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Crystal structures of a natural and a Cs-exchanged clinoptilolite

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ABSTRACT

The crystal structures of natural and Cs-exchanged silica-rich clinoptilolite have been refined in space group *C*2/*m* using single-crystal X-ray diffraction data ($R = 0.062$ and 0.083 respectively; all reflections). Chemical formulae of the two structures are $Na_{1.3}K_{1.2}Ca_{1.55}Al_{6.2}Si_{29.8}O_{72}\cdot 23H_2O$ and $Cs_{3.8}Ca_{1.2}Al_{6.1}Si_{29.7}O_{72}\cdot 19H_2O$. Unit-cell dimensions of the two are virtually identical ($a = 17.633$ Å, $b = 17.941$ Å, $c = 7.400$ Å, and $\beta = 116.39°$ for the natural sample, and $a = 17.692$ Å, $b = 17.945$ Å, $c = 7.404$ Å, and $\beta = 116.36°$ for the Cs-exchanged sample). The positions of extra-framework cations in the natural sample are similar to those reported previously, except that there is no atom at the position ascribed to Mg, consistent with the low Mg content of the sample. Cs occupies split positions near high-symmetry special positions that are unrelated to the cation positions in the natural sample. All Cs positions have relatively long Cs-H_2O and Cs-O distances ranging from 3.0 to 3.5 Å.

INTRODUCTION

Clinoptilolite is among the most abundant natural zeolites in rocks of continental origin. It typically occurs as a pervasive alteration product of silicic volcanic glass, composing up to 90% of some horizons in nonwelded rhyolitic tuffs of the Great Basin and Basin and Range physiographic provinces of the western United States. Because of its high cation-exchange capacity, clinoptilolite is used commercially for water purification, as an additive to animal feeds, and in a variety of other applications. Clinoptilolite is also a major component in tuffs at the Nevada Test Site, a large reservation in southern Nevada used for underground testing of nuclear weapons, and it may be used for future isolation of high-level radioactive wastes (Smyth, 1982; Broxton et al., 1987).

Clinoptilolite is isostructural with heulandite and has an approximate chemical formula: $(Ca,Na,K)_6Al_6Si_{30}O_{72}\cdot 24H_2O$. Clinoptilolite has been distinguished from heulandite on the basis of cation content, with clinoptilolite having alkali cations dominant [(Na + K) > Ca] and heulandite having Ca > (Na + K) (Mason and Sand, 1960). However, it may be preferable to base the distinction on the Al content, with clinoptilolite having Si/Al > 4 and heulandite having Si/Al < 4 (Boles, 1972). Clinoptilolite generally contains somewhat less water than heulandite (Mumpton, 1960; Bish, 1988), and retains crystallinity to significantly higher temperatures in short-duration laboratory heating experiments (Mumpton, 1960). However, such heating experiments do not imply thermal stability. Natural clinoptilolites appear to have formed at temperatures of 20 to 85 °C, and may break down at temperatures of 70 to 120 °C (Iijima, 1982; Bish, 1984). Clinoptilolite has been transformed to analcime at 100 °C in the laboratory (Boles, 1971). Some stability relations have been reviewed by Smyth (1982) and Iijima (1982).

Despite its widespread occurrence, crystals of clinoptilolite greater than 50 μm in greatest dimension are rare. Consequently relatively few structural studies have been carried out on natural or cation-exchanged varieties. Merkle and Slaughter (1968) refined the structure of a heulandite sample in space group *Cm*. Alberti (1975) refined the structure of a clinoptilolite sample from Agoura, California, and another from Alpe di Siusi, Italy. Koyama and Takéuchi (1977) refined the structure of one sample from Agoura, California, and another from Kuruma, Japan. Crystal structures of cation-exchanged varieties have not been studied although several cation-exchanged heulandite samples have been studied (Mortier and Pearce, 1982).

Because of its widespread occurrence in rocks surrounding potential and existing repositories for radioactive wastes and its high specific preference for the heavy alkalis, Cs and Rb (Vaughan, 1978), that occur in those wastes, clinoptilolite may be able to play a role in the containment of those wastes in the natural environment. In order to better understand the nature of this specific preference for Cs, we have undertaken a structural study of a natural and Cs-exchanged sample from Richardson Ranch, near Bend, Oregon. At this locality, reddish single crystals up to 2 mm in greatest dimension occur in a fine-grained white matrix of clinoptilolite in an altered vitric tuff. The sample was kindly provided by Dr. J. R. Boles.

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Table 1. Electron microprobe analyses of natural and Cs-exchanged clinoptilolite samples

Element	Natural	Cs-exchanged
Wt% Oxide		
SiO_2	68.44	58.39
Al_2O_3	11.86	10.12
FeO	0.46	0.41
MgO	0.12	0.13
CaO	3.26	2.25
Na_2O	1.51	0.02
K_2O	2.14	0.18
Cs_2O	0.00	17.26
Cl	0.00	tr (<0.2)
Total	86.67	88.78
H_2O (diff)	13.32	11.22
Per 72 oxygens		
Si	29.82	29.73
Al	6.19	6.07
Fe	0.17	0.18
Mg	0.09	0.10
Ca	1.55	1.23
Na	1.30	0.02
K	1.21	0.12
Cs	0.00	3.75
H_2O	23.01	19.05
Si/Al	4.82	4.90

Note: Analysis conditions 15 kV, 4 nA, 20-μm beam diameter.

Table 2. Unit cell dimensions, calculated formula weights, molar volumes (Z = 1) and densities of natural and Cs-exchanged clinoptilolite

Parameter	Natural	Cs-exchanged
a (Å)	17.633(8)	17.692(5)
b (Å)	17.941(8)	17.945(3)
c (Å)	7.400(4)	7.404(5)
β (°)	116.39(3)	116.36(3)
Cell volume (Å^3)	2097.06	2106.23
Formula weight (g)	2710.2	3046.8
Molar volume (cm^3)	1263.06	1268.58
Density (calc)(g/cm^3)	2.146	2.402

Chemical analysis and cation exchange

The natural sample was analyzed using a JEOL 8600 electron microprobe, with a 20 μm diameter beam spot, an accelerating voltage of 15 kV, and a sample current of 4 nA. Results are presented in Table 1 as an average of ten analyses. With an Al/Si ratio of 4.85 and (Na + K) > Ca (Table 1), this sample is well within the composition range of clinoptilolite.

Several crystals were separated from the sample and immersed in 2*M* CsCl solution at 20° C. These were allowed to stand in a closed container for approximately six weeks. The crystals were removed from the solution, mounted in epoxy, and analyzed by electron probe. The crystals were strongly zoned, with Cs_2O contents >6 wt% at the rims and less than 2 wt% in the centers.

The crystals were returned to the 2*M* CsCl solution and heated to approximately 70 °C for ten days. Electron probe analyses of these crystals showed relatively uniform Cs_2O contents of 16 to 17.5 wt% across the grains. The average chemical analysis is given in Table 1. It appears from this analysis that there was nearly complete exchange of the alkalis for Cs but less complete exchange of the Ca.

X-ray diffraction

An {010} cleavage-fragment crystal of the natural clinoptilolite approximately 320 × 370 × 80 μm in size was selected for diffraction study. A 12-h exposure on a precession camera (45 kV, 20 mA Zr-filtered Mo radiation) showed relatively sharp reflections, no evidence of twinning, and no evidence of reflections violating space group *C*2/*m*. The crystal was mounted on a Picker X-ray diffractometer with Krisel automation. The crystal was centered and oriented, and the cell refined using automatic centering parameters of six strong X-ray reflections with $2\theta > 35°$ in each of the eight octants of reciprocal space. These cell data are reported in Table 2.

X-ray intensity data for reflections ranging from 5 to 50° 2θ were measured automatically using constant-precision scans resulting in 1994 intensity observations. These data were corrected for Lorentz and polarization effects and absorption using the program ABSORB obtained from L. W. Finger (Carnegie Institution of Washington). Symmetrically-equivalent reflection intensities were averaged, resulting in 1809 unique intensity data, of which 1521 were greater than 3σ, estimated from counting statistics.

A similar crystal of the Cs-exchanged material that was approximately 340 × 400 × 50 μm in size was selected for study. A 12-h exposure on a precession camera (45 kV, 20 mA Zr-filtered Mo radiation) showed relatively sharp reflections, no evidence of twinning, and no evidence of reflections violating space group *C*2/*m*. The crystal was mounted on the diffractometer, centered, oriented, and the cell refined using automatic centering parameters of six strong X-ray reflections with $2\theta > 35°$ in each of the eight octants of reciprocal space (Table 2).

The X-ray intensities of the exchanged crystal were considerably weaker than those from the natural sample. X-ray intensity data for reflections ranging from 5 to 45° 2θ were measured automatically using constant-precision scans resulting in 3126 intensity observations, representing two redundant, equivalent sets (one hemisphere). These data were corrected for Lorentz and polarization effects and absorption using the program ABSORB. Symmetrically equivalent reflection intensities were averaged resulting in 1367 unique intensity data, of which 957 were

Table 3. Details of data measurement and refinement procedures

Parameter	Natural	Cs-exchanged
Measured intensities	1994	2996
Unique intensities	1809	1367
Unique intensities > 2σ	1521	957
2θ minimum	5	5
2θ maximum	50	45
Final R unweighted		
All reflections	0.062	0.083
Observed reflections	0.052	0.057

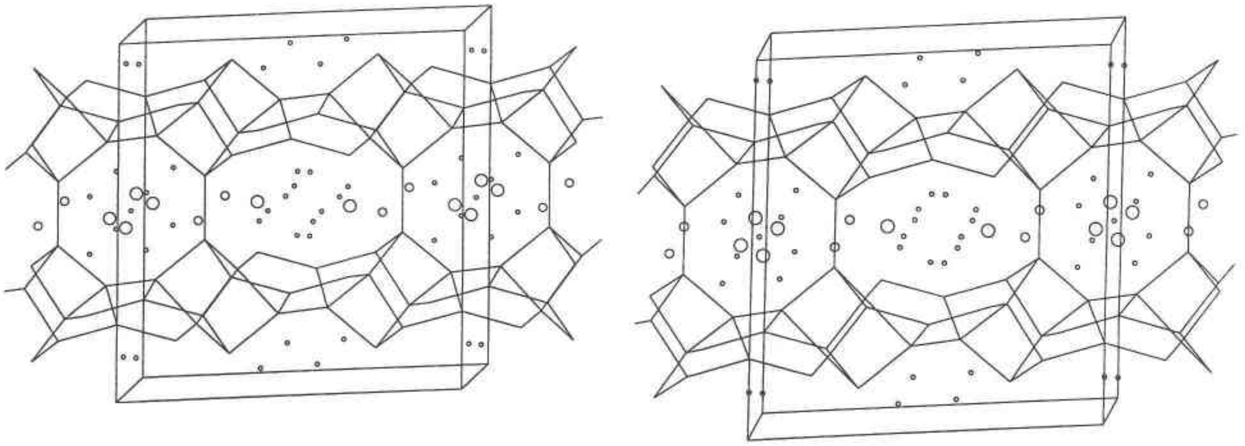

Fig. 1. Schematic stereoscopic view looking approximately down *c* (*b*-vertical) of natural clinoptilolite from Richardson Ranch showing exchangeable cations and water molecules (small circles). Tetrahedral framework is shown schematically with O atoms removed and tetrahedral cations located at intersections.

greater than 3σ estimated from counting statistics. Details of the data collection procedure are presented in Table 3.

STRUCTURE REFINEMENTS

All structure refinements were done using the program RFINE4 (Finger and Prince, 1975), and Fourier maps were prepared using FOUR (Finger and Prince, 1975). Scattering factors for fully ionized cations and O atoms obtained from Cromer and Mann (1968) were used for the framework and exchangeable cations, and neutral O (Cromer and Mann, 1968) was used to represent water molecules throughout.

For the natural clinoptilolite, the initial positional and thermal parameters were those obtained by Koyama and Takéuchi (1977) for their sample from Agoura, California. After an initial cycle of refinement of the overall scale factor, six cycles of refinement of the positional and isotropic thermal parameters of the framework cations and oxygens reduced the *R* value for all reflections to approximately 0.15. Subsequently, with the framework fixed, refinement of the positional, occupancy, and isotropic thermal parameters for the extra-framework cations and water molecules was carried out, reducing *R* to 0.12. Then, with these extra-framework positions fixed, six cycles of least-squares refinement of the framework positional and anisotropic thermal parameters reduced *R* to 0.08. At this stage a Fourier map of the structure was prepared in order to look for additional extra-framework positions. Occupancies of the M4 and W1 positions reported by Koyama and Takéuchi (1977) refined to near zero occupancies and so these atoms were removed from the atom list. W5 was moved off the twofold axis into a general position, as in the refinement of Alberti (1975). An additional six cycles of refinement of all atom positions and anisotropic thermal parameters resulted in a final *R* value of 0.052 for observed intensities.

At this point cation-oxygen distances were computed in an attempt to estimate occupancies. The tetrahedral Al/Si ratios were estimated from the mean T-O distances using the figures and method outlined by Gottardi and Alberti (1988). The distances and angles used for this calculation are reported in Tables 7 and 8. The exchangeable cation coordinations were computed, and that for the M3 position was found to be substantially larger than those for the other two and had a slightly shallower electrostatic site potential. For the final refinement cycles, K was assigned to this site and the total occupancy refined. M1 and M2 positions had nearly equal electrostatic site potentials and mean distances. Na and Ca were assigned to these positions and occupancies refined. A final four cycles of refinement of the occupancies and thermal parameters of the exchangeable cation sites left *R* unchanged at 0.052 for observed reflections. Final atom positions, occupancies, and thermal parameters are reported in Table 4. Final observed and calculated structure factors are available as Table 6.[1] Cation-oxygen distances, polyhedral volumes, distortion indices, and Al-contents of the tetrahedral sites are reported in Table 7. Bridging oxygen angles used for the Al occupancy determination are reported in Table 8. Coordinations of the extra-framework cations are reported in Table 9. Figure 1 is a schematic, stereoscopic drawing of the framework showing the extra-framework cations and water molecules.

For the Cs-exchanged clinoptilolite, the initial positional and thermal parameters were those obtained from the natural sample. After an initial cycle of refinement of the overall scale factor, six cycles of refinement of the positional and isotropic thermal parameters of the framework cations and O atoms reduced *R* for all reflections to approximately 0.24. Subsequently, with the framework fixed, refinement of the positional, occupancy, and iso-

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[1] A copy of Table 6 may be ordered as Document AM-90-432 from the Business Office, Mineralogical Society of America, 1625 I Street, N.W., Suite 414, Washington, D.C. 20006, U.S.A. Please remit $5.00 in advance for the microfiche.

TABLE 4. Occupancy, positional, and thermal parameters for natural clinoptilolite

Atom	occ(tot)	x	y	z	B_{iso}	$\beta_{11} \times 10^4$	$\beta_{22} \times 10^4$	$\beta_{33} \times 10^4$	$\beta_{12} \times 10^4$	$\beta_{13} \times 10^4$	$\beta_{23} \times 10^4$
T(1)	1.00	0.1789(1)	0.1705(1)	0.0953(3)	1.12	6.2(8)	10.4(7)	70(5)	−0.4(6)	6.3(16)	1.8(15)
T(2)	1.00	0.2131(1)	0.4104(1)	0.5030(3)	1.15	9.2(8)	7.2(7)	81(5)	0.6(6)	8.7(17)	0.3(15)
T(3)	1.00	0.2080(1)	0.1907(1)	0.7152(3)	1.13	8.7(8)	9.3(7)	67(5)	0.2(6)	8.1(17)	0.7(15)
T(4)	1.00	0.0654(1)	0.2989(1)	0.4129(3)	1.13	6.5(8)	10.3(7)	71(5)	−0.0(6)	6.6(16)	1.0(15)
T(5)	1.00	0	0.2160(2)	0	1.17	4.5(11)	11.6(11)	72(7)	0	3.0(20)	0
O(1)	1.00	0.1973(5)	½	0.4571(12)	2.55	29(4)	8(3)	180(20)	0	18(8)	0
O(2)	1.00	0.2320(4)	0.1212(3)	0.6138(9)	2.42	22(3)	20(2)	159(16)	−3(2)	33(6)	−19(5)
O(3)	1.00	0.1835(4)	0.1565(4)	0.8859(9)	2.66	29(3)	21(2)	138(16)	−3(2)	29(6)	−1(5)
O(4)	1.00	0.2356(4)	0.1065(3)	0.2518(9)	2.38	22(3)	18(2)	146(16)	7(2)	24(5)	4(5)
O(5)	1.00	0	0.3245(5)	½	2.91	26(4)	24(4)	212(26)	0	48(9)	0
O(6)	1.00	0.0811(3)	0.1614(3)	0.0570(9)	2.12	9(2)	15(2)	187(17)	−1(2)	17(5)	−1(5)
O(7)	1.00	0.1274(4)	0.2343(4)	0.5484(9)	3.28	25(3)	25(3)	163(17)	7(2)	1(6)	15(6)
O(8)	1.00	0.0110(4)	0.2682(4)	0.1857(9)	2.67	17(3)	26(3)	148(16)	2(2)	15(5)	−17(5)
O(9)	1.00	0.2119(4)	0.2534(3)	0.1830(9)	2.36	15(2)	15(2)	199(17)	−5(2)	23(5)	−14(5)
O(10)	1.00	0.1174(3)	0.3723(3)	0.4079(9)	2.41	16(2)	16(2)	200(18)	−5(2)	26(5)	−2(5)
M(1)	0.50(1)	0.1478(4)	0	0.6661(8)	5.8	75(4)	27(2)	320(18)	0	52(6)	0
M(2)	0.39(1)	0.0404(3)	½	0.2167(8)	3.8	15(2)	22(2)	293(18)	0	−4(4)	0
M(3)	0.64(1)	0.2344(4)	½	0.0252(10)	8.7	116(4)	37(2)	780(28)	0	218(9)	0
W(2)	0.98(5)	0.0798(15)	0	0.8531(53)	30	158(19)	105(14)	2570(280)	0	−37(52)	0
W(3)	0.89(2)	0.0798(4)	0.4190(4)	0.9655(11)	7.4	60(4)	45(3)	385(25)	−7(3)	−6(3)	32(7)
W(4)	1.00(2)	0	½	½	6.7	58(6)	35(5)	562(50)	0	82(15)	0
W(5)	0.36(2)	0.0202(17)	0.0901(12)	0.525(15)	15.5	42(22)	67(11)	1480(190)	−22(10)	−8(22)	126(56)
W(6)	0.81(3)	0.0865(10)	0	0.2654(30)	12.2	85(10)	90(10)	1010(100)	0	159(25)	0

tropic thermal parameters for the extra-framework cations and waters were carried out reducing the *R* to 0.20. Then, with these extra-framework positions fixed, six cycles of least-squares refinement of the framework positional and anisotropic thermal parameters reduced the *R* to 0.18. At this stage a difference-Fourier map of the structure was calculated to look for additional extra-framework positions. Additional, partially occupied cation sites were defined as M4 and M5. A final six cycles of refinement of all atom positions and anisotropic thermal parameters resulted in a final unweighted *R* value of 0.057 for observed reflections. Final atom positions, occupancies, and thermal parameters are reported in Table 5. Final observed and calculated structure factors are available as Table 6.[1] Cation-oxygen distances, polyhedral volumes, and distortion indices of the tetrahedral sites are reported in Table 7. Bridging oxygen angles are reported in Table 8. Coordinations of the extra-framework cations are reported in Table 9. Figure 2 is a schematic, stereoscopic drawing of the framework showing the extra-framework cations and waters.

DISCUSSION

Cell translations and space group

The unit-cell parameters obtained for the natural clinoptilolite sample are consistent with those obtained for samples of similar composition by previous workers

TABLE 5. Occupancy, positional, and thermal parameters for Cs-exchanged clinoptilolite

Atom	occ(tot)	x	y	z	B_{iso}	$\beta_{11} \times 10^4$	$\beta_{22} \times 10^4$	$\beta_{33} \times 10^4$	$\beta_{12} \times 10^4$	$\beta_{13} \times 10^4$	$\beta_{23} \times 10^4$
T(1)	1.00	0.1781(2)	0.1699(2)	0.0937(4)	0.98	5(1)	13(1)	38(7)	0(1)	5(2)	3(2)
T(2)	1.00	0.2139(2)	0.4107(2)	0.5069(4)	1.00	9(1)	8(1)	58(7)	0(1)	9(2)	1(2)
T(3)	1.00	0.2096(2)	0.1903(1)	0.7167(4)	1.06	9(1)	10(1)	46(7)	1(1)	5(2)	3(2)
T(4)	1.00	0.0674(2)	0.2976(2)	0.4183(4)	1.06	8(1)	11(1)	46(7)	−1(1)	5(2)	1(2)
T(5)	1.00	0	0.2179(2)	0	1.05	6(1)	11(1)	49(9)	0	2(3)	0
O(1)	1.00	0.1965(6)	0.5	0.4622(13)	2.34	28(5)	9(4)	121(27)	0	6(9)	0
O(2)	1.00	0.2359(4)	0.1210(4)	0.6183(10)	2.76	32(4)	20(3)	156(20)	−5(3)	37(7)	−16(7)
O(3)	1.00	0.1867(4)	0.1553(4)	0.8885(10)	2.74	32(4)	22(3)	133(20)	0(3)	33(7)	0(7)
O(4)	1.00	0.2298(4)	0.1048(4)	0.2501(10)	2.70	27(4)	22(3)	122(19)	6(3)	17(7)	9(6)
O(5)	1.00	0	0.3209(6)	½	3.29	34(6)	29(5)	203(30)	0	55(11)	0
O(6)	1.00	0.0790(5)	0.1639(4)	0.0456(11)	2.04	13(4)	17(3)	158(20)	2(3)	25(7)	−2(7)
O(7)	1.00	0.1272(5)	0.2304(4)	0.5487(11)	3.27	26(4)	22(3)	174(21)	10(3)	2(7)	31(7)
O(8)	1.00	0.0157(4)	0.2707(5)	0.1868(10)	2.74	27(4)	26(3)	88(18)	4(3)	9(7)	−16(6)
O(9)	1.00	0.2131(4)	0.2516(4)	0.1843(10)	2.65	21(4)	19(3)	186(20)	−5(3)	26(7)	−15(7)
O(10)	1.00	0.1199(4)	0.3717(4)	0.4279(10)	2.80	21(4)	20(3)	211(21)	−8(3)	31(7)	−2(7)
M(1)	0.179(7)	0.0283(13)	0	0.1274(36)	11.2	196(88)	7(3)	1800(200)	0	510(80)	0
M(2)	0.217(3)	−0.0116(42)	½	0.474(15)	3.66	3(20)	17(2)	0330(150)	0	20(20)	0
M(3)	0.088(8)	0.1913(25)	½	−0.0327(64)	8.56	71(11)	107(15)	0750(130)	0	−10(30)	0
M(4)	0.184(9)	0.0593(13)	0	0.2521(22)	7.34	68(7)	72(7)	580(50)	0	90(10)	0
M(5)	0.327(5)	0.2829(8)	0	0.9799(19)	7.01	164(12)	13(2)	380(40)	0	210(20)	0
W(1)	1.0(1)	0.3809(16)	½	0.3011(41)	20.5	185(25)	35(13)	1750(170)	0	−250(40)	0
W(2)	1.0(1)	0.4229(9)	0.0771(8)	0.0379(20)	10.0	125(12)	70(7)	563(8)	−16(7)	−70(20)	16(14)
W(3)	0.64(8)	0.5412(9)	0	0.2141(21)	0.89(8)						

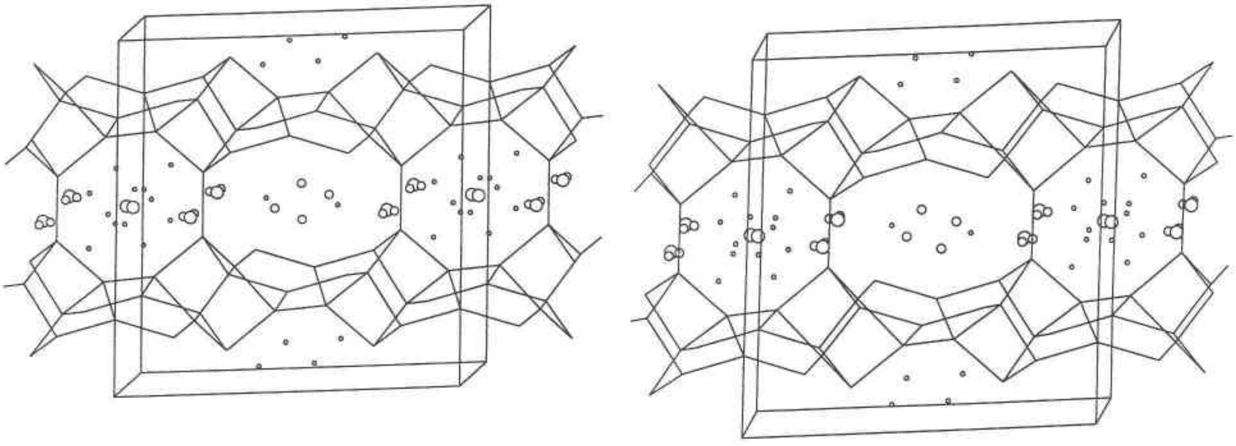

Fig. 2. Schematic stereoscopic view looking approximately down *c* (*b*-vertical) of Cs-exchanged clinoptilolite from Richardson Ranch showing exchangeable cations and water molecules (small circles).

(Boles, 1972; Alberti, 1975; Koyama and Takéuchi, 1977; Bish, 1988). There appears to be very little change in the cell parameters with Cs exchange. The values of *b, c,* and β of the exchanged crystal are identical to those of the natural crystal, and the *a* dimension and cell volume differ by less than 0.5%.

Table 7. Cation-oxygen distances (Å), occupancies, and distortion parameters for tetrahedral sites in natural and Cs-exchanged clinoptilolite

Atoms	Natural	Cs-exchanged
T1-O3	1.607(7)	1.614(8)
-O4	1.621(6)	1.613(7)
-O6	1.627(5)	1.630(7)
-O9	1.624(6)	1.617(7)
⟨Ti-O⟩	1.620	1.619
Al-content	0.13	0.12
Polyhedral Vol	2.174	2.179
Quad. Elong.	1.0006	1.0007
T2-O1	1.641(8)	1.638(9)
-O2	1.658(6)	1.644(7)
-O4	1.656(6)	1.648(7)
-O10	1.660(5)	1.653(7)
⟨T2-O⟩	1.654	1.646
Al-content	0.33	0.29
Polyhedral Vol	2.284	2.317
Quad. Elong.	1.0010	1.0013
T3-O2	1.606(6)	1.611(7)
-O3	1.626(7)	1.623(7)
-O7	1.611(7)	1.606(8)
-O9	1.619(6)	1.614(7)
⟨T3-O⟩	1.616	1.614
Al-content	0.10	0.10
Polyhedral Vol	2.153	2.162
Quad. Elong.	1.0008	1.0006
T4-O10	1.614(5)	1.605(6)
-O7	1.603(7)	1.612(8)
-O5	1.618(4)	1.613(5)
-O8	1.618(7)	1.617(7)
⟨T4-O⟩	1.613	1.612
Al-content	0.08	0.08
Polyhedral Vol	2.146	2.152
Quad. Elong.	1.0013	1.0008
T5-O6(×2)	1.627(7)	1.609(8)
-O8(×2)	1.602(6)	1.596(7)
⟨T5-O⟩	1.614	1.6022
Al-content	0.09	0.01
Polyhedral Vol	2.106	2.155
Quad. Elong.	1.0016	1.0013

Although $h + k$ odd reflections were not measured systematically, no evidence of these reflections was observed in zero-level *b*-axis (*h*0*l*) precession photographs exposed for 12 h. Further, both structures refined well in *C*2/*m* with no evidence of split positions for framework atoms or nonpositive-definite temperature factors for any of the framework or extra-framework atoms, with the exception of one partially occupied water position in the Cs-exchanged sample. We therefore conclude that both structures have space group symmetry *C*2/*m*.

Al/Si ratios and ordering

The tetrahedral Al/Si ratios (Table 7) were estimated from the mean T-O distances using the figures and method outlined by Gottardi and Alberti (1988). Consistent with previous studies, the tetrahedral sites show significant ordering of Al into T2 (Table 7). The Si/Al ratio of the whole natural sample obtained from the T-O distances is 5.47, compared to 4.82 obtained from the electron-microprobe chemical analysis (Table 1). The cause of this discrepancy is not readily apparent, although T-O distances obtained from both structures are comparable, and the standard errors are relatively small and corre-

Table 8. Bridging oxygen angles (°) in frameworks of natural and Cs-exchanged clinoptilolite

Angle	Natural	Cs-exchanged
T2-O1-T2	156.8(3)	156.2(4)
T3-O2-T2	147.7(3)	149.2(4)
T3-O3-T1	146.6(3)	146.7(4)
T1-O4-T2	140.8(3)	141.4(4)
T4-O5-T4	147.0(3)	150.0(4)
T1-O6-T5	136.6(3)	139.1(4)
T3-O7-T4	162.6(3)	158.1(4)
T4-O8-T5	151.7(3)	153.5(4)
T1-O9-T3	146.8(3)	149.9(4)
T2-O10-T4	143.8(3)	146.9(4)

spond to ± about 2% of Al occupancy. In either case, this is the most Si-rich and Al-poor clinoptilolite yet studied by single-crystal methods.

Table 9. Exchangeable cation coordination in natural and Cs-exchanged clinoptilolite

Natural		Cs-exchanged	
Atoms	Distance (Å)	Atoms	Distance (Å)
M1-O2(2)	2.756	M1-O6(2)	3.210
-W5(2)	2.584	-O6(2)	3.424
-W2	2.197	-W1	3.379
-W6	2.667	-M1	0.895
⟨M1-O/W⟩(6)	2.591	⟨M1-O/W⟩(5)	3.329
Inferred occupancy		Occupancy	
Na	0.24	Cs	0.18
Ca	0.37	M2-O5(2)	3.221
Total	0.61	-O10(2)	3.394
M2-O1	2.538	-O10(2)	3.276
-O10(2)	2.718	-W2(2)	3.224
-W4	2.496	(-W3	2.586)
-W3(2)	2.425	(-W3	2.483)
-W3(2)	2.683	(-M2	0.420)
⟨M2-O/W⟩(8)	2.586	⟨M2-O/W⟩(8)	3.279
Inferred occupancy		Occupancy	
Na	0.28	Cs	0.22
Ca	0.22	M3-O2(2)	3.493
Total	0.50	-O3(2)	3.400
M3-O3(2)	3.093	-O4(2)	3.193
-O4(2)	3.016	-W1(1)	3.167
-W3(2)	2.944	-W2(2)	2.420
-W2	2.987	(-M5	0.434)
⟨M3-O/W⟩(7)	3.013	⟨M3-OW⟩(9)	3.131
Inferred occupancy		Occupancy	
K	0.67	Cs	0.09
		M4-O6(2)	3.432
		-W1	2.928
		-W1	3.310
		(-M1	0.895)
		⟨M4-O/W⟩(4)	3.276
		Occupancy	
		Cs	0.184
		M5-O1	3.441
		-O2(2)	3.256
		-O3(2)	3.189
		-O4(2)	3.188
		-W1	2.735
		-W2(2)	2.677
		(-M3	0.435)
		⟨M5-O/W⟩(10)	3.080
		Occupancy	
		Cs	0.327

Extra-framework cations

The total number of extra-framework cations in the structure refinement is in good agreement with the chemical analysis. The positions of the extra-framework cations in the natural sample (Fig. 1) are very similar to those determined by Koyama and Takéuchi (1977) for their sample from Kuruma, Japan (with a low Mg content). We see no evidence of an atom at the position corresponding to their Mg atom at M4 in their sample from Agoura, California, which is consistent with the low Mg content of our sample.

Somewhat surprising is our observation that the extra-framework cation positions change completely with Cs substitution. The Cs atoms occupy five sites (Fig. 2), none of which corresponds to extra-framework cation sites of the natural sample. Each of the Cs sites has a low occupancy factor and lies close to another partially occupied Cs site so that there appears to be a large amount of positional disorder in the Cs atoms. Incoherent scattering of X-rays from these Cs atoms might account for the much lower diffraction intensities observed for this sample relative to the natural sample. The M1 site lies on the mirror close to the $2/m$ position at the cell origin, so that if fully occupied, there would be a very short (0.9 Å) M1-M1 distance. Similarly, M2 lies on the mirror, close to the $2/m$ position at (0, ½, ½), so that if fully occupied, it too would have an unreasonably short (0.4 Å) M2-M2 distance. Further, sites M3 and M5 are very close 0.4 Å) yet refined independently with low correlation coefficients of corresponding parameters. The M4 position also shows a short distance to M1 (0.8 Å).

With all extra-framework atoms in this structure modeled as Cs, the total number of Cs atoms per formula unit determined in the structure refinement (3.98) is in good agreement with the chemical analysis (1.2 Ca + 3.5 Cs) (if one Ca has 0.36 times as many electrons as Cs). The splitting of positions and low occupancies of the extra-framework cation sites, however, makes it rather difficult to infer cation ordering in these sites from interatomic distances. There is a significant amount of Ca remaining in the exchanged crystal, but because of the much lower scattering factor of Ca, it is impossible to refine occupancies directly when none of the sites approaches full occupancy. Therefore, any assignment of site occupancies from these data would be speculative.

Water molecules

The total number of water molecules observed in each of the structure refinements is significantly less than determined by difference from 100% for the microprobe chemical analysis. In the natural sample, the total number of water molecules in the cell determined by X-ray structure refinement is 19.2 as compared to 23 reported in the microprobe analysis. In the Cs-exchanged sample, only 14.6 water molecules are reported in the X-ray structure compared to 19 in the chemical analysis. Final difference-Fourier maps of both structures showed no sharp peaks that could be ascribed to a well ordered water position.

Total water contents of several cation-exchanged clinoptilolite samples determined by thermo-gravimetric analysis were reported by Bish (1988). Using a linear combination of his results, we estimate approximately 13.1 wt% H_2O (=22 water molecules per formula unit) for a sample with 30% K, 32% Na, 38% Ca and 9.6 wt% H_2O (=16.3 water molecules per formula) for a sample with 75% Cs, 25% Ca. These values are in fair agreement with our chemical analyses for both samples, indicating that there are probably more water molecules present than were detected by the X-ray structure refinement. It is likely then that positional disorder owing to water molecules lying in low-occupancy sites causes a significant number of them to be undetectable in the difference-Fourier.

CONCLUSIONS

The crystal structures of natural and Cs-exchanged silica-rich clinoptilolite samples have been refined in space group *C2/m* using single-crystal X-ray diffraction data. The structures have a slightly higher Si/Al ratio than previously reported clinoptilolite structures.

The positions of extra-framework cations in the natural sample are similar to those reported previously, except that there appears to be no atom at the position ascribed to Mg by Koyama and Takéuchi (1977), which is consistent with the low Mg content of the current sample.

In the Cs-exchanged sample, Cs occupies split positions near high-symmetry special positions that are unrelated to the exchangeable cation sites in the natural sample. All Cs positions have relatively long Cs-H_2O and Cs-O distances ranging from 3.0 to 3.5 Å. There are significantly fewer water molecules in the Cs-exchanged sample than in the natural sample. These observations imply that there is not a simple one-for-one cation exchange taking place, but a complete rearrangement of exchangeable cation sites and waters of hydration in the exchange process. Further, these relations imply that a small amount of water is lost from the zeolite concomitant with the exchange. These conclusions may prove useful in geochemical modeling of radionuclide migration in zeolite-bearing rocks.

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REFERENCES CITED

Alberti, A. (1975) The crystal structures of two clinoptilolites. Tschermaks Mineralogische und Petrographische Mitteilungen, 22, 25–37.

Bish, D.L. (1984) Effects of exchangeable cation composition on the thermal expansion/contraction of clinoptilolite. Clays and Clay Minerals, 32, 444–452.

Bish, D.L. (1988) Effects of composition on the dehydration behavior of clinoptilolite and heulandite. In D. Kallo and H. S. Sherry, Eds., Occurrence properties, and utilization of natural zeoliates, p. 565–576. Akademiai Kiado, Budapest.

Boles, J.R. (1971) Synthesis of analcime from natural heulandite and clinoptilolite. American Mineralogist, 56, 1724–1734.

Boles, J.R. (1972) Composition, optical properties, cell dimensions, and thermal stability of some heulandite-group zeolites. American Mineralogist, 57, 1452–1493.

Broxton, D. E., Bish, D. L., and Warren, R. G. (1987) Distribution and chemistry of diagenetic minerals at Yucca Mountain, Nye County, Nevada. Clays and Clay Minerals, 35, 89–110.

Cromer, D. T., and Mann, J.B. (1968) X-ray scattering factors computed from numerical Hartree-Fock wave functions. Acta Crystallographica A24, 321–324.

Finger, L.W., and Prince, E. (1975) A System of Fortran IV Computer Programs for Crystal Structure Computations. U.S. National Bureau of Standards Technical Note 854.

Gottardi, G., and Alberti, A. (1988) The tetrahedral framework of natural zeolites: silicon-aluminim distribution. In D. Kallo and H.S. Sherry, Eds., Occurrence, properties and utilization of natural zeolites, p. 223–244. Akademiai Kiado, Budapest.

Iijima, A. (1982) Geology of natural zeolites and zeolitic rocks. Proceedings Fifth Int'l Conf. on Zeolites, Heyden, London, 175–198.

Koyama, K., and Takéuchi, Y. (1977) Clinoptilolite: The distribution of potassium atoms and its role in thermal stability. Zeitschrift für Kristallographie, 145, 216–239.

Mason, B., and Sand, L.B. (1960) Clinoptilolite from Patagonia: The relationship between clinoptilolite and heulandite. American Mineralogist 45, 341–350.

Merkle, A.B., and Slaugher, M. (1968) Determination and refinement of the structure of heulandite. American Mineralogist, 53, 1120–1138.

Mortier, W.J., and Pearce, J.R. (1980) Thermal stability of the heulandite-type framework: Crystal structure of the calcium-ammonium form dehydrated at 483K. EOS 61, 685.

Mumpton, F.A. (1960) Clinoptilolite redefined. American Mineralogist, 53, 1120–1138.

Smyth, J.R. (1982) Zeolite stability and radioactive waste isolation in volcanic rocks. Journal of Geology, 90, 195–201.

Vaughan, D.E.W. (1978) Properties of natural zeolites. In L.B. Sand and F.A. Mumpton, Eds. Natural zeolites: Occurrence, properties, use, p. 353–371. Pergamon, New York.

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