AIIM

Association for Information and Image Management
1100 Wayne Avenue, Suite 1100
Silver Spring, Maryland 20910
301/587-8202

Centimeter

1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 mm

1 2 3 4 5

Inches

LA-UR 93-2254

Conf-9306100--3

Los Alamos National Laboratory is operated by the University of California for the United States Department of Energy under contract W-7405-ENG-36.

TITLE: K/AR DATING OF CLINOPTILOLITE, MORDENITE, AND ASSOCIATED CLAYS FROM YUCCA MOUNTAINS, NEVADA

AUTHOR(S): GIDAY WOLDEGABRIEL

SUBMITTED TO: INTERNATIONAL ZEOLITE CONFERENCE
JUNE 20-28, 1993, BOISE, ID

Los Alamos

Los Alamos National Laboratory
Los Alamos, New Mexico 87545

FORM NO. 836 R4
ST. NO. 2629 581

MASTER

K/Ar Dating of Clinoptilolites, Mordenite, and Associated Clays From Yucca Mountain, Nevada

Giday WoldeGabriel, Earth and Environmental Sciences Division, EES-1, MS D462, Los Alamos National Laboratory, Los Alamos, New Mexico 87545

ABSTRACT

Alkali zeolites are the dominant secondary minerals in the zeolite-rich sections of the altered Miocene tuffs at Yucca Mountain. According to SEM studies smectite predates alkali zeolites. Mordenite in the dissolved-shard cavities post-dates clinoptilolite crystals, whereas authigenic K-feldspar occurs locally in voids on top of smectite ribbons and mordenite fibers.

K/Ar dates ranging from 2-13 Ma suggest that clinoptilolites can retain K and radiogenic Ar. The dates increase with depth, and samples from below the static water level yield mostly older dates than those from above the water table. Although the clinoptilolites are contaminated by minor amounts of microcrystalline feldspars, the older K/Ar dates (≥8.5 Ma) are similar to illite/smectites (9-12 Ma) separated from dated zeolites and from underlying units and may reflect primary crystallization ages. Similar clinoptilolite K/Ar dates on either side of the static water level may also indicate fluctuation in the ground water stand in the past. Ion-exchanged clinoptilolites gave older dates because of K removal. The older K/Ar dates from the saturated zone are not due to this kind of process because clinoptilolites have strong selectivity for K over other major cations in a ground water environment.

Ar loss from clinoptilolites during continued diagenetic reactions of older zeolites (e.g., clinoptilolite to mordenite), dehydration processes in the unsaturated zone, and contamination by feldspars and illite/smectites are probably responsible for the range in the K/Ar results. The similarity between illite/smectite and some of the clinoptilolite and mordenite K/Ar dates from the saturated zone suggest that dating of K-rich zeolites may provide useful information on the timing of diagenesis in low-temperature environments (e.g., zeolitization processes).

INTRODUCTION

Zeolites are abundant in the geologic record in both continental and marine environments. The purpose of the present study is to evaluate the utility of K-bearing zeolites for dating by the K/Ar method to determine the time of zeolite diagenesis at Yucca Mountain, Nevada (Fig. 1). At Yucca Mountain, K-rich clinoptilolite and possibly mordenite are the only potentially K/Ar dateable secondary minerals present in the zeolite-rich tuffs except for some illite/smectites (≥10% illite layers) associated with these minerals. Direct dating of K-rich clinoptilolite, the most abundant zeolite in the altered tuffs, is important to delineate zeolite chronology as part of the site characterization of Yucca Mountain.

Mineralogical and geochronological information from altered rocks can provide information on the geologic history of an area. For example, illite/smectites from different geologic settings have been characterized and dated by the K/Ar method to constrain burial and thermal history of a basin (Aronson and Hower, 1976; Elliott et al., 1991), contact metamorphism around plutons (Aronson and Lee, 1986), and hydrothermal activity and mineralization in volcanic fields (WoldeGabriel and Goff, 1989).

Minerals must retain radiogenic Ar and and K and resist alteration and incorporation of extraneous Ar and K in order to be useful for K/Ar dating (Dalrymple and Lanphere, 1969; Faure, 1986). These conditions are apparently satisfied by illitic clays, micas, authigenic feldspars, etc. Because zeolites have an aluminosilicate framework containing large cavities and channels that allow cations, water molecules, and certain gases to move readily in and out of the crystal structure (Vaughan, 1978), there has been limited research on the use of zeolites for dating.

A number of direct and indirect dating methods (i.e., K/Ar, Rb/Sr, and fission track) have been applied to various zeolites from continental and marine geologic settings. For example, Hay (1963) used secondary minerals such as celadonite and authigenic feldspar to show that zeolite formation from the alteration of volcanic glass in an open-system is relatively rapid. The diagenetic minerals in the John Day Formation of

Oregon are similar in age to the primary rocks, implying that the alteration occurred soon after the tuffs were deposited.

Bernat et al. (1970) dated phillipsite separates (5-37 μm) from Pacific Ocean floor deposits by the K/Ar method and found that the apparent ages generally increased with depth within the sedimentary column and with decreasing size fractions of the samples. However, the results were disqualified because of contamination by relict minerals and gain of K by the phillipsite in the absence of radiogenic Ar during growth. Phillipsite Rb/Sr apparent age (14.7 Ma) from a middle Eocene volcanosedimentary deposit in the southern Pacific Ocean floor was interpreted to represent the cessation of chemical exchange in the middle Miocene due to induration and destruction of permeable pathways (Clauer, 1982). According to Clauer (1982), the diagenetic reaction between the zeolites and fluids in the environment did not cease until long after the unit was deposited.

Chabazite, stilbite, and heulandite from basaltic flows were dated by the fission track method. Most of the apparent ages (40.8 - 55.4 Ma) were slightly younger than the age of the lavas (54.6 - 55.2 Ma) hosting them (Koul et al., 1981).

Variable K/Ar apparent ages of 1.0 to 14.3 Ma were obtained on clinoptilolites from a lacustrine volcaniclastic section of early to middle Miocene age in western Turkey (Gundogdu et al., 1989). According to the authors, the variation in clinoptilolite dates is related to the permeability of the host rock from which the clinoptilolite was separated (i.e., impermeable rocks gave older dates). Diagenetic reactions induced chemical exchanges and loss of radiogenic Ar from clinoptilolites in the permeable altered tuffaceous rocks; thereby giving younger dates.

Previous studies have dated illite/smectites by the K/Ar method to explore the timing of hydrothermal alteration and diagenesis of clays and zeolites at Yucca Mountain (Aronson and Bish, 1987). Illite/smectites from subsurface altered tuff units underlying the zeolite-rich zone at Yucca Mountain yielded a narrow range of K/Ar results (9-12 Ma) (Aronson and Bish, 1987; Bish et al., 1990). The present study expands upon these reconnaissance K/Ar studies of clays from Yucca Mountain.

GEOLOGICAL BACKGROUND

Yucca Mountain is located in the southwest Nevada volcanic field (Fig. 1). It is an east-tilted fault block consisting of a thick sequence of tuffs erupted from the middle to late Miocene Timber Mountain-Oasis Valley caldera complex located to the north and west (Byers et al., 1976; Christiansen et al., 1977). The volcanic rocks are 1.2 to >1.8 km thick (Spengler et al., 1981; Scott and Castellanos, 1984; Carr et al., 1984) and range in age from 11.45 to 15.1 Ma (Sawyer et al., 1990). The upper volcanic units belong to the voluminous Tiva Canyon (1000 km^3) and Topopah Spring (1200 km^3) Members of the Paintbrush Tuff that erupted about 12.70 and 12.75 Ma, respectively, from the Timber Mountain - Oasis Valley caldera complex and are underlain in descending order by the Calico Hills Formation (12.9 Ma), the Crater Flat Tuff (13.1 Ma), the Lithic Ridge Tuff (13.85 Ma), and older unnamed ash-flow tuff units whose sources have not been well constrained (Carr et al., 1984; Sawyer et al., 1990).

The alteration minerals at Yucca Mountain are grouped broadly into four diagenetic zones with authigenic minerals that are progressively less hydrous with depth (Smyth and Caporuscio, 1981; Broxton et al., 1987; Bish and Chipera, 1989). These vertically zoned zeolitized tuff units formed in an open chemical system resulting in major mobilization of alkalis and alkaline earths (Broxton et al., 1987; Peterman et al., 1993). Structural and stratigraphic relations of the altered Yucca Mountain tuff sequence suggest that zeolitization processes were completed by about 11.6 Ma (Levy, 1984, 1991).

ANALYTICAL METHODS

Outcrop samples from areas north and northeast of Yucca Mountain and several core samples from five drill holes were selected for study (Fig. 1). Petrographic evidences indicate that most of the zeolites in the altered tuffs are fine grained (≤40 μm). All samples contained ≥30% clinoptilolite in the original bulk sample (Bish and Chipera, 1989). The samples were selected to be representative of zeolitic tuffs above and below the water table and to provide spatial coverage of the Yucca Mountain area. Selected samples were analyzed by SEM to examine paragenetic relations among the alteration minerals.

Clinoptilolite, Mordenite, and Illite/Smectite Separations

The zeolitized tuff samples were crushed and pulverized, after which the zeolites and clays were extracted by sedimentation in deionized water (Chipera and Bish, 1989). Additional purification of zeolites was carried out using a mixture of s-tetrabromoethane and acetone with a density range of 2.1 g/cm^3 to 2.45 g/cm^3 to separate clinoptilolite from other, generally denser primary and authigenic minerals by centrifugation. Although clinoptilolite has a measured density of 2.1 to 2.2 g/cm^3 (Roberts et al., 1989) and is much less dense than other common minerals found in the tuff matrix, the heavy-liquid mineral separations were not completely effective.

X-Ray Diffraction Analysis

Different size fractions were analyzed using X-ray diffraction (XRD). Random and oriented mounts were prepared and analyzed by an automated Siemens D-500 diffractometer using Cu Kα radiation, 0.02° 2θ steps, and counting time of 1 s per step for all mounts (2-36° 2θ). Standard XRD patterns were used to identify the zeolites and associated alteration minerals.

K/Ar Dating

About 130 to 200 mg of clinoptilolite, mordenite, and illite/smectite fractions (0.1-0.35, 1-3, and 3-20 μm) were used for Ar extraction. Ar measurements were made using an MS10 mass spectrometer equipped with an online, multiloaded extraction system and a bulb-pipetted ^{38}Ar tracer calibrated with the LP-6 biotite interlaboratory standard at 19.3 x 10^{10} moles/g of radiogenic Ar (Odin et al., 1982). The K content was determined in duplicate by flame photometer using a lithium internal standard. K/Ar apparent ages were calculated using ^{40}K abundance and decay constants proposed by Steiger and Jager (1977).

The total percentage (σ) uncertainties in the calculated K/Ar dates represent the combination of errors from the determination of radiogenic Ar contents of samples (Cox and Dalrymple, 1967), K_2O analysis, and sample inhomogeneity. Replicate analyses of standards analyzed with the unknown samples for K (LP-6 and U. S. Geological Survey standards BCR-1 and G-2) and Ar (LP-6) vary by less than 2 % from the accepted values. The precision of multiple analysis of some of the unknown samples, especially the clinoptilolites that yielded younger dates, is not as good as the results obtained from the standard samples. The apparent variation of the dates is sometimes greater than can be explained by analytical error alone.

ANALYTICAL RESULTS

Clinoptilolite makes up ≥75% of the purified samples except for some of the separates from the Tram Member that contain abundant finely crystalline quartz with minor amounts of feldspar (e.g., Fig. 2). The dated illite/smectites are randomly interstratified (10-20 % illite layers) and contain minor amounts of clinoptilolite and mordenite. The mordenite fraction contains quartz and possibly trace amounts of feldspar. Mordenite, opal-CT, cristobalite, quartz, and feldspar are common impurities in the clinoptilolite separates; of these, the K-bearing phases such as mordenite, feldspar, and illite/smectite can have a significant effect on the dates. Heating results indicate no heulandite in the dated samples. Table 1 summarizes the mineralogical and K/Ar results of clinoptilolite, mordenite, and illite/smectites separated by sedimentation in deionized water and heavy liquids. The analytical data are presented in descending stratigraphic order starting with the Topopah Spring Member of the Paintbrush Tuff.

Topopah Spring Member

Three zeolitized tuff samples were obtained from different levels of the Topopah Spring Member in the unsaturated zone of USW G-2 and G-4. Clinoptilolite and opal-CT are the dominant secondary minerals.

The clinoptilolite K/Ar dates are much younger compared with the age of eruption (12.75 Ma, Sawyer et al., 1990) and increase with depth within the unit from a sample with no radiogenic Ar to 4.2 Ma. The shallow sample (G-2 762) has a low K content (1.99 wt%) and yielded very low radiogenic Ar (<1 %). Two samples from the lower part of the Topopah Spring Member belong to the zone of pervasive zeolitic alteration. The samples are from different drill holes that are about 4 km apart and yielded similar apparent ages of 4.1 Ma and 4.2 Ma (WoldeGabriel et al., 1992).

Calico Hills Formation

Clinoptilolite fractions were separated from several zeolitized surface and subsurface samples of the Calico Hills Formation at Yucca Mountain and vicinity. Outcrop samples at and north of the Prow Pass at the northern end of Yucca Mountain (Fig. 1) contain abundant clinoptilolite and mordenite with trace amounts of opal-CT (Fig. 2). SEM examinations of both surface samples indicate more mordenite compared with corresponding subsurface samples (WoldeGabriel et al., 1993, in review). The mordenite crystals occur on top of the clinoptilolites. The secondary mineral assemblages in the unsaturated and saturated zones of drill holes USW G-1, G-2, and G-4 are similar to the outcrop samples except for minor contents of quartz, feldspar, and illite/smectite in the core samples.

The Clinoptilolite K/Ar results (1.5 to 4.8 Ma) yielded younger dates compared with the mid-Miocene age of the tuff of Calico Hills (12.9 Ma, Sawyer et al., 1990). Clinoptilolites from the outcrop range between 1.5 and 3.5 Ma (Table 1), whereas those from the drill holes yielded dates of 2 to 4.8 Ma and like the Topopah Spring Member, the dates increase with depth within the unit (WoldeGabriel et al., 1992).

Prow Pass Member

Several samples selected from the Prow Pass Member of the Crater Flat Tuff in the unsaturated and saturated zones of UE-25P #1, USW G-1, G-2, GU-3, and G-4 contain abundant altered shards that are replaced by illite/smectite (≤10 % illite layers), clinoptilolite, mordenite, opal-CT, and authigenic alkali feldspar as indicated by XRD and SEM analyses. Based on grain relations from SEM studies, the crystallization sequence for the authigenic minerals is illite/smectite, clinoptilolite, mordenite, and analcime (WoldeGabriel et al., 1993, in review).

The K/Ar dates range from 4.1 to 13 Ma and increase with depth within the Prow Pass Member. The oldest clinoptilolite dates are from saturated zone samples in the lower part of the Prow Pass section and are similar to the eruption age of the unit (13.1 Ma, Sawyer et al., 1990). A date of 13.3 Ma was obtained on clinoptilolite fractions from G-2 3250.5 - 3250.7 (Table 1). The illite/smectite separate from G-2 3250.5 - 3250.7 also yielded a similar date (12.7 Ma). However, the clinoptilolite fraction is contaminated with traces of finely crystalline feldspars and illite/smectites. Although an apparent age 11 Ma was obtained on G-2 3191.5-3192 (WoldeGabriel etal., 1992), it decreased to 7 Ma after purification by heavy liquid. This was also true for sample UE-25P #1 1740 - 1750 that changed from 8.5 to 6.0 Ma after treatment. However, a K/Ar date of 8.4 Ma was obtained on a less contaminated clinoptilolite (UE-25P #1 1790 - 1800).

Bullfrog Member

A clinoptilolite separate (1-3 μm) from the Bullfrog Member (G-3 2013.1-2013.4) of the Crater Flat Tuff in the unsaturated zone of USW GU-3/G-3 contains minor amounts opal-CT and no mordenite. However, another sample from the lower part of the Bullfrog Member in the saturated zone of USW G-4 (G-4 2716.5 - 2716.8) contains mordenite, quartz, and trace amount of feldspar.

The clinoptilolite from the Bullfrog Member (3.9 Ma) is very similar to a number of clinoptilolite dates from the unsaturated portion of the Topopah Spring Member of the Paintbrush Tuff (4.2 Ma), the tuff of Calico Hills (4.1 Ma and 3.9 Ma), and the Prow Pass Member of the Crater Flat Tuff in USW G-4 (4.4 Ma) (WoldeGabriel etal., 1992). The mordenite date (12.3 Ma) is similar to the older clinoptilolites and illite/smectites from the saturated zone.

Tram Member

The samples from the Tram Member of the Crater Flat Tuff in drill holes USW G-1 and G-3 contain clinoptilolite, quartz, and analcime with minor amounts of mordenite, illite/smectite, and microcrystalline feldspar. The amount of feldspar contaminants in the clinoptilolite separates is generally higher for Tram Member and underlying tuff samples compared with similar fractions obtained from the overlying altered units. Heavy-liquid treatment to reduce the microcrystalline quartz and feldspar contents from the dated samples was not significantly effective as noted in the XRD patterns of the untreated and treated aliquots. SEM analysis of G-3 3854.7 - 3854.9 indicates that most of the secondary minerals occur as direct replacements of the original vitric pyroclasts except for smectite which also occurs in the matrix and in altered minerals (i.e., feldspars and biotites) (WoldeGabriel et al., 1993, in review).

Similar dates (9 - 10 Ma) were obtained on the Tram Member samples. A date of 10 Ma was obtained on a heavy-liquid treated sample (G-1 3288.5 - 3288.6). Samples G-3 3589 and G-3 3854.7 - 3854.9 also yielded dates of 9 and 10.4 Ma, respectively (Table 1).

Unnamed Older Tuffs (Units B and C)

Two samples from informal units B (G-1 5458.4 - 5458.5) and C (G-1 5560) of the unnamed Older Tuffs in drill hole USW G-1 contain clinoptilolite, mordenite, quartz, feldspar, and illite/smectite (15 - 25 % illite layers). The SEM results indicate that the phenocrysts (feldspars and biotites) and matrix in these samples are replaced by illite/smectite, authigenic K-feldspar, clinoptilolite, and mordenite (WoldeGabriel et al., 1993, in review)

These tuffs underlie the Lithic Ridge Tuff (13.85 Ma, Sawyer et al., 1990). Dates of 12 Ma were obtained on both clinoptilolite fractions from units B (G-1 5458.4 - 5458.5) and C (G-1 5560) and are similar to the dates from the Tram Member. These dates represent maximum apparent ages because of the feldspar and illite/smectite contaminations. An illite/smectite fraction from G-1 5458 - 5458.5 yielded a younger date (8.8 Ma) compared with the clinoptilolite (12 Ma) separated from the same sample.

DISCUSSION

The significance of the dating results of the selected clinoptilolite-rich fractions, mordenite, and illite/smectites from the unsaturated and saturated zones are discussed. This is a reconnaissance study and the interpretations and conclusions are subject to revision as more data are acquired on the factors controlling the behaviors of Ar and K in alkali zeolites in different geologic environments.

Distribution of Clinoptilolite, Mordenite, and Clay K/Ar Dates

The dating results demonstrate that clinoptilolites retain at least part or all of their radiogenic Ar depending on the effects of post-crystallization processes and environments. This observation is important because zeolites are commonly perceived as unsuitable for radiometric age determinations because their open framework structure implies an inability to retain radiogenic Ar.

A striking aspect of the dates obtained is the consistent pattern of increasing apparent age with depth (Fig. 3). This pattern is repeated in USW G-1, G-2, GU-3/G-3, and G-4 drill holes across the Yucca Mountain block. Dates from surface and near-surface samples range between 2 and 4 Ma, whereas those from the lower part of the unsaturated zone yielded dates of 4 to 5 Ma. The dates below the static water level increase from 4 to 13 Ma with depth. The oldest dates are similar to the eruption ages of the volcanic units hosting the secondary minerals and may represent the original zeolite and illite/smectite crystallization ages. These initial results are promising because co-existing minerals such as mordenite and illite/smectite fractions separated from clinoptilolite-rich samples corroborate the clinoptilolite apparent ages.

Why do the clinoptilolite K/Ar dates systematically vary with depth within the unsaturated and saturated zones? Can the dates and the variation in the dates be related to any geological processes at Yucca Mountain? Variations in the clinoptilolite apparent ages may be related to contamination of zeolites by microcrystalline feldspars and illite/smectite clays, post-zeolite crystallization cation-exchange reactions, and Ar loss during intermittent saturation changes within the zeolite-rich sections. The effects of other factors such as the inheritance of extraneous Ar during the alteration of the host rocks and zeolite crystallization, Ar loss from clinoptilolites from volcanic-related heating of Yucca Mountain, and gain and loss of K by and from clinoptilolites during fluid migration especially in the unsaturated zone of the drill holes may be insignificant compared with the other processes mentioned above.

Contamination of clinoptilolite fractions by K-bearing primary and secondary minerals contribute to the variation of the K/Ar dates. For example, K and Ar determinations were made on clinoptilolites before and after purification by heavy liquids. In seven of nine samples, K, Ar, and apparent ages are greater in clinoptilolite separates analyzed before heavy-liquid treatment (WoldeGabriel et al., 1993, in review). The greater K contents and older apparent ages of these pre-treatment fractions are therefore attributed to the presence of contaminants such as microcrystalline feldspars (i.e., primary and/or authigenic) and illite/smectite. Few authigenic feldspars are present with the zeolites, and paragenetic relations indicate that they postdate the clinoptilolites. Thus, most of the contaminants are fine-grained feldspar impurities that are probably pyrogenic and/or crystallized during high-temperature devitrification soon after the tuffs were deposited. The presence of these micrometer-size (≤3 μm) feldspars will tend to increase the apparent ages determined for contaminated clinoptilolite separates. These results demonstrate the necessity for carefully screening clinoptilolite separates for the presence of contaminants.

Smectite occurs with zeolites in the unsaturated zone of the drill holes (Bish and Chipera, 1989). Collapse of smectite layers creates pore spaces that could provide pathways for fluid migration (Eberl, 1984). Post-clinoptilolite-crystallization chemical interactions with percolating fluids in the unsaturated zone can affect the Ar and K contents of the clinoptilolites. Evidence for percolation of fluids from the surface is provided by the similarity in Sr, $\delta^{18}O$, and $\delta^{13}C$ isotope compositions and trace element chemistry between pedogenic carbonate and pore-space and fracture-filling calcites in the unsaturated zone (Marshall et al., 1992, Whelan and Stuckless, 1992; Vaniman, 1993). In most cases, the clinoptilolites in the unsaturated zone occur in close association with mordenite grains. This is consistent with the report that some of the mordenite formed at the expense of clinoptilolite in drill hole samples at Yucca Mountain (Sheppard et al., 1988); such alteration potentially results in Ar loss and a decrease in the K/Ar date. For example, clinoptilolite K/Ar dates (1-14 Ma) from middle Miocene zeolite-rich tuffs in western Turkey were attributed to post-crystallization chemical exchange in permeable zones and the range of dates was interpreted to represent the cessation of water/rock interactions during the progressive decrease in permeability (Gundogdu et al., 1989). The cessation of chemical exchange between fluids and diagenetic minerals due to impermeability and the subsequent retention of isotopic signatures by the minerals are also indicated by their Rb/Sr composition. Clauer (1982) reported that a middle Miocene (14.7 Ma) Rb/Sr isotopic age on phillipsite from the Pacific Ocean floor represented the end of induration processes (i.e., end of diagenetic reactions between zeolites and pore fluids) in middle Eocene volcanogenic sediments.

At Yucca Mountain, the effects of intermittent saturation on the Ar and cation contents of the clinoptilolites from the unsaturated zone are not well understood. Barrer and Vaughan (1969) suggested that Ar can readily diffuse through the structure of heulandite (isostructural to clinoptilolite) although this can be minimized by rehydration until the sample is heated to 110°C. Increased atomic displacement and disorder in the tetrahedral framework was noted during dehydration of alkali zeolites (Bish 1988; Armbruster, 1993). These processes could increase Ar loss from the clinoptilolite structure.

The similarity of the K/Ar clinoptilolite dates (4 - 5 Ma, Fig. 3) in the lower and upper parts of the unsaturated and saturated zones, respectively across Yucca Mountain is probably related to fluctuations in ground water stands in the past. Water in the zeolite structure probably inhibited Ar loss in the vicinity of the static water level compared with outcrop and near surface samples during intermittent saturations. With few exceptions, most of the unsaturated zone samples are about 100 m above the present day static water level (Fig. 3). Evidences for variations in ground water levels within the unsaturated zone are also indicated by mineralogical and Sr, $\delta^{18}O$, and $\delta^{13}C$ isotopic data (Levy, 1991; Whelan and Stuckless, 1992; Marshall et al., 1993).

Thermal effects as a cause for Ar loss from clinoptilolites in the unsaturated zone are unlikely since the secondary mineral assemblage (i.e., smectite, clinoptilolite, opal-CT, etc.) in the zeolite-rich sections at Yucca Mountain is characteristic of low-temperature diagenetic environment. For example, the upper stability limit for both clinoptilolite and smectite is about 100°C (Bish, 1989). Thus, the temperature in the zeolite zone may not have been high enough to cause Ar loss from the clinoptilolite. However, the long term (> 1 million years) effect of relatively low temperature on Ar migration in clinoptilolites is unknown. Gundogdu et al. (1989) examined the Ar retention ability of clinoptilolites during dehydration by degassing the samples under vacuum at 25, 60, and 100°C for 12 hours and obtained similar apparent ages suggesting minimal Ar loss. Preliminary quadrupole mass spectrometric analysis of gases from tuff of Calico Hills clinoptilolite samples heated in vacuum indicates that Ar is released at temperatures greater than 200 °C.

Excess Ar in clinoptilolites can result in dates older than the crystallization ages. Is it possible that the older clinoptilolite K/Ar dates from the saturated zone are due to Ar that was not generated by an in-situ decay of ^{40}K in the clinoptilolites? Independent studies indicate that excess Ar in the clinoptilolites is minimal because the alteration of the tuffs at Yucca Mountain was completed rapidly. For example, the clinoptilolite dates are similar to illite/smectite ages (9-12 Ma; Aronson and Bish, 1987) and the results from both secondary minerals approach the time of eruption of the major tuff units at Yucca Mountain (11.6-15.1 Ma; Sawyer et al., 1990). Moreover, stratigraphic and structural relations of the altered Yucca Mountain tuff sequence suggest that zeolite formation was completed between 11.6 and 12.8 Ma (Levy, 1991).

Clinoptilolites with extraneous K yield younger apparent ages. The silicic tuffs at Yucca mountain are alkali-rich. Chemical changes during alteration can be evaluated by comparing altered and stratigraphically equivalent unaltered samples (Peterman et al., 1993). This approach can establish criteria to estimate the increase or decrease of a particular element during alteration. Gain of K by the clinoptilolites during fluid migration in the unsaturated zone cannot be ruled out as a cause for the variation in the K/Ar dates. Generally, the clinoptilolite fractions from the unsaturated zone have higher K contents compared with those from the saturated zone, and this may be due to the selective removal of K from the percolating fluids (e.g., Ames, 1961). However, based on microprobe data of single crystals (Broxton et al., 1986), the distribution of K-rich clinoptilolites in USW G-1, G-2, GU-3/G-3, and G-4 is variable. For example, the clinoptilolites from the Calico Hills Formation and the Prow Pass Member of the Crater Flat Tuff in USW G-1, the Topopah Spring, the Calico Hills Formation, and some of the Prow Pass samples in USW G-2, the Prow Pass Member in USW G-3, and the Calico Hills Formation and some of the Prow Pass samples from USW G-4 contain higher K_2O (2-6 wt %) compared with the overlying and underlying units in each of the drill holes.

Because zeolitization in the Calico Hills Formation and the underlying Crater Flat Tuff was completed prior to the eruption of the Topopah Spring Member of the Paintbrush Tuff (Levy, 1984, 1991), the K content of the clinoptilolites in the Calico Hills Formation and the Prow Pass Member probably was acquired before the alteration of the overlying Topopah Spring Member. The distribution of the K-rich clinoptilolites in the drill holes suggests that the modification of the K contents after the alteration of the Topopah Spring Member from percolating fluids may be minimal except along fractures because of the significant decrease in permeability during the crystallization of zeolites and clays. Lander and Hay (1993) reported significant decrease in permeability in altered tuffs relative to laterally equivalent unaltered units. Moreover, low permeability was invoked to explain the occurrence of precursor clinoptilolites and mordenites with analcime in Tertiary sediments; analcime forms from alkalic, silicic zeolites (Iijima, 1978; Surdam and Sheppard, 1978). Assuming the clinoptilolites formed in the late Miocene based on the stratigraphic and structural relations (Levy, 1991), the K-clinoptilolites would have generated enough radiogenic Ar to give apparent ages older than the 2 Ma obtained on outcrop and near-surface samples. Thus, Ar loss by post-crystallization alteration and/or diffusion during dehydration seems to be a more plausible reason for the variation in the clinoptilolite K/Ar dates in the unsaturated zone than the gain of K.

Loss of K from clinoptilolites in the saturated zone can result in older dates. This was demonstrated by ion-exchange experiments of clinoptilolites with chloride solutions of Na, Ba, and Cs (WoldeGabriel et al., 1992). The ion-exchange experiments indicate that the type of cations (e.g., Cs, Ba, K, Sr, etc.) in the exchange solution and the duration of exchange have a measurable effect on the K content of the dated clinoptilolites. The results suggest that K was removed stepwise, with variable effect on the Ar in the clinoptilolite structure, yielding older K/Ar dates. Clinoptilolite is selective for Cs, Ba, and Sr over other cations (Ames, 1961; Bish, 1988), however, the effect of these cations on the K content of the dated clinoptilolites is insignificant because their total concentrations in both the zeolitic tuffs (≤0.1 wt% Ba, Cs, and Sr) and the ground water are very low. The concentrations of Cs, Ba, and Sr are also low compared with the major cations in ground water. In a ground water environment, the order of cation preference by clinoptilolite is K > Ca > Na and Ca > Mg (Ames, 1961). A strong selectivity for K over other cations suggests that K loss from the clinoptilolites in the saturated zone was unlikely. Moreover, chemical compositions of present day water samples from several wells in the Yucca Mountain area indicate lower amounts of K than Na and Ca (Benson et al., 1983). Based on the generalized information presented above, the older clinoptilolite K/Ar dates may not be due to excess Ar and/or K depletion because the dates are similar to illite/smectite ages and to the eruption ages of the tuffs.

CONCLUSIONS

The secondary minerals from the altered tuffs at Yucca Mountain consist of smectitic clays, zeolites, silica, and K-feldspar. The clinoptilolite separates are generally contaminated by mordenite, opal-CT, quartz, finely crystalline primary feldspar, and illite/smectite in the 1 - 3 μm fractions.

The variation in the K/Ar dates may be due to several factors such as (1) modification of the K and Ar contents during chemical exchange between percolating fluids and the older clinoptilolites resulting in partial alteration of clinoptilolite to mordenite and possibly to analcime; (2) Ar loss from prolonged dehydration of clinoptilolites in the unsaturated zone; (3) impermeability in the host rocks preventing fluid migration and chemical exchange; and (4) the effect of hydration immobilizing Ar in the framework structure of clinoptilolite, etc. No apparent evidence was noted in the mineral assemblage to suggest that Ar loss from the clinoptilolite was triggered by major thermal effects at Yucca mountain. The clinoptilolite K/Ar dates reflect the dynamic interplay of fluid chemistry and host-rock permeability because water/mineral interaction induces chemical exchanges, destruction of diagenetic minerals, and loss or gain of K and radiogenic Ar during alteration, resulting in variable dates. The older clinoptilolites, although contaminated by minor amounts of feldspars, probably have not been modified by subsequent diagenetic reactions. In the saturated zone water may have immobilized Ar in the clinoptilolite structure. These older dates are correlative to illite/smectite dates from drill hole samples below the zeolitized tuff units at Yucca Mountain and approach the depositional ages of the tephras.

Despite the variation in dates, the K/Ar results have demonstrated that clinoptilolites can be dated because they can retain their Ar and K. Partial Ar loss and K gain or both may be responsible for the younger dates in the unsaturated zone. In the saturated zone, the older dates are not due to excess Ar because alteration of the tuffs was completed rapidly as supported by stratigraphic and structural evidence. Moreover, K loss from the clinoptilolites is not a viable explanation because clinoptilolites are selective for K compared with other major cations in ground water.

More data are needed to evaluate the utility of alkali zeolites for dating. Nonetheless, the consistency of the preliminary clinoptilolite K/Ar dates is encouraging because similar apparent ages were obtained on clinoptilolites from drill hole samples across Yucca Mountain. Various other authigenic minerals are being investigated to evaluate the relevance and reliability of the clinoptilolite K/Ar dates.

ACKNOWLEDGMENT

This work was supported by the Yucca Mountain Site Characterization Project Office as part of the Civilian Radioactive Waste Management Program of the U.S. Department of Energy. We thank Jim Aronson of the Geological Sciences, Case Western Reserve University in Cleveland, Ohio, for allowing us use of the K/Ar laboratory and Dave Norman of the Department of Geoscience, New Mexico Institute of Mining and Technology for help and use of the quadrupole mass spectrometer. Typing and editorial support by Barbara Hahn and drafting by Anthony Garcia and James Archuleta are greatly appreciated. The report benefited from the review of Dave Vaniman.

REFERENCES

Ames, L. L., Jr.(1961) Cation sieve properties of the open zeolites chabazite, mordenite, erionite, and clinoptilolite: American Mineralogist 45, 689-700.

Armbruster, T. (1993) Dehydration mechanism of clinoptilolite and heulandite: single-crystal X-ray study of Na-poor, Ca-, K-, Mg-rich clinoptilolite at 100 K: American Mineralogist 78, 260-264.

Aronson, J. L. and Bish, D. L. (1987) Distribution, K/Ar dates, and origin of illite/smectite in tuffs from cores USW G-1 and USW G-2, Yucca Mountain, Nevada, a potential high-level radioactive waste repository: Clay Mineral Society 24th Annual Meeting, Socorro, New Mexico 25.

Aronson, J. L. and Lee, M. (1986) K/Ar systematics of bentonite and shale in contact metamorphic zone, Cerrillos, New Mexico: Clays and Clay Minerals 34, 483-487.

Aronson, J. L. and Hower, J. (1976) The mechanism of burial metamorphism of argillaceous sediments: 2. radiogenic argon evidence: Geological Society of America Bulletin 87, 738-744.

Barrer, R. M. and Vaughan, D. E. W. (1969) Sorption and diffusion of rare gases in heulandite and stilbite: Surface Science 14, 77-92.

Benson, L. V., Robinson, J. H., Blankennagel, R. K., and Ogard, A. E. (1983) Chemical composition of ground water and the location of permeable zones in the Yucca Mountain area, Nevada: U. S. Geological Survey Open-File Report 83-853 19.

Bernat, M., Bieri, R. H., Koide, M., Griffin, J. J., and Goldberg, E. D. (1970) Uranium, thorium, K, and Ar in marine phillipsites: Geochem. Cosmochim. Acta 34, 1063-1071.

Bish, D. L., Vaniman, D. T., and Aronson, J. L. (1990) Interpretation of paleohydrologic and paleothermal conditions in a volcanic sequence using mineralogical and K/Ar dating information: The Geological Society of America Abstracts with Program, Dallas A57.

Bish, D. L. and Chipera, S. J. (1989) Revised mineralogic summary of Yucca Mountain, Nevada: Los Alamos National Laboratory Report, LA-11497-MS 68 p. (1989).

Bish, D.L. (1989) Evaluation of past and future alterations in tuff at Yucca Mountain, Nevada, based on clay mineralogy of Drill Cores USW G-1, G-2, and G-3: LosAlamos National Laboratory Report LA-10667 40.

Bish, D. L. (1988) 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, H. S., eds., Akadémiai Kiadó, Budapest, 565-576.

Broxton, D. E., Bish, D. L., and Warren, R. G. (1987) Distribution and Chemistry of Diagenetic Minerals at Yucca Mountain, Nye County, Nevada: Clays and Clay Minerals 35, No.2, 89-110.

Broxton, D. E., Warren, R. G., Hagan, R. C., and Luedemann, G., "Chemistry of diagenetically-altered tuffs at a potential nuclear waste repository, Yucca Mountain, Nye County, Nevada," Los Alamos National Laboratory Report, LA-10802-MS, 160 p. (1986)

Byers, F. M., Jr., Carr, W. J., Orkild, P. P., Quinlivan, W. D., Sargent, K. A. (1976) Volcanic suites and related cauldrons of Timber Mountain-Oasis Valley caldera complex, southern Nevada: U. S. Geological Survey Professional Paper 919 70 pp.

Carr, W. J., Byers, F. M., Jr., and Orkild, P. P. (1984) Stratigraphic and volcanotectonic relations of Crater Flat Tuff and some older volcanic units, Nye County, Nevada: U. S. Geological Survey Open-File Report, 84-114, 42 pp.

Chipera, S. J., and Bish, D. L. (1989) Zeolite purification/separation procedure. Los Alamos National Laboratory Yucca Mountain Site Characterization Project Detailed Procedure: TWS-ESS-DP-110, R1 4pp.

Christiansen, R. L., Lipman, P. W., Carr, W. J., Byers, F. M., Jr., Orkild, P. P., and Sargent, K. A. (1977)Timber Mountain-Oasis Valley caldera complex of southern Nevada: Geological Society of America Bulletin 88, 943-959.

Clauer, N. (1982) Strontium isotopes of Tertiary phillipsites from the Southern Pacific: Timing of the geochemical evolution: J. Sed. Petrol. 88, 1003-1009.

Cox, A. and Dalrymple, G. B. (1967) Statistical analysis of geomagnetic reversal data and the precision of potassium-argon dating: J. Geophys. Res. 72, No 10, 2603-2614.

Dalrymple, G. B. and Lanphere, M. A. (1969) K-Ar dating: W. H. Freeman, San Francisco, 258 pp.

Eberl, D. D. (1984) Clay mineral formation and transformation in rocks and soils: Phil. Trans. R. Soc. London A311, 241-257.

Elliott, C. W., Aronson, J. L., Matisoff, G., and Gautier, D. L. (1991) Kinetics of the smectite to illite transformation in the Denver basin: Clay mineral, K-Ar data, and mathematical model results: The American Association of Petroleum Geologists 75, No.3, 436-462.

Faure, G. (1986) Principles of Isotope Geology (2nd ed.): John Wiley and Sons, New York, 589 pp.

Gundogdu, M. N., Bonnet-Courtois, C., and Clauer, N. (1989) Isotope and chemical signatures of sedimentary smectite and diagenetic clinoptilolite of lacustrine Neogene basin near Bigadic, Western Turkey: Applied Geochemistry 4, 635-644.

Hay, R. L. (1963) Stratigraphy and zeolites diagenesis of the John Day Formation of Oregon: University of Calif. Publ. Geol. Sci. 42, 199-262.

Iijima, A. (1978) Geological occurrences of zeolites in marine environments: in Natural Zeolites, Occurrences, Properties, Use L. B. Sand and F. A.Mumpton eds., Pergamon Press, Oxford, 175-198.

Koul, S. L., Chdderton, L. T., and Brooks, C. K. (1981) Fission track dating of zeolites: Nature 294, 347-350

Lander, R. H. and Hay, R. L. (1993) Hydrogeologic control on zeolite diagenesis of the White River sequence: Geological Society of America Bulletin 105, 361-376.

Levy, S. S. (1991) Mineralogic alteration history and paleohydrology at Yucca Mountain, Nevada: in Proc. 2nd Annual Int. Conf. on High Level Radioactive Waste Management, Las Vegas, 1991 American Nuclear Society and American Society of Civil Engineers, La Grange, Il and New York, NY, 477-485

Levy, S. S. (1984) Petrology of samples from drill holes USW H-3, H-4, and H-5, Yucca Mountain, Nevada: Los Alamos National Laboratory Report, LA-9706-MS, 77 pp.

Marshall, B. D., Whelan, J. F., Peterman, Z. E., Futa, K., Mahan, S. A., and Stuckless, J. S. (1992) Isotopic studies of fracture coatings at Yucca Mountain, Nevada, U.S.A.:in Proc. of the International Symposium on Water-Rock Interaction-WRI-7 1992, Y. K. Kharaka and A. S. Maest, eds., A.A. Balkema, Rotterdam, 737-740.

Marshall, B. D., Peterman, Z. E., and Stuckless, J. S. (1993) Strontium isotopic evidence for a higher water table at Yucca Mountain: in Proc. 4th Annual Int. Conf. on High Level Radioactive Waste Management, Las Vegas, 1993, American Nuclear Society and American Society of Civil Engineers, La Grange, Il and New York, NY.

Odin, G. S., and 35 collaborators (1982) Interlaboratory standards for dating purposes: in Numerical Dating in Stratigraphy, G. S. Odin, ed., John Wiley and Sons, Ltd., Chichester, 124-150.

Peterman, Z. E., Spengler, R. W., Singer, F. R., and Dickerson, R. P. (1993) Isotopic and trace element variability in altered and unaltered tuffs at Yucca Mountain: in Proc. 4th Annual Int. Conf. on High Level Radioactive Waste Management, Las Vegas, 1993, American Nuclear Society and American Society of Civil Engineers, La Grange, Il and New York, NY, 1940-1947.

Roberts, W. C., Campbell, T. J., and Rapp, G. R. Jr., eds., (1989) Encyclopedia of Minerals, 2nd Ed., Van Nostrand Reinhold Co., New York.

Robison, J. H. (1984) Ground-water level data and preliminary potentiometric-surface maps, Yucca Mountain and vicinity, Nye County, Nevada: U.S. Geological Survey Water-Resources Investigations Report 84-931 22pp.

Sawyer, D. A., Fleck, R. J., Lanphere, M. A., Warren, R. G., and Broxton, D. E. (1990) Episodic volcanism in the Southwest Nevada Volcanic Field: New $^{40}Ar/^{39}Ar$ geochronologic results: EOS, American Geophysical Union Transactions 1296.

Scott, R., and Castellanos, M. (1984) Preliminary report on the geologic character of the drill holes USW GU-3/G-3: U. S.Geological Survey Open-File Report, 84-491, 121 pp.

Sheppard, R. A., Gude, A. J., 3rd, and Fitzpatric, J. J. (1988) Distribution, characterization, and genesis of mordenite in Miocene silicic tuffs at Yucca Mountain, Nye County, Nevada: U. S. Geological Survey Bulletin 1777, 22 pp.

Smyth, J. R. and Caporuscio, F. A. (1981) Review of the thermal stability and cation exchange properties of the zeolites minerals clinoptilolite, mordenite, and analcime: Applications to radioactive waste isolation in Silicic tuffs: Los Alamos National Laboratory Report, LA-8841-MS, 30 pp. (1981).

Spengler, R. W., Byers, F. M., Jr., and Warner, J. B. (1981) Stratigraphy and structure of volcanic rocks in drill hole USW G-1, Yucca Mountain, Nye County, Nevada: U. S. Geological Survey Open-File Report, 81-1349, 50 pp.

Steiger, R. H. and Jager, E. (1977) Subcommission on geochronology: Convention on the use of decay constants in geo- and cosmochronology: Earth and Planetary Science Letters 36, 359-362.

Surdam R. C. and Sheppard, R. A. (1978) Zeolites in saline, alkaline-lake deposits: in Natural Zeolites, Occurrences, Properties, Use L. B. Sand and F. A.Mumpton eds., Pergamon Press, Oxford, 145-174.

Vaniman, D. T. (1993) Calcite deposits in fractures at Yucca Mountain, Nevada: in Proc. 4th Annual Int. Conf. on High Level Radioactive Waste Management, Las Vegas, 1993, American Nuclear Society and American Society of Civil Engineers, La Grange, Il and New York, NY, 1935-1939.

Vaughan, D. E. W. (1978) Properties of natural zeolites: in Natural Zeolites, Occurrences, Properties, Use L. B. Sand and F. A.Mumpton eds., Pergamon Press, Oxford, 353-371.

Whelan, J. F. and Stuckless, J. S. (1992) Paleohydrologic implications of the stable isotopic composition of secondary calcite within the tertiary volcanic rocks of Yucca mountain, Nevada: in Proc. 3rd Annual Int. Conf. on High Level Radioactive Waste Management, Las Vegas, 1992 American Nuclear Society and American Society of Civil Engineers, La Grange, Il and New York, NY, 1572-1581.

WoldeGabriel, G., Broxton, D. E., Bish, D. L., and Chipera. S. J. (1993) Mineralogy and clinoptilolite K/Ar results from Yucca Mountain, Nevada, USA: A potential high-level radioactive waste repository site, Los Alamos National Laboratory Report (in YMSCP review)

WoldeGabriel, G., Broxton, D. E., Bish, D. L., and Chipera. S. J. (1992) Preliminary assessment of clinoptilolite K/Ar results from Yucca mountain, Nevada, USA: A potential high-level radioactive waste repository site: in Proc. of the International Symposium on Water-Rock Interaction-WRI-7 1992, Y. K. Kharaka and A. S. Maest, eds., A.A. Balkema, Rotterdam, 457-461.

WoldeGabriel, G. and Goff, F. (1989) Temporal relations of volcanism and hydrothermal systems in two areas of the Jemez volcanic field, New Mexico: Geology 17, 986-989.

Table 1 Mineralogical and K/Ar analyses of clinoptilolite and mordenite (1-3μm and 2-30μm) and illite/smectite (0.1-0.35μm) fractions from the Yucca Mountain zeolitized tuff units

Stratigraphic Units	Sample I.D.	Depth (m)	Depth to Water Table (m)[1]	Size Fraction (μm)	Authigenic Minerals[2]	Age[3] (Ma,σ[4])
Calico Hills	3-15-82-8	Outcrop	N/A	1-3	C, M, CT	2.6±0.8
Calico Hills	3-15-82-8	"	N/A	1-3	C, M, CT	3.5±0.5
Calico Hills	3-15-82-8	"	N/A	1-3	c, M, CT	3.1±0.6
Calico Hills	3-15-82-8	"	N/A	3-20	C, M, CT	1.5±0.4
Calico Hills	3-15-82-8	"	N/A	3-20	C, M, CT	2.0±0.4
Calico Hills	G-1 1561+6	475.8	571.7	1-3	C, M, CT	3.1±0.5
Calico Hills	G-1 1561+	475.8	"	1-3	C, M, CT	1.9±0.6
Calico hills	G-4 1734.3-1734.6+	528.5	539.5	1-3	C, M, CT	4.8±2.4
Prow Pass	G-1 2190.8-2190.9+	667.5	571.7	1-3	C, M, CT	4.3±1.2
Prow Pass	G-2 3191.5-3192.0+	972.9	524.9	1-3	C, Q, F, I/S	7.0±0.7
Prow Pass	G-2 3250-3325.7	990.6	"	1-3	C, A, Q, F, I/S	13.3±1.4
Prow Pass	G-2 3250-3325.7	990.6	"	0.1-0.35	I/S	12.7±3.0
Prow Pass	G-4 1779.6-1779.9+	542.2	539.5	3-20	C, M, CT	4.1±0.4
Prow Pass	G-4 1779.6-1779.9+	542.2	"	1-3	C, M, CT	4.1±0.3
Prow Pass	UE25P#1 1740-1750+	530.4-545.6	383.9	1-3	C, M, CT	6.0±1.0
Prow Pass	UE25P#1 1790-1800	545.6-548.6	"	1-3	C, M, CT	8.4±0.8
Bullfrog	G-4 2716.5-2716.8	827.8	539.5	1-3	M, Q, F	12.3±0.8
Tram	G-1 3288.5-3288.6+	1002.2	571.7	1-3	C, M, A, Q, F, I/S	10.0±0.4
Tram	G-3 3589+	1094.1	750.3	1-3	C, Q, F, I/S	9.0±0.5
Tram	G-3 3854.7-3854.9	1174.9	"	1-3	C, M, Q, F, I/S	10.4±0.3
Older Tuff (B)	G-1 5458.4-5458.5	1663.6	571.7	1-3	C, Q, F, I/S	12.0±0.9
Older Tuff (B)	G-1 5458.4-5458.5	1663.6	"	0.1-0.35	I/S	8.8±1.0
Older Tuff (C)	G-1 5560	1694.7	"	1-3	C, M, Q, F, I/S	12.3±0.9

[1]Data on water table depth is from Robison, 1984
[2]C = clinoptilolite, M = mordenite, CT = opal-CT, Q = quartz, F = feldspar, I/S = ilite smectite.
[3]Determined from decay constants and isotopic abundance of ^{40}K according to Steiger and Jager, 1977.
[4]Total percentage error
[5]Numbers in paranthesis are % radiogenic Ar
[6]Heavy-liquid treated clinoptilolites.

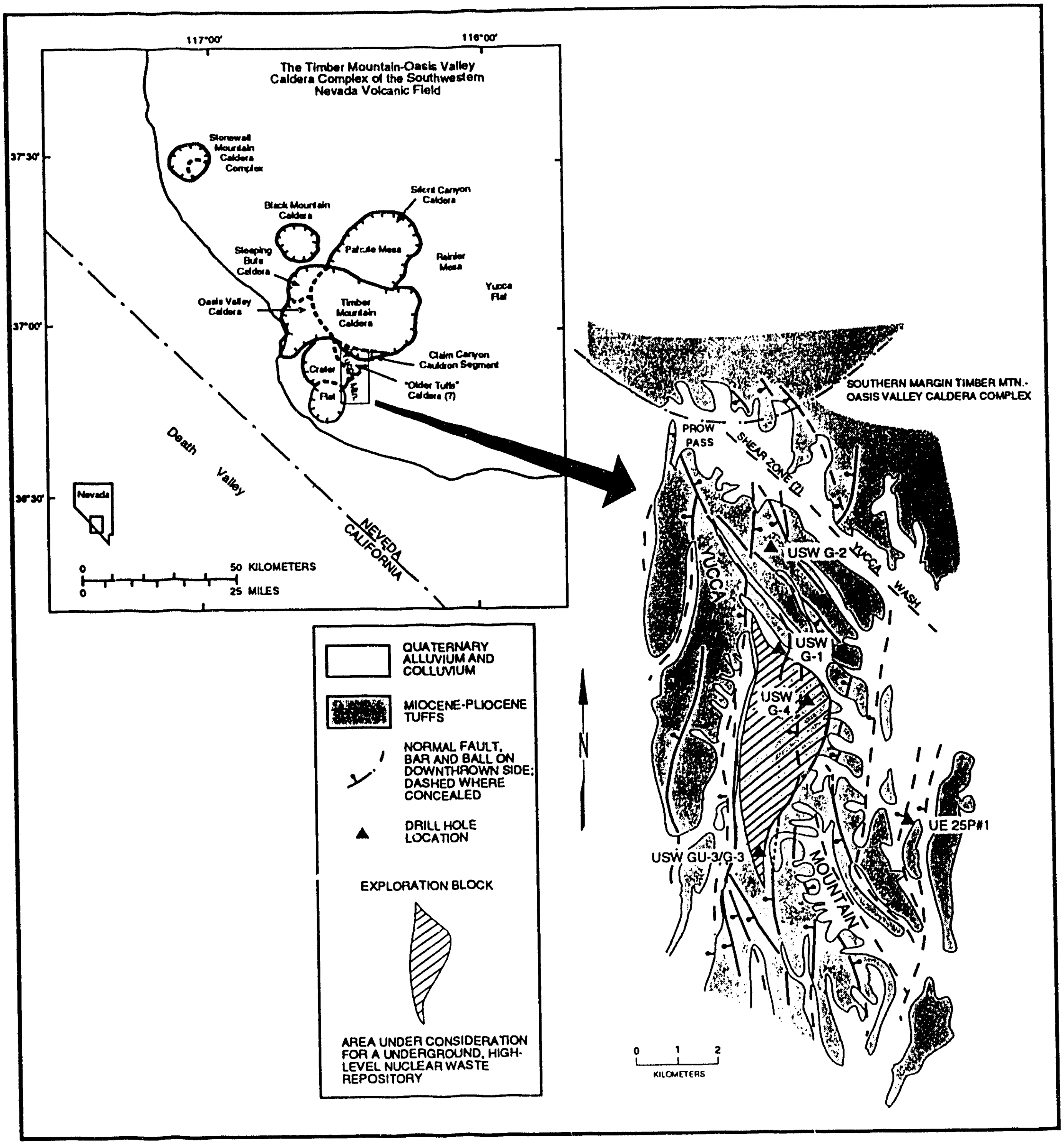

Figure 1. Location map of Yucca Mountain, Nevada. Solid triangles indicate the locations of the exploratory drill holes. Inset map shows the location of Yucca Mountain with reference to the Timber Mountain-Oasis Valley caldera complex (adapted from Scott and Castellanos, 1984).

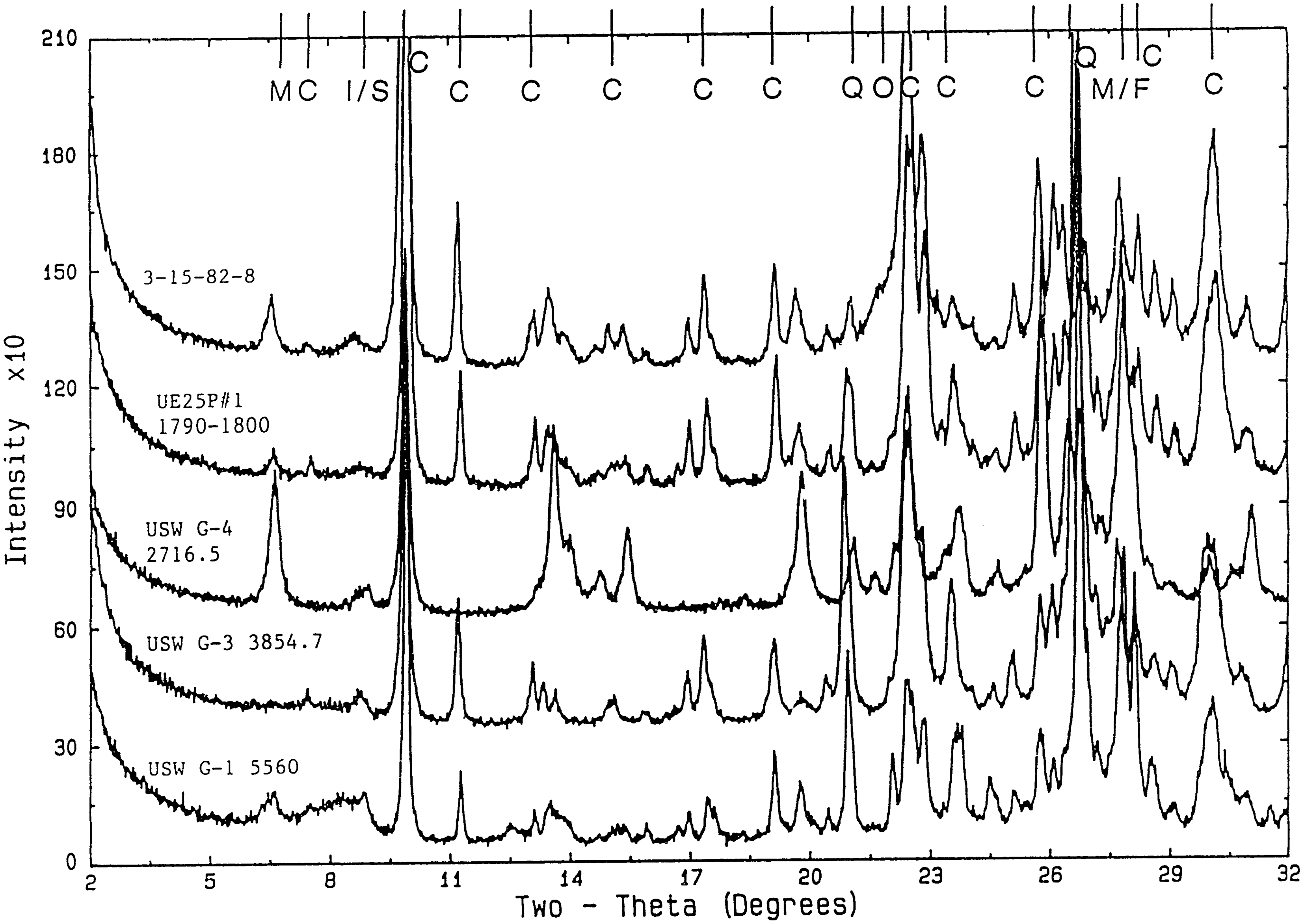

Figure 2. Representative X-ray diffraction patterns of clinoptilolite fractions (1-3μm) from the outcrop (3-15-82-8, Calico Hills Formation), and the drill holes UE-25P #1 (Prow Pass Member), USW G-1 (G-1 5560, Older Tuffs), USW G-3 (G-3 3854.7, Tram Member), and USW G-4 (G-4 2716.5, Bullfrog Member). The patterns represent clinoptilolite (C), mordenite (M), feldspar (F), illite/smectite (I/S), quartz (Q), and opal-CT (O).

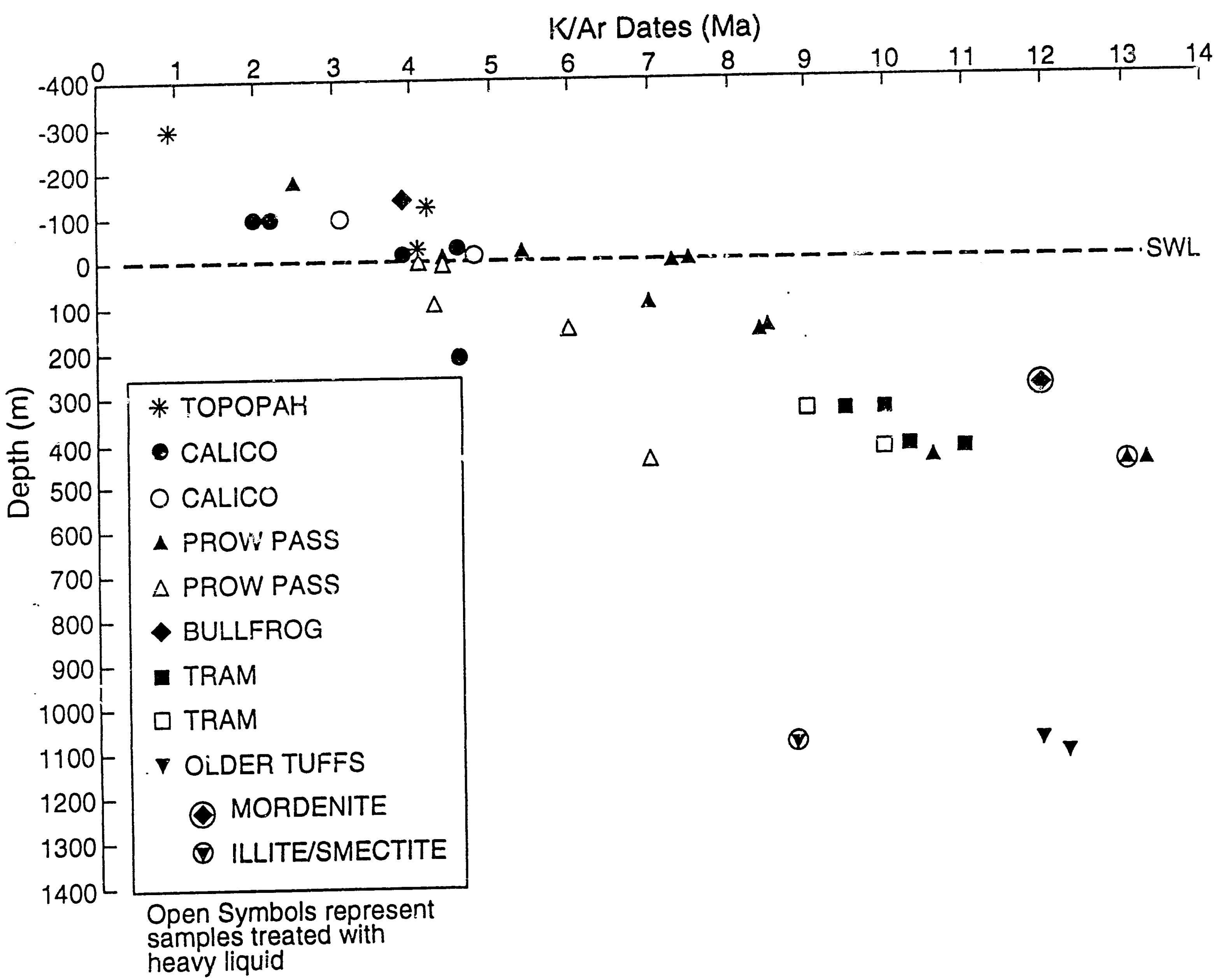

Figure 3. Variation of clinoptilolite, mordenite, and illite/smectite K/Ar dates with reference to the static water level (SWL) in the drill holes. Some samples plot along the saturated-unsaturated transition zone. The units in the box are arranged in stratigraphic order.

DATE

FILMED

9/8/93

END