

Cation ordering in synthetic and natural Ni-Mg olivine

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Abstract

The crystal structures of natural liebenbergite— $(\text{Ni}_{1.52}\text{Co}_{0.05}\text{Fe}_{0.09}\text{Mg}_{0.34})\text{SiO}_4$ —from Barberton, South Africa, and of synthetic liebenbergite— $(\text{Ni}_{1.16}\text{Mg}_{0.84})\text{SiO}_4$ —synthesized at 500°C, have been studied in order to determine the intracrystalline Ni-Mg distribution. The natural liebenbergite is fully ordered, with M1 occupied only by Ni, whereas the synthetic sample is only partially ordered with $K_D = [\text{Mg}(\text{M2}) \cdot \text{Ni}(\text{M1})]/[\text{Ni}(\text{M2}) \cdot \text{Mg}(\text{M1})] = 9.9(4)$, $\Delta G_{\text{ex}}^{\circ} = -3.5$ kcal/mole. Comparison with the results of Rajamani *et al.* (1975), who found $K_D = 9.2(2)$ and $\Delta G_{\text{ex}}^{\circ} = -6.9$ kcal/mole for a sample synthesized at 1280°C, implies that the 500°C synthetic sample in the present study crystallized metastably in a disordered or partially ordered state and ordering proceeded slowly.

Although site size effects are small in Fe-Mg, Ni-Mg, and Co-Mg olivines, the crystal field stabilization energy is important in determining the observed cation distribution in Ni-Mg and Co-Mg olivines. Electronegativity or covalency effects are known only qualitatively, but there is a preference of less electronegative ions (Mg, Ca) for M2.

Ordering of Ni into the M1 site of olivine should appreciably affect Ni partitioning between olivine and melt, and activity-composition relations have been examined assuming ideal solution behavior. Deviations from Raoult's law increase with increasing order, but variations in activity coefficients are less than 10 percent below 10 mole% Ni.

Introduction

Although nickel is a common and important minor constituent in olivines, liebenbergite, the nickel-rich olivine, has been found only in the unusual Bon Accord deposit in Barberton, South Africa. The material at Bon Accord originally filled interstices between trevorite grains in the assemblage trevorite-nickel serpentine-nickel ludwigite-bunsenite-violarite-millerite-gaspeite-nimite but is now almost completely replaced by secondary nickel serpentine. Only small irregular crystals remain in the serpentine matrix (de Waal and Calk, 1973). The liebenbergite appears to have formed at about 730°C and less than 2 kbar during thermal metamorphism, possibly of a nickel-rich meteorite (de Waal, 1978). I have obtained crystals of liebenbergite through the courtesy of Dr. de Waal.

The natural occurrence of liebenbergite presents us with the unique opportunity to examine a mineral

that previously had been studied in synthetic form only (*e.g.* Rajamani *et al.*, 1975). The natural sample equilibrated over a long period at a fairly low temperature (730°C), so it should possess an equilibrium distribution of cations. Typical synthesis experiments are of short duration at high temperature. For example, the Ni-Mg olivine examined by Rajamani *et al.* (1975) was crystallized at 1280°C and cooled in several days yielding a zoned crystal. The authors questioned whether the observed K_D , $[\text{Mg}(\text{M2}) \cdot \text{Ni}(\text{M1})]/[\text{Ni}(\text{M2}) \cdot \text{Mg}(\text{M1})]$, represented an equilibrium distribution of cations.

During a study of hydrous nickel-magnesium silicates (Brindley *et al.*, 1979), euhedral crystals of liebenbergite were synthesized by reacting natural pimelite (nickel-magnesium talc) at 500°C and 2.1 kbar for 4 weeks. These crystals should differ significantly from the products of short-term reactions at temperatures in excess of 1200°C.

Numerous studies have focused on the nature and causes of intracrystalline cation distributions in natural and synthetic olivines (see Rajamani *et al.*, 1975, for a summary). In an attempt to understand order-

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ing in transition metal olivines, site populations have been determined for synthetic Ni-Mg olivine (Rajamani *et al.*, 1975) and synthetic Co-Mg olivine (Ghose and Wan, 1974). However, there is disagreement regarding the factors contributing to site preference energies. Based on site preference energies calculated from observed K_D values, Ghose and Wan (1974) suggested that ordering in transition metal olivines could not be explained on the basis of crystal field theory but is due to the preference of the larger ion for M2 and more covalent bonding of transition metals in M1. On the other hand, using experimental crystal field splitting values for hydrated crystals and the K_D values for synthetic Co-Mg and Ni-Mg olivines, Walsh *et al.* (1976) suggested that ordering differences in transition metal olivines could be explained by crystal field theory. Rajamani *et al.* (1975) concluded that the observed site preferences of divalent Fe, Co, Ni, and Mg in olivines are determined by a competition between ionic size, electronegativity, and crystal field effects.

In this study the cation distributions of both the natural and the low-temperature synthetic liebenbergites are determined and the energetic factors controlling ordering are evaluated. In addition, because Ni-Mg olivines appear to be partially ordered even at high temperatures (Rajamani *et al.*, 1975), it is necessary to examine the effects of cation ordering on the partitioning of Ni between olivine and melt.

Experimental

The synthetic liebenbergite was analyzed on an ETEC microprobe using pure forsterite, fayalite, and liebenbergite as standards. The crystals were not significantly zoned and contained only the cations Ni, Mg, and Si in appreciable amounts. The average of six analyses gave the formula shown in Table 1; the

Ni:Mg ratio is essentially identical to that of the starting material. Liebenbergite from Bon Accord was analyzed by de Waal and Calk and the average for eight separate grain analyses gave the formula: $(\text{Ni}_{1.52}\text{Mg}_{0.33}\text{Co}_{0.05}\text{Fe}_{0.12})\text{Si}_{10.99}\text{O}_4$. The same Bon Accord crystal used for X-ray intensity data collection was analyzed using a Harwell Si(Li) detector and pulse processor (Statham, 1976), employing the correction procedures of Sweatman and Long (1969). The analysis yielded the formula in Table 1 and revealed no significant zoning.

The cell parameters of both crystals were refined using 12 reflections with 2θ greater than 40° measured on an automated Picker diffractometer and are listed in Table 1 along with other relevant crystal data.

Intensities of 1090 (synthetic) and 933 (natural) nonequivalent reflections were collected at 20°C using a Picker diffractometer with Zr-filtered (syn.) and Nb-filtered (natural) $\text{MoK}\alpha$ radiation. All data were corrected for Lorentz and polarization effects, and the natural liebenbergite data were corrected for absorption using numerical integration techniques (Burnham, 1966). Transmission factors varied from 0.24 to 0.34. Refinement was carried out using the least-squares program RFINE (Finger, 1969) with the atom parameters obtained by Rajamani *et al.* (1975) for an Ni-Mg olivine as the initial model. The compositions were constrained to the formulae in Table 1, allowing occupancies of Ni and Mg in the M1 and M2 sites to vary. The Co and Fe in the natural sample were treated as Ni to simplify the refinement. The contents of M1 were allowed to vary in the natural liebenbergite, resulting in an occupancy of $\text{Ni}_{1.05}\text{Mg}_{-0.05}$, so the occupancy was fixed at $\text{Ni}_{1.0}$. The calculated occupancy may be due to a systematic absorption error, but nonabsorption-corrected data yielded the same unrealistic occupancy. Neutral atomic scattering factors (Doyle and Turner, 1968) and anomalous dispersion corrections (Templeton, 1968) were employed.

Final refinement, during which a scale factor, secondary extinction parameter, positional and anisotropic thermal parameters, and occupancies of M1 and M2 were allowed to vary, gave unweighted R factors of 4.7 percent (5.8 percent wtd.) for the synthetic material and 2.9 percent (2.6 percent wtd.) for natural liebenbergite. Reflections were weighted as $w = 1/\sigma_F^2$, where σ_F is the estimated standard deviation of the observation defined by Burnham *et al.* (1971). Refined occupancies and positional and thermal parameters are given in Table 2; selected interatomic

Table 1. Liebenbergite crystal data

	Synthetic	Natural
a (Å)	4.7366(4)*	4.7311(2)
b	10.164(2)	10.1797(6)
c	5.9322(5)	5.9408(3)
V (Å ³)	285.59(5)	286.12(4)
Crystal Size	0.2x0.1x0.1 mm.	0.20x0.17x0.16 mm.
Linear Absorption Coefficient	81.9 cm ⁻¹	112.62 cm ⁻¹
Composition	$(\text{Ni}_{1.16}\text{Mg}_{0.84})\text{Si}_{10}$	$(\text{Ni}_{1.52}\text{Co}_{0.05}\text{Fe}_{0.09}\text{Mg}_{0.34})\text{Si}_{10}$
No. Refl. ($I > 2\sigma$)	1079	860
Extinction Corr.	None	0.135×10^{-6}

* Calculated standard errors in parentheses refer to the last decimal place quoted.

Table 2. Positional parameters and temperature factors for natural and synthetic Ni-Mg olivine

		Natural	Synthetic			Natural	Synthetic				
M1	Ni	1.00	0.830(3)	0(1)	x	0.7671(5)	0.7676(5)				
	Mg	0.00	0.170			y	0.0925(2)	0.0931(2)			
	x	0.0	0.0			z	0.25	0.25			
	y	0.0	0.0			β_{11}	0.0048(8)	0.0046(6)			
	z	0.0	0.0			β_{22}	0.0013(2)	0.0011(1)			
	β_{11}	0.0046(2)*	0.0053(2)			β_{33}	0.0025(4)	0.0031(4)			
	β_{22}	0.0010(1)	0.0008(1)			β_{12}	0.0000(3)	0.0000(2)			
	β_{33}	0.0025(1)	0.0029(1)			Beq	0.45(3)	0.43			
	β_{12}	-0.0001(1)	0.0000(1)			0(2)	x	0.2190(5)	0.2199(5)		
	β_{13}	-0.0003(1)	-0.0003(1)					y	0.4455(2)	0.4456(2)	
	β_{23}	-0.0002(1)	-0.0002(1)					z	0.25	0.25	
	** Beq	0.40(1)	0.40					β_{11}	0.0057(8)	0.0057(6)	
	M2	Ni	0.66					0.33	β_{22}	0.0009(1)	0.0006(1)
		Mg	0.34					0.67	β_{33}	0.0031(5)	0.0042(4)
x		0.9903(1)	0.9909(1)	β_{12}	-0.0002(3)			0.0001(2)			
y		0.2747(1)	0.2748(1)	Beq	0.44(3)			0.45			
z		0.25	0.25	0(3)	x			0.2755(3)	0.2752(3)		
β_{11}		0.0057(2)	0.0063(3)					y	0.1625(1)	0.1625(1)	
β_{22}		0.0008(1)	0.0006(1)					z	0.0310(3)	0.0311(3)	
β_{33}		0.0028(1)	0.0033(2)					β_{11}	0.0059(5)	0.0061(5)	
*** β_{12}		0.0000(1)	0.0000(1)					β_{22}	0.0011(1)	0.0010(1)	
Beq		0.41(1)	0.43					β_{33}	0.0034(3)	0.0036(3)	
Si		x	0.4265(1)			0.4263(2)	β_{12}	-0.0003(2)	-0.0001(2)		
		y	0.0938(1)			0.0937(2)	β_{13}	0.0001(4)	0.0001(3)		
		z	0.25			0.25	β_{23}	0.0003(2)	0.0004(1)		
		β_{11}	0.0044(3)			0.0052(3)	Beq	0.49(2)	0.48		
	β_{22}	0.0007(1)	0.0005(1)								
	β_{33}	0.0026(2)	0.0030(2)								
	β_{12}	0.0000(1)	0.0001(1)								
	Beq	0.36(1)	0.37								

* Numbers in parentheses are calculated standard errors and refer to the last digit quoted.

** Beq is the isotropic equivalent of the anisotropic temperature factor (Hamilton, 1959).

*** $\beta_{13} = \beta_{23} = 0$ for M(2), Si, 0(1), and 0(2).

distances, in Table 3. Tables of observed and calculated structure factors are on deposit at the Business Office of the Mineralogical Society of America.²

Discussion

The results for both crystals are similar to those obtained by Rajamani *et al.* (1975), and the positional parameters in Table 2 for the synthetic liebenbergite agree with theirs within the limits of uncertainty. As expected from the higher concentration of Ni in these samples, M1-O and M2-O distances are slightly shorter than those found by Rajamani *et al.* (1975). The M1-O and M2-O distances in natural

liebenbergite are longer than would be expected from the refined occupancies, probably because of small amounts of Fe and Co distributed in both M1 and M2. Significant enrichment of Ni on the smaller M1 site (Rajamani *et al.*, 1975) is confirmed; the natural liebenbergite is fully ordered and the synthetic sample has a K_D of 9.9(4) (at 500°C, $\Delta G_{ex}^\circ = -RT \ln K = -3.5$ kcal/mole), significantly larger than that obtained by Rajamani *et al.* (1975), 9.2(2) (at 1280°C, $\Delta G_{ex}^\circ = -6.9$ kcal/mole).

The Ni-Mg distribution in the natural liebenbergite is probably close to equilibrium. If we use the ΔG_{ex}° obtained from the results of Rajamani *et al.* (1975), assuming $\Delta S_{ex}^\circ \approx 0$, K_D would equal 31.2 at 730°C for the natural sample. This K_D corresponds to a cation distribution of $(Ni_{0.985}Mg_{0.015})_{M1} (Ni_{0.675}Mg_{0.325})_{M2}$, in good agreement with the present results. Thus, the ordering observed by Rajamani *et*

² To obtain a copy of this table, order Document AM-81-160 from the Mineralogical Society of America, Business Office, 2000 Florida Avenue, N.W., Washington, D.C. 20009. Please remit \$1.00 in advance for the microfiche.

Table 3. Interatomic distances in natural and synthetic Ni-Mg olivine

	Natural	Synthetic
<u>M1 Octahedron</u>		
* {2} M1 - O(1)	2.075(2) ^o	2.075(2)
{2} M1 - O(2)	2.069(2)	2.065(2)
{2} M1 - O(3)	2.114(1)	2.112(1)
Mean M1 - O	2.086	2.084
<u>M2 Octahedron</u>		
{1} M2 - O(1)	2.134(2)	2.128(2)
{1} M2 - O(2)	2.048(2)	2.047(2)
{2} M2 - O(3)	2.056(2)	2.057(2)
{2} M2 - O(3)	2.195(2)	2.191(2)
Mean M2 - O	2.114	2.112
<u>Si Tetrahedron</u>		
{1} Si - O(1)	1.611(2)	1.617(3)
{1} Si - O(2)	1.660(2)	1.657(2)
{2} Si - O(3)	1.641(2)	1.639(2)
Mean Si - O	1.638	1.638

* Numbers in brackets refer to the multiplicity of the bond, and calculated standard errors in parentheses refer to the last digit quoted.

al. (1975) for their synthetic olivine is close to equilibrium at 1280°C. If ΔG_{ex}^o does not vary significantly with temperature, the K_D of 9.9 for the material grown at 500°C does not represent a closer approach to equilibrium than a high-temperature synthesis of short duration. At 500°C, ΔG_{ex}^o is significantly smaller than at 1280°C. The sample synthesized at 500°C probably crystallized metastably in a disordered or partially ordered state and further ordering proceeded slowly, yielding a low ΔG_{ex}^o value.

Energetics of order-disorder

Although a number of investigators have appealed to crystal field theory to explain the observed cation ordering in olivines, Ghose and Wan (1974) concluded that the distribution of transition metal ions in olivines could not be accounted for by crystal field theory. They observed that Co^{2+} shows a strong preference for the M1 site in olivine but less preference for the more distorted orthopyroxene M2 site. Partly because of this, Ghose and Wan (1974) felt that ionic size and different covalent bonding on M1 and M2 in olivines would explain the observed ordering more quantitatively. These conclusions are in part due to the failure of Ghose and Wan (1974) to consider crystal field site-size effects in addition to site distortion criteria.

The stabilization gained by a transition element ion on a particular site is due to a number of factors, including an interplay between the crystal field stabi-

lization energy ($\Delta \propto 1/r^5$) and the stabilization due to distortion ($\delta \propto$ site distortion). It is very important to note that δ is typically one to three orders of magnitude smaller than Δ . Depending on electronic configuration, the relative importance of these two terms will vary: d^8 ions (Ni^{2+}) are not affected by distortions and are affected to the greatest extent by size differences, whereas d^7 (Co^{2+}) and d^6 (Fe^{2+}) ions are influenced by both site size and distortion. The crystal field site preference energy (SPE) is thus related to both Δ and δ ; the SPE is approximately $6/5(\Delta_1 - \Delta_2)$ for Ni^{2+} , $4/5(\Delta_1 - \Delta_2) + 1/3(2\delta_1 - \delta_2)$ for Co^{2+} , and $2/5(\Delta_1 - \Delta_2) + 1/3(\delta_1 - 2\delta_2)Fe^{2+}$ (Burns, 1970). The symbols Δ_1 and Δ_2 represent the crystal field splitting parameters for the ions in M1 and M2 respectively, and δ_1 and δ_2 are the t_{2g} orbital splitting parameters related to distortion. Of these three ions, Fe^{2+} is the least affected by size differences, and distortion differences are important in controlling site occupancies of Fe^{2+} . In fact, Walsh *et al.* (1974) showed that the observed Fe^{2+} distribution in olivines is due to a close balance between the crystal field stabilization energy (CFSE) and Jahn-Teller effects. An illustration of the importance of the CFSE's can be obtained by comparing the stabilization energies for Fe^{2+} , Co^{2+} , and Ni^{2+} , 11.9, 21.3, and 29.6 kcal/mole respectively (Burns, 1970, p. 19) with the measured site preference energies (ΔG_{ex}^o). This is similar to the Ghose and Wan (1974) plot of ΔG_{ex}^o versus the ionic radii of Fe^{2+} , Co^{2+} , and Ni^{2+} . Using the values of ΔG_{ex}^o given by Ghose and Wan (0.5, 4.0, 6.5 kcal/mole), we find a linear relation between CFSE and ΔG_{ex}^o .

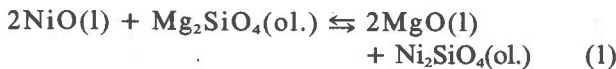
Although crystal field effects are important in determining site populations, crystal field theory cannot explain all of the observed ordering in olivines and orthopyroxenes (Ghose and Wan, 1974). We can obtain an idea of the relative cation-size ("ionic") contribution to site preferences from the results of Bish (1980). His electrostatic calculations on model ordered and antioderred structures suggest a small (≈ 2 kcal/mole preference of Ni^{2+} for the M1 site of $NiMgSiO_4$ and negligible preference of Fe^{2+} and Co^{2+} for either octahedral site in $FeMgSiO_4$ and $CoMgSiO_4$ respectively. Although electronegativity and site covalency contributions are not well known, qualitative predictions can be made. Brown and Fenn (1979) predicted that the more electronegative ions (Fe, Ni, Co) will prefer the M1 site, and the electropositive ions (Mg, Ca) will prefer M2, the site with the more negative site potential. One can make similar predictions using the results of a charge density study of forsterite (G. V. Gibbs, personal communication,

1980). A higher residual charge is found on M2 than on M1, demonstrating that the bonding at M1 is more covalent. Again, the more electropositive ions will prefer the more ionic M2 site.

Implications of cation ordering for Ni partitioning

The partitioning of trace elements between olivine and melts is important and widely studied. The nickel distribution coefficient, $Ni^{olivine}/Ni^{melt}$, is particularly useful as a petrogenetic indicator (e.g., Hakli and Wright, 1967). Not only does Ni partitioning between olivine and melt give us information concerning igneous processes (Wood and Fraser, 1976), but variations in Ni distribution coefficients with melt composition can provide useful insights into silicate melt structures (Leeman, 1978). Thus it is important to examine the possible effects of cation ordering on Ni partitioning.

The exchange reaction for Ni partitioning can be written in the form:

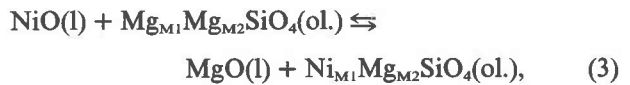


(Wood and Fraser, 1976). The equilibrium constant for this reaction is:

$$K = \frac{[MgO]^2 \cdot [Ni_2SiO_{4ol.}]}{[NiO]^2 \cdot [Mg_2SiO_{4ol.}]}, \quad (2)$$

where square brackets denote activities. At high temperatures, transition element olivines are considered to behave nearly as ideal solutions (Masse *et al.*, 1966; Schwerdtfeger and Muan, 1966; Nafziger and Muan, 1967; Campbell and Roeder, 1968) and activity coefficients are commonly assumed to be one (e.g., Leeman and Lindstrom, 1978). However, as Mysen (1979) noted, we have no proof that activity coefficients are constant for the Ni-Mg olivine series in the temperature range of interest.

Although Fe-Mg olivines show little tendency to order, Co-Mg olivines and Ni-Mg olivines exhibit considerable ordering of the transition metal ion into M1. Complete ordering in natural liebenbergite demonstrates the strong site preference of Ni for M1, and the results of Rajamani *et al.* (1975) for the synthetic Ni-Mg olivine crystallized at 1280°C show that Ni exhibits pronounced site preference even at high temperatures. In the extreme case, if we assume that the olivine crystallizes with complete ordering of Ni onto M1, equation (1) may more correctly be written for the low Ni concentration range:



and the equilibrium constant is:

$$K = \frac{[MgO] \cdot [Ni_{M1}Mg_{M2}SiO_{4ol.}]}{[NiO] \cdot [Mg_{M1}Mg_{M2}SiO_{4ol.}]}. \quad (4)$$

As an approximation, we may examine the effects of ordering on activity-composition relations using the statistical thermodynamic treatment described by Mueller *et al.* (1970) and Kerrick and Darken (1975). For the case of complete disorder, or ideal mixing on one type of site, $a_{NiSi_{0.5}O_2} = X_{NiSi_{0.5}O_2}$, and for ordering, or ideal mixing on two types of sites, $a_{NiSi_{0.5}O_2} = [(\theta_{Ni}^{M1}) \cdot (\theta_{Ni}^{M2})]^{\frac{1}{2}}$, where θ_{Ni}^{M1} and θ_{Ni}^{M2} represent the fractional occupancy of Ni on M1 and M2, respectively. Activity-composition relations for the Ni-Mg olivine series are shown in Figure 1 for several values of K_D , 1.0 (disorder), 10.0, 100.0, and ∞ (complete order).

Under the constraints of the initial assumptions, we can see from these relations (Figure 1) that appreciable ordering of Ni into M1 will give rise to noticeable negative deviations from ideal Raoult's law behavior and appreciably different behavior for the Mg and Ni end-members. With small ΔV (≈ 3 percent), these deviations will be reflected in changes in K_D with Ni concentrations. An alternative approach is to examine the behavior of γ_i , the activity coefficient, with composition for various values of K_D (Figure 2).

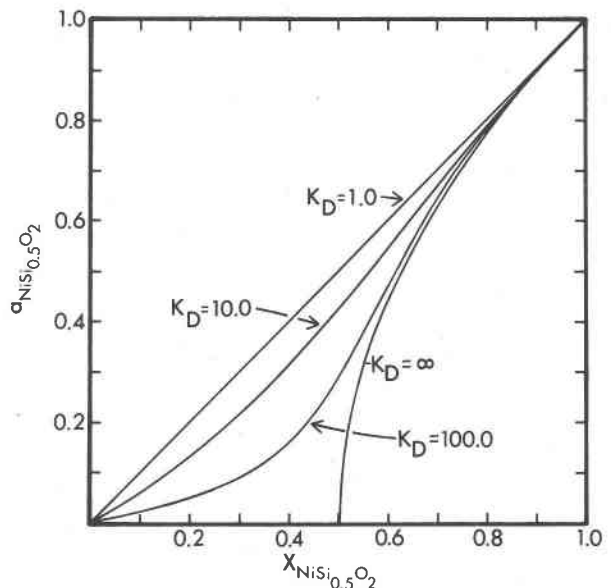


Fig. 1. Activity-composition relations for $NiSi_{0.5}O_2$ in $(Ni,Mg)_2SiO_4$ olivines for several values of K_D .

There is considerable discussion in the literature concerning the manner in which Ni dissolves in olivine (see Mysen, 1979, and Leeman and Lindstrom, 1978). Mysen (1976, 1978, 1979) concluded that solution of Ni in forsterite followed Henry's law up to a maximum of ≈ 1000 ppm Ni. However, Leeman and Lindstrom (1978) found no deviations from Henry's law behavior from 0.04 percent to at least 1 percent Ni, and Hart and Davis (1974) found Henry's law behavior from below 0.94 percent to 9.51 percent NiO in olivine. Although the statistical thermodynamic treatment is admittedly simplistic and seldom predicts mixing properties accurately, it does illustrate the possible effects of cation ordering on Ni partitioning. We would predict from Figures 1 and 2 that Henry's law behavior is approached in the low Ni concentration range commonly observed in natural rocks. However, at concentrations greater than ≈ 10 mole percent $\text{NiSi}_{0.5}\text{O}_2$, the activity coefficient for partially ordered olivines varies rapidly with composition. If more data were available, a more accurate treatment involving regular solution theory could conceivably predict deviations from Henry's law at lower concentrations.

Conclusions

Crystal structure refinements of natural and synthetic (500°C) liebenbergite crystals confirm the high degree of cation ordering found for a high temperature (1280°C) synthetic liebenbergite by Rajamani *et al.* (1975). Although the synthetic sample was reacted for one month at 500°C , it appears to have crystallized in a partially ordered state or ordered very slowly, while the natural sample exhibits complete ordering of Ni into M1.

Crystal field stabilization energies are important in determining the observed cation distributions in Ni-Mg and Co-Mg olivines, in agreement with Rajamani *et al.* (1975). The cation size or ionic effects can be approximately calculated (Bish, 1980) and are small for Fe-Mg, Ni-Mg, and Co-Mg olivines, although electronegativity or covalency effects are less well known. Relationships are emerging that suggest that less electronegative ions such as Mg and Ca prefer M2, and the more electronegative ions, Fe, Co, and Ni, prefer M1. Competition between all of these factors, rather than any single factor, determines the total site preference energy.

In light of the extensive cation ordering found in Ni-Mg olivines even at 1280°C , it is important to

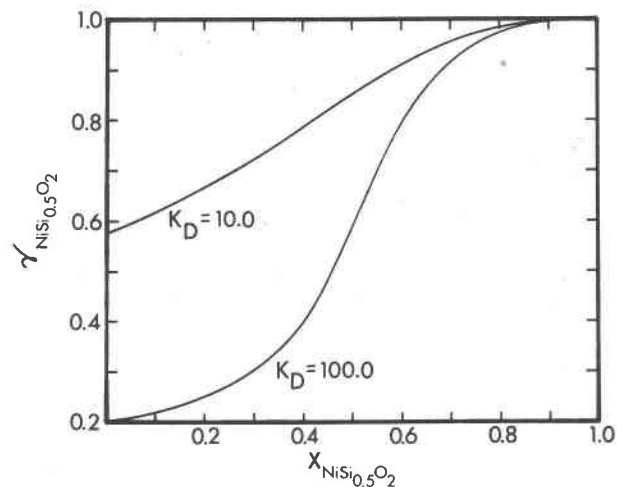


Fig. 2. Variation of γ_i , the activity coefficient of $\text{NiSi}_{0.5}\text{O}_2$, with composition for two values of K_D .

consider the effects of ordering on the partitioning of Ni between olivine and melt. A simple analysis assuming ideal mixing shows that activity-composition relations for Ni-Mg olivines may differ appreciably depending on whether the olivine crystallizes with an ordered or disordered distribution of Ni. One may expect large deviations from Raoult's law behavior and a different behavior for the Mg and Ni end-members due to cation ordering. Although literature data suggest that activity coefficients are close to one at high temperatures, further study is needed in the range 900 to 1100°C where ordering may be important.

These results provide few constraints on the origin of the natural liebenbergite. All plausible modes of origin of the Bon Accord deposit involve the presence of an iron-nickel metal phase prior to intrusion of the associated Nelspruit granite and the formation of the liebenbergite assemblage during the metamorphism of the metal phase by the granite (de Waal, 1980). Complete ordering in the natural liebenbergite is compatible with a long period of metamorphism at approximately 730°C and subsequent slow cooling, but we cannot discount other modes of formation involving metamorphism and slow cooling. In order to interpret the detailed history of the liebenbergite, quantitative data on the kinetics of order-disorder in Fe-containing Ni-Mg olivines are required.

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