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Cation Ordering in Ni-Mg Olivine

V. RAJAMANI,[1]

Department of Earth and Space Sciences, State University of New York,
Stony Brook, New York 11794

GORDON E. BROWN,

Department of Geology, Stanford University,
Stanford, California 94305

AND C. T. PREWITT

Department of Earth and Space Sciences, State University of New York,
Stony Brook, New York 11794

Abstract

A synthetic crystal of Ni-Mg olivine—$Ni_{1.03}Mg_{0.97}SiO_4$; a = 4.7366(4); b = 10.1716(13); c = 5.9374(4) Å—has been investigated by X-ray methods in order to determine the intracrystalline distribution of Ni and Mg. Anisotropic least squares refinement of the structure, including cation occupancies, to $R = 0.029$ indicates significant ordering of Ni on $M1$ (0.767 Ni + 0.233 Mg; $\sigma = \pm 0.002$ Ni) and of Mg on $M2$ (0.737 Mg + 0.263 Ni). The intracrystalline distribution coefficient, K_D = (Mg[$M2$]/Ni[$M2$])/(Mg[$M1$]/Ni[$M1$]), equals 9.22. This amount of Ni-Mg ordering is surprising in view of the small size difference [Δr = 0.03 Å] between the two cations and the slight ordering observed in some Fe-Mg olivines [K_D = 1.00 − 1.30] and suggests that crystal field effects strongly favor Ni on the $M1$ site of olivine, in agreement with the predictions of Burns (1970a) and others. Comparison of the available site occupancy data for transition metal olivines and pyroxenes indicates that site preferences of divalent Fe, Co, Ni, and Mg depend on a balance between such crystal chemical factors as cation size, charge, electronegativity, crystal field effects, and the nature of the two octahedral sites in each structure. In particular, the differences in residual charge, ζ, at these sites [$Z_{M1(ol)} = Z_{M2(ol)} = \zeta_{M2(pyx)} = 0.0$; $\zeta_{M1(pyx)} = -0.66$ v.u.] enhances the ordering of transition metal cations on the $M2$ site of pyroxenes relative to Mg.

Introduction

Inter- and intra-crystalline distributions of cations in the structures of rock-forming silicates have been and continue to be the subjects of intense investigation by mineralogists and petrologists because of their potentially useful applications as geothermometers and geobarometers involving igneous and metamorphic rocks. For example, geothermometers based on intra-crystalline exchange of Fe^{2+} and Mg in ortho- and clinopyroxenes and of Al and Si in the alkali feldspars are well known, as is the one based on inter-crystalline exchange of Ni between augite and olivine. Crystal chemical factors that govern cation distributions are not yet completely understood and the problem gains additional complexity when transition metal cations are involved. For these cations, two other crystal chemical factors, (1) their variable oxidation states and (2) crystal field stabilization energies [CFSE], become moderately important in addition to other common atomic properties such as charge, radius, electronegativity and polarizability. A number of authors have emphasized the importance of CFSE gained by these cations in mineral structures in determining their distribution within and between minerals during magmatic crystallization or metamorphism (Williams, 1959; Burns and Fyfe, 1964; Curtis, 1964; Schwarcz, 1967; Matsui and Banno, 1969; Burns, 1970a). Applying crystal field theory to the problem of cation ordering in the two crystallographically distinct octahedral sites of the olivine and orthopyroxene structures, Burns (1970a) predicted the cation distributions listed in Table 1. These predictions have been experimentally verified for Fe-Mn and Mg-Mn olivines (Brown, 1970; Huggins, 1973) and for Fe-Mg pyroxenes (Ghose,

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[1] Present Address: Department of Geology, University of Toronto, Toronto, Ontario, Canada.

TABLE 1. Predicted Cation Distribution in Olivine and Orthopyroxene*

M-Cations	Δr(Å)	Olivine M1	Olivine M2	Orthopyroxene M1	Orthopyroxene M2
Mg - Ni	0.03	Ni	Mg	Ni	Mg
Mg - Co	0.025	Co	Mg	Mg	Co
Mg - Fe	0.06	Mg	Fe	Mg	Fe
Mg - Mn	0.11	Mg	Mn	Mg	Mn
Mn - Fe	0.05	Fe	Mn	Fe	Mn

* after Burns (1970a)

1965; and many others since). However, for Fe-Mg olivines, the problem of ordering in the two cation sites, *M*1 [C_i or $\bar{1}$ point symmetry] and *M*2 [C_s or *m* point symmetry], has become a controversial subject because there is no general agreement among the various investigators who have studied the problem using different mineralogical techniques. For example, Burns (1970a, b) suggested that there is almost complete disorder to slight enrichment of iron in the larger *M*2 site of olivine based on optical absorption spectroscopy. However, a number of recent X-ray and Mössbauer studies of lunar and terrestrial olivines have shown that the larger cation, Fe^{2+}, has a slight but significant preference for the smaller *M*1 site (Finger, 1970; Bush, Hafner, and Virgo, 1970; Finger and Virgo, 1971; Virgo and Hafner, 1972; Brown and Prewitt, 1973; Wenk and Raymond, 1973; Smyth and Hazen, 1973). The results of these studies are shown in Figure 1, where intra-crystalline distribution coefficient, K_D [K_D = (Mg[*M*2]/Fe[*M*2])/(Mg[*M*1]/Fe[*M*1])], is plotted against mole percent fayalite. Figure 1 shows that Fe^{2+} is slightly enriched in *M*1 [$K_D > 1$] and that there is no significant correlation of K_D with composition. Furthermore, it should be noted that for the natural Fe-Mg olivines examined so far, cooling histories tend to have only minor and apparently opposite influence on Fe-Mg ordering—*i.e.*, olivines crystallized from a rapidly cooled magma were found to show relatively more ordering (enrichment of Fe in the *M*1 site) than those from slowly cooled igneous and metamorphic rocks (Finger and Virgo, 1971; Brown and Prewitt, 1973; Wenk and Raymond, 1973).

Crystal chemical reasons for the observed enrichment of Fe^{2+} in the smaller *M*1 site of olivine, although only slight, are by no means conclusive. Indeed, if the relative sizes of $^{VI}Mg^{2+}$ and $^{VI}Fe^{2+}$ [0.72 and 0.78 Å, respectively] and crystal field stabilization of Fe^{2+} in the two sites[2] were mainly responsible for cation site preferences, Fe^{2+} would be expected to show an enrichment in the larger *M*2 site as Burns has predicted. Even though the site preference energy of Fe^{2+}, as calculated by Burns, for the *M*2 site of olivine [0.2 to 0.8 kcal/mole] is larger than that for the *M*2 site of orthopyroxene [0.2 kcal/mole], in which Fe^{2+} is strongly preferred, the majority of olivines studied show slight ordering of Fe^{2+} in the *M*1 site. If the calculations of Burns are correct, these differences suggest that neither crystal field effects, alone, nor cation size, alone, controls Fe-Mg ordering in these cases.

The present study was undertaken in order to understand better the factors controlling site preferences of transition metal cations such as $Fe^{2+}(d^6)$, $Co^{2+}(d^7)$, and $Ni^{2+}(d^8)$ in the olivine and pyroxene structures. For this purpose we chose to investigate Ni-Mg ordering in a synthetic Ni-Mg olivine

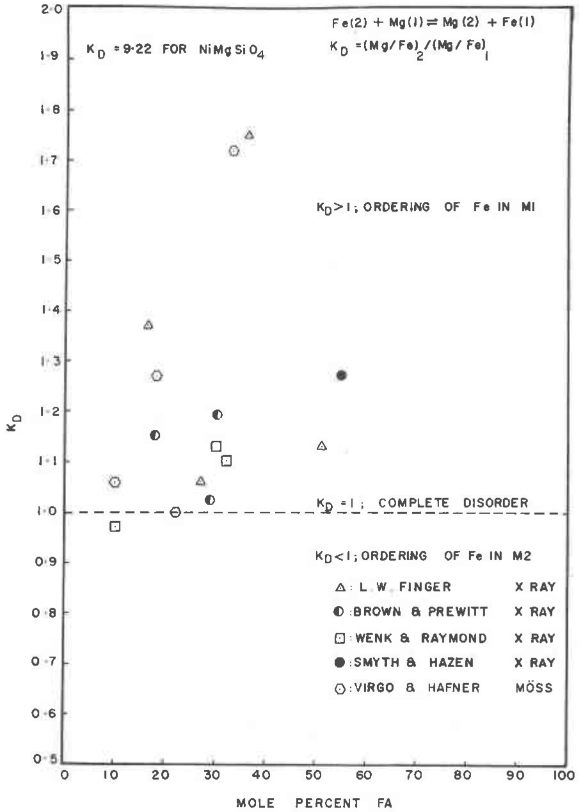

FIG. 1. Comparison of Fe/Mg intracrystalline distributions (expressed as K_D) as a function of fayalite content for fifteen Fe-Mg olivines. Data are from Finger (1970), Virgo and Hafner (1972), Brown and Prewitt (1973), Wenk and Raymond (1973), and Smyth and Hazen (1973).

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[2] Burns (1970a) has calculated the CFSE of Fe^{2+} for the two sites in olivine and found that iron has site preference energy [CFSE(*M*2) − CFSE(*M*1)] for the *M*2 site, which varies between 0.8 and 0.2 kcal/mole in the composition range Fa_{96} to Fa_{12}.

using X-ray diffraction techniques. We felt that because of the relatively small size difference between Ni and Mg [0.03 Å; see Table 1], crystal field effects could be examined more or less independently from the effects of cation size. Additional impetus for this study derives from earlier spectroscopic studies of Ni-Mg olivines and pyroxenes which are not conclusive. Infrared studies of synthetic Ni-Mg olivines by Tarte (1963) and Duke and Stephens (1964) are ambiguous concerning Ni-Mg ordering and, as interpreted by Huggins (1973), are contradictory. Optical absorption spectra of synthetic Ni-Mg olivines (Reinen, 1968) and clinopyroxenes (White, McCarthy, and Scheetz, 1971) have been interpreted as evidence of preferential ordering of Ni into the *M*1 site of olivine and the *M*2 site of pyroxene. These assignments agree with the Ni-Mg distributions as deduced by Matsui and Syono (1968) for synthetic olivines and by Matsui, Syono, Akimoto, and Kitayama (1968) for synthetic orthopyroxenes based on deviations of cell parameter *versus* composition plots from linearity. However, they disagree with the theoretical prediction of Burns (1970a; see Table 1) in the case of orthopyroxene and the results of a statistical study by Dasgupta (1972); see also a rebuttal by Burns (1972) in the case of olivine. The present study, which was reported earlier (Brown, Rajamani, and Prewitt, 1973), was carried out to help resolve these differences.

Experimental Details

The crystals used in this study were grown in $NaWO_4 \cdot 2H_2O$ flux by Dr. Jun Ito of Harvard University. $NiCO_3$, $Mg(OH)_2$, and H_2SiO_4 were used as starting materials, and cooling was accomplished in two steps—from 1280°C to 1000°C at 5°C per hour and from 1000°C the temperature was lowered to room temperature by turning off the power supply to the furnace. A small [~0.15 mm diam.], euhedral, transparent, emerald-green crystal, displaying sharp, uniform optical extinction under crossed nicols, was first examined by precession photography, which confirmed it to be an olivine with cell parameters $a = 4.74$, $b = 10.17$, $c = 5.94$ Å [all ±0.01 Å]; $\alpha = \beta = \gamma = 90.00°$. After the collection of intensity data, described below, this crystal was chemically analyzed using an ARL electron microprobe. Homogeneous crystals of synthetic Ni olivine, Fo_{33}, and An_{43} were used as standards for Ni, Mg, and Si, respectively. The crystal was found to be moderately zoned with respect to Ni and Mg, which vary inversely across the crystal. Analyses were first carried out in the standard fashion with focused beam, then followed by analysis with the electron beam broadened. Both data sets were reduced following the method of Bence and Albee (1968), each resulting in the average composition shown in Table 2. Because of the relatively high oxide total [$\Sigma = 102.9$, see Table 2], a second analysis was performed using an enstatite glass as standard for Mg and Si; however, the results were unchanged and the high total remains unexplained.

TABLE 2. Crystal Data for Ni-Mg Olivine

Method of Synthesis

$NiCO_3 + Mg(OH)_2 + H_2SiO_4$ $[NaWO_4 \cdot 2H_2O$ flux$]$ $\xrightarrow[72\ hrs]{1280°C}$ $NiMgSiO_4$

Cooled at 5°C/hr from 1280°C to 1000°C, then natural quench

Microprobe Composition

NiO: 44.8 % MgO: 22.7 % SiO_2: 35.4 % $Ni_{1.03}Mg_{0.97}SiO_4$

Space Group	Calculated Density	Linear Absorption Coefficient
Pbnm	4.09 gm/cm^3	75.65 cm^{-1}

Cell Parameters[1] (Å)

$a = 4.7366(4)$; $b = 10.1716(13)$; $c = 5.9374(4)$; $V = 286.06(4)$ Å^3

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[1] Numbers in parentheses are estimated standard errors (1σ) and refer to the last decimal place quoted.

The intensities of approximately 650 independent reflections in the range 1 − 70° 2θ were collected in the ω-2θ mode on an automated Picker diffractometer employing graphite monochromatized MoKα radiation. Lorentz and polarization corrections were applied in the standard fashion, and refinement of the structure was initiated using L. W. Finger's RFINE least squares program, neutral atomic scattering factors of Doyle and Turner (1968), and the positional and thermal parameters obtained by Brown and Prewitt for a lunar olivine [12052]. No absorption correction was applied prior to refinement. Occupancies of Ni and Mg in the two octahedral sites were allowed to vary with the chemistry of these sites constrained to 1.03 Ni + 0.97 Mg. Final anisotropic refinement of the structure which included scale factor, secondary extinction parameter, positional and thermal parameters, and occupancy of Ni and Mg in the two cation sites resulted in an unweighted *R* factor of 2.9 percent. Unit weights were used in both isotropic and anisotropic refinements. The refined parameters are listed in Table 3. Interatomic distances were calculated from the refined positional parameters using L. W. Finger's ERROR program and are listed in Table 4.

A second crystal was used to obtain precise cell

TABLE 3. Positional and Thermal Parameters of Synthetic Ni-Mg Olivine Compared with Olivine (12052) of Brown and Prewitt (1973)

Site		Ni-Mg Olivine	Fe-Mg Olivine (12052)
M1		0.767(2)* Ni 0.233 Mg	0.675 Mg 0.325 Fe
	x	0.0	0.0
	y	0.0	0.0
	z	0.0	0.0
	B	0.26(1)	0.36(2)
M2		0.737 Mg 0.263 Ni	0.705 Mg 0.285 Fe + 0.010 Ca
	x	0.9907(1)	0.9877(1)
	y	0.2750(1)	0.2783(1)
	z	0.25	0.25
	B	0.27(1)	0.34(2)
Si	x	0.4260(1)	0.4276(1)
	y	0.0937(2)	0.0952(1)
	z	0.25	0.25
	B	0.30(2)	0.29(2)
O(1)	x	0.7672(4)	0.7659(3)
	y	0.0931(2)	0.0920(1)
	z	0.25	0.25
	B	0.44(3)	0.44(3)
O(2)	x	0.2193(4)	0.2181(3)
	y	0.4451(2)	0.4493(1)
	z	0.25	0.25
	B	0.42(3)	0.42(3)
O(3)	x	0.2755(3)	0.2809(2)
	y	0.1625(1)	0.1637(1)
	z	0.0316(2)	0.0340(3)
	B	0.45(3)	0.55(2)
R**		0.029	0.025

* The numbers in parentheses represent calculated standard errors (1σ) and refer to the uncertainty in the last decimal place.

** $R = \Sigma[|F_o| - |F_c|]/\Sigma|F_o|$

parameters based on least squares refinement using the 2θ values of 22 reflections ($2\theta \geq 30°$) measured on a Picker diffractometer. These parameters (see Table 2) compare well with those obtained for crystal 1 using the precession camera. However, precession cell parameters were used in all calculations and are plotted in Figure 2.

Results and Discussion

In spite of the uncertainties in the microprobe composition of the Ni-Mg olivine crystal used in this study (see experimental details), we are reasonably confident that our structural model, including the composition reported in Table 2, is consistent with the X-ray intensity data. Past experience with a number of structural refinements of olivines of various compositions has shown that the isotropic temperature factors of the *M*1 and *M*2 sites are sensitive to errors in chemical compositions when the two major octahedral cations present differ significantly in scattering power [*e.g.*, $\Delta > 50$ percent over the entire $\sin\theta/\lambda$ range for Ni or Fe *versus* Mg] and when other systematic errors are negligible. An incorrect deficiency of scattering power in one of the two octahedral sites of the model structure normally results in an unusually small isotropic thermal parameter, *B*, whereas an incorrect excess results in an unusually large *B*. For example, the assignment of an incorrect excess of 0.16 Fe^{2+} and 0.15 Fe^{2+} to the *M*1 and *M*2 sites, respectively, of a lunar olivine (12018; correct composition = Fa_{18}; Brown and Prewitt, 1973, their Table 10) resulted in *B* values of 0.64Å^2 for the *M*1 and *M*2 sites and an unweighted *R* factor of 3.5 percent. When the correct composition was used, the *B* values refined to 0.38Å^2 with an *R* factor of 2.3 percent. Well-refined, room-temperature olivine structural models of various compositions generally exhibit isotropic *B*'s for the *M*1 and *M*2 sites in the range 0.20 to 0.45Å^2 (Birle, Gibbs, Moore, and Smith, 1968; Brown, 1970; Finger, 1970; Wenk and Raymond, 1973; Brown and Prewitt, 1973; Smyth and Hazen, 1973). The thermal param-

TABLE 4. Interatomic Distances (Å) in Ni-Mg Olivine Compared with Synthetic Ni_2SiO_4 (Brown, 1970) and Synthetic Forsterite (Smyth and Hazen, 1973)

Polyhedron	Ni_2SiO_4	Ni-Mg Olivine	Forsterite
M1 Octahedron			
*[2] M1 - O(1)	2.065	2.079	2.085
[2] M1 - O(2)	2.062	2.071	2.069
[2] M1 - O(3)	2.102	2.114	2.132
Mean M1 - O	2.076	2.088	2.095
M2 Octahedron			
[1] M2 - O(1)	2.110	2.131	2.183
[1] M2 - O(2)	2.041	2.040	2.051
[2] M2 - O(3)	2.051	2.061	2.067
[2] M2 - O(3)	2.178	2.194	2.216
Mean M2 - O	2.102	2.114	2.133
Si Tetrahedron			
[1] Si - O(1)	1.613	1.617	1.615
[1] Si - O(2)	1.663	1.660	1.654
[2] Si - O(3)	1.641	1.638	1.635
Mean Si - O	1.641	1.638	1.635

* The numbers in brackets refer to the multiplicity of the bond. Estimated standard errors (1σ) for the M1-O, M2-O and Si-O distances are ±0.002 Å.

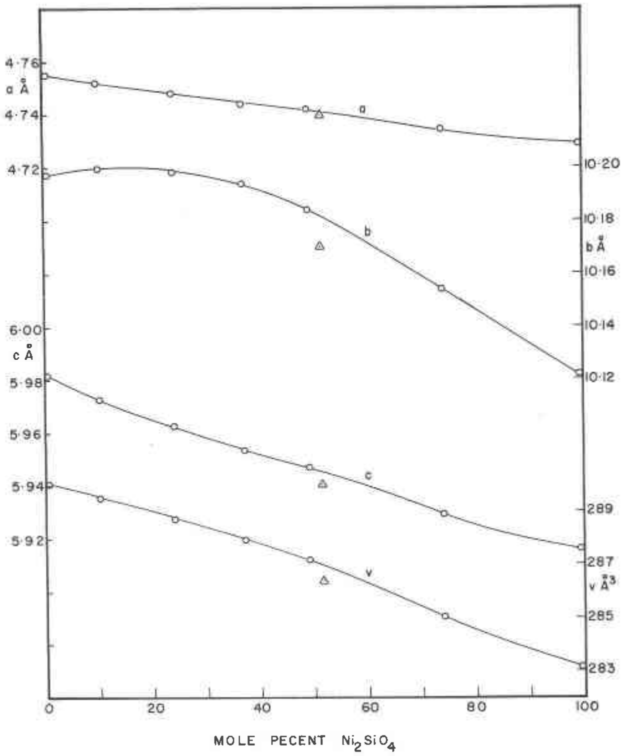

FIG. 2. Plot of cell parameters *versus* mole percent Ni_2SiO_4 for Ni-Mg olivine solid solution series (after Matsui and Syono, 1968). Data points from this study are shown as triangles.

eters for the *M*1 and *M*2 sites of Ni-Mg olivine, 0.26 and 0.27Å^2, respectively, are centered in this range of values and support our assigned octahedral site chemistry.

Comparison of the cell parameters of Ni-Mg olivine obtained in the present study with those reported by Matsui and Syono (1968) for the Ni-Mg solid solution series shows that our *b* cell parameter is significantly smaller than the value reported by these authors for similar compositions (Fig. 2). The reason for this discrepancy is not clear; however, the high probability that our sample does not possess an equilibrium intracrystalline distribution of Ni and Mg between *M*1 and *M*2 may explain it in part. Another possible explanation is that the excess volume of mixing in the Ni-Mg solid solution series may not be as large as reported by Matsui and Syono (1968).

The general structural details of olivine have been thoroughly discussed by Birle *et al* (1968) and therefore do not warrant further discussion here. Interatomic distances of Ni-Mg olivine are compared with those of Ni_2SiO_4 (Brown, 1970) and Mg_2SiO_4 (Smyth and Hazen, 1973) in Table 4. Although the *M*1 and *M*2 sites of Ni-Mg olivine contain predominately Ni and Mg, respectively, the mean *M*1-O distance [2.088 Å] lies closest to that of forsterite [*M*1-O = 2.095 Å; *M*2-O = 2.133 Å], whereas, the mean *M*2-O distance [2.114 Å] lies closest to that of Ni_2SiO_4 [*M*1-O = 2.076 Å; *M*2-O = 2.102 Å].

The refined cation occupancies in the two octahedral sites (listed in Table 3) indicate that Ni is strongly enriched in the *M*1 site. The distribution coefficient, K_D, as defined earlier, is 9.22, which is almost an order of magnitude larger than 1.75, the previous maximum value observed by Finger and Virgo (1971). Because the crystal was moderately zoned, the observed K_D may not represent the equilibrium distribution of Ni and Mg in the two sites. Therefore, high temperature structural studies are being conducted to establish the equilibrium distribution of these cations.

The observed enrichment of Ni in the smaller *M*1 site of the olivine structure is in good agreement with previous suggestions and predictions (Reinen, 1968; Burns, 1970a; Huggins, 1973). However, the degree or magnitude of ordering is somewhat surprising if we consider the difference in the effective ionic radii of $^{VI}Ni^{2+}$ and $^{VI}Mg^{2+}$ [$\Delta r = 0.03$ Å], compared to the larger radii difference between $^{VI}Fe^{2+}$ and $^{VI}Mg^{2+}$ [$\Delta r = 0.06$ Å]. Possible reasons for this strong ordering include the following: (a) The *M*1 site in the olivine structure is inherently smaller than the *M*2 site even when both sites are occupied exclusively by Mg; therefore, because $^{VI}Ni^{2+}$ is smaller than $^{VI}Mg^{2+}$, it should prefer the smaller site. (b) Because the *M*1 site is smaller, the magnitude of crystal field splitting [Δ_o] of the *d* orbitals of a transition metal cation should be larger in the *M*1 site (since $\Delta_o \sim 1/(M\text{-}O)^5$), assuming that both *M*1 and *M*2 are equally distorted octahedra. Therefore Ni^{2+} [d^8] would gain greater CFSE in the *M*1 site. (c) In the olivine structure, both cation sites, *M*1 and *M*2, are distorted from true octahedral symmetry. Ni^{2+}, however, does not gain additional stabilization in a distorted octahedral site because of its unique electronic configuration (Burns, 1970a, p. 123). Thus, all of the above factors are simultaneously responsible for the observed enrichment of Ni in the *M*1 site relative to Mg. The intracrystalline cation distribution in Ni-Mg olivine is analogous to that of Fe-Mg orthopyroxene where Fe^{2+} is enriched in the *M*2 site. Here again, cation size, cation-site size and its distortion, and CFSE act together in the same direction, leading to significant enrichment of Fe in the *M*2 site relative to Mg.

TABLE 5. Comparison of Cation Environments in the Olivine and Orthopyroxene Structures at 24°C

	Forsterite[1]			Enstatite[2]		
	M1	M2	Δ	M1	M2	Δ
M - O (Å)	2.101	2.135	0.034	2.070	2.158	0.088
Bond Angle Variance[3] (°)	114.6	107.8	6.8	29.2	211.8	182.6
Average Charge Imbalance (v.u.)	0.0	0.0	0.0	-0.66	0.0	-0.66
CFSE[4] for Fe^{2+} (Kcal/mole)	12.9	13.1	0.2	11.5	11.7	0.2

[1] Distances and angles for bond angle variance calculation taken from Birle et al (1968).

[2] Distances and angles taken from Morimoto and Koto (1969).

[3] Bond angle variance as defined by Robinson et al (1971) is given by

$$\sigma_\theta^2 \text{ (oct.)} = \sum_{i=1}^{12} (\theta - 90)^2 / 11$$

[4] From Burns (1970a)

It is interesting to compare the observed site preferences of transition metal cations in the olivine structure with those observed in the orthopyroxene structure so that reasons for their site preferences may be understood. We wish to emphasize here that in addition to crystal chemical properties of these cations, the differences in the cation site environments within the structure (listed in Table 5) are important in determining cation site preferences. From Table 5, it is evident that the differences in the cation environment in olivine are relatively minor compared to the corresponding differences in orthopyroxene. Ghose, Okamura, Wan, and Ohashi (1974) used X-ray diffraction techniques to show that in orthopyroxene, preference for the *M*2 octahedral site is in the order: $Mn^{2+} > Zn^{2+} > Fe^{2+} > Co^{2+}$; they found that Ni^{2+} has a slight preference for the *M*1 site.

The available intracrystalline distribution coefficients in the two structures are plotted against the effective ionic radii of these cations in Figure 3 (see caption for details). In spite of the large differences in the cation environments of the orthopyroxene structure relative to the olivine structure, Ni is only slightly enriched in the *M*1 site of orthopyroxene. Furthermore, Co shows a strong preference for the *M*2 site in orthopyroxene in contrast to its strong preference for the *M*1 site in olivine (Ghose *et al,* 1974). If cation size, site size, and crystal-field stabilization alone were mainly responsible for cation-site preferences, then Ni should exhibit a greater enrichment in the *M*1 site of orthopyroxene compared to its enrichment in olivine. It can be inferred, therefore, that other factors are acting against the enrichment of Ni in the *M*1 site of orthopyroxene. One such factor is the "ionicity" of the cation site. From charge balance considerations, the anions surrounding the *M*2 site are neutral on the average, and the site is thought to be associated with a higher degree of covalency than the *M*1 site (Ghose, 1962; Burnham, Ohashi, Hafner, and Virgo, 1971; O'Nions and Smith, 1973). Therefore, transition metal cations, such as Fe^{2+}, Co^{2+}, and Ni^{2+}, which are capable of forming more covalent bonds than Mg^{2+}, would tend to prefer the *M*2 site. Conversely, the more electropositive Mg^{2+} would tend to prefer the more highly charged, "ionic" *M*1 site. Although $^{VI}Zn^{2+}$ is smaller than $^{VI}Fe^{2+}$ and gains no CFSE, the smaller K_D value reported for Zn^{2+} (Fig. 3) in orthopyroxene compared to the value for Fe^{2+} could be due to its tendency to form more covalent bonds. Thus the observed cation ordering in the structures of olivine and orthopyroxene leads to the conclusion that the site preferences of iron, cobalt, nickel, and

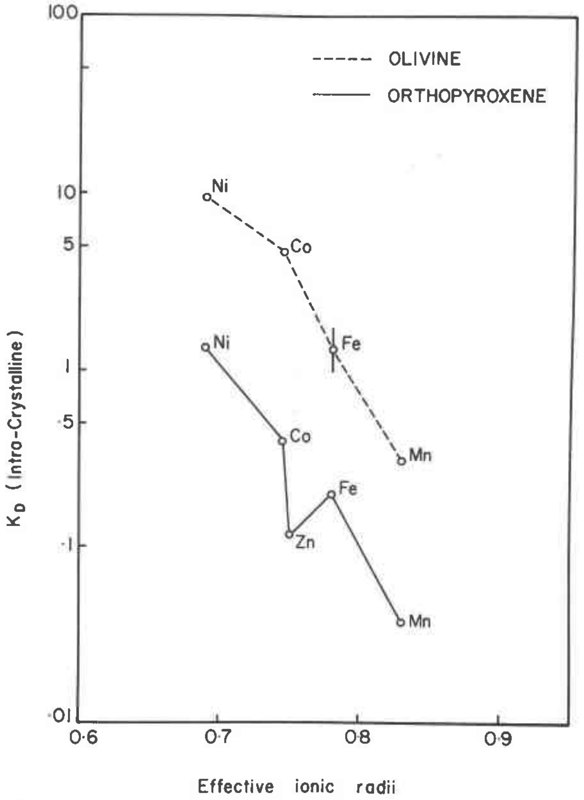

FIG. 3. Log-linear plot of intracrystalline distribution coefficient (K_D as defined in Fig. 1) *versus* effective ionic radii for a number of transition metal olivines and orthopyroxenes. Data are from the following sources: Ni-Mg olivine (this study); Co-Mg olivine (Ghose *et al,* 1974); Fe-Mg olivine (see references given in Fig. 1); Mn-Fe olivine (Brown, 1970); Ni-Mg, Co-Mg, Zn-Mg, Fe-Mg, and Mn-Mg orthopyroxenes (Ghose *et al,* 1974). The vertical line through the point for Fe-Mg olivines expresses the range in K_D values.

magnesium depend on a balance between various crystal chemical factors including cation size, charge, electronegativity, crystal-field stabilization energy for transition metal cations, and the nature of the cation sites (particularly their differences).

As mentioned earlier, the differences in the cation site environments of olivine are small but significant. It appears that the small size difference between the *M*1 and *M*2 sites is sufficient to cause significant ordering of Ni and Co in the structure because of the high CFSE they gain in *M*1. Wood (1974) calculated the CFSE of Ni^{2+} in the two octahedral sites of Ni-olivine based on crystal field spectra and reports values of 27.3 kcal/gram atom for *M*1 and 25.7 kcal/gram atom for *M*2. For Fe the site differences apparently are not sufficient to cause strong ordering in *M*1. Cation size, site size, and its distortion effects (which would favor Fe^{2+} in the *M*2 site) are just compensated by the higher CFSE gained by Fe^{2+} in the *M*1 site (because of its smaller *M*–O distance). Detailed calculations on the CFSE of Fe^{2+} in the two sites of the olivine structure using room temperature crystal data indicated to Walsh, Donnay, and Donnay (1974) that Fe^{2+} has negligible preference for the *M*1 site (site preference energy being little less than one per cent of the energy gained by Fe^{2+} in the *M*1 site). At high temperatures (500°C and above), the differences in the cation environments may be enhanced, as indicated by the high temperature structural studies of Fe-Mg olivines (Brown and Prewitt, 1973), so as to cause an increased enrichment of iron in the *M*1 site (Smyth and Hazen, 1973).

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