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Giday WoldeGabriel
David E. Broxton
David L. Bish
Steve J. Chipera

Los Alamos
NATIONAL LABORATORY
Los Alamos, New Mexico 87545

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MINERALOGY AND CLINOPTILOLITE K/AR RESULTS FROM YUCCA MOUNTAIN, NEVADA, USA: A POTENTIAL HIGH-LEVEL RADIOACTIVE WASTE REPOSITORY SITE

by

Giday WoldeGabriel, David E. Broxton, David L. Bish, and Steve J. Chipera

ABSTRACT

The Yucca Mountain Site Characterization Project is investigating Yucca Mountain, Nevada, as a potential site for a high-level nuclear waste repository. An important aspect of this evaluation is to understand the geologic history of the site including the diagenetic processes that are largely responsible for the present-day chemical and physical properties of the altered tuffs. This study evaluates the use of K/Ar geochronology in determining the alteration history of the zeolitized portions of Miocene tuffs at Yucca Mountain. Clinoptilolite is not generally regarded as suitable for dating because of its open structure and large ion-exchange capacity. However, it is the most abundant zeolite at Yucca Mountain and was selected for this study to assess the feasibility of dating the zeolitization process and/or subsequent processes that may have affected the zeolites. In this study we examine the ability of this mineral to retain all or part of its K and radiogenic Ar during diagenesis and evaluate the usefulness of the clinoptilolite K/Ar dates for determining the history of alteration.

Zeolites and associated diagenetic minerals formed by alteration of volcanic glass at Yucca Mountain and other available data suggest that zeolites have subsequently been modified by interactions with groundwater. Preliminary scanning electron microscope (SEM) results suggest that smectites were formed first from the alteration of shards and pyrogenic minerals, followed by the formation of alkali zeolites. Generally, mordenite in the dissolved-shard cavities post-dates clinoptilolite crystals. Authigenic K-feldspar occurs locally in voids on top of smectite ribbons and mordenite fibers.

The preliminary K/Ar dates ranging from 2–13 Ma suggest that the clinoptilolites can retain K and radiogenic Ar. Although the clinoptilolites are contaminated by minor amounts of microcrystalline feldspars, the older K/Ar dates (≥9.0 Ma) are similar to illite/smectite ages (9–12 Ma). The K/Ar dates increase with depth, and samples from below the static water level yield mostly older dates than those from above the water table. The older clinoptilolite dates may reflect primary crystallization ages, whereas the younger dates probably represent Ar loss by diffusion and continued diagenetic reactions of older zeolites with percolating fluids.

Ion-exchange experiments with alkaline solutions significantly reduced the K contents of clinoptilolites, whereas the Ar concentrations were variably affected, thereby generally resulting in older apparent ages. Internal consistency of the clinoptilolite K/Ar results at different levels within the drill holes and the similarity between illite/smectite and some of the clinoptilolite K/Ar dates from the saturated zone suggest that dating of K-rich zeolites may provide useful information for assessing the zeolitization process.

I. INTRODUCTION

The Yucca Mountain Site Characterization Project of the U.S. Department of Energy is conducting multi-disciplinary studies to assess the suitability of Yucca Mountain to host the nation's first high-level radioactive waste repository (U.S.DOE/RW-0160, 1988). Considerable information is now available on the mineralogy and petrology of the altered rocks at the potential repository site (e.g., Vaniman *et al.,* 1984; Broxton *et al.,* 1987; Bish and Chipera, 1989). These data indicate that zeolites and other diagenetic minerals occur in laterally extensive beds throughout the Yucca Mountain area (Broxton *et al.,* 1986, 1987; Bish and Chipera, 1989). The presence of zeolitized tuffs was a major reason for choosing this site; favorable physical and chemical properties of zeolites are important barriers to radionuclide migration (Daniels *et al.,* 1982; Thomas, 1987; Meijer, 1992). This study evaluates the application of the K/Ar method to determine the timing of zeolitization and of subsequent chemical exchange in tuffs at Yucca Mountain. Direct dating of K-rich clinoptilolite, the most abundant zeolite in the altered tuffs, would be the most desirable way to investigate zeolite chronology; however, clinoptilolite is not generally regarded as a suitable mineral for dating by the K/Ar method because of its large ion-exchange capacity and open-framework structure. Therefore, our main objectives in this study are to examine the ability of clinoptilolite to retain all or part of its K and radiogenic Ar, and to evaluate the usefulness of the K/Ar dates from this mineral for determining the history of alteration.

Secondary or authigenic minerals provide information on the temporal and spatial relations of processes that are essential to the understanding of 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 the type and timing of the processes responsible for their formation (e.g., Aronson and Lee, 1986; WoldeGabriel and Goff, 1989). Minerals must retain radiogenic Ar and resist alteration and incorporation of extraneous Ar in order to be useful for K/Ar dating (Dalrymple and Lanphere, 1969; Faure, 1986). These conditions are apparently satisfied by illitic clays. However, there are major structural differences between illitic clays and zeolites that may affect the usefulness of the zeolites as reliable K/Ar clocks. For example, illite/smectite sheet silicates are characterized by lower cation exchange capacity compared with zeolites, which 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).

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 considered unreliable because of contamination by relict minerals and gain of K by the phillipsite in the absence of radiogenic Ar during growth. The 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 caused by induration of the host rock and the 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. Hay (1963, 1978) was able to show that zeolite formation from the alteration of volcanic glass in an open system is relatively rapid. He used authigenic K-feldspar and celadonite to constrain the time of alteration in zeolitized tuff units of the John Day Formation in Oregon. The diagenetic minerals are similar in age to the primary rocks, implying that the alteration occurred soon after the tuffs were deposited.

Clinoptilolites separated from a lacustrine volcaniclastic section of early to middle Miocene age in western Turkey were dated by the K/Ar method and yielded variable apparent ages of 1.0 to 14.3 Ma (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. In contrast to these results, minimal Ar loss was reported during low-temperature dehydration (≤100°C) (Gundogdu *et al.*, 1989) and during surface hydration and heating (Barrer and Vaughan, 1969).

Previous studies have dated illite/smectites and zeolites 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 from the northern part of Yucca Mountain yielded a narrow range of K/Ar results (9–12 Ma) (Aronson and Bish, 1987). The present study expands upon these preliminary K/Ar studies of clays from Yucca Mountain.

II. 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 volcanic sequence is underlain by late Proterozoic and Paleozoic rocks (300–600 Ma) composed of limestone, dolomite, shale, argillite, and quartzite. These pre-Tertiary rocks do not crop out at Yucca Mountain; however, drill hole UE-25P #1,

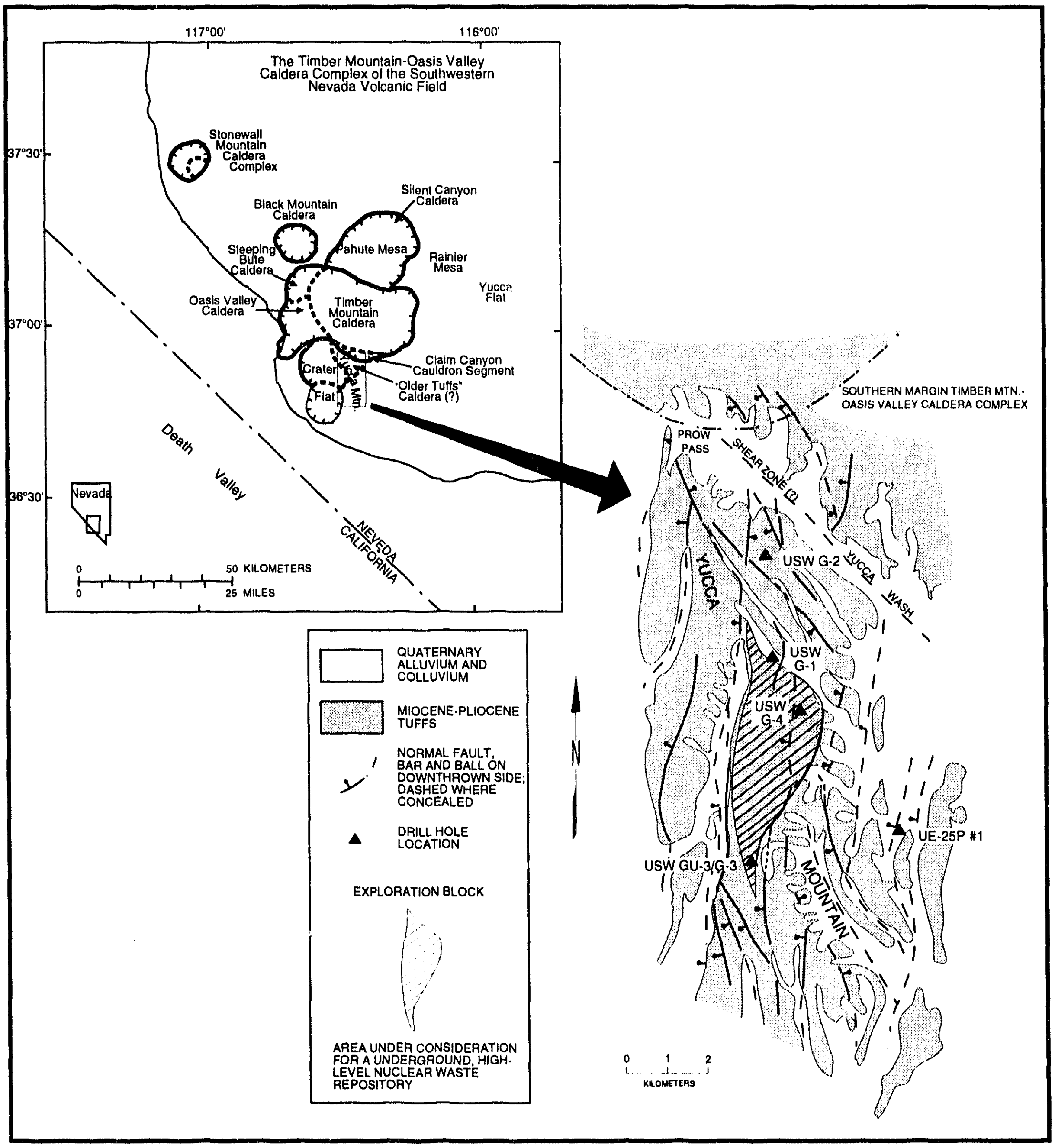

Figure 1. Location map of the Yucca Mountain, Nevada. Solid triangles indicate the locations of the exploratory drill holes. Inset map shows the location of Yucca Mountain with reference to the Timber Mountain-Oasis Valley caldera complex (adapted from Scott and Castellanos, 1984).

located about 3 km southeast of the potential repository (Figs. 1 and 2), penetrated a Paleozoic dolomite sequence below a depth of 1244 m (Carr *et al.,* 1986).

As shown in Figure 2, the volcanic sequence at Yucca Mountain consists of silicic ash-flow tuffs, bedded tuffs, and minor lavas and flow breccias (Spengler *et al.,* 1981; Maldonado and Koether, 1983; Scott and Castellanos, 1984). 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 tuff of Calico Hills (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 altered tuff units at Yucca Mountain are grouped broadly into four diagenetic zones which are defined by authigenic minerals that are progressively less hydrous with depth (Smyth and Caporuscio, 1981; Broxton *et al.,* 1987; Bish and Chipera, 1989). The diagenetic mineral assemblage in Zone I consists of fresh glass with minor smectite, opal, and Ca-rich clinoptilolite and grades downward into Zone II, where the glass is completely replaced by clinoptilolite, mordenite, and opal with minor amounts of K-feldspar, quartz, and smectite. Zone III is characterized by analcime, K-feldspar, quartz, and minor calcite and smectite, whereas the altered tuffs in Zone IV contain albite, K-feldspar, quartz with lesser amounts of calcite, and illite/smectites. The zeolitized tuffs contain minor amounts of smectite (<10% by volume); however, in the deeper levels of USW G-1 and G-2, R1 to $R\geq3$ interstratified illite/smectites are present reflecting the effects of high-temperature (200°C–275°C) hydrothermal alteration of late to middle Miocene age (9–12 Ma) (Bish, 1989). These vertically zoned zeolitized tuff units exemplify alteration in an open chemical system resulting in major mobilization of alkalis and alkaline earths (e.g., Hay, 1963; Hoover, 1968; Walton, 1975; Hay and Sheppard, 1977; Broxton *et al.,* 1987).

According to Levy (1984, 1991), the zeolites and clays at Yucca Mountain formed in three episodes. The earliest episode resulted in the formation of clinoptilolite and opal-CT within the tuff of Calico Hills and the Crater Flat Tuff; this alteration occurred prior to the eruption of the Topopah Spring Member (12.75 Ma). The second episode of alteration was represented by the crystallization of heulandite and smectite within the vitrophyre in the Topopah Spring Member during cooling of the unit. The third episode of alteration was represented by the crystallization of clinoptilolite in the Topopah Spring Member and underlying units in structurally low areas. Based on geopetal structures in the zeolitized tuff units, Levy (1984) suggested that zeolitization processes were completed by about 11.6 Ma. This age is consistent with the timing of "third-episode" zeolitization (12.8–11.6 Ma) constrained from stratigraphic

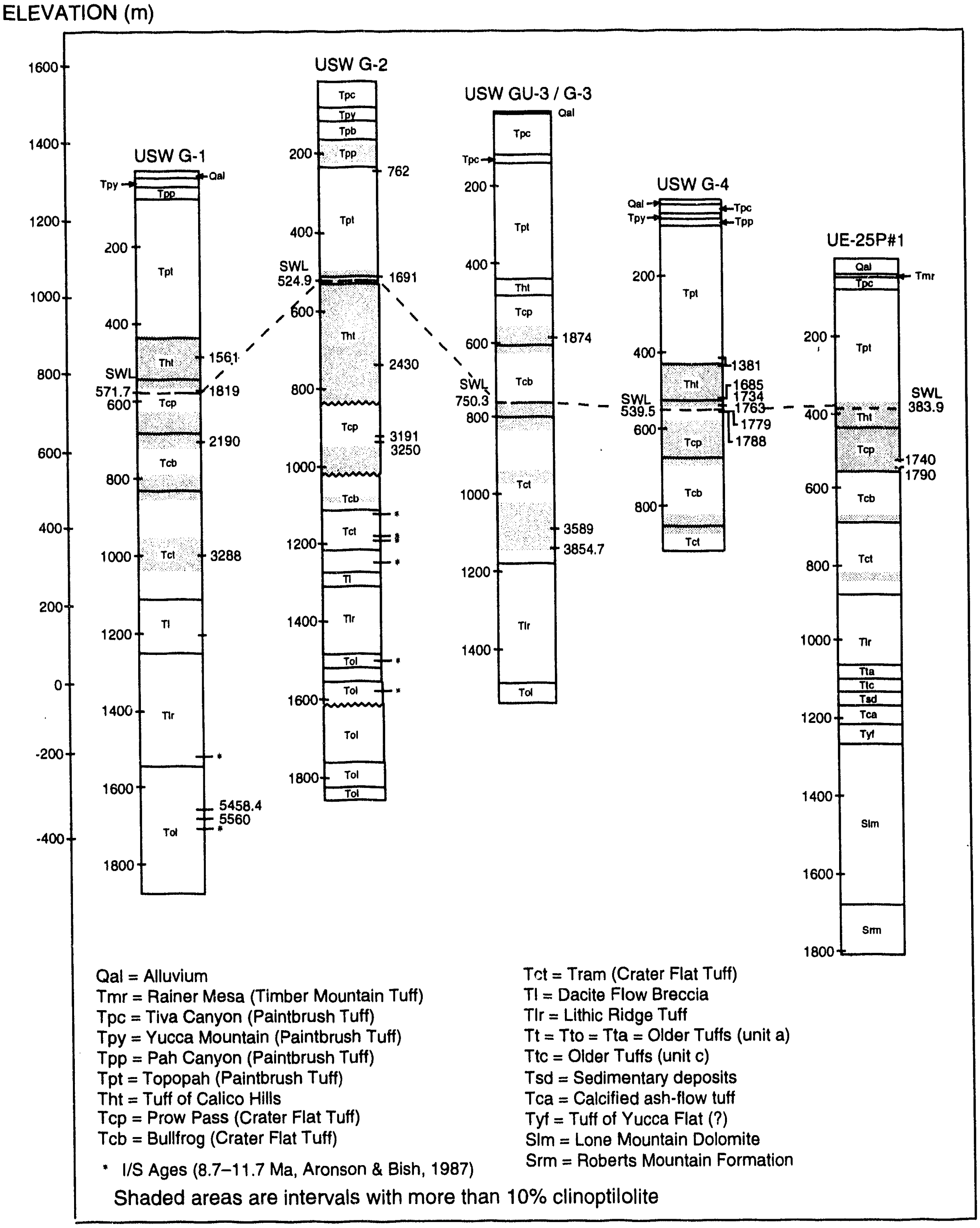

Figure 2. Stratigraphy of the Yucca Mountain exploratory drill holes (Maldonado and Koether, 1983; Scott and Castellanos, 1984; Spengler and Chornack, 1984; Caporuscio *et al.,* 1982; Carr *et al.,* 1986). Shaded areas are intervals with more than 10% clinoptilolite (Bish and Chipera, 1989). The locations of the drill holes are indicated in Figure 1. Numbers on the left and right sides of the columns represent depth in meters and sample locations in feet, respectively. Static water level (SWL) depths are in meters (Robison, 1984).

and structural relations of the altered Yucca Mountain tuff sequence, although the two lines of evidence are not entirely independent (Levy, 1991).

III. ANALYTICAL METHODS

Two outcrop samples from areas north and northeast of Yucca Mountain and 26 core samples and one cutting from five drill holes in the vicinity of the exploration block were selected for study. Although clinoptilolite-rich altered tuffs were selected for this study, all samples contained ≥30% clinoptilolite in the original bulk sample (Bish and Chipera, 1989); most of the nonzeolitic minerals were removed by sedimentation in water and/or by organic heavy-liquid separation as described below. 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. The approach of the present study is as follows:

(1) Highly zeolitized core samples were selected for dating from levels above and below the static water level; emphasis was placed on selection of samples just above and below the static water level. Outcrop samples of zeolitized tuff of Calico Hills were also selected for study. Selected samples were analyzed by scanning electron microscope (SEM) to examine paragenetic relations among the alteration minerals.

(2) Diagenetic minerals were separated into different size fractions by sedimentation in deionized water and using organic heavy liquid and centrifugation. The mineralogy of these separates was characterized using X-ray diffraction (XRD) analysis.

(3) Ion-exchange experiments were performed on selected clinoptilolites to evaluate the effects of such processes on the apparent ages of the zeolites.

(4) Selected diagenetic minerals (e.g., clinoptilolite) were dated using the K/Ar method after thorough cleaning by dialysis in deionized water.

(5) The results of age determinations were assessed, and the suitability of alkali zeolites for use in dating of alteration processes at Yucca Mountain was evaluated.

A. Clinoptilolite Separations

The zeolitized tuff samples were crushed and pulverized after which the zeolite was purified or extracted by sedimentation in deionized water (Chipera and Bish, 1989). During mineral separations, the diagenetic and fine-grained primary minerals were concentrated in the finer fractions (1–3 and 3–20 μm). Additional purification 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. The clinoptilolite-rich light fractions (e.g., <2.2 g/cm^3) from the heavy-liquid separations contain mordenite in addition to minor amounts of opal-CT, cristobalite, clays, and finely crystalline quartz and feldspars as indicated using XRD analysis. Because clinoptilolite and mordenite have similar densities, no attempt was made to separate them from each other. The clinoptilolite fractions enriched by heavy-liquid separations were thoroughly cleaned (up to 10 times) in acetone using magnetic stirrers and an ultrasonic probe and followed by centrifugation each time. This cleaning is essential because, if samples are not cleaned properly, the Ar-40 signal in mass spectrometry may be masked by hydrocarbons from the heavy liquid (Bernat *et al.,* 1970). Generally, this should not be a problem because the argon is cleaned by hot getter that react with all elements except for the noble gases during extraction in the K/Ar system.

Because clinoptilolite is characterized by open structure and large ion-exchange capacity, the effects of the organic heavy liquid and acetone treatments on the Ar and K contents during mineral separations and cleaning were evaluated by dating treated and untreated aliquots of two fairly pure tuff of Calico Hills clinoptilolite fractions from the unsaturated zone of USW G-1 (G-1 1561) and G-4 (G-4 1734.3–1734.6). Seven other samples were treated with heavy liquid to remove quartz, feldspar, and other contaminants from the clinoptilolites.

B. Ion-Exchange Experiments

Clinoptilolites are highly selective for Cs, Sr, Ba, K, Ca, Na, etc. (Ames, 1961; Bish, 1988) and may scavenge these cations from ground waters. Neutron activation analyses of smectite- and zeolite-rich Yucca Mountain tuffs indicate the presence of higher amounts of Cs, Sr, and Ba compared with the unaltered vitric tuffs (Broxton *et al.,* 1986). Moreover, water samples from wells at Yucca Mountain contain variable amounts of alkaline and alkaline earth cations (Benson *et al.,* 1983) that can exchange with the zeolites. The effect of cation exchange on K and Ar in clinoptilolite was evaluated by dating ion-exchanged samples. Removal or addition of K without a similar effect on the radiogenic Ar will tend to increase or decrease the apparent ages of the dated clinoptilolites, respectively. In most cases, Ar loss or gain causes greater variation in the apparent ages of samples than K variability. The effect of cation exchange on the clinoptilolites was investigated by treating selected samples with 1 M NaCl, CsCl, and $BaCl_2$ solutions. During the exchange experiment, the alkaline solutions were mixed with splits of clinoptilolites (1–3 µm) and continuously agitated by magnetic stirrer and heated to about 50°C in a water bath for 48 and 72 hours. A new batch of solution was added every 24 hours after the older solution was removed by centrifugation.

Splits of G-2 762 from the Topopah Spring Member of the Paintbrush Tuff were exchanged with 1 M NaCl and CsCl solutions for 72 hours. Fractions of the Prow Pass sample (G-1 1819) were also exchanged with 1 M NaCl and $BaCl_2$ solutions for both 48 and 72 hours.

C. X-Ray Diffraction Analysis

Different size fractions were analyzed using 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 X-ray patterns were used to identify the zeolites and associated alteration minerals. The non-zeolite minerals are enriched in the coarser fractions (>3 μm) and the clays are present in the finer separates (<1 μm). Splits of the 1–3 μm clinoptilolite fraction were heated at 450°C for 12 hours to distinguish between heulandite and clinoptilolite (Mumpton, 1960). Representative X-ray patterns of the dated clinoptilolites from the various units are included in the presentation.

D. K/Ar Dating

About 130 to 200 mg of clinoptilolite fractions (1–3 and 3–20 μm) were used for Ar extraction. The K/Ar system was prebaked for about 12 hours after loading the samples. During the prebaking, the samples were covered and cooled using a copper coil with continuous running water. 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 19.3×10^{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 greater than can be explained by analytical error alone.

IV. ANALYTICAL RESULTS

Mineralogic analyses of purified clinoptilolite fractions are presented in Table I. 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 and analcime. The randomly interstratified illite/smectite clays contain ≤10% illite layers and are therefore low in K. Mordenite, opal-CT, cristobalite, quartz, and feldspar are the common impurities in these mineral separates; of these, the K-bearing phases such as mordenite and feldspar can have a significant effect on the determined dates. The X-ray patterns of the clinoptilolites were not affected after heating the separates at 450°C for 12 hours, suggesting the absence of heulandite in the dated samples. Table II summarizes the K/Ar results for the clinoptilolite fractions separated by sedimentation in deionized water, and the apparent ages of clinoptilolite fractions before and after heavy-liquid separations are presented in Table III. The dating results of the clinoptilolites exchanged with the chloride solutions are given in Table IV. The analytical data are presented in descending stratigraphic order starting with the Topopah Spring Member of the Paintbrush Tuff as shown in Figure 2.

A. Topopah Spring Member

1. Alteration Minerals. 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. The shallowest sample (G-2 762) is from nonwelded tuff at the top of the unit and is dominated by clinoptilolite except for minor amounts of opal-CT in the finer fraction (1–3 µm) (Fig. 3 and Table I). Portions of this sample were exchanged with $BaCl_2$ and CsCl solutions for 72 hours with no apparent variations in the XRD patterns.

The zeolite separates from nonwelded tuffs in the lower part of the Topopah Spring Member (e.g., G-2 1691–1691.5) are dominated by clinoptilolite and contain trace amounts of mordenite, opal-CT, cristobalite, feldspar, and illite/smectite (<5% illite layers). Most of the clinoptilolite is concentrated in the 1–3 µm fraction along with minor amounts of mordenite and opal-CT (Fig. 3 and Table I). Similar authigenic mineral assemblages are present in sample G-4 1381 from the lower part of the Topopah Spring Member in USW G-4 except that mordenite is absent.

2. K/Ar Data. The clinoptilolite K/Ar dates increase with depth within the Topopah Spring Member from a sample (USW G-2 762) with insignificant amount of radiogenic Ar to 4.2 Ma (Table II). The clinoptilolite separate from G-2 762 is from a zone of Ca-rich zeolite tuff from the nonwelded top of

Table I. Mineralogical assemblages separated from altered Yucca Mountain tuff units. Clinoptilolite is the dominant (≥75) mineral except for quartz in some of the deeper samples. CPT = clinoptilolite, MOR = mordenite, I/S = illite/smectite, FEL = feldspar, and ANL = analcime.

Sample ID	Stratigraphic Units	Depth (m)	Size Fraction (µm)	Authigenic* Minerals
3-15-82-8	Calico Hills	outcrop	1–3	CPT, MOR, opal-CT
3-15-82-8	Calico Hills	outcrop	3–20	CPT, MOR, opal-CT
82FB-4	Calico Hills	outcrop	3–20	CPT, MOR, opal-CT
USW G-1 1561	Calico Hills	475.8	1–3	CPT, MOR, opal-CT
USW G-1 1819	Prow Pass	554.4	1–3	CPT, MOR, opal-CT, quartz
USW G-1 2190.8–2190.0	Prow Pass	667.5	1–3	CPT, MOR, FEL, opal-CT, quartz
USW G-1 3288.5–3288.6	Tram	1002.2	1–3	CPT, MOR, quartz, FEL, ANL, I/S
USW G-1 5458.4–5458.5	Tuff (Unit B)	1663.6	1–3	CPT, quartz, FEL, I/S
USW G-1 5560	Tuff (Unit C)	1694.7	1–3	CPT, MOR, quartz, I/S, FEL
USW G-2 762	Topopah Spring	232.2	1–3	CPT, opal-CT
USW G-2 2430	Calico Hills	740.7	1–3	CPT, MOR, opal-CT,I/S, FEL
USW G-2 1691–1691.5	Topopah Spring	515.5	1–3	CPT, MOR, opal-CT
USW G-2 3191.5–3192.0	Prow Pass	972.9	1–3	CPT, quartz, FEL, I/S
USW G-2 3250–3250.7	Prow Pass	990.6	1–3	CPT, ANL, MOR, quartz, FEL, I/S
USW GU-3 1874	Prow Pass	571.2	1–3	CPT, opal-CT
USW G-3 2013.1–2013.4	Bullfrog	613.6	1–3	CPT, opal-CT
USW G-3 3589	Tram	1094.1	1–3	CPT, quartz, FEL, I/S
USW G-3 3854.7–3854.9	Tram	1174.9	1–3	CPT, FEL, MOR, quartz, I/S
USW G-4 1381	Topopah Spring	420.9	1–3	CPT, opal-CT
USW G-4 1685.2–1685.4	Calico Hills	513.6	1–3	CPT, opal-CT
USW G-4 1734.3–1734.6	Calico Hills	528.5	1–3	CPT, MOR, opal-CT
USW G-4 1763.2–1763.5	Prow Pass	537.4	1–3	CPT, opal-CT, MOR, FEL, quartz
USW G-4 1779.6–1779.9	Prow Pass	542.2	1–3	CPT, opal-CT, MOR, FEL, quartz
USW G-4 1788.4–1788.7	Prow Pass	545	1–3	CPT, opal-CT, FEL, quartz
UE-25P#1 1740–1750	Prow Pass	530.4	1–3	CPT, opal-CT, MOR, FEL
UE-25P#1 1790–1800	Prow Pass	545.6–548.6	1–3	CPT, MOR, opal-CT

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* Most of the feldspar and quartz are primary.

Table II. K/Ar analyses of clinoptilolite (1–3 µm and 3–20 µm) fractions from the Yucca Mountain zeolitized tuff units. The stratigraphic sequence is represented by the Topopah Spring Member of the Paintbrush Tuff, the tuff of Calico Hills, the Prow Pass, the Bullfrog, and the Tram Members of the Crater Flat Tuff, and the Older Tuffs in descending order.

Sample ID	Depth (m)	Stratigraphic Unit	Depth to Water Table* (m)	Size Fraction (µm)	Weight (g)	K_2O Wt.%	^{40}Ar§ (10^{-11} mol/g)	^{40}Ar§ (%)	Age† (m.y., σ)
3-15-82-8	Outcrop	Calico Hills	**	1–3	0.1599	5.49	2.0271	8	2.6±0.8
3-15-82-8	"	"	"	1–3	0.1677	6.13	3.1094	15	3.5±0.5
3-15-82-8	"	"	"	3–20	0.1685	5.83	1.6997	10	2.0±0.4
3-15-82-8	"	"	"	3–20	0.1765	5.47	1.1439	8	1.5±0.4
USW G-1 5458.4–5458.5	1663.6	Older Tuffs	571.7	1–3	0.1837	3.58	6.1866	22	12.0±0.9
USW G-1 5560	1694.7	"	"	1–3	0.1653	3.25	5.7686	23	12.3±0.9
USW G-2 1691–1691.5	515.4	Topopah Spring	524.9	1–3	0.1548	4.13	2.3731	10	4.0±0.7
USW G-2 2430	740.7	Calico Hills	"	1–3	0.1672	3.47	2.2875	17	4.6±0.5
USW G-2 3250–3325.7	990.6	Prow Pass	"	1–3	0.1925	1.64	3.1446	17	13.3±1.0
USW GU-3 1874	571.2	"	750.3	1–3	0.1697	3.99	1.4002	8	2.4±0.6
USW GU-3 2013.15–2013.4	613.6	Bullfrog	"	1–3	0.1573	4.64	2.5681	19	3.8±0.3
USW G-3 3854.7–3854.9	1174.9	Tram	"	1–3	0.1664	4.02	6.0061	45	10.4±0.3
USW G-4 1381	420.9	Topopah Spring	539.5	1–3	0.1895	4.79	2.8756	9	4.2±0.9
USW G-4 1685.2–1685.4	513.6	Calico Hills	"	1–3	0.1560	5.42	3.5271	22	4.5±0.3
USW G-4 1788.4–1788.7	545.2	Prow Pass	"	1–3	0.1629	6.85	7.1259	34	7.2±0.3
UE-25P#1 1740–1750	530.4-545.6	"	383.9	1–3	0.1527	4.72	5.6841	18	8.4±0.8
UE-25P#1 1790–1800	545.6-548.6	"	"	1–3	0.1803	3.24	3.9166	19	8.4±0.8

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§ Radiogenic
† Determined from decay constants and isotopic abundance of ^{40}K according to Steiger and Jager, 1977
* Data on water table depth from surface are from Robison, 1984.
** Depth to water table not known
σ Total percentage error

Table III. K/Ar analyses of clinoptilolite (1–3 μm and 3–20 μm) fractions from the Yucca Mountain zeolitized tuff units before and after heavy-liquid treatment.

Sample ID	Depth (m)	Stratigraphic Unit	Depth to Water Table[#] (m)	Size Fraction (μm)	Weight (g)	K_2O Wt.%	^{40}Ar[§] (10^{-11} mol/g)	^{40}Ar[§] (%)	Age[†] (m.y., σ)
USW G-1 1561	475.8	Calico Hills	571.7	1–3	0.1254	4.96	1.5677	8	2.2±0.6
USW G-1 1561	475.8	"	"	1–3	0.1340	4.96	1.4006	10	2.0±0.4
USW G-1 1561[+]	475.8	"	"	1–3	0.1349	4.99	2.2210	15	3.1±0.4
USW G-1 1561[+]	475.8	"	"	1–3	0.1628	4.87	1.3491	7	1.9±0.6
USW G-1 2190.8–2190.9	667.5	Prow Pass Member	"	1–3	0.1760	4.86	4.7995	26	6.9±0.4
USW G-1 2190.8–2190.9[+]	667.5	"	"	1-3	0.1372	4.38	2.7158	7	4.3±1.0
USW G-1 3288.5–3288.6	1002.2	Tram Member	"	1–3	0.1535	4.85	7.3396	35	10.5±0.4
USW G-1 3288.5–3288.6[+]	1002.2	"	"	1–3	0.1301	4.64	6.7043	35	10.0±0.4
USW G-2 3191.5–3192.0	972.9	Prow Pass Member	524.9	1–3	0.1500	3.73	5.6058	27	10.4±0.6
USW G-2 3191.5–3192.0[+]	972.9	"	"	1–3	0.0524	2.30	2.3145	20	7.0±0.7
USW G-3 3589	1094.1	Tram Member	750.3	1–3	0.1569	6.12	8.2727	33	9.9±0.5
USW G-3 3589	1094.1	"	"	1–3	0.1800	5.66	8.0722	44	10.0±0.3
USW G-3 3589[+]	1094.1	"	"	1–3	0.0714	5.10	6.6200	29	9.0±0.5
USW G-4 1734.3–1734.6	528.5	Calico Hills	539.5	1–3	0.1548	3.28	1.8338	5	3.8±1.0
USW G-4 1734.3–1734.6[+]	528.5	"	"	1–3	0.1467	3.29	2.2847	4	4.8±2.0
USW G-4 1763.2–1763.5	537.4	Prow Pass Member	"	1–3	0.1572	3.09	1.9400	10	4.4±0.8
USW G-4 1779.6–1779.9	542.2	"	"	1–3	0.1623	7.13	7.6142	43	7.4±0.2
USW G-4 1779.6–1779.9[+]	542.2	"	"	3–20	0.1744	4.34	2.7582	24	4.4±0.3
USW G-4 1779.6–1779.9[+]	542.2	"	"	1–3	0.1721	4.30	2.5421	18	4.1±0.4
UE-25P#1 1740–1750[+]	530.4–545.6	"	383.9	3–20	0.2141	2.60	2.2415	11	6.0±1.0

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§ Radiogenic
† Determined from decay constants and isotopic abundance of ^{40}K according to Steiger and Jager, 1977
\+ Heavy-liquid treated
\# Data on water table depth are from Robison, 1984.
σ Total percentage error

Table IV. K/Ar analyses of cation-exchanged clinoptilolite (1–3 μm) fractions from the Yucca Mountain zeolitized tuff unit.

Sample ID	Depth (m)	Stratigraphic Unit	Depth to Water Table# (m)	Size Fraction (μm)	Weight (g)	K_2O Wt.%	^{40}Ar§ (10^{-11} mol/g)	^{40}Ar§ (%)	Age† (m.y., σ)
USW G-1 1819	554.4	Prow Pass	571.7	1–3	0.1961	4.91	3.7616	18	5.3±0.5
USW G-1 1819-NaCl, 48 hr.	554.4	"	"	1–3	0.1532	3.55	3.5081	19	6.9±0.6
USW G-1 1819-$BaCl_2$, 48 hr.	554.4	"	"	1–3	0.1540	3.20	3.4008	16	7.4±0.8
USW G-1 1819-$BaCl_2$, 72 hr.	554.4	"	"	1–3	0.1708	3.97	4.7366	20	8.3±0.7
USW G-1 1819-CsCl, 72 hr.	554.4	"	"	1–3	0.2439	3.63	4.5633	14	8.7±1.0

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§ Radiogenic

† Determined from decay constants and isotopic abundance of ^{40}K according to Steiger and Jager, 1977

\# Data on water table depth are from Robison, 1984.

σ Total percentage error

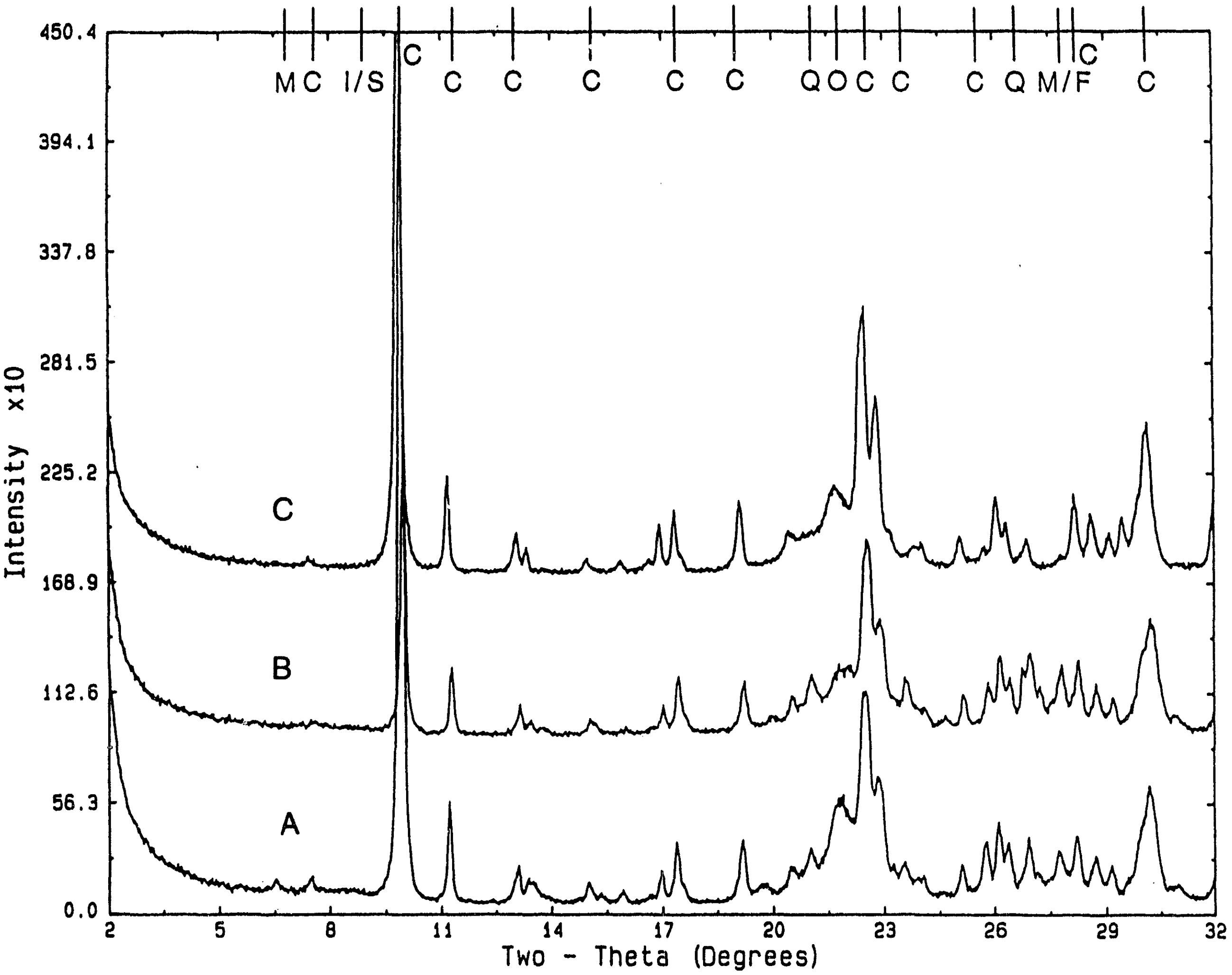


Figure 3. Representative X-ray diffraction patterns of clinoptilolite fractions (1–3 µm) from the unsaturated zone of the Topopah Spring Member of the Paintbrush Tuff. The patterns represent clinoptilolite (C), mordenite (M), feldspar (F), and opal-CT (O). A = G-2 1691, B = G-4 1381, and C = G-2 762.

the unit. This Ca-rich zone of zeolitic alteration extends upward into the overlying Pah Canyon Member and represents a local zone of alteration in diagenetic Zone I (Broxton *et al.*, 1987). This sample has a low K content (1.99 wt %) and is loaded with atmospheric Ar (>99%); the K/Ar date is not reliable. Although the amount of K was significantly reduced in the NaCl- and CsCl-exchanged fractions, the exchanged aliquots did not have enough radiogenic Ar to calculate apparent ages.

Two samples from the lower part of the Topopah Spring Member belong to the upper part of diagenetic Zone II, the zone of pervasive zeolitic alteration. The samples, obtained from drill holes that are about 4 km apart, yielded similar apparent ages of 4.1 Ma (G-2 1691–1691.5) and 4.2 Ma (G-4 1381) (Table II).

B. Tuff of Calico Hills

1. Alteration Minerals. Clinoptilolite fractions were separated from several zeolitized surface and subsurface samples of the tuff of Calico Hills at Yucca Mountain and vicinity. The alteration mineral assemblages are typical of diagenetic Zone II. Clinoptilolite fractions were separated from samples 3-15-82-8 (1–3 µm and 3–20 µm) and 82FB-4 (3–20 µm) of zeolitized tuff of Calico Hills obtained from outcrops at and north of Prow Pass at the northern end of Yucca Mountain (Fig. 1). The samples contain abundant clinoptilolite and mordenite with trace amounts of opal-CT (Fig. 4 and Table I). The clinoptilolites from outcrop samples are K-rich (≥5 wt % K_2O) compared with similar minerals obtained from the drill holes (Table II). SEM examinations of both surface samples indicate the occurrence of abundant mordenite associated with and draping clinoptilolite crystals (Figs. 5a and 5b).

Clinoptilolite with trace amounts of mordenite and opal-CT are present in G-1 1561 from the unsaturated zone of drill hole USW G-1, whereas a correlative sample from the saturated zone of USW G-2 (G-2 2430) is dominated by clinoptilolite with mordenite and traces of opal-CT, feldspar, and illite/smectite (<5% illite layers) (Figs. 4, 5c, and 5d). Clinoptilolite with minor amounts of mordenite and opal-CT are present in the 1–3 µm fraction. The alteration minerals from the tuff of Calico Hills in the unsaturated zone of USW G-4 (G-4 1685.2 and G-4 1734.3–1734.6) are dominated by clinoptilolite with some mordenite and opal-CT (Fig. 4 and Table I). The surface samples contain more mordenite than the correlative drill hole samples selected for this study (Fig. 4).

2. K/Ar Data. The K/Ar results for the size fractions of surface sample 3-15-82-8 are variable, with dates of 2.6 Ma and 1.5 Ma obtained on the finer (1–3 µm) and coarser (3–20 µm) fractions, respectively. The K_2O contents in the finer (1–3 µm) and coarser (3–20 µm) fractions are similar. Repeat analyses of

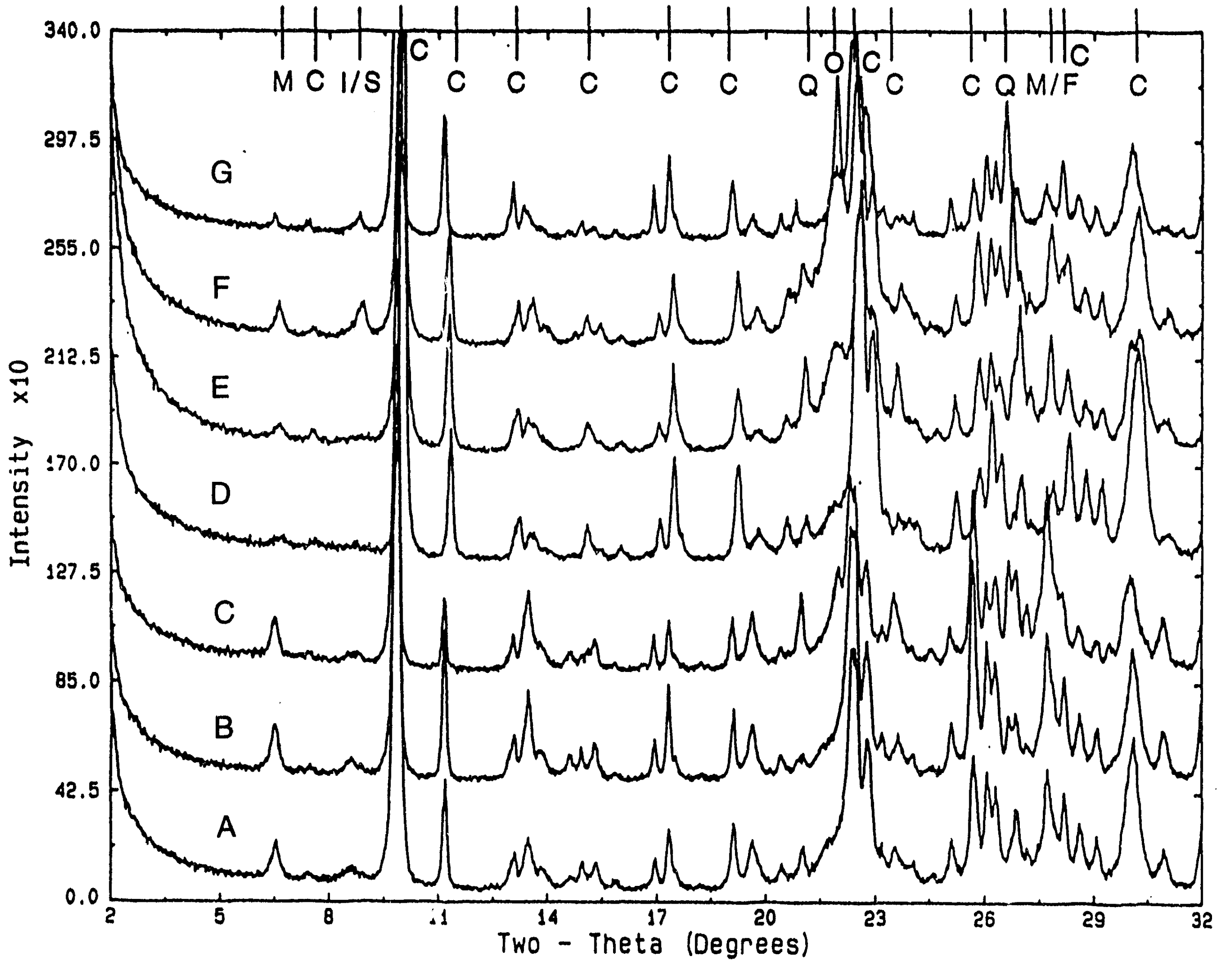


Figure 4. Representative X-ray diffraction patterns of clinoptilolite fractions (1–3 μm) from the unsaturated and saturated (G-2 2430) zones of the tuff of Calico Hills. The samples are from the outcrop (A = 3-15-82-8 [1–3 μm] B = 3-15-82-8 [3–20 μm], and C = 82FB-4) and drill holes (D = G-1 1561, E = G-4 1685.2–1685.4, F = G-4 1734.3–1734.6, and G = G-2 2430). The patterns represent clinoptilolite (C), feldspar (F), mordenite (M), opal-CT (O), and quartz (Q).

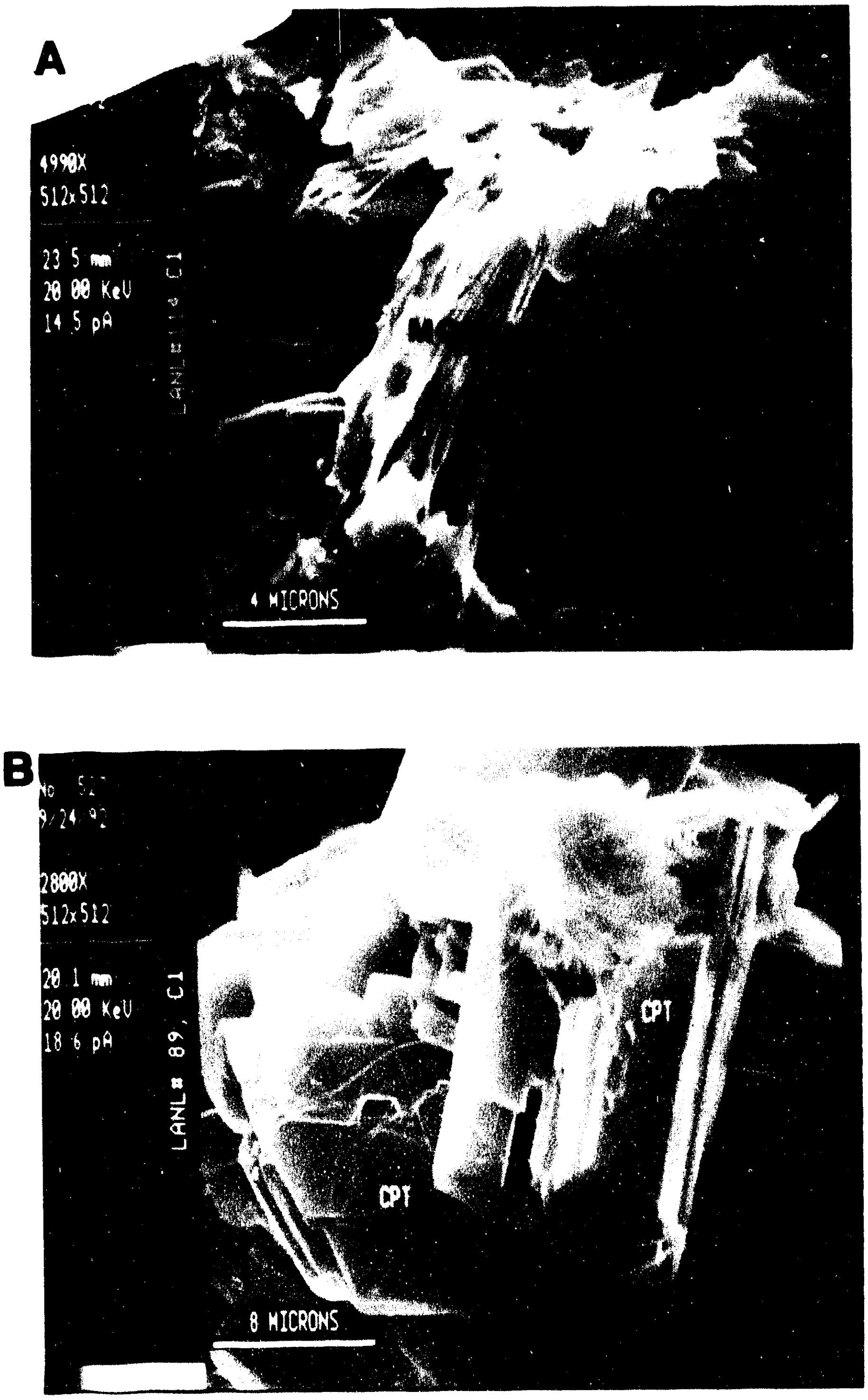


Figure 5. Representative SEM images of tuff of Calico Hill samples from outcrops (A = 82FB-4 = LANL#114, C1; and B = 3-15-82-8 = LANL#89, C1) and drill holes (C and D = USW G-2 2430). The samples contain abundant mordenite fibers in close association with euhedral clinoptilolites.

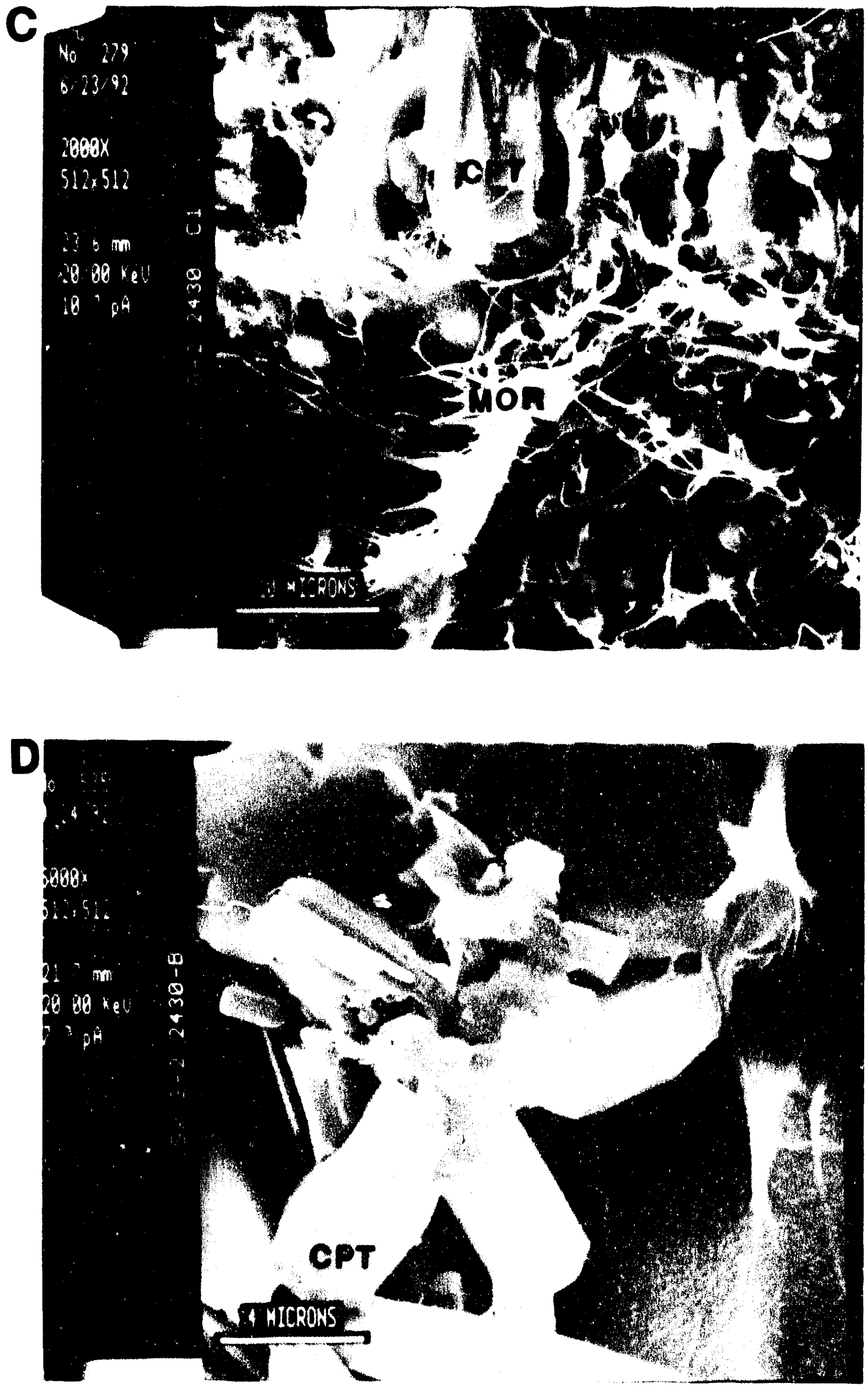


Figure 5. (Continued)

these two fractions showed higher K_2O and radiogenic Ar contents and yielded older dates of 3.5 Ma (1–3 µm) and 2.0 Ma (3–20 µm).

The K/Ar dates from the tuff of Calico Hills in each drill hole generally increase with depth. Duplicate analyses of sample G-1 1561, a zeolitic tuff 97 m above the static water level, yielded similar dates of 2.0 and 2.2 Ma. The heavy-liquid treated aliquot yielded an older date (3.1 Ma), but the result (2.1 Ma) of a repeat analysis is similar to the apparent age of the untreated fraction (Table III).

C. Prow Pass Member

1. Alteration Minerals. Ten samples of zeolitic Prow Pass tuff from 5 drill holes were processed in this study. All of the samples investigated are from diagenetic Zone II and contain abundant altered shards that are totally replaced by clinoptilolite and mordenite (Fig. 6). The samples were obtained from the unsaturated and saturated zones of UE-25P#1 and USW G-1, G-2, GU-3, and G-4. Representative XRD patterns from the unsaturated- and saturated-zone samples are given in Figure 7.

Samples prepared by both sedimentation and heavy-liquid mineral separation were dated using the K/Ar method. The two samples from USW G-1 are from above (G-1 1819) and below (G-1 2190.8–2190.9) the static water level. Both contain similar alteration minerals of clinoptilolite and mordenite with traces of opal-CT and quartz (Table I). The amount of mordenite associated with clinoptilolite is much higher in G-1 1819 (unsaturated zone) than in the underlying sample G-1 2190.8–2190.9 from the saturated zone. Unlike G-1 1819, minor amounts of finely crystalline feldspar are present in G-1 2190.8–2190.9. XRD patterns of ion-exchanged clinoptilolite fractions of G-1 1819 are similar to the untreated sample except for the reduced mordenite peak intensity from the $BaCl_2$ exchange (Fig. 8).

Two samples of clinoptilolite-rich tuff from the lower part of the Prow Pass Member in USW G-2 (G-2 3191.5–3192 and G-2 3250.5–3250.7) were also studied. Clinoptilolite with minor amounts of quartz, feldspar, and illite/smectite (<10% illite layers) is present in the 1–3 µm fraction of both samples. G-2 3250.5–3250.7 also contains mordenite and analcime. SEM images of G-2 3250.5–3250.7 indicate abundant smectite, clinoptilolite, and mordenite in the matrix and altered shards. Based on grain relations, the crystallization sequence for the authigenic minerals is smectite, clinoptilolite, mordenite, and analcime (Fig. 6b).

The clinoptilolite separate (1–3 µm) from GU-3 1874 contains minor amounts of opal-CT, whereas other samples from the same unit in USW G-4 (G-4 1763.2–1763.5, G-4 1779.6–1779-9, and G-4 1788.4–1788.7) have quartz and feldspar as trace components in addition to clinoptilolite, mordenite, and

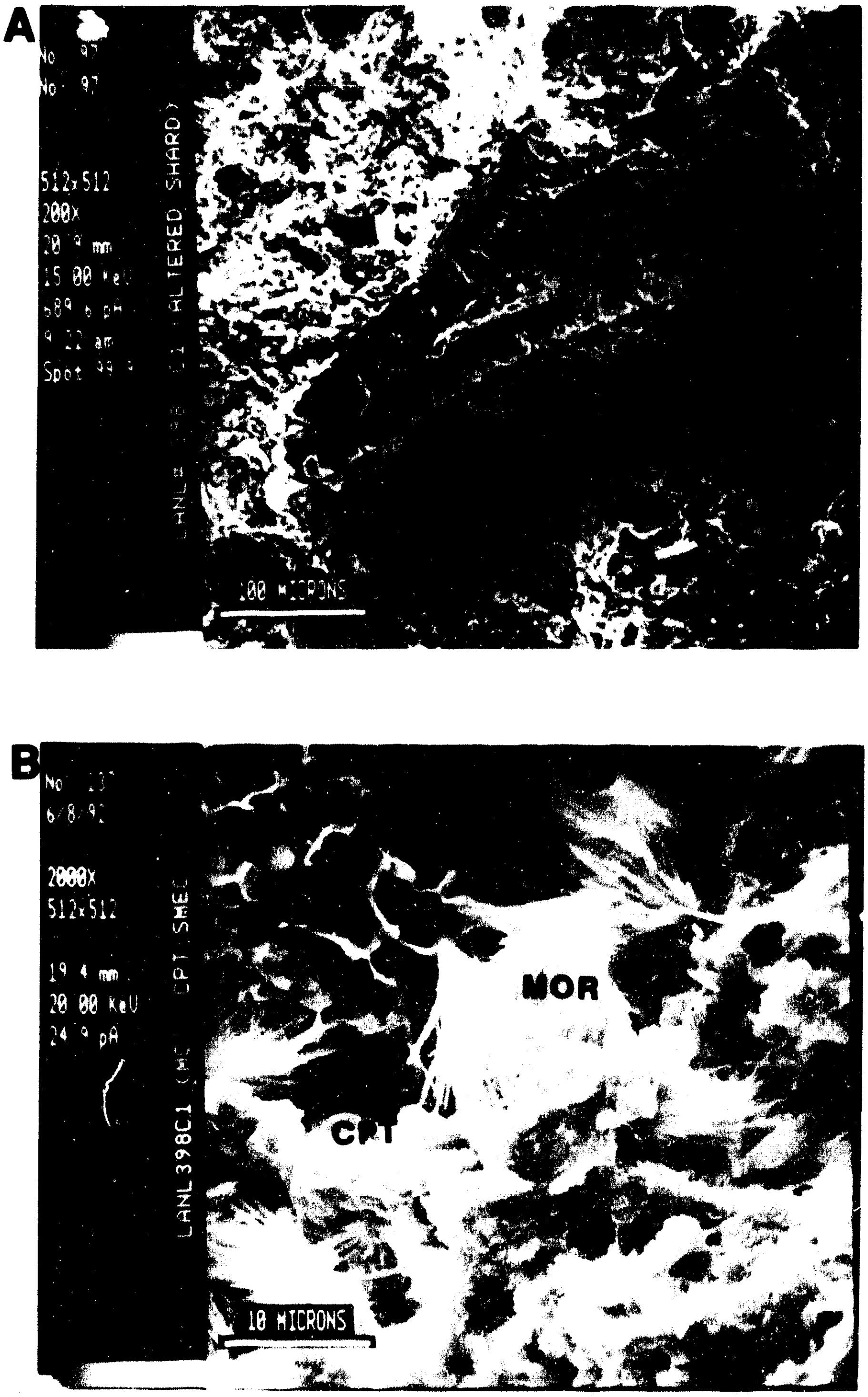
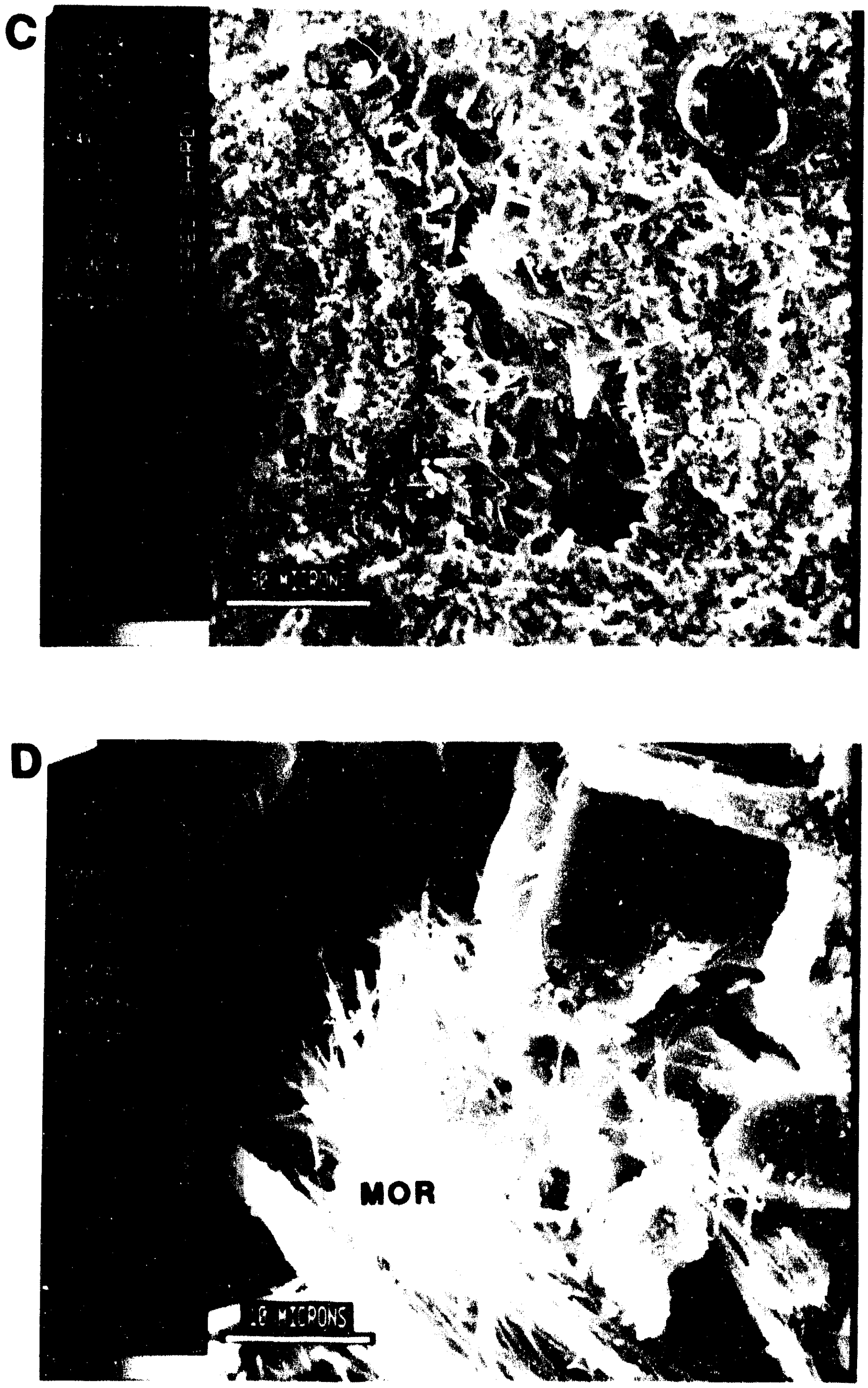


Figure 6. Representative SEM images from the Prow Pass Member of the Crater Flat Tuff in USW G-2 and UE-25P#1 drill holes. The sample from USW G-2 (A and B = LANL#398 C1 = G-2 3250.0–3250.7) contains an altered shard (A) that is replaced (B) by smectite, clinoptilolite, and mordenite. The sample from UE-25P#1 (1790–1800) also contains an altered shard (C) partially filled with clinoptilolite crystals and mordenite (D). The matrices in both samples are dominated by smectite and zeolites as direct replacements of the primary volcanic glass.



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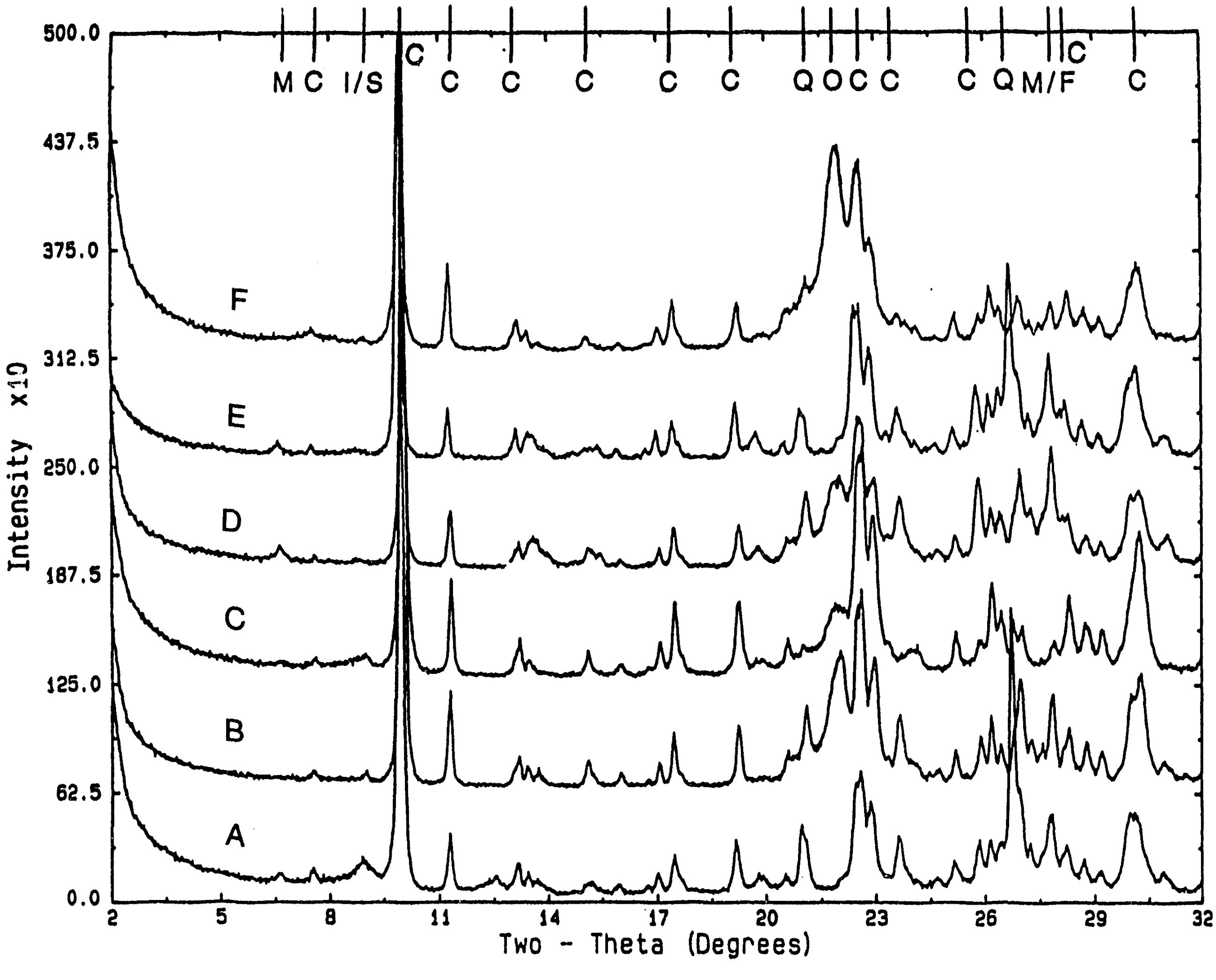

Figure 7. Representative X-ray patterns of clinoptilolite fractions (1–3 μm) from the Prow Pass Member samples in the unsaturated and saturated zones of UE-25P#1 and USW G-1, G-2, GU-3, and G-4 drill holes. The patterns represent clinoptilolite (C) feldspar (F), mordenite (M), opal-CT (O), and quartz (Q). A = G-2 3191.5–3192, B = G-1 2190.8–2190, C = GU-3 1874, D = G-1 1819, E = UE-25P#1 1790–1800, and F = G-4 1763. A, B, and E are from the saturated zone.

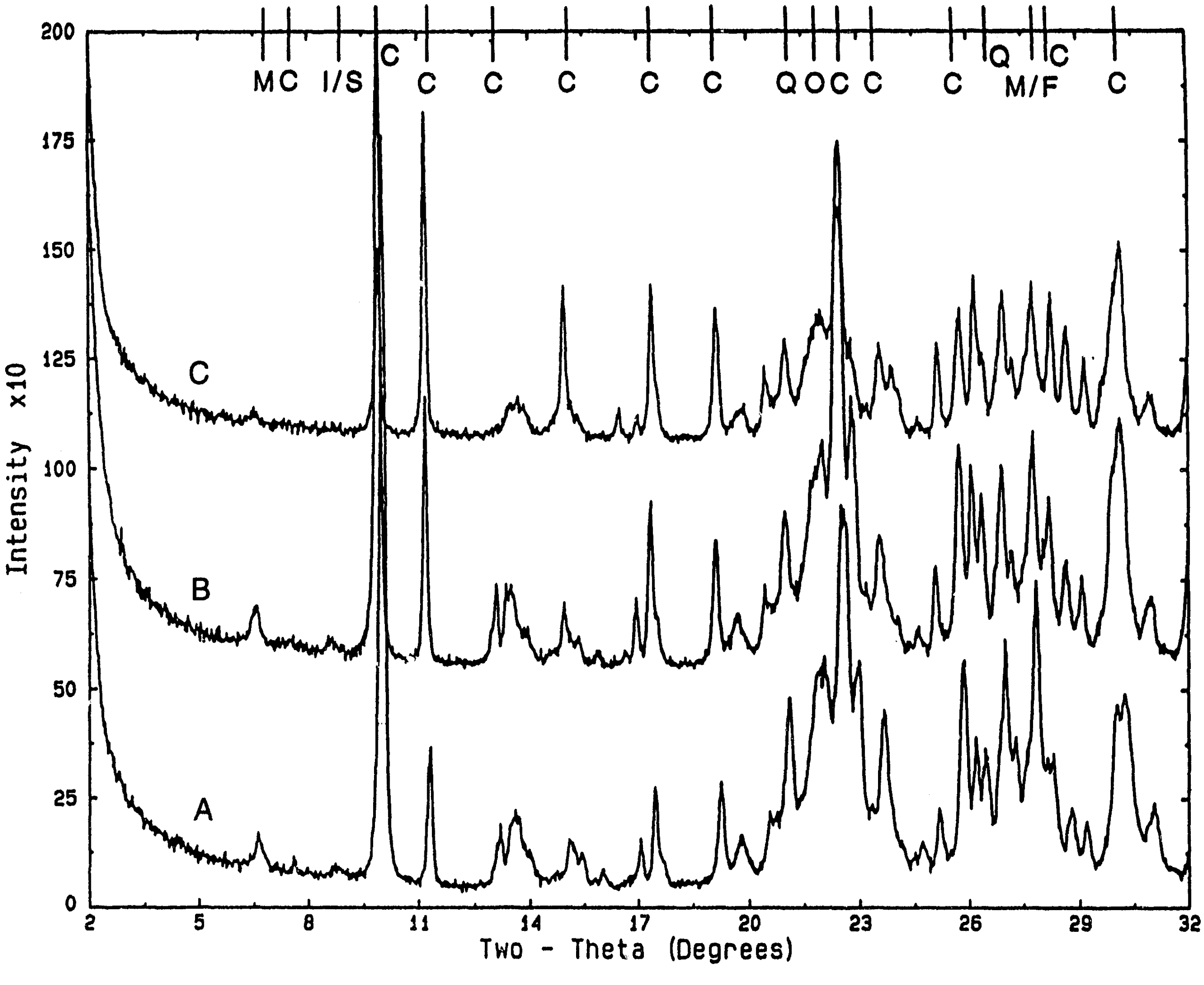

Figure 8. Representative X-ray patterns of ion-exchanged clinoptilolite separates (1–3 μ) from USW G-1 1819. The untreated (A), NaCl (B), and $BaCl_2$ (C) exchanged patterns are similar except for the decrease in mordenite peak intensity in (C). The patterns represent clinoptilolite (C), feldspar (F), mordenite (M), opal-CT (O), quartz (Q).

opal-CT in the same size fraction (1–3 µm). The amount of opal-CT is higher in the clinoptilolite separates from the unsaturated zone (Fig. 7).

Two samples from the lower part of the Prow Pass Member in UE-25P#1 (1740–1750 and 1790–1800) contain clinoptilolite, opal-CT, feldspar, and mordenite in the 1–3 µm fraction (Fig. 7 and Table I). These samples were obtained about 150 m below the static water level. SEM data from UE-25P#1 1790–1800 indicate the total replacement of shards by clinoptilolite and mordenite (Fig. 6).

2. **Ar Data.** The K/Ar dates range from 2.5 to 13 Ma and increase with depth within the Prow Pass Member. In USW G-1, two samples close to the present-day static water level from the unsaturated (G-1 1819) and saturated (G-1 2190.8–2190.9) zones yielded dates of 5.3 Ma and 6.9 Ma, respectively. Abundant mordenite and traces of feldspar are present in the dated clinoptilolite fractions as contaminants that may be responsible for the range in the apparent ages. The Na- and Ba-exchanged aliquots of G-1 1819 give older dates of 6.9, 7.4, 8.3, and 8.7 Ma consistent with the partial replacement of K without drastically affecting the Ar contents.

The oldest clinoptilolite dates (7–13 Ma) were obtained from samples in the lower part of the Prow Pass section in USW G-2 and may represent true ages or may be affected by other K-bearing authigenic and/or primary phases. For example, clinoptilolite fractions from G-2 3191.5–3192 gave a date of 11 Ma and a clinoptilolite separate from the lowermost sample (G-2 3250.5–3250.7) yielded a date of 13.3 Ma (Table II). However, both samples are contaminated with traces of finely crystalline feldspars and illite/smectite (Fig. 9 and Table I). The apparent age of G-2 3191.5–3192 decreased to 7 Ma after purification by heavy liquid (Table III).

The youngest clinoptilolite date (2.4 Ma) from a zeolitic Prow Pass tuff sample was obtained from the unsaturated zone of USW GU-3 (GU-3 1874). In USW G-4, a date of 4.4 Ma was obtained on a clinoptilolite separate from the unsaturated zone, whereas those from the saturated zone are older with dates of 7.2 and 7.4 Ma. The younger date (4.4 Ma) is from a sample (G-4 1763.2–1763.5) about 4 m above the static water level, whereas the older samples (7.2 and 7.4 Ma) were obtained about 1–3 m below it.

Three clinoptilolite separates from two zeolitic samples were dated from the saturated zone of UE-25P#1. Two size fractions of UE-25P#1 1740–1750 yielded dates of 6.0 Ma (3–20 µm) and 8.4 Ma (1–3 µm) (Tables II and III). The coarser fraction (3–20 µm) with a date of 6.0 Ma was purified by heavy-liquid separation. The decrease in the K/Ar result is consistent with the removal of feldspar contaminants in the coarser fraction (Fig. 9). However, a K/Ar date of 8.4 Ma was obtained on a less contaminated clinoptilolite from an underlying sample (UE-25P#1 1790–1800).

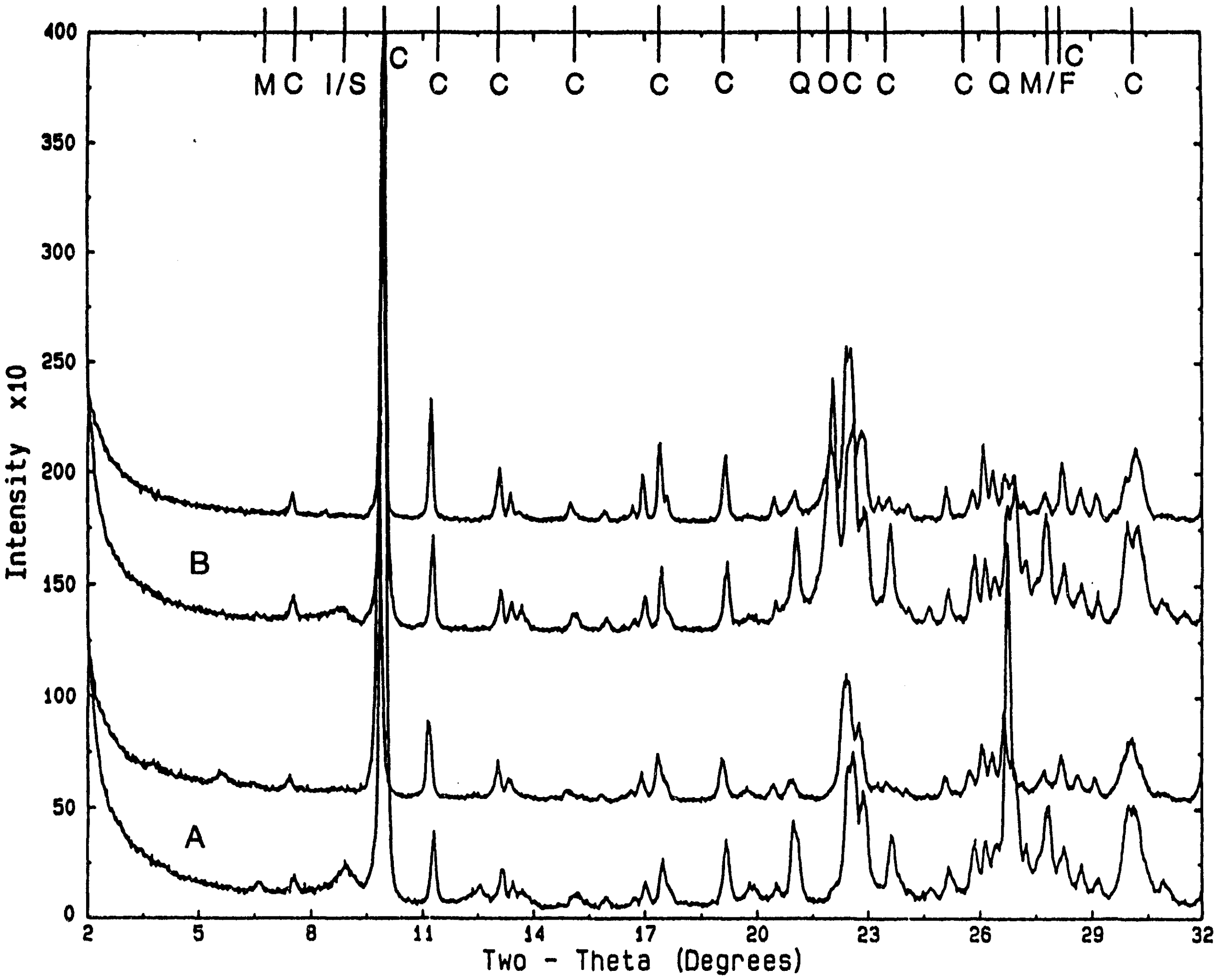

Figure 9. Representative X-ray patterns of clinoptilolite fractions (1–3 μm) from the Prow Pass Member of the Crater Flat Tuff before and after heavy-liquid separations. The samples are from the saturated zones of USW G-2 (A = G-2 3191.5–3192) and UE-25P#1 (B = 1740–1750). The heavy-liquid treated samples are above the untreated ones. The patterns represent clinoptilolite (C), feldspar (F), mordenite (M), opal-CT (O), quartz (Q).

The data from the unsaturated zone are more variable than those obtained from the saturated zone of the same unit. The variation in the K/Ar dates in the unsaturated zone samples seems to reflect the location of these samples with respect to the static water level. For example, the youngest date (2.4 Ma) from USW GU-3/G-3 is 150 m above the static water level, whereas dates of 5.3 Ma and 4.4 Ma were obtained from G-1 1819 and G-4 1763.2 that are close to the static water level, about 18 m and 4 m, respectively, above the static water level. Clinoptilolites from the saturated zone just below the static water level generally yielded older dates.

D. Bullfrog Member

1. Alteration Minerals. The clinoptilolite separate (1–3 µm) from the Bullfrog Member (G-3 2013.1–2013.4) of the Crater Flat Tuff contains minor amounts opal-CT (Table I). This sample is from the unsaturated zone of USW G-3. Unlike the separate from the overlying Prow Pass Member sample (GU-3 1874), mordenite was not detected in the altered Bullfrog fraction (1–3 µm).

2. K/Ar Data. The clinoptilolite (G-3 2013.15) from the Bullfrog Member, dated at 3.8 Ma, is older than a similar fraction from the overlying Prow Pass Member (GU-3 1847, 2.4 Ma). However, this date (3.8 Ma) is very similar to a number of clinoptilolite dates from the unsaturated portion of diagenetic Zone II including the Topopah Spring Member of the Paintbrush Tuff (G-4 1381, 4.2 Ma); the tuff of Calico Hills (G-2 1691–1691.5, 4.0 Ma and G-4 1734.3, 3.8 Ma); and the Prow Pass Member of the Crater Flat Tuff in USW G-4 (G-4 1763.2–1763.5, 4.4 Ma) (Tables II and III). Samples G-3 2013.15 and G-4 1381 are more than 100 m above the static water level, whereas most of the other samples with similar K/Ar dates are a few meters (<15 m) above it.

E. Tram Member

1. Alteration Minerals. Three samples from the altered Tram Member of the Crater Flat Tuff in USW G-1 and G-3 contain clinoptilolite and quartz with minor amounts of mordenite, illite/smectite, and microcrystalline feldspar in the finer fractions (1–3 µm) (Fig. 10 and Table I). Two of the samples (G-3 3589 and G-3 3854.7–3854.9) are from the lower part of diagenetic Zone II, and one sample (G-1 3288.5–3288.6) is from the upper part of diagenetic Zone III. The amount of feldspar contaminants in the clinoptilolite separates is generally higher for the Tram Member and underlying tuff samples compared with similar fractions obtained from the overlying altered units. 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 that occurs in the matrix and on altered feldspars.

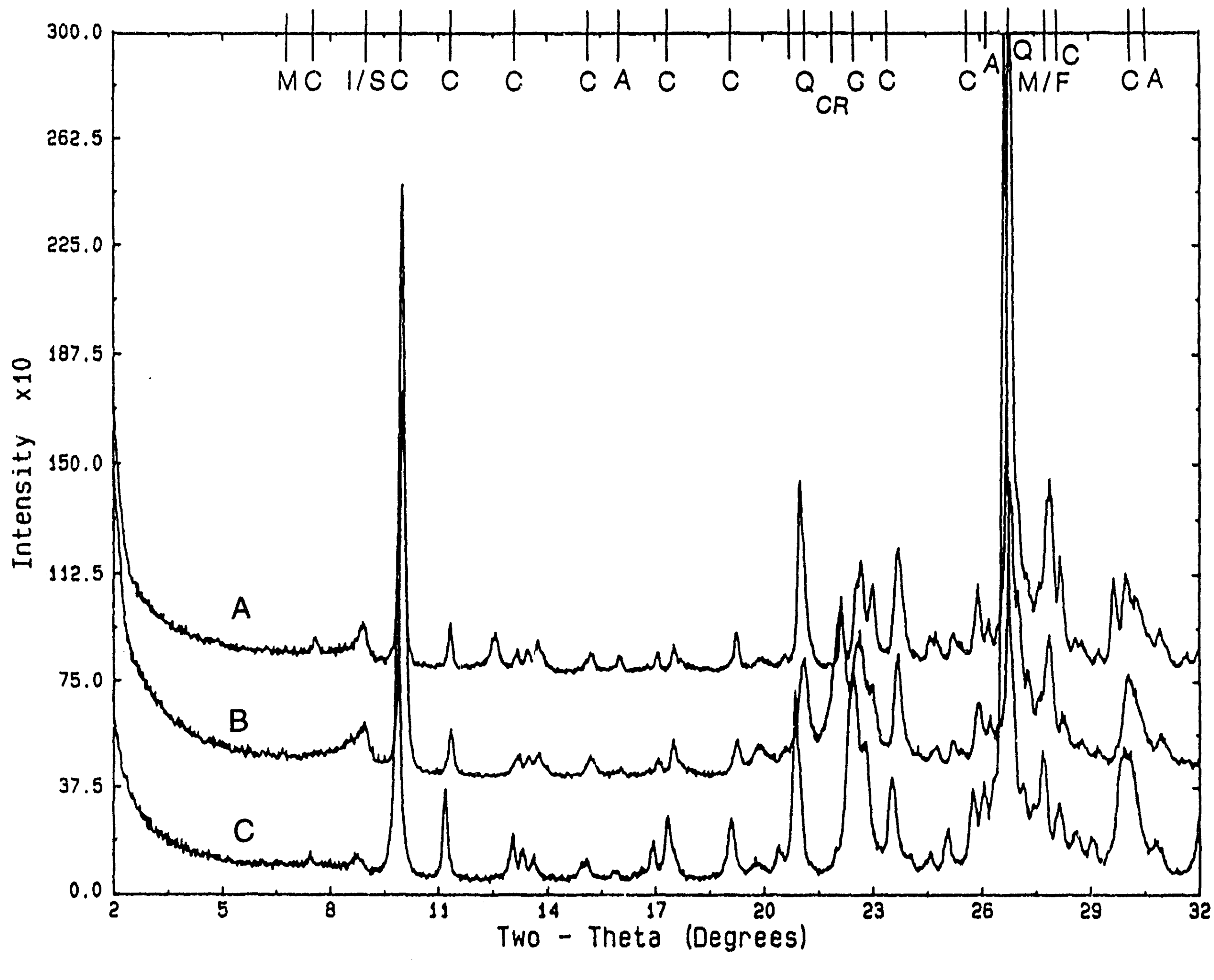

Figure 10. Representative X-ray patterns of clinoptilolite fractions from the Tram Member of the Crater Flat Tuff in USW G-1 (G-1 3288.5 = A) and G-3 (G-3 3589 = B and G-3 3854.7–3854.9 = C) drill holes. The clinoptilolite (C) separates contain abundant quartz (Q) and analcime (A) with minor amounts of feldspar (F), mordenite (M), illite/smectite (I/S), and cristobalite (CR).

The clinoptilolite separates were treated with organic heavy liquid to reduce the microcrystalline feldspar and quartz contaminants except for G-3 3854.7–3854.9 from the lower part of the unit. Only minor differences were noted in the XRD patterns of the untreated and heavy-liquid treated samples because the quartz and feldspar contaminants did not separate effectively during the process.

2. K/Ar Data. Three clinoptilolite fractions (1–3 μm) from the Tram Member samples in USW G-1 and G-3 yielded similar dates (10–11 Ma). A date of 10.5 Ma was obtained on the clinoptilolite separate from G-1 3288.5–3288.6, similar to the 10 Ma apparent age of the heavy-liquid treated fraction. Samples G-3 3589 and G-3 3854.7–3854.9 also yielded identical dates of 10 Ma (Tables II and III). The result of a repeat analysis of G-3 3589 (10 Ma) is similar to the initial date (10 Ma), whereas an aliquot processed by heavy liquid is slightly younger with a date of 9 Ma.

The clinoptilolite fractions from the Tram Member samples are contaminated by finely crystalline feldspars and illite/smectite (Fig. 10), and an attempt to remove the feldspars by heavy liquid was not effective. This is apparent in the XRD patterns and in the K/Ar results of the treated samples that are similar to the untreated fractions (e.g., G-1 3288.5–3288.6 and G-3 3589).

F. Unnamed Older Tuffs (Units B and C)

1. Alteration Minerals. 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 (<10% illite layers) in the 1–3 μm fractions (Fig. 11); both of these samples are from diagenetic Zone IV. 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 (Fig. 12). The zeolites in the matrix are direct replacements of the primary phases because no euhedral secondary minerals were recognized in these samples.

2. K/Ar Data. Dates of 12 Ma were obtained on the clinoptilolite fractions from units B (G-1 5458.4–5458.5) and C (G-1 5560) of the Older Tuffs (Table II). These dates are similar to K/Ar results of clinoptilolites from the Tram Member. Because the clinoptilolite fractions from the older tuffs are contaminated by minor amounts of feldspars and illite/smectite, the K/Ar results represent maximum ages. An attempt will be made to purify the clinoptilolite fractions by heavy liquid for redating.

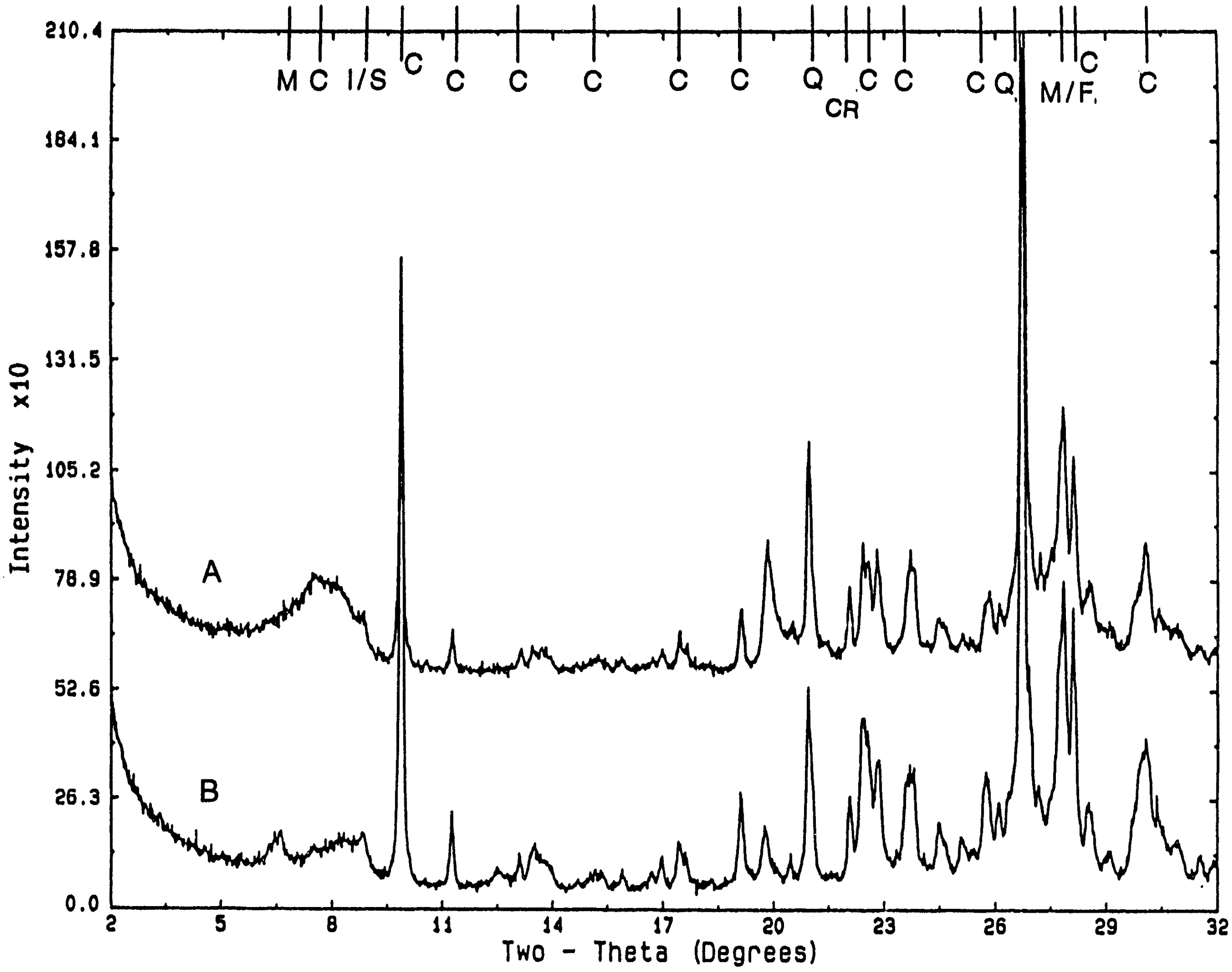

Figure 11. X-ray patterns of clinoptilolite (C) separates (1–3 μm) from USW G-1 5458.7 (A) and G-1 5560 (B). Quartz (Q), feldspar (F), mordenite (M), illite/smectite (I/S), and cristobalite (CR) are present in the clinoptilolite fraction.

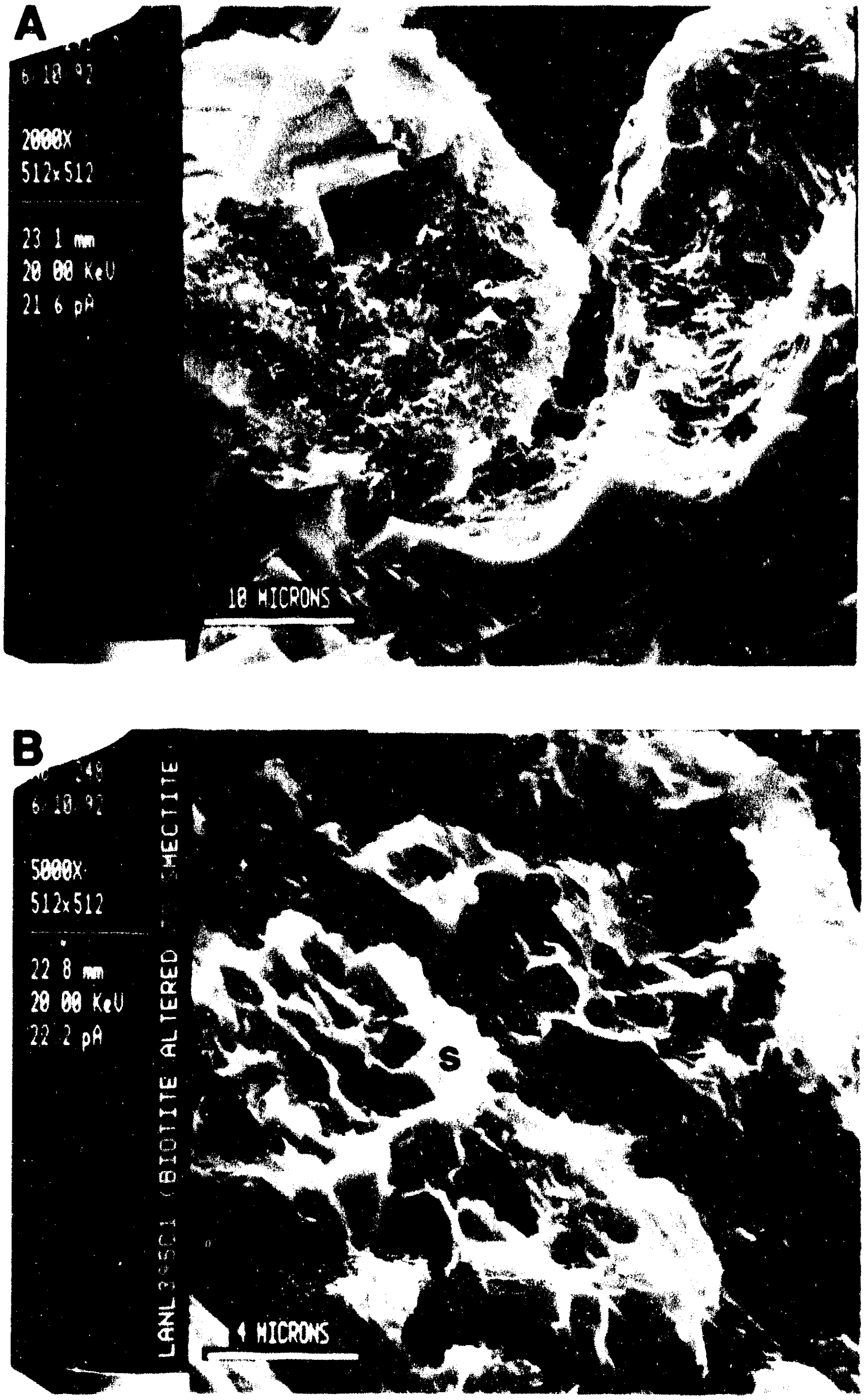

Figure 12. SEM images of USW G-1 5560 showing smectite flakes (S) on altered feldspar (A) and biotite (B). The matrix with dissolution channels contains clinoptilolites and smectites (C). Authigenic K-feldspar (K) is present on top of smectite flakes (D).

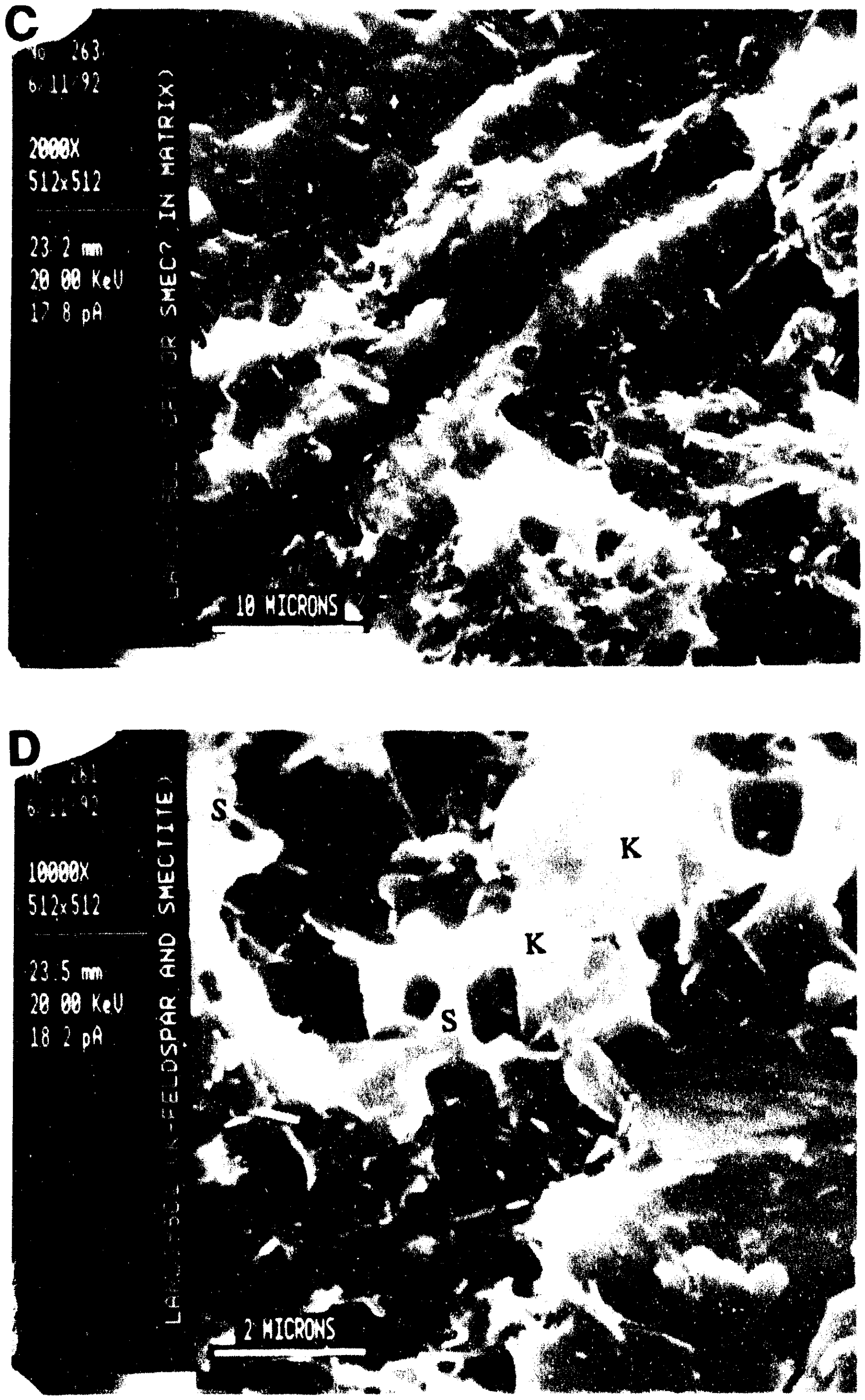

Figure 12. (Continued)

V. DISCUSSION

At Yucca Mountain, clinoptilolite is the dominant K-rich mineral in the zeolite zones of the altered tuffs and occurs in close association with various combinations of mordenite, opal-CT, illite/smectite, authigenic feldspar, and primary finely crystalline quartz and feldspar. A brief description of the distribution and relations of these secondary minerals is outlined. This is followed by an evaluation of the significance of the dating results of the selected clinoptilolite-rich fractions from the unsaturated and saturated zones.

A. Distribution and Textural Relations of Secondary Minerals

Textural evidence from SEM studies on selected samples indicates that the alteration minerals at Yucca Mountain formed in a paragenetic sequence of illite/smectite, clinoptilolite, mordenite, and authigenic feldspar. Illite/smectites (≤10% illite) formed early during alteration of the originally vitric pyroclasts (Fig. 6b). Illites are present in the deeper parts of drill holes USW G-1 and G-2 due to hydrothermal and diagenetic reactions of precursor smectites (Bish, 1989). The illite/smectites are present in partially altered biotites, feldspars, and in dissolution channels and voids in the matrix in some of the deeper samples from the saturated zone (Fig. 12). The alkali zeolites (clinoptilolite, mordenite, etc.) in the altered tuffs directly replace volcanic shards, pumice lapilli, and ash of the tuff matrix; zeolites are particularly conspicuous as euhedral crystals in voids of dissolved shards and vesicles (Figs. 5 and 6). Clinoptilolite predates mordenite in all of the samples examined and the euhedral clinoptilolite crystals are generally oriented perpendicular to the shard-matrix reaction boundary (Figs. 5 and 6). Mordenite occurs as fibrous webs and postdates clinoptilolites. This relation is consistent with the suggestion that some of the mordenite crystallized from the alteration of clinoptilolites (Sheppard *et al.*, 1988). Mordenite is not as widely distributed in the drill hole samples as clinoptilolite (Bish and Chipera, 1989), but rather has a more restricted distribution in certain surface and subsurface altered samples. It is found generally in the northern part of Yucca Mountain close to the Timber Mountain-Oasis Valley caldera complex. Considering that some of the mordenite formed by replacing clinoptilolite (Sheppard *et al.*, 1988), its limited distribution in the drill holes may be due to minimal alteration of clinoptilolite. For example, factors such as low permeability or slow rate of reaction were considered responsible for the occurrence of precursor clinoptilolites and mordenites with analcime in Tertiary sediments (Iijima, 1978). Analcime forms from alkali, silicic zeolites (Surdam and Sheppard, 1978). Authigenic K-feldspars are not as abundant as the clays and alkali zeolites and often postdate clinoptilolites.

B. Clinoptilolite K/Ar Dates

The most important result of this study is that we were able to demonstrate that clinoptilolites retain at least part of their radiogenic Ar which indicates that it may be possible to constrain the timing of alteration of Yucca Mountain tuffs by applying radiometric dating techniques. This finding is important because zeolites have usually been perceived as unsuitable for radiometric age determinations because of their open-framework structure which implies an inability to retain radiogenic Ar. Our study demonstrates that Ar retention does occur in zeolites and that geologically reasonable K/Ar ages can be derived from the dating of clinoptilolite.

A striking aspect of the dates obtained is the consistent pattern of increasing apparent age with depth (Fig. 13). This pattern is repeated in USW G-1, G-2, GU-3/G-3, and G-4 drill holes and is distributed over a wide area. Clinoptilolite dates range from about 2 Ma in outcrop samples and in the upper parts of drill holes to about 13 Ma in the lower parts of the volcanic pile. Significantly, the oldest dates obtained closely approach the eruption ages of the volcanic units hosting the secondary minerals. These older dates may represent the original clinoptilolite crystallization age. Although we consider these initial results to be promising, we caution that the preliminary dates reported herein have not been confirmed by independent dating of co-existing minerals (e.g., authigenic feldspars) whose suitability for K/Ar dating is widely accepted. In addition, diagenesis at Yucca Mountain took place in an open chemical system, and post-crystallization cation-exchange reactions and Ar mobility should be expected in clinoptilolite. Therefore, when one interprets the K/Ar dates, the possibility that the dates represent a combination of original ages and overprinting by later water/rock interactions must be considered.

Contamination of clinoptilolite fractions by K-bearing primary and secondary minerals is partly responsible for the variation in the K/Ar results. 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. The greater K contents and older apparent ages of these pre-treatment fractions are therefore attributed to the presence of contaminants such as feldspars (i.e., primary, devitrification, and/or authigenic phases) and illite/smectite (Fig. 9). Few authigenic feldspars are present with the zeolites, and paragenetic relations (Fig. 12d) 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.

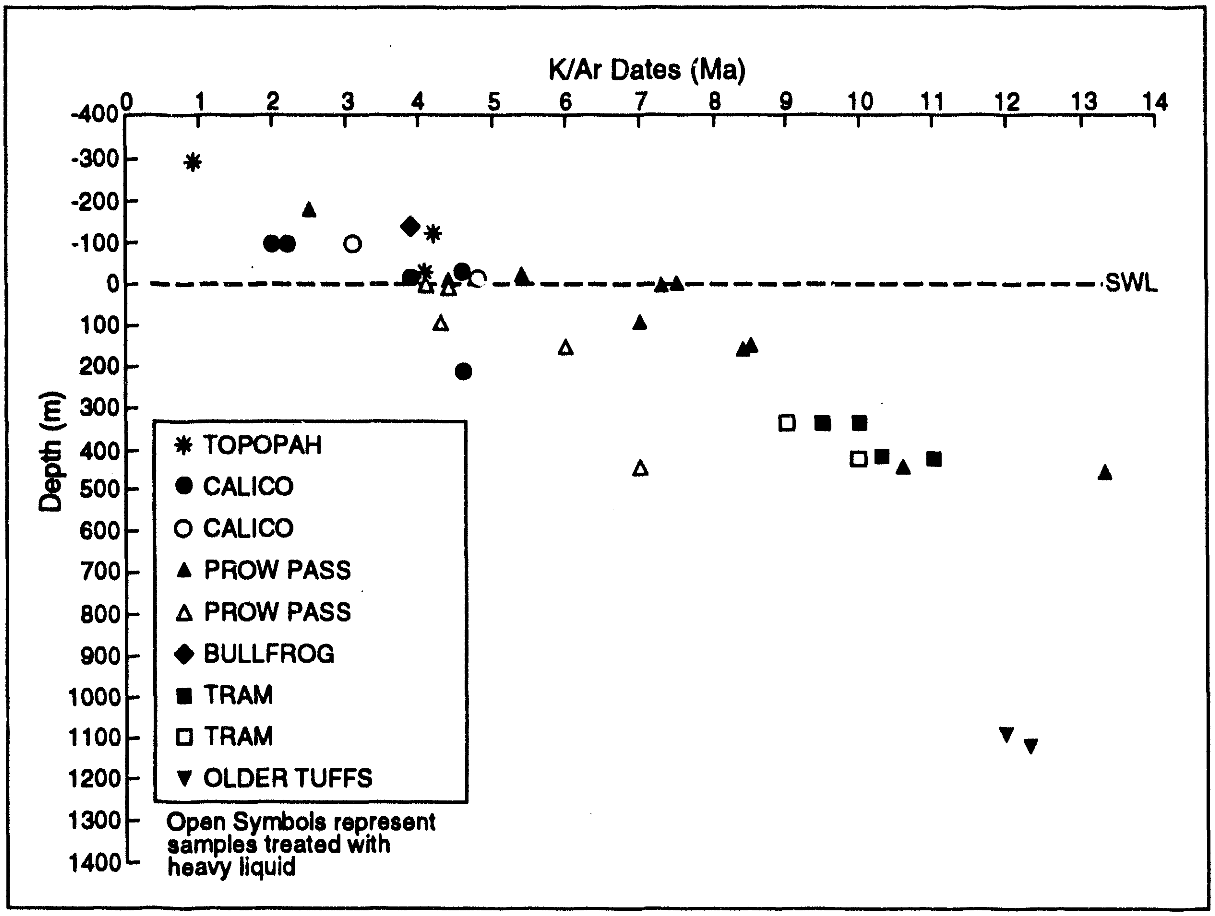

Figure 13. Variation of preliminary clinoptilolite K/Ar dates with depth. The points are plotted with reference to the static water level (SWL). The units in the box are arranged in stratigraphic order.

Although feldspars, quartz, and clays were removed from some of the heavy-liquid treated clinoptilolites (Fig. 9), the effect of this organic liquid on the zeolites is not understood. For example, two fairly pure clinoptilolite fractions (G-1 1561 and G-4 1734.3–1734.6) from the tuff of Calico Hills yielded dates older than the untreated samples (Table III). One of the samples (G-1 1561) was redated and the result is similar to the initial sample separated by sedimentation only.

C. Distribution of Clinoptilolite K/Ar Dates

As briefly stated above, the preliminary clinoptilolite K/Ar dates from the drill holes at Yucca Mountain are variable and increase with depth (Fig. 13). 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 Ma to 13 Ma with depth. 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? Several factors (e.g., post-crystallization alteration, thermal effects, and hydration and dehydration processes) that can affect the Ar and K contents of the zeolites both in the unsaturated and saturated zones are briefly outlined.

Thermal effects causing Ar loss from clinoptilolites in the unsaturated zone are unlikely since the secondary mineral assemblage (e.g., smectite, clinoptilolite, and opal-CT) in the zeolite-rich sections at Yucca Mountain is characteristic of low-temperature diagenetic environment. For example, the stability range 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) effects of relatively low temperature on Ar migration in clinoptilolites are unknown. Alternatively, post-crystallization chemical interactions can result in dissolution and Ar loss because zeolite diagenesis at Yucca Mountain has taken place in an open chemical system (Broxton *et al.,* 1987). 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 isotope composition between pedogenic carbonate and fracture-filling calcites in the unsaturated zone (Marshall *et al.,* 1992). In most cases, the clinoptilolites in the unsaturated zone occur in close association with younger 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. Examples of post-crystallization alteration and its effects on the isotopic composition of secondary minerals have been reported for clinoptilolites and phillipsite. Variations in 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 results were interpreted to represent the cessation of water/rock interactions (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. In another example, Clauer (1982) reported that a middle Miocene (14.7 Ma) Rb/Sr isotopic age on phillipsites 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.

In the unsaturated zone, the effects of hydration and dehydration processes on the Ar contents of the clinoptilolites are not well understood. Barrer and Vaughan (1969) suggested that Ar can readily diffuse through the structure of heulandite (isostructural to clinoptilolite). However, the diffusion is minimized by rehydration until the sample is heated to 110°C. Gundogdu *et al.* (1989) examined the Ar retention ability of clinoptilolites during dehydration by degassing aliquots of a sample in vacuum at 25°C, 60°C, and 100°C 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.

The distribution of water and its role in heulandite-group minerals are well documented (Bish, 1984, 1988). Detailed experimental studies on the dehydration and thermal expansion/contraction of clinoptilolite and heulandite suggest that these zeolites dehydrate in a stepwise process and that water loss results in volume contraction. Thus, Ar loss may be minimized by its large molecular size (3.8Å), and the presence of water probably reduces its mobility through the channels and cavities of the clinoptilolites during intermittent saturation changes in the unsaturated zone.

The unaltered silicic rocks 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 a criteria to estimate the increase or decrease of a particular element during alteration. Secondary gain of K by the clinoptilolites during episodes of fluid migrations 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 addition of K into the clinoptilolite 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 tuff of Calico Hills and the Prow Pass Member of the Crater Flat Tuff in USW G-1, the Topopah Spring, the tuff of Calico Hills, and some of the Prow Pass samples in USW G-2, the Prow Pass Member in USW G-3, and the tuff of Calico Hills and some of the Prow Pass samples from USW G-4 (Fig. 2) contain higher K_2O (2–6 wt %) compared with the overlying and underlying units in each of the drill holes. Because zeolitization in the tuff of Calico Hills 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 tuff of Calico Hills 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 insignificant except along fractures because of the destruction of permeable zones by the crystallization of zeolites and clays. 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 much older (10–12 Ma) than the 2 Ma dates actually obtained on outcrop and near-surface samples. Thus, Ar loss by post-crystallization alteration and/or diffusion seems to be a more plausible reason for the variation in the clinoptilolite K/Ar dates in the unsaturated zone.

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) and/or the likely time of geothermal alteration associated with the Timber Mountain-Oasis Valley caldera complex to the north. 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).

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. The ion-exchange experiments indicate that the type of cations (e.g., Cs, Ba, K, and Sr) 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 (Table IV). 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 minimal 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 minimal. 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.

VI. CONCLUSIONS

The secondary minerals from the altered tuffs at Yucca Mountain are dominated by smectitic clays, zeolites, silica, and K-feldspar. The secondary minerals are generally contaminated by finely crystalline primary feldspar in the 1–3 μm fractions. Preliminary SEM results indicate that the smectites formed first and were followed by alkali zeolites and K-feldspar.

The preliminary clinoptilolite K/Ar dates increase with depth. Clinoptilolites in the shallow unsaturated zone yielded the youngest K/Ar dates (2–4 Ma), whereas those from the unsaturated-saturated transition zone gave intermediate results (4–5 Ma). Zeolites from the saturated zone range between 4 and 13 Ma.

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 exchanges 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 exchanges; and (4) the effect of hydration immobilizing Ar in the framework structure of clinoptilolite, etc. 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 (e.g., equilibration and recrystallization of clinoptilolites with changing ground water conditions), 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 (e.g., primary, devitrified, and/or authigenic phases), 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. Ar loss and K gain or both may be responsible for the younger dates in the unsaturated zone; however, this cannot be firmly established until confirmed by dates from cogenetic secondary minerals. 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 and understand the mechanism of Ar retention by the framework structure of the clinoptilolites. The effects of post-crystallization ion exchange during water/rock interactions and intermittent saturation changes in the unsaturated zone coupled with sample preparation procedures may account for the observed variations in the K/Ar dates obtained in this study. 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.

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