis can be summarized as follows:

1. The disturbed zone was assumed to extend to a position 560 meters (m) below the midplane of the 45 m thick repository horizon.
2. The region between the disturbed zone and the water table was discretized into 963 vertical prisms, each measuring 76.3 m square; each prism was divided into 3.105 m thick elements.
3. Recharge flux was assumed to be uniformly distributed in time and space; 0.6 mm/yr was adopted as a baseline value.
4. A value of saturated matrix hydraulic conductivity for each element within a particular hydrogeologic unit obtained by statistical sampling methods from a frequency distribution fitted to the matrix hydraulic conductivity data for that particular unit.
5. The randomly selected value of hydraulic conductivity was compared with the value of flux; if the flux value was less than 0.95 times the saturated matrix hydraulic conductivity, it was assumed that the flow within that element was entirely in the porous rock matrix, and a value for matrix effective porosity was then chosen by random sampling from the frequency distribution of porosity values for the appropriate hydrogeologic unit.
6. Water particle velocity for each of the elements for which only matrix flow was assumed to occur was calculated by dividing the flux value by the samples effective porosity, assuming a hydraulic gradient equal to 1.0, then modified to account for partial saturation.
7. If the ratio of flux to the randomly sampled value of saturated matrix hydraulic conductivity was equal to or greater than 0.95, it was assumed that fracture flow occurred for that quantity of flux in excess of 0.95 times the saturated matrix hydraulic conductivity.
8. An effective porosity of 0.0001 was assumed for all fracture flow, and the velocity of flow in fractures for each element was determined by dividing the calculated value for flux in the fractures by 0.0001.
9. The shorter of matrix or fracture flow time was considered to be the "travel time" through any individual element.
10. Ground-water travel time in each of the 963 vertical prisms was calculated as the sum of travel times in all of the 3.06 m thick elements comprising the individual prisms.
11. The procedure was repeated ten times for each prism to provide a representation of the variation in travel time due to the variation in hydraulic parameters.

The selection of a disturbed-zone boundary 40 m below the midplane of a 45 m thick envelope containing the underground facilities (Sinnock, et al., 1986, p. 18) is essentially arbitrary. Although the disqualifying condition addressed in the EA applies to pre-waste emplacement conditions, application of the disqualifying condition to a particular site requires that the extent of the disturbed zone during the 1,000 years following waste emplacement be known. Until a quantitative evaluation of convective heat transfer and associated mineral alterations is demonstrated, the approximate extent of the disturbed zone will not be known.

Discretization of the region between the repository horizon and the water table appears to have been guided by convenience rather than a rational choice of element size based on a geostatistically valid correlation length. Since the model does not allow for a nonuniform wetting front (fingering) in individual prisms; this phenomenon is likely to occur on a scale much smaller than the 76.2 m horizontal grid size. The assumed vertical correlation distance is of critical importance in determining the travel time through a vertical prism. This is because the equivalent permeability of a vertical prism is defined by the harmonic mean permeability of the individual layers; the harmonic mean is weighed toward the properties of the least-permeable elements. The greater the number of elements, the greater the probability that a low permeability, but not so low as to require fracture flow) will be assigned to one or more elements in the prism. Sinnock, et al., (1986, p. 58) have concluded that the travel-time distribution is apparently most sensitive to flux, correlation lengths, and spatial variations of saturated matrix hydraulic conductivity. Also, "...the sensitivity of the travel times to the correlation lengths suggests how prudent it is to perform a carefully designed testing program for determining the correlation length of all key parameters influencing flow velocities" (Sinnock, et al., 1986, p. 50). A key point is that "...neither the vertical correlation length nor the horizontal correlation length has been determined for the hydrogeological units at Yucca Mountain..." (Sinnock, et al., 1986, p. 15). Vertical correlation length was therefore considered a "free" variable in simulations of unsaturated-zone travel time (Sinnock, et al., 1986, p. 15). If the vertical correlation length is assumed to be at least as great as the thickness of each unit, travel times for approximately two percent of the prisms are less than 1,000 years, even with a flux of only 0.5 mm/yr (Sinnock, et al., 1986, p. 48 to 49). The EA states that:

"This approach yields higher, but probably physically unrealistic, estimates of the probability of continuous fracture flow and rapid matrix flow than the (3.05 - meter) interval sampling method..." (DOE, 1986, section 6.3.1.1, part 6.3.1.1.5, p. 6-150, paragraph 4, lines 11 to 13, and p. 6-162 first partial paragraph, lines 1 to 23),

ignoring evidence such as that presented by Spengler, et al., 1987, p. 25 and 27) that preferred orientations of joints and type and percent of joint fillings in the Topopah Spring Member and the tuffaceous beds of Calico Hills are nearly identical. Vertical correlation lengths may, therefore, be even greater than individual unit thicknesses.

The baseline flux value used for travel-time calculations is 0.5 mm/yr, a value thought by Wilson (1985) to be a "reasonable and conservative" upper bound flux for Yucca Mountain. Using a trial flux value of 1.0 mm/yr, Sinnock, et al., (1986, p. 52) found that a "substantial" proportion of flow paths have travel time of less than 10,000 years. It is emphasized that the nonconservative 3.05 m vertical correlation length was obtained during adjustments of flux; results of simulations that incorporate conservative vertical correlation lengths, and conservative flux rates have not been made available. Given the extreme sensitivity of travel time to flux rate (Peters, et al., 1986, p. 30 to 33) and the very real uncertainty in flux (discussed earlier in this review) we consider the range of flux values utilized in trial calculations of travel time to be incomplete.

Lognormal frequency distributions were fitted to available saturated matrix hydraulic conductivity data from the hydrogeologic units at Yucca Mountain; these distributions were then randomly sampled during each simulation to provide estimates of saturated matrix hydraulic conductivity for each block in the discretized region. Fitting a set of data with a lognormal distribution has two effects; the influence of extremely high values are minimized, and the logarithms take on the characteristics of a normally distribute population. Sinnock, et al., (1985, p. 35) have made a conceptual error by fitting bimodal distributions of saturated matrix hydraulic conductivity data from the Calico Hills vitric unit and Prow Pass welded unit with lognormal distributions.

The assumptions that only matrix flow occurs when the flux rate is less than 0.95 times the saturated matrix hydraulic conductivity is open to question. Skin effects on fractures and hysteresis in the moisture-content dependent characteristics of the rockmass will cause fracture flow to dominate (over matrix flow) earlier and more extensively than otherwise expected (see Montazer and Wilson, 1984, p. 25

for a discussion of hysteresis). As recognized by Montazer and Wilson (1984, p. 25) a secondary hysteresis effect, due to air entrapment in matrix blocks during wetting, would further promote fracture flow during recharge events. Hysteresis and skin effects both escape mention in the EA, and the sensitivity of the analysis to the assumed constant relationship between flux and saturated hydraulic conductivity is not addressed.

The concept of relative permeability discussed at length by Weeks and Wilson (1984, p. 12 to 13) appears to have been ignored in the treatment by Sinnock, et al., (1985) and subsequently in the EA. If matrix hydraulic conductivities had been adjusted downward to account for the effects of partial saturation, a proportional increase in fracture flow would result.

Flow velocity through fractures has been obtained from an assumed fracture porosity and an assumed flux excess above the amount transmitted by the matrix. Hydraulic tests on fractured specimens by Peters, et al., (1985, p. 54) indicate fracture apertures up to 67 microns in the Topopah Spring welded unit and 31 microns in the zeolitized Calico Hills unit. Corresponding fracture hydraulic conductivities are 3.78×10^{-3} and 7.9×10^{-4} m/s, respectively; under a unit hydraulic gradient water could move from the repository horizon to the water table in fractures such as these in less than one week! Ogard, et al., (1983, p. 44) report fractures in the Topopah Spring welded unit with apertures exceeding 250 microns.

Saturated Zone Travel Time:

Basic data utilized by the DOE in the calculation of saturated zone travel time at Yucca Mountain is as follows:

1. Potentiometric data from 32 drillholes in the vicinity of Yucca Mountain (DOE, 1986, vol. II, section 6.3.2.2, part 6.3.1.1.5, p. 6-148, fig. 60-3).
2. Fracture effective porosities calculated by multiplying the fracture density from Scott, et al., (1983) by the effective aperture (calculated from a relationship provided by Freeze and Cherry (1979, p. 74).
3. Saturated hydraulic conductivities from tests on wells UE-25b#1 (Lahoud, et al., 1984) and J-13 (Thordarson, 1983).

Sinnock, et al., (1986) are referred to as the source of fig. 56-3 in the EA (DOE, 1986, vol. II, section 6.3.1.1, part 6.3.1.1.5, p. 6-148, fig. 6-3 caption); no similar figure appears in Sinnock, et al., (1985); Robison (1984) is not cited in Sinnock, et al., (1986). A similar figure does appear in Sinnock, et al., (1985, p. 19). No summary of water-level fluctuations in individual boreholes is yet available in the published literature. Although numerous wells are known to be equipped with pressure transducers and data-logging devices.

Fracture effective porosities for the zone of saturation were computed from a theoretical relationship between hydraulic conductivity of the fractured rock, fracture density, and fracture aperture (Snow, 1968, as cited in Freeze and Cherry, 1979, p. 74). This relationship is strictly applicable only to a single set of planar joints with constant aperture. Orientation bias, due to the relative orientation of fractures and the borehole, was accounted for through the relationship:

$$F_c = (\sin A)^{-1} \cdot F_m$$

where: F_c = fractures per cubic meter.

F_m = linear fracture frequency.

A = acute angle between the core axis and an individual fracture set.

This procedure converts all fractures to a single hypothetical set normal to the core axis.

Unfortunately, this simplistic approach to the estimation of fracture parameters does not account for contrasting properties of individual fracture sets, which are likely to differ in preferred orientation, roughness, hydraulic aperture, mineral content, etc. The SEM image of a fracture in the lower, nonwelded portion of the Topopah Spring Member (Carlos, 1984, p. 32, fig. 31) illustrates how variable the aperture and roughness of individual fractures are likely to be in the field environment. Analysis that does not account for hydraulic properties of individual fracture sites, connectivities of the fracture sets, and hydraulic significance of fracture intersections markedly increases the uncertainty for the analysis.

Results of hydraulic testing at well J-13 indicate that "850 m²/day probably is a reasonable maximum value for transmissivity (of the Topopah Spring Member)" (Thordarson, 1983, p. 49). Dividing this transmissivity by the 308.5 m thickness of the tested interval yields a hydraulic conductivity of 2.75 m/day (1,000 m/year). Examination of core recovery data from J-13 (Thordarson, 1983, p. 14) indicates that highly fractured intervals are quite localized, so the hydraulic conductivities of the producing intervals are probably much higher than the average value given above. Recent work by Erickson and Galloway (1984) has resulted in hydraulic conductivity estimates of between 59.56 m/day (21.7 km/year) and 74.3 m/day (27.1 km/yr) for fractured intervals in the Bullfrog and Tram Members of the Crater Flat Tuff. These values contrast sharply with the assumed hydraulic conductivity of 1.0 m/day used in the EA for a calculation of saturated-zone travel time in the indurated tuffs.

ADDITIONAL WORK NEEDED:

Review of the DOE documents which establish site-characterization programs.

RECOMMENDED PROGRAM:

Objective:

Continue to track the DOE site-characterization program in key issue areas, where the database and/or DOE approach is deficient.

EXISTING PROGRAM:

Review of the SCP and work plans.

Appendix E-II

**Review of: Consultation Draft of the Site Characterization Plan : Yucca Mountain Site, Nevada
Research and Development Area, Nevada
January 1988 (DOE/RW-0160) by DOE, p. 2 to 28.**

Review of Technical Documents

ISSUE:

The technical accuracy of the U.S. Department of Energy Site Characterization Plan : Yucca Mountain Site, Nevada Research and Development Area, Nevada : Consultation Draft : Nuclear Waste Policy Act (Section 113) (DOE/RW-0160), vols. 1 to 8, 1988 (CD-SCP) for Yucca Mountain.

OBJECTIVES OF ACTIVITY:

Review the CD-SCP, especially its hydrogeologically related activity, in terms of: 1) conceptual completeness and focus; 2) appropriateness of methodology to accomplish stated objectives; 3) availability of supportive technology; and 4) probability of success and/or feasibility.

ACTIVITY SUMMARY:

The following elements of the CD-SCP were reviewed in terms of the four points (2a, b, c, and d) listed above:

- Geohydrology Program
- Geochemistry Program
- Rock Characteristics Program
- Climate Program
- Thermal and Mechanical Rock Properties Program
- Waste Package Program
- Performance Assessment Program

The review was structured into three basic parts:

- Overview Comments - which deals with general impressions;
- Issue Resolution Comments - deals specifically with several of the most important hydrogeologic issues; and
- Activity Reviews - (Appendix 1) which contains each individual's review of the technical activities.

FINDINGS:

The following comments have been abstracted from the review of the CD-SCP by MAI:

OVERVIEW COMMENTS

GENERAL COMMENTS

The following objectives of the CD-SCP are stated in the Annotated Outline for Site Characterization Plans (DOE, February 1987, p. xii to xiv):

The purpose of the SCP is to provide a document in which the DOE:

- Describes the site, design of a repository and engineered barriers appropriate to the site, waste packages, emplacement environment, and performance analysis in sufficient detail so that the planned site characterization program may be understood.

- Identifies the uncertainties and limitations on site- and design-related information developed during site screening, including issues that need further investigation or for which additional assurance is needed.
- Describes the detailed programs for additional work, including performance confirmation, to (1) resolve outstanding issues, (2) reduce uncertainties in the data, and (3) make site suitability findings relative to DOE siting guidelines, 10 CFR 960.

The SCP will provide a vehicle for early NRC, State, Indian tribal, and public input on the DOE's data-gathering and development work so as to avoid postponing issues to the point where modifications would involve major delays or disruptions in the program. Early review of the DOE's site characterization plans as presented in the SCP will provide an opportunity for the NRC to evaluate whether the DOE's proposed program is likely to generate data suitable to support a license application." (OGR/B-5, p. xiii).

We find that the CD-SCP substantially, but not completely, meets the above first objective. We find that it does not consistently meet the second and third objectives. It does not consistently describe the detailed programs to: 1) resolve outstanding issues; 2) reduce uncertainties in the data; and 3) make site suitability findings relative to the DOE siting guidelines, 10 CFR 960.

We find that the CD-SCP does not entirely establish what is known about the Yucca Mountain from site-exploration activities to date. Many if not most aspects and findings are freely and fully discussed, but key findings, such as evidence of perched water within the vadose zone, and important observations of gas-circulation gradients within the vadose zone, are omitted. These omitted observations could prove to be the most fundamental findings to date with respect to the site's ability to isolate waste.

We find also, with respect to the above point two objective, that a major issue of fracture flow in the vadose zone has been deemed so unimportant that the resolution activity is to be primarily laboratory experiments. Therefore, we judge the CD-SCP fundamentally deficient with respect to resolving the issue by reducing or eliminating the uncertainties about fracture flow in the vadose zone.

We find that, with respect to the above, the CD-SCP often fails to provide enough details in the activity plans to confidently judge the plans.

The following questions are intended to be addressed by the SCP (DOE, OGR/B-5, February 1987):

- Have the important information needs and unresolved issues been identified?
- Does the SCP specifically address these information needs and present program plans to obtain the needed information?
- Are the methods of testing and analysis proposed for the planned site characterization program appropriate?
- Have alternative methods of testing and analysis been identified and evaluated, and has an adequate basis been provided for the selection of the methods to be used?
- Will the data to be collected and the reliability of the collection methods and analysis be of adequate quality to support site selection and a future license application?
- Have the testing plans been based on the performance requirements of the Mined Geologic Disposal System (MGDS) components, and are the tests adequate to enable evaluation of whether or not the MGDS components will perform as required?

We recognize aspects where the CD-SCP is seriously deficient in all of the above points of question. We think that important negative answers can be given for the first five questions when aspects of vadose-zone hydrology are considered. Point six, discussion of whether tests are adequate to enable evaluation of the expected performance of the MGDS, is not recognized in the CD-SCP. We assume that such testing call upon characterizing a combination of dynamic thermal loading and unloading, multiphase water transport, and dissolution processes based on in-situ geochemistry, all acting upon the engineered barriers.

We find the CD-SCP, when judged by the data development/analyses activities, unlikely to create a technical program that will establish viable databases to resolve or answer several of the important issues. The basis for this statement can be further examined in Appendix I reviews. A summary of this appendix reviews is shown in Table 1 (appendix reviews are not included in this report). Many activities are poorly designed and/or focused with respect to available technology. Many others are not feasible with respect to combinations of time, financial resources, and human and laboratory resources. Idealistic approaches, with much modeling in the face of little or no data and marked uncertainties with respect to processes operating, characterize the planned technical program. The CD-SCP is very consistent in calling upon numerical models (using existing, or newly developed, and/or to be developed codes) for the resolution of the characterization issues created by the complexity of the site and the very limited databases.

Our opinion is that the CD-SCP activities need to be carefully screened, focused, and modified into feasible, well-coordinated activity programs that could be completed in five or six years. Each program (investigation, study, and activity) needs the benefit of peer review by experts experienced in both theory and field investigation.

Further, an appropriate SCP would clearly identify and rank the most likely fatal flaws (issues) of the geologic-barrier system of the site to prioritize and coordinate site characterization studies. This has not been done; the CD-SCP generally fails to establish a vadose-zone fracture flow/travel time issue resolution program that will work, and totally ignores the need for a research program to establish the impacts of the thermal envelope, and the associated extent of the disturbed zone with the induced hydrothermal system. Such a disturbed system has major potential to impact waste isolation.

DISCLAIMER

We find the disclaimer printed on the back cover of each volume to be inappropriate to the work presented. It says that the report was prepared as an account of work sponsored by the United States Government, but neither the U.S. Government nor the U.S. Department of Energy, nor employees make any warranty, nor assumes legal liability or responsibility, etc. It also states that the views and opinions of authors expressed herein do not necessarily state or reflect those of the United State Government nor an agency thereof.

The DOE is clearly the author of the CD-SCP, as no authorship is shown other than the U.S. DOE. If the above disclaimer were to be used in an appropriate manner, the majority of the CD-SCP should be backed by specific authorships. Specific authors would be appropriate for the expert opinion and judgment desirable in the planned activities of exploration and research. We find by omitting the specific technical authorship, the DOE may have, perhaps inadvertently, diminished the technical quality of the CD-SCP. We suggest the DOE recognize the scientific and technical challenge of characterizing Yucca Mountain, and appropriately indicate specific authorship on scientific and technical activities in the SCP.

DOE GOALS

A very disquieting presentation characteristic of the CD-SCP is the apparent perception that the given site, Yucca Mountain, in terms of geologic-barrier performance, can be made better or worse, just as an engineered system can be made better or worse by design changes. This conceptual approach has flavored the DOE selection process (Draft Environmental Assessment and Environmental Assessment

documents) and continues in the CD-SCP. Explicit examples occur throughout the CD-SCP discussions and in tables, such as Table 8.3.1.5-1 on pages 8.3.1.5-4 and 5. This table, dealing with site performance during a climate change, shows a column of initiating events or processes, and another correlating column entitled "tentative goal", which gives the currently perceived extreme values that would be acceptable. Such a title "tentative goal" would be appropriate for an engineered barrier where engineered design determines performance. A natural system, the geologic barrier, can not be altered once the site has been selected. There is no goal, therefore; there is only performance characterization. Geologic and hydrogeologic aspects can only be characterized to varying degrees of accuracy as to how they will perform in waste isolation. Therefore, if the DOE correctly perceived that its mission is to characterize the site to establish if the repository should be built, the many "tentative goal" columns would be better named "performance requirement" or "tentative performance requirement." The term "goal" is widely used in the CD-SCP, and should not be used for the SCP for uncontrollable geologic and hydrologic aspects of the specific site. Performance goals are fine for engineered aspects.

CD-SCP CONTENTS AND TECHNICAL REVIEW

The CD-SCP is so massive and complex in terms of topical scope and objectives that the reader is easily diverted from the true intent of the document. The SCP is the program of exploration and research, both in the laboratory and in the field. Therefore, we have focused our review efforts not on the very extensive organizational discussions and rationalizations, but on the descriptions of the programs of exploration and research.

We believe that success or failure in reaching confident site characterization will depend heavily on the SCP adopted by the DOE. We base this belief on the following: 1) the choice of a repository-horizon environment that is totally unknown from a hydrogeologic perspective; 2) the ten years of effort already expended on Nevada Test Site (NTS) and the Yucca Mountain characterization; and 3) the continuing high degree of uncertainty with respect to many critical performance aspects of the site. Therefore, the CD-SCP has been reviewed in anticipation of discovering the technical program the DOE would mount to resolve the many issues and performance questions.

Activities are the technical and/or scientific efforts planned for site characterization. The CD-SCP links activities, where there is a usually brief discussion of the planned objectives, methods, and associated elements, to studies, generally composed of one or more activities, to investigations, which are composed of studies, to programs. All have been organized and rationalized with respect to characterization issues from the perspective of licensing requirements. The CD-SCP provides reasonable planning discussions at these levels. However, the activities are a better measure of the planned site characterization, and we give, in general, very low marks for the activities.

We have reviewed each activity (Appendix I summary is given in Table 1) in our topical areas of responsibility because we recognize them as the only fundamental investigative activities in the CD-SCP. These activities, when executed, must provide the information to deal definitively with all issues and have the power to characterize the site. Unfortunately, we have found that many activities are only at the conceptual stage at best, and would be better judged when work plans and technical procedures become available. In response to this very real problem, we were forced to review the activities from an expert opinion mode, generally reading between the lines and judging the activity from several perspectives.

Technical Review Criteria: The four criteria adopted in the activity reviews: 1) conceptual completeness and focus; 2) appropriateness of methodology to accomplish stated objectives; 3) availability of supportive technology; and 4) probability of success and/or feasibility, warrant brief discussion. There are, however, no detailed work plans or technical procedures for each activity upon which we can base an in-depth review. Our ability to review conceptual aspects of a given activity is, therefore, better than our ability to review methodology, since the details of methodology are often not complete. Any activity, if it falls in any of the four categories, fails to establish what is required for site characterization and/or issue resolution. For example, one might find in a review that conceptual completeness or focus is rated low, and the other three aspects much higher. This would indicate that in our opinion, the activity can be performed in terms of methodology, available technology, and that there are the necessary resources for feasible execution, but it will not likely answer the correct questions. Conversely, we also find many of the activities more or less conceptually appropriate and focused, but unlikely to be successful because of deficiencies in methodology, available technology, or the likely availability of resources (including time).

In the reviews of the activities we find that, out of a total of 190 individual activities, we judge that 163 (about 86%) will not be successful in terms of the site characterization objectives (Table 1). When analyzed by program, we find only in one program (Climate) where there can be some important progress towards site characterization.

Table 1. Summary of MAI Reviews of CD-SCP Activities

<u>CD-SCP PROGRAM</u>	<u>YES</u>	<u>NO</u>	<u>TOTAL REVIEWED</u>
Geohydrology (8.3.1.2)	6(4)	51(47)	57(51)
Geochemistry (8.3.1.3)	4	33(29)	37(33)
Rock Characteristics (8.3.1.4)	1	5	6
Climate (8.3.1.5)	14(12)	15(14)	29(26)
Thermal and Mechanical Rock Properties (8.3.1.15)	2	2	4
Waste Package (8.3.4)	1	14(13)	15(14)
Performance Assessment (8.3.5)			
a. Engineered Barrier System (8.3.5.10)	3	23	26
b. Total System (8.3.5.13)	0	30	30
Total (without duplication)	31(27)	173(163)	204(190)

The DOE has, or could have, at its disposal, the best scientific facilities and cadre of scientists in the nation. Such resources have not been effectively tapped in the development of the CD-SCP. We think it productive to offer the probable reasons for our review findings:

- I. The site-selection and licensing criteria demand knowledge about natural systems that is not normally established at the scales of consideration and the levels of confidence required.
- II. The DOE has selected an entirely undocumented and little studied hydrogeologic environment for the repository at Yucca Mountain. There are few if any useful databases from similar environments in the world, and there are no proven techniques of study with respect to several key issues.
- III. Fractured, and somewhat porous rock imposes a well-known but analytically intractable degree of complexity to fluid-flow systems, as does the vadose-zone position of the repository horizon. It is known that conventional mathematical models and established field-test procedures will not perform adequately in both the saturated and vadose zones of the Yucca Mountain environment.
- IV. The host-rock stability is uncertain due to its origin and composition when subjected to the heat of the thermal envelope.
- V. The primary (and possibly only) waste-isolation attribute of the Yucca Mountain site is its location in an arid climate. The mechanics and site-specific conditions of recharge are unknown in these arid climates for most classes of terrane, including that represented by Yucca Mountain.

The above factors relate to the thoroughness of the technical questions being asked, the very limited preexisting knowledge, and the complexity of the site. The following, however, relate to the DOE program:

- VI. There is little evidence that the DOE has followed the expert advice offered by early peer-review groups. The characterization program continues to be weak in the same areas as the site-selection program (useful field studies lacking, useless models dominating).

- VII. There is little evidence of peer review in the development of the majority of the CD-SCP activities. Only one program, climate change, seems to have had the benefit of independent peer review, and we judge half of the activities may succeed, which is a major improvement over all other programs.
- VIII. There is ample evidence that many activities have been conceived and written, or perhaps rewritten, by authors with limited experience and training in the topical areas, and that these activities have not been reviewed by experts.

Points six through eight disappoint us. They indicate one or a combination of the following: 1) the DOE management has failed to recognize the complexity of the site (has not taken or used expert advice appropriately); 2) the DOE management has made a determination that careful characterization is not necessary, nor perhaps desirable; and/or 3) the DOE has failed to effectively develop and manage the required scientific program to confidently select and characterize the site.

PERFORMANCE ISSUES

The following sections are discussions and specific comments focused on selected performance issues:

PERFORMANCE ISSUE 1.1

The ability of a mined repository to limit radionuclide releases to the accessible environment is fundamentally dependent on geologic and hydrologic conditions at the site which, combined, establish the degree of the geologic barrier a specific site offers. Intrinsic properties such as permeability provide one general measure of site quality, while the chemistry of the rock-water system determines the mobility of radionuclides as well as the necessary desirable designs for the waste packages. Key Issue I in the Office of Geologic Repositories issues hierarchy relates to whether the mined geologic-disposal system at Yucca Mountain will isolate the radioactive waste from the accessible environment after closure in accordance with the requirements set forth in 40 CFR Part 191, 10 CFR Part 60, and 10 CFR Part 960 (CD-SCP, p. 8.2-2). Performance Issue 1.1, "Will the mined geologic disposal system meet the system performance objective for limiting radionuclide releases to the accessible environment as required by 10 CFR 60.112 and 40 CFR 191.13?" (CD-SCP, p. 8.2-3), dictates information needs 1.1.1 through 1.1.5 of section 8.3.5.13 of the CD-SCP, "Total System Performance":

Information Need (CD-SCP)

- 1.1.1 Site information needed to calculate releases to the accessible environment.
- 1.1.2 A set of potentially significant release scenario classes that address all events and processes that may affect the geologic repository.
- 1.1.3 Calculational models for predicting releases to the accessible environment attending realizations of the potentially significant release scenario classes.
- 1.1.4 Determination of the radionuclide releases to the accessible environment associated with realizations of potentially significant release scenario classes.
- 1.1.5 Probabilistic estimates for the radionuclide releases to the accessible environment considering all significant release scenarios.

Geochemistry

8.3.1.7 Overview of Rock Dissolution.....

8.3.1.7.1 Investigation: Rates of dissolution of crystalline and noncrystalline components in tuff.

Comments:

1. The use of the word "investigation" in the title/header is misleading; no investigation is planned.
2. Previous comments (Mifflin & Associates, Inc.) regarding the dissolution section of the EA have been ignored.
3. Specifically, considering the listed conclusions (p. 8.3.1.7-1) regarding dissolution in the EA, restated in the CD-SCP: the second conclusion regarding mineral insolubility is decidedly incorrect and not based on any factual information of which we are aware.

The first part of the fourth conclusion, insolubility of minerals comprising the host rock in and around Yucca Mountain, is incorrect as well; therefore the second part of the fourth conclusion, "significant subsurface rock dissolution is not a credible process leading to radionuclide releases greater than those allowable..." is incorrect information and contradicts current experiments (J. D. Rimstidt, personal communication, 1988) that suggest important mass transport occurs under nonequilibrium conditions (i.e., thermal gradients expected under repository conditions).

8.3.1.7.1.1 Application of Results

In general, there are no results when no investigations were specifically conducted to consider dissolution. The CD-SCP is illogical when it applies speculative conclusions from the EA to this important site-characterization issue. There are no results, only speculative and totally unsupported conclusions, to address higher-level findings concerning dissolution.

The dissolution question affects favorable conditions 3, 4, and 7 (Table 8.3.5.17-1) and potentially-adverse conditions (Table 8.3.5.17-2) 5, 7, 8, 10, and especially 23 (potential for future perched water bodies that may saturate portions of the underground facility).

Scenarios to characterize potentially-adverse condition [PAC] 5 do not address changes in the hydrologic conditions caused by the heat envelope generated by the repository after a few hundred years.

Scenarios regarding PAC 7 (ground-water geochemistry conditions that could increase solubility or chemical reactivity of the engineered-barrier system) do not address the thermal regime imposed by the waste repository, particularly the hydrochemical and mineralogical reactions that will accompany vaporization and condensation in fractures.

No scenarios concerning PAC 10 (dissolution) will be characterized further by DOE because their available information appears adequate to them. This is a serious flaw in the CD-SCP, since the assumption that dissolution will not occur has no basis in fact.

Scenarios regarding PAC 23, the potential for existing or future perched-water bodies that might saturate portions of the repository, do not include any that may result from actual storage of waste canisters in the repository over the several hundred years of perturbing thermal influences. Only the potential for perched-water bodies that may form under present [preclosure] conditions will be considered by the DOE. This is a serious shortcoming in DOE's site-characterization plans considering the amount of water vapor that will be driven from the rock matrix in the greater than 95°C portion of the thermal envelope.

If the DOE continues to assume that host rock and minerals are insoluble, then many other CD-SCP activities are inappropriate, such as 8.3.1.3.2.2.1 (History of mineralogic and geochemical alteration...); 8.3.1.3.2.2.2 (Smectite, zeolite, manganese minerals, glass dehydration and transformation); 8.3.1.3.3.2 (Kinetics and thermodynamics of mineral evolution); 8.3.4.2.4.1.1 (Rock-water interactions at elevated temperatures); 8.3.4.2.4.1.7 (Numerical analysis and modeling of rock-water interaction); and 8.3.4.2.4.2 (Repository horizon rock-water interaction). The CD-SCP dissolution program is totally deficient. The aforementioned studies and activities need to be integrated into a dissolution program.

General Comments: Geochemistry Section

The following items represent our major concerns regarding the geochemistry program in the CD-SCP. For specific comments, see the activity review sheets and the specific comment section of this review.

1. The continued use of water from well J-13 as a reference water for all experimental work is not justified. Most of the credit taken by DOE for ground-water travel time is postulated to occur in the vadose zone and therefore most of the retardation should also occur in the vadose zone. Thus, obtaining chemical analyses of a vadose-zone water should be of the highest priority in the CD-SCP. The range of vadose-waters compositions should be determined as quickly as possible. As experiments and modeling employing J-13 water may have to be redone, it would be judicious of DOE to suspend those activities utilizing J-13 water until the vadose-water chemistry is characterized.

2. Another serious problem involves extrapolating laboratory sorption data (determination of K_d 's and retardation factors) to actual field conditions. Not enough importance is being attached to this subject. It is extremely difficult to envisage how data from experiments employing crushed tuff could be correlated to the field with any scientifically valid confidence. Crushing tuff generates new surfaces with attendant high-surface energies and nonrepresentative sorption characteristics. Furthermore, the mineralogy of the new rock surfaces from a modal standpoint is not known and should not be assumed from modal mineralogy of a whole rock sample. This may partially account for the unexplained scatter in previous experimental work and the differences between crushed tuff and solid core experiments. Highest priority should be assigned to validating the proposed experimental approach through field tests of sorption/retardation before additional resources are wasted in this extensively practiced but totally unproven methodology.
3. A major concern is the undue emphasis placed on modeling before experimental methodology is proven and meaningful field data are collected. Vast resources will apparently be directed to modeling efforts before sufficient information is collected to justify modeling.
4. Samples to be utilized in activities/studies are not clearly identified, nor are sample collection and preservation techniques. Very little is known about the site to date because of sampling difficulties.
5. Analytical methodology is not always indicated.
6. Technical procedures are not determined.
7. There are major inconsistencies in planned activities from one section to another.
8. Incomplete or wrong methodologies are used in many cases to obtain the desired information (See Appendix I Specific comments).

General Comments: Issue 1.1 Resolution Strategy

1. DOE continues to assume that matrix flow predominates over fracture flow in the vadose zone and that the matrix must be saturated for fracture flow to occur. No data exists to support these assumptions; in fact, based on suction-head data for the various rock units, these tuff units are most likely effectively saturated and therefore fracture flow should predominate.
2. DOE continues to assume that the percolation flux is uniformly distributed in space and time. This is highly speculative, not realistic nor conservative, and not supported by any data.
3. The dissolution scenarios (among others) have been ruled "not sufficiently credible to warrant further consideration" (DOE, 1986) by a "panel of experts". The same ruling was incredulously rendered for the bedded and domed salt sites. This ruling was not made by an independent panel of scientifically and/or technically recognized geochemists; but rather it was a DOE panel with, apparently, very limited expertise in the main subject area.
4. The DOE should convene a panel of recognized practicing geochemists and charge these experts with the tasks of evaluation of the rock-dissolution questions, particularly in light of the thermal envelope and the water content of the repository-rock horizon. Then it needs to follow the panel recommendations on appropriate rock-dissolution studies and add these to the SCP, if appropriate.
5. Under "Performance Parameters for Scenario Class C-3 [Table 8.3.5.13-14., p. 8.3.5.13-63] (changes in unsaturated zone rock hydrologic and geochemical properties)", no consideration is

given to the effect of waste emplacement in the repository. Specifically, those changes in rock-water geochemistry and hydrologic properties surrounding the repository level that may result in the formation of a perched-water body in the vadose zone above and below the repository, such as permeability and porosity changes brought about by refluxing of vadose-zone waters due to the thermal pulse of decaying waste.

6. Individual evaluation of topical scenarios for the purpose of eliminating scenarios with insignificant consequences may overlook the coupling that may occur between two or more processes/events that could produce significant consequences for the release of radionuclides to the accessible environment. We think this has occurred: the DOE has omitted the most obvious scenario of water vapor driven from the thermal envelope condensing in the cooler fractures that surround the repository horizon and returning to the boiling zone by gravitational forces.

Summary Comments: Issue 1.1 Resolution Strategy

Probabilistic estimates of radionuclide releases to the accessible environment must be based on sound, statistically valid, data and not on unproven DOE assumptions such as:

1. Matrix flow predominates in vadose zone;
2. percolation flux is areally and temporarily uniformly distributed; and
3. batch sorption experiments employing crushed tuff are representative of field conditions;
4. nor on statistically biased data such as were used by Sinnock, et al. (1986).

Until the aforementioned assumptions are proven by site characterization or changed to conservative assumptions, and sound statistical and geostatistical techniques are employed to evaluate data, the resolution of issues will continue to be flawed.

PERFORMANCE ISSUE 1.3:

Important "special" sources of ground water that are in close proximity to a repository should be well-characterized. Key Issue I in the Office of Geologic Repositories Issues hierarchy relates to whether the mined geologic-disposal system at Yucca Mountain will isolate the radioactive waste from the accessible environment after closure in accordance with the requirements set forth in 40 CFR Part 191, 10 CFR Part 60, and 10 CFR Part 960 (CD-SCP, p. 8.2-2). Performance Issue 1.3, "Will the mined geologic disposal system meet the requirements for the protection of special sources of ground water as required by 40 CFR 191.16?" (CD-SCP, p. 8.2-3), dictates information needs 1.3.1 and 1.3.2 of section 8.3.5.15 of the CD-SCP, "Ground-water Protection".

Information Need (CD-SCP)

- 1.3.1 Determination whether any Class 1 or special sources of ground water exist at Yucca Mountain, within the controlled area, or within 5 km of the controlled area boundary
- 1.3.2 Determine for all special sources whether concentrations of waste products in the ground water during the first 1,000 years after disposal could exceed the limits established in 40 CFR 191.16.

Section 191.16 of 40 CFR Part 191 was added to the final EPA rule to provide protection for those individuals in the vicinity of a disposal system (FR 38072, September 19, 1985). The CD-SCP (p. 8.3.5.15-1) provides the following explanation of EPA water-source designations:

"An aquifer must meet several criteria to be designated as a special source. The first step in the evaluation is to establish whether the aquifer is a Class I source as defined by the EPA Ground Water Protection Strategy of 1984 (EPA, 1984). The conditions that must be met for designation as a Class I source are (1) that the source is highly vulnerable to contamination because of the hydrologic characteristics and (2) that the source is irreplaceable in that no reasonable alternative is available to substantial populations or that the source is ecologically vital in that it provides baseflow to a sensitive ecological system.

If an aquifer meets the criteria for a Class I source, the next step is to determine whether it qualifies as a special source of ground water. 40 CFR 191.12 defines a special source of groundwater as "those Class I ground waters identified in accordance with the agency's Ground-Water Protection Strategy . . . that: (1) are within the controlled area encompassing a disposal system or less than 5 km beyond the controlled area [the controlled area is the actual area chosen according to the 40 CFR 191.12 definition of the controlled area]; (2) are supplying drinking water for thousands of persons as of the date that the [DOE] chooses a location within that area for detailed characterization as a potential site for a disposal system (e.g., in accordance with Section 112(b) (1)(B) of the Nuclear Waste Policy Act); and (3) are irreplaceable in that no reasonable alternative source of drinking water is available to that population."

A valley-fill aquifer, a tuff aquifer, and a carbonate aquifer are present at Yucca Mountain. DOE states that only the valley-fill aquifer was serving a population of thousands of persons at the time that the site was chosen for characterization (CD-SCP, Section 3.8). DOE also offers a preliminary determination that no potential special sources of ground water are present at the site, below the site, within the boundaries of the controlled area, or within 5 km of the controlled area boundary (CD-SCP, p. 8.3.5.15-6). The hydrologic feasibility of developing the lower carbonate aquifer must consider the possibility of interbasin diversion of baseflow to the Ash Meadows Springs (Section 8.3.1.9.2). DOE also considers that the Ash Meadows area is part of a different ground-water subbasin (Ash Meadows) from the Alkali Flat-Furnace Creek Ranch ground-water subbasin, which contains Yucca Mountain (Section 3.6).

The content of Section 8.3.1.9.2 (Investigation: Studies to provide the information required on present and future value of energy, mineral, land, and ground-water resources) suggests that the CD-SCP does not intend to refine the very poor understanding of the western margin of the Ash Meadows flow system between Yucca Mountain and Ash Meadows. The projection of this boundary north of Lathrop Wells is entirely speculative. DOE plans an analysis 1.3.1.1. (p. 8.3.5.15-7) to determine whether any aquifers near the site meet the Class I or special-source criteria. This analysis consists of two activities (1.3.1.1.1 and 1.3.1.1.2). These pull hydrologic data from other activities and demographic information into an assessment.

Comments and Discussion

DOE prefers to ignore that the western extent of the Ash Meadows' ground-water flow system is highly uncertain, as well as the carbonate aquifer's uncertain relations with the tuff aquifers of Yucca Mountain and the valley-fill aquifer in Amargosa Valley.

Yucca Mountain overlies the fragmented western extent of a regional-carbonate aquifer (Winograd and Thordarson, 1975), which discharges on the order of 17,000 acre-feet per year of good-quality ground water near Ash Meadows. Structural relationships probably control the extent of the carbonate aquifer in this area. Four major Mesozoic thrust faults that involve the subvolcanic rocks are projected through the Yucca Mountain-Jackass Flats area by Wernicke (1988). From southeast to northwest, these are the Clery-Spector Range Thrust, the Schaub Peak-Mine Mountain (?) Thrust, an equivalent of the back-facing Panama Thrust, and the Last Chance Thrust. These thrust sheets involve a nearly complete Paleozoic section that is known to include major aquifers in the region. If, as Carr and Monsen (1988) suggest, the breakaway zone for the Fluorspar Canyon Fault is west of Yucca Mountain and faults at Yucca Mountain are genetically related to the Crater Flat graben system, then Paleozoic carbonates could underlie the entire Yucca Mountain-Jackass Flats area. In the absence of large-magnitude Cenozoic extension, the Tertiary section would be expected to be underlain by an allochthonous wedge corresponding to rocks between the Marble Canyon and White Top Thrusts, and equivalents. The Cottonwood Mountains, southern Funeral Mountains, southern Bare Mountain, and Mine Mountain (NTS) offer the best exposures of tectonic elements that could be structurally analogous to those beneath Yucca Mountain. In the Grapevine Mountains, the same structural level of the fold and thrust belt is exposed, but Cenozoic rotation and extensional overprinting have confused relations among pre-Tertiary units there somewhat more than in the other listed areas.

The Mesozoic fold and thrust belt that may underlie Yucca Mountain consists of several discrete thrust sheets with stratigraphic throws of up to 5 km and the full spectrum of brittle through ductile behavior. A key question is whether extensional crustal thinning has removed Paleozoic carbonates from beneath Yucca Mountain, and if the Silurian dolomite in UE25-p#1 is part of the laterally continuous carbonate aquifers which discharges at Ash Meadows. The northwest strike of prethrust normal faults in the Spring Mountains region indicates that hydraulic relations in and beneath the thrust sheets between Yucca Mountain and the northern Spector Range-Ash Meadows area should be explored. Because of the water-resource potential of the regional-carbonate aquifer, an understanding of flow paths within it is needed to resolve performance issue 1.3. The carbonate aquifer serves as a water supply for NTS activities and supports the unique and endangered ecology of the Ash Meadows area, including the Devil's Hole part of Death Valley National Monument. In addition, the major spring areas in Death Valley National Monument are the principal water supply for the Furnace Creek area and may be part of the carbonate-aquifer system.

The available evidence indicates that:

1. The alluvial aquifer is Class 1.
2. The tuff aquifer is Class 1 because it is a prime recharge source to the alluvial aquifer.

3. The carbonate aquifers that discharge at Ash Meadows and at Death Valley are Class 1.

We see that the "special source" designation can only be confidently resolved by determining the flow-system relationships and boundary conditions between the three aquifers known to exist in the vicinity of the controlled area. The CD-SCP has no data collection activities that will produce a definitive database and it therefore offers no useful plan to resolve the ground-water protection "special source" issues.

PERFORMANCE ISSUE 1.6

The statutory requirement for evaluation of ground-water travel time (GWTT) presupposes a need for understanding the geometry and geologic controls on ground-water flow. Key Issue 1 in the Office of Geologic Repositories Issues hierarchy relates to whether the mined geologic-disposal system at Yucca Mountain will isolate the radioactive waste from the accessible environment after closure in accordance with the requirements set forth in 40 CFR Part 191, 10 CFR Part 60, and 10 CFR Part 960 (CD-SCP, p. 8.2-2.). Performance Issue 1.6, "Will the site meet the performance objective for prewaste-emplacment ground-water travel time as required by 10 CFR 60.113" (CD-SCP, p. 8.2-5), dictates information needs 1.6.1 through 1.6.5 of section 8.3.5.12 of the CD-SCP, "Ground-water Travel Time":

Information Need (CD-SCP)

- 1.6.1 Site information and design concepts needed to identify the fastest path of likely radionuclide travel and to calculate the ground-water travel time along that path.
- 1.6.2 Computational models to predict ground-water travel times between the disturbed zone and the accessible environment.
- 1.6.3 Identification of the paths of likely radionuclide travel from the disturbed zone to the accessible environment and identification of the fastest path.
- 1.6.4 Determination of the prewaste-emplacment ground-water travel time along the fastest path of likely radionuclide travel from the disturbed zone to the accessible environment.
- 1.6.5 Boundary of the disturbed zone.

The success of several investigations in the geochemistry program will depend on recognition of ground-water flow paths:

CD-SCP Section

- 8.3.1.3.1 Investigation: studies to provide information on water chemistry within the potential emplacement horizon and along potential flow paths;
- 8.3.1.3.2 Investigation: Studies to provide information on mineralogy, petrology, and rock chemistry within the potential emplacement horizon and along potential flow paths;
- 8.3.1.3.4 Investigation: Studies to provide the information required on radionuclide retardation by sorption processes along flow paths to the accessible environment;
- 8.3.1.3.5 Investigation: Studies to provide the information required on radionuclide retardation by precipitation processes along flow paths to the accessible environment;
- 8.3.1.3.6 Investigation: Studies to provide the information required on radionuclide retardation by dispersive, diffusive, and advective transport processes along flow paths to the accessible environment;
- 8.3.1.3.7 Investigation: Studies to provide the information required on radionuclide retardation by all processes along flow paths to the accessible environment; and
- 8.3.1.3.8 Investigation: Studies to provide the information required on retardation of gaseous radionuclides along flow paths to the accessible environment.

The conceptual framework for calculating ground-water travel time requires identification of "likely" flow paths to the accessible environment, along which travel times are calculated, and a disturbed-zone boundary from which calculations are begun. The original disturbed-zone concept was based on a near-field region of difficult-to-model flow processes (48 FR 35280, 35281, July 8, 1981). Later, the NRC (Gordon, et al., 1986) proposed to restrict the disturbed-zone definition to include only a region of intrinsic-property changes. However, this later proposal has not been formally adopted by the NRC probably because of the large region of hydrothermal (heat-pipe) effects that may develop around emplaced waste, including non-Darcian fracture flow as condensate accumulates. Intrinsic-property changes will probably accompany boiling and condensation of pore fluids, so even if the restricted definition of the disturbed-zone boundary, such as proposed by Gordon, et al. (1986) were adopted by the NRC, the boundary may extend a considerable distance above and below the repository.

Ground-Water Flow Path

It appears that the DOE is approaching the problem of ground-water flow paths from the following perspectives:

1. Calculate flow paths using two-dimensional porous-medium model.
2. Map the intersection of land surface with a composite regional potentiometric surface that rises and falls over geologic time.
3. Determine physical-property conditions that govern fracture versus matrix flow.
4. Investigate apparently steep and apparently flat regions in the composite potentiometric surface by drilling additional WT-holes and by conducting tracer tests.
5. Prepare a plan to investigate the hydrologic significance of the Ghost Dance Fault.

<u>Perspective</u>	<u>CD-SCP Section</u>	<u>Methodology</u>
Calculation based on fluid potentials	8.3.5.12.3.1.2	Numerical Model
Intersection of composite regional potentiometric surface with land surface	8.3.1.2	Reexamine and redatate paludal deposits
Determine physical-property conditions that govern fracture vs. matrix flow	8.3.1.2.3	Develop empirical relations from laboratory tests
Investigate steep and flat regions in composite potentiometric surface	8.3.1.2.3.1	Drill WT-holes, hydrology hole, and possibly southern tracer test complex
Investigate steep and flat regions in composite potentiometric surface	8.3.1.2.2.3.3	Solitario Canyon horizontal borehole
Investigate hydrologic significance of Ghost Dance Fault	8.3.1.2.2.6	Develop plan only

Disturbed Zone

DOE proposes to develop a disturbed-zone definition (8.3.5.12.5.2, activity 1.6.5.2), and reevaluate that definition based on saturated and unsaturated-zone system investigations (8.3.1.2.2 and 8.3.1.2.3). We strongly suggest that it would be fundamental for the SCP to include activities that delineate the extent and character of the disturbed zone as now defined.

The disturbed zone is an important focus of State of Nevada review activities. We find that the zone of difficult-to-understand (and characterize) processes (46 FR 35280, 35281, July 8, 1981) has been equated conceptually by the DOE to the zone of intrinsic-property changes. The central concept of a zone of intrinsic-property changes appears in most, if not all, DOE-sponsored literature that requires a disturbed-zone definition (Langkopf, 1987 and CD-SCP, Section 8.3.5.12.5, for example). However, even if there were no intrinsic property changes whatsoever, heat-driven changes in the hydrologic system at Yucca Mountain can reasonably be expected to be profound (and extraordinarily complex from a modeling perspective). These hydrothermal processes can be reasonably expected to occur within 100 years of repository loading based on simple calculations using DOE's physical-property values.

The CD-SCP assumes that the NRC draft generic technical position (Gordon, et al., 1986) will be adopted formally by the NRC. The State of Nevada has pointed out to the NRC that that draft position fails to consider the hydrothermal effects of the waste, causing multiphase fluid flow. It is obvious that the more restricted (in space) the disturbed-zone definition, the longer the flow paths in the vadose zone along which travel times are calculated, and the longer the travel times in any flow scenario.

The potential hydrothermal effects in the vadose zone of Yucca Mountain due to waste-generated temperatures which exceed the boiling temperature of water is generally unrecognized¹ in the CD-SCP. Our analysis indicates marked increases in both vapor and liquid-phase flow are expected due to the strong thermal envelope generated by the waste. In the fractured-rock environment, the complexity of heat and mass-transfer processes and associated solution-mineral reactions will be greatly increased by the multiphase liquid and vapor-flow environment. We estimate that about 10,000 acre-feet of water are present within the volume of rock that is expected to reach boiling temperature within 100 years.

The CD-SCP definition of the disturbed zone ignores the importance of multiphase fluid transport. The CD-SCP definition is not as defined and intended in 10 CFR 60.2 (46 FR 35280, 35281, July 8, 1981). Instead of a mechanically disturbed zone of the current DOE definition (measured as extending several meters from the repository horizon) hydrothermal effects have the potential to extend downward and upward tens to hundreds of meters from the repository horizon.

Based on our findings of: a) a high probability of field-scale hydrothermal multiphase (heat-pipe) effects occurring during repository loading, and b) the resultant zone of vaporization and condensation that could extend upward and downward significant distances from the repository horizon, we believe that a zone of intrinsic property changes is not conservative as a basis for defining the disturbed zone. Physical and chemical changes within the zone of vaporization and condensation would be difficult to characterize by direct observation, and will be impossible to predict accurately based on initial conditions only. The DOE needs to address and establish a research program to resolve both the thermal and hydrothermal effects in the repository performance in the SCP.

CD-SCP Ground-Water Travel Time Strategy

The DOE recognizes the "reasonable assurance" licensing requirement (10 CFR 60.101(a)(2)) that the ground-water travel time at Yucca Mountain is at least 1,000 years leaves this issue ambiguous as to what constitutes data of sufficient quantity and quality (p. 8.3.5.12-10).

1. Langkopf (1987) refers to unpublished modeling studies by J. Gauthier and R. R. Peters in a 1986 internal memorandum (SANDIA) where water redistribution was considered from the repository midline to below the repository. Their reported findings support our scenario of total water expulsion as vapor in a 100-year period. However, their model assumes the matrix would absorb the moisture.

CD-SCP states (p. 8.0-9):

"The top-level strategy focuses strongly on the investigations of the characteristics of the flow in the unsaturated zone, relying heavily on the current view that the percolation is low and that the water in the unsaturated zone is tightly confined within the rock matrix. If these concepts can be confirmed, then the general objective for the system and for the post closure performance of the engineered and natural barriers are very likely to be met. As part of these investigations, the program will address alternative concepts including flow in fractures, lateral movement of water at rock interfaces in the unsaturated zone, and the effect on the flow of structural features such as faults. The ability of the unsaturated rock to hold water and limit contact of water with the waste packages will also be investigated."

We find that the CD-SCP approach indicated by the above warrants both applause and criticism. The correct issues have been identified, including ground-water travel times, but the characterization approach is to prove conditions and processes favorable to waste isolation. This would make good sense if there were established technologies, in-depth understanding of the processes, simple natural systems, and well understood analog environments. This is not the case for the vadose zone at Yucca Mountain. The SCP therefore needs to be structured to test for the unacceptable conditions, and for the most part, it falls in terms of the vadose-zone issues.

Vadose-Zone Conceptual Model Comments

The CD-SCP investigation 8.3.1.2.2 entitled "Studies to provide a description of the unsaturated zone hydrologic system at the site" presents the DOE's purpose and objective as "to develop a model of the unsaturated-zone hydrologic system at Yucca Mountain that will assist in assessing the suitability of the site to contain and isolate waste." It is also stated that in developing the model the needed information will be provided through ten studies to characterize the flow and transport through the Yucca Mountain unsaturated zone. The major studies planned to be conducted by DOE during site characterization address the areas of unsaturated-zone infiltration, percolation, gaseous-phase circulation, and hydrochemistry. Appendix I indicates our opinion of the general failure of these investigations to adequately establish site characterization objectives.

The CD-SCP conceptual model of water flow through the vadose zone is generally based on the assumption of steady-state downward flow. A second assumption is that the water flux through the vadose zone is so small that most water flow is through the matrix of the rock and not through fractures. A third assumption is that matrix flow will predominate through the repository horizon (Topopah Spring). This assumption largely depends upon the hypothesis that excess recharge is both diverted away from the repository horizon and retarded by capillary and permeability barriers at the contacts between the Tiva Canyon welded unit and the underlying Paintbrush Tuff nonwelded unit; and between the Topopah Spring welded unit and the overlying Paintbrush Tuff nonwelded unit.

The CD-SCP vadose-zone conceptual model is articulated on p. 3-207 to 3-213. In reviewing the CD-SCP, we have become aware of two important facts. First, the CD-SCP does not seriously consider conservative conceptual models that fit the limited site-specific data and the open-literature data. Second, the CD-SCP conceptual model, amazingly, perfectly satisfies all of the following conditions:

- (i) Low moisture flux in the host rock and in the overlying and underlying hydrogeologic units;
- (ii) A water table sufficiently below the underground facility such that fully saturated voids contiguous with the water table do not encounter the underground facility;
- (iii) A laterally extensive, low-permeability, hydrogeologic unit above the host rock that would inhibit the downward movement of water or divert downward-moving water to a location beyond the limits of the underground facility;

- (iv) A host rock that provides for free drainage; or
- (v) A climatic regime in which the average annual historic precipitation is a small percentage of the average annual potential evapotranspiration." (10 CFR 60.122(b)(8)).

The above, of course, are the NRC favorable conditions for a repository in a vadose-zone environment.

We think the CD-SCP conceptual model of flow of water through the vadose zone is not based on nor supported by the available technical data. The estimated downward ground-water flux may be low in the light of published data. Estimates of the downward vertical matrix flux (no fracture flow) through the repository-horizon host rock range from a low value of 0.003 mm/year (based on laboratory determinations on core, Weeks and Wilson, 1984) to a high of 10 mm/yr (Sass and Lachenbruch, 1982) based on the geothermal-gradient analyses. Montazer and Wilson (1984) data from borehole UZ-1 show negative (upward) flux of approximately 1 to 2 mm/yr in the Topopah Spring unit. They also estimated that a downward flux through the same unit to be 1 mm/yr based on geometric mean of the saturated hydraulic-conductivity measurements on core samples assuming a hydraulic gradient of one. However, Montazer and Wilson (1985) reported that the measured hydraulic conductivity of two saturated samples was two-orders-of-magnitude greater than the geometric mean. For the Paintbrush Tuff nonwelded unit, they estimated that a vertical flux of 0.1 to about 100 mm/yr may be occurring. Additional uncertainty on the estimated flux under present conditions is introduced by recharge estimates of 4.5 mm/yr (Rush, 1970) to 5 mm/yr (Waddell, et al., 1984). These estimates of recharge are inconsistent with the postulated 1 mm/yr by the CD-SCP. If the saturated-matrix conductivity of the Topopah Spring unit is limited to a maximum of 1 mm/yr as DOE indicates, then the vadose flux could pass through the repository-horizon host rock (Topopah Spring) as fracture flow.

The CD-SCP conceptual model also assumes by implication that the recharge throughout the proposed repository boundary area is uniformly distributed. In desert terrane such as the Yucca Mountain site, the recharge may be low and variable. However, much of the recharge is certainly concentrated and focused beneath washes, in and through open and exposed fractures, and through faults in the rock matrix of the repository block. It is very likely that most of the recharge occurs through the fractures and in turn gives rise to the flux values that shorten dramatically the ground-water travel times through the vadose zone toward the accessible environment.

The CD-SCP assumption that a capillary barrier exists at the contacts between the Tiva Canyon welded unit and the underlying Paintbrush Tuff nonwelded unit, and between the Topopah Spring welded unit and the overlying Paintbrush Tuff nonwelded unit is unlikely based on the available information provided by DOE. There is no data or evidence that recharge moves laterally down dip at the contact between the fractures networks of the Tiva Canyon welded unit and the matrix of the Paintbrush Tuff nonwelded unit. To date, no field or laboratory data have been published by DOE which indicate that saturated conditions have been observed at or near the contact. It is unlikely that water will move laterally over any significant distance until the tuff is almost saturated.

In addition to the above, the CD-SCP postulates the existence of a capillary barrier between the Paintbrush Tuff nonwelded and the Topopah Spring units. There is no evidence that water is present across this contact or as a general condition across the site. Therefore, there is no basis to assume that "excess recharge" has been stored or that significant lateral flow is occurring within this unit.

The CD-SCP discusses (on pages 8.3.1.2-248 to 250) the use of the geochemical approach to evaluate and determine the flow direction, water flux, and ground-water travel time in the unsaturated zone by isotopic techniques. It also states:

"Pore fluids from the matrix and near fractures will be extracted from exploratory shaft rubble core for chemical and isotope analyses.", "Fracture fluids are expected to permeate the surrounding matrix.", and "Fluids from samples with moisture contents less than 11 percent (including samples that have been squeezed and centrifuged) will be extracted using the vacuum distillation method."

This technique may be useful in estimating and evaluating the ground-water travel times of water in the matrix. However, it is not clear from the CD-SCP how water in the fractures, especially the Topopah Spring unit, will be sampled for the geochemical isotopic technique. Nowhere under any activity is it explained how fracture waters will be sampled and analyzed when encountered. There are no activities that address field determination of saturated fractures, or ephemeral fracture flow. Other problems that are not addressed by the CD-SCP are the distributed nature of recharge over the repository block, the scale at which data is developed, the three-dimensional distribution in space of data collection, and the manner in which interpretations of these data will be made. Based on surface mapping and the core data, there are several million fractures within the repository block and every one of these is a possible conduit for both liquid and vapor flow. In addition, there are very significant lithologic units and associated facies that can markedly impact matrix-hydraulic conductivities. We find no activities that recognize and deal effectively with these problems.

Vadose Zone Boreholes: The CD-SCP activity 8.3.1.2.3.2 (p. 8.3.1.2-14) entitled "Site vertical borehole studies" describes the DOE investigation which involves dry drilling and coring of nine planned boreholes that will range in depth from 122 to 460 meters below the land surface. We are surprised by the apparent strategy of the vadose-zone drilling program. Based on the existing data on moisture in the vadose zone, it could be interpreted that the drilling plan has been designed to avoid developing additional data on perched water, or resolving already developed ambiguous data. Specifically UZ-14, near UZ-1, has a design depth of 120 m. Thus, it will avoid encountering known saturation at 387 m, which stopped UZ-1 drilling. Also, it will not provide any data to resolve the ambiguous potential records of UZ-1 in the Topopah Spring.

In addition, all the deep boreholes (UZ-9, UZ-9a, UZ-9b, UZ-2, UZ-3, UZ-10) are useless with respect to evaluating the occurrence and extent of perched water at or below the repository horizon in the repository block. UZ-2 and UZ-3 are shallower than UZ-6 and located very close to UZ-6, hence no new data on the distribution of perched water is likely to be established. UZ-9, UZ-9a, UZ-9b, and UZ-10 are too far from the repository block to be representative of the block conditions. All the rest of the boreholes are too shallow to develop data at or below the repository horizon. Such a plan is unlikely to establish new information on perched water and it can not resolve existing questions about already encountered perched water.

We find that the same two drilling techniques previously used in site-selection studies are planned for all future surface based vadose-zone studies. Both of these drilling methods have serious weaknesses that are well known to DOE from experience, and these weaknesses seriously impact the ability of the DOE to characterize the vadose zone. The ODEX method is slow and has produced a depth maximum of around 400 feet. The reverse-air vacuum produces a large diameter borehole, can not drill through perched water, produces unstable boreholes in fractured tuff, and is unnecessarily costly. The moisture data from UZ-1 and UZ-6 are compromised by the large diameter of the borehole and the prolonged drilling time.

Vadose Zone Siting Criteria: The NRC siting criteria set forth in 10 CFR 60.122 consist of two sets of conditions namely, the first set (10 CFR 60.122(b)) encompasses favorable conditions and the second set (10 CFR 60.122(c)) encompasses the potentially adverse conditions. The NRC siting criteria include the requirement that DOE must demonstrate and show by analysis that the potentially adverse conditions, if present at the site, do not affect significantly the ability of the geologic repository to meet the performance objective related to isolation of the waste. The CD-SCP sets out a plan to prove a conceptual model of favorable conditions. In doing so, it fails to provide a plan of activities that test for unfavorable conditions in the vadose zone.

Concluding Vadose Zone Comments

The confident characterization of the vadose-moisture regime of Yucca Mountain fractured tuff is the most important hydrogeological site-characterization objective. Based on our technical review of the CD-SCP, the following observations are warranted:

1. The methodologies proposed by DOE for obtaining in-situ physical measurements of moisture conditions in vadose-zone fractured tuff are based on porous media models which are inappropriate for fractured tuff; therefore, the proposed methodologies are highly experimental and have questionable probability of success.
2. Within fractured rocks, such as in the vadose zone of Yucca Mountain, the unresolved problem of an appropriate scale of data collection is not being addressed. The CD-SCP is not clear on how this scale problem is going to be resolved.
3. There is no new approach in the CD-SCP for establishing confident travel times in the saturated zone. We suggest that the SCP should contain field-oriented research activities that attempt to establish the scale(s) at which the tuff aquifers can be treated as equivalent porous media between the repository block and the accessible environment.
4. The heavy reliance on computer and numerical codes developed for characterizing the liquid, vapor, heat, and radionuclide transport within the fractured rocks is disturbing because of the general absence of a reliable validation methodology and the continuing unavailability of reliable field data at various scales (laboratory versus repository scale).

Saturated Zone and Regional Hydrogeology

A key component of hydrogeologic characterization is establishment of relations between geologic elements of the system and fluid flow. Boundary conditions for any region of interest are primarily due to geologic controls either directly, as in the case of an impermeable barrier to flow, or intrinsically, as in the case of a natural conduit.

In the summary of significant results from Chapter 1 (Geology) of the CD-SCP, the following statements are made:

"Planned studies will identify and characterize the subvolcanic rocks and delineate their contact with overlying volcanic rocks (Section 8.3.1.17) to allow for refinement of hydrologic and tectonic models." (CD-SCP, p. 1-323).

Also,

"Inactive faults and fractures, in their role as hydrologic barriers and conduits, may also influence the hydrology in the repository area for the postclosure period (Chapter 3)." (CD-SCP, p. 1-328).

Chapter 3 of the CD-SCP summarizes the present state of knowledge concerning the hydrology of the Yucca Mountain site. Two sections, 3.7.4.2, "Ground-Water Flow Paths During the Quaternary Period," and 3.9.3.1, "Accessible Environment and Credible Pathways," relate to flow-path and travel-time issues.

The CD-SCP states on p. 3-198:

"Tests are planned to evaluate the conditions under which flow in fractures and faults may occur (Section 8.3.1.2.3), thus aiding in the definition of flow paths in the unsaturated zone."

Also,

"...because of the nearly flat potentiometric surface under parts of Yucca Mountain, specific flowpath directions are currently difficult to define. Furthermore, the degree of anisotropy has not been evaluated. Additional water-table holes and extensive multiple-well and single-well tracer tests may help define anisotropy, hydraulic connections, and probable flow paths in the saturated zone (refer to Section 8.3.1.2.3.1)."

According to a statement on p. 3-105, Section 8.3.1.2 includes studies to reexamine and redatate spring and marsh deposits from the south end of Crater Flat and south of Yucca Mountain.

Regarding ground-water flow paths during the Quaternary period, the CD-SCP states on p. 3-107:

"...the occurrence of calcitic veins, tuffs, and marsh deposits kilometers to tens of kilometers upgradient from areas of modern ground-water discharge indicates that flow to points of ground-water discharge were shorter in the past."

Evidence of possible megascale channeling in carbonate rocks of the southern Great Basin has been available in the open literature for over a decade. The CD-SCP reiterates the results of Winograd and Pearson (1976):

"[Winograd and Pearson] have shown a radiocarbon anomaly in Crystal Pool to probably be caused by megascale channeling, with water moving to this discharge point at velocities appreciably greater than those to adjacent springs." (CD-SCP, p. 3-102).

Structural Control on Flow Paths: As stated on p. 8.3.1.17-186, the tectonic synthesis will be applied to information need 1.6.1 (Section 8.3.5.12.1), "site information and design concepts needed to identify the fastest path of likely radionuclide travel and to calculate the ground-water travel time along that path." This is one component of the ground-water travel time issue, as outlined on p. 8.3.5.12-23 in a discussion of interrelationships of information needs. DOE indicates that tectonic synthesis will also be applied to investigations 8.3.1.2.1 (regional hydrologic system) and 8.3.1.4.2 (geologic framework).

We have reviewed the CD-SCP for investigation activities planned to assess the hydrologic significance of geologic structure in the Yucca Mountain region. We looked for evidence that hydrologic test drilling is effectively integrated with geologic-characterization activities. The basis for our review comments is Table 8.3.1.4-2, "Site Characterization Plan Proposed Drilling Requirements," which lists proposed boreholes and associated CD-SCP activities.

Only one activity of the CD-SCP is squarely aimed at characterizing the hydrogeologic significance of a discrete repository-scale geologic structure. Activity 8.3.1.2.3.1.1, "Solitario Canyon Fault Study in the Saturated Zone," will attempt to determine whether the Solitario Canyon Fault is a barrier to eastward movement of ground water through the repository block. Two new WT-holes will be drilled near the Solitario Canyon Fault, plus a new hydrologic test hole (production well) east of the fault on the ridge crest of Yucca Mountain, designated H-7. A long-term pumping test intended to observe pumping response across the Solitario Canyon Fault is planned. We commend this effort but question why similar studies are not planned to evaluate other known structures, such as the Ghost Dance Fault.

Steep hydraulic gradients immediately upgradient of the repository appear to have focused DOE's attention with respect to mission objectives. Activity 8.3.1.2.3.1.2, "Site Potentiometric-Level Evaluation," calls for two water-table drillholes near Drill Hole Wash to obtain additional data on the steep hydraulic gradient in this area, and another two water-table drillholes south and east of the repository site. It is evident from the discussion on p. 8.3.1.2-302 that data from geologic drillhole USW G-5 will be used to help determine the probable cause and nature of the steep hydraulic gradient north of Drill Hole Wash. Conversely, the region inferred to be down the hydraulic gradient receives virtually no attention in terms of possible structural controls and hydraulic connection with underlying and overlying aquifer lithologies.

No plans are given for assessment of preferred flow paths in carbonate rock between Yucca Mountain and Ash Meadows, or refinement of the inferred western boundary of the Ash Meadows ground-water flow system. Activity 8.3.1.2.3.1.6, "Well Testing with Conservative Tracers Throughout the Site," calls for a possible second multiple-well tracer test complex in a location "where the physical rock properties are significantly different from those of the C-hole location" (CD-SCP, p. 8.3.1.2-327). There is no discussion of the many distinct geologic controls on fluid flow that might be investigated with tracers, nor is there any elaboration of the role of tracers in developing a hydrologic characterization of structural discontinuities. Most importantly, the building of a statistically meaningful sampling rationale from available data is not evident in the geohydrology program.

Hydrologic Effects of Regional Strain Features: Calcite veins in Pliocene and younger rocks at Ash Meadows strike $N40^{\circ} \pm 10^{\circ}E$ (Winograd and Szabo, 1986; CD-SCP, 1988). This is approximately at right angles to the direction of regional Cenozoic extension. Although major northeast-trending structures exist in the Yucca Mountain region, the CD-SCP does not appear to address the possibility that they might represent conduits to ground-water flow because of their fundamentally dilational character.

The CD-SCP alludes to the possible, but unknown hydrologic significance of detachment faults in the following statement:

"If detachment faults exist at depth below the site, their relevance to repository design and performance as potential sources of ground motion, rupture, or hydrologic conduits or barriers hinges on their age, depth, and nature of the intersection of the detachment faults with the steeply-dipping Quaternary normal faults within the site area" (DOE CD-SCP, p. 8.3.1.17-132).

The possible hydrogeologic significance of detachment faults is therefore recognized in the CD-SCP, but no studies are presented for hydrogeologic assessment of detachment faults. The structural studies that focus on particular groups of faults near Yucca Mountain are disjointed from a hydrogeologic perspective, with the exception of Solitario Canyon Fault studies, since they do not include hydrogeologic objectives. One of the stated objectives of activity 8.3.1.17.4.12.1 (Evaluate Tectonic Processes and Tectonic Stability at the Site) is to "...evaluate the regional extent of detachment faults...and evaluate regional extent of Paleozoic rocks known to be aquifers, aquitards, or to provide favored surfaces of detachment or thrusting" (DOE CD-SCP, p. 8.3.1.17-181). The description of this activity given on p. 8.3.1.17-182 of the CD-SCP provides for topical reports on "Quaternary wrench faulting, detachment faulting, normal faulting, and left-lateral strike-slip faulting." Gravity and magnetic maps will be compiled, and "geologic cross sections showing inferred subsurface structural and stratigraphic geometry will be prepared." Nowhere, however, do we find a statement of any clear hydrogeologic objective accompanied by a testing methodology, in these tectonic studies.

We have been unable to judge the merits of DOE's proposed borehole locations since locations given in the CD-SCP are inconsistent and generally unjustified. For example, we note major discrepancies between proposed borehole locations given in Section 8.3.1.2.3.1.2 "Activity: Site Potentiometric Level Evaluation," and Section 8.3.1.4.1 "Investigation: Development of an Integrated Drilling Program." If, as stated on p. 8.3.1.4-18 of the CD-SCP, each proposed drillhole represents a

source of data intended to answer a particular requirement of design or performance assessment, then all proposed holes should be precisely located and comprehensively justified. Furthermore, if Figure 8.3.1.4-2 contains a mixture of randomly-located and judiciously-sited holes, they should be clearly distinguished.

The difficulty in defining flow paths in the saturated zone for travel-time calculations is due, as stated on p. 8.3.1.2-295 of the CD-SCP, to the fact that hydraulic tests at Yucca Mountain have failed to identify definitive hydrostratigraphic units:

"If pervasive fracturing crosses stratigraphic boundaries and accounts for orders of magnitude greater hydraulic conductivity than does the matrix, it may not be appropriate to simulate ground-water flow within a framework of hydrostratigraphic units."

As indicated earlier, only one activity, 8.3.1.2.3.1.1, "Solitario Canyon Fault Study in the Saturated Zone," is focused directly on determining the hydrologic role of a discrete geologic structure. While it is recognized that "...flow down the Ghost Dance Fault could result in concentrated flow in a part of the repository horizon" (CD-SCP, p. 8.3.1.2-255), a plan to characterize flux in the Ghost Dance Fault has not been presented in the CD-SCP.

There is no provision in the CD-SCP for hydrogeologic assessment of (discrete) geologic discontinuities in a geostatistically robust (rigorous) fashion. Plans have been made for a limited analysis of the hydrogeologic significance of the Solitario Canyon Fault, and as yet no plan exists for analysis of the Ghost Dance Fault. Activities proposed in the CD-SCP to provide flow-path characterization offer little hope of resolving performance issue 1.6 with respect to flow in the saturated zone. A comprehensive drilling and testing program that includes an assessment of the hydrogeologic character of representative geologic structures (or areas) is absent from the CD-SCP. The CD-SCP fails to focus site-characterization activities on real (as opposed to simulated) flow paths.

INTERPRETATION OF FINDINGS:

The CD-SCP is seriously deficient in establishing a site characterization program that will resolve key licensing issues.

ADDITIONAL WORK REQUIRED:

A comparison of the new SCP (published in December 1988) with our "Review of Consultation Draft of the Site Characterization Plan ... of January 1988".

RECOMMENDED PROGRAM (objectives/activities):

Objective:

Review of the SCP, especially its hydrogeologically related activity, in terms of: 1) conceptual completeness and focus; 2) appropriateness of methodology to accomplish stated objectives; 3) availability of supportive technology; and 4) probability of success and/or feasibility.

EXISTING PROGRAM:

Review of the revised SCP.

Appendix E-III

Technical Meetings/Symposia Attended

Technical Meetings/Symposia Attended

Date	Sponsor	Meeting/Symposia
23 Jan. 1987	US-DOE	DOE Environmental and Socioeconomic Monitoring and Mitigation Plans : Background on Site Characterization Activities.
26 to 28 Jan. 1987	Princeton University	Contaminant Transport Modeling Seminar/Short Course.
10 to 12 Feb. 1987	National Water Well Association (NWWA)	Solving Ground Water Problems with Models.
24 to 28 Feb. 1987	US-NRC	NRC Field Trip in Southern Nevada.
27-30 Apr. 1987	Nuclear Structure Research Laboratory, University of Rochester	Fourth International Symposium on Accelerator Mass Spectrometry.
17-21 May 1987	American Geophysical Union (AGU)	AGU Spring Meeting.
18-21 May 1987	NWWA-Association of Ground Water Scientists and US-EPA-EMSL	First National Outdoor Action Conference on Aquifer Restoration, Ground Water Monitoring and Geophysical Methods.
27 to 29 May 1987	US-DOE/USGS/SAIC	Peer Review on Calcite and Opaline Silica Deposits Located along Faults Near Yucca Mountain.
15-16 Jun. 1987	Sandia National Laboratory	Uncertainties in Groundwater Travel Time Calculations at Yucca Mountain, Nevada, Second Meeting.
23-26 Jun. 1987	Continuing Education in Engineering, U. C. Berkeley Extension	Aqueous Corrosion - Theory and Analysis.
8 to 9 Jul. 1987	US-NRC	Review of USGS Program.
30 Jul. to 9 Aug. 1987	International Union for Quaternary Research (INQUA)	Congress XII: INQUA.
11 to 16 Sept. 1987	GSA	Paleoenvironmental Interpretation of Paleosols Penrose Conference.
06 to 08 Oct. 1987	Minerals and Geotechnical Logging Society	Second International Symposium on Borehole Geophysics for Minerals, Geotechnical and Ground Water Applications.
03 to 06 Oct. 1987	Colorado Section of the American Institute of Professional Geologists and the Computer Oriented Geological Society	Computer-Aided Methods and Modeling in Geology and Engineering.

18 to 22 Oct. 1987	Clay Minerals Society (CMS)	Clay Minerals Society Meeting.
24 to 29 Oct. 1987	GSA	Geological Society of America Meeting and Short Course.
07 to 10 Dec. 1987	AGU	AGU Fall Meeting.
16 to 18 Feb. 1988	Association of Ground Water Scientists and Engineers	Ground Water Geochemistry Conference.
22 to 26 Feb. 1988	DOE/USGS.	NNWSI-USGS Trench 14, Busted Butte Carbonate/Opal Hydrogenic Deposits Sampling Field Trip.
Feb. 1988	Nevada Water Resources Association	Nevada Water Resources Association Meeting.
29 to 31 Mar. 1988	GSA	GSA Cordilleran Section Meeting.
23 to 26 May 1988	Association of Ground Water Scientists and Engineers and the US-EPA-EMSL.	Second National Outdoor Action Conference on Restoration, Ground Water Monitoring and Geophysical Methods.

MAI Field Trips:

29 May 1987	Crater Flat Preliminary Age Dating Field Studies.
June 1987	Field Mapping at Corn Creek Flat.
June 1987	Reconnaissance Study of the distribution of packrat middens of Pleistocene age in Fortymile Wash, Sandy Valley, Coyote Springs, and L. Pahrnagat Valley.
20 and 25 August 1987	Colloid Sampling in Oasis Valley and Ash Meadows.
October 1987	Tecopa Basin field trip
November 1987	Reconnaissance Studies of "Lacustrine Life deposits in Piute Valley, Searchlight, Nevada) and Coyote Springs.
27 to 30 December 1987	Field Trip to Pahrump Valley and Tecopa Valley
February 1988	Tecopa area field trip.
February 1988	Tecopa area field trip.
February to April 1988	Field trip to collect pack rat middens along the White River drainage system.