

LA--10667-MS

UC-7
Issued: March 1989

DE89 008317

*Evaluation of Past and Future Alterations
in Tuff at Yucca Mountain, Nevada,
Based on the Clay Mineralogy of
Drill Cores USW G-1, G-2, and G-3*

David L. Bish

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

MASTER

EB

EVALUATION OF PAST AND FUTURE ALTERATIONS IN TUFF AT YUCCA MOUNTAIN, NEVADA, BASED ON THE CLAY MINERALOGY OF DRILL CORES USW G-1, G-2, AND G-3

by

David L. Bish

ABSTRACT

The tuffs at Yucca Mountain in south-central Nevada are being studied by the Yucca Mountain Project (YMP) to determine their suitability for a high-level radioactive waste repository. For predictive purposes, it is important to understand the alteration history of Yucca Mountain and to know how the minerals in Yucca Mountain tuffs respond to changing conditions such as elevated temperatures. The clay mineralogy of these tuffs has been examined using x-ray powder diffraction, and approximate temperatures of alteration have been determined using available clay mineral data and fluid inclusion analyses. Also, several illites from drill holes USW G-1 and G-2 have been dated using K/Ar techniques, yielding ages of about 11 Myr. The clay minerals in Yucca Mountain tuffs are predominantly interstratified illite/smectites, with minor amounts of chlorite, kaolinite, and interstratified chlorite/smectite at depth in USW G-1 and G-2. The reactions observed for these illite/smectites are similar to those observed in pelitic rocks. With depth, the illite/smectites transform from random interstratifications ($R=0$) through ordered intermediates ($R=1$) to illite in USW G-2 and to Kalkberg ($R\geq 3$) interstratifications in USW G-1. The illite/smectites in USW G-3 have not significantly transformed. It appears that the illites in deeper rocks result from hydrothermal and diagenetic reactions of earlier-formed smectites. These data demonstrate that the rocks at depth in the northern end of Yucca Mountain were significantly altered about 11 Myr ago. Both clay mineralogy and fluid inclusions suggest that the rocks at depth in USW G-2 have been subjected to postdepositional temperatures of at least 275°C, those in USW G-1 have reached 200°C, and USW G-3 rocks probably have not exceeded 100°C.

The temperature estimates from clay mineral and fluid inclusion data suggest stability limits for several minerals at Yucca Mountain. Clinoptilolite became unstable at about 100°C, mordenite was not a major phase above 130°C, and analcime transformed to albite above 175° to 200°C. It appears that cristobalite transformed to quartz at about 90° to 100°C in USW G-2 but must have reacted at considerably lower temperatures in USW G-3. Comparison of the clay mineral data with the bulk-rock mineralogy shows that the reactions seen with increasing depth are coupled. Clinoptilolite and cristobalite disappear approximately simultaneously in USW G-2 and G-3, supporting aqueous silica activity as the 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. Breakdown of clinoptilolite probably provided the source of Ca for calcite, Mg for chlorite, K for illite/smectites found deeper in the section, and Na for analcime and albite.

The vertical distribution of minerals across Yucca Mountain demonstrates that the alteration at depth is most profound to the north in USW G-2, and there is little evidence for elevated-temperature alteration in USW G-3. Drill cores USW G-1 and UE-25a#1 show the

effects of hydrothermal alteration, but at a greater depth and to a lesser extent than in USW G-2. The observed alteration mineralogy and the age of illites in USW G-1 and G-2 are consistent with Timber Mountain volcanism about 11 Myr ago as the source of hydrothermal alteration. The available data suggest that no significant hydrothermal alteration has occurred since Timber Mountain time.

Using the rocks in USW G-1, G-2, and G-3 as natural analogs to alteration under the thermal effects of a waste repository 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 life of the repository. However, the zeolites in zeolite interval I, directly underlying the candidate repository horizon, may transform at the predicted repository temperatures. The reaction of clinoptilolite to analcime in interval I may require the transformation of all of the abundant opal-CT and glass to quartz in these unsaturated-zone rocks.

I. INTRODUCTION

The secondary minerals in the ash-flow and bedded tuffs at Yucca Mountain near the Nevada Test Site (NTS) in south-central Nevada (Fig. 1) are being studied as part of a comprehensive investigation to determine the suitability of the tuffs for an underground high-level radioactive waste repository. The study of this area, sponsored by the Yucca Mountain Project (YMP) of the U.S. Department of Energy, includes a concern with the past alteration history and future alteration of the tuffs and associated volcanic rocks at Yucca Mountain. It is particularly important to understand the secondary minerals in these rocks, including zeolites and clays, because of their high sorption capacity for many waste elements and their relatively low thermal stability. The relationship between bulk-rock sorption capacity and mineralogy has been described by Bish et al. (1984b). They showed that the sorption of many elements was related to the bulk-rock clinoptilolite, mordenite, and smectite contents and that clinoptilolite and smectite were the minerals most important to sorption. Smyth (1982) emphasized the problems involved with the low thermal stability of the clinoptilolite and mordenite in the tuffs but did not discuss clay minerals. Bish et al. (1982) discussed the thermal stability of both zeolites and smectites.

It is noteworthy that whereas the distribution of zeolites (mordenite, clinoptilolite, and analcime) in Yucca Mountain is stratified, smectites are present in small to moderate amounts (1-10%) in virtually all stratigraphic units in Yucca Mountain. This was first shown in the preliminary description of the clay mineralogy of the Bullfrog and Tram Members of the Crater Flat Tuff from drill core USW G-1 (Bish 1981). That report, which included a summary of the effects of elevated temperatures on illite/smectites, described the conditions of clay formation in USW G-1. Evidence from smectites shallower than 1067 m (3500 ft) in USW G-1 suggested that clay formation postdated zeolite crystallization, although the exact timing was unclear. Comparisons of the zeolite zonation in Yucca Mountain with data from Iijima (1975, 1980) suggested that a steeper geothermal gradient existed in the past (Smyth, 1982), but other studies of the clay minerals (Bish 1981) suggested that diagenetic temperatures were never over 100°C. Based

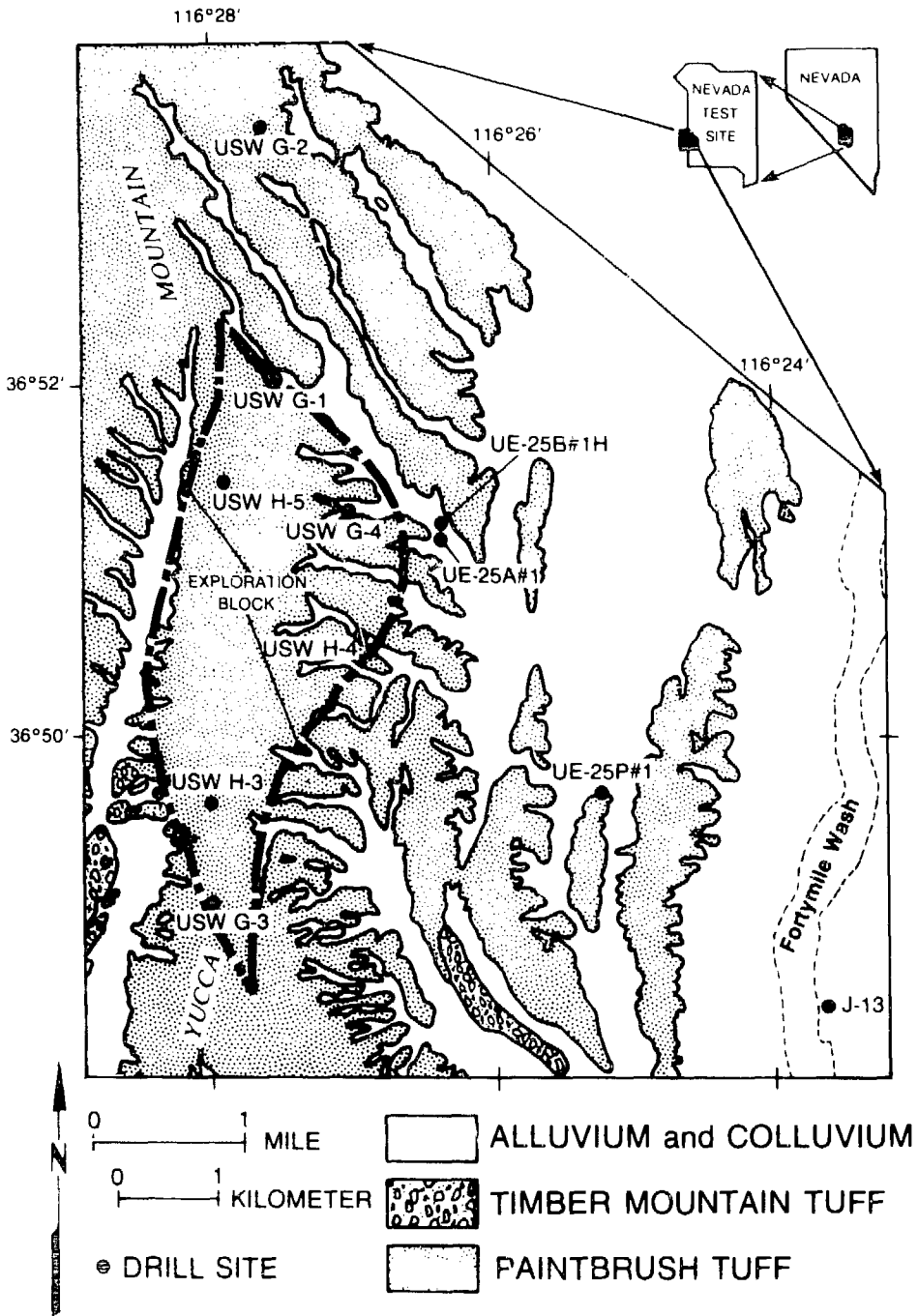


Fig. 1

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

on further studies of the zeolites at Yucca Mountain (Broxton et al. 1986), it now appears that higher temperatures need not be invoked to explain the zeolite distribution in Yucca Mountain; smectite and zeolite formation may have been contemporaneous.

After the preliminary work on the clay mineralogy in USW G-1, a more complete study of the clays in drill holes USW G-1, G-2, and G-3 was undertaken. This was done not only to outline the clay mineral abundances as a function of depth in these drill cores but also to obtain information on the timing, extent, and temperature of alteration in the tuffs of Yucca Mountain.

The transformation of smectite to illite with increasing temperature in pelitic rocks has been thoroughly studied and well documented (Burst 1959; Perry and Hower 1970, 1972; Hower et al. 1976; Hoffman and Hower 1979; Hower and Altaner 1983). When an abundant supply of potassium exists, 100% expandable smectites react through a series of intermediate interstratified illite/smectites to a nonexpandable illite containing additional potassium and aluminum. This reaction is influenced by several variables, including time, temperature, mineralogic assemblage, and water composition (Eberl and Hower 1976; Howard 1981; McCubbin and Patton 1981; Roberson and Lahann 1981). Because the extent of this reaction is highly temperature dependent (Eberl and Hower 1976; Hower and Altaner 1983), it is possible to obtain consistent estimates of the temperatures to which a particular illite/smectite has been subjected, given sufficient K, Al, and reaction time.

The reaction of smectite to illite in nonpelitic rocks has received considerably less attention, but it appears that the general trends with temperature noted above for pelitic rocks hold for other rocks (Steiner 1968; Inoue et al. 1978; Bish and Semarge 1982; Hower and Altaner 1983). Roberson and Lahann (1981) have shown, however, that the addition of >100 ppm Mg, Ca, or Na to K-bearing solutions significantly inhibits the reaction of smectite to illite, and Howard (1981) proposed that competing ions in interstitial waters influence the illitization reaction as much as the supply of K. Unfortunately, it is difficult to extrapolate their results to a system with a composition typical of present-day J-13 well (Fig. 1) water at Yucca Mountain (~2 ppm Mg, ~13 ppm Ca, ~5 ppm K⁺, and ~50 ppm Na) (Bish et al. 1984a; Ogard and Kerrisk 1984). The composition of the paleogroundwater is not known, but 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. Given the age of the tuffs in Yucca Mountain (~12 to 16 Myr), the amount of time available for reaction, and the observed illite/smectites, there is no evidence for suppression of the smectite-to-illite reaction in tuffs due to groundwater composition effects.

Ideally, it should be possible to map out the distribution of clay minerals in Yucca Mountain, to determine the time and temperature at which the minerals formed, and to map out the extent of hydrothermal alteration in Yucca Mountain. A very important application of this time-temperature information will be predicting the effects of prolonged high temperatures on the mineral assemblages in possible repository horizons. To aid prediction of these effects, the alteration observed in deeper parts of drill holes may 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, e.g., the requirement that higher than natural temperatures be used to increase recrystallization rates, with the associated problem of extrapolating high-temperature kinetics to low temperatures. The work described here deals mainly with correlations of temperatures of reactions and zeolite assemblages in the tuffs. If the zeolites in Yucca Mountain formed early and were subjected to the same temperature and pressure conditions as the smectites, the clay mineralogy should provide information on the stability ranges of the zeolites in Yucca Mountain.

This report addresses topics of concern for evaluating the long-term changes that may occur in Yucca Mountain tuffs as a result of the heat load imposed by a waste repository. By determining the temperatures of clay mineral formation, it is possible to assess the temperatures at which clinoptilolite, mordenite, and analcime transformed to other mineral assemblages in the past at Yucca Mountain. This study of natural, thermally induced transformations at Yucca Mountain provides one method for predicting the repository-induced thermal alteration of existing secondary minerals within the thermal aureole around the repository.

Additionally, this report presents the first information available for the timing of past hydrothermal alteration at depth below Yucca Mountain. This information indicates that post-placement hydrothermal alteration at Yucca Mountain is an old event, probably correlated with Timber Mountain igneous activity. No mineralogical evidence exists to suggest that significant hydrothermal activity has occurred more recently than 11 Myr ago.

II EXPERIMENTAL METHODS

Many techniques are used for clay mineral identification (e.g., Jackson 1979; Brindley and Brown 1980), but specific techniques are required depending on the rock type and information desired. For this reason, the procedures used in our work will be described in detail.

We typically start with drill core samples that have been brushed or washed clean of surface contaminants. After breaking a 2- to 4-cm slice of core into pieces smaller than about 0.5 cm, the sample is loaded into a shatterbox and crushed for 5 minutes. After crushing the entire slice of core by portions in the shatterbox, the crushed powder is mixed and stored in plastic vials. The use of large amounts of sample and subsequent homogenization of powder is important because of the typical inhomogeneity of tuffs. We use an automated Siemens D-500 diffractometer in our powder x-ray diffraction analysis, and we count for 0.6 to 2.0 seconds every $0.02^\circ 2\theta$, using a rotating sample holder when quantitative results are desired.

For clay mineral separations, 20-50 g of powdered sample are suspended in 500 to 700 ml of deionized water in a 1000-ml beaker. To disaggregate the sample, the beaker with suspended sample is vibrated in an ultrasonic bath for at least 1 hour or with an ultrasonic probe for 15 minutes. After disaggregation, the beaker is covered for about 4 hours to allow the coarsest material to sediment out.

The material remaining in suspension is decanted into centrifuge tubes and centrifuged at 2500 rpm for 30 minutes. We have found this speed and time sufficient to remove all quartz, feldspar, and zeolites from suspension. After centrifugation, the supernatant is decanted into other centrifuge tubes and centrifuged at a speed of 8000 rpm for 1 hour. This centrifugation sediments the fine clay fraction ($<1 \mu\text{m}$). The material at the bottom of the tubes is saved for analysis. If the supernatant is cloudy, it is centrifuged at 15 000 rpm for 45 minutes, and the sediment is removed and saved. This ultrafine fraction sediment ($<0.1 \mu\text{m}$) is ideal for making oriented mounts of clays for x-ray diffraction. A layered sediment with a clear, gel-like top layer and an opaque bottom layer is often observed after centrifuging the ultrafine fraction. When this occurs, separate oriented mounts of the two materials are prepared.

The above procedure provides clay mineral concentrates that can be used for chemical analysis and x-ray diffraction. X-ray powder diffraction of clay minerals usually involves the preparation of two types of mounts: (1) oriented thin films and (2) "random" cavity mounts. Many procedures exist for producing oriented mounts (see Brindley and Brown 1980, p. 309). We employ the method of sedimentation from an aqueous suspension under gravity onto a glass slide. Our procedure is to suspend 50-150 mg of the $<1\text{-}\mu\text{m}$ or $<0.1\text{-}\mu\text{m}$ clay fraction in 10 to 20 ml of deionized water contained in a small beaker. Suspension may be improved by ultrasonic vibration if necessary. This suspension is dripped from an eye dropper or pipette onto a clean, dry, level glass slide appropriately sized for the diffractometer sample holder. Only enough sample to completely cover the slide is used, and the slide is not overfilled. The suspension is allowed to dry undisturbed on the glass slide, and no more suspension is added after drying begins. Several points must be considered when making an oriented clay mount. If one is interested in ratios of basal 00l intensities or in absolute intensities, extra care must be taken in mount preparation. The sample area must be large enough so that the x-ray beam is fully contained within the sample at all angles of interest. If the sample is too narrow, a portion of the beam will be outside of the sample area at low angles where the beam has significant divergence, and low-angle peak intensities will be low when compared to higher-angle peaks for which the beam is completely within the sample. It is also important to consider the thickness of the oriented sample. If one is interested in accurate intensities, the sample should be effectively infinitely thick at the maximum angle of interest (see Brindley and Brown 1980, pp. 309-310; Reynolds 1980, p. 299). For typical specimens, thicknesses on the order of 30-50 μm are required at $30^\circ 2\theta_{\text{Cu}}$, and for accurate intensities at high angles, at least 20 mg of clay per cm^2 are required. These thicknesses are typically not obtained with sedimentation on a glass slide. Reynolds (1980, p. 299) also discussed the effects of sample displacement from the goniometer axis of rotation. The errors are largest at low angles and follow the relation (Parrish and Wilson 1959)

$$\Delta 2\theta = 2S \cos\theta/R$$

where $\Delta 2\theta$ is the error in radians, S is the sample displacement in cm, and R is the goniometer radius in cm. When one considers this relation, the drawbacks to thick smear mounts on glass slides are obvious.

Finally, it is useful to have a homogeneous particle size, and if the above centrifugation procedure is followed, this requirement should be met.

Oriented mounts are useful primarily because a highly oriented clay specimen yields only the 00 l series of basal reflections with little or no evidence of hkl reflections (because clays have excellent 00 l cleavage). The basal spacing yielded by patterns of oriented mounts is related to the type of layers present, and this technique is thus very useful for clay mineral identification. These are also the most commonly used mounts in the study of interstratified clay minerals; techniques employed in the investigation of these more complex clays are given below.

In contrast to oriented mounts, "random" cavity mounts are employed when one is interested in the complete diffraction pattern, including hkl reflections. Random powder mounts are used also to determine whether a clay is dioctahedral or trioctahedral. The 060 or 06 l reflection located about $60^\circ 2\theta_{Cu}$ is often used for this purpose; dioctahedral minerals yield reflections with spacings between 1.48 and 1.50 Å, whereas trioctahedral minerals have $d(060)$ values about 1.53 to 1.55 Å. Just as with oriented mounts, there are a variety of methods for producing random mounts (see Brindley and Brown 1980, pp. 310-311). One of the most common techniques used to produce a random orientation is to pack a powder into a shallow cavity in a glass, aluminum, stainless steel, or plastic holder, but the surface smoothing process inevitably produces some preferred orientation. An alternative method is filling shallow cavities from the rear. Unless one is interested in a truly random orientation, one of these methods should suffice.

Numerous treatments are employed in the identification of clay minerals. These usually can be carried out with oriented mounts, and the treatments include cation saturation, solvation with a polar organic liquid (including water at different vapor pressures), and heating. The literature on such techniques is voluminous, and only those treatments employed in this study will be discussed here. Untreated material is usually examined first, and either oriented or random mounts may be employed. A useful initial indication of the type of clay mineral one is working with may be gained from the 00 l basal reflections. The basal spacings and intensities expected for a variety of clay minerals are listed by Brindley and Brown (1980, p. 323). Because the study described below is concerned only with smectites and illite/smectites, the other clay minerals will not be discussed. Further information on identification of nonsmectites can be obtained from Brown (1972) and Brindley and Brown (1980).

The swelling behavior of smectites is a well-known phenomenon and is discussed at length in Brown (1972), Brindley and Brown (1980), and Bish (1988). Depending upon relative humidity, layer charge, and interlayer composition, smectites have a range of basal spacings from ~10 Å to ~19 Å under room conditions. Because it is a major factor, the relative humidity should always be noted when recording an x-ray diffraction pattern of a smectite. Our standard analysis routine involves recording an x-ray pattern of an oriented clay separate under room conditions, usually 10 to 40% relative humidity, and noting whether the smectite has 0, 1, 2, or 3 layers of water in the interlayer. From this information and using data in Gillery (1959) and Suquet et al. (1975), knowledge of the interlayer composition of the

smectite can be obtained. At the relative humidity in our laboratory, we normally see evidence for a potassium-rich interlayer (0 water layers) or a mixed sodium, calcium, potassium interlayer (1 to 2 water layers). After examining the oriented mount under room conditions, the mount is placed in an ethylene glycol vapor for at least 12 hours at about 50°C. Martin (1982) has shown that the minimum contact time for a Mg-montmorillonite in ethylene glycol to obtain a regular ethylene glycol-smectite complex is 4 hours. A diffraction pattern of the ethylene glycol-solvated smectite is made immediately after removing the sample from the ethylene glycol vapor. Solvation of smectites with ethylene glycol yields a stable well-ordered complex that gives an easily interpretable x-ray pattern regardless of whether or not interstratified illite is present.

To interpret the patterns of ethylene glycol-solvated illite/smectite interstratifications, we use the method of Reynolds (1980) (see also Reynolds and Hower 1970; Srodon 1980; Hower 1981). The approximate percentage of illite (or 10 Å) layers was estimated using techniques described by Reynolds (1980) and Srodon (1980), and the estimates were refined by calculating patterns using a FORTRAN version of Reynolds' (1980) program. Examples of these calculated patterns are shown in Fig. 2. The proportions of expanded and collapsed components are indicated above the individual patterns. All calculations were done with an ethylene glycol-smectite complex thickness of 16.6 Å. The small peaks on either side of the main peak at about 5.2° 2θ for the 99% smectite/1% illite and the peaks at about 27° 2θ for the Kalkberg-ordered clays are due to series termination errors and are not representative of what is observed with natural samples (see Reynolds 1980, p. 264). The random-powder Lorentz-polarization factor was used for all calculations of randomly interstratified illite/(glycol)smectite (R=0), allevardite (R=1, IS ordered), and pure illite. The single-crystal Lorentz-polarization factor was used in calculations of Kalkberg-ordered (R≥3, ISII long-range-ordered) illite/(glycol)smectite below 20° 2θ because this form of the Lorentz-polarization factor is more applicable to well-oriented samples on a powder diffractometer without an incident-beam Soller slit (Siemens D-500). These different types of ordering (Kalkberg, allevardite) are often described using the term "Reichweite," denoted R (Reynolds 1980). In an interstratified layer sequence, R denotes the most distant layer that affects the probability of occurrence of the final layer. Therefore R=0 denotes a randomly interstratified illite/smectite because a given layer has no influence on the probability of occurrence of the next layer. Nearest-neighbor ordering, or allevardite-ordered illite/smectite (Reynolds and Hower 1970), in which there is a regular, ordered alternation of layers is denoted R=1. Kalkberg-ordered illite/smectites or ISII long-range-ordered illite/smectites are R≥3. Few occurrences of R=2 interstratifications have been documented, and illite/smectites seem to go rapidly from R=1 to R=3 or R≥3. In addition, evidence exists for longer-range ordering than R=3 in Kalkberg-ordered illite/smectites, hence the term R≥3 is often used for such clays.

The calculated patterns allow several parameters to be estimated, including the percentage of 10 Å layers interstratified with smectite layers, the thickness of the ethylene glycol-smectite complex, and the degree of ordering of the interstratification. Srodon (1980) discussed the relationship between the

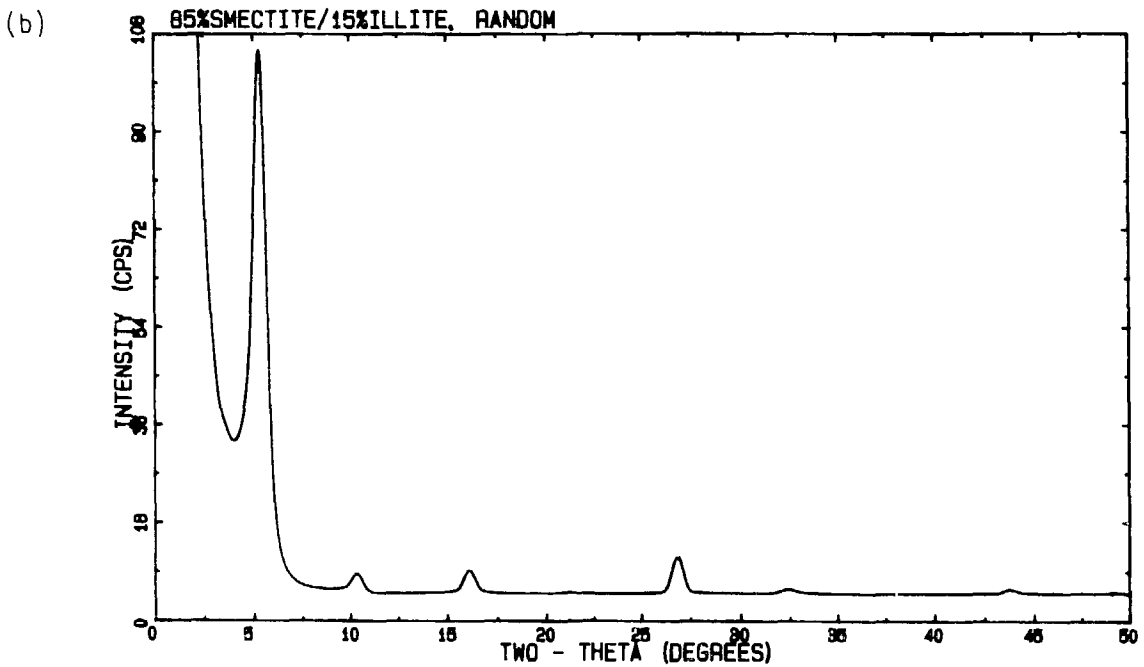
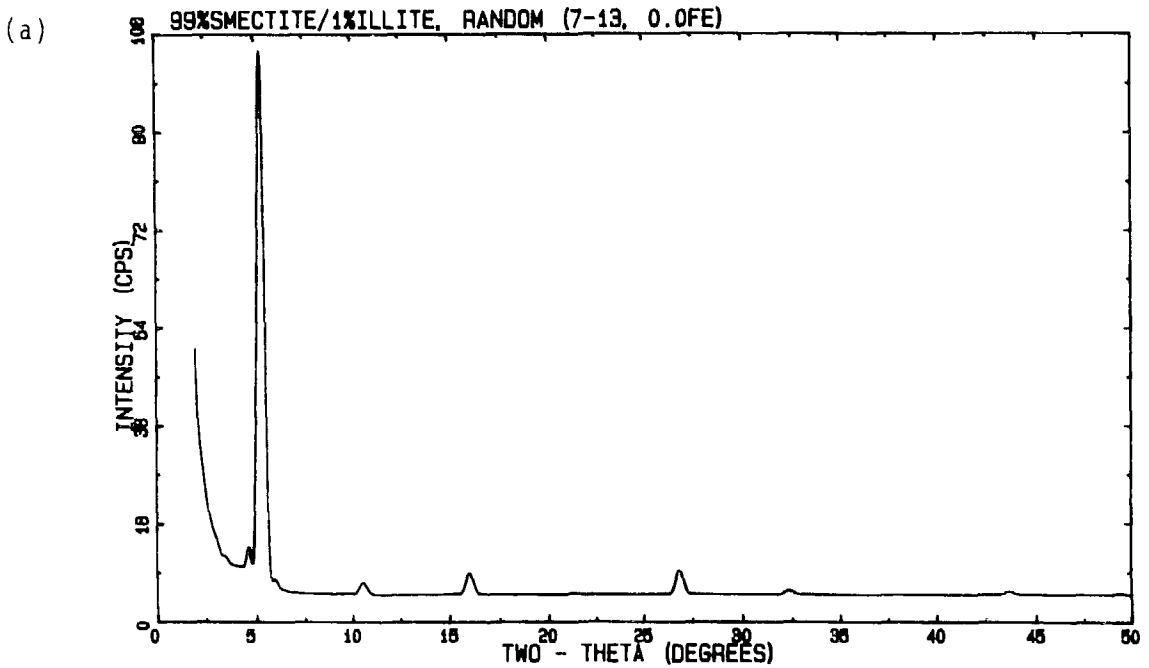
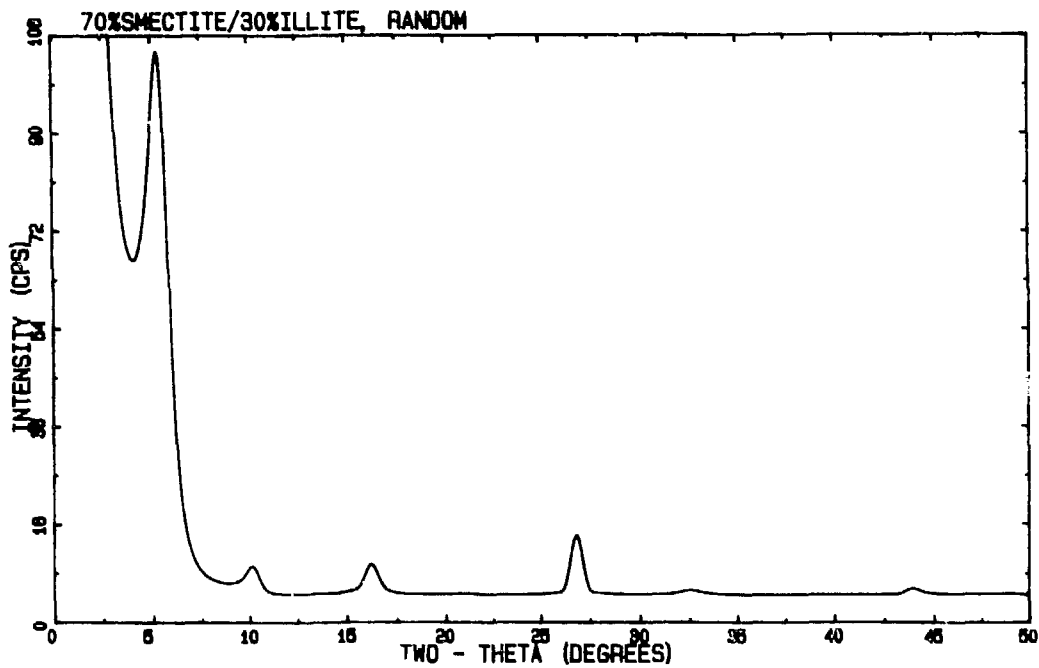


Fig. 2.

Calculated x-ray diffraction patterns ($\text{CuK}\alpha$) of interstratified illite/ smectites. The number of layers in individual crystallites (N) equals 7 to 13 for a), d), e), and h), equals 4 to 10 for b) and c), and equals 9 to 15 for f) and 10 to 16 for g).

(c)



(d)

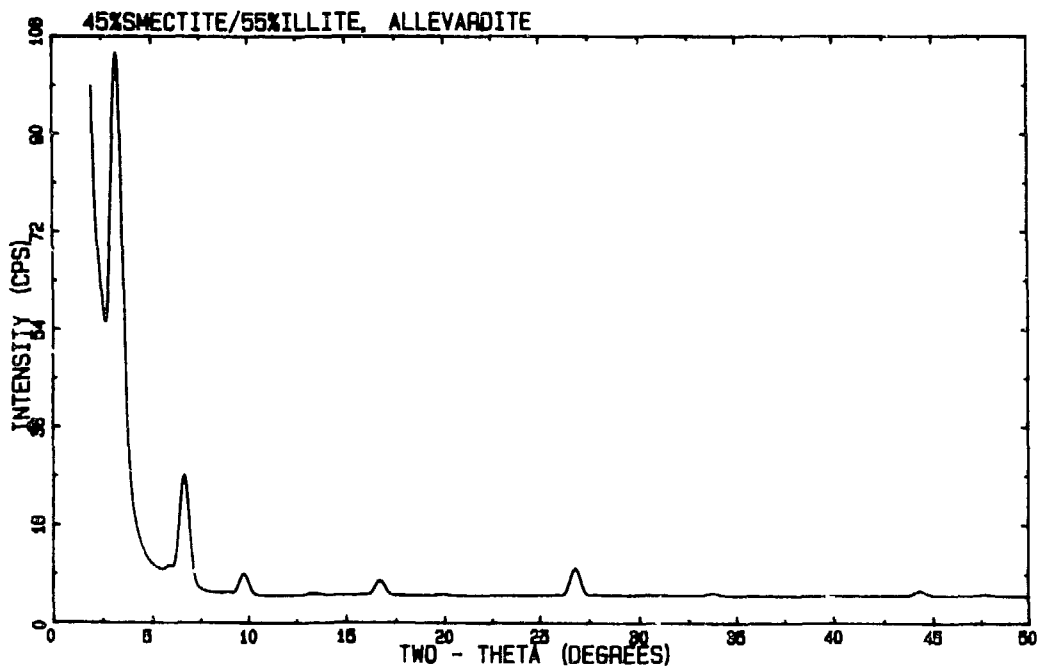


Fig. 2. (cont)

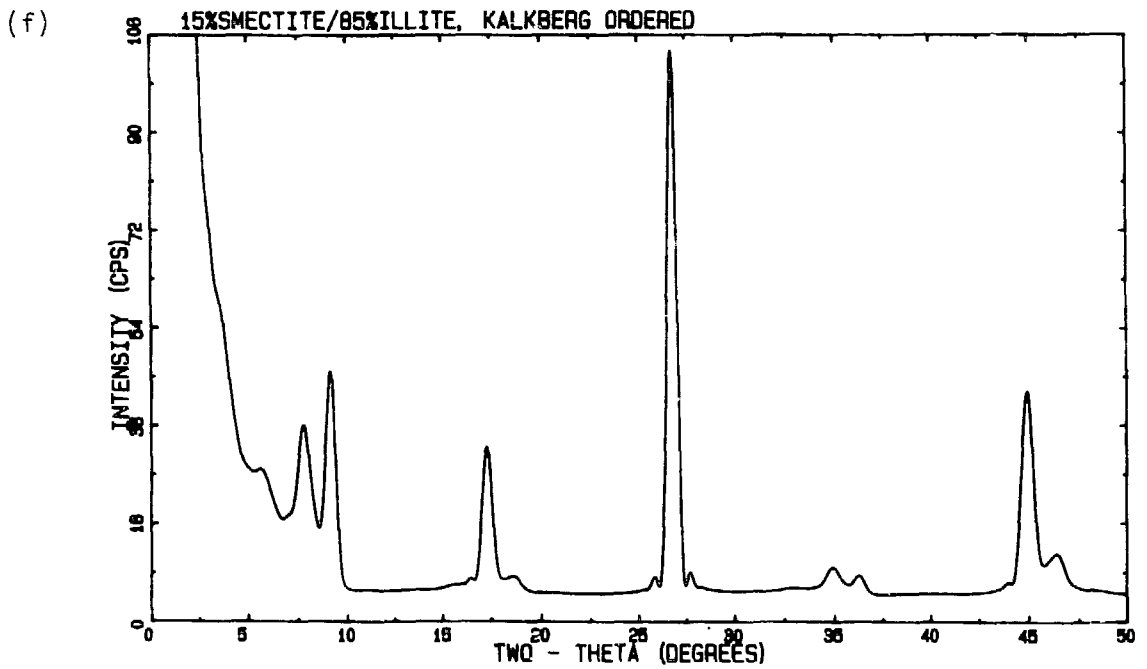
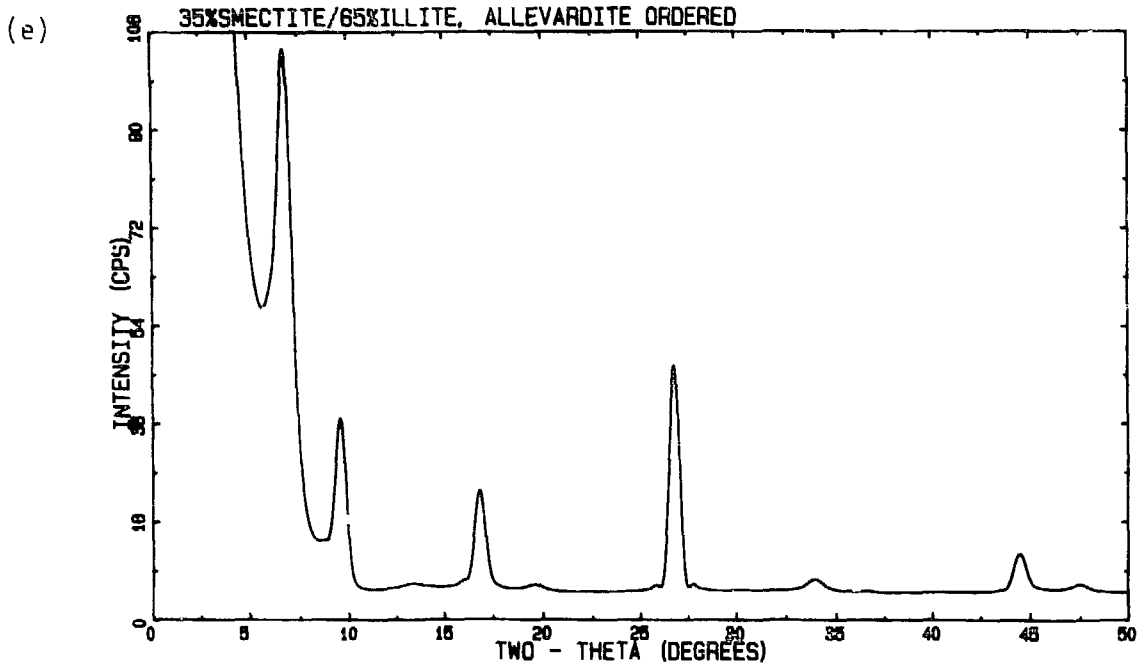
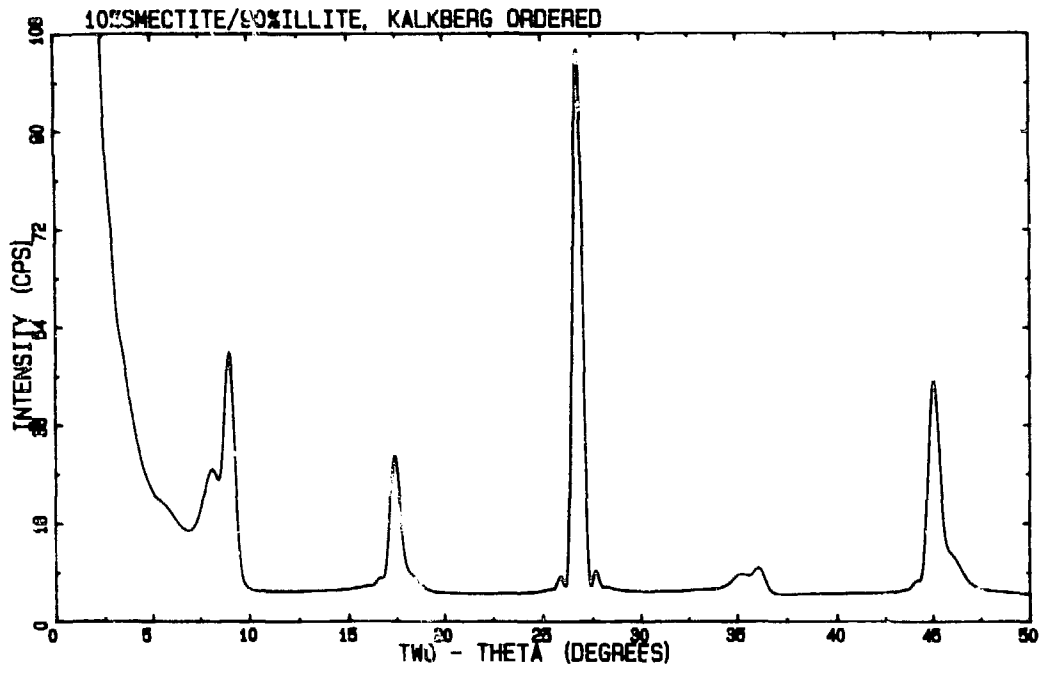


Fig. 2. (cont)

(g)



(h)

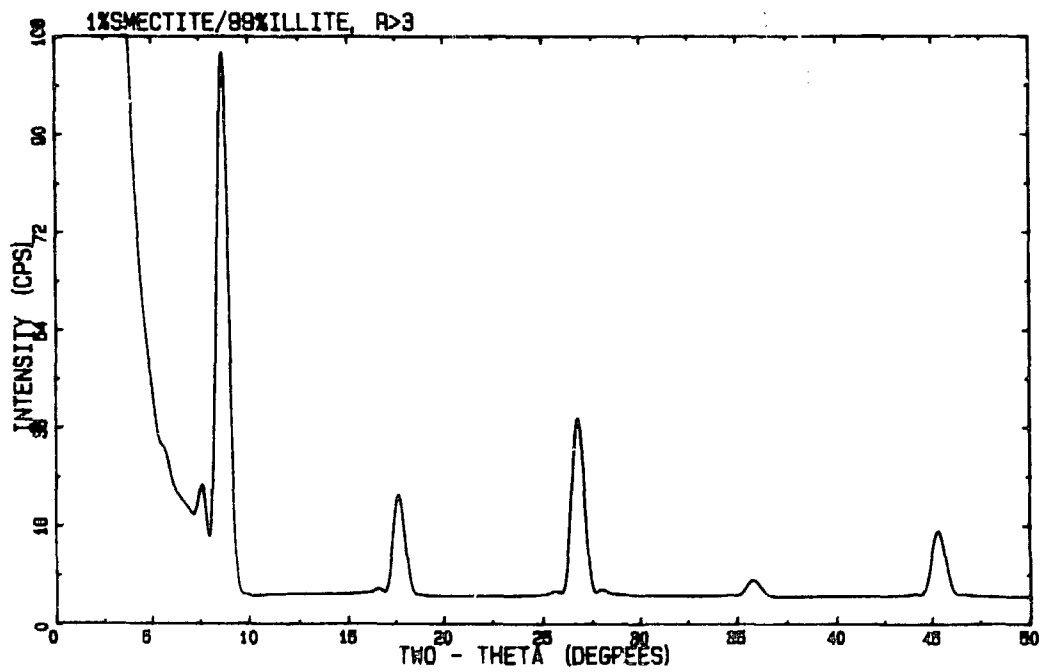


Fig. 2. (cont)

ethylene glycol-smectite complex thickness and layer charge; in general, a low ethylene glycol-smectite complex thickness is correlated with a higher layer charge and a high cation exchange capacity. Reynolds (1980) discussed interstratification at length, including methods of determining ordering and the type of interstratification.

In the course of our routine examinations, we usually do not perform any other treatment on the clay. However, if other clay minerals are suspected or if the smectite appears unusual, we perform a variety of other tests including potassium saturation, lithium saturation (Greene-Kelley 1955; Bystrom-Brusowitz 1975), water solvation, and heat treatments (see Brindley and Brown 1980). Unambiguous identification of kaolinite and/or chlorite in these rocks was usually difficult because of the small amounts of the phases present. Both phases have major reflections near 12° - 2θ in x-ray powder patterns, and discrimination was attempted based on the presence or absence of a reflection near 6° 2θ (chlorite has a reflection here) or on the basis of heating experiments. However, results were usually ambiguous due to the small concentrations, and values reported here are best estimates.

In addition to examining the clay mineralogy by x-ray diffraction, fluid inclusions were examined in calcite, fluorite, and quartz in USW G-2 and G-3, using techniques described by Roedder (1984) in order to obtain additional information on the temperatures associated with the formation and alteration of the minerals in Yucca Mountain tuffs. In general only calcite and fluorite contained secondary inclusions that might provide information on secondary alteration conditions, and inclusions large enough to study were very rare. Primary inclusions in phases such as quartz were not usually examined since they yield very high initial depositional temperatures.

III. RESULTS AND DISCUSSION

Examples of the x-ray powder diffraction patterns of the clays from USW G-1 and G-2 are shown in Fig. 3 and can be compared with the calculated patterns in Fig. 2. The results for the clays from USW G-1, G-2, and G-3 are presented in Tables I, II, and III; data for the clays from the upper portion of G-1 are in Bish (1981). These data include percent illite layers, type of interstratification, the ethylene glycol-smectite complex thickness, and the basal spacing at $20 \pm 10\%$ relative humidity. In USW G-1, the clays shallower than 1448 m (4750 ft) in depth are randomly interstratified illite/smectites ($R=0$) with greater than 80% expandable layers. Below 1448 m (4750 ft), ordered illite-rich interstratifications occur, with Kalkberg-interstratified illite/smectites ($R \geq 3$) and chlorite occurring below 1718-m (5637-ft) depth. The clays from USW G-2 are randomly interstratified illite/smectites ($R=0$) with $<10\%$ illite layers shallower than 1053 m (3454 ft). Kaolinite appears and there is an abrupt increase in interstratified illite in the illite/smectites below about 1106 m (3627 ft), with minor $R=1$ ordering appearing at 1097 m (3600 ft), well-ordered $R=1$ interstratifications occurring at 1128 m (3700 ft), and long-range ordered Kalkberg-type interstratifications ($R \geq 3$) occurring between 1158-m (3800-ft) and 1524-m (5000-ft) depth. Discrete illite predominates below 1524 m (5000 ft), with lesser amounts of chlorite, randomly interstratified chlorite/smectite, and 100%

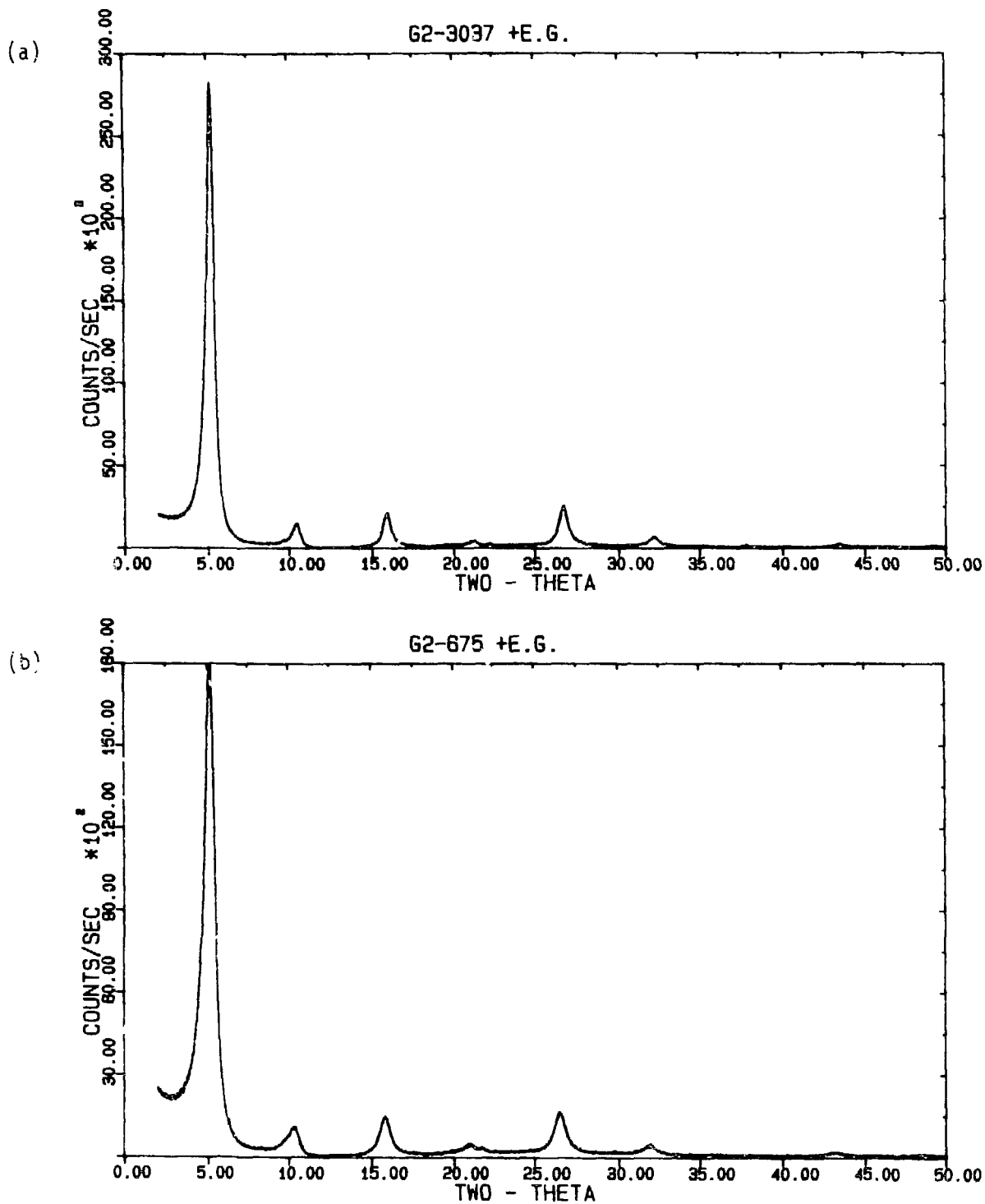


Fig. 3.

Measured x-ray diffraction patterns ($\text{CuK}\alpha$) of ethylene-glycol saturated illite/smectites from USW G-1 and G-2. Depth in feet is indicated in each sample title, e.g., G2-3037 is a sample from USW G-2 at 3037-ft (925.7-m) depth.

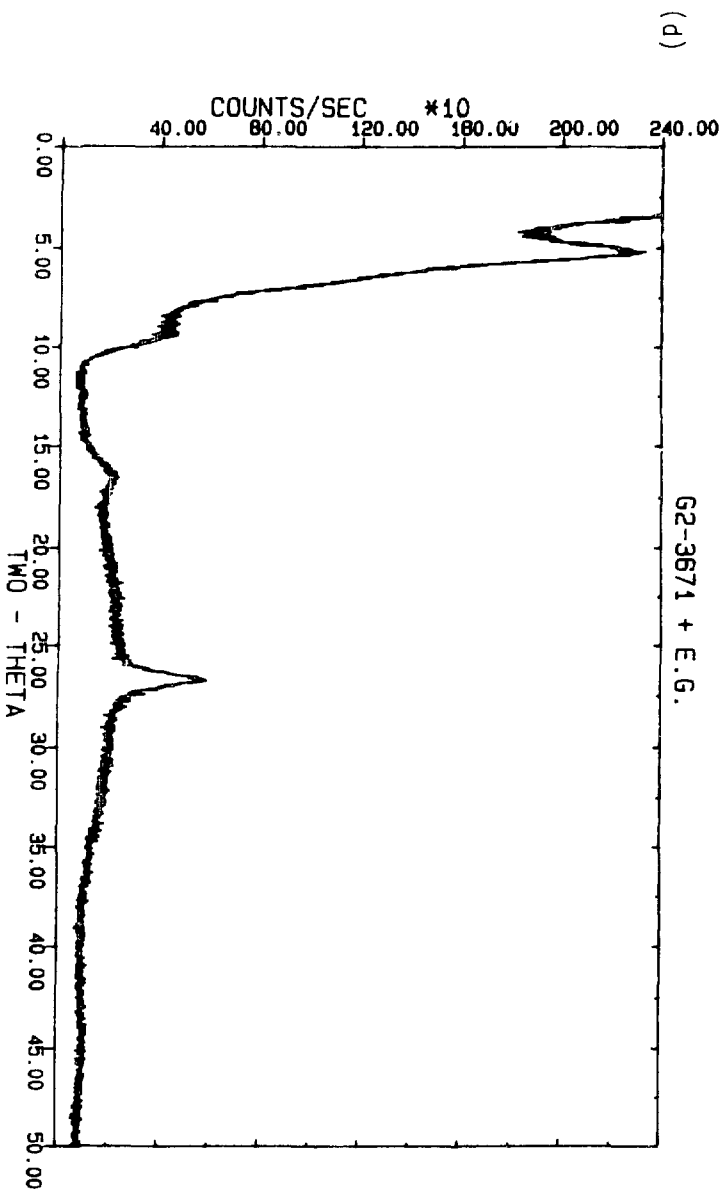
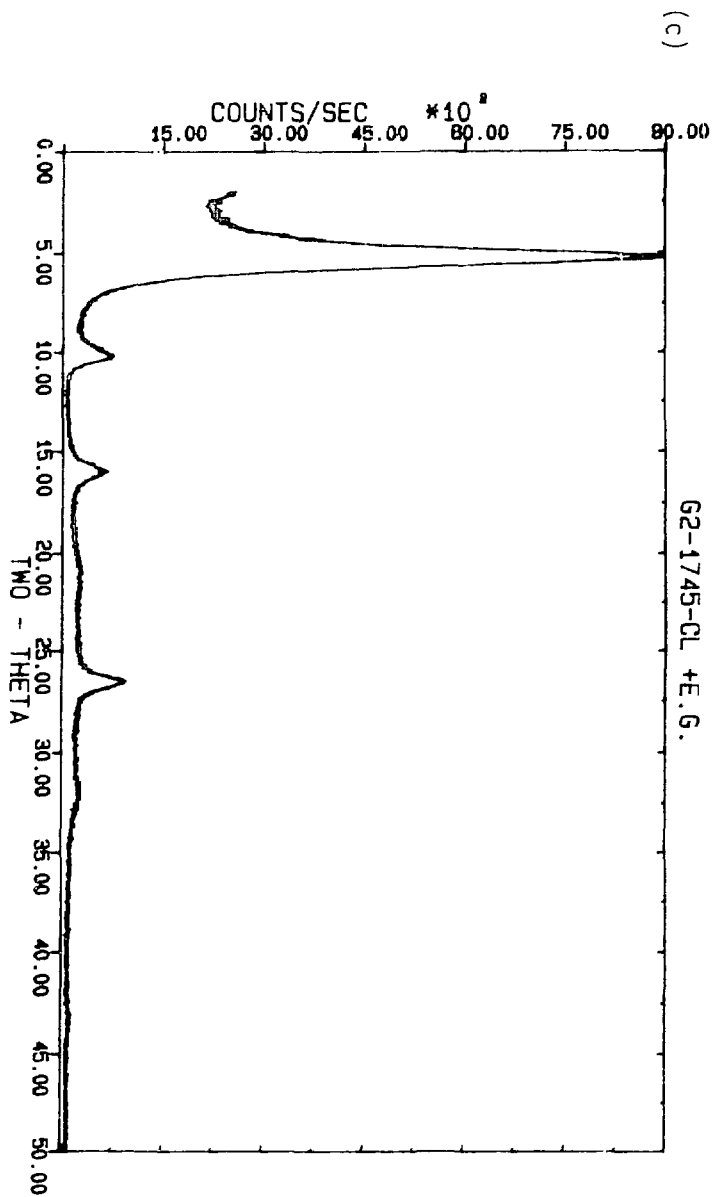


Fig. 3. (cont)

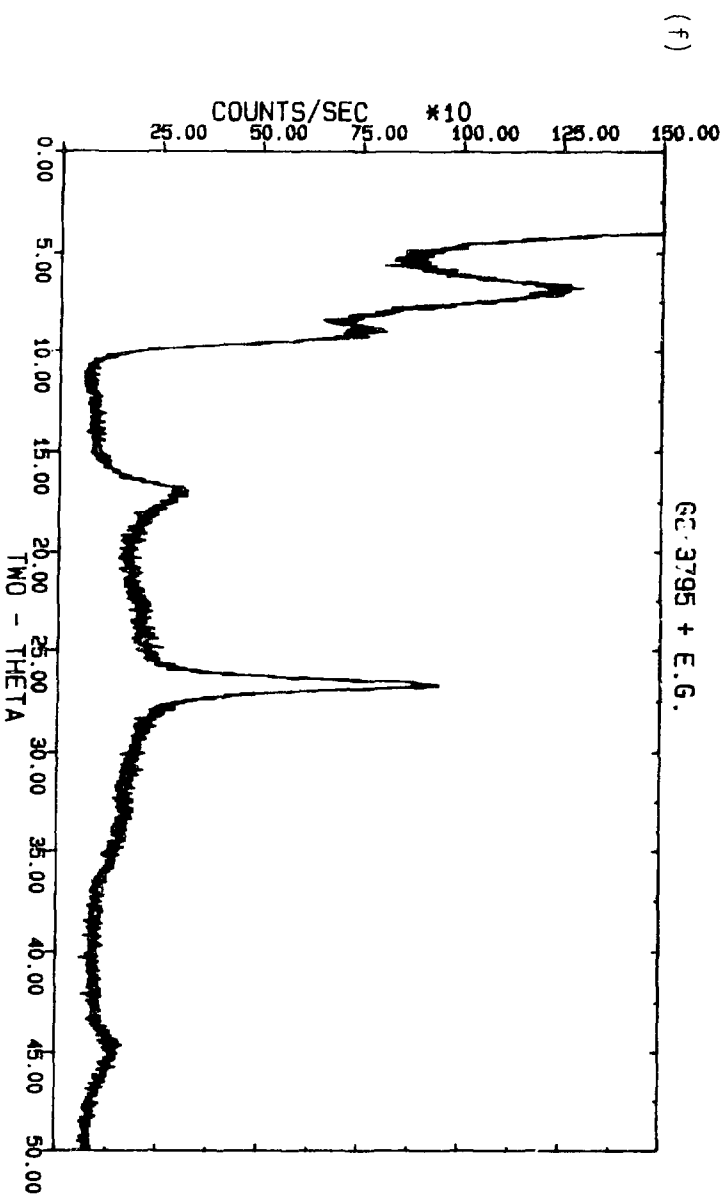
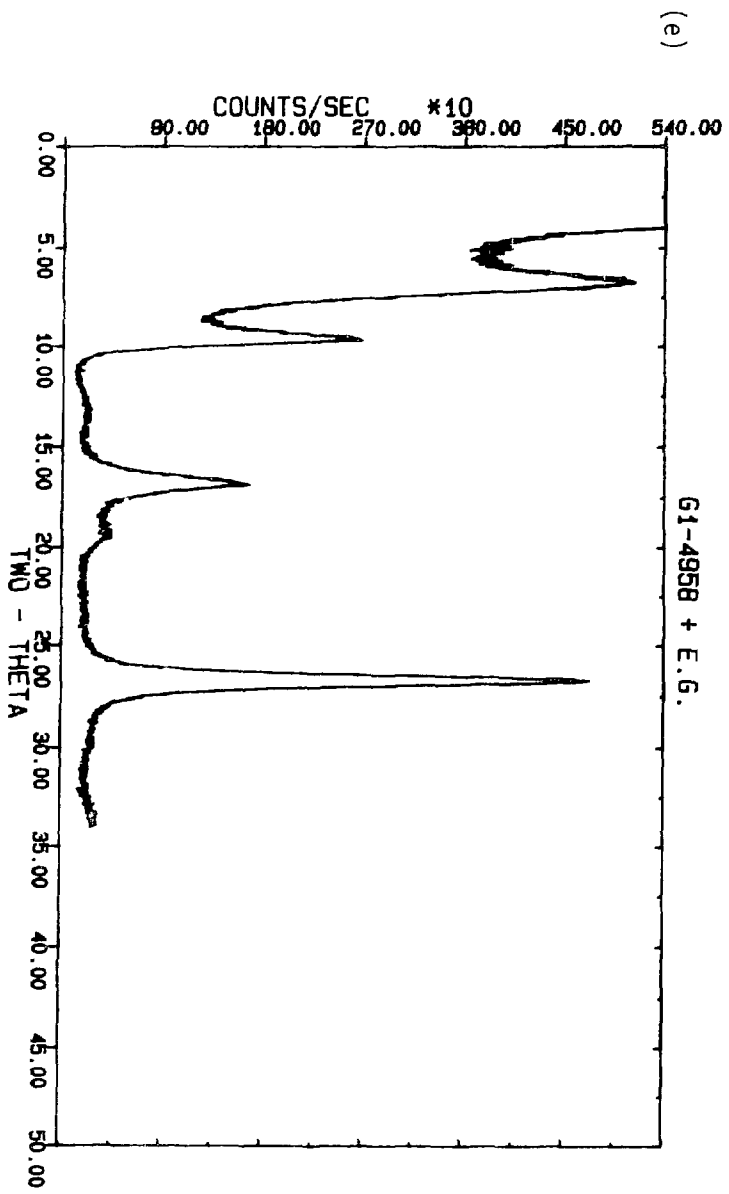
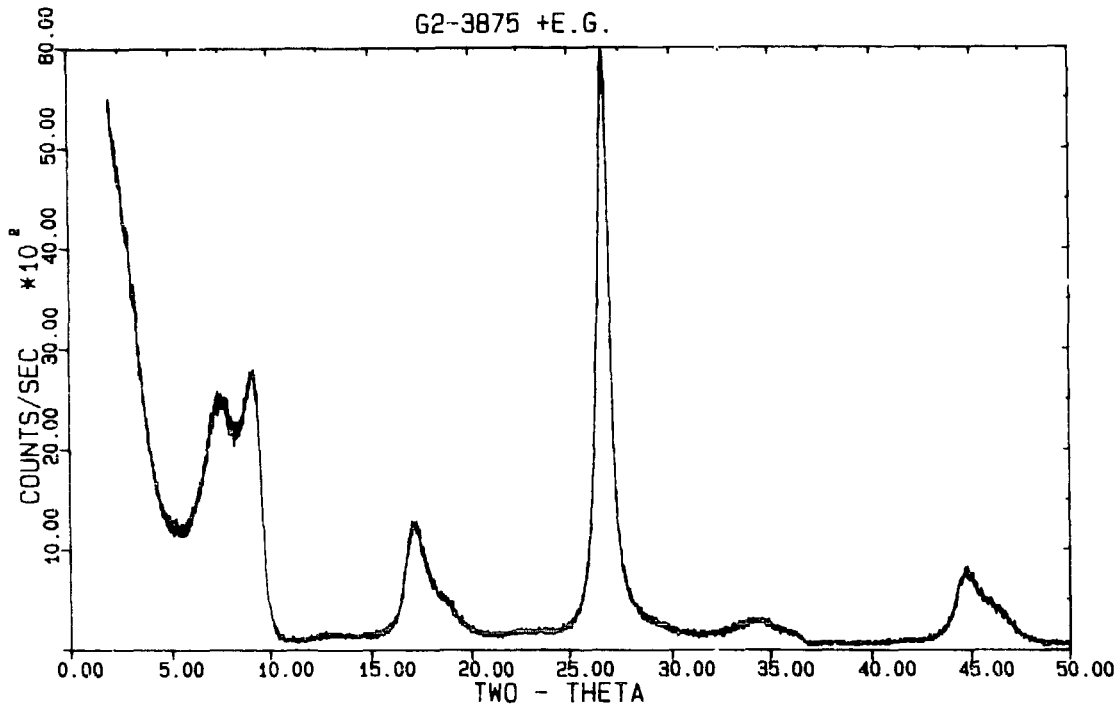


Fig. 3. (cont)

(g)



(h)

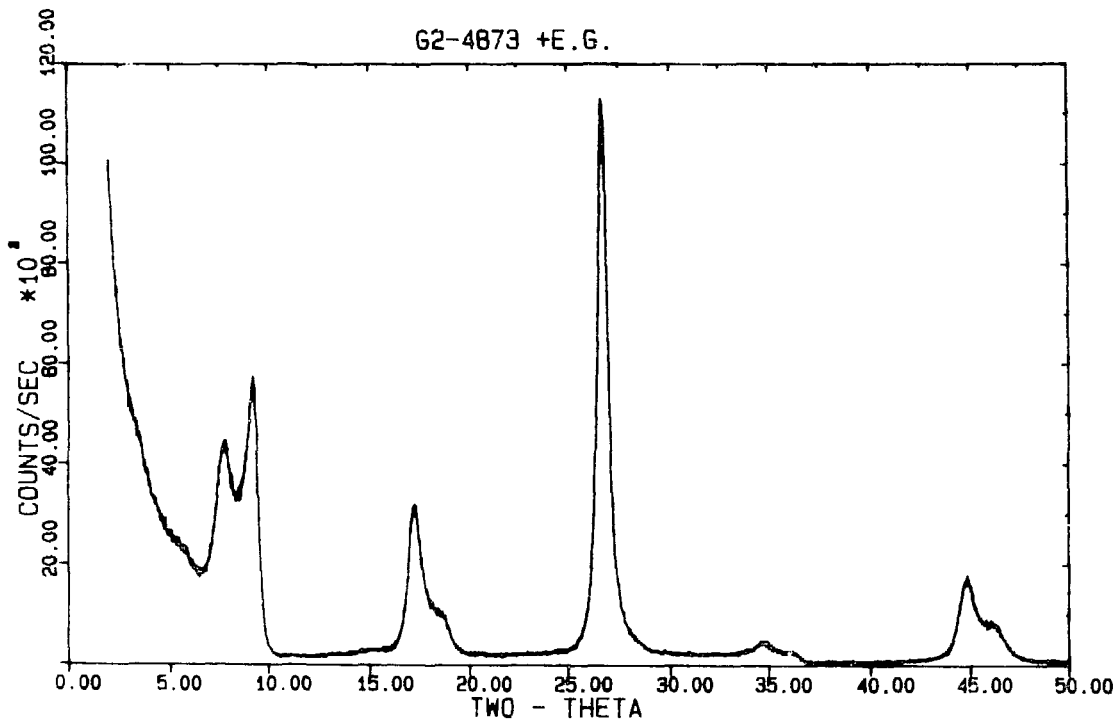


Fig. 3. (cont)

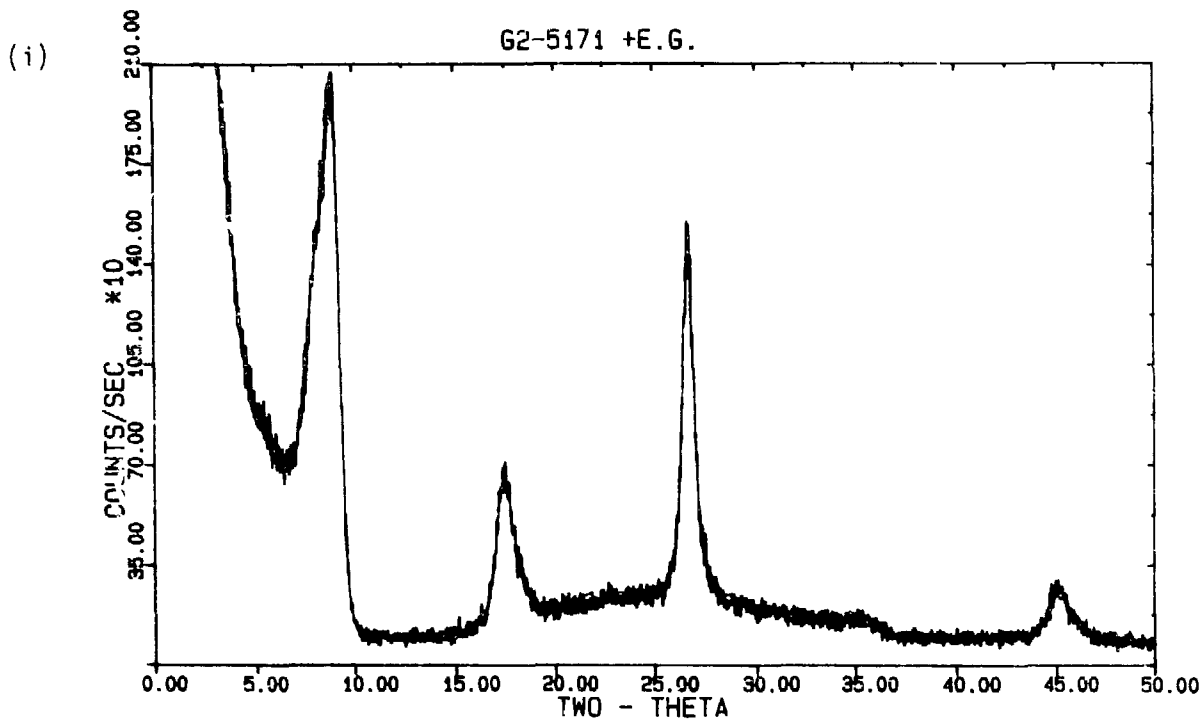


Fig. 3 (cont)

TABLE I

X-RAY DIFFRACTION RESULTS FOR CLAY MINERALS FROM USW G-1
20±10% RELATIVE HUMIDITY

<u>Sample No.</u>	<u>% Illite Layers</u>	<u>Type of Inter-stratification</u>	<u>EG-Smectite Thickness (Å)</u>	<u>(001) at Room Temperature (Å)</u>
G1-1286	10	Random	16.85	13.1Å
3621 dark	20	"	16.9	12.2
3621 clear	15	"	16.9	11.8
3810 dark	20	"	16.9	12.2
3810 clear	20	"	16.85	11.9
3940 dark	20	"	16.7	11.9
3940 clear	25	"	16.8	12.1
4246 dark	20	"	16.75	13.7
4400	25	"	16.6	14.1
4556	20	"	16.65	14.3
4750	50-60	"	16.6	13.7, 11.3
4958	60	Alleverdite	16.65	11.4
4998	30	Random	16.7	12.7
5339 dark	30	"	16.75	14.0
5339 clear	30	"	16.75	13.6
5534	40	"	16.75	11.9
5637	85-90	Kalkberg	16.5	10.5+Chl ^a
5898	80-90	"	16.55	11.0
5980	85-90	"	16.6	10.9+Chl ^a

^aChl = Chlorite.

TABLE II
X-RAY DIFFRACTION RESULTS FOR CLAY MINERALS FROM USW G-2 CORE
20±10% RELATIVE HUMIDITY

Sample No.	% Illite Layers	Type of Inter-stratification	EG-Smectite Thickness (Å)	(001) at Room Temperature (Å)
G2-338	<5	Random	16.70	14.0
501	<5	"	16.70	14.4
675	~5	"	13.75	13.4
743	<5	"	16.70	12.4
921	<5	"	16.65	13.2
1032	<5	"	16.65	13.0
1382	<5	"	16.70	12.6
1634	~5	"	16.70	10.2
1745 clear	10	"	16.75	11.9
2667	10	"	-	10.3
3037	<5	"	16.60	13.5
3250	~5	"	16.55	10.2
3454 clear	10	"	16.55	12.3
3454 dark	15	"	16.60	10.1
3492	15	"	16.8	10.2
3512	20	"	16.65	10.1
3578	~5	"	16.65	10.2
3627	40-50	Minor ordering	16.55	10.1
3671	60	" "	16.60	10.2
3720 clear	~70	Allevardite	16.70	10.5
3720 dark	70	"	16.70	10.2
3724	~80	"	16.65	10.1
3750	80	"	16.60	10.1
3795	80	"	16.60	10.1
3833	80	Allevardite, some long-range order	16.60	10.1
3875	90	Kalkberg	16.60	10.1
3933	90	"	16.60	10.0
4005	70	Minor ordering	16.60	10.1
4090 clear	20	Random	16.60	13.0, 10.1
4090 dark	20	"	16.60	10.1, 13.4

TABLE II (cont)

Sample No.	% Illite Layers	Type of Interstratification	EG-Smectite Thickness (Å)	(001) at Room Temperature (Å)
4167		Illite + randomly interstratified chlorite/smectite		10.2
4467	85	Kalkberg	16.55	10.2
4873	90	"	16.60	10.1
4885	90	Kalkberg + smectite	16.60	10.1
4949 clear	<5	Random	16.65	12.6
4949 dark	<5	"	16.60	10.5, 12.6
5171	>95	Illite		10.3
5369		Illite + discrete smectite/ 20% illite	16.6	10.16
5538		Illite + chlorite	10.1	
5657		Illite + chlorite	10.3	
5696		Illite + chlorite + smectite	16.65	10.5
5820		Randomly interstratified chlorite-smectite, 60-80% chlorite, minor ordering		
5931	>95	Illite	-	10.3

TABLE III

X-RAY DIFFRACTION DATA FOR CLAY MINERALS FROM USW G-3 CORE
20±10% RELATIVE HUMIDITY

Sample No.	% Illite Layers	Type of Interstratification	EG-Smectite Thickness (Å)	(001) at Room Temperature (Å)
G3-315.7	10-20	Random	16.7	13.5
332.5	10-20	"	16.75	13.9
414.3	10-20	"	16.8	13.0
1344.8	(poorly ordered, no higher orders of (001))		13.9	
1394.6	10-20	"	16.7	.a
1438.2	10-20	"	16.7	12.5
1493.7	10-20	"	16.7	-
2189.0	10-20	"	16.7	12.9
3170.5	10-20	"	16.7	12.5
3228.0	5-15	"	16.75	13.7
3264.4 clear	5-15	"	16.8	12.0
3264.4 dark	5-15	"	16.8	12.1
3310.9 clear	5-15	"	16.75	-
3310.9 dark	0-10	"	16.75	12.3
3315.1 super ^b	10-20	"	16.7	11.9
3315.1 clear	0-5	"	16.7	12.4
3315.1 dark	5-15	"	16.8	-
3799.0 clear	5-15	"	16.95	10.0
3799.0 dark	5-15	"	17.0	10.0
3847.5 clear	5-15	"	17.0	9.7
3847.5 dark	5-15	"	17.0	9.8
4288.9 clear	10-20	"	16.65	13.0
4288.9 dark	5-15	"	16.7	-
4439.0 clear	5-15	"	16.7	12.1
4439.0 dark	5-15	"	16.75	13.8
4706.9	10-20	"	16.65	14.2
4857.5 clear	15-25	"	16.80	12.0
4857.5 dark	5-15	"	16.70	13.8
4964.3 clear	15-25	"	16.7	14.1
4964.3 dark	15-25	"	16.65	13.0

^aNot measured.

^bSuper = supernatant.

expandable smectite. Incomplete collapse of heat-treated smectites from USW G-1 and G-2 suggests that many of the smectites in the deeper portions of these drill holes are partially chloritized. G-3 clays are all randomly interstratified illite/smectites ($R=0$) with fewer than 25% illite layers. No consistent trends are obvious in the ethylene glycol-smectite complex thickness in these cores, although there is a tendency for the complex thickness to decrease in the deeper samples. This is consistent with an increase in smectite layer charge with depth.

The (001) spacings at room temperature and 20% relative humidity suggest (Gillery 1959; Suquet et al. 1975) that the illite/smectites in G-1, G-2, and G-3 are predominantly Na-Ca saturated, but the G-2 clays become more K rich below 457-m (1500-ft) depth. These conclusions from x-ray data are in agreement with limited microprobe data for clays from these cores (Caporuscio et al. 1982; Vaniman et al. 1984). These data show that the illite/smectites abruptly increase in K content below 975 m (3200 ft) in USW G-2, and illite/smectites shallower than 975 m (3200 ft) have $Ca \geq Na \gg K$. Below 1067 m (3500 ft), the interlayer cation is predominantly K. Data for USW G-3 clays show subequal Ca and Na with variable K, but K tends to increase with depth below about 1372 m (4500 ft).

The transformations in clay mineralogy with depth can yield information concerning the temperatures to which the rocks have been subjected by employing the data of Hower and Altaner (1983). Figure 4a is a summary diagram of the relationship between temperature and the extent of the smectite-to-illite reaction, incorporating data from pelitic rocks as well as active geothermal areas (Steiner 1968; Eslinger and Savin 1973; Hoffman and Hower 1979; McDowell and Elders 1980). Figure 4b shows an example of the relationship between expandability and temperature for a Gulf Coast well at lower temperatures (Perry and Hower 1970). Application of Fig. 4 to the clay mineral data for G-1, G-2, and G-3 cores yields the schematic paleotemperature profiles shown in Fig. 5. The present-day measured geothermal gradients (Sass et al. 1983) are shown on Fig. 5 for comparison. The schematic profiles in Fig. 5 are considerably steeper than the present-day gradients; it is thus apparent from these clay mineral data that a significant thermal event has occurred in the northern end of Yucca Mountain but has not appreciably affected the rocks in USW G-3 at the southern end of Yucca Mountain. The schematic paleotemperatures in Fig. 5 assume long enough reaction times that kinetic effects are not limiting. Hower and Altaner (1983) and Thompson and Jennings (1985) concluded that the reactions below 150°C involving randomly interstratified illite/smectites ($R=0$) and alleverdite ($R=1$) are kinetically controlled; in a prograde sequence, alleverdite ($R=1$) is formed at 90 to 100°C over long reaction times ($>10^7$ years) but at 130° to 150°C over short reaction times ($<10^6$ years). Apparently these clay mineral reactions are not kinetically limited at temperatures over 130° to 150°C.

It is unclear why the apparent thermal gradient is so steep in USW G-2 and why the percent illite in the illite/smectites rises so abruptly at about 1067-m (3500-ft) depth. The static water level at the time of alteration may have been deep, but 1067 m (3500 ft) is probably an unrealistic depth for the static water level, particularly during times of increased rainfall. This abrupt change near 1067 m is probably related to

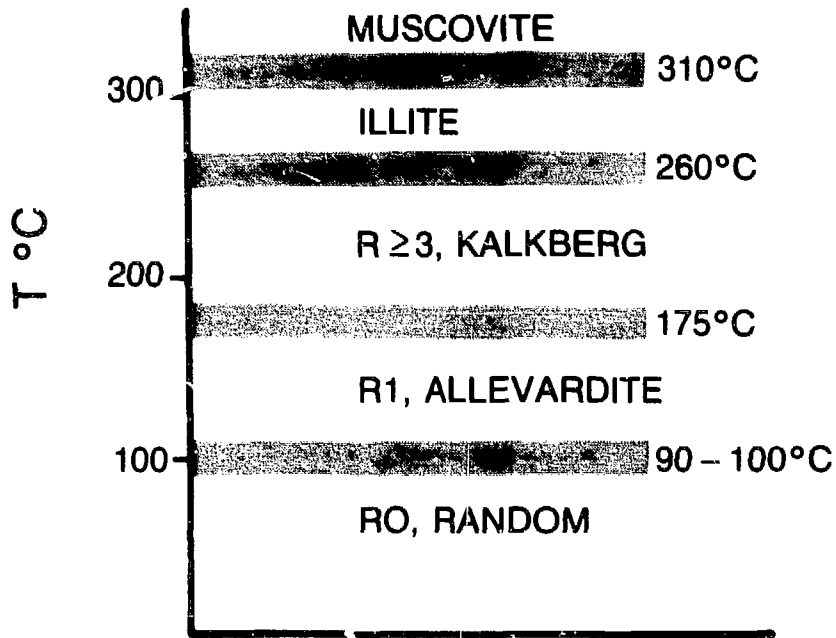


Fig. 4a.

Relationship between temperature and extent of smectite-to-illite reaction (Hower and Altaner 1983).

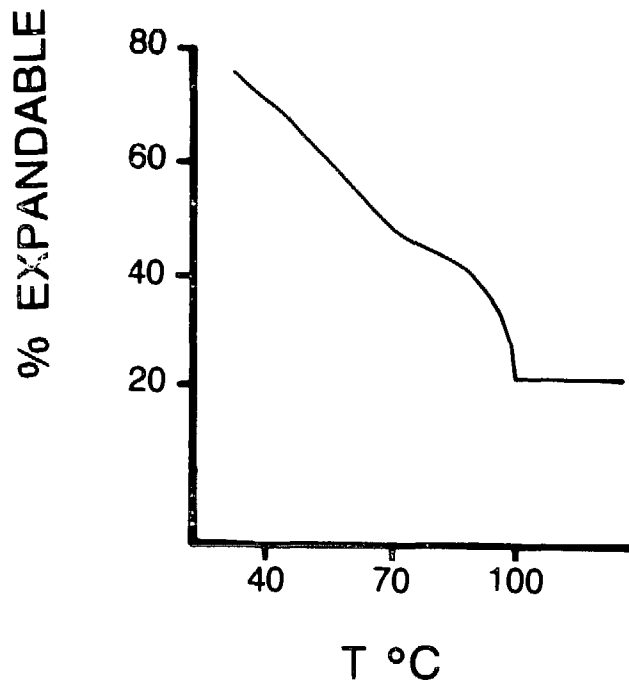


Fig. 4b.

Relationship between expandability and temperature for illite/smectites from a Gulf Coast well (Perry and Hower 1970).

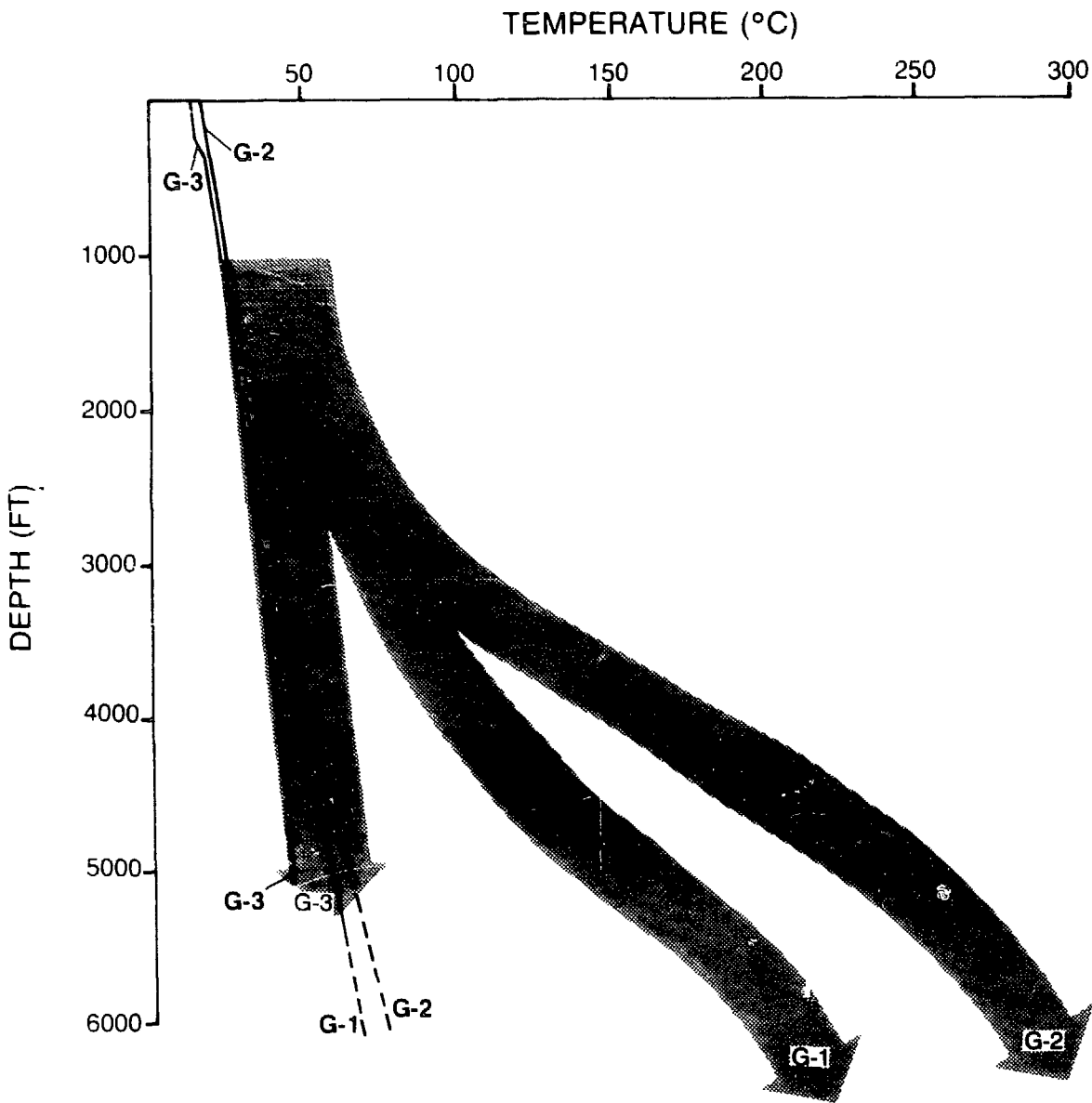


Fig. 5.

Schematic paleotemperatures for USW G-1, G-2, and G-3 estimated from clay mineral reactions and fluid inclusion data (broad, arrowed lines) with the present-day measured temperature profiles from Sass et al. (1983) (solid narrow lines).

a change from a zone that was meteorically cooled (convective) to a conductive zone. The paleogeothermal gradient presented in Fig. 5 for USW G-2 is very similar to present-day thermal gradient curves found in geothermal areas. For example, Swanberg and Combs (1986) presented the temperature-depth plot for a drill hole in Newberry Volcano, Oregon. Their plot revealed virtually constant temperature to a depth of about 1000 m (3280 ft), at which point the temperature increased abruptly by at least 30°C and took on a conductive character. They postulated that the observed change at about 1000 m is due to a transition from younger porous rocks to older, more silicic rocks unaffected by the regional groundwater flow. The remarkable similarity between the gradients in Fig. 5 and many of those measured today suggests that similar conditions may have existed at Yucca Mountain 11 Myr ago. It is likely that the rain curtain extended to approximately 1000-m depth in USW G-2, and the hydrothermal fluids responsible for rock alteration did not appreciably interact with shallower rocks.

Potentially valuable data concerning other mineral reactions in tuffs can be obtained by examining the changes in bulk mineralogy with depth and correlating these changes with the clay mineral reactions and the paleotemperatures estimated from the clay minerals. The bulk mineralogy determined by x-ray powder diffraction of drill holes USW G-1, G-2, and G-3 has been presented by Bish et al. (1981), Caporuscio et al. (1982), and Vaniman et al. (1984), respectively. Noteworthy variations in mineralogy include the gradation from unaltered volcanic glass to clinoptilolite and mordenite to analcime and finally to authigenic albite with depth. The 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 the 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 may depend on whether the silica activity is controlled by cristobalite or quartz. The time interval over which clinoptilolite would remain stable would be determined by the rate of reaction of cristobalite to quartz. Other mineralogic variations with depth include the disappearance of tridymite, opal-CT, and cristobalite and the appearance of calcite and chlorite. In addition, pyrite, barite, and fluorite have been identified below 1067 m (3500 ft) in USW G-2; these three phases may be suggestive of hydrothermal alteration rather than diagenetic alteration through the action of groundwater.

Results of analysis of the few fluid inclusions found in secondary minerals from G-2 and G-3 yield temperatures below and above, respectively, those determined by the clay minerals. Inclusions in calcite from G-2 yielded homogenization temperatures of 94° to 115°C in G2-5379 [G2-5379 refers to a sample

from USW G-2 at 1640-m (5379-ft) depth], 147°C in G2-5762, and 202° to 239°C in G2-5820. Freezing temperatures ranged from -0.1° to -0.6°C, reflecting low salinities in the inclusions. Homogenization temperatures in calcite from G-3 were 101° to 227°C in GU3-103, 125° to 170°C in GU3-429, and 97°C in G3-4803. Lack of mineralogical data to support elevated alteration temperatures suggests that the higher temperature inclusions in the upper part of USW G-3 probably formed during the initial deposition or cooling of the tuffs. Alternatively, the relatively high homogenization temperatures in the shallow GU3 calcites may be a result of re-equilibration or variable initial vapor-to-liquid ratios (Goldstein 1986).

A. Zeolite Stabilities

Figures 6, 7, and 8 show comparisons of the clay mineralogy with the bulk mineralogy for USW G-1, G-2, and G-3 cores, respectively. From these figures, Fig. 4, and Tables I, II, and III, approximate upper temperature limits at which zeolites have broken down in Yucca Mountain can be obtained. The clays in USW G-2 reflect higher temperatures than those from G-1 or G-3. It is clear from G-1 and G-2 that clinoptilolite was not part of the stable mineral assemblage at the depth/temperature at which ordered illite/smectite interstratifications occur. The temperature range for the onset of ordering is 90 to 100°C for reaction times in excess of 10^7 years. For shorter reaction times ($<10^6$ yr), temperatures of 130 to 150°C are required for the formation of allevardite ($R=1$) (Hower and Altaner 1983). Mordenite disappears in G-2 below 1091-m (3578-ft) depth; the illite/smectite at 1106 m (3627 ft) is the shallowest to exhibit measurable ordering, suggesting that the mordenite upper stability limit is 100 to 130°C. Analcime is rare below 1097 m (3600 ft) and virtually absent below 1372 m (4500 ft). The disappearance with depth of analcime as a major phase near the first appearance of Kalkberg-type interstratifications ($R\geq 3$) in G-2 implies an upper stability limit for analcime of 175 to 200°C, in agreement with limited experimental data (Liou 1971). The zeolite mineralogy in USW G-3 shows the trends obvious in USW G-1 and G-2, but the clay mineralogy suggests that temperatures have not been significantly elevated in G-3. It may be that an additional factor, perhaps water chemistry, was the controlling factor in zeolite reactions in USW G-3 in the absence of significantly elevated temperatures.

B. Chlorite Occurrence

Chlorite and randomly interstratified chlorite/smectite both occur with illite/smectite and illite in the deeper portions of USW G-1 and G-2. In addition, some of the deeper smectites in these two drill holes appear to be partially chloritized and show hindered collapse upon heating. 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 may be intermediate between shallower smectites and the deeper chlorites, as proposed by Inoue (1985) for his field area. 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)

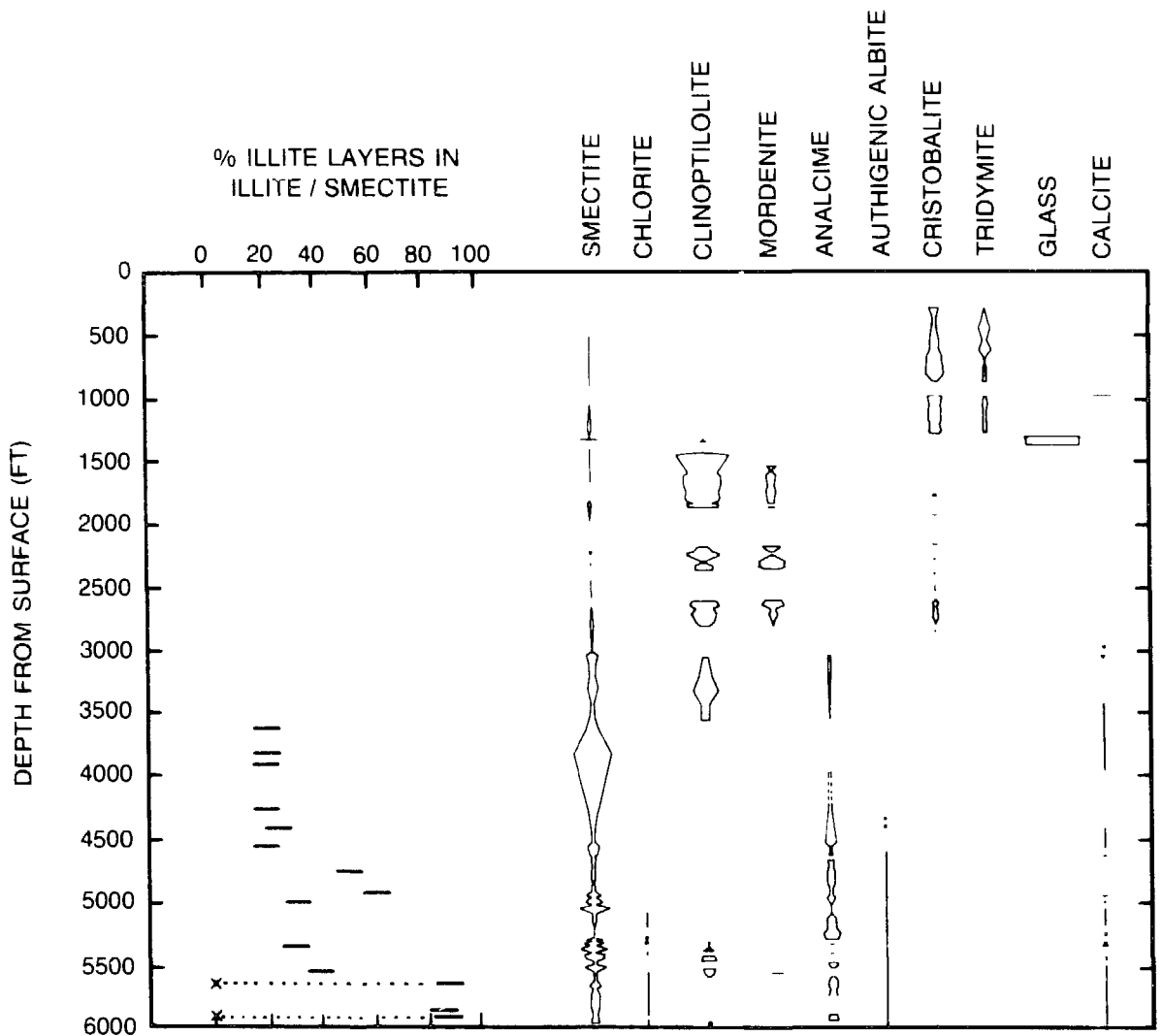


Fig. 6.

Mineral and glass abundances compared with clay mineralogy in drill core USW G-1 determined by x-ray diffraction. Occurrences of authigenic albite were determined by optical examination and are not quantitative. Dotted horizontal lines connecting clay minerals indicate that the phases are coexisting.

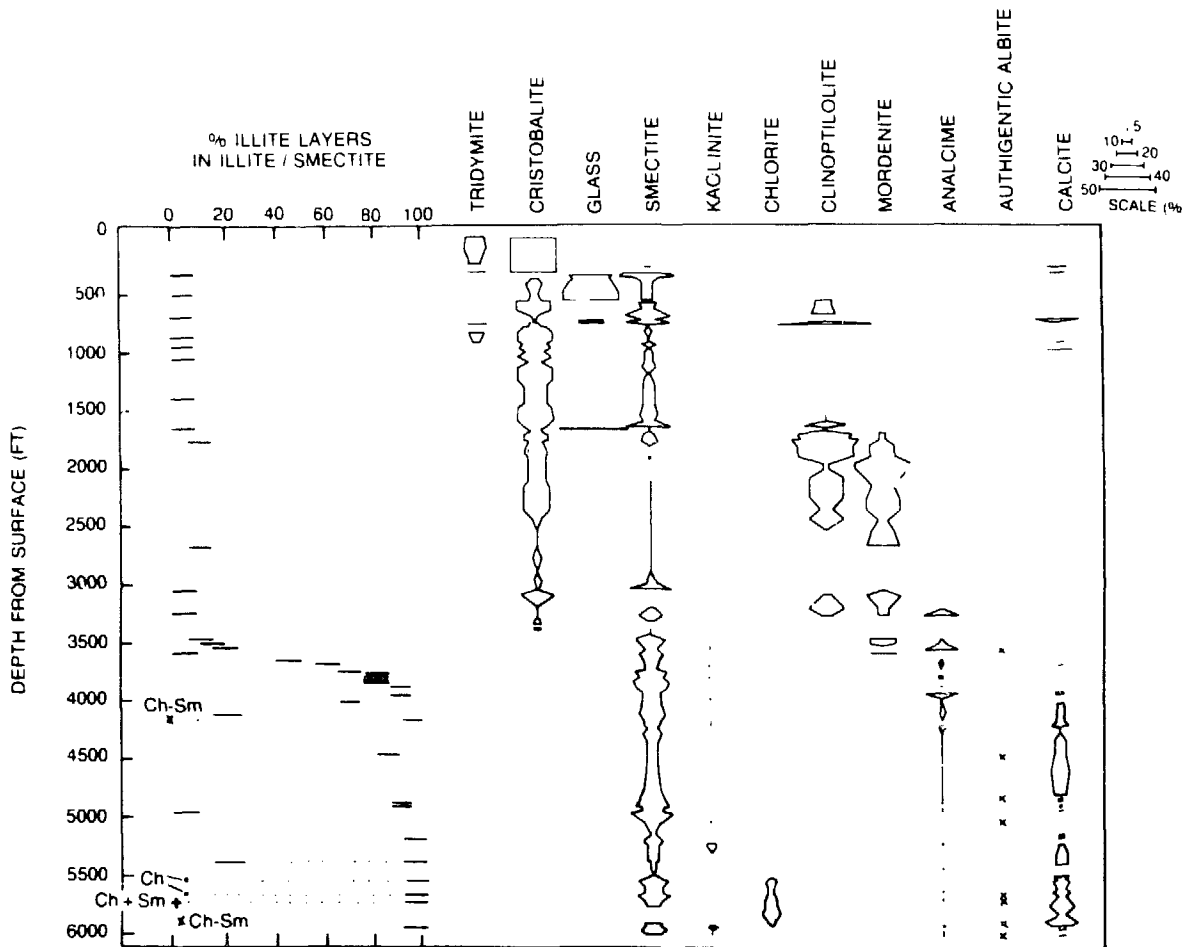


Fig. 7.

Mineral and glass abundances compared with clay mineralogy in drill core USW G-2 determined by x-ray diffraction. Occurrences of authigenic albite were determined by optical examination and are not quantitative. Dotted horizontal lines connecting clay minerals indicate that the phases are coexisting. An "X" signifies the occurrence of randomly interstratified chlorite/smectite, a "+" signifies the occurrence of chlorite + smectite, and a "#####" denotes the presence of chlorite.

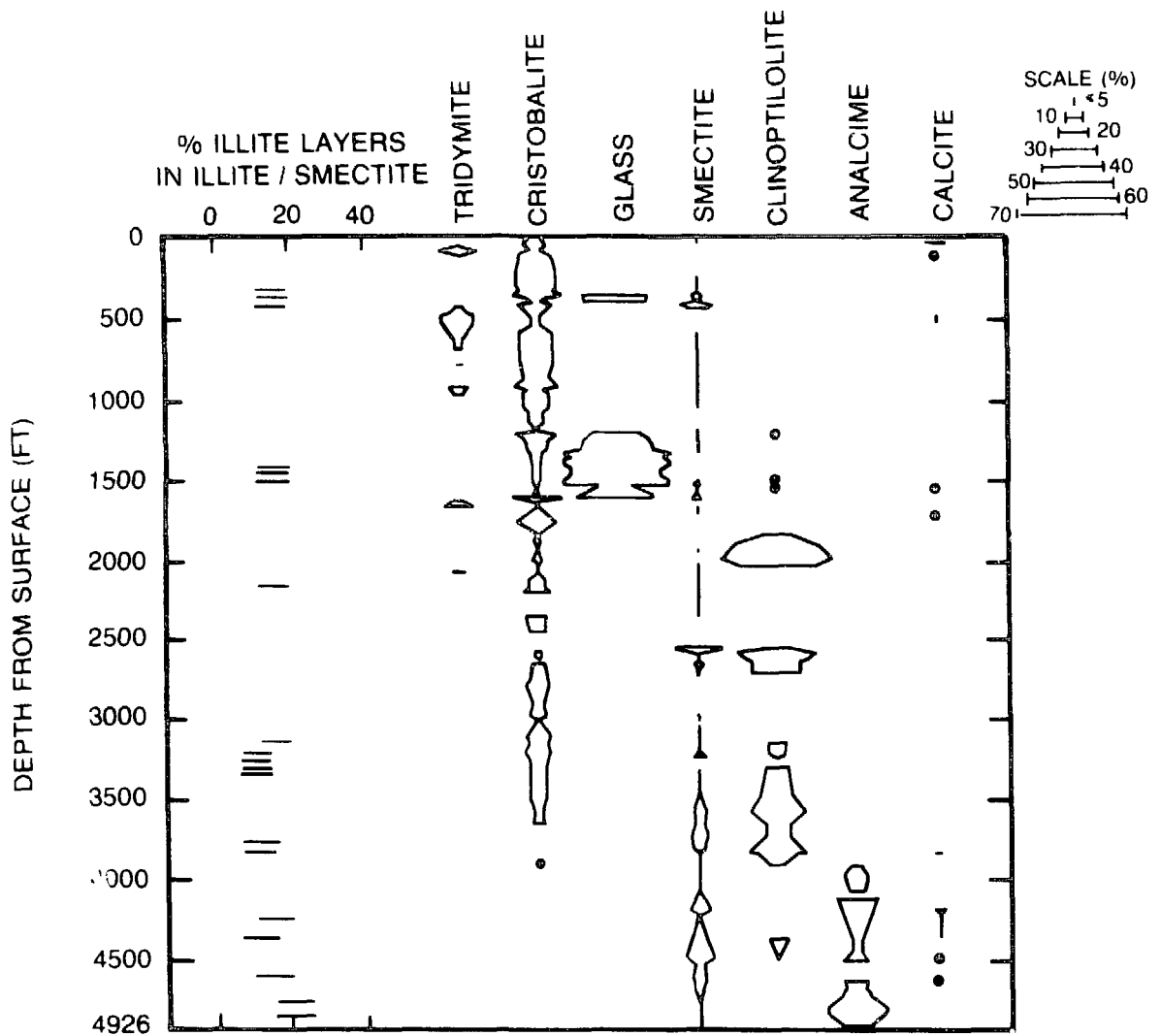


Fig. 8.

Mineral and glass abundances compared with clay mineralogy in drill core USW G-3 determined by x-ray diffraction. Authigenic albite was not found in this drill core. 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).

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. As noted by Broxton et al. (1986), the clinoptilolites in Yucca Mountain tuffs contain significant Mg whereas analcime and authigenic albite contain little or no Mg or Fe. In addition, chlorite and/or chlorite/smectite do not coexist with clinoptilolite at Yucca Mountain.

C. Silica Phases

Several transformations among silica phases in Yucca Mountain are obvious in Figs. 6, 7, and 8. 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 is well documented (Iijima 1978), as is the instability of tridymite and cristobalite in altering 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, was the most important factor in mineral evolution in volcanic rocks at the Nevada Test Site. The x-ray diffraction data for USW G-1, G-2, and G-3 shown in Figs. 6, 7, and 8 reveal a consistent trend in mineralogy with depth. It is noteworthy that the disappearance of clinoptilolite and mordenite as major phases coincides quite 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 a temperature obtained from the clay minerals 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 perhaps destabilizing clinoptilolite.

D. Alteration Timing

Yucca Mountain is in an area that has been volcanically active in the past, and it is bordered by numerous ancient caldera complexes (Byers et al. 1976) (Fig. 9). The Timber Mountain caldera complex is adjacent to Yucca Mountain to the north, and it or an associated cauldron segment are likely sources of the hydrothermal alteration that is apparent in drill core G-2 and less so in G-1. We have obtained preliminary K/Ar dates from illite/smectites in G-1 and G-2; sample G1-5637 yielded an age of 10.9 ± 0.6 Myr, and G2-3875 and G2-5171 both gave ages of 11.0 ± 0.6 Myr. These ages are statistically equivalent to the age of the Timber Mountain tuff, 11.3 ± 0.3 Myr (Marvin et al. 1970). The internal concordance of the three illite ages at different depths in wells USW G-1 and G-2, the increasing intensity of alteration in well G-2 closer to Timber Mountain, and the agreement of the ages with the age of Timber Mountain activity all

* Information provided by J. Aronson, Case Western Reserve University (1986).

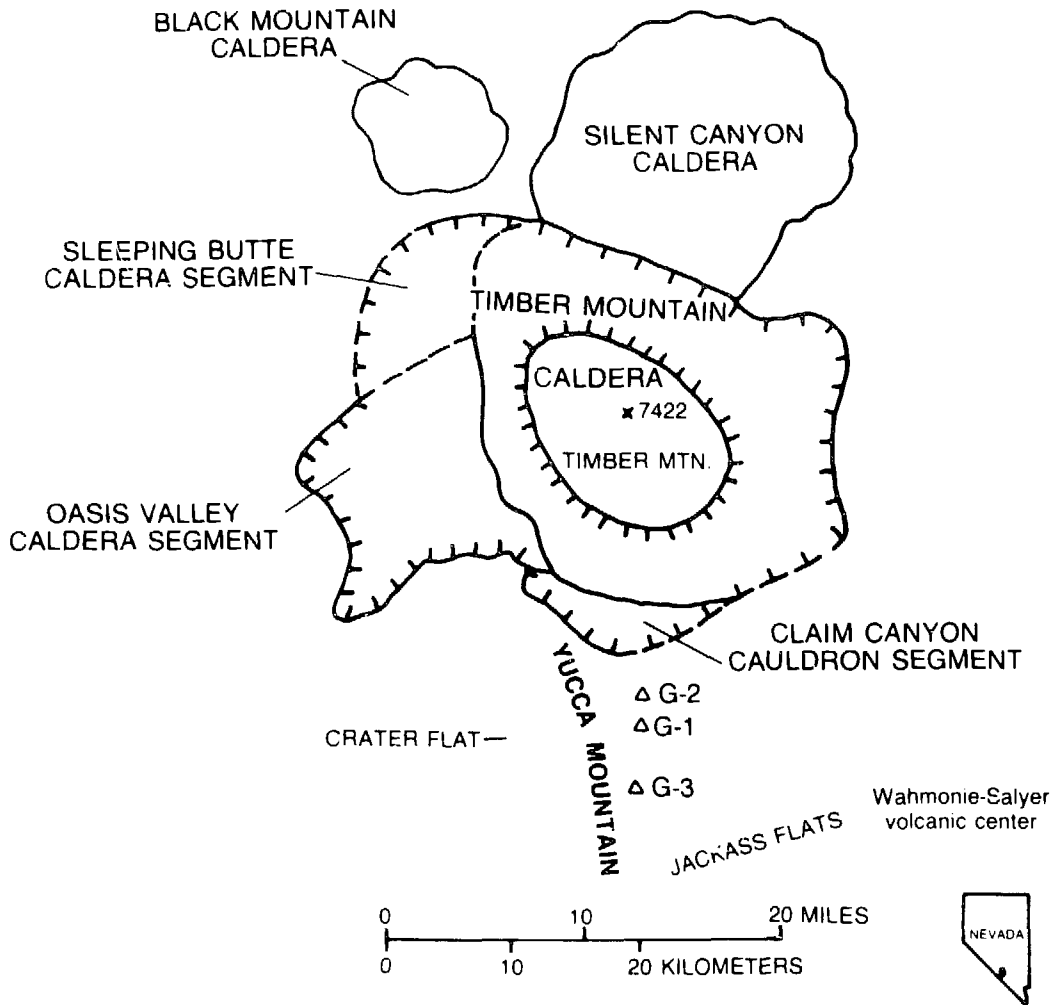


Fig. 9.

Southwestern Nevada volcanic field, Nye County, Nevada, showing the location of the Timber Mountain caldera and other volcanic centers with respect to Yucca Mountain from Byers et al. (1976). 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 (dashed where indefinite). Heavy lines with hatchure marks to the outside represent the periphery of the Timber Mountain resurgent dome. Drill cores USW G-1, G-2, and G-3 are shown.

argue that hydrothermal effects of the Timber Mountain activity are responsible for the illitization at depth in these two wells. Alternatively, the illitization could have taken place earlier when this area was equally volcanically active, for example during Paintbrush or Crater Flat volcanism. If this were the case, the 11-Myr ages would then represent resetting of the older illite K/Ar system due to reheating during Timber Mountain activity. The blocking temperature below which illites quantitatively retain argon is not well established. K/Ar results on deep Gulf Coast wells indicate this blocking temperature is at least 160°C, and consistent results from other areas suggest it may be as high as 200° to 225°C.* In any case, the illite ages argue that the alteration either formed or was strongly affected by Timber Mountain activity 11 Myr ago, and the rocks have not been significantly reheated since.

However, evidence exists for continued low-temperature formation of minerals in USW G-1 and G-2. This is demonstrated by illite/smectites with a low percentage of collapsed (illite) layers occurring deeper than higher temperature-ordered illite/smectites in both G-1 and G-2 (e.g., G1-4998, G1-5339, G2-4090, and G2-4949). In addition, one sample examined (G2-5369) contained both discrete illite and randomly interstratified illite/smectite with about 80% expandable layers. It therefore appears that clay formation has continued since the waning of the Timber Mountain hydrothermal alteration event. An alternate but unlikely interpretation is that the low-illite illite/smectites could have been subjected to elevated temperatures, but the reaction to illite did not proceed due to a low K or Al supply. The occurrence of coexisting discrete illite and randomly interstratified illite/smectite does not support this alternate interpretation.

E. 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 tuffs in a repository environment. These studies include research in the dehydration behavior of minerals in tuffs (Bish 1984, 1988) 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 significantly reducing the cation sorptive capacity of the rocks. Smyth advised constraining the maximum temperature in zeolitized tuff to 85°C to prevent reaction. Smyth's conclusions were based on field observations. 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 at these temperatures, 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).

* Information provided by J. Aronson, Case Western Reserve University (1986).

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 water composition (including the activity of water), this approach assumes that future water compositions will be approximately the same as those present during the alteration in Yucca Mountain 11 Myr ago. This may be a reasonable assumption, but conditions have probably changed significantly in the past 11 Myr. Present-day waters are likely much more dilute than those present during and shortly after zeolitization and clay mineral alteration. In addition, waters surrounding the repository environment may vary significantly in composition, particularly if they are concentrated by evaporation. However, for the alterations seen at Yucca Mountain, the clay mineralogy data suggest an upper temperature limit of 90° to 100°C for clinoptilolite, 100° to 130°C for mordenite, and 175° to 200°C for analcime. Coupling these data with models of the thermal profiles around a repository in tuff as a function of time (Johnstone et al. 1984) and mineral distribution data from Bish and Vaniman (1985) demonstrates that reaction of clinoptilolite to analcime should not occur in the thick, zeolitized tuff of Calico Hills underlying the candidate repository horizon. However, zeolite interval I, the first zeolite-bearing horizon below the candidate repository horizon (Bish et al. 1984a), may be significantly heated by the repository thermal pulse, and reactions among the zeolites and smectites may occur in this zone. The calculations of Johnstone et al. (1984) show that this interval will approach 90°C after about 1000 years. If the cristobalite and opal-CT in this interval react to form quartz and the aqueous silica concentration decreases, the clinoptilolite may then transform to analcime. However, there is a large amount of glass/opal-CT in interval I (Bish and Vaniman 1985) and this interval is in the unsaturated zone. Therefore, it is questionable whether the aqueous silica concentration will be controlled by quartz in the lifetime of a repository.

IV. SUMMARY AND CONCLUSIONS

These mineralogical data demonstrate that the rocks at depth in the northern end of Yucca Mountain have been significantly altered early in their history. The clay mineral reactions are similar to what has been observed in pelitic rocks, with close to 100% expandable randomly interstratified illite/smectites ($R=0$) transforming through ordered intermediates ($R=1$, $R\geq 3$) to illite with depth (increasing temperature) in USW G-2 and to Kalkberg ($R\geq 3$) interstratifications in USW G-1. The illite/smectites 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.

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 data from USW G-2 and G-3 showing the approximately simultaneous disappearance of

crystalite and clinoptilolite. Clinoptilolite appears to have transformed to analcime at about 100°C in USW G-1 and G-2. However, analcime occurs in USW G-3 although mineralogic data suggest that temperatures did not reach 100°C. Thus there are indications that water chemistry may have exerted as great or greater an influence than temperature on the reaction of clinoptilolite to analcime in Yucca Mountain, in agreement with field observations elsewhere (Iijima 1975). The kinetics of the cristobalite-to-quartz reaction may have influenced the clinoptilolite-to-analcime reaction by controlling the aqueous silica concentration.

The reaction of clinoptilolite to analcime in USW G-2 also 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 opposite to what is observed in pelitic rocks, probably reflecting the differences in mineral assemblages (Hower et al. 1976). It is likely that the breakdown of clinoptilolite provided the source of Mg for chlorite formation and the source of 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 the K in the deeper illite/smectites, and the analcime and albite incorporated the Na from the clinoptilolite. The interstratified chlorite/smectites appear to be intermediate between shallower smectites and deeper chlorites, similar to what was observed by Inoue (1985).

Based on estimates from clay 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 G-3 rocks [about 305 m (1000 ft) shallower than G-1 and G-2] probably have not exceeded 100°C. These data can be used to apply limits to 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° to 200°C. It also appears that cristobalite transformed to quartz at about 90° to 100°C in USW G-2 but must have reacted at considerably lower temperatures in USW G-3.

The vertical distribution of minerals across Yucca Mountain demonstrates that deep 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. The mineralogy and clay chemistry from UE-25a#1, farther to the southeast along Drill Hole Wash, suggest that this drill core was also subjected to hydrothermal alteration (Caporuscio et al. 1982). Data suggest that the shallower Paintbrush Tuff Members (12-13 Myr) have not been significantly altered in any of the drill holes examined. The alteration mineralogy distribution and the age of illites in USW G-1 and G-2 (about 11 Myr) are consistent with Timber Mountain volcanism as the source of hydrothermal alteration. The widespread distribution of volcanic centers in the area suggests that alteration may have occurred before Timber Mountain volcanism (Paintbrush volcanism), perhaps culminating with Timber Mountain volcanism at about 11 Myr. It is noteworthy that the

mineralogical data suggest that no hydrothermal alteration has occurred since the Timber Mountain event about 11 Myr ago.

Use of the rocks in USW G-1, G-2, and 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 required life of the repository. However, zeolite interval I directly underlying the potential repository (Bish et al. 1984a) may transform at the temperatures predicted by thermal models (Johnstone et al. 1984). The reaction of clinoptilolite to analcime may require the transformation of the opal-CT and glass in this interval to quartz to lower the aqueous silica activity, a questionable scenario over the lifetime of a repository considering the abundance of opal-CT and glass and the unsaturated nature of the rocks at this depth.

ACKNOWLEDGMENTS

I am grateful to D. Vaniman, D. Krier, R. Raymond, S. Chipera, and C. Duffy of the Los Alamos National Laboratory and to D. Horton for constructive reviews of this manuscript. I have also benefitted from discussions with J. Aronson, Case Western Reserve University.

REFERENCES

- Bish, D. L., "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). NNA.870406.0238
- Bish, D. L., "Effects of Exchangeable Cation Composition on the Thermal Expansion/Contraction of Clinoptilolite," *Clays and Clay Minerals*, 32, 444-452 (1984).
- Bish, D. L., "Effects of Composition on the Dehydration Behavior of Clinoptilolite and Heulandite," in Occurrence, Properties and Utilization of Natural Zeolites, D. Kallo and H. S. Sherry, Eds. (Akademiai Kiado, Budapest, 1988).
- Bish, D. L., "Smectite Dehydration and Stability: Applications to Radioactive Waste Isolation at Yucca Mountain," Los Alamos National Laboratory report LA-11023-MS (March 1988).
- Bish, D. L., and R. E. Semarge, "Mineralogic Variations in a Silicic Tuff Sequence: Evidence for Diagenetic and Hydrothermal Reactions," *Clay Minerals Society*, 19th Annual Meeting, Hilo, Hawaii, p. 42 (August 1982). NNA.870406.0234
- Bish, D. L., and D. T. Vaniman, "Mineralogic Summary of Yucca Mountain, Nevada," Los Alamos National Laboratory report LA-10543-MS (October 1985). NNA.870407.0330
- Bish, D. L., 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). NNA.870406.0158

- Bish, D. L., D. T. Vaniman, F. M. Byers, Jr., and D. E. Broxton, "Summary of the Mineralogy-Petrology of Tuffs of Yucca Mountain and the Secondary-Phase Thermal Stability in Tuffs," Los Alamos National Laboratory report LA-9321-MS (November 1982).
- Bish, D. L., A. E. Ogard, D. T. Vaniman, and L. Benson, "Mineralogy-Petrology and Groundwater Geochemistry of Yucca Mountain Tuffs," *Materials Research Society Symposium Proceedings*, 26, 283-291 (1984a).
- Bish, D. L., D. T. Vaniman, R. S. Rundberg, K. Wolfsberg, W. R. Daniels, and D. E. Broxton, "Natural Sorptive Barriers in Yucca Mountain, Nevada, for Long-Term Isolation of High-Level Waste," in Radioactive Waste Management, Vol. 3 (International Atomic Energy Agency, 1984b), 415-432. NNA.870406.0085
- Blacic, J. D., D. T. Vaniman, D. L. Bish, C. J. Duffy, and R. C. Gooley, "Effects of Long-Term Exposure of Tuffs to High-Level Nuclear Waste Repository Conditions: Final Report," Los Alamos National Laboratory report LA-9330-MS (1986).
- Brindley, G. W., and G. Brown, Crystal Structures of Clay Minerals and Their X-Ray Identification (Mineralogical Society, London, 1950).
- Brown, G., The X-Ray Identification and Crystal Structures of Clay Minerals (Mineralogical Society, London, 1972).
- Broxton, D. E., D. L. Bish, and R. G. Warren, "Distribution and Chemistry of Diagenetic Minerals at Yucca Mountain, Nye County, Nevada," submitted to *Clays and Clay Minerals* (1986).
- Burst, J. F., "Post-Diagenetic Clay Mineral-Environmental Relationships in the Gulf Coast Eocene in *Clays and Clay Minerals*," *Clays and Clay Minerals*, 6, 327-341 (1959).
- Byers, F. M., Jr., W. J. Carr, P. P. Orkild, W. D. Quinlivan, and K. A. Sargent, "Volcanic Suites and Related Cauldrons of Timber Mountain-Oasis Valley Caldera Complex, Southern Nevada," U. S. Geological Survey Professional Paper 919 (1976).
- Bystrom-Brusewitz, A. M., "Studies on the Li Test to Distinguish Between Beidellite and Montmorillonite," *Proceedings of the International Clay Conference*, 419-428 (1975).
- Caporuscio, F., D. Vaniman, D. Bish, D. Broxton, B. Amey, G. Heiken, F. Byers, R. Gooley, and E. Semarge, "Petrologic Studies of Drill Cores USW-G2 and UE25b-1H, Yucca Mountain, Nevada," Los Alamos National Laboratory report LA-9255-MS (July 1982). NNA.870519.0041
- Duffy, C. J., "Hydrothermal Stability Studies," in "Research and Development Related to the Nevada Nuclear Waste Storage Investigations July 1-September 30, 1982," W. R. Daniels, B. R. Erdal, and D. T. Vaniman, Comp., Los Alamos National Laboratory progress report LA-9577-PR (March 1983a).
- Duffy, C. J., "Permeability, Porosity, and Hydrothermal Reactions," in "Research and Development Related to the Nevada Nuclear Waste Storage Investigations January 1-March 30, 1983," K. Wolfsberg, D. T. Vaniman, and A. E. Ogard, Comp., Los Alamos National Laboratory progress report LA-9793-PR (June 1983b).
- Duffy, C. J., "Hydrothermal Geochemistry," in "Research and Development Related to the Nevada Nuclear Waste Storage Investigations July 1-September 30, 1982," K. Wolfsberg and D. T. Vaniman, Comp., Los Alamos National Laboratory progress report LA-10032-PR (August 1984).

- Eberl, D., and J. Hower, "Kinetics of Illite Formation," *Geological Society America Bulletin*, 87, 1326-1330 (1976).
- Ernst, W. G., and S. E. Calvert, "An Experimental Study of the Recrystallization of Porcelanite and Its Bearing on the Origin of Some Bedded Cherts," *American Journal of Science*, 267-A, 114-133 (1969).
- Eslinger, E. V., and S. M. Savin, "Mineralogy and Oxygen Isotope Geochemistry of the Hydrothermally Altered Rocks of the Ohaki-Broadlands, New Zealand Geothermal Area," *American Journal of Science*, 273, 240-267 (1973).
- Gillery, F. H., "Adsorption-Desorption Characteristics of Synthetic Montmorillonoids in Humid Atmospheres," *American Mineralogist*, 44, 806-818 (1959).
- Goldstein, R. H., "Re-equilibration of Fluid Inclusions in Low-Temperature Calcium-Carbonate Cement," *Geology*, 14, 792-795 (1986).
- Greene-Kelly, R., "Dehydration of the Montmorillonite Minerals," *Mineralogical Magazine*, 30, 604-615 (1955).
- Hoffman, J., and J. Hower, "Clay Mineral Assemblages as Low Grade Metamorphic Geothermometers: Application to the Thrust Faulted Disturbed Belt of Montana, U.S.A.," *Society of Economic Paleontologists and Mineralogists, Special Publication 26*, 55-79 (1979).
- Howard, J. J., "Lithium and Potassium Saturation of Illite/Smectite Clays from Interlaminated Shales and Sandstones," *Clays and Clay Minerals*, 29, 136-142 (1981).
- Hower, J., "X-Ray Diffraction Identification of Mixed-Layer Clay Minerals," in *Clays and The Resource Geologist*, Chap. 3, F. J. Longstaffe, Ed. (Mineralogical Association of Canada, Calgary, 1981, 39-59).
- Hower, J., and S. P. Altaner, "The Petrologic Significance of Illite/Smectite," *Clay Minerals Society, 20th Annual Meeting, Buffalo, New York*, p. 40 (October 1983).
- Hower, J., E. V. Eslinger, M. E. Hower, and E. A. Perry, "Mechanism of Burial Metamorphism of Argillaceous Sediments: 1. Mineralogical and Chemical Evidence," *Geological Society of America Bulletin*, 87, 725-737 (1976).
- Iijima, A., "Effect of Pore Water to Clinoptilolite-Analcime-Albite Reaction Series," *Journal of the Faculty of Science, University of Tokyo*, 19, 133-147 (1975).
- Iijima, A., "Geological Occurrences of Zeolite in Marine Environments," in *Natural Zeolites: Occurrence, Properties, Use*, L. B. Sand and F. A. Mumpton, Eds. (Pergamon Press, New York, 1978).
- Iijima, A., "Geology of Natural Zeolites and Zeolitic Rocks," in "Proceedings of the 5th International Conference on Zeolites," L.V.C. Rees, Ed. (Heyden, London, 103-118, 1980).
- Inoue, A., "Conversion of Smectite to Chlorite in Acidic Pyroclastic Rocks in the Hokuroku Kuroko District, Northeast Japan," *International Clay Conference, Denver, Colorado*, p. 109 (1985).
- Inoue, A. H. Minato, and M. Utada, "Mineralogical Properties and Occurrence of Illite/Montmorillonite Mixed Layer Minerals Formed from Miocene Volcanic Glass in Waga-Omono District," *Clay Science*, 5, 123-136 (1978).
- Jackson, M. L., *Soil Chemical Analysis--Advanced Course*, 2nd ed., published by author, Madison, Wisconsin (1979).

- Johnstone, J. K., R. R. Peters, and P. F. Gnirk, "Unit Evaluation at Yucca Mountain, Nevada Test Site: Summary Report and Recommendations," Sandia National Laboratories report SAND 83-0372 (June 1984).
- Kano, K., "Ordering of Opal-CT in Diagenesis," *Geochemical Journal*, 17, 87-93 (1983).
- Kano, K., and K. Taguchi, "Experimental Study on the Ordering of Opal-CT," *Geochemical Journal*, 16, 33-41 (1982).
- Kerrisk, J. F., "Reaction-Path Calculations of Groundwater Chemistry and Mineral Formation at Rainier Mesa, Nevada," Los Alamos National Laboratory report LA-9912-MS (December 1983).
- Knauss, K. G., and W. B. Beiriger, "Report on Static Hydrothermal Alteration Studies of Topopah Spring Tuff Wafers in J-13 Water at 150°C," Lawrence Livermore National Laboratory report UCRL-53576 (August 1984).
- Liou, J. G., "Analcime Equilibria," *Lithos*, 4, 389-402 (1971).
- Martin, R. T., "Evaluation of Solvation Methods for Expandable Layers," Clay Mineral Society, Short Course Notes, August 6, 1982, Hilo, Hawaii (1982).
- Marvin, R. F., F. M. Byers, Jr., H. H. Mehnert, P. P. Orkild, and T. W. Stern. "Radiometric Ages and Stratigraphic Sequence of Volcanic and Plutonic Rocks, Southern Nye and Western Lincoln Counties, Nevada," *Geological Society of America Bulletin*, 81, 2657-2676 (1970).
- McCubbin, D. G., and J. W. Patton, "Burial Diagenesis of Illite/Smectite: The Kinetic Model," Annual Meeting American Association of Petroleum Geologists, San Francisco, California, 1981 (Abstract).
- McDowell, S. D., and W. A. Elders, "Authigenic Layer Silicate Minerals in Borehole Elmore 1, Salton Sea Geothermal Field, California, USA," *Contributions to Mineralogy and Petrology*, 74, 293-310 (1980).
- Ogard, A. E., and J. F. Kerrisk, "Groundwater Chemistry Along Flow Paths Between a Proposed Repository Site and the Accessible Environment," Los Alamos National Laboratory report LA-10188-MS (November 1984).
- Parrish, W., and A. J. C. Wilson, "Precision Measurements of Lattice Parameters of Polycrystalline Specimens," in *International Tables for X-Ray Crystallography*, Vol 2., K. Lonsdale, Ed. (Kynoch Press, Birmingham, 1959) 216-234.
- Perry, E., and J. Hower, "Burial Diagenesis in Gulf Coast Pelitic Sediments," *Clays and Clay Minerals*, 18, 165-177 (1970).
- Perry, E. A., Jr., and J. Hower, "Late-Stage Dehydration in Deeply Buried Pelitic Sediments," *American Association of Petroleum Geologists Bulletin*, 56, 2013-2021 (1972).
- Reynolds, R. C., "Interstratified Clay Minerals," in *Crystal Structures of Clay Minerals and Their X-Ray Identification*, Chap. 4, G. W. Brindley and G. Brown, Eds. (Mineralogical Society, London, 1980) 249-304.
- Reynolds, R. C., and J. Hower, "The Nature of Interlayering in Mixed-Layer Illite/Montmorillonite," *Clays and Clay Minerals*, 18, 25-36 (1970).
- Roberson, H. E., and R. W. Lahann, "Smectite to Illite Conversion Rates: Effects of Solution Chemistry," *Clays and Clay Minerals*, 29, 129-135 (1981).

- Roedder, E., Fluid Inclusions, Reviews in Mineralogy, Vol. 12, Mineralogical Society of America (1984).
- Sass, J., A. Lachenbruch, F. Grubb, and T. Moses, "Status of Thermal Observations at Yucca Mountain, Nevada," U.S. Geological Survey Letter Report (April 1983).
- Smyth, J. R., "Zeolite Stability Constraints on Radioactive Waste Isolation in Zeolite-Bearing Volcanic Rocks," *Journal of Geology*, 90, 195-201 (1982).
- Srodon, J., "Precise Identification of Illite/Smectite Interstratifications by X-Ray Powder Diffraction," *Clays and Clay Minerals*, 28, 401-411 (1980).
- Steiner, A. "Clay Minerals in Hydrothermally Altered Rocks at Wairakei, New Zealand," *Clays and Clay Minerals*, 16, 193-213 (1968).
- Suquet, H., C. De La Calle, and H. Pezerat, "Swelling and Structural Organization of Saponite," *Clays and Clay Minerals*, 23, 1-9 (1975).
- Swanberg, C. A., and J. Combs, "Geothermal Drilling in the Cascade Range: Preliminary Results from a 1387-m Core Hole, Newberry Volcano, Oregon," *EOS, Transactions of the American Geophysical Union*, 67, 578-580 (1986).
- Thompson, G., and S. Jennings, "Kinetic Factors Affecting the Diagenetic Transformation of Smectite to Illite," *Proceedings of the International Clay Conference, Denver, Colorado*, 239 (1985).
- Vaniman, D., D. Bish, D. Broxton, F. Byers, G. Heiken, B. Carlos, E. Semarge, F. Caporuscio, and R. Gooley, "Variations in Authigenic Mineralogy and Sorptive Zeolite Abundance at Yucca Mountain, Nevada, Based on Studies of Drill Cores USW GU-3 and G-3," Los Alamos National Laboratory report LA-9707-MS (June 1984). NNA.870519.0043