

See Packet 4 for

97



Department of Energy

Waste Management Operations Office
CENTER P. O. Box 14100

Las Vegas, NV 89114-4100 WM Record File

'84 OCT 12 A10:43

WM Project 11
Docket No. _____
PDR
LPDR

Distribution:

Coplan

(Return to WM, 623-SS)

ok

OCT 10 1984

Seth M. Coplan, Section Leader
NTS Project Section
Repository Projects Branch
Division of Waste Management
U.S. Nuclear Regulatory Commission
Washington, D.C. 20555

GEOCHEMISTRY MEETING SUMMARY

As requested in your letter of September 11, 1984, a signed copy of the summary for the July 10-12 Geochemistry Meeting held at Los Alamos, New Mexico is attached. Enclosures 1 through 4 to the summary are also included.

We agree with your suggestion that summaries for future technical meetings should be finalized and signed at the conclusion of the meeting. Agendas prepared for future technical meetings will provide for sufficient time to draft, type, review, and finalize the summaries.

Please contact J. S. Szymanski of my office if you have any questions regarding this matter.

Donald L. Vieth
Donald L. Vieth, Director
Waste Management Project Office

WMPO:JSS:119

Enclosures:
As stated

- cc w/encl:
N. K. Stablein, NRC, Washington, D.C.
P. T. Prestholt, NRC, Las Vegas, NV
M. A. Gora, SAI, Las Vegas, NV
D. T. Oakley, LANL, Los Alamos, NM
G. L. DePoorter, LANL, Los Alamos, NM
M. B. Blanchard, WMPO, DOE/NV

8411090185 841010
PDR WASTE
WM-11 PDR

1027/84/97 H

391

See folder for Mr.
To Captain A.M. Voth
10-10-84

NRC-DOE GEOCHEMISTRY MEETING SUMMARY
JULY 10-12, 1984

LOS ALAMOS NATIONAL LABORATORY
LOS ALAMOS, NEW MEXICO

Attendees

A list of attendees and their organizational affiliations is attached as Enclosure i.

Background/Facts

An agenda, and copies of viewgraphs used by the NRC and DOE speakers, are attached as Enclosures 2, 3, and 4 respectively.

Observations

The NRC had the following observations:

1. The meeting was conducted in a professional manner and provided a useful exchange of information. The NNWSI speakers encouraged open, productive discussion.
2. The current and previous workshop agendas were structured along the technical disciplines that are being explored by NNWSI. This leads to presentations that appear to give only limited attention to potential licensing issues and application of planned investigations, data, or information to resolution of those issues. Restructuring the agenda of future meetings by issue (for example, the NRC site issues presented at this meeting) would be one way of addressing this NNWSI shortcoming.
3. USGS has described alternative conceptual models regarding movement of water in unsaturated fractured tuff. The alternatives differ with respect to how much water moves through fractures as opposed to the rock matrix itself. Also, there is uncertainty as to how much recharge occurs at the site (between 0.1 and 8 mm per year). As a result, there is a wide range of possible groundwater residence times that are consistent with what is now known about the Yucca Mountain site. In planning investigations of geochemical processes at the site and in interpreting the results of investigations completed to date, the NNWSI have assumed the hydrologic conditions and models that lead to the longer, less conservative residence times. It is the NRC staff's view that these assumptions are still questionable. Accordingly, the staff considers that the full range of residence times should be considered by the NNWSI in planning and interpreting the geochemistry investigations.
4. Values for many geochemical parameters will be needed to support site performance assessment calculations of future behavior, as required by 10 CFR 60. "Accurate" values (i.e. values to be existent) for given parameters under future repository conditions may be difficult to establish by measurement or calculation. The use of bounding values and limiting geochemical conditions, which would support reasonably

conservative performance assessment calculations, could simplify the collection of needed information. The NNWSI Program seems to be giving little consideration to a reasonably conservative vs "accurate" performance analysis, i.e. the collection of limiting or bounding values. Greater consideration of a reasonably conservative approach by NNWSI could greatly facilitate licensing decisions.

5. The solubility or apparent concentration limit of radionuclides in site groundwater/rock systems is likely to be an important barrier to the migration of radioactivity from emplaced waste to the accessible environment. The rate of radionuclide release can be no greater than the product of the apparent concentration limit and the groundwater volumetric flux.

Several aspects of the NNWSI approach to radionuclide solubility may be subject to concern. These include:

- (1) A possible over reliance on solubility values based on geochemical models rather than experimental measurements. Solubility calculations must assume equilibrium which may not be appropriate, and rely on a thermodynamic data base, which may be inadequate for some elements, particularly actinides at elevated temperatures, as well as aluminosilicates.
- (2) Neither the solubility measurements nor the modeling calculations seem to be giving enough emphasis to the effects of altered groundwater composition on radionuclide solubility. The in situ groundwater composition will be altered by contact with waste package and engineered facility components at elevated temperature and radiation fields during migration. It would be desirable to consider the solubility of radionuclides in this altered groundwater. This solubility may be the most representative of the source terms for far-field analysis.

6. The mineralogy/petrology program may have much to offer the overall hydrology program. Information was presented regarding mineralization both in the rock matrix and in fractures above the water table. The origin of such mineralization could shed light on which of the alternative conceptual models for unsaturated zone flow is most nearly correct. Also, fracture density and mineralogy offers an opportunity to determine the paleo flow currents through the Topopah Springs. These data/observations may lead to useful information on mineral stabilities on a repository time scale and aid in extrapolating laboratory data to the long term and in determining paleo flow paths. The NRC staff considers that mineralogy studies should be pursued and factored into whatever interpretations are made regarding groundwater movement in the unsaturated zone.
7. Reaction path calculations pertaining to rock/water interactions have been done by the NNWSI using the assumption of a closed system. These calculations bear on determining the design bases for the engineered barriers. The NRC staff would encourage that open-system calculations be done as well.

8. The potential physiochemical effects of kinetics have not been adequately addressed in NNWSI studies of mineral stabilities. The NRC staff believes that certain features of Yucca Mountain petrology and mineralogy (e.g. variation of zeolite mineralogy with depth) may be more correctly explained if the potential role of kinetics is investigated fully.
9. In this meeting there was little discussion of groundwater flow paths and rates of flow in the saturated zone, and, likewise, little mention of geochemical conditions along potential radionuclide migration routes in this zone. Additional information on groundwater flow paths and geochemical conditions in the saturated zone beneath Yucca Mountain is required for a complete and accurate assessment of the potential radionuclide isolation performance of the Yucca Mountain site.
10. One phenomenon that may pertain to movement of water in the unsaturated zone is cycles of wetting and drying. Such cycles would affect many unsaturated zone geochemical processes in a variety of ways -- some of which are obvious and others more subtle. Some of the more subtle aspects do not appear to have received full consideration in NNWSI studies. For example, proposals to empirically determine unsaturated zone groundwater travel times by ³⁶Cl dating do not seem to have fully considered the implications of wet-dry cycles with respect to how Cl samples might be emplaced and interpreted for dating.
11. Ionic species in the groundwater of the unsaturated zone may be concentrated due to evaporation and condensation in the near field. Upon cooling, potential flow of these fluids to the Calico Hills may adversely affect the radionuclide sorptive capacity of the tuffaceous host rocks. It is the view of the NRC staff that such a scenario be addressed.
12. The model of secondary mineral (zeolite) stability is important to future decisions about the location of the repository horizon and the choice of a suitable backfill. Two theoretical models have been proposed for zeolite diagenesis at Yucca Mountain. The more recent model suggests that the secondary mineral stability is controlled primarily by the activity of SiO₂ in solution and is not strongly affected by temperature. At present, this model is not well supported by available data and relies on a number of assumptions. In particular, the phase(s) controlling silica activity and the mineral stability fields are not known. It is the less conservative of the two models since it implies that irreversible phase (mineralogical) changes will not occur in the vicinity of the waste at temperatures less than 200°C. An earlier model suggested that mineral stability at Yucca Mountain would be a strong function of temperature. This more conservative model should not be abandoned but should be considered an alternate working hypotheses until more field, experimental and theoretical data have been obtained.
13. Studies of clay mineral and zeolite dehydration under vacuum do not seem to provide any direct or indirect ("baseline") data that bear on investigations of the behavior of repository host rocks under thermal loading. A much more relevant approach is to investigate clay mineral and zeolite dehydration under prescribed and controlled temperature (T) and

partial pressure of H_2O (P_{H_2O}) conditions that mimic T- P_{H_2O} conditions that are expected to develop in the near field of an HLW repository in tuff beneath Yucca Mountain.

14. From the workshop presentations, it is not clear that a sound approach has been developed by NNWSI for determining that all significant species are included in the data base for geochemical modeling and for picking the controlling solid for modeling solubilities in specific groundwaters.
15. The in situ tests of fracture transport planned for the exploratory shaft may not have adequately addressed problems of interpretation of results due to (1) multiple fractures; (2) plume formation and position of sample borings within that plume; (3) extrapolation from 2 m to 2 km; and (4) the fact that only one result will be obtained, not allowing adequate estimation of uncertainty of that result.
16. Colloids have been suggested as a possible means for radionuclide transport; hence research on colloids and their properties may be warranted. However, the applicability of the colloid work, as described in the workshop, to repository performance assessment is not clear.
17. The sorption work should be guided more by consideration of key nuclides than it appeared to be from the presentations.
18. It is still not clear how results of experiments, particularly sorption work with high water/rock ratios (water-dominated system) are going to be applied to the unsaturated zone with very small water/rock ratios (rock-dominated system).
19. Simple models may often be most useful for sensitivity analysis. Use of a model as complicated as TRACR3D may not be warranted. Analytical models may be more appropriate at this time.
20. There is a need for a conceptual geochemical model of mineral stability that integrates the field observations and the laboratory work; until this is done the experimental work, no matter how well conceived, will appear unrelated to repository performance.
21. The defense wastes at SRL likely will not be stored in South Carolina but will be sent to a national repository. The NNWSI geochemistry program apparently has not considered inclusion of defense wastes (in addition to spent fuel and reprocessing wastes) in their site analysis scheme. It would be desirable for NNWSI to do so.

The DOE had the following observations:

1. Workshop was generally useful; it acquainted us with NRC concerns, especially with respect to characterizing the unsaturated zone. The value of the workshop should be weighed against that of data reviews.
2. Speakers were required to skip back and forth, referring to other talks that were presented out of logical sequence due to the NRC-imposed agenda.

3. DOE understands that it is NRC's view that in developing plans there is a lot of room for professional judgment at this time; DOE fully concurs.
4. Regulatory framework is still evolving and is ambiguous. Regulatory uncertainties that affect project direction due to delays in issuing of definitive positions exist for: 10 CFR 60 including the unsaturated zone amendment; 40 CFR 191, Draft 4 especially with respect to the definition for accessible environment; rewriting of Reg. Guide 4.17; and technical guidelines on solubility, which are being rewritten (communication at the workshop level would be more helpful as opposed to written interaction on proposed changes).
5. In lieu of these regulations, meaningful interaction between NNWSI and NRC is desirable. However, DOE is responsible for the planning and direction of the Project. NRC and NNWSI both expect sensitivity analysis to redirect emphasis on the Project. NRC should recognize that Project redirection takes time and proper planning as well as requiring sound reasons that are related to the overall issue of radiological safety of the public and environment.
6. NRC staff need to become familiar with simplifying assumptions that can be made in the TRACR3D radionuclide transport code.

The State of Nevada had the following observations:

1. Since the age of the waters in the various parts of the repository system is important, it is critical to consider all age dating techniques. We have heard exhaustive discussions on the use of ^{36}Cl . Is there a program to look at other age-dating techniques such as He, ^3H , Kr, and I? All of these methods have problems, but they may be complimentary. The stable isotopes such as D, ^{18}O , and ^{13}C should also be examined. These efforts should be coordinated with the USGS programs.
2. If Rainier Mesa is intended to be an analog to Yucca Mountain, then there needs to be a more comprehensive understanding of the hydrologic and geochemistry conditions. Our experience indicates Rainier Mesa may be a valid analog.
3. Since so many parameters are dependent upon knowing unsaturated zone water chemistry and actual in situ saturation, a program should be identified to obtain these data.
4. DOE studies have used hydrologic parameters to determine water flow rates in the unsaturated zone. This approach is based on numerous assumptions. There need to be examples of where these techniques have been used successfully.
5. What is the Los Alamos program to determine actual input water quality to the bedrock? This seems to be an important parameter to the current experiments and modeling activities.
6. We understand that both NRC and DOE have developed heat flow codes and are modeling the proposed Yucca Mountain Repository. We would request complete description and documentation of these activities.

7. Discussions have identified that some very minor minerals may contribute ions to the complexing of radionuclides. We feel that it is important to have a program to identify the amounts and locations of these minerals.
8. A statement was made that manganese oxides coat some fracture surfaces. Since flow may occur in these fractures, these coatings should not be ignored. Particular attention should also be paid to sorption experiments on natural fracture surfaces both in the field and in the laboratory.
9. Geostatistics should be used to identify alternative flow paths to the accessible environment. Particular attention should be given to potential flow paths that bypass zeolites or other sorptive minerals, as a worst-case scenario.
10. If laboratory experiments and modeling continue to use reducing conditions as one possible scenario, then more information is needed on Redox conditions in the repository block in both the saturated and unsaturated zones. The mineralogy/petrology data should be integrated with the geochemical data in establishing a more complete understanding of redox conditions.
11. If the repository is to be located in the unsaturated zone, then vapor and aerosol transport should be considered. We heard little discussion on this subject at this workshop.
12. We feel that multiple working hypotheses must be considered in developing the geochemical and mineralogical/petrological research plans for NNWSI. Our perception from this workshop is that most of the research evolved from single hypotheses. We do not feel that this is the best approach to assess the characteristics of the Yucca Mountain site.

Agreements

1. DOE and NRC agreed to conduct discussions concerning the results of numerical simulations of pore water movement under the influence of thermal fields.
2. DOE and NRC agreed to conduct discussions concerning a restructuring of the format and emphasis of future technical meetings. Specifically, a format is needed that addresses more narrowly defined issues that focus on specific phases of repository performance; for example, radionuclide transport in the unsaturated zone.

Open Items

As noted

DOE Requests of NRC

1. Would like to see the QA Review Plan as soon as possible.
2. Would like to get the technical positions on Sorption, Solubility, and Mineralogy/Redox conditions as quickly as possible.

3. Would like NRC to review the Los Alamos Geochemistry Program Plan and provide feedback.

NRC Requests of DOE

1. Correlation of the Los Alamos work plan with "issues" as presented.

Jerry S. Szymanski

Jerry S. Szymanski
Waste Management Project Office
DOE/NV
Oct. 1 1984.

Seth M. Coplan

Seth M. Coplan
Division of Waste Management
US NRC
9/7/84

Enclosure 1

NNWSI/NRC GEOCHEMISTRY WORKSHOP ATTENDEES

JULY 10-12, 1984

LOS ALAMOS NATIONAL LABORATORY

<u>Name</u>	<u>Organization</u>	<u>FTS Phone Number</u>
Aamodt, Paul L.	Los Alamos	843-7960
Beaton, John A.	Los Alamos	843-9805
Bermanis, Henry L.	Weston	202-963-6821
Bilhorn, Susan G.	NRC	
Bish, David L.	Los Alamos	843-4337
Blencoe, James G.	NRC/ORNL	624-7041
Brown, Lee F.	Los Alamos	843-8067
Broxton, David E.	Los Alamos	843-2492
Bryant, Ernest A.	Los Alamos	843-4498
Byers, Frank M.	Los Alamos	843-8753
Campbell, Katherine	Los Alamos	843-2799
Carlos, Barbara H.	Los Alamos	843-6879
Coplan, Seth M.	NRC	427-4177
Crowe, Bruce M.	Los Alamos	843-4299
DePoorter, Gerald L.	Los Alamos	843-1033
Duffy, Clarence J.	Los Alamos	843-5154
Elzeftawy, Atef	NRC	427-4675
Erdal, Bruce R.	Los Alamos	843-5338
Essington, Edward H.	Los Alamos	843-3057
Fiore, Joy H.	SAI/NV	575-1203
Fuentes, H.	Los Alamos	843-3004
Furman, Marvin J.	DOE/HQ	444-7062
Gloria, Michael A.	SAI/NV	575-1463
Grisham, Genevieve F.	Los Alamos	843-5321
Hess, John W.	State of Nevada	702-798-8882
Jacobson, Roger L.	State of Nevada	702-673-7373
Johnson, Carl A.	State of Nevada	702-885-3744
Johnson, Mark	Los Alamos	843-3308

NNWSI/NRC GEOCHEMISTRY WORKSHOP ATTENDEES

<u>Name</u>	<u>Organization</u>	<u>FTS Phone Number</u>
Kelmers, Donald A.	NRC/ORNL	624-6870
Kerrisk, Jerry F.	Los Alamos	843-3348
Knauss, Kevin	LLNL	532-1372
Kovach, Linda A.	NRC	427-4693
Levy, Schon S.	Los Alamos	843-9504
Meijer, Arend	Los Alamos	843-0831
Merson, Thomas J.	Los Alamos	843-5726
Michels, Ronald D.	Los Alamos	843-5816
Myers, C. Wes	Los Alamos	843-6722
Nitsche, Heino	LBL	451-4483
Norris, A. Edward	Los Alamos	843-5442
Oakley, Donald T.	Los Alamos	843-1310
Ogard, Allen E.	Los Alamos	843-6344
Ortiz, Terri	SNL	846-0267
Panno, Samuel V.	Weston	202-963-6848
Planner, Harry N.	Los Alamos	843-1582
Polzer, Wilfred L.	Los Alamos	843-3073
Prestholt, Paul T.	NRC	598-6125
Rowley, John C.	Los Alamos	843-1378
Rundberg, Robert S.	Los Alamos	843-4559
Siegel, Malcolm D.	NRC/SNL	846-5448
Stablein, Newton K.	NRC	427-4611
Starmer, R. John	NRC	427-4541
Szymanski, Jerry S.	WMPO/NV	575-1503
Thomas, Kimberly W.	Los Alamos	843-4379
Travis, Bryan J.	Los Alamos	843-1254
Vaniman, David T.	Los Alamos	843-1165
Wolery, Thomas J.	LLNL	532-5789

Enclosure 2

NNWSI/NRC GEOCHEMISTRY WORKSHOP AGENDA

JULY 10-12, 1984

LOS ALAMOS NATIONAL LABORATORY

Tuesday - July 10, 1984

- 8:00 a.m. Registration
- 8:15 a.m. Welcome/Introductions - D. T. Oakley
- 8:30 a.m. Technical Overview for Workshop - DOE Representative
- 9:30 a.m. Break
- 9:45 a.m. LOS ALAMOS PRESENTATION
Overview and Geochemistry Program Plan - G. L. DePoorter
- 10:15 a.m. NRC PRESENTATION
Geochemical Issues Specific to NNWSI
- 10:45 a.m. Discussion - Los Alamos and NRC
- 11:45 a.m. Lunch
- 12:45 p.m. SESSION I: UNSATURATED ZONE PROCESSES
Overview - R. S. Rundberg (Los Alamos)
- 1:05 p.m. NRC Comments
- 1:15 p.m. Discussion - Los Alamos and NRC
Discussion Presentations
Unsaturated Zone Transport (including Vapor) - B. J. Travis
Unsaturated Zone Water Chemistry - A. E. Ogard
Suggested Discussion Topic
Relation between Saturated and Unsaturated Zone
Geochemical Processes
- 2:45 p.m. Break
- 3:00 p.m. SESSION II: ROCK-WATER INTERACTIONS
Presentations
Unsaturated Zone Travel Time
³⁶Cl Experiment for ES - A. E. Norris
Rock-water Equilibrium - C. J. Duffy
Reaction Path Calculations - J. F. Kerrisk
- 3:30 p.m. NRC Comments
- 3:40 p.m. Discussion - Los Alamos and NRC
Suggested Discussion Topic
Equilibrium vs. Kinetic Effects
- 4:45 p.m. End of Session

NNWSI/NRC GEOCHEMISTRY WORKSHOP AGENDA

Wednesday, July 11, 1984

- 8:00 a.m. **SESSION III: 3-D MINERALOGY AND SORPTION STRATIGRAPHY**
Mineralogy/Petrology Update - D. T. Vaniman (Los Alamos)
- 8:20 a.m. NRC Comments
- 8:30 a.m. Discussion - Los Alamos and NRC
Discussion Presentation - Los Alamos
Evaluation of Statistical Methods - K. Campbell
Suggested Discussion Topics
3-D Mineralogy and Sorptive Mineral Stratigraphy
Fracture Mineralogy
Determining Paleo Flow Paths from Present Mineralogy
- 10:00 a.m. Break
- 10:15 a.m. **SESSION IV: MINERAL STABILITY**
LOS ALAMOS PRESENTATION
Mineral Stability
- 10:20 - 10:35 Hydrothermal Stability - C. J. Duffy
10:35 - 10:50 Thermal Stability - D. Bish
- 10:50 a.m. NRC Comments
- 11:00 a.m. Discussion - Los Alamos and NRC
- 12:00 Noon Lunch
- 1:00 p.m. **SESSION V: KEY RADIONUCLIDES AND SOLUBILITY**
Key Radionuclides - J. F. Kerrisk (Los Alamos)
- 1:10 p.m. NRC Comments
- 1:15 p.m. **NRC PRESENTATION**
Solubility
- 1:35 p.m. Los Alamos Comments
- 1:45 p.m. EQ3/6 Geochemical Model - T. Wolery (LLNL)
- 2:00 p.m. NRC Comments
- 2:10 p.m. **LOS ALAMOS PRESENTATION**
Solubility and Speciation
- 2:10 - 2:40 Solubility Calculations - J. F. Kerrisk
2:40 - 3:00 Solubility Measurements - Los Alamos
3:00 - 3:20 Solubility Measurements - LBL

NNWSI/NRC GEOCHEMISTRY WORKSHOP AGENDA

Wednesday, July 11, 1984

- 3:20 p.m. Break**
- 3:40 p.m. Discussion - Los Alamos and NRC
Suggested Discussion Topics
Key Radionuclides
Solubility and Speciation of Key Radionuclides**
- 4:00 p.m. SESSION VI: REDOX CONDITIONS AND REDOX BUFFERING
Los Alamos Presentation - A. E. Ogard**
- 4:20 p.m. NRC Comments**
- 4:30 p.m. Discussion - Los Alamos and NRC
Suggested Discussion Topics
Redox Conditions in the Unsaturated Zone
Redox Buffering by Fe-Ti Minerals**
- 4:45 p.m. End of Session**

NNWSI/NRC GEOCHEMISTRY WORKSHOP AGENDA

Thursday, July 12, 1984

- 8:00 a.m. SESSION VII: TRANSPORT MODELING AND MATRIX DIFFUSION**
Transport Modeling - B. J. Travis (Los Alamos)
- 8:20 a.m. NRC Comments**
- 8:30 a.m. Discussion - Los Alamos and NRC**
Discussion Presentations - Los Alamos
Fracture Flow Experiments (Laboratory and ES)
Diffusion Experiments (Laboratory and ES)
Colloid Size Determination
Discussion Topics:
Matrix Diffusion
Vapor Transport
Aerosol Transport of Radionuclides
- 9:45 a.m. Break**
- 10:00 a.m. SESSION VIII: SORPTION**
Update on Sorption - K. W. Thomas (Los Alamos)
- 10:35 a.m. NRC Comments**
- 10:45 a.m. Discussion - Los Alamos and NRC**
Suggested Discussion Topics
Sorption Measurements on Crushed vs Intact Samples
Batch vs Flow Experiments
Effects of Water Composition and Redox Conditions
Sorption Kinetics
Key Radionuclides
- 12:00 Noon Lunch**
- 1:00 p.m. Preparation of Minutes and Closeout**
- 3:30 p.m. Feedback and Discussion**
- 4:45 p.m. End of Workshop**

Enclosure 3

Technical Position

It is the position of the NRC staff that based on our current level of knowledge of the NNWSI site, assessment of the Technical Criteria of 10CFR60 in terms of the performance elements of NUREG-0960 requires that, at a minimum, the following issues concerning geochemistry be addressed.

3.0 Geochemistry

- 3.1. What are the geochemical conditions preceding waste emplacement in the saturated/unsaturated zone?
 - 3.1.1 What is the mineralogy/petrology/chemistry of the backfill, disturbed zone/farfield host rock prior to waste emplacement?
 - 3.1.2 What is the mineralogy/petrology/chemistry along potential release pathways of the disturbed zone/farfield host rock prior to waste emplacement?
 - 3.1.3 What are the geochemical conditions of the groundwater in the disturbed zone/farfield in the saturated/unsaturated zone.
- 3.2 What are the geochemical conditions/processes following waste emplacement, in the saturated/unsaturated zone?
 - 3.2.1 How are the mineral stabilities of the Yucca Mountain tuffs affected by anticipated changes in the temperature and pressure?
 - 3.2.1.1 What is the rock/groundwater ratio in the backfill, disturbed zone/farfield in the saturated/unsaturated zone through time?
 - 3.2.1.2 Can chemical equilibrium be assumed in rock/water interactions under various flow regimes in the saturated/unsaturated zone?
 - 3.2.2 What is the anticipated spatial distribution of alteration products due to increased temperatures and altered fluid flow paths.

- 3.2.3 What are the anticipated geochemical conditions of the groundwater due to increased temperature within the unsaturated/saturated zone?
- 3.3 What are the anticipated geochemical processes/conditions affecting release and transport of the radionuclides in the saturated/unsaturated zone?
 - 3.3.1 How does solubility/concentration of radionuclides under differing flow regimes affect transport?
 - 3.3.1.1 How does precipitation/co-precipitation affect radionuclide migration/retardation from the vicinity of the outermost packing material/rock/backfill interfaces to the accessible environment through time?
 - 3.3.1.2 How does speciation affect radionuclide solubility?
 - 3.3.1.3 How do colloids/particulates affect the solubility of radionuclides?
 - 3.3.2 What is the importance of reaction and sorption kinetics in radionuclide migration/retardation in the disturbed zone/farfield environment under various flow regimes?
 - 3.3.3 How do redox conditions of the groundwater and redox buffering potential of Fe-Ti oxides affect radionuclide speciation/retardation?
 - 3.3.3.1 What are the effects of gamma and alpha radiolysis products on backfill and disturbed zone/farfield host rock relevant to radionuclide transport?
 - 3.3.4 How does backfill and disturbed zone/farfield mineralogy (under anticipated flow regimes) influence radionuclide migration through time?
 - 3.3.5 How do colloids/particulates/organics under differing flow regimes affect radionuclide migration/retardation in the disturbed zone/far field through time?

- 3.3.6 How does matrix diffusion affect radionuclide migration/retardation in the disturbed zone/farfield through time?
- 3.3.7 How does vapor transport affect radionuclide migration/retardation in the disturbed zone/farfield through time?

L. KOVACH
NRC WORKSHOP
7-10-84

DEFINITIONS

SITE ISSUE

A QUESTION ABOUT A SPECIFIC SITE THAT MUST BE ADDRESSED AND RESOLVED TO COMPLETE THE LICENSING ASSESSMENT OF SITE SUITABILITY AND/OR DESIGN SUITABILITY IN TERMS OF 10 CFR PART 60.
(NEED NOT BE CONTROVERSIAL.)

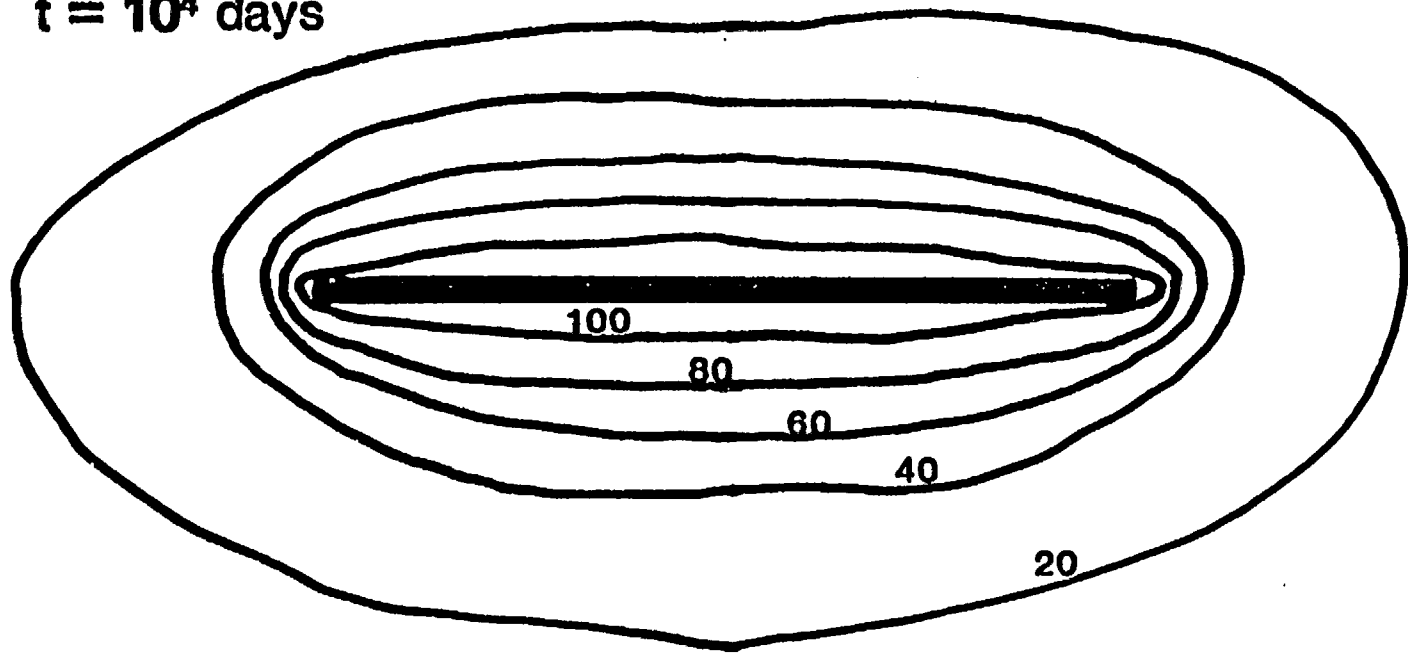
PERFORMANCE ISSUE

A BROAD QUESTION CONCERNING THE OPERATION OR LONG-TERM PERFORMANCE OF THE VARIOUS COMPONENTS OF THE REPOSITORY SYSTEM.



ambient = 25°C

t = 10⁴ days



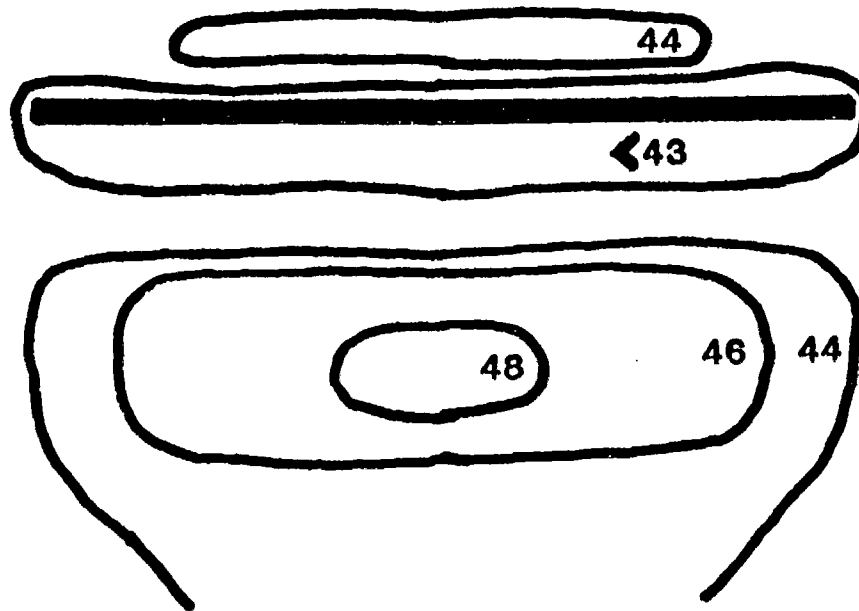
2-D TEMPERATURE PROFILE

RECHARGE = 1 cm/yr

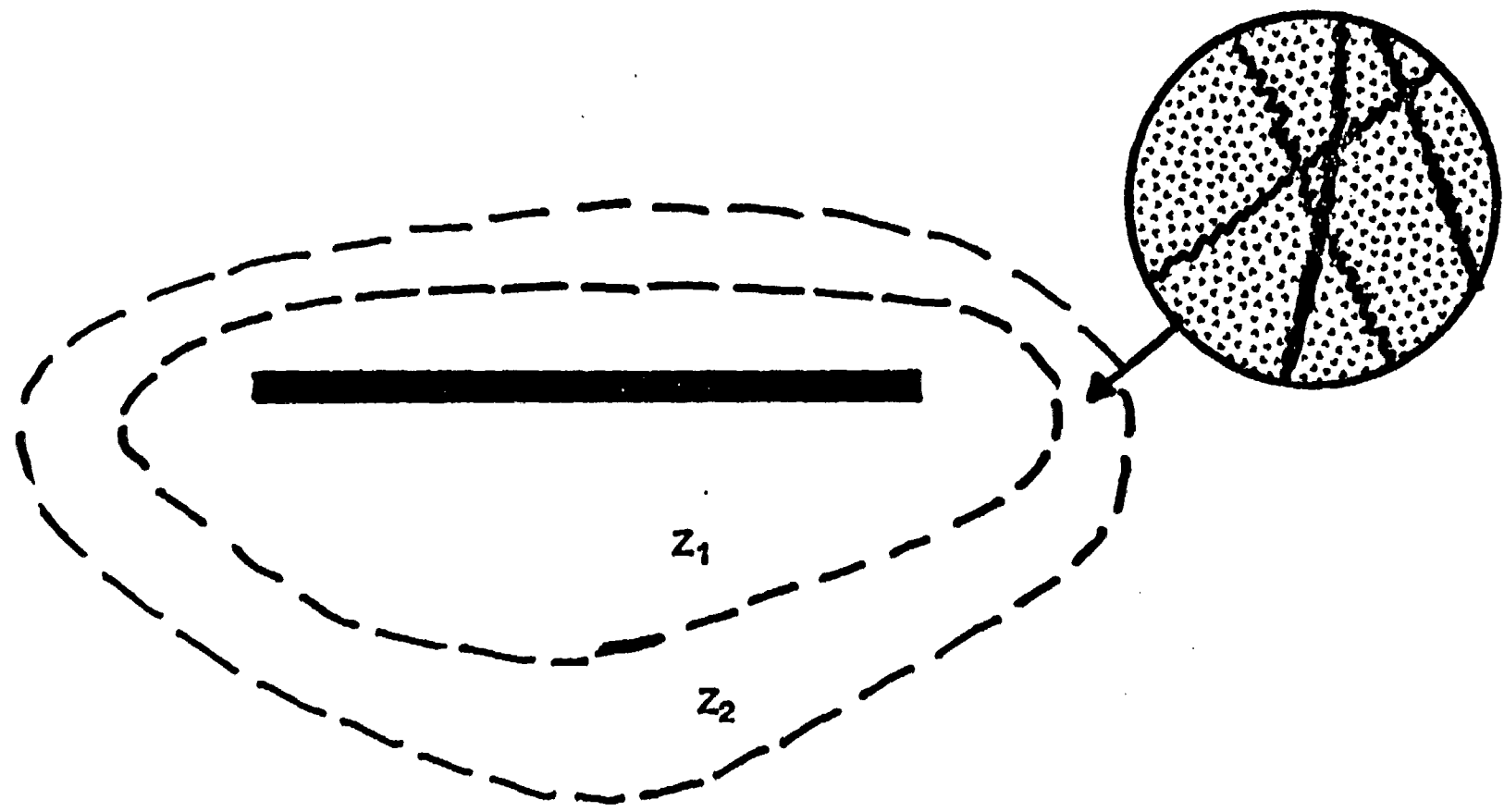
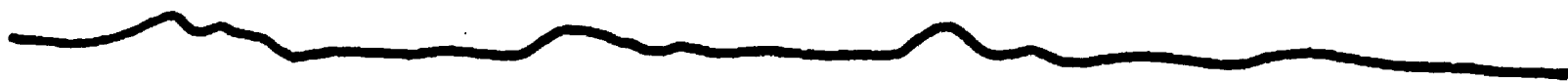


ambient = 43%
saturation

$t = 10^4$ days



2-D SATURATION PROFILE.



MINERAL ZONATION

GEOCHEMICAL ISSUES FOR NNWSI

1. WHAT ARE THE GEOCHEMICAL CONDITIONS PRECEDING WASTE EMPLACEMENT IN THE SATURATED/UNSATURATED ZONE?
2. WHAT ARE THE GEOCHEMICAL CONDITIONS/PROCESSES FOLLOWING WASTE EMPLACEMENT IN THE SATURATED/UNSATURATED ZONE?
3. WHAT ARE THE GEOCHEMICAL PROCESSES/CONDITIONS AFFECTING RELEASE AND TRANSPORT OF THE RADIONUCLIDES IN THE SATURATED/UNSATURATED ZONE?

GEOCHEMICAL CONDITIONS PRECEDING WASTE EMPLACEMENT

1. MINERALOGY/PETROLOGY/CHEMISTRY OF THE BACKFILL
AND FAR FIELD HOST ROCK
2. MINERALOGY/PETROLOGY/CHEMISTRY ALONG POTENTIAL
RELEASE PATHWAYS
3. GEOCHEMICAL CONDITIONS OF THE GROUNDWATER

GEOCHEMICAL CONDITIONS FOLLOWING WASTE EMPLACEMENT

1. MINERAL STABILITIES OF BACKFILL AND HOST ROCK
2. SPATIAL DISTRIBUTION OF ALTERATION PRODUCTS
3. GEOCHEMICAL CONDITIONS OF THE GROUNDWATER

SUMMARY OF GEOCHEMICAL ISSUES

INITIAL CONDITIONS

GEOCHEMICAL CONDITIONS PRECEDING WASTE EMPLACEMENT

MINERALOGY

MINERALOGY ALONG RELEASE PATHWAYS

GROUNDWATER GEOCHEMISTRY

CHANGING CONDITIONS

GEOCHEMICAL CONDITIONS FOLLOWING WASTE EMPLACEMENT

MINERAL STABILITIES

SPATIAL DISTRIBUTION OF ALTERATION

GROUNDWATER CONDITIONS

RELEASE AND TRANSPORT

GEOCHEMICAL PROCESSES AFFECTING RELEASE AND TRANSPORT OF RADIONUCLIDES

SOLUBILITY/CONCENTRATION

REACTION/SORPTION KINETICS

REDOX

MINERALOGY

COLLOIDS/PARTICULATES/ORGANICS

MATRIX DIFFUSION

VAPOR TRANSPORT

GEOCHEMICAL PROCESSES AFFECTING RELEASE AND TRANSPORT OF RADIONUCLIDES

1. SOLUBILITY/CONCENTRATION OF RADIONUCLIDES
2. REACTION/SORPTION KINETICS
3. REDOX CONDITIONS
4. MINERALOGY
5. COLLOID/PARTICULATES/ORGANICS
6. MATRIX DIFFUSION
7. VAPOR TRANSPORT

BRIEFING ON THE NRC GENERIC TECHNICAL POSITION
ON
"SOLUBILITY"

R J STARMER

NRC/NNWSI GEOCHEMISTRY TECHNICAL MEETING
LOS ALAMOS, NEW MEXICO
JULY 11, 1984

BACKGROUND

SOLUBILITY IS A RELATIVELY SIMPLE CHEMICAL CONCEPT WHICH MAY BE DEFINED PRECISELY IN TERMS OF EQUILIBRIUM CHEMICAL THERMODYNAMICS. THE MEASURE OF SOLUBILITY IS MORE DIFFICULT, EVEN IN SIMPLE SYSTEMS. IN THE REPOSITORY ENVIRONMENT, SOLUBILITY CAN BE DEFINED ONLY IN AN OPERATIONAL SENSE. ANY ATTEMPT TO DEFINE OR USE THE TERM SOLUBILITY IS OPEN TO LENGTHY DISCUSSION. THIS REQUIRES A STATEMENT OF THE NRC STAFF POSITION ON THE SUBJECT.

SOLUBILITY. A property of a substance by virtue of which it forms mixtures with other substances which are chemically and physically homogeneous throughout. The degree of solubility (often spoken of as "solubility") is the concentration of a solute in a saturated solution at any given temperature. The degree of solubility of most substances increases with rise in temperature, but there are cases (notably the organic salts of calcium) where a substance is more soluble in cold than in hot solvents.

The solubility of a given element is the sum of the stoichiometric concentrations of all dissolved species containing the element.

solubility. The ability or tendency of one substance to blend uniformly with another, e.g., solid in liquid, liquid in liquid, gas in liquid, gas in gas. Solids vary from 0 to 100% in their degree of solubility in liquids, depending on the chemical nature of the substances; to the extent that they are soluble, they lose their crystalline form and become molecularly or ionically dispersed in the solvent to form a true solution.

solubility (Chem.). The mass of a dissolved substance which will saturate 100 g of a solvent under stated conditions.

solubility [PHYS CHEM] The ability of a substance to form a solution with another substance.

SOLUBILITY, REAL. In the case of salts which form a solution in a given solvent in which the salt exists partly as unionized molecules and partly as ions, the maximum concentration of unionized salt that may exist under equilibrium conditions is called the real solubility, and the maximum total concentration of ionized and unionized salt is called the apparent solubility.

GARRELS AND CHRIST (1965) P. 55:

"THE SOLUBILITY OF A GIVEN ELEMENT IS THE SUM OF THE STOICHIOMETRIC
CONCENTRATIONS OF ALL DISSOLVED SPECIES CONTAINING THE ELEMENT."

SOLUBILITY OF SOMETHING

USE OF "SOLUBILITY" ESTIMATES

- 1) SCREENING FOR KEY RADIONUCLIDES
- 2) A WASTE PACKAGE PERFORMANCE MEASURE
- 1) A FAR-FIELD PERFORMANCE ASSESSMENT SOURCE TERM

STATEMENT OF POSITION

Each site which takes credit for solubility should design a minimum set of experiments to produce an information base adequate for licensing.

The set of experiments can be minimized if the following points are considered.

1. The range and proportions of solid compositions in the system that could react with ingressing or egressing waters;
2. The range of repository water compositions needed for determining radionuclide solution concentrations; and
3. The sources and effects of uncertainties.

- 1) USE A MATRIX OF COMBINATIONS OF WATER AND MATERIALS WHICH IS RATIONAL AND SUPPORTABLE
- 2) DETERMINE ALTERED GROUNDWATER COMPOSITIONS
- 3) DETERMINE "SOLUBILITY" (MAXIMUM STEADY-STATE CONCENTRATION) LIMITS FOR THESE WATER COMPOSITIONS AT PRESSURES AND TEMPERATURES OF THE MATRIX SET UP IN (1) ABOVE IN THE ABSENCE OF THE REACTING SOLIDS

ASSUMPTIONS

- o Knowledge of radionuclide solution concentration will be essential to near field and far field radionuclide transport modeling.
- o It is feasible to determine maximum concentration of radionuclides in a representative site-specific hydrothermal system via laboratory experiments.
- o A conservative assessment of radionuclide solution concentration should be based on approach to equilibrium from oversaturation.
- o Solubility measurements in the absence of other geochemical mechanisms give a conservative estimate of radionuclide concentration.

IF ALL DISSOLVED COMPONENTS ARE PRESENT IN THE PRECONDITIONED WATER

THEN

THE FIRST (AND ONLY POSSIBLE) PRECIPITATE OR SUITE OF PRECIPITATES WILL
BE THE CONTROLLING SOLID(S)

UNCERTAINTY

Water/Rock ratio

Colloids/Particulates

Supersaturation

Kinetics

Other suggested sources of uncertainty could include:

- o Use of defionized, distilled or synthetic ground waters,**
 - o Proportions of mineral solids versus radionuclide solids, and**
 - o The extrapolation of short-term results to predicted long-term results.**
-

MODELING

Alone, models are not suitable for estimating source term concentrations. Sources^{of} problems with calculations are:

1. equilibrium is assumed

Unrealistic in view of changing T, mineralogy, pH, and redox conditions. Also, these calculations generate solubilities in most stable state, hence nonconservative.

2. incomplete mass transfer

3. data base limitations

4. experimental verification

Enclosure 4

NNWSI/NRC GEOCHEMISTRY WORKSHOP

July 10-12, 1984

LOS ALAMOS NATIONAL LABORATORY

VIEW GRAPHS AND BACKUP DATA

•

OVERVIEW AND GEOCHEMISTRY PROGRAM PLAN



Los Alamos

WBS 2.3 SITE

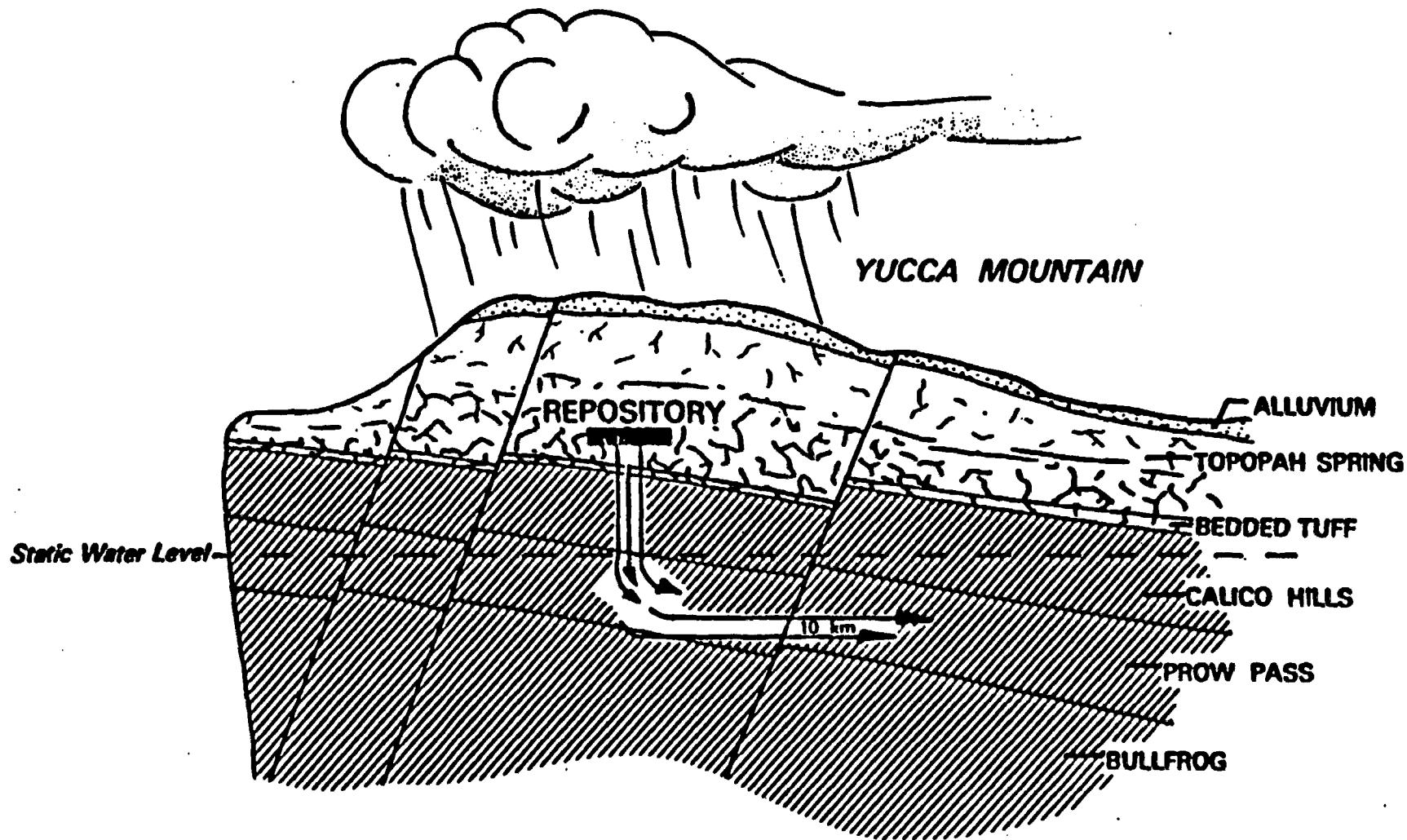
LOS ALAMOS NATIONAL LABORATORY CONTRIBUTION

WBS 2.3.1 GEOCHEMISTRY

WBS 2.3.2 MINERALOGY/PETROLOGY



CONCEPTUAL RADIONUCLIDE TRANSPORT PATH





Los Alamos

WBS 2.3.1 GEOCHEMISTRY

- GROUNDWATER CHEMISTRY
- SOLUBILITY DETERMINATION
- SORPTION AND PRECIPITATION
- DYNAMIC TRANSPORT PROCESSES
- RETARDATION SENSITIVITY ANALYSIS
- APPLIED DIFFUSION
- HYDROTHERMAL GEOCHEMISTRY
- NATURAL ISOTOPE CHEMISTRY



Los Alamos

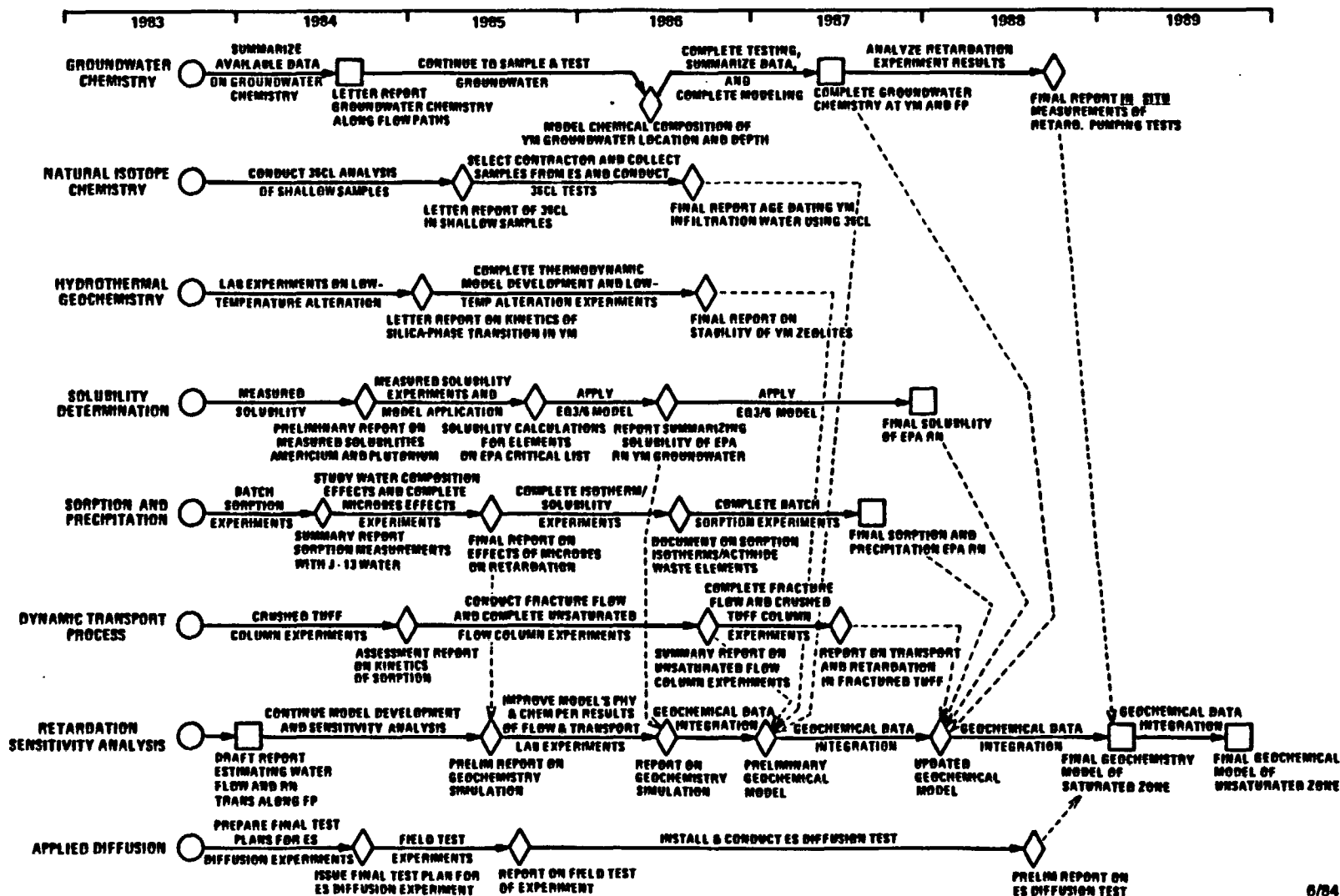
WBS 2.3.2 MINERALOGY/PETROLOGY

- **HOST ROCK STRATIGRAPHY AND MINERALOGY**
- **THREE-DIMENSIONAL DATA BASE FOR MINERALOGY/
PETROLOGY OF TRANSPORT PATHWAYS**
- **FRACTURE MINERALOGY**
- **MINERALOGIC CONTROLS ON RADIONUCLIDE
MOBILITY (Eh AND pH)**
- **HEAT LOAD EFFECTS ON PHYSICAL AND SORPTIVE
PROPERTIES OF MINERALS**
- **ALTERATION HISTORY OF YUCCA MOUNTAIN**



2.3.1 GEOCHEMISTRY SUMMARY NETWORK

Los Alamos

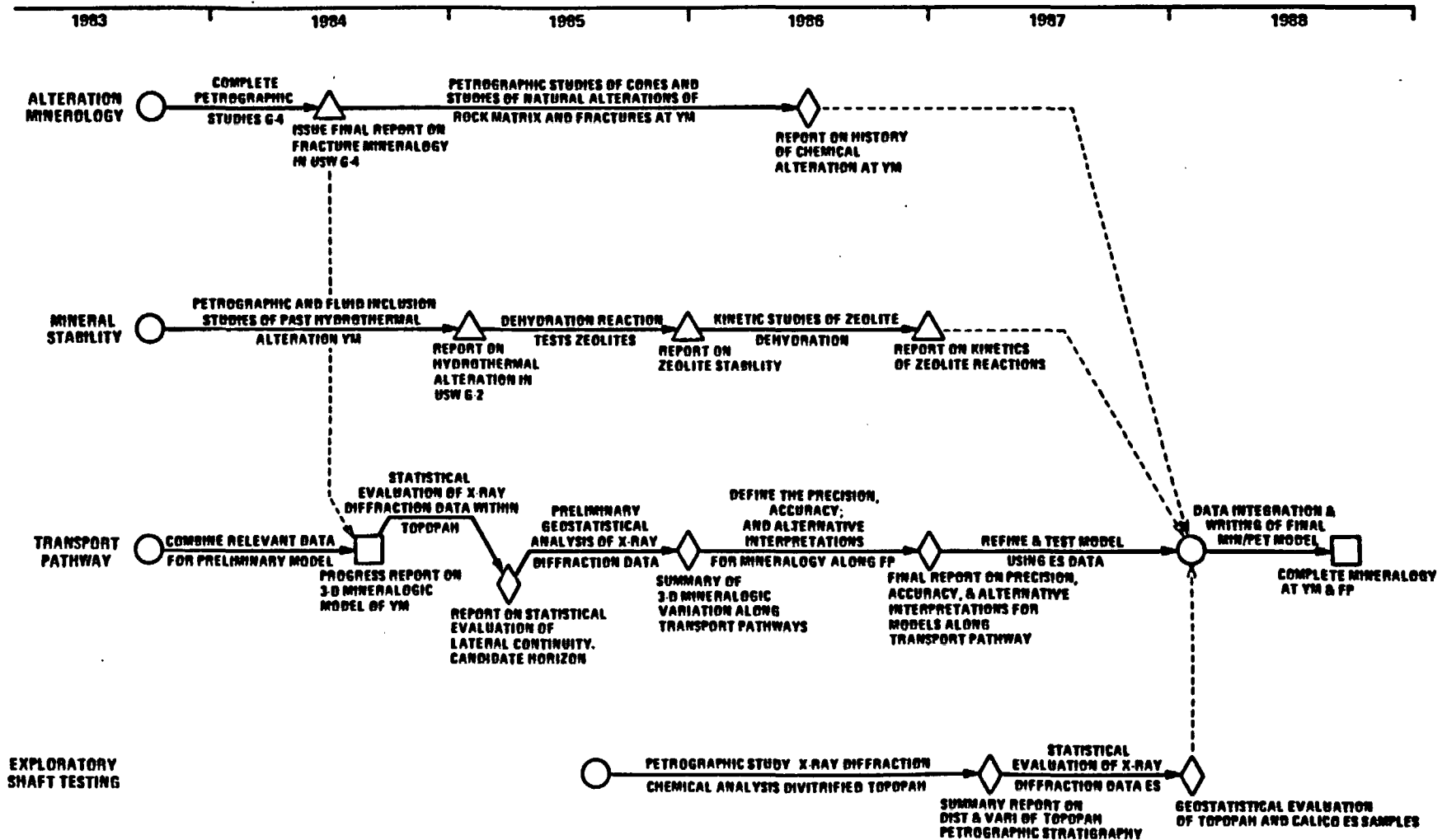




2.3.2

Los Alamos

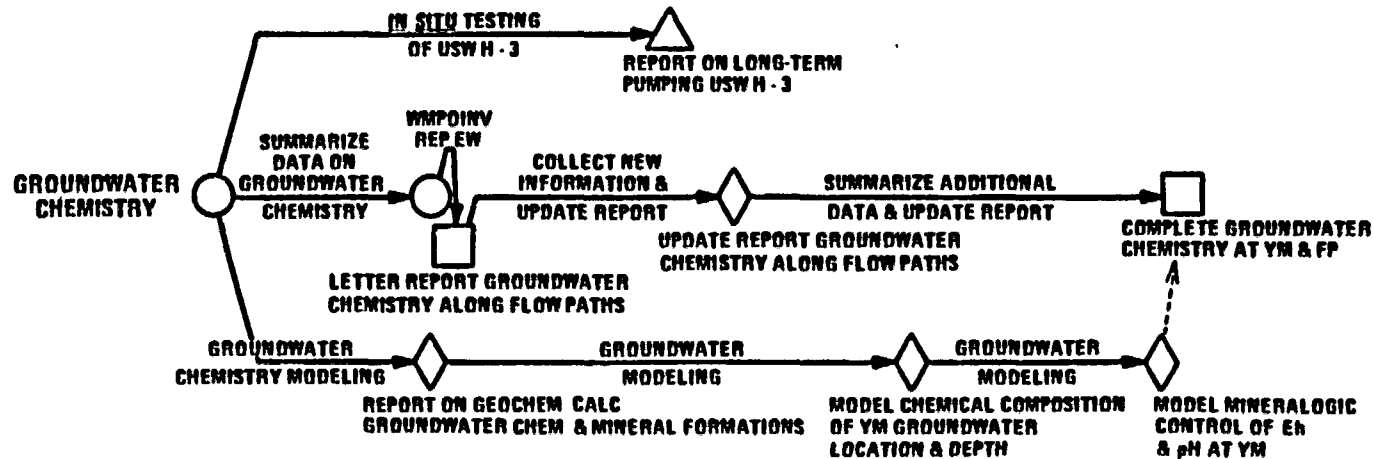
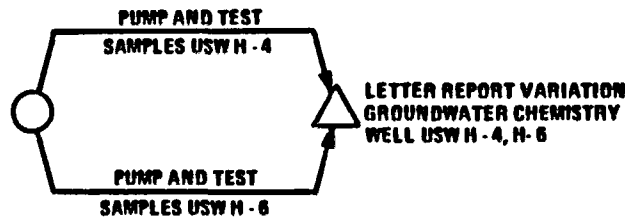
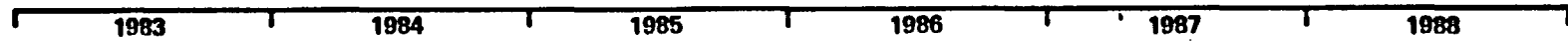
MINERALOGY/PETROLOGY SUMMARY NETWORK



BACKUP VIEWGRAPHS AND DATA

2.3.1.1 GROUNDWATER CHEMISTRY NETWORK

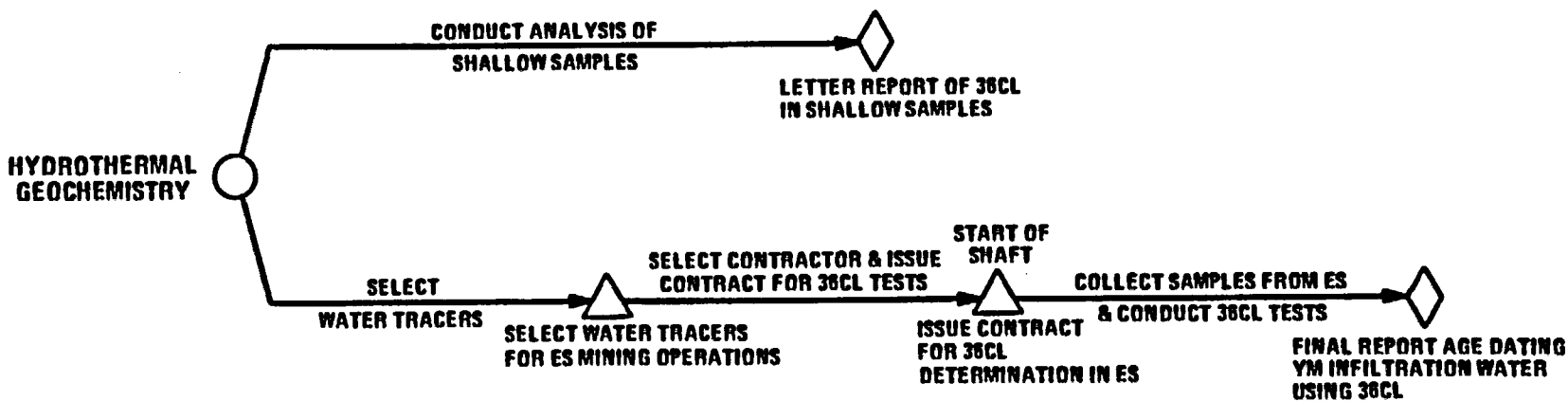
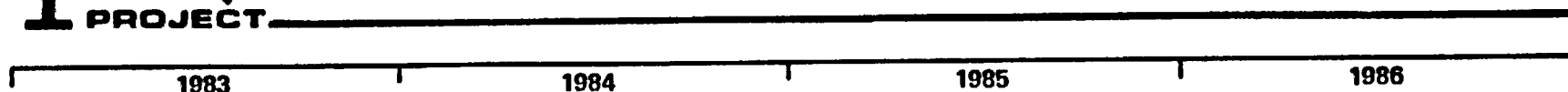
Los Alamos



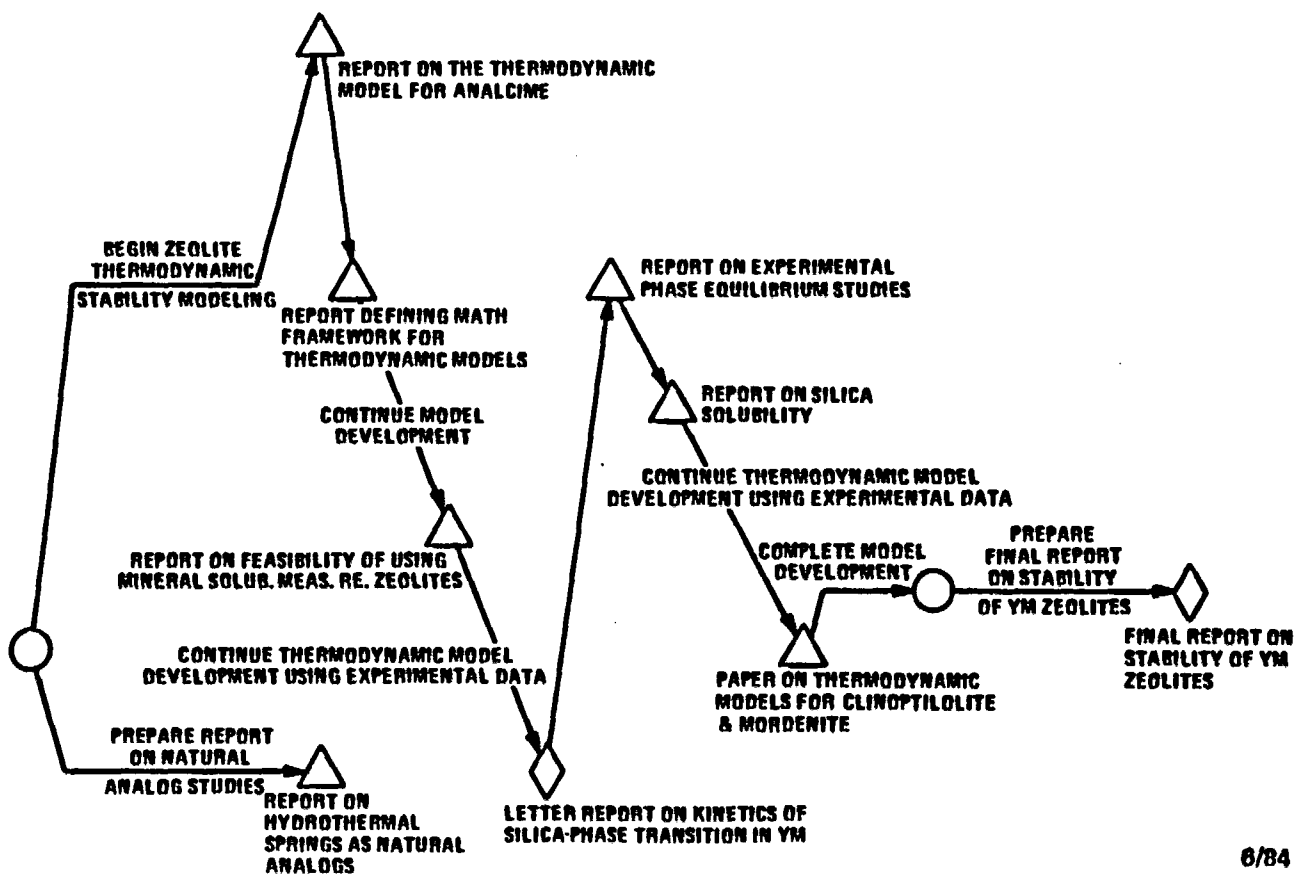
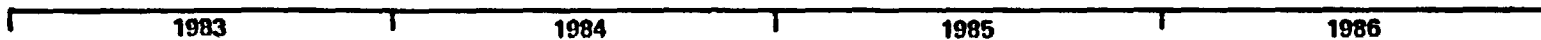


2.3.1.2 NATURAL ISOTOPE CHEMISTRY NETWORK

Los Alamos

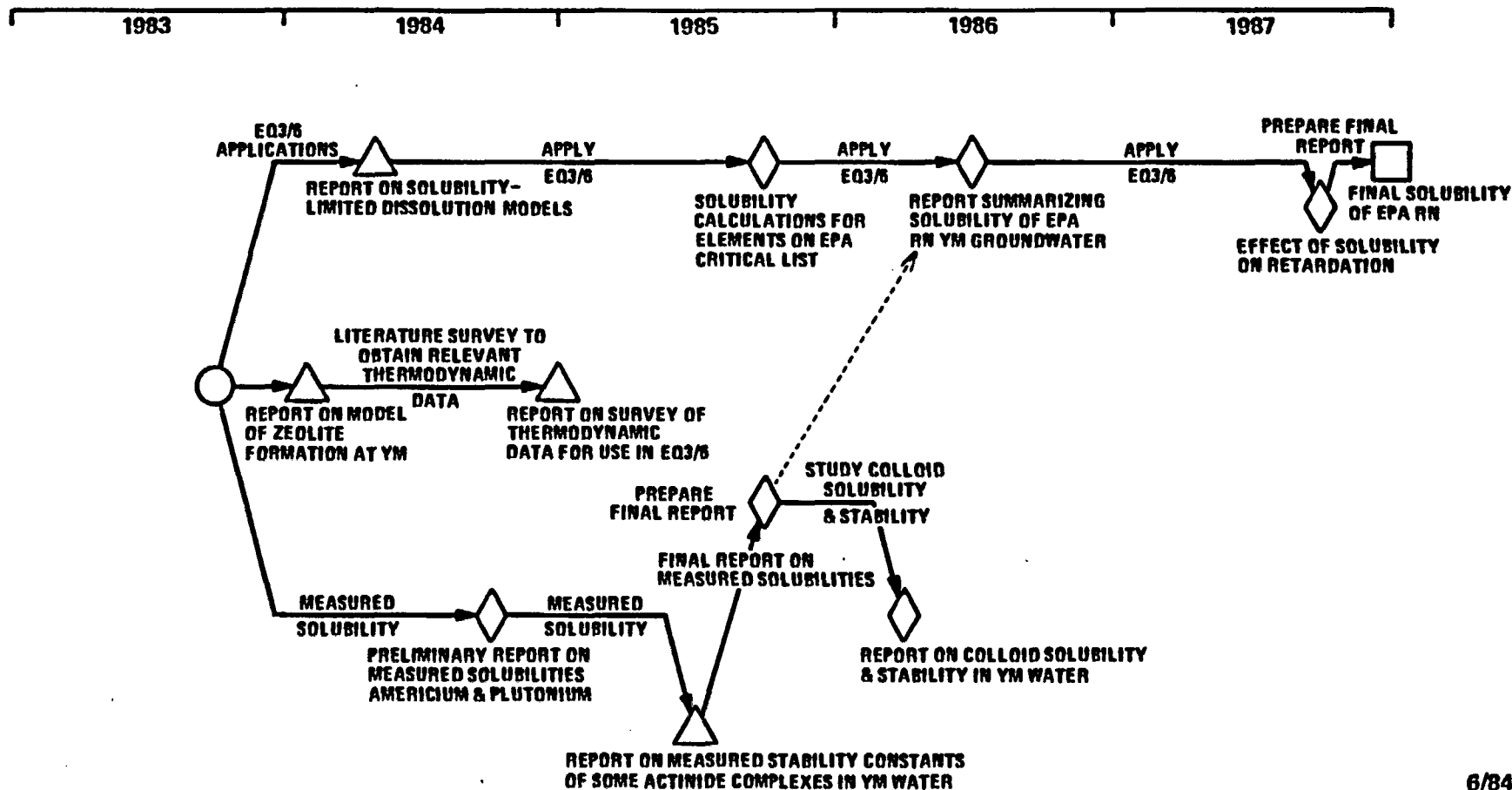


**2.3.1.3 HYDROTHERMAL
GEOCHEMISTRY NETWORK**



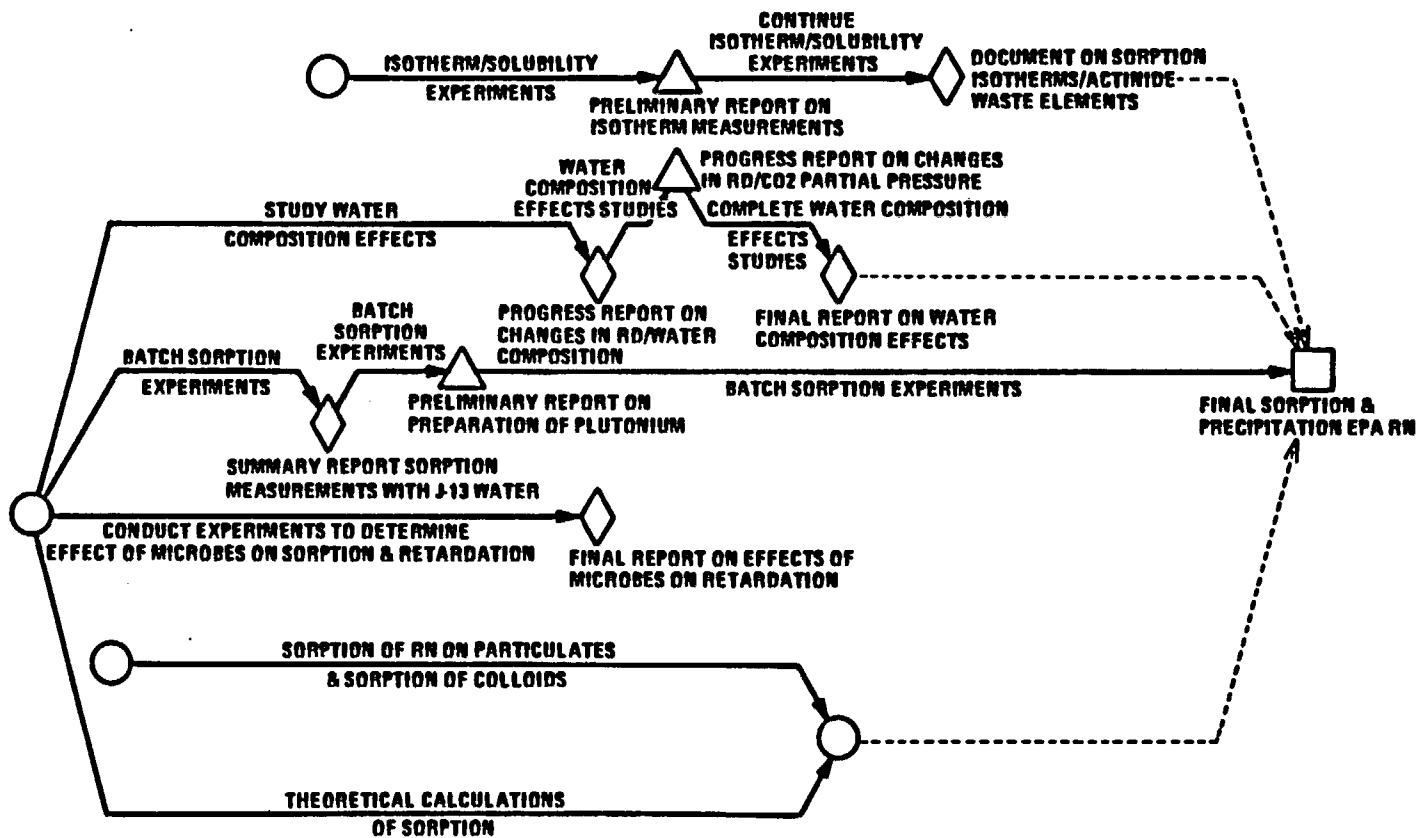
2.3.1.4 SOLUBILITY DETERMINATION NETWORK

Los Alamos

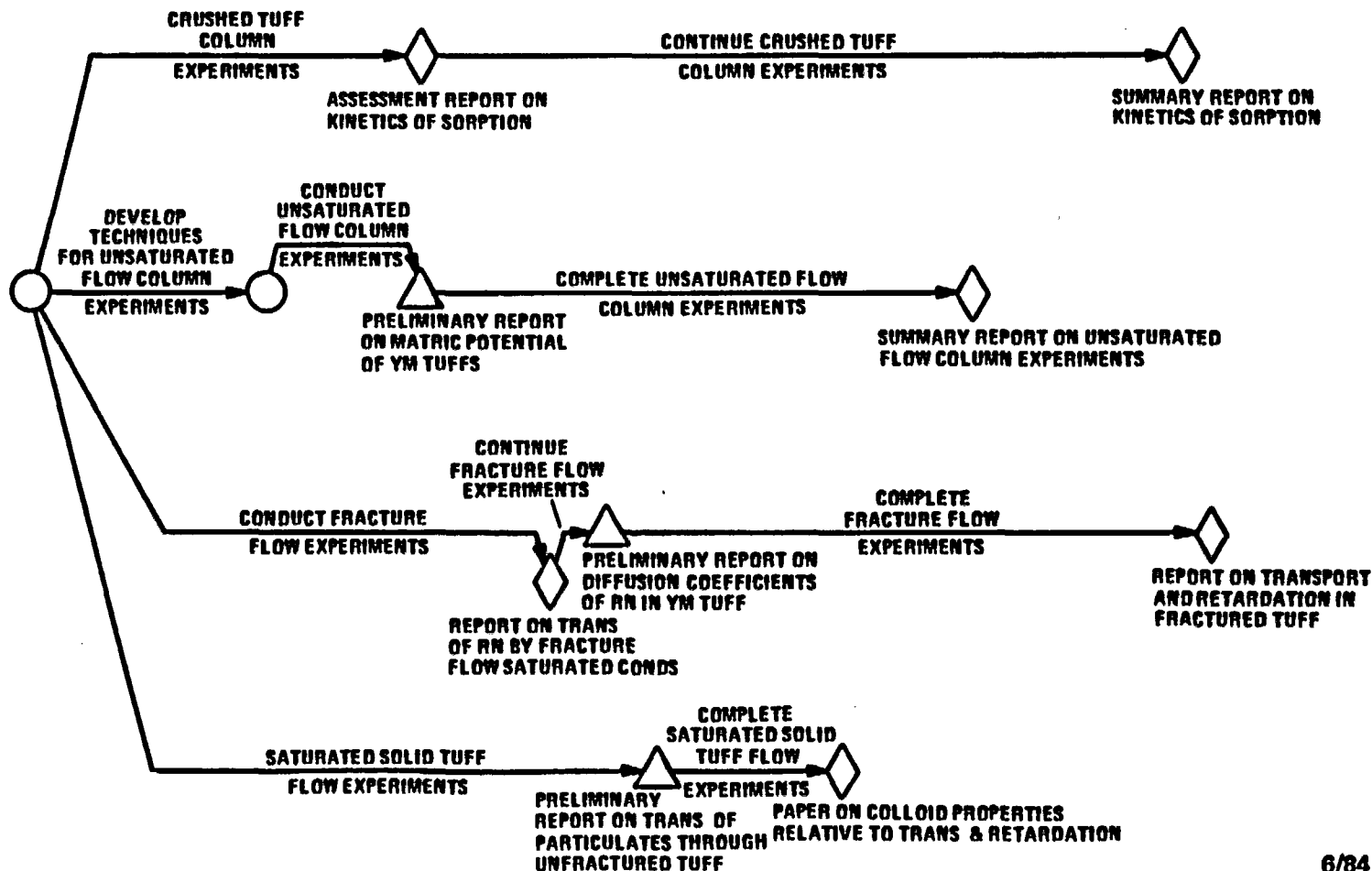


2.3.1.5 SORPTION AND PRECIPITATION NETWORK

1983 1984 1985 1986 1987

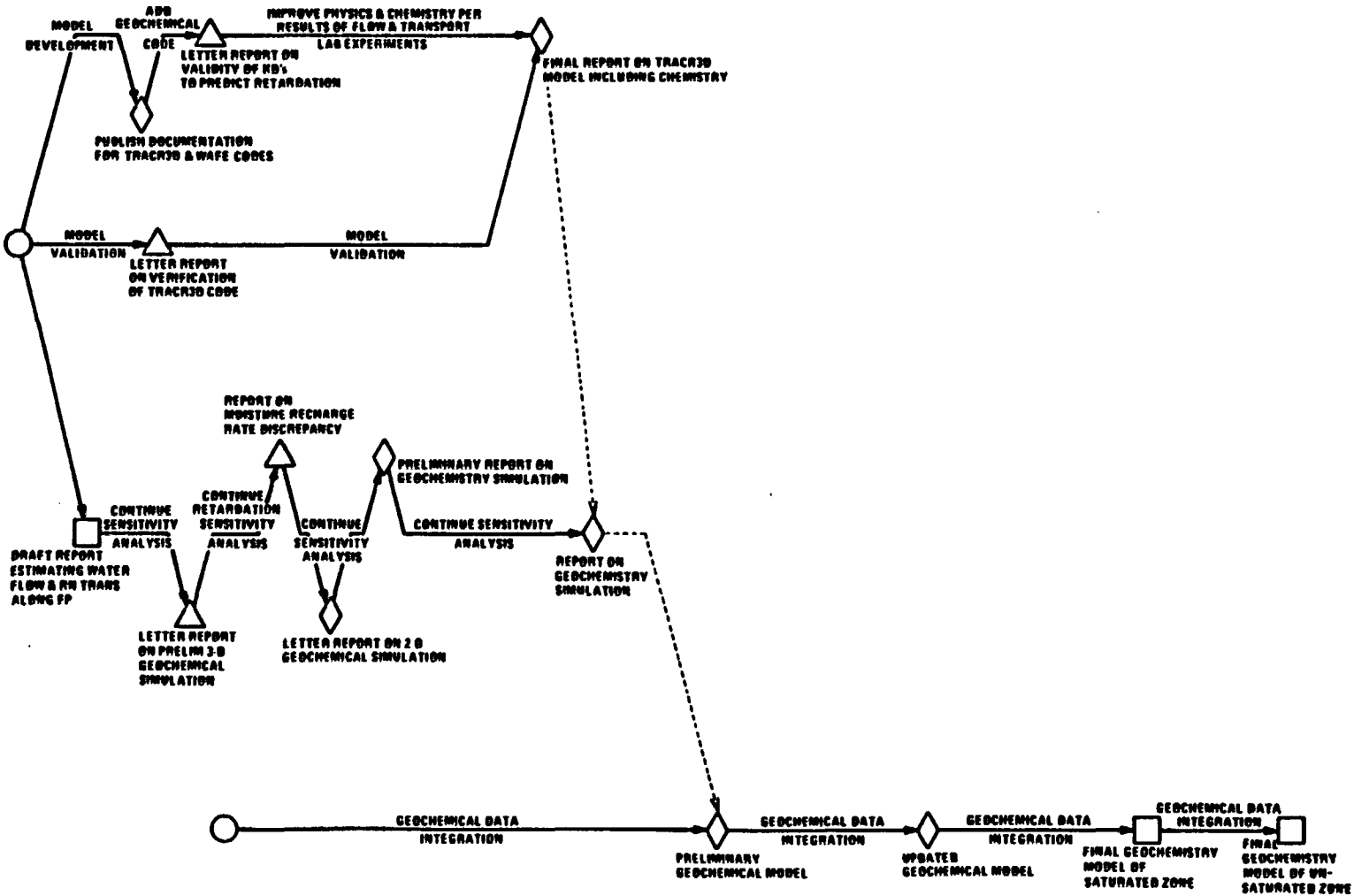


2.3.1.6 DYNAMIC TRANSPORT PROCESS NETWORK



2.3.1.7 RETARDATION SENSITIVITY ANALYSIS NETWORK

1983 1984 1985 1986 1987 1988 1989

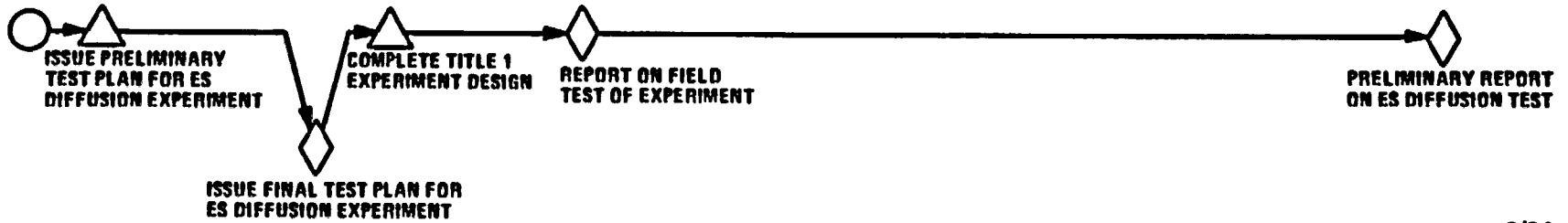




2.3.1.8 APPLIED DIFFUSION NETWORK

Los Alamos

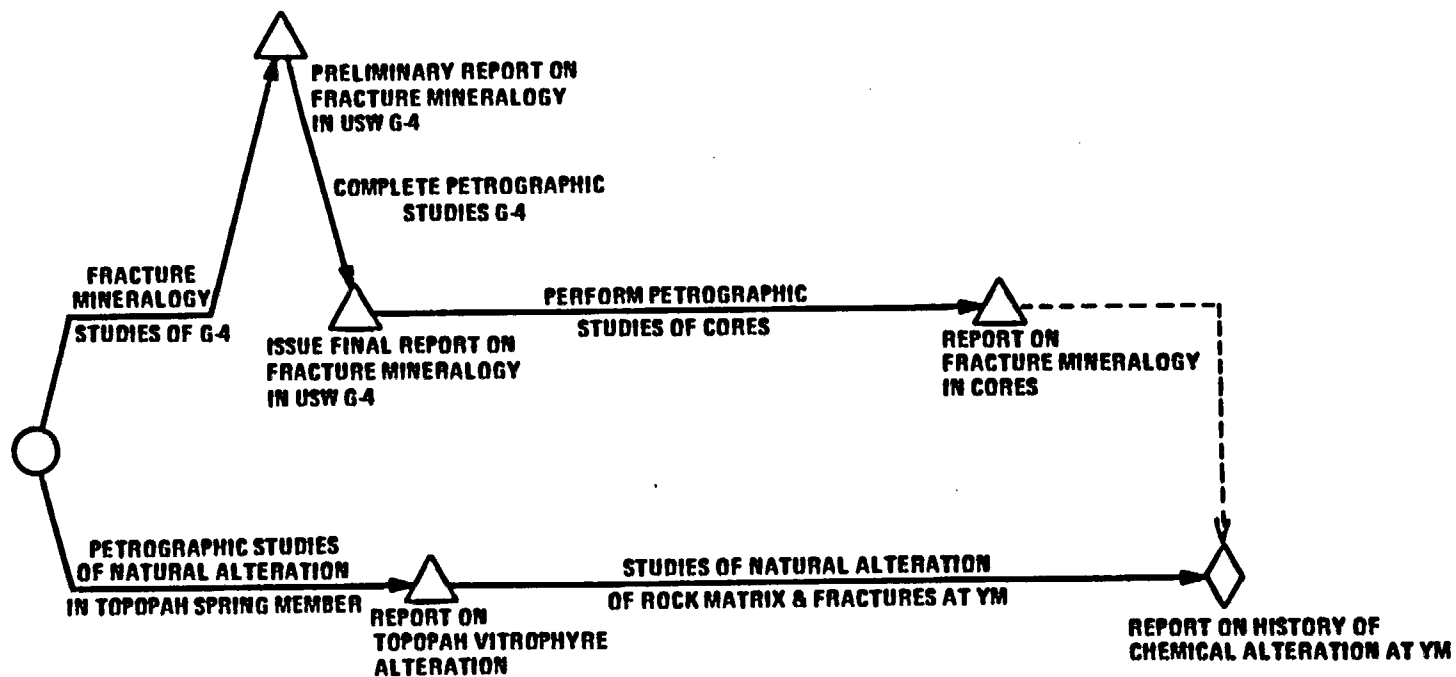
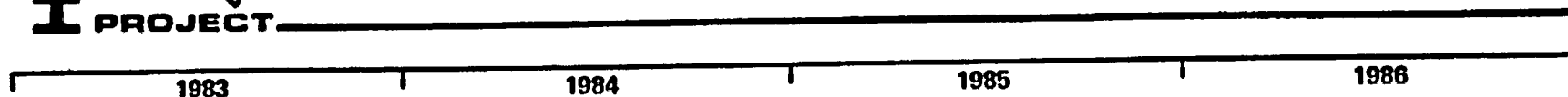
1983 1984 1985 1986 1987 1988





2.3.2.1 ALTERATION MINERALOGY NETWORK

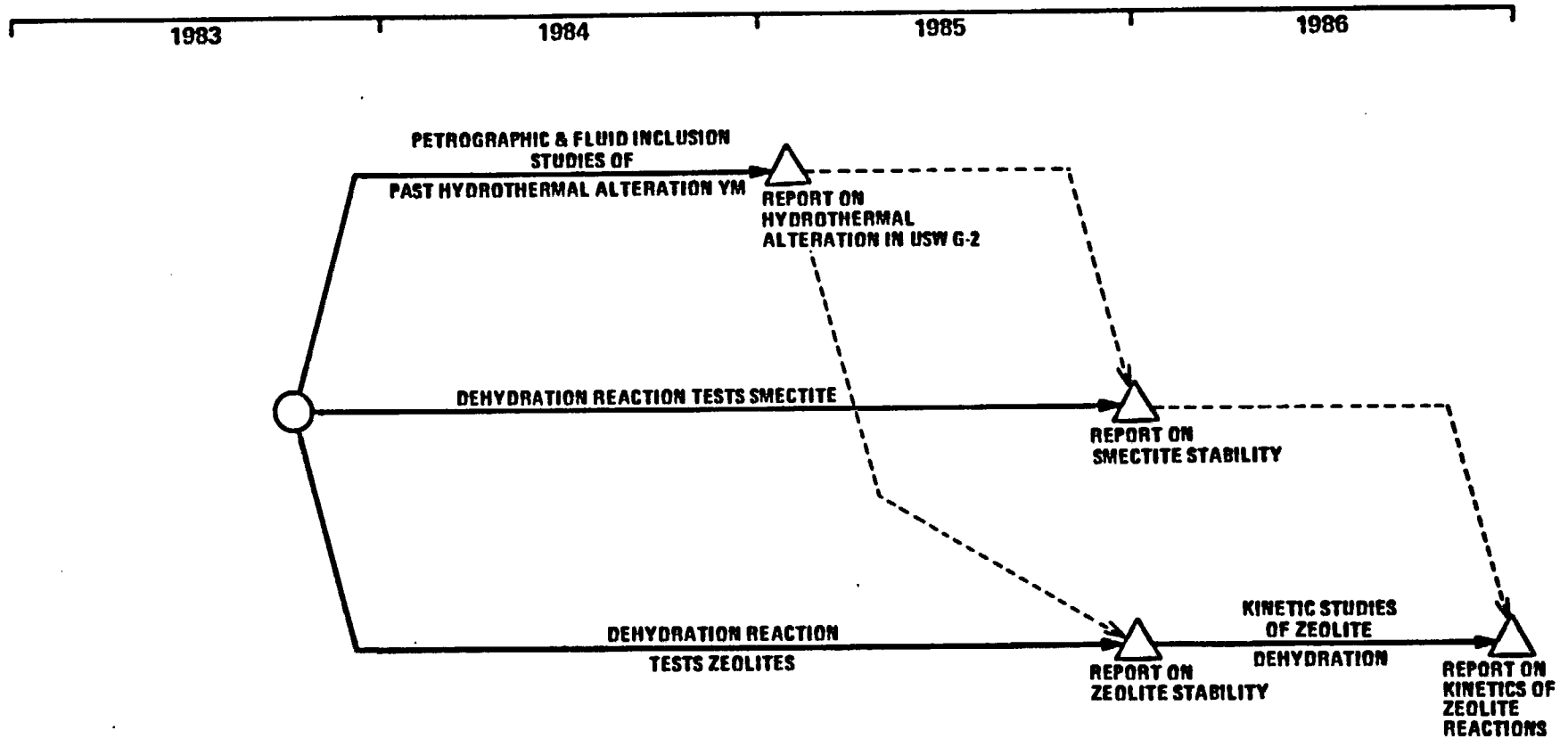
Los Alamos





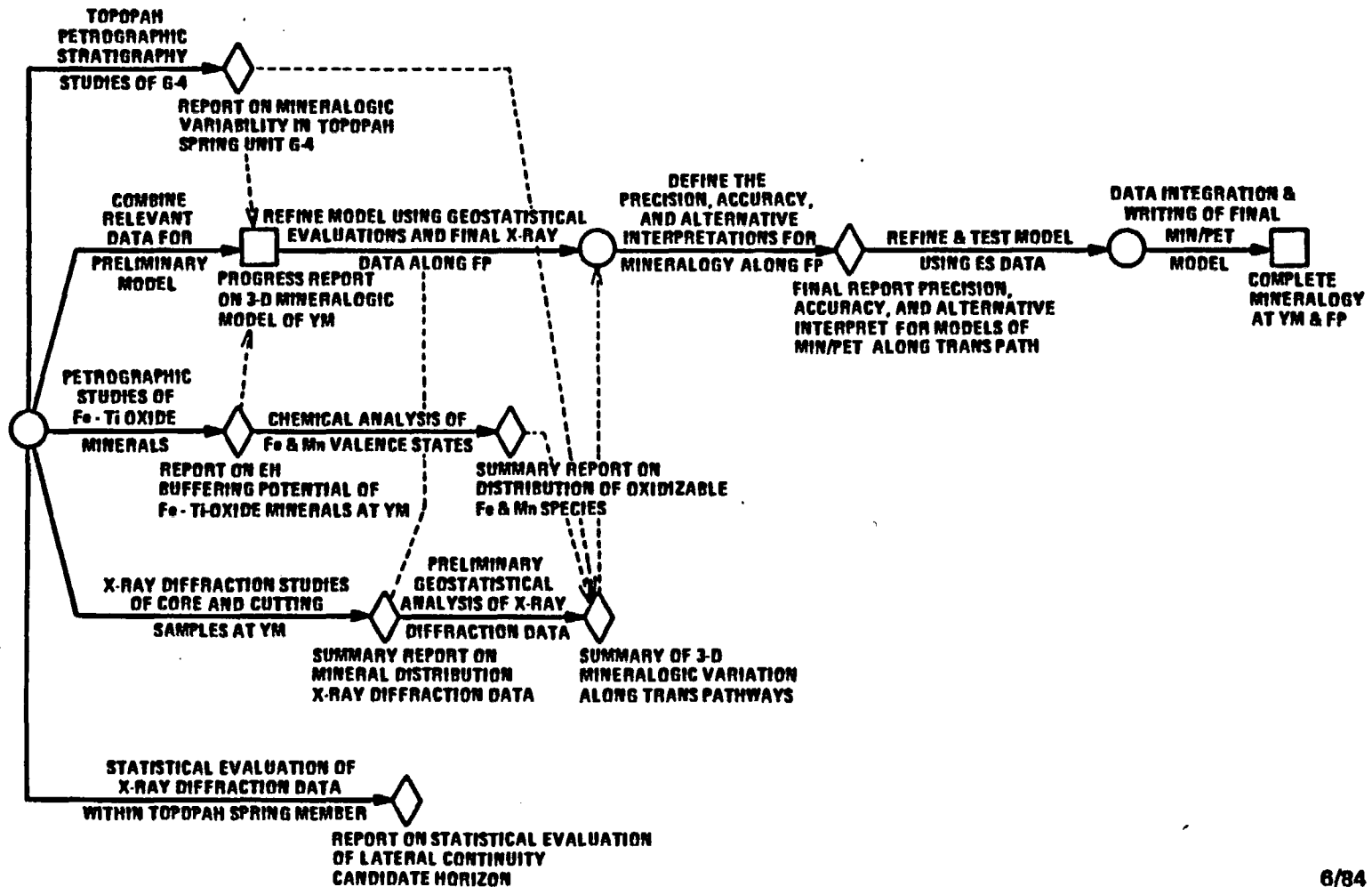
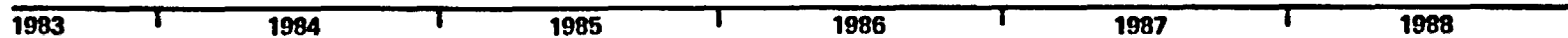
2.3.2.2 MINERAL STABILITY NETWORK

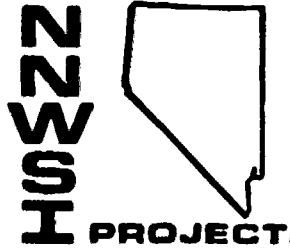
Los Alamos



2.3.2.3 TRANSPORT PATHWAY NETWORK

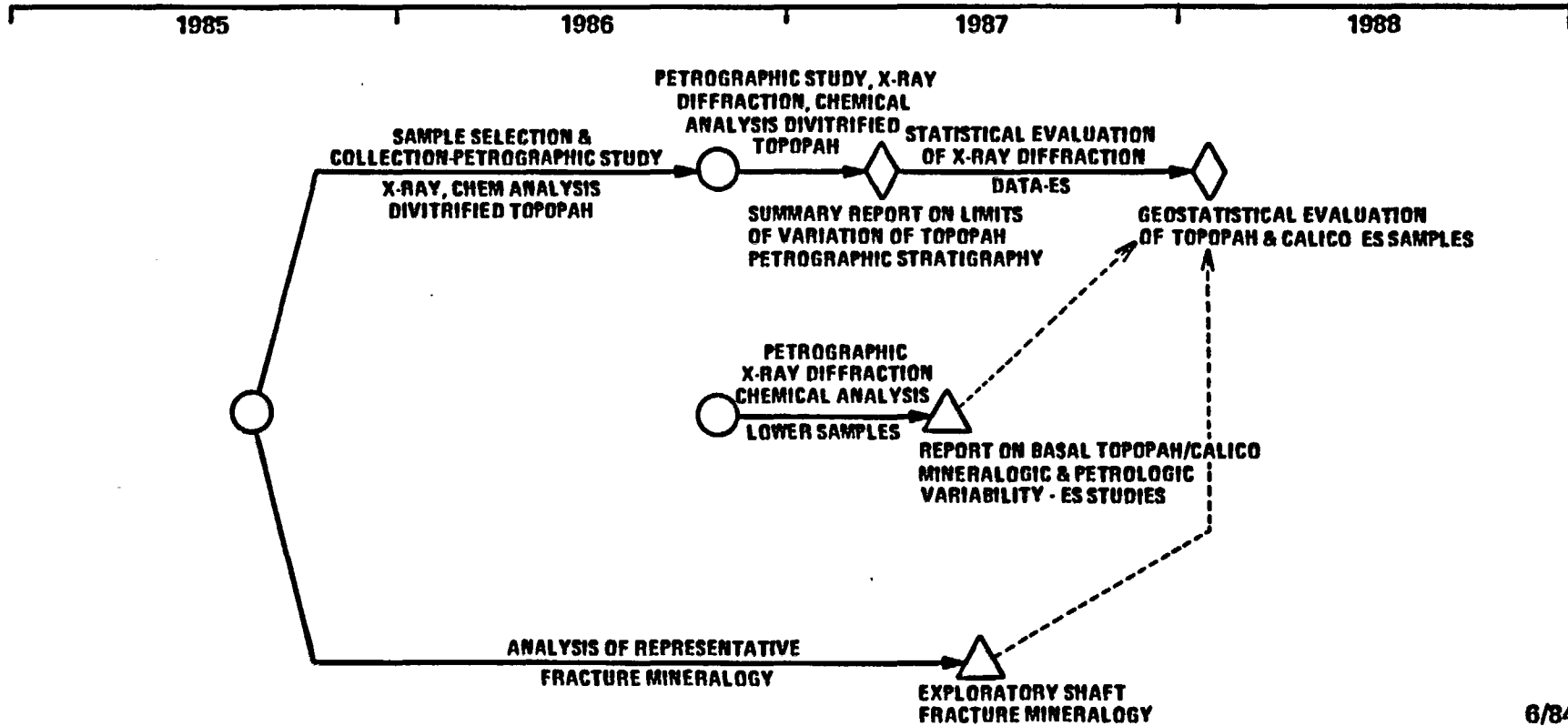
Los Alamos





2.3.2.4 EXPLORATORY SHAFT TESTING NETWORK

Los Alamos



UNSATURATED ZONE PROCESSES



NNWSI PROGRAM
UNSATURATED ZONE PROCESSES – OVERVIEW

Los Alamos

TRANSPORT PROCESSES IN THE UNSATURATED ZONE

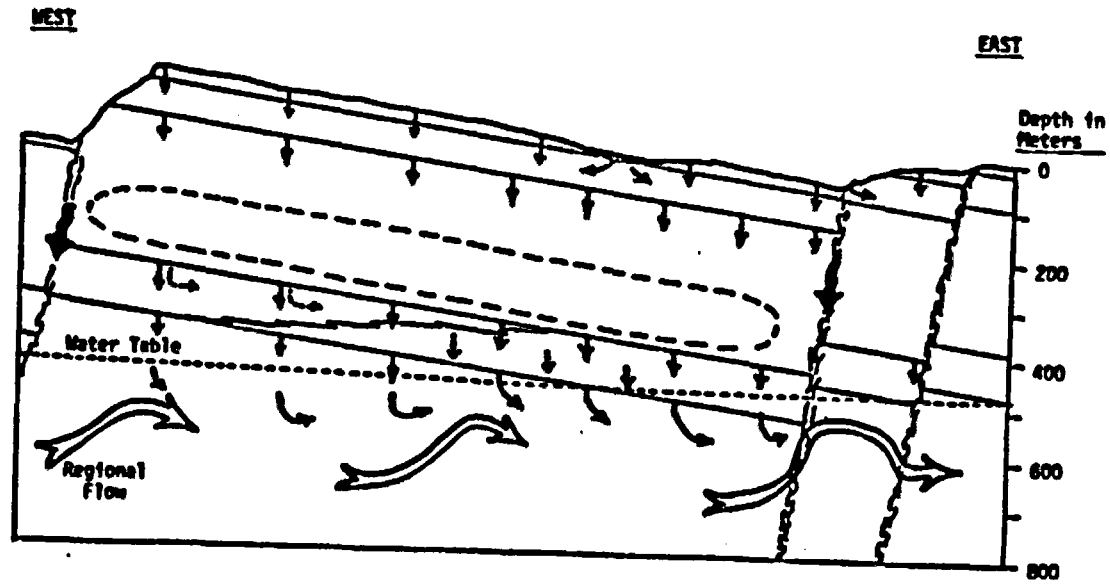
- 1. ADVECTION**
- 2. DIFFUSION**
- 3. SORPTION/PECIPITATION**
- 4. VAPOR MOVEMENT**
- 5. FILTRATION**



NNWSI PROGRAM

UNSATURATED ZONE PROCESSES - OVERVIEW

Los Alamos

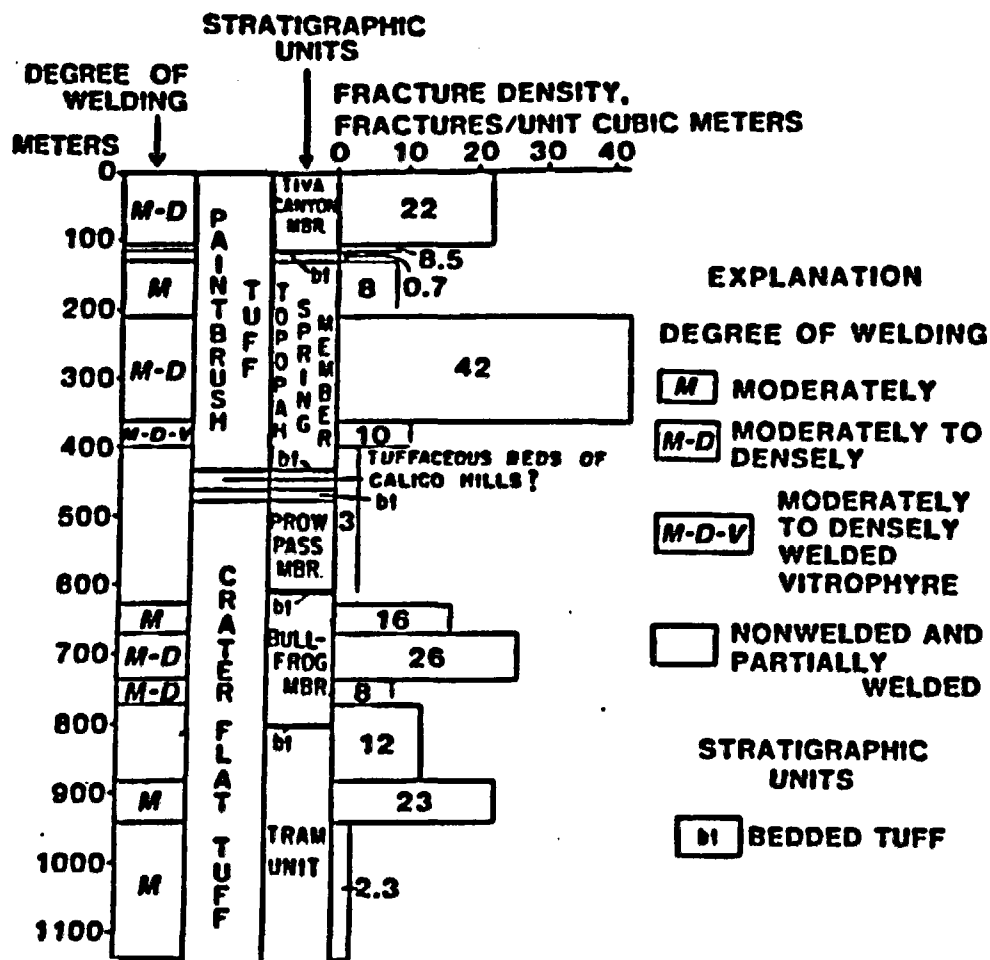




NNWSI PROGRAM

UNSATURATED ZONE PROCESSES - OVERVIEW

Los Alamos





NNWSI PROGRAM

UNSATURATED ZONE PROCESSES – OVERVIEW

Los Alamos

FLOW CHARACTERISTICS

AFFECTED BY MATRIC POTENTIAL

PERMEABILITY DEPENDS ON SATURATION

DIFFUSIVITY DEPENDS ON SATURATION

DISPERSIVITY MAY DEPEND ON SATURATION

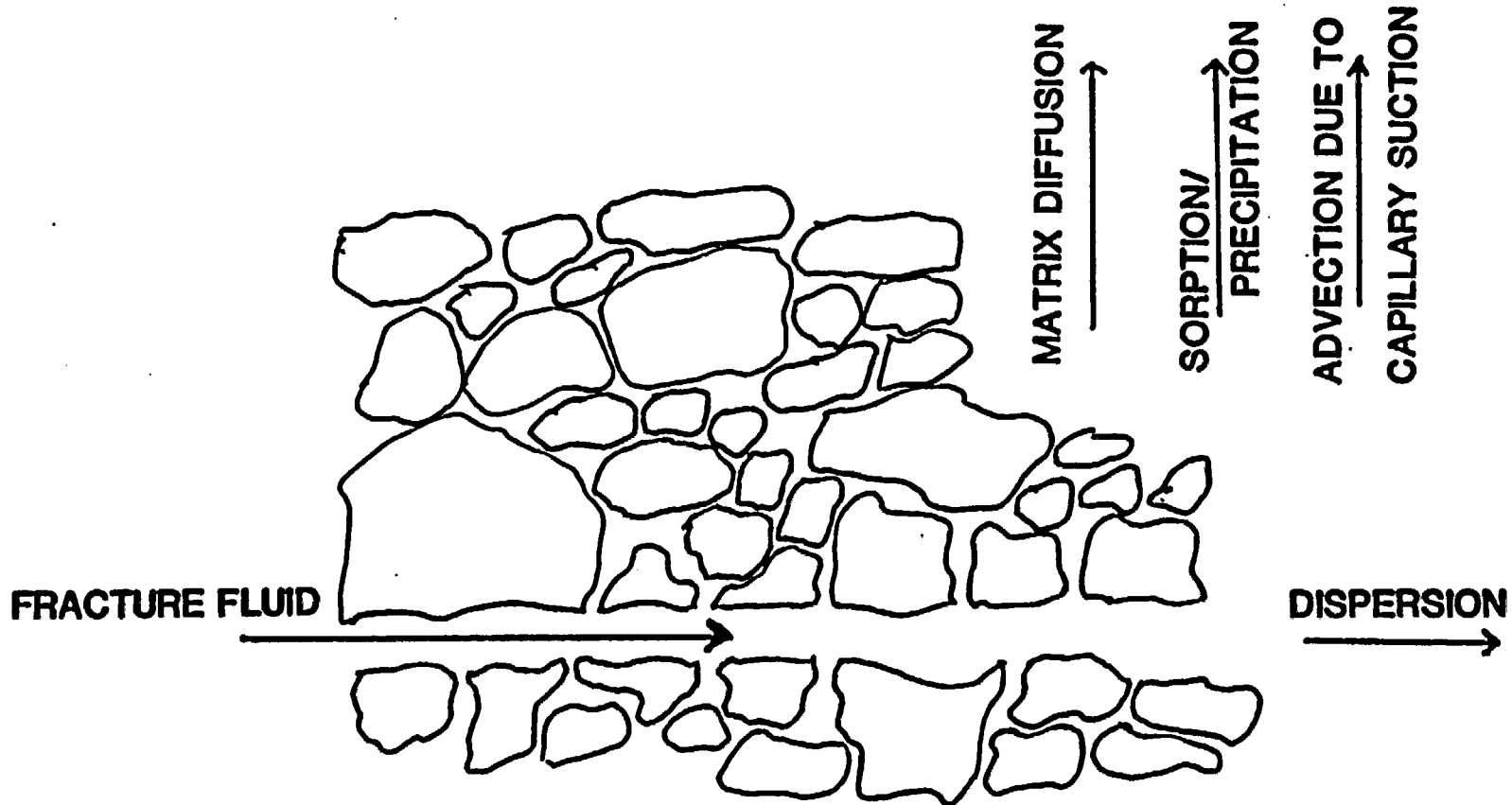
**FRACTURE VS. POROUS FLOW DEPENDING ON
INFILTRATION RATE**



NNWSI PROGRAM
UNSATURATED ZONE PROCESSES - OVERVIEW

Los Alamos

FRACTURE FLOW IN UNSATURATED TUFF





NNWSI PROGRAM

UNSATURATED ZONE PROCESSES - OVERVIEW

Los Alamos

PRESENT KNOWLEDGE OF TRANSPORT IN THE
YUCCA MOUNTAIN UNSATURATED ZONE

MATRIC POTENTIAL / POROSIMETRY DATA

SATURATION VS. DEPTH

DIFFUSIVITY AT 100 % SATURATION

MATRIX PERMEABILITY AT 100 % SATURATION

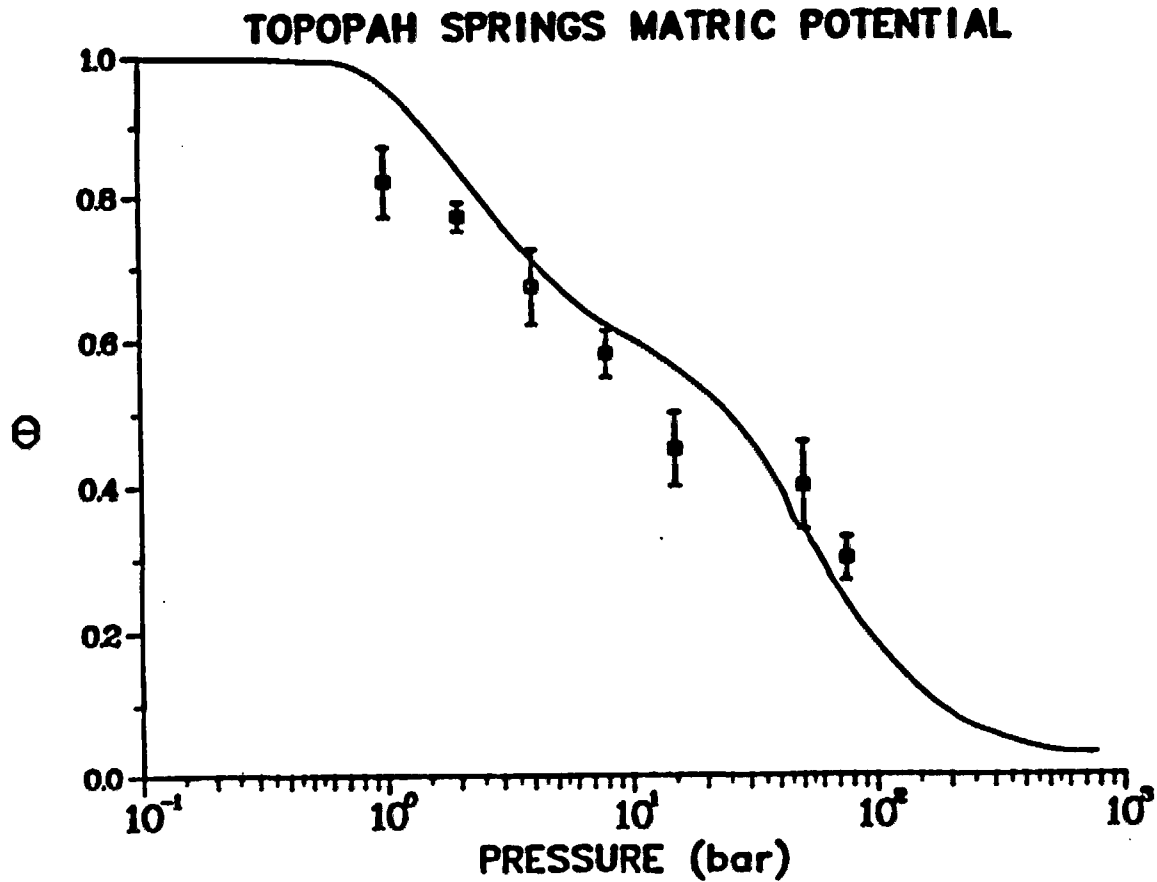
TRACR3D CALCULATIONS OF FRACTURE FLOW
SCENARIOS



NNWSI PROGRAM

UNSATURATED ZONE PROCESSES - OVERVIEW

Los Alamos





NNWSI PROGRAM
UNSATURATED ZONE PROCESSES - OVERVIEW

Los Alamos

PLANNED EXPERIMENTS

DIFFUSION VS SATURATION

**SATURATED FRACTURE FLOW WITH UNSATURATED
MATRIX**

ES TRANSPORT EXPERIMENTS



NNWSI PROGRAM
UNSATURATED ZONE PROCESSES - OVERVIEW

Los Alamos

POSSIBLE SUPPLEMENTRY EXPERIMENTS

**INFILTRATION OF TRACED WATER INTO
PARTIALLY SATURATED TUFF**

**ADVECTION DRIVEN BY MATRIC
POTENTIAL ONLY**

**USING ALL CURRENT TRACERS
INCLUDING PARTICULATE**

**VAPOR TRANSPORT VIA PERCOLATION
EXPERIMENT**

**USING GAS TRACERS HAVING
DIFFERENT SOLUBILITIES**



NNWSI PROGRAM
UNSATURATED ZONE PROCESSES - OVERVIEW

Los Alamos

OPEN QUESTIONS

HOW DOES VAPOR MOVEMENT AFFECT

- 1. DISSOLUTION/PRECIPITATION OF MINERALS**
- 2. PORE WATER AGE DATING**
- 3. WASTE PACKAGE DISSOLUTION**
- 4. MIGRATION OF VOLATILE WASTE ELEMENTS**

Q26

GEOCHEMISTRY OF WATER

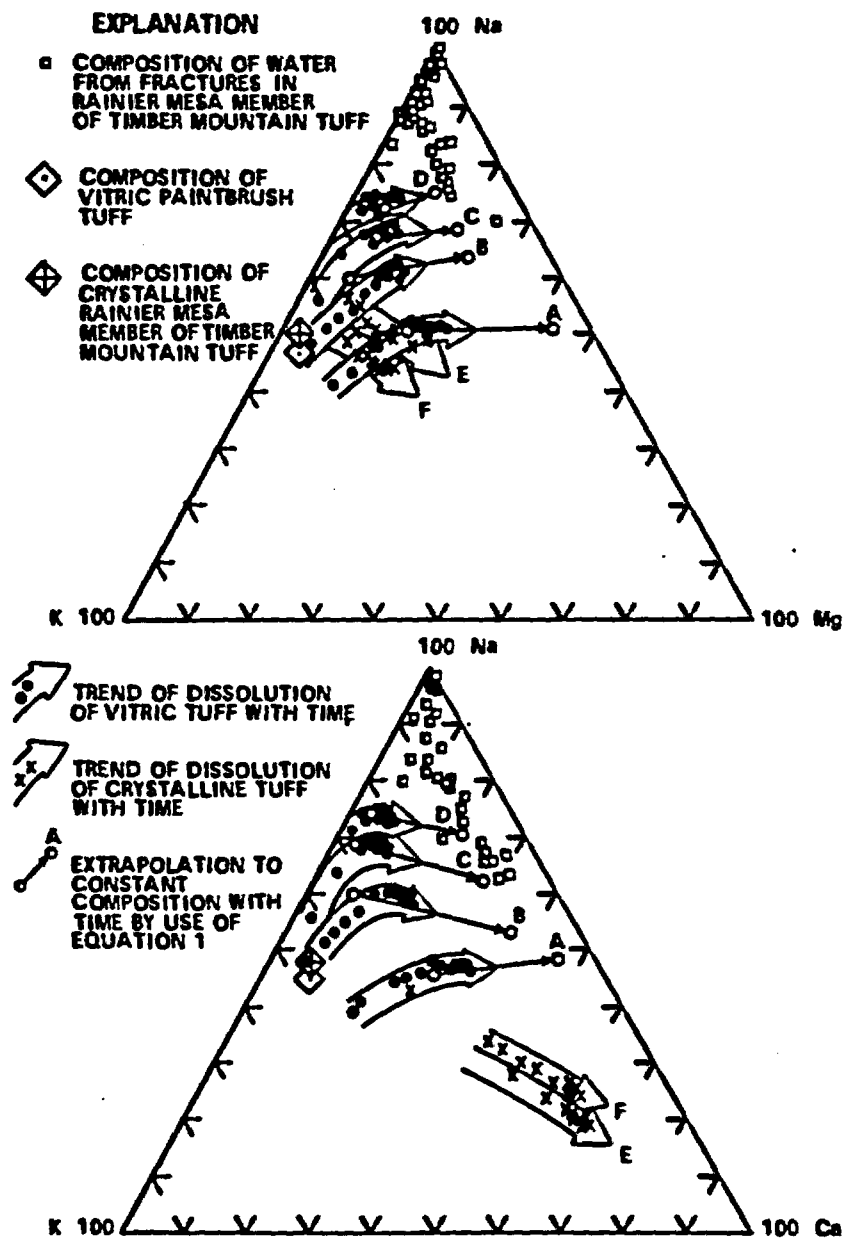


FIGURE 11.—Relative mole fractions of cations in the tuffaceous rocks, fracture waters, and experimental solutions.

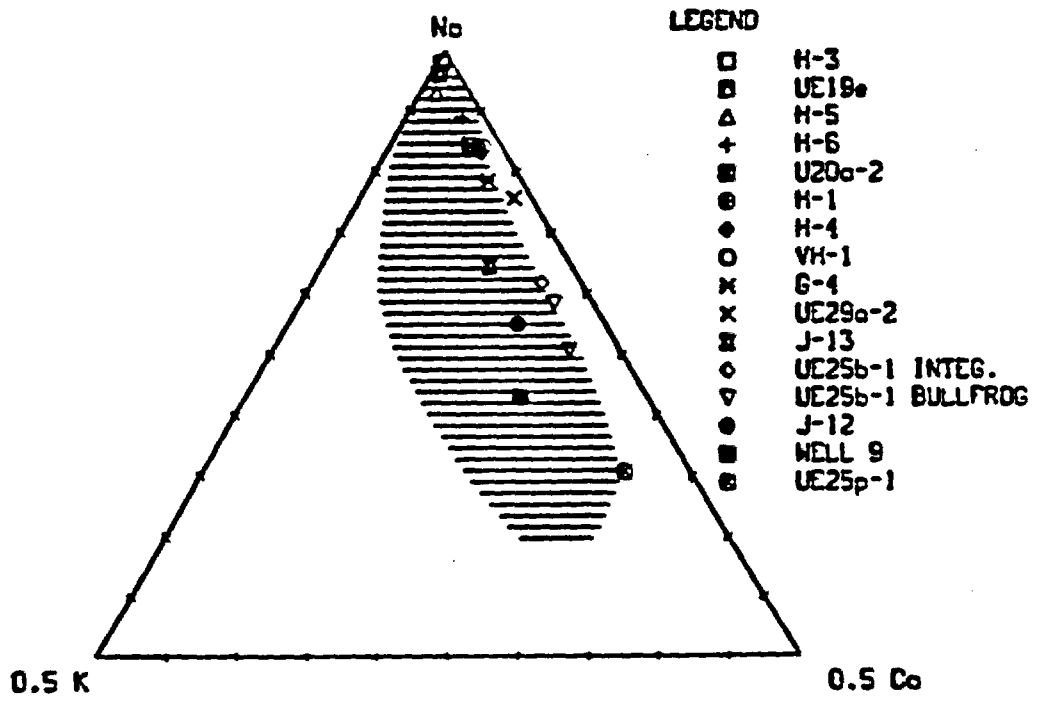


Fig. 3. Relative Na-K-Ca concentration in Yucca Mountain water.

BACKUP VIEWGRAPHS AND DATA



GROUND WATER CHEMISTRY

**A. OGARD, P. WANEX, A. MITCHELL, M. CISNEROS,
AND S. MAESTAS**

- **AFFECTS SPECIATION, SOLUBILITY, TRANSPORT, AND RETARDATION**
- **VARIES SPATIALLY**
- **AIDS IN FLOWPATH MODELING**

Los Alamos

REPRESENTATIVE GROUNDWATERS

USW H-3

UE25p#1

J-13

SNOW OR RAIN

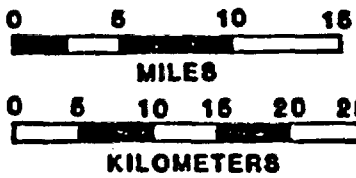
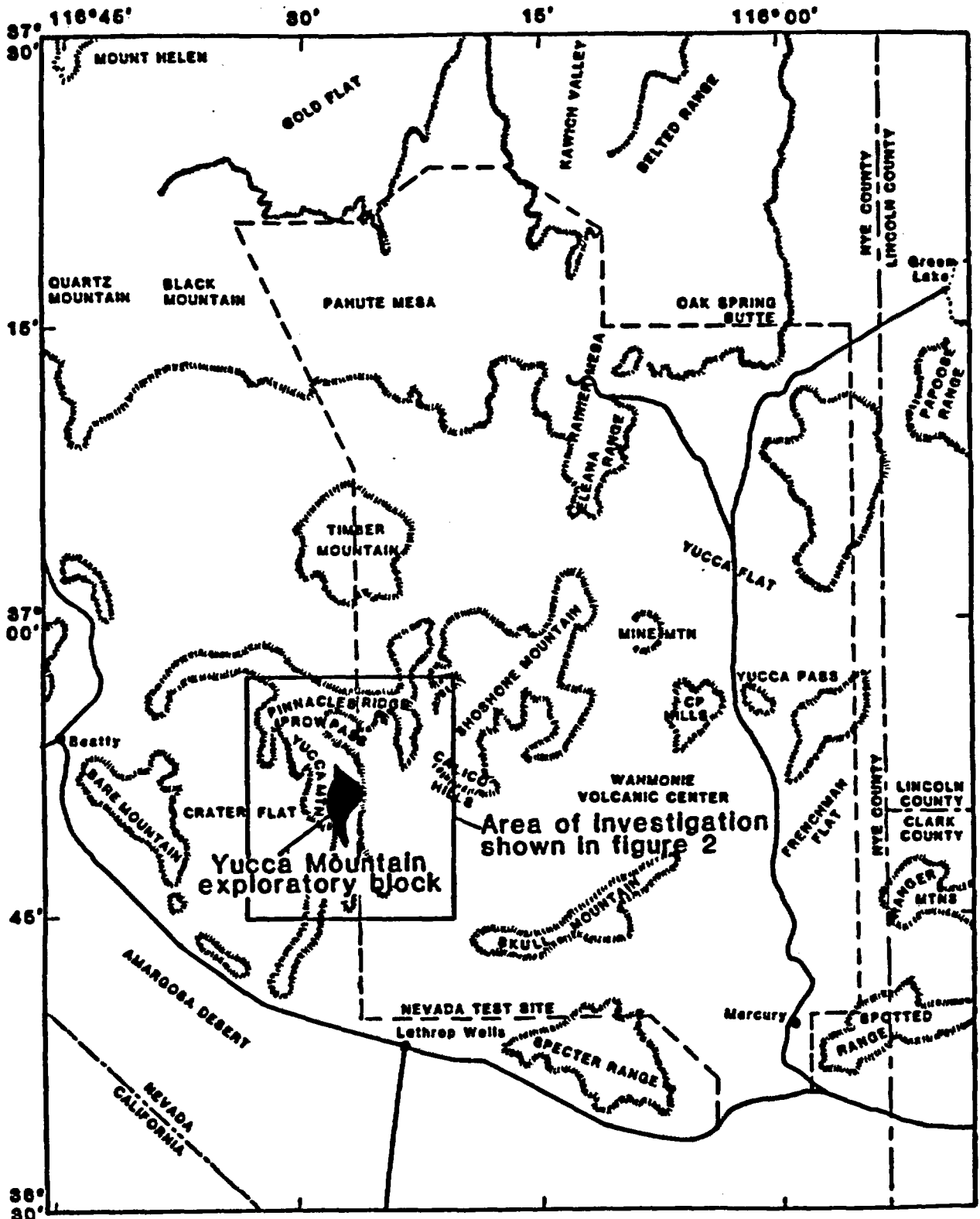
BELOW REPOSITORY

PALEOZOIC AQUIFER

SURROUNDING AQUIFER

JUVENILE RECHARGE

Los Alamos



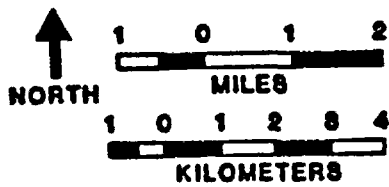
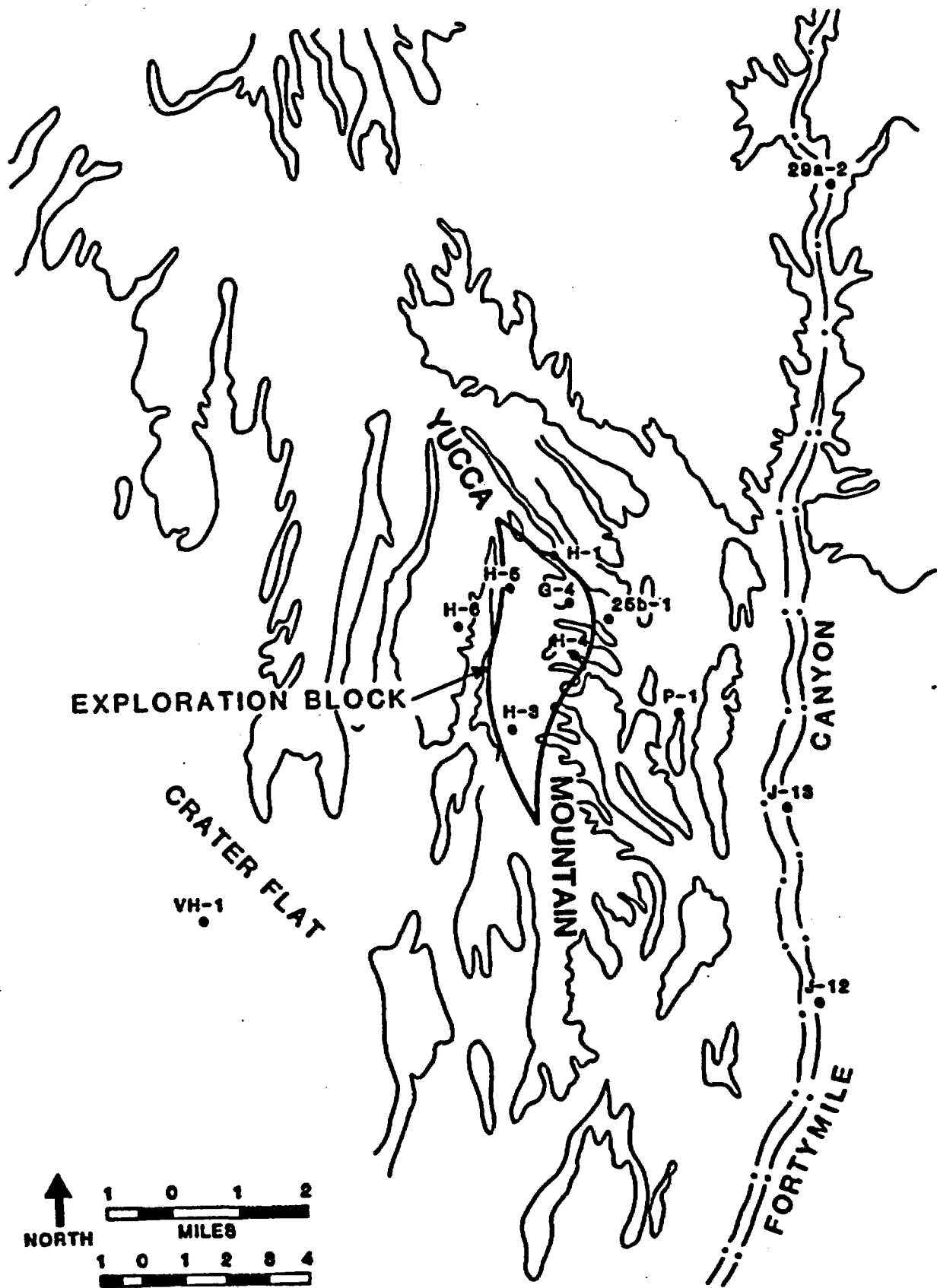


TABLE I
 ELEMENTAL CONCENTRATIONS OF GROUNDWATERS
 FROM THE VICINITY OF YUCCA MOUNTAIN

Well No.	Field pH	Concentration (mg/l)								
		Ca	Mg	Na	K	Li	Fe	Mn	Al	Si
USW VH-1 ^a	7.5	10	1.5	80	1.9	0.090				23
USW H-6	7.4	5.5	0.22	74	2.1	0.10	0.12	0.04	0.12	20.0
USW H-3	9.4	0.8	0.01	124	1.5	0.22	0.13	0.01	0.51	16.9
USW H-5	7.1	1.1	0.03	54	2.3	0.04	0.01	N.D.	0.17	17.4
USW G-4	7.1	9.2	0.15	56	2.5	0.08	0.04	0.02	0.02	19.6
USW H-1 ^a	7.5	6.2	<0.1	51	1.6	0.04				19
USW H-4	7.4	10.8	0.19	84	2.6	0.16	0.03	0.005	0.04	25.9
UE-25b#1 ^b	7.7	19.7	0.68	56	3.3	0.28	0.04	0.004	0.03	31.5
UE-25b#1 ^c	7.2	18.4	0.68	46	2.5	0.30	0.69	0.36	0.04	28.7
UE-25b#1 ^d	7.3	17.9	0.66	37	3.0	0.17	0.08	0.07	0.06	28.8
J-13	6.9	11.5	1.76	45	5.3	0.06	0.04	0.001	0.03	30.0
UE-29a#2	7.0	11.1	0.34	51	1.2	0.10	0.05	0.03	0.04	25.8
J-12 ^a	7.1	14	2.1	38	5.1					25
UE-25p#1	6.7	87.8	31.9	171	13.4	0.32	<0.1	<0.1	0.1	30

^aData from L. Benson et al.¹

^bIntegral water sample.

^cBullfrog zone, 4th day.

^dBullfrog zone, 28th day.

Note: Ionic or molecular species are not listed; concentration is based on the element.

TABLE II
ANION CONCENTRATIONS AND OTHER MEASUREMENTS
OF GROUNDWATERS IN THE VICINITY OF YUCCA MOUNTAIN

Well No.	Concentration (mg/L)								
	F ⁻	Cl ⁻	SO ₄ ²⁻	HCO ₃ ⁻	NO ₂ ⁻	NO ₃ ⁻	O ₂	Eh ^f	Detergent
USW VH-1 ^a	2.7	10	45	165					
USW H-6	4.1	7.7	27.5		N.D. ^e	5.3	5.6	395	
USW H-3	5.4	8.3	31.2		<0.10	0.2	<0.1	-143	<0.02
USW H-5	1.3	5.7	14.6		N.D.	8.6	6.3	353	<0.005
USW G-4	2.4	5.5	15.7		N.D.	5.5	6.4	402	
USW H-1 ^a	1.0	5.8	19	122					
USW H-4	4.5	6.2	23.9		N.D.	4.7	5.8	216	>2
UE-25b#1 ^b	1.2	7.1	20.6		N.D.	0.6	1.8	220	
UE-25b#1 ^c	1.5	9.8	21.0		0.5	2.2	<0.1	-18	2.7
UE-25b#1 ^d	1.2	6.6	20.3		N.D.	4.5	1.8	160	0.02
J-13	2.1	6.4	18.1		N.D.	10.1	5.7		N.D.
UE-29a#2	0.56	8.3	22.7		N.D.	18.7	5.7	305	
J-12 ^a	2.1	7.3	22	119					
UE-25p#1	3.5	37	129		N.D.	<0.1		360	<0.2

^aData from L. Benson et al.¹

^bIntegral water sample.

^cBullfrog zone, 4th day.

^dBullfrog zone, 28th day.

^eN.D. = not detected.

^fmV vs H₂ electrode.

TABLE III
 ELEMENTAL CONCENTRATIONS OF GROUNDWATER
 FROM THE VICINITY OF YUCCA MOUNTAIN

Well No.	Field	Concentration (mmols/l)								
	pH	Ca	Mg	Na	K	Li	Fe	Mn	Al	Si
USW VH-1 ^a	7.5	0.25	0.06	3.48	0.049	0.013				0.83
USW H-6	7.4	0.14	0.009	3.22	0.053	0.014	0.002	0.0007	0.004	0.71
USW H-3	9.4	0.02	0.0002	5.39	0.038	0.032	0.002	0.0002	0.019	0.60
USW H-5	7.1	0.03	0.001	2.35	0.059	0.006	0.0002	N.D.	0.006	0.62
USW G-4	7.1	0.23	0.007	2.43	0.064	0.012	0.0007	0.0004	0.0007	0.70
USW H-1 ^a	7.5	0.15	<0.004	2.22	0.041	0.006				0.71
USW H-4	7.4	0.27	0.008	3.65	0.066	0.023	0.0005	N.D.	0.001	0.92
UE-25b#1 ^b	7.7	0.49	0.028	2.43	0.084	0.040	0.0007	N.D.	0.001	1.12
UE-25b#1 ^c	7.2	0.46	0.028	2.00	0.064	0.043	0.012	0.006	0.001	1.02
UE-25b#1 ^d	7.3	0.45	0.027	1.61	0.077	0.024	0.001	0.001	0.002	1.03
J-13	6.9	0.29	0.072	1.96	0.136	0.009	0.0008	0.00002	0.0010	1.07
UE-29a#2	7.0	0.28	0.014	2.22	0.031	0.014	0.0009	0.0005	0.001	0.92
J-12 ^a	7.1	0.35	0.086	1.65	0.130					0.90
UE-25p#1	6.7	2.19	1.312	7.43	0.343	0.046	<0.002	0.002	0.003	0.62

^aData from L. Benson et al.¹

^bIntegral water sample.

^cBullfrog zone, 4th day.

^dBullfrog zone, 28th day.

TABLE IV
ANION CONCENTRATIONS OF GROUNDWATER
IN THE VICINITY OF YUCCA MOUNTAIN

Well No.	Concentrations (mmols/l)					
	F^-	Cl^-	SO_4^{2-}	Alkalinity	NO_2^-	NO_3^-
USW VH-1 ^a	0.14	0.28	0.47			
USW H-6	0.22	0.22	0.29	2.75	N.D. ^e	0.09
USW H-3	0.28	0.23	0.32	4.72	<0.002	0.003
USW H-5	0.07	0.16	0.15	2.00	N.D.	0.14
USW G-4	0.13	0.16	0.16	2.34	N.D.	0.09
USW H-1 ^a	0.05	0.16	0.20			
USW H-4	0.24	0.17	0.25	2.82	N.D.	0.08
UE-25b#1 ^b	0.06	0.20	0.21	2.20	N.D.	0.01
UE-25b#1 ^c	0.08	0.28	0.22	2.41	0.011	0.03
UE-25b#1 ^d	0.06	0.19	0.21	2.13	N.D.	0.07
J-13	0.11	0.18	0.19	2.34	N.D.	0.16
UE-29a#2	0.03	0.23	0.24	1.77	N.D.	0.30
J-12 ^a	0.13	0.21	0.23			
UE-25p#1	0.18	1.04	1.34	11.44	N.D.	<0.002

^aData from L. Benson et al.¹

^bIntegral water sample.

^cBullfrog zone, 4th day.

^dBullfrog zone, 28th day.

^eN.D. = not detected.

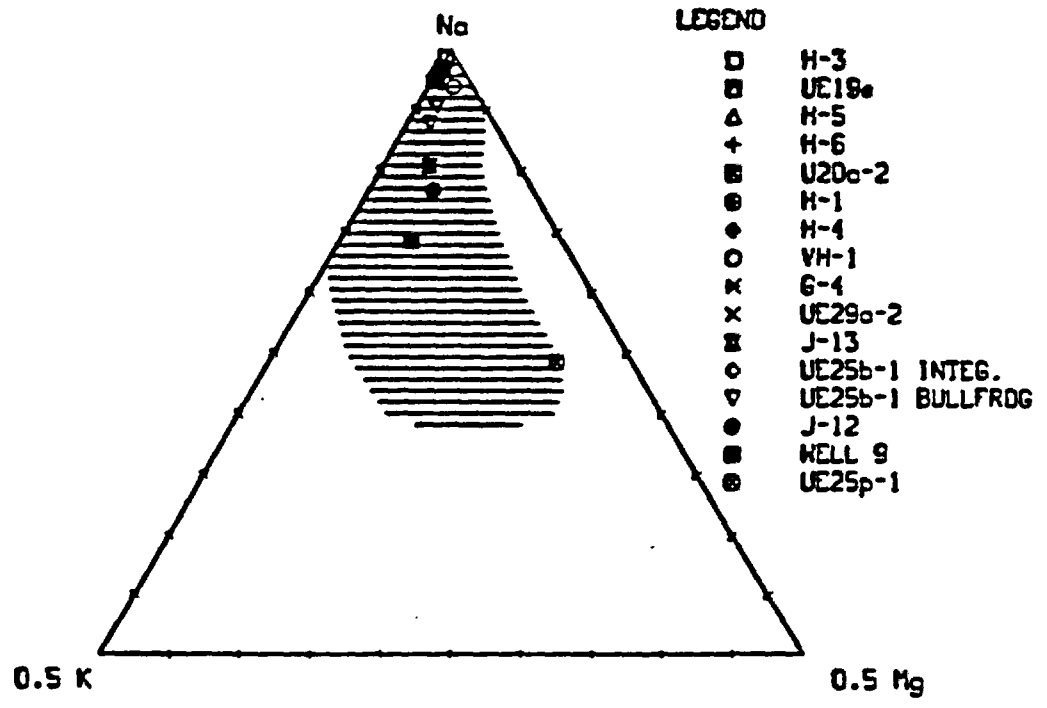


Fig. 4. Relative Na-K-Mg concentration in Yucca Mountain water.

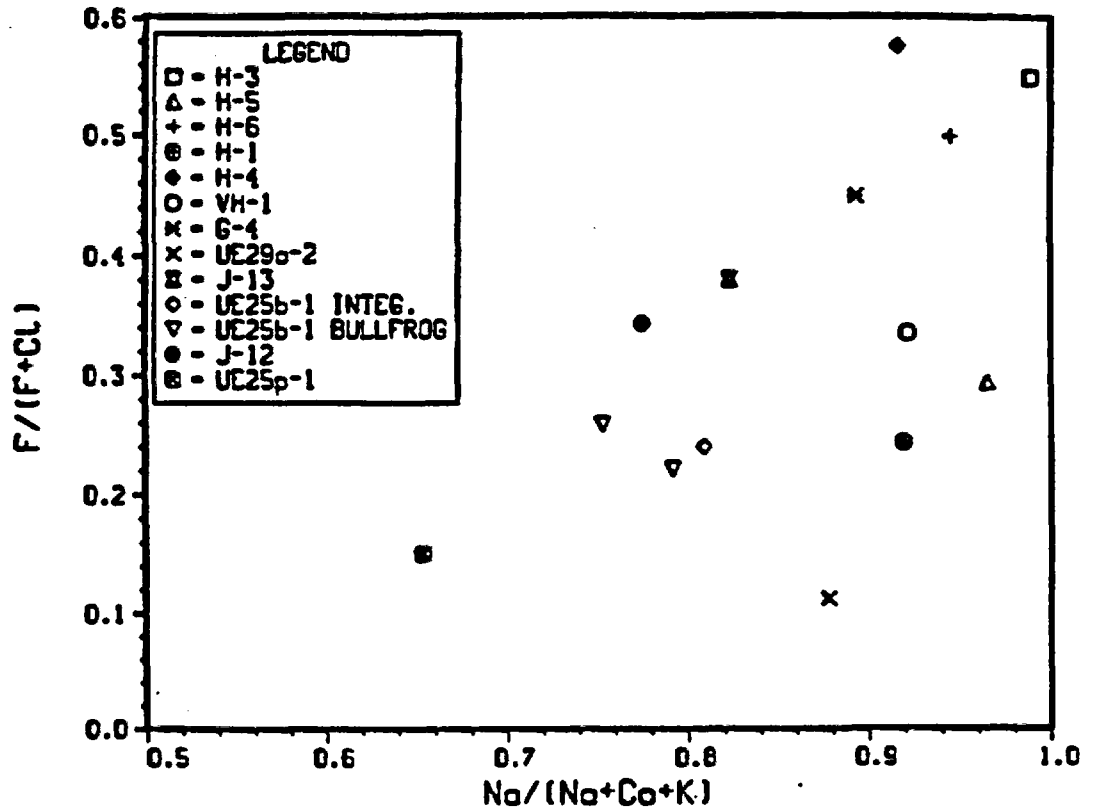


Fig. 10. Relative fluoride content as a function of relative sodium content for waters from Yucca Mountain.

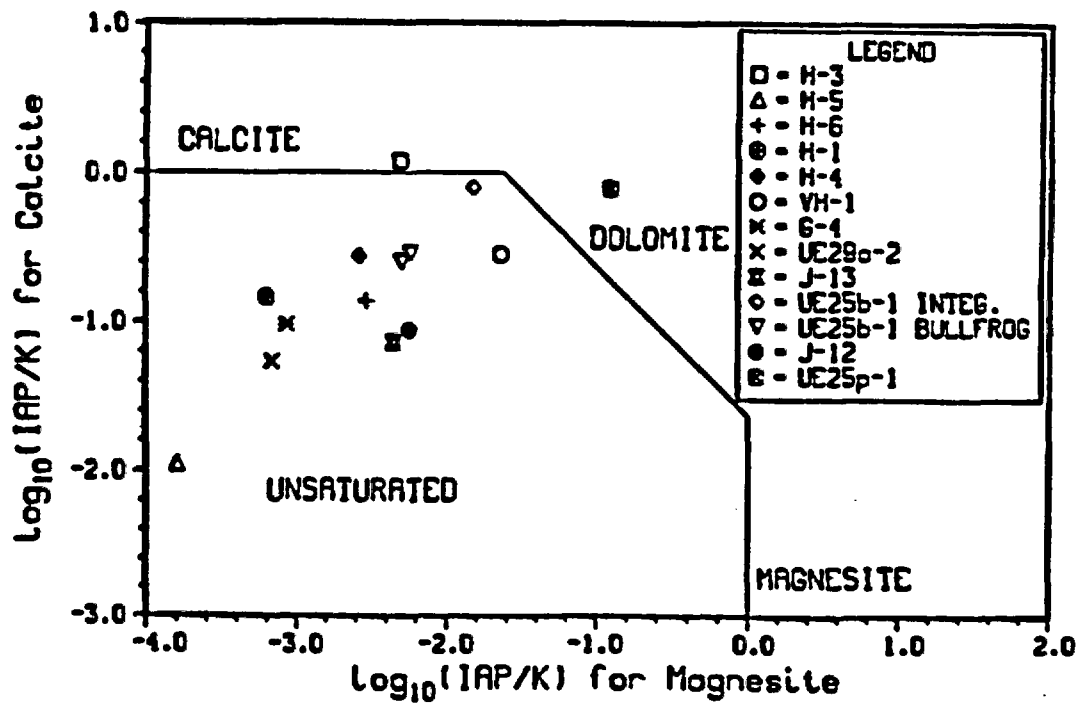


Fig. 11. Ratio of ion activity product to equilibrium constant for calcite as a function of the ratio for magnesite for waters from Yucca Mountain. The dolomite saturation line is also shown.

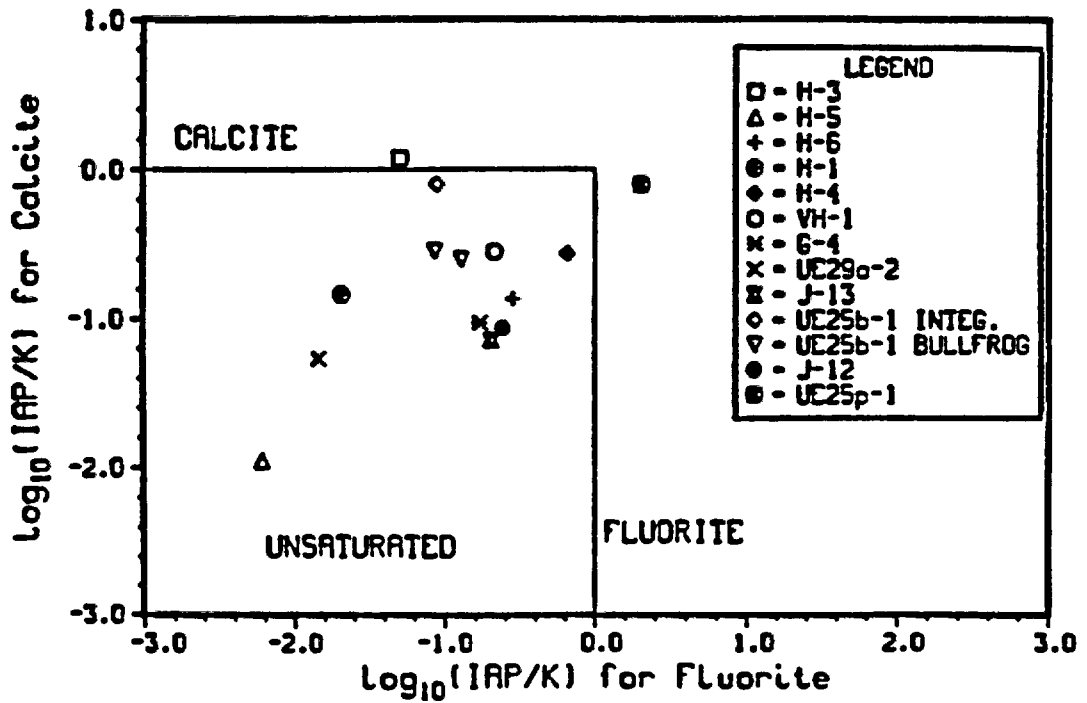


Fig. 12. Ratio of ion activity product to equilibrium constant for calcite as a function of the ratio for fluorite for water from Yucca Mountain.

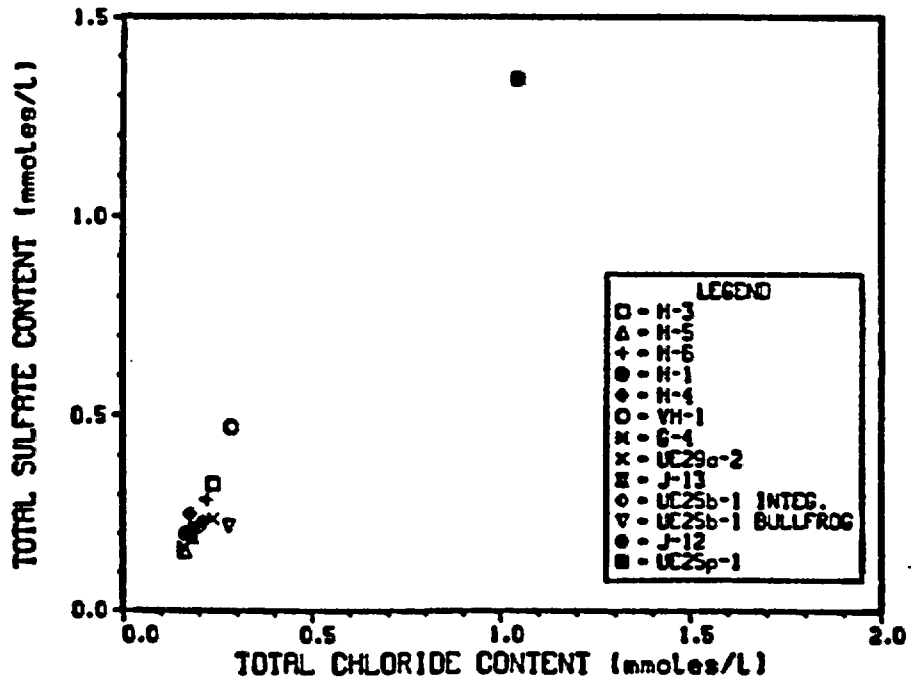


Fig. 13. Total sulfate content as a function of total chloride content for water from Yucca Mountain (see also Fig. 14).

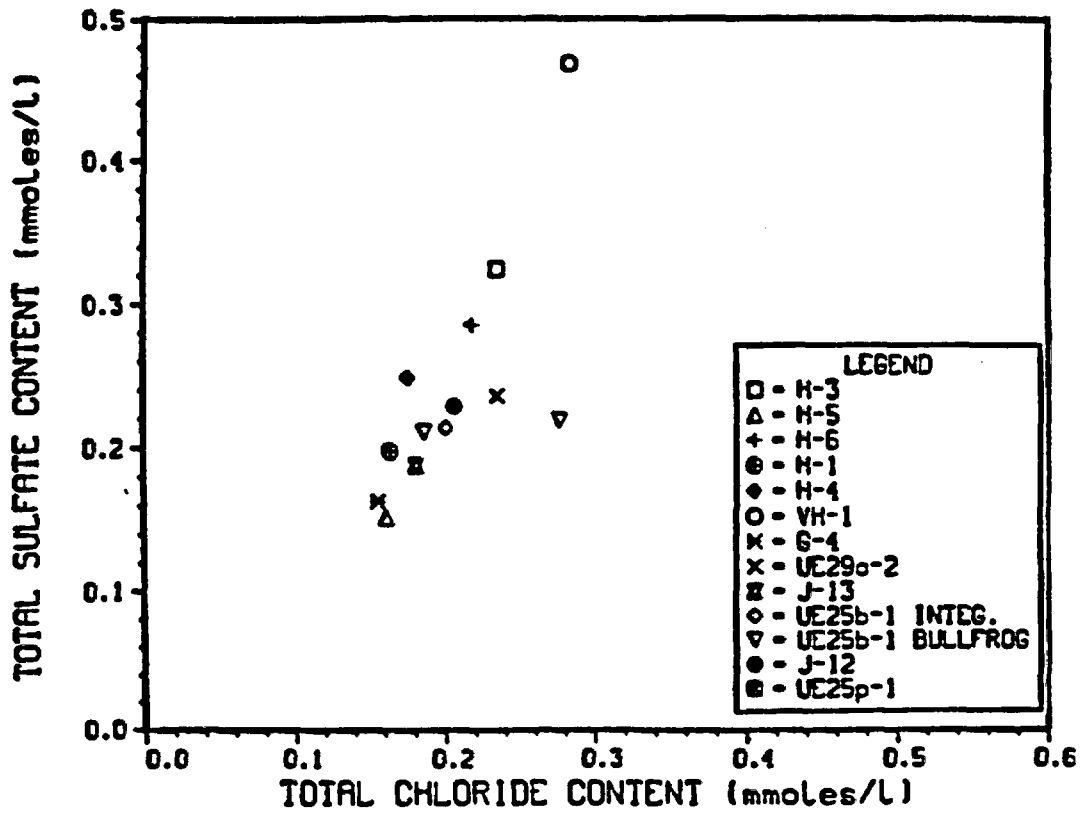


Fig. 14. Total sulfate content as a function of total chloride content for water from Yucca Mountain—expanded scale (see also Fig. 13).

ROCK-WATER INTERACTIONS

^{36}Cl Experiment for the Exploratory Shaft

Rock-Water Equilibrium

Reaction Path Calculations

^{36}Cl Surface Experiment



³⁶Cl WATER MOVEMENT TRACER RATIONALE

Los Alamos

**10CFR60.113: *PREEMPLACEMENT GROUNDWATER TRAVEL TIME
TO ACCESSIBLE ENVIRONMENT AT LEAST 1000 YEARS
OR AS SPECIFIED BY COMMISSION***

10CFR60.112: *EPA RELEASE STANDARDS*

**NNWSI INFORMATION NEED 1.2.3: *HYDROLOGIC TRAVEL TIME IN
UNSATURATED ZONE***

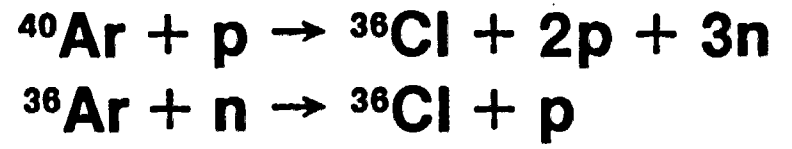
+

LA-5027-1-67

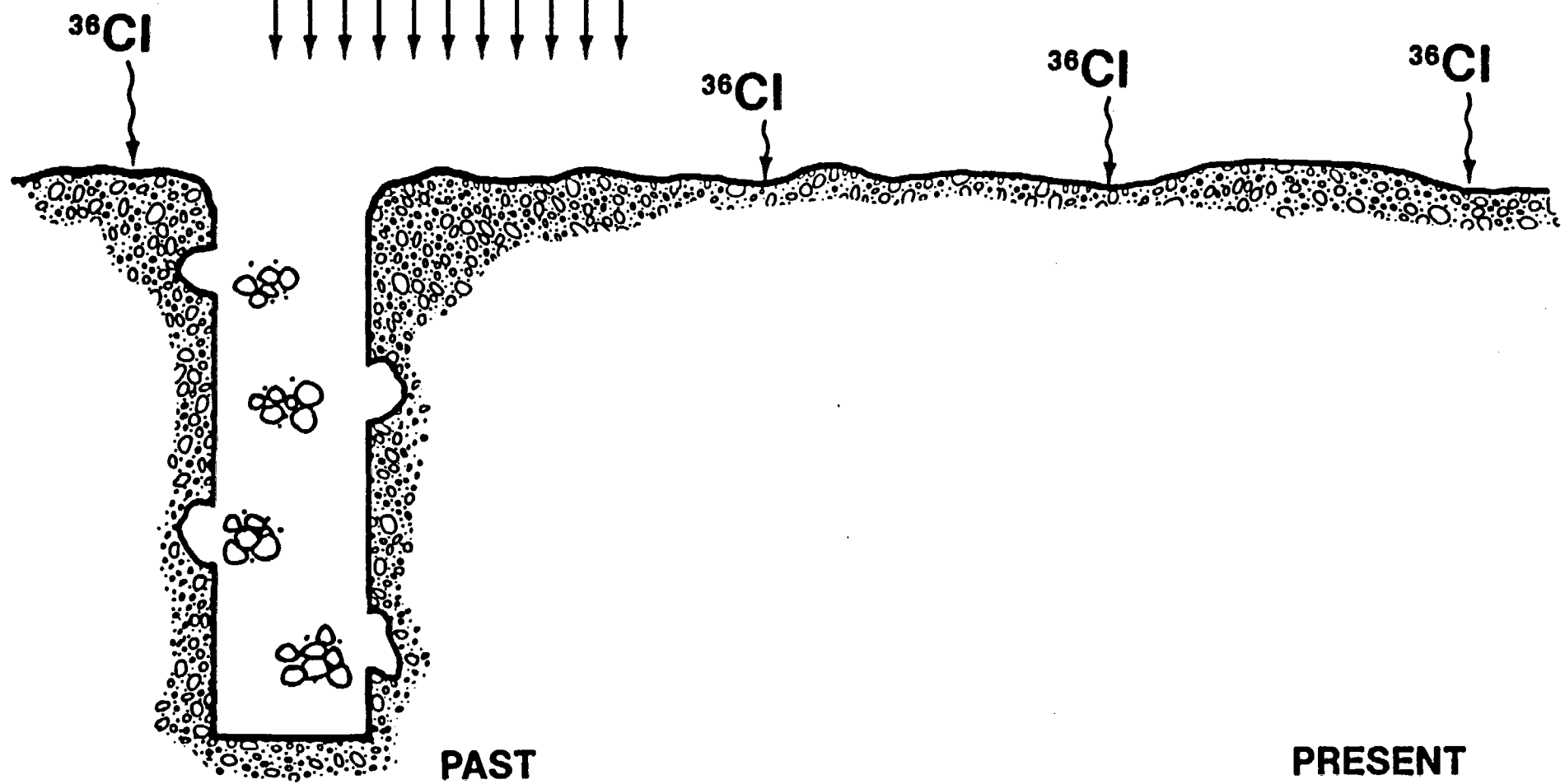
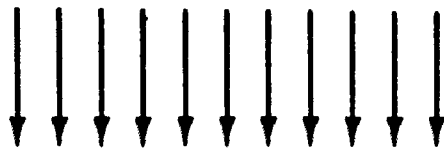


³⁶Cl WATER MOVEMENT TRACER

Los Alamos



COSMIC RAYS



PAST

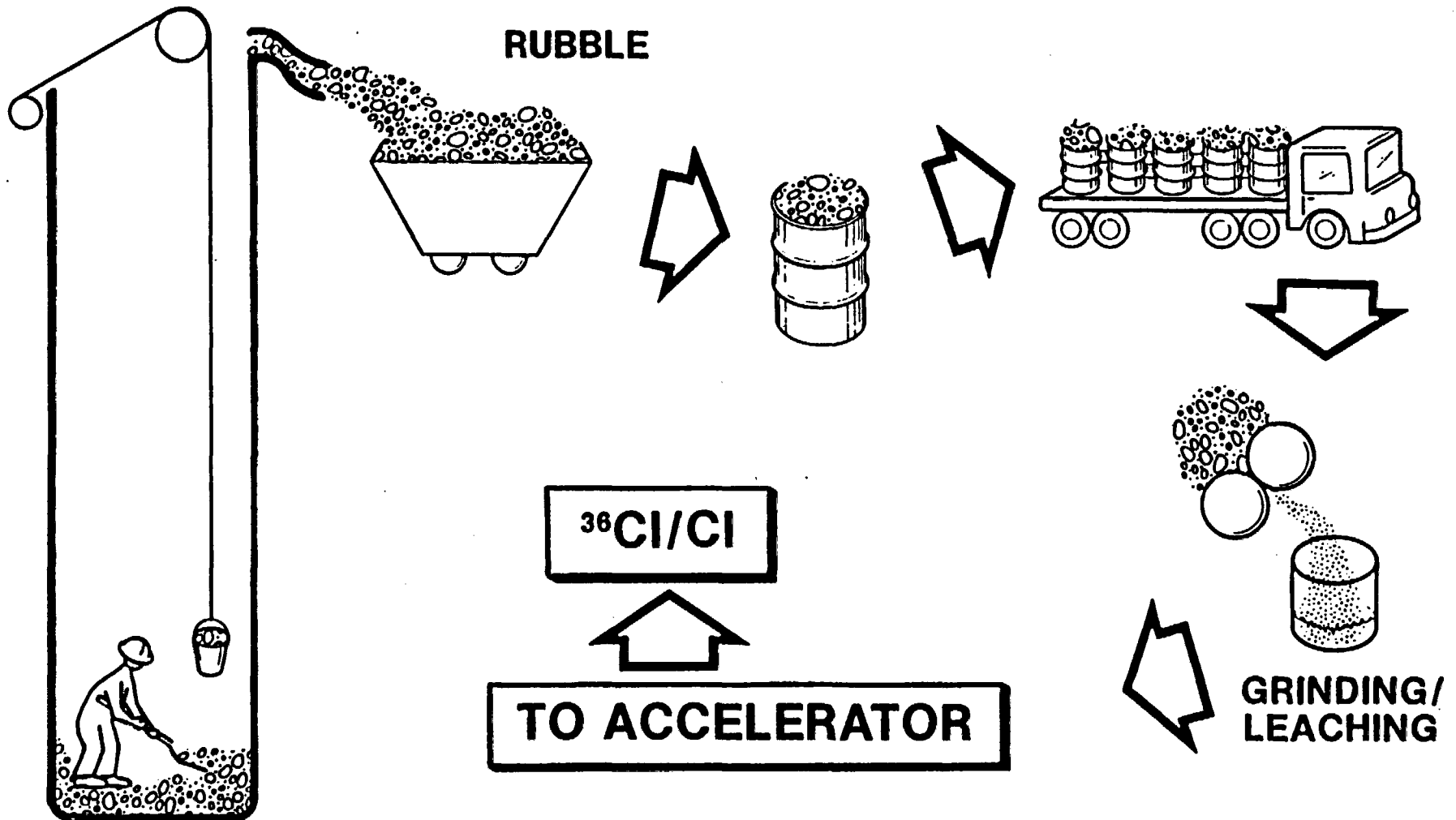
PRESENT

+



³⁶Cl WATER MOVEMENT TRACER

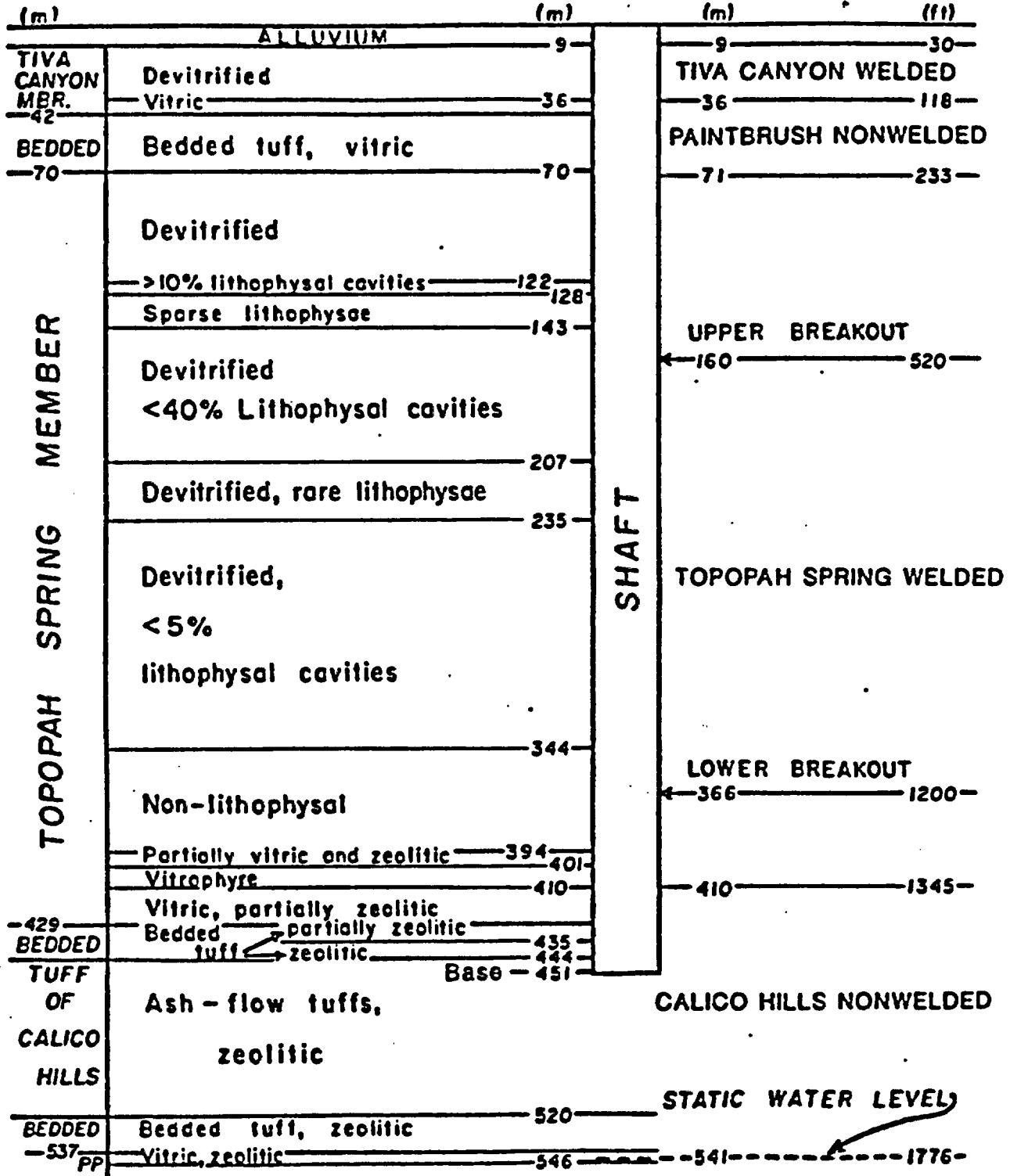
Los Alamos



FORMAL STRATIGRAPHY

PREDICTED FROM G-4 LITHOLOGY

HYDROGEOLOGIC UNITS





**³⁶Cl WATER MOVEMENT TRACER
INACTIVE CHLORIDE
INTERFERENCE**

Los Alamos

- **WELL J-13 WATER 15 mg/L Cl⁻**
- **EFFECT MITIGATED BY**
 - **DOWNHOLE WATER TRACER**
 - **LARGE BLOCKS**
- **CHLORIDE IN TUFF**
 - **MEASURED**
 - **SHORT LEACHING TIME**



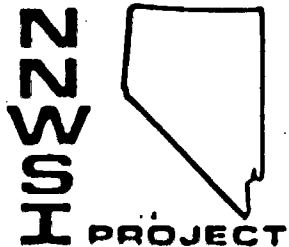
**^{36}Cl WATER MOVEMENT TRACER
CHLORIDE CHARACTERISTICS
AS A WATER MOVEMENT TRACER**

Los Alamos

WHY ^{36}Cl ?

- CHLORIDE MOVEMENT IS UPPER BOUND FOR $\text{T}_c \text{O}_4^-$ AND I^-
- NON SORBING
- LOW RATE OF ISOTOPIC EXCHANGE
- NO VAPOR-PHASE TRANSPORT
- HALF-LIFE RANGE 5×10^4 TO 2×10^6 YEARS

∴ UNIQUE CHARACTERISTICS, BUT COMPLEMENTARY TO ^{14}C DATING



³⁶Cl WATER MOVEMENT TRACER SUMMARY

Los Alamos

- **³⁶Cl/Cl MEASURED IN ~30 SAMPLES AS EXPLORATORY SHAFT IS MINED**
- **UNSATURATED ZONE PORE WATER DATED BETWEEN 5×10^4 AND 2×10^6 YEARS**
- **BOMB PULSE WILL INDICATE FRACTURE FLOW**
- **DATA USED FOR**
 - **CORRECT MODELING OF UNSATURATED ZONE HYDROLOGIC FLOW**
 - **10CFR60.113 REQUIREMENT OF 1000-YEAR FLOW**
 - **SETTING LIMIT ON $T_c O_4^-$ AND I^- MOVEMENT**
- **COMPLEMENTS OTHER PORE WATER DATING TECHNIQUES**



ROCK-WATER INTERACTIONS
EQUILIBRIUM?

Los Alamos

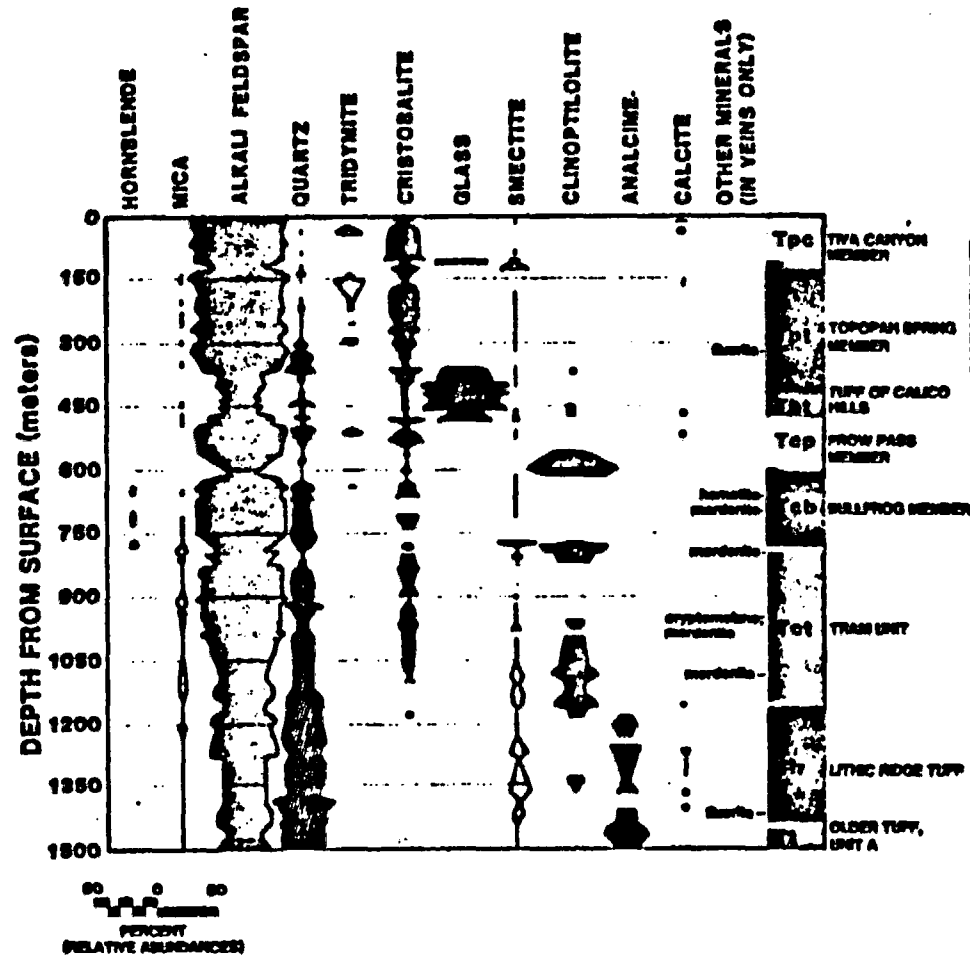
SOLID PHASES ARE NOT ALL IN EQUILIBRIUM
FLUID COMPOSITION IS CONTROLLED BY ROCK
THE SYSTEM IS NOT IN EQUILIBRIUM
EQUILIBRIUM MODELING IS USEFUL



MINERAL ABUNDANCES

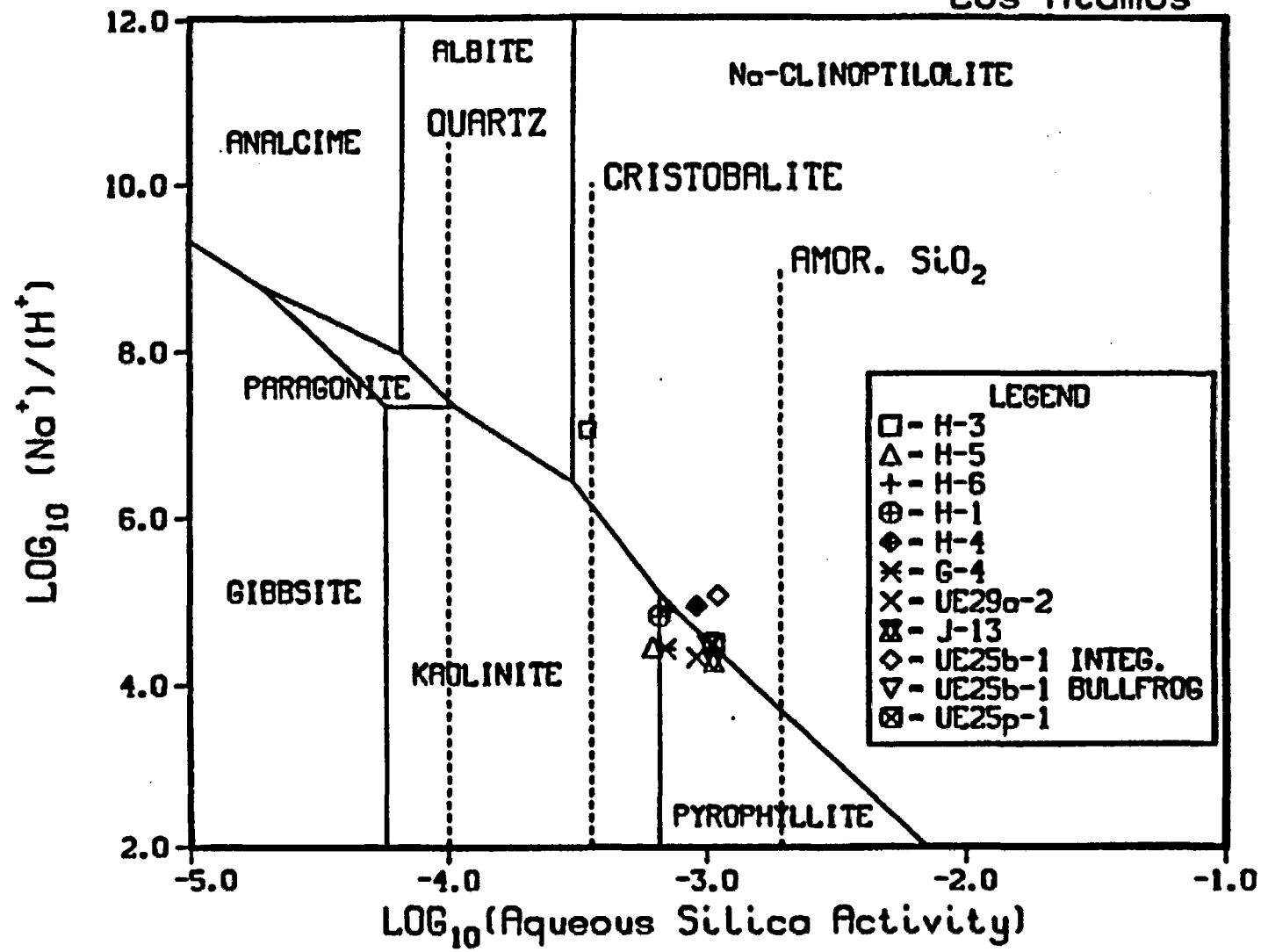
DRILL HOLES USW GU-3/G-3

Los Alamos



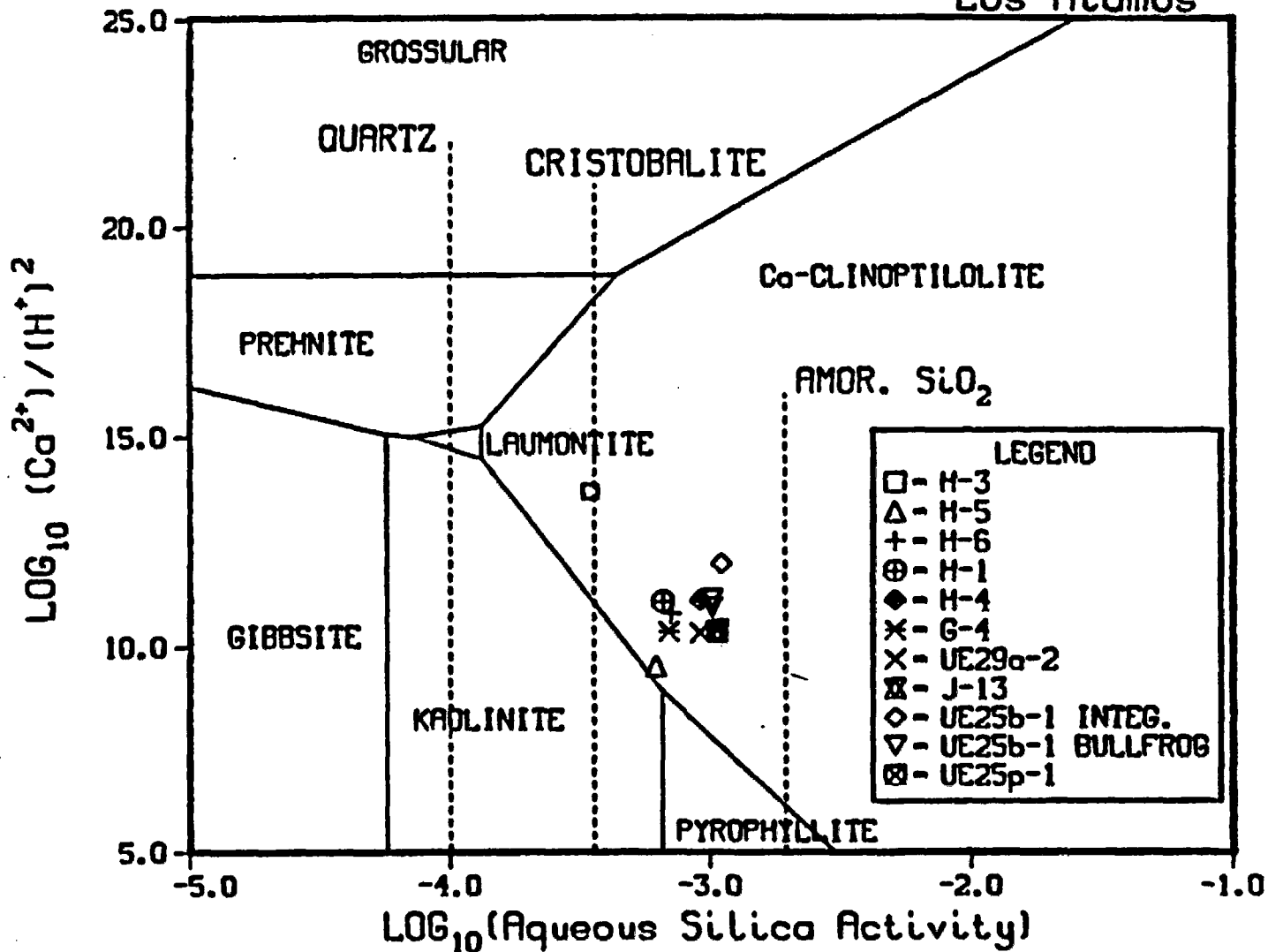
Na-Si-AL PHASE DIAGRAM AT 25°C

Los Alamos



Ca-Si-AL PHASE DIAGRAM AT 25°C

Los Alamos





USEFULNESS OF EQUILIBRIUM MODELING
WHAT EQUILIBRIA ARE CLOSELY APPROACHED?

Los Alamos

SILICON AND ALUMINUM
FORM SILICATE FRAMEWORKS
ARE NOT EASILY EXCHANGED WITH WATER
EQUILIBRATION MAY BE POOR

SODIUM, POTASSIUM, AND CALCIUM
MORE EASILY EXCHANGED
EQUILIBRIUM MORE CLOSELY APPROACHED



MINERAL-WATER MODEL

Los Alamos

- * WATER COMPOSITION AND LOCAL MINERALS IN TUFFACEOUS AQUIFER RESULT FROM DISSOLUTION OF VOLCANIC GLASS.

- * EQ3/6 REACTION-PATH MODEL OF RAINIER MESA MINERAL FORMATION (LA-9912-MS).



MINERAL-WATER MODEL

Los Alamos

- * GLASS DISSOLUTION IN WATER WITH DISSOLVED CO₂.
- * CATION LEACH RATES FROM GLASS A FUNCTION OF pH.
- * AQUEOUS SILICA ACTIVITY CONTROLLED BY SUPPRESSING PRECIPITATION OF SILICA MINERALS.



MINERAL-WATER MODEL

Los Alamos

ESTIMATED ZEOLITE FORMATION CONSTANTS

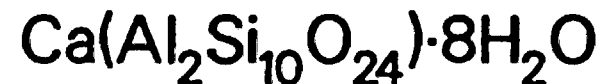
- * CLINOPTILOLITE, MORDENITE, AND HEULANDITE.
- * METHOD DEVELOPED BY Chen - USE DATA FOR OTHER SILICATES FROM EQ3/6 DATA BASE.



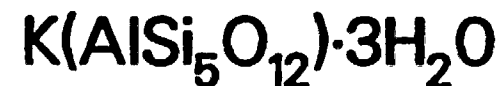
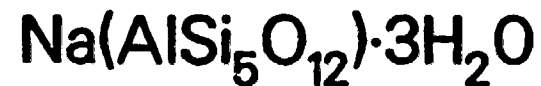
MINERAL-WATER MODEL

Los Alamos

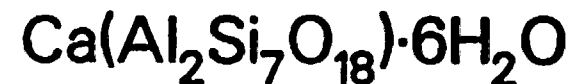
* CLINOPTILOLITE



* MORDENITE



* HEULANDITE





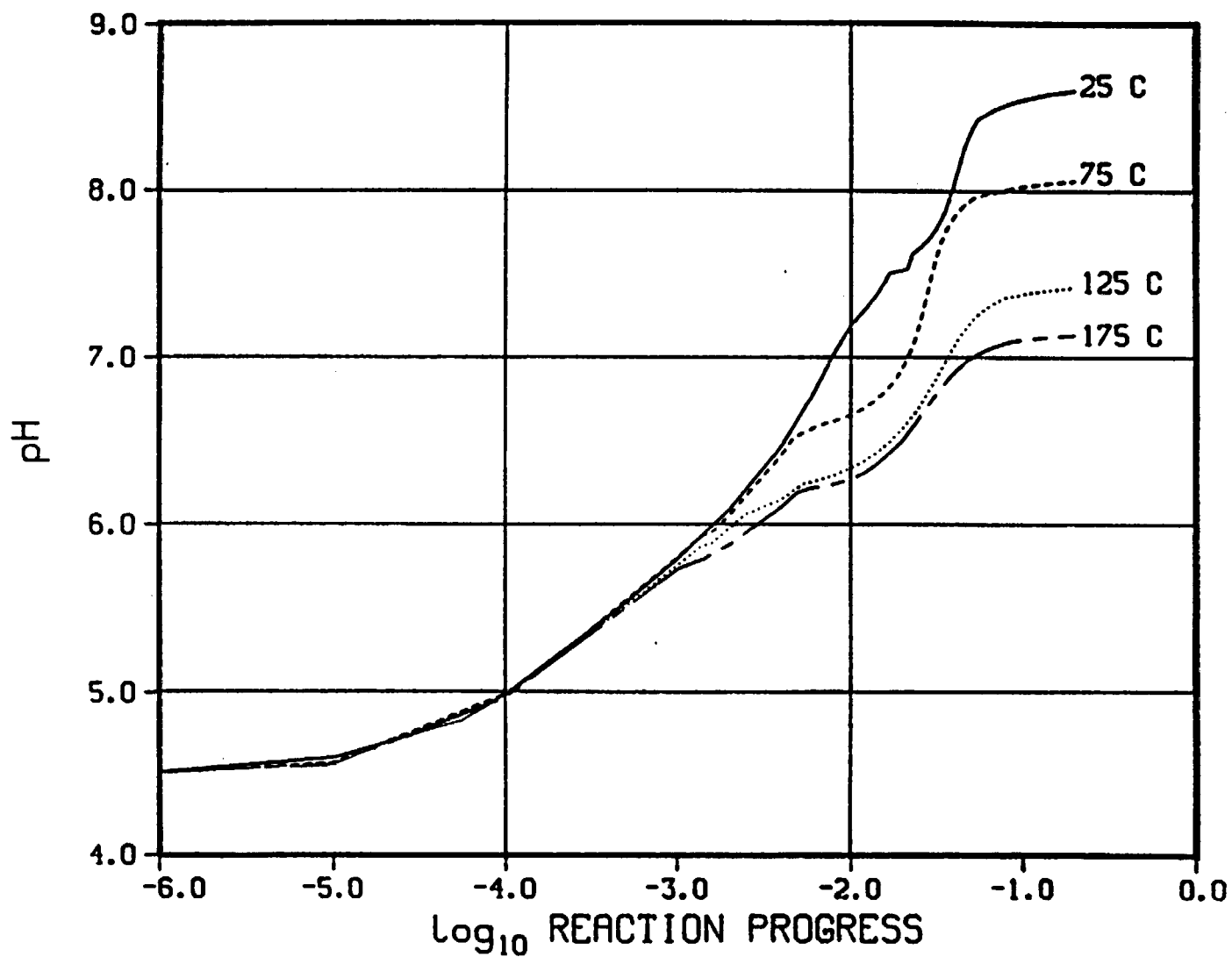
MINERAL-WATER MODEL

Los Alamos

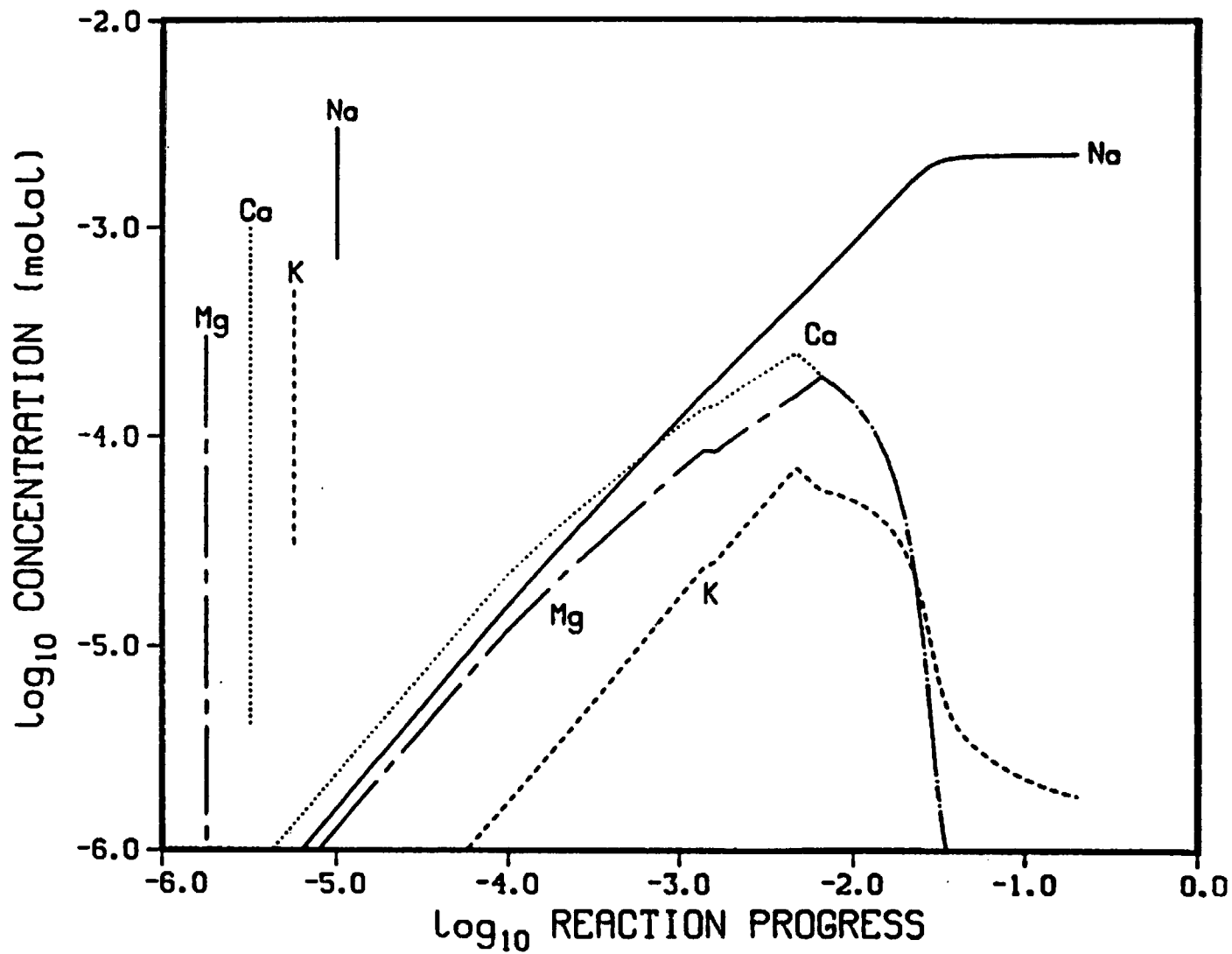
RESULTS WITH CRISTOBALITE CONTROLLING AQUEOUS SILICA ACTIVITY

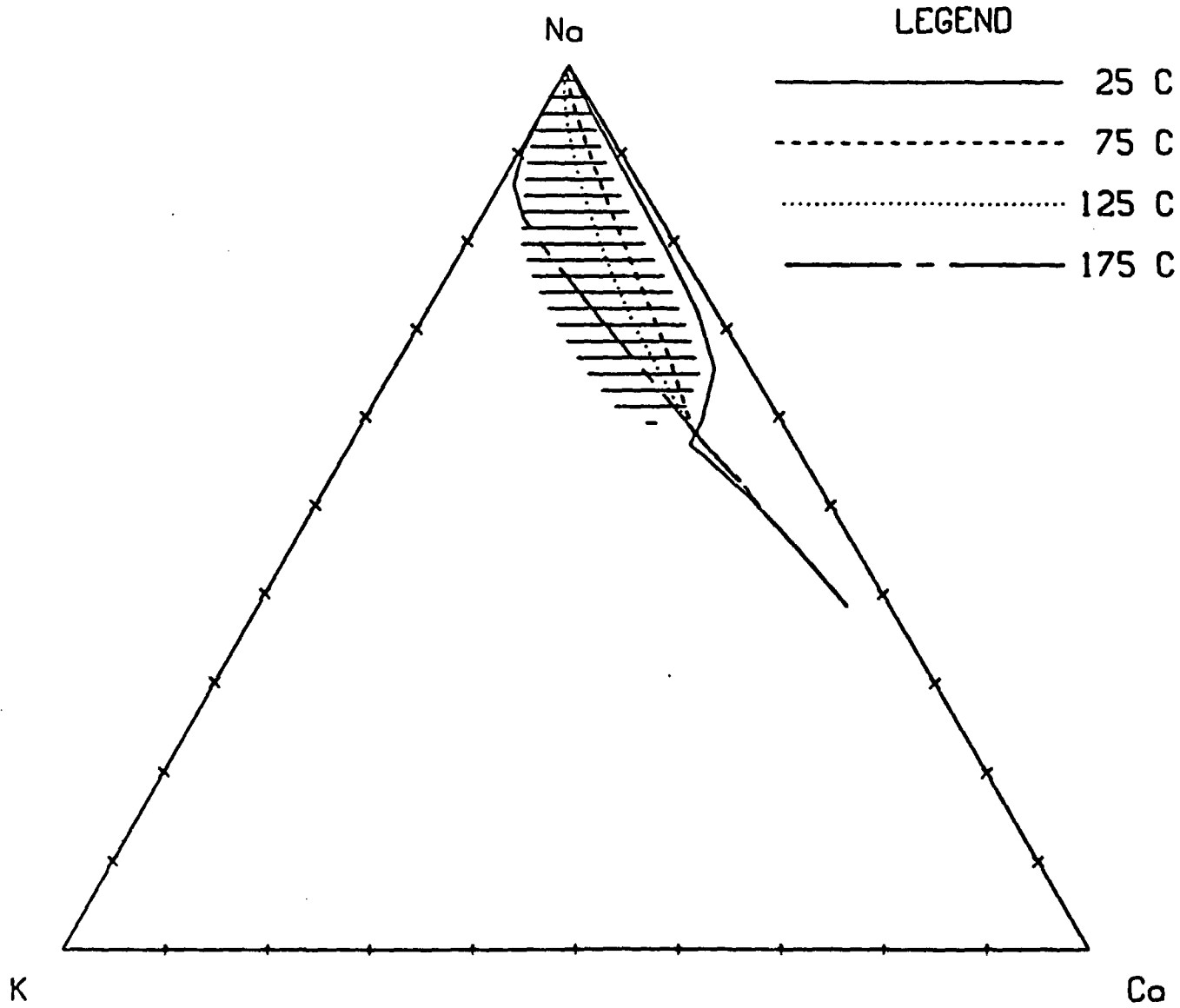
- * MINERAL PRECIPITATES ARE CRISTOBALITE, SMECTITE CLAYS, CLINOPTILOLITE, AND MORDENITE.
- * WATER IS PRIMARILY A SODIUM-BICARBONATE WATER.

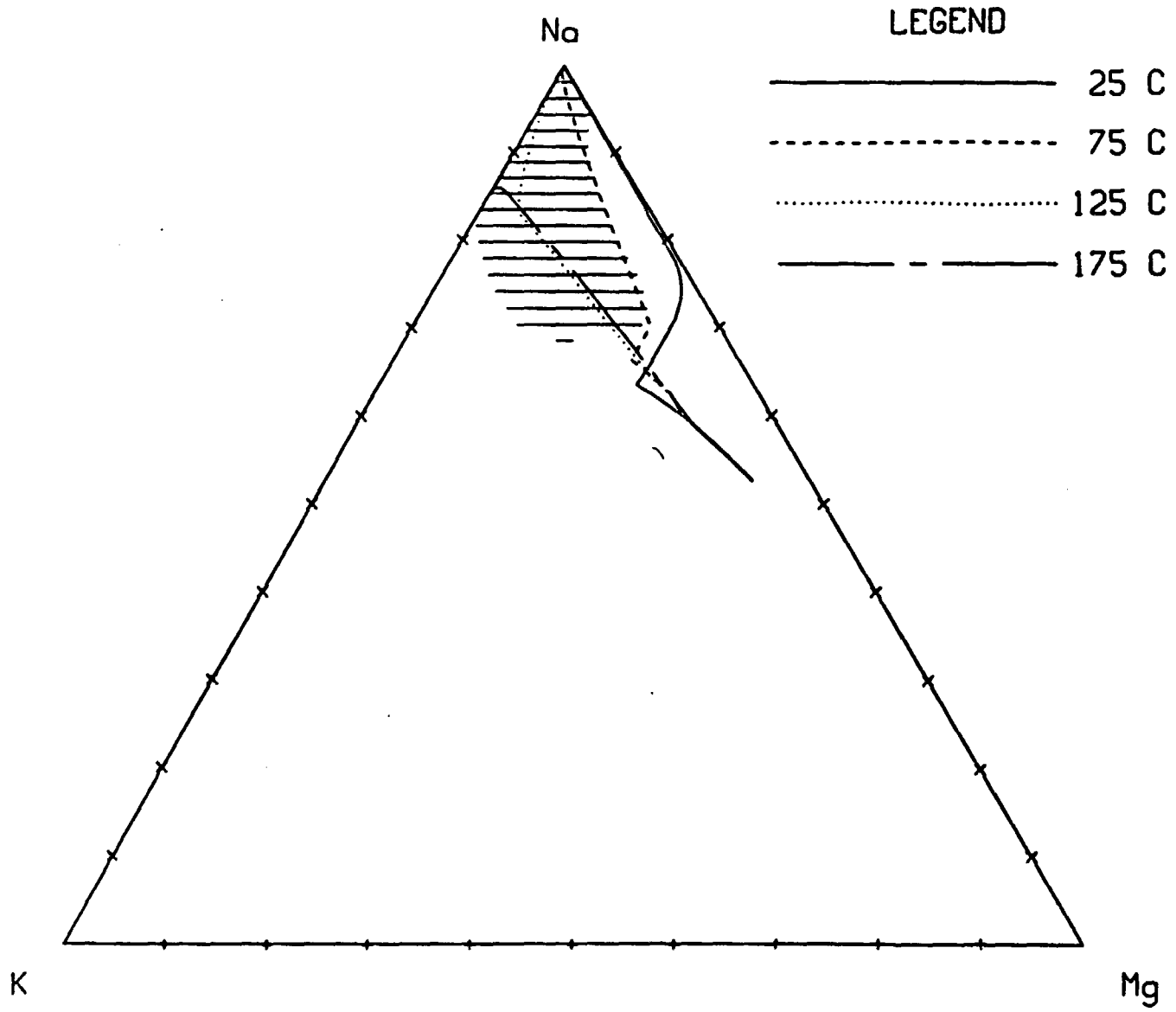
SOLUTION pH - QTZ CHALC NONTRON SUPPRESSED



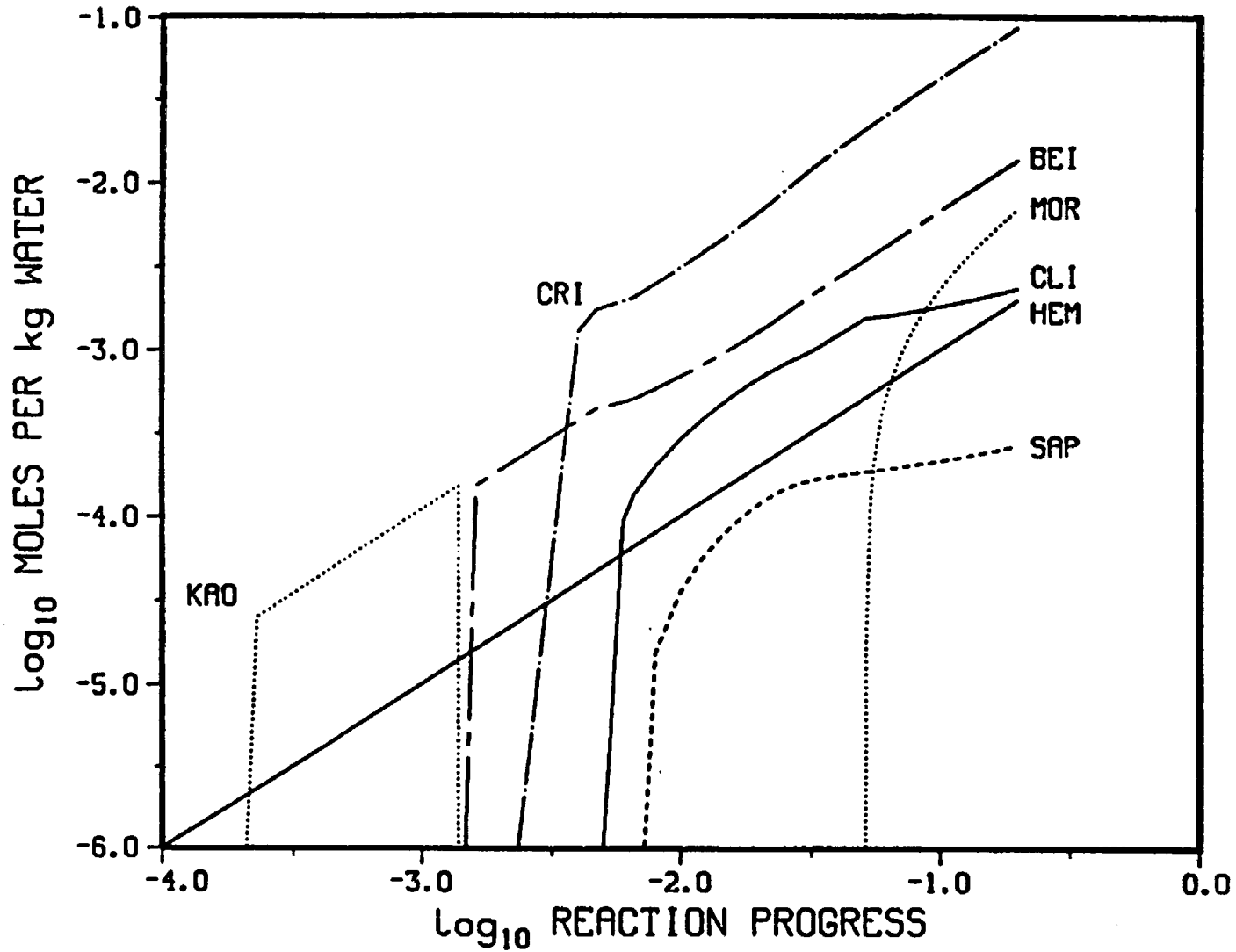
75 C SUPPRESS OTZ CHALC NONTRON



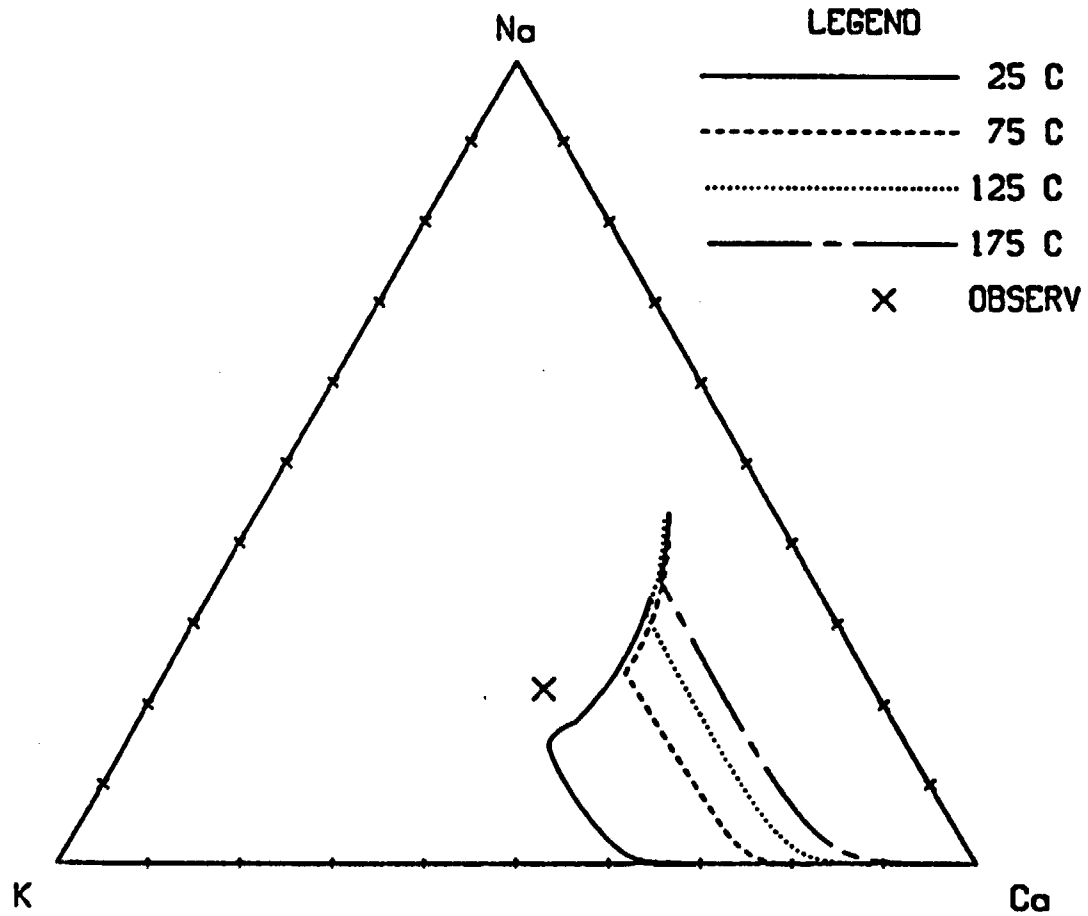




75 C SUPPRESS OTZ CHALC NONTRON



CLINOPTILOLITE COMPOSITION





MINERAL-WATER MODEL

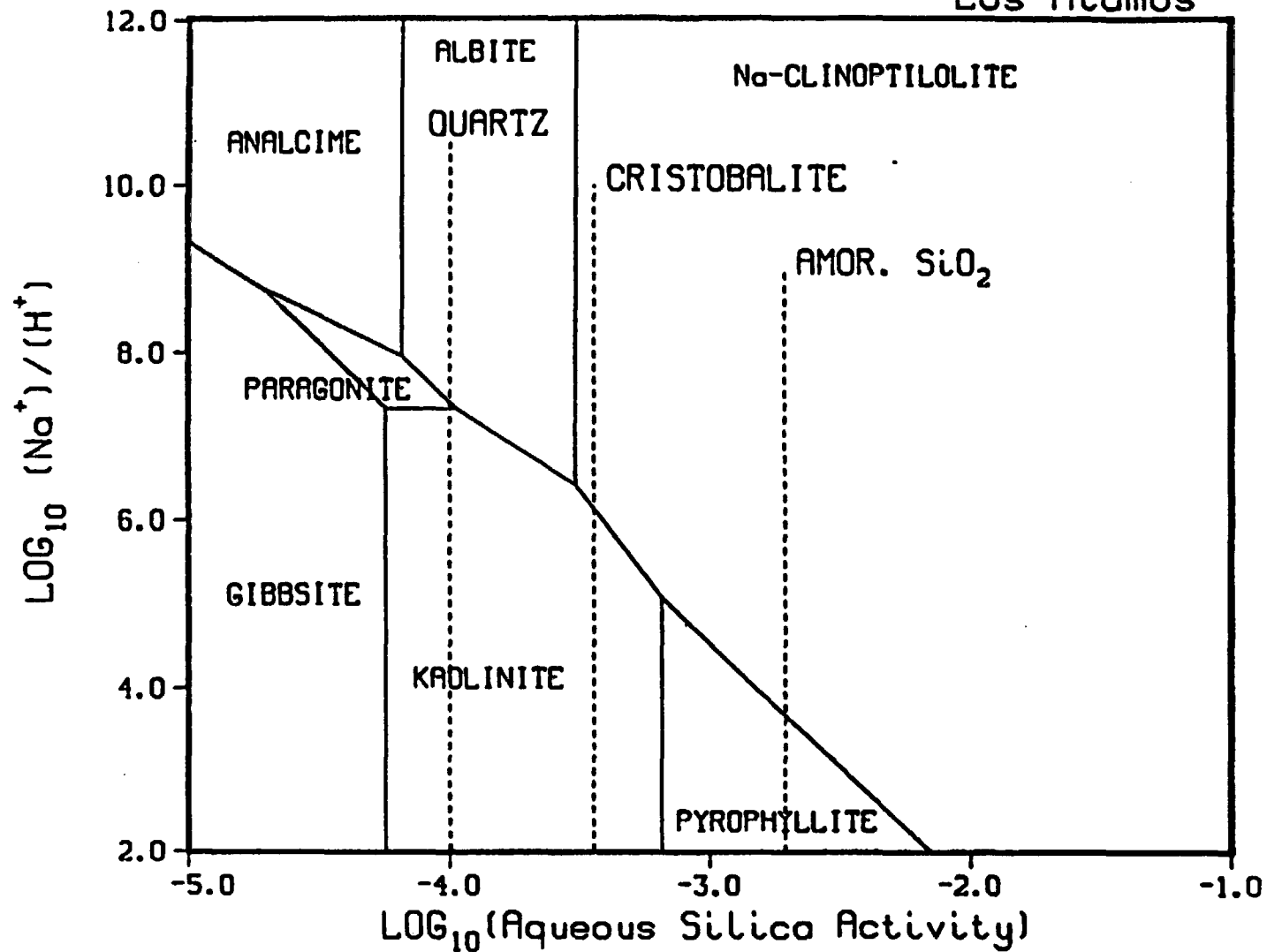
Los Alamos

RESULTS WITH QUARTZ CONTROLLING AQUEOUS SILICA ACTIVITY

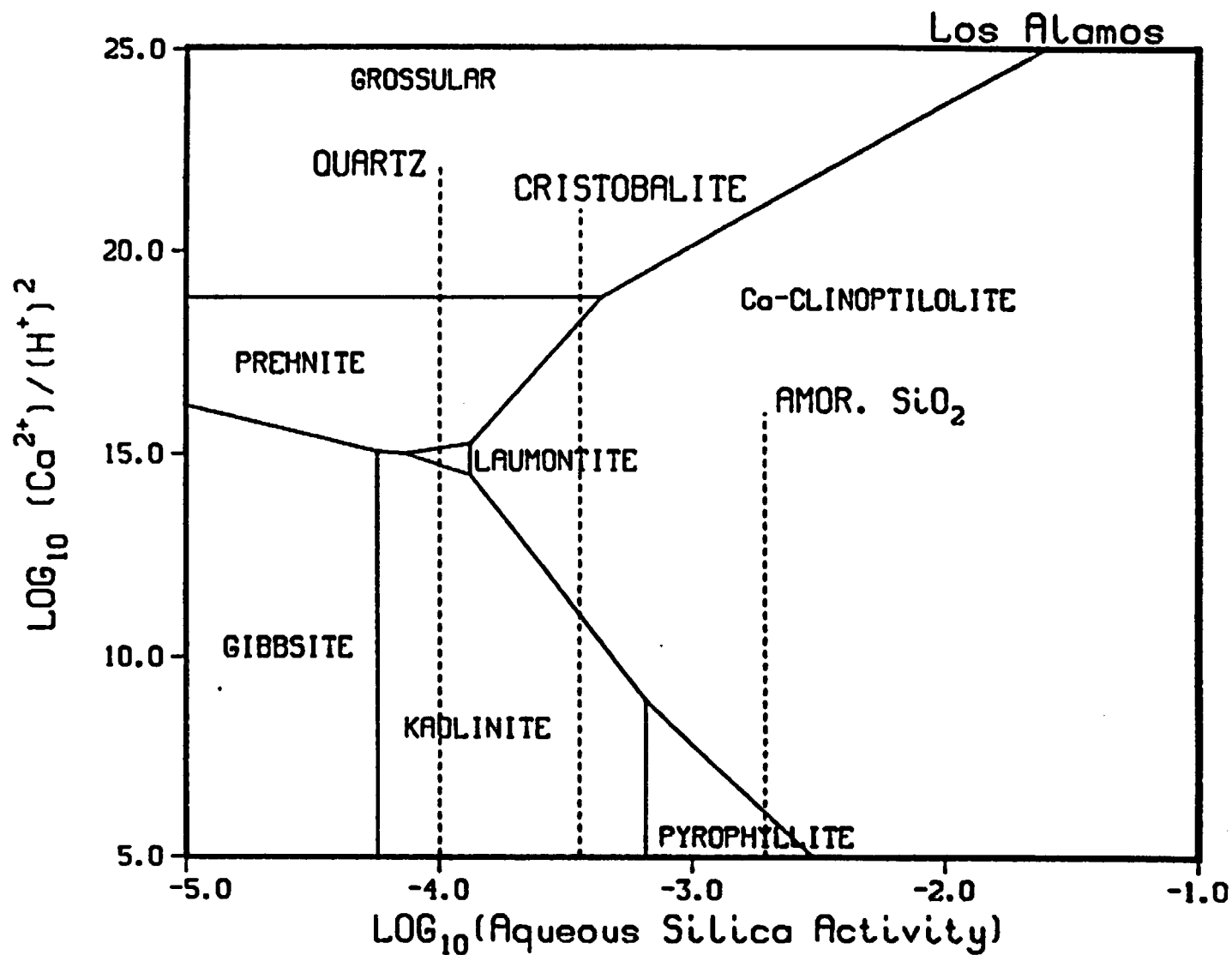
- * MINERAL PRECIPITATES ARE QUARTZ AND VARIOUS CLAYS; ALBITE UNDER SOME CONDITIONS.
- * WATER IS PRIMARILY A SODIUM-BICARBONATE WATER; HIGHER pH.

Na-Si-AL PHASE DIAGRAM AT 25°C

Los Alamos



Ca-Si-AL PHASE DIAGRAM AT 25°C





MINERAL-WATER MODEL

Los Alamos

CONCLUSIONS FROM THE MODEL

- * AQUEOUS SILICA ACTIVITY CONTROLS THE STABILITY OF ZEOLITES CLINOPTILOLITE AND MORDENITE.
- * ESTIMATED ZEOLITE FORMATION CONSTANTS ARE REASONABLE.



^{36}Cl FALLOUT
(ATOMS $^{36}\text{Cl}/\text{m}^2\text{sec}$)

Los Alamos

PRE-1953	16
1953-1964	23,000
POST-1964	22

**USEFUL FOR TRACING INFILTRATION RATE
OVER LAST 25 YEARS.**

RELATED STUDIES
GREENLAND ICE CORE
BORDEN LAND FILL
SOCORRO SANDY LOAM



BOMB PULSE AND BORDEN LANDFILL

(BENTLEY, 1982)

Los Alamos

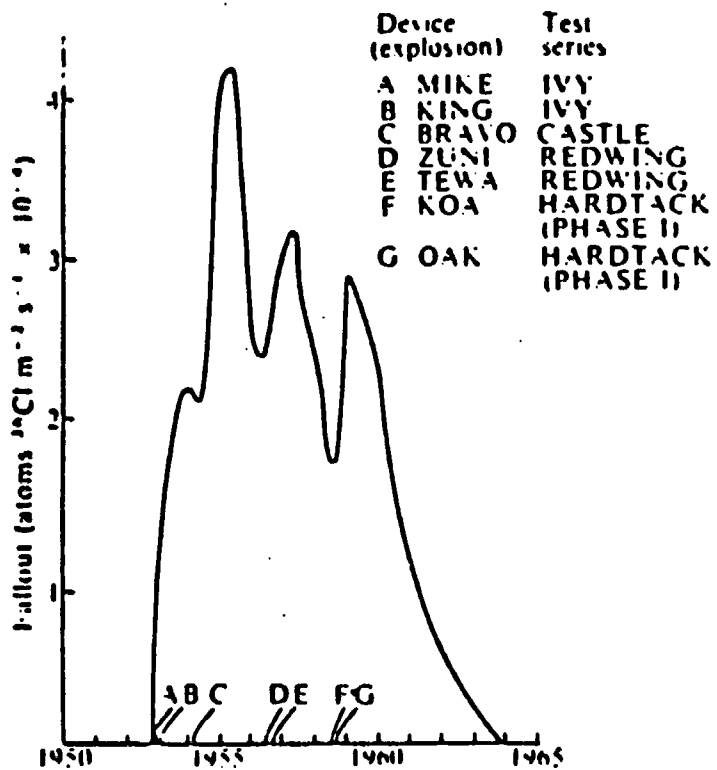
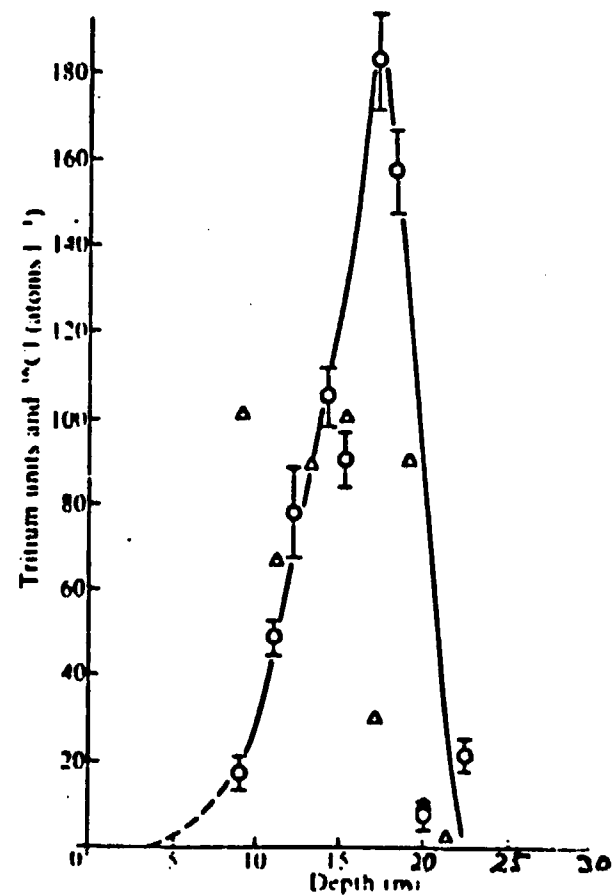


Fig. 1 Fallout of thermonuclear ^{36}Cl predicted by the atmospheric box model.





ICE CORE AND SANDY LOAM (ELMORE, 1982; BENTLEY, UNPUBLISHED)

Los Alamos

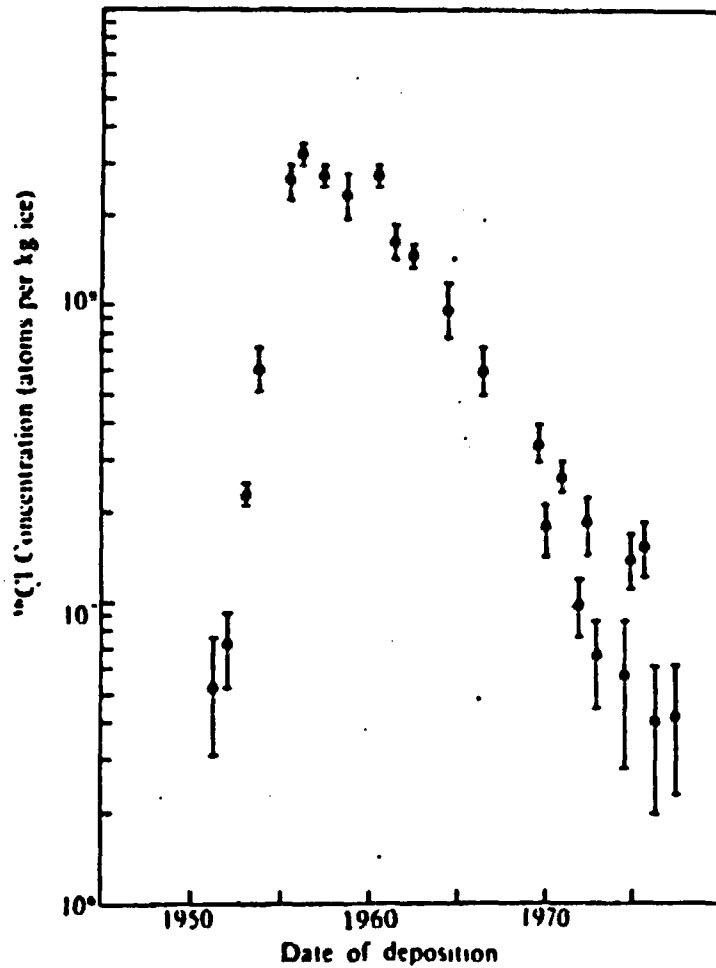


Fig. 1 The ^{36}Cl profile in an ice core drilled at Dye 3, Greenland, showing the large pulse that resulted from activation of ^{35}Cl during marine nuclear weapons tests. The age scale was determined by counting the seasonal variations in $\delta^{18}\text{O}$.

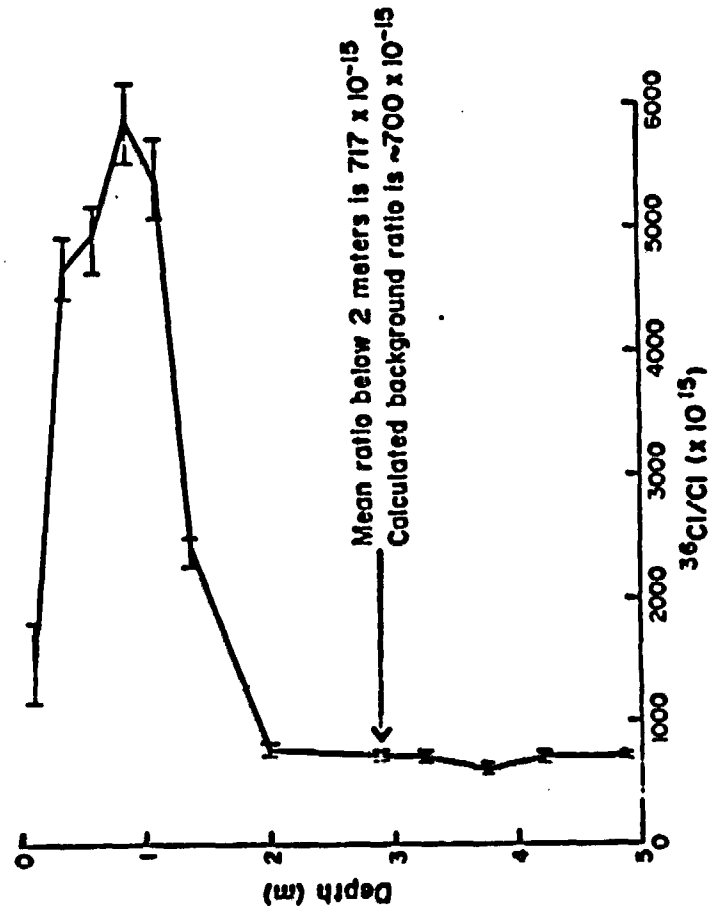


Figure 1. The $^{36}\text{Cl}/\text{Cl}$ ratio of soil-water solutions in the vadose zone from a vertical borehole near Socorro, New Mexico



NNWSI PROGRAM
BOMB PULSE ^{36}Cl INFILTRATION

Los Alamos

PICK SAMPLING SITES
NEAR EXPLORATORY SHAFT
FRACTURED LOCATION ON YUCCA MOUNTAIN CREST
YUCCA WASH

DETERMINE CHLORIDE PROFILES

DETERMINE $^{36}\text{Cl}/\text{Cl}$ PROFILES

SUBCONTRACTOR - HYDRO GEO CHEM, INC.

3-D MINERALOGY AND SORPTION STRATIGRAPHY

Mineralogy/Petrology Update

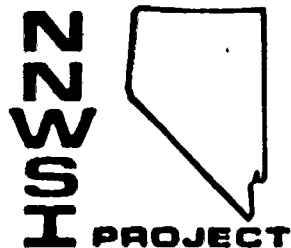
Evaluation of Statistical Methods



MINERALOGY/PETROLOGY PLAN

Los Alamos

- **TRANSPORT PATHWAY MINERALOGY**
 - A) **HOST ROCK**
 - B) **AWAY FROM THE REPOSITORY**
- **ALTERATION MINERALS**
 - A) **ALTERATION HISTORY**
 - B) **MINERALS IN FRACTURES**
- **MINERAL STABILITY**
 - A) **PAST HISTORY OF YUCCA MOUNTAIN**
 - B) **SMECTITE DEHYDRATION**
 - C) **ZEOLITE DEHYDRATION AND REACTION KINETICS**
- **EXPLORATORY SHAFT TESTING**
 - A) **DEEP SAMPLES WITH MAPPED-OUT RELATIONS**
 - B) **EXPOSURE OF CONTACTS BETWEEN MAJOR PETROLOGIC INTERVALS**



HOST ROCK: YUCCA MOUNTAIN

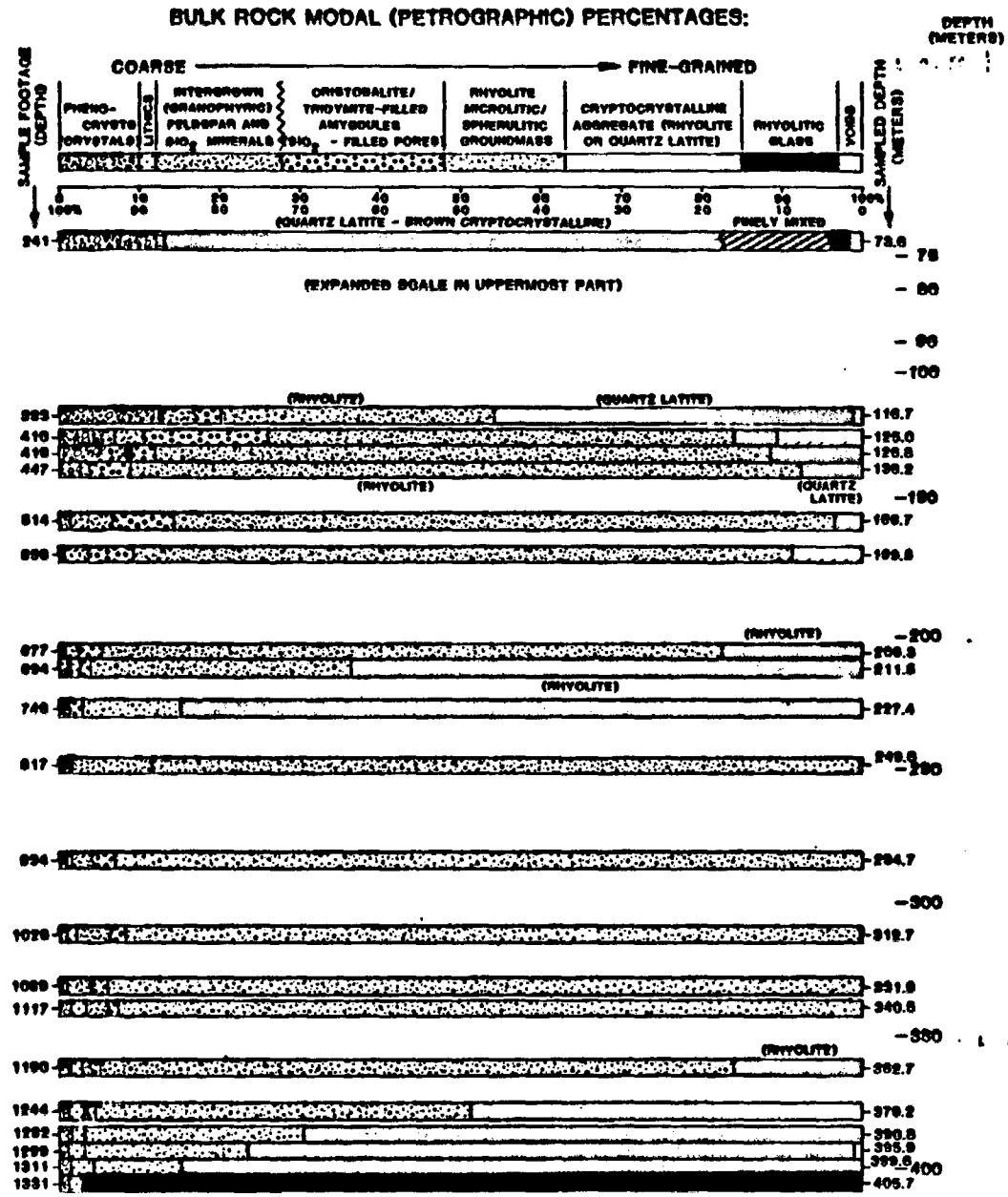
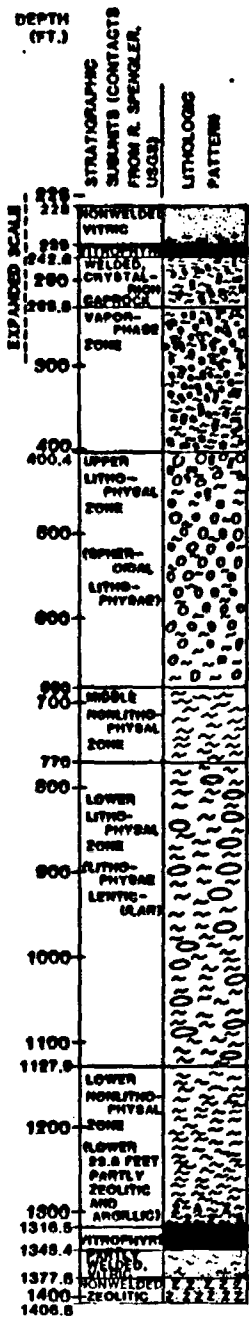
Los Alamos

● TRANSPORT PATHWAYS -

**POSSIBILITY OF SLOW TRANSPORT IN THE UNSATURATED
ZONE: SIGNIFICANT RETARDATION MAY OCCUR IN OR NEAR THE
HOST ROCK**

● KNOWLEDGE OF THE HOST ROCK -

- A) FOR ACCURATE DETERMINATION OF POSITION DURING
CONSTRUCTION (E.G. - CONSTRUCTION ACROSS FAULT
OFFSETS)**
- B) FOR TRANSFER OF RESULTS FROM LOCAL STUDIES TO OTHER
PARTS OF THE EXPLORATION BLOCK**

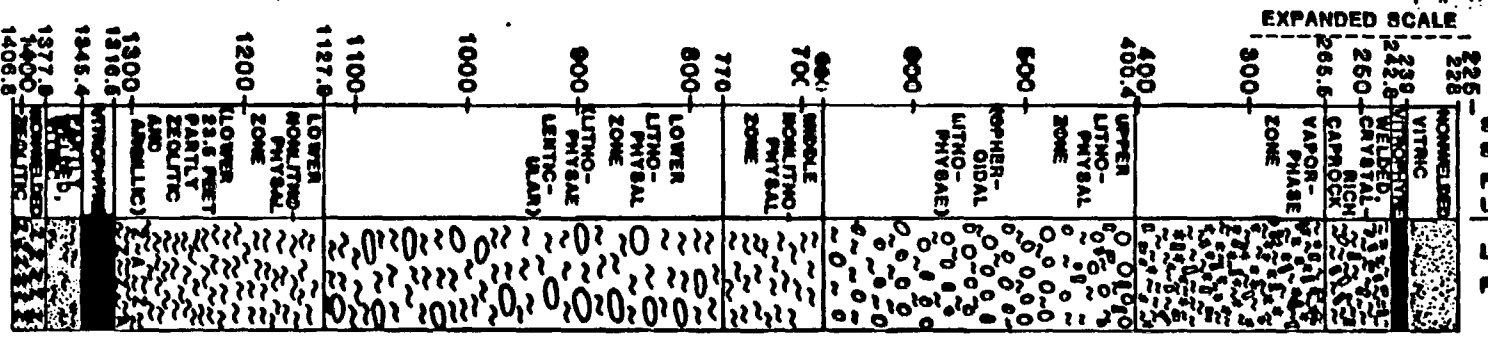


USW G-4

DEPTH (FT.)

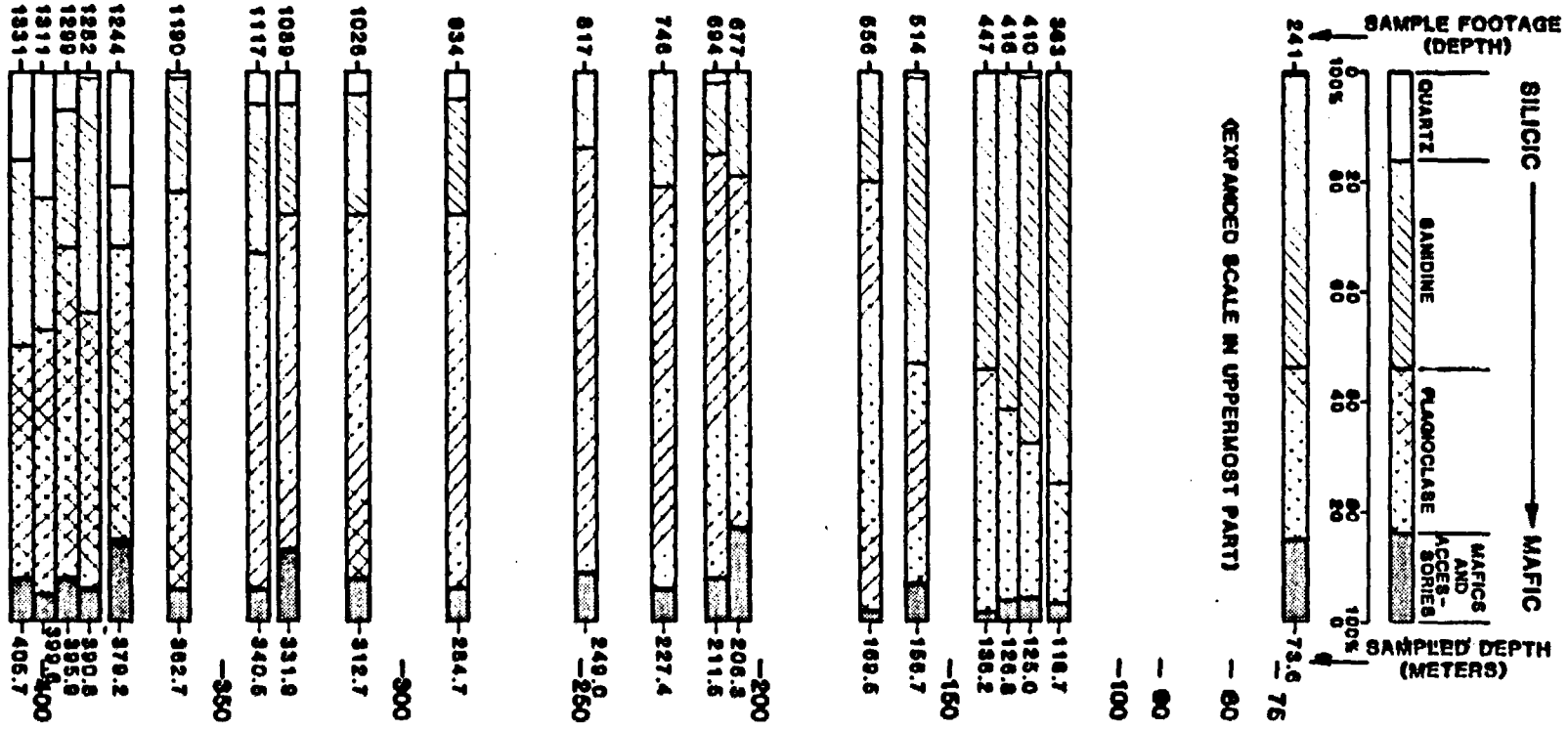
STRATIGRAPHIC SUBUNITS (CONTACTS FROM R. SPENGLER, USGS)

LITHOLOGIC PATTERN



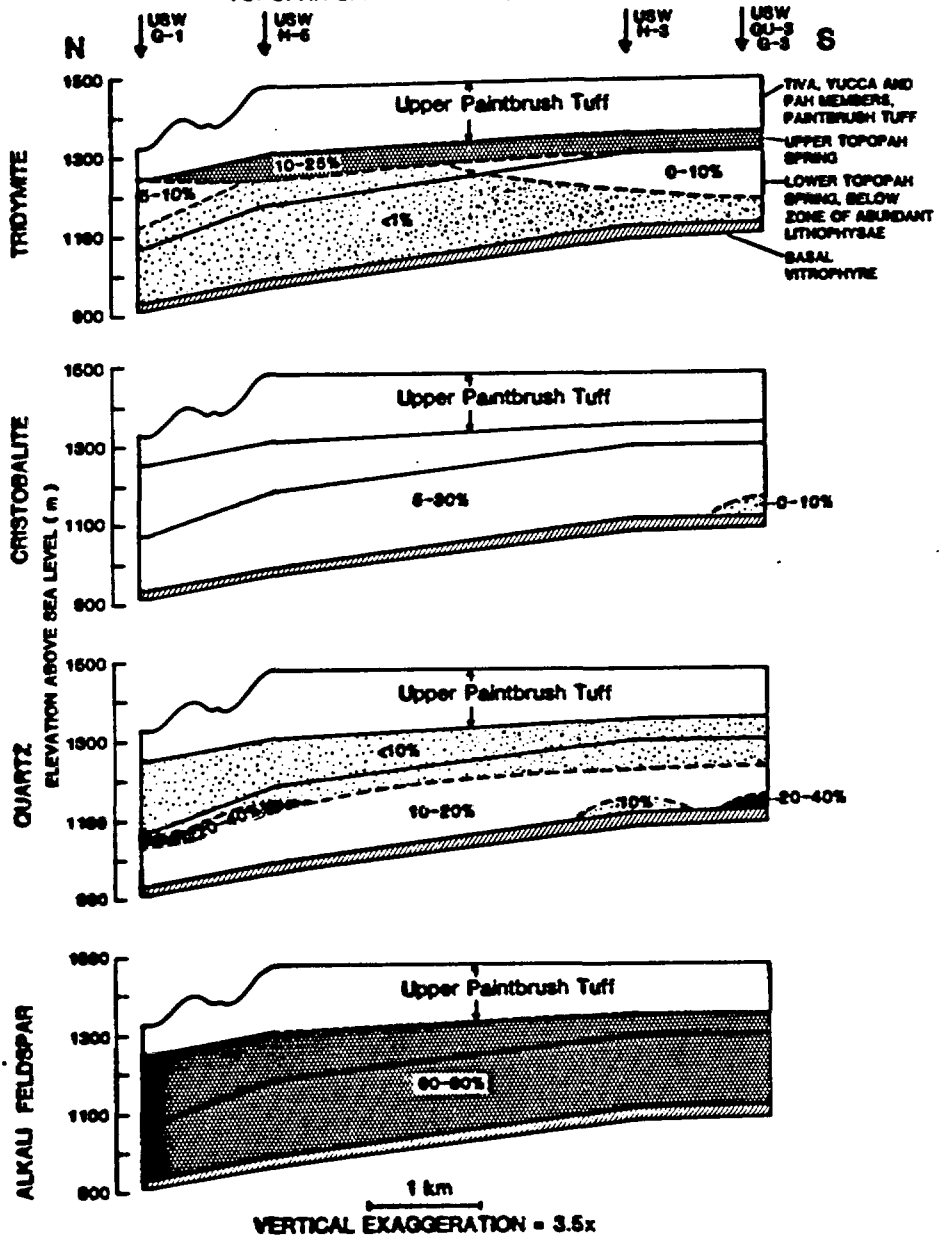
CRYSTAL (PHENOCRYST) PERCENTAGES

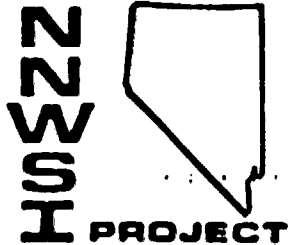
DEPTH (METERS)



USW G-4

MAJOR MINERAL COMPONENTS IN THE DEVITRIFIED TOPOPAH SPRING MEMBER, PAINTBRUSH TUFF.





ROCK TYPES BEYOND THE REPOSITORY: YUCCA MOUNTAIN

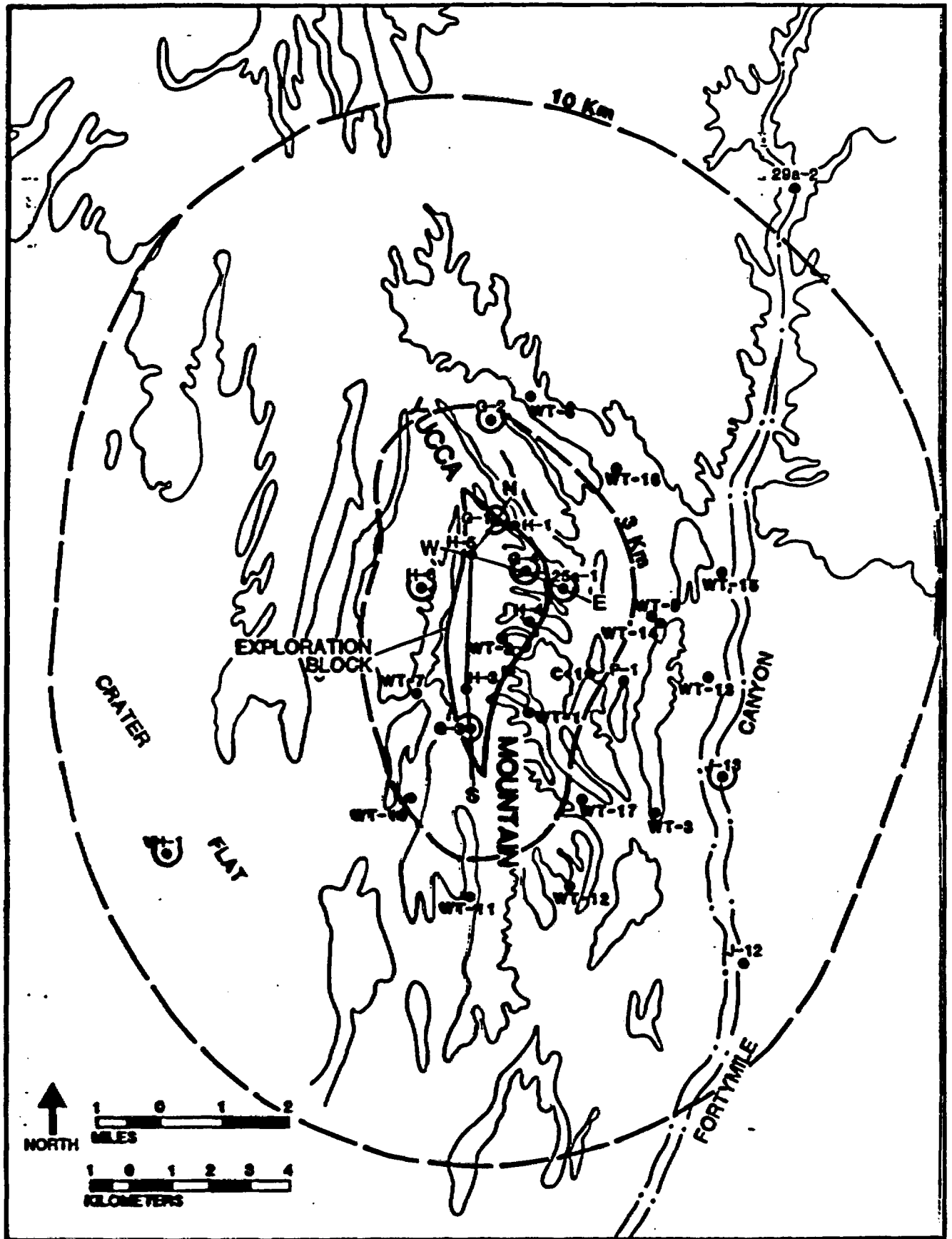
Los Alamos

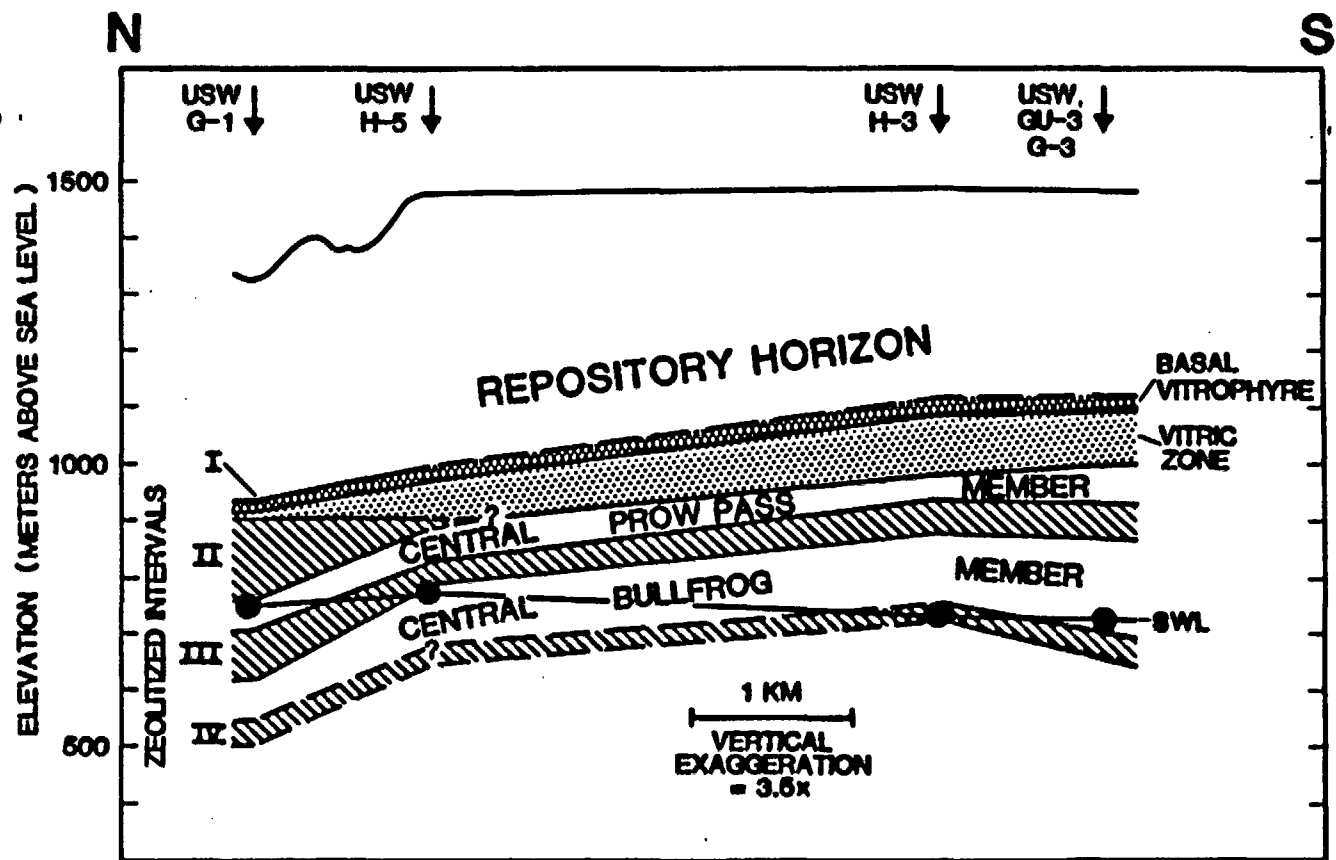
● CLASSIFICATION OF SIGNIFICANT LITHOLOGIC VARIANTS NEAR THE REPOSITORY

- A) DEVITRIFIED TUFF (ALKALI FELDSPARS & SILICA MINERALS)
- B) ZEOLITES AND CLAY (HEULANDITE, CLINOPTILOLITE & SMECTITE)
- C) VITROPHYRE (DENSE GLASS)
- D) VITRIC TUFF (POORLY CONSOLIDATED GLASS)

● CLASSIFICATION OF SIGNIFICANT LITHOLOGIC VARIANTS AWAY FROM THE REPOSITORY

- A) DEVITRIFIED TUFF (ALKALI FELDSPARS & SILICA MINERALS)
- B) ZEOLITIZED TUFF (CLINOPTILOLITE & MORDENITE)
 - 1) FOUR MAPPABLE ZEOLITIZATION INTERVALS



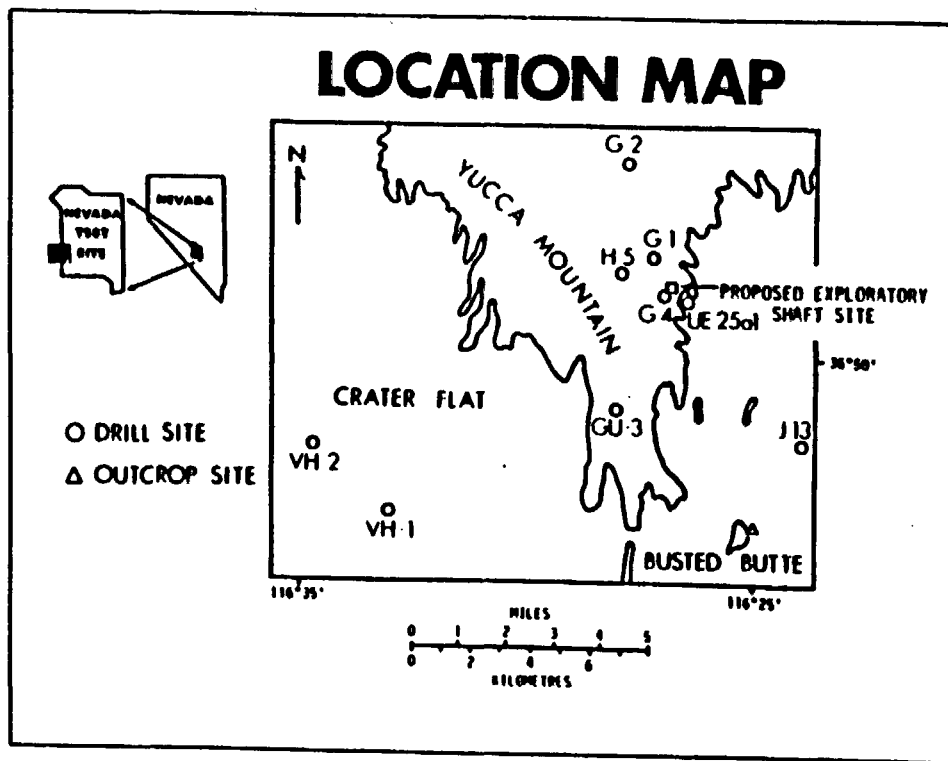




OXYGEN ISOTOPE GEOTHERMOMETRY

from quartz fracture filling in altered Tpt vitrophyre

USW VH-2 3565 ft (1086.6 m) depth



Los Alamos



OXYGEN ISOTOPE GEOTHERMOMETRY

Data needed to calculate temperature:

- $\delta^{18}\text{O}$ of quartz -- determined in lab
- assumed or known $\delta^{18}\text{O}$ of water that deposited the quartz
- relationship between temperature and quartz-water oxygen isotope fractionation factor (experimentally determined – published)

Los Alamos

OXYGEN ISOTOPE GEOTHERMOMETRY

Oxygen isotope fractionation factor:

$$\alpha = 1000 + \delta^{18}\text{O}_{\text{quartz}} / 1000 + \delta^{18}\text{O}_{\text{water}}$$

Temperature—fractionation factor relationship:

(Friedman and O'Neil, 1977)

$$T^{\circ}\text{C} = \frac{3.38 \times 10^6}{10^3 \ln \alpha + 2.90} - 273$$

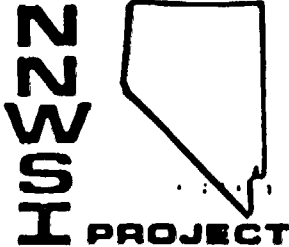
$$= 91 \text{ or } 95^{\circ}\text{C} \quad \text{VH-2 3565}$$



GEOPETAL STUDIES – SUMMARY

- **Tectonic tilting recorded by geopetal structures in zeolitized tuffs probably occurred before 11.3 million years ago.**
- **The age of zeolitization at Yucca Mountain is also probably pre–11.3 million years ago, based on textural relations in zeolitized tuffs.**

Los Alamos



ALTERATION MINERALS IN FRACTURES: YUCCA MOUNTAIN

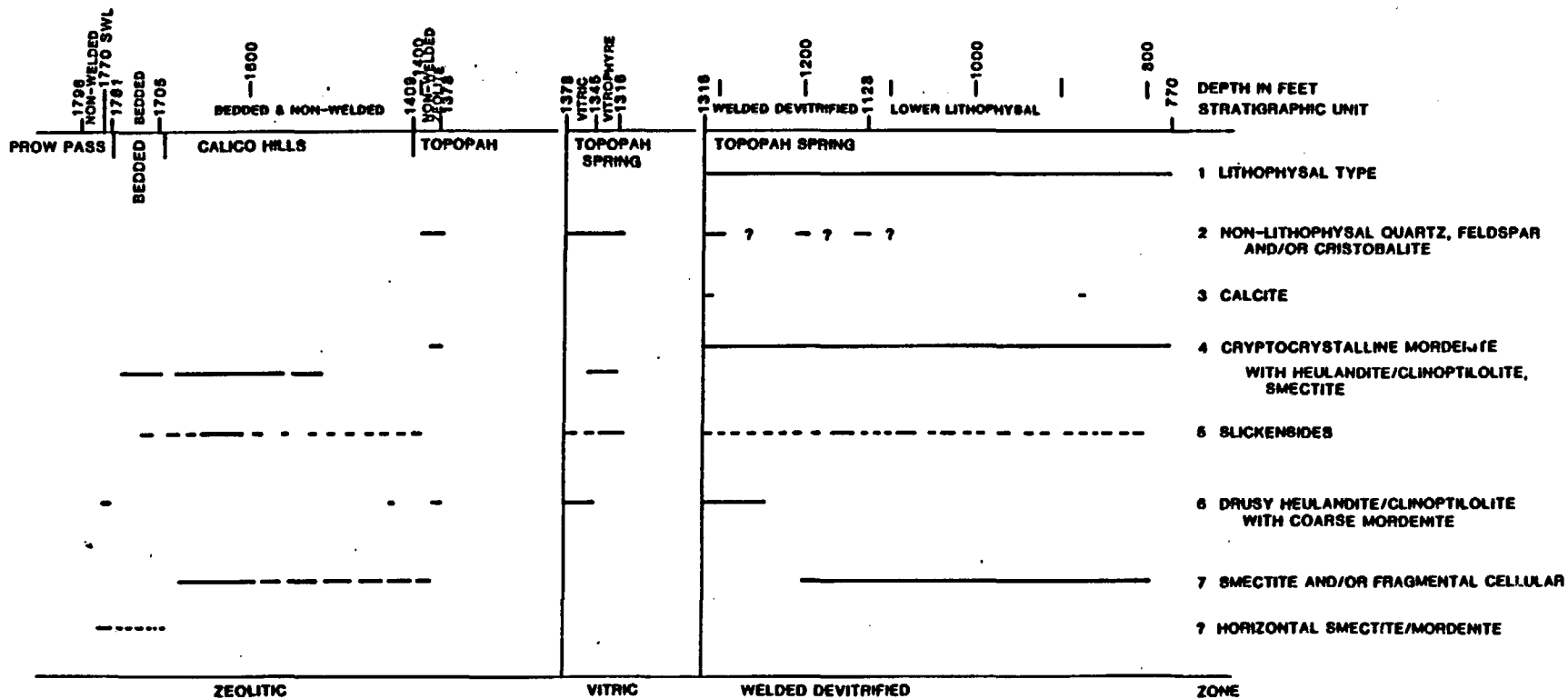
Los Alamos

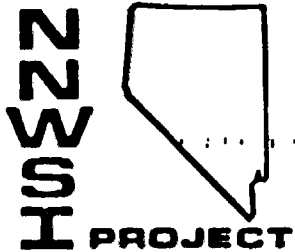
- **THE GREATEST DIFFERENCES BETWEEN FRACTURE MINERALOGY AND ROCK-MATRIX MINERALOGY OCCUR IN DEVITRIFIED OR GLASSY TUFFS**
- **ZEOLITES IN FRACTURES OCCUR FAR ABOVE THEIR SHALLOWEST OCCURRENCES AS BULK-ROCK ALTERATION PRODUCTS**
- **HEULANDITE IN UPPER FRACTURES AND NEAR THE LOWER TOPOPAH SPRING VITROPHYRE MAY HAVE AN ORIGIN VERY DIFFERENT FROM CLINOPTILOLITE IN LOWER ZEOLITIZED INTERVALS**

X-RAY DIFFRACTION ANALYSES OF FRACTURE FILLINGS USW G-4 UNSATURATED ZONE

	Unit	Sample	Estimated % of Fracture Surface Coated	Estimated Max. % Rock Contamination	Smectite	Ch. Zeolite/ Heulandite	Mordenite	Quartz	Cristobalite	Alkali Feldspar	Trigymite
Topopah Spring Member	Lower Lithophysal	810	40	5	23 ± 5		59 ± 10	18 ± 3			
		887	90	30	2 ± 1			12 ± 2	5 ± 3	74 ± 10	7 ± 4
		984	100	20				79 ± 5	~1	14 ± 5	6 ± 3
		1001	10	40	~1			21 ± 4	5 ± 3	73 ± 10	
		1008	100	15	~1		11 ± 5	40 ± 5	10 ± 5	38 ± 10	
		1038 X	100	20	15 ± 5			24 ± 8	5 ± 3	36 ± 10	20 ± 5
		1072 #1	100	30				65 ± 5	~1	22 ± 10	12 ± 4
		1072 #2	30	30	~1		7 ± 4	14 ± 1	8 ± 4	61 ± 10	9 ± 4
		1083 #3	90	10	6 ± 2			9 ± 2	5 ± 3	66 ± 10	14 ± 5
	Welded Devitrified "Candidate Host Rock"	1148	50	25	2 ± 1			22 ± 8	7 ± 4	69 ± 10	
		1160	50	10				32 ± 5	6 ± 4	62 ± 10	
		1173	25	10	3 ± 1		58 ± 15	23 ± 7	16 ± 7		
		1201	95	50				43 ± 9	9 ± 4	48 ± 15	
		1244	60	15	~1			40 ± 5	8 ± 4	51 ± 10	
		1254 #1	100	15			52 ± 10	13 ± 5	20 ± 2	15 ± 5	
Calico Hills	Vitrophyre	1254 #3	100	10		47 ± 10 H	11 ± 5	26 ± 5	16 ± 4		
		1258	100	5	7 ± 3	29 ± 5		12 ± 3	7 ± 4	45 ± 10	
		1309	90	5		100 H					
	Vitric	1341 blue	100	50	2 ± 1	20 ± 10	12 ± 6	5 ± 3	6 ± 4	55 ± 10	
		1341 cream	100	10	67 ± 10	28 ± 10		5 ± 4			
	Nonwelded	1341 beige	35	10	5 ± 2	80 ± 10 H	15 ± 5				
		1350	100	20	20 ± 10	80 ± 10					
	Zeolitic	1362	20	>50	3 ± 1	42 ± 10	18 ± 5		6 ± 4		31 ± 10
		1381	100	50	~1	67 ± 10 C			32 ± 5		
		1436	100	20	~1	99 C					
1513		100	20		55 ± 10	22 ± 10	2 ± 2	15 ± 8		6 ± 2	
Proow Pass	Nonwelded	1542	100	15	2 ± 1	74 ± 10	24 ± 10				
		1643	100	20		20 ± 10	80 ± 10				
	1694	Not readily discernible from rock matrix		2 ± 1	70 ± 10	28 ± 10					
	1707	70	10		4 ± 2	96 ± 4					
	1716	30	50		25 ± 10	25 ± 10	18 ± 3		27 ± 10	5 ± 2	
Nonwelded SWL	1763 white	100	Can't tell as intergrown with rock grains		88 ± 10	8 ± 3			4 ± 2		
	1763 orange	100			68 ± 10	23 ± 10	5 ± 3		4 ± 3		

SEQUENCE OF FRACTURE COATINGS IN THE UNSATURATED ZONE OF USW G-4





POSSIBLE APPROACHES TO THE DETERMINATION OF "PALEO" WATER SYSTEMS (YUCCA MOUNTAIN)

Los Alamos

● PALEO FLOW PATHS -

Sr-ISOTOPIC VARIATIONS BETWEEN ZEOLITE GROUPS (UPWARD

FLOW, DOWNWARD FLOW; DISTANT OR LOCAL TRANSPORT?)

● PALEO WATER LEVELS -

A) PRESERVATION OF UNPROTECTED, NONWELDED GLASS SHARDS

B) TEXTURAL TRANSFORMATIONS WITHIN CLINOPTILOLITE

OCCURRENCES

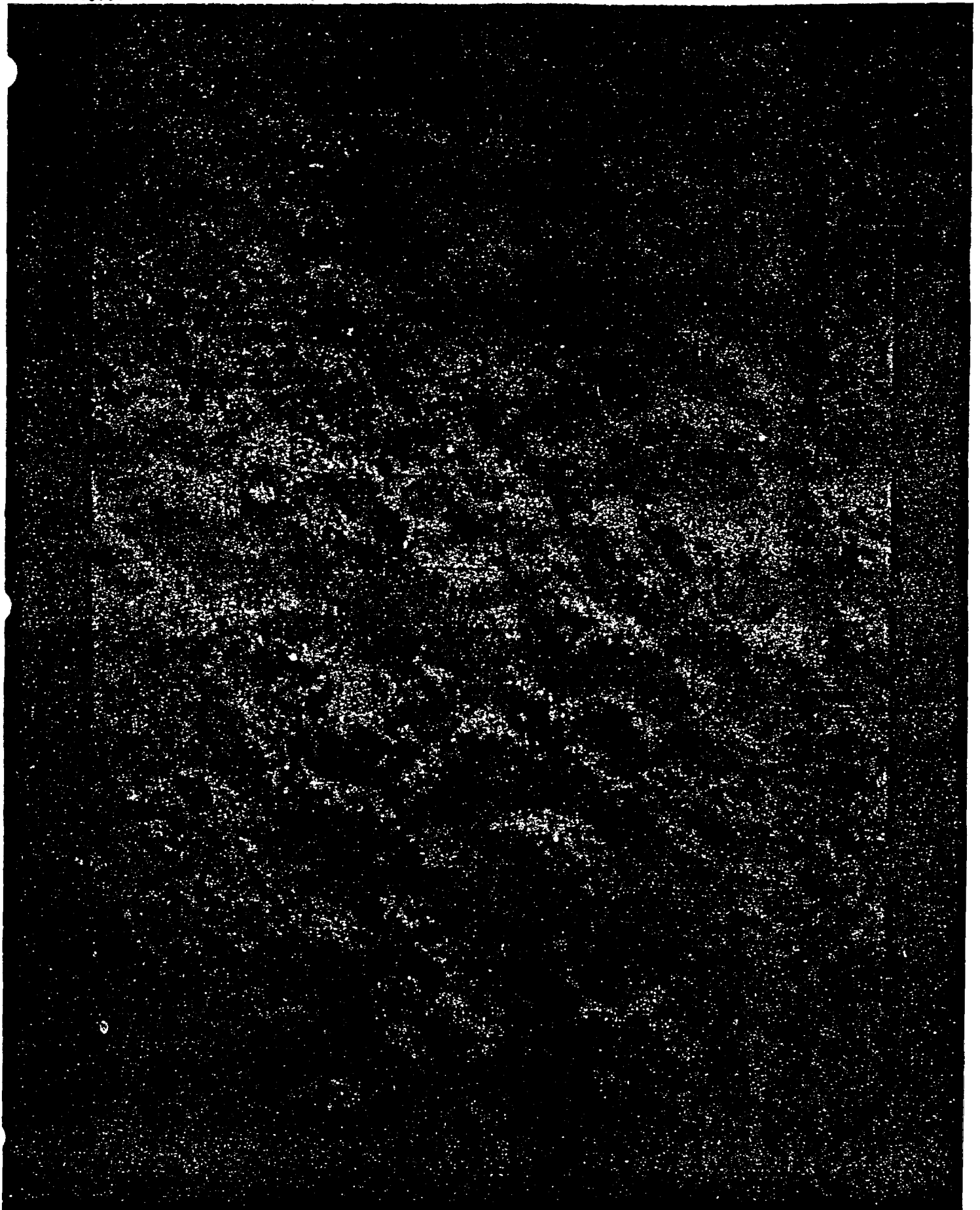
Sr - ISOTOPIC DIFFERENCES BETWEEN CARBONATE AND TUFF SOURCES

Source Rock	Rb (ppm)	Sr (ppm)	$^{87}\text{Sr}/^{86}\text{Sr}$	Comments
I. Caliche				
Carboniferous carbonates	1-40	200-1000	0.7077-0.7085	Reworked Paleozoic carbonate materials may be the dominant components of the caliche layer at Yucca Mountain. Presented here are worldwide averages taken from Peterman et al., 1970 and Veizer, 1974.
Devonian carbonates	"	"	0.7078-0.7084	
Silurian carbonates	"	"	0.7088	
Ordovician carbonates	"	"	0.7077-0.7088	
Cambrian carbonates	"	"	0.7089-0.7094	
II. Paintbrush Tuffs				
Tiva Canyon Member	56-103	142-205	0.7075-0.7135	The 0.7075 $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of the Tiva Canyon Member is typical of quartz latitic caprocks. However, these caprocks have generally devitrified to stable mineral phases and are not subject to dissolution. Ratios taken from Noble and Hedge, 1969.
Pah Canyon Member	ND	ND	0.7101	
Topopah Spring Member	125-195	22-110	0.7107-0.7179	
All Tuffs	56-195	22-205	0.7075-0.7179	

POLAROID

CA 226022 37 C

1542 2 1/2 m





1.1 30000-010

BOGAVOID

1310

5mm



EVALUATION OF STATISTICAL METHODS

K. CAMPBELL AND M. JOHNSON

Los Alamos

STATISTICAL METHODS FOR:

- A. EXTRAPOLATION OF LIMITED BOREHOLE DATA
(MAPPING PROBLEM)**

- B. DETERMINING THE VARIATION IN MINERALOGIC
COMPOSITION OF THE REPOSITORY HORIZON
AND ALONG POTENTIAL FLOW PATHS**



EVALUATION OF STATISTICAL METHODS

DATA SETS

Los Alamos

A. FOR MAPPING PETROLOGIC ZONES BELOW REPOSITORY HORIZONS:

- UP TO FOURTEEN HOLES (FIVE CONTINUOUSLY CORED)
- CONTACTS BETWEEN ZONES KNOWN TO WITHIN ONE TO FOUR METERS

B. FOR DETERMINING MINERALOGIC VARIABILITY WITHIN THE TOPOPAH SPRING MEMBER OF THE EXPLORATION BLOCK:

- UP TO FIVE HOLES (TWO CONTINUOUSLY CORED)
- X-RAY DIFFRACTION MEASUREMENTS OF CRISTOBALITE, TRIDYMITTE, SMECTITE, QUARTZ AND ALKALI-FELDSPAR



EVALUATION OF STATISTICAL METHODS

A. EXTRAPOLATION: QUESTIONS

Los Alamos

- WHAT TECHNIQUES ARE AVAILABLE?
- WHAT IS THE MAGNITUDE OF ERROR ASSOCIATED WITH ESTIMATES OF THICKNESS AND DEPTH OF PETROLOGIC ZONES ACROSS THE EXPLORATION BLOCK?
- WHAT SAMPLING (BOREHOLE) DENSITY WOULD BE REQUIRED TO REFINE THESE ESTIMATES TO A SPECIFIED LEVEL OF PRECISION?



EVALUATION OF STATISTICAL METHODS

A. EXTRAPOLATION TECHNIQUES

Los Alamos

- TREND SURFACE FITTING WITH STANDARD PREDICTION ERRORS OR "JACKKNIFED" ERROR ESTIMATES
- KRIGING, WITH STANDARD KRIGING ERROR AND "JACKKNIFED" EVALUATION OF MODEL FIT



EVALUATION OF STATISTICAL METHODS

A. EXTRAPOLATION: TREND SURFACE FITTING

Los Alamos

- SMALL DATA SET MEANS CHOICE OF SURFACE FORM LIMITED TO FORMS WITH FEW PARAMETERS (E.G., QUADRATIC)
- POOR FIT AND LARGE ERROR ESTIMATES
- POSSIBLY USEFUL AS PRELIMINARY TO KRIGING



EVALUATION OF STATISTICAL METHODS

A. EXTRAPOLATION: KRIGING

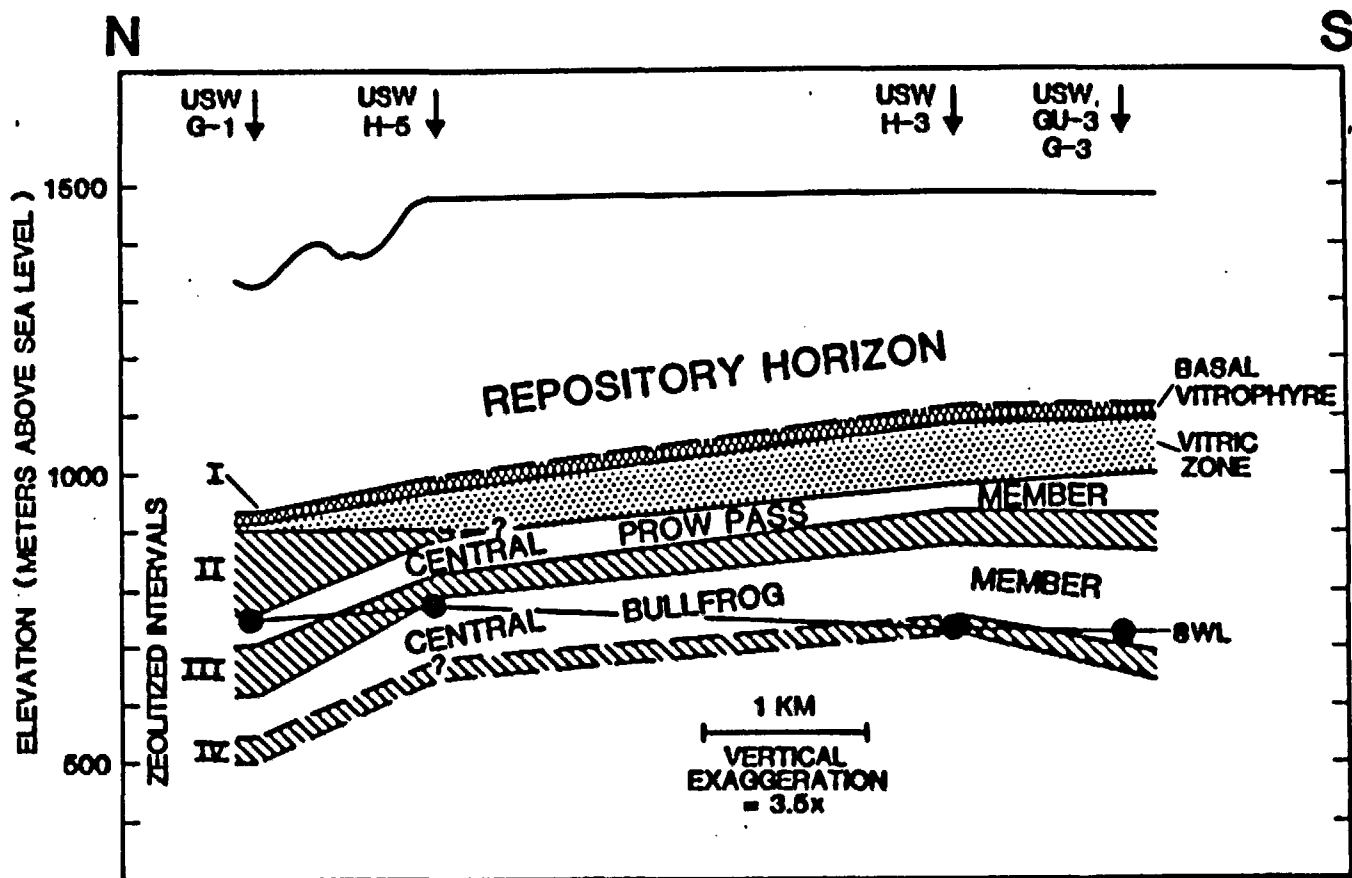
Los Alamos

- SMALL DATA SET MEANS CHOICE OF MODEL

IS SOMEWHAT ARBITRARY; VARIABILITY OF

RAW VARIOGRAM IS LARGE.

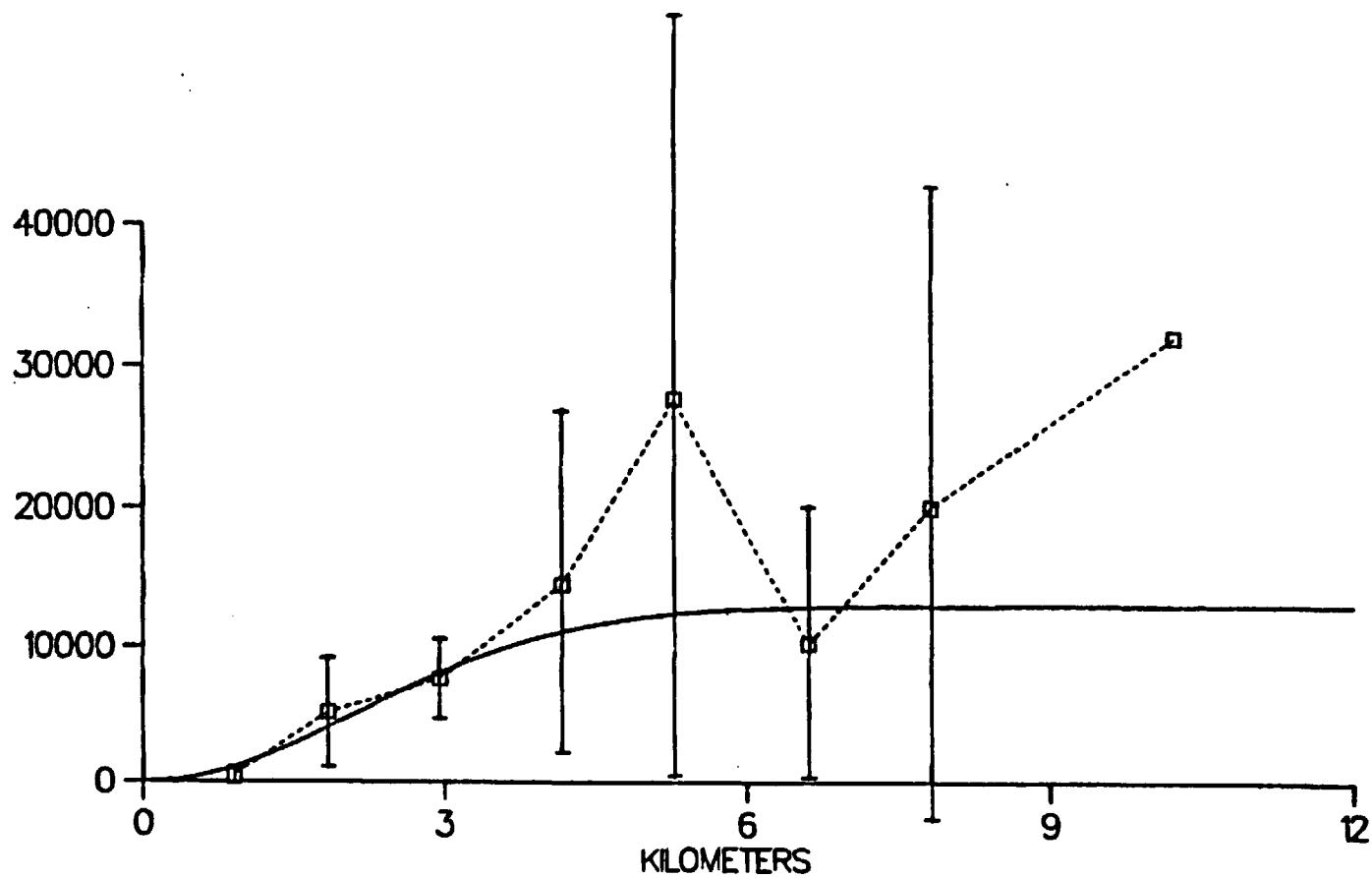
- REASONABLE ERROR ESTIMATES CAN BE OBTAINED.





TOP OF VITRIC ZONE
RAW VARIOGRAM AND GAUSSIAN MODEL

Los Alamos

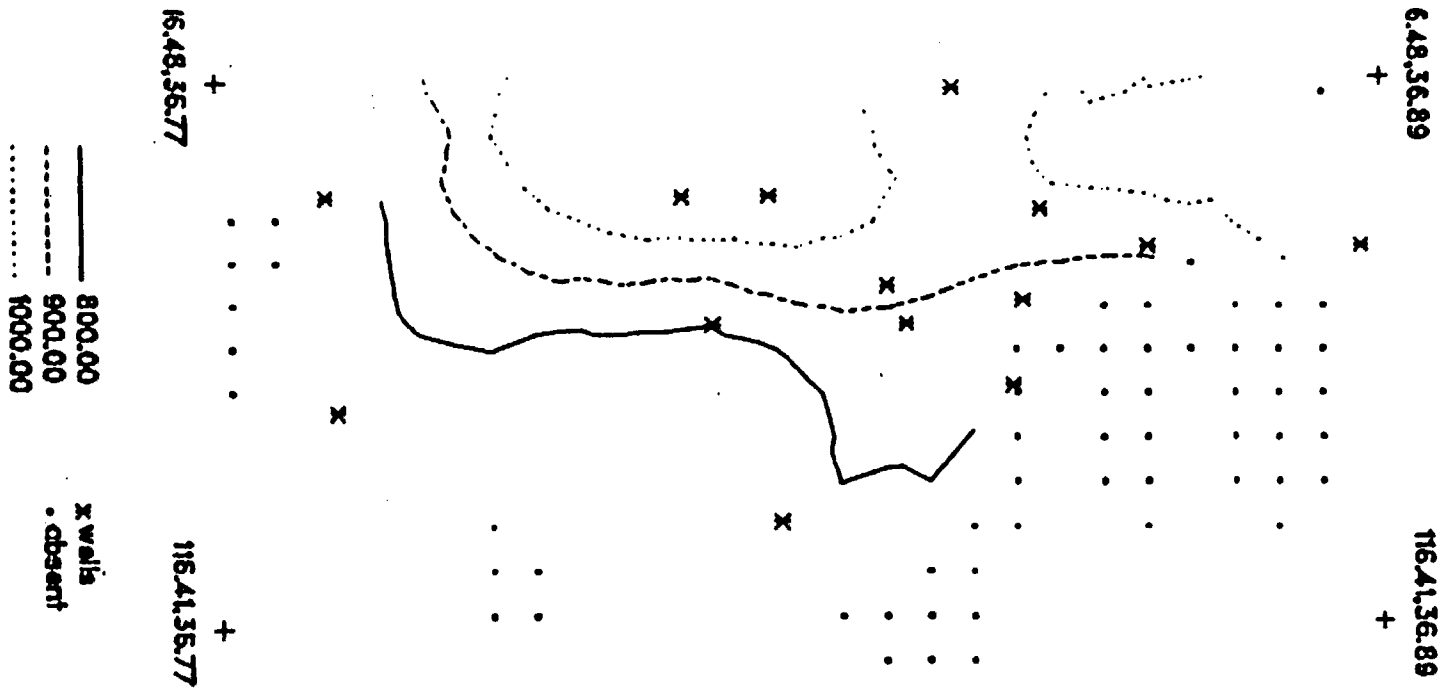


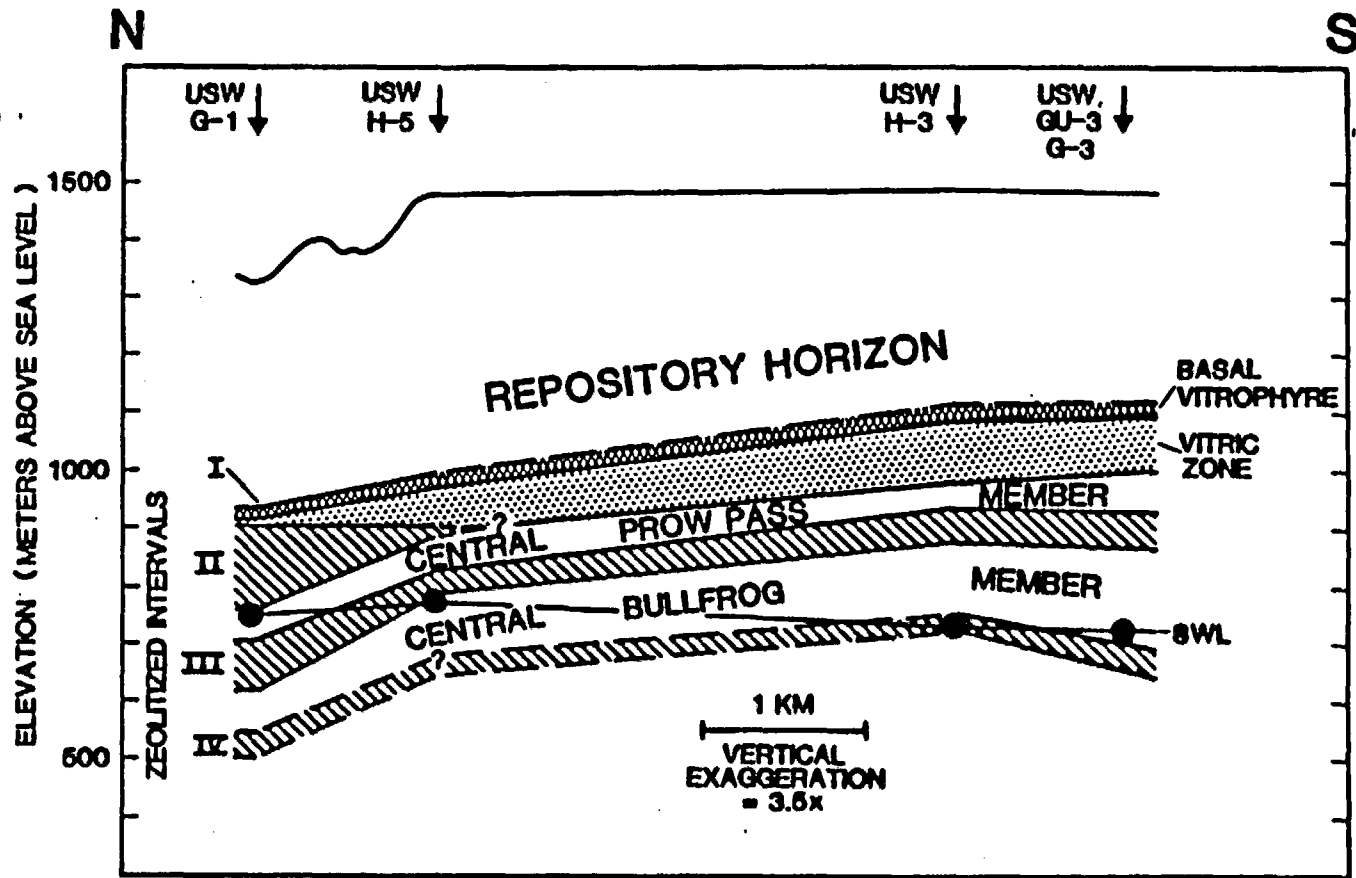


TOP OF VITRIC ZONE (METERS)

"KRIGED" MAP

Los Alamos



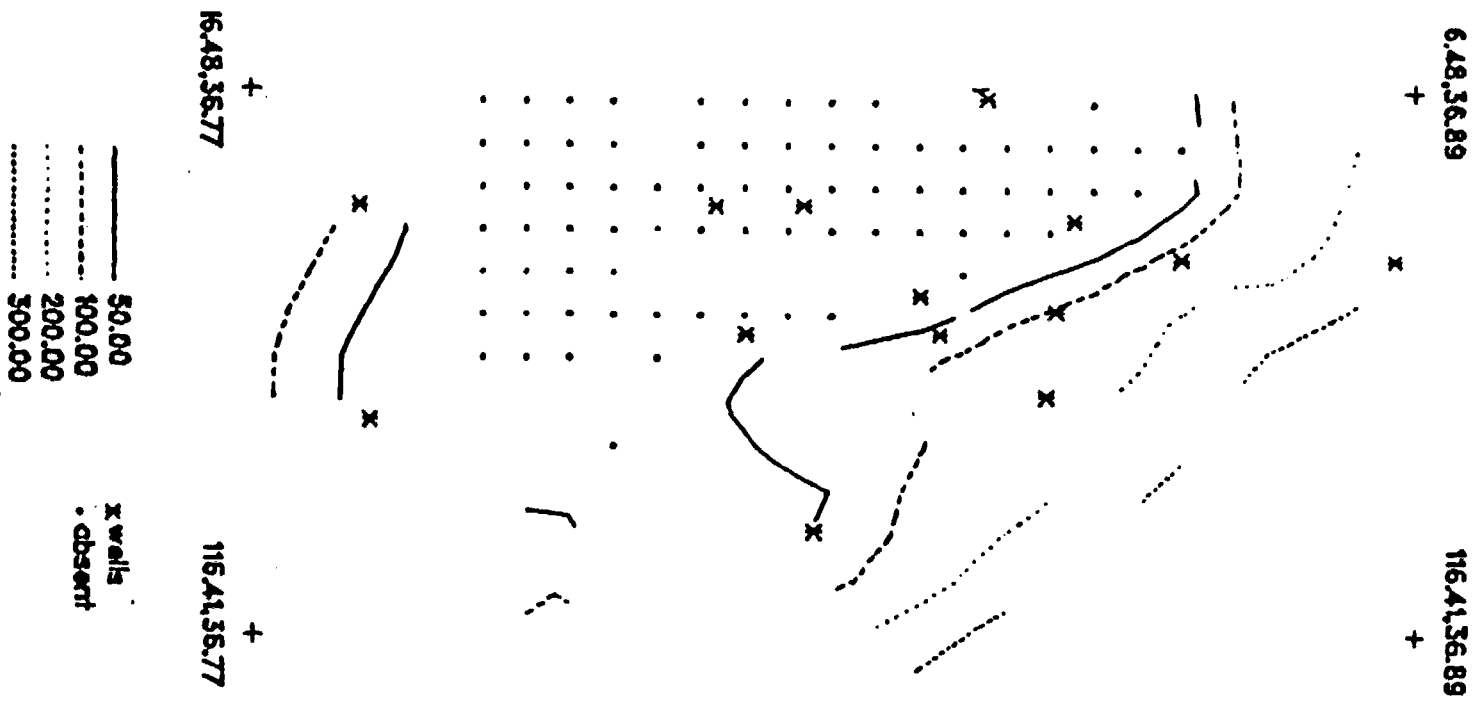




THICKNESS OF ZEOLITE II (METERS)

"KRIGED" MAP

Los Alamos



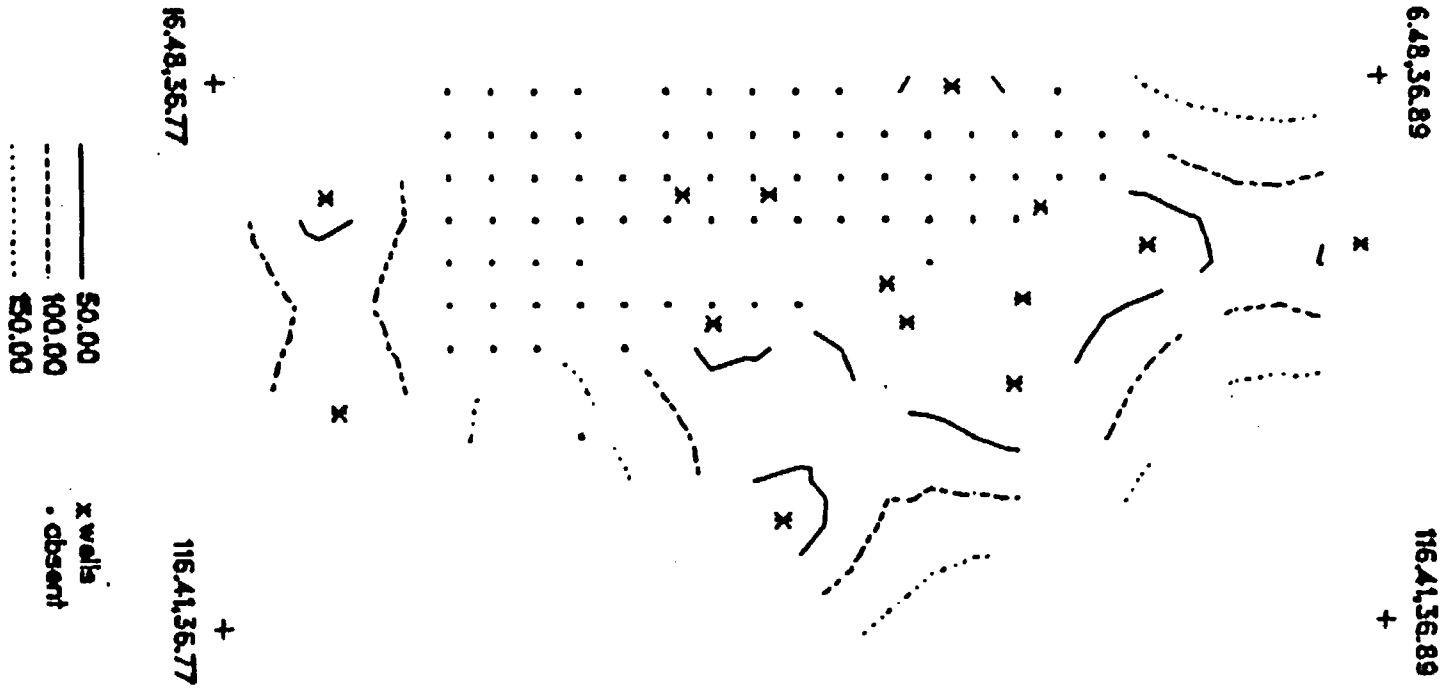
50.00
100.00
200.00
500.00

x wells
• absent



THICKNESS OF ZEOLITE II (METERS)
KRIGING ERROR (HALF OF 95% CONFIDENCE INTERVAL)

Los Alamos





EVALUATION OF STATISTICAL METHODS

B. MINERALOGIC VARIATION: QUESTIONS

Los Alamos

- HOW DOES THE VARIABILITY BETWEEN HOLES COMPARE TO THE VARIABILITY WITHIN HOLES?
- HOW DO X-RAY DIFFRACTION RESULTS COMPARE WITH PETROLOGIC ASSESSMENTS?
- CAN ESTIMATES OF VARIABILITY BE IMPROVED BY DRILLING MORE HOLES OR BY ANALYZING MORE SAMPLES FROM AVAILABLE HOLES?



EVALUATION OF STATISTICAL METHODS

B. MINERALOGIC VARIATION: TECHNIQUES

Los Alamos

- **ANALYSIS OF VARIANCE (ANOVA) FOR
ZONE AND BOREHOLE EFFECTS**

- **CANONICAL DISCRIMINATION FOR
COMPARISON OF MINERALOGIC AND
PETROLOGIC ASSESSMENT**



EVALUATION OF STATISTICAL METHODS

B. MINERALOGIC VARIATION: ANOVA

Los Alamos

- TWO-WAY ANOVA FOR INDIVIDUAL MINERALS SUGGESTS STRONG BOREHOLE EFFECTS AND BOREHOLE-ZONE INTERACTIONS, IMPLYING LACK OF HOMOGENEITY BETWEEN HOLES.
- SOME LINEAR COMBINATIONS (E.G., QUARTZ PLUS SMECTITE) EXHIBIT ONLY ZONE EFFECTS.



EVALUATION OF STATISTICAL METHODS

B. MINERALOGIC VARIATION: CANONICAL DISCRIMINATION

Los Alamos

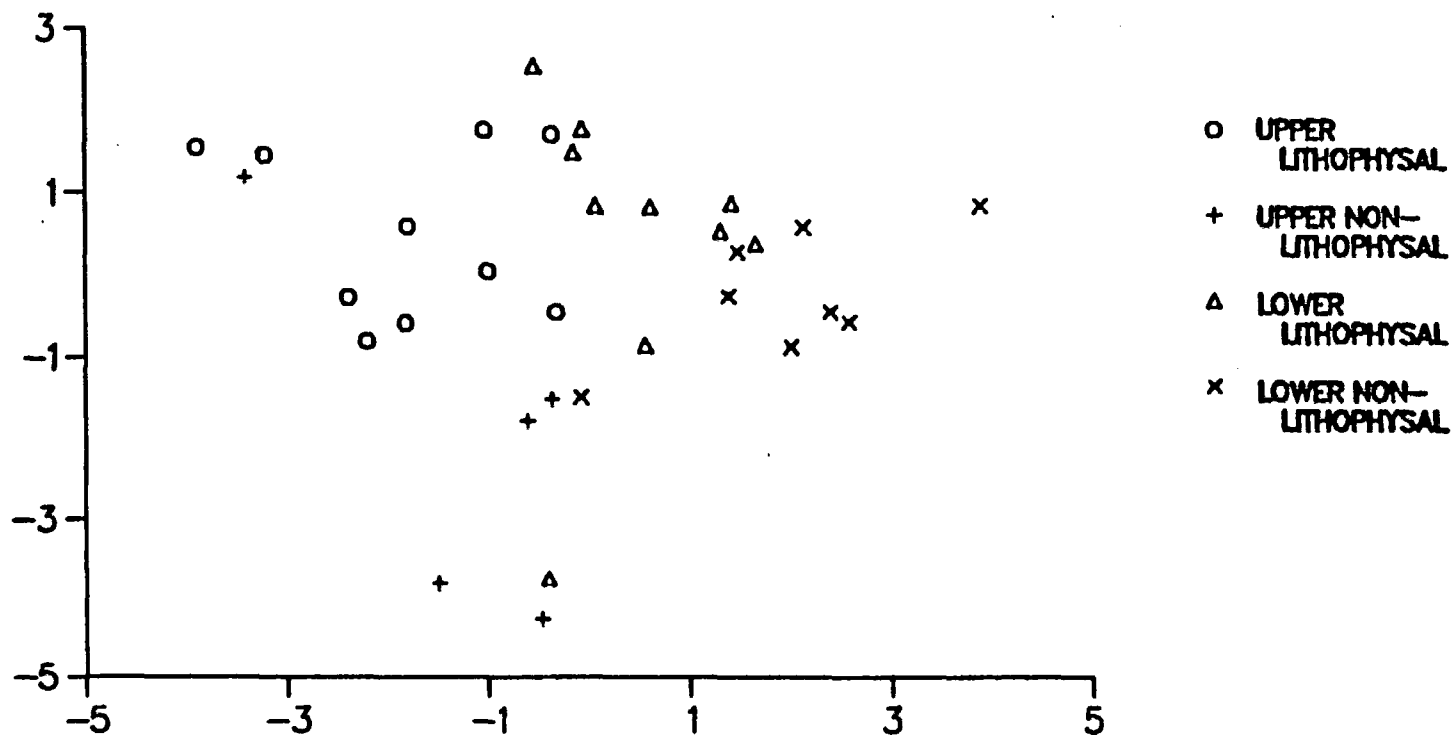
- **GOOD MATCH BETWEEN PETROLOGIC AND MINERALOGIC ASSESSMENT FOR G-3 AND G-4.**
- **PREPARATION OF SAMPLES IS VERY IMPORTANT.**
- **ACCURACY OF X-RAY DIFFRACTION MEASUREMENTS ON CONSISTENTLY PREPARED SAMPLES IS SUFFICIENT TO BE USEFUL.**



CANONICAL DISCRIMINATE MAP

BASED ON X-RAY DIFFRACTION DATA FOR G-3 AND G-4

Los Alamos

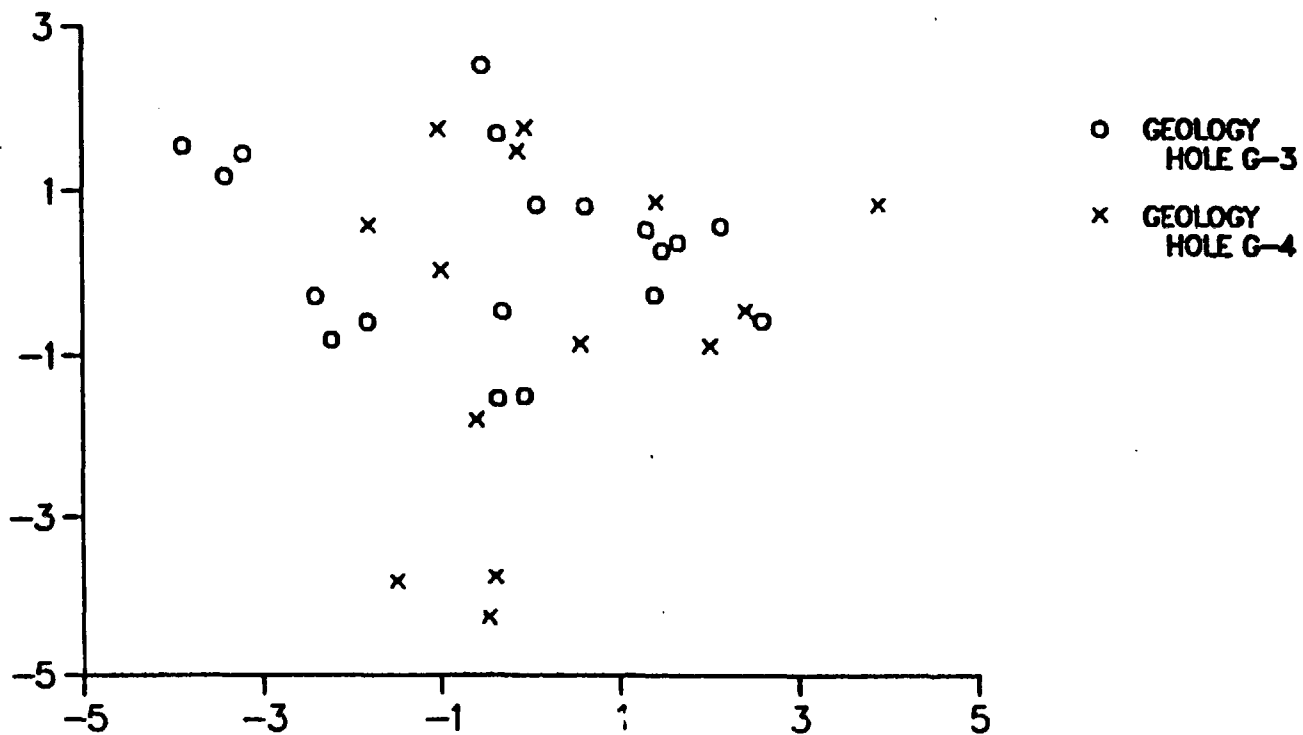




CANONICAL DISCRIMINATE MAP

BASED ON X-RAY DIFFRACTION DATA FOR G-3 AND G-4

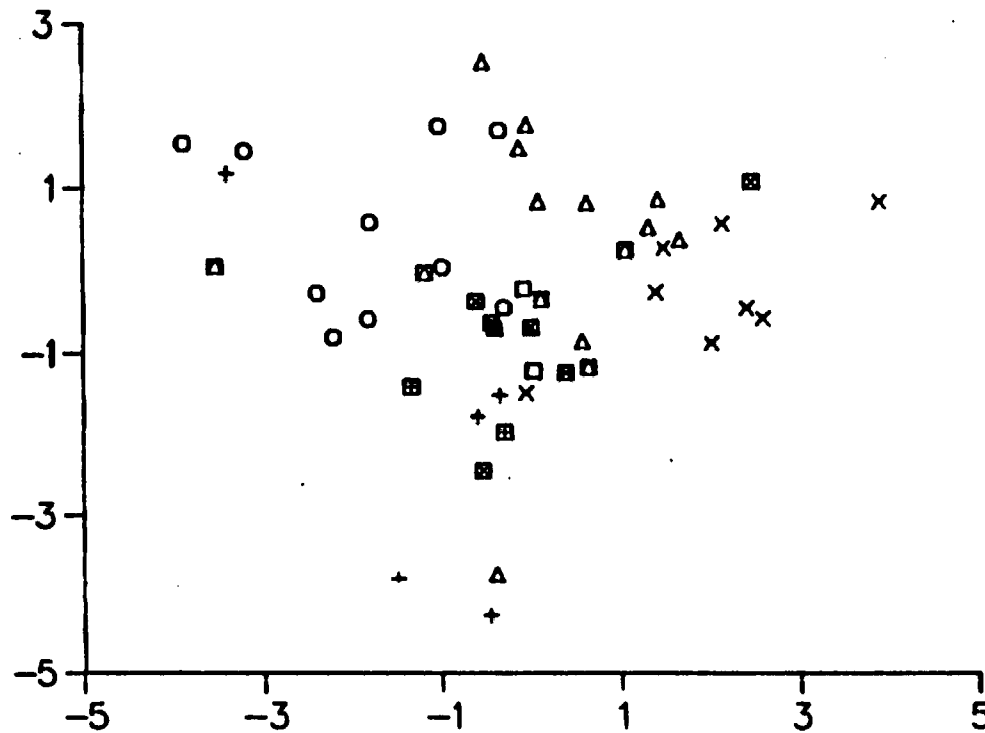
Los Alamos





CANONICAL DISCRIMINATE MAP
INCLUDING DATA FOR H-3, H-4 AND H-5

Los Alamos



MINERAL STABILITY

Hydrothermal Stability

Thermal Stability



MINERAL STABILITY

WHY IS IT IMPORTANT?

Los Alamos

WILL SORPTIVE MINERALS REMAIN
THROUGHOUT REPOSITORY LIFETIME?

PREDICTION OF CHEMICAL CONDITIONS

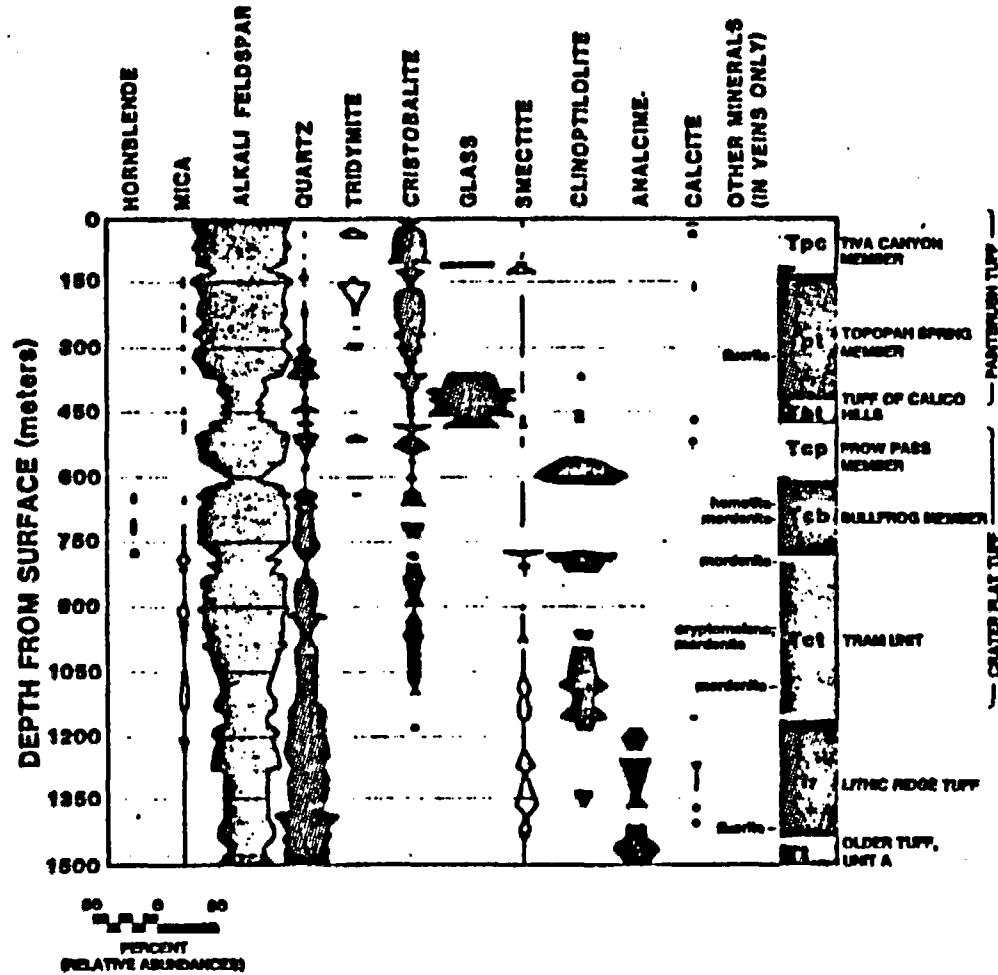
CONSTRAINTS ON PAST HYDROLOGIC CONDITIONS



MINERAL ABUNDANCES

DRILL HOLES USW GU-3/G-3

Los Alamos





IS THE MINERALOGY IN YUCCA MOUNTAIN STABLE?

NO

Los Alamos

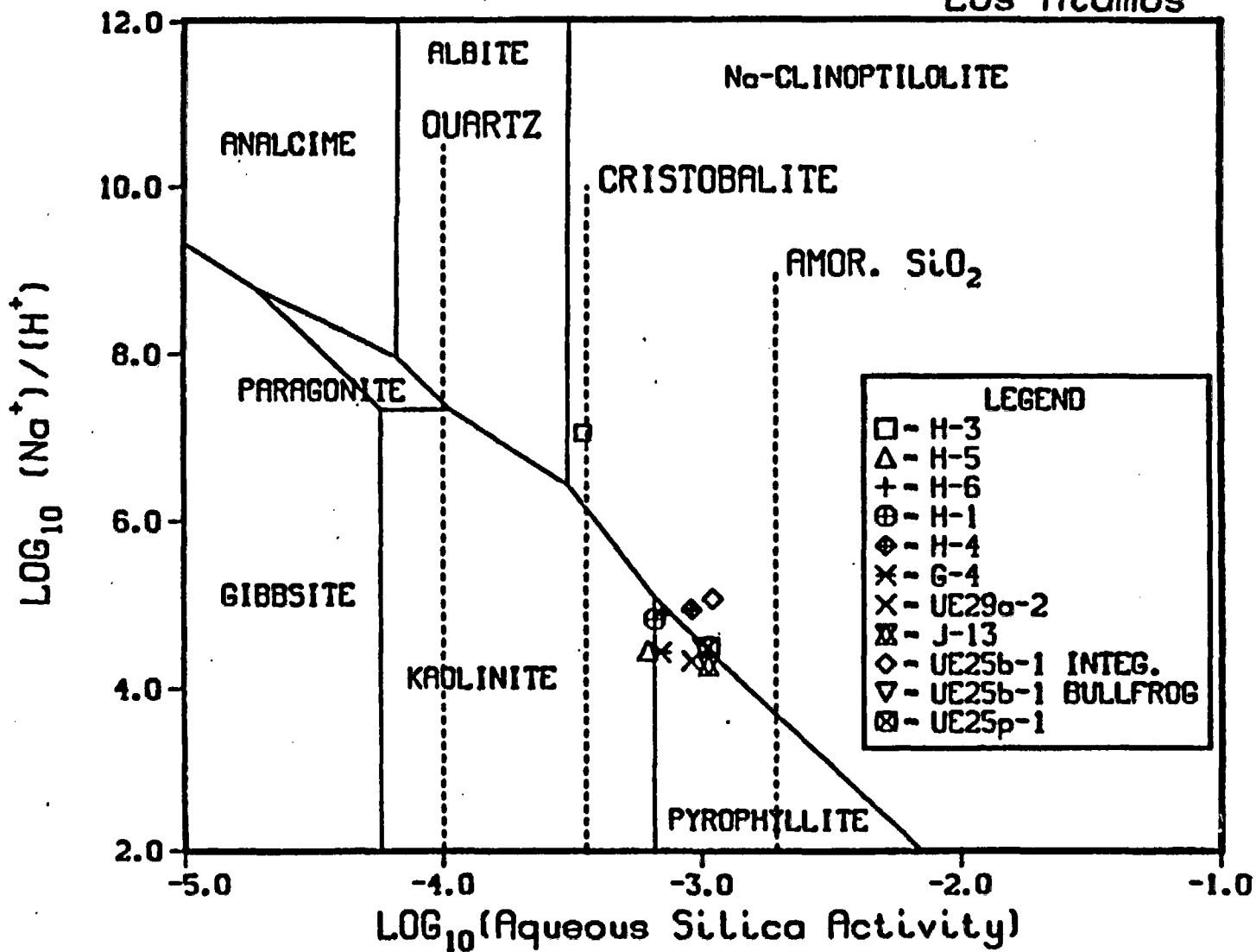
THE MINERALOGY IN YUCCA IS EVOLVING
TOWARD LOW SILICA ACTIVITIES

SIGNIFICANT CHANGE ON REPOSITORY TIMESCALE
IS UNLIKELY

IF CLINOPTILOLITE BREAKS DOWN IT IS
LIKELY TO PRODUCE CLAYS

Na-Si-AL PHASE DIAGRAM AT 25°C

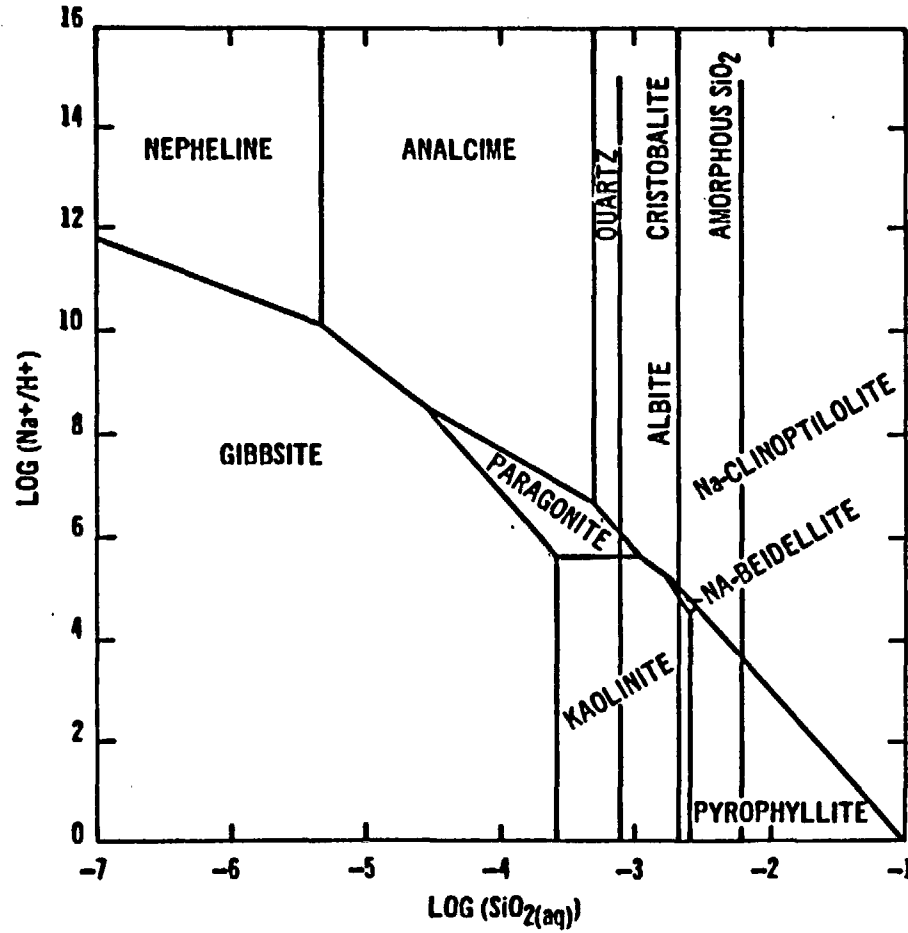
Los Alamos





CALCULATED PHASE EQUILIBRIA AT 100 C
SYSTEM SODIUM-ALUMINUM-SILICON

Los Alamos





MINERAL STABILITY
IMPORTANT PARAMETERS

Los Alamos

ACTIVITY OF SiO_2

LITHOSTATIC PRESSURE

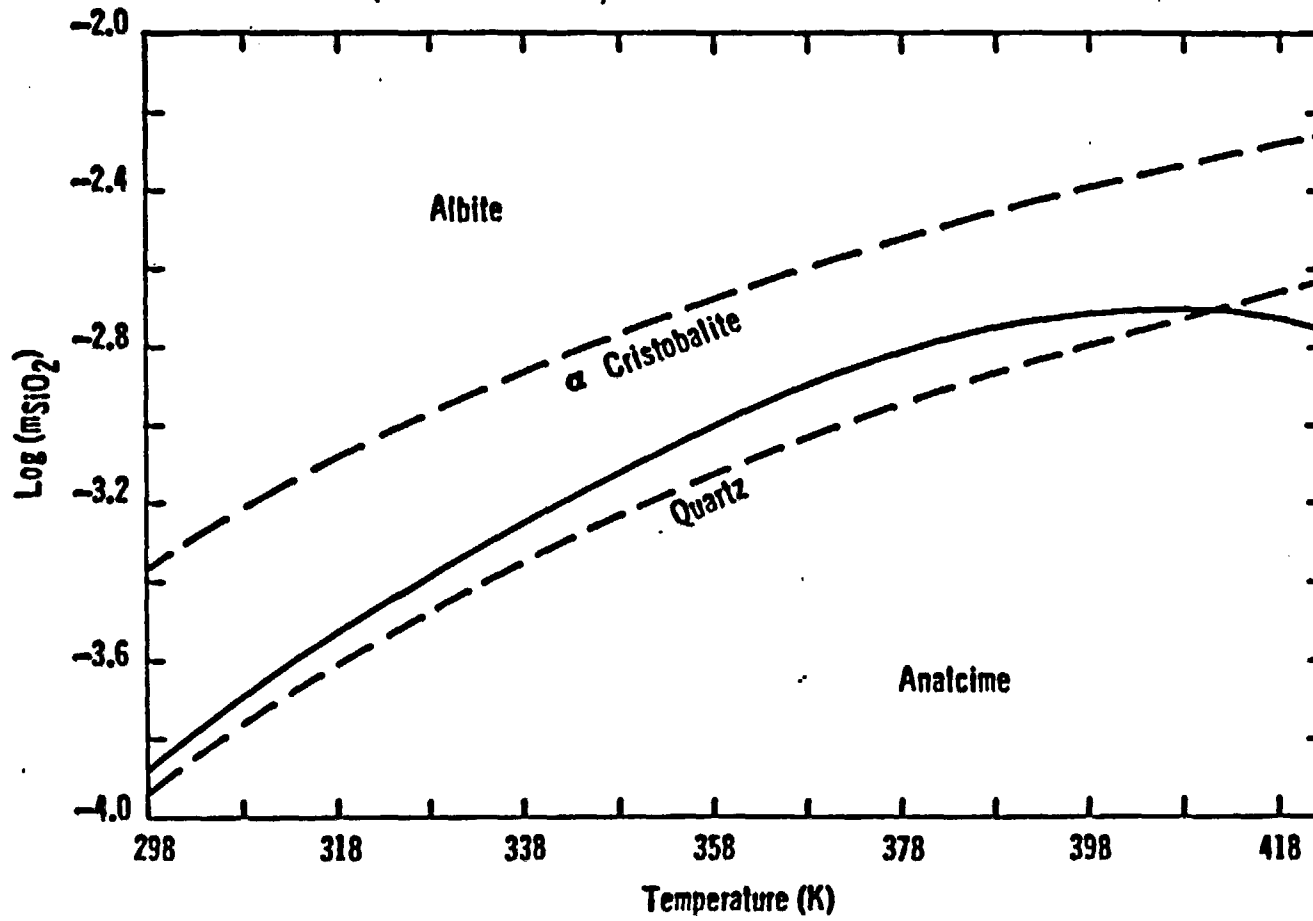
WATER PRESSURE

TEMPERATURE



EFFECT OF SILICA ACTIVITY ON ANALCIME STABILITY

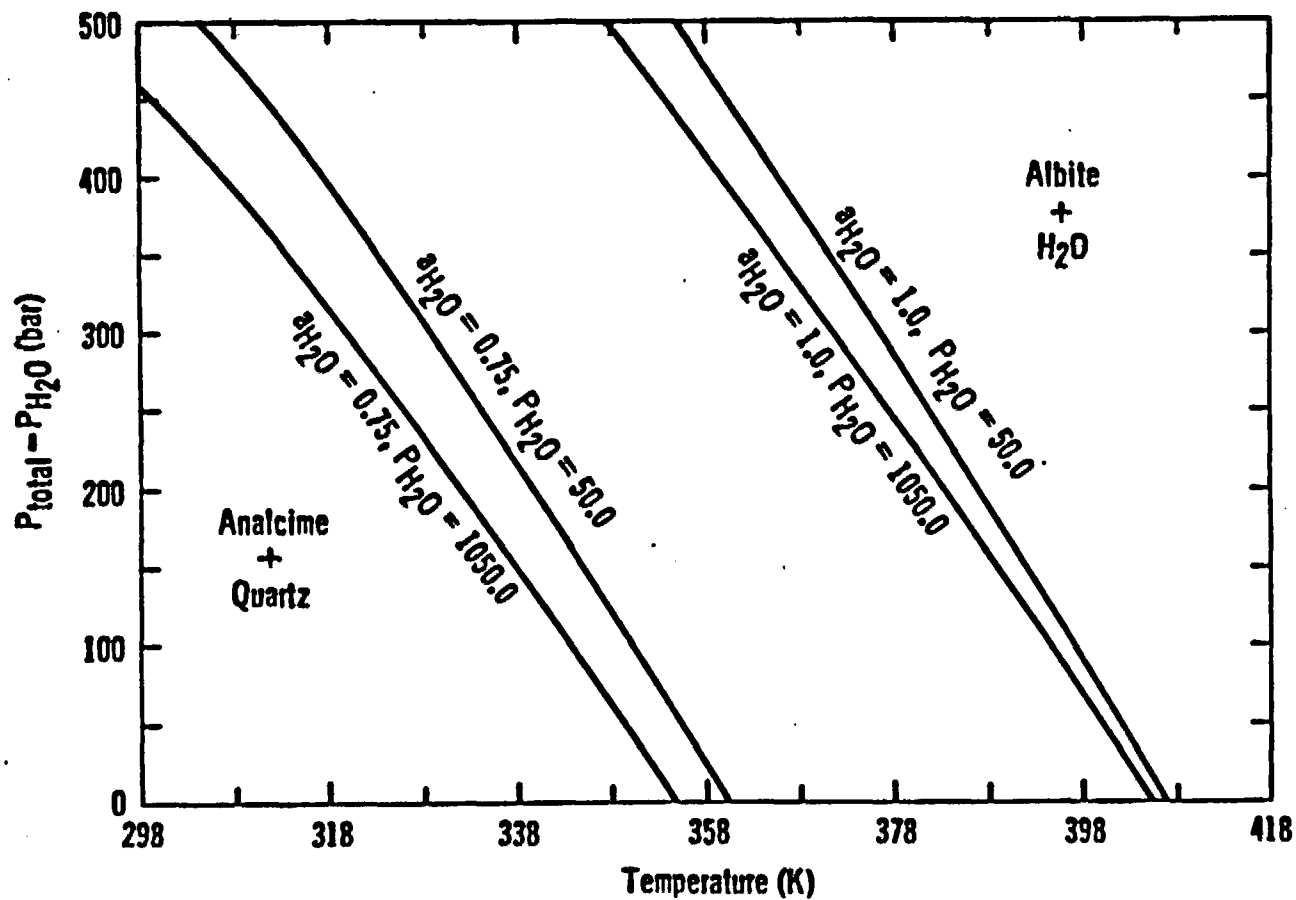
Los Alamos





EFFECT OF LITHOSTATIC MINUS WATER PRESSURE ON ANALCIME STABILITY

Los Alamos





IMPORTANT ADDITIONAL DATA NEEDED

Los Alamos

THERMODYNAMIC DATA ON CLAY AND
ZEOLITE ENDMEMBERS

THERMODYNAMICS OF CLAY AND ZEOLITE
SOLID SOLUTIONS

KNOWLEDGE OF CONTROLS ON SILICA POLYMORPH
DISSOLUTION AND PRECIPITATION



MINERAL THERMODYNAMIC MODELS

DATA NEEDED

Los Alamos

DATA

REFERENCE FREE ENERGY

HEAT CAPACITY

ENTROPY OF MIXING

VOLUME

EXPERIMENTAL TECHNIQUES

X-RAY DIFFRACTION

MAGIC ANGLE NMR

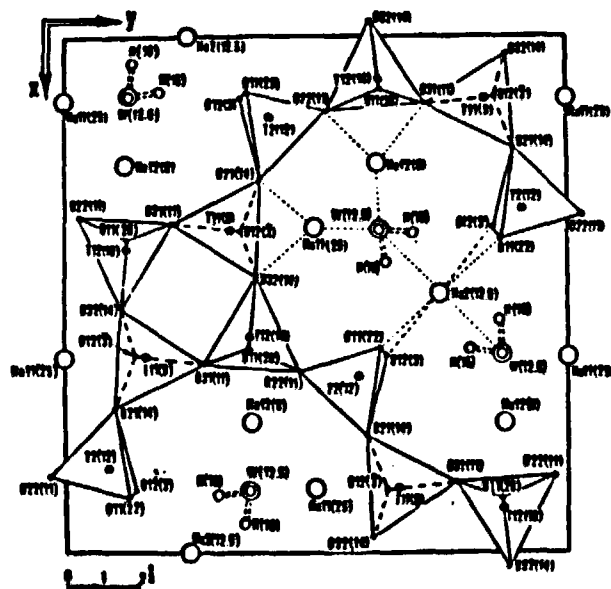
CALORIMETRY

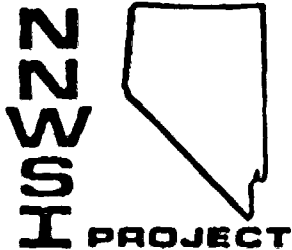
PHASE EQUILIBRIA DETERMINATIONS

SOLUBILITY MEASUREMENTS

CRYSTAL STRUCTURE OF ANALCIME

Los Alamos





ZEOLITE AND SMECTITE THERMAL STABILITY

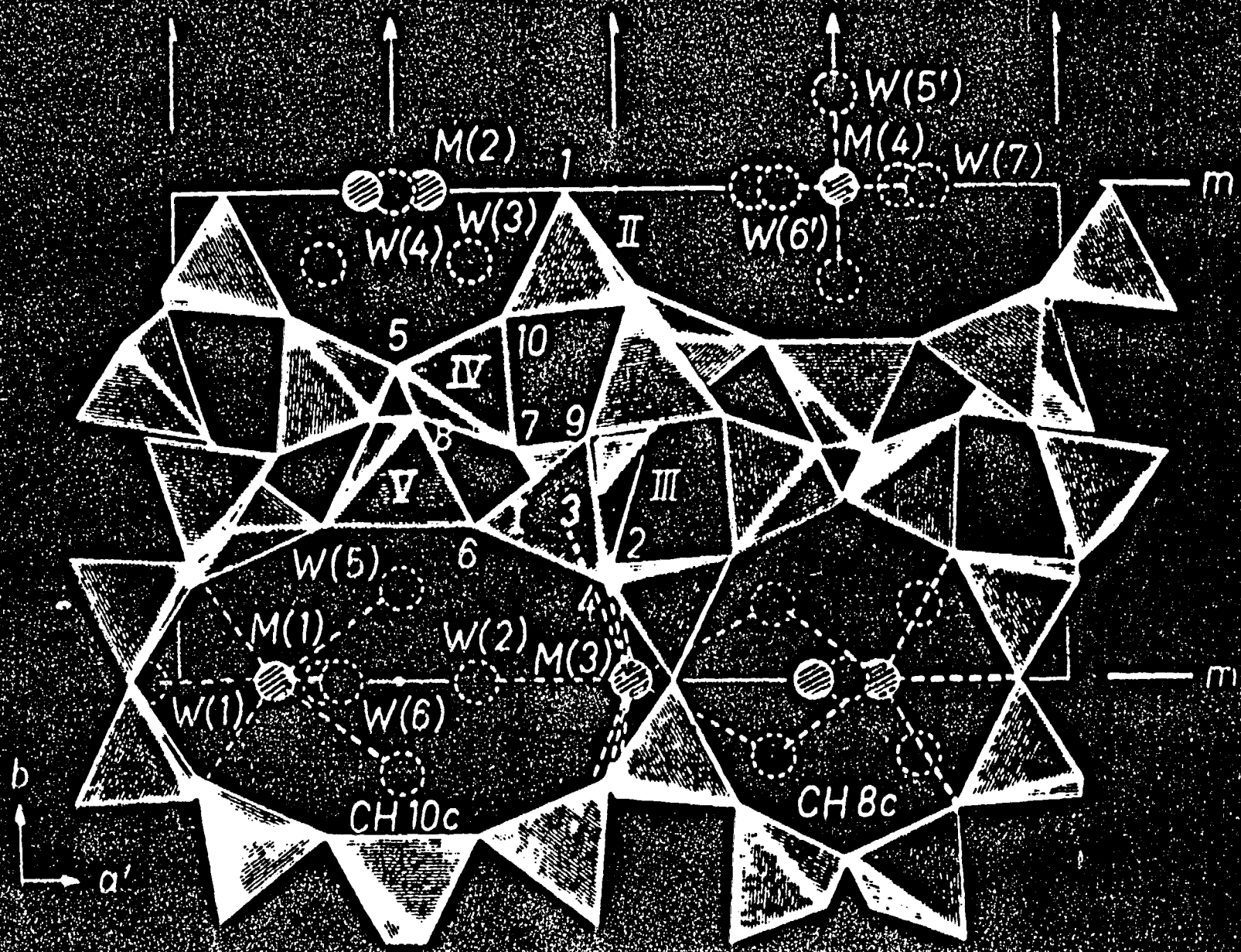
Los Alamos

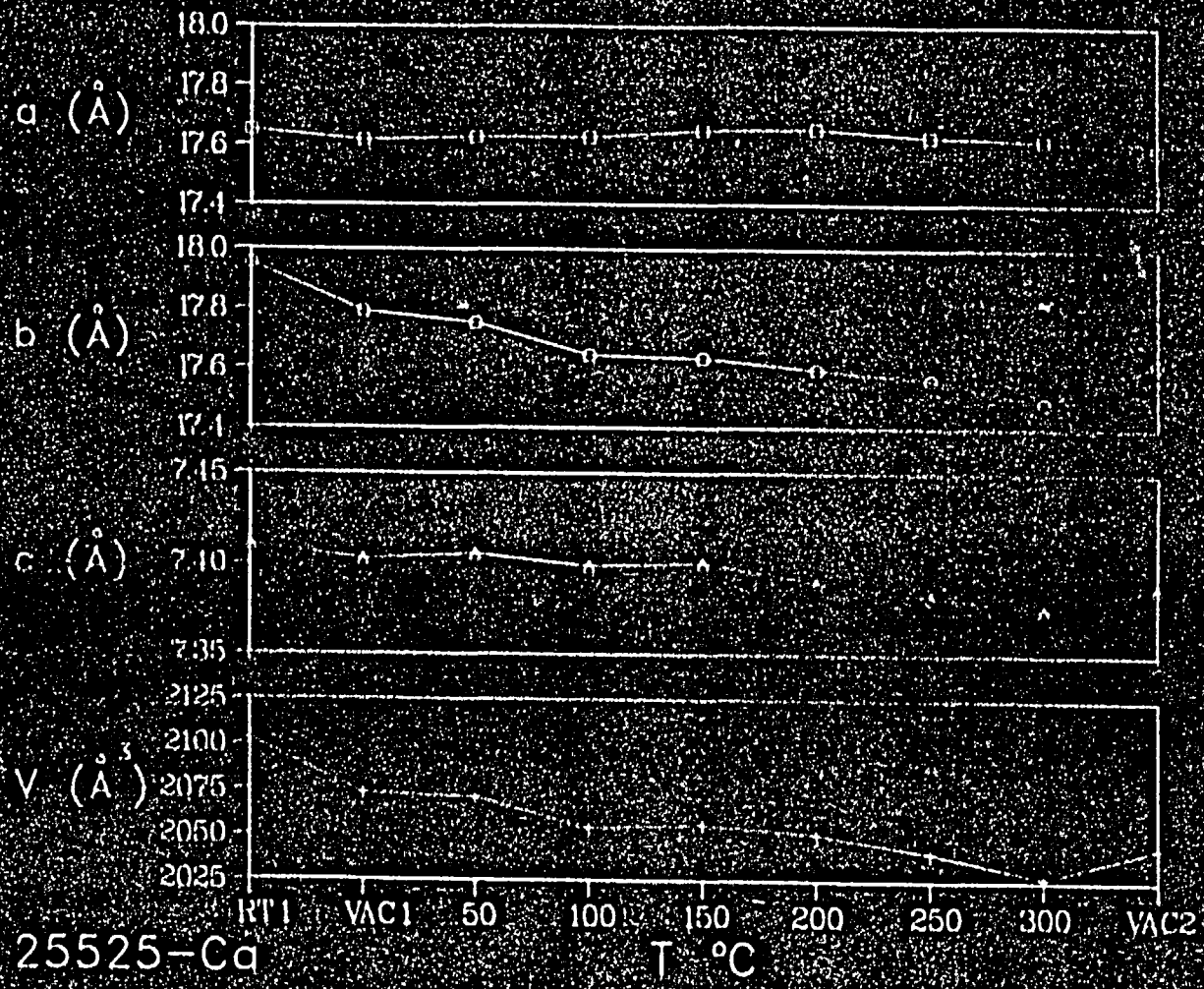
- **IMPORTANT MINERAL REACTIONS CAN OCCUR IN A PARTIALLY SATURATED ENVIRONMENT AT TEMPERATURES BELOW 200°C.**
 - **SMECTITE DEHYDRATION - IRREVERSIBLE?**
 - **CLINOPTILOLITE DEHYDRATION**
 - **GLASS DEHYDRATION**

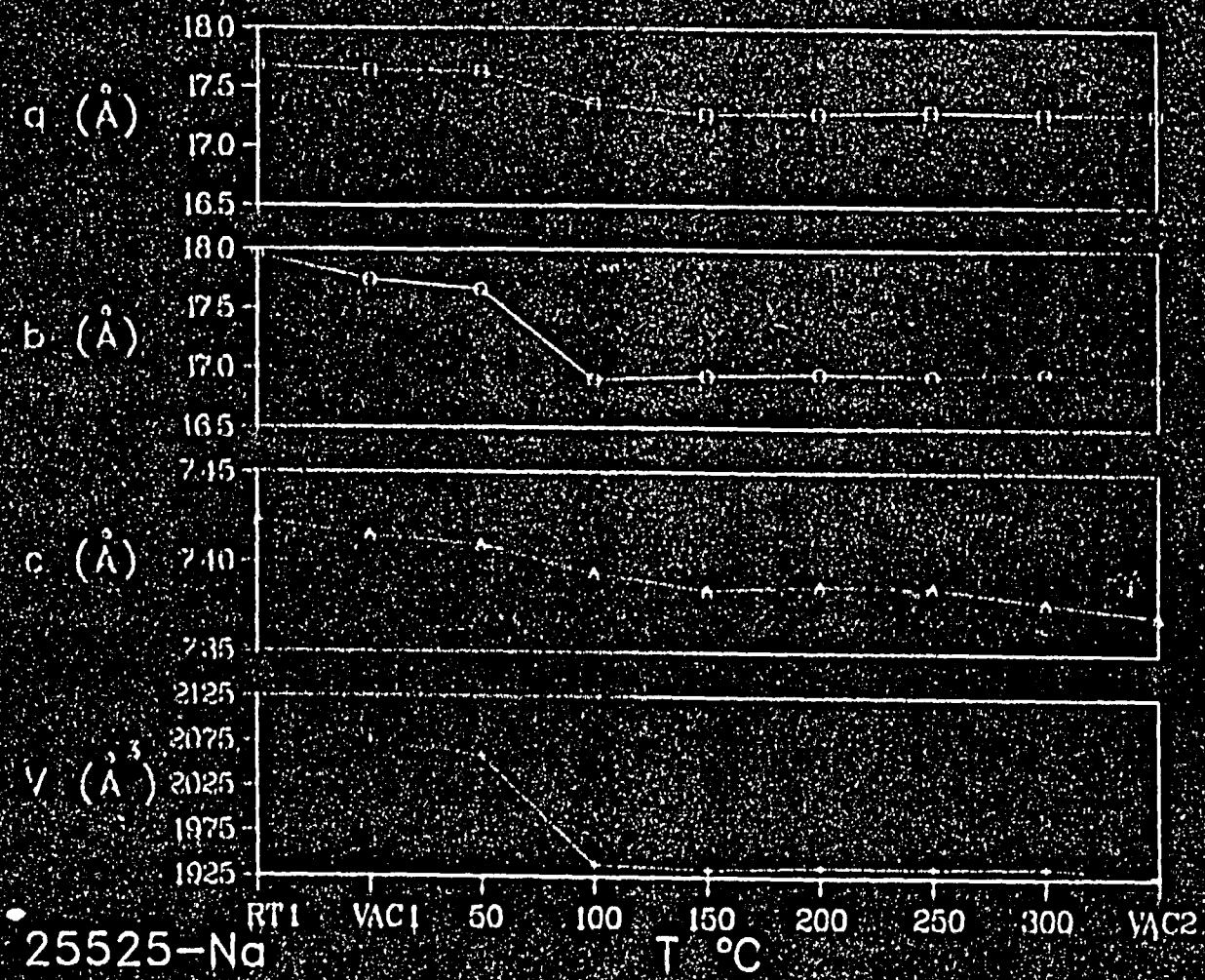
- **THESE REACTIONS WILL ONLY BE IMPORTANT IN THE NEAR FIELD BUT POTENTIALLY CAN AFFECT RETARDATION BY SORPTION AND ROCK PERMEABILITY**

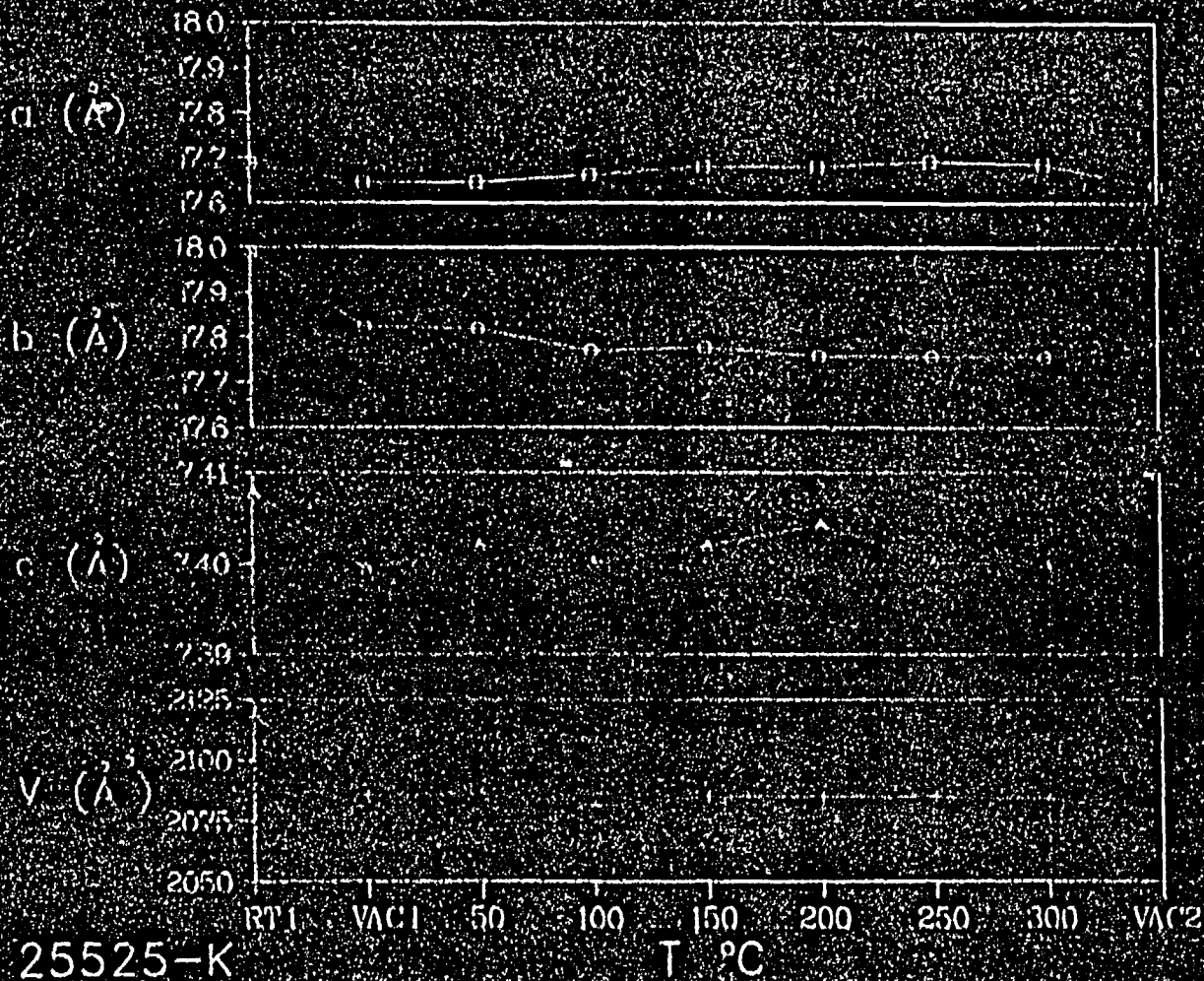
- **EXPERIMENTS CONDUCTED**
 - **EFFECTS OF HEATING ON CLINOPTILOLITE, HEULANDITE, AND MORDENITE VOLUME**
 - **DEHYDRATION BEHAVIOR OF CLINOPTILOLITES, HEULANDITE, MORDENITE, AND VOLCANIC GLASS.**
 - **KINETICS OF DEHYDRATION OF Ca-CLINOPTILOLITE**

- **EXPERIMENTS PLANNED**
 - **KINETICS OF DEHYDRATION OF CLINOPTILOLITES**
 - **EFFECT OF PH_2O ON SMECTITE AND ZEOLITE DEHYDRATION**



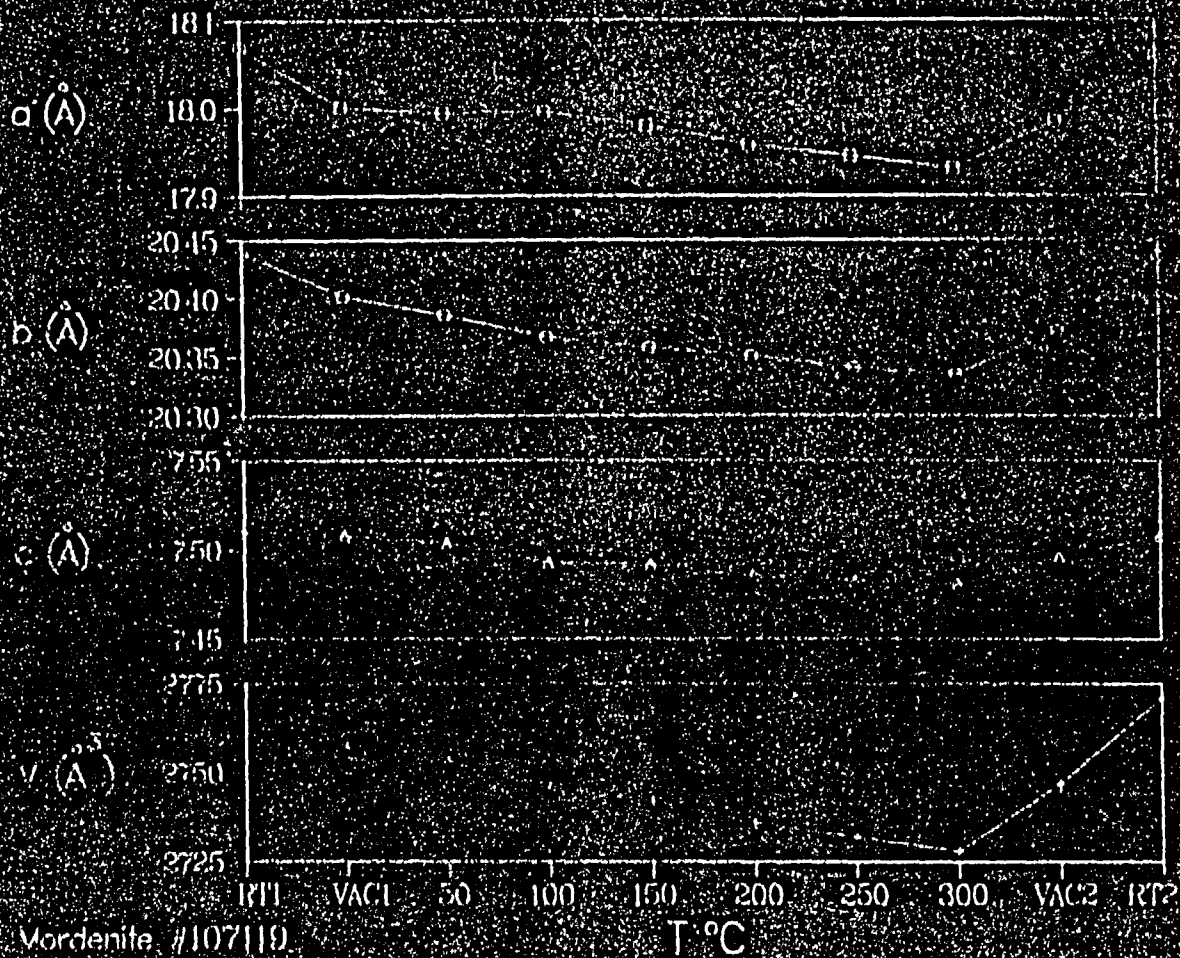


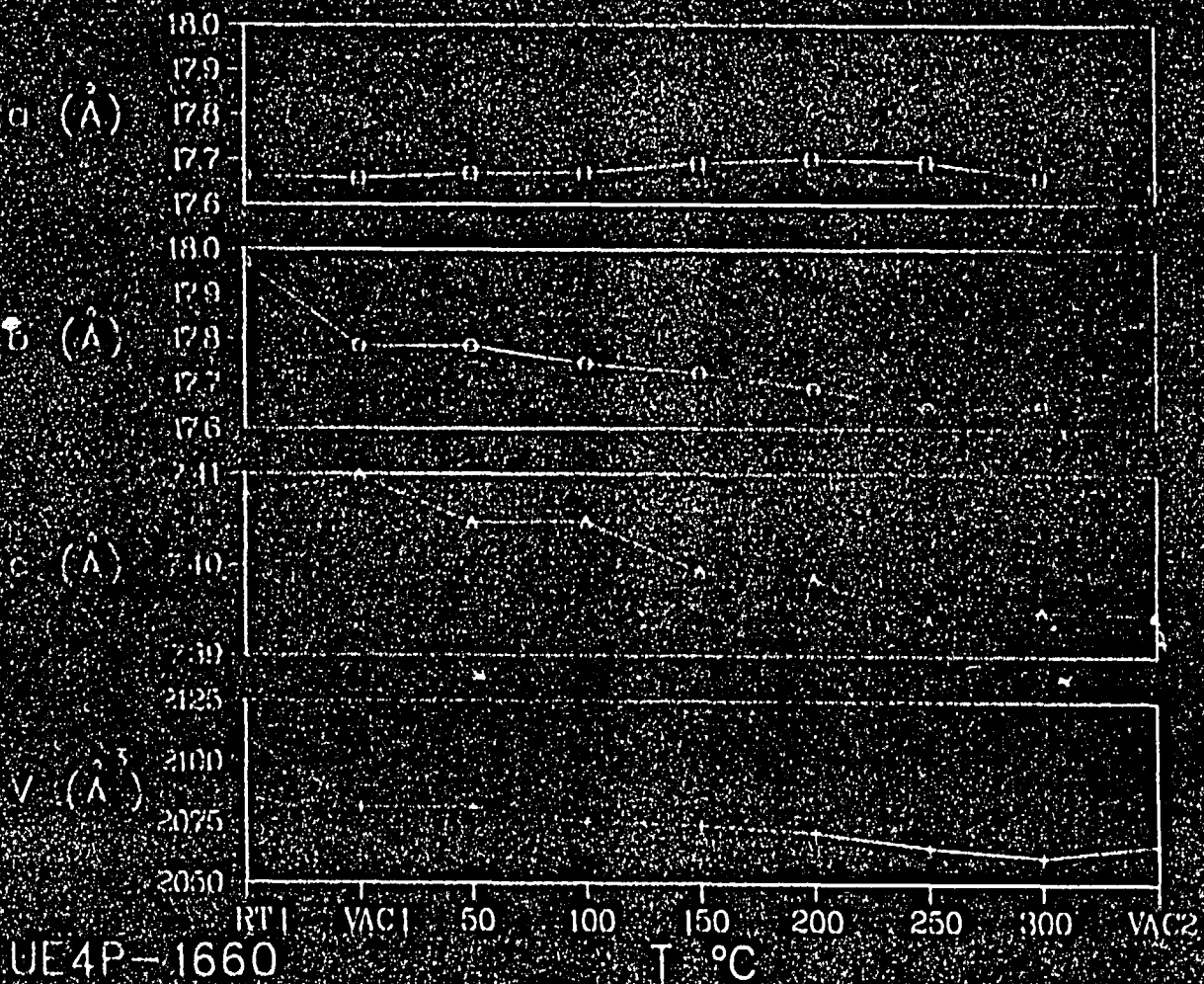


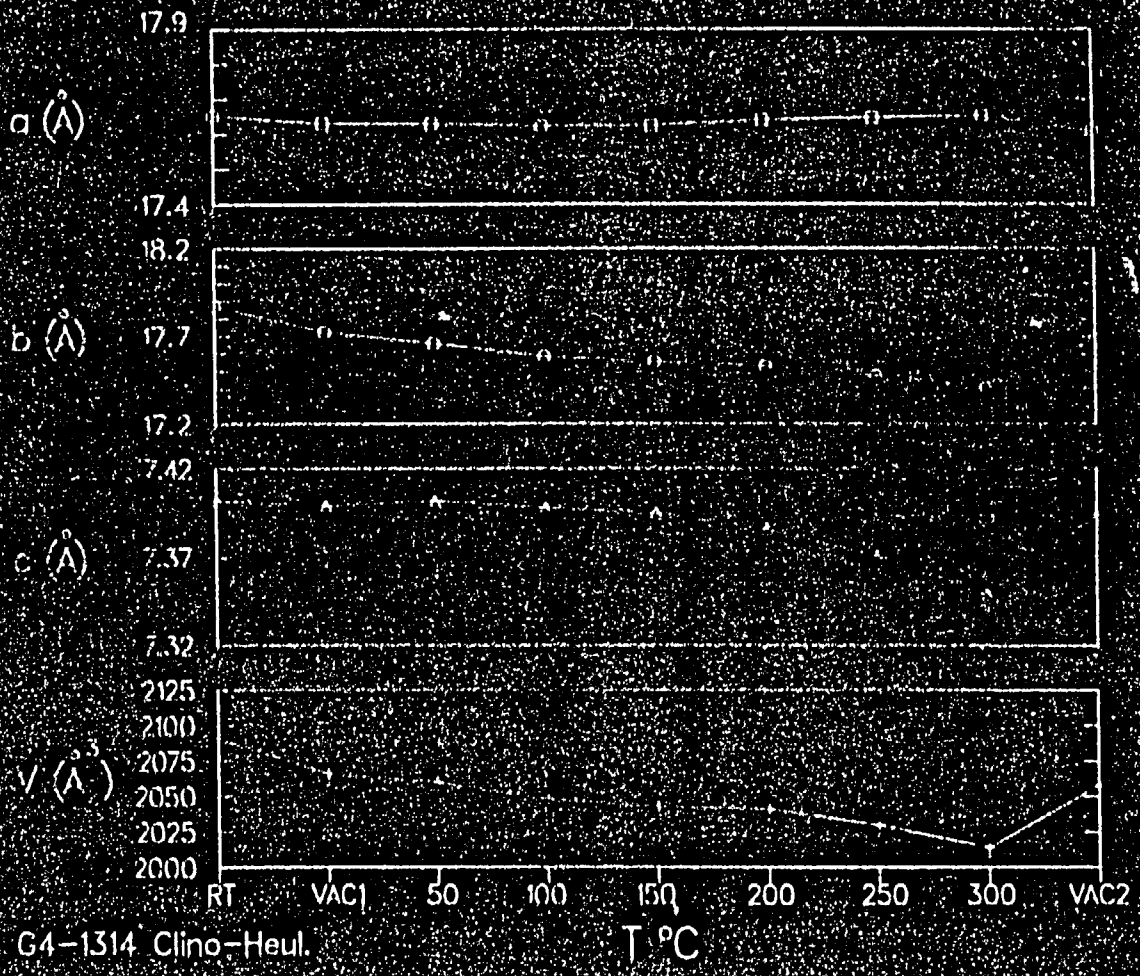


25525-K

T °C

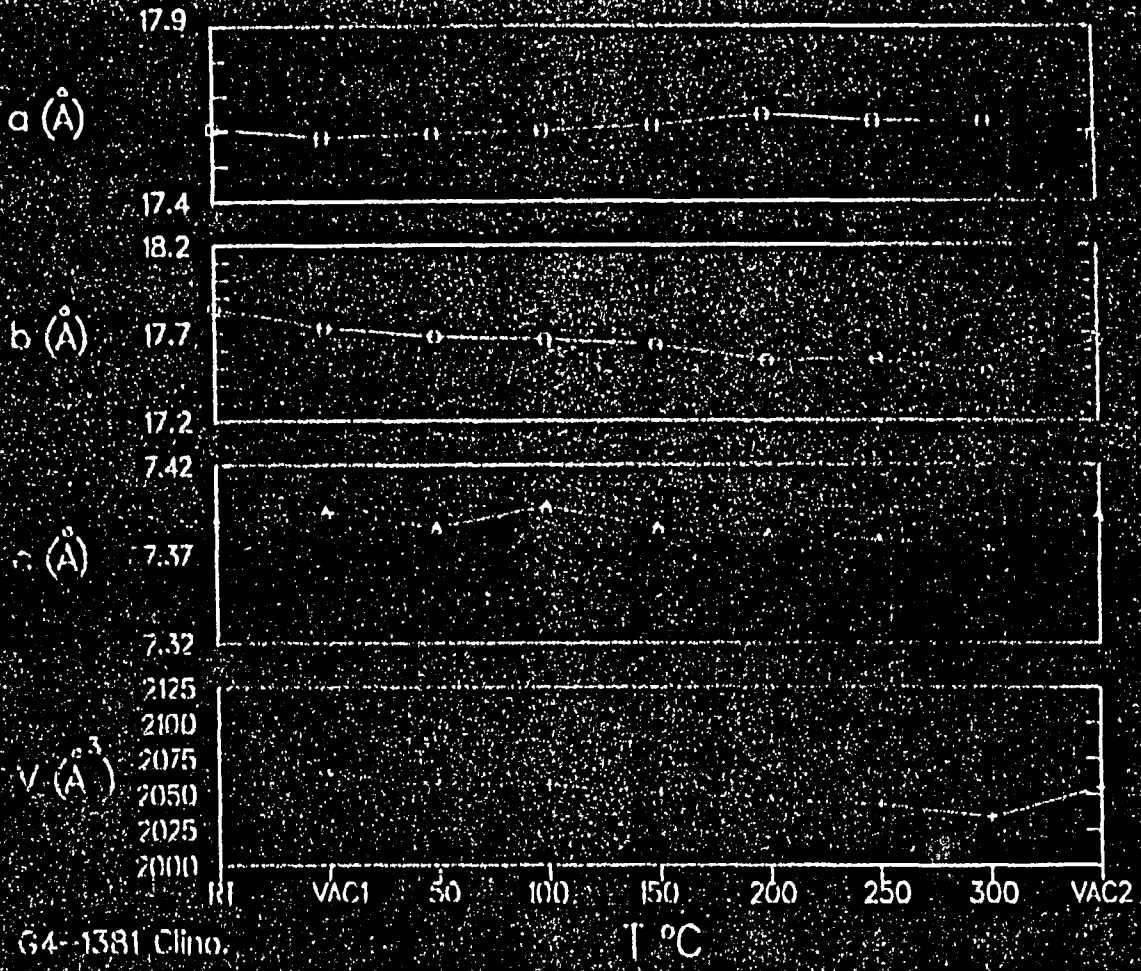






G4-1314 Clino-Heul.

T °C



G4-1381 Clino.

KEY RADIONUCLIDES AND SOLUBILITY

Key Radionuclides

Solubility Calculations

Solubility Measurements



IMPORTANT RADIONUCLIDES

Los Alamos

- * REPOSITORY INVENTORY - WHICH RADIONUCLIDES ARE PRESENT IN LARGE QUANTITIES?
- * EPA LIMITS - HOW WELL MUST DIFFERENT RADIONUCLIDES BE CONTAINED?
- * RETARDATION PROCESSES - WHICH PROCESSES AFFECT WHICH ELEMENTS?

REPOSITORY INVENTORY

(Ci/1000MTHM)

	100 yr	1000 yr	10,000 yr	100,000 yr
PWR spent fuel				
A. P.	3.21×10^5	8.40×10^3	6.40×10^3	2.47×10^3
Act.	6.79×10^6	1.72×10^6	4.43×10^5	3.87×10^4
F. P.	3.39×10^7	1.93×10^4	1.86×10^4	1.43×10^4
Total	4.10×10^7	1.75×10^6	4.68×10^5	5.55×10^4
PWR HLW				
A. P.	3.21×10^5	8.40×10^3	6.40×10^3	2.47×10^3
Act.	3.21×10^5	8.27×10^4	2.05×10^4	2.53×10^3
F. P.	3.35×10^7	1.92×10^4	1.85×10^4	1.42×10^4
Total	3.41×10^7	1.10×10^5	4.54×10^4	1.92×10^4

Los Alamos

REPOSITORY INVENTORY

Primary Radionuclides (% total activity)

	100 yr	1000 yr	10,000 yr	100,000 yr
PWR spent fuel	^{137}Cs 49%* ^{90}Sr 34%* ^{241}Am 9% ^{238}Pu 3%	^{241}Am 51% ^{240}Pu 27% ^{239}Pu 17% ^{239}Np 1%	^{239}Pu 51% ^{240}Pu 39% ^{99}Tc 3% ^{243}Am 1%	^{239}Pu 32% ^{99}Tc 17% ^{93}Zr 6%* ^{59}Ni 4%
PWR HLW	^{137}Cs 58%* ^{90}Sr 41%* ^{241}Am 0.5%	^{241}Am 38% ^{243}Am 14% ^{239}Np 14% ^{99}Tc 12%	^{99}Tc 28% ^{243}Am 15% ^{239}Np 15% ^{59}Ni 10%	^{99}Tc 49% ^{93}Zr 18%* ^{59}Ni 11% ^{239}Pu 3%

* Activity of short-lived daughters included.

Los Alamos

RADIONUCLIDES - EPA LIMITS

Cumulative release limits at 10000 yr (Ci/1000MTHM)

$^{241}\text{Am} = 100$	$^{240}\text{Pu} = 100$
$^{243}\text{Am} = 100$	$^{242}\text{Pu} = 100$
$^{14}\text{C} = 100$	$^{226}\text{Ra} = 100$
$^{135}\text{Cs} = 1000$	$^{90}\text{Sr} = 1000$
$^{137}\text{Cs} = 1000$	$^{99}\text{Tc} = 10000$
$^{237}\text{Np} = 100$	$^{126}\text{Sn} = 1000$
$^{238}\text{Pu} = 100$	other $\alpha = 100$
$^{239}\text{Pu} = 100$	other non- $\alpha = 1000$

Los Alamos

RADIONUCLIDES - OLD EPA LIMITS

Cumulative release limits at 10000 yr (Ci/1000MTHM)

$^{241}\text{Am} = 10$	$^{240}\text{Pu} = 100$
$^{243}\text{Am} = 4$	$^{242}\text{Pu} = 100$
$^{14}\text{C} = 200$	$^{226}\text{Ra} = 3$
$^{135}\text{Cs} = 2000$	$^{90}\text{Sr} = 80$
$^{137}\text{Cs} = 500$	$^{99}\text{Tc} = 10000$
$^{237}\text{Np} = 20$	$^{126}\text{Sn} = 80$
$^{238}\text{Pu} = 400$	other $\alpha = 10$
$^{239}\text{Pu} = 100$	other non- $\alpha = 500$

Los Alamos

RADIONUCLIDES - PWR SPENT FUEL

(order based on curie content/EPA limit)

100 yr	1000 yr	10,000 yr	100,000 yr
²⁴¹ Am	²⁴¹ Am	²³⁹ Pu	²³⁹ Pu
¹³⁷ Cs	²⁴⁰ Pu	²⁴⁰ Pu	²³⁴ U
⁹⁰ Sr	²³⁹ Pu	²⁴³ Am	²⁴² Pu
²³⁸ Pu	²⁴³ Am	²³⁴ U	²³⁷ Np
²⁴⁰ Pu	²³⁴ U	²⁴² Pu	²²⁶ Ra
²³⁹ Pu	²⁴² Pu	²³⁷ Np	²³⁰ Th
²⁴¹ Pu	¹⁴ C	⁵⁹ Ni	²³³ U
²⁴⁴ Cm	²³⁷ Np	¹⁴ C	²³⁶ U
⁶³ Ni	²³⁸ Pu	²³⁶ U	²²⁹ Th
²⁴³ Am	⁵⁹ Ni	²³⁸ U	²³⁸ U

Los Alamos

RADIONUCLIDES - PWR HLW

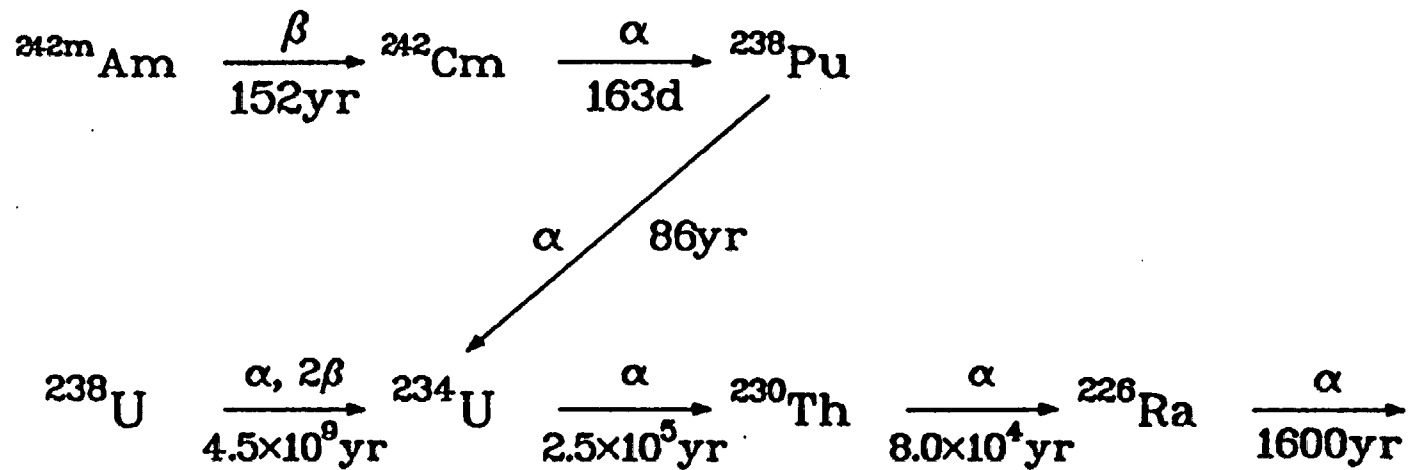
(order based on curie content/EPA limit)

100 yr	1000 yr	10,000 yr	100,000 yr
^{137}Cs	^{241}Am	^{243}Am	^{239}Pu
^{90}Sr	^{243}Am	^{239}Pu	^{237}Np
^{241}Am	^{240}Pu	^{240}Pu	^{59}Ni
^{238}Pu	^{239}Pu	^{59}Ni	^{93}Zr
^{244}Cm	^{14}C	^{237}Np	$^{93\text{m}}\text{Nb}$
^{63}Ni	^{59}Ni	^{14}C	^{233}U
^{243}Am	^{237}Np	^{93}Zr	^{229}Th
^{151}Sm	^{93}Zr	$^{93\text{m}}\text{Nb}$	^{99}Tc
^{240}Pu	$^{93\text{m}}\text{Nb}$	^{99}Tc	^{126}Sn
^{242}Cm	^{99}Tc	^{94}Nb	^{234}U

Los Alamos

RADIONUCLIDES

^{226}Ra decay scheme



Los Alamos



History

- **First created in 1975 to model hydrothermal reactions between sea water and basalt**
- **Present development is focused on interactions in geologic disposal of nuclear waste**

Calculate

- **Chemical speciation (simple ions and complexes) in aqueous solutions**
- **Thermodynamic equilibrium in rock/water systems**
- **Progress of reacting rock/water systems (kinetic model)**

Status

- **Operational in current mode at LLNL, other national laboratories, universities, and industry**
- **We are continuing to improve these codes and extend their capabilities**

Current status of geochemical modeling in nuclear waste management



- **The importance of using geochemical codes to make long-term predictions of radionuclide migration is well established.**
- **EQ3/6 is the geochemical code now being upgraded for use by the Nevada Nuclear Waste Storage Investigations (NNWSI) and Office of Nuclear Waste Isolation (ONWI) Programs.**
- **Geochemical modeling task plans for both the tuff (NNWSI) and salt (ONWI) programs have been developed.**
- **The current geochemical modeling work includes code and data base development tasks, but does NOT include basic research.**

EQ3/6 IS A CODE PACKAGE CONSISTING OF

- EQ3NR - SPECIATION-SOLUBILITY CODE
- EQ6 - REACTION-PATH CODE
- MCRT - THERMODYNAMIC DATA PROCESSOR
- DATA FILES
- DATA FILE PREPROCESSORS
- EQ6 GRAPHICS POSTPROCESSOR

STATUS OF EQ3/6 DOCUMENTATION

- EQ3NR USER'S GUIDE (1983)
- EQ6 USER'S GUIDE (IN REVISION, TBP 1984)
- EQ3/6 BRINE MODIFICATIONS (IN REVISION, TBP 1984)
- MCRT USER'S GUIDE (NO DRAFT YET, TBP 1984)
- EQ6 GRAPHICS GUIDE (1ST DRAFT, TBP 1984)
- EQ6 FIXED FUGACITY (IN REVISION, TBP 1984)
- EQ6 PPTN KINETICS (IN PREPARATION, TBP 1984)

EQ3/6 VERSION 3245 IS NOW UNDER DEVELOPMENT

IMPROVEMENTS INCLUDE

- BRINE MODELING CAPABILITY
(PITZER'S EQUATIONS)
- "ECONOMY" MODE FOR SOME EQ6 CALCULATIONS
- PRECIPITATION KINETICS
(SIMPLE TREATMENT AT PRESENT)
- FULLY DOCUMENTED THERMODYNAMIC DATA FILE

EQ3NR - A MULTI-OPTION SPECIATION-SOLUBILITY CODE

- MODELS THE THERMODYNAMIC STATE OF AN AQUEOUS SOLUTION

- TYPICAL INPUTS
 - PH, OTHER SPECIFIC ION ELECTRODE MEASUREMENTS
 - EH (NOT RECOMMENDED)
 - TOTAL CONCENTRATIONS
 - ELECTRICAL BALANCE (ADJUST SPECIFIED ION)
 - SOLUBILITY EQUILIBRIA (ASSUMPTIONS)
 - GAS EQUILIBRIA (ASSUMPTIONS)

- TYPICAL OUTPUTS
 - PH
 - REDOX POTENTIALS
 - FREE CONCENTRATIONS
 - TOTAL CONCENTRATIONS
 - DEGREE OF ELECTRICAL IMBALANCE
 - SATURATION INDICES
 - A MODEL OF THE WATER TO FEED TO EQ6

EQ6 - A MULTI-OPTION REACTION PATH CODE

- MODELS THE PATH OF A REACTING AQUEOUS SYSTEM
(EXAMPLE: WATER + ROCK)

- NON-EQUILIBRIUM MASS TRANSFER IS TREATED BY EITHER
 - SIMPLE TITRATION (OLD)
 - KINETIC RATE LAWS (NEW)

- PREDICTS EVOLUTION OF FLUID COMPOSITION AND
FORMATION OF SECONDARY SOLIDS

- TEMPERATURE CAN BE CONSTANT OR VARIABLE

EQ6 MODELS MORE THAN ONE KIND OF PHYSICAL SYSTEM

- **ZERO-DIM: CLOSED SYSTEM, THERMODYNAMICALLY HOMOGENEOUS
(GOOD MATCH TO ROCKING DICKSON AUTOCLAVES)**
- **PSEUDO-ONE-DIM: FLOW-THROUGH OPEN SYSTEM, FOLLOWS A PACKET OF WATER**
- **PSEUDO-ONE-DIM: FLOW-THROUGH OPEN SYSTEM, FOCUSED ON A FIXED VOLUME
(E.G., A FLOW-THROUGH LEACHING CELL) - PLANNED**
- **ONE-DIM: FEASIBLE BUT NOT PLANNED**

EQ3/6 code development tasks planned for the NNWSI (tuff) and ONWI (salt) Programs, 1984 to 1988



1. Precipitation Kinetics

Complements the existing EQ6 capability to model dissolution kinetics. Will eventually be expanded to include second-order effects and nucleation phenomena.

2. Fixed Fugacity Option

Allows us to model systems open to gases; especially the unsaturated zone, which contains a large reservoir of CO₂ and O₂.

3. Sorption

Our eventual goal is the capability to model complex sorption isotherms, sorption kinetics and non-equilibrium sorption processes which control radionuclide migration.

Code development tasks (continued)



4. Redox Disequilibrium and Kinetics

Allows us to model systems where redox couples are not in equilibrium with each other. Redox kinetics will be incorporated into EQ6 for modeling corrosion experiments.

5. Glass/Water Interactions Model

To model waste glass leaching, code modifications will be needed to account for the effect of diffusion, the development of an alteration layer and other effects.

6. Radiolysis

Allows us to model the effect of radiolysis products on leaching, corrosion and other processes operating in the waste package environment.

Code development tasks (continued)



7. Site-Mixing Concept

Solid solutions are now represented in EQ3/6 as percentages of end-member components. To model reactions involving clays and zeolites, a more sophisticated approach such as the site-mixing concept is needed.

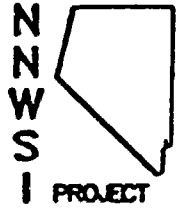
Other Tasks That May Be Included

1. Geochemical Flow Model

May be needed to model flow-through leaching experiments.

2. Isotopic Fractionation

May be needed to model the preferential substitution of one isotope for another of the same element in a solid or aqueous phase.



RETARDATION PROCESSES

Los Alamos

- * SOLUBILITY
WHICH ELEMENTS HAVE LOW SOLUBILITY?
HOW WILL SOLUBILITY LIMIT TRANSPORT?

- * SORPTION
WHICH ELEMENTS HAVE HIGH K_d ?

- * PHYSICAL PROCESSES

- * RETARDATION OF GASES OR VAPORS
 ^{14}C , ^{129}I , VOLATILE OXIDES



EXPERIMENTAL MEASUREMENTS

Los Alamos

- * SORPTION - U, Pu, Np, Am, Th, Ba, Ra, Cs, Sr, Tc, Sn, Se, Ce, Eu, I, Pr.
- * SOLUBILITY AND SPECIATION - Pu, Am, Np.



SOLUBILITY AND SPECIATION

Los Alamos

- * DETERMINATION OF SOLUBILITY
 - CALCULATIONS.
 - MEASUREMENTS.

- * USE OF SOLUBILITY DATA
 - RADIONUCLIDE DISSOLUTION MODELS.



SOLUBILITY AND SPECIATION

Los Alamos

- * DEVELOP A THERMODYNAMIC DATA BASE FOR WASTE ELEMENTS.**

- * CALCULATE SOLUBILITY AND SPECIATION IN WATER AT YUCCA MOUNTAIN.**

- * VALIDATE MODEL BY COMPARASON WITH EXPERIMENTS.**

- * USE EMPIRICAL SOLUBILITY DATA WHERE NECESSARY.**



SOLUBILITY AND SPECIATION

Los Alamos

SOLUBILITY AND SPECIATION CALCULATIONS WITH EQ3/6

- * THREE WATERS - J-13, UE25p-1,
AND H-3.
- * SIX ELEMENTS - U, Pu, Am,
Sr, Ra, AND Tc.

WATER COMPOSITIONS

	J-13	UE25p-1	H-3
Na ⁺ (mm/l)	1.96	7.43	5.39
K ⁺ (mm/l)	0.14	0.34	0.04
Ca ²⁺ (mm/l)	0.29	2.19	0.02
Mg ²⁺ (mm/l)	0.07	1.31	0.00
SiO ₂ (aq) (mm/l)	1.07	0.62	0.60
CO ₃ ²⁻ (total) (mm/l)	2.81	16.1	4.04
Cl ⁻ (mm/l)	0.18	1.04	0.23
SO ₄ ²⁻ (mm/l)	0.19	1.34	0.32
F ⁻ (mm/l)	0.11	0.18	0.28
pH	7.0	6.7	9.4
Eh (mV)	700	360	-143

Los Alamos

URANIUM

	J-13	UE25p-1	H-3
Solub. (m/l)	3.65×10^{-3}	1.74×10^{-3}	4.05×10^{-8}
Solid	Schoepite	Rutherfordine	Uraninite
Primary Aqueous Species	$(\text{UO}_2)_2\text{CO}_3(\text{OH})_3^-$ (98%) $\text{UO}_2(\text{CO}_3)_2^{2-}$ (1%)	$\text{UO}_2(\text{CO}_3)_2^{2-}$ (54%) $(\text{UO}_2)_2\text{CO}_3(\text{OH})_3^-$ (31%) $\text{UO}_2(\text{CO}_3)_3^{4-}$ (13%) UO_2CO_3 (2%)	$\text{UO}_2(\text{CO}_3)_3^{4-}$ (86%) $\text{U}(\text{OH})_5^-$ (8%) $\text{UO}_2(\text{CO}_3)_2^{2-}$ (7%)

Los Alamos

PLUTONIUM

	J-13	UE25p-1	H-3
Solub. (m/l)	1.79×10^{-6}	3.11×10^{-8}	1.33×10^{-5}
Solid	$\text{Pu}(\text{OH})_4$	$\text{Pu}(\text{OH})_4$	$\text{Pu}(\text{OH})_4$
Primary Aqueous Species	PuO_2^+ (71%) PuO_2F_3^- (20%) $\text{Pu}(\text{OH})_5^-$ (3%) $\text{PuO}_2(\text{CO}_3)_2^{2-}$ (2%) $\text{PuO}_2\text{F}_4^{2-}$ (2%)	$\text{Pu}(\text{OH})_5^-$ (94%) $\text{Pu}(\text{OH})_4$ (6%)	$\text{Pu}(\text{OH})_5^-$ (100%)

Los Alamos

AMERICIUM

	J-13	UE25p-1	H-3
Solub. (m/l)	9.87×10^{-9}	2.16×10^{-8}	6.85×10^{-10}
Solid	$\text{Am}(\text{OH})\text{CO}_3$	$\text{Am}(\text{OH})\text{CO}_3$	$\text{Am}(\text{OH})\text{CO}_3$
Primary Aqueous Species	AmCO_3^+ (80%) AmOH^{2+} (8%) AmF^{2+} (4%) Am^{3+} (3%) $\text{Am}(\text{CO}_3)_2^-$ (3%)	AmCO_3^+ (83%) $\text{Am}(\text{CO}_3)_2^-$ (6%) AmF^{2+} (4%) AmSO_4^+ (2%) AmOH^{2+} (2%) Am^{3+} (2%)	$\text{Am}(\text{CO}_3)_2^-$ (46%) $\text{Am}(\text{OH})_3$ (36%) $\text{Am}(\text{OH})_2^+$ (12%) AmCO_3^+ (5%)

Los Alamos

STRONTIUM

	J-13	UE25p-1	H-3
Solub. (m/l)	8.04×10^{-4}	5.27×10^{-4}	3.28×10^{-6}
Solid	Strontianite	Strontianite	Strontianite
Primary Aqueous Species	Sr^{2+} (96%) SrSO_4 (4%)	Sr^{2+} (86%) SrSO_4 (14%)	Sr^{2+} (96%) SrSO_4 (4%)

Los Alamos

RADIUM

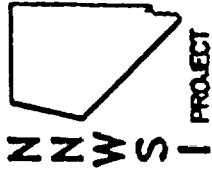
	J-13	UE25p-1	H-3
Solub. (m/l)	3.39×10^{-7}	9.29×10^{-8}	2.94×10^{-7}
Solid	RaSO_4	RaSO_4	RaSO_4
Primary Aqueous Species	Ra^{2+} (99%)	Ra^{2+} (99%)	Ra^{2+} (99%)

Los Alamos

TECHNETIUM

	J-13	UE25p-1	H-3
Solub. (m/l)	Large	Large	2.06×10^{-12}
Solid	----	----	Tc_3O_4
Primary Aqueous Species	TcO_4^- (100%)	TcO_4^- (100%)	TcO_4^- (91%) $\text{TcO}(\text{OH})_2$ (9%)

Los Alamos



RADIONUCLIDE DISSOLUTION

Los Alamos

- * ASSESS THE IMPORTANCE OF SOLUBILITY IN LIMITING RADIONUCLIDE DISSOLUTION
(LA-9995-MS).
- * TWO DISSOLUTION MODELS:
 - SATURATION LIMITED.
 - DIFFUSION LIMITED.



RADIONUCLIDE DISSOLUTION

Los Alamos

SATURATION-LIMITED MODEL

- * WATER FLOW THROUGH THE REPOSITORY IS SATURATED WITH WASTE ELEMENTS.
- * SIMPLE.
- * CONSERVATIVE.

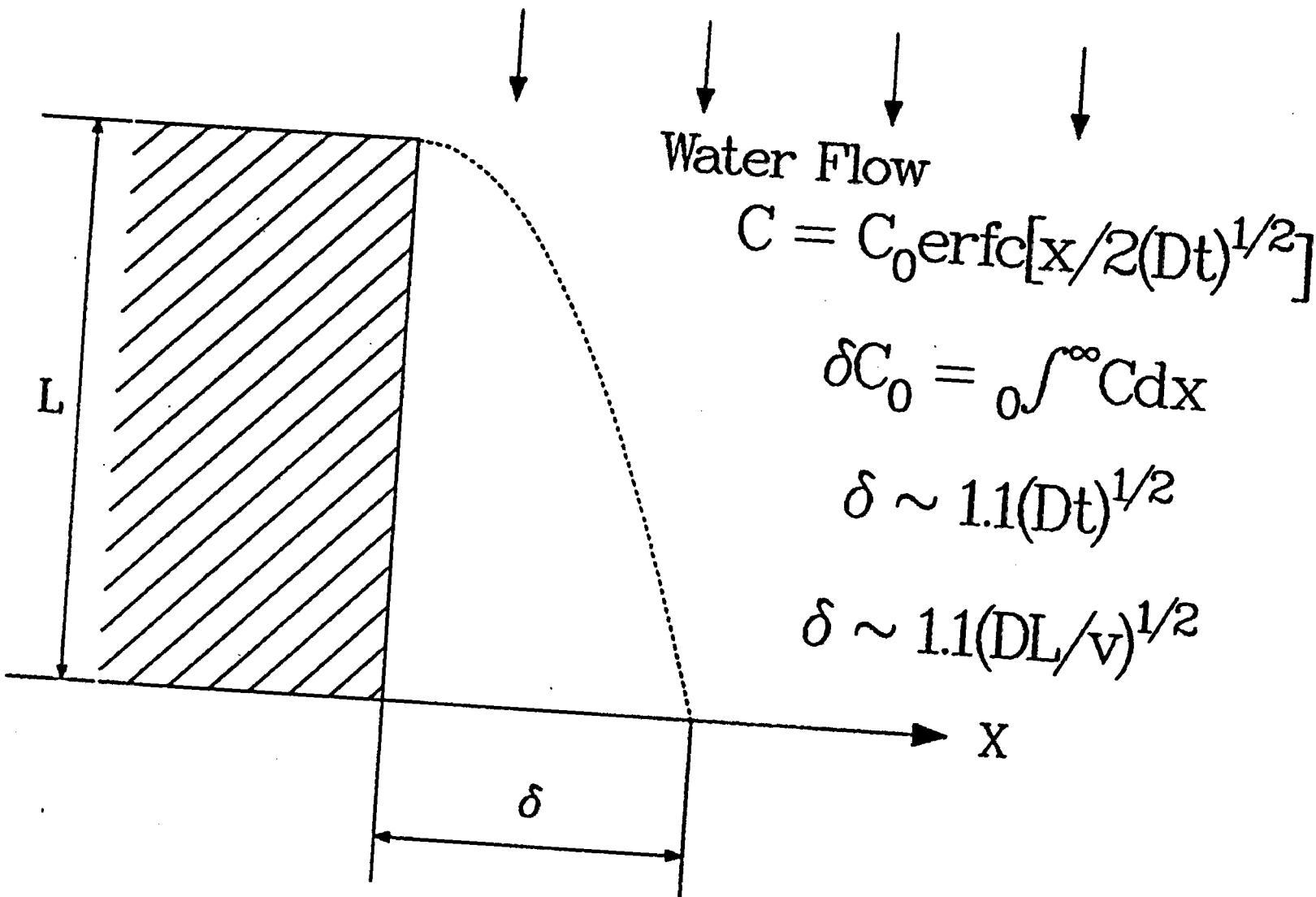


RADIONUCLIDE DISSOLUTION

Los Alamos

DIFFUSION-LIMITED MODEL

- * DIFFUSION OF WASTE ELEMENTS INTO WATER FLOWING PAST WASTE LIMITS DISSOLUTION.
- * WASTE ELEMENTS SATURATED AT WATER/WASTE INTERFACE.
- * COMPLEX.
- * REALISTIC.



Los Alamos

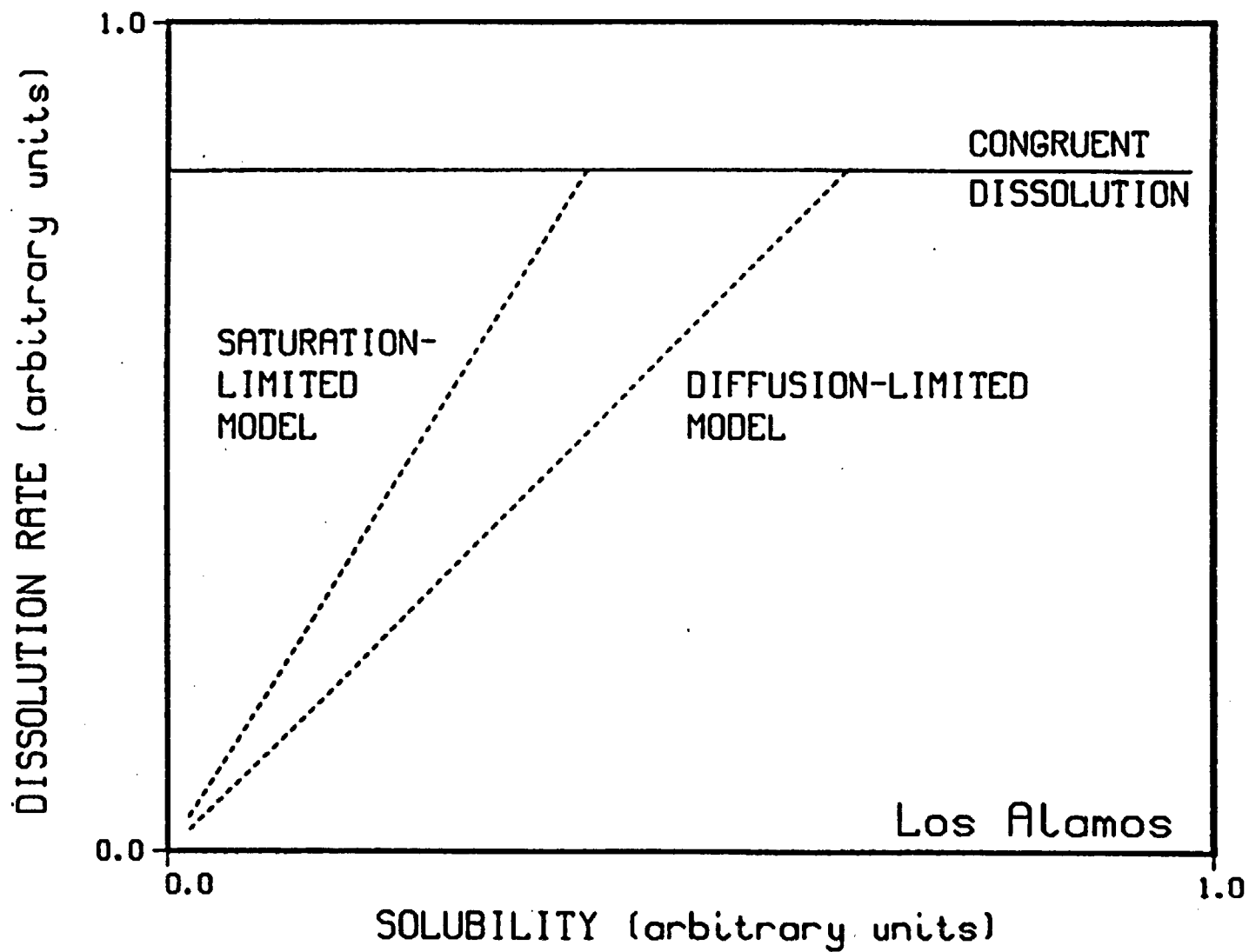


RADIONUCLIDE DISSOLUTION

Los Alamos

- * COMPARE SOLUBILITY-LIMITED DISSOLUTION WITH BULK WASTE-FORM DISSOLUTION.
- * ELEMENTS WITH A DISSOLUTION RATE LESS THAN THE BULK FRACTIONAL DISSOLUTION RATE ARE LIMITED BY SOLUBILITY.
- * ELEMENTS WITH A DISSOLUTION RATE GREATER THAN THE BULK FRACTIONAL DISSOLUTION RATE ARE LIMITED BY BULK WASTE DISSOLUTION.

DISSOLUTION RATE VS SOLUBILITY



RADIONUCLIDE DISSOLUTION

Waste element solubilities (m/l)
(oxidizing conditions in Well J-13 water)

Am = 1.0×10^{-8}	Cs = large
Pu = 1.8×10^{-6}	Tc = large
U = 2.1×10^{-4}	Np = 3.0×10^{-3}
Sr = 9.4×10^{-4}	Ra = 1.0×10^{-7}
C = large	Sn = 1.0×10^{-9}

Los Alamos

RADIONUCLIDE DISSOLUTION

NOMINAL MODEL PARAMETERS

Recharge rate = 8 mm/yr.

Repository area = 114 m²/MTHM.

Water flow = 910 l/MTHM yr.

Bulk dissolution rate = 1.0×10^{-4} /yr.

Rock porosity = 10 %.

Water velocity = 8.0×10^{-2} m/yr.

Diffusion coef. = 1.0×10^{-10} m²/yr.

L = 4.5 m (SF) or 3.0 m (HLW).

Los Alamos



RADIONUCLIDE DISSOLUTION

Los Alamos

SOLUBILITY-LIMITED DISSOLUTION

* SPENT FUEL:

SLM - U, Pu, Am, Sn.

DLM - U, Pu, Am, Sn, Ra.

* HIGH LEVEL WASTE:

SLM - Am, Sn.

DLM - U, Pu, Am, Sn.

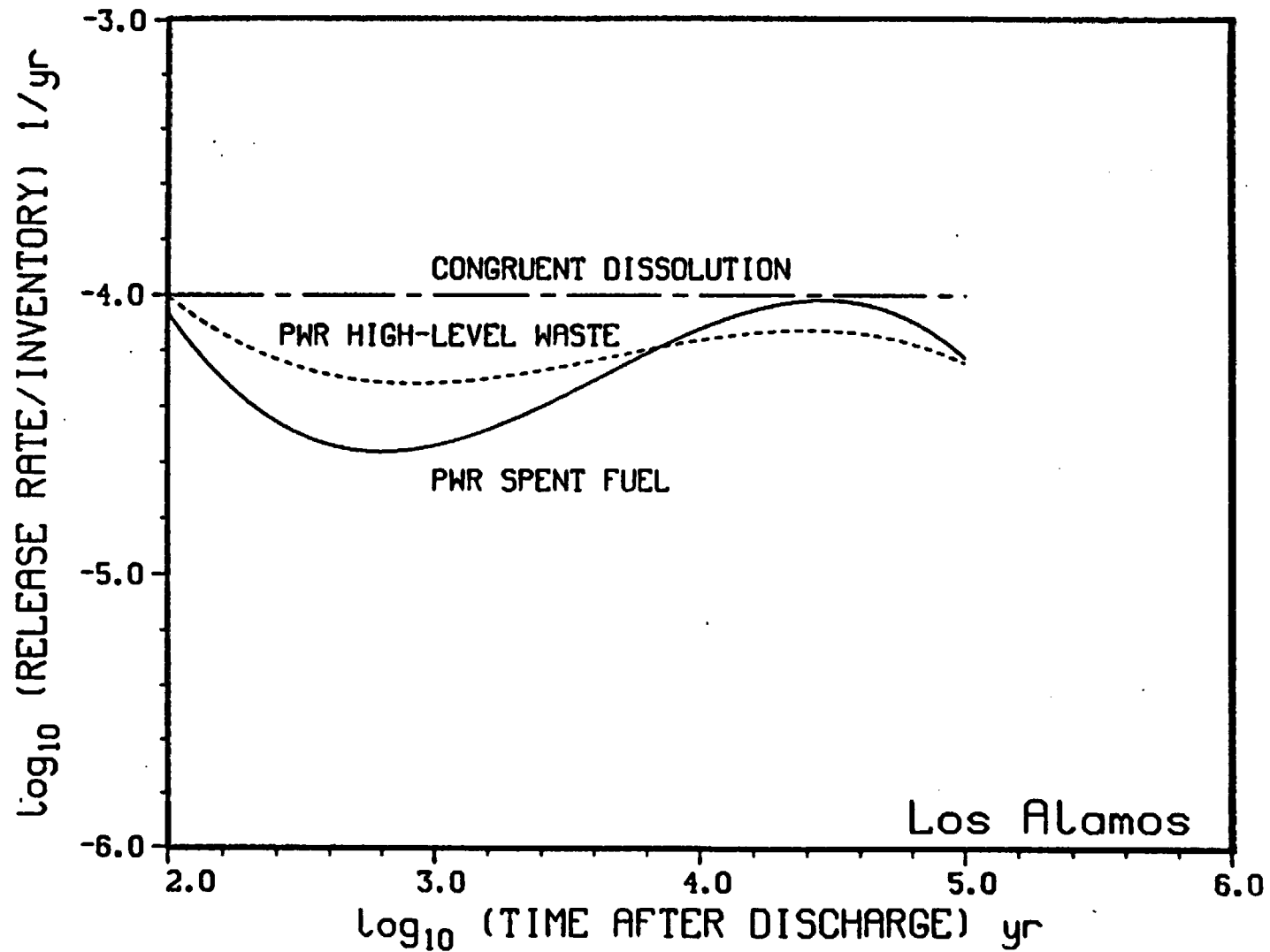


RADIONUCLIDE DISSOLUTION

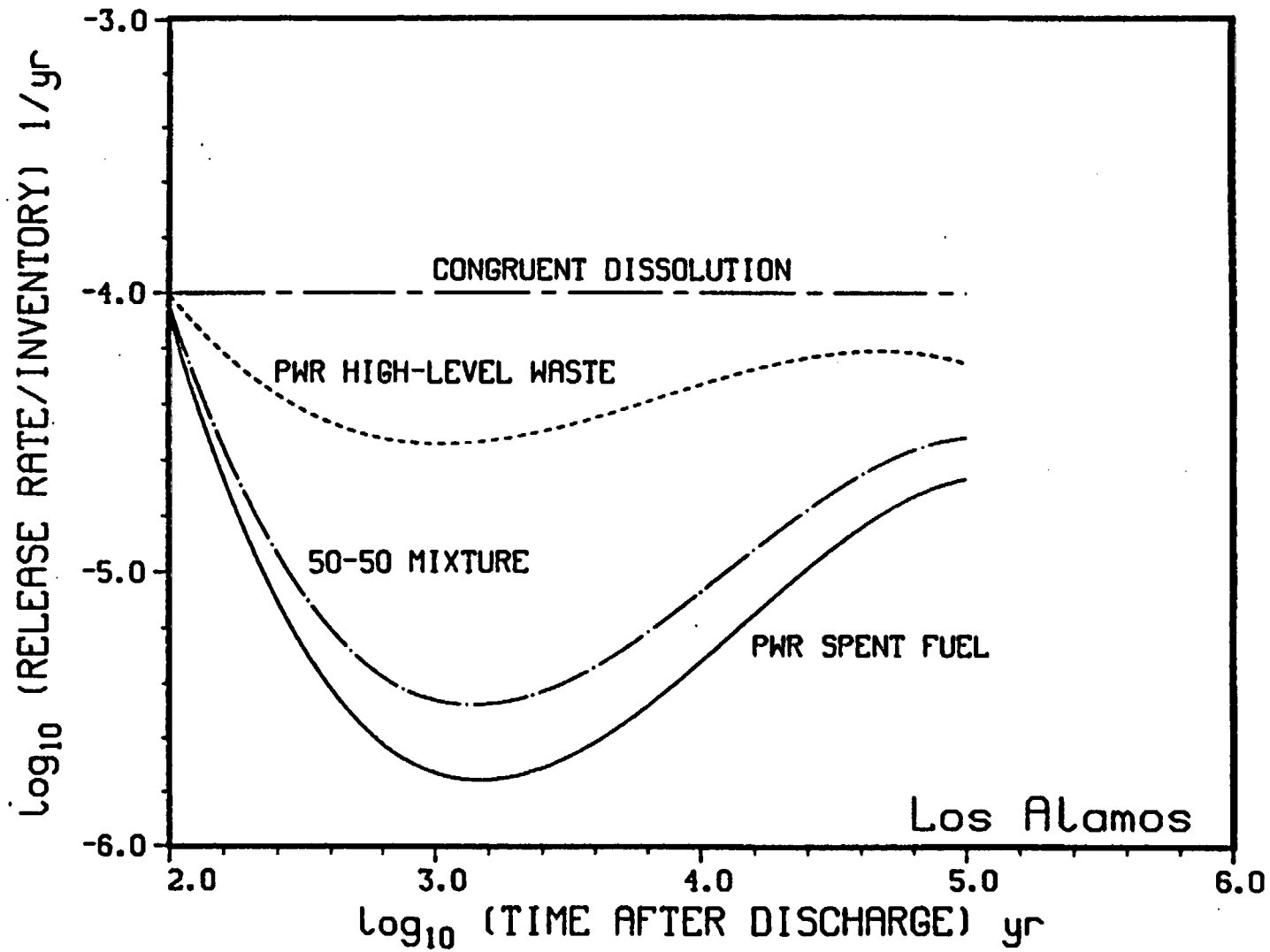
Los Alamos

- * OVERALL MEASURE OF THE EFFECT OF SOLUBILITY IS THE RATIO OF THE RELEASE RATE OF RADIOACTIVITY (Ci/MTHM yr) TO THE REPOSITORY INVENTORY (Ci/MTHM).
- * COMPARE SOLUBILITY-LIMITED DISSOLUTION WITH BULK WASTE DISSOLUTION.

SATURATION-LIMITED RADIOACTIVITY RELEASE



DIFFUSION-LIMITED RADIOACTIVITY RELEASE





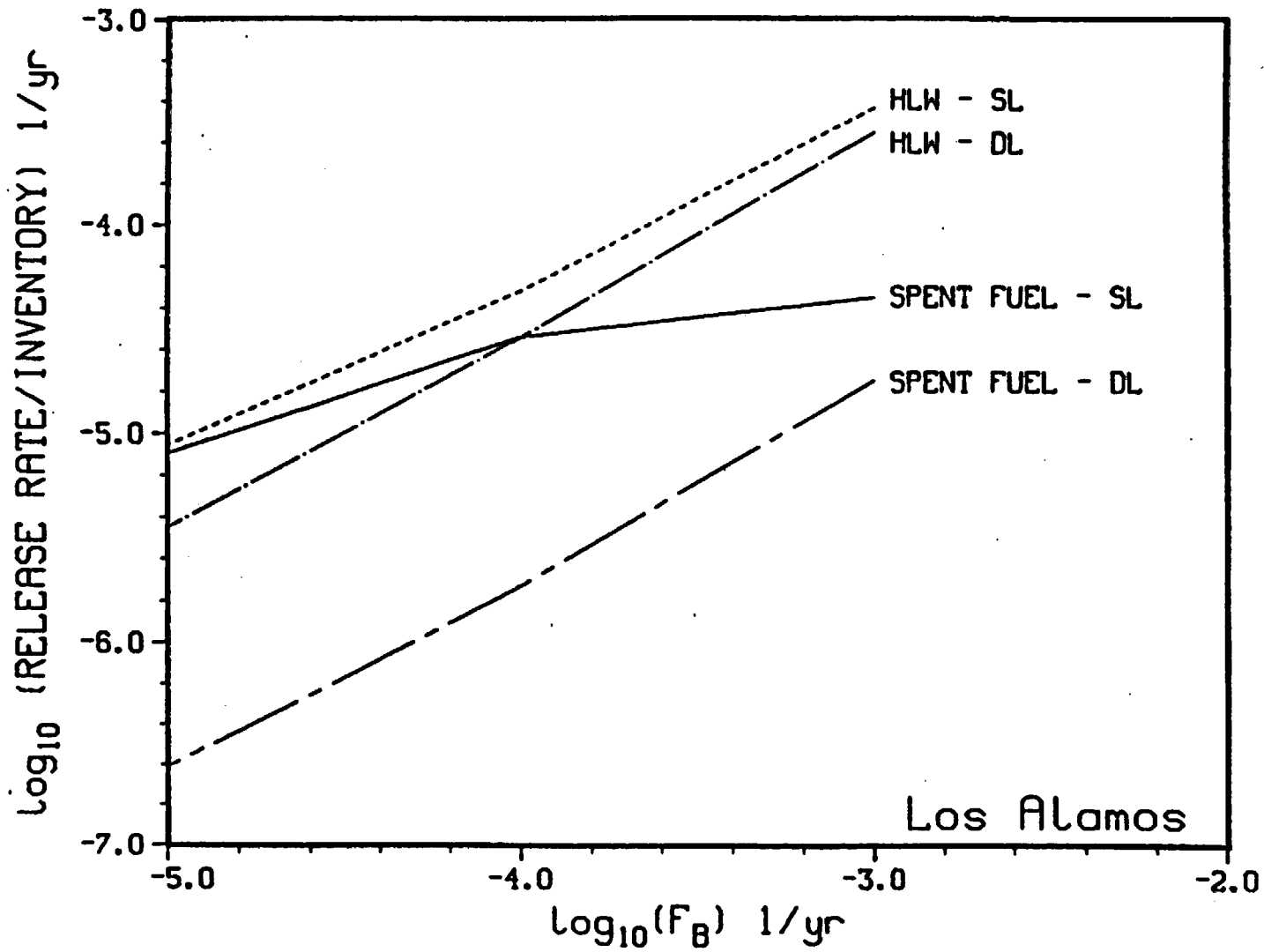
RADIONUCLIDE DISSOLUTION

Los Alamos

EFFECT OF VARYING MODEL PARAMETERS

- * WATER RECHARGE RATE.
- * WASTE ELEMENT SOLUBILITIES.
- * BULK FRACTIONAL DISSOLUTION RATE.

EFFECT OF BULK DISSOLUTION RATE AT 1000 YEARS



RADIONUCLIDE DISSOLUTION

EFFECT OF VARYING PARAMETERS - AT 1000 yr.

(Release rate/inventory (1/yr))

	Nominal	Reduced Recharge ^a	Reduced Solubility ^b
Sat.-limited model			
Spent fuel	2.9×10^{-5}	4.5×10^{-6}	2.1×10^{-6}
HLW	4.8×10^{-5}	3.7×10^{-5}	3.3×10^{-5}
Diff.-limited model			
Spent fuel	1.9×10^{-6}	1.8×10^{-6}	9.5×10^{-7}
HLW	2.9×10^{-5}	2.8×10^{-5}	1.7×10^{-5}

^afactor of 10.

^bfactor of 100.

Los Alamos

RADIONUCLIDES - PWR SPENT FUEL DIFFUSION-LIMITED MODEL RESULTS

(order based on release rate/EPA limit)

100 yr	1000 yr	10,000 yr	100,000 yr
^{137}Cs	^{14}C	^{237}Np	^{237}Np
^{90}Sr	^{237}Np	^{14}C	^{226}Ra
^{14}C	^{240}Pu	^{239}Pu	^{239}Pu
^{238}Pu	^{239}Pu	^{240}Pu	^{99}Tc
^{240}Pu	^{241}Am	^{226}Ra	^{135}Cs
^{237}Np	^{99}Tc	^{99}Tc	^{242}Pu
^{239}Pu	^{135}Cs	^{135}Cs	^{234}U
^{241}Am	^{226}Ra	^{243}Am	^{243}Am
^{99}Tc	^{243}Am	^{242}Pu	^{233}U

Los Alamos

RADIONUCLIDES - PWR HLW DIFFUSION-LIMITED MODEL RESULTS

(order based on release rate/EPA limit)

100 yr	1000 yr	10,000 yr	100,000 yr
^{137}Cs	^{14}C	^{14}C	^{239}Pu
^{90}Sr	^{240}Pu	^{239}Pu	^{237}Np
^{238}Pu	^{237}Np	^{237}Np	^{99}Tc
^{14}C	^{239}Pu	^{240}Pu	^{135}Cs
^{240}Pu	^{99}Tc	^{99}Tc	^{226}Ra
^{237}Np	^{135}Cs	^{135}Cs	^{233}U
^{239}Pu	^{241}Am	^{243}Am	^{234}U
^{99}Tc	^{238}Pu	^{234}U	^{242}Pu
^{241}Pu	^{234}U	^{226}Ra	^{243}Am

Los Alamos

COMPARISON OF RADIONUCLIDE IMPORTANCE CRITERIA-SPENT FUEL

	INVENTORY	INVENTORY EPA LIMIT	RELEASE RATE EPA LIMIT
1000 yr	²⁴¹ Am ²⁴⁰ Pu ²³⁹ Pu ²⁴³ Am	²⁴¹ Am ²⁴⁰ Pu ²³⁹ Pu ²⁴³ Am	¹⁴ C ²³⁷ Np ²⁴⁰ Pu ²³⁹ Pu
10000 yr	²³⁹ Pu ²⁴⁰ Pu ⁹⁹ Tc ²⁴³ Am	²³⁹ Pu ²⁴⁰ Pu ²⁴³ Am ²³⁴ U	²³⁷ Np ¹⁴ C ²³⁹ Pu ²⁴⁰ Pu
100000 yr	²³⁹ Pu ⁹⁹ Tc ⁹³ Zr ⁵⁹ Ni	²³⁹ Pu ²³⁴ U ²⁴² Pu ²³⁷ Np	²³⁷ Np ²²⁶ Ra ²³⁹ Pu ⁹⁹ Tc

* Diffusion-limited model.

Los Alamos



Los Alamos

COLLOIDAL $^{239}\text{PuO}_2$

SOLUBILITY

DISSOLUTION

RADIOLYTIC EFFECTS

PRELIMINARY RESULTS, RESEARCH IN PROGRESS.

D. E. HOBART, T. W. NEWTON, P. D. PALMER

REACTIONS

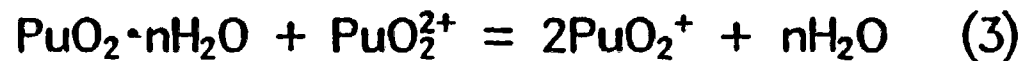
SOLUBILITY IN ACID



DISSOLUTION WITH OXIDATION

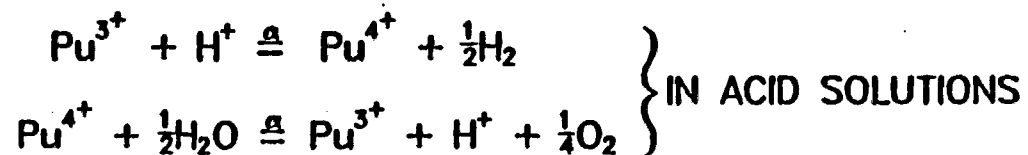
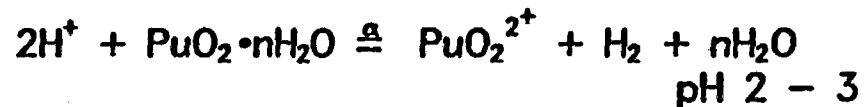
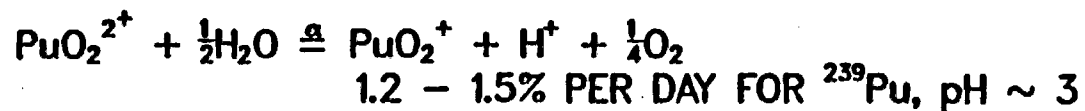


SPECIAL CASE



$$Q_3 = (\text{PuO}_2^+)^2 / (\text{PuO}_2^{2+})$$

NET RADIATION EFFECTS

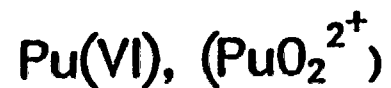


(REACTIVE SPECIES: H_2O_2 , H, OH, HO_2)



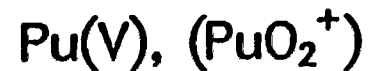
Los Alamos

ANALYTICAL METHODS



SPECTROPHOTOMETRY IN 0.6 M HClO_4

AT 830.3 nm, $\epsilon \sim 525 \text{ M}^{-1}\text{cm}^{-1}$.



SPECTROPHOTOMETRY AFTER ADDING Ce(IV)

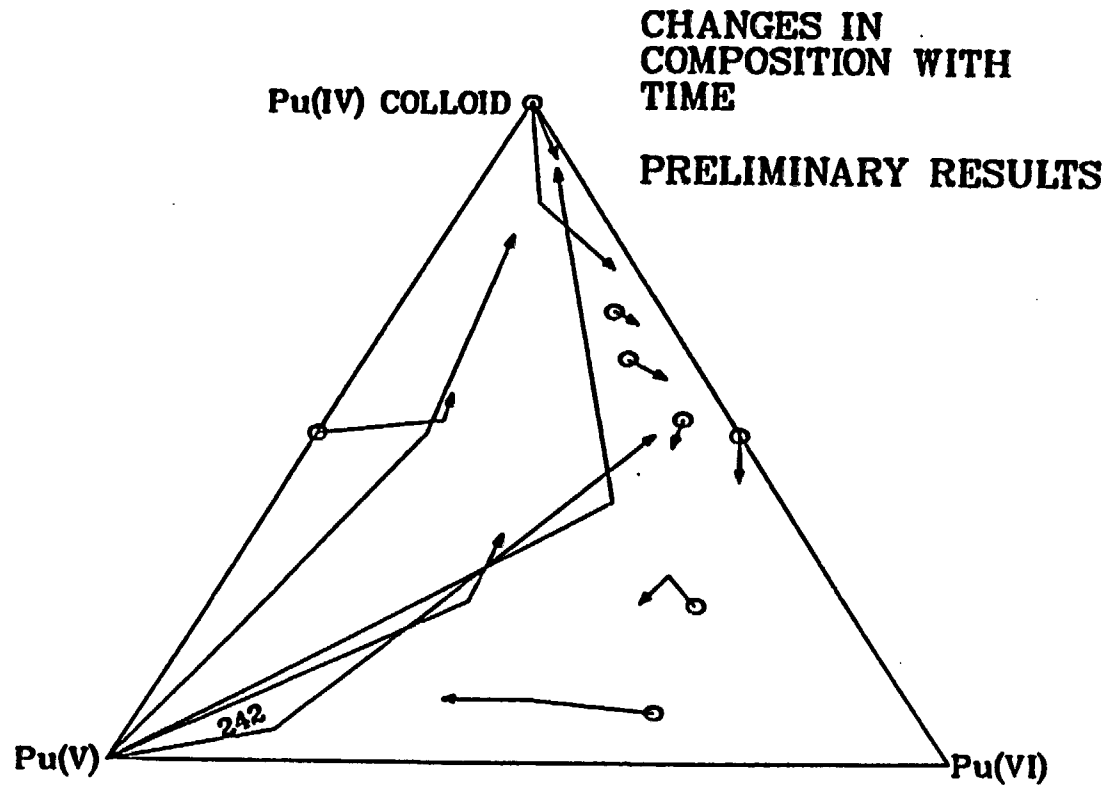
TO CONVERT Pu(V) TO Pu(VI) . Ce(IV)

OXIDIZES Pu(V) RAPIDLY BUT Pu(IV) OR

COLLOIDAL Pu(IV) VERY SLOWLY.

EXPERIMENTS

1. PuO_2^+ ALLOWED TO DISPROPORTIONATE, BOTH ^{239}Pu AND ^{242}Pu USED.
2. PURIFIED COLLOIDAL SUSPENSIONS ALLOWED TO "DISSOLVE".
3. MIXTURES OF COLLOIDAL Pu(IV) WITH PuO_2^{2+} AND/OR PuO_2^+ ANALYZED AS A FUNCTION OF TIME.

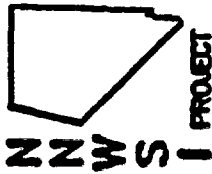




Los Alamos

PRELIMINARY RESULTS

1. NET OXIDATION AND NET REDUCTION WERE BOTH OBSERVED.
2. Pu(V) UNDERGOES BOTH DISPROPORTIONATION AND REDUCTION.
3. COLLOIDAL Pu(IV) DISSOLVES BY OXIDATION, PRIMARILY TO Pu(VI).
4. AT CONSTANT INITIAL Pu(VI)/Pu(V) RATIOS, THE BEHAVIOR DEPENDS ON THE CONCENTRATION OF COLLOID.
5. THERE IS NO DIRECT EVIDENCE FOR REPROPORTIONATION OF Pu(V).



Los Alamos

PRIMITIVE MODEL

REACTION	RATE DEPENDS ON:
$2\text{Pu(V)} = \text{Pu(IV)}_{\text{col}} + \text{Pu(VI)}$	Pu(V) , COLLOID
$\text{Pu(VI)} \xrightarrow{\alpha} \text{Pu(V)}$	TOTAL Pu
$\text{Pu(IV)}_{\text{col}} \xrightarrow{\alpha} \text{Pu(VI)}$	TOTAL Pu

LAWRENCE BERKELEY LABORATORY

H. NITSCHKE AND N. EDELSTEIN

SOLUBILITY OF SELECTED ACTINIDE IONS IN 0.1 M NaClO₄ AT

PH 7 AND IN GROUNDWATER (J-13) OF THE

NEVADA STORAGE SITE

- experiment still in progress

COMPARISON OF EXPERIMENTAL CONDITIONS IN NaClO₄ SOLUTION

AND IN J-13 GROUNDWATER

- a) NaClO₄ solution
 - pH 7
 - 0.1 M ionic strength
 - non-complexing
 - actinide solubility only controlled by hydroxide formation
 - will give "simple" understanding of solubility (baseline)
- b) J-13 groundwater
 - pH 7
 - 0.1 M ionic strength
 - complexing (CO₂, SO₄, NO₃, Cl, F, PO₄)
 - actinide solubility controlled by complexing ability of ligands
 - will give "complex overall picture"
 - results can be compared with values gained by modeling

GOAL OF EXPERIMENT

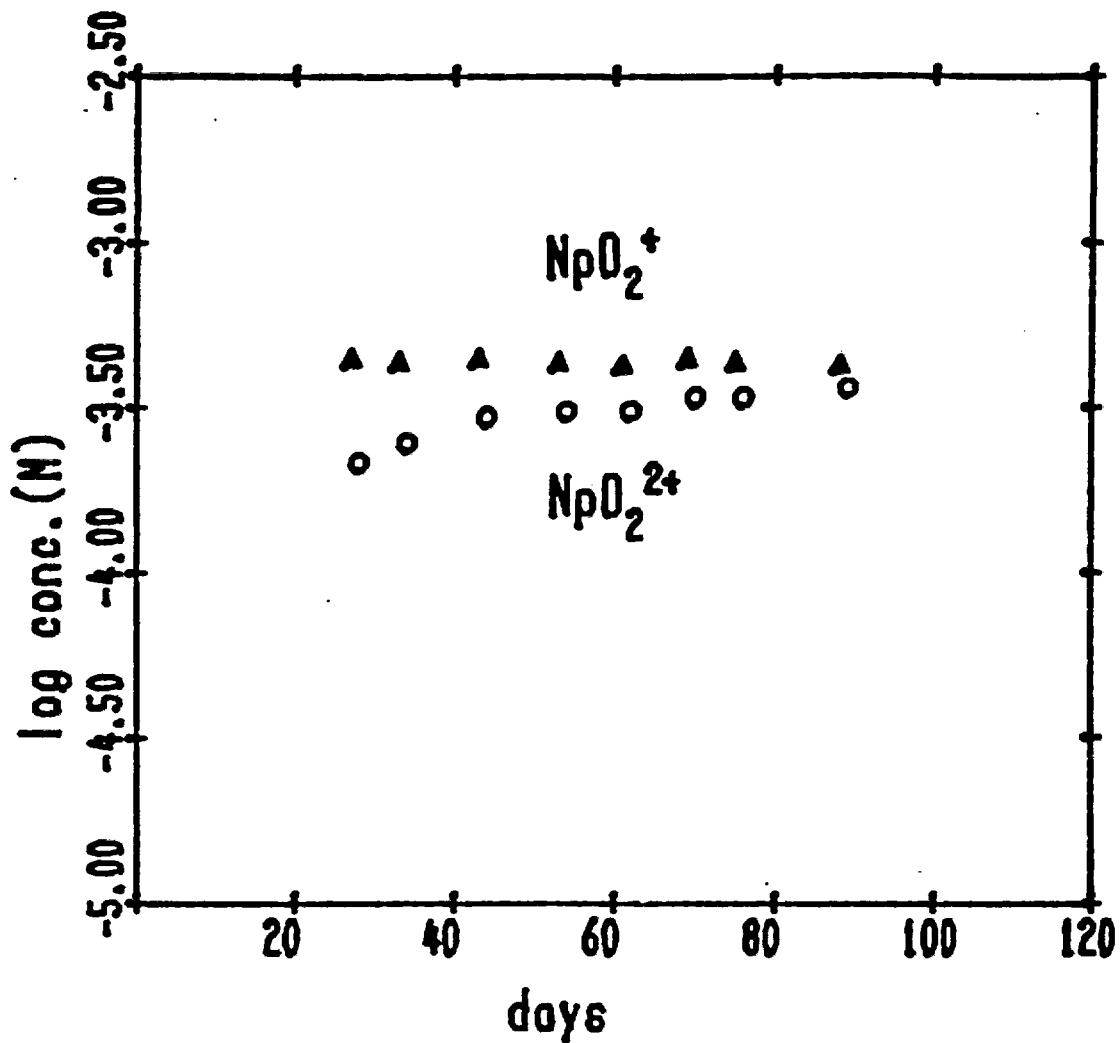
- determine actinide solubility
- identify oxidation state in solution
- characterize solid phase
- DETERMINE PERTURBATION OF SOLUBILITY BY LIGANDS

EXPERIMENTAL CONDITIONS

- actinide ions have specific oxidation state
- oxidation state was
 - adjusted by electrochemistry
 - verified by absorption spectrophotometry
- background electrolyte 0.1 M NaClO_4
- pH 7.0 ± 0.1 , controlled by pH-stat, $25 \pm 1^\circ\text{C}$
- inert atmosphere
- samples were shaken continuously
- solution filtered through 2 nm filters

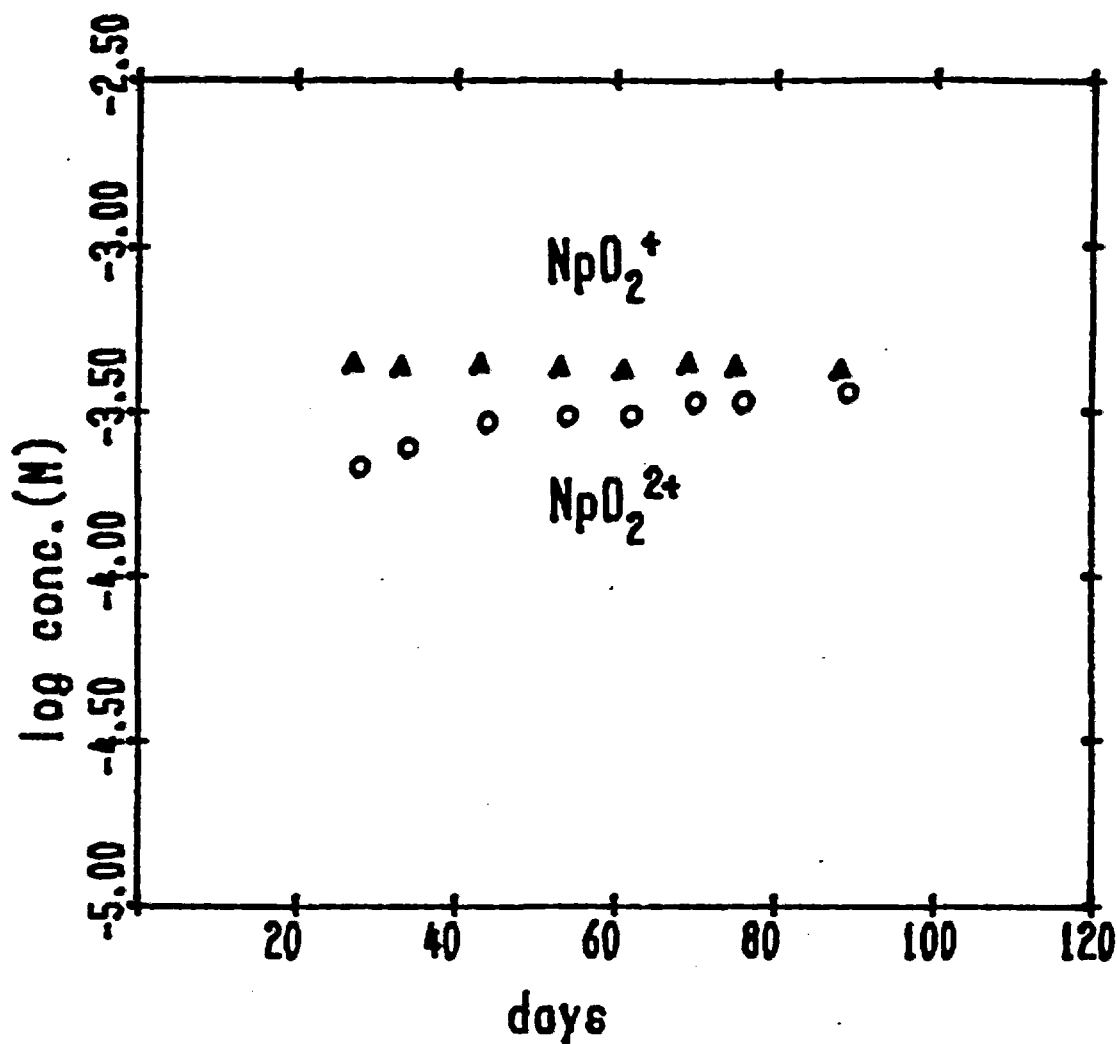
actinide ions used in experiment:

- $^{237}\text{NpO}_2^+$
- $^{237}\text{NpO}_2^{2+}$
- $^{243}\text{Am}^{3+}$
- $^{242}\text{Pu}^{4+}$
- $^{242}\text{PuO}_2^+$
- $^{242}\text{PuO}_2^{2+}$



Initial NpO_2^+

- $c = 10^{-3.36 \pm 0.01} \text{ M}$
- Kraus and Nelson (48):
amorphous $\text{NpO}_2(\text{OH})$, $c \leq 10^{-2.3} \text{ M}$ (pH 7)
- Np in solution is NpO_2^+ (V)

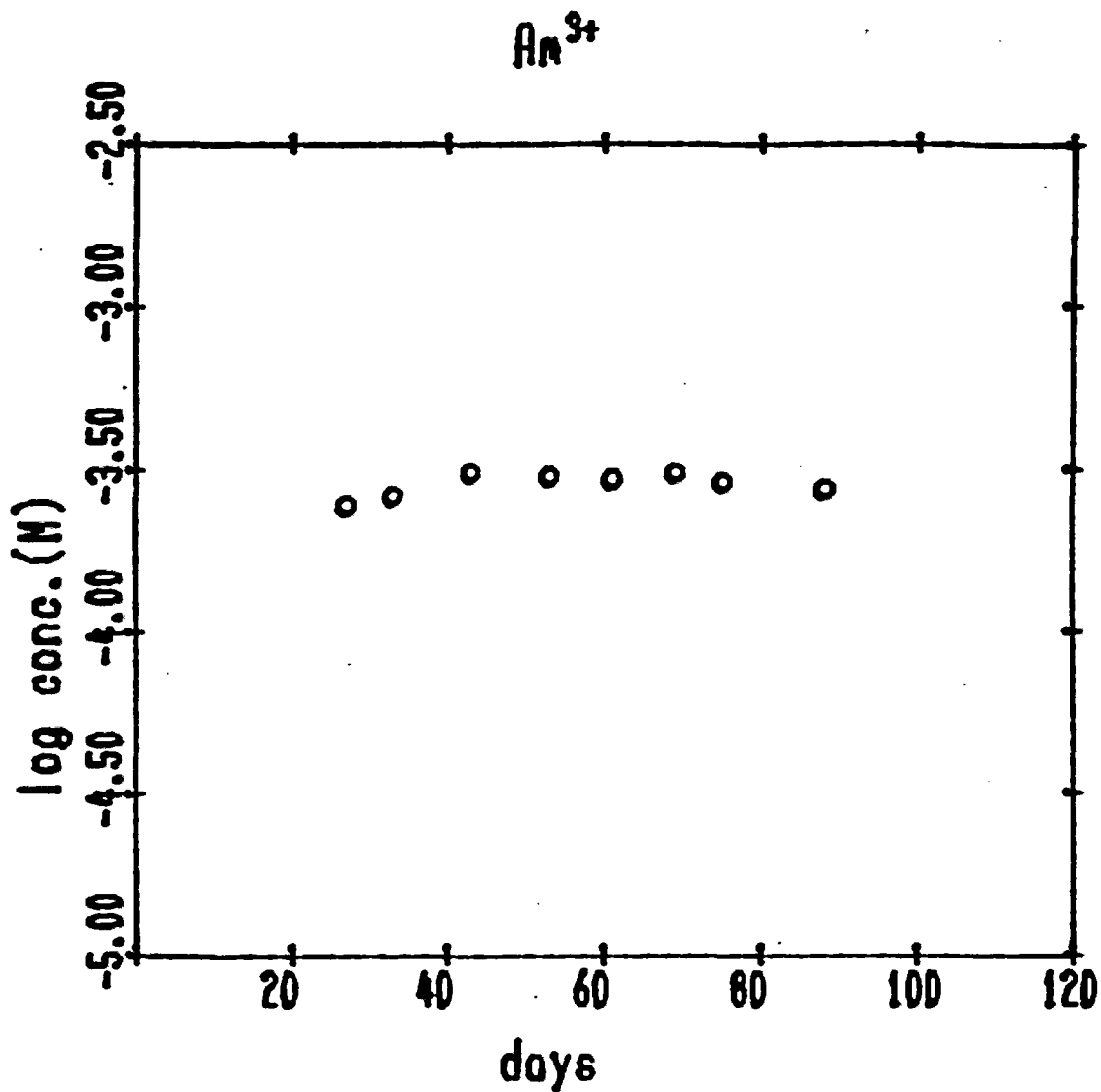


Initial NpO_2^{2+}

- $c = 10^{-3.46 \pm 0.02} \text{ M}$
- Kraus and Nelson (48):
amorphous $\text{NpO}_2(\text{OH})_2$, $c \leq 10^{-7.4} \text{ M}$ (pH 7)
- Np in solution is NpO_2^+ (V)

Conclusion

- solubility value for initially NpO_2^+ and NpO_2^{2+} is close to each other
- oxidation state in solution is V for both cases

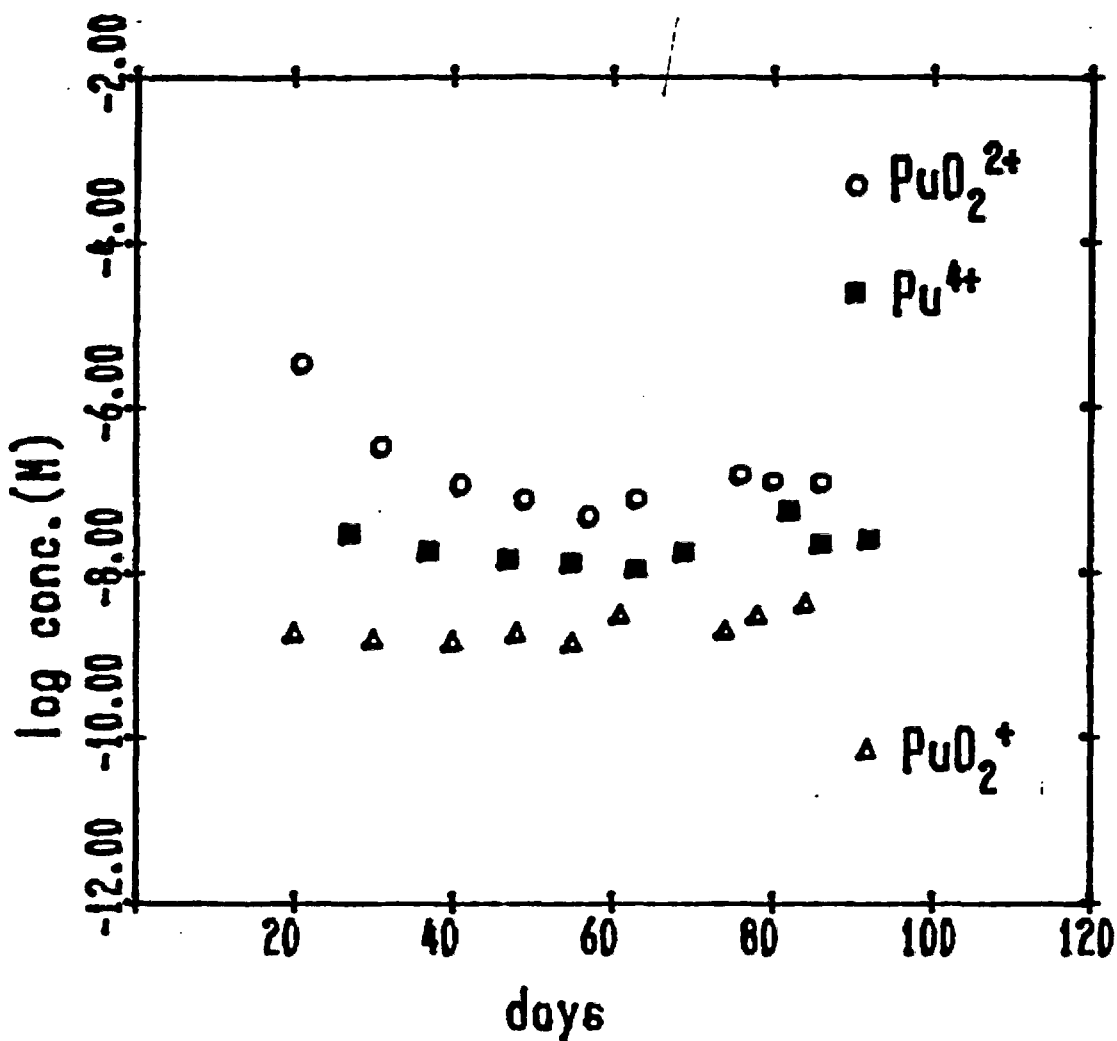


Initial Am^{3+}

- $c = 10^{-3.53 \pm 0.02} \text{ M}$
- Rai, et al. (82)
amorphous $^{243}\text{Am}(\text{OH})_3$, $c \cong 10^{-3.5} \text{ M}$ ($I = 0.02 \text{ M}$)
- Silva (82)
crystalline $^{243}\text{Am}(\text{OH})_3$, $c \cong 10^{-4.5} \text{ M}$ ($I = 0.1 \text{ M}$)
- Am in solution is Am^{3+}

Conclusion

- Value agrees well with Rai's value for amorphous $^{243}\text{Am}(\text{OH})_3$
- solid phase probably amorphous $\text{Am}(\text{OH})_3$
- oxidation state in solution did not change

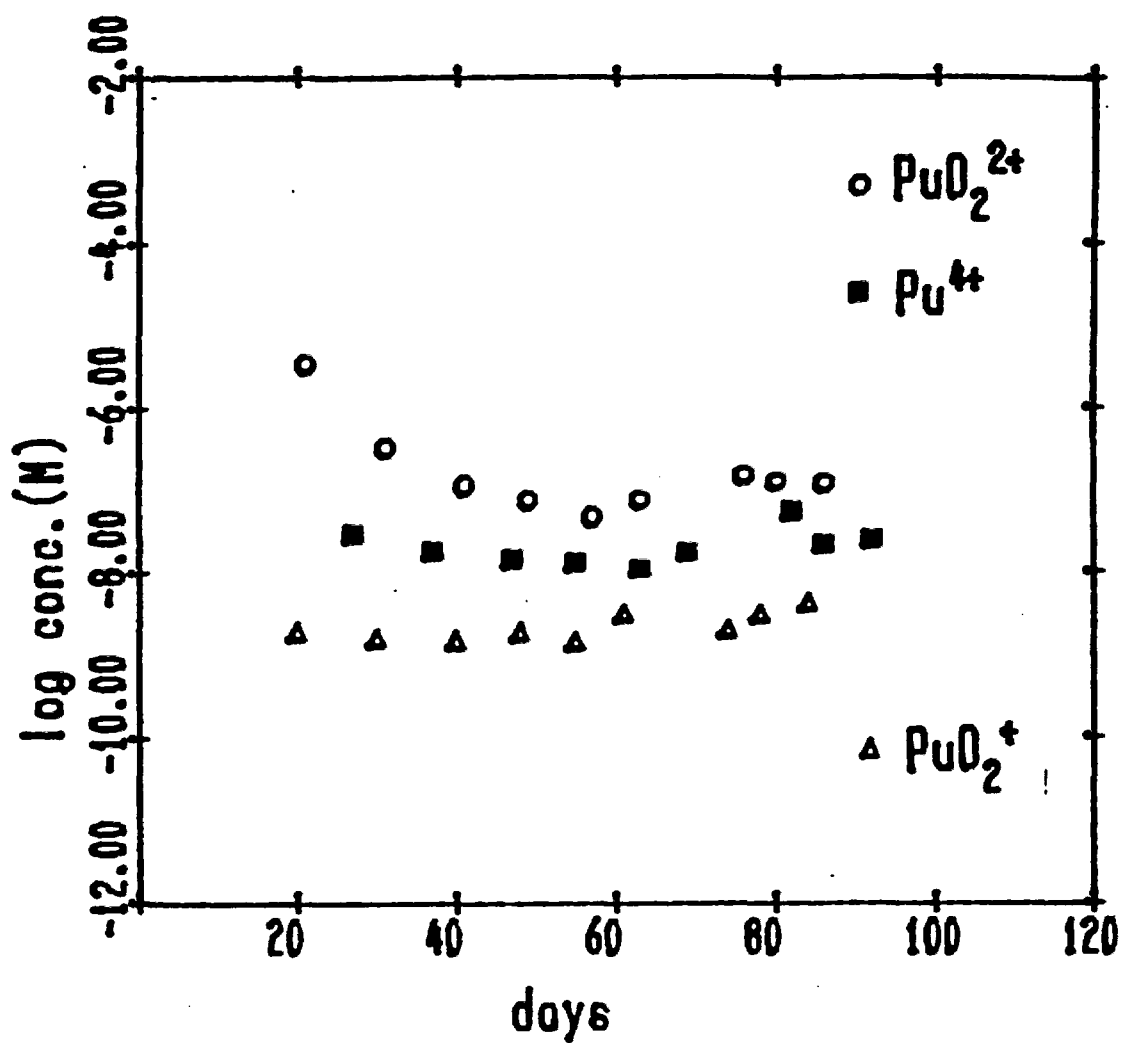


Initial Pu^{4+}

- $c = 10^{-7.56 \pm 0.22} \text{ M}$
- Rai and Ryan (82):
 PuO_2 crystalline, $c \cong 10^{-8} \text{ M}$ (pH 7)
 $\text{PuO}_2 \times \text{H}_2\text{O}$ amorphous, $c \cong 10^{-6.5} \text{ M}$ (pH 7)

Initial PuO_2^+

- $c = 10^{-8.51 \pm 0.14} \text{ M}$
- Baes and Mesmer:
amorphous $\text{PuO}_2(\text{OH})$, $c \cong 10^{-1.6} \text{ M}$ (pH 7)



Initial PuO_2^{2+}

- $c = 10^{-6.93 \pm 0.13} \text{ M}$
- Baes and Mesmer:
amorphous $\text{NpO}_2(\text{OH})_2$, $c \leq 10^{-7.4} \text{ M}$ (pH 7)

Problem

Low Pu concentration in solution requires method other than absorption spectrophotometry for oxidation state determination.

TTA, pH 0		TTA, pH 4		LoF ₃		HEXONE	
IV	III, V, VI, P	III, IV	V, VI, P	III, IV, P	V, VI	IV, VI	III, V, P

Pu ⁴⁺	0.8±0.2	99.2±0.2	2.0±1.3	98.0±1.3	2.6±1.6	96.8±0.6	29.9±7.4	70.1±7.4
	(95.1±8.2)		(91.8±11.0)		(86.8±7.1)		(101.4±46.6)	

PuO ₂ ⁺	2.2±2.0	97.3±1.3	1.6±0.6	98.4±0.6	5.2±4.3	94.9±4.3	27.0±15.5	72.9±15.2
	(101.7±5.7)		(96.0±1.6)		(97.3±1.1)		(95.8±2.9)	

PuO ₂ ²⁺	1.4±0.8	98.7±0.8	0.6±0.1	99.4±0.1	2.9±1.6	97.1±1.6	15.8±15.8	84.2±15.8
	(99.7±0.2)		(98.4±0.5)		(93.5±0.4)		(85.4±5.2)	

All values in %

Values in parentheses are overall chemical yield

CONCLUSION

Pu⁴⁺

- solubility value is within literature values for crystalline PuO₂ and amorphous PuO₂ x H₂O
- oxidation states in solution are
 - III + IV + V ≤ 5%
 - V + VI ~97%
 - V ~60%-75%

PuO₂⁺

- solubility value is much smaller than literature value for amorphous PuO₂(OH)
- oxidation states in solution are
 - III + IV + V ≤ 10.0%
 - V + VI ~90%-98%
 - V ~50%-70%

PuO₂²⁺

- solubility value agrees with literature value for amorphous NpO₂(OH)₂ and UO₂(OH)₂
- oxidation states in solution are
 - III + IV + V ≤ 5%
 - V + VI ~97%
 - V ~65%-80%

Work in Progress:

- a) Study of solids by X-ray powder diffraction
- b) repetition of experiments with J-13 groundwater

SUMMARY

- a) Gave solubility values at pH 7 in 0.1 M non-complexing solution of initially
 - NpO_2^+
 - NpO_2^{2+}
 - Am^{3+}
 - Pu^{4+}
 - PuO_2^+
 - PuO_2^{2+}
- b) Studied oxidation state distribution in solution phase by either absorption spectrophotometry or extraction/coprecipitation method

REDOX CONDITIONS AND REDOX BUFFERING

REDOX BUFFERING

FE²⁺ - TI OXIDES 0.16 - 0.33 v/o

DENSITY OF TUFF 2g/cm³

EQUIVALENTS FE²⁺ 20-40/m³

REPOSITORY LOADING

<u>WASTE ELEMENT</u>	<u>EQUIVALENTS</u>
Np	4.19 x 10 ⁵
Pu	4.36 x 10 ⁶
Tc	1.63 x 10 ⁶
U	5.64 x 10 ⁶
TOTAL	5.70 x 10⁸

3-6m OF TUFF THE SIZE OF THE REPOSITORY
CONTAINS THIS AMOUNT OF FE²⁺.

Los Alamos



FERROUS/FERRIC IRON DISTRIBUTION IN TUFF MINERALS AND ROCKS AT YUCCA MOUNTAIN

Los Alamos

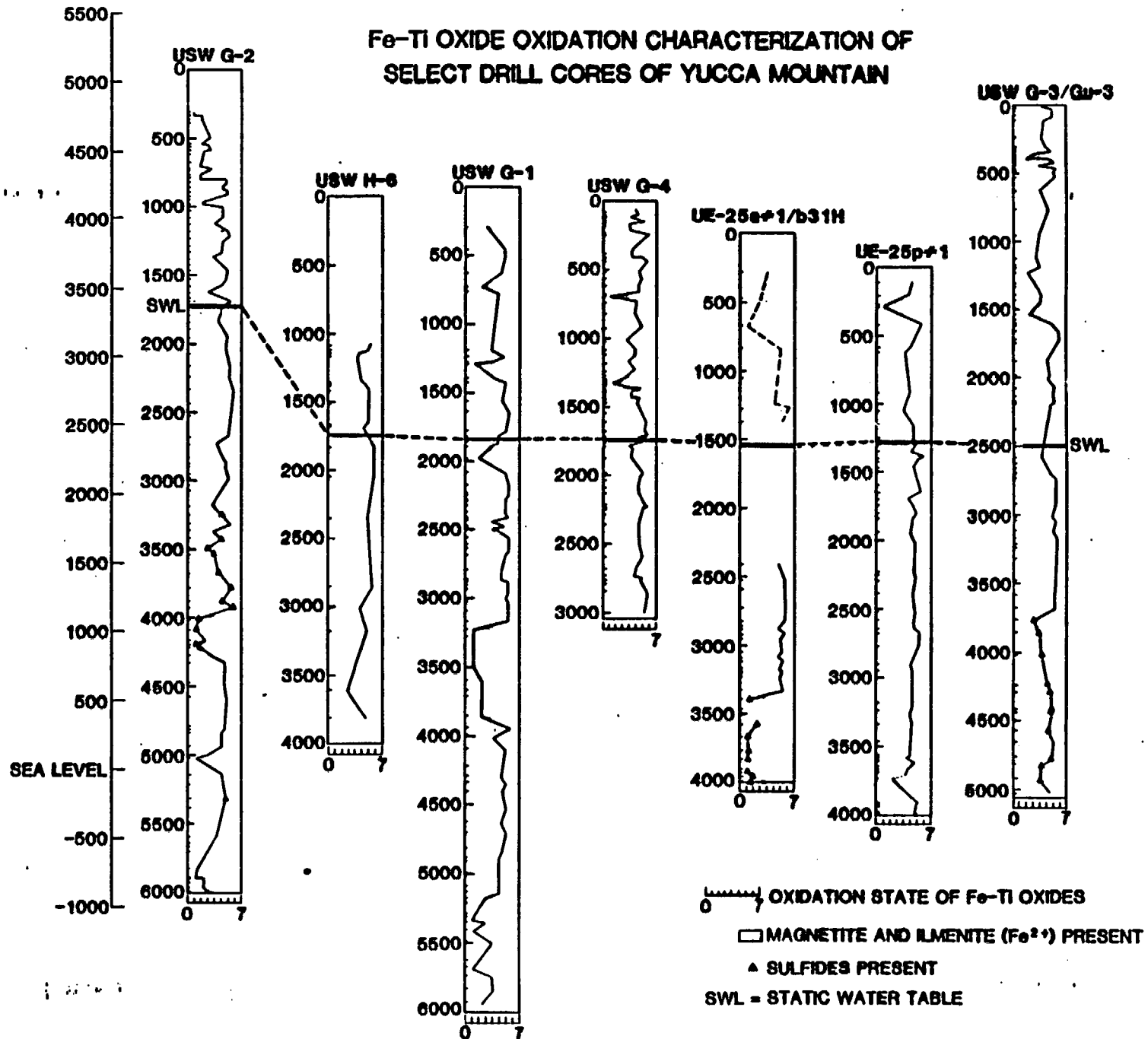
● **MINERALS**

- A) OXIDATION - EXSOLUTION IN Fe, TI-OXIDE MINERALS: WIDELY
SCATTERED FERROUS REMNANTS**
- B) FERROUS IRON IN SULFIDE - BEARING ROCKS AT DEPTH**

● **ROCKS**

- RETENTION OF SOME FERROUS IRON IN ROCKS OF THE LOWER...
TOPOPAH SPRING VITROPHYRE**

Fe-Ti OXIDE OXIDATION CHARACTERIZATION OF SELECT DRILL CORES OF YUCCA MOUNTAIN



WEIGHT - PERCENT FeO IN SAMPLES FROM USW G-4

(DETECTION LIMIT = 0.2% FeO)

DEVITRIFIED TOPOPAH

1089	FT	0%
1190	FT	0%

ZEOLITE INTERVAL I

1314	FT	0%
------	----	----

LOWER TOPOPAH VITROPHYRE

1330	FT	0.3%
------	----	------



ZEOLITE INTERVAL II

1438	FT	0%
1544	FT	0%

CENTRAL PROW PASS MEMBER

1871	FT	0%
------	----	----

ZEOLITE INTERVAL III

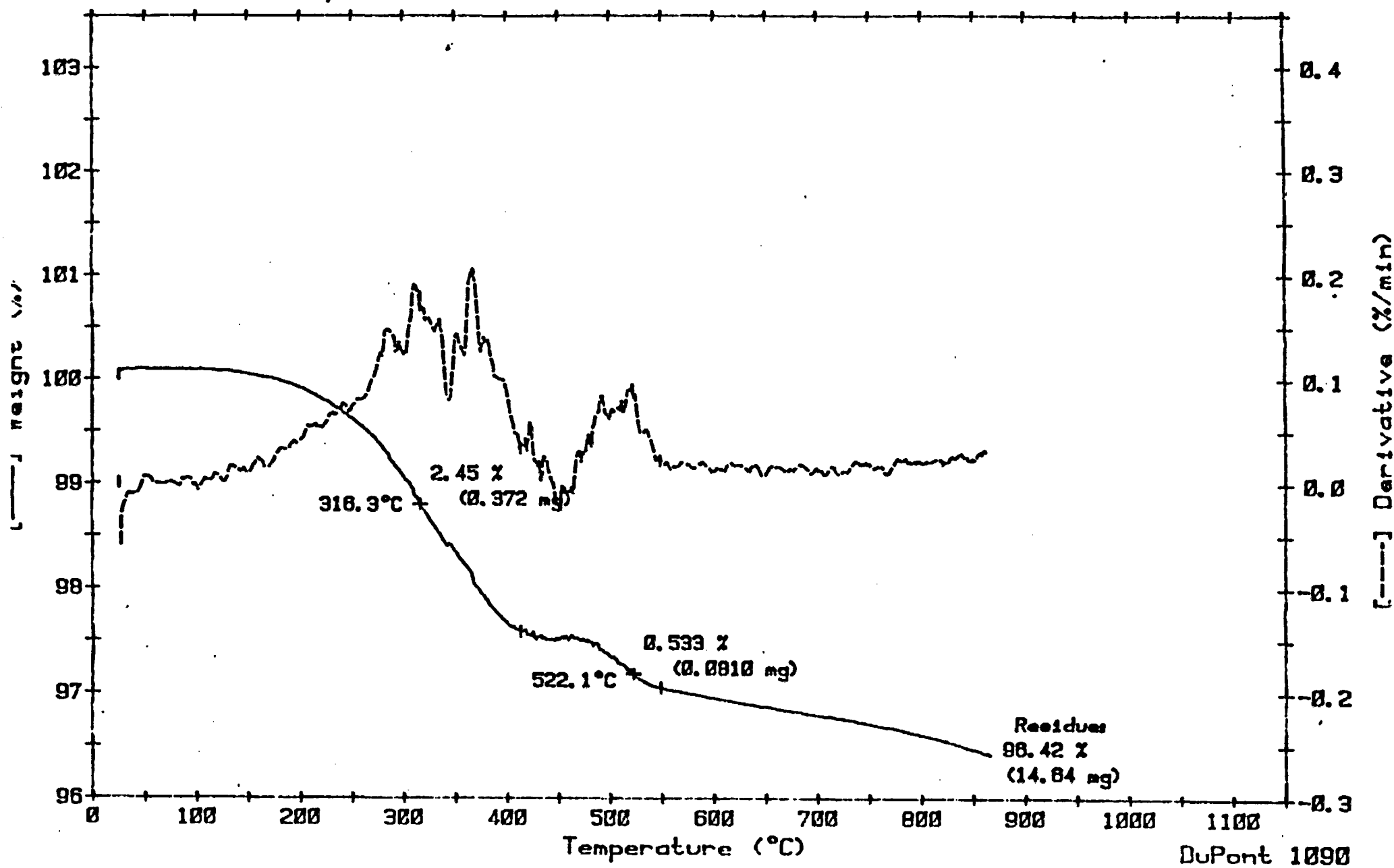
2100	FT	0%
------	----	----

CENTRAL BULLFROG MEMBER

2516	FT	0%
------	----	----

ZEOLITE INTERVAL IV

2716	FT	0%
2823	FT	0%



THERMOGRAVIMETRIC ANALYSIS OF TOPOPAH SPRING VITROPHYRE
(DRY N₂ PURGE)

DuPont 1090

REDOX BUFFERING

Fe^{2+} - Ti OXIDES 0.16 - 0.33 %
DENSITY OF TUFF 2 g/cm³
EQUIVALENTS Fe^{2+} 20-40 /m³

REPOSITORY LOADING

<u>WASTE ELEMENT</u>	<u>EQUIVALENTS</u>
Np	4.19×10^5
Pu	4.36×10^6
Tc	1.63×10^6
U	5.64×10^8
TOTAL	5.70×10^8

3-6 m OF TUFF THE SIZE
OF THE REPOSITORY CONTAINS
THIS AMOUNT OF Fe^{2+} .

LOS ALAMOS

TRANSPORT MODELING AND MATRIX DIFFUSION

Fracture Flow Experiment

Diffusion Experiment



THREE QUESTIONS TO ANSWER -

Los Alamos

- * How do fractures affect flow through unsaturated tuff?
- * How well can the fractured and unfractured layers retard radionuclide transport?
- * What is the effect of waste heat load on hydrology?



USES OF MODELS

Los Alamos

- predictive : what will happen
- sensitivity analyses: which processes or interactions are most important?
- interpretive: can it explain a lab. or field experiment?
- characterization: (inverse problem) what must flow properties be to produce given observations?
- experimental design: special case of predictive mode



SOME AREAS OF UNCERTAINTY IN MODELING

Los Alamos

- CHEMISTRY IN UNSATURATED SOIL/ROCK
vapor-rock interactions
(hydro-thermo-chemical)
- FRACTURE FLOW – Is it important in unsaturated rock?
- COLLOID migration
precipitates
particulates
- STOCHASTIC BEHAVIOR
need mean $c = c(x_1, x_2, \dots, x_n)$
and variance $c = f(x_1, \dots, x_n, \sigma_1, \dots, \sigma_n)$
where $x_i =$ variable, $r_i =$ uncertainty in x_i
- COUPLED PROCESSES
flux $J_i = \sum_j L_{ij} F_j$ where F_j are driving forces
what are L_{ij} ?, especially what are L_{ij} , $i \neq j$?



INGREDIENTS FOR BUILDING MODELS

Los Alamos

-
- conservation equations (mass, momentum, energy)
 - equations of state
 - conceptual model of microphysics which can be integrated to provide macroscopic constitutive relations,

e.g., $\kappa(\sigma, \varepsilon)$: permeability as fcn. of saturation and porosity

$\varepsilon(P, T, C)$: porosity as fcn. of pressure, temperature, concentrations.

Limitations of models due mainly to shortcomings of idealized microphysics and/or to inadequate equations of state.



Los Alamos

SIMPLE ANALYSIS OF TRANSPORT IN FRACTURED ROCK



MODEL ASSUMES

ASSUMPTIONS—MASS CONCENTRATION EQUATIONS

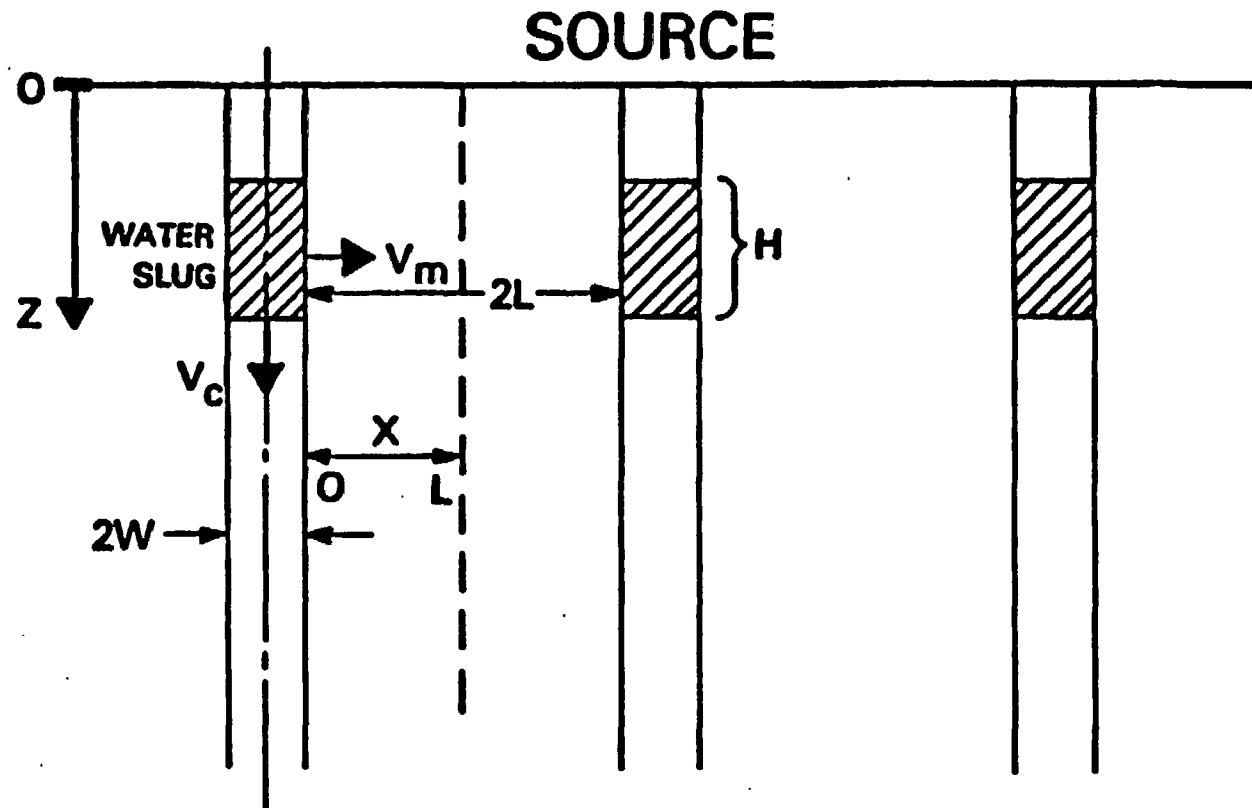
Los Alamos

1. One dimensional, steady state, two dissolved species.
2. Fixed concentration boundary conditions at $z = 0$.
3. Radioactive decay. $x \rightarrow c$ and $y \rightarrow d$
4. Reversible adsorption of dissolved species on both the matrix and the colloids.
5. No sources except at $z = 0$.
6. Constant porous matrix properties, porosity, permeability, density, and chemical composition.



Scenario Used for Fracture Flow Analysis

Los Alamos





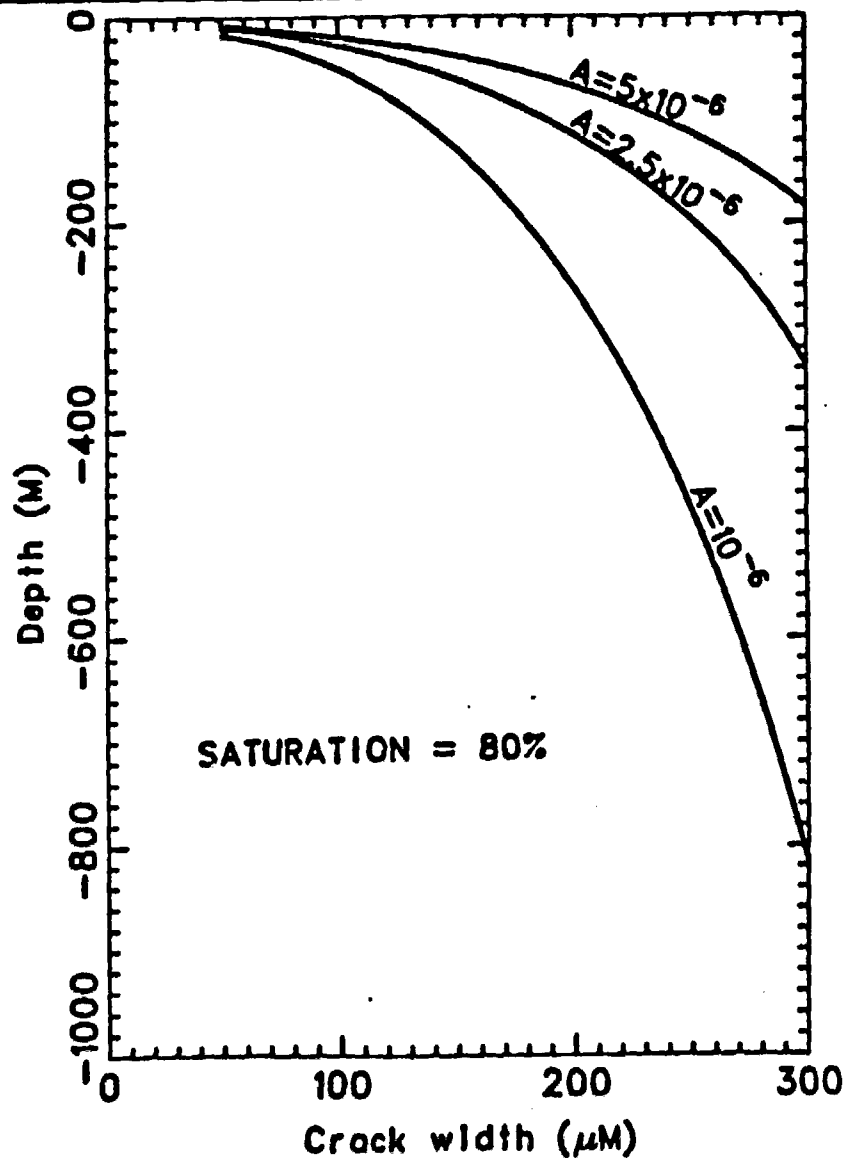
Los Alamos

WATER FLOW IN UNSATURATED FRACTURED ROCK



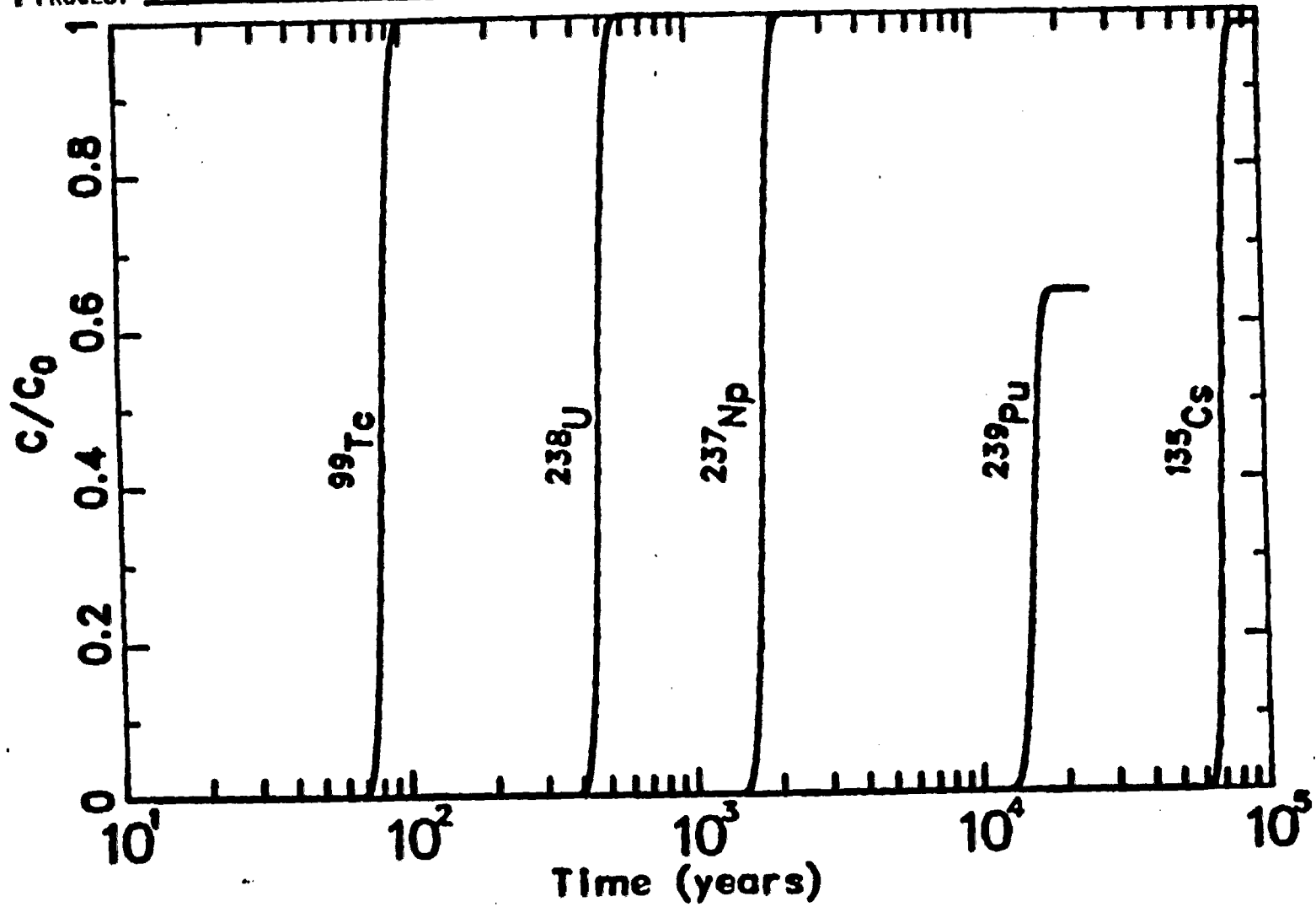
Depth Reached by Water Slug vs. Crack Width and Diffusion Coefficient A

Los Alamos



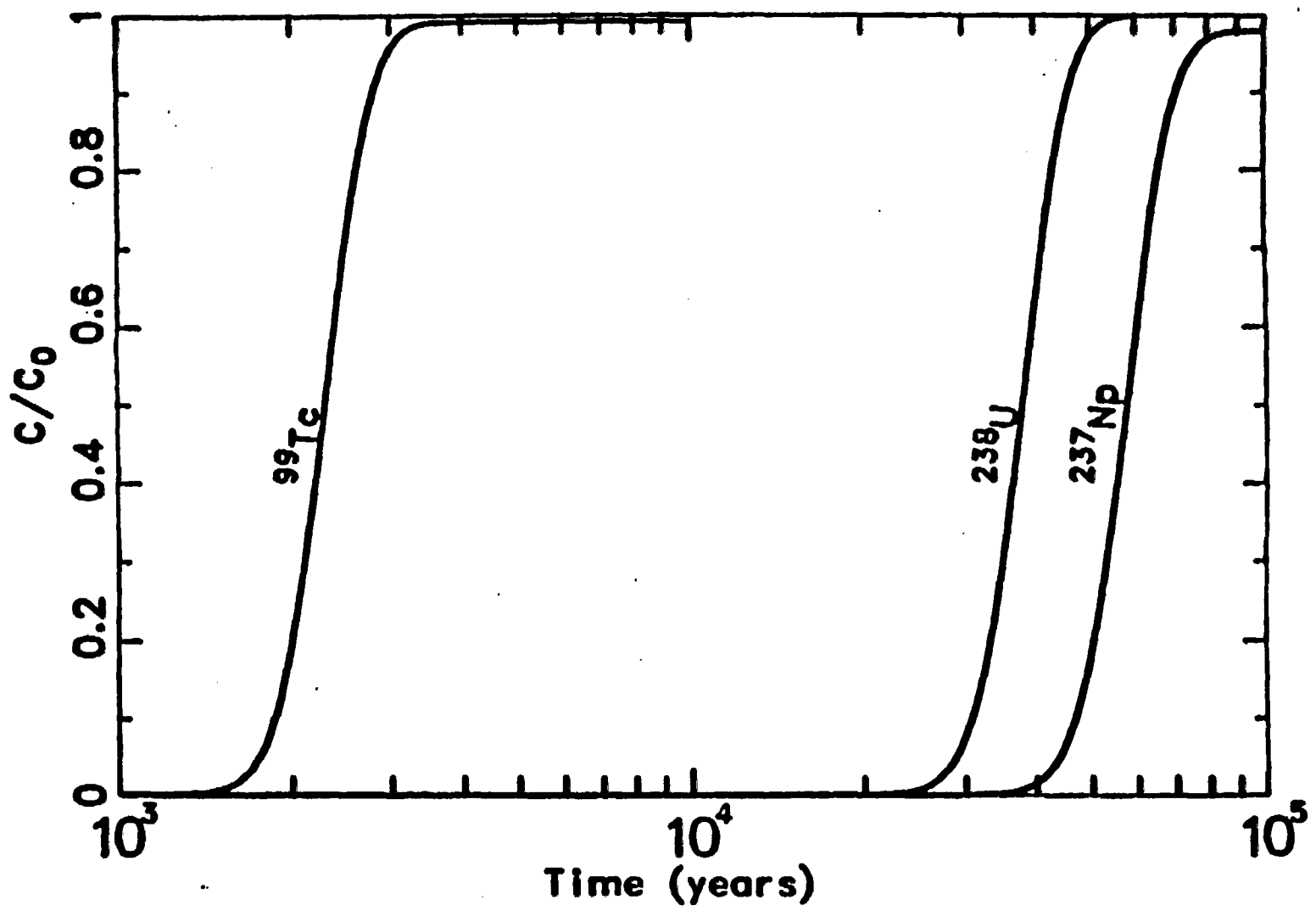
N
N
W
S
PROJECT

Concentration Histories for Topopah Springs Tuff
at Bottom of 50 m Layer, for 100 μm Crack
Los Alamos



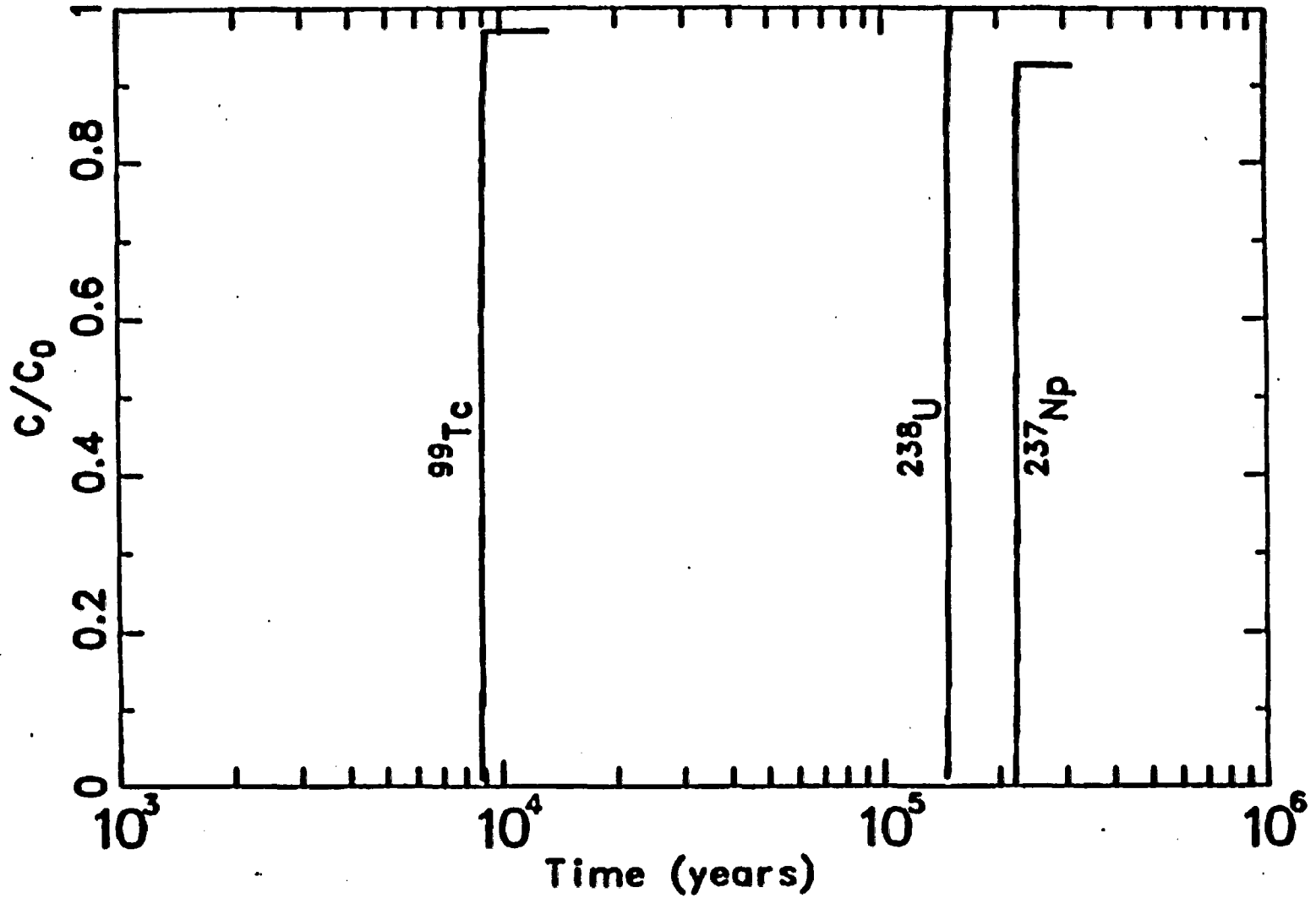


Concentration Histories for Calico Hills Tuff
at Bottom of 135 m Layer, for 100 μm Crack
Los Alamos





Concentration Histories for Calico Hills Tuff at
Bottom of 135 m Layer, for Porous Flow of 0.03 m/y
Los Alamos





Los Alamos

Coupling of RADIOCOLLOID Equations with Geo-Transport Equations

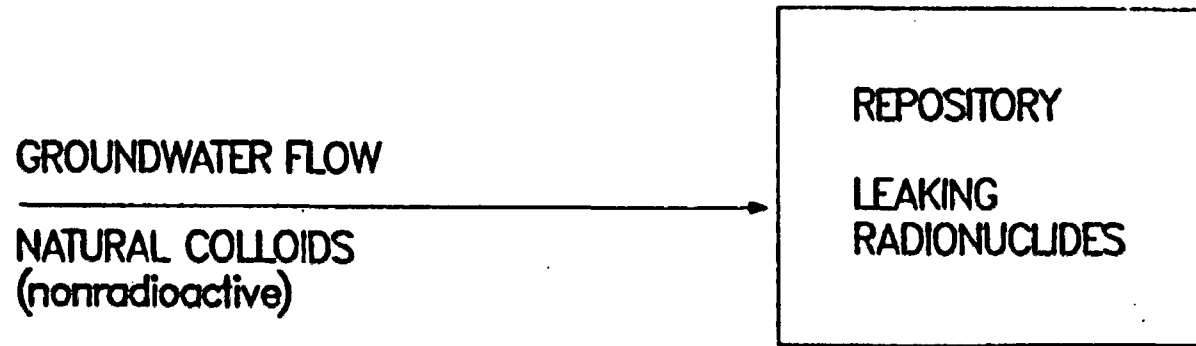
TRACR3D ENHANCEMENT



PSEUDOCOLLOIDS

Los Alamos

Naturally occurring (pseudo) colloids travel with the flowing groundwater into the repository where they contact and absorb a portion of the dissolved nuclides.

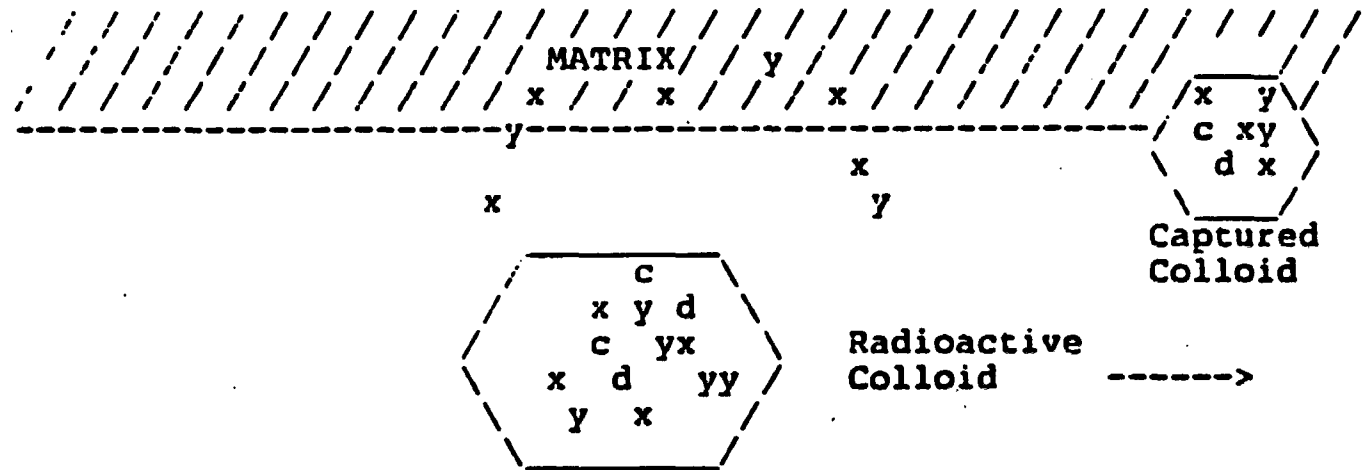




Transport of Radiocolloids

Los Alamos

As the radioactive colloids migrate downstream of the repository, several phenomena are occurring simultaneously. Included are colloid capture, radioactive decay, and adsorption/desorption of dissolved species from the pseudocolloids and rock matrix.





EXPERIMENTAL STUDIES

Los Alamos

LABORATORY

- LANL--Colloid Size Distributions and Concentrations
- PNL--Adsorption of Actinides on Iron Silicates and Clay
- Georgia Tech--Column and Adsorption Studies using Kaolinite
- Sweden--Formation of Actinide Colloids
Column Study
- Canada--Soil Column Studies with Plutonium
- Italy--Leached Borosilicate Glass followed by Column Tests
- Germany--Adsorption of Actinides on Natural Colloids

Field Sites

- LANL--DP Waste Site
- Canada--Low Level Waste Site (early release of cesium,
etc.)



MODEL ASSUMPTIONS

COLLOIDS--POPULATION BALANCE **Los Alamos**

1. Treatment of both pseudo and true colloids. The code initially will consider only one chemical type of pseudo and one type of true colloid. This reduces the complexity and storage requirements of the code. If necessary, these restrictions could later be relaxed.
2. The size distribution of the pseudocolloids remains fixed. The true colloids can exhibit both birth and growth behavior. Colloids are assumed to be in stable dilute concentrations; thus no coalescence or agglomeration is considered.
3. Colloids can adsorb/desorb two species (nuclides x and y). (The population balance coupled to the mass transport equations for species x and y). One or both of the dissolved species may form true colloids.
4. Irreversible colloid capture on the matrix.



MODEL ASSUMPTIONS

COLLOIDS—POPULATION BALANCE

Los Alamos

5. Pseudocolloids neither grow nor dissolve. The amount of radionuclides adsorbed is assumed to be only a monolayer; thus, not effecting the size nor mass of the initial pseudocolloid size distribution.
6. The colloid capture rate expression may be a function of particle size.
7. Initially the natural colloids are nonradioactive and of a given size distribution.
8. The concentration of pseudocolloids is changed only by capture. No additional sources or sinks.
9. One dimensional problem, constant fluid/colloid velocity, constant boundary colloid concentration and size distribution.
(at $z = 0$)
10. Radioactive decay of adsorbed species. No chain reactions.



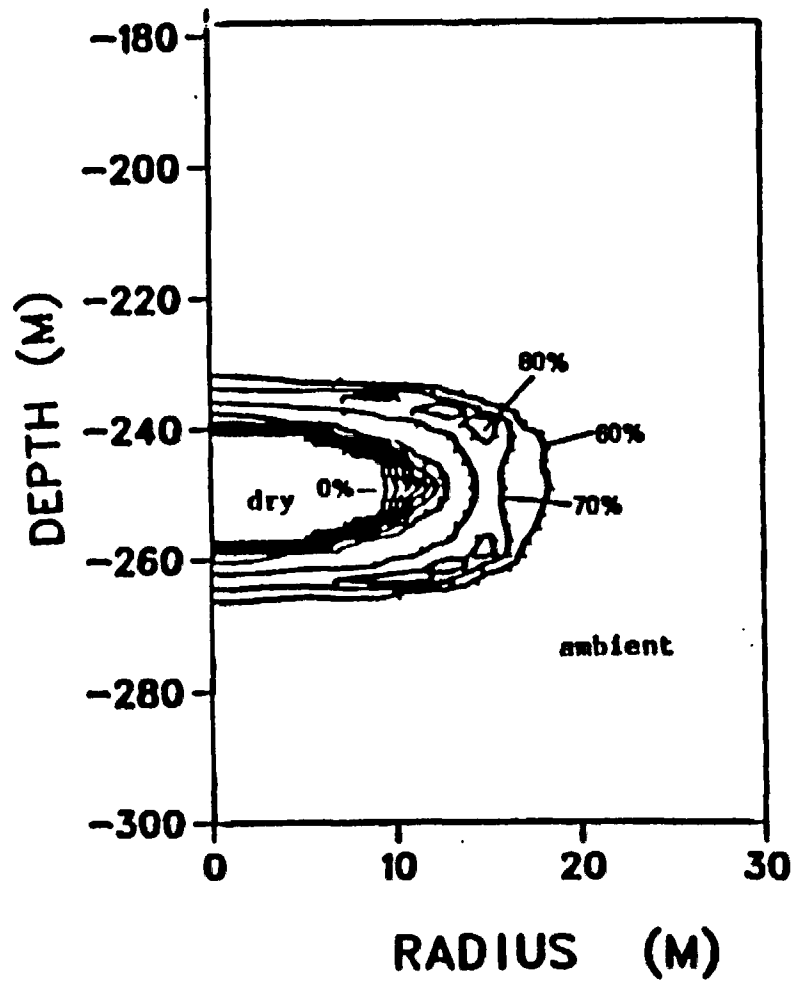
Los Alamos

GENERATION OF TWO PHASE FLOW BY WASTE HEAT LOAD



Water Saturation Contours 50 years After Emplacement of Heat Load

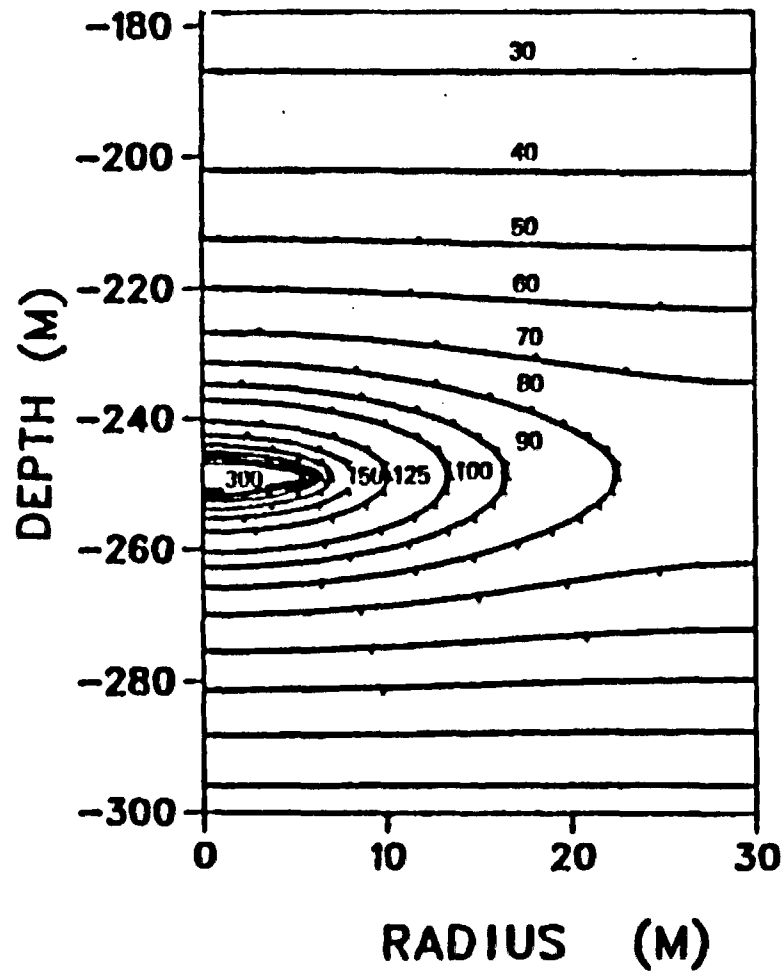
Los Alamos





Temperature Contours 50 years After Emplacement of Heat Load

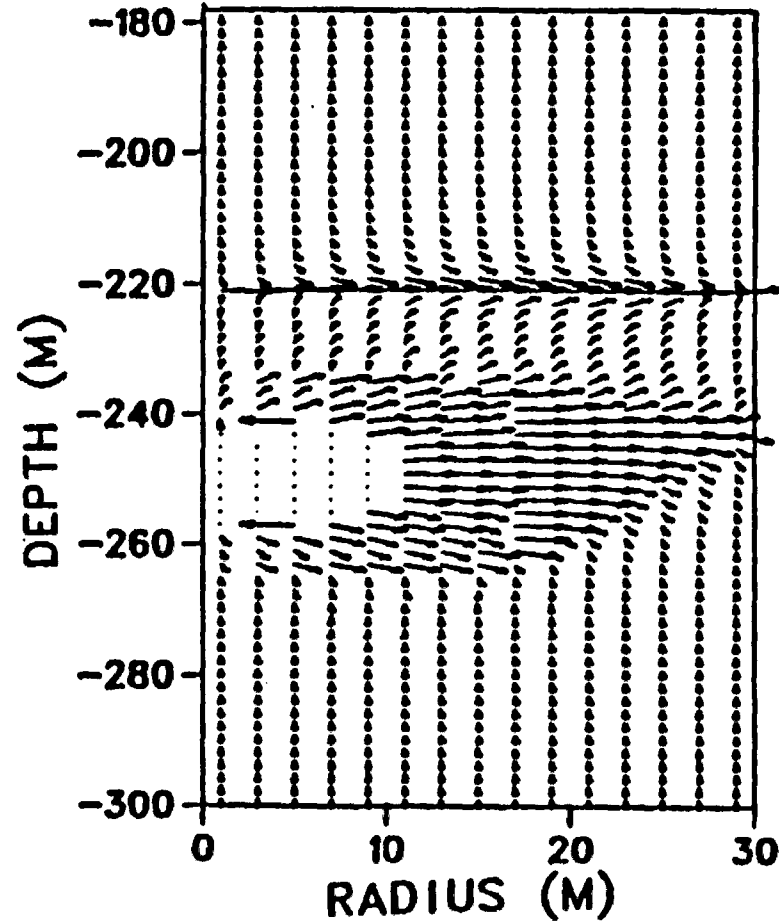
Los Alamos





Water Velocity Vector Field 50 years After Emplacement of Heat Load

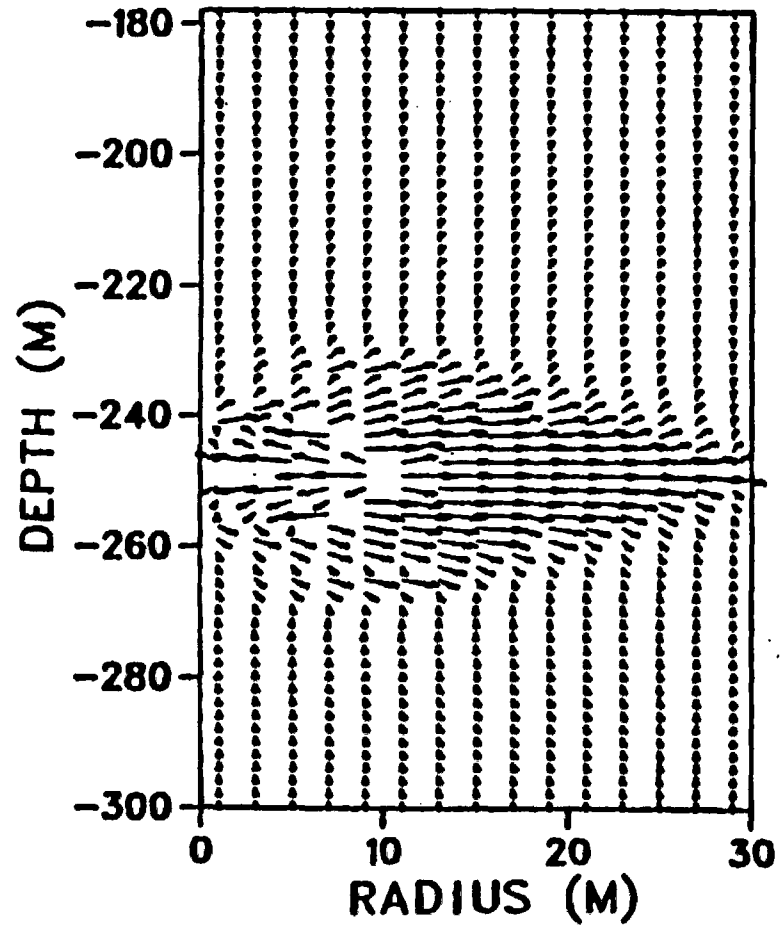
Los Alamos





Vapor + Air Velocity Vector Field 50 years After Emplacement of Heat Load.

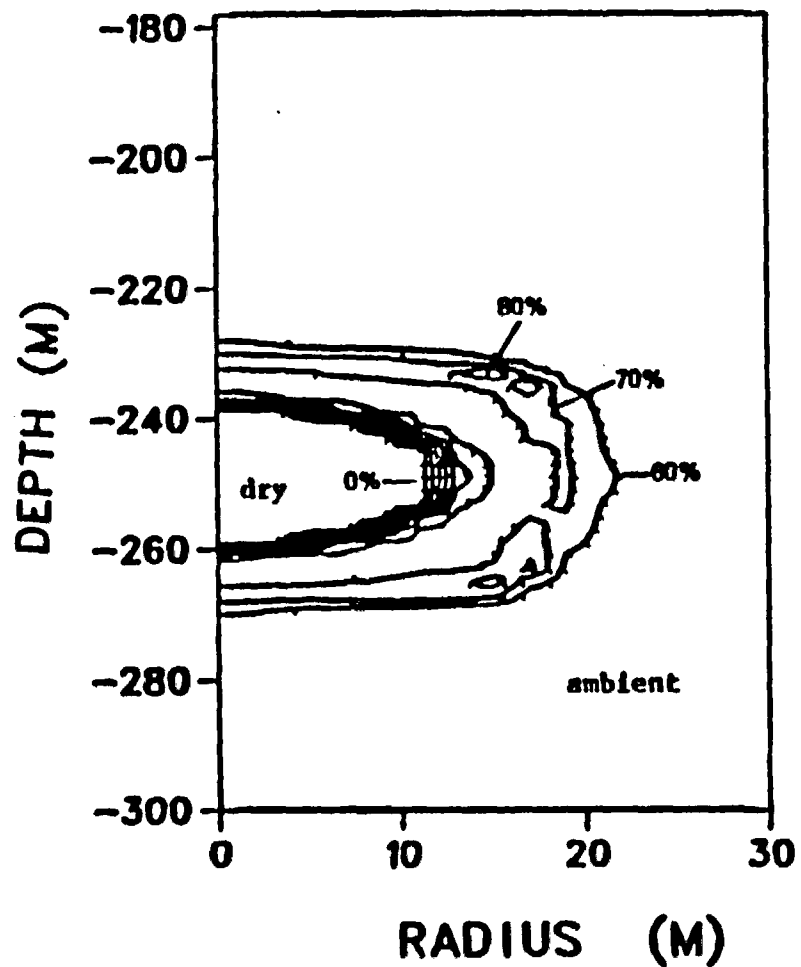
Los Alamos





Water Saturation Contours 100 years After Emplacement of Heat Load

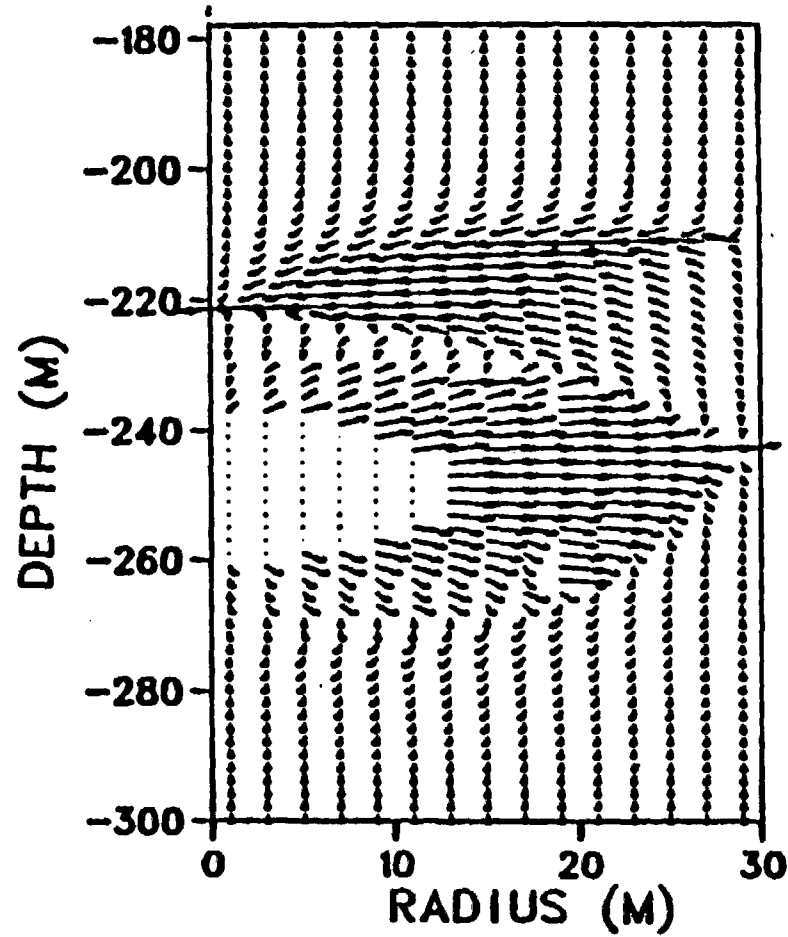
Los Alamos





Water Velocity Vector Field 100 years After Emplacement of Heat Load

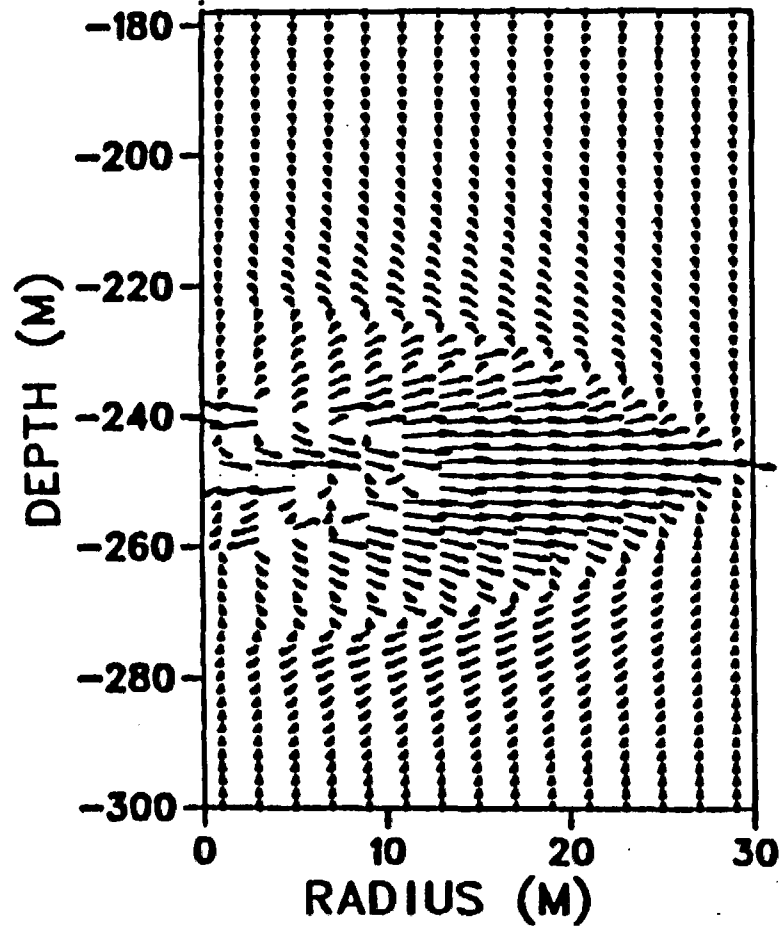
Los Alamos





Vapor + Air Velocity Vector Field 100 years After Emplacement of Heat Load

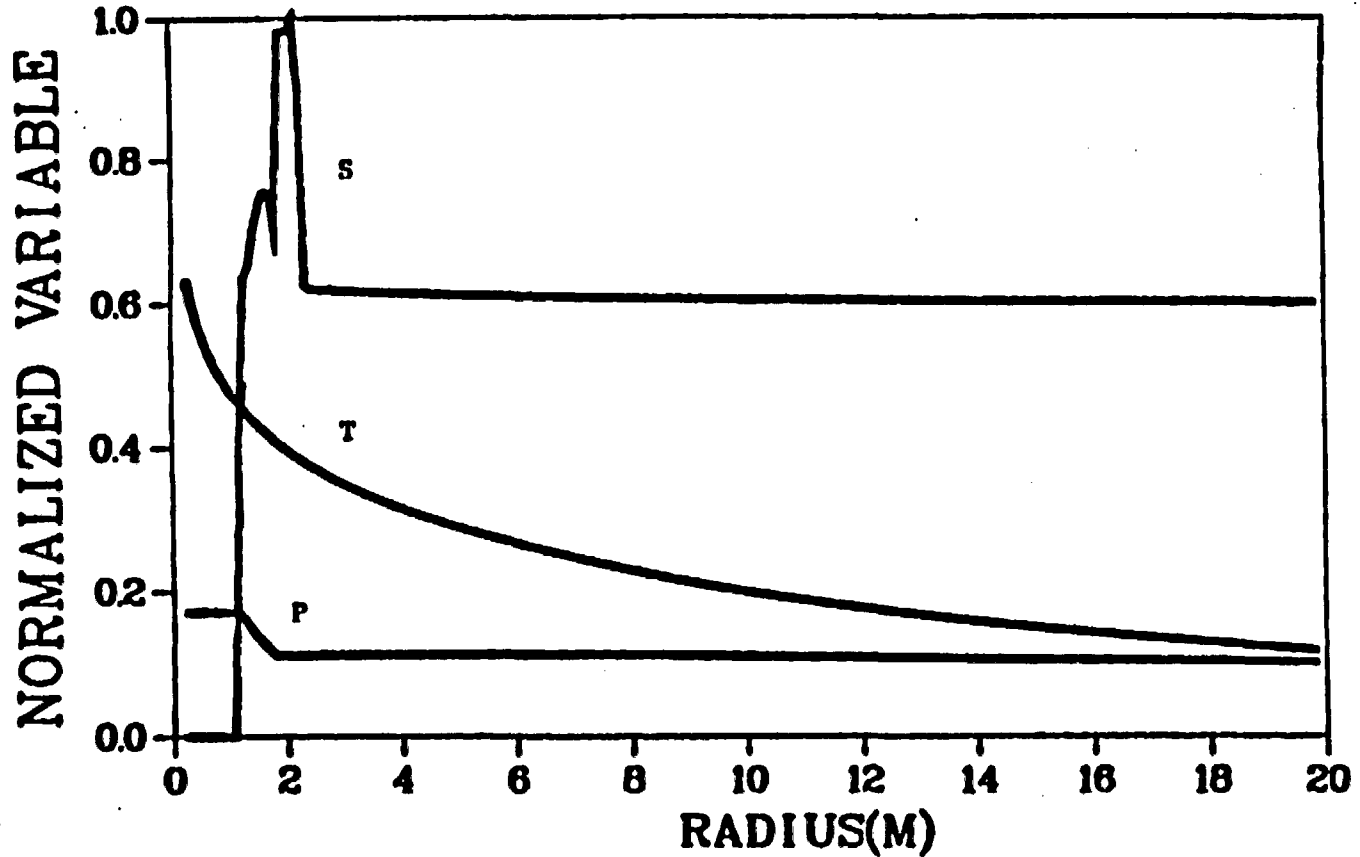
Los Alamos





Saturation (S), Temperature (T), and Pressure (P)
Profiles at 20 years for No Venting Case

Los Alamos



PRESSURE (KPA)
FLUID TEMP(CELSIUS)
SATURATION

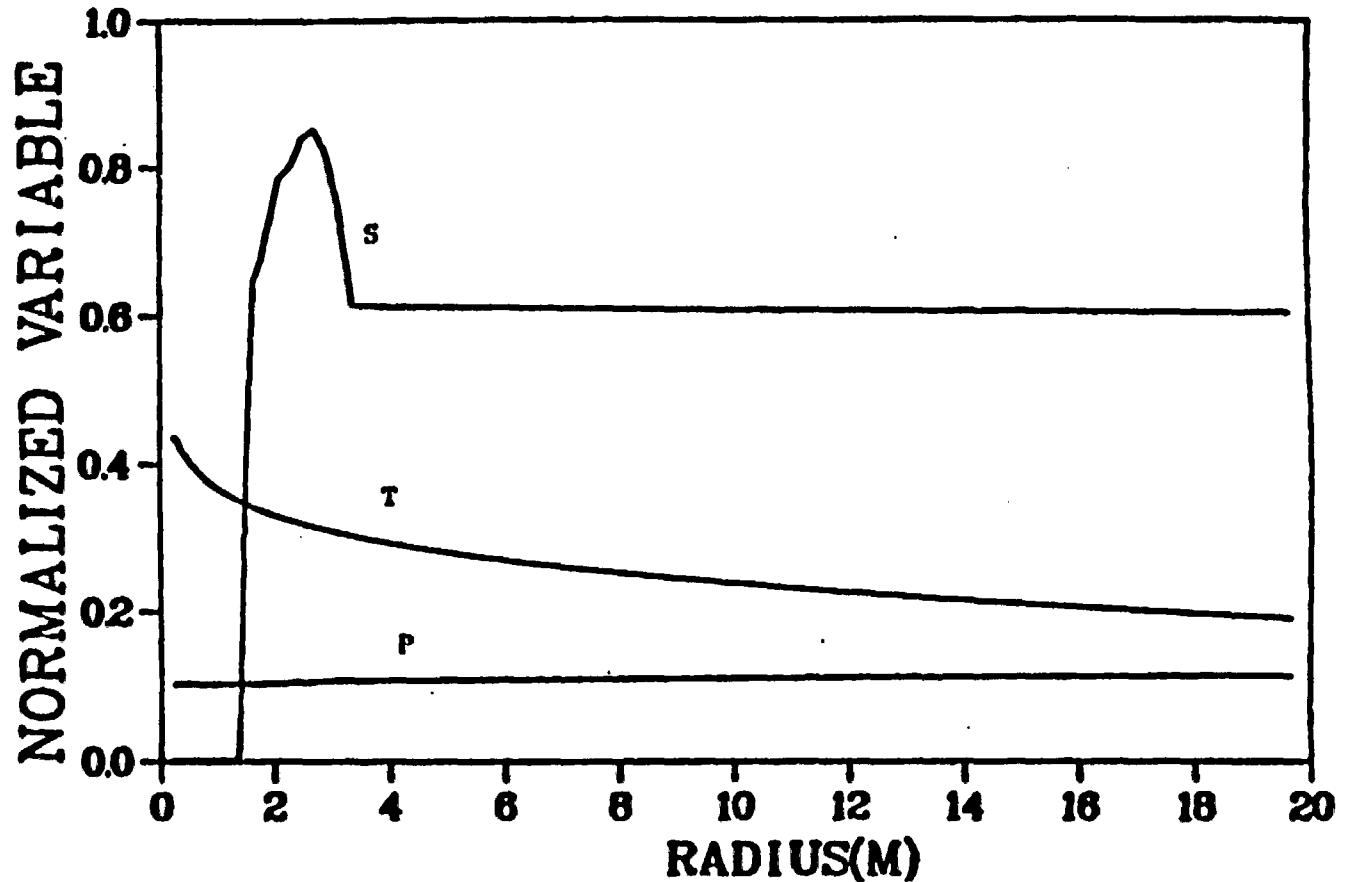
MIN= 0.
MIN= 0.
MIN= 0.

RANGE= .100E+04
RANGE= 250E+03
RANGE= .100E+01



Saturation (S), Temperature (T), and Pressure (P)
Profiles at 50 years for No Venting Case

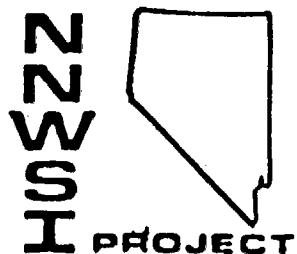
Los Alamos



PRESSURE (KPA)
FLUID TEMP(CELSIUS)
SATURATION

MIN= 0.
MIN= 0.
MIN= 0.

RANGE= .100E+04
RANGE= .250E+03
RANGE= .100E+01

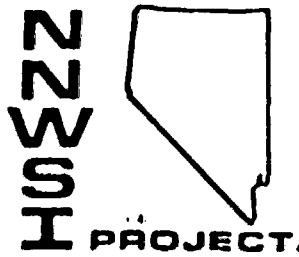


DIFFUSION TEST RATIONALE

Los Alamos

- **10CFR60.112: *EPA RELEASE STANDARDS***
- **NNWSI INFORMATION NEED 1.3.3: *BOUNDS ON EFFECTIVE RETARDATION IN DISPERSION/DIFFUSION/ADVECTIVE TRANSPORT PROCESS***

+

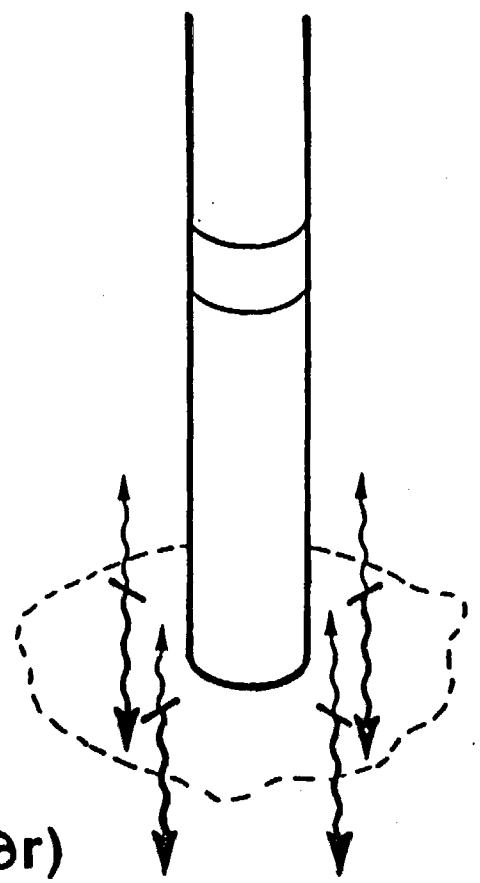
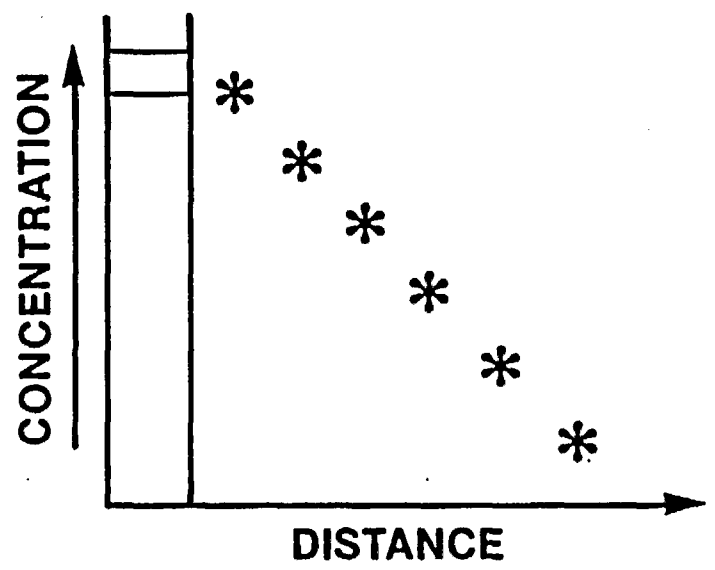
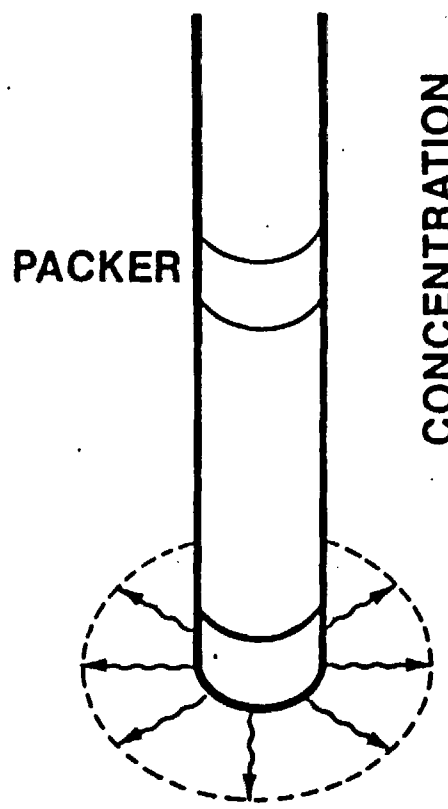


DIFFUSION TEST

Los Alamos

WITHOUT WATER FLOW

WITH WATER FLOW



$$\frac{\partial C}{\partial t} = D \frac{1}{r} \frac{\partial}{\partial r} (r \frac{\partial C}{\partial r})$$

+



DIFFUSION TEST EXPERIMENTAL GOALS

Los Alamos

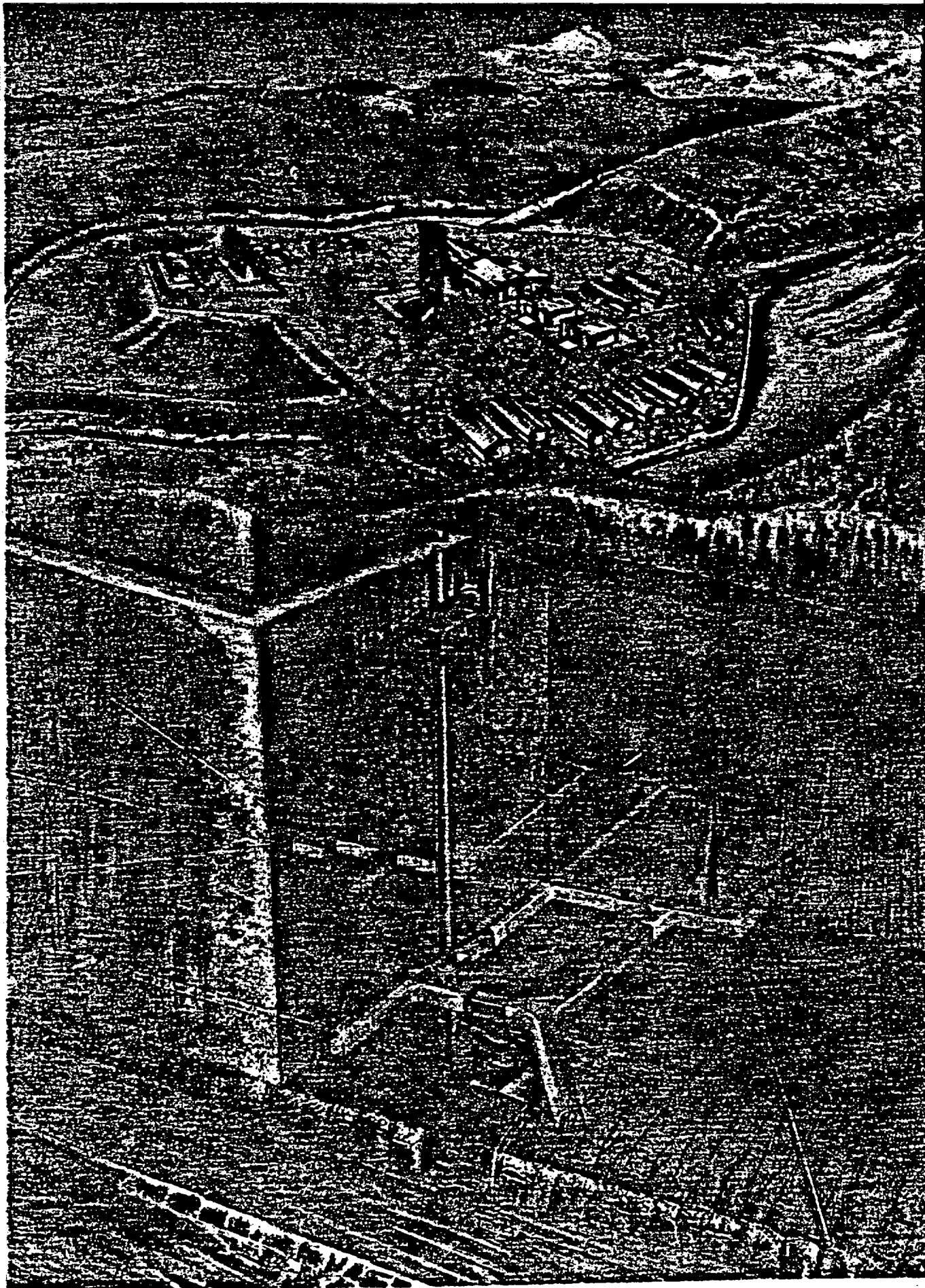
- **DIFFUSIVITY OF AQUEOUS SOLUTES INTO WATER-FILLED PORES IN**
 - **TOPOPAH SPRING TUFF**
 - **CALICO HILLS TUFF**
- **MEASURE IN LABORATORY**
- **EXTRAPOLATE TO FIELD**
 - **LITHOSTATIC LOAD**
 - **SATURATION**
- **CHECK EXTRAPOLATION**
- **USE FIELD RESULTS FOR TRANSPORT CODE CALCULATIONS**

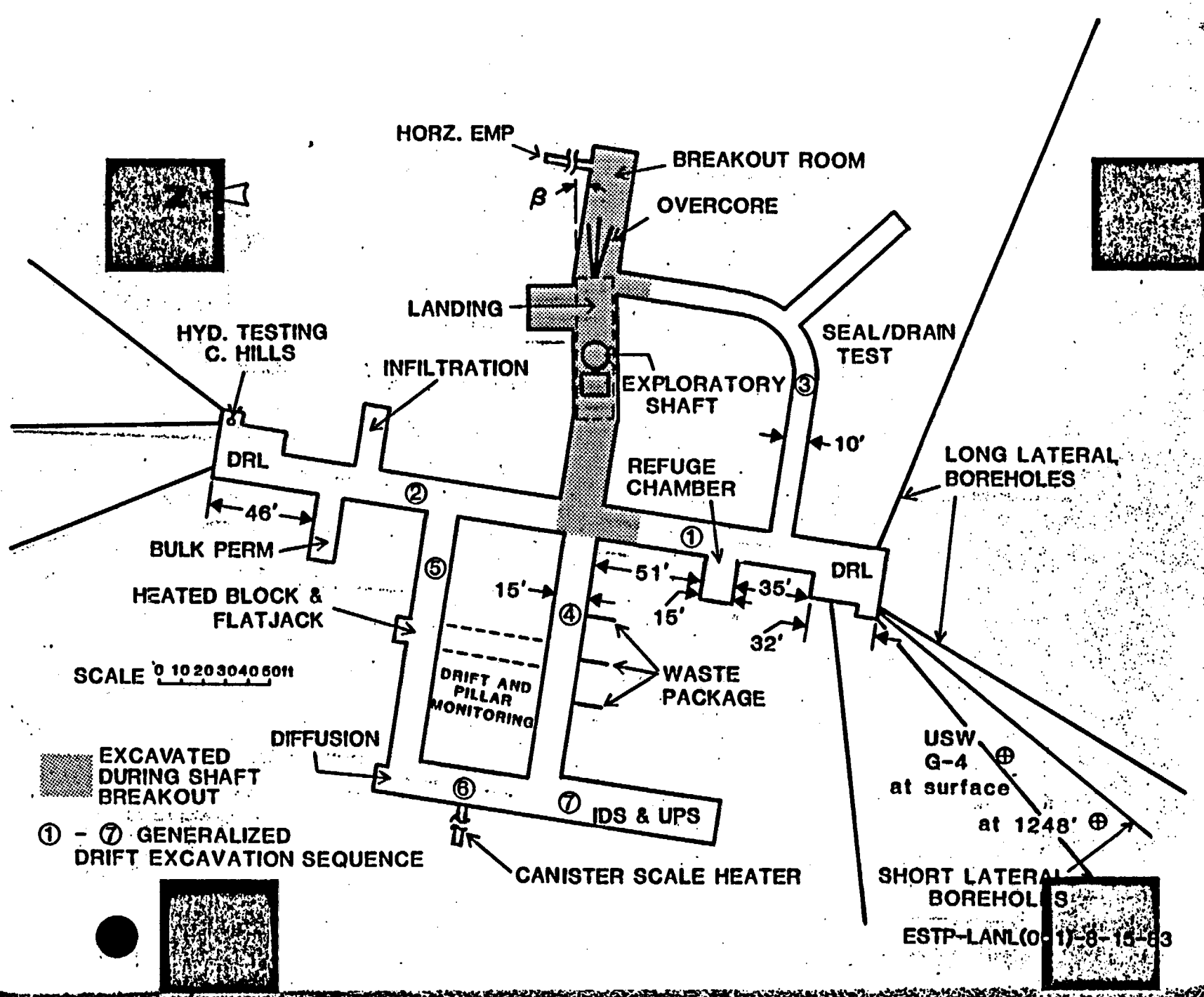


DIFFUSION TEST LOCATIONS

Los Alamos

- **EXPLORATORY SHAFT**
 - MAIN TEST FACILITY – TOPOPAH SPRING TUFF
 - DRILL ROOM – TUFFACEOUS BEDS OF CALICO HILLS
- **NEVADA TEST SITE**
 - PACKER TESTING
 - OVERCORING TECHNIQUE DEVELOPMENT
- **LOS ALAMOS**
 - TRACER SELECTION
 - LABORATORY-SCALE EXPERIMENTS
 - QUANTITATIVE ANALYSES OF OVERCORED MATERIAL
 - COMPUTATIONS





HORZ. EMP

BREAKOUT ROOM

OVERCORE

LANDING

SEAL/DRAIN TEST

HYD. TESTING C. HILLS

INFILTRATION

EXPLORATORY SHAFT

REFUGE CHAMBER

LONG LATERAL BOREHOLES

DRL

BULK PERM

HEATED BLOCK & FLATJACK

DRL

SCALE 0 10 20 30 40 50 60 ft

DRIFT AND PILLAR MONITORING

WASTE PACKAGE

USW G-4 at surface

at 1248'

SHORT LATERAL BOREHOLES

ESTP-LANL(0-1)-8-15-83

EXCAVATED DURING SHAFT BREAKOUT

① - ⑦ GENERALIZED DRIFT EXCAVATION SEQUENCE

CANISTER SCALE HEATER

IDS & UPS

DIFFUSION

②

⑤

15'

④

51'

15'

32'

③

10'

46'

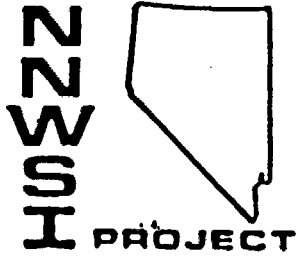
①

⑥

⑦

⑧

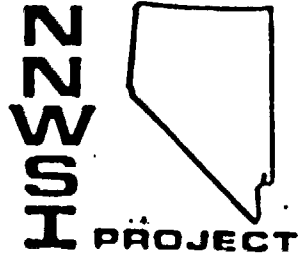
β



DIFFUSION TEST TECHNIQUE

Los Alamos

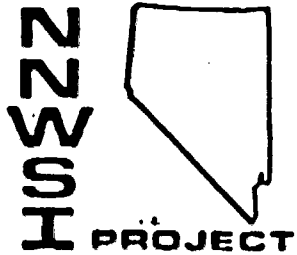
- SELECT TRACERS
- VERIFY PACKER PERFORMANCE
- DEVELOP OVERCORE TECHNIQUE
- LABORATORY DIFFUSIVITY MEASUREMENT
- DRILL *IN SITU* HOLES ~5 cm DIAMETER, 10 m DEEP
- INTRODUCE TRACERS
- SEAL FOR 3 MONTHS TO 1 YEAR
- OVERCORE
- ANALYZE FOR SOLUTE CONCENTRATION WITH DISTANCE FROM EMPLACEMENT
- DERIVE DIFFUSIVITY, D



DIFFUSION TEST EXPECTED VALUE

Los Alamos

- $D \sim 10^{-7} \text{ cm}^2/\text{s}$
- DIFFUSION DISTANCE $\sim 7 \text{ cm}/\text{YEAR}$



DIFFUSION TEST SUMMARY

Los Alamos

- **MEASURE D IN EXPLORATORY SHAFT IN**
 - **MAIN UNDERGROUND FACILITY (TOPOPAH SPRING)**
 - **DRILL ROOM AT BOTTOM (CALICO HILLS)**
- **COMPARE LABORATORY AND FIELD RESULTS**
- **SEARCH FOR INHOMOGENEOUS DIFFUSION TO MEASURE MATRIX FLOW**
- **USE FIELD D VALUES FOR TRANSPORT CODE CALCULATIONS OF RADIONUCLIDE RETARDATION**



PROPOSED ES FRACTURE FLOW EXPERIMENTS

PURPOSES OF PROPOSED EXPERIMENTS

Los Alamos

1. Confirmation of codes
2. Determination of parameters in codes



PROPOSED ES FRACTURE FLOW EXPERIMENTS

LOCATIONS OF PROPOSED EXPERIMENTS

Los Alamos

1. Welded portion of Topopah Springs member
2. Calico Hills tuff
3. Transition region between welded and nonwelded portions of Topopah Springs member



PROPOSED ES FRACTURE FLOW EXPERIMENTS

PROGRAM FOR PROPOSED EXPERIMENTS

Los Alamos

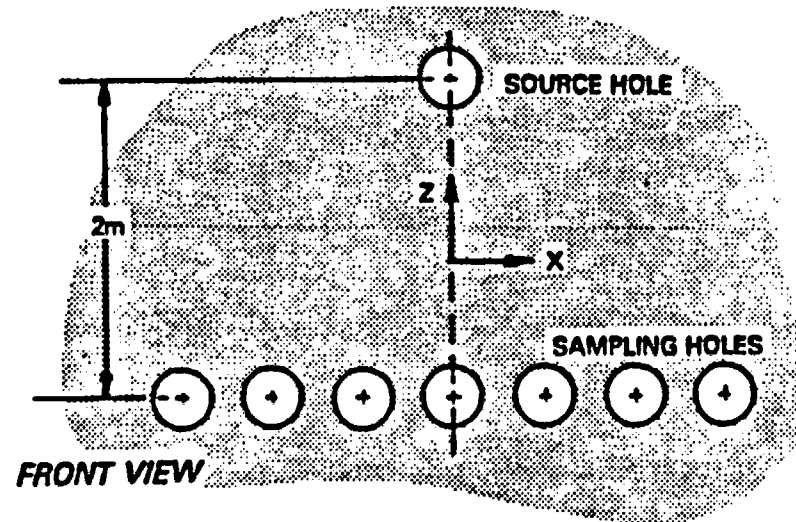
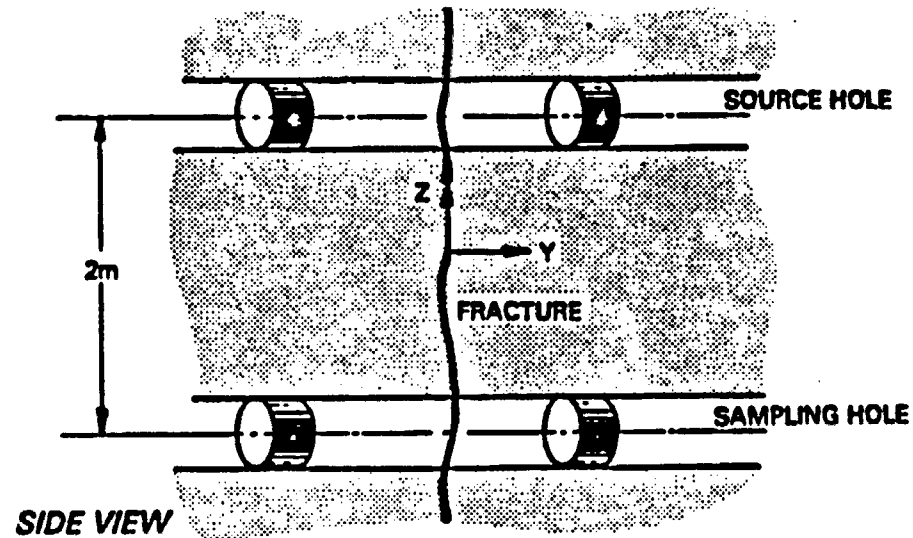
- 1. Predict transport of water and solutes in test location using numerical codes**
- 2. Drill source hole**
- 3. Inject water containing suite of solutes and some particulates -- injected flows greater than natural flows, so measurable transport can occur**
- 4. Drill sampling holes where calculations predict flow**
- 5. Analyze water from sampling holes and compare with predictions**



PROPOSED ES FRACTURE FLOW EXPERIMENTS

IDEALIZED SITUATION FOR SAMPLE CALCULATION

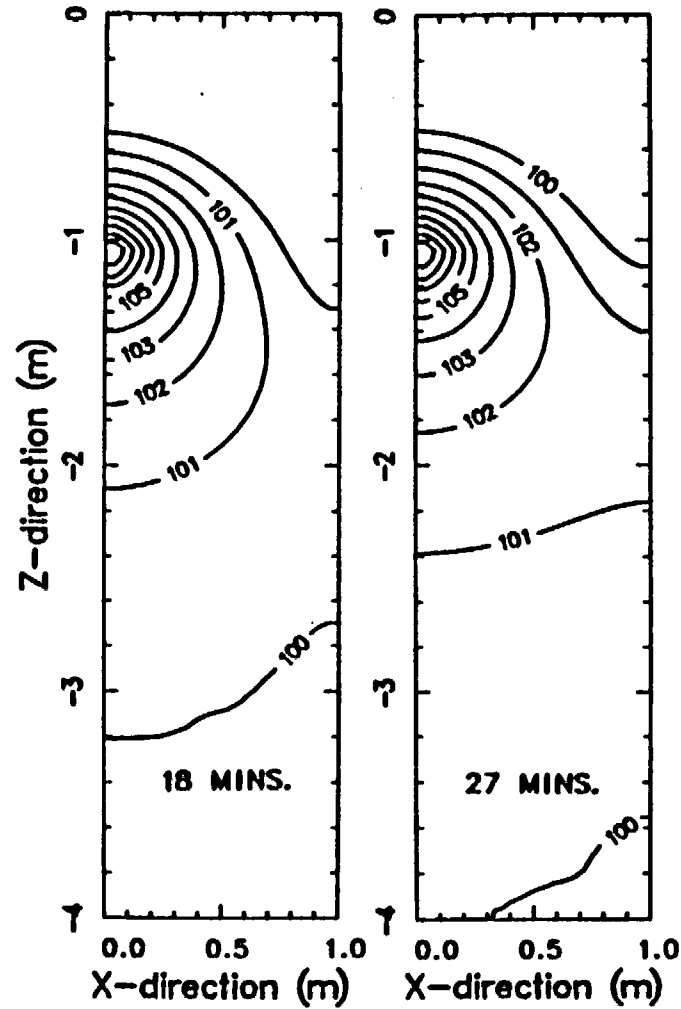
Los Alamos





Water Pressure Contours (10^4 dyne/cm²) at Indicated Times on X-Z Plane of Crack

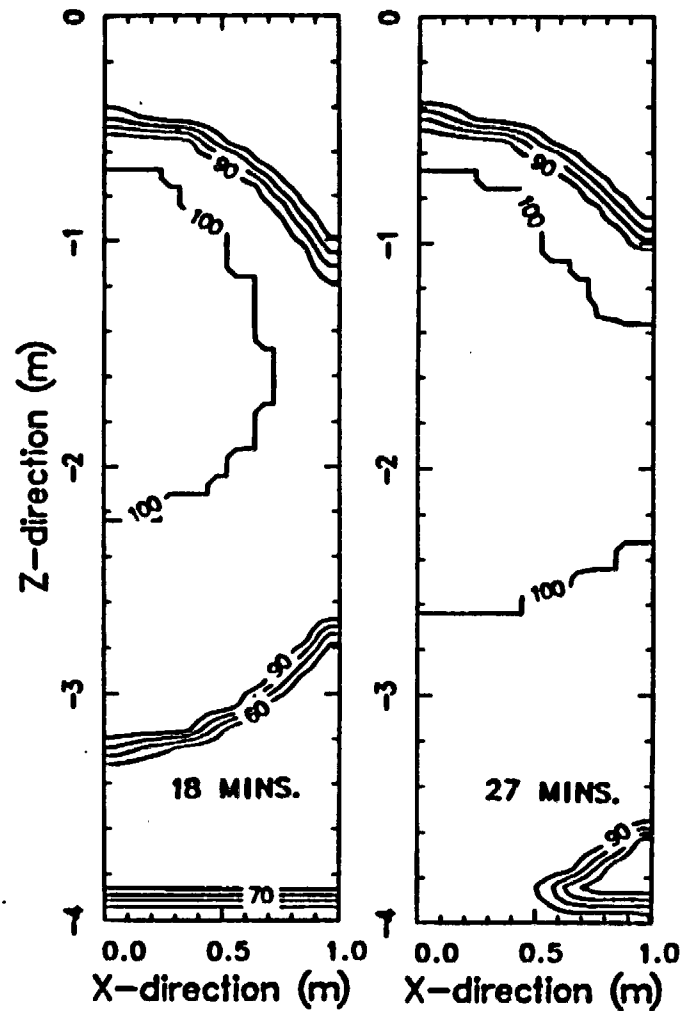
Los Alamos





Water Saturation Contours at Indicated Times on X-Z Plane of Crack

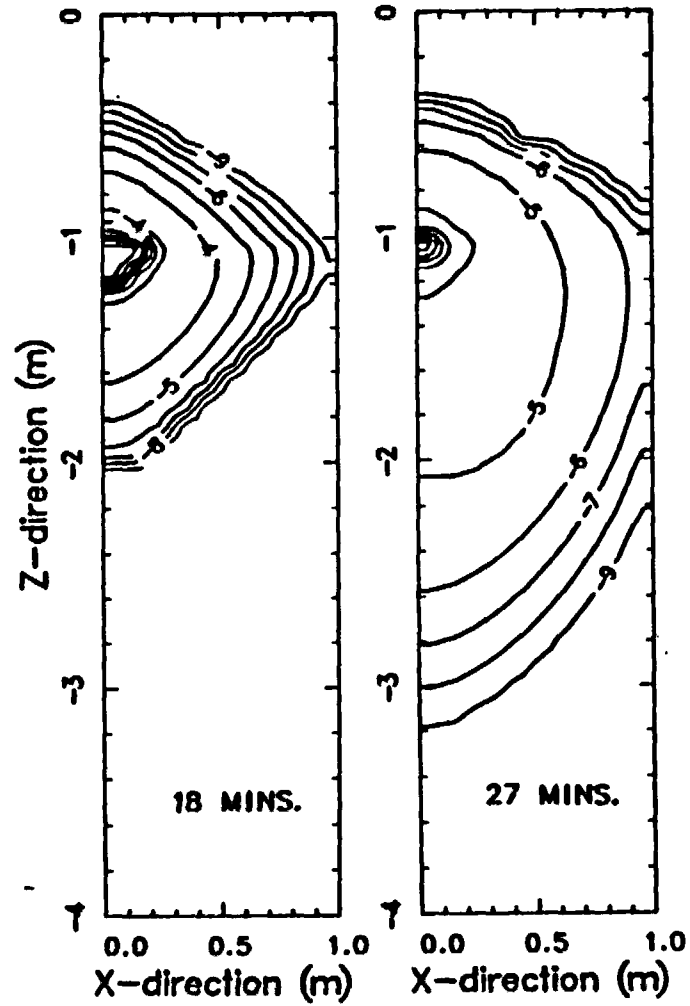
Los Alamos





Tracer Concentration Contours (log-gm/cm³) at Indicated Times on X-Z Plane of Crack

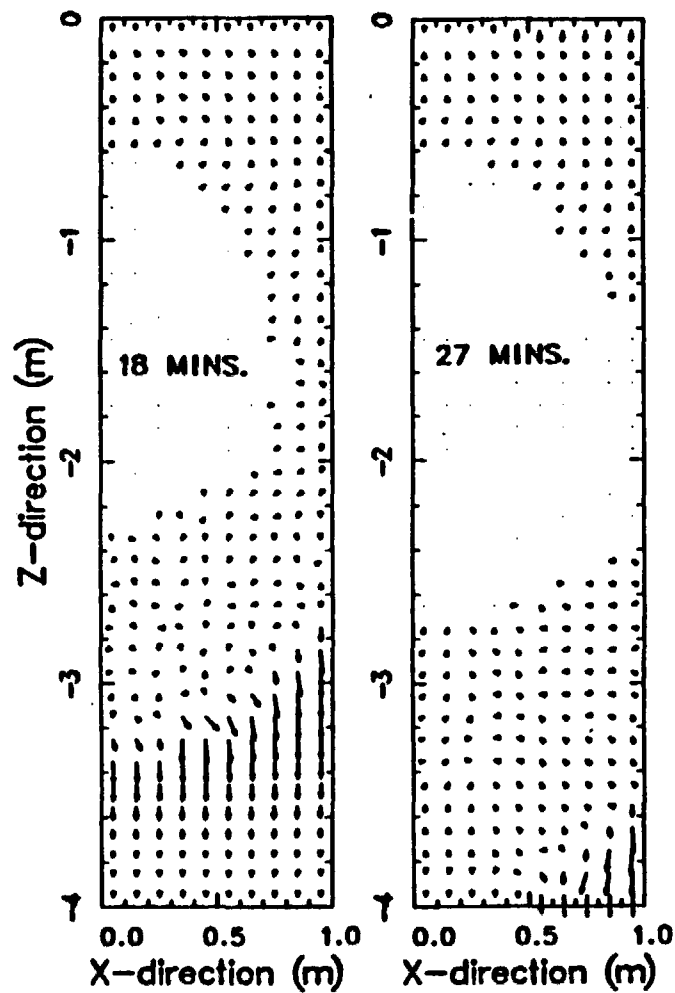
Los Alamos





Air Velocity Vector Field at Indicated Times on X-Z Plane of Crack

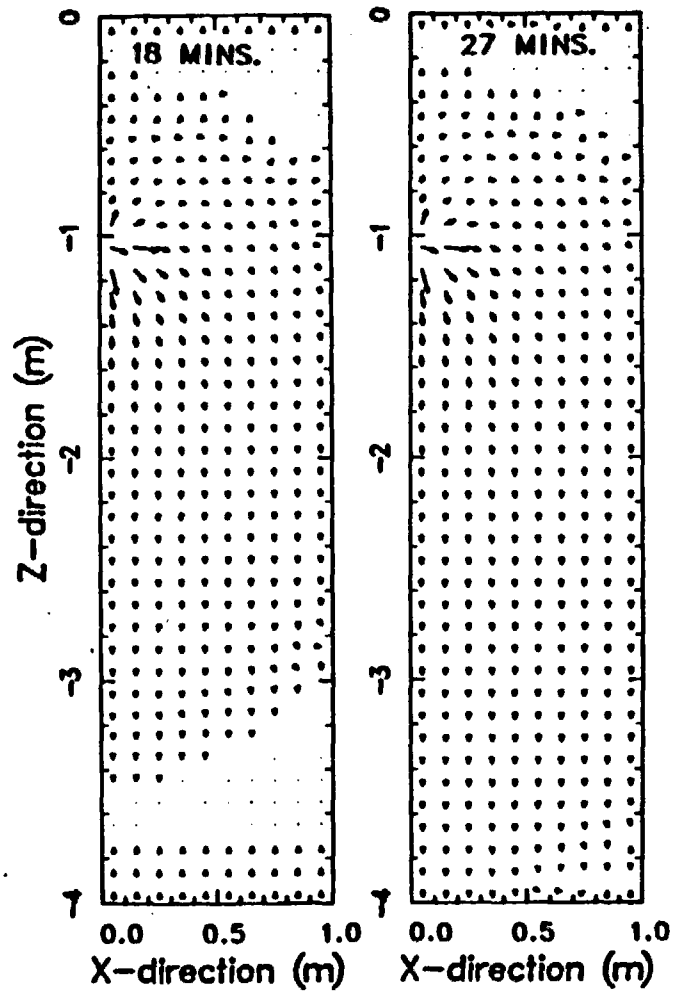
Los Alamos





Water Velocity Vector Field at Indicated Times on X-Z Plane of Crack

Los Alamos



SORPTION



SORPTION AND PRECIPITATION

Los Alamos

UPDATE ON SORPTION AND PRECIPITATION

Kim Thomas

INC-11, Los Alamos

NRC Geochemistry Workshop

July 10-13, 1984



SORPTION RATIOS FOR THORIUM IN J-13 GROUNDWATER

Los Alamos

CORE	TRACED FEED pH	TRACED FEED CONCENTRATION (M)	SORPTION RATIOS (ml/g) ^a		
			EXPERIMENTAL VALUE (pH)	EXPERIMENTAL VALUE (pH)	AVERAGE
G1-1292	5.61	5.39×10^{-8}	566 (7.52)	389 (7.52)	478(63)
G1-2233	5.75	1.07×10^{-7}	266 (7.00)	421 (6.93)	344(55)
G1-2289	5.76	5.86×10^{-8}	140 (6.89)	146 (6.86)	143(2)
G1-2363	5.60	6.52×10^{-8}	940 (6.83)	1484 (6.82)	1213(193)

^aSORPTION TIME WAS 12 DAYS



ANALYSIS OF WELL J-13 WATER PRE-TREATED WITH YUCCA MOUNTAIN TUFF

Los Alamos

<u>SAMPLE NO.</u>	<u>Mg</u> <u>(ppm)</u>	<u>Mn</u> <u>(ppm)</u>	<u>Si</u> <u>(ppm)</u>	<u>Fe</u> <u>(ppm)</u>	<u>Sr</u> <u>(ppm)</u>	<u>Ba</u> <u>(ppm)</u>
ORIGINAL GROUNDWATER	1.76	0.012	31.8	0.011	0.039	0.001
g1-2840	1.660	0.009	33.2	0.007	0.037	0.002
g4-1502	0.016	0.001	23.0	0.016	0.001	0.001
gu3-1301	1.040	0.026	25.7	0.050	0.073	0.003

<u>SAMPLE NO.</u>	<u>V</u> <u>(ppm)</u>	<u>Ti</u> <u>(ppm)</u>	<u>Ca</u> <u>(ppm)</u>	<u>Li</u> <u>(ppm)</u>	<u>K</u> <u>(ppm)</u>	<u>Al</u> <u>(ppm)</u>
ORIGINAL GROUNDWATER	0.021	0.028	11.5	0.060	5.26	0.025
g1-2840	0.010	0.001	11.90	0.057	5.07	0.010
g4-1502	0.000	0.007	0.24	0.050	3.08	0.066
gu3-1301	0.017	0.018	11.10	0.078	6.18	0.031

**ANALYSIS OF WELL J-13 WATER PRE-TREATED
WITH YUCCA MOUNTAIN TUFF (cont)**

<u>SAMPLE NO.</u>	<u>Na</u> <u>(ppm)</u>	<u>F</u> <u>(ppm)</u>	<u>Cl</u> <u>(ppm)</u>	<u>NO₂</u> <u>(ppm)</u>	<u>NO₃</u> <u>(ppm)</u>	<u>SO₄</u> <u>(ppm)</u>	<u>pH</u>	<u>Alk</u>
ORIGINAL GROUNDWATER	45.1	2.1	6.4	-	10.1	18.1	6.9	2.339
g1-2840	48	2.5	7.7	0.00	8.8	18.6	7.56	1.922
g4-1502	51	2.6	8.4	0.00	7.1	19.8	8.09	2.082
gu3-1301	46	2.7	8.8	0.20	8.1	19.0	8.52	2.001



ANALYSIS OF WELL UE25p#1 WATER PRE-TREATED WITH YUCCA MOUNTAIN TUFF

Los Alamos

<u>SAMPLE NO.</u>	Mg (ppm)	Mn (ppm)	Si (ppm)	Fe (ppm)	Sr (ppm)	Ba (ppm)
ORIGINAL GROUNDWATER	31.9	0.103	17.4	0.045	0.390	0.260
G1-2233-2	14.5	0.045	15.6	0.030	0.009	0.006
GU-3-1301-2	26.7	0.015	13.7	0.021	0.009	0.059

<u>SAMPLE NO.</u>	V (ppm)	Ti (ppm)	Ca (ppm)	Li (ppm)	K (ppm)	Al (ppm)
ORIGINAL GROUNDWATER	0.023	0.039	87.8	0.720	13.4	0.139
G1-2233-2	0.011	0.010	15.8	0.557	8.00	0.063
GU-3-1301-2	0.021	0.022	19.5	0.557	9.51	0.064

**ANALYSIS OF WELL UE25p#1 WATER PRE-TREATED
WITH YUCCA MOUNTAIN TUFF (cont)**

<u>SAMPLE NO.</u>	<u>Na (ppm)</u>	<u>F (ppm)</u>	<u>Cl (ppm)</u>	<u>NO₂ (ppm)</u>	<u>NO₃ (ppm)</u>	<u>Br (ppm)</u>
ORIGINAL GROUNDWATER	110.	3.5	37.	-	<0.1	-
G1-2233-2	192.	4.2	34.8	-	-	-
GU-3-1301-2	106.	3.9	34.2	-	-	-

<u>SAMPLE NO.</u>	<u>PO₄ (ppm)</u>	<u>SO₄ (ppm)</u>	<u>pH</u>	<u>Alk meq/l</u>
ORIGINAL GROUNDWATER	-	129.	6.7	11.448
G1-2233-2	-	195.	8.97	10.848
GU-3-1301-2	-	189.	8.91	6.771

COMMENT

HCO₃ = 698
CO₃ = 22.8; HCO₃ = 569
CO₃ = 14.6; HCO₃ = 354



SORPTION RATIOS IN UE-25p#1, J-13, AND DEIONIZED WATERS

Los Alamos

		SORPTION RATIOS (ml/g)	
CORE	ELEMENT	UE-25p#1	J-13
GU3-1301	Sr	10(2)	32(8)
	Cs	45(5)	160(35)
	Ba	82(18)	570(60)
	Eu	>17 000	75(12)

		SORPTION RATIOS (ml/g)		
CORE	ELEMENT	UE-25p#1	J-13	DEIONIZED
G1-2233	Sr	2 000(330)	48 000(3 000)	>56 000
	Cs	7 500(1 100)	13 500(800)	13 000(1 600)
	Ba	41 000(6 300)	250 000(30 000)	55 000(5 300)
	Eu	>5 600	900(200)	810(100)



COMPARISON OF TIN SORPTION RATIOS IN J-13 AND UE-25p#1^a GROUNDWATERS

Los Alamos

<u>CORE</u>	SORPTION RATIOS (ml/g)		DESORPTION RATIOS (ml/g)	
	<u>J-13</u>	<u>UE-25#1</u>	<u>J-13</u>	<u>UE-25#1</u>
G1-2840	283	20000	780	18400
GU3-1301	168	4000	1280	6750
G4-1502	215	800	500	300
G1-2901	22000	35800	38000	52500

^aWATER FROM DEPTH 1298-1792m.



LONG-TERM Tc AND Np SORPTION RATIOS

Los Alamos

CORE	ELEMENT	pH RANGE	TRACER CONC. (M)	SORPTION RATIO (ml/g)
				CONTACT TIME: UP TO 9 MONTH
G4-1502	Tc	8.71-9.00	8×10^{-10}	0-0.02
	Np	8.32-8.70	1×10^{-10}	4.0-5.1
GU3-1301	Tc	8.41-8.72	7×10^{-10}	0-0.04
	Np	8.46-8.67	6×10^{-11}	1.7-2.2
GU3-916	Tc	8.51-8.83	6×10^{-10}	0.13-0.81
	Np	8.08-8.76	6×10^{-11}	4.8-5.4



Am AND Pu SHORT-TERM SORPTION RATIOS ON TUFF G4-1502

Los Alamos

SORPTION TIME	SORPTION RATIO (ml/g)	
	Am	Pu
1 h	490 (20)	19 (1)
4 h	715 (5)	22 (1.2)
1 d	1100 (60)	27 (1)
2 d	1200 (5)	34 (2.3)
3 d	1450 (50)	34 (2.9)
1 wk	1900 (20)	36 (1)
3 wk	1550 (10)	34 (1)
6 wk	1400 (5)	43 (1)



**COMPARISON OF SORPTION RATIOS^a
(R_d) MEASURED UNDER ATMOSPHERIC AND
 N_2 -CONTROLLED-ATMOSPHERE CONDITIONS^b Los Alamos**

<u>ELEMENT</u>	<u>EFFECT ON R_d VALUE</u>
Cs	NONE
Sr	NONE
Ba	NONE
Ce	NONE
Eu	NONE
Na	NONE
Se	NONE
Mn	LOWER IN CA (FACTORS OF 3 TO 4)
Sn	LOWER IN CA (FACTOR OF 2)
Am	NONE
Pu	HIGHER IN CA (FACTOR OF 2)
Tc	HIGHER IN CA (FACTOR OF ≥ 10)
U	HIGHER IN CA ^c (FACTORS OF 2 TO 3)
Np	HIGHER IN CA (FACTOR OF 2)

^aTUFF STUDIED: YM-22, YM-38, YM-54

^bCA = CONTROLLED ATMOSPHERE; NITROGEN, ≤ 0.2 ppm
OXYGEN, AND ≤ 20 ppm CARBON DIOXIDE.

^cYM-38 (ZEOLITIZED) TUFF ONLY; OTHERWISE NO EFFECT.



COMPARISON OF N_p SORPTION RATIOS UNDER AMBIENT AND CO_2 -CONTROLLED ATMOSPHERES

Los Alamos

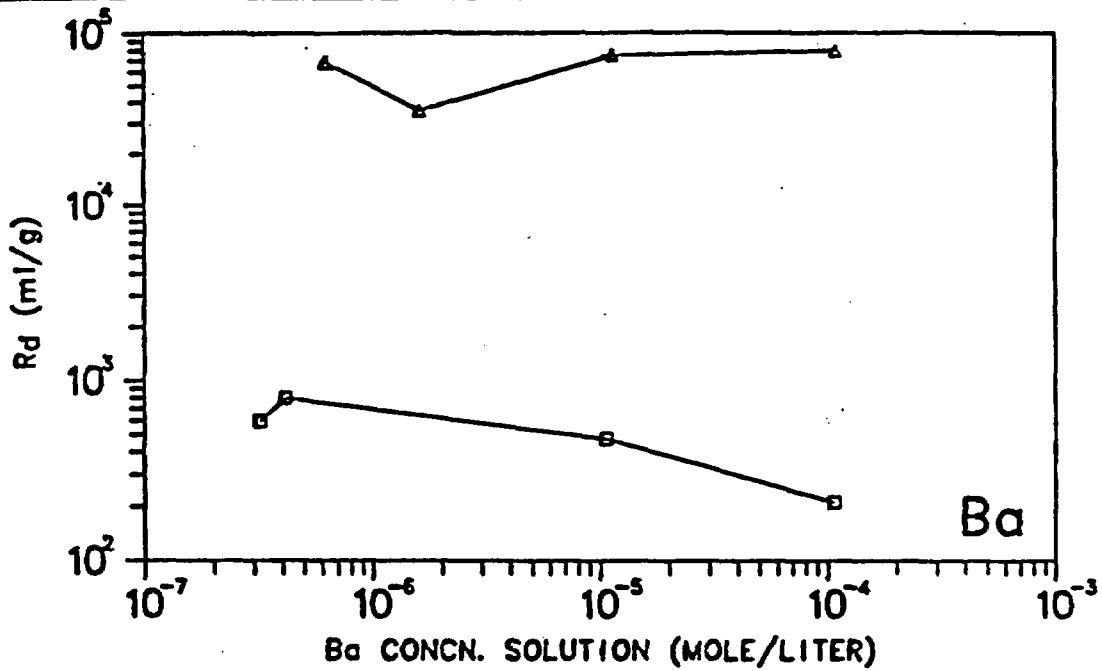
CORE	ATMOSPHERE	SORPTION RATIO (ml/g)
GU3-1203	AMBIENT	0.49
	CO_2	0.35
GU3-1301	AMBIENT	1.7
	CO_2	2.1
G4-1608	AMBIENT	6.3
	CO_2	5.4



**Np ISOTHERM SORPTION RATIOS UNDER
CO₂ - CONTROLLED ATMOSPHERIC CONDITIONS**

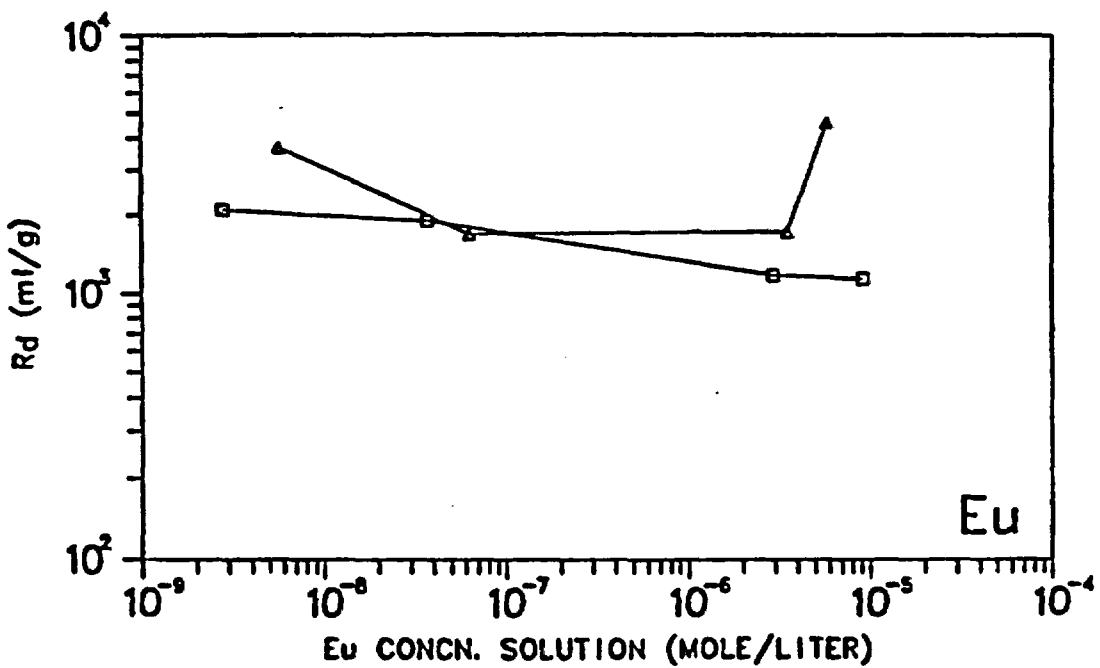
Los Alamos

Np CONC (M)	SORPTION RATIO (ml/g)
6 x 10 ⁻⁴	2.4
3 x 10 ⁻⁴	0.94
7 x 10 ⁻⁵	3.4
3 x 10 ⁻⁵	3.3
8 x 10 ⁻⁶	4.9
3 x 10 ⁻⁶	5.0
7 x 10 ⁻⁷	5.0
4 x 10 ⁻⁷	5.2
2 x 10 ⁻¹¹	5.4



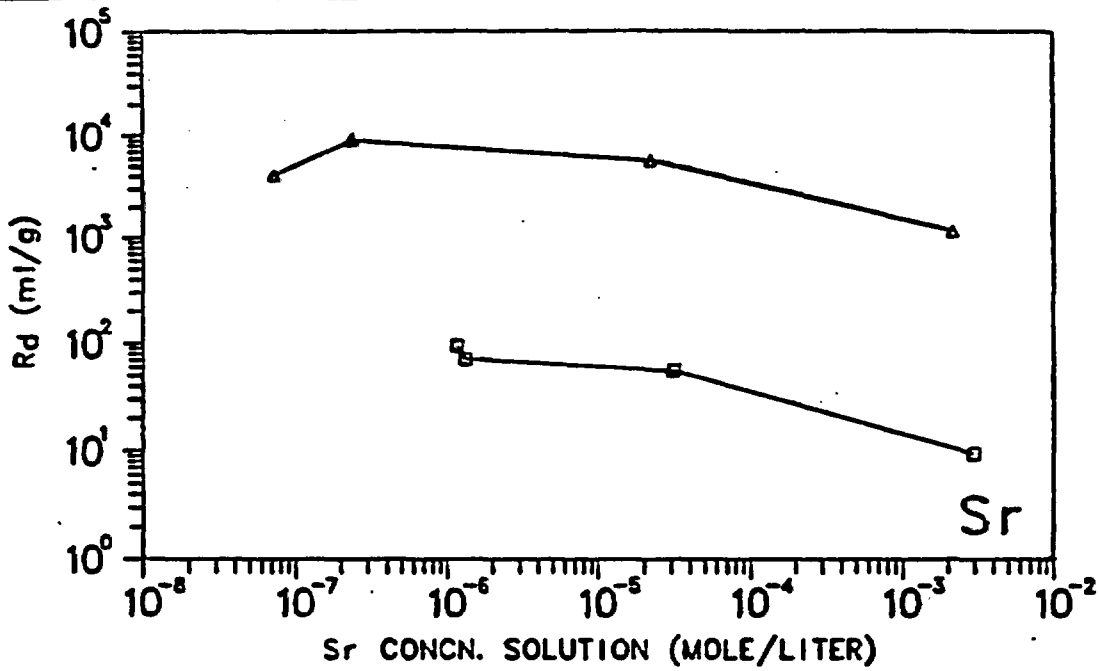
75-500 μ m
 AMBIENT TEMPERATURE

□ YM-22
 Δ YM-38



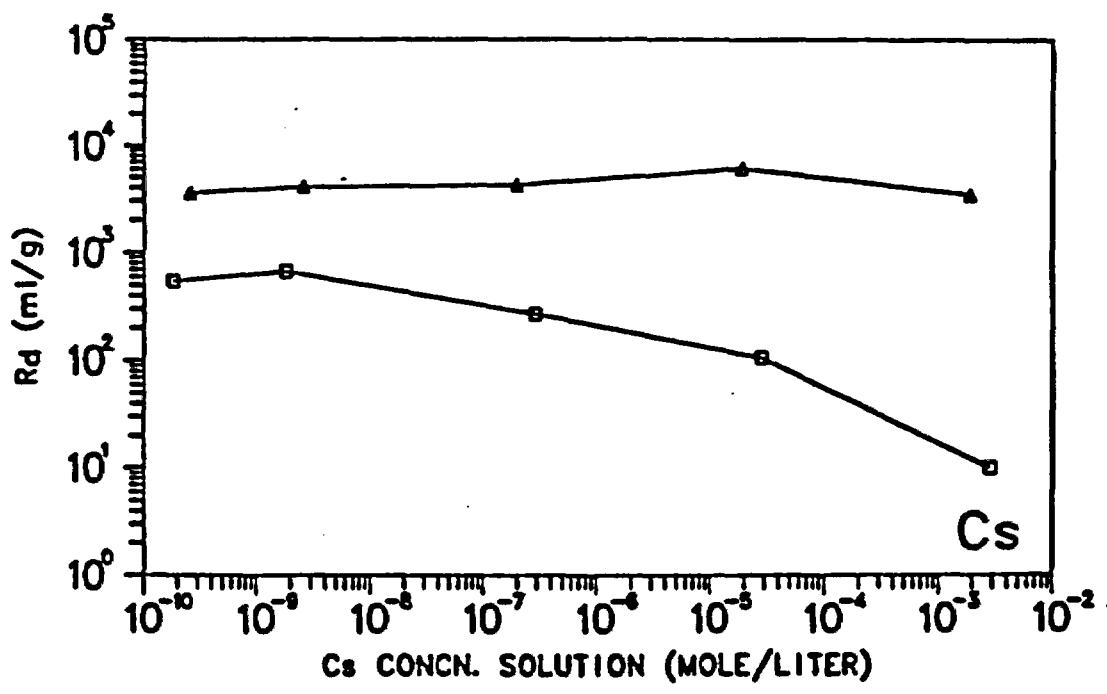
75-500 μ m
 AMBIENT TEMPERATURE

□ YM-22
 Δ YM-38



75-500 μ m
 AMBIENT TEMPERATURE

□ YM-22
 Δ YM-38



75-500 μ m
 AMBIENT TEMPERATURE

□ YM-22
 Δ YM-38



COMPARISON OF AVERAGE SORPTION RATIOS
FROM BATCH AND CIRCULATING-SYSTEM
SORPTION MEASUREMENTS

Los Alamos

BATCH R_d -TO-CIRCULATING SYSTEM R_d RATIO

	Sr	Cs	Ba	Am	Pu
<u>ZEOLITIZED TUFFS</u>					
JA-37	0.74(0.04)	0.34(0.03)	0.88(0.18)	8.2(3.3)	1.4(0.3)
YM-49				2.0(0.7)	0.40(0.15)
<u>DEVITRIFIED TUFFS</u>					
YM-22	2.0(0.2)	0.59(0.09)	7.5(0.7)		
YM-54	1.3(0.2)	1.3(0.3)	1.6(0.6)		
G1-1883				1.4(0.1)	1.4(0.4)



SUMMARY OF DIFFERENCES IN SORPTION RATIOS BETWEEN CRUSHED-ROCK COLUMN AND BATCH MEASUREMENTS

Los Alamos

CORE	⁸⁵ Sr	¹³⁷ Cs	¹³³ Ba
YM-54	0	0	0
YM-38	N.A.	C (1.45)	N.A.
YM-22	0	0	0
JA-37	B (2.08)	0	N.A.
JA-32	0	N.A.	N.A.
GI-3658	B (11.8)	B (1.18)	B (1.91)
GI-3116	-	-	0
GI-2363	0	-	-
GI-2233	0	C	0
GI-1982	0	0	B (1.18)
GI-1883	0	0	B (1.23)
GI-1292	0	C	-



R_d COMPARISON: TUFF WAFERS VS CRUSHED TUFF

Los Alamos

<u>TUFF SAMPLE</u>	<u>ELEMENT</u>	<u>R_d (WAFER) (ml/g)</u>	<u>R_d (BATCH) (ml/g)</u>
G-1-1883	Sr	27	22
	Cs	230	190
	Ba	210	180
G-1-1982	Sr	80	62
	Cs	1000	1200
	Ba	710	800
G-1-1436 (DESORPTION)	Sr	96500	87000
	Cs	14900	24000

BACKUP VIEWGRAPHS AND DATA

LONG-TERM TECHNETIUM SORPTION RATIOS

Core	Tracer Feed pH	Traced Feed Concentration (M)	Sorption Time	Sorption Ratios (m ² /g)		
				Experimental Values (pH)		Average
G-4-1502	8.74	8 x 10 ⁻¹⁰	6 weeks	0.042 (8.60)	-0.003 (8.60)	0.02(0.02)
			13 weeks	0.06 (9.00)	-0.038 (8.81)	0.01(0.05)
			6 months	-0.085 (8.65)	-0.09 (8.65)	0
			9 months	-0.06 (8.71)	-0.05 (8.75)	0
GU-3-1301	8.67	7 x 10 ⁻¹⁰	6 weeks	0.058 (8.41)	0.022 (8.47)	0.04(0.02)
			13 weeks	0.065 (8.63)	0.002 (8.69)	0.03(0.03)
			6 months	-0.003 (8.60)	0.004 (8.61)	0
			9 months	0.013 (8.70)	0.031 (8.72)	0.02(0.01)
GU-3-916	8.57	6 x 10 ⁻¹⁰	6 weeks	0.50 (8.51)	0.94 (8.57)	0.72(.2)
			13 weeks	0.33 (8.75)	1.3 (8.70)	0.81(0.5)
			6 months	0.81 (8.61)	0.44 (8.66)	0.62(0.2)
			9 months	0.14 (8.81)	0.11 (8.83)	0.13(0.02)

LONG-TERM NEPTUNIUM SORPTION RATIOS

Core	Tracer Feed pH	Traced Feed Concentration (M)	Sorpton Time	Sorpton Ratios (mL/g)		
				Experimental Values (pH)		Average
G-4-1502	8.72	1×10^{-10}	6 weeks	4.6 (8.33)	3.5 (8.32)	4.0(1)
			3 months	5.1 (8.66)	3.4 (8.70)	4.3(1)
			6 months	4.7 (8.44)	5.0 (8.49)	4.8(1)
			9 months	5.2 (8.37)	5.0 (8.53)	5.1(1)
GU-3-1301	8.4	2×10^{-11}	6 weeks	1.8 (8.53)	1.7 (8.54)	1.7(1)
			3 months	2.3 (8.63)	2.1 (8.65)	2.2(1)
	8.6	6×10^{-11}	3 months	2.1 (8.65)	1.9 (8.67)	2.0(1)
			6 months	2.2 (8.55)	2.3 (8.62)	2.2(1)
			9 months	1.9 (8.46)	1.8 (8.47)	1.9(1)
			6 weeks	4.8 (8.76)	4.9 (8.65)	4.8(1)
GU-3-916	Not Available	6×10^{-11}	3 months	5.1 (8.69)	5.4 (8.68)	5.3(1)
			6 months	5.6 (8.48)	5.2 (8.54)	5.4(1)
			9 months	5.1 (8.24)	5.1 (8.08)	5.1(1)

NEPTUNIUM ISOTHERM SORPTION RATIOS UNDER
 CO_2 -CONTROLLED ATMOSPHERIC CONDITIONS^a

Traced Feed Concentration (M)	Traced Feed pH	Sorption Ratios (ml/g)		
		Experimental Values (pH)		Average Value ^b
6×10^{-4}	7.0	2.0 (6.4)	2.7 (6.3)	2.4(1)
3×10^{-4}	7.2	1.3 (6.4)	0.57 (6.5)	0.94(1)
7×10^{-5}	7.3	3.5 (6.7)	3.2 (6.7)	3.4(1)
3×10^{-5}	7.2	3.4 (6.7)	3.1 (6.7)	3.3(1)
8×10^{-6}	7.3	4.7 (6.7)	5.1 (6.7)	4.9(1)
3×10^{-6}	7.3	4.5 (6.7)	5.4 (6.7)	5.0(1)
7×10^{-7}	7.3	5.2 (6.7)	4.7 (6.7)	5.0(1)
4×10^{-7}	7.3	4.4 (6.7)	5.9 (6.7)	5.2(1)
2×10^{-11}	7.2	5.2 (6.7)	5.6 (6.8)	5.4(1)

^aCore was G-4-1608, 75-500 μm . Atmosphere was enriched in CO_2 to ~5%. Sorption was for 6 weeks.

^bNumbers in parentheses are standard deviations of the mean.

AMERICIUM AND PLUTONIUM SHORT-TERM SORPTION RATIOS ON USW G-4-1502 CRUSHED ROCK^a

Sorption Time	Am ^b				Pu ^c			
	pH Values		R _d (mg/g)		pH Values		R _d (mg/g)	
	Feed ^d	Sample	Individual	Average ^e	Feed ^d	Sample	Individual	Average ^e
1 hour		8.3	470			8.4	19	
	8.5	8.3	510	490(20)	8.4	8.2	20	19(1)
4 hour		8.4	720			8.2	24	
	8.5	8.4	710	715(5)	8.4	8.1	21	22(1.2)
1 day		8.3	1000			8.3	26	
	8.5	8.4	1200	1100(60)	8.4	8.3	28	27(1)
2 day		8.4	1200			8.3	36	
	8.5	8.4	1200	1200(5)	8.4	8.3	31	34(2.3)
3 day		8.3	1500			8.4	31	
	8.5	8.3	1400	1450(50)	8.4	8.4	38	34(2.9)
1 week		8.5	1800			8.3	36	
	8.5	8.4	2000	1900(20)	8.4	8.3	37	36(1)
3 week		8.5	1600			8.5	34	
	8.5	8.5	1500	1550(10)	8.4	8.5	34	34(1)
6 week		8.5	1400			8.6	44	
	8.5	8.5	1400	1400(5)	8.4	8.6	43	43(1)

^aThe rock particle size was 75-500 μm.

^bThe americium concentration was 1.3×10^{-8} M.

^cThe plutonium concentration was 3.1×10^{-8} M.

^dAliquots of the same americium or plutonium feed solutions were used for all of these experiments.

^eThe values in parentheses are the standard deviation of the means.

THE 3- AND 6-WEEK SORPTION MEASUREMENTS FOR PLUTONIUM AND AMERICIUM

Core	Core Sorption Category	Sorption Time (weeks)	Pu		Am	
			R_d (ml/g)	R_d	R_d (ml/g)	R_d
JA-37	Devitrified, Smectite	3	~300		18 000	
		6	~490	1.63	37 000	2.06
YM-22	Devitrified	3	37		1500	
		6	64	1.73	1100	0.73
YM-38	Zeolitized	3	58		6100	
		6	120	2.07	5200	0.85
YM-49	Zeolite and Glass	3	140		2900	
		6	~180	1.29	2800	0.97
YM-54	Devitrified	3	52		150	
		6	81	1.56	160	1.07
G-1-1292	Glass	3	~160			
		6	~530	3.31	Not Measured	
G-1-1883	Devitrified	3	~51		4200	
		6	~72	1.41	4500	1.07
G-4-1502	Zeolitized	3	34(1)		1550(10)	
		6	43(1)	1.26	1400(5)	0.90

COMPARISON OF NEPTUNIUM SORPTION RATIOS UNDER AMBIENT
AND CO₂-CONTROLLED ATMOSPHERIC CONDITIONS

Core ^a	Atmospheric Conditions ^b	Traced Feed pH	Traced Feed Concentration (M)	Sorption Ratio ^c (m ₂ /g)		
				Experimental Value (pH)	Average Value ^d	Value
GU-3-1203	Ambient	8.6	3 x 10 ⁻¹¹	0.5 (8.4)	0.49 (8.5)	0.49(1)
	CO ₂	7.1	6 x 10 ⁻¹¹	0.36 (6.8)	0.35 (6.8)	0.35(1)
GU-3-1301	Ambient	8.4	2 x 10 ⁻¹¹	1.8 (8.53)	1.7 (8.54)	1.7(1)
	CO ₂	---	2.5 x 10 ⁻¹¹	2.1 (6.65)	2.1 (6.63)	2.1(1)
G-4-1608	Ambient	8.7	3.5 x 10 ⁻¹¹	6.1 (8.3)	6.6 (8.4)	6.3(1)
	CO ₂	7.2	2 x 10 ⁻¹¹	5.2 (6.7)	5.6 (6.8)	5.4(1)

^aFraction size was 75-500 μm.

^bCO₂-atmosphere was controlled to be enriched to ~5% in CO₂.

^cSorption times were 6 weeks.

^dNumbers in parentheses are standard deviations of the mean.

AVERAGE SORPTION RATIOS FROM BATCH AND
CIRCULATING-SYSTEM SORPTION MEASUREMENTS

<u>Element</u>	<u>Tuff Core</u>	R_d (ml/g)	
		<u>Batch</u>	<u>Circulating System</u>
Sr	YM-22	53(3)	27(2)
	YM-54	62(12)	45(3)
	YM-37	287(14)	390(10)
Cs	YM-22	290(30)	490(50)
	YM-54	180(40)	120(10)
	JA-37	610(40)	1800(80)
Ba	YM-22	900(30)	120(10)
	YM-54	400(150)	130(10)
	JA-37	760(150)	860(40)
Am	YM-49	4300(1400)	2200(300)
	JA-37	28 000(10000)	3400(600)
	G-1-1883	4700(300)	3300(100)
Pu	YM-49	230(50)	570(170)
	JA-37	400(70)	290(20)
	G-1-1883	77(11)	56(11)

SUMMARY OF DIFFERENCES IN SORPTION RATIOS BETWEEN
CRUSHED-ROCK COLUMN AND BATCH MEASUREMENTS^a

Core	<u>⁸⁵Sr</u>	<u>¹³⁷Cs</u>	<u>¹³³Ba</u>
YM-54	0	0	0
YM-38		C > B (1.45)	
YM-22	C < B ^b	0	C < B ^b
JA-37	C < B (2.08)	C > B (1.36) ^b	
JA-32	0		
G-1-3658	C < B (11.8)	C < B (1.18)	C < B (1.91)
G-1-3116	C < B	C < B	0
G-1-2901	C < B	C < B	C < B
G-1-2476	C < B	C < B	C < B
G-1-2363	0	C < B	C < B
G-1-2233	0	C > B	0
G-1-1982	0	0	C < B (1.18)
G-1-1883	0	0	C < B (1.23)
G-1-1292	0	C > B	C < B

^a"0" indicates the column R_d value fell within the range of measured batch values or that the ranges overlapped (if more than one column measurement was made). C < B or C > B indicates the column R_d value was less than or greater than the batch R_d value. If a number follows in parentheses, it is the factor by which column and batch values differ. Numbers are not given when only batch data on unwashed fractions are unavailable for comparison. This is because the apparent differences between column and batch values may not be real.

^bC = B when results from the "circulating" type of batch measurements are included.

SORPTION OF WAFERS ON TUFF G-1-1883^a

Time (hours)	R_d (ml/g)		
	Sr	Cs	Ba
2.55	0.85	11	7.5
4.53	8.8	25	20
6.00	11	32	26
10.0	18	63	50
15.0	22	75	61
21.1	26	100	87
24.0	27	100	93
120	24	190	130
144	25	210	140
192	26	230	140
305	24	230	150
(504)	(22)	(190)	(180)
869	27	230	210
[Column]	[14;28]	[129;283]	[85;162]

SORPTION ON WAFERS OF TUFF G-1-1982^a

Time (hours)	R_d (ml/g)		
	Sr	Cs	Ba
5.0	17	65	45
7.0	30	110	78
12.0	36	180	130
16.0	45	190	170
112	84	620	580
136	86	670	560
190	88	760	560
303	84	750	650
(336)	(53)	(1120)	(670)
(504)	(62)	(1200)	(800)
860	80	1000	710
[Column]	[53]	[1350;1720]	[483]

^aThe numbers in parentheses are the contact time and average R_d values from batch measurements with washed fractions >38 μ m.