Superstructure of laihunite-3M ($\square_{0.40}$Fe$^{2+}_{0.80}$Fe$^{3+}_{0.80}$SiO$_4$)

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Abstract

Laihunite, $\square_{0.40}$Fe$^{2+}_{0.80}$Fe$^{3+}_{0.80}$SiO$_4$, is a nonstoichiometric olivine-type mineral and shows superstructures with $2c$ and $3c$ repeats of the basic olivine structure. The superstructure of laihunite-3M was determined in $P2_1/b$ (a = unique axis) symmetry with 1889 reflections collected from a twinned specimen. The cell dimensions are a = 4.805(2) Å, b = 10.189(9) Å, c = 17.403(9) Å and α = 91.0(2)°.

The average structure was used as a starting model for the superstructure. Each equivalent octahedral site for Fe atoms in the average structure differentiates into two or three nonequivalent sites in the superstructure, resulting in translation of the c axis three times that of the average structure of olivine. The site occupancies and bond distances of the octahedral sites for cations in the structure indicate the following distribution: M1A (1.0Fe^{2+}), M1B (0.82Fe^{2+} + 0.18Mg), M2A (0.20Fe^{2+} + 0.80Fe^{3+}), M2B (0.20Fe^{2+} + 0.80Fe^{3+}), VA (vacant), and VB (0.67Fe^{2+}).

Introduction

Laihunite is an iron silicate of olivine structure with a composition of Fe$^{2+}_{0.8}$Fe$^{3+}_{0.8}$SiO$_4$. This mineral was first described from a magnetite ore of Liaoning province, China (Laihunite Research Group of China, 1976), and later from a metamorphic rock (Ying et al., 1981), druses of tuff (Kondoh et al., 1983; Matsuura et al., 1983) and other rock types (Sueno et al., 1985). Laihunite has also been synthesized by oxidation of fayalite in air (Kondoh et al., 1983).

The X-ray Laboratory, Guiyang Institute of Geochemistry (1976), carried out the first X-ray study of laihunite and reported orthorhombic symmetry and space group $Pb2_1m$. Ferrifayalite Research Group (1976) revealed that the mineral was of monoclinic symmetry and space group $P2_1/b$. The research group (1976) and Fu et al. (1979) determined the structure and confirmed that laihunite has a distorted olivine structure with Fe vacancies.

Though Fu et al. (1979) reported that laihunite crystals commonly occur with fine twinning on (001), Shen et al. (1980) and Kitamura et al. (1984) noticed that the apparent twinning of laihunite was better explained by a pseudotwin relation on (001). Shen et al. (1980), Li et al. (1981), and Kitamura et al. (1984) found superlattice reflections along the **c*** axis in laihunite, which indicated a c axis in laihunite double or triple that of the c axis in

olivine. Taking into account these results, Tamada et al. (1983) determined the average structure of laihunite-3M based on the space group of $P2_1/b$ by using the intensities of the main reflections collected by a four-circle diffractometer. Laihunite with different superlattices named according to the Ramsdell system is described in this paper as laihunite-2M (laihunite-$Mab2c$) and laihunite-3M (laihunite-$Mab3c$) (with the modified Gard notation system in parentheses) (Bailey, 1978). Laihunite of possible monoclinic symmetry (Kondoh et al., 1984) is described as laihunite-1PM (laihunite-$PMabc$).

In the present study, the superstructure of laihunite-3M has been determined in order to find the ordering scheme of Fe^{2+}, Fe^{3+}, and vacancies among the octahedral sites in the olivine-type structure and to elucidate the possible relationships between the superstructure and nonstoichiometry in the olivine-type structure.

Average structure of laihunite-3M

The present study on laihunite-3M has been initiated from the average structure (Tamada et al., 1983). The average structure of laihunite-3M (called hereafter the average structure for simplicity) is essentially isomorphous with sarcopside (Moore, 1972), (Fe,Mn)$_3$(PO$_4$)$_2$ (Calvo and Faggiani, 1975), and (Ni,Zn)$_3$(PO$_4$)$_2$ (Nord, 1982). The cell dimensions are a = 4.805(2) Å, b = 10.189(9) Å, c = 5.801(1) Å and α = 91.0(2)°.

The space group of $P2_1/b$ (a = unique axis) has been chosen for the average structure to refer to the setting
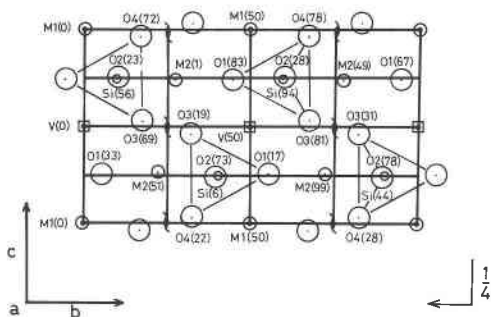
Fig. 1. Average structure of laihunite-3*M* projected on (100) (Tamada et al., 1983). The height of each atom is given by a percentage of the *a* repeat. The SiO_4 tetrahedra are indicated.

Table 2. Chemical and crystallographic data of laihunite-3*M*

Ideal chemical formula	$\square_{0.4}Fe^{2+}_{0.8}Fe^{3+}_{0.8}SiO_4$.*
Bulk chemical formula	$Fe^{2+}_{0.53}Mg_{0.03}Fe^{3+}_{1.03}Si_{0.94}O_4$**
ρ_{obs} (g·cm⁻³)	3.92†
ρ_{calc} (g·cm⁻³)	4.11
Space group	$P2_1/b$ (unique axis = *a*)
Z	12
μ(MoKα) (cm⁻¹)	81.51
Cell parameters	
a	4.805(2) Å
b	10.189(9) Å
c	17.403(9) Å
α	91.0(2)°
V	851.7(9) Å³

* An ideal chemical formula of $Fe^{2+}_{0.5}Fe^{3+}_{1.0}SiO_4$ was first assumed for laihunite by the X-ray laboratory, Guiyang Institute of Geochemistry (1976). However, the analysis of the average structure of laihunite-3*M* (Tamada et al., 1983) has shown that the ideal chemical formula is $\square_{0.4}Fe^{2+}_{0.8}Fe^{3+}_{0.8}SiO_4$.
** Kitamura et al. (1984).
† Laihunite Research Group (1976).

chosen by the Chinese groups (e.g., Fu et al., 1979), which differs from the traditional setting of the olivine structure (e.g., Birle et al., 1968) in the position of the origin. The origin of the unit cell of the average structure corresponds to (½,½,½) in the olivine unit cell. Because of symmetry reduction in the average structure in comparison with olivine, the notation of sites in the average structure has been chosen differently from that in olivine after the Chinese researchers (Fig. 1) (Tamada et al., 1983). In the average structure, the V and M(1) sites correspond to the M(1) site in the olivine structure. The M(2) and T sites are same in both structures, though the O(1) and O(2) sites of the average structure correspond to O(2) and O(1) of olivine, respectively. Both O(3) and O(4) sites are derived from O(3) of the olivine structure by symmetry reduction.

The average structure obtained by Tamada et al. (1983) shows that the V and M(1) sites have 0.22 and 0.94 Fe atoms, respectively, whereas the M(2) site is fully occupied by Fe (Table 1). Therefore, the chemical composition of laihunite estimated from the average structure is $\square_{0.42}(Fe^{2+},Fe^{3+})_{1.58}SiO_4$. If the charge neutrality in the chemical formula and the small amount of Mg present (0.03 in Table 2) are taken into account, the composition becomes $\square_{0.40}Fe^{2+}_{0.77}Mg_{0.03}Fe^{3+}_{0.80}SiO_4$. The composition is in good agreement with that obtained by wet-chemical analysis (Zhang et al., 1981). The bond distances of the octahedral sites indicate the occupancies of Fe^{2+}, Mg, and

Fe^{3+} ions as follows, M(1) ($0.91Fe^{2+}$ + 0.06Mg), M(2) ($0.20Fe^{2+}$ + $0.80Fe^{3+}$), and V ($0.22Fe^{2+}$).

EXPERIMENTAL METHOD

The specimen of laihunite-3*M* is the same one that was used in the previous study on the average structure (Tamada et al., 1983). The apparent bulk chemical composition of the specimen was determined by electron probe to be $Fe^{2+}_{0.53}Mg_{0.03}Fe^{3+}_{1.03}Si_{0.94}O_4$, but this value was obtained for a mixture of magnetite and laihunite (Kitamura et al., 1984). The determination of the average structure has shown that the composition of the laihunite is $\square_{0.40}(Fe^{2+},Fe^{3+})_{1.60}SiO_4$, neglecting the small amount of Mg in the structure. This composition has been used in the present study.

The space group of the superstructure is $P2_1/b$ (*a* = unique) (Kitamura et al., 1984), the same as that of the average structure. The chemical and crystallographic data of laihunite-3*M* are shown in Table 2.

The specimen shows a pseudotwin relation as described in the previous paper (Tamada et al., 1983), and most reflections from the two pseudotwin individuals were completely or partly superimposed upon each other. The intensities of the reflections were counted as one reflection using a four-circle automatic diffractometer. The experimental conditions in collecting the intensity data of the main and superlattice reflections are given in Table 3. Among the observed 1889 reflections, 1751 reflections are stronger than 3σ, where σ represents the standard deviation of the measured intensity. These intensities were corrected for Lorentz and polarization effects, but no correction was made for absorption because of the small size of the specimen and the complexity in absorption caused by the pseudotwin relation. In the process of the structure analysis, the intensities of all the reflections were divided into two sets of intensities corresponding to the twin individuals where the ratio of the intensities of the pseudotwin individuals was assumed to be the ratio of the calculated intensities in the previous cycle.

Atomic scattering factors and dispersion corrections for neutral Fe, Si, and O atoms were taken from the *International Tables for X-ray Crystallography*, Volume IV (1974). No distinction between Fe^{2+} and Fe^{3+} ions in the atomic scattering factors was made. The Mg content was fixed to be zero throughout the analysis, because of the very limited amount. The computer program

Table 1. Occupancies, atomic coordinates, and temperature factors of the average structure of laihunite-3*M* (Tamada et al., 1983)

Site	n*	Occupancy	*x*	*y*	*z*	B_{eq} (Å²)
M1	2	Fe 0.938(4)	0.0	0.0	0.0	0.98
M2	4	Fe 1.0	0.0048(2)	0.2737(1)	0.7421(2)	0.73
T	4	Si 1.004(5)	0.0595(3)	0.4041(2)	0.2491(4)	0.61
O1	4		0.3266(10)	0.0543(5)	0.2566(9)	0.86
O2	4		0.2239(9)	0.1047(5)	0.7544(10)	0.88
O3	4		0.6964(11)	0.1771(5)	0.5339(9)	1.10
O4	4		0.2167(9)	0.3272(4)	0.0327(8)	0.38
V	2	Fe 0.222(4)	0.5	0.5	0.5	1.67

* *n* = multiplicity of the sites.

Table 3. Experimental conditions in collecting the intensity data of laihunite-3*M*

Specimen used (mm)	rectangular 0.15 × 0.17 × 0.25
Monochromator	graphite
Radiation	X-ray (MoKα)
Collimator (mm)	1.0
2θ range	2θ ≤ 80°
Scanning speed	2°/min
Maximum repetition of scanning	3
Scanning width	(1.5 + 0.5 tan θ)°
Collected reflections	1889
Used reflections	1889 (3277)*
Diffractometer	RIGAKU 5UD

* The superposed intensities of original 1889 reflections were divided into 3277 reflections for the twin individual.

Fig. 2. Crystal structure of laihunite-3*M* projected on (100). The arrows indicate the shifts of atoms parallel to (100) from the average structure (Fig. 1). The length of the arrow indicates ten times the real shift. The shifts along the **a** axis are shown by the number (×10⁻³ Å) beside the arrows.

RFINE was used for the refinement after minor changes for twinning (Tamada et al., 1983). The program FOURIER (written by Iitaka and Matsusaki) was also used for the difference Fourier synthesis.

Structure determination

The average structure determined by Tamada et al. (1983) (Table 1) was used as a starting model for the superstructure determination. The notations of the sites in the superstructure are, in principle, the same as those in the average structure. Because the *c* axis of the superstructure cell is three times larger than the *c* axis of the average cell, each of the general sites in the average structure differentiates into three crystallographically different A, B, and C sites, and each of the special V and M(1) sites are converted into only two A and B sites (Fig. 2).

Since the average structure has the octahedral V sites, which include vacancies of cations, it is most likely that the superstructure takes place by ordering of the vacancies between the V sites, or VA and VB sites. At the initial stage of the analysis, two most possible models with different distributions of Fe vacancies, model I and model II, were examined by using the reflections only at low Bragg angles, because the scattering factors of the sites with different vacancies strongly affect the intensities at low Bragg angles. In model I, all Fe atoms at the V sites in the average structure are concentrated into the VA site, while, in model II, they are concentrated into the VB site. In both models, all the other parameters were fixed to be the same as those in the average structure; for example, the Fe occupancies in the M1A and M1B sites were kept at 0.94 as in the average structure.

Only 74 superstructure reflections of low Bragg angles (2θ < 30°), which were converted to 139 reflections of a twin individual, were used to check the two models by using the least-squares refinement and difference Fourier methods. The Fe occupancies at the VA, VB, M1A, and M1B sites were refined in both models without changing the total Fe contents at the V and M1 sites of the average structure. Model II showed occupancies of 1.02 and 0.90 for the M1A and M1B sites, respectively, and 0.01 and 0.64 for the VA and VB sites, respectively. However, the Fe occupancies at the VA and VB sites converged to 0.43 and −0.20, respectively, in model I. Thus, model II was adopted for further refinements (Shen et al., 1982).

Refinement procedure

Determination of the atomic positions in the superstructure was first performed with heavy Fe atoms and then with Si and light oxygen atoms. The refl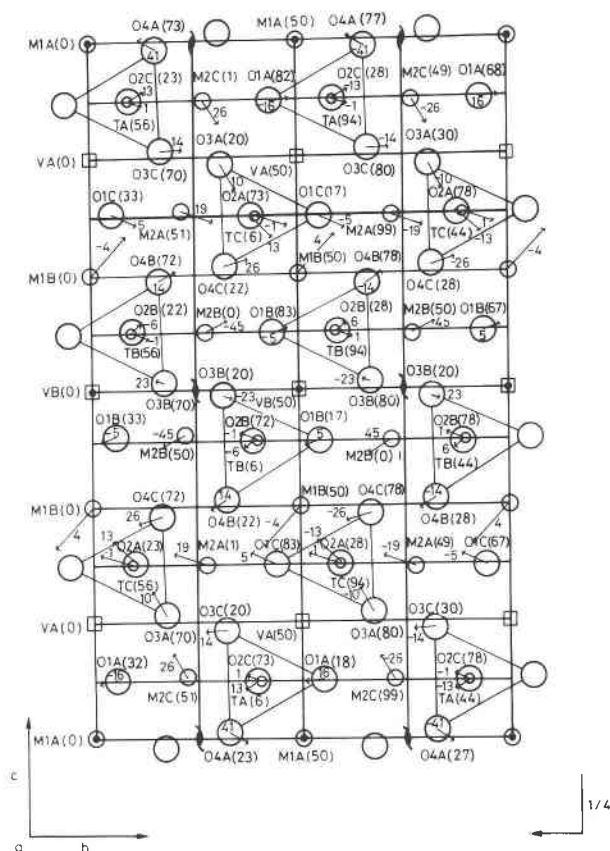ections of low Bragg angles were initially used and those of higher Bragg angles were carefully added with the progress of the refinements as follows.

The atomic positions of only the M sites were first refined starting from the average model, by using the main and superstructure reflections with only 2θ < 40°. All the parameters of the other atoms were kept as in the average structure and the temperature factor of 0.5 was used for all atoms. The reflections with 2θ < 60° were further added in the refinement, and the atomic positions of the M and T sites were separately refined. For the final stage the 2θ range was extended to 80°. After the refinement of the scale factor and the atomic positions of the M sites, the atomic positions of the T sites and of oxygen atoms were refined. The isotropic temperature factors of the cations and those of the anions were successively refined. At this stage, complete ordering of Fe atoms was obtained at the V and M1 sites with 0.01 and 0.67 in the VA and VB sites, respectively, and 1.00 and 0.91 in M1A and M1B, respectively. The difference Fourier sections showed significant residual electron densities at the cation sites, indicating anisotropic temperature factors for cations. Thus, the isotropic temperature factors for cations were switched to the anisotropic ones, and they were refined until no significant residual electron densities were observed around the cation sites in the difference Fourier map.

The final *R* and R_w values were converged to 0.116 and 0.110, respectively, for all 1889 reflections. Tables 4 and 5 report the

Table 4a. Final occupancies, atomic coordinates, and isotropic temperature factors ($Å^2$) of laihunite-3M

Site	n^*	Occupancy	x	y	z	B_{eq}
M1A	2	1.00	0.0	0.0	0.0	0.63
M1B	4	0.907(4)	0.0008(5)	0.0089(2)	0.3278(1)	0.65
M2A	4	1.00	0.0088(5)	0.2660(2)	0.2488(1)	0.37
M2B	4	1.00	−0.0045(5)	0.2788(2)	0.5823(1)	0.53
M2C	4	1.00	0.0102(5)	0.2770(2)	0.9109(1)	0.73
TA	4	1.00	0.0597(8)	0.4008(4)	0.0837(3)	0.63
TB	4	1.00	0.0594(8)	0.4000(4)	0.4174(3)	0.42
TC	4	1.00	0.0593(8)	0.4118(3)	0.7483(3)	0.40
O1A	4	1.00	0.323(2)	0.0501(9)	0.0851(7)	1.06
O1B	4	1.00	0.326(2)	0.0508(8)	0.4181(6)	0.89
O1C	4	1.00	0.328(2)	0.0603(9)	0.7506(7)	0.46
O2A	4	1.00	0.227(2)	0.0993(8)	0.2545(7)	0.38
O2B	4	1.00	0.223(2)	0.1065(8)	0.5857(6)	0.98
O2C	4	1.00	0.227(2)	0.1079(9)	0.9193(7)	0.76
O3A	4	1.00	0.699(2)	0.1738(9)	0.1815(7)	0.71
O3B	4	1.00	0.701(2)	0.1752(8)	0.5116(6)	0.78
O3C	4	1.00	0.699(2)	0.1820(9)	0.8448(6)	0.61
O4A	4	1.00	0.225(2)	0.3313(8)	0.0094(7)	0.58
O4B	4	1.00	0.220(2)	0.3236(8)	0.3429(6)	0.72
O4C	4	1.00	0.222(2)	0.3329(8)	0.6785(7)	0.66
VA	4	0.00	0.5	0.5	0.1667	0.50
VB	4	0.666(8)	0.5	0.5	0.5	1.40

* n = multiplicity of sites.

Table 4b. Anisotropic temperature factors of cations of laihunite-3M ($\times 10^{-4}$)

Site	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
M1A	3(4)	23(1)	8(1)	3(2)	1(2)	6(1)
M1B	31(4)	15(1)	9(1)	−6(2)	−2(1)	−2(0)
M2A	3(3)	6(1)	7(0)	2(1)	−1(1)	−1(0)
M2B	6(3)	21(1)	5(0)	10(2)	−2(1)	0(0)
M2C	48(4)	19(1)	8(0)	2(2)	4(1)	3(0)
TA	23(7)	20(2)	7(1)	−2(3)	1(2)	−1(1)
TB	−13(6)	18(2)	6(1)	−1(3)	−4(2)	2(1)
TC	1(1)	8(1)	7(1)	5(2)	2(2)	1(1)

final atomic coordinates, temperature factors, interatomic distances, and other important structure features.[1]

DISCUSSIONS OF THE STRUCTURE

The superstructure of laihunite-3M is projected on (100) (Fig. 2). Fe atoms preferentially occupy the VB site and leave the VA site completely vacant. The shift of each atom from the original position in the average structure is pointed out by an arrow and by a number beside it in Figure 2. The length of the arrow exaggerates the real shift by a factor of 10 and the adjacent number gives the shift interval along the a axis (multiplied by 10^{-3} Å). The atoms in the upper half of the projection tend to shift to the right, and those in the lower half to the left. The ordering of Fe atoms in the VA and VB sites and the shift of atoms result in a modulated structure with a 3c repeat.

The interatomic distances (Table 5) are calculated by the program UMBADTEA. The interatomic distances range from 1.604 to 1.687 Å for T–O, 2.017 to 2.288 Å for M1–O, 1.919 to 2.252 Å for M2–O, and 2.119 to 2.357 Å for V–O. The mean M1–O and M2–O distances are 2.164 and 2.046 Å, respectively, which are close to the sums of the ionic radii of Fe^{2+} and O^{2-}, 2.180, and of Fe^{3+} and O^{2-}, 2.045 Å. Therefore, the major parts of the M1 and M2 sites are occupied by Fe^{2+} and Fe^{3+} ions, respectively. The mean VB–O distance, 2.200 Å, is slightly greater than the mean M1–O distance indicating that the Fe atoms at the VB sites are divalent.

The small amount of vacancies at the M1 site in the average structure has been concentrated in the M1B site, and the M1A site is completely filled with Fe atoms. If the neglected Mg atoms occupy this M1B site as suggested by Tamada et al. (1983), the apparent deficiency can be nearly compensated because of the difference in scattering power between Fe and Mg atoms. Thus, in this laihunite-3M, the final site occupancies are estimated to be M1A (1.00Fe^{2+}), M1B (0.87 Fe^{2+} + 0.08Mg), M2A (0.20Fe^{2+} + 0.80Fe^{3+}), M2B (0.20Fe^{2+} + 0.80Fe^{3+}), M2C (0.20Fe^{2+} + 0.80Fe^{3+}), VA (vacant) and VB (0.67 Fe^{2+}). The total composition is $\Box_{0.40}Fe^{2+}_{0.77}Mg^{2+}_{0.03}Fe^{3+}_{0.80}SiO_4$.

The structure of laihunite-3M apparently indicates that laihunite is adaptable to nonstoichiometry because of partial occupancy or vacancy of the octahedral M1 and V sites. However, existence of the superlattice structures of natural laihunite with only c, 2c, and 3c periods strongly suggests that the ordered distribution of vacancies among the M1 and V sites takes place so as to result in the superlattice modulation along the c axis. If the M2 sites are completely occupied by Fe^{3+} ions, all the V sites must become vacant. This results in the most Fe^{3+}-rich composition of laihunite, $\Box_{0.5}Fe^{2+}_{0.5}Fe^{3+}_{1.0}SiO_4$ with the basic translation, laihunite-1M.

Apparent wide ranges of the Fe^{3+}/Fe^{2+} ratio in natural "ferrifayalite" have been reported to be due to an intergrowth of laihunite and fayalite with domain sizes of about 5 μm or more (Schaefer, 1983, 1985). These results indicate the existence of a miscibility gap between fayalite ($Fe^{2+}_2SiO_4$) and laihunite with endmember composition ($Fe^{2+}_{0.5}Fe^{3+}_{1.0}SiO_4$). Furthermore, laihunite itself usually occurs in domain textures with magnetite at the domain boundaries with thicknesses of a few nanometers (Kitamura et al., 1984). Thus, the apparent chemical compositions of laihunite are for the mixtures of laihunite and magnetite, even if the fayalite domains are excluded. Oxidized products of fayalite in air indicate that laihunite-2M occurs in areas of higher oxidation condition than laihunite-3M (Kondoh et al., 1983, 1985). Thus, laihunite-2M probably has greater Fe^{3+} content and more vacancies than does laihunite-3M.

The occurrence of limited superlattice structures of laihunite, the possible relationship between the superstructure and composition and the observations of fine intergrowths of laihunite and fayalite indicate the existence of

Table 5. Interatomic distances (Å) and angles (°) of laihunite-3M

TA tetrahedron

TA–O1A	1.621(1)	O1A–O2C	2.696(1)	113.48(2)
–O2C	1.604(1)	O1A–O3C	2.681(4)	109.8(1)
–O3C	1.657(2)	O1A–O4A	2.580(4)	103.4(1)
–O4A	1.666(2)	O2C–O3C	2.728(2)	113.53(4)
		O2C–O4A	2.764(1)	115.36(5)
		O3C–O4A	2.547(1)	100.07(4)
Mean	1.637(1)		2.666(1)	109.27(2)

TB tetrahedron

TB–O1B	1.633(1)	O1B–O2B	2.698(1)	112.11(2)
–O2B	1.620(1)	O1B–O3B	2.629(4)	108.1(1)
–O3B	1.615(2)	O1B–O4B	2.648(4)	105.8(1)
–O4B	1.687(2)	O2B–O3B	2.732(1)	115.25(4)
		O2B–O4B	2.779(1)	114.36(5)
		O3B–O4B	2.534(1)	100.20(4)
Mean	1.639(1)		2.670(1)	109.30(2)

TC tetrahedron

TC–O1C	1.608(1)	O1C–O2A	2.690(1)	113.78(1)
–O2A	1.604(1)	O1C–O3A	2.684(4)	110.7(1)
–O3A	1.655(2)	O1C–O4C	2.626(4)	107.8(1)
–O4C	1.644(2)	O2A–O3A	2.715(2)	112.83(4)
		O2A–O4C	2.736(1)	114.77(5)
		O3A–O4C	2.442(1)	95.54(4)
Mean	1.628(1)		2.649(1)	109.24(2)

M1A octahedron

M1A–O1A	2.201(1) × 2	O1A–O2C	2.993(2) × 2	88.08(5) × 2
–O2C	2.103(3) × 2	O1A–O2C	3.094(1) × 2	91.92(5) × 2
–O4A	2.176(1) × 2	O1A–O4A	3.535(2) × 2	107.8(1) × 2
		O1A–O4A	2.580(4) × 2	72.2(1) × 2
		O2C–O4A	2.775(1) × 2	80.9(1) × 2
		O2C–O4A	3.257(5) × 2	99.1(1) × 2
Mean	2.160(1)		3.039(1)	90.00(3)

M1B octahedron

M1B–O1B	2.288(2)	O1B–O2A	2.936(2)	85.75(6)
–O1C	2.145(1)	O1B–O2B	2.084(1)	88.88(4)
–O2A	2.017(3)	O1B–O4B	2.648(4)	72.5(1)
–O2B	2.112(3)	O1B–O4C	3.564(2)	103.7(1)
–O4B	2.191(1)	O1C–O2A	3.120(1)	97.06(6)
–O4C	2.243(2)	O1C–O2B	2.960(2)	88.09(4)
		O1C–O4B	3.556(2)	110.2(1)
		O1C–O4C	2.626(4)	73.5(2)
		O2A–O4B	3.237(5)	100.5(1)
		O2A–O4C	2.771(1)	81.0(1)
		O2B–O4B	2.805(1)	81.3(1)
		O2B–O4C	3.257(5)	96.8(1)
Mean	2.166(1)		3.047(1)	89.94(3)

M2A octahedron

M2A–O1C	1.972(1)	O1C–O3A	3.002(4)	94.7(1)
–O2A	1.999(1)	O1C–O3C	2.710(3)	87.4(2)
–O3A	2.107(2)	O1C–O4B	2.767(3)	88.2(2)
–O3C	1.950(2)	O1C–O4C	3.109(5)	98.3(1)
–O4B	2.004(2)	O2A–O3A	2.943(2)	91.5(1)
–O4C	2.135(2)	O2A–O3C	2.847(5)	92.3(1)
		O2A–O4B	2.732(5)	86.1(1)
		O2A–O4C	2.771(1)	84.1(1)
		O3A–O3C	2.860(1)	89.55(6)
		O3A–O4C	2.442(1)	70.30(4)
		O3C–O4B	3.267(2)	111.45(3)
		O4B–O4C	2.893(1)	88.63(6)
Mean	2.028(1)		2.862(1)	90.21(3)

Table 5—*Continued*

M2B octahedron

M2B–O1B	1.919(1)	O1B–O3B	2.728(3)	89.0(2)
–O2B	2.069(1)	O1B–O3B	3.087(4)	98.9(1)
–O3B	1.973(1)	O1B–O4B	3.134(5)	100.9(1)
–O3B	2.141(2)	O1B–O4B	2.816(3)	89.9(2)
–O4B	2.143(2)	O2B–O3B	2.821(5)	88.5(2)
–O4C	2.064(2)	O2B–O3B	2.909(1)	87.4(1)
		O2B–O4B	2.805(1)	83.5(1)
		O2B–O4C	2.793(5)	85.0(1)
		O3B–O3B	2.878(1)	88.70(6)
		O3B–O4B	2.534(1)	72.52(4)
		O3B–O4C	3.310(2)	110.12(3)
		O4B–O4C	2.915(4)	87.65(6)
Mean	2.052(1)		2.894(1)	90.17(3)

M2C octahedron

M2C–O1A	1.978(1)	O1A–O3A	2.752(3)	89.9(2)
–O2C	2.019(1)	O1A–O3C	3.030(4)	95.6(1)
–O3A	1.919(2)	O1A–O4A	2.822(3)	88.4(2)
–O3C	2.111(2)	O1A–O4A	3.211(5)	98.5(1)
–O4A	2.067(2)	O2C–O3A	2.859(5)	93.0(2)
–O4A	2.252(2)	O2C–O3C	2.950(2)	91.2(1)
		O2C–O4A	2.741(5)	84.3(1)
		O2C–O4A	2.775(1)	80.9(1)
		O3A–O3C	2.854(1)	90.05(6)
		O3A–O4A	3.323(2)	112.86(3)
		O3C–O4A	2.547(1)	71.35(4)
		O4A–O4A	2.934(1)	85.45(6)
Mean	2.058(1)		2.900(1)	90.12(3)

VA octahedron

VA–O1A	2.171(1)	O1A–O2A	3.017(2)	89.38(5)
–O1C	2.227(2)	O1A–O2C	2.696(1)	91.76(5)
–O2A	2.119(3)	O1A–O3A	2.752(3)	109.6(1)
–O2C	2.139(3)	O1A–O3C	2.681(4)	72.5(1)
–O3A	2.299(1)	O1C–O2A	2.690(1)	91.74(1)
–O3C	2.357(1)	O1C–O2C	3.007(2)	87.03(5)
		O1C–O3A	2.684(4)	72.7(1)
		O1C–O3C	2.710(2)	105.2(1)
		O2A–O3A	2.715(2)	83.5(1)
		O2A–O3C	3.340(6)	96.4(1)
		O2C–O3A	3.357(6)	98.2(1)
		O2C–O3C	2.728(2)	81.9(1)
Mean	2.219(1)		2.865(1)	89.99(3)

VB octahedron

VB–O1B	2.185(1) × 2	O1B–O2B	3.003(2) × 2	88.47(5) × 2
–O2B	2.119(3) × 2	O1B–O2B	3.084(1) × 2	91.53(5) × 2
–O3B	2.297(1) × 2	O1B–O3B	2.629(4) × 2	71.8(1) × 2
		O1B–O3B	3.631(2) × 2	108.2(1) × 2
		O2B–O3B	3.327(6) × 2	97.7(1) × 2
		O2B–O3B	2.909(1) × 2	82.3(1) × 2
Mean	2.200(1)		3.097(1)	90.00(3)

some immiscibility between fayalite and laihunite in nature.

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