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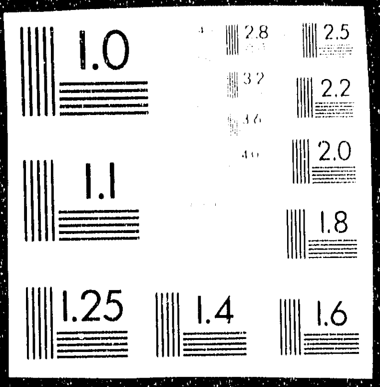

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TITLE: PRELIMINARY ASSESSMENT OF CLINOPTILOLITE K/AR RESULTS FROM YUCCA MOUNTAIN, NEVADA: A POTENTIAL HIGH-LEVEL RADIOACTIVE WASTE REPOSITORY SITE

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Preliminary assessment of clinoptilolite K/Ar results from Yucca Mountain, Nevada: a potential high-level radioactive waste repository site

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ABSTRACT: At Yucca Mountain, evidence for at least three distinct temporal groups of clinoptilolites can be delineated from the preliminary K/Ar dates (2 - 3 Ma; 4 - 5 Ma; 7 - 11 Ma). The older K/Ar dates that are similar to published illite/smectite ages (9-12 Ma) may be crystallization ages, whereas the younger dates probably represent continued diagenetic reactions of older clinoptilolites with percolating fluids. The K/Ar dates increase with depth, suggesting minimal argon loss in the deeper samples. Internal consistency of the clinoptilolite K/Ar results at different levels within the drill holes suggest that dating of K-rich zeolites may provide useful information for assessing the zeolitization at Yucca Mountain. Variations in the K/Ar dates are probably related to Ar loss during dissolution of older clinoptilolites and to contamination by finely crystalline feldspars.

INTRODUCTION

Yucca Mountain is located in the southwest Nevada volcanic field. It is an east-tilted fault block underlain by 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). These tuffs range in age from 11.45 to 15.1 Ma (Kistler, 1968; Marvin *et al.*, 1970; Sawyer *et al.*, 1990). Those rocks that were not devitrified soon after emplacement have been extensively altered, and the zeolitized tuff units at Yucca Mountain are broadly grouped 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). Based on stratigraphic and structural relations, the zeolitization processes at Yucca Mountain were completed in the Middle Miocene (11.6-12.8 Ma) (Levy, 1991).

The present study is an attempt to determine the timing of zeolitization using clinoptilolite, expanding upon the work of earlier preliminary K/Ar studies of clays (8.7-11.7 Ma) and zeolites (2-7 Ma) at Yucca Mountain (Aronson and Bish, 1987; Bish *et al.*, 1990; Aronson and Bish, unpublished data). This work was exploratory, since clinoptilolite is not generally regarded as an ideal mineral for dating by the K/Ar method because of its large ion-exchange capacity and open-framework structure. A total of 21 core samples from five drill holes at Yucca Mountain were selected for study. All samples contained ≥30% clinoptilolite (Bish and Chipera, 1989); most of the nonzeolitic minerals were removed by sedimentation in deionized water (Chipera and Bish, 1989) and/or by organic heavy-liquid separations. The effect of the organic heavy liquid and acetone on the Ar and K contents during sample preparations and cleaning was examined by dating untreated and heavy liquid-treated clinoptilolite separates from the same sample. The K/Ar dates from the clinoptilolites separated by heavy liquid are not included here because the analyses are not yet completed. However, initial results indicate that the dated clinoptilolites responded variably to the organic heavy-liquid treatment. In some pure separates the K/Ar dates increased after treatment, whereas in most of the other samples the apparent ages dropped significantly probably because of the removal of primary and authigenic feldspar contaminants. No variation in the clinoptilolite K/Ar results was noted in the third group of samples. The effect of cation exchange on zeolite dates was evaluated by treating some clinoptilolite separates with 1 N NaCl, CsCl, and $BaCl_2$ solutions for 48 and 72 hours.

The mineral separates were analyzed by X-ray diffraction. Random and oriented mounts were prepared and analyzed with 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). Clinoptilolite-rich fractions from the X-ray analyses were selected for K/Ar dating (Table 1). About 50 to 200 mg of clinoptilolite separates (1-3 and 3-20 μm) were weighed for Ar measurements and analyzed 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. 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).

ANALYTICAL RESULTS

Mineralogic and K/Ar data are given in stratigraphic order in Table 1. Clinoptilolite makes up ≥75% of the purified samples. Mordenite and minor amounts of opal, feldspar and quartz are the main contaminants. The apparent ages generally increase with depth within each individual unit and within the stratigraphic sequence in the drill holes.

TABLE 1. Mineralogical assemblages of zeolite and clay fractions (1-3μm) separated from altered Yucca Mountain tuff units. Clinoptilolite is the dominant (≥75%) authigenic mineral. CPT=clinoptilolite, MOR=mordenite, I/S=illite/smectite, FEL=feldspar.

Stratigraphic Units	Sample I.D.	Depth (m)	Size Fraction (μm)	Authigenic Minerals	Age† (Ma,2σ)§
Topopah Spring Member	USW G-2 1691-1691.5	515.5	1-3	CPT, MOR, Opal CT	4.1 ± 0.1 (10%)
Topopah Spring Member	USW G-4 1381	420.9	1-3	CPT, Opal CT	4.2 ± 0.1 (10%)
Calico Hills	USW G-1 1561	475.8	1-3	CPT, MOR, Opal CT	2.2 ± 0.1 (8%)
Calico Hills	USW G-1 1561	475.8	1-3	CPT, MOR, Opal CT	2.0 ± 0.1 (10%)
Calico Hills	USW G-2 2430	740.7	1-3	CPT, Opal CT, MOR	4.6 ± 0.2 (18%)
Calico Hills	USW G-4 1685.2-1685.4	513.6	1-3	CPT, Opal CT,	4.6 ± 0.1 (23%)
Calico Hills	USW G-4 1734.3-1734.6	528.5	1-3	CPT, MOR, Opal CT	3.9 ± 0.2 (5%)
Prow Pass Member	USW G-1 1819	554.4	1-3	CPT, MOR, Opal CT	5.4 ± 0.1 (18%)
Prow Pass Member	USW G-1 1819	554.4	1-3	CPT, MOR, Opal CT	7.0 ± 0.2 (20%)*
Prow Pass Member	USW G-1 1819	554.4	1-3	CPT, MOR, Opal CT	7.5 ± 0.2 (16%)**
Prow Pass Member	USW G-1 1819	554.4	1-3	CPT, MOR, Opal CT	8.4 ± 0.2 (20%)***
Prow Pass Member	USW G-1 2190.8-2190.0	667.5	1-3	CPT, MOR, Opal CT	6.9 ± 0.1 (26%)
Prow Pass Member	USW GU-3 1874	571.2	1-3	CPT, MOR, Opal CT	2.5 ± 0.2 (8%)
Prow Pass Member	USW G-4 1763.2-1763.5	537.4	1-3	CPT, Opal CT, MOR	4.4 ± 0.2 (10%)
Prow Pass Member	USW G-4 1779.6-1779.9	542.2	1-3	CPT, Cristobalite	7.5 ± 0.1 (44%)
Prow Pass Member	USW G-4 1788.4-1788.7	545.0	1-3	CPT, Cristobalite, FEL	7.3 ± 0.1 (44%)
Prow Pass Member	UE25P#1 1740-1750	530.4	1-3	CPT, Opal CT, MOR	8.5 ± 0.2 (18%)
Bullfrog Member	USW G-3 2013.1-2013.4	613.6	1-3	CPT, Opal CT	3.9 ± 0.1 (10%)
Tram Member	USW G-1 3288.5-3288.6	1002.2	1-3	CPT, MOR, Quartz, FEL	10.6 ± 0.2 (35%)
Tram Member	USW G-2 3191.5-3192.0	972.9	1-3	CPT, Quartz, FEL	10.6 ± 0.2 (28%)
Tram Member	USW G-3 3589	1094.1	1-3	CPT, Quartz, FEL	9.5 ± 0.2 (34%)
Tram Member	USW G-3 3589	1094.1	1-3	CPT, Quartz, FEL	10.0 ± 0.2 (45%)

† Determined from decay constants and isotopic abundance of ^{40}K according to Steiger and Jager, 1977;
* NaCl-exchanged (48 hours); ** $BaCl_2$-exchanged (48 hours); *** $BACl_2$-exchanged (72 hours); § Numbers in brackets are % radiogenic argon.

The K/Ar dates from two Topopah Spring Member samples in the lower part of the unsaturated zone are similar with dates of 4.1 and 4.2 Ma. Dates of 2 and 2.2 Ma were obtained on a near-surface tuff of Calico Hills sample, whereas those from the drill holes penetrating the lower unsaturated zone and the upper saturated zone yielded dates of 3.9 to 4.6 Ma. The K/Ar dates range from 2.5 to 7.5 Ma and increase with depth within the Prow Pass Member of the Crater Flat Tuff. Samples from the unsaturated zone (USW G-1 1819, GU-3 1874, and G-4 1763.2) yielded dates (2.5-5.3 Ma) that are younger than those from the saturated zone (6.9-7.5 Ma). A date of 5.3 Ma was obtained from USW G-1 1819, whereas the ion-exchanged splits yielded older dates of 7.0 Ma and 7.5 Ma for the fractions treated for 48 hours with NaCl and $BaCl_2$ solutions, respectively, and 8.4 Ma on a split exchanged for 72 hours with $BaCl_2$ solution. A sample from the Bullfrog Member of the Crater Flat Tuff in the unsaturated zone yielded a date of 3.9 Ma that is similar with other dated samples from the lower part of the unsaturated zone at Yucca Mountain. Clinoptilolite fractions from the Tram Member of the Crater Flat Tuff in the saturated zone yielded dates between 9 and 10.6 Ma.

DISCUSSION

As a whole, the preliminary clinoptilolite K/Ar dates from the drill holes at Yucca Mountain are variable and cluster into at least three distinct groupings (2 - 3 Ma, 4 - 5 Ma, and 7 -11 Ma). However, the dating results from similar levels are generally concordant between drill holes. For example, dates from near-surface samples range between 2 and 3 Ma, whereas those from the lower part of the unsaturated zone yielded older dates of 4 to 5 Ma. The dates below the the static water level indicate a similar pattern whereby they increase with depth from 4 Ma to 11 Ma from the upper to the lower parts of the saturated zone. The younger dates may represent the dissolution of older clinoptilolites and the crystallization of more clinoptilolite as well as new phases such as mordenite, adularia, clays, etc., as indicated by SEM data. Except for the older apparent ages (9-11 Ma) from the lower part of the clinoptilolite-rich section of the saturated zone, most of the dates probably represent the termination of diagenetic processes. The older dates are similar to published illite/smectite ages (9-12 Ma) from USW G-1 and G-2 (Aronson and Bish, 1987; Bish *et al.*, 1990). The difference in the K/Ar dates can be related to Ar loss during diagenetic reactions with changing pore water chemistry as indicated by the presence of abundant dissolution pits and the growth of mordenite on older clinoptilolite within the unsaturated and saturated zones. This process is consistent with the negative correlation noted between the clinoptilolite K/Ar dates and mordenite content. The effect of permeability on the K/Ar data is generally indicated by the dated clinoptilolites from the subsurface tuff of Calico Hills. SEM data indicates that the amount of mordenite decreases with depth, whereas the K/Ar dates increased from 2 to 4.6 Ma. This variation in age may be related to progressive sealing of permeable zones by mordenite crystallization with depth within the unsaturated zone. Permeability and hydraulic conductivity values from nonwelded and zeolitized tuff of Calico Hills in USW G-1 and G-4 close to the dated samples are extremely low (1.21×10^{-6} - 4.77×10^{-8} darcy and 1.16×10^{-11} - 4.59×10^{-13} m/s) (Rutherford *et al.*, 1989). According to Gundogdu *et al.* (1989), altered Miocene tuffs from western Turkey yielded older clinoptilolite K/Ar dates from impermeable units compared with samples from permeable rocks. Thus, the permeability and mordenite content seem to suggest that the clinoptilolite K/Ar results were affected by fluid chemistry and the availability of fluid pathways.

The ion-exchange experiments suggest that saline, alkaline fluids with certain cations (e.g., Cs, Ba, Na, Sr, etc.) can strip the potassium from clinoptilolites without affecting the radiogenic argon resulting in older dates. Clinoptilolite is more selective for Cs, Ba, and Sr than other cations (Ames, 1961; Bish, 1988). Because the altered tuffs contain minor amounts of these cations (0.1 wt % of Ba, Cs, and Sr) (Broxton *et al.*, 1986), the effect of cation exchange on the K content and the K/Ar results must have been insignificant. For example, the clinoptilolites in the lower part of the saturated zone are K-rich (4-5 wt %) and yielded older K/Ar dates (9-11 Ma). More ion-exchange experiments are being carried out to check if K is continuously replaced during an extended period of exchange (> 72 hours) or if it remains constant after a certain time. Samples from such an experiment will be dated to determine whether the K/Ar dates approach the probable crystallization age or not.

This study is exploratory and we recognize that the interpretations discussed above are preliminary. Other datable paragenetic minerals (illite/smectite, mordenite, adularia, etc.) are being investigated to evaluate the results from the clinoptilolite K/Ar dating.

SUMMARY

Clinoptilolites from the unsaturated zone yielded younger dates compared with similar zeolites from the underlying saturated zone. The variation in the K/Ar dates may be related to Ar loss during the partial conversion of clinoptilolites to mordenite and other diagenetic minerals (i.e., clays, adularia, etc.) and to contamination by finely crystalline feldspars. Temporal correlation between some of the clinoptilolites and illite/smectite clays suggests that the alteration process started in the late Miocene.

More data are needed to evaluate and understand the mechanism of Ar retention by clinoptilolites. So far, the precision of the preliminary clinoptilolite K/Ar dates are acceptable and similar results suggest some sensible meaning to the dates obtained.

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