342
7/22/81
M.S.

(1)

Dr. 2849

LA-8841-MS

B5861

MASTER

Review of the Thermal Stability and Cation Exchange Properties of the Zeolite Minerals Clinoptilolite, Mordenite, and Analcime: Applications to Radioactive Waste Isolation in Silicic Tuff

University of California

LOS ALAMOS SCIENTIFIC LABORATORY
Post Office Box 1663 Los Alamos, New Mexico 87545

REVIEW OF THE THERMAL STABILITY AND CATION EXCHANGE PROPERTIES OF THE ZEOLITE MINERALS CLINOPTILOLITE, MORDENITE, AND ANALCIME: APPLICATIONS TO RADIOACTIVE WASTE ISOLATION IN SILICIC TUFF

by

J. R. Smyth and F. A. Caporuscio

ABSTRACT

Silicic tuffs of the southern Great Basin and basalts of the Columbia River Plateau are under investigation as potential host rocks for high- and intermediate-level radioactive wastes. Nonwelded and partially welded tuffs may contain major amounts (>50%) of the zeolite minerals clinoptilolite, mordenite, and analcime. Densely welded tuffs and some basalt flows may contain clinoptilolite as fracture filling that limits the permeability of these rocks. The cation exchange properties of these zeolite minerals allow them to pose a formidable natural barrier to the migration of cationic species of various radionuclides in aqueous solutions. However, these minerals are unstable at elevated temperatures and at low water-vapor pressures and may break down either by reversible dehydration or by irreversible mineralogical reactions.

All the breakdown reactions occurring at increased temperature involve a net volume reduction and evolution of fluids. Thus, they may provide a pathway (shrinkage fractures) and a driving force (fluid pressure) for release of radionuclides to the biosphere. These reactions may be avoided by keeping zeolite-bearing horizons saturated with water and below about 85°C. This may restrict allowable gross thermal loadings in waste repositories in volcanic rocks.

I. INTRODUCTION

Zeolites are open-framework aluminosilicate minerals of the general formula $(Na_2, K_2, Ca)_x\ Al_{x/2}\ Si_{2-x/2}\ O_4 \cdot yH_2O$. Each aluminum and silicon is coordinated by four oxygens, each of which is shared with another aluminosilicate tetrahedron to form a three-dimensional framework. The framework encloses large regular cavities into which hydrated large radius cations (Na, K, Ca, Mg, Fe, Cs, Sr, Rb, and Ba) fit to balance the net negative charge on the framework left by the substitution of aluminum for silicon. The large cations and their waters of hydration are loosely bound and are readily exchangeable. The water is largely neutral (not required for stoichiometry) and may exist in variable amounts within any given structure. The structures are also capable of incorporating and sometimes entrapping ammonia, noble gases, and complex organic molecules and are used extensively in industry as catalysts and ion sieves. The variable cation radii and amounts of water are accommodated by expansion and collapse of the framework as evidenced by measurable expansion and contraction of the unit cell.

Natural zeolites, with few exceptions, are found in rocks that are generally known to have formed or altered at temperatures less than 200°C. They are most common in porous volcaniclastic rocks and in sediments that contain a significant volcanic component, both of which have undergone burial diagenesis at temperatures below 200°C. Zeolites are also common in near-surface sediments in saline alkaline lake environments, particularly in regions where there is a significant volcanic glass component in the sediments. Zeolites are known to undergo complex solid-state mineralogical reactions at temperatures as low as 50°C (Sheppard and Gude [illegible]; Mariner and Surdam 1970; Boles and Coombs 1976; Iijima [illegible]).

Silicic tuffs, which have undergone variable amounts of zeolitization, are under consideration as a medium for the long-term isolation of high-level radioactive wastes (Smyth et al. [illegible], Smyth and Sykes 1980, Sykes and Smyth 1980). One potential site in such a medium is located in southern Nye County, Nevada (Heiken and Bevier [illegible], Sykes et al. [illegible], Spengler et al. 1979) at Yucca Mountain, on and immediately adjacent to the Nevada Test Site (NTS). The principal zeolite phases in these rocks are clinoptilolite, mordenite, and analcime. They may comprise 90 [illegible] of some horizons. Inasmuch as heat-generating wastes may be placed in such a medium, it is imperative to understand the types of mineralogical reactions and the conditions under which they may occur so that such reactions may either be avoided or allowed for in the repository design. Further, understanding some of the physical properties of these minerals will be useful in interpretation of results of experimental work on these rocks.

Reactions that may occur in these rocks at temperatures below 200°C are of two types: simple reversible dehydration and complex mineralogical phase inversions. The first of these involves the loss of loosely bound water of hydration in the zeolite. This water is not required for stoichiometry of the zeolite and may be lost reversibly without damage to the aluminosilicate framework. However, loss of the water can cause contraction of the unit cell (and hence individual grains) of up to 10% by volume (Boles 1971, 1972) with concomitant development and propagation of fractures and loss of mechanical strength. The second type of reaction involves complete recrystallization and exchange of cations and/or water with the environment. Such reactions may evolve (or incorporate) significant quantities of water, result in volume changes in large quantities of rock, and alter physical and chemical properties of rock and incorporated fluids.

This report reviews the literature on the mineralogy and some physical and chemical properties of the principal zeolite phases that occur at Yucca Mountain, Nevada (clinoptilolite, mordenite, and analcime) and the dehydration and mineralogical reactions that occur among these phases at temperatures below 200°C. Based on this literature review, some preliminary experiments have been performed to outline and refine some potential effects and conditions of such reactions in the rocks of Yucca Mountain. The preliminary experiments and the literature review can then be used to outline further experiments that may be required to precisely understand these reactions.

II. LITERATURE REVIEW

A. The Mineralogy of Clinoptilolite and Heulandite

Clinoptilolite and heulandite are isostructural, differing principally in the large cation and Al/Si ratio. Unit cells and approximate chemical formulae are given in Table I. Heulandite is the name given to the calcium- and aluminum-rich end-member and clinoptilolite to the sodium-, potassium-, and silicon-rich end-member. Laboratory synthesis of these phases is experimentally difficult (Goto 1977), and there has been discussion in the literature (Mumpton 1960, Mason and Sand 1960, Shepard 1961, Boles 1972, Alietti 1972) whether complete crystalline solution exists. However, sufficient intermediate compositions have now been reported from natural specimens to conclude that there is no compositional gap between the end-members (Boles 1972).

TABLE I

UNIT CELL AND CHEMICAL FORMULA FOR CLINOPTILOLITE MORDENITE AND ANALCIME

		Unit Cell			Space	
Mineral	a	b	c	β	Group	Formula
Clinoptilolite[a]	17.63	17.97	7.39	116.3°[a]	C2/m	$Na_6[Al_6\ Si_{30}\ O_{72}]\ 24\ H_2O$[d]
Heulandite	17.72	17.86	7.43	116.4°[a]	C2/m	$Ca_4[Al_8\ Si_{28}\ O_{72}]\ 24\ H_2O$
Mordenite	18.10	20.48	7.52[b]		Cmcm	$Na_8[Al_8\ Si_{40}\ O_{96}]\ 24\ H_2O$[d]
Analcime	13.723		13.686[c]		$I4_1/acd$	$Na_{15}[Al_{15}\ Si_{33}\ O_{96}]\ 16\ H_2O$[c]
	13.733	13.729	13.712[c]		Ibca	$Na_{16}[Al_{16}\ Si_{32}\ O_{96}]\ 16\ H_2O$[c]

---

[a] Boles 1972
[b] Passaglia 1975
[c] Mazzi and Galli 1978
[d] Gottardi 1978

The extremes of composition have somewhat different physical properties. The clinoptilolite end-member is substantially more stable with respect to short-term heating in the laboratory than is heulandite. Indeed, Mumpton (1960) suggested differentiation of the two on the basis of a heating test to 400°C for 16 to 24 h: heulandite becomes x-ray amorphous whereas clinoptilolite retains its crystallinity. Several workers (Boles 1972, Alietti 1972, Riecker and Rooney 1968) have shown that clinoptilolite may retain its crystal structure and mechanical strength to temperatures as high as 750°C for short periods (<24 h) under dry conditions (1 atm air), whereas heulandite may begin to break down irreversibly at temperatures as low as 250°C. However, resistance to short-term dry heating should not be taken to indicate thermodynamic stability. Although Boles (1971, 1972) prefers to differentiate the two end-members on the basis of composition, he has performed numerous heating experiments to delineate thermal stability (see Sec. II, D.)

Clinoptilolite is one of the most abundant of natural zeolites. It is common in diagenetically altered silicic tuffs, where it replaces glass pyroclasts and fills pores. It can comprise 90% or more of some horizons. In these rocks it appears to be among the first-formed zeolites, forming directly from glass and occurring nearest the surface. It is also common in saline-alkaline lake deposits such as Lake Tecopa, Inyo County, California (Sheppard and Gude 1968) in which glass is a significant detrital component. Further, it is common in deep-sea sediments, where it occurs at some depth in the sediment column and may replace phillipsite, which occurs at the top of the column (Boles 1977, Boles and Wise 1978, Kastner and Stonecipher 1978). With very few exceptions, high-silica, high-alkali clinoptilolite is extremely fine-grained (<20 μm) and is not known to occur or form in environments where temperatures exceed 100°C.

As mentioned earlier, heulandite and clinoptilolite are isostructural. Although cell edges do appear to be related to composition (Boles 1972), they are greatly affected by hydration state, making the two extremely difficult to reliably distinguish by x-ray powder diffraction methods. The crystal structure was determined for a heulandite by Merkle and Slaughter (1968), and since then, four additional structures have been reported. Two of these are for heulandites (Alberti 1972, Bartl 1973), the latter by neutron diffraction, and two for macrocrystalline clinoptilolite (Alberti 1975). A stereo plot of the structure is given in Fig. 1. The structure is monoclinic with space group *C2/m*; however, aluminum-silicon ordering in the framework may reduce the symmetry to *Cm* (Merkle and Slaughter 1968) or *I2/m* with a doubling of the unit cell (Bartl 1973).

The structure of clinoptilolite consists of linked 4- and 5- membered rings forming layers in the *a*-*c* plane separated by 8-ring and 10-ring channels parallel to *c* with approximate dimensions of 4.4 by 3.0 Å and 7.9 by 3.5 Å, respectively. The exchangeable cation sites lie in the channels close to the 8- and 10-rings. The cation exchange properties of natural clinoptilolites and heulandites have been extensively investigated and indicate extremely high selectivity for cesium and a high selectivity for strontium. Ames (1959, 1960,

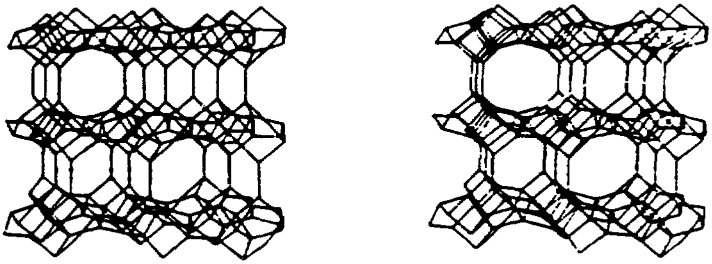

Fig. 1.
Stereo pair diagram of the framework of clinoptilolite and heulandite (after Meier and Olsen 1978). View is along the axis of the 8- and 10-ring channels (*c*). The *b*-axis is horizontal, parallel to the page.

1960, 1961, 1962a, b, 1963, 1964, 1965) has investigated the use of natural clinoptilolite to scavenge ^{137}Cs and ^{90}Sr from radioactive waste streams. This ability of natural clinoptilolite to selectively remove these elements from solution by ion exchange, particularly in high concentrations of competing ions, allows natural clinoptilolite tuff to form an extremely effective barrier to migration of these ions. It is cesium and strontium that can contribute up to 80% of the specific activity of radioactive wastes from the commercial fuel cycle in the period from 10 to 600 years after fission. Further, Honstead et al. (1960) showed that rare earth ions and ^{60}Co can also be isolated by clinoptilolite ion-exchange properties. Some ion exchange and sorption properties of natural clinoptilolite are reviewed in Tables II and III.

TABLE II

SORPTION PROPERTIES OF CLINOPTILOLITE, MORDENITE, AND ANALCIME[a]

	Si/Al	Diffusion Control		Sorption	Sorption Properties[b]				pH Stability
Mineral	Range	Ring Type	Ring Size (Å)	Site Type	H_2O	N_2	nC_4H_{10}	C_6H_6	Limit[c]
Clinoptilolite	2.7-5.3	10 8	7.9 by 3.5 4.4 by 3.0	Channel	14	11	4	9	<2
Mordenite	4.4-5.5	12	7.0 by 6.7	Channel	15	15.4	6.5	8.8	<2
Analcime	2.0-2.7	6	2.8 by 2.8	Channel	8	0	0	0	~5

---

[a] Modified after Vaughan 1978.
[b] Approximate maximum reported values (wt%).
[c] pH at which structural degradation is detectable.

TABLE III

ION EXCHANGE PROPERTIES OF CLINOPTILOLITE[a]

Mineral	Si/Al (Exchange Capacity)	Original Cations	Exchange Selectivities
Clinoptilolite	2.7 - 5.3	Na, K, Ca	$Cs^+ > K^+ > Sr^{++} = Ba^{++} > Ca^{++} >> Na^+ > Li^+$ $Pb^{++} > Ag^+ > Cd^{++} \simeq Zn^{++} > Ca^+ > Na^+$
Mordenite	4.4 - 5.5	Na, Ca	$Cs^+ > K^+ > NH^{4+} > Na^+ > Ba^{++} > Li^+$ $NH_4^+ > Na^+ > Mn^{++} > Cu^{++} > C^{2+} \sim Zn^{++} > Ni^{++}$
Analcime	2.0 - 2.7	Na	Complicated by ion sieving

---

[a] Modified after Vaughan 1978.

B. Mineralogy of Mordenite

Mordenite is a zeolite of commonly fibrous habit. It is very simliar in chemical composition and water content to alkali clinoptilolite and has the approximate formula $(Na_2, K_2, Ca)_4\ Al_8Si_{40}O_{96} \cdot 28H_2O$ (Passaglia 1975). However, the Al/Si ratio is much less variable. The mineral species ptilolite, flokite, and arduinite have been shown to be identical to mordenite (Davis 1958) and these names are no longer in use.

The crystal structure was determined by Meier (1968) and is orthorhombic with space group Cmcm (Table I). Recent refinements of the structures of dehydrated mordenites (Schlenker et al. 1979a,b) also give this space group. A stereo pair drawing of the framework is given in Fig. 2 showing the chains of five-membered rings parallel to c, which are connected through double eight-membered rings in the a-c place. These are joined to form large 12-ring channels parallel to c with double 8-ring prisms forming side pockets in the a-c plane. Adjacent eight-ring prisms are offset by c/2 so that the path between large channels is constricted, and diffusion within the structure is limited to molecules with diameters less than about 2.8 Å. Structural offset of the large channels limits access to the structure to molecules with diameters less than about 4.2 Å (Vaughan 1978). Because of this cage-like effect, natural mordenite has been used to mechanically entrap ^{85}Kr which can diffuse into the structure at elevated temperatures (Barrer and Vaughan 1971, Brown et al. 1977, Benedict 1979). Some sorption and cation exchange properties of

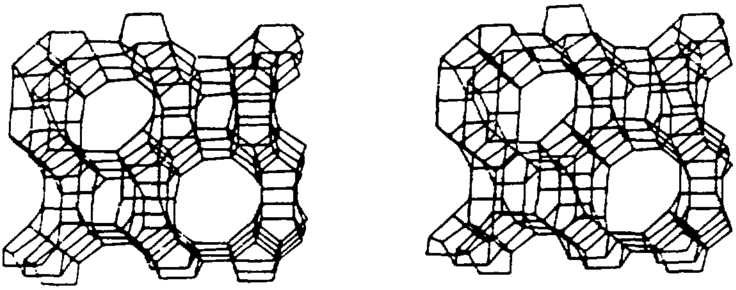

Fig. 2.
Stereo pair diagram of framework of mordenite (after Meier and Olsen 1978). View is parallel to c.

natural mordenites are reviewed in Tables II and III. Mordenite is stable in acid solutions (up to 2 mol HCl), and acid treatments are used to increase ion exchange capacities of natural mordenites.

Mordenite is common in altered silicic tuff deposited in marine and continental environments where it can be a major constituent of some rocks. At the NTS, it is commonly closely associated with clinoptilolite and cristobalite in the deeper clinoptilolite zones where it comprises up to 40% of some horizons (Hoover 1968, Heiken and Bevier 1978). Mordenite also occurs in saline-alkaline lake environments where it can form nearly pure monomineralic rocks (Sheppard and Gude 1968, 1969, Surdam and Sheppard 1978).

C. Mineralogy of Analcime

Analcime is a sodium-rich zeolite with the ideal formula $NaAlSi_2O_6 \cdot H_2O$; however, natural analcimes range in composition from about $Na_{16}Al_{16}Si_{32}O_{96} \cdot 16H_2O$ to about $Na_{13}Al_{13}Si_{35}O_{96} \cdot nH_2O$ (Coombs and Whetten 1968). Although the calcium analogue exists as the mineral wairakite ($Ca_8Al_{16}Si_{32}O_{96} \cdot 16H_2O$) as do intermediate compositions, calcic analcimes are more common in high-temperature hydrothermal environments (Harada et al. 1972, Liou 1971). Analcimes from diagenetically altered alkalic silicic tuffs tend to be nearly calcium free and silica rich (Coombs and Whetten 1968, Heiken and Bevier 1978) although calcic analcimes have been reported from such environments (for example, Surdam and Parker 1979). The cesium analogue also exists as the mineral pollucite (the principal ore of cesium), but extensive crystalline solution between the cesium and sodium end-members has not been reported. Natural analcime has a substantially lower water content and higher density than either clinoptilolite or mordenite.

The holosymmetry of the analcime framework is cubic, space group Ia3d (Table I) (Taylor 1930, Calleri and Ferraris 1964, Knowles et al. 1965, Ferraris et al. 1972). Natural analcimes, however, commonly show evidence of noncubic symmetry and are typically optically birefringent to varying degrees. This has been related to aluminum-silicon ordering in the framework in violation of cubic symmetry. Mazzi and Galli (1978) have successfully refined analcime crystal structures in the tetragonal space group $I\ 4_1/acd$ and in the orthorhombic space group Ibca, both subgroups of the cubic Ia3d. A stereo pair diagram of the framework is given in Fig. 3.

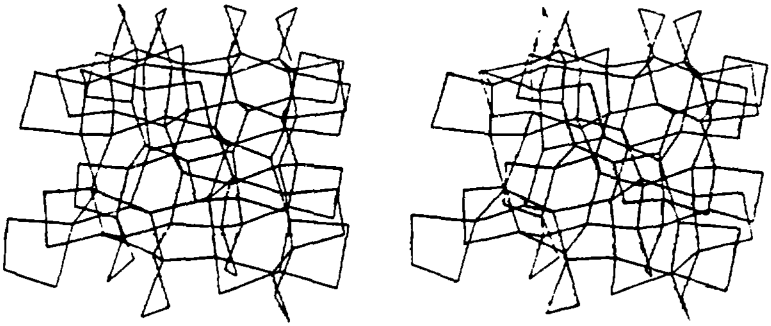

Fig. 3.
Stereo pair diagram of the framework of analcime (after Meier and Olsen 1978). The lack of channels is evident when compared with Figs. 1 and 2.

The cubic structure consists of four-, six-, and eight-membered rings linked to form nonintersecting channels and cavities. Because of the dense structure and isolated channels and cavities, the analcime structure does not readily sorb molecules larger than about 3.0 Å diam, and ion exchange is extremely limited particularly at room temperature. At elevated temperatures, sodium can be replaced by potassium, silver, thallium, ammonia, and rubidium; however, only negligible exchange occurs with lithium, magnesium, calcium, and barium (Vaughan 1978). Cesium has been shown to exchange very slowly (Barrer and Rees 1960, Callahan and Kay 1966).

Analcime is the only member of the zeolite group that appears to occur as primary magmatic crystals in the groundmass of some basalts (Deer et al. 1964). However Liou (1971) and Thompson (1971) have shown that analcime breaks down to nepheline plus albite at 200°C and 100 MPa (1 kbar) water pressure, and it may be that the apparent igneous occurrences are either secondary or metastable. Saha (1959) has shown that analcime is kinetically favored and crystallizes readily from glasses ranging in composition from nepheline to albite. Analcime is widespread as a secondary alteration mineral in silicic tuffs that have undergone burial diagenesis or low-grade hydrothermal alteration. In this paragenesis, it commonly pseudomorphs and replaces clinoptilolite and mordenite. Here it may compose up to 90% of some rocks although it is more commonly intergrown with significant amounts of quartz, cristobalite, and albite. Analcime also occurs in hydrothermally altered tuffs and sediments (for example, Seki and Oki 1969, Honda and Muffler 1970) and is a minor constituent in saline-alkaline lake deposits (Sheppard and Gude 1968).

D. Dehydration Stability

Literature on the thermal stability of clinoptilolite and heulandite is complex and, in places, conflicting. However, such studies are of two principal types: those done at one atmosphere pressure or less, and those done at elevated water pressures. The former principally address dehydration reactions to metastable states, whereas the latter address the thermodynamic stability of clinoptilolite relative to other zeolite phases. Both types of reaction may constrain design of a waste repository in or near clinoptilolite-bearing rocks. Literature on the thermodynamic stability of clinoptilolite will be reviewed under "Burial Diagenesis" below. The dehydration of these minerals may cause water loss under unsaturated conditions, possibly affecting the stability of mine tunnels or, in a worst case, control temperature and water pressure conditions during a thermal excursion. In either case, the reactions warrant investigation.

Because heating tests in dry atmospheres have been used to differentiate clinoptilolite from heulandite (Mumpton 1960, Alietti 1972, Boles 1972), there exists considerable information on the thermal stability of these minerals under such conditions. Breger et al. (1970) describe a complex polymorphism in clinoptilolite based on x-ray powder diffraction and infrared spectroscopy. These and subsequent workers (Boles 1971, 1972, Alietti 1972) describe discrete contracted phases, a B phase and an intermediate I phase, which occur on heating in the range 200 to 300°C, followed by cooling. The more alkalic and silicic the clinoptilolite, the higher the temperature at which the contracted phases appear. The more calcic and aluminous heulandites become x-ray amorphous above 250°C, whereas the more alkalic and silicic clinoptilolites do not become x-ray amorphous until heated above 750°C. The contracted phases were observed to revert to the normal structure after cooling and being allowed to re-equilibrate with atmospheric moisture. It is inferred that the contracted phases result from reversible loss of loosely bound water with concomitant collapse of the aluminosilicate framework. The contracted phases appear to have decreased in volume by up to 10%. Single-crystal observations of the dehydration of these minerals are in progress (Mortier and Pearce 1980), so it should soon be possible to conclude if the contracted phases are discrete, definable states or if all intermediate states may exist. Such observations will be extremely useful for interpretation of dehydration phenomena and how they might affect physical properties, mechanical strength in particular.

Mordenite behaves similarly to clinoptilolite on dehydration (for example, Schlenker et al. 1979a,b). It releases loosely bound water on increased temperature up to approximately 300°C. Water loss is accompanied by a reduction in unit cell volume of up to 8%. Loss of crystallinity begins above 400°C. No detailed information on the dehydration behavior of analcime was found in the literature. Analcime might be expected to exhibit similar effects; however, they will probably be much less pronounced and occur at higher temperatures because of the substantially lower water content, higher density, and apparent higher temperature of paragenesis of analcime relative to clinoptilolite and mordenite.

E. Burial Diagenesis

Zeolite grade metamorphism was defined to be the lowest grade of regional metamorphic alteration of rocks by Fyfe et al. (1958) based on the early work of Coombs (1953). It occurs at temperatures below 200°C and pressures below 300 MPa (3 kbar) (for example, Winkler 1965, Turner and Verhoogen 1960) and is typical of low-grade burial and contact metamorphic assemblages (Hay 1966, Coombs 1970, Sheppard 1971, Hay 1978, Barrows 1980). It is only recently that the zeolite grade has been subdivided into zones that are consistent, mappable, and correlated between rocks of differing composition, and that temperatures have been tentatively assigned to boundaries (Iijima 1975, 1978, 1980). The temperature ranges of these zones are also known to vary with the composition of pore fluids, particularly with sodium ion concentration.

Zeolite zones defined by Iijima (1975, 1980) are based on zeolite mineralogies replacing volcanic glass in two types of sequences: an alkali zeolite reaction series and a calcic reaction series. Zone boundaries are defined on the basis of the more common alkali series, which is typical of diagenetically altered silicic tuff.

> "Four diagenetic zones are constructed; namely, Zone I is a zeolite-free zone characterized by glass shards which alter principally, or sometimes wholly to smectite and opal; Zone II is a zone characterized by clinoptilolite, mordenite, or both which originate from

acidic glass; Zone III is a zone characterized by analcime replacing the precursor zeolites, which often coexist as relic; and Zone IV is a zone characterized by albite replacing analcime." (Iijima, 1980).

The mineralogy of the various zones is shown diagrammatically in Fig. 4.

Several lines of evidence have been used to establish temperatures of boundaries between zones. The top of Zone III, marked by the appearance of analcime, has been observed in drill holes penetrating thick sequences of Quaternary marine tuffs currently undergoing burial diagenesis in the Niigata, Akita, and Tenpoku oil fields of Japan (Iijima and Utada 1971, Iijima 1975, 1978, 1980, Iijima and Ohwa 1980). Borehole logs give a narrow temperature range of 84 to 91°C for the transition. It appears to occur over a large depth range (1700 to 3500 m), indicating that temperature rather than pressure (total or water) is the controlling variable. This is in very good agreement with the experimental work of Boles (1971) who converted clinoptilolite to analcime at 100°C in pore fluids of 0.1 mol NaCl plus 0.01 mol Na_2CO_3 in 21 days. In the drill holes, the top of Zone IV is observed at 120 to 124°C over a depth range of 2500 to 4500 m, again indicating that temperature rather than pressure is the controlling variable.

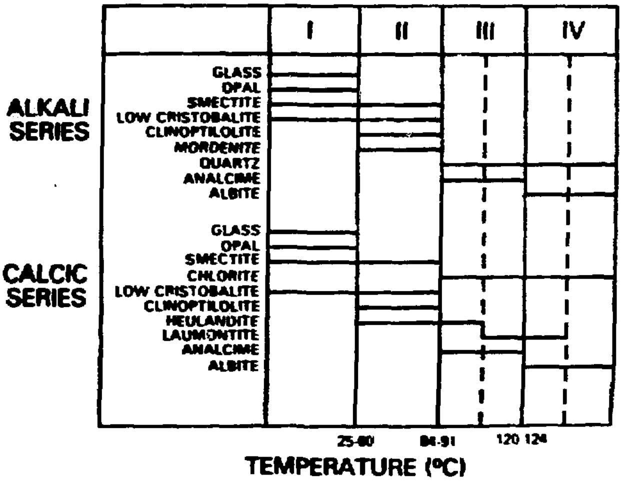

Fig. 4.

Zeolite zone mineralogy for alkali and calcic zeolite series (after Iijima 1980). Approximate temperatures of boundaries between zones at bottom of figure are given by Iijima, 1980 for marine tuffs with high concentrations of Na+ in pore fluids (Iijima and Ohwa 1980).

The top of Zone II is observed at temperatures of 25 to 60°C over a depth range of 635 to 1900 m. The wider temperature range indicates that this reaction is perhaps more sensitive to pressure or pore water composition. Iijima (1975) has summarized the effects of pore water composition on the temperatures of the Zone II/III and Zone III/IV boundaries. His conclusions are presented diagrammatically in Fig. 5 and permit a rough extrapolation to lower sodium ion concentrations. If sufficient sodium ion is available for conversion of alkali clinoptilolite to analcime at concentrations below 1000 ppm, then the reaction should proceed at temperatures of 90 to 100°C at concentrations typical of waters in tuff with open continental hydrologic systems.

In summary, the literature on the mineralogy, chemistry, occurrences, and thermal stability of zeoloite minerals typical of the alkali-zeolite sequence

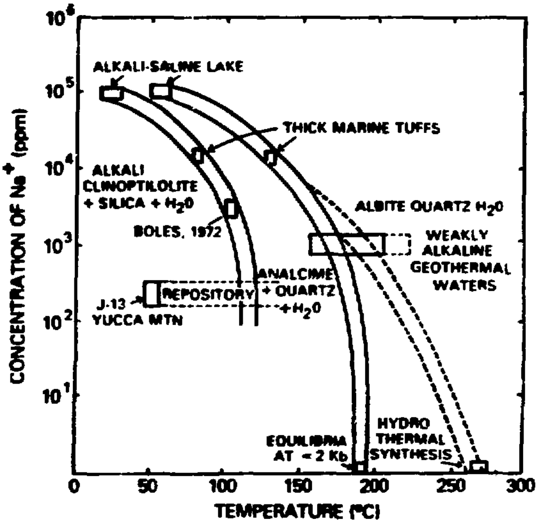

Fig. 5.

Plot of Na+ concentration vs temperature for reactions bounding zeolite zones (after Iijima 1975). The lowest temperature and concentration field is for the assemblage alkali clinoptilolite + silica + H_2O and corresponds to Zone II (Fig. 4). The reaction of this assemblage to analcime + quartz + H_2O is delineated by three data points: temperatures of saline alkaline lakes, those of thick marine tuffs and the laboratory experiment of Boles 1972. The reaction of the assemblage analcime + quartz + H_2O (Zone III) to albite + quartz + H_2O is bounded by four data points: saline alkaline lakes, thick marine tuffs, weakly alkaline geothermal waters (for example, Honda and Muffler 1970), and some laboratory experiments (for example, Liou 1971, Saha 1959). The composition of water from drill hole J-13 in Jackass Flat is plotted at the approximate ambient temperature of possible repository horizons at Yucca Mountain.

in continental tuffs has been reviewed. Sorption and cation exchange selectivity offer a substantial advantage of these rocks over other media for long-term isolation of radioactive wastes. The relatively low thermal stability of these minerals, however, may constrain the allowable temperatures and hence waste emplacement densities for any repository of high-level wastes or spent reactor fuel elements.

III. CONSTRAINTS ON REPOSITORY CONDITIONS

A. Dehydration Reactions

Although it is not currently contemplated to emplace radioactive waste directly into zeolitized horizons, rocks containing major amounts of clinoptilolite and mordenite surround potential repository horizons at Yucca Mountain. Also, zeolites are important fracture-filling minerals that may control permeability in basalts of the Columbia River Plateau. Simple dehydration of natural clinoptilolite and mordenite is viewed as being of secondary importance to repository design relative to the mineralogical reactions discussed below. However, inasmuch as these reactions may cause degradation of mine tunnels and pillars or open fractures, some preliminary experiments have been carried out to delineate or bound dehydration reaction conditions.

The first experiment (Appendix A) observed the time required for a small cylinder of clinoptilolite-rich tuff to reach hydration equilibrium with laboratory air at 95°C (relative humidity <20% at 20°C) after being hydrated in a water-saturated environment at 95°C. The results indicate a rapid decrease in volume and weight in the first few hours with essentially no changes in weight and volume after about 8 h. Essentially complete rehydration occurred after replacing in the saturated environment for 8 h. The results of this experiment show that the hydration state of clinoptilolite is much more a function of partial pressure of water than of temperature. Although the water in the zeolite is only loosely bound, it does have some binding energy and does not behave thermodynamically like liquid water. From this, one may conclude that if the zeolite is in equilibrium with liquid water at the same temperature, it should be fully hydrated, and that major dehydration (that is, loss of greater than 3% water by weight) can only occur if the partial pressure of water is less than the vapor or pore pressure.

However, the above inference pertains only to major dehydration effects, and minor dehydration (loss of 2% or less water by weight) may also become significant. For example, if clinoptilolite is under an external water pressure of 30 bar (= 300-m waterhead) and the temperature is raised from 35 to 85°C, the "fully-hydrated" state at the higher temperature may contain less water than at the lower temperature. Within the limits of current knowledge, this amount could be as much as 1 or 2 wt%; and if so, pressures in excess of the hydrostatic head could develop in and around the heated, saturated zeolitized horizon. This could have a significant effect on the hydrology of the repository site. To evaluate such effects, data on amounts of hydration water in these zeolite minerals as a function of water pressure and temperature are required. It is here strongly recommended that such measurements be undertaken, particularly in the temperature range 30 to 100°C and pressure range 0.5 to 30 bar.

A second experiment (Appendix B) recorded changes in weight and volume for specimens of differing mineralogy on heating in a dry environment at several temperatures for a minimum of 8 h each. Three nonwelded specimens, one high in clinoptilolite, one high in analcime, and one high in glass, and one welded devitrified specimen high in quartz, feldspar, and cristobalite were selected. The results reflect a very large difference in dehydration behavior of the various minerals. The welded devitrified and the nonwelded vitric specimens showed near zero weight loss on heating as might be expected from the near absence of hydrous minerals. The analcime specimen showed a total weight loss of about 5% and the clinoptilolite about 10%, which is consistent with their relative water contents. These results closely correlate with hydrous mineral water contents and not with porosity or bulk density.

It is possible to conclude from these simple experiments that major dehydration (greater than 3 wt% water) of clinoptilolite would only occur in a repository at mine tunnel surfaces if liquid water were not present or in rock masses if boiling should occur. If temperatures in the repository are not to exceed 100°C, the latter should not be a problem. If heated mine tunnels are cooled by surface air, the former could become a problem; however, it could easily be avoided by wetting down tunnel surfaces. If boiling should occur in rock masses by some accident or severe miscalculation, dehydration of clinoptilolite with decrease in volume, propagation of fractures, and evolution of large amounts of water could become a severe problem.

Although major dehydration of these minerals should not occur in the temperature range 20 to 85°C with water pressures in excess of one atmosphere, small changes in the water contents of up to 1 or 2% are possible. Inasmuch as such changes may affect the local hydrology, they need to be evaluated. To do this, it will be necessary to undertake careful differential thermal analysis of the dehydration process and to measure the water contents of clinoptilolite as a function of water pressure at various temperatures.

B. Mineralogical Reactions

As pointed out, clinoptilolite and mordenite have a somewhat limited thermal stability and break down to denser, less hydrous phases (analcime and albite, progressively) at temperatures below 150°C under conditions that could conceivably be achieved in the rock volume surrounding a waste repository. Although the reactions might possibly result in more inherently stable rocks, and the recrystallization might fix migrating radionuclides, potential negative effects are currently unknown and unpredictable. In particular, the reactions can release large amounts of water, cause significant volume decreases and development and propagation of fractures, and completely alter the physical and chemical properties of the rock.

Because kinetic and other thermodynamic parameters of these reactions are unknown, it is currently impossible to accurately model or predict the effects. It therefore seems advisable to avoid conditions that might induce such reactions. This may place a significant constraint on waste emplacement densities (thermal loading) in any repository at Yucca Mountain. The reaction of clinoptilolite to analcime is the one that appears to take place at the lowest temperatures and hence has the greatest potential to constrain thermal loadings. This reaction has been observed in the laboratory in pore fluids moderately concentrated in sodium ion (approximately 5000 ppm at pH 11) at 100°C in as little as 21 days (Boles 1971). Also, analcime is reported to be forming in the field at temperatures as low as 85°C in slightly more concentrated sodic pore fluids (approx 10 000 ppm at pH 8.5) (Fig. 5, Iijima 1975). Ground water at Yucca Mountain is of substantially lower sodium ion concentrations and pH. Water from well J-13 in western Jackass Flat has sodium ion concentrations of approximately 200 ppm and a pH of 7.8 to 8.2. This water comes from fracture permeability in the densely welded, nonzeolitized Topopah Springs member of the Paintbrush Tuff and may not be representative of pore water in zeolitized horizons. However, it is not expected that such waters will exceed 1000 ppm in sodium ion concentrations. It is known that sufficient sodium ion concentrations did exist in the past for the reaction to proceed at depths greater than 3500 feet in drill hole USW-G1.

Plotting the expected sodium ion concentrations at Yucca Mountain in Fig. 5, we would predict that the reaction of clinoptilolite to analcime will probably begin at about 105°C. However, Boles (1971) did not do experiments below 100°C or attempt to reverse the reaction, so his work does not provide a lower temperature bound for the reaction. Also, sodium ion concentrations _in situ_ could be as high as 1000 ppm, so a safe lower bound for the beginning of the reaction could be set at about 95°C. Allowing a further 10% margin of error in thermal calculations, it seems advisable to constrain temperature maxima for zeolitized horizons adjoining any nonzeolitized repository horizon to a maximum of 85°C.

Figure 6 is a plot of the observed geothermal gradient in USW-G1. Also plotted are the maximum paleogeothermal gradient as inferred from the first appearance of analcime and albitized tuffs in USW-G1 and the temperature of the Zone II-Zone III (clinoptilolite-analcime) transition. It appears from this figure that maximum temperature _rises_ in zeolitized zones adjacent to potential repository horizons will be limited to about 50°C.

Preliminary thermal models for a repository located at 800-m depths in tuff of Yucca Mountain indicate that temperatures in clinoptilolite zones will not exceed 85°C if reprocessed high-level waste is emplaced at a gross thermal loading of 75 kW/acre (Tyler and Langkopf 1980). However, calculations for spent fuel emplaced at the same loading indicate that temperatures in zeolitized zones may reach 110 to 120°C. Any potential problem can be avoided by lowering the gross thermal loading for spent fuel. More precise thermal models will of course be required to estimate maximum allowable thermal loadings.

IV. CONCLUSIONS

Literature review shows that the instability of clinoptilolite may constrain repository heat loadings at Yucca Mountain. To prevent dehydration of clinoptilolite, wetting of mine tunnel and shaft surfaces may be required if dry air is used to cool heated geologic formations during the active life

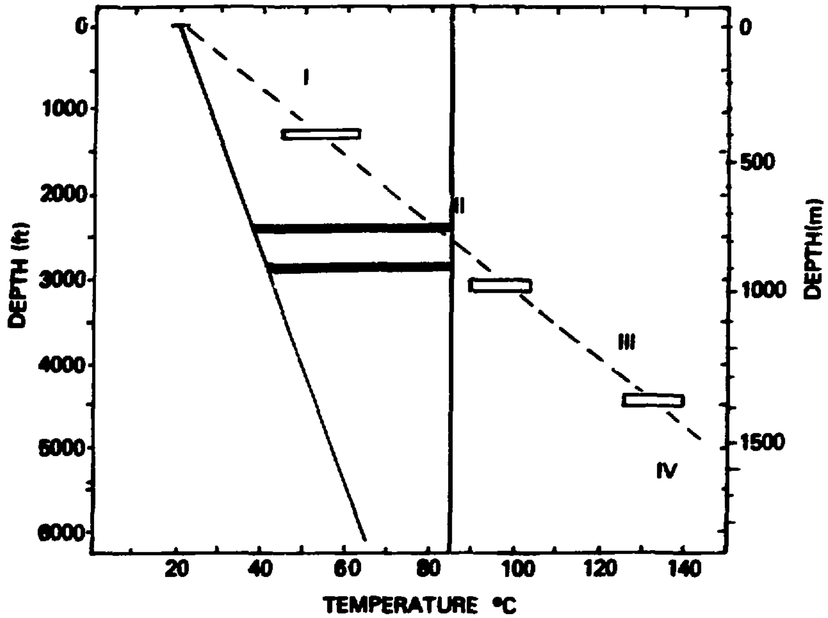

Fig. 6.

Plot of approximate temperature vs depth for drill hole USW-G1 (solid line). Also shown is a maximum paleogeotherm (dashed line) based on the observed zeolite zonal boundaries (boxes). Roman numerals indicate zeolite zones. The 85°C temperature limit is shown as a vertical solid line. Possible repository locations in the centers of two zeolite-free horizons 60 to 100 m thick are shown with horizontal bars extending to the 85°C limit. The length of the bar corresponds to the maximum allowable induced temperature increases resulting from emplaced wastes.

of the repository. Otherwise, major dehydration of clinoptilolite should not become a problem unless boiling of interstitial water should occur. Boiling should not occur if thermal constraints imposed by potential mineralogical reactions are observed. It is possible that minor dehydration (less than 2 wt% water loss) could occur in the temperature range 20 to 85°C and at water pressures greater than one atmosphere and affect local hydrology. These effects might be evaluated by measurement of water content as a function of water pressure and temperature.

It is possible to place a fairly firm constraint on the maximum temperature of clinoptilolite horizons based on mineralogical reactions. There is substantial evidence to suggest that in environments similar to Yucca Mountain, clinoptilolite and mordenite break down at temperatures above 95°C. To avoid consequences of these reactions, temperatures in zeolitized horizons should not exceed about 85°C. This will limit temperature rises in rocks 30 to 50 m above potential emplacement horizons to about 50°C. If this constraint is exceeded, the reactions may provide both a pathway (shrinkage fractures) and driving force (evolved fluid) for release of radionuclides to the biosphere.

ACKNOWLEDGMENT

This work was supported by the U.S. Department of Energy through its Nevada Operations Office as part of the Nevada Nuclear Waste Storage Investigations. The work was performed at Los Alamos National Laboratory, which is operated by the University of California under contract W-7405-ENG-36. Helpful reviews of the manuscript were received from D. Hoover, A. Waters, J. Whetten, and B. Crowe.

REFERENCES

Alberti, A., "On the Crystal Structure of the Zeolite Heulandite," Tschermaks Mineral. Petrogr. Mitt. 18, 129-146 (1972).

Alberti, A., "The Crystal Structure of Two Clinoptilolites," Tschermaks Mineral. Petrogr. Mitt. 22, 25-37 (1975).

Alietti, A., "Polymorphism and Crystal Chemistry Heulandites and Clinoptilolites," Am. Mineral. 57, 1437-1451 (1972).

Ames, L. L., "Zeolitic Extraction of Cesium from Aqueous Solutions," U.S. A.E.C. HW62607 (1959) 25 p.

Ames, L. L., "Cation Sieve Properties of Clinoptilolite," Am. Mineral. 45, 689-700 (1960).

Ames, L. L., "Cation Sieve Properties of the Open Zeolites Chabazite, Mordenite, Erionite, and Clinoptilolite," Am. Mineral. 46, 1120-1131 (1961).

Ames, L. L., "Kinetics of Cesium Reactions with Some Inorganic Cation Exchange Materials," Am. Mineral. 47, 1067-1078 (1962a).

Ames, L. L., "Effect of Base Cation on the Cesium Kinetics of Clinoptilolite," Am. Mineral. 47, 1310-1316 (1962b).

Ames, L. L., "Mass Action Relationships of Some Zeolites in the Region of High Competing Ion Concentrations," Am. Mineral. 49, 868-882 (1963).

Ames, L. L., "Some Zeolite Equilibria with Alkali Metal Cations," Am. Mineral. 49, 127-145 (1964).

Ames, L. L., "Self-Diffusion of Some Cations in Open Zeolites," Am. Mineral. 50, 465-475 (1965).

Barrer, R. M. and L. V. C. Rees, "Self-Diffusion of Alkali Metals in Analcime," Trans. Faraday Soc. 56, 709-721 (1960).

Barrer, R. M. and D. E. W. Vaughan, "Trapping of Inert Gases in Sodalite and Cancrinite Crystals," J. Phys. Chem. Solids 32, 731-743 (1971).

Barrows, K. J., "Zeolitization of Miocene Volcaniclastic Rocks, Southern Desatoya Mountains, Nevada," Geol. Soc. Am. Bull. 91, 199-210 (1980).

Bartl, H., "Neutronenbeugungsuntersuchung des Zeolithes Heulandit," Z. Kristallogr. 137, 440-441 (1973).

Benedict, R. W., Technical and Economic Feasibility of Zeolite Encapsulating for Krypton-85 Storage, ENICO-1011 Idaho National Engineering Laboratory (1979).

Boles, J. R., "Synthesis of Analcime from Natural Heulandite and Clinoptilolite," Am. Mineral. 56, 1724-1734 (1971).

Boles, J. R., "Composition, Optical Properties, Cell Dimensions, and Thermal Stability of Some Heulandite Group Zeolites," Am. Mineral. 57, 1463-1493 (1972).

Boles, J. R., "Zeolites in Deep-Sea Sediments," Mineral. Soc. Am. Short Course Notes 4, 137-163 (1977).

Boles, J. R. and D. S. Coombs, "Mineral Reactions in Zeolitic Triassic Tuff, Hokonui Hills, New Zealand," Geol. Soc. Am. Bull. 86, 63-173 (1976).

Boles, J. R. and W. S. Wise, "Nature and Origin of Deep-Sea Clinoptilolite," in Natural Zeolites: Occurrence, Properties, Use, L. B. Sand and F. A. Mumpton, Eds. (Pergamon Press, Elmsford, New York, 1978) 144-158.

Breger, I. A., J. C. Chandler, and P. Zubovic, "An Infrared Study of Water in Heulandite and Clinoptilolite," Am. Mineral. 55, 825-840 (1970).

Brown, R. A., M. Hoza, and D. A. Knecht, "^{85}Kr Storage by Zeolite Encapsulation," Proc. 14th ERDA Air Clean. Conf. (Springfield, Virginia, 1977) CONF-760822 ^{1}, 118-131, NTIS.

Callahan, C. M. and M. A. Kay, " Ion Exchange in Fused Salts - I. A Comparison of Ion Exchanger Characteristics of Fine Mineral Exchangers," J. Inorg. Nucl. Chem. 28, 233-244 (1966).

Calleri, M. and G. Ferraris, "Struttura dell'analcime: $NaAlSi_2O_6 \cdot H_2O$," Atti Accad. Sci. Torino, 98, 821-846 (1964).

Coombs, D. S., "The Nature and Alteration of Some Triassic Sediments from Southland, New Zealand," Trans. R. Soc. N.Z., Geology, 82, 65-109 (1953).

Coombs, D. S., "Present Status of the Zeolite Facies," Am. Chem. Soc. Adv. Chem. Ser. 101, 317-327 (1970).

Coombs, D. S. and J. T. Whetten, "Composition of Analcime from Sedimentary and Burial Metamorphic Rocks," Geol. Soc. Am. Bull. 78, 259-268 (1968).

Davis, R. J., "Mordenite, Ptilolite, Flokite and Arduinite," Mineral. Mag. 31, 887-888 (1958).

Deer, W. A., R. A. Howie, and J. Zussman, Rock-Forming Minerals 4, Framework Silicates (Longmans, London, 1964) 338-350.

Ferraris, G., D. W. Jones and J. Yerkess, "A Neutron-Diffraction Study of the Crystal Structure of Analcime, $NaAlSi_2O_6 \cdot H_2O$," Z. Kristallogr. 135, 240-252 (1972).

Fyfe, W. S., F. J. Turner and J. Verhoogen, "Metamorphic Reactions and Metamorphic Facies," Geol. Soc. Am. Mem. 85, 215-217 (1958).

Gottardi, G., "Mineralogy and Crystal Chemistry of Zeolites," in Natural Zeolites: Occurrence, Properties, Use, L. B. Sand and F. A. Mumpton, Eds. (Pergamon Press, Elmsford, New York, 1978), 31-44.

Goto, Y., "Synthesis of Clinoptilolite," Am. Mineral. 62, 330-332 (1977).

Harada, K., K. Tanaka, and K. Nagashima, "New Data on the Analcime - Wairakite Series," Am. Mineral. 57, 924-931 (1972).

Hay, R. L., "Zeolites and Zeolitic Reactions in Sedimentary Rocks," Geol. Soc. Am. Spec. Pap. 85, 130 (1966).

Hay, R. L., "Geologic Occurrence of Zeolites," in Natural Zeolites: Occurrence, Properties, Use, L. B. Sand and F. A. Mumpton, Eds., (Pergamon Press, Elmsford, New York, 1978) 135-143.

Heiken, G. H. and M. L. Bevier, "Petrology of Tuff Units from the J-13 Drill Site, Jackass Flats, Nevada," Los Alamos National Laboratory report LA-7563-MS (1978).

Honda, S. and L. J. P. Muffler, "Hydrothermal Alteration in Core from Research Drill Hole Y-1, Upper Geyser Basin, Yellowstone National Park, Wyoming," Am. Mineral. 55, 1714-1737 (1970).

Honstead, J. F., J. L. Nelson, B. W. Mercer, and W. A. Haney, "Waste Fixation on Minerals," U.S.A.E.C. Rpt. No. TID-7613 (1960).

Hoover, D. L., "Genesis of Zeolites, Nevada Test Site," in Nevada Test Site, Geol. Soc. Am. Mem. 110, 275-284 (1968).

Iijima, A., "Effect of Pore Water to Clinoptilolite - Analcime - Albite Reaction series," J. Fac. Sci. Univ. Tokyo, Sec II, 19, 133-147 (1975).

Iijima, A., "Geological Occurrences of Zeolite in Marine Environments," in Natural Zeolites: Occurrence, Properties, Use, L. B. Sand and F. A. Mumpton, Eds. (Pergamon Press, Elmsford, New York, 1978) 175-198.

Iijima, A., "Geology of Natural Zeolites and Zeolitic Rocks," in Proc. Fifth Int. Conf. Zeolites, L. V. Rees, Ed. (Heyden, London, 1980) 103-118.

Iijima, A. and I. Ohwa, "Zeolitic Burial Diagenesis in Creta-Tertiary Geosynclinal Deposits of Central Hokkaido, Japan," in Proc. Fifth Int. Conf. Zeolites, L. V. C. Rees, Ed. (Heyden, London, 1980) 139-148.

Iijima, A. and M. Utada, "Present-day Zeolitic Diagenesis of the Neogene Geosynclinal Deposits in the Niigata Oil Field, Japan," Am. Chem. Soc. Adv. in Chem. Ser. 101, Molecular Sieve Zeolites - 1, 342-349 (1971).

Kastner, M. A. and S. A. Stonecipher, "Zeolites in Deep-Sea Sediments," in National Zeolites: Occurrence, Properties, Use, L. B. Sand and F. A. Mumpton, Eds. (Pergamon Press, Elmsford, New York, 1978) 127-134.

Knowles, C. R., F. F. Rinaldi, and J. V. Smith, "Refinement of the Crystal Structure of Analcime," Indian Mineral. 6, 127-140 (1965).

Liou, J. G., "Analcime Equilibria," Lithos 4, 389-402 (1971).

Mariner, R. H. and R. C. Surdam, "Alkalinity and Formation of Zeolites in Saline Alkaline Lakes," Science 170, 977-980 (1970).

Mason, B. and L. B. Sand, "Clinoptilolite from Patagonia: The Relationship Between Clinoptilolite and Heulandite," Am. Mineral. 45, 341-350 (1960).

Mazzi, F. and E. Galli, "Is Each Analcime Different?," Am. Mineral. 63, 448-460 (1978).

Meier, W. M., "The Crystal Structure of Mordenite (Ptilolite)," Z. Kristallogr. 115, 439-450 (1968).

Meier, W. M. and P. M. Olsen, Crystal Structures of Natural and Synthetic Zeolites, (Clay Minerals Society, New York, 1978), 56 p. (1978).

Merkle, A. B. and M. Slaughter, "Determination and Refinement of the Crystal Structure of Heulandite," Am. Mineral. 53, 1120-1138 (1968).

Mortier, W. J. and J. R. Pearce, "Thermal Stability of the Heulandite-Type Framework: Crystal Structure of the Calcium-Ammonium Form Dehydrated at 483K," (abstract) EOS Trans. Am. Geophys. Union 61, 685 (1980).

Mumpton, F. A., "Clinoptilolite Redefined," Am. Mineral. 45, 351-369 (1960).

Passaglia, E., "The Crystal Chemistry of Mordenites," Contrib. Mineral. Petr. 50, 65-77 (1975).

Riecker, R. E. and T. P. Rooney "Shear Strength and Weakening of Zeolitized Tuff from the Nevada Test Site, Nevada," Am. Mineral. 52, 1174-1178 (1968).

Saha, P., "Geochemical and X-ray Investigation of Natural and Synthetic Analcites," Am. Mineral. 44, 300-313 (1959).

Schlenker, J. L., J. J. Pluth, and J. V. Smith, "Positions of Cations and Molecules in Zeolites with the Mordenite-Type Framework VIII. Dehydrated Sodium-Exchanged Mordenite," Mater. Res. Bull. 14, 751-758 (1979a).

Schlenker, J. L., J. J. Pluth, and J. V. Smith, "Positions of Cations and Molecules in Zeolites with the Mordenite-Type Framework IX. Dehydrated H-Mordenite Via Acid Exchange," Mater. Res. Bull. 14, 849-856 (1979b).

Seki, Y. and Y. Oki, "Wairakite - Analcime Solid Solutions from Low-Grade Metamorphic Rocks of the Tanzawa Mountains, Central Japan," Mineral. J. 6, 36-45 (1969).

Shepard, A. O., "A Heulandite-Like Mineral Associated with Clinoptilolite in Tuffs Of Oak Spring Formation, Nevada Test Site, Nye County, Nevada," U.S. Geol. Surv. Prof. Pap. 424-C, 320-323 (1961).

Sheppard, R. A., "Zeolites in Sedimentary Rocks," U.S. Geol. Surv. Prof. Pap. 820, 689-695 (1971).

Sheppard, R. A. and A. J. Gude, 3rd, "Distribution and Genesis of Authigenic Silicate Minerals in Tuffs of Pleistocene Lake Tecopa, Inyo County, California," U.S. Geol. Surv. Prof. Pap. 597, 38 p. (1968).

Sheppard, R. A. and A. J. Gude, 3rd, "Diagenesis of Tuffs in the Barstow Formation, Mud Hills, San Bernardino County, California," U.S. Geol. Surv. Prof. Pap. 634, 34 p. (1969).

Sheppard, R. A. and A. J. Gude, 3rd, "Zeolites and Associated Authigenic Silicate Minerals in Tuffaceous Rocks of the Big Sandy Formation, Mojave County, Arizona," U.S. Geol. Surv. Prof. Pap. 830, 36 p. (1973).

Smyth, J. R., B. M. Crowe, and P. M. Halleck, "Evaluation of the Concept of Terminal Storage of Radioactive Wastes in Silicic Pyroclastic Rocks," Los Alamos National Laboratory report (internal document, 1978).

Smyth, J. R. and M. L. Sykes, "Tuff Properties: Mineral and Petrology, General Description," in *Evaluation of Tuff as a Medium for a Nuclear Waste Repository*, J. K. Johnstone and K. Wolfsberg, Eds. (Sandia Laboratories, Albuquerque SAND-80-1464, 1980), 25-27.

Spengler, R. W., D. C. Muller, and R. B. Livermore, "Preliminary Report on the Geology and Geophysics of Drill Hole UE25a-1, Yucca Mountain, Nevada Test Site," U.S. Geol. Surv. Open File Report 79-1244, 43 p. (1979).

Surdam, R. C. and R. A. Sheppard, "Zeolites in Saline, Alkaline-Lake Deposits," in *Natural Zeolites: Occurrence, Properties, Use*, L. B. Sand and F. A. Mumpton, Eds. (Pergamon Press, Elmsford, New York, 1978) 145-174.

Surdam, R. C. and R. D. Parker, "Authigenic Aluminosilicate Minerals in the Tuffaceous Rocks of the Green River Formation, Wyoming," Geol. Soc. Am. Bull. 83, 689-700 (1979).

Sykes, M. L., G. H. Heiken, and J. R. Smyth, "Mineralogy and Petrology of Tuff Units from the UE25a-1 Drill Site, Yucca Mountain, Nevada," Los Alamos National Laboratory report LA-8139-MS (1979).

Sykes, M. L. and J. R. Smyth, "Tuff Properties: Mineralogy and Petrology Location Specific Studies," in Evaluation of Tuff as a Medium for a Nuclear Waste Repository, J. K. Johnstone and K. Wolfsberg, Eds. (Sandia Laboratories, Albuquerque, SAND-80-1464, 1980), 27-36.

Taylor, W. H., "The Structure of Analcite ($NaAlSi_2O_6 \cdot H_2O$)," Z. Kristallogr., 74, 1-19 (1930).

Thompson, A. B., "Analcite - Albite Equilibria at Low Temperatures," Am. J. Sci. 271, 79-92 (1971).

Turner, F. J. and J. Verhoogen, Igneous and Metamorphic Petrology, (McGraw Hill, New York, 1960).

Tyler, L. D. and B. S. Langkopf, "Mine Design Working Group," in Evolution of Tuff as a Medium for a Nuclear Waste Repository, J. K. Johnstone and K. Wolfsberg, Eds. (Sandia Laboratories, Albuquerque, SAND-80-1464, 1980), 85-96.

Vaughan, D. E. W., "Properties of Natural Zeolites," in Natural Zeolites: Occurrence, Properties, Use, L. B. Sand and F. A. Mumpton, Eds. (Pergamon Press, Elmsford, New York, 1978), 353-371.

Winkler, H. G. F., Petrogenesis of Metamorphic Rocks, (Springer-Verlag, New York, 1965), 136-143.

APPENDIX A

HYDRATION AND DEHYDRATION OF A CLINOPTILOLITE-RICH CORE FROM YUCCA MOUNTAIN

I. PURPOSE

To determine the rate of density change in a clinoptilolite-rich core sample of Yucca Mountain tuff upon hydration followed by constant temperature.

II. SAMPLE

YM-38: altered, zeolitized, nonwelded, vitric tuff. The zeolites have a median (Ca = Na + K) clinoptilolite composition. The phenocrysts are quartz, plagioclase, and sanidine.

III. PROCEDURE

Measurements were made for a core of YM-38 tuff approximately 2 cm in length and 2.5 cm in diameter. The sample core was weighed to 0.001 and measured for both length and diameter to 0.01 of an inch; these measurements were repeated three times prior to the test. Average values were then used to calculate volume and density for the sample. These measurements were also performed after each run was completed.

The core was placed in a water-filled desiccator for 48 h at 91°C and the density of the core was remeasured. The hydrated sample was then maintained at a constant temperature of approximately 95° (±3°) in a drying oven. The density of the core was remeasured after 0.5, 1, 2, 3, 8, 16, and 32 h (±10 min.). Following the 32-h dehydration, the core was returned to the desiccator for 48 h at 92°C for rehydration.

IV. RESULTS

Complete results are presented in Table A-I and Fig. A-1. During the initial hydration run, sample YM-38 exhibited similar increases in weight (6.15%) and in density (5.72%). Subsequent heating resulted in a weight loss of 9% and a density decrease of 6.14%. Weight and density parameters show little variation between the 16- and 32-h runs, possibly indicating approach to hydration equilibrium during this time. After rehydration the density was 3.04% lower than that following the first hydration.

V. CONCLUSIONS

The 6.15 wt% gain during the initial hydration test indicates that the zeolite in the YM-38 tuff core was not fully hydrated before this experiment began. The experiment shows that significant weight and volume changes in clinoptilolite tuff can occur below 100°C with changes in the partial pressure of water. Because such changes may critically affect the ground-water flow regime in the vicinity of a waste repository, it is important to continue the investigation of equilibrium reactions between zeolite and ground water under low temperature (<100°C) conditions.

The volume of the core (Fig. A-1) generally decreased as the time of heating was increased. To avoid the rapid re-equilibration with atmospheric moisture, measurements were made while the samples were still warm. Although thermal expansion is known to be small relative to volume changes resulting from hydration, the small initial volume increase may simply reflect thermal expansion. After 1 h of heating, the shrinkage of the clinoptilolite unit cell (determined by x-ray analysis) upon dehydration becomes dominant and produces a net volume decrease.

After rehydration the sample exhibited lower weight and density and a larger volume relative to the initial hydration run. The weight loss following rehydration may be due to nonreversible dehydration.

TABLE A-I
AVERAGE VOLUME AND DENSITY FOR YM-38 MAINTAINED AT 91-95°C

Time(h)[a]	Weight(g)	V(cm^3)	Density(g/cm^3)
BH	18.6257	10.2077	1.8247
H	19.7703	10.2490	1.9290
0.5	19.2063	10.2590	1.8721
1.0	18.8235	10.2814	1.8308
2.0	18.5134	10.2028	1.8018
3.0	18.3237	10.1698	1.8018
8.0[b]	18.0710	10.1823	1.7747
16.0	18.0709	10.1689	1.7771
32.0	17.9906	10.1526	1.7720
RH	19.2272	10.2798	1.8704

---

[a] BH is before hydration, H is after hydration, and RH is rehydration after 32 h at 95°C.

[b] Out of sequence.

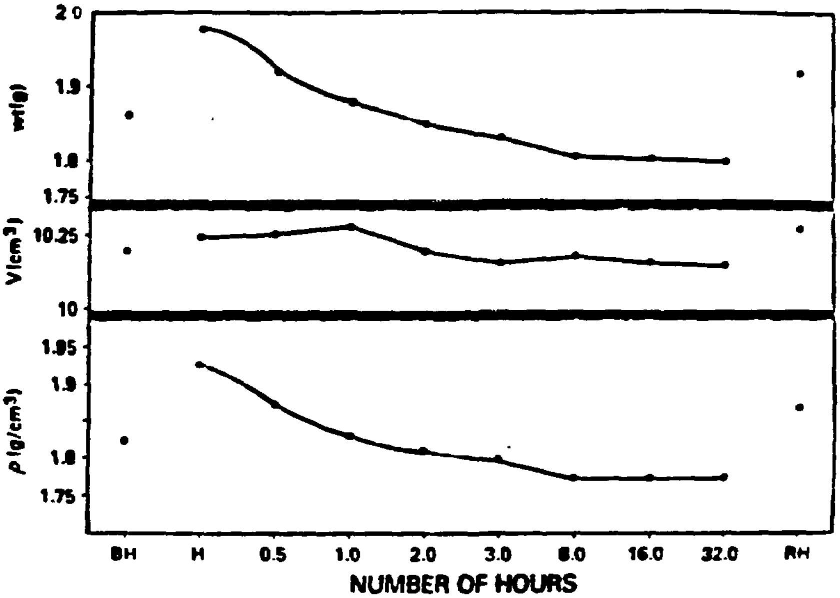

Fig. A-1.
Cumulative changes in density, volume, and weight for clinoptilolite tuff sample YM-38 heated at 95°C as a function of time. Initial values (BH) are for the shelf-dried specimen, and final values (RH) are after rehydration.

The volume increase following rehydration may be due to slight thermal expansion or to fractures introduced by shrinkage of clinoptilolite by dehydration. More tests are required to determine if there are residual nonreversible hydration-dehydration effects in this zeolitized tuff.

APPENDIX B

EFFECTS OF MINERALOGY ON WEIGHT AND VOLUME CHANGES IN SELECTED TUFF SAMPLES ON HEATING TO 400°C

I. PURPOSE

To record density changes in tuff samples of various mineralogies at different temperatures.

II. SAMPLE DESCRIPTION

JA-5	Tiva Canyon Member, Paintbrush Tuff. Welded, vitric tuff. Phenocrysts are primarily quartz and sanidine.
JA-26	Prow Pass Member, Crater Flat Tuff. Nonwelded, zeolitized (analcime) ash-flow tuff. Phenocrysts are quartz, plagioclase, and K-spar.
YM-40	Bedded tuff of Calico Hills. Altered, nonwelded vitric tuff. Zeolitized with Na + K-rich clinoptilolite. Phenocrysts are quartz, sanidine, and plagioclase.
B	Central portion of Bandelier Tuff. Nonwelded, nonzeolitized, ash-flow tuff with large pumice fragments and moderate amount of lithic fragments.

III. PROCEDURE

Cores (approximately 1-in. diam and 1-1/2-in. length) of each sample were cut and weighed three times to the nearest 0.001 g. The diameter and length of each core were also measured three times to 0.01 in. Volumes and densities were calculated using these values.

Each core was heated in a temperature-controlled muffle furnace (±1°C) for a period of 48 h (±15 min.); weight, length, and diameter were redetermined as above for temperatures of 100, 200, 300, and 400°C to yield volume and density as a function of temperature (Table B-I). Changes in the measured and calculated properties between 25 and 400°C are given in Table B-II.

TABLE B-I
WEIGHTS, VOLUMES, AND DENSITIES OF SAMPLES USED FOR HEATER EXPERIMENTS[a]

Temp (°C)	JA-5 Wt	JA-5 V	JA-5 ρ	JA-26 Wt	JA-26 V	JA-26 ρ	YM-40 Wt	YM-40 V	YM-40 ρ	B Wt	B V	B ρ
25	33.3060	15.3002	2.1646	26.4739	14.7298	1.7973	25.0519	15.2242	1.6456	21.8045	15.2346	1.4352
100	33.3217	15.3716	2.1677	26.3044	14.7281	1.7914	23.9593	15.2202	1.5742	21.0674	15.2797	1.4305
200	33.2956	15.3061	2.1640	25.9479	14.7472	1.7595	23.0069	15.1218	1.5275	21.0428	15.3407	1.4238
300	33.2876	15.4644	2.1525	25.5673	14.7302	1.7341	22.6073	15.0639	1.5067	21.0313	15.4192	1.4159
400	33.2042	15.5318	2.1430	25.5327	14.7206	1.7346	22.5008	14.9996	1.5060	21.0204	15.3045	1.4109
500	33.2799	15.6001	2.1322	25.4000	14.7246	1.7310	22.5045	14.9524	1.5061	21.0261	15.3706	1.4192

---

[a] V is volume and is density.

TABLE B-II
CHANGES IN PROPERTIES, 25 TO 400°C OF SAMPLES USED FOR HEATER EXPERIMENTS[a]

	JA-5	JA-26	YM-40	B
Wt (g)	-0.1061	-0.9051	-2.5474	-0.0384
h (cm)	+0.0290	-0.0043	-0.0094	+0.0094
r (cm)	+0.0030	+0.0007	-0.0094	+0.0040
V (cm^3)	+0.2199	-0.0053	-0.2718	+0.1440
ρ (g/cm^3)	-0.0374	-0.0063	-0.1404	-0.0160

---

[a] h is height, r is radius, V is volume, and ρ is density.

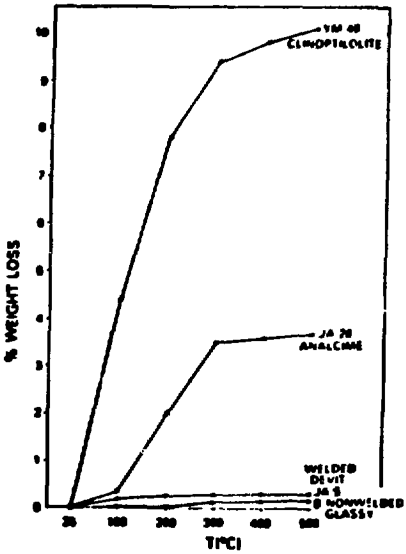

Fig. B-1.
Cumulative percent weight loss for tuff samples of various mineralogies.

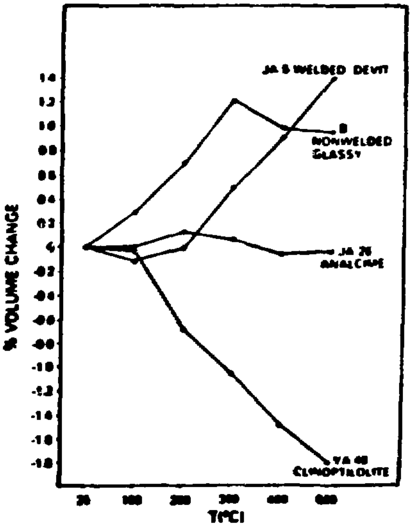

Fig. B-2.
Cumulative percent volume change on heating for tuff samples.

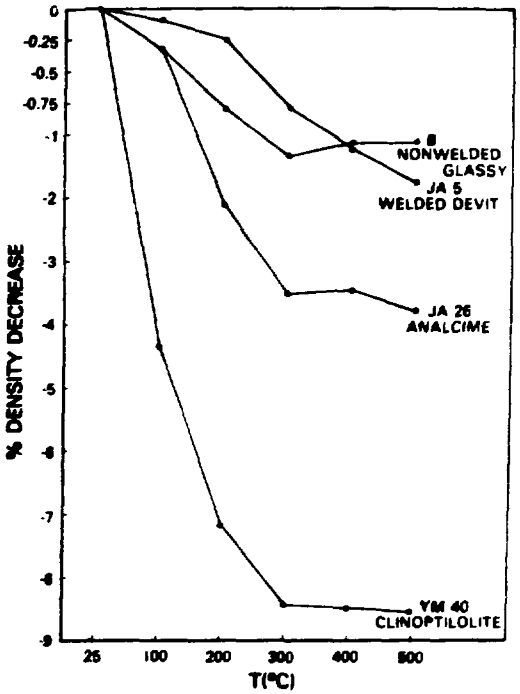

Fig. B-3.
Cumulative percent density change on heating for tuff samples. Clinoptilolite present in YM-40. Not only was all loosely bound water driven off, but minor amounts of tightly bound water may have also been driven out of the clinoptilolite. The volume decrease in YM-40 is probably due to contraction of the clinoptilolite unit cell upon heating.

IV. CONCLUSIONS

Experimental results (see Figs. B-1, B-2, and B-3) indicate a range in thermomechanical properties for tuff samples that depend primarily upon the nature and proportion of zeolite minerals present. Density decreases in the zeolite-free JA-5 and B cores were similar and are due primarily to volume increases upon heating because weight changes were negligible. The density decrease in sample JA-26, however, was due to weight loss coupled with negligible volume change. Weight loss in JA-26 is attributed to water loss from analcime in the tuff. The density decrease of sample YM-40 is due to a fractional weight loss that is much greater than the fractional volume loss. The relatively high weight loss is also due to dehydration of the zeolite phase.