

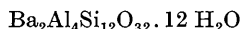
The Crystal Structure of Harmotome, $\text{Ba}_2\text{Al}_4\text{Si}_{12}\text{O}_{32} \cdot 12\text{H}_2\text{O}$

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The crystal structure of harmotome has been determined. There is one chemical unit of



in the unit cell of symmetry $P2_1$ with

$$a_0 = 9.87, b_0 = 14.14, c_0 = 8.72 \text{ \AA}; \beta = 124^\circ 50'.$$

The crystal is pseudorhombic; upon transformations: $a_0' = a_0$, $b_0' = b_0$ and $c_0' = 2c_0 + a_0$, the new β angle becomes as nearly 90° as $90^\circ 23'$. The (y, z) coordinates of atoms were determined from the Patterson (100) projection with the aid of the minimum function method. A simplified sharpening procedure was applied to the Patterson (010) projection to evade the difficulty in identifying Ba–Ba peaks due to serious overlappings. Information obtained from this procedure and from the pseudosymmetry of the crystal made it possible to locate Ba atoms in the projection, and the framework of the structure was derived from the minimum function. The refinements were started on the basis of space group $P2_1/m$, since the statistical test of the diffracted X-ray intensities suggested a nearly centrosymmetric arrangement of atoms, and the deviations from it were taken into consideration at the final stage.

The structure is based upon a three-dimensional aluminosilicate framework composed of four- and eight-membered rings of oxygen tetrahedra, and bears close resemblance to the feldspar structures. Through the framework, channels run along [100] and [010], barium atoms and water molecules being situated in them. Barium atoms are surrounded by six oxygen atoms and four water molecules. The cruciform twinning characteristic of the crystal is satisfactorily explained by the structure. Probable differences in structures between harmotome and phillipsite were suggested.

The zeolites are classified into three groups according to the features of frameworks composed of silicon (aluminium)–oxygen tetrahedra in their structures. The first group is the fibrous zeolites, the structures of which can be described as built up of parallel strings of the tetrahedra, and natrolite, thomsonite and edingtonite are the typical members of this group. The second is the group notable for their perfect lamellar cleavage, and the crystal structures are supposed to be based upon some kind of sheet framework. Heulandite, stilbite, and brewsterite, for example, belong to this group. The last group, of which analcite, chabazite and phillipsite are the important members, consists of crystals which have neither fibrous feature nor perfect lamellar cleavage.

Among these minerals in the last group, the structures of the first two have been determined by Taylor (1930) and by Dent & Smith (1958) respectively, but phillipsite has so far baffled our efforts. In order to obtain the systematic knowledge on the structural principle of this group of zeolites, therefore, it is essential to determine the structure of this crystal, and the structure analysis of harmotome, the mineral presumably isomorphous with phillipsite, was attempted in hope that barium atoms in it might make solution of the problem much easier.

Another problem in view upon the structure analysis

was on a peculiar character of the crystals; they are invariably piezoelectric in spite of their holohedral forms. This kind of pseudosymmetry, often disclosed optically and referred to as optical anomaly, has also been observed with other members of this group such as analcite and chabazite (Taylor, 1930; Wyart, 1933; Stewart, 1941; Ventriglia, 1953).

1. Experimental

The crystals used in this study are from Andreasberg, Hartz, Germany. They are colorless and often twinned on (001) and (021), and larger ones are more than $2 \times 2 \text{ mm.}^2$ in cross-section. For intensity measurement, rods with the diameter of about 0.2 mm. were prepared, and reflections were recorded, by multiple film technique, in Weissenberg photographs taken with $\text{Cu K}\alpha$ about the a - and b -axes. Intensities were measured with a microphotometer and were checked by visual comparison. The relative intensities, corrected for the Lorentz and polarization factors, were put on to an absolute scale using Wilson's statistical method. No correction for absorption or extinction was made.

A close survey on the chemical formula of the mineral, based on the data appeared in Doelter's Handbuch (1921) as well as Meier's analysis (1939),

showed that the composition of the specimens under examination is best represented by



which is approximately equal to the conventional formula of the mineral, $\text{Ba}_2\text{Al}_4\text{Si}_{12}\text{O}_{32} \cdot 12\text{H}_2\text{O}$. Therefore, the latter simple formula was adopted throughout the course of the structure analysis, and the alkali contents were taken into consideration only at the final stage.

2. Unit cell and space group

Harmotome is monoclinic and the cell dimensions obtained from Weissenberg and powder patterns are:

$$a_0 = 9.87 \pm 0.01, \quad b_0 = 14.14 \pm 0.01, \quad c_0 = 8.72 \pm 0.01 \text{ \AA}, \\ \beta = 124^\circ 50' \pm 10', \quad \text{and } V = 999 \text{ \AA}^3.$$

These are in good agreement with the values reported by Sekanina & Wyart (1937). There is one chemical unit of $\text{Ba}_2\text{Al}_4\text{Si}_{12}\text{O}_{32} \cdot 12\text{H}_2\text{O}$ in the unit cell, giving $\rho_c = 2.43$ in comparison with $\rho_o = 2.35$.

The $0k0$ reflections with k odd are absent, no other systematic absence being observed. Therefore, the possible space group is either $P2_1/m$ or $P2_1$ as was concluded by the above authors (1937). A test for piezoelectricity was carried out by the method developed by Iitaka (1956). The result was positive and especially in the direction of the b -axis the effect was rather strong, indicating the true space group to be $P2_1(C_2^2)$.

Kalp & Klotsch (1944) suggested, as the result of their study on the symmetry of vicinal faces on (010), (100) and (101), that harmotome is orthorhombic. In fact, if we convert the axes into a new set so as to satisfy the relations: $a'_0 = a_0$, $b'_0 = b_0$ and $c'_0 = 2c_0 + a_0$, we can regard the lattice approximately as a base-centred orthorhombic one, since the new β angle becomes as nearly 90° as $90^\circ 23'$. An additional evidence of the pseudorhombic nature of harmotome

was observed in intensity distribution in the X-ray diffraction patterns; the patterns are, in a fairly good approximation, symmetrical by reflection across the plane $l=0$ in reciprocal space. Then, since the $h'k'0$ reflections with k' odd are all very weak, on neglect of these the possible space group of the pseudorhombic structure may be said to correspond to $Bm2_1b(C_{2v}^{12})$. This space group was of great help to determine the positions of barium atoms as will be seen later.

3. Structure analysis

As stated above, the true space group of the crystal is $P2_1$. However, since the morphological aspects of this mineral always simulate a holohedral symmetry, we assumed in the first place that the main part of the structure would be constructed almost centrosymmetrically, and started the analysis on the basis of the centrosymmetric space group $P2_1/m$.

A Patterson (100) projection was prepared as shown in Fig. 1. Since the plane group of the projection along the a -axis of the space group is pg , the plane group of the corresponding Patterson projection is pgm . Ba-Ba peaks must therefore lie along the line $y = \frac{1}{2}$, because there are only two barium atoms in the unit cell. In fact, three peaks are observed along the line as designated by A , B and C in Fig. 1. Accordingly, three kinds of minimum functions were prepared, each by assuming each of these peaks as corresponding to a Ba-Ba distance. It has become clear from these diagrams that the first two do not give us a clue to the solution, failing to indicate any reasonable linkage of oxygen tetrahedra, but the last one renders a promising interpretation as follows.

Besides the peak of a barium atom, there are two salient peaks in an asymmetric unit of the M_2 map as shown in Fig. 2. If we assign two silicon (aluminium) atoms and one oxygen atom combined to each of the peaks and the remaining oxygen atoms to some of the

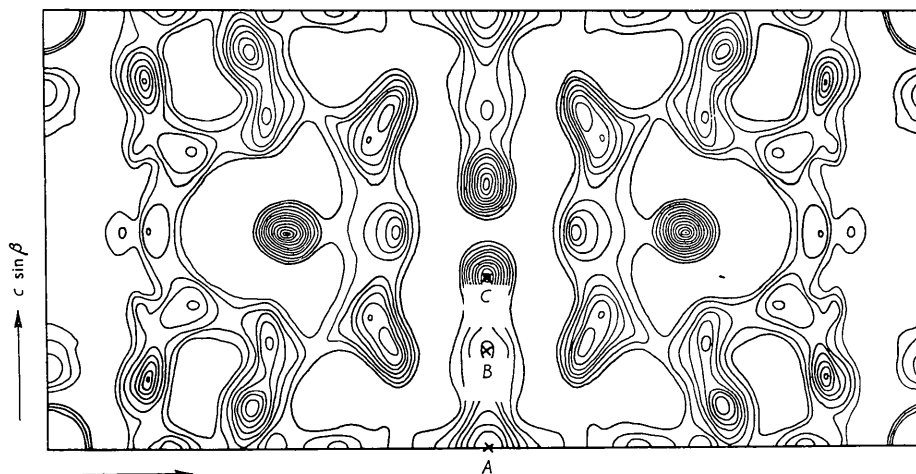


Fig. 1. Patterson (100) projection, $P(y, z)$. Contours are at equal but arbitrary intervals.

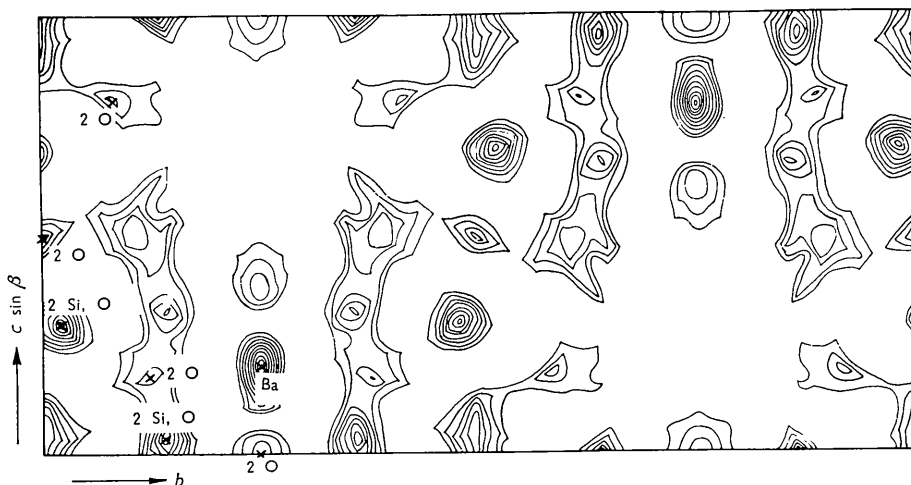


Fig. 2. Minimum function (M_2) derived from $P(y, z)$ by assuming peak C in Fig. 1 as corresponding to a Ba–Ba distance.

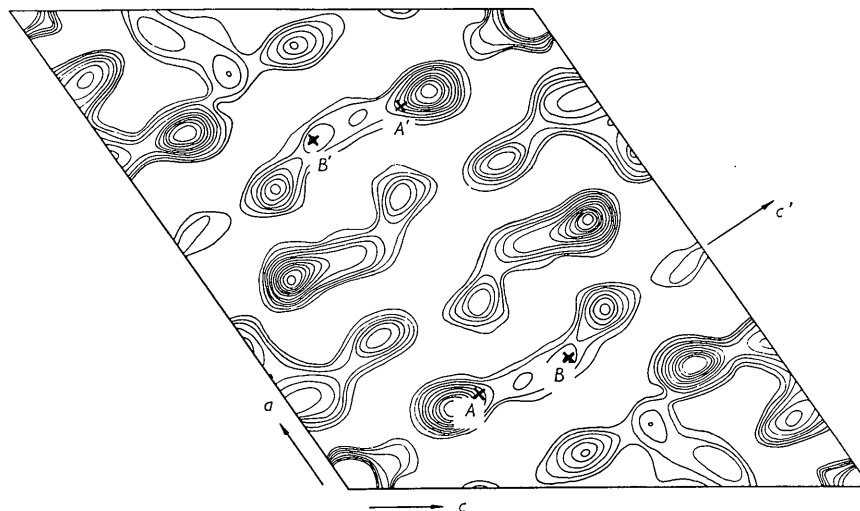


Fig. 3. Patterson (010) projection, $P(x, z)$. Contours are at equal but arbitrary intervals.

other peaks, we can obtain a three-dimensional linkage of four-membered rings of tetrahedra. The $0kl$ structure factors were then calculated using the parameters estimated from the M_2 map. Though the contributions by water molecules were altogether neglected at this stage, a considerably good agreement between observed and calculated structure factors was obtained, giving the R -factor 0.35.

Next, the Patterson function $P(x, z)$ was calculated to determine the x -parameters (Fig. 3). Since the period along the direction of the projection is as long as 14 Å, some overlappings seem to be so serious as to obscure Ba–Ba peaks. However, the knowledge on the pseudosymmetry of the crystal provided a clue to the identification of the peaks. The space group of the pseudorhombic structure is $Bm2_1b$ and there are four barium atoms in the converted unit cell, so that these must lie on the mirror planes, occupying a set

of fourfold positions: $0, y', z'$; $0, \bar{y}', \frac{1}{2} + z'$; $\frac{1}{2}, \frac{1}{2} + y', z'$; $\frac{1}{2}, \frac{1}{2} - y', \frac{1}{2} + z'$, and the corresponding Patterson peaks in the b -axis projection must lie along the lines $x' = 0$ and $x' = \frac{1}{2}$. Since the z -parameter of the atom has been found from the a -axis projection as about 0.200, the possible peaks are either A and its equivalent or B and its equivalent in Fig. 3.

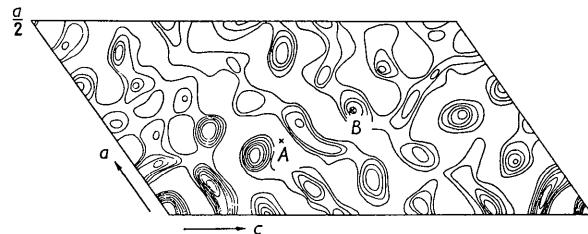


Fig. 4. Simplified sharpened-Patterson function calculated with the $h0l$ terms having $\sin \theta/\lambda > 0.45$.

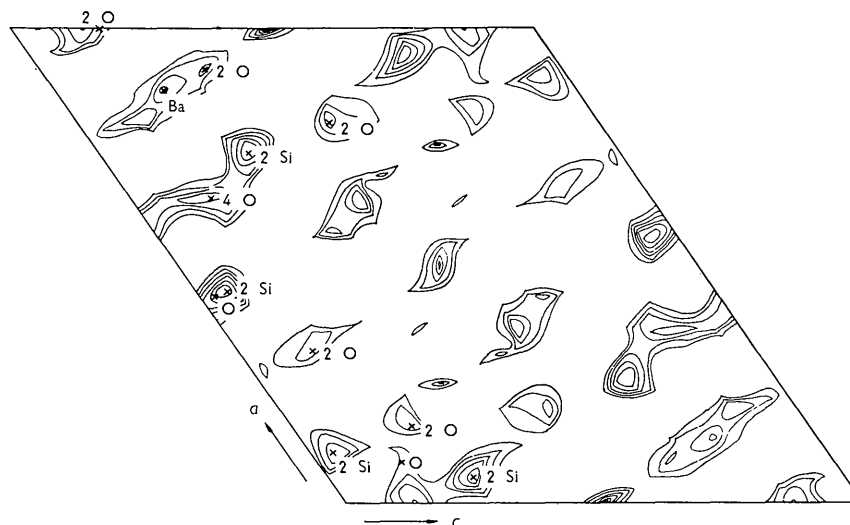


Fig. 5. Minimum function (M_2) derived from $P(x, z)$ by assuming peak B in Fig. 3 as corresponding to a Ba–Ba distance.

An attempt was then made to choose the correct set of Ba–Ba peaks by preparing minimum functions and trying to deduce a reasonable structure from either of these sets. This procedure was, however, proved to become too diversified, since three structural models derivable by choosing peak A and one by choosing peak B seemed to be equally probable, all giving the same (100) projection. Now, there are 708 electrons in the unit cell, 440 of which belong to oxygen ions and water molecules. So, if we can find some method of reducing the contributions by these constituents to the Patterson function, difficulty in identifying the Ba–Ba peaks due to overlappings should be much ameliorated, and the following procedure was found to answer the purpose.

Since the atomic scattering factor for an oxygen ion decreases with the increase of $\sin \theta$ more rapidly than those for cations in this crystal, if a sharpened Patterson function is calculated, it will enhance the contributions by cations in contrast with those by oxygen ions. For this purpose, however, it is not necessary to follow the ordinary procedure of postulating point atoms for sharpened Patterson synthesis, but it suffices to calculate a function consisting of F^2 terms whose $\sin \theta/\lambda$'s are larger than an appropriate value. This simplified sharpened-function corresponds to the convolution of the Patterson function with the Fourier transform of a pulse function, while the ordinary one to the convolution of the Patterson function with the transform of a function whose value is $1/\hat{f}^2$ up to the maximum reciprocal coordinate for the observation and is zero thereafter. A simplified sharpened-function was actually calculated by employing the $h0l$ terms having their $\sin \theta/\lambda$'s larger than 0.45 as shown in Fig. 4, and it was found that peak B , rather inconspicuous in the previous Patterson map, had become a relatively high peak in the new map, while peak A had completely disappeared from the line

$z=0.200$. Hence, the Ba–Ba peaks were unequivocally identified as B and its equivalent.

Now that the correct set of Ba–Ba peaks had been obtained as above, the (010) projection of the structure was produced as shown in Fig. 5. This structure was refined by successive Fourier syntheses, during the course of which the positions of some of the water molecules were determined, and the R -factor decreased to 0.29 from its initial value, 0.47.

4. Refinement of the structure

The structure thus derived was based upon the centrosymmetric space group $P2_1/m$. Therefore, it seemed then worthwhile to estimate at what stage of refinement we should be able to look for the deviation of the structure from the centrosymmetric arrangement. For this purpose, a statistical test for symmetry centres was carried out as follows.

In the first place, in order to make the results of the test reliable, we must eliminate the disturbance due to heavy atoms in the crystal under examination. Average must therefore be taken over such a set of reflections that throughout these the contributions by the heavy atoms are comparable in magnitude with one another (Collin, 1955; Sim, 1958). For the case considered here, this requirement will quite easily be satisfied for the $0kl$ reflections by taking advantage of the fact that the y - and z -coordinates of the barium atom happen to be simple fractions as $y=0.250$ and $z=0.200$. Namely, it is possible to divide the reflections into six sets in such a way that the absolute values of the contributions by the atoms to the geometrical structure factors are to remain exactly constant for whole reflections in each set. On the other hand, it is obvious that to make the above grouping is to render the number of reflections in each set too small, so that for the actual calculation the combined prob-

ability distributions $N(z)$'s were taken according to the relation,

$$N(z) = \frac{\sum_{i=1}^6 m_i N_i \langle \langle I \rangle \rangle / \langle \langle I_i \rangle \rangle}{\sum_{i=1}^6 m_i},$$

where N_i is the probability distribution for the i th set, m_i the total number of reflections in the set, $\langle I_i \rangle$ the averaged intensity of the set and $\langle \langle I \rangle \rangle$ the averaged value for whole reflections. The theoretical $N(z)$ for centrosymmetric and non-centrosymmetric arrangements, both corresponding to the case under examination, are shown in Fig. 6 with the observed values. The figure indicates that, as far as the X-ray data are concerned, the crystal can be regarded as centrosymmetric in a close approximation.

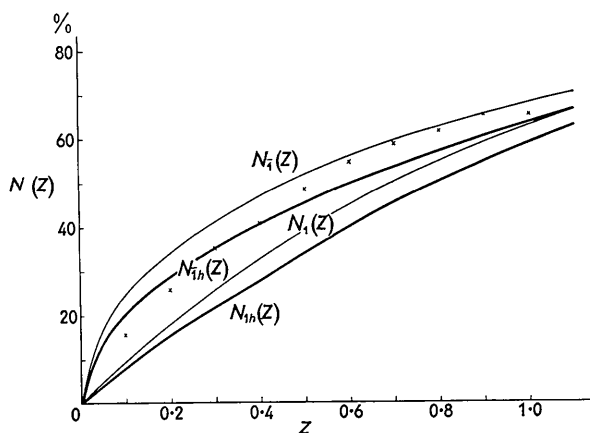


Fig. 6. Intensity distribution of the $0kl$ reflections. The probability distribution curves for the centric case, $N\bar{1}h(z)$, and for the non-centric case, $N1h(z)$, both obtained after eliminating the disturbance due to barium atoms, are shown by thick lines. Ordinary curves for the centric case, $N\bar{1}(z)$, and for the non-centric case, $N1(z)$ are also given for comparison. Observed values are indicated by crosses.

According to the above result, refinements were still continued on the centrosymmetric space group, and five and seven cycles of refinements were made about the a - and the b -axis projections respectively, both by means of the difference Fourier method. During these processes, the remaining water molecules were allocated to either conclusive or probable positions and the R -factors were reduced to 0.20 for $F(0kl)$'s and to 0.18 for $F(h0l)$'s.

Some signs of departures of the structure from the centrosymmetric arrangement were then revealed as follows; firstly, peaks for some of silicon (aluminium) and oxygen atoms in these projections showed oval appearances, indicating deviations of the atomic positions from the centrosymmetrically related pairs, and secondly, peaks for the water molecules at probable positions were about half as high as those for the others at conclusive positions and some peaks with the heights equal to those of the former peaks were observed at unexpected positions, both suggesting necessity of re-distributing the molecules in a non-

centrosymmetric way. From this stage onward, therefore, the departures were taken into consideration and refinements were carried out, on the basis of the non-centrosymmetric space group $P2_1$, both by difference Fourier syntheses and by steepest descents on 105 hkl reflections picked up by random sampling. The final results are as listed in Table 1 and as shown by the Fourier maps in Fig. 7(a) and (b), and the R -factors are 0.143 and 0.148 for $0kl$ and $h0l$ reflections respectively. The calculated structure factors are also given in Table 2 for comparison with the observed ones.

Table 1. Final atomic coordinates and temperature factors

Atom	x	y	z	B
Ba	0.136	0.750	0.806	1.5 Å ²
Si ₁	0.267	0.978	0.716	1
Si ₂	0.580	0.860	0.987	1
Si ₃	0.943	0.986	0.710	1
Si ₄	0.883	0.859	0.965	1
Si ₅	0.733	0.019	0.284	1
Si ₆	0.420	0.140	0.013	1
Si ₇	0.057	0.009	0.290	1
Si ₈	0.117	0.141	0.035	1
O ₁	0.897	0.908	0.810	3
O ₂	0.356	0.078	0.832	3
O ₃	0.382	0.885	0.826	1
O ₄	0.987	0.090	0.836	3
O ₅	0.099	0.962	0.710	1
O ₆	0.693	0.878	0.910	1
O ₇	0.213	0.993	0.505	1
O ₈	0.412	0.250	0.969	2
O ₉	0.084	0.250	0.007	2
O ₁₀	0.103	0.092	0.190	3
O ₁₁	0.644	0.922	0.168	3
O ₁₂	0.618	0.112	0.174	1
O ₁₃	0.013	0.910	0.164	3
O ₁₄	0.901	0.038	0.290	1
O ₁₅	0.307	0.122	0.090	1
O ₁₆	0.787	0.007	0.495	1
H ₂ O-1	0.118	0.750	0.452	3
H ₂ O-2	0.284	0.858	0.133	3
H ₂ O-3	0.471	0.915	0.524	3
H ₂ O-4	0.783	0.750	0.508	3
H ₂ O-5	0.317	0.642	0.128	3
H ₂ O-6	0.505	0.683	0.524	3

5. Description of the structure and discussion

The interatomic distances are given in Table 3. The mean standard deviations of the atomic coordinates, calculated with Cruickshank's equation (1949a, b) by making allowance for the absence of the centre of symmetry, are 0.002 Å for Ba, 0.004 Å for Si(Al), 0.012 Å for O and 0.022 Å for H₂O. Another set of values, derived from Booth's equation (Booth & Britten, 1948) by assuming the relative error of the observed structure factors as 0.1, are 0.005 Å for Ba, 0.014 Å for Si(Al), 0.034 Å for O and 0.041 Å for H₂O.

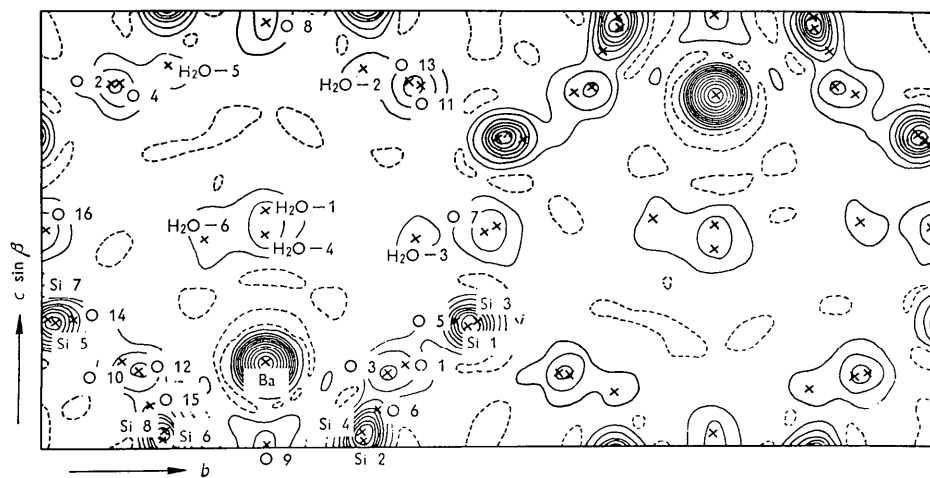
Each silicon or aluminium atom is surrounded tetrahedrally by four oxygen atoms, and the tetrahedra are linked together by sharing each corner, constructing a three-dimensional aluminosilicate framework. This framework essentially consists of

Table 2. *Observed and calculated structure factors*

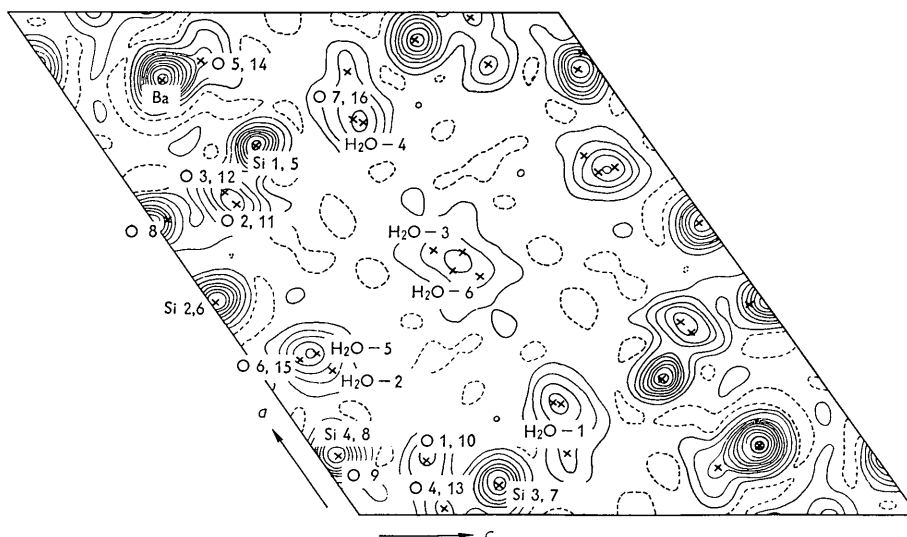
hkl	$ F_o $	$ F_c $	$\alpha/2\pi$	hkl	$ F_o $	$ F_c $	$\alpha/2\pi$	hkl	$ F_o $	$ F_c $	$\alpha/2\pi$	hkl	$ F_o $	$ F_c $	$\alpha/2\pi$
100	84	107	0	$\bar{8}03$	42	40	0.5	$\bar{3}07$	83	72	0	061	39	40	0.518
200	0	2	0	903	0	2	0	407	50	34	0	071	32	26	0.021
300	29	36	0.5	$\bar{1}0,0,3$	25	31	0	$\bar{5}07$	42	44	0	081	67	70	0.986
400	109	103	0.5	$\bar{1}1,0,3$	9	34	0	$\bar{6}07$	69	67	0.5	091	123	118	0.494
500	65	70	0.5					$\bar{7}07$	31	20	0.5	0,10,1	79	76	0.498
600	58	52	0.5	704	0	7	0	$\bar{8}07$	53	50	0.5	0,11,1	27	20	0.448
700	56	57	0	604	39	24	0.5	907	62	70	0.5	0,12,1	20	20	0.516
800	39	41	0	504	45	37	0	$\bar{1}0,0,7$	20	3	0	0,13,1	64	74	0.488
900	0	6	0	404	15	6	0.5	$\bar{1}1,0,7$	28	31	0	0,14,1	26	21	0.033
10,0,0	6	4	0.5	304	107	112	0.5	$\bar{1}2,0,7$	55	63	0	0,15,1	24	15	0.056
				204	33	29	0.5					0,16,1	21	11	0.037
901	59	57	0	104	37	38	0.5	208	23	29	0.5	0,17,1	46	46	0.481
801	28	29	0	004	119	112	0	108	42	38	0.5	0,18,1	32	34	0.509
701	0	11	0	$\bar{1}04$	99	90	0	008	35	31	0.5				
601	59	68	0.5	$\bar{2}04$	64	66	0	$\bar{1}08$	47	47	0.5	012	71	64	0.495
501	76	73	0.5	$\bar{3}04$	0	10	0	$\bar{2}08$	37	41	0	022	81	74	0.498
401	130	145	0.5	404	32	28	0.5	$\bar{3}08$	84	80	0	032	72	68	0.008
301	28	26	0	$\bar{5}04$	86	86	0.5	408	47	45	0	042	99	118	0.521
201	40	36	0	604	100	103	0.5	$\bar{5}08$	37	41	0	052	17	6	0.797
101	80	85	0	$\bar{7}04$	31	18	0	$\bar{6}08$	11	24	0.5	062	64	51	0.024
001	109	136	0	804	41	29	0	708	11	13	0.5	072	80	87	0.994
$\bar{1}01$	82	91	0.5	904	42	43	0	$\bar{8}08$	47	53	0.5	082	11	14	0.363
$\bar{2}01$	21	13	0	$\bar{1}0,0,4$	41	40	0	908	0	10	0	092	55	39	0.503
$\bar{3}01$	47	49	0	$\bar{1}1,0,4$	17	14	0.5	$\bar{1}0,0,8$	59	72	0	0,10,2	39	32	0.482
$\bar{4}01$	53	59	0.5	$\bar{1}2,0,4$	35	42	0.5	$\bar{1}1,0,8$	12	13	0	0,11,2	38	34	0.992
$\bar{5}01$	52	58	0					$\bar{1}2,0,8$	0	10	0	0,12,2	59	41	0.482
$\bar{6}01$	44	40	0	605	13	15	0					0,13,2	13	1	0.750
701	144	133	0	505	30	30	0	009	26	32	0.5	0,14,2	64	60	0.994
801	14	10	0.5	405	71	76	0.5	$\bar{1}09$	18	14	0	0,15,2	38	45	0.988
901	30	31	0.5	305	87	90	0.5	$\bar{2}09$	29	43	0	0,16,2	10	3	0.585
$\bar{1}0,0,1$	24	10	0	205	9	7	0	$\bar{3}09$	23	23	0	0,17,2	18	11	0.550
$\bar{1}1,0,1$	15	21	0.5	105	27	17	0.5	409	41	36	0.5				
				005	26	24	0	$\bar{5}09$	36	32	0.5	013	43	30	0.988
802	22	13	0.5	$\bar{1}05$	32	31	0	609	46	50	0.5	023	72	68	0.001
702	19	5	0.5	$\bar{2}05$	81	67	0	$\bar{7}09$	25	25	0.5	033	31	37	0.514
602	15	8	0	$\bar{3}05$	12	3	0	809	0	4	0.5	043	34	31	0.449
502	0	3	0	405	141	159	0.5	909	47	51	0	053	107	101	0.006
402	23	18	0.5	$\bar{5}05$	9	20	0.5	$\bar{1}0,0,9$	51	53	0	063	132	136	0.992
302	13	17	0	605	31	11	0	$\bar{1}1,0,9$	7	5	0.5	073	11	7	0.977
202	39	43	0	705	80	64	0					083	17	7	0.693
102	109	111	0.5	805	55	55	0	$\bar{2},0,10$	0	3	0.5	093	34	45	0.984
002	40	38	0.5	905	56	51	0	$\bar{3},0,10$	0	3	0.5	0,10,3	19	7	0.531
$\bar{1}02$	109	117	0.5	$\bar{1}0,0,5$	42	23	0	4,0,10	29	26	0.5	0,11,3	0	6	0.903
$\bar{2}02$	11	8	0.5	$\bar{1}1,0,5$	30	27	0.5	5,0,10	21	21	0.5	0,12,3	59	61	0.512
$\bar{3}02$	130	122	0.5	$\bar{1}2,0,5$	19	12	0.5	6,0,10	46	52	0.5	0,13,3	63	64	0.985
$\bar{4}02$	85	86	0					7,0,10	25	21	0.5	0,14,3	63	56	0.003
$\bar{5}02$	106	108	0	406	17	24	0.5	8,0,10	33	5	0	0,15,3	0	4	0.750
602	53	49	0.5	306	0	5	0.5	9,0,10	9	5	0	0,16,3	24	29	0.490
702	0	12	0.5	206	33	39	0	$\bar{1}0,0,10$	9	9	0.5	0,17,3	14	20	0.980
802	54	47	0.5	106	13	2	0	$\bar{1}1,0,10$	18	23	0.5				
902	16	14	0	006	84	82	0					014	28	31	0.006
$\bar{1}0,0,2$	46	51	0	$\bar{1}06$	0	1	0	$\bar{6},0,11$	14	19	0	024	11	12	0.979
$\bar{1}1,0,2$	0	3	0	$\bar{2}06$	0	3	0.5	7,0,11	27	33	0	034	108	101	0.494
				306	62	61	0.5	8,0,11	0	0	0.5	044	55	57	0.971
803	30	38	0.5	406	64	64	0.5					054	50	53	0.990
703	33	29	0	506	77	75	0	020	21	4	0.739	064	42	42	0.008
603	10	5	0.5	606	29	36	0.5	040	53	62	0.928	074	89	84	0.499
503	20	24	0	706	45	41	0.5	060	68	52	0.494	084	63	60	0.005
403	14	17	0	806	0	1	0.5	080	187	200	0.002	094	13	18	0.459
303	21	37	0	906	0	1	0.5	0,10,0	89	69	0.511	0,10,4	34	26	0.511
203	9	13	0	$\bar{1}0,0,6$	27	7	0.5	0,12,0	62	62	0.002	0,11,4	50	57	0.491
103	94	107	0.5	$\bar{1}1,0,6$	12	9	0.5	0,14,0	0	10	0.574	0,12,4	12	18	0.004
003	90	73	0.5	$\bar{1}2,0,6$	62	55	0	0,16,0	53	42	0.987	0,13,4	37	33	0.028
$\bar{1}03$	101	97	0					0,18,0	54	65	0.496	0,14,4	11	14	0.965
$\bar{2}03$	78	78	0	307	21	23	0					0,15,4	60	61	0.488
303	28	29	0	207	19	12	0	011	103	119	0.501	0,16,4	0	8	0.970
403	59	42	0	107	0	8	0	021	79	85	0.494				
503	64	55	0.5	007	35	35	0	031	35	34	0.996	015	22	28	0.510
603	214	213	0.5	$\bar{1}07$	33	24	0.5	041	128	142	0.473	025	115	122	0.499
703	56	48	0.5	$\bar{2}07$	33	34	0	051	89	104	0.493	035	54	55	0.507

Table 2 (cont.)

hkl	$ F_o $	$ F_c $	$\alpha/2\pi$	hkl	$ F_o $	$ F_c $	$\alpha/2\pi$	hkl	$ F_o $	$ F_c $	$\alpha/2\pi$	hkl	$ F_o $	$ F_c $	$\alpha/2\pi$
045	49	38	0.464	016	72	64	0.496	017	51	57	0.502	018	12	5	0.460
055	34	34	0.027	026	23	29	0.504	027	63	57	0.997	028	17	17	0.003
065	89	94	0.497	036	39	37	0.009	037	0	10	0.962	038	25	27	0.490
075	23	27	0.484	046	0	4	0.625	047	0	6	0.479	048	32	36	0.504
085	36	29	0.998	056	24	26	0.965	057	0	6	0.115	058	16	15	0.975
095	23	25	0.501	066	32	28	0.487	067	55	53	0.992	068	33	36	0.006
0,10,5	63	74	0.495	076	69	74	0.993	077	27	25	0.009	078	23	31	0.497
0,11,5	0	10	0.475	086	33	37	0.006	087	0	7	0.908	088	18	20	0.487
0,12,5	27	22	0.010	096	32	29	0.508	097	51	47	0.503				
0,13,5	18	15	0.995	0,10,6	27	26	0.502	0,10,7	11	10	0.968	019	14	18	0.995
0,14,5	19	16	0.468	0,11,6	55	64	0.991	0,11,7	20	21	0.004	029	29	33	0.495
0,15,5	25	33	0.489	0,12,6	21	24	0.011								
				0,13,6	15	20	0.985								



(a)



(b)

Fig. 7. Electron density projection along (a) the a -axis and (b) the b -axis. Contours are at the intervals of $8 \text{ e.}\text{\AA}^{-2}$ and $16 \text{ e.}\text{\AA}^{-2}$ below and above $56 \text{ e.}\text{\AA}^{-2}$ respectively, zero contours being dotted.

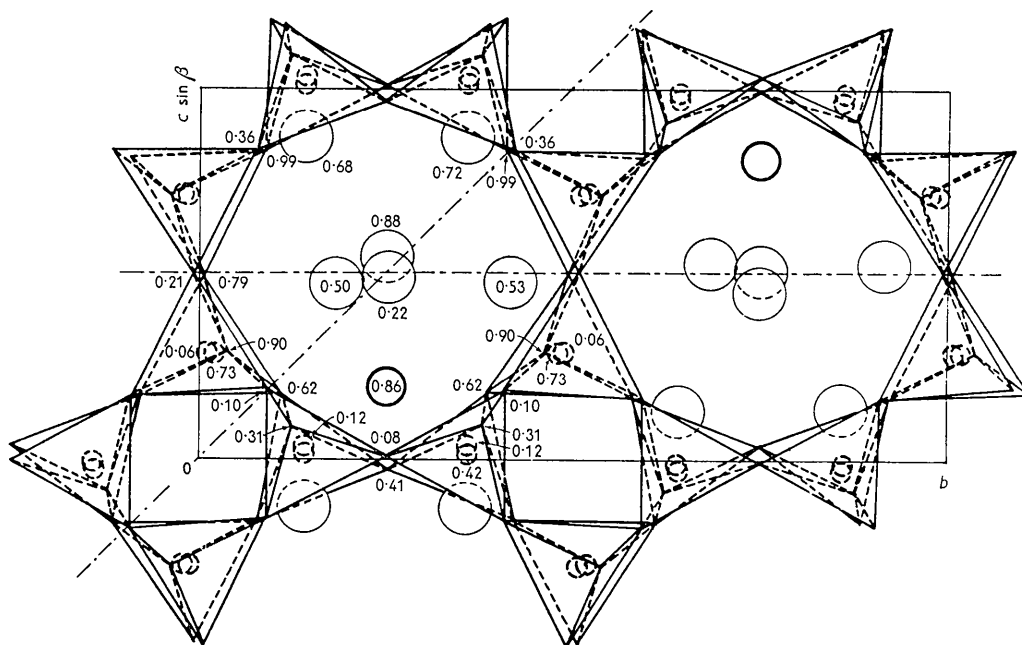


Fig. 8(a).

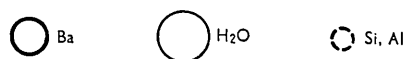
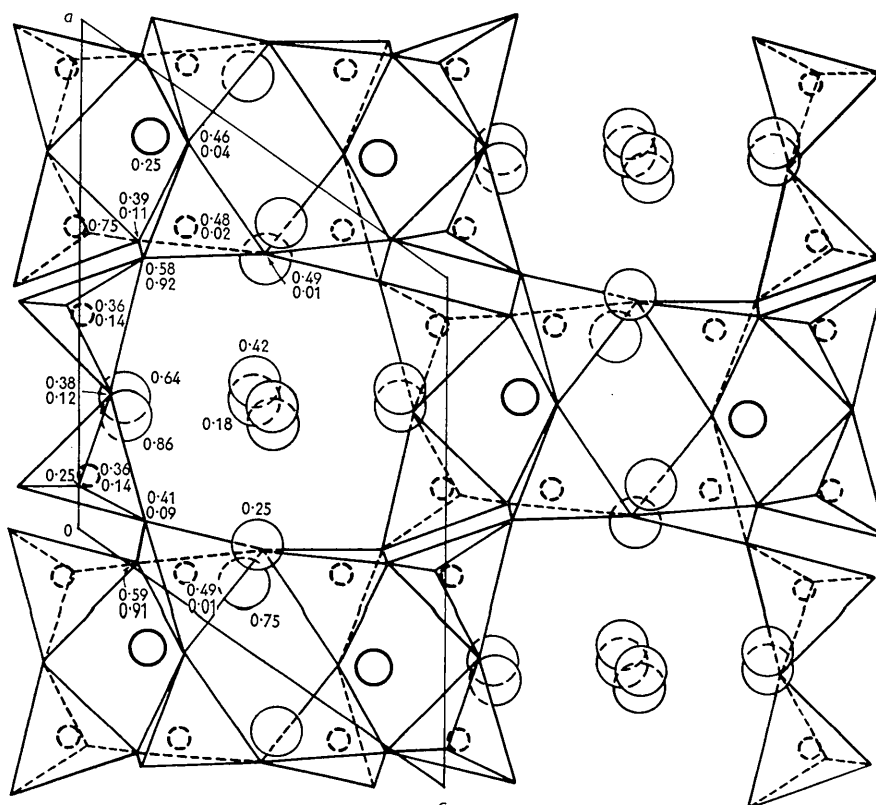


Fig. 8(b).

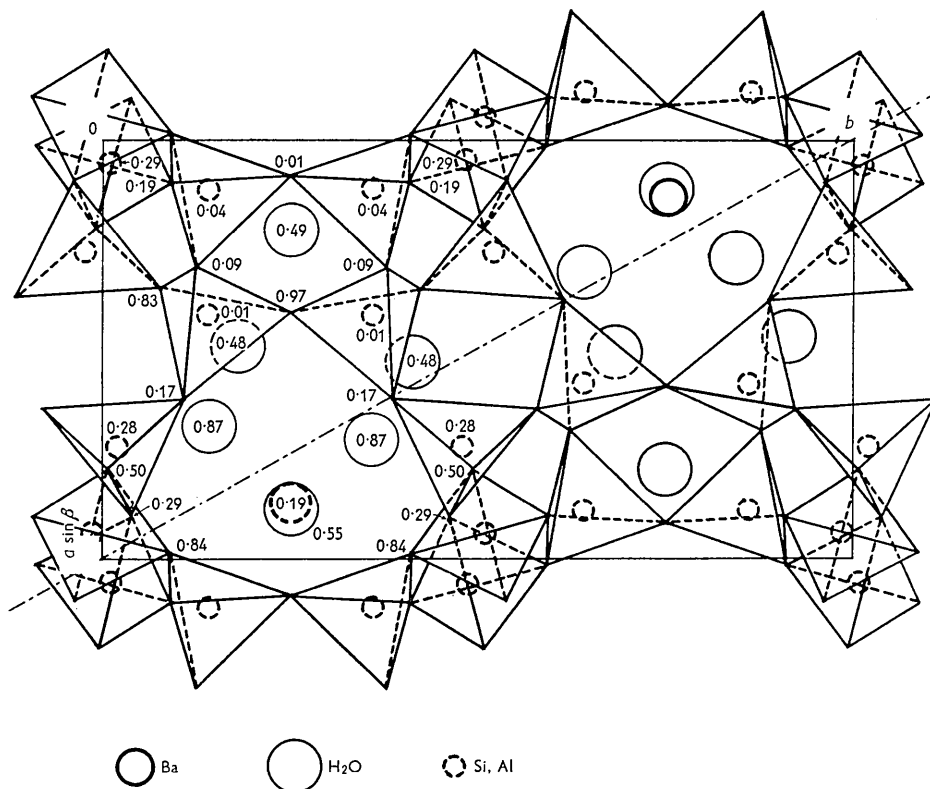


Fig. 8(c).

Fig. 8. Schematic drawings of the structure of harmotome viewed along (a) the a -axis, (b) the b -axis and (c) the c -axis. The numbers indicate atomic coordinates parallel to the axes of projection, and the dashed and dotted lines the probable positions of composition planes of twinning.

four- and eight-membered rings of tetrahedra as is illustrated in Fig. 8 and closely resembles to those in sanidine and in paracelsian. In fact, if we look upon these frameworks as built up of parallel strings of tetrahedra, which run in the a -direction in the case of harmotome, we shall find that the constituent strings are one and the same kind throughout these frameworks, only the ways of their lateral binding being different from one another as seen in Fig. 9.

Through the framework and along the a - and b -axes of harmotome, two sets of open channels run, in which barium atoms and water molecules are situated. The minimum width of the channels along the a -axis is about 4 Å and those along the b -axis have the cross-section of 3×4 Å². These two sets of channels cross at right angle, leaving spacious vacancies at the intersections.

The edge-lengths of silicon (aluminium)-oxygen

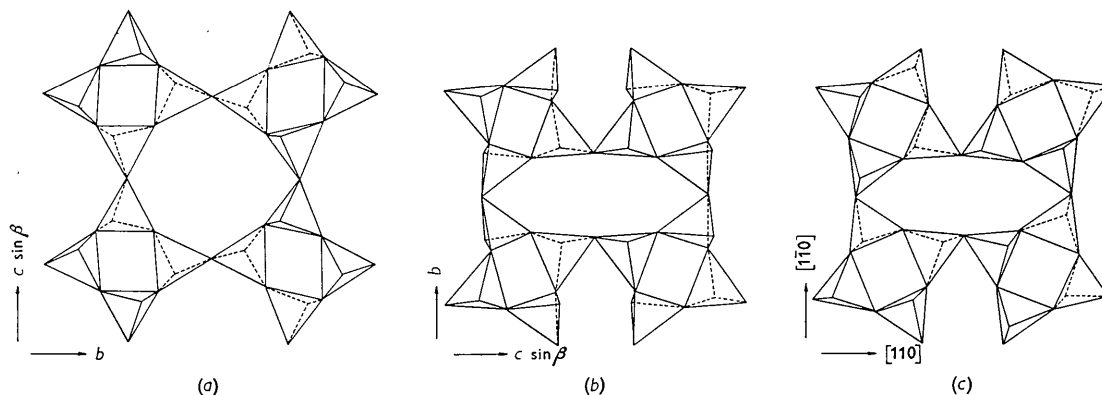


Fig. 9. Comparison of the aluminosilicate frameworks (a) in harmotome, (b) in sanidine and (c) in paracelsian.

Table 3. *Interatomic distances*

Si-O	Si ₁ -O ₂	1.67 Å	Si ₅ -O ₁₁	1.63 Å
	-O ₃	1.64	-O ₁₂	1.64
	-O ₅	1.65	-O ₁₄	1.65
	-O ₇	1.61	-O ₁₆	1.61
	Mean	1.64	Mean	1.63
	Si ₂ -O ₃	1.67	Si ₆ -O ₂	1.59
	-O ₆	1.62	-O ₈	1.59
	-O ₈	1.59	-O ₁₂	1.68
	-O ₁₁	1.59	-O ₁₅	1.62
	Mean	1.62	Mean	1.62
	Si ₃ -O ₁	1.62	Si ₇ -O ₇	1.62
	-O ₄	1.74	-O ₁₀	1.67
	-O ₅	1.58	-O ₁₃	1.68
-O ₁₆	1.64	-O ₁₄	1.59	
Mean	1.64	Mean	1.64	
Si ₄ -O ₁	1.59	Si ₈ -O ₄	1.62	
-O ₆	1.67	-O ₉	1.57	
-O ₉	1.57	-O ₁₀	1.59	
-O ₁₃	1.62	-O ₁₅	1.67	
Mean	1.61	Mean	1.61	
O-O	Si ₁ O ₂ -O ₃	2.74 Å	Si ₅ O ₁₁ -O ₁₂	2.70 Å
	O ₂ -O ₅	2.68	O ₁₁ -O ₁₄	2.68
	O ₂ -O ₇	2.64	O ₁₁ -O ₁₆	2.64
	O ₃ -O ₅	2.61	O ₁₂ -O ₁₄	2.59
	O ₃ -O ₇	2.76	O ₁₂ -O ₁₆	2.74
	O ₅ -O ₇	2.64	O ₁₄ -O ₁₆	2.64
	Mean	2.68	Mean	2.66
	Si ₂ O ₃ -O ₆	2.72	Si ₆ O ₂ -O ₈	2.63
	O ₃ -O ₈	2.61	O ₂ -O ₁₂	2.65
	O ₃ -O ₁₁	2.65	O ₂ -O ₁₅	2.63
	O ₆ -O ₈	2.59	O ₈ -O ₁₂	2.64
	O ₆ -O ₁₁	2.63	O ₈ -O ₁₅	2.59
	O ₈ -O ₁₁	2.63	O ₁₂ -O ₁₅	2.72
	Mean	2.64	Mean	2.64
	Si ₃ O ₁ -O ₄	2.69	Si ₇ O ₇ -O ₁₀	2.70
	O ₁ -O ₅	2.70	O ₇ -O ₁₃	2.72
	O ₁ -O ₁₆	2.70	O ₇ -O ₁₄	2.61
	O ₄ -O ₅	2.66	O ₁₀ -O ₁₃	2.69
	O ₄ -O ₁₆	2.72	O ₁₀ -O ₁₄	2.70
	O ₅ -O ₁₆	2.61	O ₁₃ -O ₁₄	2.66
	Mean	2.68	Mean	2.68
	Si ₄ O ₁ -O ₆	2.65	Si ₈ O ₄ -O ₉	2.57
	O ₁ -O ₉	2.69	O ₄ -O ₁₀	2.61
	O ₁ -O ₁₃	2.61	O ₄ -O ₁₅	2.66
O ₆ -O ₉	2.61	O ₉ -O ₁₀	2.69	
O ₆ -O ₁₃	2.66	O ₉ -O ₁₅	2.61	
O ₉ -O ₁₃	2.58	O ₁₀ -O ₁₅	2.65	
Mean	2.63	Mean	2.63	
Ba-	Ba-O ₁	3.26 Å	Ba-H ₂ O-1	2.99 Å
	-O ₃	3.02	-H ₂ O-2	2.80
	-O ₅	3.08	-H ₂ O-4	2.92
	-O ₁₀	3.26	-H ₂ O-5	2.77
	-O ₁₂	3.04		
	-O ₁₄	3.08		
H ₂ O-	H ₂ O-1-Ba	2.99	H ₂ O-4-Ba	2.92
	-O ₄	3.09	-H ₂ O-6	2.98
	-O ₁₃	3.09	-O ₁	3.13
			-O ₁₁	3.45
	H ₂ O-2-Ba	2.80	H ₂ O-5-Ba	2.77
	-O ₁₃	2.93	-O ₂	3.17
	-H ₂ O-3	2.91	-H ₂ O-6	2.90
	H ₂ O-3-H ₂ O-2	2.91	H ₂ O-6-H ₂ O-4	2.98
	-O ₆	2.83	-H ₂ O-5	2.90
	-O ₇	2.69	-O ₁₅	2.89

tetrahedra are in good agreement with those in other silicates, ranging from 2.57 Å to 2.76 Å. The tetrahedra can be classified into two groups: one sharing one oxygen atom with a barium atom, and the other sharing two oxygen atoms with a barium atom. These two groups of tetrahedra may be considered as suggesting an ordering of silicon and aluminium in such a way that a tetrahedron in the former group is occupied by Si⁴⁺, while that in the latter group by $\frac{1}{2}(\text{Si}^{4+} + \text{Al}^{3+})$.

Barium atoms are surrounded by six oxygen atoms and four water molecules and the coordination polyhedron is irregular. Eight of twelve water molecules in a unit cell are bound to barium atoms, but the remainder are not, being surrounded either by one oxygen atom and two water molecules or by two oxygen atoms and one water molecule. The coordinations around the molecules are all triangular, except that around H₂O-4 which is tetrahedral.

Though almost all the atoms are arranged nearly in a centrosymmetric structure, two of the water molecules in an asymmetric unit are largely deviated from it. This is probably the reason why piezoelectricity is observed with the crystal, while the statistical distribution of the diffracted X-ray intensities as well as the morphological habit suggests a centrosymmetric structure.

Harmotome invariably contains a small amount of alkali, one atom per unit cell in the specimens investigated, which has been neglected altogether during the course of the structure determination. Examination of the structure thus determined shows that there are three probable positions for the atoms around (0.15, 0.25, 0.72), (0.07, 0.11, 0.58) and (0.07, 0.39, 0.58). However, no appreciable peak is found at any of these positions and this might suggest a statistical distribution of the atoms over the points.

The cruciform twins characteristic of harmotome are well explained with the structure determined here. The twinning planes of the fourling are (001) and (021), and it is quite easy to obtain the structural model of the fourling if we take the following planes as composition planes; one parallel to (001) containing the O₇ atom, and the other parallel to (021) passing through the origin, both indicated by dashed and dotted lines in Fig. 8(a). Sometimes, another type of twin is observed, having (110) as the twinning plane. It is also possible to envisage the model by slight shifts of atomic positions on and near the composition plane along the position shown by a dashed and dotted line in Fig. 8(c).

Finally, consideration must be made on the relation between harmotome and phillipsite. Since these two kinds of minerals are similar to each other in their unit cell dimensions, chemical compositions and crystal habits, they have been considered to be isomorphous. However, the space for a barium atom in the harmotome structure described above is too wide for a calcium atom in phillipsite, and it seems impossible,

by any slight shifts of neighbouring oxygen atoms, to make the coordination polyhedron contracted so as to fit a calcium atom. This situation may be relevant to the difference in the amount of alkali contents in these minerals, namely phillipsite contains two alkali atoms per unit cell, while harmotome only one atom or less. Thus, the arrangement of metal atoms and water molecules in phillipsite is probably considerably different from that in harmotome. In fact, the results of our preliminary investigation into the structure of phillipsite seem to suggest that its aluminosilicate framework may take a configuration somewhat different from the one in harmotome, though we still believe that these two are essentially of identical structural scheme.

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On the Method of Least Squares as Applied to the Refinement of Crystal Structures

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The effect of off-diagonal terms of the normal equations of least-squares on the refinement of parameters (both positional and thermal) is discussed critically. It is shown that the usual procedure of neglecting the off-diagonal terms during refinement of positional parameters in a three-dimensional structure, or in a projection without overlap of atoms, is valid only if the structure or the projection concerned is centrosymmetric and the axes are orthogonal. If the structure is non-centrosymmetric and contains atoms or groups of atoms which are centrosymmetric and which contribute predominantly to the structure factor, then a new type of overlap termed 'inverse overlap' has to be taken into account. The inverse overlap is particularly significant since it can occur in three dimensions. Finally it is shown that in the refinement of thermal parameters the linear approximation formula is not valid and all the off-diagonal terms involving the B_{ij} 's which occur for the particular symmetry have to be included in the refinement.

1. Introduction

Since it was first suggested by Hughes (1941), the method of least-squares has been widely used in crystal-structure analysis. However, no critical examination of the method, particularly the effect of off-diagonal terms, as applied to the structural refinement seems to be available in the literature. Such a study was undertaken by the author and the results obtained are presented in this paper.

The usual procedure of neglecting the off-diagonal terms in the refinement of three-dimensional structures, and in two dimensional projections without overlap, although justifiable in centrosymmetric structures, is not valid for non-centrosymmetric structures containing atoms or groups which are centrosymmetric and which contribute predominantly to the structure factor. Under these conditions it is necessary to take into account what may be termed the 'inverse overlap' of atoms. The linear-approximation formula