Cation ordering in Fe–Mn silicate olivines

HANS ANNERSTEN, JACOB ADETUNJI AND ANESTIS FILIPPIDIS

Department of Mineralogy and Petrology
Institute of Geology, University of Uppsala
Box 555, S-75122, Uppsala, Sweden

Abstract

The cation distribution in synthetic and natural (Fe,Mn) olivines has been investigated by use of Mössbauer spectroscopy. A partially ordered distribution with Mn^{2+} entering the M2 site and Fe^{2+} entering the M1 site was observed which, however, becomes more disordered at higher temperature of quenching. Gibbs free energy of exchange for the reaction

$$Mn^{2+}(M1) + Fe^{2+}(M2) = Mn^{2+}(M2) + Fe^{2+}(M1)$$

at 1000°C is -3.5 kcal/mole. The observed variations in the a and b parameters of the solid solution series are in general agreement with the expected order–disorder behavior (Lumpkin et al., 1983) but would suggest a higher degree of Fe order into M1 than the results we obtained from Mössbauer spectra.

Introduction

Cation order–disorder in silicate olivines has recently attracted the attention of many crystallographers (see Brown, 1982 for review). In the common Fe–Mg olivines, Fe^{2+} and Mg^{2+} are found by various methods to be almost randomly distributed over the two non-equivalent M1 and M2 octahedral sites. However, other divalent ions such as Ni and Co are strongly fractionated into the M1 site while Mn, Ca and Zn (?) tend to prefer the M2 site in olivine. Furthermore, ordering of some cations in the olivine structures is strongly dependent on the thermal history of the sample, and the potential for geothermometry has been postulated. Although Fe–Mg olivines are found always to be nearly disordered, the (Mg–Mn) olivines are highly ordered at lower temperatures and tend to disorder at higher temperatures (Lumpkin et al., 1983).

Cation order–disorder in olivines is mainly understood using ionic size criteria (Ghose, 1976) or in terms of crystal field stabilization energy (Burns, 1970), and cation ordering may therefore strongly depend on the type of ions occupying the available sites in the olivine structure. Crystal structure refinements of the octahedral site occupancies in silicate olivine have been restricted mainly to Mg-containing olivines. By use of the Mössbauer effect, cation distribution of Fe^{2+}-bearing olivines can be obtained, and the present study will show the distribution of Fe and Mn, which can add valuable information to the crystalline solid solution behavior and relate the cation ordering to lattice parameters as developed by Lumpkin and Ribbe (1983).

Experimental methods

The present study was performed on five synthetic samples and one natural knebelite (OL 6) from Dannemora, Sweden (collection number 273/13 of the Institute of Geology, Uppsala). The synthetic Fe–Mn olivines were prepared from oxide mixtures, melted in an arc furnace and homogenized at 1000°C in vacuo. Optical examination of the homogenized samples shows minute amounts of opaque phases (magnetite) at the grain boundaries, which could be magnetically separated after crushing the sample to a fine powder. Microprobe analysis of the homogenized samples indicated no zoning of the grains (size 100–150 μm), but a slightly lower iron content than the original oxide mixtures. The computer-corrected microprobe analyses are shown in Table 1. X-ray diffraction analyses show no trace of impurities in the powdered olivines. Cell parameters were obtained by using Si as standard and a computer refinement of 15–26 reflections. Table 1 and Figure 1 show the values obtained for Fe–Mn olivines.

The natural sample, obtained from a coarse-grained skarn rock, was found to be close to the join Fe_2SiO_4–Mn_2SiO_4 with only 1.4 wt.% MgO and trace amounts of CaO. The rock unit, which contained this sample, belongs to a regionally metamorphosed iron formation (Magnusson, 1944) which suffered amphibolite facies conditions of around 500–550°C.

The ^{57}Fe Mössbauer spectra were obtained with the powder absorber at elevated temperature. The best resolution of the two absorption doublets, arising from ^{57}Fe at the M1 and M2 sites in olivine, was obtained at 587 K

Table 1. Compositions and cell parameters of investigated Fe–Mn olivines

Sample	OL 1	OL 2	OL 3	OL 4	OL 5	OL 6	OL 6 B
SiO$_2$ wt-%	30.1	30.0	28.5	29.2	28.7	29.1	
FeO	6.0	21.0	34.1	48.9	63.6	38.7	
MnO	63.9	49.0	37.4	21.9	7.7	30.7	
Σ	100.0	100.0	100.0	100.0	100.0	100.0 [1]	
Number of cations on the basis of 4 oxygens							
Si	1.01	1.01	0.97	0.99	0.98	0.98	
Fe^{2+}	0.17	0.59	0.97	1.39	1.82	1.09	
Mn	1.81	1.40	1.08	0.63	0.22	0.88	
X^{Fe}	0.09	0.30	0.47	0.69	0.89	0.55	
X^{Mn}	0.91	0.70	0.53	0.31	0.11	0.44	
Cell parameters							
a Å	4.936(1)	4.871(3)	4.856(2)	4.840(2)	4.826(1)	4.852(2)	4.850(1)
b Å	10.603(2)	10.594(3)	10.585(2)	10.556(2)	10.514(2)	10.575(3)	10.559(2)
c Å	6.241(2)	6.200(2)	6.168(2)	6.135(2)	6.105(1)	6.142(2)	6.149(1)
V Å^3	324.0	319.9	317.0	313.5	309.8	315.1	314.9

[1] The sum includes 1.40 wt-% MgO and 0.1 wt-% CaO

OL 6 B = OL 6 heated at 1000°C 7 days

using equipment and the technique described by Annersten et al. (1982). Site occupancies of Fe in olivine were obtained from the corrected areas under the respective absorption doublets. The applied correction factors were obtained from experimental data on fayalite, Fe$_2$SiO$_4$ (Annersten et al., 1982), which show a slight difference in recoil-free fractions for iron in M1 and M2 sites in olivine at *elevated temperature*. The following expression was therefore used to calculate the iron site occupancy:

$$X_{M1}^{Fe} = \frac{A_{M1}}{A_{tot}} \cdot f_{M1} \text{ and } X_{M2}^{Fe} = \frac{A_{M2}}{A_{tot}} \cdot f_{M2},$$

where A$_{tot}$ denotes the total resonance absorption and A$_{M1}$ and A$_{M2}$ the area under the respective absorption doublet. f$_{M1}$ and f$_{M2}$ are ratios of the recoil free fractions in M1 and M2, respectively. The experimentally observed values from Annersten et al. (1982) yield f$_{M1}$ = 1.01 and f$_{M2}$ = 0.99 measured at 560 K. These factors indicate that the iron occupancy is underestimated in M1 and overestimated in M2 by the measured Mössbauer spectra at elevated temperature. Computer fitted spectra are shown in Figure 2 from the investigated olivines and Tables 2 and 3 give the obtained Mössbauer parameters and site occupancies.

Results and discussion

X-ray diffraction analysis

The variations of the *a*, *b*, *c* and *V* for the crystalline solid solution (Fe,Mn)$_2$SiO$_4$ are shown in Table 1 and

plotted in Figure 1. An appreciable curvature of the cell dimensions is observed for the solid solution series. The most pronounced deviation from a linear relationship is shown by *b*. The curvature reflects an ordered substitution of the cations among the two non-equivalent octahedral sites.

Lumpkin and Ribbe (1983) recently discussed the relationship between cation distribution and lattice parameters in silicate olivine structures. They concluded that *a* is highly correlated to the mean ionic radius of the M1 cation (r$_{M1}$) while *b* is largely dependent on the mean radius of the M2 cations (r$_{M2}$). The cell volume and *c* were found to be functions of the radius of both cations.
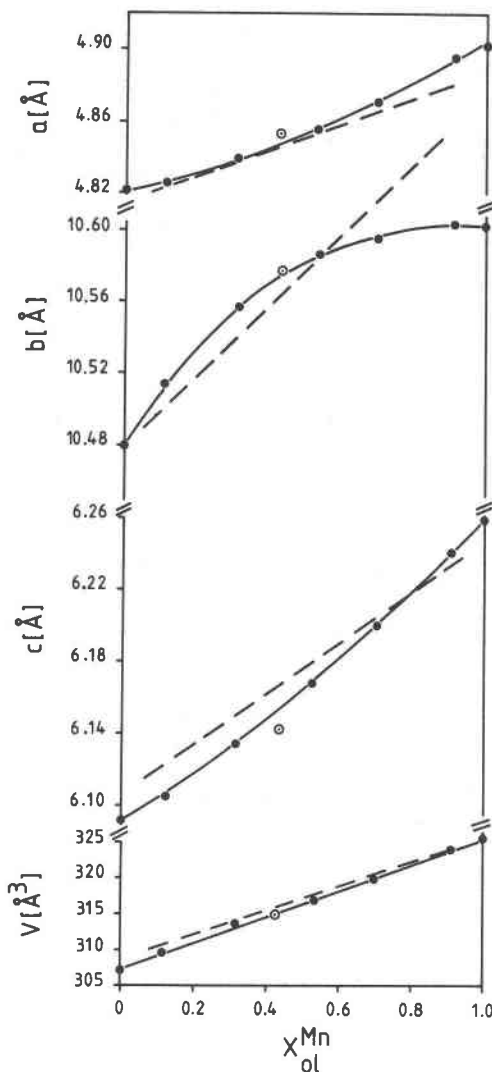

Fig. 1. Cell parameter variations in the (Fe,Mn)$_2$SiO$_4$ solid solution series. Solid dots are synthetic samples, open circles are natural samples (unheated). Dashed line calculated cell parameter variations from regression equation (Lumpkin and Ribbe, 1983).

The interpretation of the present results is thus that the larger Mn^{2+} ion is mainly ordered into the M2 sites in olivine when substituting for iron. At higher manganese content, however, Mn has to enter the M1 site and the high sensitivity to the *b*-axis dimension is lost. A stronger curvature in *a* can be recognized beyond $X^{Mn} \approx 0.5$, although it is not so pronounced as that shown by the change in *b* (cf. Lumpkin and Ribbe, 1983). Our site occupancy data (cf. Table 3) permitted us to use the general formula developed by Lumpkin and Ribbe (1983) relating lattice parameters to effective ionic radius of present cations in olivine. Using the radii given by Shannon (1976) for Fe^{2+} and Mn^{2+}, the formula resulted in a variation of the calculated lattice dimensions for the present synthetic (Fe–Mn) olivines shown by the broken line in Figure 1. Our data are in general agreement, considering the large correction factors applied by Lumpkin and Ribbe (1983).

The natural sample, although not strictly a binary (Fe–Mn) solid solution, has cell dimensions that approach the solid curves shown in Figure 1 for the synthetic (Fe–Mn) olivines. However, especially large changes were observed in the *b*-dimension upon heating the natural sample at 1000°C for one week. The observed 0.017Å decrease in *b* (Sample OL 6 B, Table 1) is indicative of an increased disorder of the cations among the M1 and M2 sites in the model presented by Lumpkin and Ribbe
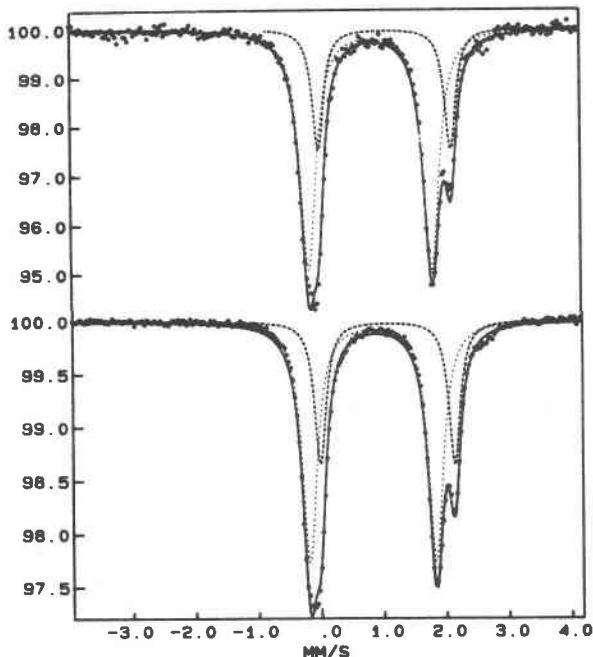
Table 2. Mössbauer parameters of ^{57}Fe in Fe–Mn olivines. Absorber $T = 587$ K

Sample	IS[1] mm/s M1	M2	ΔE_Q mm/s M1	M2	FWHH mm/s	Intensity % M1	M2
OL 1	0.88	0.99	2.12	2.19	0.29	74.7	25.3
OL 2	0.85	1.03	2.06	2.14	0.29	66.7	33.3
OL 3	0.84	1.06	2.04	2.15	0.31	64.4	35.6
OL 4	0.81	1.05	2.00	2.14	0.30	59.3	40.7
OL 5	0.80	1.05	2.06	2.19	0.26	54.3	45.7
OL 6	0.83	1.06	1.97	2.11	0.30	73.7	26.3
OL 6 B	0.82	1.06	2.02	2.14	0.25	68.4	33.2

1) IS relative to natural iron at room temperature

Estimated error for IS an $\Delta E_Q \approx \pm$ 0.01 mm/s, for intensity $\pm$ 2%

(1983). This observation is also in agreement with the cation distribution in natural and heated olivine obtained from Mössbauer spectra (see below). This feature strengthens the importance of having full control of crystallization conditions when using *d*-spacing of olivine X-ray diffraction pattern for compositional determination. For example, the commonly used d_{130}, d_{131}, and d_{112} reflections in crystal chemical studies of olivine, were observed to be 2.852, 2.586, and 2.518Å for the natural olivine compared to the heated natural sample where the same reflections measured 2.848, 2.584, and 2.521Å, respectively.

Mössbauer spectroscopy

The observed Mössbauer parameters (cf. Table 2 and Fig. 3) give valuable information on the bonding of iron in $(Fe,Mn)_2SiO_4$ solid solution series. The distinct difference in the isomer shifts between iron at the M1 and M2 sites in olivine clearly indicates a stronger covalent bonding character of iron in M1. The observed difference is

Fig. 2. Mössbauer spectra obtained at 587 K of natural sample Ol 6 (upper spectrum) and heated sample (lower spectrum). The full line is the sum of the absorption intensity from computer fitting two absorption doublets. ···· absorption doublet from ^{57}Fe in M1 site, ---- absorption doublet from ^{57}Fe in M2 site.

Table 3. Site occupancy in Fe^{2+} in Fe–Mn olivines from Mössbauer spectra

Sample	X^{Fe}_{ol}	X^{Fe}_{M1}	X^{Fe}_{M2}	K_D[1]
OL 1	0.09	0.135	0.045	3.33
OL 2	0.30	0.404	0.197	2.76
OL 3	0.47	0.611	0.331	3.17
OL 4	0.69	0.826	0.556	3.79
OL 5	0.89	0.976	0.805	9.85
OL 6	0.53	0.789	0.276	
OL 6 B	0.53	0.732	0.348	

$$1) \quad K_D = \frac{X^{Fe}_{M1} (1-X^{Fe}_{M2})}{(1-X^{Fe}_{M1}) X^{Fe}_{M2}}$$
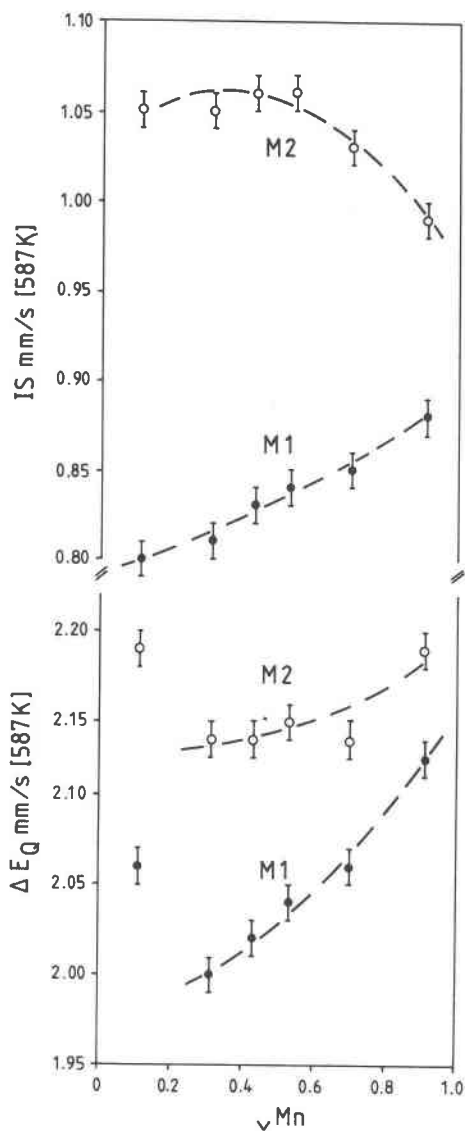
Fig. 3. Variations in the ^{57}Fe Mössbauer parameters for iron in the M1 and M2 sites in the $(Fe,Mn)_2SiO_4$ solid solution series.

in quadrupole splitting with increasing Mn substitution is most likely due to electrostatic changes coupled to the different types of substituting ions.

Iron–manganese distribution in olivine

The measured site occupancy of iron in (Fe–Mn) olivine (Table 3) clearly shows an ordered substitution of Fe^{2+} into the M1 site. The site preference, however, of Fe^{2+} for the M1 site, is temperature dependent as indicated by the naturally heated sample (cf. Fig. 4). It is not known if the heated sample (1000°C) represents an equilibrium distribution, but it approaches the distribution observed for the synthetic olivines annealed at the same temperature. We may express the intracrystalline exchange by the following reaction:

$$Mn^{2+}(M1) + Fe^{2+}(M2) = Mn^{2+}(M2) + Fe^{2+}(M1) \quad (1)$$
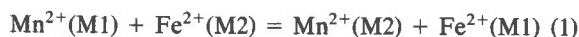
with the following equilibrium constant, assuming ideal solid solution:

$$K_a = \frac{X_{M1}^{Fe} \cdot (1 - X_{M2}^{Fe})}{(1 - X_{M1}^{Fe}) \cdot X_{M2}^{Fe}} \quad (a)$$

This approaches the expression for the distribution coefficient (cf. Table 3). The mean value for K_D observed for the synthetic olivines is 3.8. This value, when inserted in

$$\Delta G° = -RT \ln K_a \quad (b)$$

gives a Gibbs free energy of exchange of -3.5 kcal/mole (-14 kJ/mole), indicating a significant preference of Fe^{2+} for the M1 site in $(Fe,Mn)_2SiO_4$. This value can be
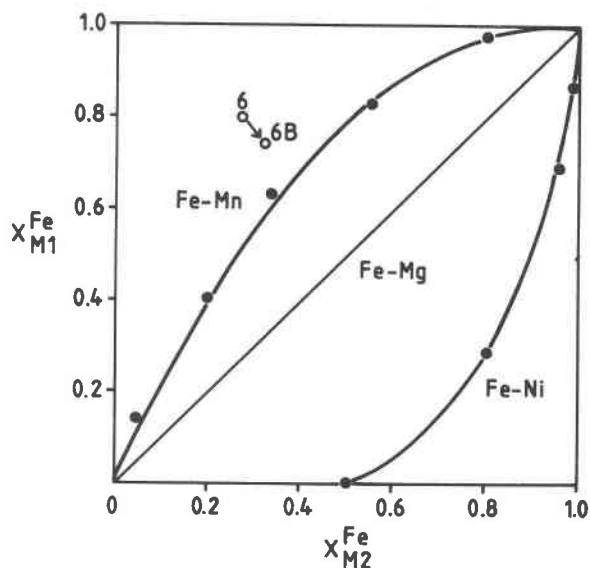

Fig. 4. Iron site occupancy in iron-bearing olivines based on Mössbauer data. Fe–Ni from Annersten et al. (1982); Fe–Mg distribution is close to unity (Brown, 1982); Fe–Mn (this study). Notice the change in ordering of the natural sample when heated (sample OL 6 B).

suggested to arise mainly from the shorter M–O distances observed at the M1 site. The smooth increase of the M1 isomer shifts with increasing manganese substitution is correlated to the increase in the M1–O bond distances with substitution of the larger Mn^{2+} ion (Tang Kai et al., 1980). Isomer shift variations of iron in the M2 site are less regular but show an opposite trend to those associated with the M1 site.

Quadrupole interactions are complex interactions between the iron nucleus and the electric field gradient from the surrounding lattice. The smaller quadrupole splitting observed for the M1 site is in agreement with the slightly larger distortion of the M1 polyhedra (Brown, 1980). Since the bond angle strain will not markedly change with substitution of Mn for Fe in olivine, the observed increase

compared with Gibbs free energy found for $(Fe,Mg)_2$ SiO_4, close to zero kcal/mole (Bush et al., 1970) or the high positive value for $(Ni,Fe)_2SiO_4$ of 6 kcal/mole (Annersten et al., 1982).

The observed Fe–Mn distribution is similar to that observed for Mg–Mn distribution in $(Mg,Mn)_2SiO_4$ (Brown, 1970; Francis and Ribbe, 1980; Lumpkin and Ribbe, 1983). Ordering of cations in the olivine structure is readily explained by ionic size criteria or crystal field stabilization energy. Although exceptions are found (Lumpkin and Ribbe, 1983) these two features seem to account for the major ordering scheme observed in olivines, sometimes in combination. It is therefore interesting to note that iron with an approximately equal preference for both the M1 and M2 octahedral sites in olivine (Walsh et al., 1974) is forced to accept an ordering into the M1 site by entrance into the larger M2 cation site of the larger Mn^{2+} ion, which is not stabilized by the crystal field.

Earlier we discussed the significance of the cation order–disorder in olivine and its manifestation in the lattice parameters. Our data on the cation distribution using Mössbauer spectra may be compared with the observed lattice parameters in an a–b plot based on the equations and correction factors in Table 2 of Lumpkin et al. (1983) (see Fig. 5). It is to be noted that the construction of the a–b plot involves corrections to account for the differences in the observed parameters and the theoretical parameters calculated according to the formula given by

Lumpkin and Ribbe (1983). The observed a–b parameters in the plot are in good agreement with the measured X_{ol}^{Fe}, considering the experimental errors involved in the determination of the cell parameters. The synthetic samples all fall on a smooth distribution line, which, however, suggests a more ordered cation distribution than the observed cation distribution indicated from the Mössbauer spectra (full line in Fig. 5). The position of the natural sample OL 6 falling on the synthetic distribution line seems puzzling at first sight. However, corrections of the a and b parameters for the 4 mole % Mg_2SiO_4 in solid solution ($a = -0.003$Å and $b = 0.013$Å assuming random distribution of Mg among M1 and M2) displace the point well towards the ordered corner of the plot. As shown by the plot, heating of the natural sample increases the disorder, resulting in a decrease in the b parameter. The apparently good agreement between the cation distribution observed in the natural sample, obtained from XRD data and Mössbauer spectra, has to be judged in the light of the corrections accounting for the Mg_2SiO_4 solid solution. It is, of course, not to be expected that perfect agreement between the two methods for observing cation order–disorder in olivine will be obtained. Mössbauer absorption spectra measures exclusively the iron population and is a direct method. Cell parameter variations are related to very complex features (see the discussion of Lumpkin and Ribbe, 1983, and Lumpkin et al., 1983) in the solid crystal, which today are less well known. The
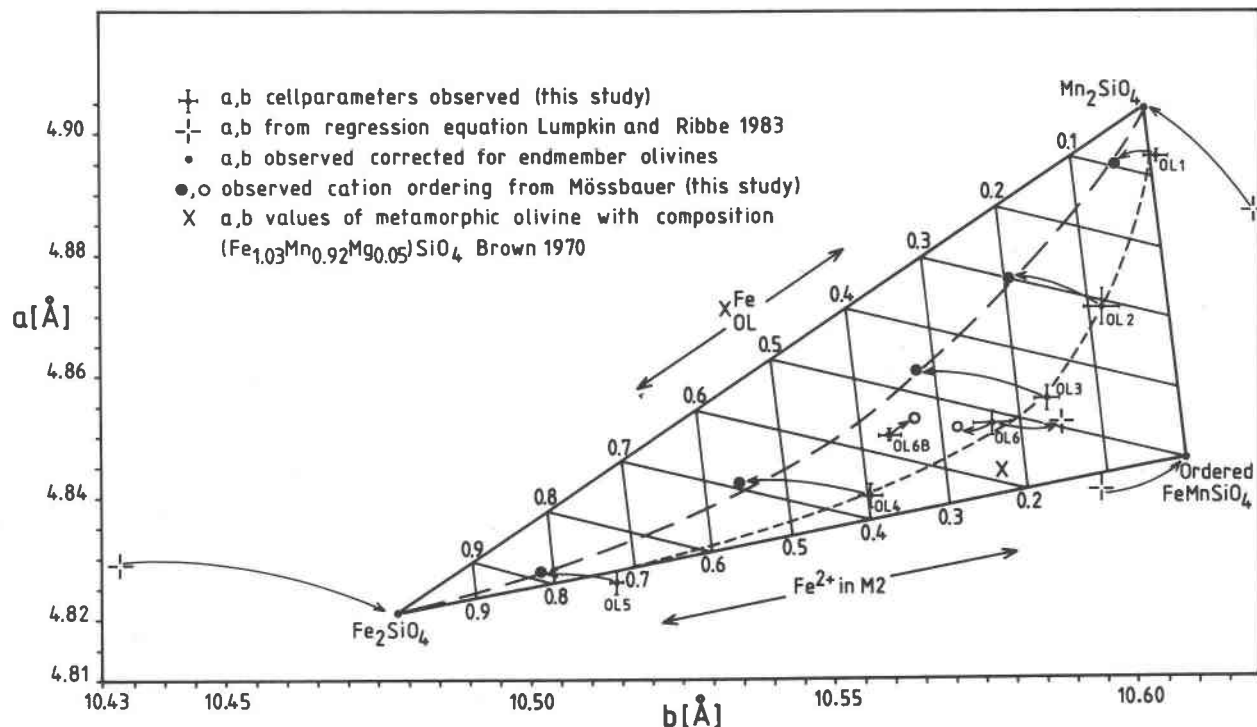

Fig. 5. Site occupancy of iron in $(Fe,Mn)_2SiO_4$ solid solution inferred from an a–b plot (Lumpkin et al., 1983) and corresponding site occupancy obtained by Mössbauer effect data.

present investigation has confirmed that order–disorder has a major influence on the *a–b* cell parameters in olivine solid solutions.

Acknowledgments

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