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Zeolites of the Phillipsite Family. Refinement of the Crystal Structures of Phillipsite and Harmotome

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Phillipsite ($K_{\sim 2}Ca_{\sim 1\cdot 5}Na_{\sim 0\cdot 4}Al_{\sim 5}Si_{\sim 10}O_{32}.12H_2O$) and harmotome ($Ba_{\sim 2}Ca_{\sim 0\cdot 5}Al_{\sim 5}Si_{\sim 11}O_{32}.12H_2O$) were found to be isostructural with the same cationic sites and water-molecule distribution within an almost identical framework. Both minerals crystallize in the monoclinic system ($P2_1$ or $P2_1/m$) with respective cell dimensions: $a=9\cdot865$ (2), $b=14\cdot300$ (4), $c=8\cdot668$ (2) Å, $\beta=124\cdot20$ (3)°, and $a=9\cdot879$ (2), $b=14\cdot139$ (2), $c=8\cdot693$ (2) Å, $\beta=124\cdot81$ (1)°. Intensity data from a 4-circle diffractometer were refined by least-squares and Fourier techniques to respective R's of 0·063 and 0·047. The aluminosilicate framework is topologically identical to that found by earlier workers. No evidence for Si,Al ordering was found. All cations and water molecules were unequivocally located although some water molecules showed large atomic displacements. There are two cation sites: one, fully occupied by K in phillipsite and Ba in harmotome, is surrounded by eight framework oxygens and four water molecules. The other site is partially occupied by Ca and Na in a distorted octahedral coordination with two framework oxygens and four water molecules. Two of the water molecules associated with Ca showed large atomic displacements consistent with partial occupancy of the Ca site. Refinement of harmotome in $P2_1$ was unsuccessful and the structure is best described in $P2_1/m$.

Introduction

Although morphological and optical studies in the 19th and 20th centuries on minerals of the phillipsite family consistently indicated monoclinic symmetry, Steinfink (1962) solved and refined the crystal structure of a Na-rich phillipsite with $a=9\cdot96$, $b=14\cdot25$, $c=14\cdot25$ Å in the orthorhombic space group $B2mb$. Independently, Sadanaga, Marumo & Takéuchi (1961) solved and refined the crystal structure of harmotome with $a=9\cdot87$, $b=14\cdot14$, $c=8\cdot72$ Å and $\beta=124°\,50'$ in $P2_1$. Their work was carried out on a specimen of harmotome from the same locality as the present sample (Andreasberg, Hartz, Germany) but the chemical composition they quote has more Na and less Ca than ours. The aluminosilicate frameworks of the two structures are topologically identical and the transformation matrix from the orthorhombic to monoclinic cell is $100/010/-\frac{1}{2}0-\frac{1}{2}$. Černý (1964) pointed out that Steinfink's orthorhombic cell is merely a geometric average from complex twinning. Both Steinfink (1962) and Sadanaga *et al.* (1961) had difficulty with the locations and occupancies of the exchangeable cations and water molecules, a common problem with zeolites.

This and work to follow were undertaken (*a*) to prove that phillipsite and harmotome do indeed share the same topology of the aluminosilicate framework, (*b*) to determine the Si,Al distribution and framework geometry of several varieties with extreme chemical compositions, (*c*) to determine the location of and bonding between exchangeable cations and water molecules, and (*d*) to explain the twin laws and look for possible intergrowths analogous to feldspar perthites.

Experimental

A single crystal (0·1 × 0·06 × 0·05 mm rectangular parallelepiped) of phillipsite from Casal Brunori, Rome, Italy (#3 of Galli & Loschi Ghittoni, 1972) and one of harmotome (0·15 × 0·10 × 0·10 mm rectangular parallelepiped) were obtained by cutting penetration twins until only one set of X-ray diffractions was observed. The only extinction condition is absence for k odd in $0k0$ indicating $P2_1$ or $P2_1/m$ as possible space groups for both minerals.

Unit-cell parameters [phillipsite: $a=9\cdot865$ (2), $b=14\cdot300$ (4), $c=8\cdot668$ (2) Å, $\beta=124\cdot20$ (3)°; harmotome: $a=9\cdot879$ (2), $b=14\cdot139$ (2), $c=8\cdot693$ (2) Å, $\beta=124\cdot81$ (1)°] were determined by the least-squares refinement of 30 high 2θ values (Burnham, 1962). The 2θ values were measured on a Picker-FACS-1 diffractometer at room temperature and determined by averaging 4 half-height-peak settings (plus and minus 2θ). The chosen cell transforms to the reduced standard cell by means of the matrix: 101/00–1/010.

A wet chemical analysis of phillipsite by Galli & Loschi Ghittoni (1972) on the same specimen from which the single crystal came gave $K_{1\cdot 99}Ca_{2\cdot 09}Na_{0\cdot 29}Ba_{0\cdot 01}Si_{9\cdot 51}Al_{6\cdot 45}O_{32}.13\cdot 5H_2O$. This compares with $K_{2\cdot 0}Ca_{1\cdot 7}Na_{0\cdot 4}Si_{10\cdot 6}Al_{5\cdot 3}O_{32}.?H_2O$ from our electron microprobe analysis on some crystals obtained from the same radial aggregate as the one used in the structure determination; note that water content cannot be measured directly by electron microprobe. Galli & Loschi Ghittoni (1972) found that the

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measured density of 2·20 (2) g cm^{-3} was close to the value of 2·242 g cm^{-3} calculated for 32 oxygen atoms per cell. Natural phillipsites range widely in Na, K, Ca substitution (*e.g.* Galli & Loschi Ghittoni, 1972) and their composition can be represented by the ideal chemical formula: $K_2Ca_nNa_{2-n}Al_{4+n}Si_{12-n}O_{32}.12H_2O$ with $n \le 2$.

Chemical analyses of the same specimen of harmotome used in the present work were carried out by both the wet method and X-ray fluorescence (F. Rinaldi, personal communication). The two sets of data agree very well giving an average cell content of $K_{0\cdot07}Ca_{0\cdot46}Ba_{1\cdot92}Si_{11\cdot26}Al_{4\cdot65}O_{32}.11\cdot80H_2O$. The water content was determined by TGA. The calculated density from the above formula is 2·416 g cm^{-3} compared to the observed density of 2·35 g cm^{-3} (Sadanaga *et al.*, 1961).

Intensity data collection was carried out on a Picker FACS-1 automated single-crystal diffractometer with θ–2θ scans; 3300 diffractions (about two equivalent sets) were measured for phillipsite [$(\sin\theta/\lambda)_{\max}=0\cdot562$] using Cu $K\alpha$ radiation ($\lambda=1\cdot5418$ Å) which after averaging produced 1416 unique diffractions and 6470 diffractions (about 2 equivalent sets) were measured for harmotome [$(\sin\theta/\lambda)_{\max}=0\cdot7035$] using graphite-monochromatized Mo $K\alpha$ radiation ($\lambda=0\cdot71069$) which after averaging produced 2839 unique diffractions.

The estimated errors in the intensities (σ_I) were calculated using:

$$\sigma_I=[S+t^2B+k^2(S+tB)^2]^{1/2}$$

where S = peak scan counts, B = total background counts, t = ratio of peak to background observation times, k = instability constant (0·01).

The equivalent diffractions were averaged using

$$\bar{I}=\sum_i (I_i/\sigma_i^2)/\sum_i (1/\sigma_i^2)\;, \quad \bar{\sigma}_I=[1/\sum (1/\sigma_i^2)]^{1/2}$$

where I_i and σ_i are the intensity and the standard deviation of the ith equivalent diffraction. The intensity data were corrected for Lorentz and polarization effects, but no absorption correction was applied in either case because the crystals were small and equidimensional. The linear absorption coefficient for phillipsite was $\mu_{\mathrm{Cu}\,K\alpha}=92\cdot3$ cm^{-1} and for harmotome $\mu_{\mathrm{Mo}\,K\alpha}=25\cdot8$ cm^{-1}, yielding a maximum error in the relative structure factors of 5 and 3 percent respectively.

The $\bar{\sigma}_I$'s were converted to the estimated errors in the relative structure factors (σ_F) by $\sigma_F=[(\bar{I}+\bar{\sigma}_I)/\mathrm{Lp}]^{1/2}-(\bar{I}/\mathrm{Lp})^{1/2}$ with Lp = Lorentz and polarization factors.

Structure refinements

For phillipsite initial phases were assigned from a structure-factor calculation (*NUCLS*, a modified version of *ORFLS* by Busing, Martin & Levy, 1962) that used, after proper transformation, the parameters of the framework atoms [except for O(8) and O(9)] given for harmotome by Sadanaga *et al.* (1961). A value of R = 0·35 was obtained. A second structure-factor calculation, after adding the positional parameters for K and three water molecules, gave $R=0\cdot24$. From then on, an alternation of Fourier calculations, combining the calculated phases with the observed moduli, and of least-squares refinements, yielded $R=0\cdot135$ after 4 cycles. A difference-Fourier synthesis was calculated and the resulting electron density map allowed the location of Ca and two more water molecules $W(4)$ and $W(5)$. Moreover the K site at this stage appeared to consist of two half-atoms 0·4 Å apart. In two more cycles the isotropic least-squares refinement converged, with $R=0\cdot082$ (Rinaldi, Pluth & Smith, 1973).

For harmotome initial phasing was obtained from a structure-factor calculation that used the atomic parameters derived previously for phillipsite. Ca was excluded, Ba was introduced in place of K, and 3 of the water molecules [$W(1)$, $W(2)$ and $W(5)$] corresponding respectively to $H_2O(4)$, $H_2O(1)$ and $H_2O(6)$ in the model of Sadanaga *et al.* (1961), were also used. The first cycle of least-squares refinement yielded R = 0·25. After 2 more cycles R dropped to 0·067 (isotropic). A difference-Fourier synthesis allowed the location of Ca and two more water molecules [$W(3)$ and $W(4)$].

During the isotropic refinements, populations and thermal parameters were refined simultaneously. All populations except Ca refined close to the values of full occupancy that were used in the partially anisotropic refinements. In both cases anisotropic temperature factors were applied to all non-framework atoms, and the occupancy of Ca was varied: the refinements converged in 5 cycles for phillipsite and in 6 for harmotome. The maximum shifts in phillipsite (0·2– 1·35σ) appeared in the thermal parameters of $W(4)$ and $W(5)$ as discussed below. In harmotome the maximum shifts (0·7–1·3σ) appeared in the thermal parameters of $W(5)$ and Ca respectively.

The X-ray models give the chemical formulas: $Ca_{1\cdot65}K_2Si_{10\cdot7}Al_{5\cdot3}O_{32}.12H_2O$ for phillipsite and $Ca_{0\cdot6}Ba_2Si_{12}Al_4O_{32}.12H_2O$ for harmotome. The final cycle of least-squares refinement minimized $\sum w||F_o|-|F_c||^2$ with $w=(1/\sigma_F)^2$. The final reliability factors were $R=0\cdot063$, $R_w=0\cdot057$ and $S=4\cdot254$ for phillipsite; and $R=0\cdot047$, $R_w=0\cdot039$ and $s=3\cdot317$ for harmotome, where

$$R=\sum ||F_o|-|F_c||/\sum |F_o|\;,$$
$$R_w=[(\sum w||F_o|-|F_c||^2)/\sum w|F_o|^2]^{1/2}$$
$$S=[(\sum w||F_o|-|F_c||^2)/(n_o-n_v)]^{1/2}\;,$$

n_o = number of diffractions, n_v = number of parameters.

Atomic scattering factors (Mann, 1968) were used for K^+, Ba^{2+}, Ca^{2+}, O^- and [$\frac{1}{3}Al^+ + \frac{2}{3}Si^{2+}$] (for which Al^+ was interpolated between Al and Al^{3+} and Si^{2+} between Si and Si^{4+}) for phillipsite, and [$\frac{1}{4}Al^+ + \frac{3}{4}Si^{2+}$] for harmotome. Anomalous scattering corrections (Cromer & Liberman, 1970) were applied to all atoms.

The final models were checked by difference-Fourier synthesis. In phillipsite the electron density map shows residual but not well defined areas of maximum height (1·2 e Å^{-3}) around *W*(4) and *W*(5). No significant electron density was found around any of the framework atoms. Possible deviation of the structure of phillipsite from the space group assumed in the refinement was also checked by statistical tests on the intensity distribution. The zero-moment test of Howells, Phillips & Rogers (1950) and the distribution of *E*'s (see Table 1) both gave an overall suggestion of centrosymmetry. The suggestion of no significant departure from the centrosymmetric arrangement from both the difference Fourier map and the statistical tests confirmed the choice of $P2_1/m$ as the more probable space group. However, the statistical half-occupancy of the Ca,Na site must result in at least local violation of the assumed mirror plane. Unfortunately it was not possible from the X-ray data to determine whether the Ca,Na atoms occupy the sites at random or whether domains occur. Whatever the actual situation, the apparent large thermal vibrations of neighboring atoms must result from averaging of positions affected by choice of occupancy of the Ca,Na sites.

Table 1. *Distribution of* $|E|$*'s*

	Phillipsite	Harmotome	$\bar{1}$	1
Av. $\lvert E\rvert$	0·783	0·834	0·798	0·886
Av. $\lvert E\rvert^2$	0·985	1·008	1·000	1·000
Av. $\lvert E^2-1\rvert$	0·988	0·902	0·968	0·736
$\lvert E\rvert > 1$ %	28·9	33·4	32·0	36·8
$\lvert E\rvert > 2$ %	4·8	3·7	5·0	1·8
$\lvert E\rvert > 3$ %	0·38	0·07	0·30	0·01

None of the peaks present in the difference Fourier map of harmotome gave a definite suggestion of deviation from the model and its symmetry, although some

Table 2. *Positional, thermal and population parameters*

(*a*) Phillipsite

Atom type	Population	*x*/*a*	*y*/*b*	*z*/*c*	*B* (Å^2)
T(1)	4	0·7362 (2)	0·0248 (1)	0·2805 (3)	1·08 (4)
T(2)	4	0·4206 (2)	0·1409 (1)	0·0019 (3)	1·06 (4)
T(3)	4	0·0604 (2)	0·0078 (1)	0·2844 (3)	1·11 (4)
T(4)	4	0·1204 (2)	0·1396 (1)	0·0421 (3)	1·14 (4)
O(1)	4	0·1335 (6)	0·0976 (3)	0·2289 (7)	2·04 (10)
O(2)	4	0·6445 (6)	0·5766 (3)	0·1878 (6)	1·94 (10)
O(3)	4	0·6100 (5)	0·1130 (3)	0·1728 (6)	1·89 (10)
O(4)	4	0·0254 (5)	0·9154 (3)	0·1494 (6)	1·85 (10)
O(5)	4	0·8957 (6)	0·0440 (3)	0·2713 (7)	2·06 (10)
O(6)	4	0·3022 (6)	0·3738 (3)	0·0783 (7)	2·32 (10)
O(7)	4	0·7872 (5)	0·4795 (3)	0·4982 (6)	1·90 (10)
O(8)	2	0·5814 (8)	$\frac{3}{4}$	0·0616 (9)	1·94 (13)
O(9)	2	0·0665 (8)	$\frac{1}{4}$	0·0196 (9)	2·12 (14)
K	2	0·8480 (3)	$\frac{1}{4}$	0·2076 (4)	2·4 (4)*
Ca	1·65 (2)	0·6080 (4)	0·6262 (3)	0·4401 (5)	2·14 (15)*
W(1)	2	0·7551 (12)	$\frac{3}{4}$	0·4733 (12)	7·8 (5)*
W(2)	2	0·1552 (13)	$\frac{3}{4}$	0·4382 (13)	7·3 (5)*
W(3)	4	0·3208 (8)	0·8525 (6)	0·1740 (10)	8·8 (4)*
W(4)	2	0·5085 (14)	$\frac{1}{4}$	0·4384 (16)	18·7 (1·0)*
W(5)	2	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	16·6 (9)*

* *B*'s from last cycle of isotropic refinement.

(*b*) Harmotome

Atom type	Population	*x*/*a*	*y*/*b*	*z*/*c*	*B* (Å^2)
T(1)	4	0·7367 (1)	0·0248 (1)	0·2840 (1)	0·82 (2)
T(2)	4	0·4214 (1)	0·1410 (1)	0·0136 (1)	0·77 (2)
T(3)	4	0·0577 (1)	0·0075 (1)	0·2898 (1)	0·78 (2)
T(4)	4	0·1216 (1)	0·1390 (1)	0·0375 (1)	0·85 (2)
O(1)	4	0·1042 (4)	0·0896 (2)	0·1958 (4)	2·45 (6)
O(2)	4	0·6470 (3)	0·5726 (2)	0·1679 (4)	1·80 (5)
O(3)	4	0·6163 (3)	0·1186 (2)	0·1792 (4)	1·58 (4)
O(4)	4	0·0050 (3)	0·9083 (2)	0·1711 (4)	2·05 (5)
O(5)	4	0·9057 (3)	0·0515 (2)	0·2955 (3)	1·47 (4)
O(6)	4	0·3137 (3)	0·3709 (2)	0·1017 (4)	1·84 (5)
O(7)	4	0·7808 (3)	0·4856 (2)	0·4976 (4)	1·68 (5)
O(8)	2	0·5885 (5)	$\frac{3}{4}$	0·0573 (5)	1·76 (7)
O(9)	2	0·0661 (5)	$\frac{1}{4}$	0·0256 (6)	1·99 (7)
Ba	2	0·86290 (5)	$\frac{1}{4}$	0·19441 (5)	1·79 (2)*
Ca	0·60 (3)	0·5869 (20)	0·6286 (13)	0·4799 (25)	–
W(1)	2	0·8004 (8)	$\frac{3}{4}$	0·4889 (7)	5·5 (6)*
W(2)	2	0·1148 (8)	$\frac{3}{4}$	0·4593 (7)	4·8 (6)*
W(3)	4	0·3027 (5)	0·8628 (3)	0·1324 (5)	5·8 (3)*
W(4)	2	0·4611 (17)	$\frac{3}{4}$	0·5134 (13)	47 (4)*
W(5)	2	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	35 (2)*

* *B*'s from last cycle of isotropic refinement.

of them (maximum height 1 e Å^{-3}) occurred in the vicinity of framework atoms.

The zero-moment test of Howells, Phillips & Rogers (1950), and the distribution of E's (Karle, Dragonette & Brenner, 1965), plotted between the characteristic curves of centrosymmetric and non-centrosymmetric structures. The piezoelectric effect observed in harmotome (Iitaka, 1953) may indicate absence of a center of symmetry. Perhaps domains are formed. Further measurements on this effect are desirable.

On the basis of the small uncertainty suggested by these tests and by the difference-Fourier synthesis an attempt was made to refine the structure of harmotome in P2$_1$. The initial atomic coordinates were shifted by 0·01–0·02 Å in the direction suggested by the difference Fourier peaks. After 6 cycles the positional parameters of the tetrahedral atoms were back very close to their original values and the same happened to Ba. The thermal parameters of two oxygens and Ca were still erratic after the sixth cycle and the correlation coefficients of several of the parameters developed very high values. A bond-distance calculation showed that the tetrahedra were much more irregular than in the first refinement with T–O distances varying between 1·59 and 1·71 Å in the same tetrahedron. The cation coordination was not improved either. A value of R= 0·08 was reached when the refinement in $P2_1$ was abandoned.

The structure of harmotome is therefore best described in $P2_1/m$. As for phillipsite the violation of the assumed symmetry may be confined to the statistical distribution of the sorbates in the zeolitic channels, and in particular to the partial occupancy of the Ca site. The effect of this is more pronounced than in phillipsite but still far from producing a truly non-centrosymmetric structure.

The results of the refinements are given in Table 2 (positional and population parameters), Table 3* (structure factors), Table 4 (anisotropic thermal parameters), Table 5* (r.m.s. components and directions of thermal displacement), Tables 6, 7 and 8 (interatomic distances), and Table 9* (O–W–O angles). Interatomic distances and angles were calculated by the program *ORFFE* (Busing, Martin & Levy, 1964).

Table 6. T–O *distances*

T designates tetrahedral sites occupied by Si or Al.

	Phillipsite	Harmotome
T(1)–O(2)	1·658 (5) Å	1·637 (3) Å
T(1)–O(3)	1·644	1·663
T(1)–O(5)	1·643	1·658
T(1)–O(7)	1·659	1·654
$\overline{\text{T–O}}$	1·651	1·653
T(2)–O(2)	1·666	1·632
T(2)–O(3)	1·653	1·648
T(2)–O(6)	1·648	1·637
T(2)–O(8)	1·651	1·641
$\overline{\text{T–O}}$	1·655	1·639
T(3)–O(1)	1·671	1·629
T(3)–O(4)	1·667	1·640
T(3)–O(5)	1·647	1·652
T(3)–O(7)	1·670	1·640
$\overline{\text{T–O}}$	1·664	1·640
T(4)–O(1)	1·663	1·638
T(4)–O(4)	1·661	1·646
T(4)–O(6)	1·650	1·650
T(4)–O(9)	1·642	1·647
$\overline{\text{T–O}}$	1·654	1·645

Table 4. *Anisotropic thermal parameters*

The thermal parameters are defined as $\exp\,[-\frac{1}{4}\sum_{j=1}^{3}\sum_{i=1}^{3}B_{ij}h_ih_ja_i^*a_j^*]$.

(*a*) Phillipsite

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
K	4·4 (2)	1·90 (11)	6·4 (2)	0	3·26 (15)	0
Ca	1·6 (2)	3·5 (2)	2·0 (2)	0·43 (15)	0·45 (15)	−0·66 (15)
W(1)	8·4 (7)	9·1 (7)	2·8 (5)	0	2·9 (5)	0
W(2)	9·8 (8)	4·4 (5)	4·0 (5)	0	1·2 (5)	0
W(3)	5·3 (4)	14·5 (7)	6·2 (5)	−0·8 (4)	3·3 (4)	−1·1 (5)
W(4)	4·3 (7)	57 (3)	2·8 (6)	0	2·2 (6)	0
W(5)	4·8 (6)	24·4 (16)	17·6 (1·3)	3·2 (8)	8·1 (8)	10·9 (11)

(*b*) Harmotome

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Ba	2·605 (17)	1·239 (13)	2·053 (15)	0	1·426 (13)	0
Ca	7·8 (10)	11·6 (12)	9·3 (11)	−0·8 (8)	−0·4 (7)	1·1 (9)
W(1)	5·4 (3)	6·5 (4)	2·6 (2)	0	1·5 (2)	0
W(2)	7·3 (4)	2·7 (2)	3·0 (2)	0	2·5 (3)	0
W(3)	5·0 (2)	6·9 (3)	3·7 (2)	−0·6 (2)	2·3 (2)	−1·3 (2)
W(4)	12·8 (10)	65 (4)	2·5 (4)	0	1·8 (5)	0
W(5)	5·9 (6)	85 (6)	13·9 (10)	−5·1 (16)	6·9 (7)	−14 (2)

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Table 7. *Cation coordination*

Phillipsite		Harmotome	
2 K–O(3)	2·941 (5) Å	2 Ba–*W*(3)	2·826 (4) Å
2 K–O(5)	2·985 (4)	Ba–*W*(1)	2·861 (6)
K–*W*(2)	3·088 (11)	Ba–*W*(2)	2·890 (5)
2 K–*W*(3)	3·110 (8)	2 Ba–O(5)	2·899 (3)
K–*W*(1)	3·287 (10)	2 Ba–O(3)	3·007 (3)
K–O(9)	3·353 (7)	Ba–O(9)	3·089 (4)
2 K–O(1)	3·482 (5)	2 Ba–O(1)	3·286 (3)
K–O(8)	3·505 (7)	Ba–O(8)	3·678 (4)
$\overline{\text{K–O}}$	3·189	$\overline{\text{Ba–O}}$	3·046
Ca—*W*(1)	2·203 (7)		
Ca—*W*(5)	2·298 (4)	Ca—*W*(5)	2·060 (21)
Ca—*W*(3)	2·468 (8)	Ca—*W*(4)	2·234 (20)
Ca—O(2)	2·510 (6)	Ca—*W*(1)	2·686 (23)
Ca—O(1)	2·584 (6)	Ca—*W*(3)	2·709 (15)
Ca—O(7)	2·603 (6)	Ca—O(7)	2·728 (19)
Ca—*W*(4)	2·632 (9)	Ca—O(1)	2·782 (15)
$\overline{\text{Ca–O}}$	2·471	$\overline{\text{Ca–O}}$	2·533

Discussion

(*a*) Si, Al–O *framework*

The aluminosilicate framework is topologically the same as that proposed by Steinfink (1962) for phillipsite and by Sadanaga *et al.* (1961) for harmotome. The near uniformity of the T–O distances (Table 6) give little or no suggestion of ordering of Al and Si.

The framework consists of layers of tetrahedra composed of eight- and four-membered rings approximately perpendicular to the *a* axis (Fig. 1). The layers are linked vertically by 4-membered rings which form crankshafts with the 4-membered rings of the layers (Fig. 2). The topological relation of phillipsite to other structures with crankshafts is given by Smith (1963, 1968).

Two sets of channels are present in the structure. One parallel to the *a* axis consists of a succession of

Table 8. *Water–oxygen close contacts*

	Phillipsite	Harmotome
W(1)–O(8)	2·966 (11) Å	3·081 (7) Å
2 *W*(1)–O(1)	3·071 (8)	3·255 (5)
W(1)–*W*(2)	–	3·260 (9)
W(1)–*W*(4)	3·097 (15)	–
2 *W*(1)–O(2)	3·230 (7)	–
W(2)–*W*(4)	2·856 (15)	3·176 (16)
2 *W*(2)–O(4)	3·146 (8)	3·060 (5)
W(2)–O(9)	3·282 (11)	–
W(2)–*W*(1)	–	3·260 (9)
2 *W*(2)–O(3)	–	3·294 (5)
W(3)–*W*(3)	2·931 (17)	3·190 (10)
W(3)–*W*(4)	3·148 (13)	3·170 (9)
W(3)–*W*(5)	3·153 (8)	3·265 (4)
W(3)–O(2)	3·287 (8)	–
W(3)–O(3)	–	3·244 (5)
W(3)–O(4)	2·942 (8)	3·210 (5)
W(3)–O(5)	–	3·286 (5)
W(4)–*W*(2)	2·856 (15)	3·176 (16)
2 *W*(4)–*W*(3)	3·148 (13)	3·170 (9)
W(4)–*W*(1)	3·097 (15)	–
2 *W*(4)–O(6)	3·143 (10)	3·250 (9)
2 *W*(5)–O(7)	2·857 (4)	2·794 (3)
2 *W*(5)–O(3)	3·153 (8)	3·265 (4)

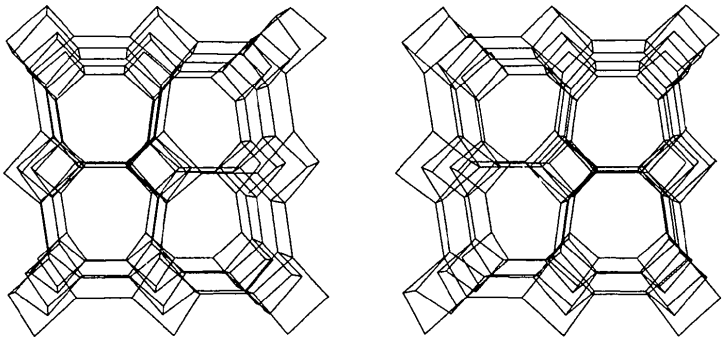


Fig. 1. Phillipsite-type framework looking down the **a** direction (*ORTEP*, Johnson, 1965).

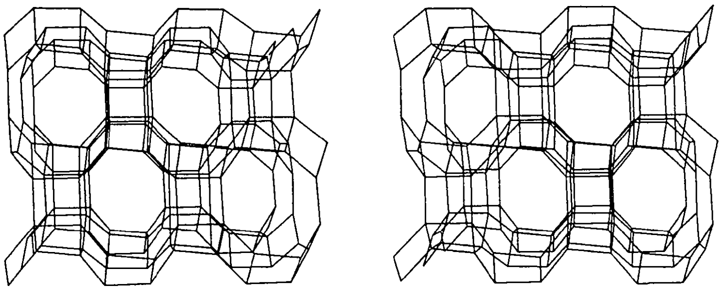


Fig. 2. Phillipsite-type framework looking down the **b** direction (*ORTEP*, Johnson, 1965).

incomplete octagonal prisms (type I) separated by a second type of incomplete octagonal prisms (type II) formed by the 8-membered rings of the layers (Fig. 1). Each octagonal prism of type I lacks two adjacent vertical edges and each octagonal prism of type II lacks six adjacent vertical edges (each prism edge, of course, is a *T*–O–*T* linkage). The minimum free diameter of these channels is 3·85 Å assuming the effective radius of oxygen to be 1·35 Å. The other set of channels runs parallel to the *b* axis and once again its openings are defined by 8-membered rings resulting from the connections between the crankshafts of the 4-membered rings (Fig. 2). These eight-membered rings are elongated along the **c*** direction and the resulting minimum width of the channels is about 2·8 Å.

The two sets of channels intersect each other and the intersections can be regarded as cages. Such a cage actually consists not only of a type II octagonal prism at the intersection, but also an adjacent type I octagonal prism.

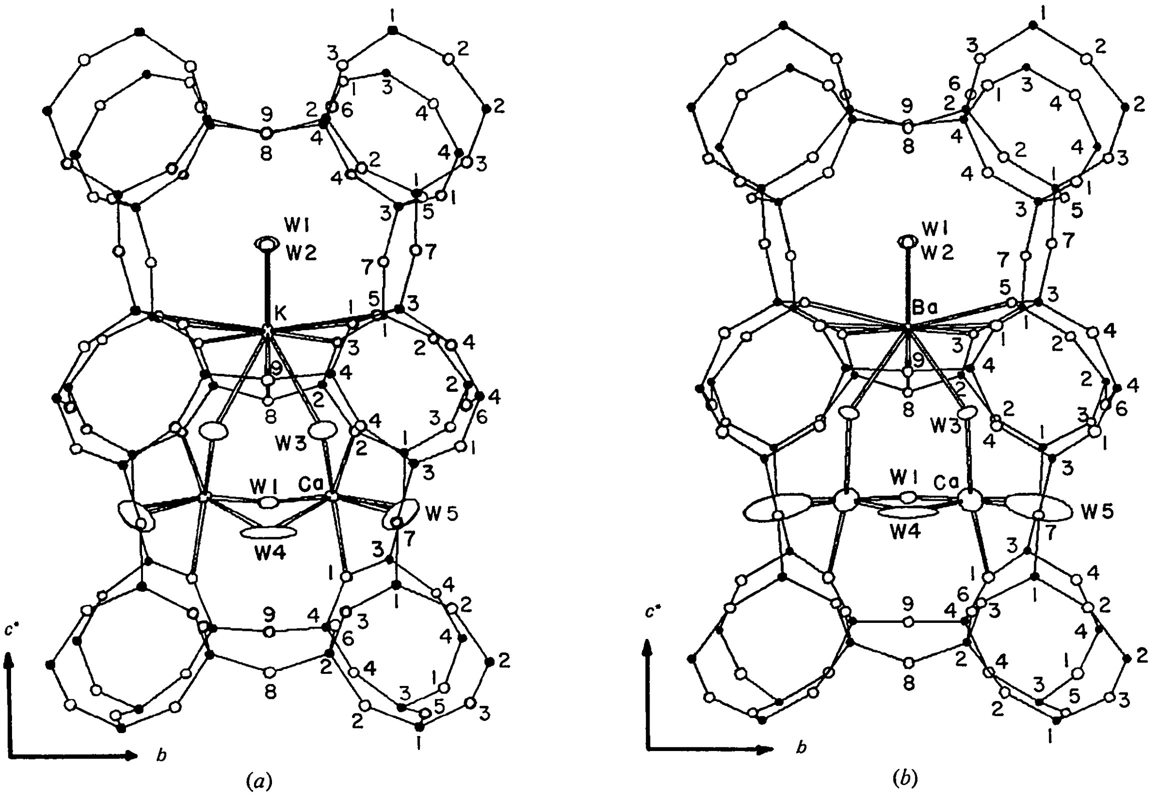
Fig. 3 gives a direct comparison of the structures of phillipsite and harmotome.

(*b*) *Cations and water molecules in phillipsite*

Each Ca atom is located near an intersection of the two sets of channels. Each K atom is located in a type I octagonal prism but in a peripheral position displaced along one of the larger channels [Fig. 3(*a*)]. The K and Ca sites alternate along these larger channels.

Both the chemical and microprobe analyses gave two K atoms per cell which checks with the X-ray estimate of full occupancy of the K site. All the distances to neighbouring atoms and molecules are long (Table 7) and although there are 12 oxygen species surrounding the K, only eight of them are within 3·3 Å [Fig. 4(*a*)]. The K atom is sitting in a cradle-shaped eight-membered ring [Fig. 3(*a*)] and it is closest to two O(3)'s and two O(5)'s. The next nearest neighbours are four water molecules [2*W*(3), *W*(1) and *W*(2)] lying at the corners of an elongated tetrahedron.

The Ca site is presumably occupied by both Ca and Na. Population refinement converged to 1·65 Ca in the four-fold site, but the chemical analysis suggests 2·09 Ca + 0·29 Na while the probe analysis suggests 1·7 Ca + 0·4 Na. For model purposes we assume that this site is half-occupied by Ca. This half-occupancy could explain the short distance (2·20 Å) to *W*(1) and the large anisotropic 'temperature' factors for the water molecules, especially *W*(4) and *W*(5). Probably the X-ray analysis yields a mean of atomic positions dependent on local occupancy of the Ca sites. The apparent 'temperature' factor [actually a mathematically-constrained root-mean-square displacement factor] consists of the summation of displacements of centers-of-motion plus true thermal vibrations which tend to



(*a*) (*b*)

Fig. 3. Positions of the cations and water molecules within the frameworks of (*a*) phillipsite and (*b*) harmotome (*ORTEP*, Johnson, 1965).

be large in zeolites. Probably the Ca atoms migrate from site to site, thereby giving a space-and-time average. Fig. 3(*a*) shows graphically how the displacements of the water molecules might occur. Suppose the Ca site to the right of the mirror plane is occupied while that to the left is vacant. Water molecule *W*(1) would be displaced to the left by ~0·3 Å, while water molecule *W*(5) would be displaced approximately to the right subject to constraints from bonding to nearby O(7) atoms. Water molecule *W*(4) would also be displaced to the right by ~0·2 Å. Water *W*(3) has several near neighbours (Table 8) and its displacement would depend on complex interactions with them. All these displacements apparently take place without any major effects on the aluminosilicate framework whose atoms show no unusual displacements from nodes obeying $P2_1/m$.

The Ca atom is surrounded by 4 water molecules and 3 oxygens for a total of 7 [Fig. 5(*a*)]. If O(2) were excluded from the coordination polyhedron of Ca the coordination would be almost regular octahedral. The distances between Ca and the water molecules are irregular but this may result merely from the statistical averaging as described in the last paragraph.

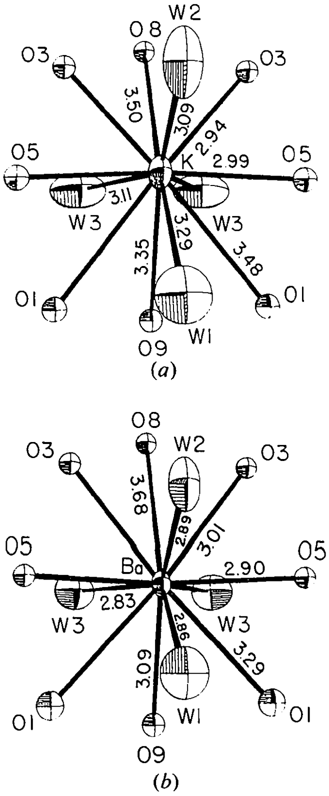
Returning to the K atoms, isotropic refinement was made on the basis of two half-atoms 0·4 Å apart. During anisotropic refinement this displacement was taken care of by the thermal parameter [see also Table 5(*a*)]. This highly anisotropic displacement of the K atom can be explained by either or both of the following: (*a*) presence of the Ca atom in one or other of the two half-occupied positions and its influence on the position of the K atom, and (*b*) by true anisotropic thermal vibration in a large cavity (note large distances in Table 7 compared with common value near 2·7 Å for K–O).

From the cation sites, speculations can be made concerning chemical substitutions in phillipsite. On a simple ionic model, Ba and Sr should substitute for K, and Na for Ca. There is no apparent restriction on occupancy in the K site and (K + Ba + Sr) should equal two per cell. Actually Galli & Loschi Ghittoni (1972) observed a range of K from 0·68 to 3·79 atoms in 22 phillipsites while the range of (K + Ba + Sr) is from 0·7 to 3·8. Again on a simple model, only one out of each pair of Ca sites would be occupied because of electrostatic repulsion, resulting in a maximum of 2Ca per cell. Actually the observed values range from 0·26 to 2·12. The number of Na atoms in phillipsite ranges up to 4·19 atoms per cell suggesting occupancy of both sites of each pair, perhaps because of lower electrostatic repulsion from a monovalent ion (the specimen with 4·19 Na also contains 0·41 Ca and 0·89 K). It is obvious that structure determinations are needed of high-K and high-Na phillipsites to clarify the structural controls on the exchangeable cations. Probably the cation contents of phillipsite correlate with the external environment at the time of crystallization, thereby fixing the Al/Si ratio, and with the later environment which controls the final content of exchangeable cations.

The water molecules *W*(1) and *W*(2) lie near the center of 8-membered rings [Fig. 3(*a*)]; *W*(3) occurs as pairs related by a plane of symmetry on the circumference of the large channels; *W*(4) occurs between two eight-rings in the center of the large channels; and *W*(5) at the center of the elongated eight-membered rings that form the smaller channels parallel to [010]. All water molecules except *W*(2) bond to Ca. The water molecule *W*(2) is within normal bonding distance of K. Because of the large *B* factors, it is not easy to determine the positions of possible hydrogen bonds: however, the distances reported in Table 8 imply a reasonable pattern of bonding to framework oxygens and other water molecules. The oxygen–water–oxygen angles are reported in Table 9.*

(*c*) *Cations and water molecules in harmotome*

The simplest explanation of the cation positions is that Ba and K occupy the large site, and Ca the small site. Ba occupies the same site occupied by K in phillipsite and it is surrounded by eight oxygens of an eight-ring and four water molecules at the corners of



(*a*)

(*b*)

Fig. 4. Nearest neighbours of the (*a*) K and (*b*) Ba atoms; 50% ellipsoids of vibration; viewed down the **c*** direction. Distances in Å. (*ORTEP*, Johnson, 1965.)

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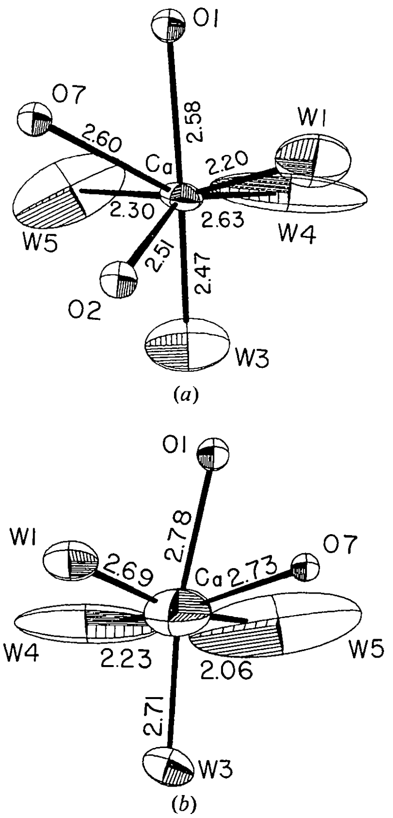
* See previous footnote.



(*a*)

(*b*)

Fig. 5. Nearest neighbours of the Ca atom in (*a*) phillipsite and (*b*) harmotome; looking down the **a** direction (*ORTEP*, Johnson, 1965).

an elongated tetrahedron [Fig. 4(*b*)]. All bond distances are long (Table 7) and some of the atoms may be too far away to be considered as part of the coordination polyhedron of Ba. The chemical analyses gave 1·92 atoms of Ba and 0·07 K per unit cell but in our X-ray model we assumed for simplicity that the site was fully occupied by Ba.

The population refinement for the Ca site converged to 0·6 Ca atom in the fourfold site, which is similar to 0·46 given by the chemical analysis. The partial occupancy of this site should allow the 2 water molecules that are bonded only to Ca [*W*(4) and *W*(5)] to occupy different positions, thereby explaining why their apparent 'thermal' parameters are even larger than in phillipsite. The same mechanism of movement of the atoms around this site advocated for phillipsite applies also to harmotome where, due to the lower occupancy of the site, a higher degree of local deviation from centrosymmetry occurs.

The Ca atom occupies the center of a slightly distorted octahedron formed by 2 oxygens and 4 water molecules [Fig. 5(*b*)]. The bond distances are generally long except for *W*(4) which is normal (2·23 Å), and *W*(5) which is too short (2·06 Å). However, these cannot be regarded as absolute distances because they are associated with very large 'thermal' parameters.

We observed the possibility of the same twinning planes reported by Sadanaga *et al.* (1961). The observations on the twinning of phillipsite and harmotome reported by Hoffman, Donnay & Donnay (1973), are also consistent with our findings.

In conclusion, when account is taken of displacements caused by partial occupancy of the Ca sites, these models for the structures of phillipsite and harmotome are consistent with the general crystal-chemical principles found for zeolite structures, and provide a satisfactory explanation of the chemical properties.

The study of a Na-rich form of phillipsite will be undertaken if a suitable crystal can be found.

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