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Clinoptilolite: the distribution of potassium atoms and its role in thermal stability

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Auszug

Die Kristallstruktur von Klinoptilolith, einem alkali- und Si-reichen Heulandit, wurde auf der Grundlage der Raumgruppe $C2/m$ entwickelt. Für einen Kristall vom Kuruma-Paß in Japan wurden die Gitterkonstanten $a = 17{,}660(4)$ Å, $b = 17{,}963(5)$ Å, $c = 7{,}400(3)$ Å, $\beta = 116{,}47(3)^\circ$ gefunden, für einen anderen, aus Agoura, U.S.A., $a = 17{,}662(4)$ Å, $b = 17{,}911(5)$ Å, $c = 7{,}407(3)$ Å, $\beta = 116{,}40(3)^\circ$ festgestellt. Im tetragonalen Gerüst vom Heulandit-Typ sind vier Lagen von Kationen, M(1) bis M(4), zu erkennen. In M(1) und M(2), den Kationlagen des Heulandits, befinden sich Na und Ca; M(1) neigt dazu, mehr Natrium aufzunehmen als M(2). Die neue Lage M(3) enthält K fast im Mittelpunkt des achtgliedrigen Rings der Kanäle parallel a. Diese Lage wird umgeben von sechs O Atomen des Gerüsts und von drei Wassermolekülen. In M(4) befindet sich Mg, oktaedrisch umgeben von sechs Wassermolekülen. Es ist sehr wahrscheinlich, daß die vier Lagen für alle Zeolithe der Heulanditgruppe charakteristisch sind. Klinoptilolith und Heulandit unterscheiden sich im Wesentlichen durch die Besetzung der Atomlagen: im Klinoptilolith sind M(1) und M(2) reich an Na, im Heulandit an Ca. M(3) ist beim Klinoptilolith im allgemeinen stärker mit Kalium besetzt als beim Heulandit. Durch Lage und Koordination von K wird die Beobachtung erklärt, daß die Anwesenheit von Kalium einer der regelnden Faktoren des thermischen Verhaltens der Zeolithe der Heulanditgruppe ist.

Abstract

The crystal structure of clinoptilolite has been worked out, based on $C2/m$, using two crystals from two different localities: one from Kuruma Pass, Japan, $a = 17.660(4)$ Å, $b = 17.963(5)$ Å, $c = 7.400(3)$ Å, $\beta = 116.47(3)^\circ$, and the other from Agoura, U. S. A., $a = 17.662(4)$ Å, $b = 17.911(5)$ Å, $c = 7.407(3)$ Å, $\beta = 116.40(3)^\circ$. In the tetrahedral framework of the heulandite type there are

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recognized four kinds of main cation positions, M(1), M(2), M(3), and M(4). At M(1) and M(2), which have so far been known as cation positions in the heulandite structure, Na and Ca are located; M(1) tends to accommodate more Na than M(2). The new position, M(3), which is specific for K, is located almost at the center of the eight-membered ring of the channel parallel to *a*. This position is coordinated by six framework oxygen atoms and three water molecules. At M(4), which is octahedrally coordinated by six water molecules, Mg is located. It is very likely that these four positions are characteristic of all members of the heulandite-group zeolites. The difference between clinoptilolite and heulandite is primarily in the difference of site content: for clinoptilolite, M(1) and M(2) are rich in Na, while for heulandite, they are rich in Ca. The occupancy of K at M(3) in clinoptilolite is, in general, higher than that of heulandite. The location and coordination of K explain the evidence that the presence of K in the structure is one of the controlling factors of the thermal behaviour of the heulandite-group zeolites.

Introduction

The name "clinoptilolite" was introduced by Shaller (1923) to represent alkali- and Si-rich members of zeolites of the heulandite group. Later, Mumpton (1960) gave a new definition of clinoptilolite based on the difference in thermal behaviour between heulandite and clinoptilolite. Upon heating up to about 450 °C, the structure of heulandite is destroyed, whereas the clinoptilolite structure persists stably up to about 700 °C. The difference has, in fact, been used to distinguish one from the other (Mumpton, 1960). Particularly in heulandite, a phase called "heulandite *B*" (Slawson, 1925) occurs before destruction. The temperature needed to start transformation to this phase was reported to be 230 °C (Mumpton, 1960), or 300 ~400 °C (Koizumi and Kiriyama, 1953; Alietti, 1967).

There is further complexity in heat behaviour of this group of zeolites. Based on heat treatment, heulandite can be classified into two types (Alietti, 1972; Boles, 1972). Type-1 heulandite is transformed to heulandite *B*, which persists at room temperature. After heating at 550 °C, type-1 heulandite no longer exhibits any powder-diffraction pattern (Alietti, 1972). On the other hand, type-2 heulandite is likewise transformed to phase *B*, which, unlike the case of type 1, tends to revert, upon cooling to room temperature, to the original phase or to an intermediate phase, *I*, which was defined by Alietti (1972) based on the (020) spacing. When heated to 550 °C, type-2 heulandite still exhibits a sharp powder pattern.

It has been surmised that these differences in thermal stability are due to the difference in Al/Si ratio (Mumpton, 1960) or to the difference in valency of exchangeable cations (MASON and SAND, 1960). These assumptions are not entirely independent and are thought to be basically acceptable. However, structural knowledge is needed to explain such an evidence that K-exchanged heulandite behaves like a typical clinoptilolite in its absence of transformation and high-temperature destruction (SHEPARD and STARKEY, 1966).

The following account presents the results of our structural study of two clinoptilolites carried out in the hope that the elucidation of the structure might throw light on the thermal behavior of clinoptilolite. The crystal structure of heulandite has been investigated by x-ray (MERKLE and SLAUGHTER, 1968; ALBERTI, 1972) and by neutron diffraction (BARTL, 1973). ALBERTI (1973) has also proposed the structure of heulandite *B*. After completion of the present study, a paper came to our attension on the structure of two clinoptilolites (ALBERTI, 1975). However, one of our crystals has a much higher potassium content than his crystals, and the potassium location we obtained is entirely different from his result.

Experimental

The source of the two clinoptilolites used for the present study, and their crystallographic data are given in Table 1. Though the space group of clinoptilolite would perhaps be *Cm* or even lower, we used *C* 2/*m* for refinements; as will be shown later, a trial of refining structure based on the acentric space group was unsuccessful as in the case of the heulandite structure worked out by ALBERTI (1972). We give in Table 2 the contents of atoms per unit cell for the two clinoptilolites. Crystals from Agoura are, compared to those from Kuruma Pass, of very good quality, showing forms, (010), (100), and (121). Electron-microprobe analyses of the crystals showed that the Ca content was considerably higher than that reported by WISE *et al.* (1969); for structure analysis we used our value. Though we did not determine the water content of Agoura clinoptilolite but calculated, by difference, the deviation from the reported value (WISE *et al.*, 1969). This is not essential for the scope of the present study.

For intensity measurements of the Kuruma clinoptilolite, we used a platy crystal fragment having dimensions of approximately $0.18 \times 0.12 \times 0.06$ mm^3. The ω-2θ scan technique was used to measure, on a Philips single-crystal diffractometer (PW-1101), a quarter of number of monochromated Cu$K\alpha$ reflection intensities

Table 1. *Crystallographic data for two clinoptilolites*

Clinoptilolite	1		2	
Locality	Kuruma Pass, Fukushima Pref., Japan		Agoura, California, U. S. A.	
	Conventional cell	Pseudorhombic cell	Conventional cell	Pseudorhombic cell*
a	17.660(4) Å	15.816 Å	17.662(4) Å	15.826 Å
b	17.963(5)	17.963	17.911(5)	17.911
c	7.400(3)	7.400	7.407(3)	7.407
β	116.47(3)°	91.71°	116.40(3)°	91.62°
Cell volume	2101 Å^3		2099 Å^3	
Space group used for refinement	$C2/m$		$C2/m$	

* These dimensions are to be compared with those given by WISE *et al.* (1969): $a = 15.85(3)$, $b = 17.89(4)$, $c = 7.41(1)$, $\beta = 91°29'(14')$. Note that the a and c axes given in their paper have been interchanged in this table.

Table 2. *Number of atoms per unit cell in clinoptilolite* (O = 72)

Atom	Kuruma	Agoura	
	(1)	(2)	(3)
Ca	1.90	1.16	0.5
Na	1.76	1.8	2.3
K	1.05	1.68	1.7
Mg	0.17	0.25	0.2
Al	6.72	6.33	6.2
Si	29.20	29.81	30
H_2O	23.7	20.1*	24

(1) Based on chemical analysis by MINATO and UTADA (1971).

(2) From microprobe analyses carried out by K. FUJINO for the present study. *The water content was calculated by difference.

(3) Average cell contents given by WISE *et al.* (1969).

up to $2\theta = 156°$. A total of 1701 independent reflections were then reduced to structure factors after due corrections for Lorentz and polarization factors as well as absorption ($\mu = 75.7$ cm^{-1}). Intensity collection for the Agoura clinoptilolite was executed in a way similar to the above. For this case, the unmodified crystal was used which had a crystal habit similar to that of the Kuruma specimen and dimensions of approximately 0.21 × 0.18 × 0.04 mm^3. For this case we measured a total of 1951 independent reflections which comprise approximately 81% of the total number of reflections in the Cu$K\alpha$ limiting sphere. Long-exposure x-ray photographs, which were taken using a high-power source of Cu$K\alpha$ radiation (40 kV, 100 mA), did not show any evidence of superstructure.

Determination and refinement of structure

Structural investigations were initiated with that of the Kuruma clinoptilolite. A test was first made of calculating structure factors based on the atomic parameters of the *Cm* structure of heulandite reported by Merkle and Slaughter (1968); this gave an R value of 0.22. For this calculation water molecules were excluded, and the form factor of Ca was used for exchangeable cations. After two cycles of refinement, using the ORFLS program (Busing, Martin and Levy, 1962), the value of R was reduced to 0.18. A three-dimensional differ-

Table 3. *Comparison of the notation of cation locations*

Heulandite			Clinoptilolite
Merkle and Slaughter (1968)	Alberti (1972)		Present work
Cm	*Cm*	*C* 2/*m*	*C* 2/*m*
Ca(2) Ca(1)	Ca(1) Ca(1B)*	Ca(1)	M(1) = Na, Ca
— Ca(3)	Ca(2) Ca(2B)*	Ca(2)	M(2) = Ca, Na
			M(3) = K
			M(4) = Mg

* For space group *C* 2/*m*, Ca(1B) is equivalent to Ca(1) by inversion, and Ca(2B) to Ca(2) by twofold rotation; for the Merkle-Slaughter's structure, the atomic location corresponding to Ca(2) of the Alberti's notation is missing.

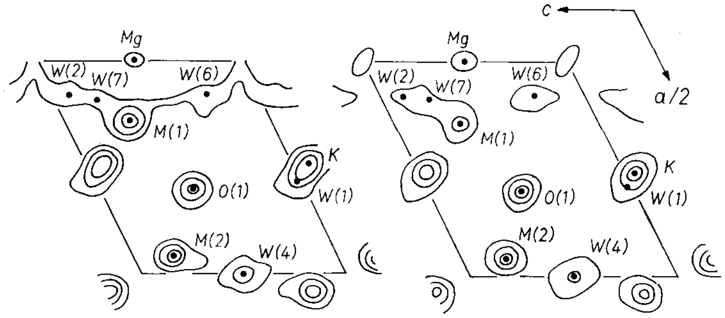


Fig. 1. Comparison of the Fourier section, $y = 0$, of the Kuruma clinoptilolite (left), and that of the Agoura clinoptilolite (right). Note that the elongation of peaks, composites of K and W(1), is more conspicuous for the Kuruma mineral than that for the Agoura mineral; the Kuruma specimen contains more of the water molecule at W(1). Densities are indicated by three contours: 1 e Å^{-3}, 5 e Å^{-3}, and 10 e Å^{-3}

ence Fourier map then revealed a peak at a location corresponding to Ca(2) in the Alberti's notation (Table 3); this position is missing in the Merkle-Slaughter structure. The map also revealed peaks corresponding to all water molecules in the Alberti structure of heulandite (ALBERTI, 1972). Thus general features of the structure of the Kuruma mineral was very closely similar to the Alberti *C*2/*m* structure of heulandite. Nevertheless, we continued the refinement based on *Cm*.

After calcium atoms at the Ca(2) position and water molecules were added, several cycles of least-squares calculations further reduced the *R* value to 0.12. During these calculations, it was observed that, if each occupancy was fixed to unity, the temperature factors of $H_2O(1)$ and $H_2O(1B)$, using ALBERTI's notation, showed unusually small values; they even showed a trend to be negative. If their temperature factors were, in turn, fixed to 1.0, the occupancy factors exceeded 1.0, to give a value of around 1.4. In the Fourier map, peak heights of these water molecules were very slightly higher than those of the cations. Noting that the peaks were elongated (Fig. 1), we decided that each of the peaks represented a cation and a water molecule. Since the peaks have neighbors of framework oxygen atoms and water molecules at distances of about 3 Å, the cation is very likely to be a potassium atom. Once the Fourier peaks were treated in this way, the temperature factors and occupancy factors did not show any unusual value.

At this stage, a calculation of bond lengths showed that the Ca(1)—O(H_2O) and Ca(1*B*)—O(H_2O) lengths were longer than the Ca(2)—O(H_2O) and Ca(2*B*)—O(H_2O) bonds. Since there are several lines of evidence (NISHI and TAKÉUCHI, 1975; TAKÉUCHI *et al.*, 1975) that in a structure in which mutual substitution between Ca and Na takes place, the Na polyhedra tend to be larger than Ca polyhedra, we assumed that Ca(1) and Ca(1*B*) were occupied by Na and Ca(2) and Ca(2*B*) by Ca. With this modification isotropic refinement then converged to give $R = 0.11$. If anisotropic thermal parameters were introduced to the framework atoms and cations, the value was reduced to 0.08. However, temperatures factors of two of the framework oxygen atoms became negative, and an unusually short Si—O bond length, 1.55 Å, was obtained. Inspection of the final electron-density

Table 4. *Atomic fractional coordinates of the Kuruma clinoptilolite*

Atom site	Occupancy and site contents	x	y	z
T(1)	1.0	0.1792(1)	0.1695(1)	0.0942(3)
T(2)	1.0	2122(1)	4107(1)	5029(3)
T(3)	1.0	2084(1)	1911(1)	7145(3)
T(4)	1.0	0656(1)	2986(1)	4134(3)
T(5)	1.0	0	2156(1)	0
O(1)	1.0	1975(5)	5	4564(13)
O(2)	1.0	2329(3)	1224(3)	6109(9)
O(3)	1.0	1835(3)	1560(3)	8810(9)
O(4)	1.0	2357(3)	1056(3)	2489(8)
O(5)	1.0	0	3214(5)	5
O(6)	1.0	0815(3)	1614(3)	0588(8)
O(7)	1.0	1273(4)	2331(4)	5461(9)
O(8)	1.0	0117(3)	2688(3)	1854(8)
O(9)	1.0	2126(3)	2525(3)	1837(8)
O(10)	1.0	1160(3)	3720(3)	4108(9)
W(1)	0.75(3)	218(1)	5	— 005(3)
W(2)	0.45(4)	087(3)	0	897(8)
W(3)	1.0	078.7(7)	419.8(7)	964(2)
W(4)	1.0	0	500	5
W(5)	0.74(4)	0	088(3)	5
W(6)	0.91(4)	083(2)	0	267(6)
W(7)	0.34(6)	094(5)	0	74(2)
M(1)	0.36(1)Na, 0.24Ca	1427(8)	0	667(2)
M(2)	0.20(1)Na, 0.26Ca	0392(5)	5	208(2)
M(3)	0.37(1)K	2562(6)	5	084(2)
M(4)	0.04(5)Mg	0	0	5

Table 5. *Anisotropic thermal parameters* ($\times 10^4$) *of the Kuruma clinoptilolite* of the form $\exp - (\beta_{11}h^2 + \cdots + 2\beta_{12}hk + \cdots)$

Atom site	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
T(1)	4.2(5)	12.1(6)	120(4)	−0.3(5)	10(1)	3(1)
T(2)	8.3(6)	8.9(5)	126(5)	0.0(5)	15(1)	2(1)
T(3)	6.3(6)	10.0(5)	113(4)	0.4(4)	13(1)	0(1)
T(4)	5.0(6)	10.9(5)	102(4)	−1.2(4)	8(1)	−1(1)
T(5)	6.0(8)	11.1(8)	114(6)	0	12(2)	0
O(1)	29(3)	14(2)	185(22)	0	30(7)	0
O(2)	26(2)	20(2)	203(15)	−1(2)	47(5)	−19(4)
O(3)	28(2)	20(2)	169(14)	−3(2)	40(5)	1(4)
O(4)	22(2)	21(2)	148(14)	11(2)	21(4)	22(4)
O(5)	31(3)	24(3)	222(23)	0	65(8)	0
O(6)	8(2)	16(2)	212(15)	1(1)	22(4)	4(4)
O(7)	25(2)	24(2)	174(15)	9(2)	5(5)	25(5)
O(8)	18(2)	24(2)	111(12)	0(2)	−3(4)	−26(4)
O(9)	14(2)	19(2)	200(15)	−6(1)	22(4)	−17(4)
O(10)	15(2)	18(2)	233(16)	−8(2)	21(5)	− 3(5)
M(1)	42(5)	12(3)	259(33)	0	33(11)	0
M(2)	12(3)	22(3)	322(27)	0	11(7)	0
M(3)	38(4)	5(2)	257(22)	0	51(8)	0

map as well as difference Fourier map did not show any substantial deviation from the symmetry, $C2/m$. We therefore, finally decided to refine the structure based on $C2/m$.

The refinement based on $C2/m$ was executed starting from the final atomic parameters obtained in the above procedure. For computations, an empirical weighting factor was used of the form $w_i = 1/(a + F_o + cF_o^2)$ (Cruickshank, 1965) with $a = 30$, $c = 0.00707$. During the refinement, it was found that the Ca(1) and Ca(2) positions in which Na and Ca respectively had been located, were, in fact, partially replaced respectively by Ca and Na. Further, the small peak at $0 0 \frac{1}{2}$ (Fig. 1) was found to be for Mg. For least-squares calculations, the following conditions were taken into account: (1) The occupancy factors of the cations and water molecules [excluding $H_2O(3)$ and $H_2O(4)$] were independently refined; no constraint was applied. (2) No constraint was applied to the isotropic temperature factors for water molecules even if they gave extremely high values. It is reasonable to assume that the high values are mainly due to positional disordering. Throughout the computations, form factors for

Table 6. *Atomic fractional coordinates of the Agoura clinoptilolite*

Atom site	Occupancy and site contents	x	y	z
T(1)	1.0	0.17906(7)	0.16943(6)	0.0963(2)
T(2)	1.0	21334(7)	41099(6)	5040(2)
T(3)	1.0	20846(7)	19034(6)	7153(2)
T(4)	1.0	06623(7)	29837(7)	4148(2)
T(5)	1.0	0	21651(9)	0
O(1)	1.0	1959(4)	5	4574(8)
O(2)	1.0	2336(2)	1204(2)	6144(6)
O(3)	1.0	1850(3)	1551(2)	8559(6)
O(4)	1.0	2333(2)	1041(2)	2509(5)
O(5)	1.0	0	3232(3)	5
O(6)	1.0	0808(2)	1627(2)	0555(5)
O(7)	1.0	1268(3)	2317(2)	5492(6)
O(8)	1.0	0122(2)	2702(2)	1856(5)
O(9)	1.0	2123(2)	2520(2)	1860(6)
O(10)	1.0	1188(2)	3718(2)	4148(6)
W(1)	0.38(4)	211(3)	500	—033(8)
W(2)	0.44(3)	084(3)	0	888(7)
W(3)	1.0	0777(6)	4206(5)	964(2)
W(4)	1.0	0	5	5
W(5)	0.76(3)	0	095(2)	5
W(6)	0.83(3)	073(2)	0	249(5)
W(7)	0.42(3)	096(3)	0	756(7)
M(1)	0.36(1) Na, 0.06 Ca	1428(11)	0	667(2)
M(2)	0.10(1) Na, 0.25 Ca	0393(4)	5	210(1)
M(3)	0.44(1) K	2413(7)	5	049(2)
M(4)	0.10(1) Mg	0	0	5

Si^{2+}, Ca^{2+}, K^+, Na^+, Mg^{2+} and O^-, were used; these were taken from the *International tables for x-ray crystallography* (1962). When we applied anisotropic temperature factors to atoms other than H_2O, the least-squares refinement finally converged to give an R value of 0.080 (weighted $R = 0.105$) for all observed reflections.

The refinement of the structure of the Agoura crystal was carried out starting with the final atomic parameters of the Kuruma mineral. For this case, the parameters a and c of the above-mentioned weighting factor, were respectively 30 and 0.0049. The final value of R was found to be 0.058 (weighted $R = 0.088$) for all measured reflections. In Table 4 and Table 5 we give final atomic parameters of the Kuruma clinoptilolite, and in Table 6 and Table 7 those of the Agoura clinoptilolite. The temperature factors of water molecules and Mg are given in Table 8.

Table 7. *Anisotropic thermal parameters* ($\times 10^4$) *of the Agoura clinoptilolite* of the form $\exp - (\beta_{11}h^2 + \cdots + 2\beta_{12}hk + \cdots)$

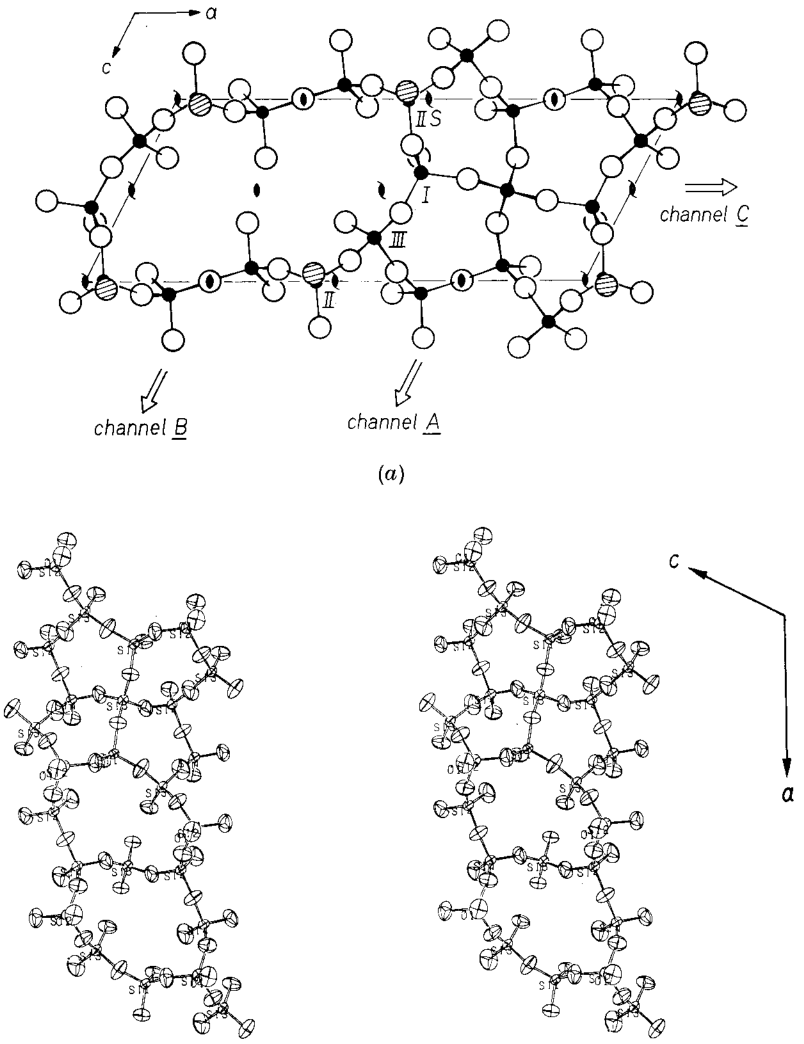
Atom site	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
T(1)	10.6(5)	10.3(3)	60(2)	0.1(3)	16.0(9)	3.2(7)
T(2)	12.6(5)	7.3(3)	70(3)	0.3(3)	16.2(9)	0.8(7)
T(3)	12.2(5)	8.7(3)	55(2)	0.7(3)	17.6(9)	0.5(7)
T(4)	10.8(5)	10.0(3)	61(3)	− 0.5(3)	15.2(9)	− 0.2(7)
T(5)	11.3(6)	10.1(5)	58(3)	0	14(1)	0
O(1)	32(2)	11(1)	146(13)	0	31(5)	0
O(2)	32(2)	18(1)	165(10)	− 0(1)	54(4)	−12(3)
O(3)	41(2)	19(1)	133(9)	− 2(1)	55(4)	2(3)
O(4)	27(2)	20(1)	92(8)	8(1)	18(3)	5(3)
O(5)	30(3)	24(2)	169(14)	0	56(5)	0
O(6)	14(1)	15(1)	152(9)	− 0(1)	24(3)	1(2)
O(7)	30(2)	21(1)	159(10)	10(1)	17(4)	24(3)
O(8)	22(2)	23(1)	103(8)	1(1)	11(3)	−21(3)
O(9)	17(1)	16(1)	178(10)	− 6(1)	25(3)	−18(3)
O(10)	22(2)	16(1)	176(10)	− 6(1)	30(3)	− 1(3)
M(1)	83(10)	15(3)	358(37)	0	79(17)	0
M(2)	20(3)	19(2)	235(20)	0	15(6)	0
M(3)	85(4)	19(1)	395(23)	0	138(9)	0

Table 8. *Temperature factors, B, of water molecules and the magnesium ion in clinoptilolite*

	Kuruma	Agoura
W(1)	4.4(3) Å²	6.2 ± 1.2 Å²
W(2)	8.8 ± 1.0	14.6 ± 1.1
W(3)	8.1(3)	9.5(2)
W(4)	7.0(5)	7.4(4)
W(5)	16.4 ± 1.4	22.1 ± 1.1
W(6)	17.7 ± 1.2	19.1 ± 1.0
W(7)	17.5 ± 2.4	10.2 ± 1.2
Mg	18.6 ± 8.2	1.1(4)

Discussion

The framework geometry of clinoptilolite is of the heulandite type (MERKLE and SLAUGHTER, 1968). The framework can be looked upon as consisting of slabs each of which is bounded by mirror planes and has a thickness of $\frac{1}{2}b \simeq 9$ Å (Fig. 2). The slabs are joined together by oxygen atoms in the mirror planes to form the framework. In the



(*a*)

(*b*)

Fig. 2. (*a*) The *b*-axis projection of the tetrahedral framework illustrating the linking of tetrahedra by shared oxygen atoms about tetrahedral cations in the slab located at $\frac{1}{4} < y < \frac{1}{2}$ (the origin is shifted to $-\frac{1}{4}$, 0, $-\frac{1}{4}$). Shaded oxygen atoms are those in the mirror plane at x, $\frac{1}{2}$, z, all other atoms being at lower levels than the mirror plane. Thus, for example, the four tetrahedra, II, III, I, and IIS, with their mirror images, form an eight-member ring. This figure therefore depicts half walls of channels, each of which is cut along its extension; the notation and the extension direction of each channel are indicated. (*b*) Corresponding stereo-plot, in which *a* is vertical

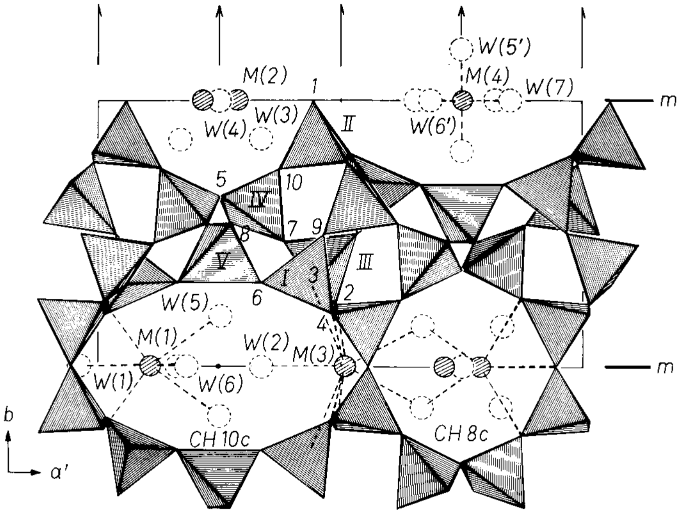


Fig. 3. The *c*-axis projection of the structure of the Agoura clinoptilolite. Notations for tetrahedra and oxygen atoms are indicated by Roman and Arabic figures respectively. To avoid confusion, only part of equivalent atoms are shown, especially in channel *A*. Symmetry axes and mirror planes are indicated. The origin is indicated by a small dot ($a' = a \sin\beta$). CH10*c* and CH8*c* respectively denote channel *A* and channel *B*

resulting framework, there are three channels (Fig. 3) which we will designate channels *A*, *B*, and *C*. The first two are parallel to *c*, and are respectively comprised of ten-member rings and eight-member rings. The third one is parallel to *a*, and comprised of eight-member rings. Though MERKLE and SLAUGHTER (1968) pointed out that there is a fourth channel of eight-member rings lying at an angle of approximately 50° to the *a* axis, the above three channels are considered to be essential for a discussion of the structure.

Distribution of Al in the framework

The T—O bond lengths are listed in Table 9. The overall mean T—O lengths are significantly smaller than those which would be found in feldspars (SMITH and BAILEY, 1963) having corresponding Al/Si ratios (Table 10). This situation suggests that the T—O bond lengths of the framework are reduced to compensate for weaker bonding to the cations. Evidence similar to this has been reported for mordenite varieties (MORTIER *et al.*, 1975); the reduction for dehydrat-

Table 9. *Interatomic distances for tetrahedra in clinoptilolite*

	Kuruma	Agoura		Kuruma	Agoura
T(1)—O(3)	1.632 Å	1.628 Å	O(3)—O(4)	2.616 Å	2.612 Å
—O(4)	1.613	1.620	—O(6)	2.665	2.652
—O(6)	1.632	1.628	—O(9)	2.694	2.690
—O(9)	1.631	1.620	O(4)—O(6)	2.643	2.644
			—O(9)	2.680	2.688
Mean	1.627	1.624	O(6)—O(9)	2.642	2.624
T(2)—O(1)	1.636	1.631	O(1)—O(2)	2.673	2.659
—O(2)	1.654	1.641	—O(4)	2.652	2.617
—O(4)	1.673	1.654	—O(10)	2.730	2.704
—O(10)	1.673	1.654	O(2)—O(4)	2.718	2.706
			—O(10)	2.745	2.713
Mean	1.659	1.645	O(4)—O(10)	2.735	2.719
T(3)—O(2)	1.610	1.618	O(2)—O(3)	2.583	2.589
—O(3)	1.609	1.623	—O(7)	2.619	2.638
—O(7)	1.607	1.602	—O(9)	2.642	2.659
—O(9)	1.614	1.628	O(3)—O(7)	2.618	2.623
			—O(9)	2.660	2.685
Mean	1.610	1.618	O(7)—O(9)	2.649	2.657
T(4)—O(5)	1.607	1.619	O(5)—O(7)	2.646	2.666
—O(7)	1.606	1.617	—O(8)	2.604	2.611
—O(8)	1.614	1.615	—O(10)	2.582	2.595
—O(10)	1.597	1.610	O(7)—O(8)	2.617	2.642
			—O(10)	2.662	2.680
Mean	1.606	1.615	O(8)—O(10)	2.662	2.627
T(5)—O(6) [× 2]	1.627	1.616	O(6)—O(6)	2.609	2.596
T(5)—O(8) [× 2]	1.608	1.612	—O(8) [× 2]	2.653	2.643
			—O(8) [× 2]	2.673	2.672
Mean	1.618	1.614	O(8)—O(8)	2.586	2.588

Estimated errors in T—O bond lengths are approximately ± 0.005 Å for the Kuruma clinoptilolite, and ± 0.004 Å for Agoura material, those in O—O distances are ± 0.009 Å for the Kuruma, and ± 0.007 Å for Agoura clinoptilolite.

ed Ca mordenite, for example, amounts to 1.9$^0/_0$. Such an effect of the T—O bond-length reduction is expected to be different between clinoptilolite and heulandite because the major cations of the former are monovalent while those of the latter are bivalent. Unfortunately, however, the two reported heulandite structures are not accurate enough to discuss the difference.

Table 10. *Comparison of mean* T—O *lengths*

	Clinoptilolite		Heulandite	
	Kuruma	Agoura	ALBERTI (1972)	MERKLE and SLAUGHTER (1968)
Major cations per cell	1.90 Ca 1.76 Na 1.05 K	1.16 Ca 1.8 Na 1.68 K	3.57 Ca 1.26 Na 0.43 K	3.5 Ca 0.4 Sr 0.9 K
Al/(Al + Si)	0.19	0.17	0.26	0.26
Mean T—O	1.625 Å	1.624 Å	1.636 Å	1.638 Å
T—O for feldspar*	1.637	1.635	1.646	1.646
Difference	−0.7%	−0.6%	−0.6%	−0.5%

* SMITH and BAILEY, 1963.

Table 11. *Distribution of* Al *over tetrahedral positions in C2/m structures of the heulandite group*

Tetrahedral position	Clinoptilolite		Heulandite *
	Kuruma	Agoura	
1	20%	17%	22%
2	42	31	42
3	9	13	27
4	6	11	12
5	14	10	28

* Calculated, based on the procedure described in the text, from the Alberti's bond lengths (ALBERTI, 1972); the results are essentially the same as those assumed by ALBERTI.

The Al distribution was estimated using the same procedure as given by MORTIER *et al.* (1975); after due corrections of the T—O bond lengths for the T—O—T angle, the fractional Al content of *i*th tetrahedron is calculated as $(l_i - L)/0.15 + r$. Here, l_i = mean T—O length of *i*th tetrahedron, L = over-all mean of T—O bond length, and r = Al/Si. The procedure is based on the assumption that Al—O is longer than Si—O by 0.15 Å. The observed mean T—O—T angles for tetrahedra are: 143.1 (142.8), 147.3 (147.7), 151.3 (151.0), 151.1 (151.8) and 144.9 (144.5)° respectively for T(1), T(2), T(3), T(4) and T(5) for Agoura clinoptilolite, the figures in parentheses being for the Kuruma clinoptilolite. In Table 11, which gives the results, we observe that Al tends to prefer (T2) over other tetrahedral positions. All oxygen atoms about T(2) are indeed bonded to cations. In the cases of the T(1) and T(3) tetrahedra, only two oxygen atoms are bonded to cations, while in the case of the T(4) tetrahedron, one oxygen atom is bonded to the cations. The lowest Al content in the T(5) tetrahedron of the Agoura clinoptilolite is in accord with the situation that no oxygen atoms about T(5) has cation neighbors.

Distribution of cations

The cation—O(H_2O) bond lengths are listed in Table 12. Among the four kinds of cation positions, M(1) and M(2) correspond to the positions which have so far been reported for the heulandite structure (MERKLE and SLAUGHTER, 1968; ALBERTI, 1972), while M(3) and M(4) are new positions which we found in the present study. Another

Table 12. M—O *distances in clinoptilolite*

		Kuruma	Agoura
M(1)	O(2) [× 2]	2.85 Å	2.82 Å
	W(1)	2.61	2.80
	W(2)	2.32	2.30
	W(5) [× 2]	2.76	2.83
	W(6)	2.66	2.77
M(2)	O(1)	2.57	2.55
	O(10) [× 2]	2.75	2.77
	W(3) [× 2]	2.38	2.36
	W(3)′ [× 2]	2.64	2.63
	W(4)	2.54	2.53
M(3)	O(2) [× 2]	3.10	3.17
	O(3) [× 2]	2.97	3.01
	O(4) [× 2]	3.16	3.08
	W(2)	2.71	2.91
	W(3) [× 2]	3.20	3.03
M(4)	W(5) [× 2]	1.59	1.70
	W(6) [× 2]	2.71	2.69
	W(7) [× 2]	1.81	1.90

Estimated errors in M—O and M—W distances are respectively ± 0.01 Å and ± 0.04 Å for the Kuruma clinoptilolite, ± 0.01 Å and ± 0.03 Å for the Agoura mineral.

position, C(3), which **Alberti** (1975) reported for the clinoptilolite structure, will be discussed later.

M(1) is located in channel *A*, being coordinated by two framework oxygen atoms, O(2) [×2], and five water molecules (Fig. 4). Among the five water molecules, W(5) is located on a twofold axis, giving rise

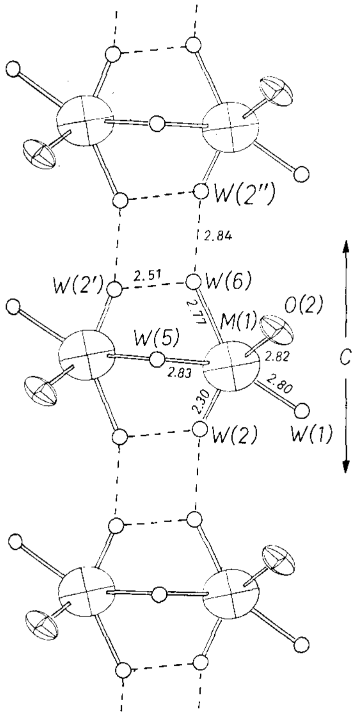


Fig. 4

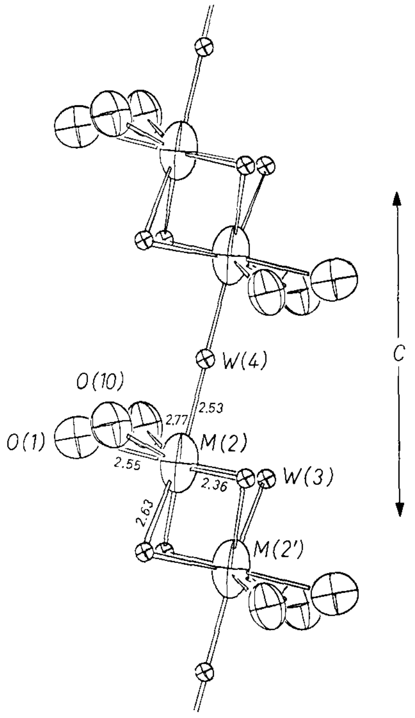


Fig. 5

Fig. 4. The contents in channel *A*, showing the arrangement of the M(1) positions and their neighbors; interatomic distances of the Agoura clinoptilolite are indicated. The broken lines do not necessarily mean hydrogen bondings. Since the occupancies of atoms at M(1) and those of water molecules are low, this kind of link is not actually formed in the channel. The water molecule, W(2) may not be associated with the atom at the M(1) position (see text)

Fig. 5. The contents in channel *B*, showing the arrangement of the M(2) position and their neighbors; interatomic distances for the Agoura clinoptilolite are indicated. This is the projection onto a plane which is rotated 10° about *c* from the (010) plane. Note that cations can not occupy simultaneously the pair of positions, M(2) and M(2'); the infinite chain as indicated in this figure is not actually formed

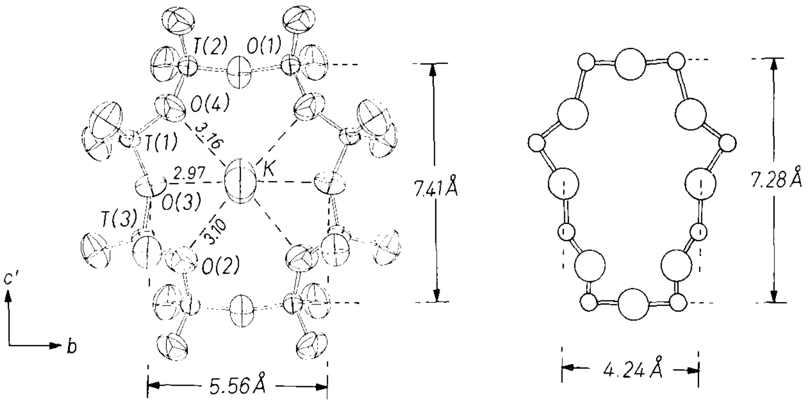


Fig. 6. The a-axis projection of the eight-member ring of channel C, showing the potassium atom at the M(3) position of the Agoura clinoptilolite (left) ($c' = c \sin \beta$). The corresponding ring in the structure of heulandite B (ALBERTI, 1973) is compared at the right, in which some of the oxygen atoms about Si are omitted

to a pair of polyhedra about M(1). In the M(1) position, there are located Na and Ca. In the cases of both the Kuruma and Agoura minerals, the content of Na in the position is higher than that of Ca. In the Agoura mineral, especially, the position is occupied essentially only by Na. ALBERTI (1975) found in his Agoura specimen a very short M(1)—W(2) distance of 1.75 Å; W(2) is not associated with M(1). Our M(1)—W(2) distances, 2.30 Å for the Agoura mineral and 2.32 Å for the Kuruma mineral, are short distances ordinarily acceptable for Na, Ca compounds. However, the low occupancy of W(2) would seem to support ALBERTI's view. We shall come to discuss this point later.

M(2), which is located in channel B, has neighbors of three framework oxygen atoms and five water molecules (Fig. 5). In this position, which is for Na and Ca, the occupancy of Ca tends to be higher than that of Na. The observed bond lengths are in good accord with the difference in site content between M(1) and M(2); the average bond length in the M(1) polyhedron is significantly longer than that in the M(2) polyhedron (Table 12). As observed in Fig. 5, M(2) and M(2)', which are related to each other by a twofold operation, are separated only by 2.76 Å; concurrent occupation of atoms in such a paired position is not likely.

M(3) is located in channel C at nearly the center of its eight-member ring. This position for K is coordinated by six framework oxygen atoms and three water molecules (Fig. 6). Since the separation between M(3) and W(1) is very small (0.71 Å for the Kuruma mineral, 0.61 Å for the Agoura mineral) and accordingly occupancies at these positions are small, it would certainly be difficult to detect the M(3) position separately from W(1) unless the crystals have high potassium contents. It is expected that, in the heulandite structures worked out by Merkle and Slaughter (1968) and by Alberti (1972), the potassium atoms are located at the positions corresponding to M(3). The M(3) possition is also close to M(1); concurrent occupation of K at M(3) and Na, Ca at M(1) is not permissible. Such a forbidden pair of atomic positions characteristic of the clinoptilolite structure is given in Table 13. The location of the potassium atoms at this position is, as will be discussed later, closely related to the thermal stability of the heulandite-group zeolites.

Table 13. *Forbidden pair of atomic positions* in clinoptilolite*

Pair	Distance between the paired positions	
	Kuruma	Agoura
M(1)—M(3)	1.91 Å	2.19 Å
—M(4)	2.26	2.26
M(2)—M(2)′	2.76	2.79
M(3)—W(1)	0.71	0.61
W(7)—W(2)	1.22	1.09
—M(1)	1.20	1.25 **
—M(3)	2.37	2.19

* The pair of atomic positions at which concurrent occupation of atoms is not permissible.

** Refer to the text.

M(4), which is occupied by Mg (or Al), is located, like M(1), in channel *A*, but at a center of inversion. Although the occupancy at this position is very small, its existence is conclusive from the results of difference syntheses and least-squares refinements. This position is coordinated by six water molecules which occupy the vertices of an octahedron (Fig. 7). Making allowance for considerable positional disorder of water molecules, we consider that the Mg—H_2O bond lengths (Table 12) are of reasonable value. As observed in Table 2, the Agoura mineral has excess of 0.14 Al for the 36 tetrahedral cations. The M(4) position may accommodate these excess atoms.

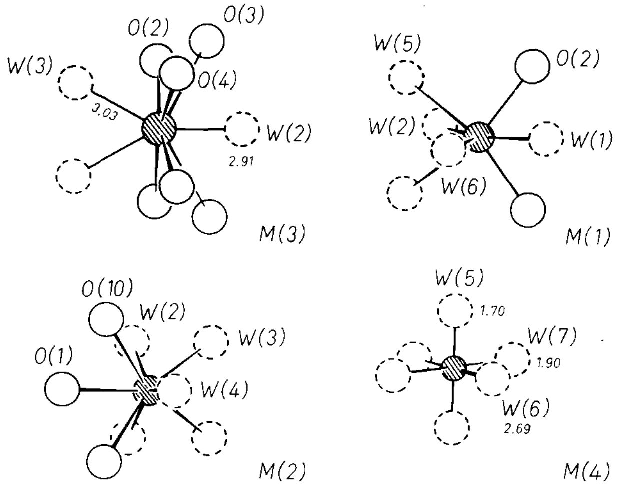


Fig. 7. Neighbors of cation positions (views approximately along the *a* axis, the mirror plane being horizontal). The atomic distances which are missing here will be found in Fig. 4, Fig. 5 or Fig. 6

Water molecules

Water molecules contained in the heulandite-group zeolites may, in general be calssified into two categories. Those which fall in the first category have a maximum occupancy, 1.0, regardless of the change in chemical composition. Those which fall in the second category have variable occupancies; their occupancy may change from one specimen to another.

We find that, for clinoptilolite, W(3) and W(4) are the constant water molecules which have the maximum occupancy. The situation is same as that of the heulandite (MERKLE and SLAUGHTER, 1968; ALBERTI, 1972). Both of the water molecules are located in channel *C* and tightly bonded to M(2) cations. The fact that W(3) and W(4) are shared by two adjacent M(2) positions (Fig. 5) is undoubtedly related to the constancy of these water molecules. W(3) has an additional cation neighbor, K, at a distance of about 3 Å.

Among water molecules which belong to the second category, W(5) and W(6) tend to have higher occupancies. This fact is explainable because these water molecules are associated with both M(1) and M(4). Though W(2) has two near cation positions, M(1) and M(3), it has very low occupancy for the both the Kuruma and Agoura minerals. In this case, W(2) would probably be associated with only M(3); the occupancy

Table 14. *Neighbors of water molecules* in clinoptilolite*

Neighbor		Distance	
		Kuruma	Agoura
W(1)	W(3) [× 2]	2.77 Å	2.74 Å
	W(7)	3.02	3.11
	O(4)	2.98	2.91
W(2)	W(6)	2.68	2.51
	W(6)	2.77	2.84
	W(5) [× 2]	3.08	3.05
	O(6) [× 2]	3.16	3.21
W(3)	W(1)	2.77	2.74
	W(3) [× 2]	2.88	2.84
	O(8)	3.09	3.02
	O(10)	3.19	3.21
W(4)	O(5) [× 2]	3.21	3.17
W(5)	W(5)	3.17	
	W(6) [× 2]	3.14	3.18
	W(2) [× 2]	3.08	3.05
	W(7)	2.41	2.52
W(6)	W(2)	2.68	2.51
	W(2)	2.77	2.84
	W(5) [× 2]	3.14	3.18
	W(7)	3.09	3.00
W(7)	W(1)	3.02	3.00
	W(5) [× 2]	2.41	2.52
	W(6)	3.09	3.11
	O(3) [× 2]	3.16	3.13

* Neighbors other than cation are given at distances less than 3.3 Å.

at this position does not vary according to the content at M(1) (Tables 6 and 8). If there is no bond between W(2) and M(1), the coordination of M(1) is, as pointed out by Alberti (1975), reduced to sixfold. The low occupancy of W(1) is explainable because it is bonded only to M(1). Neighbors of water molecules, other than cations, are listed in Table 14.

Finally, a mention should be made of the water molecule W(7) which had not been reported for heulandite (Merkle and Slaughter, 1968; Alberti, 1972). The possible existence of this new position was suggested by the Fourier maps (Fig. 1) and difference Fourier maps. It is at a reasonable distance from Mg (Table 12). Since, however, this water molecule is located, as observed in Fig. 1, in a badly elongated Fourier peak which covers the positions of M(1) and W(2), the accurate position of this water molecule is uncertain. In the least-squares procedure for the Agoura mineral, we observed a trend that W(2) was shifted towards W(7). In the case of the Agoura mineral, the Fourier peak of W(7) is more significant than that of W(2), while, in the case of the Kuruma mineral, W(2) is more significant. This situation is thought to be closely related to the Mg occupancy at M(4); the Agoura mineral contains more Mg atoms than the Kuruma mineral. In general, we may consider that there are possible water locations extended from around W(7) to W(2) (Fig. 1); the water locations in the area are variable depending upon the mode of cation occupancies at M(1), M(3) and M(4) in a crystal.

Chemical composition

Here, we conseider the maximum possible cation contents in a heulandite-group zeolite. It can be calculated based on the cation positions; among four cation positions in the space group $C2/m$, M(1), M(2), and M(3) are fourfold, while M(4) is twofold. Considering the forbidden pairs of cation positions (Table 13), and assuming that there are n ($n \leq 2$) Mg atoms per cell, we can express the maximum total number of cations, $\Sigma_{\max}$, by the following formula:

$$\Sigma_{\max} = 4\ (1.5 + \tfrac{1}{2}n)\,.$$

If Mg content is negligible, we obtain $\Sigma_{\max} = 6$. According to the reported chemical analyses for heulandite-group zeolites, the values of Σ are, in general, indeed in the range from 4—6.

However, there are some exceptions. Out of 22 chemical formulae given by ALIETTI (1972), that of specimen No. 21 gives $\Sigma = 6.52$ against a calculated $\Sigma_{\max} = 6.12$; No. 13, among 14 chemical data given by BOLES (1972), gives $\Sigma = 6.49$ against calculated $\Sigma_{\max} = 6.38$. We find noteworthy exceptions in certain chemically treated specimens: *e.g.*, a heulandite treated with KCl (SHEPARD and STARKEY, 1966) contains 8.34 K + 0.03 Na + 0.53 Ca, giving $\Sigma = 8.90$. Such a high cation content can not be accounted for from the presently available structural knowledge.

If the M(3) position is filled up by K, additional K atoms may probably occupy M(2) with adjustment of neighboring H_2O positions.

The position C(3), around the origin, which ALBERTI (1975) newly introduced to the clinoptilolite structure, would perhaps be able to accommodate K. Even if these additional positions are taken into account, the maximum possible content of K is calculated to be 8. Regarding the C(3) position, we do find in our Fourier map (Fig. 1) a very low electrondensity distribution there. However, we did not make any attempt to locate cations at the position.

The role of potassium atoms in thermal stability

As mentioned earlier, in addition to the hypotheses which have so far been given to explain the general thermal behavior of the heulandite-group zeolites, we can point out here a specific role of potassium atoms in the problem based on the potassium locations which have been brought out by the present study. Among three kinds of channels characteristic of the framework of the heulandite type, channel *C*, in which K is located, is, as argued, running parallel to *a* (Fig. 2). If we collapse the channel, a destruction of the framework must occur. Since the channel is comprised of eight-member rings, to collapse the channel, we must collapse the rings. To see this situation, we compare, in Fig. 6, an eight-member ring in the structure of Agoura clinoptilolite and a corresponding ring in heulandite *B* (ALBERTI, 1973). In this particular case, the ring in the latter structure is flattened along *b* by about 1.3 Å.

Now, we have found that the position of K is located almost at the center of such a ring, being coordinated by as many as six oxygen atoms of the ring, and three additional water molecules. An inference can then be made that the potassium atom at the position would play a role of preventing, to some extent, the ring from collaption even if the water molecules were removed. The larger the occupancy of K at the position, the more significant would be the effect. There are a number of lines of evidence which support this view. For example, of 21 samples which ALIETTI (1972) classified into three types, heulandite type 1, heulandite type 2, and clinoptilolite, No. 7, which belongs to the heulandite type 2, has a higher K content than No. 1, which belongs to the heulandite type 1, though both have almost the same Al/Si ratio. Further, SHEPARD and STARKEY (1966) reported important experimental evidence that a K-exchanged heulandite behaves just like a typical clinoptilolite in its absence of polymorphism and its high temperature of destruction.

Our result thus provides the structural basis for explaining the fact that replacement of Ca by K governs the thermal property of clinoptilolites (Alietti *et al.*, 1974). Although Alberti (1975) pointed out the role of K in a way similar to the above, he located K at the M(1) position. Our K position is more reasonable in respect to the above argument. To confirm this view, high-temperature structural studies are now in progress.

We wish to thank Prof. Y. Iitaka, Pharmaceutical Department, for making his automated diffractometer available for our study, Prof. A. Iijima for specimens of the Kuruma clinoptilolite and those of the Agoura clinoptilolite, which were studied by Wise *et al.* (1969), Prof. H. Minato and Dr. M. Utada for stimulate discussions, and Dr. K. Fujino for microprobe analyses. Dr. Y. Kudoh assisted in computation which was performed on HITAC 8700/8800 at the Computer Center of the University of Tokyo.

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