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TITLE: Ion Exchange and Dehydration Effects on Potassium and Argon Contents of Clinoptilolite

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ION EXCHANGE AND DEHYDRATION EFFECTS ON POTASSIUM AND ARGON CONTENTS OF CLINOPTILOLITE

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ABSTRACT

Zeolite-rich Miocene tuffs are an important part of the principal hydrochemical barrier to water-borne radionuclide transport from a potential high-level nuclear waste repository at Yucca Mountain, Nevada. The timing of zeolitization is an issue that relates to paleohydrology, permeability, zeolite stability, and unsaturated-zone geochemical processes. Exploratory K/Ar dating of clinoptilolite, the most abundant and widespread zeolite, shows a striking and consistent pattern of increasing apparent ages (2-13 Ma) with depth. Only the isotopic ages from the saturated zone are compatible with geologic evidence suggesting an age >10 Ma for most of the zeolites.

Factors that may be responsible for the young apparent ages in the unsaturated zone were investigated. Cation exchange with recharge water and Ar diffusion under unsaturated conditions (processes that may be characteristic of the unsaturated zone) were evaluated experimentally for their effects on K/Ar systematics. Cation exchanging a natural clinoptilolite with Ca-, Cs-, K-, and Na-chloride solutions showed minimal effects on radiogenic Ar content. However, clinoptilolite heated at 200°C for 16 hours in air lost a significant amount of its radiogenic Ar compared with minimal losses from clinoptilolite heated in water at 100°C for over 5 months. The preliminary results indicate that Ar loss from incompletely hydrated clinoptilolite may be a major factor contributing to the young apparent ages of clinoptilolite in the unsaturated zone at Yucca Mountain.

INTRODUCTION

Site suitability and licensing support information needs for the potential high-level nuclear waste repository site at Yucca Mountain, Nevada, require evaluation of geochemical processes that could affect the sorption of radionuclides. Clinoptilolite-bearing tuffs below the potential repository comprise one of the key sorptive barriers to radionuclide migration. An evaluation of natural geochemical processes affecting the stability of the zeolitic mineral assemblage should determine the timing of the low-temperature diagenetic alteration that created the zeolites and identify any evidence that the zeolites have been subsequently modified. Because the age and distribution of zeolitic rocks are indicators of changes in hydrologic regimes and geochemical processes [1], the chronology of zeolitic alteration is also directly relevant to the suitability of the site as a potential nuclear waste repository. Regulatory guidelines for license application require documentation pertaining to: (1) geochemical processes operating during the Quaternary Period that would not affect or would favorably affect the ability of a repository to isolate waste, (2) geochemical conditions that promote precipitation or sorption of radionuclides, (3) potential for changes in hydrologic conditions, such as hydraulic conductivities and potentiometric levels, that would affect the migration of radionuclides to the accessible environment, and (4) potential for the water table to rise so as to cause saturation of an underground facility located in the unsaturated zone [2]. The widespread, thick zones of pervasive zeolitization below the potential repository horizon at Yucca Mountain were probably formed during alteration of originally glassy tuffs at or below the static water level (SWL) [1]. The existence of radiometric ages within the time span of

the Quaternary Period (1.6 Ma to present) for clinoptilolites from what is now the unsaturated zone of Yucca Mountain would be of particular concern because they could be interpreted as evidence of recent static water levels much higher than present levels. Such an interpretation would be at variance with other data that suggest less extreme hydrologic fluctuations [1,3] but would certainly require technical evaluation of the dating technique and results.

Background on clinoptilolite and mordenite K/Ar dating

The major silicic tuffs at Yucca Mountain (Timber Mountain Group, Tiva Canyon and Topopah Spring Tuffs of the Paintbrush Group, Calico Hills Formation, Prow Pass, Bullfrog, and Tram Tuffs of the Crater Flat Group, and Lithic Ridge Tuff) erupted from the Timber Mountain-Oasis Valley caldera complex and nearby volcanic centers between 11.4 and 14.0 Ma [4]. Exploratory K/Ar dating of clinoptilolite, the most abundant and widespread zeolite, shows a striking and consistent pattern of increasing apparent ages (2-13 Ma) with depth [5,6]. The >10 Ma clinoptilolite, mordenite, and mixed later illite/smectite (I/S) isotopic ages from the saturated zone and the 9-12 Ma hydrothermal illite and I/S suggest that diagenetic and hydrothermal alteration at Yucca Mountain occurred contemporaneously in the near-surface and deeper sections of the altered Miocene tuffs, respectively [5,6,7]. However, several lines of evidence call into question the relatively young clinoptilolite ages from the unsaturated zone and shallow saturated zone. Petrofabric studies of zeolitic rocks suggest that clinoptilolite from the basal Topopah Spring Tuff downward formed before 11.4 Ma [1,8]. I/S ages of ~9 to 12 Ma from the unsaturated zone in drill holes USW G-1 and G-2 are compatible with the petrofabric studies but contrast with the clinoptilolite ages of ~2 to 4 Ma from similar depths in the same drill holes [5,7].

The zeolite K/Ar results themselves include examples of apparent ages that are difficult to reconcile with each other or with textural evidence of crystallization chronology. Apparent ages of clinoptilolite from the lower Prow Pass Tuff vary from 2.4 Ma for zeolite currently in the unsaturated zone to 13.3 Ma for a sample from 465 m below the present SWL. Clinoptilolites from this stratigraphic interval should all be about the same age according to a conceptual model of episodic zeolitization based on petrofabric studies [1]. The few K/Ar ages obtained from the zeolite mordenite are also in disagreement with clinoptilolite ages. Textural studies indicate that mordenite formed by diagenetic alteration of clinoptilolite [5,9], but the 7 Ma age of mordenite from the shallow saturated zone [10] is significantly older than ages of 4 to 5 Ma for clinoptilolites from 80 m above and 146 m below the dated mordenite [5]. These results are particularly significant because they suggest that the mechanism responsible for the widespread resetting of clinoptilolite apparent ages has operated independent of any resetting of K/Ar systematics specifically associated with the recrystallization of clinoptilolite to mordenite.

Given that clinoptilolite ages from the deep saturated zone are compatible with textural and isotopic data whereas ages from the unsaturated zone, especially outcrops, seem too young, we have investigated natural processes related to differences in hydrologic environment that could modify the K or Ar contents of the zeolite. Lowering of the K/Ar apparent age could result from K^+ gain by cation exchange, radiogenic Ar loss by diffusion out of the zeolite lattice channels, or a combination of both processes. The effectiveness of these mechanisms could differ in the saturated and unsaturated zones because of differences in pore water composition, water content of the zeolite lattice channels, or surface hydration of zeolite crystals.

In documenting the patterns of age variation, we have also considered the contribution of K-bearing mineral impurities [6]. Illite, I/S, and alkali feldspar are mostly ~9 to 14 Ma old and the few mordenite ages are ~7 to 8 Ma. If present as impurities, these minerals would tend to increase the apparent ages of "younger" clinoptilolites. The mineral separates produced for dating are too

small for quantitative X-ray diffraction (XRD), but qualitative XRD patterns commonly show potassic impurities. Apart from the effects of impurities on individual sample ages, there is an additional question whether systematic variations in impurity content could produce the pattern of increasing clinoptilolite age with depth. The whole-rock contents of mordenite and K-rich I/S generally increase with depth although exceptions exist. Qualitative comparisons of XRD patterns for the suites of mineral separates from any given drill hole [6] indicate about equal likelihood of increasing or decreasing potassic impurity content between consecutive samples. We conclude that potassic impurities are clearly a concern for individual samples, but no indication exists of systematic contributions to patterns of age distribution.

EXPERIMENTAL METHODS

The effects of cation exchange and heating under variable hydrologic conditions on the K and radiogenic Ar contents of clinoptilolite were evaluated experimentally to determine whether such processes could be responsible for the younger isotopic ages at Yucca Mountain. A clinoptilolite-rich rock from the late Miocene Sucker Creek Formation of Sheaville, eastern Oregon, was selected for the experiments. It is interesting to note that the K/Ar apparent ages of the Sucker Creek clinoptilolite is much younger than the suggested late Miocene time of alteration [11,12].

Zeolites were separated from other minerals by sedimentation in deionized water. Some separates were further purified by organic heavy-liquid separation. The K_2O and radiogenic Ar contents of these samples were measured before and after the ion-exchange and heating experiments. For the ion-exchange experiments, 1 M chloride solutions of Ca^{2+}, K^+, Na^+, and Cs^+ were added to several clinoptilolite aliquots (5-50 μm size fraction). Each mixture was placed in an oven at 50°C and periodically shaken. Every 24 hours the exchanged solution was removed by centrifugation and replaced by new chloride solution. The experiments were conducted as 3 and 5 exchanges for total times of 72 and 120 hours, respectively. The 120-hour exchange was intended to maximize the replacement of K^+ by alkali and alkaline earth cations. The solutions obtained by centrifugation after each step were analyzed for cation content by atomic absorption and gravimetric methods.

Aliquots of about 2 g of clinoptilolite from the same material used in the ion-exchange experiment were heated at 50°, 100°, 150°, and 200°C in air for 16 hours. Additional aliquots were placed in deionized water (2 to 1 water/sample ratio) maintained at 100°C in sealed reaction vessels for periods from one week to about six months. All aliquots were X-rayed using Cu Kα radiation on an automated Siemens D-500 diffractometer from 2 to 36° 2θ in 0.02° steps and counting for 1 s per step.

The K_2O contents of the natural, exchanged, and heated samples were determined using an atomic absorption spectrophotometer on 70 to 100 mg of each sample powder fused with $LiBO_3$ and dissolved in 3 % HNO_3 solution. Aliquots of about 120 to 250 mg of the sample powders were used for radiogenic Ar measurements using an MS 10 mass spectrometer on line with bulb-pipetted ^{38}Ar. Analyzed values of K_20 and Ar for standards USGS BCR-1 and G-2 and LP-2 were within 2.5% of published values [13,14].

RESULTS

The water-separated and heavy liquid-separated samples contain similar amounts of K_2O but the latter may have lost some of its radiogenic Ar (Table I). Additional tests would be required to identify a genuine effect of heavy-liquid separation on the radiogenic Ar content of clinoptilolite.

Table I
Experimental Conditions and Results

Experimental Conditions				Analytical Results	
Purification method	Duration of experiment	Temperature (°C)	Experimental medium	K_2O (wt %)	$^{40}Ar^*$§ (10^{-11} moles/g)
water	n.a.†	n.a.	n.a.	5.28	0.81±23.78‡
heavy liquid	n.a.	n.a.	n.a.	5.34	0.62±22.83
water	3 days	50	1 M KCl	9.22	1.04±16.30
water	5 days	50	1 M KCl	8.45	1.20±12.54
water	3 days	50	1 M $CaCl_2$	3.09	0.93±18.71
water	5 days	50	1 M $CaCl_2$	2.67	1.04±15.93
water	3 days	50	1 M NaCl	3.36	0.91±16.16
water	5 days	50	1 M NaCl	2.93	0.49±29.43
water	3 days	50	1 M CsCl	1.23	0.85±17.05
water	5 days	50	1 M CsCl	1.04	1.82±6.24
water	16 hours	50	air	5.23	1.07±23.92
water	16 hours	100	air	5.45	1.26±20.37
water	16 hours	150	air	5.49	1.02±23.63
water	16 hours	200	air	5.55	0.46±76.42
water	1 week	100	water	5.48	0.75±21.83
water	1 month	100	water	5.67	1.51±11.68
water	3 months	100	water	5.17	1.09±16.69
water	5.4 months	100	water	5.15	1.13±15.01

§ Radiogenic argon.
† n.a. = not applicable.
‡ Estimated total percentage error σ [15]. The estimated errors are probably excessive because the estimation technique is less effective for values of radiogenic argon as low as these.

Nevertheless, it seemed prudent to avoid the use of heavy liquids in preparing the starting materials for the cation-exchange and heating experiments.

Most replacement of the natural cations occurred during the first iterations of the cation-exchange experiments and decreased substantially during subsequent steps. The K_2O contents were significantly modified, as expected, whereas less drastic changes were noted in the amounts of radiogenic Ar except for the Cs-exchanged fraction from the 5-day experiment (Table I, Fig. 1a). Given the scatter in the data, there is no clear effect of the cation exchange process on radiogenic Ar content. The apparent increase in the radiogenic Ar content of the five-day Cs-exchanged clinoptilolite is not understood and should be verified by further study. We know of no mechanism to account for a genuine increase of radiogenic Ar.

The loss of about half the radiogenic Ar from the five-day Na-exchanged clinoptilolite, while not clearly a statistically significant result, is of interest. The smaller ionic radius of Na, compared to the other exchangeable cations, suggests that it may less effectively block the movement of water, cations, and gases in and out of the crystal structure. A possibility that the exchangeable cation composition of clinoptilolite could affect the retention of Ar would be worth investigating.

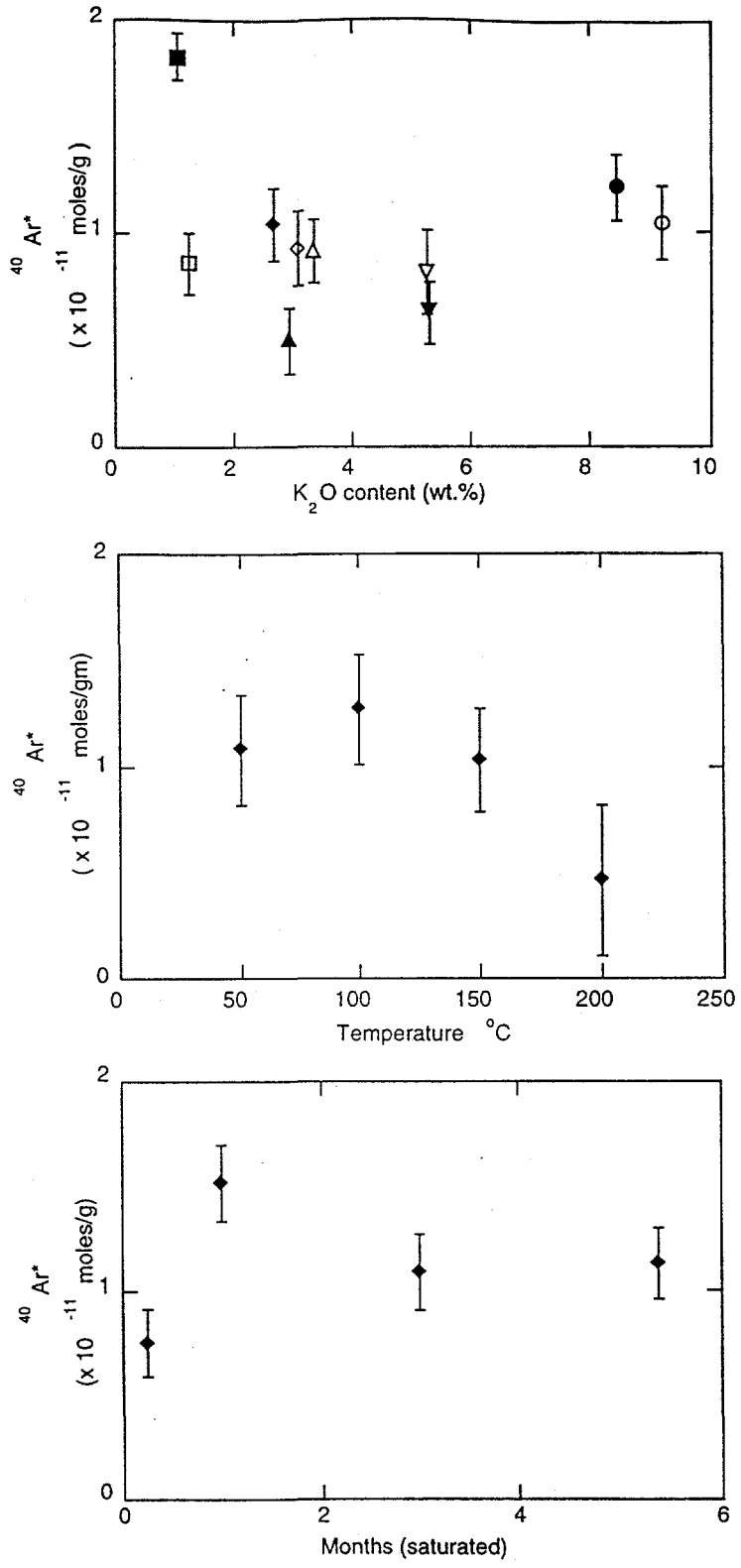

Figure 1a) Radiogenic Ar contents of cation-exchanged clinoptilolite fractions. Open and solid symbols denote fractions exchanged for three and five days, respectively. Symbols represent water-separated starting material (inverted triangle), heavy-liquid treated material (solid inverted triangle), exchange cations Ca^{2+} (diamond), Cs^{+} (square), K^{+} (circle), and Na^{+} (triangle). b) Radiogenic Ar contents of samples heated dry for 16 hours. c) Radiogenic Ar contents of samples heated in water.

About 40% of the radiogenic Ar was lost from clinoptilolite heated in air at 200°C, with inconclusive results for the samples heated at lower temperatures (Table I, Fig. 1b). Minor, possibly insignificant variations from the original radiogenic Ar content were noted in the clinoptilolite fractions heated in water at 100°C for up to six months (Table I, Fig. 1c).

IMPLICATIONS OF EXPERIMENTAL RESULTS FOR CLINOPTILOLITE DATING

The results of the cation exchange experiments suggest that the effects of cation exchange on the K/Ar systematics of clinoptilolite would likely be limited to modification of the K_2O contents. Addition of K_2O from pore fluids into the clinoptilolite structure would be consistent with the cation affinity sequence for clinoptilolite reported by Ames [16]. Unsaturated-zone waters above the zeolitized tuffs at Yucca Mountain have slightly higher chemical concentrations and higher Ca+K/Na than saturated-zone waters [17]. Comparisons of exchangeable cation compositions of clinoptilolite from the saturated and unsaturated zones do not clearly indicate any K_2O enrichment in the unsaturated zone except for a few outcrop samples [18]. Therefore we conclude that although post-crystallization K_2O enrichment may have contributed to the young apparent ages of a few surface samples, it does not account for the overall pattern of increasing ages with depth.

Substantial loss of radiogenic Ar was observed in the clinoptilolite fraction heated in air for 16 hours at 200°C. Dehydration caused by dry heating produces increased atomic displacement and disorder in the tetrahedral framework of alkali zeolites [19] and this may enhance the loss of Ar from the clinoptilolite structure. It is important to note, however, that while the dry-heating experiment was designed to accelerate any loss of Ar that might occur at low moisture content, it does not represent in situ conditions in the unsaturated zone of Yucca Mountain in terms of either temperature or humidity. Present temperatures in the unsaturated zone are no more than about 35°C [20], and the survival of the low-temperature minerals clinoptilolite, smectite, and opal-CT suggests that the diagenetic rocks in the unsaturated and shallow saturated zone have not been subjected to high temperatures.

The rate of Ar loss may also be affected by the availability of pore water to wet the surfaces of the clinoptilolite crystals. According to Barrer and Vaughan [21], Ar diffusion below 110°C can be minimized, at least for short periods of time, by surface rehydration of artificially dehydrated clinoptilolite. The pores of clinoptilolite-rich rocks above the SWL at Yucca Mountain are generally more than 70 % saturated [22]. Varying conditions of liquid undersaturation, existing within a changing recharge environment for millions of years, might contribute to the loss of radiogenic Ar.

SUMMARY AND CONCLUSIONS

The cation exchange experiments indicate that the exchangeable cation composition, including the K^+ contents, of clinoptilolite can be significantly modified with little effect on the radiogenic Ar content of the same sample. Ar depletion was apparent in a clinoptilolite fraction heated in air at 200°C. Samples heated in water at 100°C for up to six months experienced only minor, inconclusive variations in Ar content. Loss of radiogenic Ar from incompletely hydrated clinoptilolite occurs perhaps because of disorder in the clinoptilolite structure or the effects of decreased surface wetting. Thus, water appears to play an important role in the retention of Ar within the clinoptilolite structure. Other factors such as elevated thermal conditions, addition of K, and late diagenetic reactions appear to be less important in modifying the apparent ages of clinoptilolite.

The results of this work, together with data from site characterization studies, suggest that the apparent ages of clinoptilolite from the unsaturated zone of Yucca Mountain may have been reduced by diffusive loss of Ar from incompletely saturated rocks. Clinoptilolites from the vicinity of the SWL probably existed under unsaturated conditions for a shorter time and therefore were less affected than zeolites from the shallow unsaturated zone. The apparent ages of zeolites from outcrop may have been even further reduced by recent addition of K^+ from cation exchange with recharge water. The combined effects of these processes may have produced the observed pattern of increasing clinoptilolite apparent ages with depth.

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