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*Summary of the Mineralogy-Petrology of  
Tuffs of Yucca Mountain and the  
Secondary-Phase Thermal Stability in Tuffs*

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SUMMARY OF THE MINERALOGY-PETROLOGY OF TUFFS OF YUCCA MOUNTAIN  
AND THE SECONDARY-PHASE THERMAL STABILITY IN TUFFS

by

D. L. Bish, D. T. Vaniman, F. M. Byers, Jr., and D. E. Broxton

ABSTRACT

Yucca Mountain is composed of a thick sequence of silicic tuffs that are quite variable in degree of welding, alteration, and zeolitization. Tuff units above the water table are commonly devitrified or still vitric, with the exception of the zeolitized Pah Canyon Member in USW-G2. The devitrified tuffs above the water table commonly contain alkali feldspar, quartz, tridymite, and cristobalite, with minor smectite. The vitric tuffs are partly to wholly altered to sodium-calcium-saturated smectite.

Below the water table are generally densely welded nonzeolitized tuffs and less densely welded zeolite-containing tuffs. The shallowest zeolite to appear is clinoptilolite, generally occurring first in the tuffs of Calico Hills. Mordenite often occurs with clinoptilolite. With depth, both clinoptilolite and mordenite disappear as analcime appears, and analcime can persist to 1829 m depth. There is evidence for the transition of analcime to albite in the deeper sections of core examined. Whereas the zeolite distribution is stratified, smectites are ubiquitous in Yucca Mountain tuffs, composing up to 50% of some samples of core. In the southern part of Yucca Mountain, the smectites are randomly interstratified with small amounts of illite to 1829 m, but the smectites react through a series of random and ordered interstratifications with illite in rocks from the northern portion of Yucca Mountain. The clay minerals at the bottom of hole USW-G2 are illite and chlorite, reflecting paleotemperatures greater than 230°C.

The specific mineral assemblage present in Yucca Mountain tuffs has important implications in choosing a repository. The secondary phases clinoptilolite, mordenite, and smectite are very important because of their large cation sorption capacities. However, whereas densely welded tuffs containing no zeolite or glass are resistant to heating and do not dehydrate significantly, zeolitized, vitric, and smectite-containing horizons are very sensitive to minor increases in temperature. Smectites are particularly sensitive to changes in water vapor pressure and temperature, and temperature increases can lead to water evolution and large volume reductions. Similarly, clinoptilolite and mordenite begin to dehydrate below 100°C, resulting in volume

decreases. The exact effect of temperature on vitric tuffs is unclear. Under hydrothermal conditions the smectites gradually transform to nonexpanding, low sorption capacity illites, and there is evidence that this reaction has occurred in the deeper portions of USW-G2. Clinoptilolite transforms under hydrothermal conditions to analcime plus quartz with a concomitant volume decrease and water evolution. Again, there is evidence of this reaction occurring in Yucca Mountain tuffs at 80-100°C. Work is ongoing to better delineate the zeolite- and smectite-rich zones in Yucca Mountain and to better understand the effects of elevated temperatures on the phases in Yucca Mountain tuffs.

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## I. INTRODUCTION

The purpose of this report is to summarize our knowledge of the mineralogy and petrology of the tuffs of Yucca Mountain related to geologic studies for the Nevada Nuclear Waste Storage Investigations (NNWSI). The report describes the currently known range of lateral variability of the tuff units and the variation in mineralogy and petrology from unit to unit as determined through studies of core obtained from exploratory drilling. The distribution of secondary phases, including clays, zeolites, and silica phases, is also documented, and the current state of knowledge concerning the effects of temperature on these secondary phases and the resultant effects on a repository are reviewed.

Mineralogical and petrological studies of the tuffs of Yucca Mountain have been underway at Los Alamos for several years, starting with the studies of core from the J-13 drill hole (Heiken and Bevier 1979). Studies on the mineralogy-petrology of Yucca Mountain tuffs are undertaken for several reasons. In order to consider tuff as a potential repository for storage of high-level waste, a unit must be identified that has certain requisite physical properties, including high thermal conductivity, relatively high thermal stability, proximity to rocks with a high sorption potential for possible waste elements, and high physical strength. Also, this unit must be relatively thick and continuous over a scale of miles, and it should be laterally homogeneous to ensure the integrity of the entire repository and for purposes of exploration characterization. It is also important to know the past history of geologic processes affecting the rock units under investigation.

Mineralogy-petrology studies yield information on the thermal and alteration history and frequently on the hydrologic history of the rocks. Finally, examinations of deep sections of drill core provide considerable insight into the expected mineral reactions and transformations that can occur in tuffs at elevated temperatures with time.

Los Alamos geologists have examined the detailed mineralogy and petrology of core from several drill holes, J-13 (Heiken and Bevier 1979), UE25a-1 (Sykes et al. 1979, Carroll et al. 1981), USW-G1 (Bish et al. 1981, Bish 1981), UE25b-1H and USW-G2 (Caporuscio et al. 1982). The USW-G3 and USW-GU3 cores and samples from H-3, H-4, and H-5 will be examined near the end of FY 1982. During these studies, we have cooperated with the US Geological Survey in determining the stratigraphic relations, and we have examined the textures, mineralogy, and compositions of both primary and secondary phases. Initially, emphasis was placed on the primary and secondary textures in the tuffs and on the compositions of primary phases and zeolites. As these studies progressed, increased emphasis was placed on the type and distribution of secondary phases with low thermal stabilities, such as glass (perlite), zeolite, clay, and silica phases. These mineralogic and petrologic investigations have used several instrumental techniques, including optical and scanning electron microscopy, x-ray powder diffractometry, and electron probe microanalysis.

Polarizing petrographic microscopes (reflected and transmitted light) were used to examine thin sections, providing descriptions of such features as degree of welding, effects and products of primary devitrification, vapor-phase alteration, zeolitization, clay alteration, and average opaque mineral oxidation state. In general, the phases present in the fine-grained ground-mass could not be accurately identified using the petrographic microscope, and clay mineral identifications were not attempted optically. An ISI, model DS 130, scanning electron microscope (SEM) has been used to examine the pore structure and textures of tuffs, to identify phases present below the detection limits of x-ray diffraction, and to examine mineral distributions. However, only rough compositional data can be obtained with the SEM, and it is often not possible to differentiate between the different alkali-aluminum silicates present in the rocks.

Oxidation states of the iron-titanium oxides in the tuffs were determined using the series of empirical oxidation exsolution stages for cubic ( $C_1$  to  $C_7$ ) and rhombohedral ( $R_1$  to  $R_7$ ) oxides devised by Haggerty (1976). In this

classification, 1 denotes unoxidized and 7 denotes complete oxidation. Because the oxidation state of the cubic oxides in all cases closely parallels that of the rhombohedral oxides, all oxides are reported using the  $C_x$  notation. The oxidation state of the oxides is dependent on the ambient oxygen fugacity, which in turn can be related to initial rock permeability and degree of welding. The iron-titanium oxides are typically highly oxidized ( $C_5$  to  $C_7$ ) in nonwelded tuffs, and densely welded tuffs contain generally unoxidized oxides ( $C_1$  to  $C_3$ ). However, tuffs containing sulfides, carbonates, or vapor-phase alteration may not follow these generalizations.

Mineral and glass compositions were determined using an automated Cameca microprobe, with data obtained at either 10 seconds or 30 000 counts for each element. Compositions were determined from corrected peak intensities using the methods of Bence and Albee (1968). As with the SEM, it is often difficult to differentiate between compositionally similar zeolites, primarily because of the lack of data for water contents of these hydrous minerals. Also, it was usually not possible to analyze the fine-grained minerals in the groundmass, and feldspar analyses are often averages of material exsolved on a submicron scale, particularly for finely intergrown feldspars that are products of devitrification.

The method and quality of the x-ray powder diffraction analyses used to examine the tuffs have improved as the quality of the instrumentation in the laboratory has improved. Initial x-ray studies of the mineralogy of Yucca Mountain tuffs were carried out using Debye-Scherrer cameras, and results using this technique were only qualitative (Heiken and Bevier 1979, Sykes et al. 1979). Also, this technique is not well suited to clay mineral analysis. Bish et al. (1981), Carroll et al. (1981), Bish (1981), and Caporuscio et al. (1982) used a Siemens D-500 powder diffractometer using a copper target and a diffracted-beam monochromator. The techniques in the individual studies are documented in the appropriate reports, and the methods are constantly being improved. Recent analyses use -300-mesh material homogenized from a 15- to 20-g sample of core, and the powders are placed in sample mounts large enough so that the sample area fully contains the x-ray beam at the lowest angle of interest. Mineral identification is accomplished by comparison of observed patterns to standard patterns produced in this laboratory and by comparison to standards from the Joint Committee on Powder Diffraction Standards (1974). Estimation of concentrations of the various minerals present is accomplished

through comparison to in-lab standards and with consideration of the absolute scattered intensity of each phase. It is commonly assumed that significant preferred orientation is absent or constant, and this assumption is constantly verified by running duplicate diffractometer scans of different sample mounts. It is not assumed that all minerals in the tuffs have similar total scattering, even though they have approximately the same average atomic number. Absolute intensities obtained from calculated powder patterns and from standard patterns demonstrate that all minerals in the tuffs do not scatter similarly. The absolute intensity information is now used in computer programs to determine the relative percentages of different phases in the tuffs. However, because of the large number of phases present, the compositional variations in the minerals within the tuffs, and the difficulties in obtaining representative standards, concentrations given in reports are presented with appropriate notification of their sizeable uncertainties.

what, if constant but standards don't have preferred orientations?

criteria?

Clay mineral separations have often been performed in order to obtain accurate information on the clays in the tuffs. The separations require an initial dispersion of crushed samples in 600 to 1000 ml of distilled water in an ultrasonic bath. The large size fraction is deposited, and the less than 2- $\mu$ m fraction is obtained through centrifugation in a Sorvall SS-3 centrifuge. Oriented sample mounts for x-ray diffraction are prepared by dropping an aqueous suspension onto glass slides and allowing it to dry. These mounts are then used to determine the type of clay minerals present using the methods described by Bish (1981).

A separate program on mineral stability grew out of the mineralogy-petrology studies as a result of the discovery that the zeolites and clays that are advantageous from a sorption point of view may have limited thermal stability (Smyth and Caporuscio 1981). The diagenetic reaction of clinoptilolite-heulandite minerals to analcime with depth in the cores illustrates the types of reactions possible when tuffs are exposed to elevated temperatures. The purpose of this program is to identify unstable phases; to examine the effects of temperature, water pressure, and time on these phases; and to assess the effects of these phases on possible repository performance.

thermal?  
chemical

how?

## II. GENERAL DESCRIPTION OF THE TUFFS OF YUCCA MOUNTAIN

This section provides a general description of the mineralogy and petrology of tuff encountered in drill holes at Yucca Mountain, and it includes optical, microprobe, and x-ray diffraction data. Particular emphasis will be placed on the units of potential interest for a buried waste repository: the Topopah Spring Member of the Paintbrush Tuff, the tuff of Calico Hills, the Bullfrog Member of the Crater Flat Tuff, the Tram unit of the Crater Flat Tuff, and the Lithic Ridge Tuff. In the drill holes examined to date, J-13 [US Geological Survey (USGS) test well 6], UE25a-1, USW-G1, UE25b-1h, and USW-G2, the first tuff generally encountered is the Paintbrush Tuff, although the USW-G1, J-13, and UE25a-1 sections are capped by alluvium. The Paintbrush Tuff consists of the Tiva Canyon Member, the Yucca Mountain Member, the Pah Canyon Member, and the Topopah Spring Member, although some members are missing in some drill holes. The Paintbrush Tuff is underlain by the tuff of Calico Hills, and the Crater Flat Tuff occurs below the Calico Hills. The Crater Flat Tuff is made up of the Prow Pass Member, the Bullfrog Member, and the Tram unit. A dacite flow breccia locally occurs below the Crater Flat Tuff, underlain in turn by the Lithic Ridge Tuff. Below the Lithic Ridge Tuff are numerous older bedded and ash-flow tuffs and lavas that generally are more poorly characterized than the upper portions of the drill holes. A map showing the location of all drill holes examined is presented in Fig. 1. Stratigraphic relations are compared in Fig. 2 for all drill holes, and summary stratigraphic logs are given in Tables I-IV. Figures 3-6 show summary diagrams of lithology and mineral zones for all drill holes.

### PAINTBRUSH TUFF

#### Tiva Canyon Member

The Tiva Canyon Member is the uppermost unit in all drill holes except USW-G1 where it is absent, and the Tiva Canyon is covered by alluvium in all drill holes but USW-G2 and USW-G3. The alluvium was sampled only in J-13 and consisted of sandy to pebbly gravel or submature volcanic arenite. The sand grains are coated with detrital clay.

The Tiva Canyon is a vitric ash-flow sheet varying in thickness from 57.0 m in UE25a-1 to 74.8 m in J-13. The base of this unit is nonwelded and virtually unaltered, with slightly altered rhyolite shards and pumice pyroclasts. Overlying this nonwelded portion is a densely welded vitric tuff in

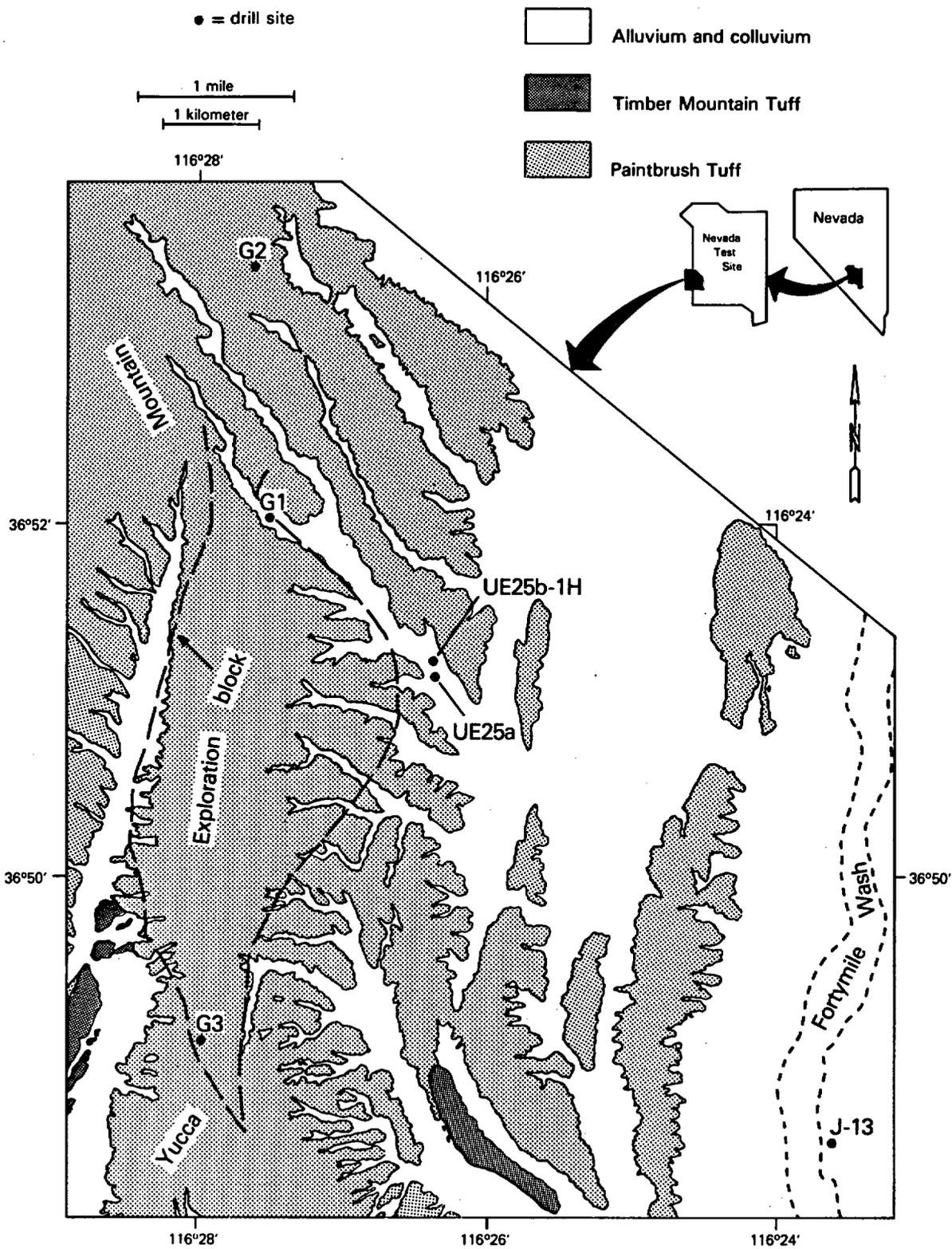


Fig. 1.

Location map of Yucca Mountain, on the southwest boundary of the Nevada Test Site. The locations of drill holes J-13, UE25a-1, UE25b-1h, USW-G1, USW-G2, and USW-G3 are indicated. Note the outline of the exploration block for the NNWSI program.



TABLE I

SUMMARY STRATIGRAPHIC LOG, WELL J-13 (USGS TEST WELL 6), JACKASS FLATS, FROM USGS DATA  
(ELEVATION, 1011.3 m; SWL,<sup>a</sup> 728.5 m).

Stratigraphic Unit	Depth to Base of Unit		Thickness of Unit		Elevation of Base of Unit	
	m	ft	m	ft	m	ft
Alluvium	132.5	435	132.5	435	878.8	2883
Paintbrush Tuff						
Tiva Canyon Member	207.7	680	74.8	245	803.6	2638
Topopah Spring Member	449.6	1475	242.3	795	561.7	1843
Tuffs of Calico Hills	530.4	1740	80.8	265	480.9	1578
Crater Flat Tuff						
Prow Pass Member	596.2	1956	65.8	216	415.1	1362
Bedded tuff	614.2	2015	18.0	59	397.1	1303
Bullfrog Member	707.1	2320	92.9	305	304.2	998
Bedded tuff	716.3	2350	9.2	30	295.0	968
Tram unit	975.4	3200	259.1	850	35.9	118
Bedded tuff	981.5	3220	6.1	20	29.8	98
Lithic Ridge Tuff	1066.2	3498	84.7+	278+	-54.9	-180

<sup>a</sup> SWL--static water level (Nuclear Hydrology Group, USGS) elevation.

TABLE II

COMPOSITE SUMMARY STRATIGRAPHIC LOG, DRILL HOLES UE25a-1 AND UE25b-1h, YUCCA MOUNTAIN, FROM USGS  
DATA (ELEVATIONS, 1198.7 AND 1200.4 m; SWL,<sup>a</sup> 728.8 AND 729.4 m).

Stratigraphic Unit (UE25a-1 to 711.2 m; UE25b-1h from 719.7 m) <sup>b</sup>	Depth to Base of Unit		Thickness of Unit		Elevation of Base of Unit	
	m	ft	m	ft	m	ft
Alluvium	9.1	30.0	9.1	30.0	1189.6	3902.7
Paintbrush Tuff						
Tiva Canyon Member	66.1	217.0	57.0	187.0	1132.6	3715.7
Bedded tuff (includes Pah Canyon Member)	82.3	270.0	16.2	53.0	1116.4	3662.7
Topopah Spring Member	414.5	1360.0	332.2	1090.0	784.2	2572.7
Tuffs of Calico Hills	559.5	1835.7	145.0	475.7	639.2	2097.0
Crater Flat Tuff						
Prow Pass Member	711.2	2333.2	151.7	497.5	487.5	1599.5
Prow Pass Member <sup>b</sup> (UE25b-1h)	719.7	2361.1			480.7	1577.2
Bullfrog Member	869.4	2852.2	149.7	491.1	331.0	1086.1
Bedded tuff	878.6	2882.5	9.2	30.3	321.8	1055.8
Tram unit	1189.0	3901.0	310.4	1018.5	11.4	37.3
Bedded tuff	1207.1	3960.2	18.1	59.2	-6.7	-21.9
Lithic Ridge Tuff	1219.9	4002.3(TD)	12.8+	42.1+	-19.5	-64.0

<sup>a</sup> SWL--Static water level (Nuclear Hydrology Group, USGS) elevations.

<sup>b</sup> Stratigraphic column break from UE25a-1 to UE25b-1h is at contact between Prow Pass and Bullfrog Members.

TABLE III  
 SUMMARY STRATIGRAPHIC LOG, DRILL HOLE USW-G1, YUCCA MOUNTAIN, FROM USGS OPEN FILE REPORT  
 81-1349 (ELEVATION, 1325.7 m; SWL,<sup>a</sup> 748.6 m).

Stratigraphic Unit	Depth to Base of Unit		Thickness of Unit		Elevation of Base of Unit	
	m	ft	m	ft	m	ft
Alluvium	18.3	60.0	18.3	60.0	1307.4	4289.3
Paintbrush Tuff						
Yucca Mountain Member	30.5	100.0	12.2	40.0	1295.2	4249.3
Bedded tuff	41.2	135.0	10.7	35.0	1284.5	4214.3
Pah Canyon Member	71.6	235.0	30.4	100.0	1254.1	4114.3
Topopah Spring Member	427.9	1403.9	356.3	1168.9	897.8	2945.4
Tuffs of Calico Hills	549.1	1801.5	121.2	397.6	776.6	2547.8
Crater Flat Tuff						
Prow Pass Member	655.9	2152.0	106.8	350.5	669.8	2197.3
Bedded tuff	662.3	2173.0	6.4	21.0	663.4	2176.3
Bullfrog Member	793.0	2601.6	130.7	428.6	532.7	1747.7
Bedded tuff	804.5	2639.4	11.5	37.8	521.2	1709.9
Tram unit	1073.5	3522.0	269.0	882.6	252.2	827.3
Bedded tuff	1084.5	3558.2	11.0	36.2	241.2	791.1
Dacite flow breccia	1194.8	3920.0	110.3	361.8	130.9	429.3
Bedded and ash-flow tuffs	1202.7	3945.8	7.9	25.8	123.0	403.5
Lithic Ridge Tuff	1499.8	4920.7	297.1	974.9	-174.1	-571.4
Bedded tuff	1505.8	4940.2	6.0	19.5	-180.1	-590.9
Older tuffs:						
Unit A (quartz rich)	1621.5	5320.0	115.7	379.8	-295.8	-970.7
Unit B (lower quartz)	1656.3	5434.0	34.8	114.0	-330.6	-1084.7
Unit C (quartz poor)	1828.8	6000.0(TD)	172.5+	566.0+	-503.1	-1650.7

<sup>a</sup> SWL--static water level (Nuclear Hydrology Group, USGS) elevation.

TABLE IV

SUMMARY STRATIGRAPHIC LOG, DRILL HOLE USW-G2, YUCCA MOUNTAIN, FROM USGS DATA  
(ELEVATION, 1553.9 m; SWL,<sup>a</sup> 1032 ± m).

Stratigraphic Unit	Depth to Base of Unit		Thickness of Unit		Elevation of Base of Unit	
	m	ft	m	ft	m	ft
Paintbrush Tuff						
Tiva Canyon Member	68.6	225.0	68.6	225.0	1485.3	4873.0
Bedded tuff	74.7	245.0	6.1	20.0	1479.2	4853.0
Yucca Mountain Member	103.9	341.0	29.2	96.0	1450.0	4757.0
Bedded tuff	151.8	498.0	47.9	157.0	1402.1	4600.0
Pah Canyon Member	222.7	730.7	70.9	232.7	1331.2	4367.3
Bedded tuff	231.5	759.4	8.8	28.7	1322.4	4338.6
Topopah Spring Member	518.5	1701.0	287.0	941.6	1035.4	3397.0
Tuffs of Calico Hills	824.2	2704.0	305.7	1003.0	729.7	2394.0
(Fault cuts out about 30 m)						
Crater Flat Tuff						
Prow Pass Member	990.8	3248.3	166.6	544.3	563.1	1849.7
Bedded tuff (faults)	1000.3	3281.9	9.5	33.6	553.6	1816.1
Bullfrog Member (faults)	1067.8	3503.4	67.5	221.5	486.1	1594.6
Bedded tuff	1089.4	3574.0	21.6	70.6	464.5	1524.0
Tram unit	1193.0	3914.0	103.6	340.0	360.9	1184.0
Bedded tuff	1243.2	4078.9	50.2	164.9	310.7	1019.1
Rhyodacite lava,						
flow breccia	1264.9	4150.0	21.7	71.1	289.0	948.0
Bedded tuff	1278.7	4195.2	13.8	45.2	275.2	902.8
Lithic Ridge Tuff	1464.0	4803.2	185.3	608.0	89.9	294.8
Bedded and ash-flow tuffs	1485.6	4874.0	21.6	70.8	68.3	224.0
Silicic lavas, breccias, and tuffs	1811.3	5942.5	325.7	1068.5	-257.4	-844.5
Older ash-flow tuff	1830.6	6006.0(TD)	19.3+	63.5+	-276.7	-907.8

<sup>a</sup> SWL--static water level (Nuclear Hydrology Group, USGS) elevation.

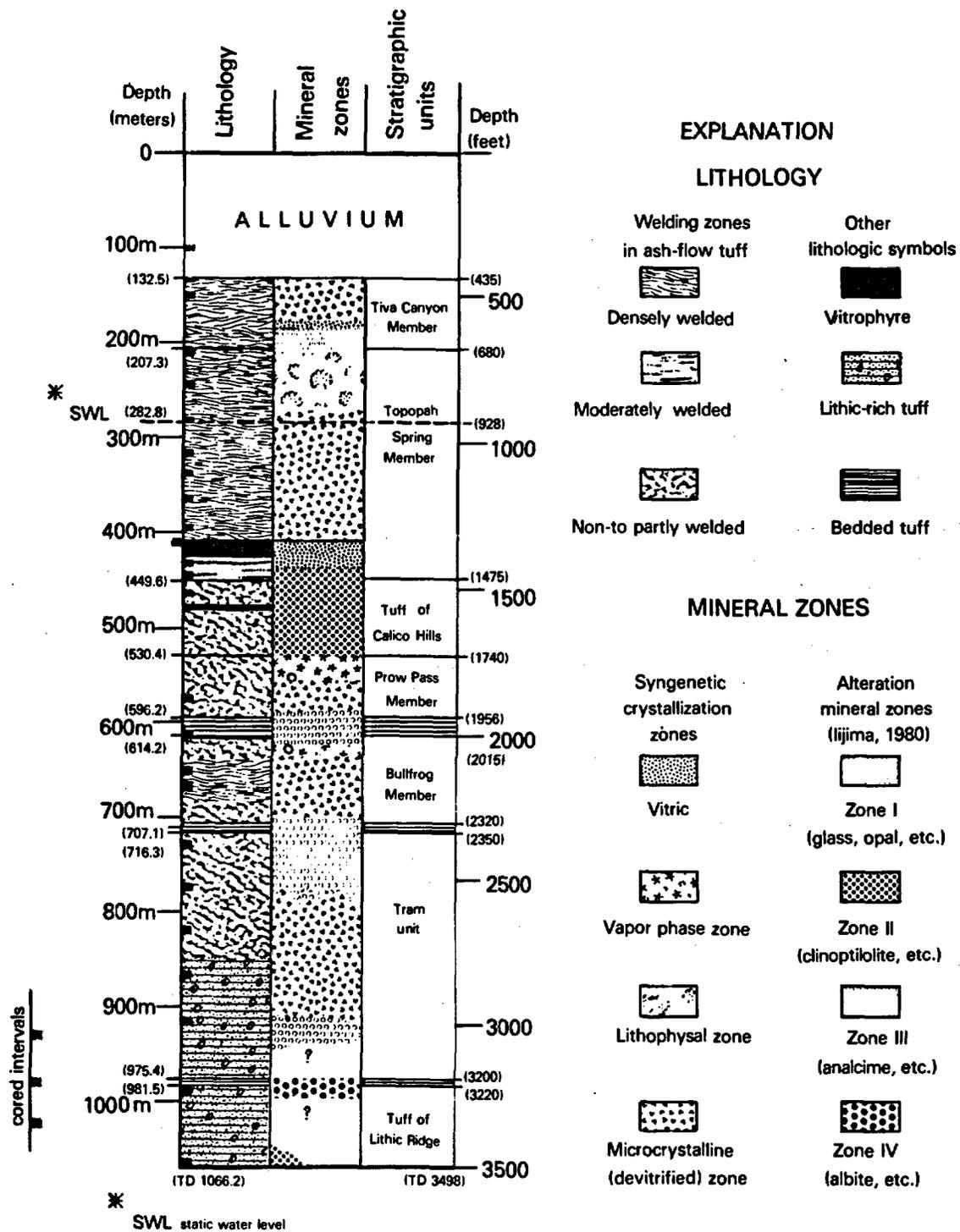


Fig. 3. Summary diagram of lithology, mineral zones mainly from stratigraphy in drill hole J-13. Mineral zones mainly from Heiken and Bevier (1979). Bedded tuff not included with any major stratigraphic unit is shown by pattern between units.

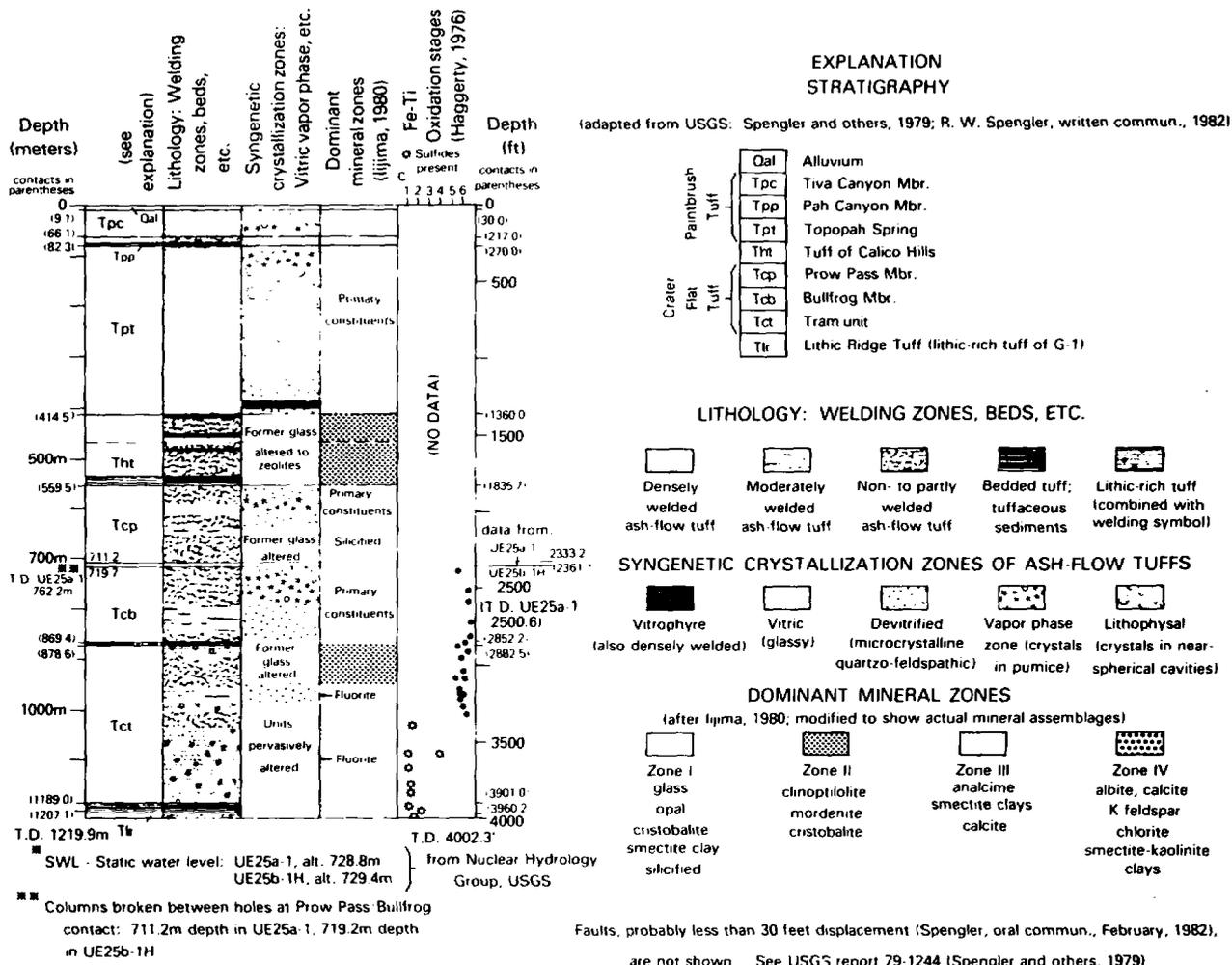


Fig. 4. Summary diagram of lithology, mineral zones, and iron-titanium oxidation stages in drill holes UE25a-1 and UE25b-1H.

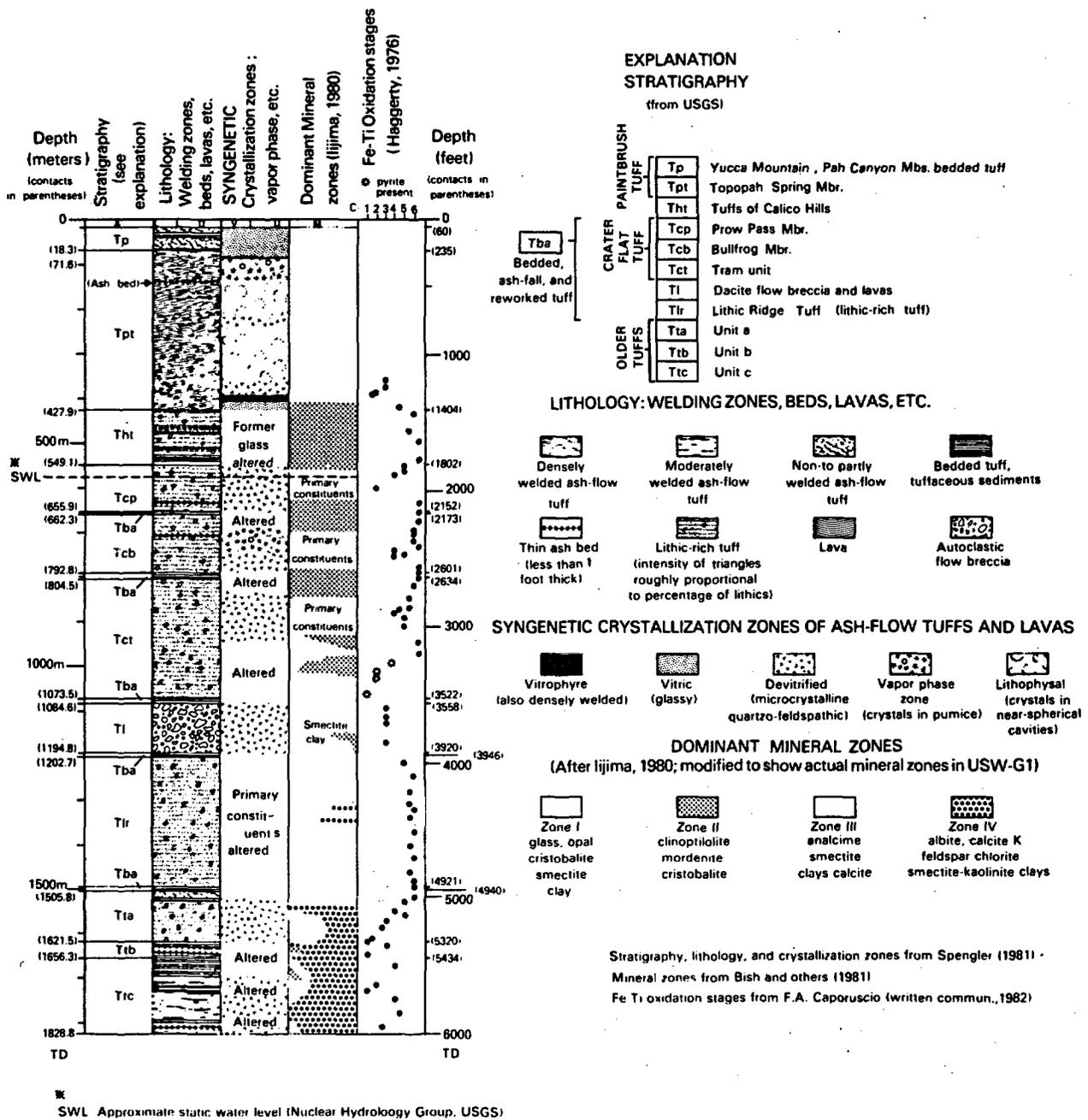


Fig. 5. Summary diagram of lithology, mineral zones, and iron-titanium oxidation stages in drill hole USW-G1.

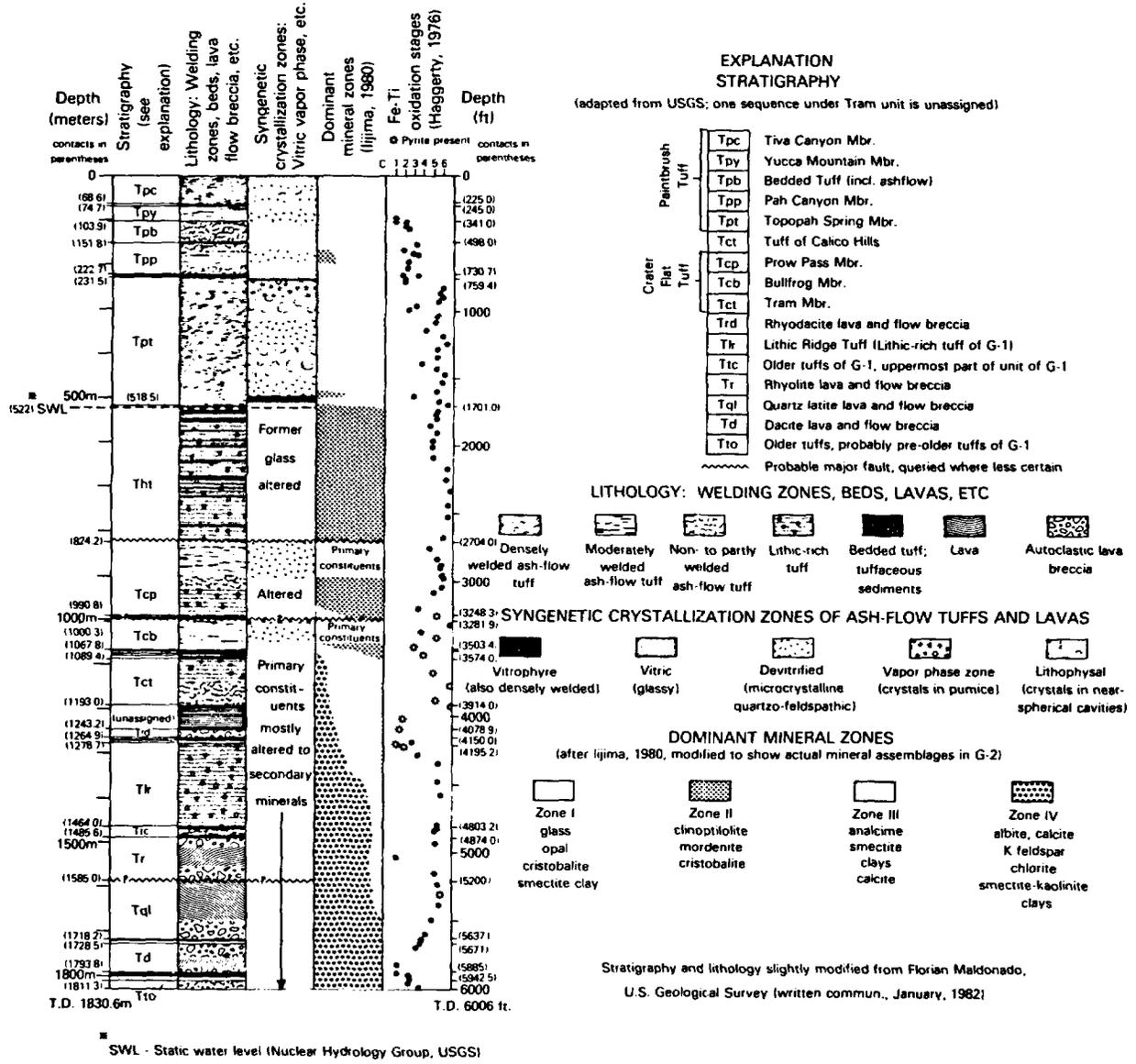


Fig. 6. Summary diagram of lithology, mineral zones, and iron-titanium oxidation stages in drill hole USW-G2.

which all glass phases have been replaced by authigenic potassium feldspar and silica minerals. Vapor-phase crystallization usually occurs as crystalline rims or fillings of vugs. In J-13, there is a systematic variation in phenocryst content from a trace near the base of the unit to 9% near the top. In UE25a-1, the phenocryst content of the Tiva Canyon unit ranges from 14% at the base to less than 5% near the top. The most common phenocrysts are sanidine, andesine/oligoclase, hornblende, and orthopyroxene, and x-ray powder diffraction reveals that the bulk mineralogy is predominantly cristobalite and alkali feldspar with minor tridymite and biotite. The few samples of Tiva Canyon that were x-rayed contained no smectites or zeolites. In general, the Tiva Canyon has a low fracture density as determined from core studies of vertical drill holes.

#### Yucca Mountain Member

The Yucca Mountain Member is the uppermost tuff in USW-G1; it underlies the Tiva Canyon in USW-G2, and it is absent in J-13 and UE25a-1 because of lateral thinning away from the source region. Because it is high in the section and sometimes unobserved, Caporuscio et al. (1982) report the only complete description of the mineralogy and petrology of the unit, and this summary is based primarily on their report. The unit is a nonwelded to partially welded ash-flow tuff and in USW-G2 consists of a basal, reworked, bedded tuff overlain by six identifiable subunits. This whole sequence forms a single cooling unit with the central 21 m moderately to densely welded and the bottom and top nonwelded. The total thickness is 12.2 m in USW-G1 and 29.2 m in USW-G2. The central welded portions of the Yucca Mountain Member are thoroughly devitrified to either cristobalite-alkali feldspar intergrowths or mixtures of smectites and alkali feldspars, and minor vapor-phase crystallization is noted by the presence of tridymite in cavities. The iron-titanium oxides are essentially unoxidized in the welded portions. The lower nonwelded unit contains well-preserved shard structures, but the groundmass and the outer margins of the glass shards have altered to authigenic smectites. The presence of unaltered glass in the central portions of the larger shards and the low oxidation state of the iron-titanium oxides indicates little if any movement of groundwater through this unit.

Sanidine and plagioclase are the two principal phenocryst phases, generally making up less than 1% of the rock, and lithic fragments also are

rare, composing less than 1% of the thin sections examined. Bulk x-ray powder diffraction analyses reveal that the tuffs of the Yucca Mountain Member examined are among the most highly altered, some containing between 30 and 60% smectite. The samples also contain minor calcite and abundant glass (perlite) and alkali feldspar.

#### Pah Canyon Member

The Pah Canyon Member occurs below the Tiva Canyon Member in UE25a-1 and below the Yucca Mountain Member in USW-G1 and USW-G2, with a thickness varying from 16.2 m in UE25a-1 to 70.9 m in USW-G2. A thin bedded tuff unit, consisting of a reworked tuff overlain by a nonwelded, largely unaltered vitric ash flow, occurs between the Yucca Mountain and the Pah Canyon in USW-G2. The Pah Canyon Member does not appear in J-13. Again, because Caporuscio et al. (1982) provide the only complete report of the mineralogy and petrology of the Pah Canyon Member, the following discussion is taken from their description.

The Pah Canyon Member of the Paintbrush Tuff consists of a thin reworked air-fall tuff overlain by five ash-flow subunits (Maldonado et al. 1982), and this sequence forms a single cooling unit with a moderately welded central zone. The upper and lower portions of the Member contain fresh glass, and the groundmass glass in the upper vitric zone is pervasively altered to smectite. Glass shards and pumice clasts in both zones are unaltered, as is the groundmass in the lower vitric zone. Significant amounts of calcite occur in open portions of the groundmass and pumice in the lower vitric zone and in the basal bedded tuff. The upper and lower vitric zones are largely glass, smectite, and alkali feldspar, with the addition of calcite in the lower vitric zone. The lower vitric zone contains more smectite (up to 50%) and less glass than the upper zone. Iron-titanium oxides in these vitric zones are only slightly to moderately oxidized even though the rocks are very permeable. The oxides and the presence of unaltered glass suggest that these rocks have not been saturated by groundwater for any significant period of time.

Between the upper and lower vitric horizons is a zone of devitrification and zeolitization that approximately coincides with the zone of moderate welding. The devitrification resulted in growth of cristobalite and sanidine in some glass shards. Following devitrification, the remaining glass was replaced by heulandite, smectite, and minor opal. Smectite appears to be the

dominant groundmass phase and is present in amounts up to 30 to 50% in this zone. Fractures within this central zone have a thin lining of vapor-phase cristobalite and sanidine, and heulandite and opal later filled these fractures. The oxidation states of the iron-titanium oxides in this zone are moderately high and, with the presence of significant amounts (up to 30%) of heulandite, suggest partial to complete saturation by groundwater. Zeolites are unusual this far above the present water table, particularly in a central, partially welded zone surrounded by two nonwelded zones, and their occurrence this high in the section has only been documented in USW-G2. A perched water table over the densely welded Topopah Spring caprock may account for this anomalous zeolite occurrence, but it is difficult to explain the lack of zeolites in the lowermost nonwelded vitric zone. Sealing of porous areas in the lower nonwelded zone by calcite before zeolitization may explain this anomaly. The clinoptilolite-heulandite zeolites in this unit are distinct from those in the lower portions of all other drill cores in that they contain little sodium and approximately three times as much calcium as potassium. These are the only zeolites in USW-G2 that have the low thermal stability characteristic of heulandites; all others at lower depths are unaffected by heating for 12 hours at 500°C.

At the bottom of the Pah Canyon Member below the lower vitric zone is a heavily zeolitized pumiceous unit. This unit contains minor tridymite and predominant heulandite and calcium-clinoptilolite. The pumices are undeformed, large, and pseudomorphed by zeolites and smectites. Phenocrysts compose a small proportion (less than 2%) of this pumiceous unit and are dominantly plagioclase.

Phenocrysts make up approximately 1% of the tuff in the lower three subunits and increase to 3 to 6% in the upper three subunits. The principal phenocrysts are sanidine and plagioclase, with minor biotite, augite, and quartz. Lithic fragments compose less than 1% of the Pah Canyon Member.

#### Topopah Spring Member

The Topopah Spring Member is one of the thickest units at Yucca Mountain, ranging from 242.3 m in J-13 to 356.3 m in USW-G1. The unit thins from north to south with the exception of the section in USW-G2 (287.0 m), which was deposited on the southern flank of the Claim Canyon Cauldron, the source area for this voluminous series of ash flows. It is the lowermost member of the

Paintbrush Tuff, occurring below the Pah Canyon Member in all drill holes except J-13, where it lies below the Tiva Canyon Member.

The Topopah Spring Member is a compound cooling unit made up of multiple ash flows. Vertical zonation in the degree of welding and crystallization are prominent lithologic features of the Member. With minor changes, the zones of welding and crystallization described by Lipman et al. (1966) for the Busted Butte section near drill hole J-13 serve as a useful framework in which to describe the mineralogy and petrology of the Topopah Spring Member. In general the unit is made up of a thick, densely welded, crystallized interior, enveloped by a thick lower vitrophyre and a thin upper vitrophyre. The lower vitrophyre grades downward into moderately welded to nonwelded ash-flow and re-worked tuff. The upper vitrophyre grades upward into moderately welded to nonwelded ash-flow and bedded tuff. The descriptions below describe each of these zones from the top of the unit to its base.

The uppermost portion of the Topopah Spring Member is made up of thin (1.7- to 2.3-m), nonwelded to moderately welded, phenocryst-poor (less than 2%) ash-flow and bedded tuffs. This uppermost zone is probably equivalent to the pumiceous unit separating the Pah Canyon and Topopah Spring Member in USW-G2 (Caporuscio et al. 1982). Zeolites (70 to 90%) have replaced the bulk of the glass in this zone in USW-G2, whereas in USW-G1 and UE25a-1, the glass is unaltered. The presence of zeolites suggests that the upper vitrophyre acted as an impermeable barrier in USW-G2 and possibly created a local perched water table. The zeolites formed in this zone are heulandite and calcium-rich clinoptilolite. Intensity of welding in pumice clasts and glass shards increases downward as the upper vitrophyre is approached.

The upper vitrophyre is present in all drill cores except J-13, where it was either eroded away or the ash flow was too distal from the source area to allow dense welding. The upper vitrophyre is composed of densely welded, partially devitrified, crystal-rich ash flows. Pumice lapilli are large (greater than 7 mm) and vitric. Disseminated hematite and rutile impart a reddish hue to otherwise clear glass in pumice lapilli. Smectites rim the margins of pumice walls and perlitic fractures. Patches of devitrified cristobalite and alkali feldspar are minor components within pumice clasts. The groundmass of the upper vitrophyre is altered, having undergone both partial devitrification and authigenic crystallization to clay. Though some shards are still clear and glassy, others have devitrified to sheafs of

cristobalite and alkali feldspar oriented parallel to the long dimension of the shards. Dark-brown clay commonly rims the shard forms. Phenocrysts are abundant in the upper vitrophyre, making up 20% of the rock. Plagioclase and alkali feldspar are the principal phenocrysts, with quartz, biotite, clinopyroxene, and iron-titanium oxides present in minor amounts.

The upper vitrophyre grades downward into the thick, moderately to densely welded crystallized interior zone of the Topapah Spring Member. This interior zone, which has complex, overlapping zones of welding and crystallization, is volumetrically the largest zone within the Member. Immediately below the upper vitrophyre this zone is densely welded, devitrified, and extremely altered by vapor-phase crystallization. This portion of interior zone corresponds to the lower part of the quartz latite caprock of Lipman et al. (1966). Pumice lapilli are flattened with most primary features obscured by devitrification. Open areas within pumice are filled by spherulites and granular aggregates of cristobalite and alkali feldspar. Spherulites are numerous and large and show multiple growth stages. Overprinted on all pumices are numerous, small pockets of tridymite. Clays and oxides are the final infill products in some tridymite pockets. The groundmass consists of devitrified axiolitic and granular shards. Smectite clay is an important component of the groundmass, giving it a dark-brown color. Vugs lined by tridymite are manifestations of vapor-phase alteration. Veins in this upper portion of the interior zone are partly to wholly filled by tridymite, calcite, and clay. The central and lower portions of the interior zone are characterized by moderately to densely welded, devitrified, vapor-phase-altered ash flows. In general the horizons of moderate welding are sandwiched between zones of dense welding and represent the join between upper and lower cooling units. Four stages of devitrification and vapor-phase crystallization growth are observed in pumice lapilli of the middle and lower portions of the central interior zone. First, small spherulites, sheaves of cristobalite, and/or axiolitic minerals nucleate on the outer margins of the pumice and grow inwards. Next, interlocking, mottled spherulites partially fill open areas in the pumice. Third, there are vapor-phase crystals of tridymite and alkali feldspar. Finally, granophyric crystallization infills interstitial regions. The groundmass in this region is characterized by high clay contents, spherulites, and granular quartz and alkali feldspar phases. Plumose, asymmetrical spherulites that cross relict pyroclast boundaries, are common in some

samples. Lithophysal cavities are abundant in areas of intense vapor-phase development. In these lithophysae, large crystals (up to 1 mm) of alkali feldspar and tridymite (retrograded to quartz) grow into partially open cavities. Fractures are common in the middle and lower portions of the central interior zone. These fractures are sealed by calcite or silica phases, or they are still open. Fractures filled by silica phases are probably contraction fractures formed during cooling of ash flows and filled by vapor-phase crystallization. Calcite-healed fractures appear to be younger than fractures filled with silicates. Open fractures clearly postdate those filled by silicates and calcite and, with zones of abundant lithophysae, may provide significant pathways for groundwater movement. Though the interior zone of the Topapah Spring consists predominantly of devitrification and vapor-phase crystallization products, Heiken and Bevier (1979) describe a zone bearing zeolites over a 27.4-m interval in densely welded rocks in the interior zone of the Member.

The lower vitrophyre of the Topapah Spring Member consists predominantly of unaltered, densely welded, rhyolitic glass. Phenocrysts are rare (1%), consisting predominantly of plagioclase and alkali feldspar and of trace amounts of iron-titanium oxides, quartz, and biotite. This vitrophyre grades upward into the thick, densely welded interior zone of the Member. In USW-G2, glass shards, the groundmass, and pumice in the densely welded interval just above the basal vitrophyre are partially replaced by clinoptilolite. In the vitrophyre, most of the glass in shards and groundmass is unaltered though veins of clinoptilolite and/or heulandite are common fracture fill in all drill holes. Pumice clasts in the vitrophyre are partially altered to clay and possibly to minor clinoptilolite. Perlitic fractures are common throughout the vitrophyre.

The lowermost portion of the Topapah Spring Member is a partly welded to nonwelded, heavily zeolitized ash flow. Shards in the lower nonwelded zone are typically large, undeformed, and completely pseudomorphed by zeolites. Clay often rims shard borders. Pumice lapilli are also generally undeformed and completely replaced by zeolites and clays. Clays coat all vesicle walls, and zeolites fill tubes. Clinoptilolite is the dominant authigenic mineral in USW-G1, USW-G2, and J-13. In UE25a-1, mordenite, clinoptilolite-heulandite, and clay are important authigenic phases. Phenocrysts are similar in abundance and composition to those in the overlying vitrophyre.

## TUFFS OF CALICO HILLS

The Tuffs of Calico Hills are variable, consisting of nonwelded ash-flow, air-fall, and reworked tuffs and ranging in thickness from 80.8 m in J-13 to 305.7 m in USW-G2. The unit comprises up to 16 nonwelded, zeolitized ash flows with thin, bedded to massive, reworked and air-fall tuffs separating each of the ash flows. The interlayered nature of the unit indicates temporally discrete eruptive events.

The Calico Hills tuffs are nonwelded in every drill core examined, and they probably were once very permeable, although profound zeolitization, noted in every core, has drastically reduced the permeability. Abundant zeolites and highly oxidized iron-titanium oxides indicate extensive interaction of groundwater with these rocks, resulting in the dissolution of glass and the deposition of low-temperature authigenic minerals. The principal authigenic minerals in all cores of Calico Hills tuff are clinoptilolite and mordenite with lesser amounts of quartz, cristobalite, and alkali feldspar. Smectite is a minor component of this unit, occurring as rims on pumice clasts and shards and generally composing less than 5% of the rock. The distribution of the zeolites, clinoptilolite and mordenite, differs substantially from core to core. Mordenite was not detected in the Calico Hills tuffs in J-13 and USW-G1, it was noted in minor amounts in UE25a-1, and it is present in amounts equal to or greater than clinoptilolite in USW-G2 below 578.8 m in the Calico Hills unit. This difference in zeolite distribution probably reflects differences in groundwater flow and chemistry. Clinoptilolite compositions vary within single cores and from hole to hole, but the numbers of calcium and potassium ions are generally subequal in the formulae. Sodium is always subordinate to calcium and potassium. The cation occupying the alkali site in clinoptilolite has important consequences for the thermal stability of the mineral, as will be discussed below.

The zeolitization process has masked almost all original glass textures in all samples examined, although some shards are pseudomorphed by clinoptilolite. Smectites are often present, lining vesicle walls and rimming pumice clasts and shards, and fractures in pumices are often filled by smectites. The groundmass of the Calico Hills unit is predominantly clinoptilolite  $\pm$  mordenite, and ubiquitous smectites are present in minor amounts. Small vugs in the groundmass are often lined with terminated crystals of clinoptilolite, but mordenite is generally absent in these vugs. In the lower half of the

unit, euhedral crystals of authigenic adularia ( $Or_{100}$ ) are often intergrown with clinoptilolite in the vugs. Vapor-phase crystallization is generally absent in the tuffs of Calico Hills. Fractures have not been frequently noted in this unit, and when they occur in USW-G2, they are usually sealed by quartz and/or smectites. Lithic fragments in the Calico Hills are primarily clasts of moderately to densely welded, vapor-phase-altered ash-flow tuffs, rhyolites, and older pumices. Lithic fragments make up 1 to 13% of the rock, with the lower portions more lithic rich, although a lithic-rich upper portion occurs in surface exposures near Prow Pass.

According to Caporuscio et al. (1982), it appears that the Calico Hills can be broken into two major lithologic units based on phenocryst abundance, size, and mineralogy. The upper portion of the unit, present in all drill cores, generally contains less than 2% phenocrysts of quartz, sanidine, plagioclase, and biotite, and the quartz crystals are often resorbed. Phenocrysts in the lower portion, present only in USW-G2, systematically increase in abundance from 6 to 9% near the top of the lower subunit to 15 to 25% near the base. Quartz, sanidine, and plagioclase are the principal phenocryst phases, with quartz and sanidine the dominant phases near the top of the subunit and plagioclase and quartz more abundant at depth. Biotite is a minor phase near the top of the subunit but increases to 10% of the rock near the base. In addition, the average size of the major and minor phenocryst phases is two to three times larger in the lower subunit than in the upper subunit. The compositions of the phenocryst phases also change systematically with depth, with the iron-magnesium ratios in biotites increasing from 0.51 to 0.55 at the base of the unit to 0.60 to 0.64 near the top and the sanidines ranging from  $Or_{71-77}$  at the base to  $Or_{66-69}$  at the top.

The phenocryst abundances and compositions, coupled with the much greater thickness of this unit in USW-G2, suggest that only the upper subunits are present in J-13, UE25a-1, and USW-G1. Phenocryst-rich tuffs correlative to the lower subunit in USW-G2 appear to be absent in the other drill cores, and microprobe data for biotites and sanidines from the other drill cores support the conclusion that only the upper, phenocryst-poor subunit is present in J-13, UE25a-1, and USW-G1 (Heiken and Bevier 1979, Sykes et al. 1979, Broxton et al. 1982).

## CRATER FLAT TUFF

### Prow Pass Member

The Prow Pass Member is the uppermost member of the Crater Flat Tuff and occurs in every drill core so far examined, ranging in thickness from 65.8 m in J-13 to 166.6 m in USW-G2. This unit comprises up to six ash-flow intervals making up a single cooling unit with a bedded, reworked air-fall tuff at the base. In USW-G1, the upper and lower portions of the ash-flow sheet are slightly to moderately welded and zeolitized, and the central portion is partially to moderately welded, with the most strongly welded part skewed toward the bottom. In USW-G2 and UE25a-1, the upper zone of the Prow Pass is more densely welded, devitrified, and fractured, and the lower zone is nonwelded and zeolitized. The upper portion of the unit may have been faulted out in USW-G2 and UE25a-1. The nonwelded to partially welded portions of the unit are typically highly oxidized and completely zeolitized to clinoptilolite and mordenite. Mordenite is subordinate to clinoptilolite in USW-G1 and UE25a-1 but is subequal to clinoptilolite in USW-G2. In USW-G2, clinoptilolite occurs predominantly pseudomorphing glass shards, whereas mordenite occurs usually in the groundmass or as void fillings. Smectite is a minor phase in USW-G1 and UE25a-1 but is predominant in the lower portion of the Prow Pass in USW-G2. The clays in the lower subunits in USW-G2 are calcium-sodium-saturated smectites with virtually no interstratified illite. The moderately welded portions of the unit show primary devitrification in shards and pumices, with fibrous cristobalite and potassium feldspar intergrowths. The iron-titanium oxides in the central welded portion of USW-G1 indicate a low degree of oxidation, but the oxides in the welded portion of USW-G2 are more oxidized, possibly because of the numerous fractures that are now filled with silica phases, hydrous manganese oxides, and hematite. Minor vapor-phase crystallization occurs only in UE25a-1. The lowermost air-fall tuff is heavily zeolitized and highly oxidized.

Phenocrysts in the Prow Pass consist of sanidine, resorbed quartz, plagioclase, and minor biotite and compose 5 to 20% of the rock. The phenocrysts in UE25a-1 serve to divide the unit into two parts, an upper crystal-rich portion and a lower crystal-poor portion. The lithic fragment abundance in the Prow Pass is variable, ranging from 1 to 5%, and consists of red siltstone, argillite, and altered welded tuffs.

### Bullfrog Member

The Bullfrog Member of the Crater Flat Tuff varies in thickness from 67.5 m in USW-G2 to 149.7 m in UE25b-1h. This unit is a compound cooling unit in USW-G1 consisting of two major units, an upper unit that is nonwelded and zeolitized and a lower unit ranging from slightly welded at the top and bottom to moderately welded within the interior. The Bullfrog in J-13 is made up of several distinctive cooling units characterized by moderate to dense welding. The remaining cores contain only a single cooling unit, but there is a large variation in the degree of welding from core to core. The Bullfrog in USW-G2 is moderately welded at the top, and the degree of welding decreases with depth to a nonwelded flow at the base of the unit, overlying bedded tuffs. In UE25b-1h, this Member is partly welded at the top, becomes more welded with depth, and then decreases in degree of welding to a slightly welded basal unit.

There also is a large variation from core to core in the amounts and types of secondary minerals present in the Bullfrog Member. Samples from J-13 contain analcime, and USW-G2 contains minor mordenite, analcime, and smectite in the lower portions of the Bullfrog Member. Mordenite and minor clinoptilolite occur only in the base of the Member in UE25b-1h. Significant zeolitization has taken place only in USW-G1, where the top and bottom of the Bullfrog Member are heavily zeolitized to clinoptilolite and mordenite, and portions of the Member contain up to 75% zeolite. Only the upper portions of the Bullfrog in USW-G1 contain significant smectites. There is a nonzeolitized interior in the Bullfrog approximately 61 m thick, surrounded above and below by about 30.5 m of zeolitized tuff. It is this zonation, with high thermal conductivity welded tuff bounded above and below by highly sorptive zeolitized tuff, that gave rise to the "sandwich" concept. The significant variation in degree of zeolitization from UE25b-1h to USW-G1 demonstrates the difficulties encountered when attempting to predict zeolitization in the Bullfrog Member.

In general, the oxidation states of the iron-titanium oxides in the Bullfrog Member are highly variable and do not correlate well with the degree of welding. It is noteworthy that the Bullfrog in USW-G2 contains pyrite, and the oxides are less oxidized than expected.

Phenocryst phases in the Bullfrog Member include embayed quartz, alkali feldspar, and plagioclase, with minor biotite, opaque oxides, and hornblende. Lithic fragments are generally scarce, usually composing less than 1% of the rock.

### Tram Unit

The Tram unit is the lowermost unit of the Crater Flat Tuff, ranging in thickness from 103.6 m in USW-G2 to 310.4 m in UE25b-1h. Petrographic descriptions demonstrate that the Tram is quite variable from hole to hole and is made up of two to three subunits varying from slightly to densely welded. The Tram contains variable proportions of lithic fragments, and it is variably zeolitized. In USW-G1, the Tram is composed of an upper devitrified ash-flow tuff, a nonwelded ash-flow tuff, and a reworked basal tuff. The upper ash flow ranges from slightly welded to nonwelded at the top to densely welded near the bottom; the upper partly welded portion is extensively zeolitized to clinoptilolite and is highly oxidized. The densely welded portion is only partially oxidized and shows evidence of vapor-phase crystallization.

The lower, nonwelded part of the Tram in USW-G1 can be divided into three intervals, all zeolitized. The upper two intervals contain clinoptilolite and are highly oxidized, and the diagenetic transformation from clinoptilolite to analcime occurs in the lowest interval. Also, the lowest portion is only slightly oxidized and contains pyrite. In USW-G1, the Tram contains very little mordenite, and the lower portion contains up to 30% smectite. The smectites are randomly interstratified with less than 30% illite layers, consistent with temperatures less than 50°C.

The Tram from USW-G2 is quite distinct from the Tram in USW-G1 and consists of two lithic-rich, nonwelded to partially welded ash flows. Phenocrysts compose up to 20% of both flows, and metamorphosed lithic fragments compose up to 90% of the upper subunit. The Tram in USW-G2 contains no clinoptilolite, only small amounts of analcime, and it contains mordenite at the top of the unit. The unit is more altered to smectites than in USW-G1, and in contrast to the almost pure smectites in USW-G1, those in USW-G2 are ordered interstratifications with up to 80% illite layers, suggesting temperatures up to 200°C. At the top of the Tram in USW-G2, the smectites go from random interstratifications with illite compatible with temperatures of less than 50°C to ordered interstratifications suggesting temperatures of 200°C and hydrothermal conditions.

The Tram unit in J-13 is vitric-crystal to vitric-lithic and welded near the top, grading downward to partially welded. Analcime is present in the lower partially welded portion. The Tram in UE25b-1h is similar to that in J-13. It can be divided into an upper, welded to moderately welded,

vitric-crystal to vitric tuff and a lower, nonwelded vitric-lithic to vitric-crystal tuff containing beds of tuffaceous sandstone. The upper subunit contains 15 to 25% phenocrysts, commonly plagioclase, and lithic fragments make up 5 to 10% of the rock. The iron-titanium oxides are highly oxidized. The lower subunit contains 7 to 15% phenocrysts, including sanidine, plagioclase, and quartz; lithic fragments, ranging in size from less than 0.5 mm to larger than thin section size, compose between 25 and 40% of the rock. Pumice and shard relicts dominate the matrix in both subunits. The Tram in UE25b-1h is generally less altered to clays than this unit in USW-G2, although sporadic horizons contain up to 50% smectite, and kaolinite is a minor phase in the lower half of the unit. Clinoptilolite and mordenite occur only in the very upper portions of the unit, and the bottom half of the unit contains analcime. The central portion of the Tram is nonzeolitized. Numerous filled fractures were examined in the Tram in UE25b-1h, and they typically contained calcite in addition to the groundmass phases. However, one fracture contained abundant fluorite and another contained todorokite, a hydrous manganese oxide. The presence of fluorite plus abundant sulfides in the groundmass strongly suggests that these tuffs have been hydrothermally altered.

#### DISCONTINUOUS UNITS BETWEEN THE TRAM AND LITHIC RIDGE TUFFS

In drill holes J-13 and UE25a-1/b-1h, the Tram unit rests directly on the Lithic Ridge Tuff. Farther to the northwest, at drill holes USW-G1 and USW-G2, these two tuff units are separated by 35.4 m to 118.3 m of dacitic to rhyodacitic flow breccias and lavas. The thicker, dacitic lavas occur in USW-G1 where the coarse flow breccia is relatively crystal poor with less than 15% plagioclase, clinopyroxene, and hornblende phenocrysts. Thinner rhyodacite flow breccias overlying lava and basal bedded rhyodacite tuff occur in USW-G2. This thin (35.4-m) sequence in USW-G2 is relatively crystal rich, with 20% phenocrysts (plagioclase, biotite, and hornblende) in the upper breccia, 35% phenocrysts (plagioclase, hornblende, and biotite) in the lower lava, and 30% phenocrysts (plagioclase with minor hornblende, biotite, and rare quartz) in the basal bedded section. The dacite and rhyodacite samples in both drill cores have relict perlitic textures that indicate the autoclastic lavas were originally vitrophyric.

In drill hole USW-G2, the rhyodacite sequence occurs some 183 m below the last abundant occurrence of sorptive zeolites (mordenite in the Bullfrog

unit). Analcime is a major alteration phase. The clay mineralogy is complex here but includes a characteristic replacement of pumice fragments by blue clay comprising a randomly interstratified smectite/illite with about 20% illite and 80% smectite layers. In drill hole USW-G1 the dacite flow breccia includes several zones with abundant clinoptilolite; analcime is absent in the dacite flow breccia but abundant above (Tram unit) and below (Lithic Ridge Tuff). The differences between USW-G1 and USW-G2 in the hydrous mineral alteration of this dacite-rhyodacite unit reflect both the deeper occurrence of the sorptive zeolites (clinoptilolite) in USW-G1 and the irregular distribution of secondary index-phases (clinoptilolite, mordenite, analcime, and albite) at depths deeper than their first appearances.

#### LITHIC RIDGE TUFF

The Lithic Ridge Tuff is present in all drill cores at Yucca Mountain and is the first major pyroclastic unit encountered below the Crater Flat Tuff. In reports from the Yucca Mountain studies published before 1982, this major unit is often misidentified or referred to informally as the lithic-rich tuff (Bish et al. 1981). Although encountered in all drill holes at Yucca Mountain, the Lithic Ridge Tuff was completely penetrated in only the two deepest holes (USW-G1 and USW-G2). The Lithic Ridge Tuff is 297.1 m thick in drill hole USW-G1 and 185.3 m thick in drill hole USW-G2. Although the Lithic Ridge Tuff is thicker in USW-G1 than in USW-G2, the section in USW-G2 includes a densely welded caprock, whereas the USW-G1 section is nonwelded to partly welded throughout. The thin (2.5 m in USW-G2), densely welded caprock of the Lithic Ridge Tuff is crystal rich, unlike the underlying crystal-lithic to lithic-crystal tuffs that form the bulk of the Lithic Ridge Tuff (204 m in USW-G2). These underlying nonwelded to partly welded tuffs range from very lithic-rich porphyritic rocks just beneath the caprock (up to 50% accidental lithic fragments, averaging about 10%, with about 9% phenocrysts, mostly of plagioclase) to lithic-poor and sparsely porphyritic rocks at the bottom of the unit (less than 5% lithic fragments and about 6% phenocrysts, mostly of sanidine). This inverse oligoclase-porphyritic to sanidine-porphyritic tuff suggests the disgorgement of a compositionally zoned magma chamber.

The population of lithic fragments is diverse. Pilotaxitic lavas of intermediate composition are predominant, but spherulitic, high-silica rhyolites are also common. Many of the accidental intermediate-composition lava

fragments have biotite and hornblende phenocrysts. Phenocrysts within the matrix of the Lithic Ridge Tuff include quartz and biotite, in addition to the feldspars described above.

The Lithic Ridge Tuff is partially altered in all drill cores. Relict shards are commonly replaced by both calcite and quartz. Calcite and albite replace many feldspars. Clays in USW-G2 include ordered interstratifications of illite and smectite, indicating formation temperatures in excess of 100°C. Randomly interstratified smectites also occur, suggesting a (later?) lower temperature clay formation. The ordered interstratified clays are commonly within relict pumices and have a characteristic blue color. Lithic Ridge Tuff is typically zeolitized by the poorly sorptive mineral analcime, although traces of the more sorptive zeolite mordenite occur within the Lithic Ridge Tuff in drill hole J-13. Pyrite development is sporadic, ranging from the Lithic Ridge caprock only in USW-G2 to a more uniform pyrite distribution in the other drill cores.

#### LOCAL VARIATIONS IN UNITS BELOW THE LITHIC RIDGE TUFF

Lithologies below the Lithic Ridge Tuff are largely unknown. These deeper volcanic units were not reached in the drilling of J-13 and UE25a-1/b-1h. The deeper units sampled in USW-G1 and USW-G2 have little or no lateral continuity. One possible unit that is continuous between these two drill holes at this depth is a thin ash flow 8.8 m thick in USW-G1 and 4.6 m thick in USW-G2. This ash flow occurs only 7.3 m below the Lithic Ridge Tuff in USW-G2 but is 156 m below the Lithic Ridge Tuff in USW-G1. Aside from this one ash flow, there are no proposed correlations between the lower 365.8 m of USW-G2 and the lower 323 m of USW-G1, below the Lithic Ridge Tuff.

Units below the Lithic Ridge Tuff in USW-G2 comprise mostly lava flows and flow breccias; in USW-G1, however, all of these lowermost units are ash flows. There are striking contrasts in composition as well as in modes of eruption and emplacement. In drill hole USW-G2 the Lithic Ridge Tuff is underlain by only 21.6 m of bedded tuff and ash flow (the thin ash flow correlated with USW-G1) with about 10% phenocrysts of plagioclase with minor sanidine, quartz, and biotite. Below this bedded and ash-flow tuff is a thick series of lavas (297.8 m) divided into three subequal units of (1) phenocryst-poor rhyolite (5% andesine phenocrysts with sanidine rims) that is flow banded or intensely brecciated, 99.4 m thick; (2) 133 m of phenocryst-rich quartz latite

(14% plagioclase, biotite, amphibole, and rare clinopyroxene phenocrysts) that may be related to quartz latite flows that crop out at the Bullfrog Mine and in Beatty Wash; and (3) a thin (10.4-m) ash flow overlies the lower 65.2 m of very phenocryst-rich dacite lava (30% plagioclase, amphibole, and clinopyroxene phenocrysts) that is marked by extreme alteration to calcite plus albite, with chlorite and barite in void spaces and in veins. The lowest 36.9 m of USW-G2 contains an older, moderately welded ash flow (19.5 m) with 10% phenocrysts (plagioclase, quartz, potassium-feldspar, amphibole, and biotite) overlain by 17.4 m of reworked tuff and a baked conglomerate at the base of the dacite lava. This lowest of the ash-flow units is older than any other unit yet sampled beneath Yucca Mountain.

Lithologies below the Lithic Ridge Tuff in USW-G1 form a major 323.1-m pyroclastic sequence with three subdivisions. The uppermost subdivision (115.7 m) is a thick ash flow similar to the Tram unit but with fewer and different lithic fragments (high-silica rhyolite). The middle subdivision (34.8 m) is a series of thin ash flows, one of which may correlate with the thin ash flow just below the Lithic Ridge Tuff in USW-G2. These middle ash flows become more mafic with depth, passing from quartz and sanidine-rich flows to plagioclase-rich flows. The lowest subdivision (172.5 m) is a more mafic series of tuffs and reworked sediments, with plagioclase, biotite, hornblende, and rare clinopyroxene phenocrysts.

Alteration of the units below the Lithic Ridge Tuff is very different in USW-G2 and USW-G1. In USW-G2 these lowest units contain few hydrous minerals with the exception of clays and sparse analcime; alteration instead has resulted in the extensive formation of calcite and albite, with chlorite below 1676 m and varied clays throughout. In contrast, the units below the Lithic Ridge Tuff in USW-G1 contain sorptive zeolites (clinoptilolite) in the middle and lower subdivisions at depths greater than 1676 m, and analcime is abundant. The occurrence of clinoptilolite at this depth is important because it indicates that sorptive zeolites are stable for geological time periods in saturated rocks where the ambient temperature is as high as 46°C.

### III. SUMMARY OF STRATIGRAPHIC UNITS AT YUCCA MOUNTAIN

As noted in the introduction, a potential repository horizon should satisfy several criteria. It should be thick, continuous, and homogeneous,

with predictable properties. The unit also should have relatively high thermal conductivity and thermal stability; it should be strong; and, ideally, it should be situated in such a way that rocks of high sorption capacity are located in the direction of groundwater flow to form a natural barrier to waste-element transport. In addition, properties such as low permeability are desirable. These criteria are very important in choosing between densely welded but possibly fractured rock and low-permeability zeolitized horizons with lower thermal conductivity and thermal stability.

There are several units at Yucca Mountain that satisfy these requirements fairly well, and it is with these criteria in mind that they will be summarized. Generally, considerable mineralogic and petrologic data exist for the cores obtained from Yucca Mountain, and more data exist for the potential target horizons, the Topopah Spring Member, tuffs of Calico Hills, the Bullfrog Member, and the Tram unit, than for other units. In general, the same is true for physical property measurements. Because only four drill cores have been examined in detail, a limitation in our knowledge of Yucca Mountain is our lack of data on the lateral continuity in mineralogy, although we have a broad understanding of the mineralogic changes with depth. Because stratigraphic thickness is affected by paleotopography, predictions of thickness also are difficult, although most units consistently thin away from their source.

#### PAINTBRUSH TUFF

All upper members of the Paintbrush Tuff, including the Tiva Canyon Member, the Yucca Mountain Member, and the Pah Canyon Member, thin from northwest to southeast and are discontinuous. The Tiva Canyon is absent in USW-G1, the Yucca Mountain is absent in J-13 and UE25a-1, and the Pah Canyon is absent in J-13. The upper members are all devitrified or still vitric with the exception of the Pah Canyon Member in USW-G2, which is zeolitized to clinoptilolite. In general, the Yucca Mountain Member is highly altered to smectite, and the vitric zones in the Pah Canyon have also been altered to smectite. The discontinuous nature of these units and their variable mineralogy make accurate prediction of their properties difficult.

The Topopah Spring Member generally thins from north to south and is one of the thickest units at Yucca Mountain. The Topopah Spring is a compound cooling unit comprising multiple ash flows, and it is typically made up of a

thick, densely welded, crystallized interior, surrounded by a thick lower vitrophyre and a thin upper vitrophyre. Both upper and lower vitrophyres contain hydrated volcanic glass that has a low thermal stability, and zeolites are present just above the upper and lower vitrophyres in USW-G2. The thick, densely welded interior of the unit exhibits the effects of vapor-phase alteration but is generally not zeolitized. However, Heiken and Bevier (1979) described a zone of zeolitization near the center of the unit in J-13. The welded interior is one of the most highly fractured horizons in Yucca Mountain, and problems with drilling-fluid loss in this horizon are commonly encountered. The Topopah Spring Member is also a major aquifer below Jackass Flat. The three main types of fractures in the Topopah Spring are (1) open, (2) silica filled, and (3) calcite filled. The oldest fractures appear to be silica filled, whereas the open fractures appear to be the youngest. The calcite-filled fractures appear to be intermediate in age, and calcite from two fractures yields minimum ages of 130 000 and 400 000 years (Caporuscio et al. 1982). An additional feature that may have deleterious effects on rock properties is the abundance of lithophysal cavities. These are vapor-phase generated pockets ranging in size from microscopic to several inches across. The Topopah Spring Member is attractive as a repository horizon in that it is very thick and continuous and has a central, densely welded zone with high thermal conductivity. It is generally bounded on the lower side by a thick zeolitized horizon that may provide a sorptive barrier or act as an aquatard. However, the Topopah is profoundly fractured; the fractures plus abundant lithophysal cavities make accurate prediction of physical properties difficult. In addition, little is known about the effects of elevated temperatures on the upper and lower vitrophyres, and this is an important area for future study. If the Topopah Spring is to be considered, investigations must be undertaken to determine the distribution and orientation of fractures and lithophysae. Also, groundwater flow paths and history in the Topopah Spring must be determined.

#### TUFF OF CALICO HILLS

The tuff of Calico Hills is generally 81 to 145 m thick in Yucca Mountain, apart from USW-G2, where it is 306 m thick. It is the only completely zeolitized unit in Yucca Mountain drill cores, containing both clinoptilolite and mordenite in variable proportions. The frequent presence of more than 75%

zeolite in the tuffs provides an excellent sorptive barrier to radionuclides, but waste loadings and the thermal stability of the zeolites must be addressed if this unit is to be considered as a possible repository horizon. It is likely that temperatures in the far field should not be allowed to exceed 80 to 100°C, although temperatures in the unsaturated near field could probably be allowed to go higher. The Calico Hills unit is generally impermeable and fractures are rare. When fractures do occur, they are typically healed by zeolites, clay, and quartz. An additional question to be answered before the Calico Hills unit is considered is the lateral continuity of the zeolitization, as there are some indications that the Calico Hills unit is vitric (nonzeolitized) in parts of the block.

#### CRATER FLAT TUFF

The uppermost unit in the Crater Flat Tuff is the Prow Pass Member, and it is typically fairly thin with a maximum thickness of 167 m. The upper portion is partially to moderately welded and devitrified, and the lower part is usually zeolitized. However, the upper portion of this unit is zeolitized in J-13. The Prow Pass is probably too thin and laterally variable to be a viable repository-unit candidate.

The Bullfrog Member is also fairly thin, with a maximum thickness of 150 m, but this unit is more laterally consistent than the Prow Pass. However, the Bullfrog does exhibit significant variations in degree of welding and zeolitization from hole to hole. The densely welded zone ranges from the bulk of the unit in UE25b-1h and J-13 down to 30 m in USW-G1 and USW-G2. More importantly, the type and position of zeolitization within this unit is quite variable. Clinoptilolite and mordenite are the major zeolite phases in USW-G1 and UE25b-1h, whereas analcime and mordenite are the common zeolites in USW-G2 and J-13. These zeolites occur in the lower parts of the Bullfrog in J-13 and UE25b-1h. Both the upper and lower portions of the unit in USW-G1 are zeolitized ("sandwich" concept), and in USW-G2 there is a zone of zeolitization approximately two-thirds of the way through the unit. Another noteworthy aspect of the mineralogy of the Bullfrog Member is the presence of sulfides in the lower portion of the unit in USW-G2. Clearly, mineral stability is a major concern with the Bullfrog Member, as is the lateral variability in mineralogy.

The Tram unit is variable in thickness, ranging from 103.6 to 310.4 m thick. The unit is thickest at USW-G1 and UE25b-1h and thins to the northwest and southeast. In general, the Tram is poorly welded with only minor zones of dense welding, and the mineralogy of the unit is quite variable. In USW-G2 and UE25b-1h, the Tram is practically devoid of zeolites, and the central portion of the unit in USW-G1 contains analcime as does a thin zone near the top of the unit in J-13. Disseminated sulfides are common in the Tram, and the presence of fluorite in some fractures suggests that the rock has been hydrothermally altered. The Tram lacks many of the features desirable in a repository horizon; it is unusual in that it is poorly welded but is also nonzeolitized. Furthermore, its lateral variability makes accurate prediction of thickness and mineralogy difficult. Clearly more information on this unit is required.

#### LITHIC RIDGE TUFF

The Lithic Ridge Tuff is one of the most laterally variable units encountered in Yucca Mountain, with a thickness varying from 185.3 to 297.1 m. Moreover, the unit has a very high lithic fragment content, yielding large and unpredictable variations in physical properties. This unit is poorly welded but is well indurated by authigenic feldspars and quartz. Additionally, fractures are sealed by calcite and quartz. It is very noteworthy that in USW-G2 and UE25b-1h, the Lithic Ridge occurs below the stability horizon for sorptive open-channel zeolites such as clinoptilolite and mordenite. In the remaining drill holes, the only zeolite present is analcime, occurring only near the top of the unit. A significant drawback to this unit is that there is little information on its physical properties, lateral variability, and source region. In addition, without better knowledge of groundwater flow, it is impossible to determine whether sorptive barriers exist between the Lithic Ridge and the accessible environment.

The units below the Lithic Ridge Tuff are very poorly characterized and understood. There is little lateral continuity to the units, and numerous stratigraphic discontinuities exist. Knowledge of these units is too limited to allow their consideration at this time.

#### IV. THERMAL STABILITY OF HYDROUS PHASES IN YUCCA MOUNTAIN TUFFS

Investigations of the thermal stability of the phases in the tuffs at Yucca Mountain are very important for several reasons, but research has only recently begun in this area. Los Alamos contributions toward solving the problem of mineral stability include Smyth and Caporuscio (1981), Bish et al. (1981), Bish (1981), Blacic et al. (1982), and Bish and Semarge (1982). The general purpose of mineral stability studies is to identify unstable phases and to examine the effects of temperature on these phases and the possible effects of thermal reactions on a repository. Both experimental and geological data will be used to provide this information, although experimental data relating to the tuffs of Yucca Mountain are scarce. Where possible, literature data on zeolite and clay mineral reactions have been used, but the applicability of these data is limited because of variations in mineralogical and chemical composition, geological environment, and experimental conditions. Therefore, considerable uncertainty exists in accurately assessing the thermal stabilities of the clays and zeolites in Yucca Mountain.

The hydrous phases, zeolites, clays, and glass (perlite), occurring in the tuffs of Yucca Mountain are very important components of both the near- and far-field environment of a repository because they can affect sorption, rock volume and strength, porosity, and permeability. In comparison to the anhydrous minerals, these hydrous phases are notable for their often low thermal stability and high reactivity. It is important to understand the thermal and chemical reactions that take place in tuffs because such reactions usually result in phases with lower sorption capacities and smaller volumes than the original phases. These effects can lead to rock strength and permeability changes in zeolite-, clay-, or glass-bearing tuffs.

Specific effects of heating tuffs containing hydrous phases include (1) reversible (low activation energy) and irreversible (high activation energy) dehydration, both involving volume decreases and possibly decreases in sorption capacity; (2) irreversible dehydroxylation (loss of structural hydroxyl groups), usually with concomitant destruction of the mineral structure; (3) accelerated rates of glass recrystallization; and (4) reaction of low-temperature minerals to more stable, less sorptive, lower volume phases stable at high temperatures.

Blacic et al. (1982) conducted a study on the effects of long-term exposure of tuffs to simulated high-level waste repository conditions. In

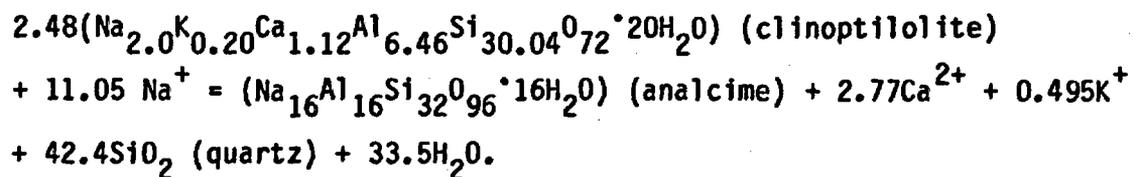
their study, they examined the physical properties of numerous core samples from Yucca Mountain both before and after exposing the samples to temperatures between 80° and 180°C under varying confining pressure and water pressure conditions. Studies were conducted of samples from seven depth levels in USW-G1 and UE25a-1 cores in an attempt to correlate changes in physical properties with changes in mineralogy and petrography. Precise correlations were difficult to make, but several useful observations were made. A sample of the Topopah Spring Member that had been exposed at 80°C for 6 months had an increase in porosity that may be correlated to the dissolution of silica, and a sample from the Bullfrog Member exposed at 180°C for 3.5 months had significant increases in tensile and compressive strength that may be correlated with a coarsening of clay crystals. One sample from the Tram unit exposed at 120°C for 2 months had a loss of feldspar and an increase in fine-grained clay content that might correlate with a slight decrease in tensile strength. Tests conducted at 120° and 180°C appeared to lead to a slight degradation of euhedral clinoptilolite crystals and suggest a crystallization of mordenite in void spaces, although there was no obvious increase in mordenite or decrease in clinoptilolite in the bulk sample. These minor changes suggest that loss of clinoptilolite and increase in mordenite may be a consequence of prolonged hydrothermal exposure at 120° to 180°C. Small-scale grain-boundary changes and variations in larger discontinuous features, such as pumice and lithic fragments, fractures, and lithophysae, are apparently very important in controlling the physical properties of tuff. Apart from these experiments, no other general mineralogical experiments on tuff have been conducted to date. Los Alamos has, however, considered numerous reactions that occur with zeolites and clay minerals and this information can usefully be integrated into the problem of tuff alteration.

#### ZEOLITES

The zeolites are probably the most important group of hydrous minerals at Yucca Mountain. The distribution of zeolites is stratified, with zeolites rarely present above the water table (Heiken and Bevier 1979, Sykes et al. 1979, Bish et al. 1981, Caporuscio et al. 1982). Clinoptilolite-heulandite and mordenite occur in major amounts in the upper portion of the saturated or paleo-saturated zones, and as a result of increasing temperature and changing water composition, these zeolites are gradually replaced by analcime with

depth. Smyth and Caporuscio (1981) reviewed the thermal stability data for clinoptilolite-heulandite, mordenite, and analcime. The extremes of composition in the clinoptilolite-heulandite series have very different physical properties. Clinoptilolite, the sodium/potassium end member of the series is stable to significantly higher temperatures than heulandite, the calcium end member. Clinoptilolites are often stable up to 750°C under dry heating, whereas heulandites break down at temperatures as low as 250°C. In addition, Shepard and Starkey (1966) demonstrated that potassium- and sodium-exchanged heulandites have higher thermal stabilities than the nonexchanged materials, showing the importance of the exchangeable cation. Based on the criteria of thermal stability and composition, only those clinoptilolite-heulandites in the very upper portions of USW-G2 are heulandites, whereas those in the lower portions, including the zeolites in the tuff of Calico Hills are clinoptilolites. Little data exist on the dehydration behavior of mordenite, a mineral making up to 50% of some Yucca Mountain tuffs. Limited experimental work suggests that mordenite forms at higher temperatures than clinoptilolite-heulandite (Hawkins et al. 1978), but these results contradict what is observed in some Yucca Mountain cores where clinoptilolite is present to greater depths than mordenite. The x-ray powder diffraction data for analcime reveal that the  $a$  parameter of analcime increases from 13.714Å at 25°C to 13.724Å at 150°C. The  $a$  parameter decreases sharply between 150° and 400°C and levels off at 800°C at a value of 13.64Å (Joint Committee on Powder Diffraction Standards 1974). It is noteworthy that little is known of the effects of time and of the partial pressure of water on the thermal stability of Yucca Mountain zeolites. Time is a particularly important factor for the isolation period of a repository.

Iijima (1975, 1980) defined four diagenetic zones in zeolite-containing rocks consisting of: zone I, a zeolite-free glass- and smectite-containing zone; zone II, characterized by clinoptilolite and/or mordenite; zone III, containing analcime replacing clinoptilolite and mordenite; and zone IV, characterized by the presence of authigenic albite. The importance of these diagenetic reactions can be seen by examining the reaction of clinoptilolite to analcime. Using an approximate composition for clinoptilolite from deeper portions of USW-G2 (Caporuscio et al. 1982) and an idealized analcime composition, the clinoptilolite to analcime reaction can be written as follows:



On a formula basis, the volume of 2.48 clinoptilolite is  $5172.21\text{\AA}^3$ , the volume of one analcime is  $2580.37\text{\AA}^3$ , and the volume of 42.4 quartz is  $1596.78\text{\AA}^3$ . Thus, this reaction involves a volume reduction of approximately 20% and evolution of considerable water. The presence of  $\text{Na}^+$  will encourage this reaction, whereas the presence of  $\text{Ca}^{2+}$  and  $\text{K}^+$  will inhibit the reaction.

Employing this zone concept and limited experimental and field evidence constraining temperatures and water compositions, Smyth and Caporuscio (1981) constructed a plot of sodium-ion concentration vs temperature for these diagenetic reactions. From the observed mineralogic data for drill hole USW-G1, they obtained a maximum paleogeotherm. However, information obtained on the clay minerals in USW-G1 (Bish et al. 1981, Bish 1981) and zeolite and clay mineral data from USW-G2 (Caporuscio et al. 1982, Bish and Semarge 1982) suggest that the zeolites in Yucca Mountain result from a combination of temperature and water composition effects. This conclusion is in agreement with those of Hoover (1968) for rocks of the Nevada Test Site. The available experimental and field data suggest that the transformation from clinoptilolite to analcime took place in the tuffs at Yucca Mountain between 80 and  $100^\circ\text{C}$ . Repository-induced transformations probably would occur at higher temperatures because of the low sodium concentrations (20 to 60 ppm) (Wolfsberg et al. 1979) occurring in groundwaters in equilibrium with the present-day tuffs. Although present-day sodium-ion concentrations in Yucca Mountain groundwaters would yield transformation temperatures of 100 to  $120^\circ\text{C}$ , it is possible that groundwater leaching nonzeolitized volcanic glass would have a higher sodium concentration than observed today, lowering the thermal stabilities of zeolites.

Although Smyth and Caporuscio (1981) inferred the temperature of the clinoptilolite to analcime transformation in Yucca Mountain tuffs, they did not address one of the most important effects, that of time. In addition, reactions involving mordenite were not described because of a lack of literature data.

## SMECTITES

Although smectites are not as abundant as zeolites, their distribution is not stratified, and they occur in small amounts in virtually all core samples examined to date (Bish et al. 1981, Bish 1981). The smectites are important because they selectively sorb certain cations, but perhaps even more important is the major effect of small changes in temperature and water pressure on smectite molar volume. Bish (1981) reviewed the effects of changes in relative humidity and temperature on smectites and noted that decreases in ambient humidity can result in decreases in smectite volume of up to 50%. Such volume changes could have profound effects on rock strength, porosity, and permeability, depending on the mode of occurrence and abundance of the smectite. Smectites typically reversibly collapse by a temperature between 100° and 200°C.

With increased temperature (dry), smectite dehydration becomes irreversible at a temperature controlled by interlayer cation composition and by time. This reaction is very likely controlled by the diffusion of the interlayer cation into the silicate layers and can occur in 24 hours at temperatures as low as 150°C. The presence of large, divalent cations ( $Ba^{2+}$ ) significantly raises the temperature of irreversible collapse to over 500°C for short-term heating. Once the smectite layers have been irreversibly collapsed, their sorption capacity is greatly decreased, although  $Cs^{1+}$  selectivity is dramatically increased. Although qualitative data exist on the effects of interlayer cation on properties, there is no information on the effects of time on the irreversible dehydration reaction. Koster van Groos (1981) has shown for one smectite that moderate water pressure significantly raises the temperature of layer collapse and dehydration, but no additional information is available on the effects of increased water pressure.

The results of low-temperature hydrothermal alteration on smectites are better documented than for zeolites, and kinetic data exist that allow qualitative prediction for the effects of prolonged elevated temperatures on the smectites in Yucca Mountain tuffs (Eberl and Hower 1976, Roberson and Lahann 1981). With increasing depth or temperature in the presence of water, smectites undergo a transition to a mica-like mineral. This reaction involves both compositional and structural changes, including a gain in interlayer potassium and additional substitution of aluminum for silicon in the tetrahedral layers. Also, the net negative charge on the layers increases and

potassium or other large univalent cations are fixed as the layers collapse to 10Å. The reaction is very sensitive to temperature, and the type of interstratified smectite/illite in the rocks is an accurate indicator of paleotemperature. In addition to being sensitive to temperature, the kinetics of the reaction are greatly influenced by water composition. The reaction is speeded by the presence of potassium and is inhibited by the presence of sodium, calcium, and magnesium.

The diagenetic reaction to an interstratified mineral has important consequences for the physical and chemical properties of the clay. The cation exchange capacity gradually decreases from values typical of pure smectites (70 to 130 meq/100g of clay) to approximately 15 meq/100g, and the amount of swelling in water and organic liquids is gradually reduced. However, the collapsed material selectively sorbs  $\text{Cs}^{1+}$ .

#### VOLCANIC GLASSES

Little data exist concerning the effects of time, temperature, and water on Yucca Mountain volcanic glass. Literature data suggest that volcanic glass alters to zeolites, but the phases resulting from hydrothermal alteration depend greatly upon glass and water compositions. Limited experimental data obtained on Yucca Mountain volcanic glasses suggest that a common product of hydrothermal alteration is cristobalite. Volcanic glass is seldom present below the water table, having either been zeolitized or altered by high-temperature devitrification processes. A major goal of future studies will be the investigation of reactivity differences between the hydrous glasses of densely welded vitrophyres and the nonwelded hydrous glasses in other vitric zones.

#### V. STUDIES NECESSARY FOR THE RESOLUTION OF ISSUES CONFRONTING NNWSI

From the perspective of mineralogic and petrologic studies, the major issue confronting NNWSI has been stated in the Federal Register (1981a): "at some point the design capabilities of the engineered system will be lost and ... the geologic setting -- the site -- must provide the isolation of wastes from the environment." The inevitability of contact between waste and the rocks local to the repository requires the resolution of two major questions. The first question concerns the distribution of sorptive minerals and glasses at Yucca Mountain: Are there sufficient natural sorptive barriers along

hydrologic pathways leading from the repository, particularly along fracture systems? The second question concerns the long-term stability of these minerals and glasses: Are these phases stable for geologically long timespans (more than 1000 years) under the thermal load of a repository housing nuclear waste? These two questions are being addressed by research in mineralogy-petrology and in mineral stability.

#### MINERALOGY-PETROLOGY

Sorption studies have shown (Wolfsberg et al. 1979, 1981) that hydrous glasses of the nonwelded zones and hydrous secondary minerals (clinoptilolite, mordenite, and smectites) show greatest promise for long-term isolation of released waste by the surrounding rocks. Surface properties, compositions, and above all the distributions of these minerals are critical to their isolation performance but are relatively unknown. Further study of these natural sorptive phases is needed. In addition to a knowledge of their composition and effective distribution, it is important to know whether these phases will remain unaltered or alter to other phases with increased sorptive capacity under repository conditions. Possible adverse alterations to nonsorptive phases must be avoided.

Research in mineralogy-petrology will concentrate on natural samples from Yucca Mountain but will not be limited to such studies. The history of alteration mineralization is no more important than the projection of future mineralization under repository conditions. For this reason, studies of possible mineral changes have been coupled to experimental studies (Blacic et al. 1982), and such studies will expand in the near future. Major focuses of both natural-sample and experimental studies of distribution, origin, and history of alteration are:

- (1) Delineation and interpretation of major compositional zonations among sorptive zeolites and clays. Present data suggest considerable variation between the sorptive capabilities of differing zeolites (for example, clinoptilolite vs mordenite); the effects of compositional variation on sorption within one zeolite type (for example, calcium- to potassium- to sodium-clinoptilolite) are still unknown. The sodium-, calcium-smectites at shallow depths in Yucca Mountain may have better sorptive capabilities than the potassium-smectites at greater depth, although this too is not well documented. Zonations of this nature present dramatic differences

between different units at Yucca Mountain that might otherwise be relegated to one oversimplified category (for example, "zeolitized"). These changes in composition also have important consequences for mineral stability; for example, calcium-heulandites have lower short-term thermal stability limits (250°C) than do sodium-, potassium-clinoptilolites (750°C).

- (2) Investigation of processes in secondary mineral growth. Samples in hand now permit a comparative study of vitric nonzeolitized and completely zeolitized Calico Hills tuff; a comparable study can be made of the Prow Pass Member of the Crater Flat Tuff. These studies may help to define limits of chemical exchange and the initial conditions of zeolite formation. Variations in the nature and abundance of clays will also lead to a better understanding of the initial conditions for clay formation.

A knowledge of transport pathways is also critical to the development of a high-level waste repository. Mineralogy of the transport pathways can have important physical and chemical effects on transport phenomena. This importance is outlined in the Federal Register (1981b), which requires an assessment of the "aperture in-filling and origin of fractures, discontinuities and heterogeneities." For the NNWSI project at Yucca Mountain, the role of fracture flow is very important. Other discontinuities and heterogeneities that must be considered include faults, lithophysae, vapor-phase cavities, and voids caused by pumice alteration. All of these are sites of potential groundwater concentration or transport. Mineralization in such features provides a geologic perspective on secondary mineralization along hydrologic pathways, and a basis for predicting the results of future groundwater waste transport. Moreover, the study of secondary mineralogy in these special localities will address the requirements for investigating the hydrologic and geochemical stability of the geologic setting since the start of the Quaternary Period.

N.B

#### MINERAL STABILITY

Because hydrous glasses and the secondary minerals, zeolites and smectites, are the key to geologic isolation of radioactive waste, it is necessary to know the long-term thermal stability of these phases. Stability data for smectites were reviewed above and by Bish (1981). Smyth and Caporuscio (1981) summarized the thermal stability data for clinoptilolite-heulandite, mordenite, and analcime. There is, however, a lack of data on the

effects of compositional variations on the thermal stability of smectites and zeolites, and much more information on the kinetics of the low-temperature alteration recrystallizations is needed.

Depending upon whether reactions in the very near field or in the far field are of concern, the alteration environment will be dry or wet, respectively. Accordingly, research in mineral stability can be broken broadly into two parts: (1) studies of the dry ( $P_{H_2O} \ll 1$  atm) stability of the zeolites, smectites, and hydrous glasses common to Yucca Mountain, and (2) research on the hydrothermal stability of zeolites and smectites and on the effects of  $P_{H_2O}$  on mineral stability.

✓ Present data suggest a compositional effect on the thermal stabilities of zeolites and smectites when heated dry. Because there are data showing significant variations in the composition of clinoptilolites and smectites with depth in Yucca Mountain, it is important to determine the effects of exchangeable cations on zeolite and smectite thermal stability. Such research, including investigations of absolute dry thermal stability, volume effects of heating, kinetics of dehydration and breakdown, and the effects of  $P_{H_2O} (\leq 1$  atm) on dehydration and breakdown reactions will be important to near- and far-field reactions and may impact studies of backfill materials. Both tuff and sodium-bentonite are possible backfill materials. Experiments on zeolites and smectites will employ ambient condition and high-temperature x-ray diffraction, using a controlled atmosphere sample cell. Samples will include standard clay and zeolite materials plus mineral separates for x-ray diffraction from Yucca Mountain. It is not possible to measure the effects of heating vitric tuffs using the x-ray diffraction techniques employed with crystalline materials, but macroscopic volume changes and weight loss can be determined as a function of temperature.

? Hydrothermal experiments will be designed to investigate the long-term stability of minerals in Yucca Mountain tuffs when exposed to elevated temperatures in the far field. As noted above and by Smyth and Caporuscio (1981), the sorptive zeolites, particularly clinoptilolite, may transform to less sorptive phases including analcime and albite. Therefore, it is critical that time-temperature-reaction data be obtained that will allow prediction of the effects of long-term, low-temperature hydrothermal alteration, and most

important will be the extraction of kinetic information from experimental data. Planned experiments include reaction of representative lithologies from Yucca Mountain at temperatures up to 400°C and water pressures of several hundred bars. Los Alamos also plans to use published kinetic data (Eberl and Hower 1976, Roberson and Lahann 1981) for the alteration of smectite to illite to interpret Yucca Mountain smectites, taking into consideration the effects of solution chemistry on reaction kinetics. Finally, very important clues to the behavior of tuffs under elevated temperature conditions may be obtained by examining the phase assemblages in deeper portions of Yucca Mountain. The mineralogy-petrology data for drill cores from Yucca Mountain therefore may provide considerable insight into potential reactions, at least below the water table.

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#### REFERENCES

- A. E. Bence and A. L. Albee "Empirical Correction Factors for Electron Microanalysis of Silicates and Oxides," *J. Geology* 76, 382-403 (1968).
- D. L. Bish, "Detailed Mineralogical Characterization of the Bullfrog and Tram Members in USW-G1, with Emphasis on Clay Mineralogy," Los Alamos National Laboratory report LA-9021-MS (October 1981).
- D. L. Bish, F. A. Caporuscio, J. F. Copp, B. M. Crowe, J. D. Purson, J. R. Smyth, and R. G. Warren, "Preliminary Stratigraphic and Petrologic Characterization of Core Samples from USW-G1, Yucca Mountain, Nevada," Los Alamos National Laboratory report LA-8840-MS (November 1981).
- D. L. Bish and R. E. Semarge, "Mineralogic Variations in a Silicic Tuff Sequence: Evidence for Diagenetic and Hydrothermal Reactions," 19th Annual Clay Minerals Society Meeting, August 9-13, 1982, Hilo, Hawaii (1982).
- J. Blacic, Ed., "Effects of Long-Term Exposure of Tuffs to High-Level Nuclear Waste Repository Conditions: Final Report," Los Alamos National Laboratory report LA-9330-MS (in preparation, 1982).
- D. Broxton, Ed., "Data Report for Mineralogy and Petrology Studies of Drill Core USW-G1," Los Alamos National Laboratory report LA-9323-MS (in preparation, 1982).

- D. Broxton, D. Vaniman, F. Caporuscio, B. Arney, and G. Heiken, "Detailed Petrographic Descriptions and Microprobe Data for Feldspars and Mafic Phenocrysts from Drill Holes USW-G2 and UE25b-1H," Los Alamos National Laboratory report LA-9324-MS (October 1982).
- F. Caporuscio, D. Vaniman, D. Bish, D. Broxton, B. Arney, G. Heiken, F. Byers, R. Gooley, and R. Semarge, "Petrologic Studies of Core from Drill Hole USW-G2 and of the Lower Crater Flat Tuff in Core from Drill Hole UE25b-1H, Yucca Mountain, Nevada," Los Alamos National Laboratory report LA-9255-MS (July 1982).
- P. I. Carroll, F. A. Caporuscio, and D. L. Bish, "Further Description of the Topopah Spring Member of the Paintbrush Tuff in Drill Holes UE25a-1 and USW-G1 and the Lithic Rich Tuff in USW-G1, Yucca Mountain, Nevada," Los Alamos National Laboratory report LA-9000-MS (November 1981).
- D. Eberl and J. Hower, "Kinetics of Illite Formation," *Geol. Soc. Am. Bull.* 87, 1326-1330 (1976).
- Federal Register, vol. 46, p. 35282 (1981a).
- Federal Register, vol. 46, p. 35287 (1981b).
- S. E. Haggerty, "Oxidation of Opaque Mineral Oxides in Basalts," in Oxide Minerals, *Min. Soc. Amer. Short Course Notes* 3, H6-100 (1976).
- D. B. Hawkins, R. A. Sheppard, and A. J. Gude, 3rd, "Hydrothermal Synthethis of Clinoptilolite and Comments on the Assemblage Phillipsite-Clinoptilolite-Mordenite," in Natural Zeolites: Occurrence, Properties, Use, L. B. Sand and F. A. Mumpton, Eds. (Pergamon Press, Elmsford, New York, 1978).
- G. H. Heiken and M. L. Bevier, "Petrology of Tuff Units from the J-13 Drill Site, Jackass Flats, Nevada," Los Alamos Scientific Laboratory report LA-7563-MS (February 1979).
- D. L. Hoover, "Genesis of Zeolites, Nevada Test Site," in Nevada Test Site, *Geol. Soc. Am. Mem.* 110, 275-284 (1968).
- A. Iijima, "Effect of Pore Water to Clinoptilolite - Analcime - Albite Reaction Series," *J. Fac. Sci. Univ. Tokyo, Sec. II* 19, 133-147 (1975).
- A. Iijima, "Geology of Natural Zeolites and Zeolitic Rocks," in Proc. Fifth Int. Conf. Zeolites, L. V. Rees, Ed. (Heyden, London, 1980), pp. 103-118.
- Joint Committee on Powder Diffraction Standards, "Selected Powder Diffraction Data for Minerals," 1st ed., (Joint Committee on Powder Diffraction Standards, Swarthmore, Pennsylvania, 1974), p. 645.
- A. F. Koster van Groos, "Determination of Dehydration Temperature of a Secondary Vug-Filling Mineral (Smectite Clay) Using a Differential Thermal Analysis at Various Pressures," Rockwell Hanford Operations report RH0-BWI-C-102 (1981).

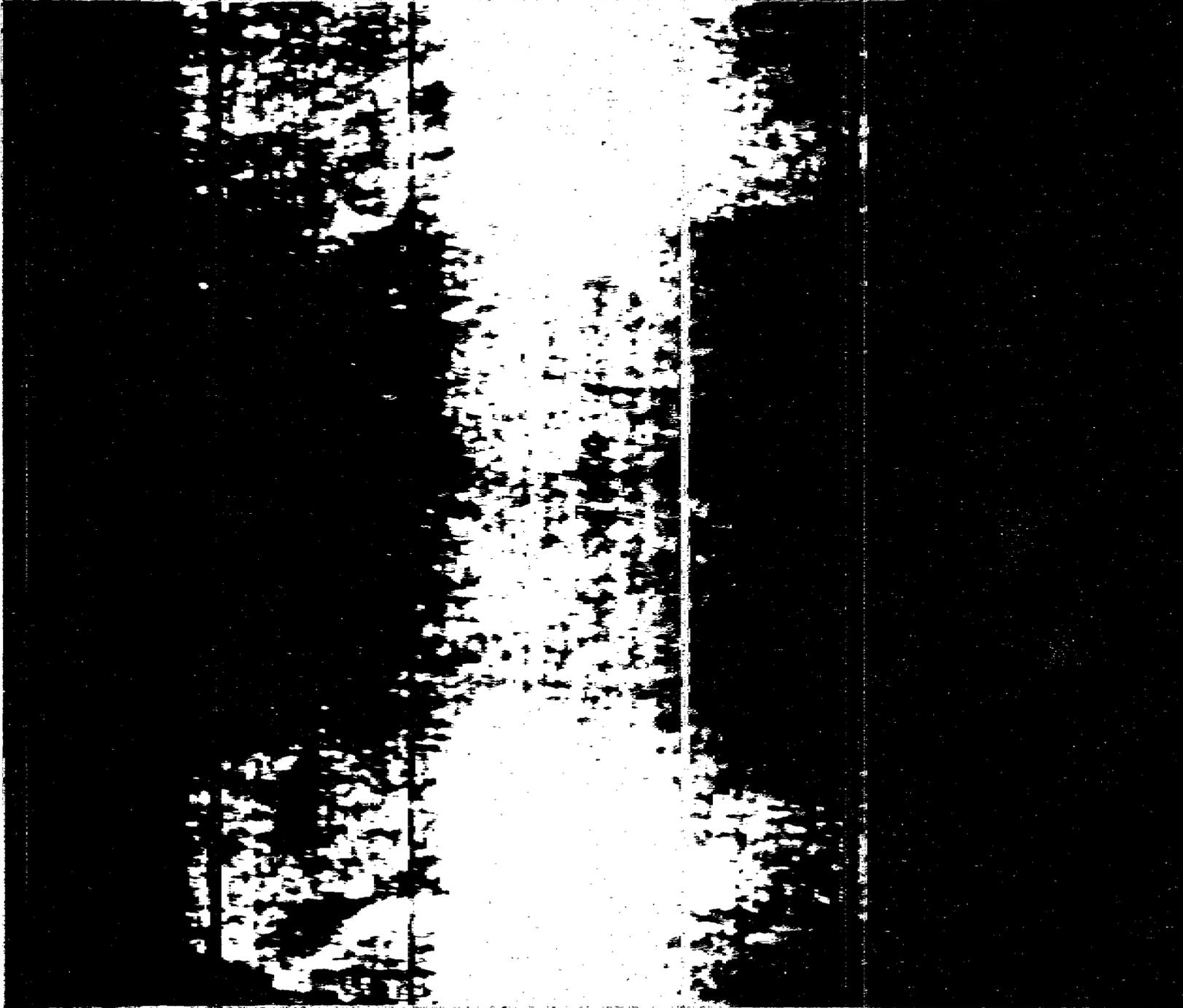
- P. W. Lipman, R. L. Christiansen, and J. T. O'Connor, "A Compositionally Zoned Ash-Flow Sheet in Southern Nevada," US Geological Survey Professional Paper 524-F, F-1 - F-47 (1966).
- F. Maldonado, D. C. Muller, and S. Koether, "Preliminary Stratigraphy, Structure, and Geophysics of USW-G2 Drill Hole, Yucca Mountain, Nye County, Nevada," US Geological Survey Open File Report (1982, in preparation).
- H. E. Roberson and R. W. Lahann, "Smectite to Illite Conversion Rates: Effects of Solution Chemistry," *Clays Clay Miner.* 29, 129-135 (1981).
- A. O. Shepard and H. C. Starkey, "The Effects of Exchanged Cations on the Thermal Behavior of Heulandite and Clinoptilolite," *Min. Soc. of India, IMA Volume*, 155-158 (1966).
- J. R. Smyth and F. A. Caporuscio, "Review of the Thermal Stability and Cation Exchange Properties of the Zeolite Minerals Clinoptilolite, Mordenite, and Analcime: Applications to Radioactive Waste Isolation in Silicic Tuff," Los Alamos National Laboratory report LA-8841-MS (June 1981).
- R. W. Spengler, D. C. Muller, and R. B. Livermore, "Preliminary Report on the Geology and Geophysics of Drill Hole UE25a-1, Yucca Mountain, Nevada Test Site," US Geological Survey Open File Report 79-1244 (1979), p. 43.
- M. L. Sykes, G. H. Heiken, and J. R. Smyth, "Mineralogy and Petrology of Tuff Units from the UE25a-1 Drill Site, Yucca Mountain, Nevada," Los Alamos Scientific Laboratory report LA-8139-MS (November 1979).
- K. Wolfsberg, R. D. Aguilar, B. P. Bayhurst, W. R. Daniels, S. J. DeVilliers, B. R. Erdal, F. O. Lawrence, S. Maestas, A. J. Mitchell, P. Q. Oliver, N. A. Raybold, R. S. Rundberg, J. L. Thompson, and E. N. Vine, "Sorpton-Desorption Studies on Tuff. III. A Continuation of Studies with Samples from Jackass Flats and Yucca Mountain, Nevada," Los Alamos National Laboratory report LA-8747-MS (May 1981).
- K. Wolfsberg, B. P. Bayhurst, B. M. Crowe, W. R. Daniels, B. R. Erdal, F. O. Lawrence, A. E. Norris, and J. R. Smyth, "Sorpton-Desorption Studies on Tuff. I. Initial Studies with Samples from the J-13 Drill Site, Jackass Flats, Nevada," Los Alamos Scientific Laboratory report LA-7480-MS (April 1979).

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