

# Cation Ordering at 1300 °C in the (Ni,Mg)-Olivine Solid Solution Series

Dan Boström

Department of Inorganic Chemistry, University of Umeå, S-901 87 Umeå, Sweden

Boström, D., 1989. Cation Ordering at 1300 °C in the (Ni,Mg)-Olivine Solid Solution Series. – Acta Chem. Scand. 43: 116–120.

Three (Ni,Mg)-olivines of different compositions, synthesized at 900 °C and then re-equilibrated at 1300 °C, were investigated by means of single-crystal X-ray diffraction methods. The least-squares refinements of the structures revealed that the crystals were partly ordered, with a preference of Ni<sup>2+</sup> for the M1 octahedral site. The intracrystalline distribution constant,  $K_D$ , was found to vary between 4.76 and 6.49. Geometrical quantities, such as octahedral volume and M-O distances, are more linearly correlated with the mole fraction,  $X(\text{Ni}^{2+})$ , than with the Ni<sup>2+</sup> content of each octahedron.

The intracrystalline partitioning of divalent cations in the olivine structure has attracted considerable attention in recent years. Several 3d cations have been found to form complete solid solutions together with Mg<sub>2</sub>SiO<sub>4</sub> (fosterite). The (Fe,Mg)<sub>2</sub>SiO<sub>4</sub> series, which is the naturally occurring series of minerals originally named olivine, exhibits only small ordering effects. In general, Fe<sup>2+</sup> is slightly enriched on the M1 octahedral site, but the situation is not entirely clear.<sup>1-6</sup> The (Co,Mg)-olivine solid solution has been found to be partly ordered.<sup>7-9</sup> Ghose and Wan<sup>7</sup> investigated a synthetic single crystal with composition (Co<sub>0.55</sub>Mg<sub>0.45</sub>)<sub>2</sub>SiO<sub>4</sub>, in which Co<sup>2+</sup> was enriched at the M1 site. The  $K_D$  value amounted to 4.60 ( $K_D = [\text{Co}_{\text{M1}}][\text{Mg}_{\text{M2}}]/[\text{Co}_{\text{M2}}][\text{Mg}_{\text{M1}}]$ , where the symbols within the square brackets represent the fractional occupancy of Co<sup>2+</sup> and Mg<sup>2+</sup> on the M1 and M2 sites. Recently, Miyake *et al.*<sup>8</sup> and Boström<sup>9</sup> have confirmed this degree of ordering in their systematic investigations of the (Co,Mg)-olivine solid solution series.

The (Ni,Mg)-olivine solid solution was first investigated by Rajamani *et al.*,<sup>10</sup> who studied a single crystal prepared by slow cooling in a flux of NaWO<sub>4</sub> · 2H<sub>2</sub>O. The olivine, with composition (Ni<sub>0.515</sub>Mg<sub>0.485</sub>)<sub>2</sub>SiO<sub>4</sub>, turned out to be moderately zoned, and showed a relatively high degree of ordering;  $K_D$  value 9.22. Bish<sup>11</sup> investigated two single crystals, one natural olivine equilibrated at 730 °C [(Ni<sub>1.52</sub>Co<sub>0.05</sub>Fe<sub>0.09</sub>Mg<sub>0.34</sub>)SiO<sub>4</sub>] and one synthetic olivine [(Ni<sub>1.16</sub>Mg<sub>0.84</sub>)SiO<sub>4</sub>] which was hydrothermally synthesized at 500 °C and 2.1 kbar. The natural olivine was found to be completely ordered, while the synthetic crystal gave a  $K_D$  value of 9.9. In the (Ni,Mg)-olivine single crystals investigated, the cation ordering is representative of the very different temperature conditions. In the first case the  $K_D$  value obtained must be taken as an average over a temperature interval;<sup>10</sup> in the last case it corresponds to a metastable state.<sup>11</sup> Recently, Boström<sup>12</sup> has made a systematic study of seven olivine single crystals in the (Ni,Mg)-series,

all of which were synthesized at a constant temperature (900 °C) using LiMoO<sub>4</sub> as solvent. The  $K_D$  values obtained indicated a considerable compositional dependence, with a higher degree of ordering towards the end members, especially on the Mg<sub>2</sub>SiO<sub>4</sub> side. A minimum value,  $K_D \approx 9$ , was found at the mole fraction  $X(\text{Ni}^{2+}) \approx 0.60$ .

The present study was undertaken to clarify the cation partitioning in (Ni,Mg)-olivine at relative high temperatures. Three single crystals of different compositions were equilibrated at 1300 °C, rapidly quenched and examined by single crystal X-ray diffraction.

## Experimental

*Preparation of single crystals.* The crystals used in this study were synthesized at 900 °C, using Li<sub>2</sub>MoO<sub>4</sub> as solvent (see Ref. 12 for details). The initial compositions of the various crystals given in Table 1 do not refer to the actual crystals used, but to crystals from the same batch. Microprobe analysis showed that the crystal composition within a batch was uniform. The final compositions in Table 1 refer to a microprobe analysis of the actual crystals investigated.

The crystals were placed in small platinum foil tubes and heated in a tube furnace to 1300 °C. The heating times were deliberately different (Table 1) in order to be able to examine possible kinetic effects. The re-equilibrations were interrupted by quenching the platinum tubes in iced-water. The effective cooling times of the samples were less than five seconds. The entire procedure was performed in air.

*X-Ray data collection.* Cell parameters for the crystals were obtained by least-squares refinement of 20 to 24 automatically centered  $K\alpha_1$  reflections with  $\sin \theta/\lambda \approx 1.1 \text{ \AA}^{-1}$ , to ensure good separation of the  $\alpha_1$  and  $\alpha_2$  peaks. X-Ray data were collected at room temperature using a Nicolet R3 four-circle diffractometer, with graphite-monochromatized

Table 1. Crystal data.

	X (Ni <sup>2+</sup> )		
	0.30	0.51	0.76
Cell dimensions			
<i>a</i> /Å	4.7473(3)	4.7395(6)	4.7344(4)
<i>b</i> /Å	10.1915(6)	10.1781(9)	10.1525(7)
<i>c</i> /Å	5.9581(4)	5.9425(6)	5.9290(4)
<i>V</i> /Å <sup>3</sup>	288.26(3)	286.66(5)	284.98(4)
Initial composition <sup>a</sup>	0.30	0.51	0.75
Time of equilibration	2d	6h	2d
Final composition <sup>b</sup>	0.30	0.51	0.76
Number of reflections with <i>I</i> > 3σ( <i>I</i> )	882	821	884
Final value of <i>R</i> <sup>c</sup>	2.06	2.48	2.92
<i>R</i> <sub>w</sub> <sup>d</sup>	3.33	2.99	4.07
<i>K</i> <sub>D</sub> value	4.76(4)	6.49(5)	6.09(12)

<sup>a</sup>Refers not to the investigated crystals but to crystals from the same batch (see Ref. 12). <sup>b</sup>Microprobe analysis of investigated crystals. <sup>c</sup>*R* = [Σ(|*F*<sub>o</sub>| - |*F*<sub>c</sub>|) / Σ|*F*<sub>o</sub>|] · 100%. <sup>d</sup>*R*<sub>w</sub> = [Σ*w*(|*F*<sub>o</sub>| - |*F*<sub>c</sub>|)<sup>2</sup> / Σ*wF*<sub>o</sub><sup>2</sup>]<sup>1/2</sup> · 100%.

Table 2. Atomic fractional coordinates, isotropic temperature factors<sup>a</sup> (*B* in Å<sup>2</sup>) and occupancy factors (*G*).

Atom	Parameter	X (Ni <sup>2+</sup> )		
		0.30	0.51	0.76
M1	<i>x</i>	0.0	0.0	0.0
	<i>y</i>	0.0	0.0	0.0
	<i>z</i>	0.0	0.0	0.0
	<i>B</i>	0.41(1)	0.36(1)	0.29(1)
(Mg)	<i>G</i>	0.275(1)	0.135(1)	0.048(1)
(Ni)	<i>G</i>	0.225(1)	0.365(1)	0.452(1)
M2	<i>x</i>	0.9908(1)	0.9908(1)	0.9917(1)
	<i>y</i>	0.2762(1)	0.2751(1)	0.2744(1)
	<i>z</i>	0.25	0.25	0.25
	<i>B</i>	0.48(1)	0.37(1)	0.31(1)
(Mg)	<i>G</i>	0.427(1)	0.353(1)	0.196(1)
(Ni)	<i>G</i>	0.073(1)	0.147(1)	0.304(1)
Si	<i>x</i>	0.4261(1)	0.4260(1)	0.4266(1)
	<i>y</i>	0.0937(1)	0.0936(1)	0.0939(1)
	<i>z</i>	0.25	0.25	0.25
	<i>B</i>	0.28(1)	0.29(1)	0.20(1)
O(1)	<i>x</i>	0.7665(2)	0.7672(2)	0.7681(3)
	<i>y</i>	0.0924(1)	0.0928(1)	0.0931(1)
	<i>z</i>	0.25	0.25	0.25
	<i>B</i>	0.37(2)	0.41(2)	0.33(2)
O(2)	<i>x</i>	0.2197(2)	0.2193(2)	0.2179(3)
	<i>y</i>	0.4462(1)	0.4458(1)	0.4453(1)
	<i>z</i>	0.25	0.25	0.25
	<i>B</i>	0.40(2)	0.42(2)	0.32(2)
O(3)	<i>x</i>	0.2765(1)	0.2758(1)	0.2754(2)
	<i>y</i>	0.1628(1)	0.1626(1)	0.1628(1)
	<i>z</i>	0.0325(1)	0.0320(1)	0.0311(1)
	<i>B</i>	0.43(1)	0.44(1)	0.34(2)

<sup>a</sup>Isotropic equivalent of the anisotropic temperature factors (Ref. 15). <sup>b</sup>0.5 represents full occupancy.

Table 3. Anisotropic-temperature-factor coefficients (β<sub>*ij*</sub> · 10<sup>4</sup>).

	<i>ij</i>	X (Ni <sup>2+</sup> )			
		0.30	0.51	0.76	
M1	11	356(11)	350(10)	389(13)	
	22	116(2)	92(2)	84(2)	
	33	304(7)	272(6)	194(8)	
	12	-7(3)	-5(3)	-1(3)	
	13	-38(5)	-37(5)	-28(5)	
	23	-27(2)	-22(2)	-22(2)	
	M2	11	524(17)	452(16)	361(15)
		22	110(3)	70(3)	66(3)
		33	363(10)	283(9)	227(10)
12		3(5)	3(4)	-4(4)	
Si	11	212(13)	239(15)	167(20)	
	22	71(2)	67(3)	56(4)	
	33	241(8)	268(9)	163(12)	
	12	3(4)	-3(5)	-10(6)	
O(1)	11	271(30)	366(38)	242(45)	
	22	103(6)	113(8)	103(10)	
	33	313(19)	306(22)	240(28)	
	12	18(11)	11(15)	-26(17)	
O(2)	11	374(31)	457(38)	355(46)	
	22	69(6)	73(7)	58(9)	
	33	399(20)	391(24)	278(30)	
	12	-8(11)	-18(14)	19(17)	
O(3)	11	390(21)	462(26)	317(32)	
	22	114(4)	107(5)	109(7)	
	33	328(13)	326(16)	198(19)	
	12	9(8)	0(10)	10(12)	
	13	-37(15)	-18(18)	-19(22)	
	23	42(6)	46(8)	34(10)	

MoK $\alpha$  radiation ( $\lambda = 0.71069\text{\AA}$ ) and  $\theta$ -2 $\theta$  scan mode ( $4.0^\circ < 2\theta < 80^\circ$ ). The scan speed varied between 2.0 and 6.0 deg · min<sup>-1</sup>. The reflection intensities and backgrounds were obtained by a conventional background-peak-background measurement. Lorentz, polarization and absorption corrections were also made, the latter by an empirical procedure supplied with the Nicolet R3 crystallographic system.

**Refinements.** The refinements were carried out in the space group *Pbnm* using the least-squares program UPALS.<sup>13</sup> Scattering factors for neutral atoms with corrections for anomalous dispersion were taken from Ref. 14. The compositions of the olivines in the refinements were constrained to the results of the microprobe analysis (see final compositions in Table 1). In the final refinement cycles, one overall scale factor, one isotropic secondary extinction parameter, positional and anisotropic temperature factors together with occupancy factors for M1 and M2 were varied. The fractional coordinates obtained for the three crystals are given in Table 2. Anisotropic temperature factors and interatomic angles are listed in Tables 3 and 4, respectively.

Table 4. Interatomic angles.

	$X(\text{Ni}^{2+})$		
	0.30	0.51	0.76
[1] <sup>a</sup> O(1)–Si–O(2)	114.23(6)	114.33(7)	114.09(9)
[2] O(1)–Si–O(3)	115.94(4)	115.99(4)	116.04(5)
[2] O(2)–Si–O(3)	102.08(4)	102.08(5)	102.03(6)
[1] O(3)–Si–O(3')	104.69(6)	104.66(7)	104.73(9)
[2] O(1)–M1–O(3)	84.85(4)	84.74(3)	84.71(5)
[2] O(1)–M1–O(3')	95.15(4)	95.26(4)	95.29(5)
[2] O(1)–M1–O(2)	86.98(3)	87.10(4)	87.26(5)
[2] O(1)–M1–O(2')	93.02(3)	92.90(4)	92.74(5)
[2] O(2)–M1–O(3')	104.82(3)	104.66(4)	104.50(5)
[2] O(2)–M1–O(3)	75.18(3)	75.34(4)	75.50(5)
[2] O(1)–M2–O(3'')	91.06(3)	91.25(3)	91.18(4)
[2] O(1)–M2–O(3)	81.27(3)	81.52(4)	81.81(5)
[2] O(2)–M2–O(3)	96.73(4)	96.73(4)	96.77(5)
[2] O(2)–M2–O(3''')	90.37(3)	90.02(4)	89.86(4)
[1] O(3)–M2–O(3')	72.04(4)	72.38(5)	72.91(6)
[2] O(3)–M2–O(3'')	88.96(2)	89.13(2)	89.16(3)
[1] O(3''')–M2–O(3''')	109.38(5)	108.79(5)	108.22(6)

<sup>a</sup>The number in square brackets refers to the multiplicity of the angle.

## Results and discussion

The shape and clearness of the crystals were affected by the re-equilibration procedure; some of the edges were rounded off and the initial gem quality of the crystals was lost. However, in spite of this rather harsh treatment, the quality of the X-ray diffraction data was surprisingly good. Standard deviations in cell parameters and final  $R$  values (Table 1) are at the same level as those for the crystals which were not heat-treated (cf. Ref. 12).

The olivine structure is well-known, and has been discussed in detail by many authors after its initial determination by Bragg and Brown.<sup>16</sup> The interested reader is referred to Brown<sup>17</sup> for a detailed description.

**Cation distribution.** Data from the present study and from the investigation of the crystals prepared of 900 °C<sup>12</sup> are visualized in Figs. 1a and 1b. The  $K_D$  values from the present study (Fig. 1a) indicate that the ordering effect is almost constant for all compositions  $X(\text{Ni}^{2+})$ . Fig. 1b shows the distribution of  $\text{Ni}^{2+}$  between the two octahedral sites M1 and M2.

There is a distinct difference with respect to the degree of ordering between the two sets of crystals obtained from 1300 °C and 900 °C. The  $K_D$  values obtained at 1300 °C are considerably lower than those at 900 °C. Consequently, on going to temperatures lower than 900 °C, the  $K_D$  values should increase considerably so as to approach complete occupancy of the M1 site by  $\text{Ni}^{2+}$ . In fact, the mineral liebenbergit<sup>11</sup> once equilibrated at 730 °C, was found to be completely ordered. It could also be mentioned that the variation in distribution with respect to the cation composi-

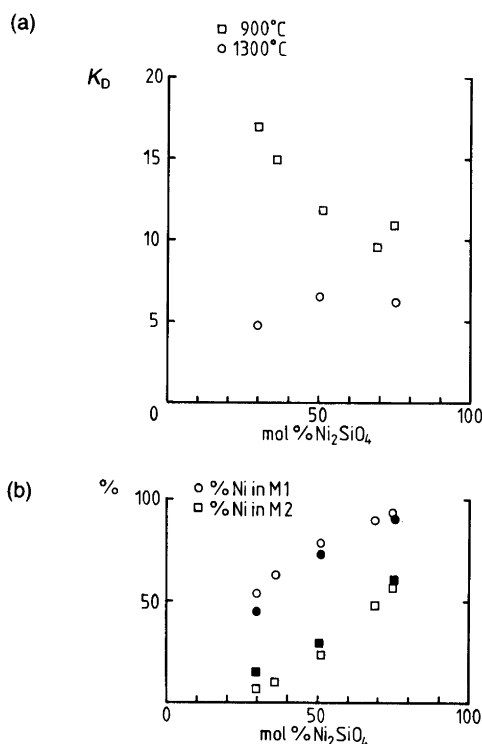


Fig. 1. (a) Variation in the intracrystalline distribution constant  $K_D$  (see text) with composition. Circles represent values from the present study and squares represent data from Ref. 12. (b) Variation in the  $\text{Ni}^{2+}$  content in M1 and M2 with the composition. Solid symbols represent values from the present study and open symbols represent data from Ref. 12.

tion which occurs at 900 °C has practically disappeared at 1300 °C.

The (Ni,Mg)-olivine sample examined by Rajamani *et al.*<sup>10</sup> was synthesized by slow cooling from 1280 °C to 1000 °C. This crystal was found to be moderately zoned, presumably due to the decrease in temperature during the synthesis. Referring to the results given in Fig. 1a, the  $K_D$  value of 9.2 given by Rajamani<sup>10</sup> reflects the intracrystalline cation distribution at about 900–1000 °C. Recently, Bostrom and Rosén<sup>18</sup> have determined the thermodynamic activity of  $\text{Ni}_2\text{SiO}_4$  in  $(\text{Ni,Mg})_2\text{SiO}_4$  solid solutions in the temperature range 920–1320 °C. The activity values thus obtained show a temperature dependence similar to that for the  $K_D$  values in the (Ni,Mg)-olivine system discussed above.

**M1 octahedron.** The smaller and more irregular octahedron M1, which is occupied preferentially by  $\text{Ni}^{2+}$ , shows a linear change in volume as a function of composition. The trends in the mean and individual M1-O distances (Table 5) for the “1300 °C olivines” show no significant departure from those recognized for the “900 °C olivines”, relationships which in general are close to being linear with respect to  $X(\text{Ni}^{2+})$ . However, considering the values displayed in Fig. 1b, it would be natural to expect quantities such as  $V_{\text{M1}}$  and mean M1-O distances to exhibit negative deviations from linea-

Table 5. Interatomic distances (Å).

	X(Ni <sup>2+</sup> )		
	0.30	0.51	0.76
[1] <sup>a</sup> Si-O(1)	1.616(1)	1.617(1)	1.616(2)
[1] Si-O(2)	1.655(1)	1.654(1)	1.657(2)
[2] Si-O(3)	1.636(1)	1.637(1)	1.639(1)
<Si-O>	1.636	1.636	1.638
[1] O(1)-O(2)	2.748(2)	2.748(2)	2.747(2)
[2] O(1)-O(3)	2.758(1)	2.758(1)	2.761(2)
[2] O(2)-O(3)	2.560(1)	2.559(1)	2.562(1)
[1] O(3)-O(3)	2.591(1)	2.591(2)	2.596(2)
<O-O>	2.633	2.662	2.665
[2] M1-O(1)	2.082(1)	2.078(1)	2.073(1)
[2] M1-O(2)	2.071(1)	2.069(1)	2.071(1)
[2] M1-O(3)	2.124(1)	2.118(1)	2.114(1)
<M1-O>	2.092	2.088	2.086
[2] O(1)-O(3)	2.838(1)	2.828(1)	2.821(1)
[2] O(1)-O(3')	3.105(1)	3.100(1)	3.094(2)
[2] O(1)-O(2)	2.858(2)	2.857(2)	2.859(2)
[2] O(1)-O(2')	3.013(1)	3.006(1)	2.999(1)
[2] O(2)-O(3')	3.325(1)	3.314(1)	3.309(2)
[2] O(2)-O(3)	2.560(1)	2.559(1)	2.562(2)
<O-O>	2.950	2.944	2.941
[1] M2-O(1)	2.154(1)	2.137(1)	2.123(2)
[1] M2-O(2)	2.045(1)	2.047(1)	2.039(2)
[2] M2-O(3)	2.203(1)	2.194(1)	2.184(1)
[2] M2-O(3'')	2.063(1)	2.061(1)	2.057(1)
<M2-O>	2.122	2.116	2.107
[2] O(1)-O(3'')	3.010(1)	3.001(1)	2.986(2)
[2] O(1)-O(3)	2.838(1)	2.828(1)	2.821(2)
[2] O(2)-O(3)	3.177(1)	3.171(1)	3.159(2)
[2] O(2)-O(3''')	2.914(1)	2.906(1)	2.893(2)
[1] O(3)-O(3')	2.591(1)	2.591(2)	2.596(2)
[2] O(3)-O(3'')	2.991(1)	2.987(1)	2.978(1)
[1] O(3''')-O(3''')	3.367(1)	3.352(2)	3.333(2)
<O-O>	2.985	2.977	2.967

<sup>a</sup>The number in square brackets refers to the multiplicity of the distances.

Table 6. Polyhedral distortion parameters<sup>a</sup> and octahedral volumes ( $V_{M1}$  and  $V_{M2}$ ).

	X(Ni <sup>2+</sup> )		
	0.30	0.51	0.76
$V_{M1}$	11.755(6)	11.688(7)	11.655(8)
$V_{M2}$	12.296(7)	12.208(7)	12.090(10)
TAV	47.7(2)	48.2(2)	48.2(3)
$OAV_{M1}$	98.8(1)	91.3(2)	89.4(2)
$OAV_{M2}$	86.0(2)	82.1(2)	77.6(2)

<sup>a</sup>TAV (tetrahedral-angle variance) =  $\sum_{j=1}^6 (A_j - 109.47)^2/5$ , where  $A_j$  values are the tetrahedral angles O-T-O. OAV (octahedral-angle variance) =  $\sum_{j=1}^{12} (A_j - 90)^2/11$ , where  $A_j$  values are the angles O-M-O.

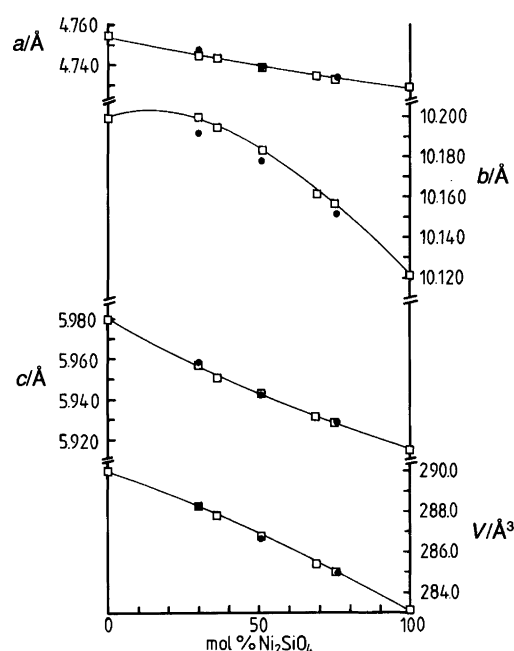


Fig. 2. Variation in the unit-cell parameters for the (Ni,Mg)-olivine solid solution. The curves and open symbols represent values from Ref. 12, and solid symbols represent values from the present study.

urity as a function of composition. On the other hand, the distortion parameter  $OAV^{19}$  (Octahedra-Angle Variance) shows a slight negative deviation, as expected.

**M2 octahedron.** The volume of the M2 octahedron shows no significant deviations from linearity as a function of the composition (Table 6). As for the M1 octahedron, the mean and individual M2-O distances conform to the values found from the “900 °C olivines”, there being a mainly linear variation with composition,  $X(Ni^{2+})$ , except for the M2-O(2) bond, which has a significantly positive deviation from linearity. Fig. 1b would suggest that geometric quantities involving M2, such as  $V_{M2}$ , M2-O and  $OAV_{M2}$ , should have negative departures. The distortion parameter, OAV, is again the only geometric parameter which agrees with the expected trend with reference to Fig. 1b, i.e. shows a slight positive deviation as a function of  $X(Ni^{2+})$ .

**Cell parameters.** The cell parameters obtained are given in Table 1 and displayed in Fig. 2 together with the corresponding values obtained for the crystals synthesized at 900 °C. There are no significant differences with regard to the  $a$ - and  $c$ -axis or the unit cell volumes for the different sets of crystals. The  $b$ -axes in the re-equilibrated crystals are significantly shorter, however. The cation ordering thus influences primarily the  $b$ -axis. This feature is not unique to the present system. In fact, the  $a$ - $b$  dimension plots for olivines as constructed by Lumpkin and Ribbe<sup>20</sup> in several cases predict an increase in the  $b$ -axis with increased octahedral cation ordering. This type of plot is based on equa-

tions in which the cell dimensions are expressed as functions of the mean M1 and M2 cation radii.

### Conclusions

The (Ni,Mg)-olivine solid solution was found to be less ordered at 1300°C than at 900°C. The variation in Ni<sup>2+</sup> distribution over the M1 and M2 sites with respect to the cation composition found at 900°C is not present at 1300°C. Octahedral geometric quantities (volume, mean and individual M–O distances) are more linearly related to  $X(\text{Ni}^{2+})$  than to the cation composition of each octahedron. The *b*-axis is significantly affected by the lower degree of ordering at 1300°C; the convexity of the *b*-curve at 900°C is smaller at 1300°C.

*Acknowledgements.* The author wishes to thank Professors Erik Rosén and John O. Thomas for valuable discussions and helpful suggestions. Thanks are also due to Professor Alberto Dal Negro for the microprobe analysis performed in Padova. Financial support from the Swedish Natural Science Research Council is gratefully acknowledged.

### References

1. Finger, L. W. *Carnegie Inst. Wash. Year Book* 69 (1970) 302.
2. Wenk, H. R. and Raymond, K. N. *Z. Kristallogr.* 137 (1973) 86.
3. Smyth, J. R. and Hazen, R. M. *Am. Mineral.* 58 (1973) 588.
4. Brown, G. E. and Prewitt, C. T. *Am. Mineral.* 58 (1973) 577.
5. Will, G. and Nover, G. *Phys. Chem. Minerals* 4 (1979) 199.
6. Basso, R., Dal Negro, A., Della Guista, A. and Rossi, G. *N. Jahrb. Mineral. Monat.* (1979) 197.
7. Ghose, S. and Wan, C. *Contrib. Mineral. Petrol.* 47 (1974) 131.
8. Miyake, M., Nakamura, H., Kojima, H. and Marumo, F. *Am. Mineral.* 72 (1987) 594.
9. Boström, D. *Acta Chem. Scand.* 43 (1989) 121.
10. Rajamani, V., Brown, G. E. and Prewitt, C. T. *Am. Mineral.* 60 (1975) 292.
11. Bish, D. L. *Am. Mineral.* 66 (1981) 770.
12. Boström, D. *Am. Mineral.* 72 (1987) 965.
13. Lundgren, J.-O. *Crystallographic Computer Programs*. Report UUIC-B13-4-05, Institute of Chemistry, University of Uppsala, Uppsala, Sweden 1982.
14. *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham 1974, Vol. IV.
15. Hamilton, W. C. *Acta Crystallogr.* 12 (1959) 609.
16. Bragg, W. L. and Brown, G. B. *Z. Kristallogr.* 63 (1926) 538.
17. Brown, G. E., Jr. *Min. Soc. Am., Rev. Mineral.* 5 (1980) 276.
18. Boström, D. and Rosén, E. *Acta Chem. Scand., Ser. A* 42 (1988) 149.
19. Robinson, K., Gibbs, G. V. and Ribbe, P. H. *Science* 172 (1971) 567.
20. Lumpkin, G. R. and Ribbe, P. H. *Am. Mineral.* 68 (1983) 164.

Received February 11, 1988.