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Fine textures of laihunite, a nonstoichiometric distorted olivine-type mineral

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Abstract

Laihunite, a nonstoichiometric distorted olivine-type mineral, has been studied by X-ray diffraction, electron-probe microanalysis, and analytical electron microscopy. Our results indicate that the laihunite is actually a mixture of laihunite and magnetite and has been derived by oxidation of fayalite. A pseudo-twin relation among the fine domains of laihunite also supports the transformation of fayalite to laihunite. The apparent composition of laihunite material obtained by EPMA and AEM is that of a mixture of laihunite and magnetite. The true composition of laihunite is nonstoichiometric, but close to a stoichiometric $Fe^{2+}Fe^{3+}_2Si_2O_8$.

Introduction

The occurrence of laihunite with the chemical composition of $Fe^{2+}_{1+x}Fe^{3+}_{2-2/3x}Si_2O_8$ ($x \simeq 0.1$) has been reported from magnetite ore (Laihunite research group, 1976), metamorphic rock (Ying *et al.*, 1981), volcanic rock (Peng, Z., private comm.), and a druse of tuff (Sueno, S., private comm.; Kondoh, S., private comm.). Laihunite has also been synthesized by oxidation of fayalite (Ginsburg *et al.*, 1962). The crystal structure is a kind of distorted olivine type with vacancies due to Fe deficiency. It is monoclinic with the space group $P2_1/b$, and the cell dimensions $a = 4.812$, $b = 10.211$, $c = 5.813$Å, and $\alpha = 90.87°$ (Fu *et al.*, 1979). The appearance of satellite reflections along the c^*-axis (Shen *et al.*, 1980, 1981; Li *et al.*, 1981) indicates the existence of superlattice structures of 2*c* and 3*c* for laihunite. Structure analysis of the 3*c* superstructure has shown an ordered arrangement of the octahedrally coordinated Fe^{2+} and Fe^{3+} ions and vacancies (Shen *et al.*, 1982). High-resolution electron microscopy has also shown the existence of the 2*c* and 3*c* superstructures and of unidentified lamellae in laihunite (Shen *et al.*, 1981; Li *et al.*, 1981).

Though the studies mentioned above indicated a close relationship between laihunite and fayalite, the mechanism of the fayalite–laihunite transformation and the character of the fine lamellar texture in laihunite are not well understood. The present investigation was carried out to elucidate the transformation process of fayalite to laihunite based on the fine textures of laihunite and fayalite.

Experimental and results

The specimens of laihunite used in this study were taken from eulysite of Hebei and of Liaoning mine, China. The eulysite from Hebei contains laihunite, fayalite with layered laihunite in (001), eulite, magnetite, and quartz (Fig. 1). A secondary electron image of the specimen (Fig. 2) indicates that wedge-shaped laihunites grew from the crystal edges of fayalite. The mineral assemblage of the eulysite is similar to that of the metamorphic rocks from Liaoning mine, China (Laihunite research group, 1976), though quartz–almandine–eulysite without fayalite has also been reported from Hebei (Ying *et al.*, 1981).

The chemical compositions of specimens from Hebei and Liaoning were determined by an electron-probe microanalyzer (EPMA) to be $Fe^{2+}_{1.06}Fe^{3+}_{2.06}Mg_{0.06}Si_{1.88}O_8$ for laihunite and $Fe^{2+}_{3.88}Mg_{0.08}Si_{2.02}O_8$ for fayalite, as the averages of 55 and 20 point analyses, respectively (Table 1). The compositions are also plotted on an $FeO–Fe_2O_3–SiO_2$ diagram (Fig. 3). The Fe^{3+} content was estimated from the deficiency from 100% of the analyses (total Fe as FeO), for which pure fayalite and forsterite were used as standards. The wet chemical analysis of laihunite from Liaoning, China (Laihunite research group, 1976) gives almost the same composition as obtained by EPMA in this investigation. A definite deficiency of Si/O from 0.25 in laihunite is observed in both chemical analyses.

X-ray study

The X-ray diffraction patterns of laihunite from both localities taken with a precession camera show, in most cases, the topotactic coexistence of one fayalite and two laihunite lattices (Fig. 4). The two laihunite lattices are in an apparent twin relation of (001). Fu *et al.* (1979) reported this relation of the two lattices as a real (001) twin. However, the c^*-axes of both lattices are not

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Table 1. Chemical composition of laihunite and fayalite obtained by electron-probe microanalysis

	Laihunite							Fayalite		
Specimen No.	1	2	3	4	5	6	7	3	4	6
Locality*	L	L	L+	L+	H	H+	H	L+	L+	H+
No. of points	6	19	6	10	5	4	5	6	10	4
	WEIGHT PERCENT									
SiO_2	30.76	32.09	31.41	32.14	31.09	32.23	31.32	29.74	30.54	29.90
FeO	64.00	63.00	62.73	62.60	63.60	61.78	62.70	69.82	68.98	69.16
MgO	0.58	0.73	0.43	0.60	0.76	0.91	0.97	0.51	0.72	1.08
Total	95.34	95.82	94.57	95.34	95.45	94.92	94.81	100.07	100.25	100.14
	CATIONS PER 4 OXYGENS									
Fe^{2+}	0.556	0.636	0.342	0.514	0.569	0.369	0.396	1.969	1.925	1.941
Fe^{3+}	1.049	0.940	1.197	1.037	1.023	1.118	1.149			
Mg	0.026	0.033	0.019	0.027	0.034	0.040	0.035	0.026	0.036	0.054
Si	0.922	0.960	0.922	0.953	0.931	0.944	0.923	1.003	1.020	1.003

The Fe^{2+}/Fe^{3+} of laihunite was estimated from the total iron analyzed as FeO to give 100% total.

*L and H represent Liaoning and Hebei, respectively. + indicates the coexistence of laihunite and fayalite.

parallel but deviate by about 0.3° from each other, indicating that the two lattices are not in an exact twin relation but in a pseudo-twin relation (Ito and Morimoto, 1957; Morimoto, 1958) as described later in more detail.

The satellite reflections corresponding to the $3c$ superstructure are clearly observed in the photograph (Fig. 4). The measured lattice constants of the subcell of laihunite are $a = 4.82$, $b = 10.2$, $c = 5.82$Å, and $\alpha = 91.1°$, and the space group of the subcell is $P2_1/b$, in agreement with the previous results (Ferrifayalite research group, 1976; Fu *et al.*, 1979). The space group of the $3c$ superlattice is also $P2_1/b$.

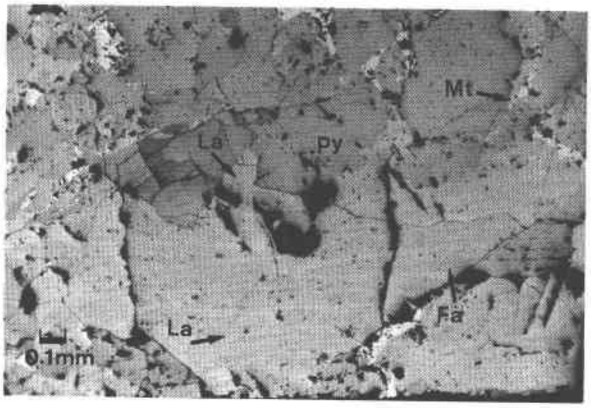

Fig. 1. Optical micrograph of eulysite from Hebei in reflected light. Fayalite (Fa) in dark gray with the layered laihunite (La) in light gray, pyroxene (Py), and magnetite (Mt) are indicated.

AEM study

Fayalite with layered laihunite from Hebei (Fig. 1) was ion-thinned and observed with a 200 kV analytical electron microscope (AEM). Though the laihunite material appears to be chemically homogeneous at the resolution

Fig. 2. Secondary electron image of fayalite and pyroxene grains from Hebei. Laihunite grew from the grain edges of fayalite into fayalite. Magnetite appears within the grain of pyroxene.

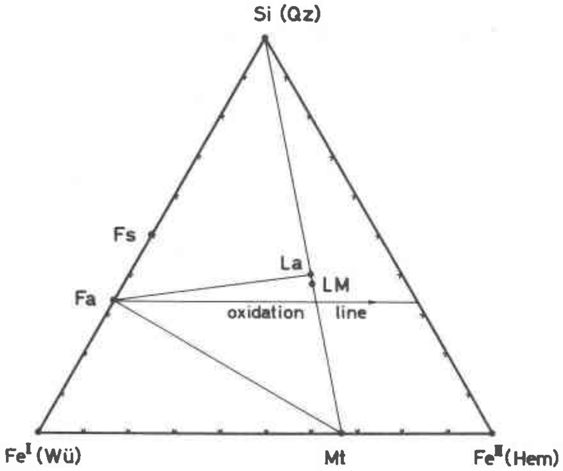

Fig. 3. The ternary FeO–Fe_2O_3–SiO_2 diagram. The composition of laihunite with fine lamellae of magnetite (LM) determined by EPMA is plotted. The oxidation line of fayalite is shown. Fs: ferrosilite, Fa: fayalite, Mt: magnetite, La: laihunite.

level of EPMA (2 μm), it is actually a mixture of laihunite and magnetite.[2] Two different types of magnetite were recognized (Fig. 5a): one forms veins several tens of nm thick and the other forms a network of thin lamellae a few nm thick at the boundaries of the fine domains of laihunite. The veins were identified to consist of fine fibrous crystals of magnetite by electron diffraction and AEM. The lamellae in laihunite are, however, too small in volume to give sharp electron diffraction spots and too fine to be analyzed by AEM with a spatial resolution of about 50 nm. Under the electron microscope, these lamellae appear to be an amorphous phase.

However, in a dark-field TEM image where fayalite and laihunite domains are dark but the magnetite vein is bright (Fig. 5b), the thin lamellae are bright, indicating that the lamellae are also magnetite. This contrast was also observed with different reflections of magnetite. Under these conditions, the lamellae consist of fine spots of different brightness and suggest that they are fine crystals of magnetite with slightly different orientations. The ratio of the areas of laihunite and magnetite was estimated to be on the order of 6:1 from the electron micrographs.

A similar intergrowth texture of laihunite with magnetite lamellae has been observed in crushed specimens of laihunite material from Liaoning. Lattice images of laihunite have also been taken from the same specimen (Fig. 6), where the coexistence of the $2c$ and $3c$ superstructures of laihunite and magnetite lamellae is clearly observed. A long exposure of the electron beam (more than several minutes) on the laihunite specimen in the electron microscope resulted in the change of laihunite to fayalite and of magnetite to hematite (Fig. 7).

A dark-field photograph (Fig. 8) taken with a reflection from one of the pseudo-twin lattices (Fig. 4) shows that the pseudo-twin domains have sizes on the order of a few hundred nm and that their boundary planes are irregular and zigzag.

The chemical compositions of fayalite and intergrown laihunite have been determined by AEM using the procedure described by Morimoto and Kitamura (1981). They are in good agreement with the results obtained by EPMA.

Discussion

The observation of a fine intergrowth of laihunite with magnetite indicates that laihunite should have less FeO component than the composition obtained by EPMA and AEM for the laihunite material. This explains the significant deficiency of Si/O of laihunite material from 0.25 mentioned above. Because the structure studies by Shen *et al.* (1982) and Tamada *et al.* (1981) indicate that all the tetrahedral sites are occupied by only Si atoms and that all octahedral sites have ordered arrangements of Fe^{2+}, Fe^{3+}, and a small proportion of vacancies, laihunite

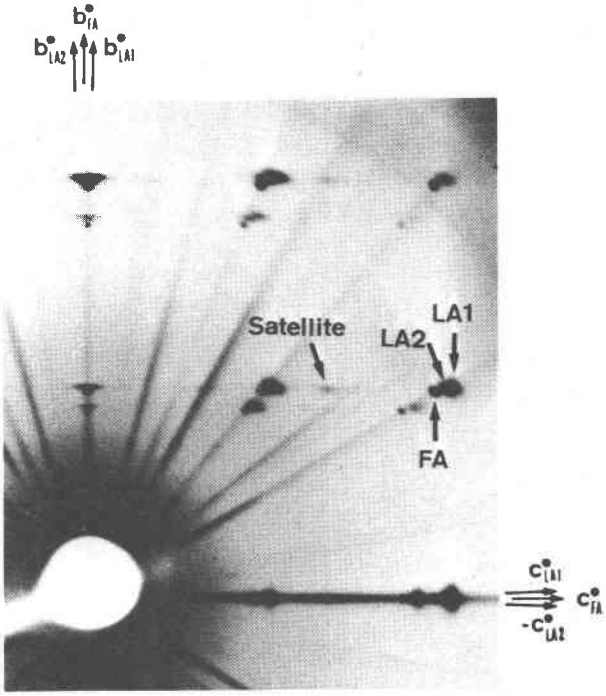

Fig. 4. X-ray diffraction pattern of laihunite coexisting with fayalite. Splitting of the reflections of laihunite shows a pseudo-twin relation of two laihunites. The b^* and c^* axes of fayalite (FA) and two laihunites (LA1 and LA2) are indicated. The superstructure reflection of laihunite is indicated as satellite.

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[2] The laihunite–magnetite intergrowth is referred to as laihunite material where it is necessary to distinguish it from laihunite in the strict sense.

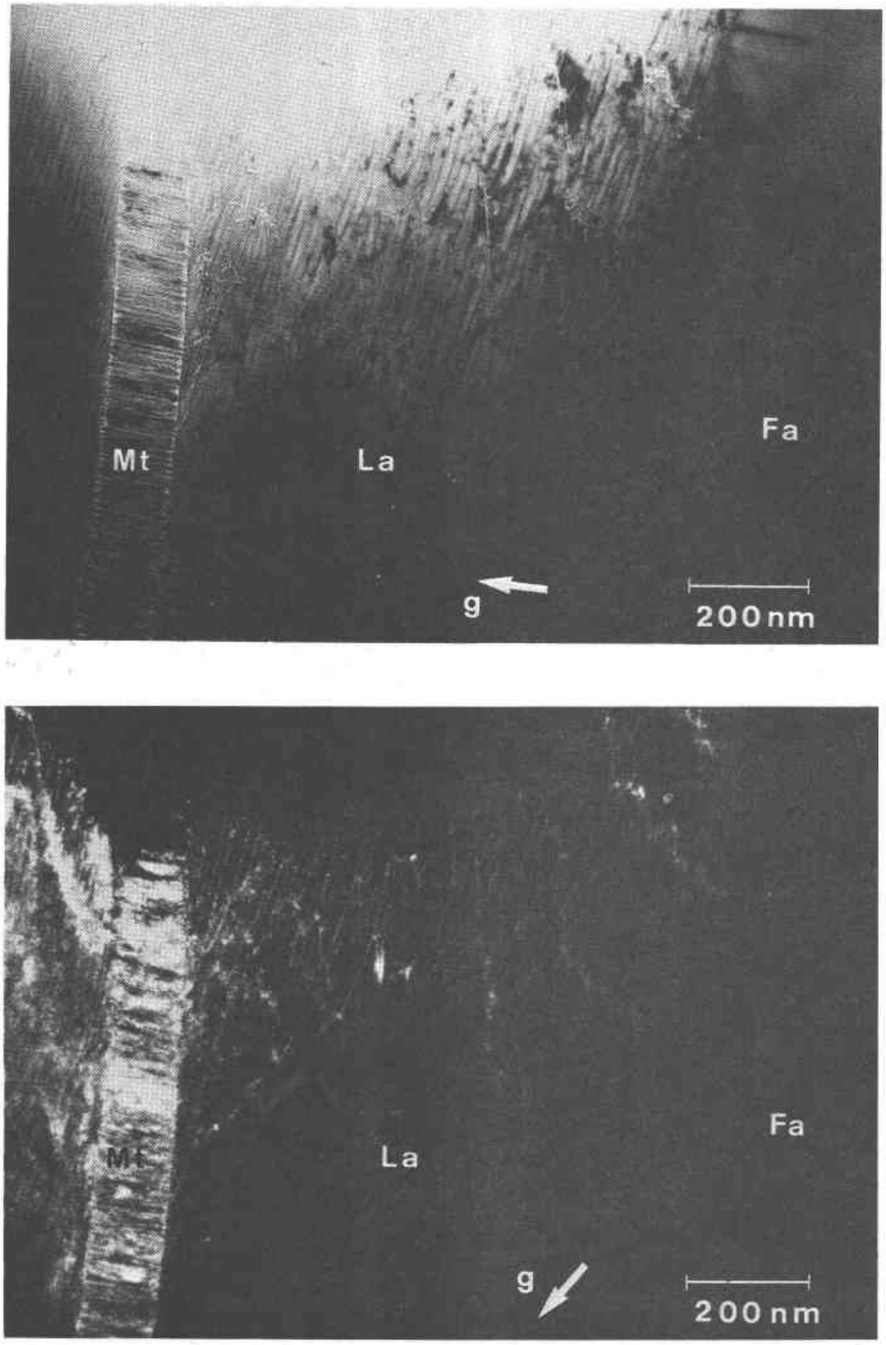

Fig. 5(a). Bright-field electron micrograph of laihunite. A vein of fibrous magnetite (Mt), laihunite (La) and fayalite (Fa) are indicated. A network of fine magnetite lamellae is observed in laihunite. The apparent interface between fayalite and laihunite is in (001) of fayalite. ($g = 004_{Fa}$). (b). Dark-field electron micrograph of the same region as Figure 5a. The magnetite vein appears bright, while laihunite domains and fayalite appear dark. The network of magnetite lamellae in laihunite appears as strings of bright spots, indicating that the lamellae consist of fine magnetite grains. ($g = 153_{Mt}$).

must have a Si/O ratio of 0.25 and a nonstoichiometric iron composition, not far from the stoichiometric $Fe^{2+}Fe_2^{3+}Si_2O_8$.

The texture of laihunite indicates that fayalite decomposed to laihunite–magnetite intergrowths. The reaction can be described as follows;

$$6Fe_2^{2+}SiO_4 + 2O_2 \rightarrow 3Fe^{2+}Fe_2^{3+}Si_2O_8 + Fe_3O_4.$$

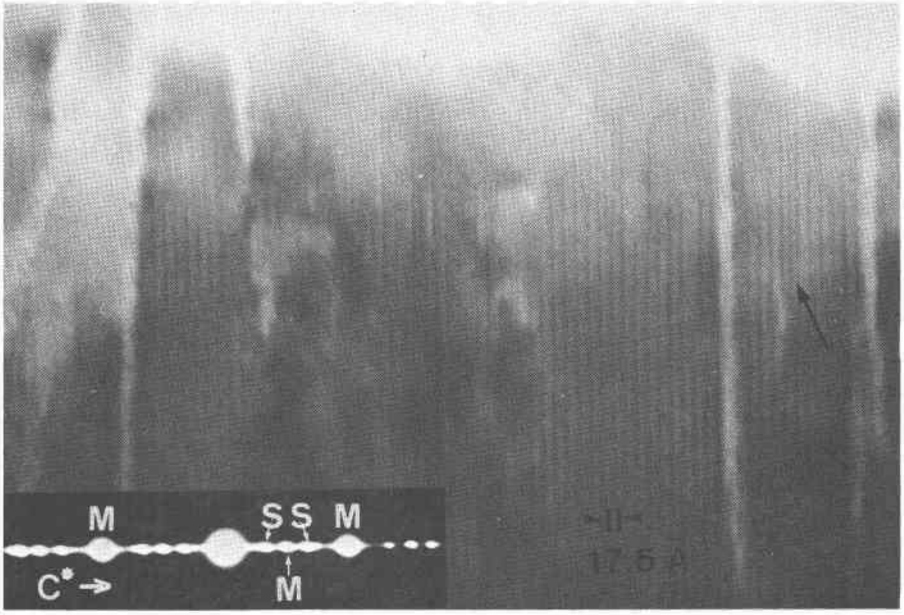

Fig. 6. Lattice image of laihunite. The electron diffraction pattern used for image formation is also presented, where M and S represent main and satellite reflections, respectively. The fringes corresponding to the $3c$ (17.5Å) superstructure are indicated. The arrow indicates the existence of $2c$ fringes in the $3c$ fringes. The white veins correspond to magnetite.

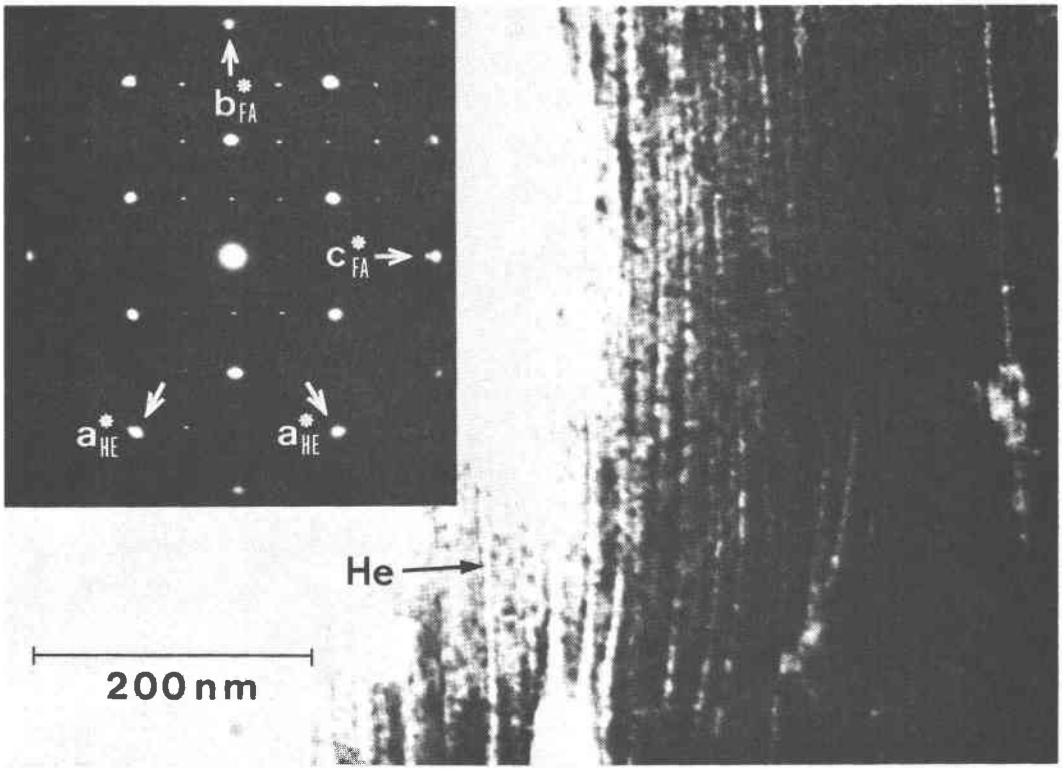

Fig. 7. Electron micrograph of fayalite with hematite lamellae which was produced from laihunite with magnetite lamellae by long exposure to the electron beam. The electron diffraction pattern shows a topotactic relation between fayalite and hematite. The orientations of fayalite and hematite are shown by the reciprocal axes b^* and c^* of fayalite and two a^*'s of hematite, respectively.

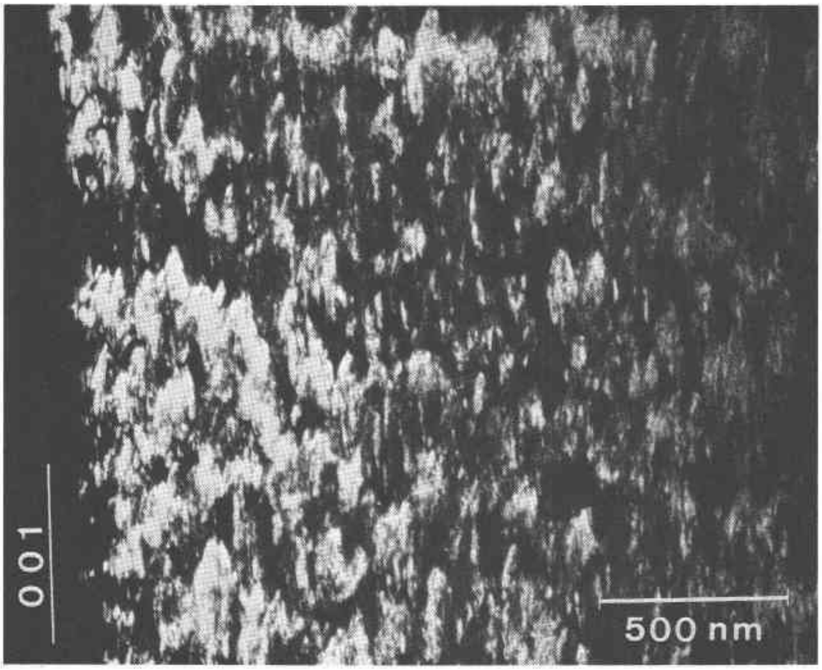

Fig. 8. Dark-field electron micrograph of laihunite taken with a reflection from the pseudo-twinned laihunite. Individual domains are nearly equal in size and have rather irregular boundaries.

The two lattices of the laihunite domains which are in an apparent twin relation share (023) or (0$\bar{2}$3) with the fayalite lattice. Because fayalite is orthorhombic, (0*kl*) and (0$\bar{k}l$) are crystallographically equivalent, while they are not equivalent in the laihunite lattices with monoclinic symmetry. Therefore, the two laihunite lattices are related by reflection through (001) of fayalite, which is an irrational plane deviating about 0.15° from the (100) of laihunite. This relation is a typical example of the pseudotwin, which was defined by Ito and Morimoto (1957) in a study of clinopyroxenes. A similar pseudo-twin relation by transformation has been described for cordierite (Kitamura and Hiroi, 1982). The psuedo-twin relation among the laihunite domains also supports the interpretation that fayalite transformed to laihunite by oxidation.

Since EPMA cannot resolve the fine textures observed under the electron microscope, the analysis should include both laihunite and the veins and lamellae of magnetite. Even in the EPMA analysis, however, the composition of laihunite is deficient in Fe/Si ratio in comparison with that of fayalite. This result indicates that some amount of the Fe_3O_4 component must have moved away from the intergrowth region of laihunite and magnetite. The magnetite grains of micron scale which are regarded to be a primary phase (Figs. 1 and 2) must have experienced further growth during the formation of laihunite by receiving the Fe_3O_4 component from the original fayalite. Large magnetites in eulite (Fig. 2) must also have been affected by this transformation process of fayalite to laihunite.

In conclusion, laihunite material, which was previously treated as a single phase, has been found to be a mixture of laihunite and magnetite produced by oxidation of fayalite.

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