Fe-deficient olivine structure type minerals from Colorado, U. S. A. and Japan

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Abstract

Fe-deficient nonstoichiometric olivine related minerals, $\square_{x/2}\text{Fe}_x^{3+}\text{Fe}_{2-(3/2)x}^{2+}\text{SiO}_4$ have been identified in samples from many localities in Colorado, U.S.A. and in Japan, where $\square$ denotes vacancies in the structure. It is possible to classify these Fe-deficient olivine minerals into several crystallographically-distinct species. Laihunite has monoclinic symmetry and this include two superstructures, the lai_hunite-2*M* and lai_hunite-3*M* types in Ramsdell notation. Lai_hunite associated with the lai_hunite-3*M* superstructure is most commonly found in rock types such as metamorphic rock, migmatite, pegmatite and is, in many cases, accompanied by magnetite. Lai_hunite associated with the lai_hunite-2*M* superstructure was found in dacite and is accompanied by hematite. Fe-deficient manganoan olivine occurs in pegmatites, has orthorhombic symmetry, and is termed as ferri-knebelite in this study in order to distinguish it from other related materials. Based on these results, it can be said that the Fe-deficient olivine minerals are fairly common in many rock types and are widespread in their occurrence.

Introduction

Laihunite is a ferric-iron bearing silicate mineral found in banded iron formations in Precambrian metamorphic rocks (Wang, 1982) and in migmatite in China (Laihunite Research Group, 1976). The ideal chemical composition is reported as $\text{Fe}_{1.6}^{3+}\text{Fe}_{0.5}^{2+}\text{SiO}_4$ (Laihunite Research Group, 1976). The basic crystal structure can be described as distorted fayalite; excess static charges caused by the substitution of Fe^{3+} for Fe^{2+} are compensated by generating vacancies at M1 octahedral sites which account for the Fe-deficiency in the $\text{M}_2^{2+}\text{SiO}_4$ composition of olivine (Fu et al., 1982, Tamada et al., 1983). Therefore, the general formula of the ferric iron bearing olivine minerals can be written as $\square_{x/2}\text{Fe}_x^{3+}\text{Fe}_{2-(3/2)x}^{2+}\text{SiO}_4$ to complete the static charge balancing in the structure, where $\square$ denotes the vacancies.

The thermodynamic stability of lai_hunite was studied by Wang (1982), who concluded that lai_hunite is stable under unusually high pressure (higher than 15kb), a temperature on the order of 600–700°C, and a relatively high oxygen fugacity. According to the above results, Wang has proposed that high pressure and high oxygen

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fugacity are mutually exclusive in common geological environments, and that this may be a reason for the rare occurrence of laihunite. However, his conclusion was based on the equilibrium among the coexisting end-member compositions of ferrosilite(Fs), fayalite(Fa) and quartz(Qtz) assemblage ($Fs = Fa + Qtz$). However, the ferrosilite includes about 3 wt.% of Mg which may greatly decrease the stability pressure of this system. Moreover, there is a possibility that laihunite is not a primary product which occurred with the ferrosilite but a secondary product resulting from the oxidation of fayalite at a lower temperature and pressure condition. At least, it can be said that laihunite can occur at normal pressure according to the study of laihunite synthesis (Kondoh *et al.*, 1985).

Schaefer (1983) studied Mössbauer spectra of several dark coloured to black fayalite specimens from various localities and reported that some of these samples contained significant amounts of Fe^{3+} , and that the Fe^{3+} ion was not contained in iron oxide inclusions in the fayalite samples. The Fe^{3+}/Fe^{2+} ratios of these samples are distributed in a broad range from 0.85 to 0.19, but are much less than that of ferrifayalite (laihunite), 1.38. However, this broad range of Fe^{3+}/Fe^{2+} ratios cannot be directly considered in connection with a continuous solid solution between fayalite and laihunite because there is a possibility that this broad distribution of Fe^{3+}/Fe^{2+} ratios may originate from a simple mixture of fayalite and laihunite on an electron microscopic scale. Therefore, it is important to investigate the possible ranges of solid solution between the two end-member phases and the possible occurrence of Fe-deficient olivine minerals from various localities.

Experimental

Samples of dark coloured to black olivines (originally labeled as "fayalite") were kindly provided for this study from several museums¹, and some specimens were collected by ourselves from rocks in many different occurrences. Several small opaque mineral tips (0.1 mm) were selected from each "fayalite" sample for single crystal X-ray study, and larger pieces were polished for EPMA analysis and for reflected light microscopy. Precession photographs for $0k1$ and $hk0$ reciprocal-lattice planes were taken for each selected mineral tip. The polished specimens were observed carefully under a reflected light microscope using polarized light and then each portion with a different reflectivity in the polished specimens was analyzed for its chemical composition using a computer-controlled JEOL-50A Electron Microprobe Analyzer at the Chemical Analysis Center, University of Tsukuba.

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¹The specimens were supplied by courtesy of U.S. National Museum, Department of Mineral Sciences (12 specimens): The American Museum of Natural History (9 specimens): The University of Tokyo (4 specimens): The Geological Survey of Canada (7 specimens).

TABLE 1. Cell parameters of fayalite and Fe-deficient olivine type minerals

Mineral locality	Fayalite ¹ synthetic	Laihunite* Cheyenne Canyon	Laihunite* Naegi	Laihunite* Kamitaga	Laihunite ² China	Ferri-knebelite ³ Suisho-yama
Occurrence space group	<i>Pbnm</i>	pegmatite <i>P2₁/b</i>	pegmatite <i>P2₁/b</i>	dacite <i>P2₁/b</i>	iron formation <i>P2₁/b</i>	pegmatite <i>Pbnm</i>
a axis(Å)	4.8211(5)	4.82	4.83	4.81	4.805(2)	4.831(1)
b axis(Å)	10.4779(7)	10.22	10.24	10.27	10.189(9)	10.310(2)
c axis(Å)	6.0889(5)	5.81	5.82	5.90	5.801(3)	5.909(1)
α angle(°)	90.0	91.3	91.1	91.2	91.0(2)	90.0
Volume(Å ³)	307.58(8)	286.1	287.8	291.4	283.9(3)	294.3(1)

* Present study. Cell parameters measured on precession photographs.

1 Schwab and Künster (1977).

2 Tamada et al. (1983).

3 Matsuura et al. (1984).

TABLE 2. EPMA chemical analysis data

Mineral locality	Laihunite* Cheyenne Canyon, USA	Laihunite* Naegi, Japan	Laihunite* Kamitaga, Japan	Laihunite ² China	Ferri-knebelite* ³ Suisho-yama, Japan
SiO ₂	29.21	31.35	32.48	31.07	30.83
FeO ¹	61.53	58.90	55.35	62.43	49.54
MnO	3.68	4.31	3.00	—	12.47
MgO	0.03	0.73	5.91	0.87	—
CaO	—	0.05	—	0.21	—
Total	94.42	95.34	96.74	95.63	92.84

1 Total iron as FeO.

2 Bulk chemical formula (Laihunite Research Group, 1976): $\text{Fe}_{1.0}^{3+}\text{Fe}_{0.58}^{2+}\text{Mg}_{0.03}\text{Si}_{0.96}\text{O}_4$;
Chemical formula defined by site occupancy refinement (Tamada et al., 1983):

$\square_{0.40}\text{Fe}_{0.80}^{2+}\text{Fe}_{0.80}^{3+}\text{SiO}_4$.

3 Chemical formula defined by EPMA and site occupancy refinement (Matsuura and Sueno, 1984): $\square_{0.31}\text{Fe}_{0.62}^{3+}\text{Fe}_{0.72}^{2+}\text{Mn}_{0.35}\text{SiO}_4$.

* Present study.

The mineralogical data of the Fe-deficient minerals observed in the present study from the four typical dark coloured “fayalite” specimens are listed with those of fayalite and original laihunite from China for comparison:

Cell parameters and cell volumes in Table 1; EPMA chemical analysis data in Table 2; *0k1* precession photographs in Figure 1; reflected light photomicrographs of polished specimens in Figure 2.

Classification and nomenclature of Fe-deficient minerals

On the systematic examination of the “fayalite” samples, we found laihunite

FIG. 1. *0kl* precession photographs of Fe-deficient olivine type minerals. Abbreviations: L=laihunite, F=fayalite, H=hematite.

(a) laihunite (from pegmatite at Cheyenne Mountain, Colorado, U.S.A.). (b) laihunite (from dacite lava at Kamitaga, Japan). Small arrows show the satellites at $c^{*'} = 1/2c^*$ position. (c) laihunite (from pegmatite at Naegi, Japan). (d) ferri-knebelite (from pegmatite at Suisho-yama, Japan). The photographs at upper right corner of (c) and (d) are the enlarged views of the 063 reflections (circled).

and related Fe-deficient olivine type minerals in the samples from many different occurrences, not only in metamorphic rocks and migmatite in which the original laihunite was found, but also in vugs in granite (Eckel, 1961), in pegmatite (Sueno *et al.*, 1984), and in druses of hypersthene dacite (Matsuura *et al.*, 1983), although these laihunite crystals are, in most cases, associated with fayalite and iron oxides such as magnetite and hematite. The estimated Fe^{3+} contents (x) in a formula of Fe-deficient olivine, $\square_{x/2}\text{Fe}_x^{3+}\text{Fe}_{2(3/2)-x}^{2+}\text{SiO}_4$, are larger than 0.62 for the all observed Fe-deficient phases, as discussed in a later part of this paper. Based on the above results, we believe that Fe-deficient olivine is a fairly common mineral in many geological occurrences. A reason for the relatively recent discovery of laihunite in “fayalite” specimens probably is a result of its optical properties. For example, laihunite is almost opaque in normal thin section and becomes translucent in a section thinner than 5–10 microns; therefore, it is easy to mistake this mineral for an opaque metal oxide or a sulfide. Another reason is the difficulty of distinguishing it from olivine in powder diffraction experiments, although the laihunite powder diffraction

FIG. 2. Reflected light photomicrographs of polished specimens. Abbreviations: L= laihunite, K=ferri-knebelite, F=fayalite, M=magnetite, A=amphibole, Q=quartz, H=hematite + amorphous silica.

(a) Cheyenne Canyon, U.S.A.; (a') Cheyenne Mountain, U.S.A.; (b) Kamitaga, Japan; (c) Naegi, Japan; (d) Suisho-yama, Japan.

pattern contains some extra peaks and the peaks are usually broader than those of fayalite (Laihunite Research Group, 1976)

In this study we found several types of crystallographically-distinct Fe-deficient minerals. Most of the mineral specimens showed monoclinic space group patterns in precession photographs, and these minerals can be classified as the laihunite species based on space group and EPMA data. However, one specimen showed orthorhombic symmetry with the space group *Pbnm*, the same as olivine, despite its containing a large amount of Fe^{3+} . It appears that the description and the definition of the Fe-deficient minerals in previous reports are incomplete, as discussed below.

In 1962, Ginzburg *et al.* first reported an olivine phase occurring in pegmatite that contained 32.19 wt% Fe_2O_3 , 26.77 wt% FeO , and 7.96 wt% MnO ; this was named ferrifayalite and described as an alteration product of manganoan fayalite although the homogeneity of the material was doubtful, and the name premature (Embrey and Fuller, 1980). Talasskite was also reported in 1934 by Nikitin (Deer *et al.*, 1962), but this mineral was transparent and different from the other Fe-deficient olivine minerals, and to our knowledge has not been studied since, although Fu *et al.* (1982) discussed the interrelations among fayalite–talasskite–laihunite. Then, the Laihunite Research Group (1976) studied an Fe-deficient mineral, $\text{Fe}^{3+}\text{Fe}_{0.5}^{2+}\text{SiO}_4$, occurring in magnetite deposits and named laihunite. The mineral was described as orthorhombic, and the X-ray Laboratory, Guiyang Institute of Geochemistry (1976), determined a preliminary crystal structure based on the space group *Pb2₁m* using Weissenberg photographs. However, the Ferrifayalite Research Group (1976) also studied an Fe-deficient olivine mineral with the same chemical composition $\text{Fe}^{3+}\text{Fe}_{0.5}^{2+}\text{SiO}_4$ under the name “ferrifayalite”, and they reported that the mineral was monoclinic with the space group *P2₁/b*. Fleischer *et al.* (1978) reviewed these studies and concluded that ferrifayalite has *P2₁/b* space group and is identical to laihunite. The Laihunite Research Group (1982) later reported that laihunite also has monoclinic symmetry and that it always shows domain-twinning.

Fu *et al.* (1982) and Tamada *et al.* (1983) succeeded in refining the crystal structure of laihunite based on the space group *P2₁/b*. However, in a site-occupancy refinement of a laihunite specimen with the bulk composition $\text{Fe}_{0.58}^{2+}\text{Mg}_{0.03}^{2+}\text{Fe}_{1.00}^{3+}\text{Si}_{0.96}\text{O}_4$ (Laihunite Research Group, 1976), Tamada *et al.* found that this mineral contains 0.40 vacancies, and they concluded that the chemical formula of this laihunite proper is $\square_{0.40}\text{Fe}_{0.80}^{2+}\text{Fe}_{0.80}^{3+}\text{SiO}_4$ where the Mg content was neglected in the refinement because the amount is small. This result is consistent with the electron microscope observation on Chinese laihunite by Kitamura *et al.* (1984) who described that the Chinese laihunite material is a mixture of laihunite and fibrous magnetite on the electron microscopic scale with the volume ratio of about 6:1, respectively. Therefore, bulk chemical composition of a laihunite specimen does not directly represent chemi-

cal composition of laihunite proper. They also found that the twinning observed in this mineral is pseudo-twinning with the composition plane of the twin individual differing from (001) of each individual by a small angle of about 0.3° .

In the previous studies, three different Fe-deficient olivine minerals have been described, excluding talasskite because this contains less Fe^{3+} ion than the others and is transparent.

- (1) Ginzburg's "ferrifayalite" which has orthorhombic symmetry and the composition of $\text{Fe}_{0.76}^{2+}\text{Mn}_{0.21}\text{Fe}_{0.69}^{3+}\text{Si}_{0.94}\text{O}_4$,
- (2) laihunite which belongs to $P2_1/b$ space group with chemical composition between $\text{Fe}_{0.53}^{2+}\text{Mg}_{0.03}^{2+}\text{Fe}_{1.00}^{3+}\text{Si}_{0.96}\text{O}_4$ and $\text{Fe}_{0.80}^{2+}\text{Fe}_{0.80}^{3+}\text{SiO}_4$,
- (3) Chinese "ferrifayalite" which may be identical to laihunite.

As a result of these studies, the definition of ferrifayalite has become confused and the existence of the orthorhombic phase is obscure. However, the orthorhombic phase (*Pbnm* space group, the same as olivine) with a chemical composition close to the original ferrifayalite reported by Ginzburg *et al.* was clearly confirmed by Matsuura and Sueno (1984). Therefore, it may be better to re-examine the differences among the Fe-deficient mineral phases. In this paper, we adopt the term "laihunite" for the monoclinic phase according to approval of the IMA Committee on New Minerals and Mineral Names and the term "ferri-knebelite" for the Fe-deficient manganese fayalite with *Pbnm* symmetry in order to avoid confusions and misunderstandings caused by the rough usage of the term "ferrifayalite" in previous reports.

Sample description

- (1) "Fayalite" specimen from El Paso county, Colorado, U.S.A.

(a) Sample 1: (American Museum of Natural History Collection; catalog number 10928. Locality: Cheyenne Canyon, Colorado, U.S.A.)

This sample is a part of the Bement collection. We do not know the exact locality for this sample other than that given on the AMNH label, but if this is a sample collected by Hidden or Hidden and Mackintosh (Eckel, 1961) at the end of the 19th century, this sample occurred in a vug in quartz and granite or pegmatite from the Cheyenne Canyon area. A dark-brownish-black opaque mass of about 1.5 g was kindly supplied from AMNH. Reflected light microscopy and EPMA analysis showed that one third of this sample is a large laihunite grain (8 mm in size) and most of the rest is a fayalite grain. The associated minerals are amphibole, magnetite, and quartz. In reflected light, laihunite shows a grayish color and a weak double reflection. The reflectivities of laihunite and the associated minerals are in the following order:

magnetite > laihunite > fayalite > amphibole > quartz.

The fayalite part is transparent and the laihunite part is opaque, and both parts are

separated by a sharp but quite complicated boundary plane.

The results of single crystal X-ray study clearly showed that laihunite is monoclinic (Figure 1) and has a pseudo-twin relation (Shen *et al.*, 1980), the same as observed by Tamada *et al.* (1983). Faint diffuse streaks with weak nodes at the $c^{*'} = 1/3c^*$ position were observed parallel to the c^* axis on long exposure precession photographs similar to that found for the laihunite specimen from China (Tamada *et al.*, 1983). This indicates the existence of a modulated structure that may result from the ordering of vacancies. All of the experimental results show that laihunite in this specimen is very similar to the original laihunite reported from China (Tables 1 and 2).

(b) Sample 2: (U.S. National Museum Collection; catalog number R3516. Locality; Cheyenne Mountain, Colorado, U.S.A.)

This sample was originally a part of the Roebling collection and may be a part of the fayalite sample collected by Hidden (1885) or by Hidden and Mackintosh (1891) from vugs in quartz and in granite on Cheyenne Mountain, Colorado or from pegmatite bodies in the Stove Mountain-St. Peters Dome area (Eckel, 1961). About 2 g of this sample was kindly supplied from USNM. This sample is mostly composed of fayalite and includes a few percent of laihunite associated with amphibole and magnetite. Opaque laihunite grains included in fayalite are 2–3 mm in maximum size and brownish-black in color, similar to the AMNH Sample. Single crystal X-ray study and optical observation revealed that this laihunite has very similar characteristics to the original laihunite from China and to Sample 1.

(2) “Fayalite” specimen from Kamitaga, Shizuoka Prefecture, Japan.

This specimen was collected by ourselves from Kamitaga dacite lava. The details of petrology of this lava are described by Kuno (1950) and include a report of the occurrence of “fayalite” in this lava. The “fayalite” crystals were grown in gas cavities of the lava associated with tridymite and a small amount of amphibole. The crystals are euhedral and 500 microns in maximum size. The color is dark-grayish-black. The reflected light observations and EPMA analyses revealed the euhedral crystal consists of four kinds of materials with different reflectivity and chemical composition, that is, the darkest part is fayalite, the second darker part is laihunite, the third darker part may be a mixture of hematite and amorphous silica, and the brightest part at the exterior of the crystal is hematite (Figure 2b). Single crystal X-ray precession photographs showed that the most of the crystals are aggregates of fayalite, laihunite, and hematite (Figure 1b), but some euhedral crystals are almost pure laihunite. Kamitaga laihunite is monoclinic and the cell parameters are slightly larger than those of the original laihunite from China. Precession photographs revealed that the laihunite diffraction spots from this specimen are always accompanied by sharp and strong satellite reflections at the $c^{*'} = 1/2c^*$ position ($c' = 2c$), as shown by small arrows in

Figure 1b, with faint diffuse streaks parallel to c^* . Therefore, this laihunite contains laihunite- $2M$ superstructure in Ramsdell notation (lahunite- $Mab2c$ in modified Gard notation, Bailey, 1978) and is different from the other laihunites collected from pegmatite and magnetite deposits which have satellite reflections with $c^{*'} = 1/3c^*$ on precession photographs (Tamada *et al.*, 1983), that is laihunite- $3M$ (lahunite- $Mab3c$), although Kitamura *et al.* (1984) observed the coexistence of the $2M$ and $3M$ superstructures of laihunite and magnetite lamellae in a dark-field TEM image.

(3) “Fayalite” specimen from Naegi and Hirukawamura area, Gifu Prefecture, Japan.

The specimens were also collected by ourselves from pegmatite blocks at several granite quarries in the Naegi and Hirukawamura areas. Most of the specimens consists of grayish-brown fayalite of about 5 cm in diameter and surrounded by biotite and plagioclase. The fayalite part is associated with magnetite, amphibole, and quartz. Laihunite is observed as irregular shaped blocks (1–3 mm in size) under a reflected light microscope. Laihunite is sometimes associated with magnetite and amphibole. However, a specimen 4 cm in diameter collected at Matsuda quarry in Naegi consisted largely of laihunite and it showed very similar chemical composition and cell parameters to the original laihunite from China (Table 1 and Figures 1c and 2c).

(4) “Fayalite” specimen from Suisho-yama, Fukushima Prefecture, Japan. (The University Museum collection of The University of Tokyo; Catalog Number Mi 23492)

The specimen is a massive block of about 10 cm in diameter and is dark grayish-brown in color. About 10 grams of the specimen were supplied for the present study. This specimen may have come from a pegmatite. EPMA analysis showed that this mineral contains 12 wt% MnO and the chemical composition is very similar to that of the original ferri-fayalite reported by Ginzburg *et al.* (1962). EPMA analysis, reflected light observation and X-ray study revealed that the grain studied mostly consisted of the “lahunite” phase with a small amount of inclusions (magnetite, amphibole and quartz) but no fayalite phase, and the whole grain (about 1 cm in diameter) is found to be a single crystal with both a uniform chemical composition and uniform cell parameters. Single crystal X-ray precession photographs showed that this mineral has an orthorhombic symmetry and the space group is $Pbnm$, although the cell parameters are considerably smaller than those of fayalite as shown in Table 1. In precession photographs, the reflections of previously described laihunite are quite diffuse or separated on the $0k1$ plane because of the twinning (Figure 1c), but the reflections of this specimen are sharp as shown in Figure 1d. For laihunite, the 001 ($l = \text{odd}$) reflection always appears with fairly strong intensity, but for the minerals with the $Pbnm$ space group, 001 ($l = \text{odd}$) reflections are never observed because of its space group restriction. These results revealed that this specimen is crystallographically different from laihunite. For this reason, we termed this mineral as “ferri-knebelite”

for distinguishing it from laihunite and the other previously reported Fe-deficient minerals. This mineral is possibly the same phase as Ginzburg's ferrifayalite but is different from Chinese ferrifayalite.

Matsuura and Sueno (1984) refined the crystal structure of this mineral using the *Pbnm* space group and found that the basic structure was very similar to the laihunite structure reported by Tamada *et al.* (1983). The refinement of site occupancy revealed that the Fe^{3+} content (x) is around 0.62. Therefore, the chemical formula of ferri-knebelite can be described as $\square_{0.31}\text{Fe}_{0.62}^{3+}\text{Fe}_{0.72}^{2+}\text{Mn}_{0.35}\text{SiO}_4$ according to the EPMA data and the site occupancy refinement. They discussed that the reasons for the preservation of orthorhombic symmetry in ferri-knebelite may depend on the disordering of vacancies in the M1 site, smaller Fe^{3+} , and higher Mn contents. The number of diffraction data used on the refinement was 651, and the final *R*-factor was 3.7%.

Discussion

Cell parameters

Figure 3 shows the variation of a , b , c and V for the fayalite (Fe_2SiO_4)–tephroite (Mn_2SiO_4) solid solution (open circles) (Annersten *et al.*, 1984) with those of ferri-knebelite which contains 0.17 mole% of the tephroite molecule (open square). The solid solution of Mn ion in fayalite causes the chemical expansion of cell parameters especially of b , c and V . However, it is clear that the Fe^{3+} ions substituting for Fe^{2+} ions in ferri-knebelite bring on a much larger rate of decrease in b (about 0.19 Å) and c (about 0.21 Å) axes and cell volume (16 Å^3) as shown by arrows in Figure 3. Figure 4 is a cell parameters vs. Fe^{3+} content (x) diagram of fayalite, ferri-knebelite, and laihunite (China) assuming that the Fe^{3+} content (x) in ferri-knebelite is 0.62 and that in laihunite from China is between 0.8 (Tamada *et al.*, 1983) and 1.0 (Laihunite Research Group, 1976). The open squares in Figure 4 are plots for the observed cell parameters of ferri-knebelite, which contain the chemical expansion effect caused by the substitution of Mn ion for Fe^{2+} ion as compared with the other two phases which have minor Mn ion contents. The solid squares are those of corrected cell parameters for the manganese-free system, estimated from the chemical expansion coefficients for Mn substitution deduced from Figure 3. The shaded area in Figure 4 lies between the two dotted lines, which are the lines connecting the cell parameters of fayalite to the corresponding cell parameters of "laihunite with $x = 1.0$ " (solid circles, bulk chemical composition determined by Laihunite Research Group, 1976) and "laihunite with $x = 0.8$ " (half solid and half open circles, determined based on the site occupancy refinement by Tamada *et al.*, 1983). This shows the range of possible Fe^{3+} mol content of Fe-deficient minerals assuming the true Fe^{3+} deficiency of Chinese laihunite is

FIG. 3. Cell parameter variations of fayalite-tephroite solid solution compared with those of ferri-knebelite (modified from Annersten et al., 1984). Arrows indicate the shrinkage of the cell parameters of ferri-knebelite.

between $x = 0.8$ to 1.0 . The corrected cell parameters of ferri-knebelite (solid squares) are plotted between these two lines and this may suggest that the shortening of b and c cell lengths and cell volume decrease in Fe-deficient minerals as compared with fayalite may be proportional to the Fe^{3+} contents. Applying this idea, the Fe^{3+} ion contents for the laihunite specimens from Cheyenne canyon and Kamitaga can be estimated as $x = 0.72$ – 0.95 and $x = 0.55$ – 0.65 as shown by the arrows (2) and (1) in Figure 4, respectively.

FIG. 4. Variation with increasing Fe^{3+} ion contents of unit cell parameters of fayalite and Fe-deficient olivine minerals. Fayalite (open circles); Ferri-knebelite (open squares; observed cell parameters, solid squares; corrected cell parameters for the Mn free system); Chinese laihunite (solid circles; bulk chemical composition, half solid and half open circles; chemical composition based on the site occupancy refinement). Arrows (1) and (2) indicate the estimated range of Fe^{3+} mol contents of laihunite from Kamitaga, Japan and Cheyenne Canyon, Colorado, U.S.A., respectively.

Mineral assemblages

The mineral assemblages of the specimens from pegmatites including those of ferri-knebelite are quite similar to each other as described below:

- (1) The boundary planes between the laihunite and fayalite phases are quite complicated and it appears that the laihunite phase has invaded the fayalite phase

along small cracks in the mineral block through an oxidization reaction (Figure 2a, 2a' and 2b).

- (2) In both the laihunite and the fayalite phase, amphibole with the grunerite composition and magnetite are observed. These two minerals are, in most of the cases, in contact with each other (Figure 2a, 2a', 2c and 2d). In some specimens, magnetite is surrounded by amphibole. This may show that magnetite and amphibole are in paragenetic relation.
- (3) Quartz and annite are observed in fayalite and laihunite blocks and these two minerals also appear to be in paragenetic relation.
- (4) Long exposure precession photographs of most laihunite specimens revealed that the laihunite diffraction spots are accompanied by faint satellite reflections at $c^* = 1/3c^*$ position (laihunite- $3M$ superstructure) and diffuse streaks.

However, in contrast to the specimens from pegmatites, the laihunite specimen obtained from dacite at Kamitaga, Japan is accompanied by hematite (Figures 1b and 2b), not magnetite, and X-ray experiments revealed that this laihunite contains the laihunite- $2M$ superstructure (Figure 1b). The exterior of the most crystals are covered by hematite, although some crystals are completely converted to hematite phase. This observation suggest that the occurrence of this laihunite specimen may be related to the weathering of fayalite.

Kondoh *et al.* (1985) studied heated fayalite crystals using an electron microscope and found several different kinds of oxidized products of submicron-scale layers arrayed from the surface of the heated crystals to the inner unreacted fayalite in the following order; "hematite + magnetite + silica", "hematite + silica", "laihunite- $2M$ ", "laihunite- $3M$ " and "fayalite". This suggest that if laihunite is accompanied by hematite, the laihunite- $2M$ structure is more stable than the laihunite- $3M$ one, and this is consistent with our observation on the laihunite specimen from Kamitaga dacite.

The determination of Fe^{3+} content in Fe-deficient minerals is not easy because of the inclusion of iron oxide minerals in the laihunite phase (Kitamura *et al.*, 1984) and this problem needs further investigation by the Mössbauer method and the analytical electron microscope. The other possible method for the estimation of Fe^{3+} content in the Fe-deficient mineral may be a comparison of the cell parameters as discussed before, but this also presents many difficulties because of the errors caused by the different order-disorder schemes of vacancies and Mn and Mg solid solutions in the structure.

It may be important to note that the boundary plane between fayalite and laihunite is very sharp for all specimens examined, and EPMA data analyzed at the center and edge parts in one laihunite grain are almost the same even for a large "laihunite" abundant grain from Suisho-yama. Moreover, in precession photographs,

the diffraction spots of fayalite and laihunite are clearly separated from each other regardless of their mutual volumes (Figure 1b). These results may suggest that the degree of oxidation reaction of laihunite, which can be shown by the x value in a formula, is uniform for a laihunite grain and each degree of oxidation may correspond to a distinct stable region at a specific environment of temperature, pressure, and oxygen fugacity. If laihunite is a temporal intermediate product during a kinetic process of oxidation from fayalite to magnetite or hematite, the massive laihunite aggregate may show a zoning of different oxidation states with different x values.

Fig. 5 shows a hypothetical phase relation of laihunite as a function of oxygen fugacity and temperature at a constant total pressure. In this system, oxygen fugacity may be defined by the assemblage laihunite(L)–magnetite(Mt)–quartz(Qtz) or laihunite(L)–hematite(Hm)–quartz(Qtz) between the HM and QFM buffers. Two possible reactions (A) and (B) are deduced from the natural assemblage (L–Qtz–Mt, L–Qtz–Mt–Hm, L–Qtz–Hm) as shown below:

Laihunite may be stable below curves (A) and (B) in Fig. 5.

FIG. 5. A hypothetical phase relation of laihunite as a function of oxygen fugacity and temperature at constant total pressure. HM and QFM are oxygen buffer curves. L=laihunite, Mt=magnetite, Hm=hematite, Qtz=quartz. Laihunite may be stable in hatched area below (A) and (B) curves.

It is clear, according to this study, that the Fe-deficient olivine-type mineral has at least two crystallographically distinct structure types, laihunite and ferri-knebelite, and these minerals are fairly common in nature although their stable regions are still obscure. A detailed study of laihunite synthesis is important for clarifying this point.

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