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PALEOGEOTHERMAL AND PALEOHYDROLOGIC CONDITIONS IN SILICIC TUFF FROM YUCCA MOUNTAIN, NEVADA

DAVID L. BISH[1] AND JAMES L. ARONSON[2]

[1] Earth and Environmental Sciences Division, Mail Stop D469, Los Alamos National Laboratory
Los Alamos, New Mexico 87545

[2] Geology Department, Case Western Reserve University
Cleveland, Ohio 44106

Abstract—The clay mineralogy of tuffs from Yucca Mountain, Nevada, the potential site of the nation's first high-level radioactive waste repository, has been studied in order to understand the alteration history of the rocks and to predict potential future alterations. Bulk-rock samples and clay-mineral separates from three drill holes at Yucca Mountain (USW G-1, USW G-2, and USW GU-3/G-3) were studied using X-ray powder diffraction, and supporting temperature information was obtained using fluid inclusion data from calcite. Twelve K/Ar dates were obtained on illite/smectite (I/S) separated from the tuffs from the two northernmost drill holes, USW G-1 and G-2. The predominant clay minerals in the Yucca Mountain tuffs are interstratified I/S, with minor amounts of chlorite and interstratified chlorite/smectite. The I/S reactions observed as a function of depth are similar to those observed for pelitic rocks; I/S transforms from R = 0 interstratifications through R = 1 and R ≥ 3 interstratifications to illite in USW G-2 and to R ≥ 3 I/S in USW G-1. The R = 0 I/S clays in USW GU-3/G-3 have not significantly transformed. K/Ar dates for the I/S samples average 10.4 my. These data suggest that the rocks at depth in the northern portion of Yucca Mountain were altered 10.0–11 my ago, soon after creation of the Timber Mountain caldera to the north. Both I/S geothermometry and fluid inclusion data suggest that the rocks at depth in USW G-2 were subjected to postdepositional temperatures of at least 275°C, those in USW G-1 reached 200°C, and rocks from USW GU-3/G-3 probably did not exceed 100°C. These data suggest that no significant hydrothermal alteration has occurred since Timber Mountain time, ~10.7 my ago.

Estimates of the temperature of formation of illite/smectites yield probable stability limits for several minerals at Yucca Mountain. Clinoptilolite apparently became unstable at about 100°C, mordenite was not a major phase above 130°C, and analcime transformed to albite above 175°–200°C. It appears that cristobalite transformed to quartz at 90°–100°C in USW G-2 but must have reacted at considerably lower temperatures (and for longer times) in USW GU-3/G-3. The reactions with increasing depth appear coupled, and clinoptilolite and cristobalite disappear approximately simultaneously, supporting aqueous silica activity as a controlling variable in the clinoptilolite-to-analcime reaction. The reaction of clinoptilolite to analcime also coincides with the appearance of calcite, chlorite, and interstratified chlorite/smectite. Although the hydrothermal fluids may have been a source for some cations, breakdown of clinoptilolite (and mordenite) probably provided the source of some of the Ca for calcite, Mg for chlorite, K for the I/S found deeper in the section, and Na for analcime and albite.

Using the rocks in USW G-1, G-2, and GU/G-3 as natural analogs to repository-induced thermal alteration suggests that the bulk of the clinoptilolite- and mordenite-bearing rocks in Yucca Mountain will not react to less sorptive phases such as analcime over the required lifetime of the potential repository. The zeolites in zeolite interval I, directly underlying the proposed repository horizon, may transform at the predicted repository temperatures. However, the reaction of clinoptilolite to analcime in interval I may require the transformation of all of the abundant opal-CT and glass to quartz, an unlikely scenario considering the unsaturated nature of these rocks and the predicted temperatures of <100°C.

Key Words—Geothermal gradients, Illite/smectite, K/Ar dating, X-ray powder diffraction, Yucca Mountain.

INTRODUCTION AND GEOLOGIC SETTING

Yucca Mountain is in the southwest Nevada volcanic field of the southern Great Basin, just south of the Timber Mountain-Oasis Valley caldera complex, which was active from about 16 to 6 my ago (Figure 1; Christiansen *et al.*, 1965, 1977; Byers *et al.*, 1976, 1989). The secondary minerals in the bedded and ash-flow tuffs at Yucca Mountain near the Nevada Test Site (NTS) in south-central Nevada are being studied as part of a comprehensive investigation to determine the suitability of the rocks to host the nation's first underground high-level radioactive waste repository. This study is sponsored by the Yucca Mountain Site Characterization Project (YMP) of the U.S. Department of Energy. The proposed repository host rock is in the lower portion of the densely welded, devitrified Topopah Spring Member of the Paintbrush Tuff at >300 m depth. One focus of this study is the determination of the extent to which past thermal events have altered the rocks and also the extent to which any future elevation of temperature will affect the rock properties. For example, evidence of recent alteration would indicate that the site may be subject to further

hydrothermal activity. Thus, the age of the last significant hydrothermal alteration activity at Yucca Mountain is important to determine. In addition, emplacement of high-level radioactive waste in the rocks will provide a significant source of heat for the next several thousand years, potentially affecting the mineralogy and properties of the surrounding rocks. The natural alteration assemblage observed in these tuffs may be used as an analog to determine the likelihood and nature of such repository-induced alteration. Accordingly, samples from the three deepest cored holes at Yucca Mountain, USW G-1, USW G-2, and USW GU-3/G-3, up to 1828 m in depth, have been studied.

The rocks at Yucca Mountain are predominantly high-silica rhyolite ash flow tuffs that range from poorly consolidated non-welded units to welded and/or devitrified units (Bish *et al.*, 1984). Where they are above the present-day static water level (SWL; 571.7 m depth in G-1, 524.9 m depth in G-2, and 750.3 m depth in GU-3/G-3), non-welded units are primarily glassy; below the SWL they are predominantly zeolitized and contain clinoptilolite, mordenite, and/or analcime. The welded, devitrified units, both above and below the SWL, contain abundant alkali feldspar, quartz with or without cristobalite and minor tridymite, and densely welded vitrophyric units remain largely glassy. Illite/smectite (I/S) is common in small amounts in the rocks, irrespective of the degree of welding. The three drill holes studied penetrated ash flow tuffs spanning Iijima's (1978) four alteration zones (glass, clinoptilolite-mordenite, analcime, albite), and there is an apparent northward increase in the degree of alteration at depth (e.g., Bish and Semarge, 1982; Smyth, 1982). The volcanic rocks at Yucca Mountain range in age from ~12.7 my at the surface to >14 my at depth (Byers *et al.*, 1989). The last significant activity at the Timber Mountain caldera occurred 11.5 and 11.3 Ma, with intracaldera activity peaking ~10.7 my ago (Jackson, 1988). Aronson and Bish (1987) and Jackson (1988) documented the occurrence of hydrothermal activity around the Timber Mountain-Oasis Valley caldera complex between 13 and 10 Ma, mostly between 11.5 and 10.0 Ma.

Considerable information on the present-day hydrothermal, hydrologic, and alteration conditions occurring near recent volcanic centers around the world is available from drill core and well logs, often obtained in connection with geothermal studies (e.g., Swanberg and Combs, 1986). Such information is, however, difficult to obtain for older inactive volcanic centers such as the Timber Mountain caldera complex, north of Yucca Mountain.

Here, the approach has been to use I/S geothermometry and K/Ar dating to obtain a semiquantitative estimate of the past thermal history. The transformation of smectite to illite with increasing temperature in pelitic rocks has been thoroughly studied and well documented (e.g., Burst, 1959; Perry and Hower, 1970, 1972; Hower *et al.*, 1976; Hoffman and Hower, 1979; Hower and Altaner, 1983). When a sufficient supply of K exists, 100% expandable smectite reacts through a series of intermediate interstratified I/S clays to a nonexpandable illite containing additional K and Al over that found in the precursor material. The reaction of smectite to illite in nonpelitic rocks such as volcanic tuffs has received considerably less attention, but it appears that the general trends with temperature noted above for pelitic rocks hold for other rocks (e.g., Steiner, 1968; Eslinger and Savin, 1973; Inoue *et al.*, 1978; Bish and Semarge, 1982; Hower and Altaner, 1983; Horton, 1985). This reaction is influenced by several variables, including time, temperature, mineralogic assemblage, and water composition (e.g., Eberl and Hower, 1976; Howard, 1981; McCubbin and Patton, 1981; Roberson and Lahann, 1981). Because the extent of this reaction is highly temperature dependent (Perry and Hower, 1970); Eberl and Hower, 1976; Hoffman and Hower, 1979; Hower and Altaner, 1983; Horton, 1985), it is sometimes possible to obtain consistent estimates of the maximum temperatures to which a particular I/S has been subjected, given sufficient K, Al, and reaction time. Thus, in favorable circumstances, the I/S data can be used to construct schematic maximum paleogeothermal gradients, and the areal changes in these gradients may be used to infer source(s) of any existing hydrothermal alteration. Although it is

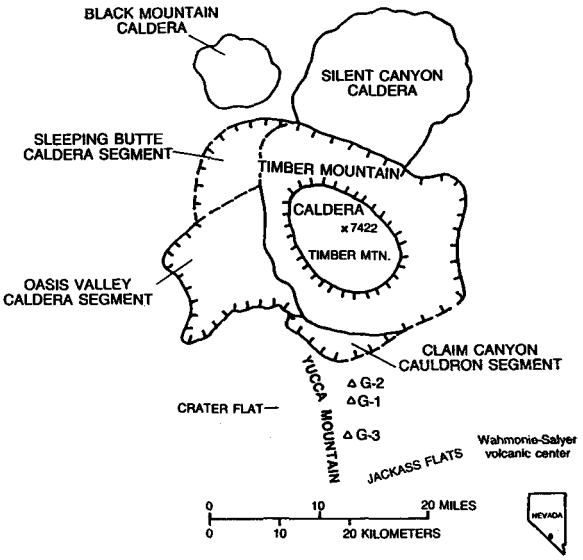

Figure 1. Southwestern Nevada volcanic field, showing the location of the Timber Mountain caldera in relation to Yucca Mountain. Heavy lines with hatchure marks to the inside represent the approximate outer limit of the Timber Mountain-Oasis Valley caldera complex, including the Sleeping Butte and Claim Canyon segments. Heavy lines with hatchure marks to the outside represent the periphery of the Timber Mountain resurgent dome. Drill holes USW G-1, G-2, and GU-3/G-3 are shown (modified from Byers *et al.*, 1976).

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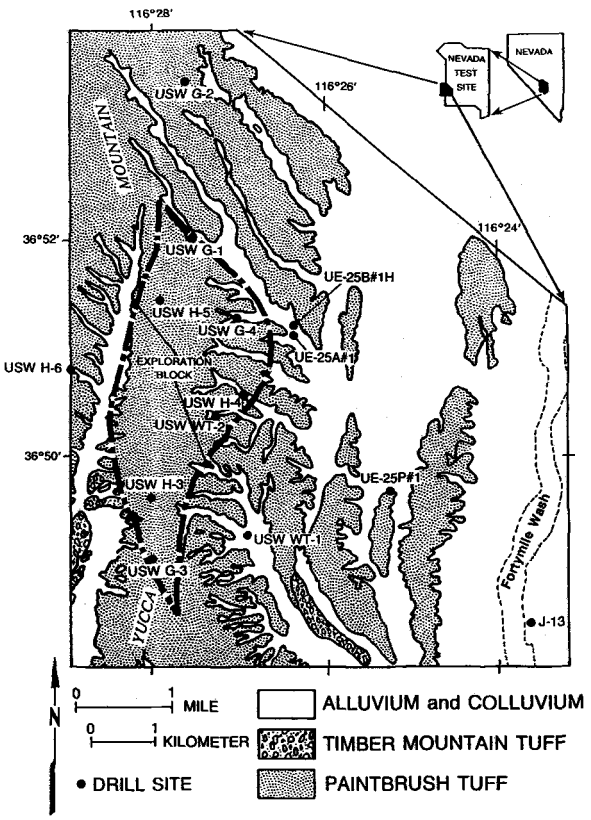

Figure 2. Location map of Yucca Mountain, Nevada, showing the approximate outline of the exploration block for the Yucca Mountain Site Characterization Project and the locations of the drill holes mentioned in the text.

difficult to extrapolate available experimental results to the Yucca Mountain paleohydrologic and paleogeothermal system, the presence of authigenic K-silicates (illite and adularia) in Yucca Mountain rocks (Caporuscio *et al.*, 1982) suggests that sufficient K and Al existed for the smectite-to-illite reaction to proceed.

In addition to using the smectite-to-illite reaction as a geothermometer, K/Ar dating methods can be applied to K-rich I/S samples to obtain reproducible estimates of the age of alteration (e.g., Aronson and Hower, 1976; Aronson and Lee, 1986; Elliott *et al.*, 1991). Thus, it should be possible to map the distribution of clay minerals in Yucca Mountain using conventional X-ray diffraction data and to determine the time and temperature of clay mineral formation. Furthermore, by establishing the correlations that exist between the clay mineral transformations and other alteration mineral assemblages, one may be able to establish the extent and timing of alteration in general at Yucca Mountain. Also, the alteration observed in deeper parts of drill holes might be used as a natural analog to repository-induced alterations. Using this natural system to provide information on reaction temperatures and products circumvents some of the problems inherent in laboratory studies, in particular the requirement that higher than expected temperatures be used to increase reaction rates, with the associated problem of extrapolating high-temperature kinetics to lower temperatures. Assuming the I/S clays record maximum alteration temperatures, inferences can be made concerning the thermal stability of associated minerals, such as the zeolites clinoptilolite and mordenite. The zeolites at Yucca Mountain apparently formed early in the mountain's history based on geopetal structures (Levy, 1991) and were presumably subjected to the same temperature and pressure conditions as the smectites.

Finally, the information on the mineral distributions, alteration temperatures, and alteration timing can be compared with data for present-day geothermal systems (e.g., Swanberg and Combs, 1986) to draw inferences about paleohydrologic conditions at Yucca Mountain. Such inferences may set limits on the elevation of past water tables and provide information on the hydrothermal circulation system that may have caused the observed alteration.

EXPERIMENTAL METHODS

All samples were obtained as drill core from drill holes USW G-1, G-2, or GU-3/G-3 at Yucca Mountain (Figure 2). Two- to 4-cm slices of core were brushed or washed clean of surface contaminants, broken into pieces smaller than ~0.5 cm, and crushed for 5 min in a tungsten carbide shatterbox. Clay mineral separations were performed by sedimentation in water, after disaggregation using an ultrasonic probe, and the < 0.1-μm or < 1-μm fraction was used to prepare oriented mounts for X-ray diffraction. There were no significant mineralogical differences between these two size fractions. In no cases were heavy liquids or any dispersants used. More than 19, 43, and 30 clay mineral separations were analyzed from USW G-1, G-2, and GU-3/G-3, respectively.

Oriented mounts for X-ray powder diffraction were prepared by sedimentation from an aqueous suspension under gravity onto a glass or cut quartz single-crystal slide; the sample area was large enough so that the X-ray beam was fully contained within the sample at all angles of interest. This preparation method did not produce mounts that were effectively infinitely thick at the maximum angle of interest, and the relative intensities were usually not used. Cavity mounts of the clay separations were prepared from dried fine fractions by front-mounting powders into a shallow cavity in a glass, Al, or stainless steel holder. The bulk-rock mineralogy reported here was described by Bish and Chipera (1989); all data were obtained using cavity-mounted powders that had been ground under acetone to < 3 μm using a Brinkmann Micro-Rapid Mill. Quantitative analyses were obtained using a combination of external- and internal-standard methods of Chung

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(1974a, 1974b), and accuracy and precision of analyses are given in Bish and Chipera (1989).

X-ray diffraction data were obtained using an automated Siemens D-500 diffractometer, counting for 0.6 to 2.0 s every 0.02° 2θ. Cavity mounts were examined under room conditions (relative humidity, RH, <30%), and oriented mounts were examined under room conditions and after solvating in ethylene glycol vapor for at least 12 hours at ~50°C. X-ray diffraction patterns of ethylene glycol-solvated I/S samples were interpreted using the methods of Reynolds (1980). The approximate percentage of illite (or 10Å) layers was estimated using techniques described by Reynolds (1980) and Środoń (1980), and the estimates were refined by calculating patterns using a FORTRAN version of Reynolds' (1980) program. If other clay minerals were suspected or if the smectite appeared unusual, a variety of other tests were performed, including K saturation, lithium saturation (Greene-Kelly, 1955; Bystrom-Brusewitz, 1975), water solvation, and heat treatments (see Brindley and Brown, 1980). Discrimination between kaolinite and/or chlorite was based on the presence or absence of a reflection near 6° 2θ or on the basis of heating experiments. However, results were usually ambiguous due to the small concentrations (<3%).

Fluid inclusions in thin-sections from USW G-2 and GU-3/G-3 were examined using techniques described by Roedder (1984). In general, only calcite contained secondary inclusions that might provide information on secondary alteration conditions, and inclusions large enough for study were very rare. Primary inclusions in phases such as quartz were not usually examined since they yielded the high temperatures typical of the primary constituents of volcanic rocks.

K/Ar dates of I/S were obtained using the methods described by Elliott and Aronson (1987) and Elliott (1988). Amounts of radiogenic Ar in the I/S samples ranged from 25–44%, and K_2O ranged from 1.78–7.56%, correlating well with the amount of collapsed layers. All age calculations used the new constants recommended by Steiger and Jager (1977). The average internal variation of replicate analyses (±0.25 my, see Table 1) was considerably less than the maximum calculated uncertainty of ±0.6 my.

Table 1. K/Ar dates (my) for I/S samples from Yucca Mountain, Nevada.

I/S	Sample[1]	Date (my)
R=0	G-2 1246.6	10.9 ± 0.5
R=0	G-2 1508.5	10.0 ± 0.5
R=1	G-1 1511.2	9.9 ± 0.6
	duplicate	10.1 ± 0.4
R=1	G-2 1133.9	8.7 ± 0.4
	duplicate	9.7 ± 0.6
	duplicate	9.9 ± 0.6
R≥3	G-1 1718.2	10.9 ± 0.6
R≥3	G-2 1181.1	11.0 ± 0.6
R≥3	G-2 1198.8	11.7 ± 0.7
	duplicate	11.3 ± 0.5
Illite	G-2 1576.1	11.0 ± 0.6
Average		10.4

[1] Drill hole and depth in meters.

RESULTS

All core samples examined contained dioctahedral I/S as the most abundant clay mineral, and other clay minerals were either uncommon or absent. The I/S mineralogy as a function of depth for the three drill holes is shown in Figures 3–5, together with the partial bulk-rock mineralogy (ubiquitous phases such as quartz, alkali feldspar, and primary biotite are not shown on the figures). In general, the I/S clays shallower than 1448 m in USW G-1 are randomly interstratified (R = 0) with <20% collapsed layers. Deeper than 1448 m, R = 1 ordered interstratifications occur, with R ≥ 3 I/S and chlorite occurring below 1718 m depth. Trends in I/S mineralogy with depth in drill hole USW G-2 are similar to those observed in USW G-1 but are displaced to shallower depths. I/S samples from <1053 m depth in USW G-2 are randomly interstratified (R = 0) with <10% collapsed layers. There is an abrupt increase in the percentage of collapsed layers below about 1106 m, with imperfect R = 1 ordering appearing at 1097 m, well-ordered R = 1 I/S occurring at 1128 m, and R ≥ 3 I/S clays occurring between 1158 and 1524 m depth. Discrete illite predominates below 1524 m, with lesser amounts of chlorite, randomly interstratified chlorite/smectite, and some 100% expandable smectites. Incomplete collapse of heat-treated I/S samples from USW G-1 and G-2 suggests that many of the clays in the deeper portions of these drill holes are partially chloritized. The I/S clays from drill hole USW GU-3/G-3 contrast with those from USW G-1 and G-2 in that they are all randomly interstratified (R = 0), with fewer than 25% collapsed layers, and they exhibit no evidence of chloritization.

Basal spacings (room temperature, 20% RH) and chemical data (Caporuscio *et al.*, 1982; Vaniman *et al.*, 1984) for I/S samples show that they are predominantly Na-Ca saturated, with a tendency to become more K rich with depth. For example, I/S shallower than 975 m in USW G-2 has Ca ≥ Na ≫ K; I/S abruptly increases in K content below 975 m depth, and those below 1067 m depth are predominantly K saturated.

In addition to the obvious trends in clay mineralogy with depth, significant parallel trends exist in the bulk-rock mineralogy shown in Figures 3–5. Most notable are the variations in zeolite mineralogy, with clinoptilolite and mordenite giving way to analcime with depth. In addition, tridymite and volcanic glass occur only in shallower rocks above the SWL, and cristobalite

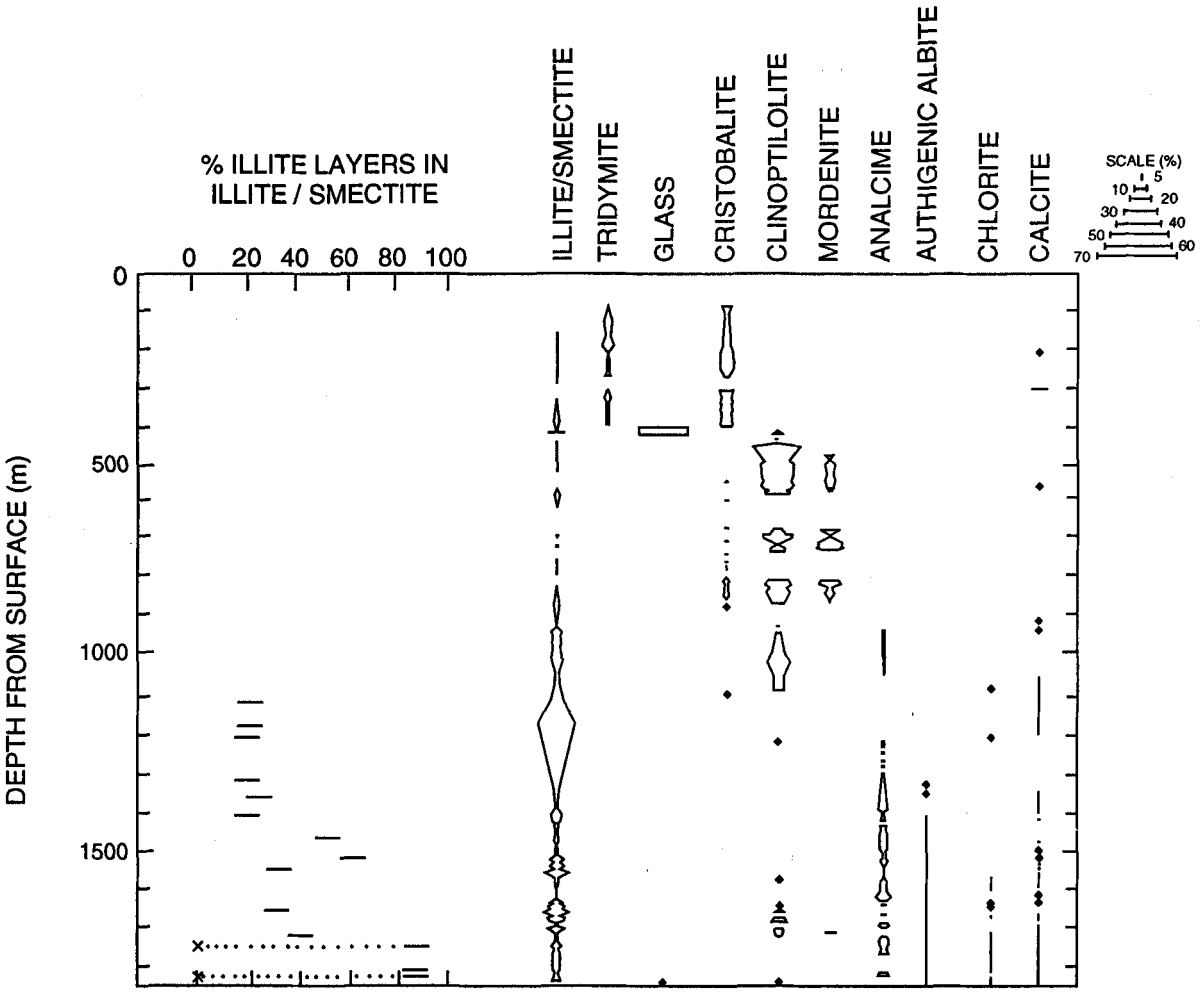

Figure 3. Mineral and glass abundances compared with clay mineralogy in drill core USW G-1 determined by X-ray powder diffraction. Occurrences of authigenic albite were determined by optical examination and are not quantitative. Amounts of phases can be estimated from the widths of the "pagodas" in comparison with the scale in the upper right-hand corner. Dotted horizontal lines connecting clay minerals indicate that the phases were coexisting in the separated fine fractions. An "×" signifies the occurrence of randomly interstratified chlorite/smectite.

disappears at intermediate depths, probably transforming to quartz (quartz is not shown on the figures). Calcite occurs sporadically in the three drill holes, but it is much more common in the deeper portions of USW G-1 and G-2. Optically identified authigenic albite (Bish *et al.*, 1981; Caporuscio *et al.*, 1982) occurs only in the deepest portions of USW G-1 and G-2.

Results of analysis of the few fluid inclusions found in secondary minerals in USW G-2 and GU-3/G-3 yield temperatures bracketing those suggested from the I/S systematics. Inclusions in calcite from USW G-2 yielded homogenization temperatures of 94° to 115°C at 1640 m depth, 147°C at 1756 m, and 202° to 239°C at 1774 m depth. Freezing temperatures for these inclusions ranged from −0.1° to −0.6°C, reflecting low salinities in the inclusions. Homogenization temperatures in calcite from USW GU-3/G-3 were 101° to 227°C at 31 m, 125° to 170°C at 130.8 m, and 97°C at 1464 m depth.

The K/Ar dates for I/S samples from USW G-1 and G-2 range from 10.0 to 11.5 my and average 10.4 my (Table 1). In general, the less illitic I/S clays yielded slightly lower K/Ar dates than the R ≥ 3 and illite clays. However, within the estimated error for an individual analysis, all of the K/Ar dates are nearly statistically equivalent.

DISCUSSION

Paleogeothermal conditions

Numerous authors have demonstrated the dependence of I/S structure and composition (i.e., degree of ordering and percentage of collapsed layers) on temperature. For example, Perry and Hower (1970) showed

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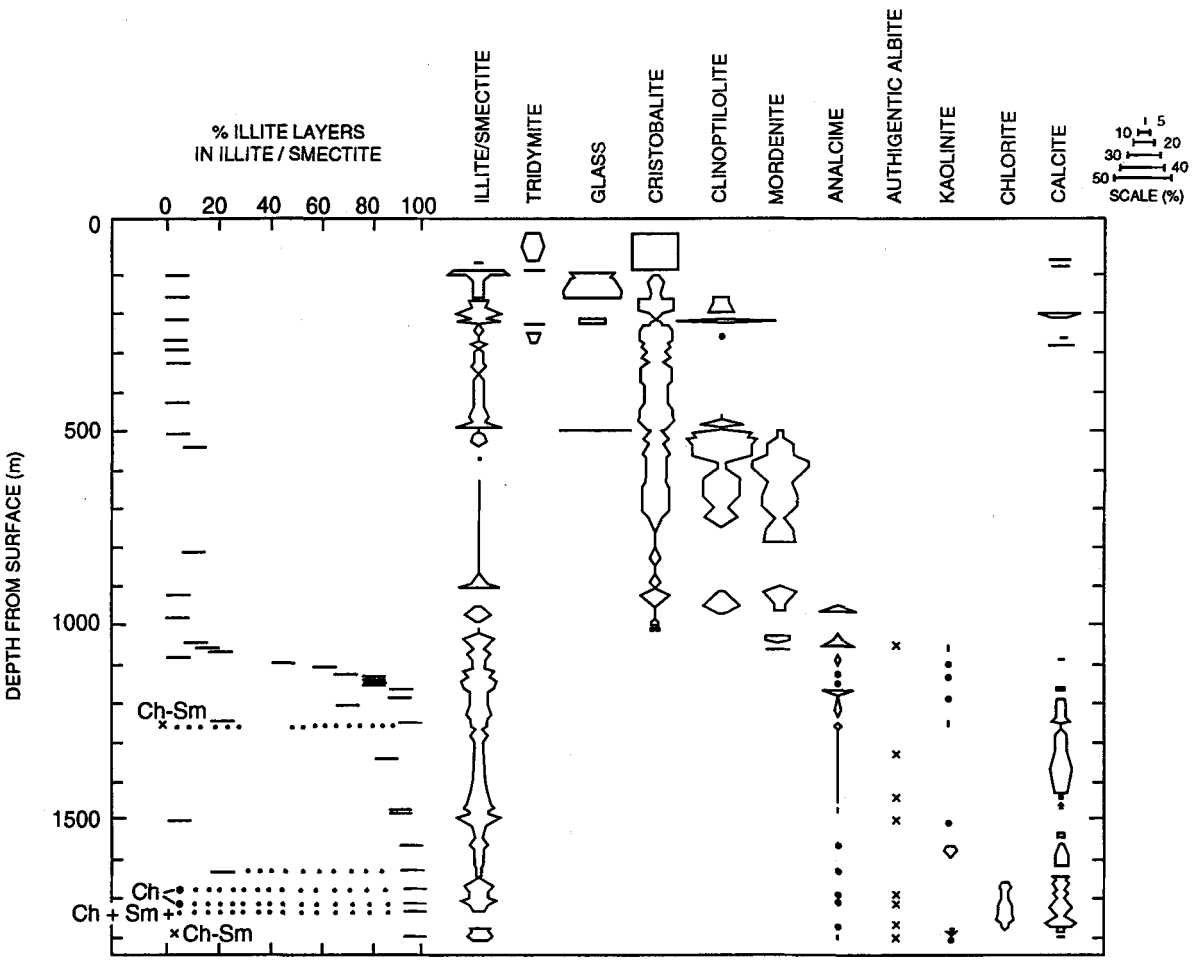

Figure 4. Mineral and glass abundances compared with clay mineralogy in drill core USW G-2 as determined by X-ray powder diffraction. Occurrences of authigenic albite were determined by optical examination and are not quantitative. Conventions as in Figure 3. A "+" signifies the occurrence of chlorite + smectite and a "•" labelled "Ch" denotes the presence of chlorite in separated fine fractions.

this relationship in comparing data from a number of Gulf Coast wells. Many subsequent studies have confirmed this temperature dependence in a variety of rock types, and Hower and Altaner (1983) illustrated this using data from both pelitic rocks and from several geothermal areas. Consistent trends emerge for a variety of rock types younger than Cretaceous age. The trends in I/S mineralogy with depth in the three Yucca Mountain drill holes may be compared with Hower and Altaner's (1983) compilation to estimate maximum temperatures to which the Yucca Mountain rocks have been subjected. Briefly, they showed that R = 1 I/S is attained at 90°-100°C for reaction times $>10^7$ yrs and at 130°–150°C for times $<10^6$ yrs. They also concluded that data from geothermal areas are consistent with those from pelitic rocks, showing that R ≥ 3 I/S is attained at ~175°C, illite appears at ~260°C, and muscovite occurs at ~310°C. Comparison of these trends with the data in Figures 3–5 yields the schematic paleotemperature profiles illustrated in Figure 6. Present-day measured geothermal gradients (Sass *et al.*, 1983) are shown on this figure for comparison. The schematic profiles for USW G-1 and G-2 in Figure 6 are considerably steeper than present-day gradients, and it is apparent that a significant thermal event has occurred in the northern end of Yucca Mountain but has not significantly affected the southern end. The schematic paleotemperatures in Figure 6 assume reaction times long enough so that kinetic effects are not limiting, and the temperatures in the deeper portions of USW G-1 and G-2, where R ≥ 3 I/S and illite occur, were apparently high enough that the smectite-to-illite reaction was not kinetically limited.

The few fluid inclusion data obtained support the I/S temperatures. Lack of evidence to support elevated alteration temperatures in GU-3/G-3 suggests that the higher temperature inclusions at 31 and 130.8 m may have formed during the initial cooling of the tuffs. More

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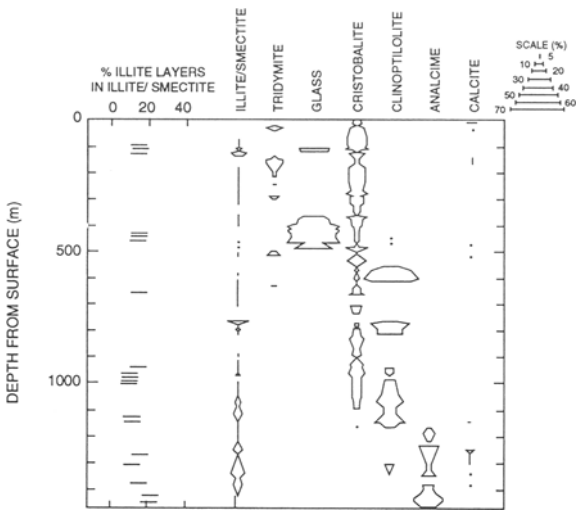

Figure 5. Mineral and glass abundances compared with clay mineralogy in drill core USW GU-3/G-3 determined by X-ray powder diffraction. Authigenic albite was not found in this drill hole. Conventions as in Figure 3. Depths below 914 m (3000 ft) in this figure are corrected for drill-hole deviation such that the total depth is shown as 1501 m (4926 ft) rather than 1533 m (5031 ft).

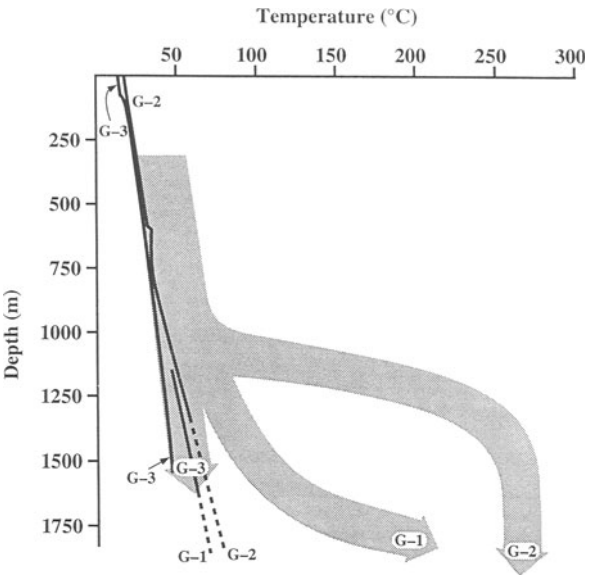

Figure 6. Schematic paleotemperatures (broad arrowed lines) for USW G-1, G-2, and GU-3/G-3 estimated from I/S mineralogy and composition and fluid-inclusion data, together with the present-day measured temperature profiles from Sass *et al.* (1983) (solid narrow lines).

likely, the relatively high homogenization temperatures in the shallow calcites are a result of re-equilibration or variable initial vapor-to-liquid ratios due to deposition in the vadose zone (Goldstein, 1986). Fluid inclusions below the SWL in G-2 (524.9 m) and GU-3/G-3 (750.3 m) are not influenced by these effects.

Alteration timing

The range in dates in Table 1 coincides with the dates published for major Timber Mountain volcanic activity (Kistler, 1968; Marvin *et al.*, 1970) (11.5 and 11.3 Ma, corrected for new constants, Steiger and Jager, 1977), and our average dates for I/S and illite closely match the dates of Timber Mountain intracaldera lava eruption (10.6–10.7 Ma, Byers *et al.*, 1989). The consistency of the I/S ages at different depths in drill holes USW G-1 and G-2, the increasing intensity of alteration observed in rocks going north toward the Timber Mountain complex, and the agreement of the I/S ages with the age of Timber Mountain volcanic activity all argue that hydrothermal effects of the Timber Mountain system are responsible for the mineralogical changes seen at depth in USW G-1 and G-2.

An alternative which we discount is that the illitization may have taken place earlier when this area was also volcanically active, for example, during Paintbrush (~12.7 my, Sawyer *et al.*, 1990) or Crater Flat (13.1 my) silicic volcanism. If this were the case, the ~11 my ages would then represent resetting of the older illite K/Ar system due to reheating during Timber Mountain volcanism. The blocking temperature above which illite and I/S rapidly lose their accumulated argon is not well established. However, the internal consistency of dates among cogenetic illitic clays of varying size fractions and the consistency of dates for a number of cases from oil well samples where samples are presently at temperatures as high as 180°C leads us to conclude that a blocking temperature of $\geq$180°C is appropriate (Aronson and Hower, 1976; Lee *et al.*, 1989; Elliott *et al.*, 1991). The blocking temperature is undoubtedly less than that of muscovite at about 350°C (Robbins, 1972), and it may be a function of the crystallite size and perfection of the I/S and, indirectly, a function of the degree of ordering and amount of collapsed layers. Considering the evidence for a moderately high blocking temperature for illite, one would expect to have observed K/Ar dates ranging as high as 12–13 my if this alternative were true.

The differences between the dates of the less illitic and the highly illitic samples warrant some discussion. It is possible that R = 0 and R = 1 I/S samples, with an average date of 9.9 my, are not as retentive of Ar as are R $\geq$ 3 I/S and illite, with an average date of 11.2 my. For example, transmission electron microscopy studies show that, in general, the crystals of more illitic I/S are more regular, well formed, and larger compared with less illitic I/S (Veblen *et al.*, 1990; Ahn and Buseck, 1990). Alternatively, it is plausible that the alteration at Yucca Mountain was progressive and what is seen in shallower cores once characterized the initial stages of alteration at depth, those initial stages now having been mostly obliterated by later higher-temperature alteration. Most of the R = 0 and R = 1

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I/S occurs at shallower depths where hydrothermal activity can be expected to have been retarded (and younger) compared with deeper R ≥ 3 I/S. Thus, the R = 0 and R = 1 dates that are as young as 9–10 my may be indicative of a 1 my duration of hydrothermal activity beneath Yucca Mountain.

Paleohydrologic conditions

Comparison of the Yucca Mountain paleogeothermal gradients (Figure 6) with those typical of modern-day geothermal systems can potentially provide information on the nature of the hydrologic system existing during hydrothermal alteration. The schematic paleogeothermal gradients for USW G-1 and G-2 in Figure 6 bear a striking resemblance to several published geothermal gradients for geothermal systems. For example, Figure 7 illustrates the temperature-depth plot for core hole GEO N-1 at Newberry Volcano, Oregon (Swanberg and Combs, 1986). The paleogeothermal gradient for USW G-2, in particular, mirrors the observed gradient in Figure 7 in many respects. Swanberg and Combs (1986) concluded that the virtually constant temperature in drill hole GEO N-1 throughout its upper 990 m represents a rain-curtain effect. The abrupt rise in temperature seen in Figure 7 is usually attributed to the existence of a permeability barrier, with shallower more permeable rocks isolated from the deeper rocks. Thus, the relatively constant inferred temperature in USW G-2 to ~1067 m depth, much deeper than the present SWL (~521.8 m), suggests that a rain-curtain effect existed and/or the rocks near or below 1067 m were relatively impermeable, thereby isolating the shallower rocks from the deeper hydrothermal system. In support of a rain-curtain effect, limited climatological data suggest that this area was much wetter ~11 my ago, before uplift of the Sierra Nevada (Hay *et al.*, 1986). However, a permeability barrier that could have effectively isolated shallower rocks from the deeper system is not obvious in USW G-2. Although there are several possible fault zones near 1000 m depth in USW G-2 (Maldonado and Koether, 1983), with significantly increased amounts of smectite below this depth, similar features are not present in USW G-1 near the depth of temperature transition. The paleogradients at Yucca Mountain also differ in detail from the gradient observed at Newberry Volcano (Figure 7) in that paleotemperatures in USW G-2 do not appear to increase significantly below about 1220 m depth, i.e., the deep system in USW G-2 was approximately isothermal rather than exhibiting the conductive geothermal gradient seen at Newberry Volcano.

The results of Forster and Smith (1990) suggest possible explanations for several of the features seen in Figure 6 and some of the discrepancies between the Newberry Volcano and Yucca Mountain geothermal gradients. Their numerical models suggest that temperatures could have been progressively set shallower

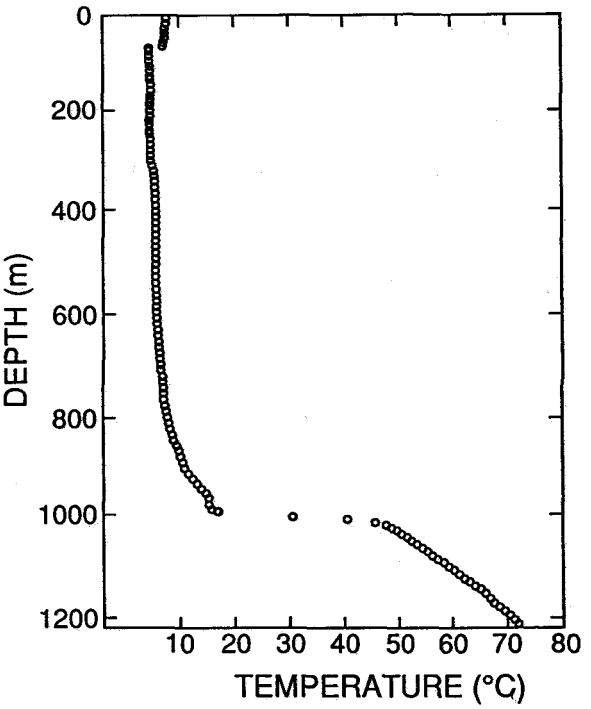

Figure 7. Measured temperature-depth plot for core hole GEO N-1, Newberry Volcano, Oregon (modified from Swanberg and Combs, 1986).

in the system as a function of time, giving the appearance of the existence of an isothermal zone. More importantly, their calculations show, for a hydrothermal system in a region of significant topography (e.g., their Figure 1.15), similar to the Timber Mountain region, that two distinct fluid flow systems can be generated without the presence of a permeability barrier. A deeper recirculating system could become chemically evolved while the shallow hydrologic system (<1–2 km depth) could be continuously recharged with fresh meteoric water. Thus a permeability barrier may not have been required to produce the type of paleogeothermal gradient shown for USW G-2 in Figure 6. The features observed at Yucca Mountain are most consistent with a hydrothermal outflow plume association, in which sufficient convective mixing occurred at depth to generate approximately isothermal conditions.

These analogies with modern-day geothermal systems suggest that the alteration observed at Yucca Mountain was associated, both spatially and temporally, with a hydrothermal outflow zone connected with the Timber Mountain caldera complex. Results of studies of modern geothermal systems such as the Jemez Mountain, New Mexico, system suggest that hydrothermal alteration surrounding a caldera complex occurs in association with late-stage intracaldera volcanic activity rather than the large-scale eruption of rhyolitic tuffs (Heiken and Goff, 1983; WoldeGabriel and Goff, 1989). The apparent isothermal nature of the

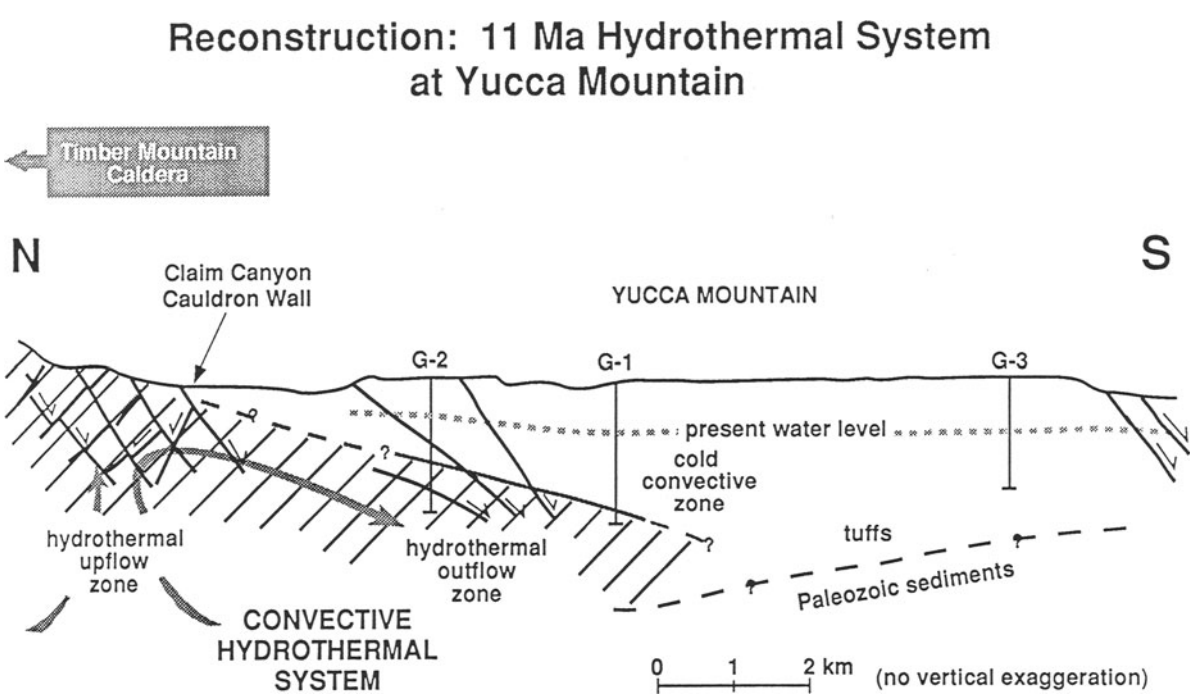

Figure 8. Reconstruction of hydrothermal circulation system near Yucca Mountain ~11 mA.

deep, high-temperature alteration zone in USW G-1 and G-2 is additional evidence supporting the presence of a hydrothermal outflow plume. A reconstruction of the hydrothermal system around Yucca Mountain ~11 my ago that is consistent with these observations is shown in Figure 8.

Interestingly, evidence exists for continued low-temperature formation of minerals at Yucca Mountain. This evidence includes I/S with a low percentage of collapsed layers occurring deeper than higher-temperature R = 1 and R ≥ 3 I/S in both USW G-1 and G-2. In addition, one sample examined (USW G-2, 1636.5 m depth) contained both discrete illite and R = 0 I/S with ~20% collapsed layers. It therefore appears that clay mineral formation has continued since the waning of the Timber Mountain hydrothermal alteration event.

Bulk-rock mineral stability

Zeolites. Potentially valuable data concerning other mineral reactions in tuffs may be obtained by examining the changes in bulk mineralogy with depth and correlating these changes with the I/S reactions and the estimated paleotemperatures. Important variations in mineralogy with depth include the gradation from unaltered volcanic glass to clinoptilolite ± mordenite to analcime and finally to authigenic albite. This sequence was first emphasized for these tuffs by Smyth (1982), who related these mineralogic changes to those documented by Iijima (1975, 1980). Smyth correlated the temperatures at which some of these reactions occurred (clinoptilolite-analcime, analcime-albite) to the Na-ion concentration of the waters. In contrast, Kerrisk (1983) conducted reaction-path calculations of mineral formation in tuffs near Yucca Mountain and concluded that aqueous silica activity was the controlling variable in the mineral evolution. He was unable to reproduce the observed mineral assemblages by varying the Na-ion concentration. Duffy (1984) also concluded that the aqueous silica concentration was the variable controlling the stability of clinoptilolite and mordenite in Yucca Mountain. He used thermodynamic calculations to show that clinoptilolite is not stable with respect to albite or analcime at any temperature when the chemical potential of silica is controlled by quartz. Thus, the stability of clinoptilolite appears to depend on whether the silica activity is controlled by cristobalite (or another relatively soluble polymorph) or quartz. The time interval over which clinoptilolite would remain stable would thus be determined by the rate of reaction of cristobalite (or glass, opal-CT) to quartz.

Approximate upper temperature limits at which zeolites have broken down in Yucca Mountain can be obtained from the mineralogic data in Figures 3–5 and the estimated paleotemperatures. For example, it is clear from the USW G-1 and G-2 data that clinoptilolite is not part of the stable mineral assemblage at the depth/temperature at which ordered I/S interstratifications occur. This implies a maximum temperature of stability of 90° to 100°C. Mordenite disappears in USW G-2 below 1091-m depth, suggesting an upper stability limit of 100° to 130°C. Finally, analcime is rare below

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1097 m and virtually absent below 1372 m in USW G-2; its disappearance as a major phase near the first appearance of R ≥ 3 I/S implies an upper stability limit for analcime of 175° to 200°C, in agreement with experimental data (Liou, 1971). The zeolite mineralogy in USW GU-3/G-3 shows the trends obvious in USW G-1 and G-2, but the I/S mineralogy suggests that temperatures have not been significantly elevated in GU-3/G-3. It is therefore likely that additional factors, probably kinetics and water chemistry (e.g., decreasing Si activity with depth), were controlling factors in zeolite reactions in USW GU-3/G-3 in the absence of significantly elevated temperatures. As discussed below, Si activity probably played a role in mineral reaction in all three holes.

The reaction of clinoptilolite to analcime coincides with the appearance of significant amounts of calcite and minor amounts of chlorite and interstratified chlorite/smectite. The increase in calcite with depth is contrary to what is observed in pelitic rocks (e.g., Hower *et al.*, 1976), reflecting either the differences in mineral assemblages or perhaps an increase in a_{CO_2} with depth (Zen, 1961) that may have been contributed by geothermal fluids. It is likely that the breakdown of clinoptilolite provided the source of at least some of the Mg for chlorite formation and the source of some of the Ca for calcite formation, although the formation of one or both of these minerals may have been associated with the hydrothermal fluids circulating at the time of alteration. The clinoptilolite probably also provided the source for at least some of the K in the deeper I/S clays and some or all of the Na for analcime and albite.

Chlorite occurrence. Chlorite and randomly interstratified chlorite/smectite both occur with I/S and illite in the deeper portions of USW G-1 and G-2. In addition, some of the deeper smectites in these drill holes appear to be partially chloritized. These occurrences are similar to those documented in silicic volcanic rocks at Wairakei, New Zealand (Steiner, 1968), and in silicic volcanic rocks in Japan (Inoue *et al.*, 1978; Inoue, 1985). Iijima (1978) also documented the occurrence of chlorite in the analcime and authigenic albite zones in altered silicic volcanic rocks. The presence of randomly interstratified chlorite/smectite in the deeper portions of drill hole USW G-2 suggests that this phase is intermediate between shallower smectites and the deeper chlorites, as proposed by Inoue (1985). In contrast to the smectite-to-illite reaction, which requires an adequate supply of K and Al, the reaction of smectite to chlorite requires additional Mg and/or Fe. Steiner (1968) suggested that the source of Mg and Fe in the silicic volcanics at Wairakei was the glassy groundmass and the alteration of magnetite to pyrite and/or epidote. However, it is likely that the source of Mg and Fe in Yucca Mountain tuffs was the clinoptilolite and mordenite that reacted to form analcime and albite. Some of the clinoptilolites in Yucca Mountain tuffs contain significant Mg, whereas analcime and authigenic albite contain little or no Mg or Fe (Broxton *et al.*, 1986). Chlorite and/or chlorite/smectite do not coexist with clinoptilolite at Yucca Mountain.

Silica phases. Several transformations between silica phases in Yucca Mountain are obvious (Figures 3–5). Among these transformations are the disappearance of glass, opal-CT, tridymite, and cristobalite with depth. The disappearance of volcanic glass and opal with depth in tuffs from other areas is well documented (Iijima, 1978), as is the instability of tridymite and cristobalite during alteration of volcanic rocks (Ernst and Calvert, 1969; Kano, 1983). As noted above, Kerrisk (1983) and Duffy (1984) concluded that decreasing aqueous silica activity, from the shallow rocks containing tridymite, cristobalite, opal, and glass to the deeper rocks containing quartz, appeared to be the most important factor in zeolite evolution in volcanic rocks at the Nevada Test Site. The X-ray diffraction data for USW G-1, G-2, and GU-3/G-3 are consistent with their ideas. It is noteworthy that the disappearance of clinoptilolite and mordenite as major phases coincides closely with the disappearance of cristobalite as a major phase, supporting the conclusions of Kerrisk (1983). The deepest occurrence of cristobalite in USW G-2 core corresponds to an I/S temperature of about 100°C. If temperature is the controlling variable in the transformation of cristobalite to quartz (Ernst and Calvert, 1969; Kano and Taguchi, 1982), then this reaction may have provided an indirect temperature control on the clinoptilolite-to-analcime reaction. The disappearance of cristobalite as a major phase would have resulted in a lower aqueous silica activity, thus destabilizing clinoptilolite.

Applications to predicting repository-induced alteration

The effects of repository-induced heating on the properties of tuffs have been studied for some time because of the importance of predicting the long-term behavior of Yucca Mountain rocks in a repository environment. Geologic emplacement of high-level radioactive waste will heat the rocks due to heat produced by the radioactive decay of the waste. Studies on the effects of repository-induced heating include research on the dehydration behavior of clays and zeolites in tuffs (Bish, 1984, 1988a, 1988b) and on the hydrothermal stability of tuffs (Blacic *et al.*, 1986; Duffy, 1983a, 1983b). In a paper on the thermal constraints on radioactive waste isolation in zeolitic tuffs, Smyth (1982) concluded that the reaction of clinoptilolite to analcime would begin at about 105°C based on data summarized by Iijima (1975), thereby giving rise to volume reductions and significantly reducing the cat-

ion sorptive capacity of the rocks. Smyth advised constraining the maximum temperature in zeolitized tuff to 85°C to prevent reaction. Laboratory research on the long-term effects of heating Yucca Mountain tuffs to relatively low temperatures (<250°C) has been hampered by the slow reaction kinetics, and laboratory experiments either have not reproduced the assemblages observed in Yucca Mountain (Duffy, 1983a, 1983b) or only do so at higher temperatures that speed reactions (Knauss and Beiriger, 1984).

A potentially effective way of circumventing the problems of slow kinetics in laboratory experiments is to use the alteration assemblages observed in Yucca Mountain, particularly in drill holes USW G-1 and G-2, as natural analogs to repository-induced thermal alterations. Because the temperatures at which reactions occur are affected by fluid composition (including the activity of water), this approach assumes that future fluid compositions will be approximately the same as those present during the alteration in Yucca Mountain ~11 my ago. This is probably a reasonable assumption, as fluid-inclusion waters are dilute. However, although present-day waters are also dilute, waters surrounding the repository environment may vary significantly from the present composition, particularly if they are concentrated by evaporation. Given these caveats, the I/S data suggest an upper temperature stability of 90° to 100°C for clinoptilolite, 100° to 130°C for mordenite, and 175° to 200°C for analcime. By combining these data with models of the thermal profiles around a repository in tuff as a function of time (Buscheck and Nitao, 1992) and with mineral distribution data from Bish and Chipera (1989), we conclude that the reaction of clinoptilolite to analcime should not occur in the thick, zeolitized tuff of Calico Hills underlying the candidate repository horizon because predicted temperatures are too low. However, zeolite interval I, above the tuff of Calico Hills and the first zeolite-bearing horizon below the candidate repository horizon (Bish *et al.*, 1984), may be significantly heated by the repository thermal pulse, and reactions among the zeolites and smectites may occur in these zones. The calculations of Buscheck and Nitao (1992) show that this interval will approach 90°C after about 1000 years. If the cristobalite and opal-CT in this interval completely react to form quartz, thereby decreasing the aqueous silica concentration, the clinoptilolite may then transform to analcime. However, there is a large amount of glass/opal-CT in interval I (Bish and Chipera, 1989) and this interval is in the unsaturated zone. Ernst and Calvert (1969) estimated that conversion of cristobalite to quartz under saturated conditions would take ~36,000 years at 100°C and 4.3 my at 50°C; all models of repository thermal behavior show that even the repository centerline temperature would be below 60°C by 10,000 years after emplacement. The transformation of volcanic glass and/or opal-CT to quartz is usually observed to proceed via a more ordered intermediate such as cristobalite (e.g., Murata and Larson, 1975) so that transformation of the existing glass and opal-CT to quartz will likely take longer than the cristobalite-to-quartz reaction. Therefore, it is highly unlikely that the aqueous silica concentration will be controlled by quartz in the required 10,000-year lifetime of a repository.

SUMMARY AND CONCLUSIONS

These mineralogical data demonstrate that the rocks at depth in the northern end of Yucca Mountain were significantly altered early in their history. The clay mineral reactions are similar to those observed in pelitic rocks, with essentially 100% expandable R = 0 I/S transforming through ordered intermediates (R = 1, R ≥ 3) to illite with depth in USW G-2 and to R ≥ 3 I/S in USW G-1. The I/S clays in USW G-3 have not significantly transformed with depth. It appears that sufficient K and Al existed in these rocks for the smectite-to-illite transformation to proceed.

Based on estimates from I/S mineralogy and fluid inclusions, the rocks at depth in USW G-2 appear to have been subjected to temperatures of at least 275°C, those in G-1 have reached about 200°C, and the deepest GU-3/G-3 rocks (about 305 m shallower than the bottoms of G-1 and G-2) probably have not exceeded 100°C. These data can be used to set limits on the temperature stability of several of the minerals in Yucca Mountain tuffs. Clinoptilolite became unstable at about 100°C, mordenite was not a major phase above 130°C, and analcime transformed to albite above 175°–200°C. It also appears that cristobalite transformed to quartz at 90°–100°C in USW G-2 but must have reacted at considerably lower temperatures (and probably over longer times) in USW GU-3/G-3. Evolution in water chemistry was probably the driving force for zeolite reactions in USW GU-3/G-3.

It is obvious that the reactions seen with increasing depth are coupled and are not only dependent on the solution chemistry but on the chemistry of the altering phases. The contention of Kerrisk (1983) that the aqueous silica activity is the variable controlling the reaction of clinoptilolite to analcime is supported by the bulk-rock mineralogical data showing the approximately simultaneous disappearance of cristobalite and clinoptilolite. Although clinoptilolite appears to have transformed to analcime at about 100°C in USW G-1 and G-2, analcime occurs in USW GU-3/G-3 although mineralogic data suggest that temperatures did not reach 100°C. Thus, there are strong indications that water chemistry exerted as great or greater an influence than temperature on the reaction of clinoptilolite to analcime in Yucca Mountain. This is in agreement with field observations elsewhere (Iijima, 1975). Reactions of glass, opal-CT, and cristobalite to quartz probably influenced the clinoptilolite-to-analcime reaction by

controlling the aqueous silica concentration, and it is likely that silica-mineral transformations are still occurring at Yucca Mountain.

The vertical distribution of minerals across Yucca Mountain demonstrates that alteration is most profound to the north in USW G-2. USW G-1 core shows the effects of hydrothermal alteration, but at a greater depth and to a lesser extent than in USW G-2, and there is little evidence for significant elevated-temperature alteration in USW G-3. Data suggest that the shallower Paintbrush Tuff Members (erupted ~12.7 my) have not been significantly altered in any of the drill holes examined. The distribution of alteration minerals and the K/Ar ages of I/S in USW G-1 and G-2 (~10.4 my) are consistent with Timber Mountain moat volcanism as the major source of hydrothermal alteration, rather than caldera-forming main ash-sheet eruptions. The rocks at depth at Yucca Mountain were apparently altered in a hydrothermal outflow plume. The nature of schematic paleogeothermal gradients suggests that a rain-curtain effect existed in USW G-2 to about ~1067 m, below which there is an abrupt rise in temperature and then the thermal gradients appear essentially isothermal. The widespread distribution of volcanic centers in the area allows for the possibility that some of the alteration may have preceded Timber Mountain volcanism, perhaps during Paintbrush volcanism, culminating with Timber Mountain volcanism, particularly the later stages, at 10–11 my. It is noteworthy, however, that the mineralogical data suggest that no hydrothermal alteration has occurred since the waning of Timber Mountain volcanism about 10 my ago.

Finally, use of the rocks in USW G-1, G-2, and GU-3/G-3 as natural analogs to alteration in a repository environment suggests that the bulk of the clinoptilolite- and mordenite-bearing rocks in Yucca Mountain will not react to less sorptive phases such as analcime and albite over the 10,000-yr required life of the repository, as anticipated temperatures are too low. However, zeolite interval I directly underlying the potential repository (Bish *et al.,* 1984) has the potential to transform at the temperatures predicted by thermal models for the repository (Buscheck and Nitao, 1992). Because the reaction of clinoptilolite to analcime appears to require the transformation of opal-CT and glass in this interval to quartz in order to lower the aqueous silica activity, it is questionable whether this reaction will occur over the lifetime of a repository considering the abundance of opal-CT and glass, the unsaturated nature of the rocks at this depth, and the anticipated temperatures mostly below 100°C.

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