

## Leucite-pollucite structure-type variability and the structure of a synthetic end-member calcium wairakite ( $\text{CaAl}_2\text{Si}_4\text{O}_{12}\cdot 2\text{H}_2\text{O}$ )

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### ABSTRACT

The structure of a synthetic end-member wairakite ( $\text{CaAl}_2\text{Si}_4\text{O}_{12}\cdot 2\text{H}_2\text{O}$ ) has been determined using Rietveld analysis of high-resolution, synchrotron X-ray powder diffraction data, and  $^{29}\text{Si}$  and  $^{27}\text{Al}$  magic angle spinning nuclear magnetic resonance spectroscopy. The framework in the synthetic sample is more disordered than that in natural wairakite. Ca is distributed over the cavity cation sites M2, M12A, M12B in the approximate proportions 0.8:0.1:0.1, respectively, with M11 being vacant.  $^{29}\text{Si}$  MAS NMR data are consistent with about 80% of the Si occupying tetrahedral T11 and T12 sites linked to two Al atoms [ $\text{Q}^+(2\text{Al})$  silicons]. Tetrahedral and cavity cation site disorder are coupled so that Al mainly occupies T2 sites, with Ca in M12A and M12B being balanced by Al in T12A and T12B; T11A and T11B sites appear to only contain Si, in agreement with the M11 site being vacant. The crystal chemistries of the wide range of stoichiometries which crystallize with the leucite/pollucite structure-type are also reviewed, with particular attention being paid to the tetrahedral ordering configurations present in these phases, and the implications to crystallographic phase transitions.

**KEYWORDS:** wairakite, leucite, pollucite, Rietveld analysis, crystal structure.

### Introduction

SILICATES with three-dimensional tetrahedral framework structures form a wide range of distinct structure types, with many representatives amongst the rock-forming minerals (e.g. silica minerals, feldspars, nepheline, leucite, sodalite, zeolites). Studies of synthetic structural analogues, many of which are distinctive in that they have rare elements substituting for the more abundant elements, have greatly aided in understanding the detailed structural behaviour of the natural minerals (Taylor, 1983; 1984; Henderson,

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1984; Torres-Martinez and West, 1989; Palmer *et al.*, 1997). From a crystal chemical point of view, such analogues allow studies to be carried out on how different chemical species influence the ordering of tetrahedral cations and/or extra-framework (cavity) cations over distinct structural sites; such ordering may lead to the occurrence of very sluggish, reconstructive phase transitions between polymorphs.

As part of a wider attempt to understand the controls and consequences of atomic substitution and cation ordering in compounds with framework structures, we are studying a series of synthetic silicates with structures related to those of the natural minerals leucite, pollucite and analcime. Another mineral with the leucite-type topology is wairakite, the analogue of analcime in which two cavity Na<sup>+</sup> cations are replaced by one Ca<sup>2+</sup> coupled with Si-Al ordering (Coombs, 1955; Takéuchi *et al.*, 1979). Natural wairakite contains a significant Na content complicating the ordering pattern to some degree. In this paper we review the chemical and structural variation of the leucite structure type, and describe the structure of synthetic Ca end-member wairakite. Our new work on wairakite is based on the application of high-resolution, synchrotron powder diffraction, and of <sup>29</sup>Si and <sup>27</sup>Al magic angle spinning, nuclear magnetic resonance spectroscopic methods.

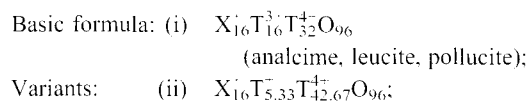
### Variable stoichiometries in the leucite structure type

The mineral leucite (KAlSi<sub>2</sub>O<sub>6</sub>) has a structure consisting of a three-dimensional framework of (Al,Si)O<sub>4</sub> tetrahedra. The ideal formulae for the natural structural analogues are: analcime NaAlSi<sub>2</sub>O<sub>6</sub>·H<sub>2</sub>O, pollucite CsAlSi<sub>2</sub>O<sub>6</sub>, and wairakite CaAl<sub>2</sub>Si<sub>4</sub>O<sub>12</sub>·2H<sub>2</sub>O; note the presence of molecular water in analcime and wairakite. The aluminosilicate framework contains two sizes of channels, the larger occupied by K in leucite, Cs in pollucite and H<sub>2</sub>O in analcime and wairakite, and the smaller by Na in analcime and Ca in wairakite (Mazzi *et al.*, 1976; Galli *et al.*, 1978).

At room temperature and pressure, pollucite is cubic with space group *la3d*, analcime is cubic *la3d* (or pseudo-cubic: tetragonal *I4<sub>1</sub>acd*, orthorhombic *lbca*, Mazzi and Galli, 1978; monoclinic *I2/a*, Pechar, 1988), while K-leucite has a distorted structure having the tetragonal space group *I4<sub>1</sub>/a*. With increasing temperature, the low-temperature, tetragonal structure in K-leucite

shows a continuous, rapid (non-quenchable), displacive transition to the high-temperature form (*la3d*; Peacor, 1968; Taylor and Henderson, 1968), perhaps via intermediate phases (Faust, 1963; Lange *et al.*, 1986; Palmer *et al.*, 1989). In this context, note that there is only a single T site in *la3d*, indicating that Al and Si must be disordered if high-leucite belongs to this space group. This in turn indicates that tetragonal low-leucite (*I4<sub>1</sub>/a*) should also have Si and Al disordered over the three T-sites, as the phase transition is too rapid to allow the possibility of Al-Si ordering. However, the situation is much more complex than this because MAS NMR for natural *I4<sub>1</sub>/a* K-leucites demonstrates partial Si-Al ordering, although there is controversy regarding the ordering scheme over the three T sites (e.g. Murdoch *et al.*, 1988; Phillips *et al.*, 1989; Kohn *et al.*, 1995; Kohn *et al.*, 1997). Clearly, such partially ordered frameworks could not transform to *la3d* symmetry, even though the lattice becomes metrically cubic above the phase transition (Palmer *et al.*, 1989).

In addition to the variations shown by Al-Si analogues, the leucite-type structure shows a wide variety of substitutions involving both tetrahedral and cavity sites. As well as K, Cs, Na and Ca occurring as cavity cation species, Rb (Henderson and Taylor, 1969; Palmer *et al.*, 1997) and Tl (Henderson and Taylor, 1969) varieties have been synthesized. In particular, the tetrahedral framework can readily accommodate a wide range of multivalent substitutions including univalent (e.g. Li) and divalent (e.g. Be, Mg, Fe, Zn, Cd, Co, Cu) ions (e.g. Roedder, 1951; Bayer, 1973; Torres-Martinez and West, 1989; Taylor, 1991; Heinrich and Baerlocher, 1991; Kohn *et al.*, 1994; England *et al.*, 1994; Bell and Henderson, 1994a, 1996). Other trivalent (e.g. B, Fe, Cr, Ga) and tetravalent (Ge) cations can be substituted for Al and Si (e.g. Ohmsbredemann *et al.*, 1986; Torres-Martinez and West, 1989; Taylor, 1991; England *et al.*, 1994; Bell and Henderson, 1994b); a P<sup>5+</sup> end member is also known (Ren *et al.*, 1990). SiO<sub>2</sub>-rich, alkali-deficient leucites can also be directly synthesized by hydrothermal methods leading to samples with cavity cation site vacancies (Henderson, 1969). The unit cell stoichiometries (anhydrous) of these 'end-members' can be expressed as follows:



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- (iii)  $X_{16}T_8^{2+}T_{40}^{4+}O_{96}$ ;
- (iv)  $X_{12}\square_4T_{12}^{3+}T_{36}^{4+}O_{96}$   
(where  $\square$  = vacancy);
- (v)  $X_{16}T_{32}^{3+}T_{16}^{5+}O_{96}$ ;
- (vi)  $X_8^2T_{16}^{3+}T_{32}^{4+}O_{96}$  (wairakite)

In the case of the phases with divalent tetrahedral cations (stoichiometry (iii) above), polymorphs exist with different numbers of T sites and different tetrahedral ordering arrangements (Heinrich and Baerlocher, 1991; Kohn *et al.*, 1991, 1994; Bell *et al.*, 1994*a, b*). For example, at room temperature,  $K_2MgSi_5O_{12}$  has been shown to be monoclinic  $P2_1/c$  with a fully ordered framework consisting of 10 Si and 2 Mg sites (Bell *et al.*, 1994*a*) and  $Cs_2CdSi_5O_{12}$  to be orthorhombic  $Pbca$  with 5 Si and 1 Mg sites (Bell *et al.*, 1994*b*).  $P2_1/c$  is a maximal sub-group of  $Pbca$  (cf.  $I4_1/a$  and  $Ia3d$  in the case of K-leucite) and Redfern and Henderson (1996) have recently shown that  $P2_1/c$   $K_2MgSi_5O_{12}$  shows an unquenchable and reversible, first-order, ferro-elastic phase transition to the  $Pbca$  structure at 350 C.

As well as the intrinsic interest in studying this varied structure type, its technological importance is reflected in recent work on aluminosilicate leucite-pollucites regarding their existing and potential uses in such areas as: fluid cracking catalysts (Kumar *et al.*, 1993); glass ceramics (e.g. Hogan and Risbud, 1991); radioactive waste disposal (e.g. Yanagisawa *et al.*, 1987); water purification (e.g. Nishioka *et al.*, 1990); dental porcelains (e.g. Mackert *et al.*, 1994); and as fast ion conductors (Palmer and Salje, 1990).

### Structure of natural wairakite

Natural wairakite, first described by Steiner (1955), invariably contains small but significant amounts of Na replacing Ca in the ideal formula (typically 0.18–1.88 wt.%  $Na_2O$ ; Aoki and Minato, 1980). Coombs (1955) carried out the first X-ray investigation and showed that it was a pseudo-cubic or pseudo-tetragonal variant of the analcime structure; he suggested that its real structure was monoclinic, either  $Ia$  or  $I2/a$ . Coombs (1955) also compared multiple twinning in wairakite to that shown by leucite and speculated that wairakite had originally crystallized as a cubic, analcime-like phase and had transformed to the low symmetry polymorph by a "non-reconstructive type of phase transforma-

tion" on cooling. Coombs suggested that the divalent Ca ions could be associated with two Al T-sites and thus inferred that wairakite had an ordered Si-Al arrangement.

Takéuchi *et al.* (1979) used single crystal X-ray methods to study a natural sample of composition  $Ca_{7.19}Na_{1.12}K_{0.1}(Si_{32.59}Al_{15.38})O_{96}\cdot 16H_2O$ , and confirmed that natural wairakite is monoclinic  $I2/a$  with a unit cell formula containing six distinct T sites (3 pairs of related sites) [T11A and T11B, T12A and T12B, T2A and T2B; each site of multiplicity 8] and four cavity cation sites (M11 and M2 each of multiplicity 8, and M12A and M12B, each of multiplicity 4). Based on T–O bond length differences, Takéuchi *et al.* showed that Si was dominantly ordered into T11A (93% Si), T11B (94%), T12A (95%), and T12B (95%) sites and Al into T2A (84%Al) and T2B (84%) sites. Note the same occupancy for each 'pair' of related T sites. Each T1(Si) site is linked to two T2(Al) and two T1(Si) sites and each T2(Al) is linked to four (T1Si) sites in accordance with the Al-avoidance principle (Loewenstein, 1954). The octahedral cavity cation M2 sites are linked to two oxygens each of adjacent Al-bearing T2A and T2B tetrahedra, and to the oxygens of two water molecules. Ca was placed in the M2 sites as close to Al as possible, in effect coupling the T-site ordering of Al to the M-site ordering of Ca so that the Al occupancy of Al in T2 effectively balances that of Ca in M2. The M-site occupancies were thus inferred to be M11 (4.2%Na, 95.8% $\square$  (vacancy)), M12A (3.4%Na, 96.6% $\square$ ), M12B (4.1%Na, 95.9% $\square$ ), M2 (89.9%Ca, 5.9%Na, 4.2% $\square$ ).

### Experimental methods

#### Synthesis

The starting material was prepared by thoroughly mixing appropriate amounts of SPECPURE amorphous  $SiO_2$ , amorphous  $Al_2O_3$  prepared by heating hydrated aluminium nitrate at 600 C, and SPECPURE  $CaCO_3$ ; X-ray fluorescence analysis showed that the anhydrous  $Al_2O_3$  contains less than 0.3wt.%  $Na_2O$ . The mixture was heated overnight at 600 C to decompose the carbonate; the product was amorphous to X-rays. About 0.5g of this mixture was sealed with excess water in a platinum tube and heated in a cold seal pressure vessel at 310 C and 2 kbars for 91 days. Using a laboratory X-ray diffractometer and  $Cu-K\alpha$  radiation, the wairakite showed a partially split 400/004 peak and the presence of a few

percent of each of quartz and anorthite as impurities. In addition,  $^{27}\text{Al}$  MAS NMR showed that a small amount of an unidentified impurity phase with octahedrally coordinated Al was present. The synthetic wairakite was fine grained (mean grain size of 10–30  $\mu\text{m}$ ) necessitating the use of powder rather than single crystal methods for structure determination.

Powder dispersed on double sided sticky tape and carbon coated was analysed on a JEOL 6400 SEM fitted with a LINK XL system high efficiency 'Pentafet' energy dispersive detector at 15 keV, 1.5 na beam current, and a 5  $\mu\text{m}$  raster. Standards used were synthetic corundum for Al and wollastonite for Si and Ca and data were reduced with LINK ZAF4 software. The mean values obtained for analyses of 5 grains ( $1\sigma$  in brackets) are  $\text{SiO}_2$  57.1(1.3),  $\text{Al}_2\text{O}_3$  23.7(1.0),  $\text{CaO}$  13.3(0.5) wt.%; Fe and Na were below detection (<0.08%). The equivalent anhydrous formula is  $\text{Ca}_{1.01}\text{Al}_{1.97}\text{Si}_{4.02}\text{O}_{12}$ , within error of the stoichiometric end-member composition. The water content of the sample was determined in duplicate by thermogravimetric analysis giving a mean value of 8.13 wt.%, very close to the theoretical value of 8.28 wt.%.

#### Synchrotron X-ray powder diffraction

The very low divergence of synchrotron radiation and the availability of high resolution diffractometers, together with Rietveld peak deconvolution techniques, allows the determination of structural data for powdered samples. Thus synchrotron X-ray powder diffraction was used to determine the structure of synthetic end-member wairakite using station 2.3 at the Daresbury Laboratory (Cernik *et al.*, 1990; Collins *et al.*, 1992). The samples were loaded onto an aluminium flat plate container 25 mm in diameter and 1 mm deep. Data were collected at room temperature over the range of 5–80 degrees  $2\theta$  using monochromatic radiation (water cooled Si (111) monochromator) of wavelength 1.40285 Å (calibrated against NIST 640b silicon standard) using steps of 0.01  $2\theta$  and counting times of 2.5 seconds per step. Each peak consists of overlapping reflections and the best estimate of peak width at half height is about 0.07  $2\theta$  showing that the sample is reasonably well crystalline despite the low synthesis temperature.

The structure was refined by the Rietveld method (Rietveld, 1969) using MPROF in the Powder Diffraction Program Library (Murray *et al.*, 1990); only data in the range 5–70  $2\theta$  (2307

peaks) were used as the signal:noise ratio higher than 70°  $2\theta$  does not allow adequate deconvolution of the very large number of low intensity, overlapping peaks in this region (Fig. 1). Refinements were carried out using neutral atom X-ray scattering factors (International Tables, volume IV, Table 2.3.1) and, because of the close similarity between those for Si and Al, T-site disorder was assumed (i.e., 1/3Al, 2/3Si on each site). The structural model was based on the results for natural wairakite, *I2/a* (Takéuchi *et al.*, 1979). In the first stage of the refinement, all the T–O distances were constrained to have a value of  $1.67 \pm 0.02$  Å. After the Rietveld refinement converged, the constraints were changed so that all T–O distances in a given tetrahedron were constrained, but T–O distances in different tetrahedra were allowed to vary. As is normal in X-ray methods, the mean refined T–O bond length for each distinct tetrahedral site can be used to infer the Si-Al occupancy for that site. During the final stages of the data reduction, the occupancies of the Ca sites and the isotropic temperature factors (B) were refined. Note that all Ca-, all T-, and all O-sites were constrained to have the same B values.

Because of the presence of anorthite and quartz as minor impurities, a three-phase Rietveld refinement was carried out using the structural parameters of Jorgensen (1978) for quartz and of Bruno *et al.* (1976) for anorthite. The final refinement gave the statistical parameters:  $R_1$  8.2,  $R_{\text{WP}}$  14.2%;  $R_{\text{exp}}$  10.9%; and goodness of fit 1.71. The errors in the structural parameters are relatively large due to the inherent problem of using powder diffraction methods to determine the structures of weakly scattering, low-symmetry materials which show only limited distortions from cubic/tetragonal symmetry. Thus the number of independent parameters to be refined was kept as small as possible because we found that more complicated structural models (e.g. taking account of T-site ordering, and entry of Ca onto the M11 site) tended to give unrealistic values for individual bond lengths and angles, which in turn distorted the mean values which we use to discuss the overall structural relations. Figure 1 shows the experimental diffraction data, the calculated positions of all possible reflections, and the plot of the differences between the experimental and calculated intensities.

#### MAS NMR

This technique is complementary to X-ray diffraction in that element-specific, short-range

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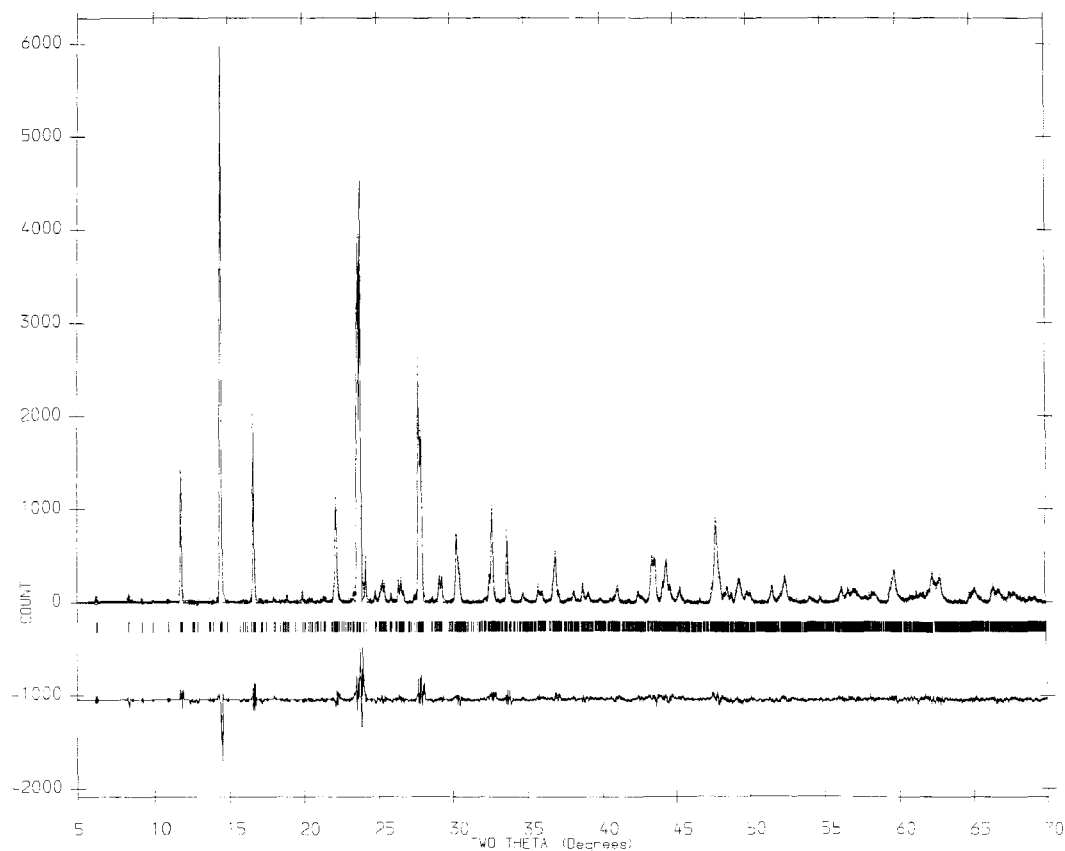


FIG. 1. High-resolution powder diffraction pattern of end-member wairakite. The upper panel shows the experimental data (spots) and calculated pattern (solid line) for the refined structure. The middle panel shows the positions of all possible reflections and the lower panel shows the difference plot  $[(I_{\text{obs}} - I_{\text{calc}})/\sigma_{\text{obs}}]$  between the experimental and calculated patterns.

order information can be obtained for both Si and Al independently, allowing inferences to be made regarding the ordering of these cations into distinct structural sites.  $^{29}\text{Si}$  NMR spectra were obtained using a Bruker MSL 360 spectrometer operating at 71.535 MHz. It was found that  $^{29}\text{Si}$  in the sample had a very long spin relaxation time ( $T_1$ ) therefore long recycle delays were required. The  $^{29}\text{Si}$  data obtained consists of the addition of 48 pulses with a 60 minute recycle decay and 92 pulses with a 30 minute delay, i.e. a total acquisition time of 94 hours. The pulse width was 2  $\mu\text{s}$  ( $\sim \pi/6$ ), the dwell time was 40  $\mu\text{s}$ , and the spinning speed 2.93 kHz.  $^{27}\text{Al}$  spectra were obtained at two magnetic fields, 14.1 T and 8.45 T using a Varian VXR 600 and the MXL 360

spectrometers, respectively. Pulse lengths of 3  $\mu\text{s}$  (high field) and 1  $\mu\text{s}$  (low field), and recycle delays of 0.5 s were used.

## Results and discussion

### *X-ray diffraction*

The synchrotron diffraction data for synthetic wairakite show a clear splitting of the pseudo-cubic {400} peaks at about  $24^\circ 2\theta$  (Fig. 1). Thirty peaks between  $10$  and  $40^\circ 2\theta$  provide the cell parameters  $a = 13.694(6)$ ,  $b = 13.644(7)$ ,  $c = 13.576(6)$  Å,  $\beta = 90.46(2)^\circ$ ; these values compare with those for natural wairakite (Takéuchi *et al.*, 1979) of 13.692(3), 13.643(3), 13.560(3),  $90.5(1)^\circ$ , respectively. The difference between the  $c$  axes

for the two samples leads to  $c/a$  ratios of 0.9916(6) and 0.9904(3), respectively, which are different at the  $1\sigma$  level. Thus the synthetic sample is slightly less distorted from the cubic pseudo-cell than the natural sample. Refined fractional atomic coordinates are given in Table 1, and mean T–O and Ca–O bond lengths, and mean T–O–T bond angles for the different T sites are summarised in Table 2. Tetrahedral and cavity cation connectivities are summarized in Table 3 (after Takéuchi *et al.*, 1979).

Initially the refinement was carried out with ‘pairs’ of T-sites (T11A and T11B; T12A and T12B; and T2A and T2B) constrained to give similar T–O bond lengths which gave the results: T11A–O 1.63, T11B–O 1.63, T12A–O 1.67, T12B–O 1.66, T2A–O 1.70, T2B–O 1.73 Å for mean bond lengths. These values suggest that T11 sites are mainly occupied by Si, T2 by Al, and

with significant Al in T12 sites. In subsequent refinements the T-sites were allowed to refine independently with the surprising result that the T12A–O and T12B–O bond lengths diverged. The final mean T–O bond lengths (in angstroms) for each tetrahedron, (compared with those from Takéuchi *et al.* in parentheses), are T11A–O 1.63 (1.609), T11B–O 1.63 (1.616), T12A–O 1.66 (1.612), T12B–O 1.61 (1.612), T2A–O 1.74 (1.726) and T2B–O 1.71 (1.732). Bearing in mind that the standard deviations of the individual T–O bond lengths in our powder refinement are  $\sim 0.02$  Å, these mean T–O values are in reasonable agreement except that the T12A tetrahedron bond lengths appear to be significantly longer for our sample. Our bond lengths for T11-type and T12B tetrahedra are close to the mean Si–O for anorthite and low albite of 1.615 Å, and those for T2 type tetrahedra are similar to the mean Al–O of 1.745 Å in these ordered feldspars; the

TABLE 1. Fractional atomic coordinates, isotropic temperature factors and Ca-site occupancies for synthetic end-member wairakite

Atom	X	Y	Z	B(iso)	Occupancy
Ca12A	0.2500	0.127(3)	0.0000	2.9(2)	0.97(3)
Ca12B	0.7500	0.385(3)	0.0000	2.9(2)	0.79(4)
Ca2	0.011(1)*	0.248(1)	0.118(1)	2.9(2)	6.24(5)
T11A	0.117(1)	0.155(1)	0.419(1)	0.29(7)	
T11B	0.877(1)	0.341(1)	0.407(1)	0.29(7)	
T12A	0.423(1)	0.130(1)	0.153(1)	0.29(7)	
T12B	0.591(1)	0.367(1)	0.164(1)	0.29(7)	
T2A	0.170(1)	0.416(1)	0.139(1)	0.29(7)	
T2B	0.844(1)	0.088(1)	0.119(1)	0.29(7)	
O11A	0.110(1)	0.350(2)	0.231(1)	0.32(9)	
O11B	0.907(1)	0.138(2)	0.217(1)	0.32(9)	
O12A	0.385(1)	0.138(2)	0.462(1)	0.32(9)	
O12B	0.599(1)	0.355(1)	0.477(1)	0.32(9)	
O21A	0.208(1)	0.116(2)	0.352(1)	0.32(9)	
O21B	0.777(1)	0.394(2)	0.374(1)	0.32(9)	
O22A	0.128(1)	0.466(1)	0.397(1)	0.32(9)	
O22B	0.834(1)	0.045(1)	0.362(1)	0.32(9)	
O31A	0.387(1)	0.224(1)	0.084(1)	0.32(9)	
O31B	0.645(1)	0.277(1)	0.112(1)	0.32(9)	
O32A	0.477(1)	0.385(2)	0.141(1)	0.32(9)	
O32B	0.545(1)	0.111(1)	0.170(1)	0.32(9)	
W A	0.137(1)	0.116(2)	0.134(1)	0.32(9)	
W B	0.880(1)	0.381(2)	0.112(1)	0.32(9)	

Cell parameters:  $a$  13.694(6),  $b$  13.644(7),  $c$  13.576(6) Å,  $\beta$  90.46(2)

Structure fit parameters:  $R_1$  8.2;  $R_{WP}$  14.2%;  $R_{exp}$  10.9%; goodness of fit 1.71

\* One sigma errors in brackets

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TABLE 2. Mean tetrahedral (T) and cavity cation (M) bond lengths, and mean inter-tetrahedral (T–O–T) angles for synthetic wairakite.

Mean bond lengths (Å)		Mean T–O–T angles (°) for each T site	This work	Takéuchi <i>et al.</i> (1979)
T11A–O	1.63(2)	T11A	144.3(2.0)	147.4(2.5)
T11B–O	1.63(2)	T11B	136.3(11.7)	139.9(8.5)
T12A–O	1.66(3)	T12A	136.5(10.1)	141.6(7.6)
T12B–O	1.61(2)	T12B	140.3(3.4)	141.9(9.1)
T2A–O	1.74(2)	T2A	141.3(4.3)	145.0(6.3)
T2B–O	1.71(2)	T2B	143.5(7.8)	140.2(11.6)
M12A–O	2.49(8)			
M12B–O	2.44(11)			
M2–O	2.47(6)			

T–O bond lengths for the T12A tetrahedra is intermediate. Based on these data, and by analogy with the work of Takéuchi *et al.*, we conclude that Si in synthetic wairakite is mainly ordered into T11 and Al into T2 sites. Based on mean T–O distances, the T12B site is occupied by Si while the T12A appears to contain a significant amount of Al; this difference is unexpected bearing in mind that these two sites are a crystallographic ‘pair’ with the same connectivities (Table 3). In this context note that the single crystal data (Takeuchi *et al.*, 1979) indicate that the bond lengths for T12A and T12B are identical.

Projections of the structure perpendicular to the *b* axis [010] and perpendicular to <111> are

shown in Fig. 2. Note that two types of four-rings of tetrahedra occur in the [010] plane, namely T11A–T2A–T11A–T2A and T11B–T2B–T11B–T2B, both with two pairs of the same species (Fig. 2*a*), while a four-ring with four different tetrahedral species, namely T11A–T12A–T11B–T12B occurs perpendicular to *c*, and similarly, four-rings containing T12A–T2A–T12B–T2B occur parallel to [100]. Figure 2*a* shows the symmetrical equivalence of the T11A and T11B, T12A and T12B, and T2A and T2B pairs of tetrahedra in the monoclinically distorted pseudo-orthorhombic cell (Takéuchi *et al.*, 1979).

In the initial refinements, Ca was placed exclusively on the M2 cation site, the site occupied

TABLE 3. Tetrahedral (T)- and cavity cation (M)-site connectivities

Site	T11A	T11B	T12A	T12B	T2A	T2B
T11A	–	–	1	1	2	–
T11B	–	–	1	1	–	2
T12A	1	1	–	–	1	1
T12B	1	1	–	–	1	1
T2A	2	–	1	1	–	–
T2B	–	2	1	1	–	–
M11*	1	1	–	–	–	–
M12A	–	–	2	–	–	–
M12B	–	–	–	2	–	–
M2	–	–	–	–	1	1

\* Ca is coordinated by 6 oxygens; two oxygens on each of the two tetrahedra shown, plus 2 waters.

