

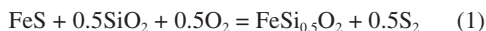
## Thermodynamics of multicomponent olivines and the solution properties of (Ni,Mg,Fe)<sub>2</sub>SiO<sub>4</sub> and (Ca,Mg,Fe)<sub>2</sub>SiO<sub>4</sub> olivines—Comment

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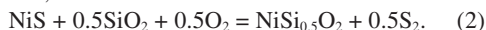
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The solution model developed in Hirschmann (1991) resulted in small to moderate negative deviations from Raoult's law for minor amounts of Ni in ternary Mg-Fe-Ni olivine; i.e., the activity coefficient of the liebenbergite component (NiSi<sub>0.5</sub>O<sub>2</sub>) in Mg-Fe-Ni olivine ( $\gamma_{\text{Ni}}$ ) was predicted to be <1. Revised solution parameters in Hirschmann (1992) reaffirmed the small to moderate negative deviations for minor Ni in Mg-rich olivine but yielded moderate positive deviations from Raoult's law for Fe-rich olivine.

These results contradicted Fleet (1989), who derived  $\gamma_{\text{Ni}}$  by equilibrating Mg-Fe-Ni olivine with (Fe,Ni)S liquid at defined  $f_{\text{S}_2}$  and  $f_{\text{O}_2}$  and 1300 to 1395 °C, and reported small to moderate positive deviations from Raoult's law for minor amounts of Ni in Mg-rich olivine. Fleet (1989) essentially considered the reactions:



and,



The important steps involved were (1) calculation of activity of FeS from Equation 1 using activity coefficients of FeSi<sub>0.5</sub>O<sub>2</sub> in olivine from Williams (1972); (2) calculation of activity of NiS by graphical integration of the Gibbs-Duhem equation across the FeS-NiS pseudobinary; and (3) calculation of  $\gamma_{\text{Ni}}$  using activity of NiS from step 2 and the linear relationship:

$$\log\gamma_{\text{Ni}} = \text{KB} + \log a_{\text{NiS}} - \log X_{\text{Ni}} \quad (3)$$

where KB is a constant, and equal to the activity of NiSi<sub>0.5</sub>O<sub>2</sub> at  $a_{\text{NiS}} = 1$ . Fleet (1989) plotted  $\log X_{\text{Ni}}$  vs.  $\log a_{\text{NiS}}$  (cf. Fig. 1) for each of the four isobaric (i.e., fixed  $f_{\text{O}_2}$  and  $f_{\text{S}_2}$ ) series of experiments (A<sub>1</sub>, A<sub>2</sub>, C, and D) in Fleet and MacRae (1987, 1988).

Hirschmann (1991) asserted that these activity coefficients for NiSi<sub>0.5</sub>O<sub>2</sub> were not likely to be correct for the following reasons: (1) the activity of FeSi<sub>0.5</sub>O<sub>2</sub> calculated from the regression equation of Williams (1972) is probably underestimated (Sack and Ghiorso 1989); (2) derivation of activities in steps 1 and 3 requires the assumption that the activity of SiO<sub>2</sub> was constant in unbuffered experiments, although this may not

have been the case; (3) the Gibbs-Duhem integration was performed across a pseudobinary over which the chemical potentials of other components were not held constant, and is therefore invalid; and (4) the sum of propagated errors is undoubtedly very large. The rebuttal arguments are as follows:

(1) The regression equation of Williams (1972) essentially optimizes the fit to the activity-composition relations of Nafziger and Muan (1967) and Kitayama and Katsura (1968) for 1200 and 1204 °C, respectively, and 1 bar, which are the studies of record for activities of MgSi<sub>0.5</sub>O<sub>2</sub> and FeSi<sub>0.5</sub>O<sub>2</sub> in binary Mg-Fe olivine (e.g., Wood and Kleppa 1981). The regression coefficients A and B for both of these sets of reference data were identical within the calculated uncertainties of ±10% in Williams (1972). The activity coefficients of FeSi<sub>0.5</sub>O<sub>2</sub> used in Fleet (1989) for Mg-Fe-Ni olivine, which was close to binary Mg-Fe composition, then, are essentially those of Nafziger and Muan (1967) and Kitayama and Katsura (1968), with a small correction for run temperatures of 1300 and 1395 °C.

(2) Fleet (1989) noted that in the controlled atmosphere experiments of Fleet and MacRae (1987, 1988), olivine and sulfide liquid coexisted with silicate liquid and (Mg,Fe,Ni)Al<sub>2</sub>O<sub>4</sub> aluminate spinel that formed by reaction of the charge with the alumina crucible. The activity of silica was constrained by the reaction:



giving,

$$a_{\text{SiO}_2} \approx \left( K_4 \frac{a_{\text{MgSi}_{0.5}\text{O}_2}^{\text{ol}} a_{\text{Al}_2\text{O}_3}^{\text{melt}}}{a_{\text{MgAl}_2\text{O}_4}^{\text{sp}}} \right)^2. \quad (5)$$

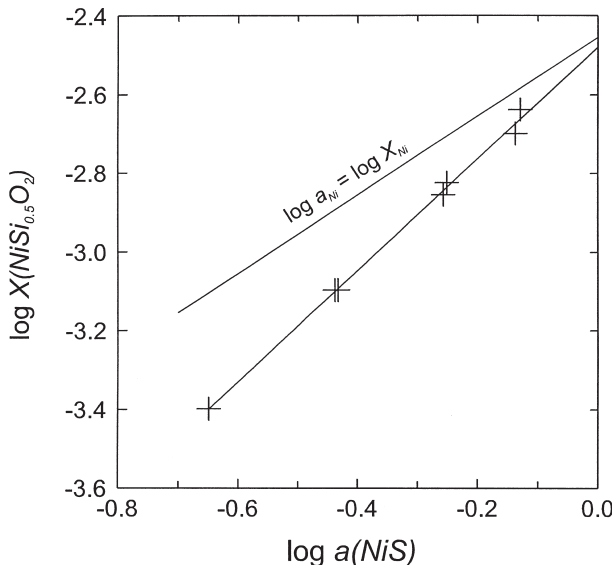
Fleet (1989) erred in suggesting that the activity of Al<sub>2</sub>O<sub>3</sub> was unity, but it is necessary only to show that it was constant within error of determination of  $\gamma_{\text{Ni}}$ . The silicate melt intergranular to olivine in the experimental products was essentially Mg-Fe aluminosilicate (99 wt%), with ~0.6 wt% Na<sub>2</sub>O and ~0.2 wt% K<sub>2</sub>O. Although the mole fractions of FeO and MgO ( $X_{\text{FeO}}$ ,  $X_{\text{MgO}}$ ) varied within each isobaric series,  $X_{\text{SiO}_2}$  and  $X_{\text{Al}_2\text{O}_3}$  remained essentially constant; e.g., for run series A<sub>2</sub> here illustrated in Figure 1,  $X_{\text{SiO}_2} = 0.533 \pm 0.023$  and  $X_{\text{Al}_2\text{O}_3} = 0.163 \pm 0.006$ . Furthermore, Fleet (1989) noted that the experimental results of Jamieson and Roeder (1984) for the distribution of Mg and Fe<sup>2+</sup> between olivine and aluminate spinel revealed

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that, within the composition interval  $\text{Fo}_{100}$  to  $\text{Fo}_{60}$ , the average value of  $X_{\text{MgSi}_{0.5}\text{O}_2}^{\text{ol}}/X_{\text{MgAl}_2\text{O}_4}^{\text{sp}}$  was 1.015, and all variation in this ratio appeared to be within the range of experimental error. Of course, these data do not demonstrate that the activity of  $\text{SiO}_2$  was constant over the restricted range of olivine composition investigated, but the maximum likely variation in it was clearly very much less than the quantity in Figure 1 associated with  $\log\gamma_{\text{Ni}}$ . For example, assuming that  $a_{\text{SiO}_2} \propto X_{\text{SiO}_2}$ , the difference between the maximum and minimum value of  $\log X_{\text{SiO}_2}$  corresponds to a shift in  $\log\gamma_{\text{Ni}}$  of +0.02, which is smaller than the symbol size used in Figure 1 (the value of  $\log\gamma_{\text{Ni}}$  for the experiment with the highest content of  $\text{SiO}_2$  actually plots below the regression line). In making the assumption that  $a_{\text{SiO}_2} \propto X_{\text{SiO}_2}$ , I note that melt structure is not a significant factor here because the silicate melts of series A<sub>2</sub> experiments were reduced ( $f_{\text{O}_2} = 10^{-8.9}$  at 1385 °C) and, therefore, Fe is unlikely to have participated in network-forming reactions.

(3) The sulfide liquid was certainly a pseudobinary solution [e.g.,  $(\text{Fe,Ni})_{1-x}(\text{S}_{1-y}\text{O}_y)$ ] and the metal/S ratio tended to increase with increase in Ni content. However, the sulfide liquid was effectively pseudobinary only in respect to minor components; the variation in  $(\text{Fe,Ni})/\text{S}/\text{O}$  within a single isobaric run series of Fleet and MacRae (1987, 1988) being minimal. It is noteworthy that magnesiowüstite solid solution presented a similar problem in Hahn and Muan (1962), yet use of their Gibbs-Duhem-derived activity coefficients of  $\text{MgO}$  and  $\text{Fe}_{1-x}\text{O}$  in  $(\text{Mg,Fe})_{1-x}\text{O}$  yielded activity-composition relations for Mg-Fe olivine that were essentially identical to those obtained independently by gas mixing (Nafziger and Muan 1967).

For the isobaric run series A<sub>2</sub> illustrated in Figure 1, the



**FIGURE 1.** Isobaric distribution for partitioning of Ni between Mg-Fe-Ni olivine and Fe-Ni monosulfide liquid at 1385 °C in controlled atmosphere experiments (pluses; series A<sub>2</sub> of Fleet and MacRae 1988; Fleet 1989). From Equation 3,  $\log\gamma_{\text{Ni}}$  is given by the difference between the activity-activity line ( $\log a_{\text{Ni}} = \log X_{\text{Ni}}$ ) and the regression line through the experimental data ( $\log X_{\text{Ni}}$ ), at given activity of NiS in the sulfide liquid ( $\log a_{\text{NiS}}$ ).

oxygen content of the most Fe-rich sulfide liquid was <0.5 wt% (Fleet and MacRae 1988), and decreased to an undetectable amount at the Ni-rich limit. On an oxygen-free basis, the S content varied from 51.2 to 49.7 at% at the Ni-rich limit. The sulfide liquids of Fleet and MacRae (1988) were homogenized in a sealed silica tube with a fitted glass rod to facilitate electron probe microanalysis (EPMA). The oxygen content was estimated visually from polished sections, but this estimate was very conservative. Brenan and Caciagli (2000) have recently reinvestigated the Fe-Ni exchange between olivine and sulfide liquid, determining oxygen in the sulfide liquid by EPMA. I also attempted analysis of oxygen in quenched monosulfide liquids using EPMA but found that the method gave unrealistically high values due to contamination by water (or oxides) in fractures and pits (unpublished research). Four experiments in Brenan and Caciagli (2000) may be compared with that for the most Fe-rich bulk composition of run series A<sub>2</sub> (OT38); they were run at 1300 °C under  $f_{\text{S}_2}$ - $f_{\text{O}_2}$  conditions that would have resulted in more oxygen and considerably less S in the sulfide-oxide liquid than in OT38. The oxygen contents reported for these four experiments ranged from 0.63 to 1.79 wt%, thus confirming both the unpublished research at UWO and the present estimate for the maximum oxygen content in the most Fe-rich sulfide product of run series A<sub>2</sub>.

Fleet (1989) obtained small to moderate positive deviations from Raoult's law for FeS and NiS in idealized  $(\text{Fe,Ni})\text{S}$  solid solution; the values of  $\gamma_{\text{FeS}}$  and  $\gamma_{\text{NiS}}$  being similar in magnitude to  $\gamma_{\text{ZnS}}$  and  $\gamma_{\text{FeS}}$  in sphalerite-structure  $(\text{Zn,Fe})\text{S}$  (Fleet 1975). The large negative deviations from Raoult's law for FeS in liquids along the  $\text{FeS-Ni}_3\text{S}_2$  join (Hsieh and Chang 1987) do not contradict Fleet (1989) because these calculated results for metal-rich liquids essentially relate to the mixing of FeS with Fe, NiS, and Ni entities. The sulfide liquid in the isobaric run series D of Fleet and MacRae (1988) was certainly metal-rich at the Ni-rich limit, but the metal:S ratio did not approach heazlewoodite stoichiometry. I emphasize that the sulfide liquid of the isobaric run series A<sub>2</sub> (Fig. 1) was generally of monosulfide composition.

(4) Errors are cumulative in the procedure of Fleet (1989), but this is compensated by robust values for activity coefficients.

The Hirschmann (1991) criticisms of Fleet (1989) are invalid, since errors associated with the isobaric run series A<sub>2</sub> (Fig. 1) are clearly minor. It is noted that the A series experiments of Fleet and MacRae (1997, 1988) were reversed, within error of measurement, by equilibrating olivine in the presence of melt and approaching the equilibrium from opposite directions, starting with pure synthetic forsterite and natural olivine.

Fleet (1989) noted that his experimental values for  $\gamma_{\text{Ni}}$  in ternary olivine were consistent with  $\gamma_{\text{Ni}} \sim 1.0$  in Mg-rich binary Ni-Mg olivine at and above 1300 °C, and in general agreement with Campbell and Roeder (1968), Seifert and O'Neill (1987), and Boström and Rosén (1988). Fleet (1989) is also supported by Snyder and Carmichael (1992), who used a completely independent experimental method to obtain values for  $\gamma_{\text{Ni}}$  in Mg-rich olivine ranging from 1.3 to 2.3. They extracted values for  $\gamma_{\text{Ni}}$  in olivine equilibrated with natural basic melts, alloy, and

gas mixtures at 1395 to 1559 K, using tabulated Gibbs free energies of olivine species ( $\text{MgSi}_{0.5}\text{O}_2$ ,  $\text{FeSi}_{0.5}\text{O}_2$ ,  $\text{NiSi}_{0.5}\text{O}_2$ ) from the oxides, their experimental activities of  $\text{MgO}$ ,  $\text{Fe}_{0.947}\text{O}$ , and  $\text{NiO}$  in the melt, and activity coefficients of forsterite and fayalite species from the Sack and Ghiorso (1989) solution model for olivine. The Snyder and Carmichael (1992) procedure is admittedly somewhat circuitous, so that different values of  $\gamma_{\text{Ni}}$  could be obtained by judicious choice of standard states and mixing model for the Ni-Fe alloy. Nevertheless, with the single exception of the 2.3 value, their activity coefficients for experiments with <8 wt% NiO in olivine are in quantitative agreement with  $\gamma_{\text{Ni}}$  derived by multiple regression analysis of the results of Fleet (1989) (unpublished research at UWO).

In Hirschmann (1991), values for  $\gamma_{\text{Ni}}$  were extracted by linear expansion of the theory for heterogeneous exchange equilibria in binary solid solutions (Thompson 1969, 1970; Sack 1980; Sack and Ghiorso 1989), which accounts for the effects of “reciprocal exchange” as well as intracrystalline partitioning exchange and binary cation interactions. The condition for equilibrium in Ni-Mg olivine is:

$$RT \ln \left( \frac{X_{\text{Ni}}^{\text{M2}} X_{\text{Mg}}^{\text{M1}}}{X_{\text{Ni}}^{\text{M1}} X_{\text{Mg}}^{\text{M2}}} \right) = \Delta \bar{G}_{\text{EX,MgNi}} \quad (6)$$

$$+ t (\Delta \bar{G}_{\text{x,MgNi}} - W_{\text{MgNi}}^{\text{M1}} - W_{\text{MgNi}}^{\text{M2}}) + q (W_{\text{MgNi}}^{\text{M2}} - W_{\text{MgNi}}^{\text{M1}})$$

where  $\Delta \bar{G}_{\text{EX,MgNi}}$  is the partial molar free energy of intracrystalline exchange,  $\Delta \bar{G}_{\text{x,MgNi}}$  is the partial molar free energy of reciprocal exchange,  $t (= X_{\text{Ni}}^{\text{M1}} - X_{\text{Ni}}^{\text{M2}})$  is the ordering parameter,  $q (= 2X_{\text{Ni}} - 1)$  is the compositional parameter,  $X_{\text{Ni}}^{\text{M2}}$  is the molar occupancy of Ni in the M2 cation site, etc., and  $W_{\text{MgNi}}^{\text{M1}}$  is the energy of interaction of Ni on Mg in the M1 site, etc. Equation 6 was made tractable by assuming that the excess partial molar entropies ( $\Delta \bar{S}_{\text{EX,MgNi}}$  and  $\Delta \bar{S}_{\text{x,MgNi}}$ ) are zero (or insignificant). Activity coefficient expressions were not given in Hirschmann (1991). I have derived the following expression by equating the microscopic and macroscopic activity terms (e.g.,  $2RT \ln a_{\text{Ni}} = RT \ln a_{\text{Ni}_2\text{SiO}_4}$ ):

$$2RT \ln \gamma_{\text{Ni}} = RT \ln \left( \frac{X_{\text{Ni}}^{\text{M1}} X_{\text{Ni}}^{\text{M2}}}{X_{\text{Ni}}^2} \right) \quad (7)$$

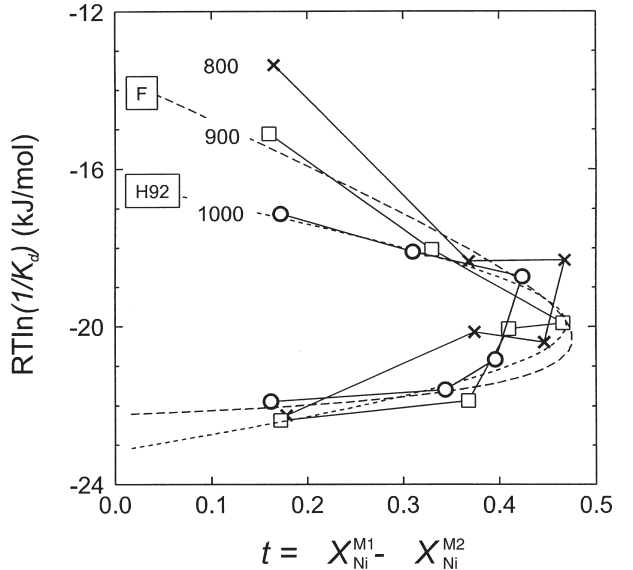
$$+ \Delta \bar{H}_{\text{x,MgNi}} (X_{\text{Mg}}^{\text{M1}} X_{\text{Mg}}^{\text{M2}}) + W_{\text{MgNi}}^{\text{M1}} (X_{\text{Mg}}^{\text{M1}})^2 + W_{\text{MgNi}}^{\text{M2}} (X_{\text{Mg}}^{\text{M2}})^2$$

where  $\Delta \bar{H}_{\text{x,MgNi}}$  is the partial molar enthalpy of reciprocal exchange. Equation 7 is consistent with equations 2.52 of Ganguly and Saxena (1987), who adapted the reciprocal exchange theory of Flood et al. (1954), and Equation 26 of Hirschmann (1991). Corresponding equations for the two-site regular solution model (without reciprocal exchange) are obtained by setting  $\Delta \bar{G}_{\text{x,MgNi}}$  and  $\Delta \bar{H}_{\text{x,MgNi}}$  in Equations 6 and 7, respectively, to zero. These equations are also readily derived by expansion of the single-site regular solution model, assuming that the energetic interaction within one site is independent of the composition of the other and that the mixing within each site follows a simple

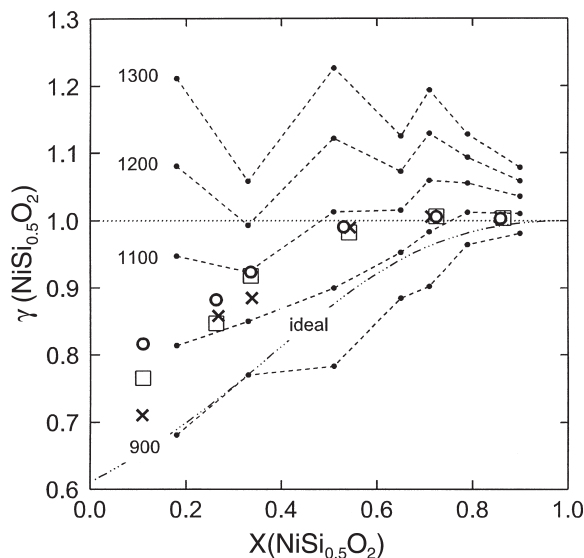
mixture behavior.

Hirschmann’s (1991) model was recalibrated in Hirschmann (1992), and then used to calculate activities of metal species in magmatic liquids (Hirschmann and Ghiorso 1994). Solution parameters for binary Ni-Mg olivine, which have a critical bearing on prediction of  $\gamma_{\text{Ni}}$  in Mg-rich ternary olivine, were based on in situ measurements of intracrystalline partitioning at 800 to 1000 °C. Activity coefficients generated by the original calibration are now redundant.

Solution parameters for the two-site regular solution model have been obtained for Hirschmann’s (1992) in situ data for the intracrystalline partitioning in Ni-Mg olivine, recognizing that  $t = 0$  at  $q = -1, 1$  and the maximum value of  $t$  is at  $q = 0$ ; e.g.,  $\Delta \bar{H}_{\text{EX,MgNi}} = [RT \ln(1/K_d)_{q=1} + RT \ln(1/K_d)_{q=-1}]/2$ , where  $\Delta \bar{H}_{\text{EX,MgNi}}$  is the partial molar enthalpy of intracrystalline exchange and  $K_d = (X_{\text{Ni}}^{\text{M1}} \times X_{\text{Mg}}^{\text{M2}})/(X_{\text{Ni}}^{\text{M2}} \times X_{\text{Mg}}^{\text{M1}})$ . This simple solution model appears to fit Hirschmann’s (1992) in situ measurements just as well as the heterogeneous exchange equilibria model (Fig. 2); evidently the status of significant reciprocal exchange in binary Ni-Mg olivine is dubious. The in situ intracrystalline partitioning data are simply too imprecise to calibrate Hirschmann’s model properly. Moreover, the scatter of the data in Figure 2 is inconsistent with equilibration of olivine crystals at 800 and 900 °C. Although intracrystalline partitioning involves exchanges among nearest-neighbor cations, long-range order requires equilibrium over crystal domains. Thus, site occupancies of refractory Mg-rich olivine determined at 800–1000 °C after short periods of annealing may simply reflect the first (rapid) step of a two-step, order-disorder process. This sugges-



**FIGURE 2.** Site occupancy in Ni-Mg olivines measured in situ at 800 (crosses), 900 (open squares) and 1000 °C (open circles) by Hirschmann (1992), expressed as plots of  $RT \ln(1/K_{d,\text{NiMg}})$  vs. ordering parameter ( $t$ ); short-dash line (H92) is fit for the heterogeneous exchange equilibria model at 900 °C (Hirschmann 1992); long-dash line (F) is fit for the two-site regular solution model at 900 °C; see Equation 6 and following discussion.



**FIGURE 3.** Activity coefficient of liebenbergite component ( $\text{NiSi}_{0.5}\text{O}_2$ ) in binary Ni-Mg olivine ( $\gamma_{\text{Ni}}$ ) calculated with Equation 7 for the heterogeneous exchange equilibria model of Hirschmann (1991; 1992) at 800 (crosses), 900 (open squares), and 1000 °C (open circles), and compared with data for 900, 1000, 1100, 1200, and 1300 °C from the emf measurements of Boström and Rosén (1988); the 1300 °C data below  $X_{\text{Ni}} = 0.65$  were obtained by extrapolation); triple dot-dash line is  $\gamma_{\text{Ni}}$  calculated for ideal mixing on M1 and M2 sites and no excess enthalpy terms at 800 °C.

tion for some control by cation diffusion or, at least, long-range cation communication is not necessarily inconsistent with the extremely high quench rates required to preserve equilibrium cation site occupancies (Akamatsu and Kumazawa 1993), because these quench rates may have been estimated with data for the initial step of rapid exchange between nearest-neighbor cations. In situ intracrystalline partitioning studies will have to be extended to much higher temperatures to fully evaluate the effect of annealing time on Hirschmann's (1992) data for 800–1000 °C.

Values of  $\gamma_{\text{Ni}}$  have been calculated for the Ni-Mg olivines studied in situ in Hirschmann (1992), using Equation 7 and his solution parameters, and are compared with data obtained from emf measurements at 927–1327 °C by Boström and Rosén (1988) in Figure 3. The heterogeneous exchange equilibria model is seen to be in poor agreement with the emf measurements except at 1000 °C, at low and high Ni content. Moreover, the activity coefficients from emf measurements show a much greater temperature dependence than the modelled values. Thus, if the emf measurements are accurate, the assumptions that  $\Delta\bar{S}_{\text{EX,MgNi}}$  and other excess entropies are zero in olivine solid solutions are invalid. These emf results show that  $\gamma_{\text{Ni}}$  varies from  $<1$  (and close to the ideal two-site mixing values) at 900 °C to  $>1$  at 1300 °C. Boström and Rosén (1988) noted that the positive deviations in their data for  $\gamma_{\text{Ni}}$  could not be explained by simple two-site ordering. Other structural features

must be present, and they suggested cation clusters or superstructures. It is likely that the loss in configurational entropy associated with intracrystalline partitioning in Ni-Mg olivine solid solutions is progressively counterbalanced by non-ideal terms associated principally with clustering on the separate (M1, M2) cation sites (Fig. 3). Independent evidence of the tendency for Ni to exist preferentially as  $^{\text{M2}}\text{Fe}^{\text{M1}}\text{NiSiO}_4$  entities in dilute solution in ternary Mg-Fe-Ni olivine is now provided by the EXAFS study of Galoisy et al. (1995).

Hirschmann (1991, 1992) demonstrated that the distribution constant ( $K_{\text{D,FeNi}}$ ) for cation exchange between Fe-Ni olivine and Fe-Ni alloy predicted by his model was in good agreement with the laboratory measurements of Campbell et al. (1979) and Seifert et al. (1988). However,  $K_{\text{D}}$  is not a very sensitive indicator of solution behavior for small departures from ideal solution, because the activity coefficient quotients (and products of activity coefficient quotients) tend to remain constant, particularly where similar cation environments exist in the two coexisting phases. A good example here is provided by the results of Snyder and Carmichael (1992);  $K_{\text{D,FeNi}}$  values for some of their experiments are apparently reproduced by Hirschmann's (1992) model, yet the values of  $\gamma_{\text{Ni}}$  for these experiments are in good agreement with Fleet (1989), as I have noted above.

In summary, Hirschmann's (1991) model for binary and ternary olivine solid solutions is suspect because it is too simplistic. It does not include cross terms for the interactions of cations between M1 and M2 sites (to account for the influence of the composition of one site on the energetic interaction within the other) and there are no excess entropy terms. It does not account for the clustering of cations in olivine, which is a ready explanation for the observation of  $\gamma_{\text{Ni}} > 1$  in Mg-rich olivine in Fleet (1989). Calibration of Hirschmann's (1991) model in both the original paper and Hirschmann (1992) is also suspect. There is no evidence for continuity in  $\gamma_{\text{Ni}}$  between values deduced from in situ intracrystalline partitioning at 800–1000 °C (Hirschmann 1992) and the higher temperature phase-equilibria studies of Campbell and Roeder (1968), Seifert and O'Neill (1987), and Boström and Rosén (1988) for Ni-Mg olivine, and Fleet (1989) and Snyder and Carmichael (1992) for Mg-rich ternary Mg-Fe-Ni olivine. I emphasize that calibration of a simple model at 800 to 1000 °C (using data of dubious value; Fig. 2) does not demonstrate that cross terms and excess entropy terms are negligible when this calibrated model is inconsistent with a wide range of higher-temperature measurements.

Finally, Fleet (1989) did not offer a general solution for the activity coefficient of liebenbergite component in ternary Mg-Fe-Ni olivine. Instead, small to moderate positive deviations from Raoult's law were reported for a limited range in temperature and composition of Mg-rich olivine. I have shown that the results for the run series A<sub>2</sub> were for monosulfide solid solution equilibrated with olivine, and that they were not invalidated by significant variation in the activity of  $\text{SiO}_2$  in the coexisting melt. These results are a critical test for thermodynamic models for  $\gamma_{\text{Ni}}$  at high temperature. However, the solution behavior of  $\text{NiSi}_{0.5}\text{O}_2$  in olivine is evidently complex and the calibration of a theoretically sound model may be too demanding for present laboratory methods.



## ACKNOWLEDGMENTS

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