Site occupancy and two-phase character of "ferrifayalite"

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Abstract

Low-temperature (down to 4.2 K) ^{57}Fe Mössbauer spectra have been taken of "ferrifayalites" (Fe^{3+}-rich fayalites) from three localities. Room-temperature spectra show two pairs of peaks, due to ferrous and ferric ions in octahedral coordination. The peaks due to ferrous iron split at low temperatures to form a pattern consistent with that of "normal" ferrous fayalite. The peaks due to ferric iron split independently to form at least one hyperfine sextet.

Based on these observations, a two-phase structure for "ferrifayalite" is proposed, in which "ferrifayalite" is composed of an intergrowth of "normal" ferrous fayalite and laihunite, $Fe^{2+}Fe_2^{3+}(SiO_4)_2$. This model is supported by scanning electron microscope (SEM) photographs showing the two phases.

In addition, infrared spectra and plots of M1 and M2 octahedra size vs. cation radius were used to estimate site occupancy of laihunite. The M2 site was found to contain ferric ions alone, whereas the M1 site contains a mixture of ferrous ions and vacancies.

Introduction

"Ferrifayalite", a variety of fayalite containing from about ten to forty weight percent Fe_2O_3, was first discovered in 1976 in China, and was given the name laihunite (Laihunite Research Group, 1976, 1982). Prior to that time, two discoveries of fayalite containing ferric iron had been made in the Soviet Union, but these discoveries remain unconfirmed. One mineral was called talasskite (Nikitin, 1934), the other ferrifayalite (Ginzburg et al., 1962). Shortly after the discovery of laihunite, two more localities were found, also in China (Ferrifayalite Research Group, 1976; Zhang et al., 1981), but these Fe^{3+}-rich fayalites were named ferrifayalite, because the discoverers believed this mineral to be the same as the mineral described by Ginzburg et al. This confusion persists in the literature today.

In this paper the term "ferrifayalite" refers in general to any fayalite containing several percent or more ferric iron, and the term laihunite refers to a sample with approximately the composition $Fe^{2+}Fe_2^{3+}(SiO_4)_2$.

Recently two[2] more "ferrifayalite" localties have been confirmed (Schaefer, 1983a,b). These were found by examination of the Mössbauer spectra of selected samples that were identified as fayalite in museum collections.

Experimental

Samples for study included "ferrifayalite" from Qianan County, China, as well as "ferrifayalites" from the more recently discovered localities of Mourne Mountains, Ireland, and Pantelleria, Italy.

The three "ferrifayalite" samples and a standard of Rockport fayalite (Palache, 1950) were each ground under acetone, examined under a microscope, and hand-picked when necessary to remove impurities. The samples were then finely ground again under acetone, and any magnetite present was removed with a hand magnet (a necessary procedure, because "ferrifayalite" and magnetite are very similar in appearance).

Sample volumes were weighed such that there would be approximately 8 mg/cm^2 Fe in the Mössbauer sample holder (Dyar, 1982, 1984), and then ground under acetone together with enough sugar to completely fill the sample holder, so that the orientations of the "ferrifayalite" particles would be randomized.

Room-temperature Mössbauer spectra were taken on an Austin Science Associates spectrometer. The γ-ray source was ^{57}Co diffused into either Pd or Rh foils having activities of 50 to 100 mc. Spectra were calibrated against metallic Fe foil. Baseline counts generally exceeded one million counts per channel. Mössbauer parameters were determined with the computer program developed by Stone et al. (1971).

Low-temperature Mössbauer spectra were taken on a spectrometer with a Ranger drive and multichannel analyzer and Janis Corporation cryogenics. Sample holders were cooled by a spray of liquid nitrogen or liquid helium, depending on the temperature desired. Temperature was monitored by a thermocouple also used to feedback information to a controller that supplied a signal to a heating element in thermal contact with the sample. The γ-ray source was ^{57}Co electroplated onto Rh, with an activity of about 100 mc. Low-temperature spectra also were calibrated against metallic Fe foil.

All samples were analyzed by powder X-ray diffraction and electron microprobe. Samples for X-ray diffraction were ground and purified as for Mössbauer analysis, but were mixed with a

small amount of fluorite as an internal standard and mounted on glass slides. $CrK\alpha$ radiation was used.

Samples, in the form either of powder or of small crystal fragments, were mounted in epoxy for electron microprobe analysis. These mounts were also used for SEM analysis.

Results

No iron oxides were detected in the samples, which were checked by room-temperature Mössbauer spectrometry with a wide velocity-range setting (oxide detection limit approx. 1 wt.%).

Electron microprobe analysis (Table 1) was used to determine the chemical composition of the samples (Schaefer, 1983a,b). All analyses were found to be similar to fayalite analyses, although they are apparently deficient in iron (compared to Rockport fayalite), due to the presence of vacancies replacing iron in the structure. Powder X-ray diffraction of the samples was used as a check of their crystallinity and as a check of their identification as a single phase. There was a positive correlation between the diffuseness of the X-ray diffraction spectra and the ferric iron content of the samples.

The specimens from Mourne Mountains and Pantelleria have different ferric iron concentrations, and neither has as much ferric iron as the Chinese "ferrifayalites". The Mössbauer spectra of all "ferrifayalite" samples are similar in appearance, with the exception of the variation in the ratio of ferric to ferrous doublet intensities (Fig. 1). Ferric–ferrous ratios were calculated from the room-temperature Mössbauer spectra (Schaefer, 1983a,b), and are summarized in Table 2. Mössbauer parameters at room temperature are summarized in Table 3.

Low-temperature Mössbauer spectra of the samples were taken at many temperatures from 215 K down to 4.2 K. Two types of spectra were seen: "normal" fayalite (Rockport fayalite), and "ferrifayalite" (Qianan County "ferrifayalite", Mourne Mountains "ferrifayalite", and Pantelleria "ferrifayalite"). The "ferrifayalite" spectra are similar in appearance to the laihunite spectrum observed by Kan and Coey (1985).

The Mössbauer spectrum of "normal" fayalite shows a single ferrous doublet at temperatures from room temperature down to 65 ± 2 K (Kündig et al., 1967; Santoro et al., 1966). At 65 K a magnetically ordered Mössbauer spectrum appears (Fig. 2). This transition is sharp, and consists of the splitting of the two-peak spectrum into a 16-peak spectrum, which results from a superposition of eight lines each produced by the two iron sites (Kündig et al., 1967), though it has not been determined which site produces which octet. There is also a pronounced λ point in specific heat measurements of fayalite at 65.0 K (Kelley, 1941).

"Ferrifayalite" spectra show two low-temperature transitions (Fig. 3). The three samples of this type differ only in the proportions of ferric to ferrous iron. Above about 100–150 K, the four-peak, room-temperature-type spectrum is seen. Below 150 K, the ferric doublet gradually decreases and is replaced by what appears to be one or more hyperfine sextets (Fig. 4). Below 100 K, the ferric doublet is absent, but the ferrous doublet is unchanged. The width of this transition probably results from inhomogeneity in the crystal, which is also indicated by the diffuseness of the X-ray spectra.

Between 50 K and 70 K (Fig. 5), a second transition is seen. This transition consists of the replacement of the ferrous doublet by the normal low-temperature fayalite spectrum. This pattern is almost entirely overshadowed by the sextet pattern from the ferric iron, particularly at lower temperatures (Fig. 6). It is difficult to tell whether the ferric peaks, also, are undergoing a transition over this temperature range, due to the extreme complexity and poor resolution of the spectra, particularly of the more ferric-rich samples.

The samples were also examined semi-quantitatively by SEM. An intergrowth texture on a scale of tens of microns was observed in the samples from Mourne Mountains (Fig. 7), Qianan County, and Pantelleria. No such texture was observed in the Rockport sample. No particulate impurities were observed in any sample.

The intergrowth texture observed consisted of two phases, in varying proportions, and was somewhat similar

Table 1. Electron microprobe analysis of "ferrifayalites" and Rockport fayalite

	Rockport		Pantelleria		Mourne Mts.		Qianan Co.	
	wt.%	formula	wt.%	formula	wt.%	formula	wt.%	formula
SiO_2	29.06±0.15	1.00±0.01	29.72±0.21	1.00±0.01	30.43±0.19	1.00±0.01	30.97±0.67	1.00±0.02
TiO_2	0.01±0.00	0.00±0.00	0.00±0.02	0.00±0.00	0.01±0.01	0.00±0.00	0.00±0.00	0.00±0.00
Al_2O_3	0.00±0.00	0.00±0.00	0.00±0.00	0.00±0.00	0.01±0.01	0.00±0.00	0.00±0.00	0.00±0.00
FeO^{**}	67.28±0.33	1.94±0.01	63.24±0.21	1.72±0.00	61.79±0.36	1.70±0.01	59.76±0.38	1.61±0.01
MgO	0.08±0.03	0.02±0.01	1.60±0.04	0.08±0.00	0.38±0.02	0.00±0.00	1.45±0.03	0.07±0.00
MnO	2.28±0.07	0.00±0.00	4.08±0.09	0.12±0.00	3.14±0.09	0.08±0.00	0.08±0.04	0.00±0.00
CaO	0.00±0.00	0.00±0.00	0.51±0.08	0.02±0.00	0.06±0.02	0.00±0.00	0.00±0.00	0.00±0.00
K_2O	0.00±0.00	0.00±0.00	0.00±0.00	0.00±0.00	0.00±0.00	0.00±0.00	0.00±0.00	0.00±0.00
Sum	98.71±0.34	2.96±0.02	99.15±0.25	2.94±0.01	95.82±0.42	2.78±0.01	92.26±0.77	2.68±0.02

*Formula based on 1 Si per molecule. Pure fayalite should have 2 Fe atoms; pure laihunite should have 1.5 Fe atoms.
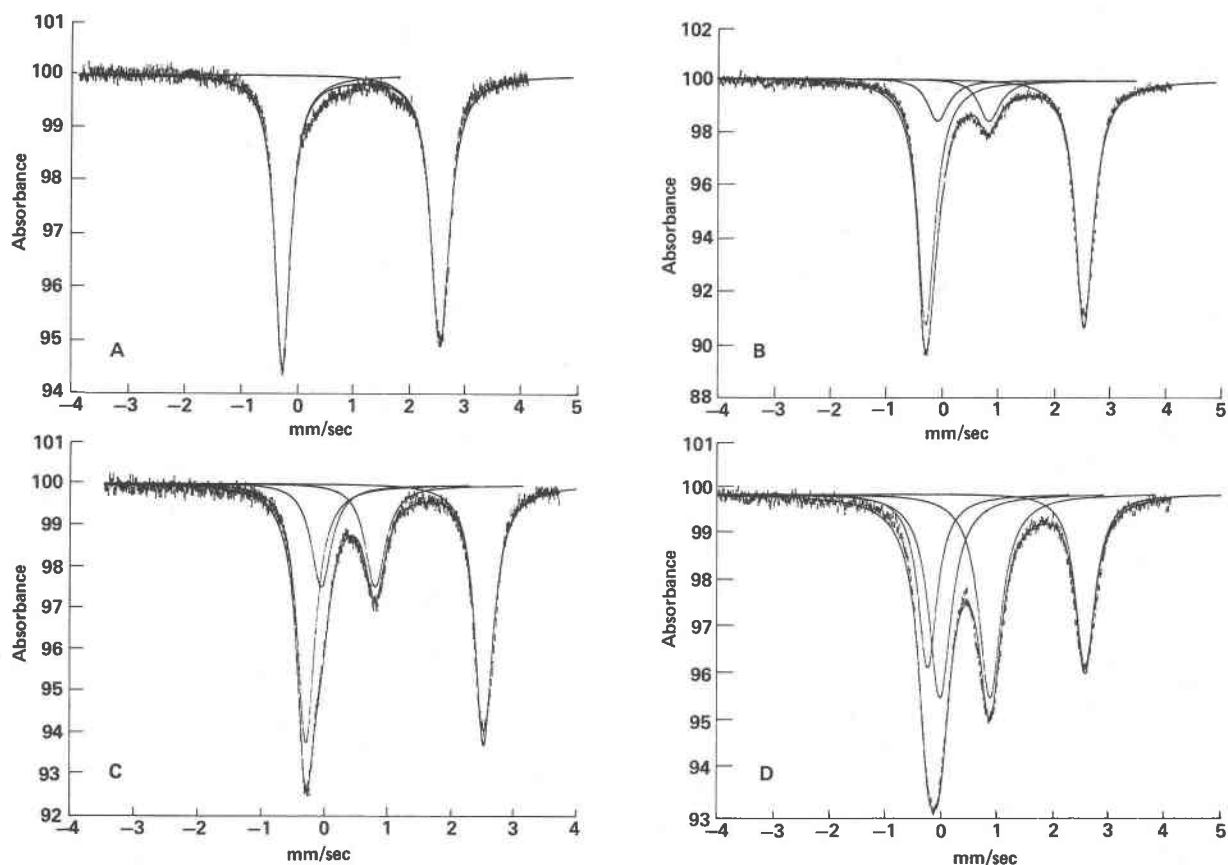
**Total iron analyzed as FeO.

Fig. 1. Room temperature Mössbauer spectra of Rockport fayalite and three "ferrifayalites". These spectra were fitted with the program described by Stone et al. (1971) (A) Rockport, Massachusetts; (B) Pantelleria, Italy; (C) Mourne Mountains, Ireland; (D) Qianan County, China.

to that observed in "ferrifayalite" from two Chinese localities (Kitamura et al. 1984). One phase was identified by backscattered electron analysis as (ferrous) fayalite, and the other phase, which had a lower iron to silicon ratio, as laihunite. Qianan County "ferrifayalite" had the largest proportion of laihunite, and Pantelleria "ferrifayalite" the smallest. No magnetite was detected.

In the spectrum from Mourne Mts., which produced the clearest SEM photographs, the laihunite domains are seen to be extensively cracked, compared to adjacent areas of the crystal containing little or no laihunite. Possible reasons for this cracking will be discussed in the next section.

Discussion

Fu et al. (1982), who have studied "ferrifayalite" by single-crystal X-ray diffraction, suggested that the laihunite structure is very similar to that of ideal $R^{2+}SiO_4$ olivines such as fayalite, but with a systematic alternation of vacant and Fe^{2+}-occupied M1 sites. The M2 sites are occupied by Fe^{3+} cations. Further work by Tamada et al. (1983) supported this hypothesis. Fu et al. also postulated the existence of two types of twin-related domains in "ferrifayalite" (which they called laihunite). The two domains, which contain different amounts of ferric iron, are irregularly distributed in the crystal, and are separated by an inhomogeneous boundary region.

The work I have done on "ferrifayalite" is consistent with the major points of Fu et al.'s hypothesis. The powder X-ray diffraction spectra indicate that the structure of "ferrifayalite" is very similar to that of fayalite; when both phases (laihunite and fayalite) are present in a sample, the spectral lines are broadened and diffuse, instead of being resolved into two different patterns. The room-temperature Mössbauer spectra indicate that both ferrous and ferric

Table 2. Ferric-ferrous ratios of samples, based on Mössbauer peak areas

Sample locality	Ferric-ferrous ratio
Rockport, MA	0
Pantelleria, Italy	0.19
Mourne Mountains, Ireland	0.46
Qianan County, China	1.38
$(Fe^{2+}_1 \square_1)^{M1}(Fe^{3+}_2)^{M2}(SiO_4)_2$	2.00

Table 3. Mössbauer parameters of "ferrifayalites" and Rockport fayalite at room temperature (in mm/sec).

Ferrous peaks	Rockport	Pantelleria	Mourne Mts.	Qianan Co.
Center shift	1.1667±0.0075	1.1542±0.0039	1.1573±0.0021	1.1687±0.0040
Quadrupole splitting	2.8077±0.0084	2.8202±0.0044	2.8164±0.0026	2.8129±0.0046
Average peak width	0.3633±0.0026	0.3872±0.0014	0.3386±0.0019	0.4161±0.0024
Ferric peaks				
Center shift	-----	0.3843±0.0043	0.4071±0.0025	0.4312±0.0036
Quadrupole splitting	-----	0.9123±0.0048	0.8523±0.0032	0.8893±0.0019
Average peak width	-----	0.4360±0.0067	0.3877±0.0045	0.4837±0.0021

iron are in octahedral coordination, in the M1 and M2 sites of olivine.

Infrared spectra of fayalite and "ferrifayalite" taken by several authors (Huggins, 1970; Zhang et al., 1981) were compared in order to estimate site populations. The strength of the band marked in Figure 8 is dependent on the average Fe^{2+} and Mn^{2+} content in the M1 site (Huggins, 1970). Because these spectra come from samples with very similar amounts of Fe and Mn (63 to 67 wt.% FeO + Fe_2O_3 and less than about 3 wt.% MnO), the variations of the strength of this band indicate a variation in the average M1 site population of iron (and manganese), as opposed to a variation in the total iron content of the samples.

The spectrum of Rockport fayalite shows the greatest intensity for this band, followed by the spectrum of Mourne Mountains "ferrifayalite". The two spectra of Chinese "ferrifayalite" are similar to one another, and show the least intensity for this band. This fact suggest that increasing ferric iron content in these samples decreases the amount of iron in the M1 site, so that the M1 site is populated with a combination of iron atoms and vacancies.

Plots were made (after Brown (1970, 1982)) of average metal–oxygen distance vs. cation radius and average oxygen-oxygen distance vs. cation radius for the M1 and M2 sites. When an average metal–oxygen distance for the M2 site of pure laihunite calculated from data given by Fu et al. (1982) is plotted and a linear variation of the parameters (determined by Brown, 1970) assumed, a cation radius of 0.645Å may be determined from the graph (Fig. 9A). This radius is very similar to the cation radius for Fe^{3+} (0.64Å) given in Shannon and Prewitt's (1969) table of cation radii, and quite different from the Fe^{2+} cation radius (0.74Å) from the same source. Plotting this Fe^{3+} cation radius and Fu et al.'s average oxygen–oxygen distance on the second graph (Fig. 9B) also produces a good fit with the line determined by Brown (1970).

This procedure cannot be duplicated with the M1 site, because there are insufficient data on the size and shape of
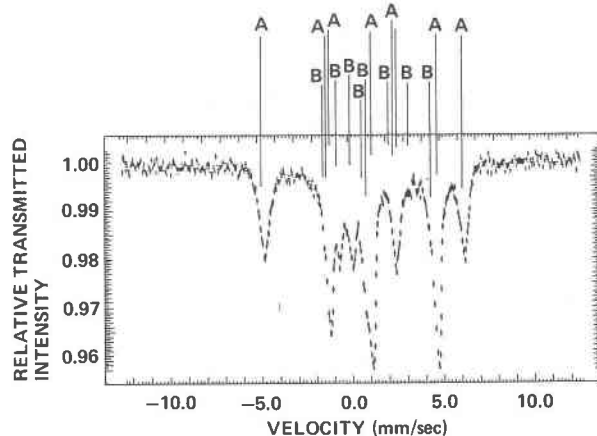

Fig. 2. 20 K Mössbauer spectrum of Rockport fayalite, with peak assignments from Kündig et al. (1967). It is not known whether the A or the B sites correspond to the M1 or the M2 sites.
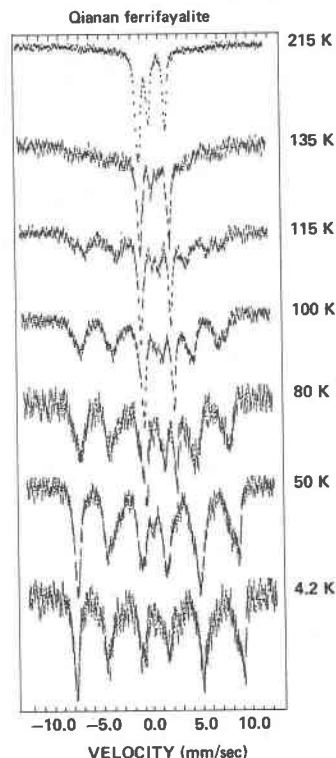

Fig. 3. Change in Qianan County "ferrifayalite" Mössbauer spectrum with temperature.
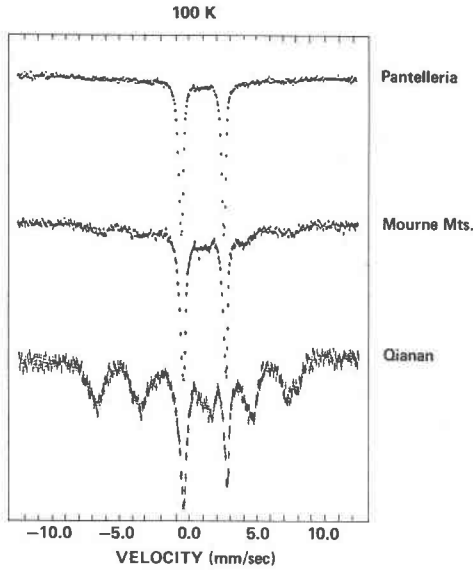
Fig. 4. Mössbauer spectra of "ferrifayalites" at 100 K.

Fig. 6. Mössbauer spectra of "ferrifayalites" at 20 K.

the vacancy sites. If values of average metal–oxygen and average oxygen–oxygen distance are taken from Fu et al., and Shannon and Prewitt's Fe^{2+} cation radius is used, disagreement with Brown's linear fit occurs (Fig. 9). This result supports the idea of vacancies concentrated in the M1 sites (distorting the average M1 site and changing its size).

A possible structure for laihunite, based on the above work and on Fu et al.'s (1982) structure refinements, is shown in Figure 10. There is a regular alternation of occupation and absence with respect to Fe^{2+} cations in the M1 site, and all the M2 sites are filled with Fe^{3+} cations. A single phase with this structure, however, should not produce the low-temperature Mössbauer spectra observed. The "ferrifayalite" low-temperature Mössbauer spectra all
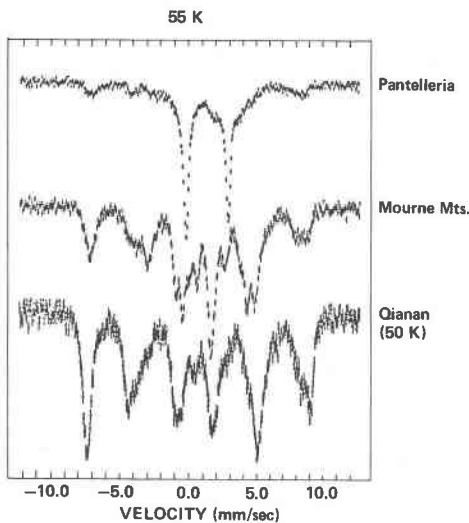

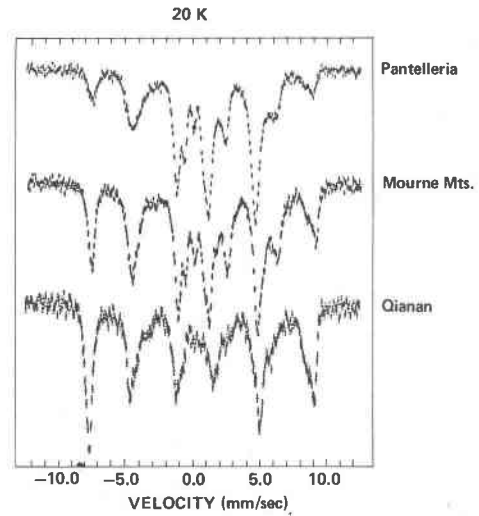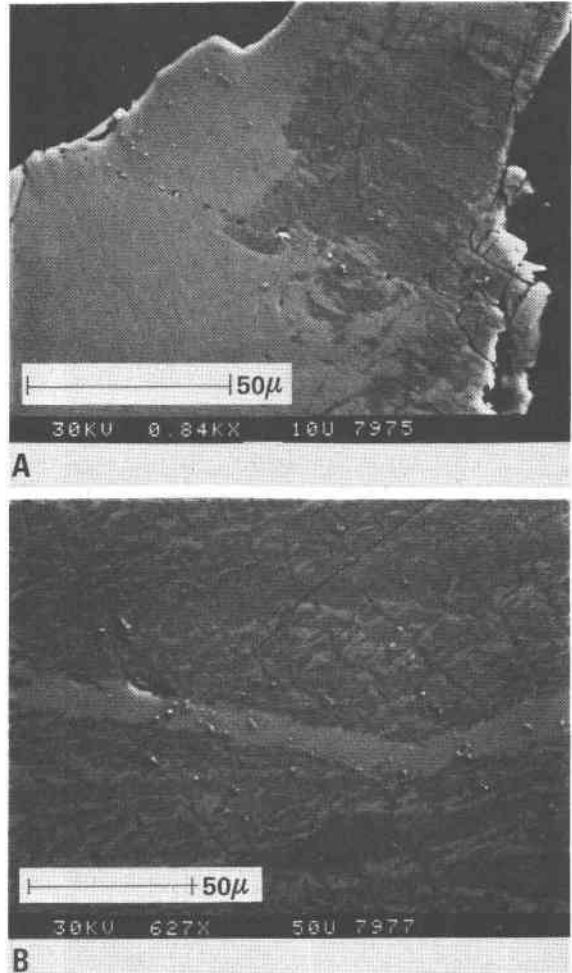Fig. 5. Mössbauer spectra of "ferrifayalites" at 55 K.

Fig. 7. SEM photographs of Mourne Mountains "ferrifayalite", showing two-phase structure and exsolution texture. Scale as shown.
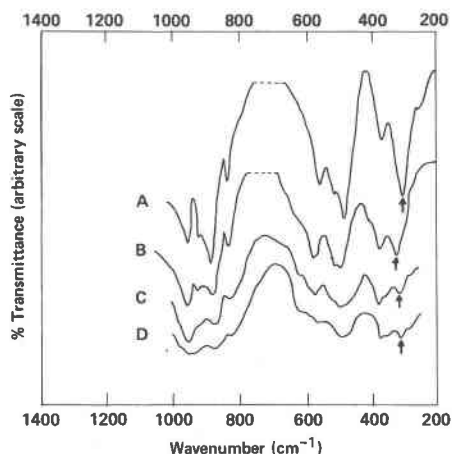
Fig. 8. Infrared spectra of Rockport fayalite and some "ferrifayalites". (A) Rockport fayalite (Huggins, 1970); (B) Mourne Mountains "ferrifayalite" (Huggins, 1970); (C) Chinese "ferrifayalite" L_{5-1} (Zhang et al., 1981); (D) Chinese "ferrifayalite" $79L_{3-4}$ (Zhang et al., 1981).

show an ordinary fayalite spectrum superimposed on another pattern. The other pattern appears to be caused by either ferric iron alone or possibly by a combination of ferric and ferrous iron[3].

This behavior indicates that the ferric and ferrous ions in "ferrifayalite" are completely magnetically uncoupled. In the suggested laihunite structure, the M1 and M2 octahedra containing ferrous and ferric iron share edges, which can result in interaction between the iron atoms. Indeed, it is difficult to arrange the ferrous and ferric ions in the olivine structure in such a way for there not to be any shared edges between their respective coordination octahedra.

Also, the presence of the normal fayalite low-temperature Mössbauer spectrum as part of the "ferrifayalite" spectrum implies the presence of ferrous ions in equal proportions on both the M1 and M2 sites, according to the magnetic model proposed by Santoro et al. (1966). This seeming contradiction in the data can be resolved if one assumes that "ferrifayalite" consists of domains of fayalite and of laihunite, intimately mixed on a very fine scale. The varying ferric–ferrous ratio of "ferrifayalite" is then seen as

the effect of mixing different proportions of fayalite with laihunite.

The presence of the ordinary fayalite Mössbauer spectrum in a "ferrifayalite" sample can now be explained as being produced by the domains of ordinary fayalite. The fact that the ferric and ferrous ions seem to be completely uncoupled is now understandable, if ferric and ferrous ions are more or less isolated from one another, segregated into the two types of domains. SEM photographs, taken to test this hypothesis, do appear to show a two-domain structure, with domain sizes of about $5\mu m$ or more.

If the laihunite structure is as is proposed, the cracks that are seen preferentially in the laihunite domains should not come as a surprise. It is very likely that a material containing such a large proportion of vacancies should be somewhat unstable and, consequently, subject to fracturing. Also, if either laihunite forms as an alteration product of ferrous fayalite, as Kitamura et al. (1984) believe, or it forms syngenetically with the fayalite, fracturing appears likely.

As an alteration product of fayalite, laihunite could be formed by the oxidation of ferrous iron in the lattice, forming vacancies to balance the charge and consequently removing ferrous ions. The resulting distortion of the lattice
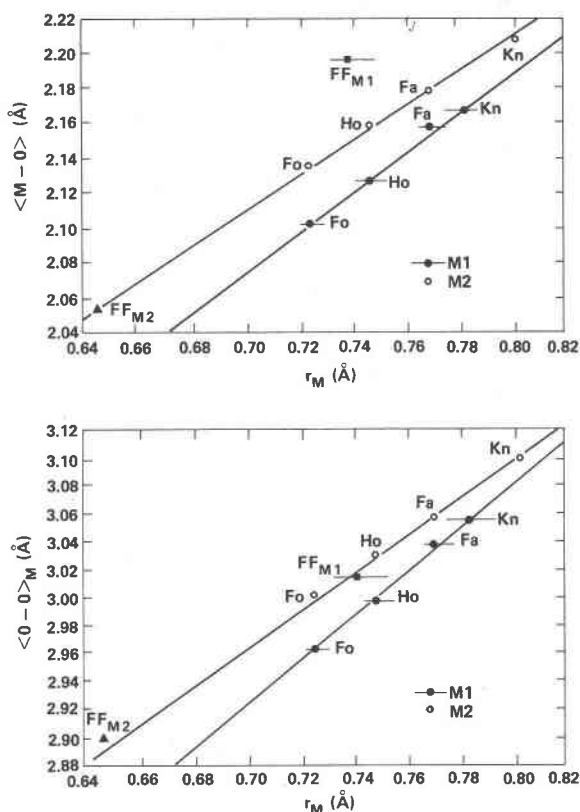
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[3] The low temperature Mössbauer spectrum of "ferrifayalite" has been interpreted by Kan Xuemin (priv. comm.) to consist of two octets produced by ferrous iron, one sextet produced by ferrous iron, and two sextets produced by ferric iron. Although this interpretation is consistent with the spectra I have observed, it is difficult to confirm, due to the extreme complexity of the spectra. If the sextet pattern is indeed due to a superposition of three sextets, one produced by ferrous iron, there should be a reduction in the intensity of the unsplit ferrous doublet over the temperature range of the ferric transition. This reduction has not been observed, but this may be in part due to the lack of a constant peak with which to compare the ferrous doublet intensity.

Fig. 9. (A) Average metal-oxygen distance vs. cation radius for the M1 and M2 sites in olivine (after Brown 1970, 1982); (B) Average oxygen–oxygen distance vs. cation radius for the M1 and M2 sites in olivine (after Brown 1970, 1982).
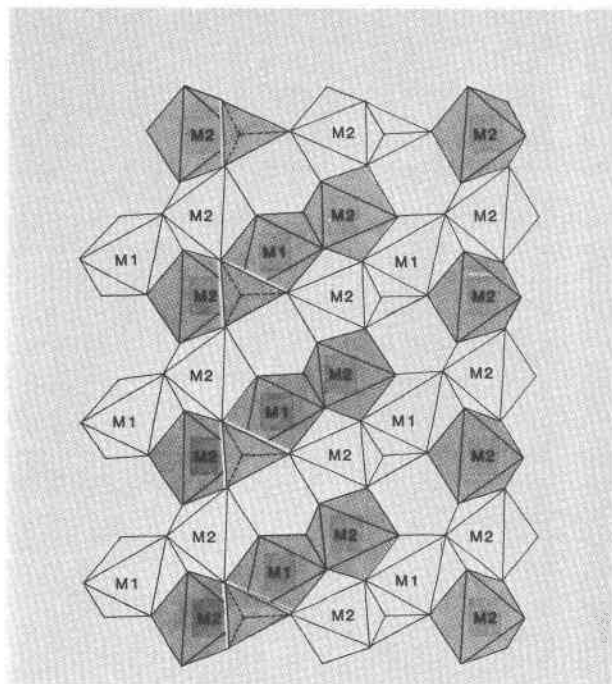
Fig. 10. A possible structure for laihunite.

could cause the observed cracks. If laihunite crystallizes with fayalite out of the melt, perhaps exsolving as the two end members of a solid solution, the difference in size of their unit cells and their difference in symmetry (monoclinic laihunite as opposed to orthorhombic fayalite) could result in enough stress to produce the observed cracks.

The part of the low-temperature "ferrifayalite" Mössbauer spectrum that remains when the fayalite spectrum is subtracted is still somewhat puzzling. Although it would appear, at first glance, to be produced by the ferric ions alone, it seem more likely that it should be produced by a combination of ferrous and ferric cations in the laihunite domains.

Summary

"Ferrifayalite" consists of two phases intimately mixed on a scale of tens of microns. One phase is ordinary ferrous fayalite. The other phase is a Fe^{3+}-rich olivine with the formula $Fe^{2+}Fe_2^{3+}(SiO_4)_2$, or, perhaps more properly, $(Fe_1^{2+}\square_1)^{M1}(Fe_2^{3+})^{M2}(SiO_4)_2$. This phase has a structure similar to fayalite, but contains only Fe^{3+} in the M2 cation site, and a (probably ordered) mixture of Fe^{2+} cations and vacancies in the M1 cation site. The two phases can be distinguished in SEM photographs.

Mössbauer spectra taken at room temperature merely show the presence of both ferrous and ferric iron in octahedral coordination, however. The low-temperature spectra are interpreted to be a superposition of the spectrum of ferrous fayalite and of laihunite. It is not possible at the present time to resolve completely the laihunite spectrum, but it seems likely that it contains as many as 18 lines, resulting from the hyperfine splitting of the lines produced by ferric and ferrous ions.

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