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The cation distribution in synthetic Mg–Fe–Ni olivines

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Abstract

Synthetic Mg–Fe–Ni olivines annealed at 1000°C have been studied. The site populations of Fe^{2+}, Mg^{2+} and Ni^{2+} among the M1 and M2 sites have been determined by a combination of Mössbauer spectroscopy and the profile-fitting technique based on X-ray powder diffraction data. The Mg^{2+}–Fe^{2+} cation distribution coefficient, $K_D = [X_{Fe}(M1) \cdot X_{Mg}(M2)]/[X_{Fe}(M2) \cdot X_{Mg}(M1)]$, is close to unity but slightly decreases with increasing nickel content. The Ni^{2+}–(Mg^{2+}+Fe^{2+}) cation distribution is close to that of Ni^{2+}–Mg^{2+} earlier reported for some synthetic Ni–Mg olivines.

Introduction

The cation distribution in natural and synthetic Mg–Fe olivines has been discussed in a great number of publications. The Mg^{2+}–Fe^{2+} distribution seems to be almost random but often with iron slightly ordered into the M1 position. The results, though, are rather confusing and sometimes contradictory. For the cation exchange reaction

$$Mg^{2+}(M1) + Fe^{2+}(M2) \rightleftarrows Mg^{2+}(M2) + Fe^{2+}(M1),$$

the cation distribution coefficient is defined as

$$K_D = [X_{Fe}(M1) \cdot X_{Mg}(M2)]/[X_{Fe}(M2) \cdot X_{Mg}(M1)].$$

K_D-values slightly above 1.0 have been reported for natural olivines of terrestrial and lunar origin (*e.g.*, Rajamani *et al.*, 1975) as well as for synthetic olivines (Warburton, 1978). This tendency of ordering is in agreement with crystal field theory (Walsh *et al.*, 1974). However, the scattering among the reported K_D-values is considerable. It now appears that the Mg^{2+}–Fe^{2+} distribution is variable as a function of temperature, oxygen fugacity, composition, and possibly pressure (Brown, 1980). Using Mössbauer spectroscopy, Virgo and Hafner (1972) observed a decrease in the cation ordering at elevated temperatures. Shinno *et al.* (1974), though, have reported increased ordering at higher temperatures from studies of natural olivines. X-ray diffraction studies of olivines at high temperatures (Brown and Prewitt, 1973) indicated little or no change in the ordering. Will and Nover (1979) have suggested that an increased oxygen partial pressure increases the ordering of Fe^{2+} into the M1 site in olivine, a feature also observed by Shinno (1981). Finally, a correlation between the composition and the Mg–Fe distribution has been suggested by Ghose *et al.* (1976), and there is slight evidence of increasing K_D-values with increasing Fe/(Mg+Fe) ratios in olivines (Finger and Virgo, 1971; Wenk and Raymond, 1973; Brown and Prewitt, 1973). In this respect the presence of other elements is also of great importance. For instance, nickel is a common constituent of natural olivines and the most nickel-rich olivine, liebenbergite, has been found to contain as much as 56.32 wt.% NiO (de Waal and Calk, 1973).

Nickel has been found to strongly prefer the smaller M1 site in Ni–Mg olivines (Rajamani *et al.*, 1975; Bish, 1981) as well as in Ni–Fe olivines (Annersten *et al.*, 1982). Nickel, even in low concentrations, may therefore affect the Mg^{2+}–Fe^{2+} distribution. In this study we have evaluated the cation distribution in one Mg–Fe and two nickel-

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Table 1. Composition and unit cell parameters for the synthetic olivines

Sample	H13	H2	H4
SiO_2 wt-%	34.8	35.6	34.8
MgO	24.2	27.4	24.0
FeO	39.0	14.4	3.3
NiO	0	23.1	39.4
Σ	98.0	100.5	101.5
Si	1.00	1.00	1.00
Mg	1.05	1.14	1.02
Fe	0.95	0.34	0.08
Ni	0	0.52	0.90
$\underline{X}_{ol}^{Mg}$	0.53	0.57	0.51
$\underline{X}_{ol}^{Fe}$	0.47	0.17	0.04
$\underline{X}_{ol}^{Ni}$	0	0.26	0.45
$\underline{a}$ (Å)	4.786(2)	4.762(4)	4.747(1)
$\underline{b}$ (Å)	10.332(2)	10.244(5)	10.193(2)
$\underline{c}$ (Å)	6.032(1)	5.989(5)	5.951(3)
$\underline{V}$ (Å^3)	298.2(2)	292.2(4)	287.9(2)

containing Mg–Fe olivines by a combination of Mössbauer spectroscopy and X-ray profile-fitting refinements in order to determine whether there is any compositional dependence on the Mg–Fe distribution.

Experimental techniques and results

Preparation and chemical analysis

The investigations have been based on well-defined synthetic samples. Oxide mixtures (reagent grade) were used as starting materials. For reasons which will be given below, X_{ol}^{Mg} was held almost constant at 0.5. Each sample was crystallized from a melt in an arc furnace in argon atmosphere. Afterwards, they were annealed at 1000°C in evacuated quartz tubes for one week, whereupon they were quenched to room temperature. Inspection of the reaction products under microscope revealed some traces of opaque crystals (metals and oxides) which were easily removed with a hand magnet. The subsequent X-ray diffraction and Mössbauer investigations revealed no trace of impurities after this separation.

Chemical analyses of the three samples (called H13, H2 and H4) were performed using microprobe techniques. From each sample at least five grains larger than 50 μm were analyzed and no zoning of the crystals was observed. The computer-corrected results (average values) are given in Table 1, together with the refined unit cell dimensions (space group *Pbnm*). The magnesium contents are similar in the three olivines. It is quite clear that unit cell volumes decrease when Fe^{2+} is replaced by the significantly smaller Ni^{2+} ions.

Mössbauer spectroscopy

Mössbauer spectra were obtained at high temperatures (673–813 K) in order to increase the resolution as described by Annersten *et al.* (1982). The results, summarized in Table 2 and Figure 1, show the site occupancies of iron (Fe^{2+}) between the M1 and M2 sites.

X-ray profile-fitting refinements

Unfortunately the Mössbauer data do not give a complete picture of the cation distribution in the H2 and H4 olivines, which contain *three* different cations. In order to evaluate the cation distribution in these, some further X-ray studies were undertaken, taking advantage of the relatively large difference in scattering power between magnesium and the two other metals and of the fact that $X_{ol}^{Mg} \approx X_{ol}^{Fe} + X_{ol}^{Ni}$. Due to lack of suitable single crystals, the profile-fitting technique was utilized, using Guinier–Hägg photographic X-ray powder diffraction data ($CrK\alpha_1$ radiation). This procedure has worked well for similar cation distribution studies (*cf.* Nord, 1977; Nord and Stefanidis, 1980). The technique is also described in some detail in these papers.

The Guinier photographs were evaluated by a

Table 2. ^{57}Fe Mössbauer data of the synthetic Mg–Fe–Ni olivines

Sample		H13	H2	H4
Absorber temp. (K)		673	813	810
IS mm/s	M1	0.84	0.71	0.73
	M2	0.90	0.77	0.79
ΔE_Q mm/s	M1	1.84	1.61	1.75
	M2	1.93	1.94	1.98
Area ratio	M1/M2	1.08(1)	0.54(1)	0.42(1)
$\underline{X}^{Fe}$	M1	0.493	0.119	0.024
	M2	0.457	0.221	0.056

IS given relative to metallic iron at room temperature. Relative errors of IS and ΔE_Q ±0.02 mm/s.

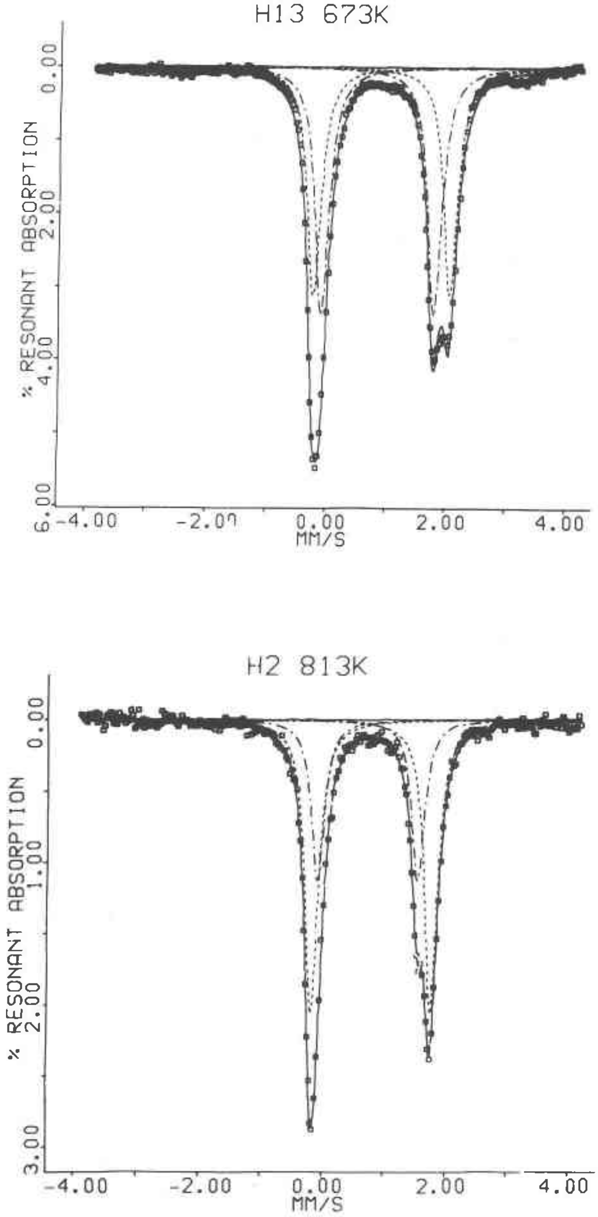

Fig. 1. Mössbauer spectra of the olivines H13 (above) and H2 (below) at elevated temperatures. Outer doublet (----) due to Fe^{2+} in the M2 site, inner doublet (- · · -) due to Fe^{2+} in the M1 site.

computer-controlled film scanner (Johansson *et al.*, 1980; P. E. Werner, Stockholm, personal communication). The net intensities of the diffraction profile, corrected for background, Lorentz and polarization effects and multiplicity factors, were then refined by Rietveld's (1969) procedure, modified for X-ray data by Malmros and Thomas (1977) and by Werner (to be published). Each profile contained 40 partly overlapping independent reflections ($0 \leq \theta \leq 45°$).

In sample H2, $(Mg_{1.14}Fe_{0.34}Ni_{0.52})SiO_4$, the distribution of iron is known from the Mössbauer study (*cf.* Table 2). The complete cation distribution in H2 can thus be expressed by means of only one parameter x defined by $(Mg_{0.36+x}Fe_{0.12}Ni_{0.52-x})^{M1}$ $(Mg_{0.78-x}Fe_{0.22}Ni_x)^{M2}$ (SiO_4), with $0 \leq x \leq 0.52$. In a preliminary step the scale factor and four intensity-profile parameters were refined, with the structure of $(Ni_{1.16}Mg_{0.84})SiO_4$ (Bish, 1981) as a starting model. The complete structure (space group *Pbnm*, No. 62) was then refined with various values of x, always in ten cycles and with 14 parameters: an overall scale factor, 11 atomic positional parameters, and two isotropic temperature factors (for metals, silicon and oxygen, respectively). The conventional R_I values *versus* x are shown in Figure 2 ($0 \leq x \leq 0.52$). (Although in disagreement with the Mössbauer results, some refinements with $x < 0$ were also carried out, now assuming iron and nickel to have equal scattering factors, in order to obtain a more complete survey of the $R_I = f(x)$ dependence.) The curve for H2 has a distinct R_I minimum of 0.085 at $x = 0.07(1)$. The standard deviations were also smallest for this refinement, thus showing that the cation distribution in H2 can be set equal to $(Mg_{0.43}Fe_{0.12}Ni_{0.45})^{M1}$ $(Mg_{0.71}Fe_{0.22}Ni_{0.07})^{M2}$ (SiO_4).

In a similar way a new cation distribution parameter x was defined for H4 by the formula $(Mg_{0.08+x}Fe_{0.02}Ni_{0.90-x})^{M1}$ $(Mg_{0.94-x}Fe_{0.06}Ni_x)^{M2}$ (SiO_4), with $0 \leq x \leq 0.90$. An R_I minimum of 0.112 was found for $x = 0.22(2)$, *cf.* Figure 2. The standard errors of x have been estimated from Figure 2. They may even be slightly larger due to the restrictions imposed upon the thermal parameters. However, earlier studies of Ni–Mg olivines have shown that the thermal parameters of M1 and M2, and also of the silicon and oxygen atoms, were similar within each compound. For instance, Rajamani *et al.* (1975) report $B(M1) = 0.26(1)$ and $B(M2) = 0.27(1)Å^2$, while Bish (1981) reports $B_{eq}(M1) = 0.40(1)$ and $B_{eq}(M2) = 0.43(1)Å^2$. The atomic parameters from the refinements of H2 and H4 are listed in Table 3. The fact that some temperature factors are negative is not uncommon with the profile-refinement technique; it is due to absorption effects. Tables of the observed and calculated integrated intensities from the two "best" refinements are available[1].

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[1] To obtain a copy of these tables, order Document AM-82-211 from the Business Office, Mineralogical Society of America, 2000 Florida Avenue, N. W., Washington, D. C. 20009. Please remit $1.00 in advance for the microfiche.

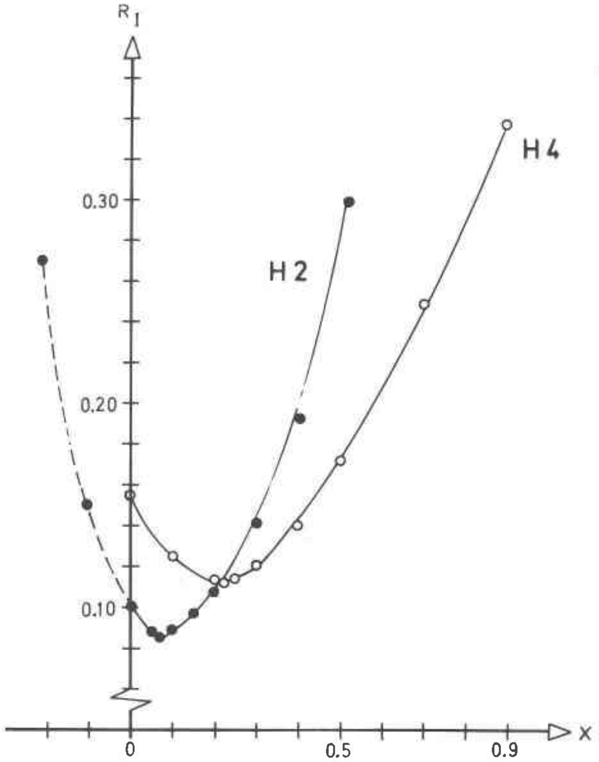

Fig. 2. The R_I-values plotted *versus* the cation distribution parameter x (see text) for H2 and H4.

Discussion

Some interatomic distances for H2 and H4 are given in Table 4. The metal–oxygen and silicon–oxygen distances are reasonable, although the standard deviations are rather large. For both samples the metal–oxygen mean distances are slightly shorter for M1 than for M2 in agreement with earlier structure refinements of Ni–Mg, Mg–Fe and many other olivines. This feature is also in accordance with the smaller isomer shift observed for ^{57}Fe at the M1 site (*cf.* Table 2). Moreover, the average M2–O distance in H2 is significantly longer than the average M1–O in agreement with the fact that the largest cation, Fe^{2+}, concentrates at M2 and the smallest, Ni^{2+}, at M1. No corresponding difference could be observed in H4 because the iron content is low in this compound.

The strong preference of Ni^{2+} for the M1 site in the olivine structure agrees well with earlier studies of Ni–Mg and Ni–Fe olivines. We will first look at the Mg^{2+}–Fe^{2+} cation distribution coefficient $K_D = [X_{Fe}(M1) \cdot X_{Mg}(M2)]/[X_{Fe}(M2) \cdot X_{Mg}(M1)]$. Our calculated K_D-values, 1.16(3), 0.89(4), and 1.00(9) for samples H13, H2, and H4, respectively, are close to unity but slightly lower for the nickel-containing olivines. However, this change may also be interpreted as dependent on the decreasing iron content. The latter tendency has also been observed in natural olivines (see review by Brown, 1980).

The cation distribution may also be viewed from a different angle. Since it is well established that the Mg^{2+}–Fe^{2+} distribution is almost random in Mg–Fe olivines (see Introduction), we can define a pseudo-distribution coefficient K'_D for the Ni^{2+}–Me^{2+} distribution (Me = Mg + Fe) by the equation

$$K'_D = [X_{Ni}(M1) \cdot X_{Me}(M2)]/[X_{Ni}(M2) \cdot X_{Me}(M1)].$$

Table 3. Atomic parameters for H2 and H4 (space group *Pbnm*)

Site		H2	H4
M1		0.43 Mg	0.30 Mg
		0.12 Fe	0.02 Fe
		0.45 Ni	0.68 Ni
	x	0	0
	y	0	0
	z	0	0
M2		0.71 Mg	0.72 Mg
		0.22 Fe	0.06 Fe
		0.07 Ni	0.22 Ni
	x	0.989(2)	0.986(2)
	y	0.278(1)	0.277(1)
	z	1/4	1/4
B(M1/M2)		-0.9(3)	+0.9(3)
Si	x	0.418(3)	0.426(4)
	y	0.098(1)	0.096(1)
	z	1/4	1/4
O(1)	x	0.776(4)	0.779(5)
	y	0.102(2)	0.101(2)
	z	1/4	1/4
O(2)	x	0.207(4)	0.207(4)
	y	0.470(2)	0.458(3)
	z	1/4	1/4
O(3)	x	0.274(3)	0.265(3)
	y	0.163(2)	0.167(2)
	z	0.029(3)	0.035(4)
B(Si/O)		-2.3(4)	-0.3(4)

The numbers within parentheses represent estimated standard deviations and refer to the uncertainty in the last decimal place

Table 4. Some interatomic distances (Å) in H2 and H4

	H2 $(Mg_{1.14}Fe_{0.34}Ni_{0.52})SiO_4$	H4 $(Mg_{1.02}Fe_{0.08}Ni_{0.90})SiO_4$
$(M1)O_6$ octahedron		
M1-O range	2.07-2.13	2.08-2.13
M1-O mean	2.11(1)	2.10(2)
$(M2)O_6$ octahedron		
M2-O range	2.05-2.23	2.05-2.16
M2-O mean	2.15(2)	2.11(2)
SiO_4 tetrahedron		
Si-O mean	1.61(2)	1.63(2)

The K'_D-values for H2 and H4 are 11(1) and 7.5(1.5), respectively. This may be compared with the corresponding values obtained for pure Ni–Mg olivines, *i.e.*, with *Me* = Mg in the equation above. Rajamani *et al.* (1975) reported $K'_D = 9.2$ for their $Ni_{1.03}Mg_{0.97}SiO_4$ olivine prepared around 1250°C while Bish (1981) obtained $K'_D = 9.9(4)$ for a $Ni_{1.16}Mg_{0.84}SiO_4$ phase synthesized at 500°C. Annersten *et al.* (1982) obtained a K'_D-value of 12.7 for $Ni_{0.97}Fe_{1.03}SiO_4$, quenched at 1000°C (*i.e.*, *Me* = Fe in the formula above).

In our three olivines, the magnesium contents are similar; this was done intentionally to avoid further confusion. Upon the introduction of nickel in the Mg–Fe olivine (and the simultaneous decrease of the iron contents) it is clear that Ni^{2+} preferentially enters the M1 sites, in accordance with size and crystal field criteria (Burns, 1970). From the discussion above on K'_D it is tempting to suggest, that among the numerous factors determining the cation distribution in olivine, the nickel ion determines the major features of the distribution pattern. Decreasing K_D-values with nickel content also show decreasing preference of Fe^{2+} for the M1 site. This may be explained from the fact that Ni^{2+} tends to shrink the M1 octahedra, which restrains iron rather than the smaller magnesium ions from residing at the M1 sites. Ghose and Wan (1974) have also suggested that ionic size criteria may be a determining factor for a compositional dependence of the Mg–Fe distribution. Furthermore, entrance of Ni^{2+} into the M1 octahedra will make these less distorted. Since divalent iron (d^6) gains extra stabilization energy in a distorted site, a decreased preference of Fe^{2+} for the M1 sites might be a consequence of an increasing nickel content.

The observed changes in the Mg–Fe distribution with composition indicate a non-ideal solid solution behavior in Mg–Fe–Ni olivines at about 1000°C. Since nickel does not seem to disorder significantly at higher temperatures, the influence of this element on the Mg–Fe distribution may be considered over a large temperature range. However, more must be known about the kinetics of the cation exchange in olivines before compositional-dependent cation distribution results can be used to interpret thermal histories of nickel-containing Mg–Fe olivines. We also believe that cation distribution studies of natural and synthetic olivines containing three or more metals are of great importance for fruitful geological interpretations.

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