

## The crystal structure of wairakite

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### Abstract

The crystal structure of wairakite has been determined and refined to  $R = 3.6\%$ , using a crystal from Onikobe, Miyagi Prefecture, Japan:  $I2/a$ ,  $a = 13.692(3)$ ,  $b = 13.643(3)$ ,  $c = 13.560(3)\text{\AA}$ ,  $\beta = 90.5(1)^\circ$ ,  $Z = \text{Ca}_{7.19}\text{Na}_{1.12}\text{K}_{0.01}(\text{Si}_{32.59}\text{Al}_{15.38})\text{O}_{96} \cdot 16\text{H}_2\text{O}$ . The location of Ca atoms is fixed to a set of eightfold positions among four distinct sets of positions available for cations, the eightfold positions being occupied by 0.899 Ca and 0.059 Na. The Na atoms are nearly evenly distributed over the available cation positions with occupancies of 0.05–0.07. The Al atoms are preferentially concentrated in two sets of tetrahedral positions associated to Ca; the Al fraction in the tetrahedral positions are the same. The ratio of Ca fraction in the Ca site to Al fraction in the tetrahedra is almost unity. These structural features characterize the monoclinic symmetry of wairakite. The occurrence of twinning on (110) characteristic of wairakite can be explained in terms of the structure. However, to elucidate structurally the nature of the wairakite–analcime solid solution, further structural study is required, particularly of crystals with intermediate compositions.

### Introduction

Wairakite,  $\text{Ca}[\text{Al}_2\text{Si}_4\text{O}_{12}] \cdot 2\text{H}_2\text{O}$  (Steiner, 1955), the calcium analogue of analcime,  $\text{Na}_2[\text{Al}_2\text{Si}_4\text{O}_{12}] \cdot 2\text{H}_2\text{O}$ , is a zeolite which occurs widely in low-grade metamorphic rocks. The first X-ray studies by Coombs (1955) showed that the mineral was a distortion derivative of analcime and had a monoclinic body-centered cell. A marked feature of wairakite crystals is the presence of complex, fine lamellar twinings which presumably originated in transformation during crystal formation (Coombs, 1955). Synthetic work by Liou (1970) showed the ex-

istence of a tetragonal disordered phase at temperatures ranging from 300 to 460°C; the transformation from the disordered phase to ordered wairakite is gradual and sluggish.

In a recent paper, Mazzi and Galli (1978) reported the existence of various non-cubic structures for analcime, primarily due to the difference in Al ordering in the analcime framework, which was originally reported as cubic with a space group  $Ia3d$  (Taylor, 1930). It is thus of particular interest to determine the mode of distribution of Al and Ca underlying the distortion of the analcime framework to yield the

monoclinic symmetry of wairakite. Infrared absorption spectra of wairakite were reported by Harada *et al.* (1972). However, in spite of the mineralogical and geological importance of this mineral, no structural study has yet been made, probably due to the complexity of twinning.

The structural study of wairakite was therefore undertaken to throw light on the conflicting views on the existence of a continuous isomorphous series between analcime and wairakite (Steiner, 1955; Ames and Sand, 1958; Coombs *et al.*, 1959; Seki, 1971; Harada and Sudo, 1976), and on the crystal chemistry of framework silicates containing Na and Ca.

### Experimental

The wairakite crystals came from Onikobe, Miyagi Prefecture, Japan. As polysynthetic twinning is inherent in wairakite, thick sections without cover glasses, as for leucite (Mazzi *et al.*, 1976) and analcime (Mazzi and Galli, 1978), were prepared from nearly twenty pieces of the crystals, and those crystals which were apparently free from twinning were selected with the polarizing microscope. Crystals so obtained were then examined by oscillation and Weissenberg methods to avoid pseudo-merohedric twins. Although theoretically merohedric twins are possible as well, twinning in this category, if it exists, can be recognized and avoided during intensity data collections. Since the twinning on (110) characteristic of wairakite is pseudo-merohedric, we may consider that the difficulty due to merohedric twinning will be negligible. We finally obtained three fragments which did not show any splitting of reflection spots. One of them was ground to a spheroid with dimensions 0.07–0.09 mm and used for subsequent X-ray experiments.

Unit-cell dimensions and diffraction intensities were measured with a Philips PW1100 automated single-crystal diffractometer at room temperature, using graphite-monochromatized  $\text{CuK}\alpha$  radiation,  $\lambda = 1.5418\text{ \AA}$ . The cell dimensions, obtained by least-squares procedure applied to the  $\sin 2\theta$  values of 30 reflections, are  $a = 13.692(3)$ ,  $b = 13.643(3)$ ,  $c = 13.560(3)\text{ \AA}$ ,  $\beta = 90.5(1)^\circ$ . The unit cell contains one formula unit which will be given later.

Diffraction intensities of a total of 4487 reflections, including  $hkl$  and  $h\bar{k}l$ , were measured in the  $\omega$ - $2\theta$  mode over the range  $2^\circ < \theta < 67^\circ$ . Intensities were corrected for Lorentz polarization effects and for absorption, the latter being carried out as a combination of the semiempirical method proposed by North *et al.* (1968) with the absorption correction for spher-

ical shape ( $\mu = 97.00\text{ cm}^{-1}$ ,  $r = 0.004\text{ cm}$ ). After averaging symmetrically-equivalent reflections, a set of 2245 independent reflections were obtained. Of these, 1561 reflections had intensities greater than  $3\sigma(F^2)$ , and 1261 greater than  $5\sigma(F^2)$ . Systematic absence of reflections agrees with that for  $I2/a$  as reported by Coombs (1955).

Electron microprobe analyses were made on the same crystal used for the X-ray measurements with the procedure reported elsewhere (Mazzi and Galli, 1978). Although we did not determine the water loss, another analysis of wairakite from the same locality (Seki, 1966) shows the almost ideal value, 16 molecules per cell, for the water content. As will be shown later, there is structural evidence that the sites for water molecules in wairakite tend to be fully occupied. Then, based on the analyses (Table 1), the chemical formula of the present material may be expressed by  $\text{Ca}_{7.19}\text{Na}_{1.12}\text{K}_{0.01}(\text{Si}_{32.59}\text{Al}_{15.38})\text{O}_{96} \cdot 16\text{H}_2\text{O}$ .

### Determination and refinement of the structure

An initial model for the monoclinic structure of wairakite was derived from the atomic parameters for orthorhombic analcime (Mazzi and Galli, 1978). Using a limited number of reflections with  $F^2 > 5\sigma(F^2)$ , we executed a test calculation of structure factors. A subsequent Fourier synthesis revealed a basic feature of the wairakite structure, giving Ca locations at a distinct set of eightfold positions which corresponds to the Na2 site in noncubic analcime and denoted here M2. The Fourier map also revealed Al locations in terms of T–O lengths. The structure was then refined with the least-squares program LINUS (Coppens and Hamilton, 1970). After eight cycles of calculation the R value was reduced to 0.09 for reflections with  $F^2 > 2\sigma(F^2)$ . The difference Fourier map at this stage revealed two sets of residual peaks significantly above the background at the positions M11 and M12A, which respectively correspond to Na11 and Na12 in orthorhombic analcime; the maximum peak heights were respectively  $1.0\text{ e \AA}^{-3}$  and  $0.5\text{ e \AA}^{-3}$ . At the position M12B, which also corresponds to Na12 in orthorhombic analcime, only a low smeared peak with maximum height of  $0.3\text{ e \AA}^{-3}$  was observed. The 1.12 Na atoms in the cell were then allocated to these three sets of positions proportionally to these maximum peak heights. Several cycles of subsequent anisotropic refinement yielded  $R = 0.06$ . However, anisotropic temperature factor coefficients for four oxygen and one silicon atoms became negative.

Acceptable results were obtained when we used a

Table 1. Chemical composition of Onikobe wairakite (wt. %)

Oxide	(1)	(2)	(3)
SiO <sub>2</sub>	55.78	54.91	55.33
TiO <sub>2</sub>		0.01	
Al <sub>2</sub> O <sub>3</sub>	22.33	22.75	23.47
Fe <sub>2</sub> O <sub>3</sub>		0.64	
CaO	11.49	11.69	12.91
FeO		0.44	
MnO		0.01	
MgO		0.23	
Na <sub>2</sub> O	0.99	0.60	
K <sub>2</sub> O	0.02	0.31	
H <sub>2</sub> O(+)		8.23	8.29
H <sub>2</sub> O(-)		0.19	
		100.01	100.00

(1) An average of electron microprobe analyses at six sampling points of the crystal used for the present study (analyst: Dr. G. Vezzalini). (2) Seki (1966). (3) For ideal chemical composition Ca[Al<sub>2</sub>Si<sub>4</sub>O<sub>12</sub>]<sub>2</sub>H<sub>2</sub>O

Table 2. Atomic coordinates and isotropic temperature factors (standard errors in parentheses)

Atom	x	y	z	B(Å <sup>2</sup> )*
M11	0.1318(53)	0.9997(53)	0.2561(54)	3.7(1.4)
M12A	0.2500	0.1203(77)	0	2.2(1.7)
M12B	0.7500	0.3763(84)	0	3.9(6)
M2	0.0115(1)	0.2474(1)	0.1160(1)	1.79
T11A	0.1122(1)	0.1580(1)	0.4175(1)	0.48
T11B	0.8714(1)	0.3381(1)	0.4056(1)	0.54
T12A	0.4221(1)	0.1310(1)	0.1599(1)	0.52
T12B	0.5971(1)	0.3728(1)	0.1682(1)	0.61
T2A	0.1753(1)	0.4112(1)	0.1370(1)	0.54
T2B	0.8474(1)	0.0856(1)	0.1176(1)	0.53
011A	0.1099(3)	0.3484(3)	0.2274(3)	1.25
011B	0.9095(3)	0.1464(3)	0.2139(3)	1.20
012A	0.3834(3)	0.1376(3)	0.4660(3)	1.16
012B	0.5983(3)	0.3501(3)	0.4791(3)	1.02
021A	0.2029(3)	0.1165(3)	0.3575(3)	1.54
021B	0.7763(3)	0.3999(3)	0.3796(3)	1.45
022A	0.1282(3)	0.4626(3)	0.3863(3)	1.41
022B	0.8355(3)	0.0357(3)	0.3548(3)	1.34
031A	0.3976(3)	0.2243(3)	0.0891(3)	1.53
031B	0.6444(3)	0.2780(3)	0.1144(3)	1.55
032A	0.4868(3)	0.3896(3)	0.1280(3)	1.65
032B	0.5405(3)	0.1218(3)	0.1639(3)	1.46
W A	0.1344(4)	0.1264(4)	0.1348(4)	5.04
W B	0.8858(4)	0.3703(4)	0.1169(4)	4.12

\* Values other than those of M11, M12A and M12B were calculated from anisotropic thermal parameters. Cation occupancies are: M11: 0.042(5) Na; M12A: 0.034(4) Na; M12B: 0.042 Na; M2: 0.89 Ca + 0.059(1) Na

set of 1452 reflections with  $F^2 > 3.5\sigma(F^2)$  after correcting intensities for anisotropic extinction effects. The results of least-squares calculations, with extinction parameters constrained to symmetry, showed that one based on the type II mosaic model (Zachariasen, 1967) gave better agreement between  $F_o$  and  $F_c$  than the other based on the type I model, giving  $R = 0.039$  (wt.  $R = 0.0362$ ) for the reflections used. The anisotropic extinction parameters obtained are:  $g_{11} = 66.2 \times 10^{-4}$ ,  $g_{22} = 42.2 \times 10^{-4}$ ,  $g_{33} = 39.5 \times 10^{-4}$ , and  $g_{13} = -31.5 \times 10^{-4}$ . A calculation shows that the largest axis of the extinction ellipsoid lies in a plane parallel to (010) and makes an angle  $33.5^\circ$  with  $c$ , and  $57.0^\circ = (\beta - 33.5)$  with  $a$ . This direction is nearly parallel to a line which passes through tetrahedral cations V (= T2A) and VI' (= T2B) as shown in Figure 4, though the physical significance of this is unknown.

For occupancy refinement, the occupancy of Ca at M2 and the total number of Na in the cell were respectively constrained to 0.899 and 1.12, as given by the chemical formula. When the constraint for Ca was released, we obtained the occupancy of 0.894(1) and a slightly better R value of 0.0342. Since, however, the significance of this value is uncertain, we adopted the Ca occupancy of 0.899. Throughout the calculations, nonionized form factors of Ca, Na, Si, Al, and O were used, as provided by Volume III of

the International Tables for X-ray Crystallography. Table 2 and Table 3<sup>1</sup> give the final positional parameters of atoms and anisotropic temperature factor coefficients respectively.

### Result and discussion

#### Cation distribution

The structure of wairakite shares the same topology as analcime. In the analcime framework, 24 cation sites are available to locate 16 Na atoms. Depending upon the mode of distribution of Na over the excess cation sites, the symmetry of analcime may be lowered from cubic (Taylor, 1930) to tetragonal or orthorhombic (Mazzi and Galli, 1978). In contrast to this, the wairakite structure has a salient feature that the cations (now Ca) occupy, among four distinct sets of cation sites (Table 2), only a specific set of eightfold positions (Fig. 1). The framework of the analcime type is then distorted to give significant differences from the analcime framework.

Since it is of basic importance to discuss the wairakite structure in comparison with analcime, we com-

<sup>1</sup> To receive a copy of Table 3 and the structure-factor table, order Document AM-79-109 from the Business Office, Mineralogical Society of America, 2000 Florida Avenue, NW, Washington, DC 20009. Please remit \$1.00 in advance for the microfiche.

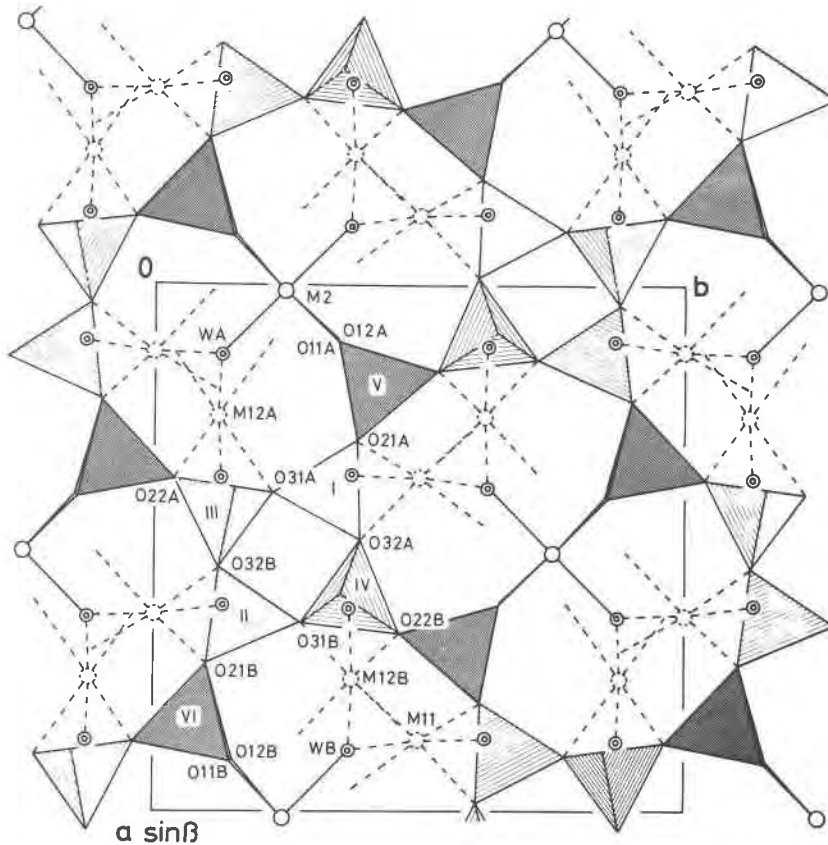


Fig. 1. The wairakite structure between  $0 \leq z \leq 1/4$ . Tetrahedra labelled by I, II, III, IV, V, and VI correspond respectively to T11A, T11B, T12A, T12B, T2A, and T2B given in Table 2; the latter two, in which Al atoms are concentrated, are densely ruled. Solid circles indicate M2 positions in which Ca is located, dotted circles partly-filled octahedral sites, and double circles water molecules.

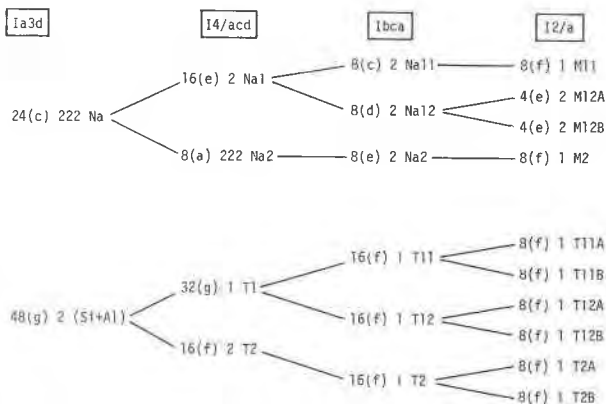


Fig. 2. Diagrams showing splittings of distinct cation sites to generate derivatives of cubic analcime. Space-group notation of equivalent points is given in the first of each triplet of symbols, point symmetry in the second, and site notation in the last. The upper diagram is for octahedral cations and the lower for tetrahedral cations.

pared in Figure 2 the notation of cation sites in wairakite and those of corresponding sites for various analcime structures (Taylor, 1930; Mazzi and Galli, 1978). In this figure, we observe how the cation site in cubic analcime is differentiated to give structures of lower symmetry. In addition to these types of reported structures for analcime, rhombohedral structures are theoretically possible. For the simple case of a rhombohedral structure with space group  $R\bar{3}c$ , the cations will be distributed over the two sets of 6(e) positions and Si/Al over the two sets of 12(f) positions.

Calcium atoms, compared to sodium, form stronger bonds to the framework oxygen atoms, thus giving rise to a contraction of the analcime framework; the O-O edges of the M2 octahedra (Table 4) are on average around 4% smaller than those of the Na2 octahedra which contain 80% Na (ANA7 in Mazzi and Galli, 1978). The Ca atoms in wairakite

Table 4. Interatomic distances (Å) and angles (°) for wairakite

Atoms	T - O	Atoms	O - O	O - T - O	Atoms	T - O	Atoms	O - O	O - T - O
T11A - O21A	1.595(4)	O21A - O12A	2.693(6)	114.7(2)	T12B - O22B	1.586(4)	O22B - O32B	2.647(6)	111.4(2)
- O12A	1.604(4)	- O31A	2.675(6)	112.9(2)	- O32A	1.618(4)	- O31B	2.591(6)	107.7(2)
- O31A	1.615(4)	- O32A	2.608(6)	108.4(2)	- O31B	1.622(4)	- O11B	2.644(6)	111.0(2)
- O32A	1.620(4)	O12A - O31A	2.524(6)	103.3(2)	- O11B	1.623(4)	O32A - O31B	2.649(6)	109.7(2)
Mean	1.609	- O32A	2.629(6)	109.3(2)	Mean	1.612	- O11B	2.608(6)	107.1(2)
		O31A - O32A	2.617(6)	108.0(2)			O31B - O11B	2.657(6)	109.2(2)
T11B - O21B	1.598(4)	O21B - O31B	2.660(6)	111.9(2)	T2A - O22B	1.708(4)	O22B - O21A	2.785(6)	107.6(2)
- O31B	1.621(4)	- O12B	2.651(6)	111.3(2)	- O21A	1.711(4)	- O12A	2.877(6)	113.2(2)
- O12B	1.622(4)	- O32B	2.600(6)	107.6(2)	- O12A	1.738(4)	- O11A	2.888(6)	113.4(2)
- O32B	1.632(4)	O31B - O12B	2.607(6)	107.0(2)	- O11A	1.748(4)	O21A - O12A	2.879(6)	113.2(2)
Mean	1.616	- O32B	2.653(6)	109.3(2)	Mean	1.726	- O11A	2.860(6)	111.5(2)
		O12B - O32B	2.661(6)	109.8(2)			O12A - O11A	2.632(6)	98.0(2)
T12A - O22A	1.578(4)	O22A - O11A	2.669(6)	113.2(2)	T2B - O21B	1.706(4)	O21B - O22A	2.763(6)	107.9(2)
- O11A	1.619(4)	- O32B	2.663(6)	112.5(2)	- O22A	1.712(4)	- O12B	2.878(6)	112.9(2)
- O32B	1.625(4)	- O31A	2.596(6)	108.2(2)	- O12B	1.749(4)	- O11B	2.901(6)	113.7(2)
- O31A	1.627(4)	O11A - O32B	2.575(6)	105.1(2)	- O11B	1.760(4)	O22A - O12B	2.879(6)	112.6(2)
Mean	1.612	- O31A	2.681(6)	111.4(2)	Mean	1.732	- O11B	2.896(6)	113.0(2)
		O32B - O31A	2.603(6)	106.3(2)			O12B - O11B	2.619(6)	96.6(2)
Atoms	M - O	Atoms	M - O	Atoms	M - O	Atoms	M - O		
M11 - O21A	2.32(7)	M12A - O22A	2.53(5)	M12B - O31B	2.52(6)	M2 - O11B	2.375(4)		
- O32B	2.42(7)			- O22B	2.60(5)	- O12B	2.379(4)		
- O21B	2.62(7)	- O31A	2.74(5)	- W B	2.434(7)	- O12A	2.409(4)		
- O32A	2.73(7)	- W A	2.430(7)			- O11A	2.409(4)		
- W A	2.39(7)					- W A	2.371(5)		
- W B	2.48(7)					- W B	2.403(5)		
Mean	2.49		2.57		2.52		2.391		

and Na in analcime share, however, the following features: (1) the temperature factors are strongly anisotropic towards associated water molecules, and (2) the octahedra about these cations are close to regular shape, with water molecules at two apices and a pair of square edges shared with the edges of tetrahedra, as shown in Figure 3. The cations are in fact coordinated by a pair of water molecules and a pair of tetrahedra. Such a coordination about cations is characteristic of the structures in the analcime-wairakite series, and is of considerable importance in discussing the crystal chemistry of this series.

The small amount of sodium atoms in the present structure are distributed nearly evenly over the four sets of cation positions including M2 (Table 5). The significance of the distribution of these minor cations was confirmed by the difference Fourier syntheses.

*Distribution of Al in the framework*

The framework of our wairakite contains 32.59 Si and 15.38 Al, yielding  $r = 0.3206$ . Here  $r$  is a value defined by  $Al/(Si + Al)$ ; for the idealized chemical composition (Table 1),  $r = 0.333$ . As will be observed in Table 4, in which T-O bond lengths are listed, the Al atoms are preferentially concentrated in a pair of

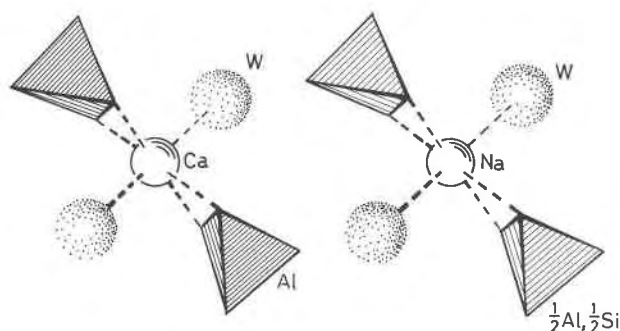


Fig. 3. Coordination of cations in the structures of the wairakite-analcime series, showing that the pair of tetrahedra about Ca are occupied by Al, while those about Na by Al/2 and Si/2.

Table 5. Occupancy in cation sites and Al fraction in tetrahedral sites

Cation site	Occupancy of cation site	Tetrahedral pair about cation site	Al fraction in tetrahedra
M11 (Na11)*	4.2(5) % Na	T11A T11B	7 % 6
M12A (Na12)	3.4(4) Na	T12A T12A'	5 5
M12B (Na12)	4.1 Na	T12B T12B'	5 5
M2 (Na2)	89.9 Ca + 5.9(1) Na	T2A T2B	84 84

\* Notations in parentheses are those for orthorhombic analcime (Mazzi and Galli, 1978). T12A' and T12B' are respectively related to T12A and T12B by twofold operation.

T2A and T2B tetrahedra. This is the pair associated with the Ca atoms. The Al distribution in the framework was estimated by the procedure given by Mortier *et al.* (1975); after due corrections of the T–O bond lengths for the T–O–T angle (Table 6), the fractional Al content of the *i*th tetrahedron is calculated as  $(l_i - L)/0.15 + r$ . Where  $l_i$  = mean T–O length of the *i*th tetrahedron,  $L$  = overall mean T–O bond length. The procedure is based on the assumption that Al–O is longer than Si–O by 0.15 Å. In Table 5, which gives the result, we observe the following features: (1) the Al fractions in the pair of tetrahedra, T2A and T2B, are identical, and (2) their values are almost the same as that of the Ca fraction in the M2 site.

Now, for the structures in general in the analcime–wairakite series, let  $p(\text{Al})$  be the average Al fraction in the pair of tetrahedra associated to a given cation site M and  $p(\text{M})$  the cation fraction in the M site. Then we find that for the Ca site in wairakite the  $p(\text{Al})/p(\text{M})$  ratio is nearly unity. On the other hand, based on the various analcime structures given by Mazzi and Galli (1978), we evaluated the ratios for 13 pairs of tetrahedra about Na sites; the average value was found to be 0.50 with standard deviation of  $\pm 0.08$  (for this calculation we excluded the tetrahedra in which the Al fractions were less than 10%). The difference in ratio between wairakite and analcime obviously suggests that Ca atoms have a stronger effect upon the framework than Na atoms.

The difference in such an effect between Ca and Na can be observed in average T–O bond lengths as well. In the present case ( $r = 0.3206$ ), the overall average of the T–O lengths (Table 4) is 1.651 Å, while for analcime with  $r = 0.3205$  (ANAl in Mazzi and

Galli, 1978) the value is 1.646 Å. Even for the case of analcime having the greater value of  $r = 0.3404$  (ANA7 in Mazzi and Galli, 1978) the value is 1.647 Å; the T–O lengths, if averaged, are smaller than those in wairakite. This situation would suggest that the T–O bond lengths in the analcime framework are reduced to compensate for weaker bonding to Na atoms. The differences in bond length, though small, are thought to be significant because similar effects have been reported in zeolite frameworks (Mortier *et al.*, 1975; Koyama and Takéuchi, 1977).

#### *Monoclinic symmetry of the framework*

In Figure 1, which shows the *c*-axis projection of the wairakite structure, we observe that the Al tetrahedra are symmetrically distributed in the twelve-membered ring; the ring simulates a 222 symmetry. In contrast with this, in the *b*-axis projection the distribution of Al tetrahedra in the twelve-membered ring is such that it gives only a twofold symmetry to the ring (Fig. 4). The arrangement of Ca atoms relative to the ring is not symmetrical, as it is in the *c*-axis projection. Note in Figure 4 that the edge, O11B–O21B, of the Al tetrahedron, T2B, is the longest edge in the framework (Table 4). This figure shows that this edge and its symmetry equivalent, in particular, are largely responsible for the monoclinic distortion of the twelve-membered ring. Thus the specific distribution of Al tetrahedra characterizes the monoclinic framework of wairakite.

#### *Neighbors of water molecules*

Each water molecule in the wairakite structure has, as in analcime, twelve neighbors of framework oxygen atoms. The distances between the water molecule and the framework oxygen atoms are from 3.133 to 3.898 Å, while in the structure of non-cubic analcime the distances are from 3.336 to 3.574 Å (Mazzi and Galli, 1978). The smallest value in wairakite occurs in the M11 octahedron, which is nearly vacant. As observed in Table 7, there are several short W–O distances, ranging from around 3.1 to 3.3 Å. It is then very likely that hydrogen bonds are formed, as in analcime (Mazzi and Galli, 1978), between water molecules and framework oxygen atoms. We calculated the valence sum at each oxygen atom following the procedure given by Donnay and Allmann (1970) and give the result in Table 8. A comparison of Table 7 and Table 8 shows that under-saturated oxygen atoms have relatively short W–O distances.

Table 6. T–O–T angles for wairakite

Oxygen atom	Neighbors	Angle
O11A	T12A, T2A	136.2°
O11B	T12B, T2B	128.6
O12A	T11A, T2A	150.6
O12B	T11B, T2B	131.8
O21A	T11A, T2A	145.1
O21B	T11B, T2B	150.3
O22A	T12A, T2B	150.0
O22B	T12B, T2A	147.9
O31A	T11A, T12A	145.9
O31B	T11B, T12B	143.2
O32A	T12B, T11A	147.9
O32B	T12A, T11B	134.2

Estimated errors in angle are  $\pm 0.2^\circ$ .

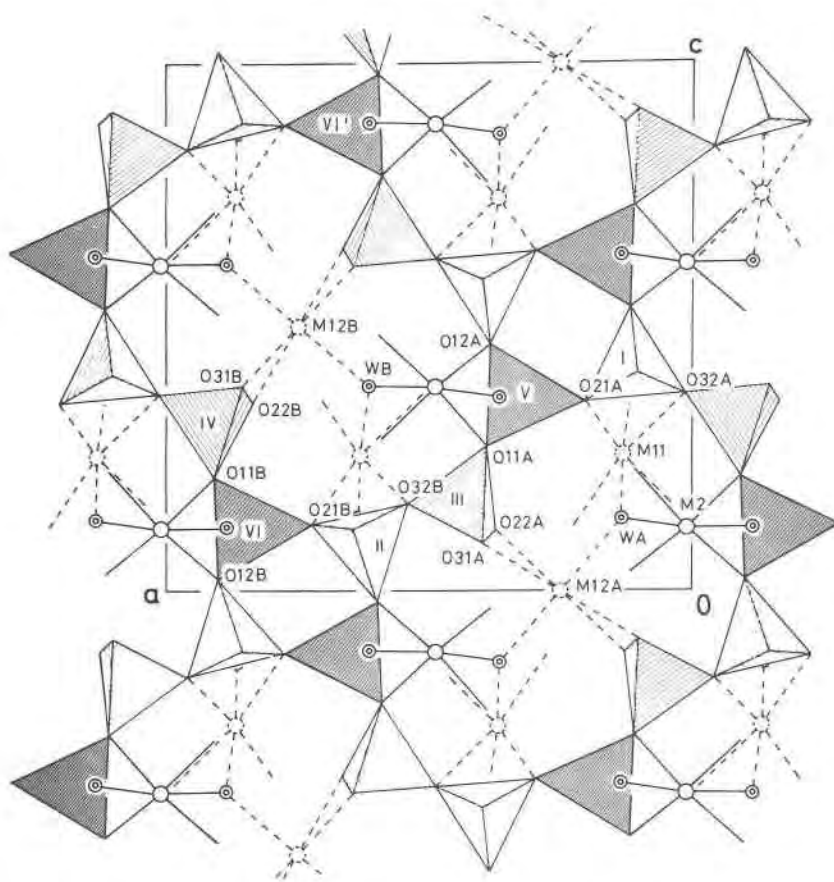


Fig. 4. The wairakite structure projected down the  $b$  axis ( $0 \leq y \leq 1/4$ ). Tetrahedra are denoted as in Fig. 1. The distribution of Al tetrahedra (densely ruled) is to be compared with that in Fig. 1.

It appears that the formation of hydrogen bonds is essential to stabilize the structure of the analcime-wairakite series. Based on the data for non-cubic analcime (Mazzi and Galli, 1978), we plotted mean Na-W and Na-O distances vs. Na contents at cation sites (Fig. 5). While Na-O distances increase with decreasing Na content, Na-W distances decrease markedly, showing that water molecules tend to approach the oxygen atoms in the octahedra about cation sites. When extrapolated to the Na-vacant point in the diagram, the Na-W distance has a value of

around 2.27Å. This means that the W-O distances in the vacant octahedra would be around 3.21Å ( $= \sqrt{2} \times 2.27$ ), provided that the octahedra are of regular shape.

For the wairakite structure, the Na-O and Na-W distances have values which are not expected from those of the analcime structure (Fig. 5). This is evidently due to the fact that water molecules in wairakite are firmly bonded to Ca in only one set of the cation sites and Al atoms in the framework are distributed in only specific pairs of tetrahedra.

Table 7. Distances (Å) between water molecules and framework oxygen atoms

	M2 octahedron				M11 octahedron				M12A/M12B octahedron*			
W A -	O11A	O11B	O12A	O12B	O21A	O21B	O32A	O32B	O22A	O22A'	O31A	O31A'
	3.297	3.282	3.506	3.543	3.157	3.329	3.639	3.644	3.483	3.583	3.857	3.343
W B -									O22B	O22B'	O31B	O31B'
	3.416	3.340	3.366	3.285	3.590	3.898	3.590	3.133	3.316	3.836	3.536	3.401

\* Oxygen atoms in the upper row belong to M12A and those in the lower belong to M12B octahedron. Estimated errors in W - O distances are  $\pm 0.009$  Å.

Table 8. Valence sums of wairakite

Bond valence (v.u.)				$\Sigma$
011A	T12A 0.986	T2A 0.729	M2 0.305	2.02
011B	T12B 0.976	T2B 0.719	M2 0.331	2.03
012A	T11A 1.009	T2A 0.734	M2 0.318	2.07
012B	T11B 0.988	T2B 0.735	M2 0.329	2.05
021A	T11A 1.026	T2A 0.782	M11 0.010	1.82
021B	T11B 1.054	T2B 0.798	M11 0.005	1.86
022A	T12A 1.068	T2B 0.789	M12A 0.004	1.86
022B	T12B 1.049	T2A 0.786	M12B 0.003	1.84
031A	T11A 0.987	T12A 0.971	M12A 0.002	1.96
031B	T11B 0.990	T12B 0.988	M12B 0.003	1.98
032A	T11A 0.978	T12B 0.986	M11 0.004	1.97
032B	T11B 0.968	T12A 0.975	M11 0.007	1.95
W A	M2 0.333	M11 0.008	M12A 0.004	0.35
W B	M2 0.324	M11 0.007	M12B 0.004	0.33

Cations are given in the first line of each pair and bond valence in the second.

### Twinning

The twinning of wairakite is, as pointed out by Coombs (1955), probably due to transformation from the high-temperature phase (Liou, 1970). Since the space group of the high-temperature phase would be  $I4/acd$  like that of tetragonal analcime, any symmetry operations in this space group which are suppressed in the space group  $I2/a$  may be considered as possible twin operations. Representative operations are  $a$  glide parallel to (001),  $b$  glide parallel to (100), and  $d$  glide parallel to (110). The twinings based on the first two operations have twin obliquity of  $0.51^\circ$ , while the twinning based on the third one has  $0.1^\circ$ . The smaller value for the twinning on (110) is in accord with the fact that this is the type of twin characteristic of wairakite (Coombs, 1955).

Assuming the above three glide planes as true symmetry elements for wairakite, we derived sets of atomic positions respectively related by these operations, and evaluated the deviations of these hypothetical atomic positions from corresponding true atomic positions. For framework oxygen atoms, the mean

deviations are: (1)  $0.400\text{\AA}$  ( $0.064\text{\AA}^2$ ) for the twinning on (110), (2)  $0.518\text{\AA}$  ( $0.040\text{\AA}^2$ ) for (100) twin, and (3)  $0.539\text{\AA}$  ( $0.032\text{\AA}^2$ ) for (001) twin, where the values in parentheses give variances. The smaller value, compared to others, for the twinning on (110) is also consistent with the frequent occurrence of twinning of this type.

### Wairakite-analcime solid solutions

The above features characteristic of the wairakite structure may be summarized as follows: (1) The location of Ca atoms is fixed to only one site, M2, among four distinct sites available for cations; (2) the Al atoms are concentrated in T2A and T2B sites both associated with Ca, and the Al fractions in T2A and T2B are the same; (3) the ratio of Ca fraction in M2

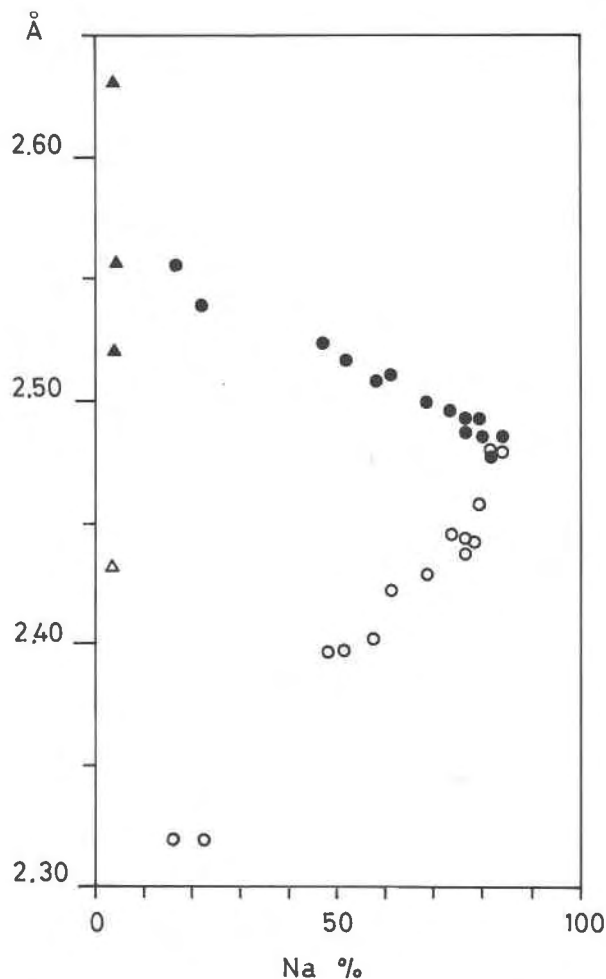


Fig. 5. Variation of Na-O distances (solid circles) and Na-W distances (open circles) vs. occupancy of Na (atom percent) in noncubic analcime structures. Solid and open triangles are respectively the entries for Na-O and Na-W distances in the wairakite structure.



to Al fraction in either tetrahedral site is unity; and (4) the small amount of Na atoms contained in the structure is evenly distributed over the cation sites, including M2.

Features (1) and (2), in particular, impose a distortion upon framework to give monoclinic symmetry, thus differentiating the wairakite structure from analcime. We may point out that the monoclinic feature of the framework will be gradually lost with decreasing Ca content (Al fraction in the tetrahedral pair decreases concomitantly) and finally vanish at a composition with the Ca/(Ca + Na) ratio of 1/3. In the structure with this composition, the Ca fraction in M2, and accordingly the Al fraction in each of the tetrahedral pair, will be 0.5; this value for the Al fraction corresponds to the maximum possible value for the analcime structure. It is however hazardous to speculate on the possible continuity of isomorphous series between analcime and wairakite only from available structural data.

Regarding the possible limit of the wairakite solid solution, Aoki (1976) appears to provide experimental evidence. He carried out hydrothermal experiments, in the temperature range 250° to 340°C, to obtain ion-exchange isotherms of the minerals in the analcime-wairakite series. Starting from natural as well as hydrothermally-prepared analcimes he synthesized wairakite and obtained the minimum value of  $\text{CaO}/(\text{CaO} + \text{Na}_2\text{O}) = 0.824$  for wairakite. This value corresponds to a Ca fraction of 0.824 in the M2 site. In this work he also pointed out that this value may be extended to lower values if the chemical composition of the framework is shifted to a more Si-rich composition than the ideal one. Among reported minerals having intermediate composition, two minerals reported by Seki and Oki (1969) have very low Ca contents; one has a composition corresponding to 66% of wairakite molecule, and the other 49%. Both minerals are actually Si-rich, the former having the Al/(Al + Si) ratio of 0.302 and the latter 0.310, compared with 0.333 for the ideal composition. However, particularly for the compositions around that of the latter, we may perhaps anticipate the existence of a superstructure or, more generally, a modulated structure. If the formation of modulated structures is really the case, the isomorphous series between analcime and wairakite may be extensive. The problem is reserved for future study.

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