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Thermodynamics of multicomponent olivines and the solution properties of $(Ni,Mg,Fe)_2SiO4$ and $(Ca,Mg,Fe)_2SiO_4$ olivine—Reply

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Fleet (2000) criticizes several aspects of the thermodynamic model for $(Ni,Mg,Fe)_2SiO_4$-bearing olivine from Hirschmann (1991) and its subsequent recalibration in my Ph.D. thesis (Hirschmann 1992). He also justifies the thermodynamic methods used by Fleet (1989) to extract activity coefficients of $NiSi_{0.5}O_2$ in olivine. I am pleased that somebody has taken the time to read parts of my Ph.D. thesis and will take this opportunity to reply to Fleet's comments on some of my early work and elaborate on the problems with Fleet (1989).

Fleet (2000) finds fault with three aspects of the thermodynamic model for $(Ni,Mg,Fe)_2SiO_4$ olivine from Hirschmann (1991, 1992). He criticizes the formulation of the model, but his contentions reflect misapprehensions regarding thermodynamic models that account for long-range ordering. He questions the quality of the ordering data used to calibrate the model, but does not acknowledge available data that corroborate the site occupancy measurements. He also disparages the accuracy of the predicted activity-composition relations, but fails to account for experimental uncertainties and discounts considerable evidence for agreement between the model and experimental constraints on $NiSi_{0.5}O_2$ olivine activities.

Fleet (2000) also defends the activity coefficients for $NiSi_{0.5}O_2$ extracted in the thermodynamic analysis of Fleet (1989). He suggests that there is *a posteriori* evidence that silica activity was nearly constant in a suite of experiments that were not designed to buffer silica but, as detailed below, there is good reason to suspect significant silica activity variation in these experiments. He reiterates evidence presented in Fleet (1989) suggesting that the oxysulfide liquids in the experiments of interest are reasonable approximations of FeS-NiS binary solutions. However, these liquids are unlikely to be close to monosulfide composition because their reported compositions are critically dependent on visual estimates of fine-grained quenched sulfide-oxide intergrowths and because significant departures from monosulfide stoichiometry are observed for oxysulfide liquids equilibrated under comparable experimental conditions in studies in which more direct analyses of the liquids were performed.

THE THERMODYNAMIC MODEL OF HIRSCHMANN (1991)

Model formulation

Hirschmann (1991) constructed a thermodynamic model for $(Ni,Mg,Fe)_2SiO_4$ olivine that accounts for non-ideal interactions between divalent cations and long-range ordering of cations between the M1 and M2 sites. Following earlier work on olivine thermodynamics (Sack 1980; Sack and Ghiorso 1989), this model incorporates a free energy of ordering ($\bar{G}_{EX}^{MgNi}$), regular-solution-like interactions on the octahedral sites (W_{MgNi}^{M1} and W_{MgNi}^{M2}) and a reciprocal term $\bar{G}_{EX}^{MgNi}$ (e.g., Wood and Nicholls 1978). Fleet (2000) examines the ordering data of Hirschmann (1992), finds satisfactory fits that neglect the reciprocal term, and concludes that incorporation of the $\bar{G}_{EX}^{MgNi}$ term in the Hirschmann (1991) model is unjustified. However, for a binary join, it is impossible to extract independent values for $\bar{G}_{EX}^{MgNi}$, W_{MgNi}^{M1}, and W_{MgNi}^{M2} from ordering data alone, as these terms are not linearly independent in the equations that describe ordering (see Eq. 19 in Hirschmann 1991). Independent values of these parameters can be found only by simultaneous examination of ordering data and of constraints on chemical potentials, such as phase equilibria or activity-composition measurements. Paradoxically, Fleet (2000) also faults the Hirschmann (1991) formulation for ignoring interactions between the M1 and M2 octahedral sites. He is apparently unaware that reciprocal terms *are* interactions between sites (e.g., Wood and Nicholls 1978; Sack 1980).

Fleet (2000) also criticizes the model of Hirschmann (1991, 1992) for failing to account for short-range clustering, which he suggests is responsible for the positive deviations from ideality inferred by Fleet (1989). However, in most cases the chief energetic effect of short-range ordering is to reduce configurational entropy and thus to reduce activity coefficients (e.g., Wood and Nicholls 1978). I agree that the role of clustering in the energetics of ferromagnesian minerals is poorly quantified and may be under-appreciated. While a comprehensive formulation incorporating short-range effects would be desirable, there is at this time no way to calibrate such a model for Ni-bearing olivine, as the study of Galoisy et al. (1995) constrains neither the extent of clustering nor its dependence on temperature or composition. The work of Hirschmann (1991, 1992) is the most detailed thermodynamic model yet formulated for Ni-Mg-Fe olivine and is consistent with the majority of available constraints, including those at very high temperature, as detailed below.

Accuracy of ordering data used to calibrate the model

In Hirschmann (1992), I recalibrated the original model presented in Hirschmann (1991) using site occupancies of $(Ni,Mg)_2SiO_4$ olivine that I determined in situ between 800 and 1000 °C. Fleet (2000) suggests that these measurements are "dubious" because he is skeptical that the crystals reached an equilibrium state of order prior to analysis. Fleet (2000) also claims that characteristic times for equilibration of order-dis-

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order are proportional to the size of the crystal, but this claim lacks theoretical or experimental justification. Because reequilibration of long-range site distributions requires only that the statistically appropriate number of Ni and Mg ions exchange positions between the M1 and M2 positions, the length scale of interest is the few-angstrom distance between neighboring octahedral sites (e.g., Ganguly and Tazzoli 1994). Note that geospeedometry using long-range ordering does not require correction for the size of crystals in the calibration experiments or the natural materials examined (e.g., Ganguly 1982).

The in situ single-crystal X-ray diffraction (XRD) site occupancies determined for $(Ni,Mg)_2SiO_4$ olivine at 800, 900, and 1000 °C by Hirschmann (1992) are corroborated by the studies of Snyder (1993) and Chen et al. (1996). Snyder (1993) (cited in preprint in Hirschmann 1992) performed in situ single crystal XRD measurements of a $(Ni_{0.606}Mg_{0.394})_2SiO_4$ olivine at 100 °C intervals between 900 and 1300 °C, and these results are in near-perfect agreement with those of Hirschmann (1992) (Fig. 1). The data of Snyder (1983) provide the high-temperature confirmation of Hirschmann's site occupancy measurements called for by Fleet (2000). Chen et al. (1996) performed a time-series experiment measuring the site occupancies of $Ni_1Mg_1SiO_4$ olivine in situ using powder XRD at 800 °C and 4 GPa and found that site occupancies approached steady state after approximately 2 hours. The crystals studied by Hirschmann (1992) at 800 °C were preheated for 24–72 hours. Additionally, the crystals studied by Chen et al. (1996) and Hirschmann (1992) approached steady state from different directions (ordering for Chen et al. 1996; disordering for Hirschmann 1992), yet record nearly identical ordering energies, which strongly suggests that both approached equilibrium.

Accuracy of predicted activity-composition relations

Fleet portrays the model of Hirschmann (1991, 1992) as being calibrated solely from order-disorder measurements and asserts that there are significant disagreements between the model and phase-equilibrium studies (Campbell and Roeder 1968; Seifert and O'Neill 1987; Boström and Rosén 1988). In fact, the model of Hirschmann (1991,1992) is calibrated from both order-disorder data and from the phase-equilibrim studies cited by Fleet (2000), and is consistent with most of the data from these studies (Figs. 2 and 3).

Fleet (2000) suggests that there are serious discrepancies between the model of Hirschmann (1991,1992) and EMF measurements of Boström and Rosén (1988), but his Figure 3 greatly exaggerates any actual disagreements because he ignores analytical uncertainty and because he extrapolates the data of Boström and Rosén (1988) to temperatures outside of their measurement intervals. As shown in Figure 2, the calibration of Hirschmann (1992) is consistent with 19 out of 23 constraints from the data of Boström and Rosén (1988) within 2σ uncertainty. It is also consistent with 4 out of 7 high-temperature, gas-mixing measurements from Campbell and Roeder (1968) (Fig. 2).

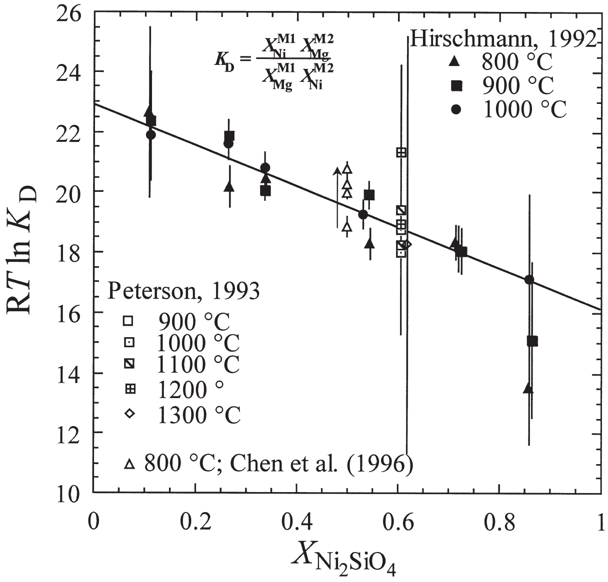

FIGURE 1. Comparison of intracrystalline partitioning of Ni and Mg determined by in situ single crystal XRD by Hirschmann (1992) at 800, 900, and 1000 °C with in situ single crystal XRD determinations of Snyder (1993) between 900 and 1300 °C and in situ powder XRD of Chen et al, (1996) at 800 °C and 4 GPa. The 1300 °C datum of Snyder (1993) has been moved to the right slightly for figure clarity. Hirschmann (1992) pre-heated crystals prior to analysis for 24–72, 15–54, and 7–25 hours at 800, 900, and 1000 °C, respectively. Fine arrow indicates direction of progressive ordering in study of Chen et al. (1996) for crystals heated for 0, 40, 62, and 109 minutes. In the study of Hirschmann (1992), XRD of unheated crystals shows that crystals became more disordered during heating. The slightly greater degree of ordering observed by Chen et al. (1996) is likely owing to the high pressure of equilibration, as ordering should increase with increasing pressure (Hirschmann 1991, 1992; Chen et al. 1996; Hazen and Navrotsky 1996). Error bars are 2σ. Solid line is the fit to model of Hirschmann (1991) that is derived in Hirschmann (1992), with $\bar{G}_{EX}^{MgNi} = -19500$ J/mol, and $(\bar{G}_X^{MgNi} - W_{MgNi}^{M1} - W_{MgNi}^{M2} = 0)$ and $(W_{MgNi}^{M2} - W_{MgNi}^{M1}) = 3400$ J/mol. These parameters are consistent both with the preferred model of Hirschmann (1992) ($\bar{G}_X^{MgNi}$=2200 kJ/mol, $W_{MgNi}^{M1} = -600$ J/mol, W_{MgNi}^{M2}=2800) and with the alternative model discussed in the text and in the caption to Figure 3. ($\bar{G}_X^{MgNi}$=7400 kJ/mol, W_{MgNi}^{M1}=2000 J/mol, W_{MgNi}^{M2}=5400 J/mol). Note that $\bar{G}_{EX}^{MgNi}$ is misprinted in Hirschmann and Ghiorso (1994) as –19750 J/mol.

Based largely on the data of Boström and Rosén (1988) and its extrapolation to high temperature, Fleet (2000) contends that mixing parameters for $(Ni,Mg)_2SiO_4$ are temperature dependent and that positive deviations from ideality are expected for Ni-poor compositions at high temperature. However, the excellent agreement between in situ ordering studies of Hirschmann (1992), Snyder (1993), and Chen et al. (1996) over 500 °C cannot be reconciled with a significant temperature dependence on those mixing parameters influencing long-range ordering (Fig. 1). It is important to note that the long-range ordering data do not specifically preclude modest positive deviations from ideality at high temperature. Indeed, it is possible to construct alternative calibrations of the Hirschmann (1991) model that produce positive deviations from ideality at high temperature (inset to Fig. 3) and that are consistent with the ordering data in Figure 1. But such models are not satisfac-

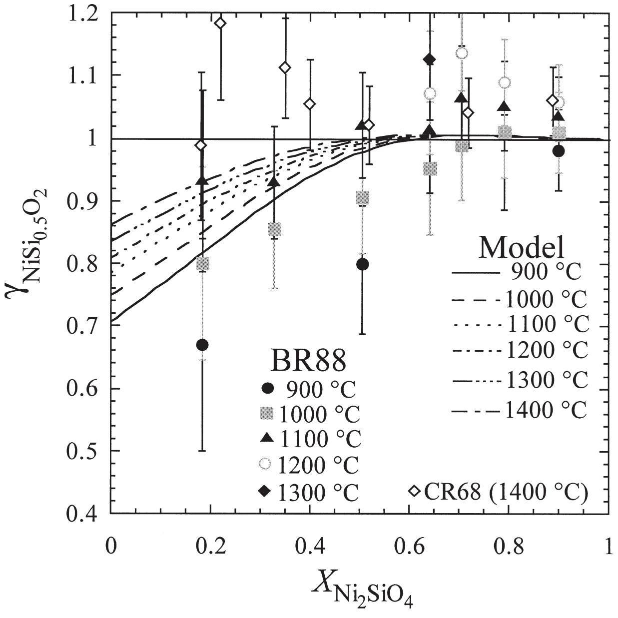

FIGURE 2. Comparison of predicted vs. experimentally determined activity coefficients for $(Ni,Mg)_2SiO_4$ olivine. EMF data from Boström and Rosén (1988) (BR88) at 100 degree intervals between 900 and 1300 °C, and gas-mixing phase equilibrium determinations from Campbell and Roeder (1968) (CR68) at 1400 °C. Error bars are 2σ. Model values are from calibration of Hirschmann (1992) with preferred olivine mixing parameters (see caption to Fig. 1). Differences between this plot and Figure 3 of Fleet (2000) are chiefly the inclusion of error bars in the former and the extrapolation of Boström and Rosén's activity coefficients beyond the temperature of measurement in the latter.

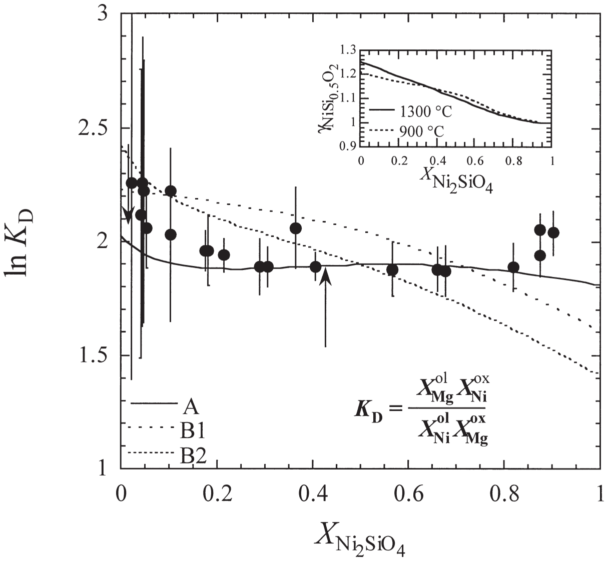

FIGURE 3. Comparison of predicted vs. experimentally determined Ni-Mg exchange between $(Ni,Mg)_2SiO_4$ olivine and (Ni,Mg)O oxide at 1300 °C and 0.5 GPa. Experimental data from Seifert and O'Neill (1987) includes synthesis experiments (solid symbols) and reversals (arrows). Error bars are 2σ. Trend A is the fit to these data from the model of Hirschmann (1991, 1992) using the preferred mixing parameters given in Figure 1, the standard state data for olivine and oxide given in Hirschmann (1991) and with $W^{ox}_{MgNi} = -2600$ J (cf. Davies and Navrotsky 1981; Hirschmann 1991). Trends B1 and B2 are predictions of alternative olivine models with $\bar{G}^{MgNi}_{EX} = -19500$ J/mol, $\bar{G}^{MgNi}_{X} = 7400$ kJ/mol, $W^{M1}_{MgNi} = 2000$ J/mol, $W^{M2}_{MgNi} = 5400$ J/mol. For trends B1 and B2, $W^{ox}_{MgNi} = 0$ and -2600 J, respectively. These alternative olivine mixing parameters produce identical predictions of olivine ordering data to the fit depicted in Figure 3, but predict large positive deviations from ideality (see inset). However, they produce poor fits to the olivine-oxide data and they violate the experimental reversals. Inset: Activity coefficients predicted by alternative olivine mixing parameters are positive at both 900 and 1300 °C.

tory, as they produce poor matches to Ni-Mg olivine-oxide exchange experiments (Fig. 3). These models also require positive deviations from ideality for Ni-poor Ni-Mg olivine at low temperature as well as high temperature (inset to Fig. 3) and are therefore in conflict with all of the data from Boström and Rosén (1988) at less than 50 mol% Ni_2SiO_4 (Fig. 2). Additionally, high temperature extrapolation of the Hirschmann (1991, 1992) model predicts successfully Fe-Ni exchange between olivine and FeNi alloy determined at high (1420–1780 °C) temperatures by Seifert et al. (1988) (Fig. 4). If positive deviations from ideality were robust features of $NiSi_{0.5}O_2$ in olivine at high temperatures, agreement between the model of Hirschmann (1991, 1992) and these data would not be possible. Finally, significant positive deviations from ideality for $(Ni,Mg)_2SiO_4$ seem unlikely, given that they are not present for (Ni,Mg)O (Davies and Navrotsky 1981) and given the small difference in ionic radii between Ni^{2+} and Mg^{2+}, as the magnitude of positive deviations from ideality in oxides and silicates generally correlates with differences in cation radii (Navrotsky 1987).

Fleet (2000) asserts that the mixing model of Hirschmann (1991, 1992) is inconsistent with activity coefficients derived from the olivine-oxide Mg-Ni exchange experiments of Seifert and O'Neill (1987) and the olivine-alloy Fe-Ni exchange studies of Campbell et al. (1979) and Snyder and Carmichael (1992). However, as Fleet notes, extraction of activity coefficients from these experiments depends critically on assumptions about standard states and mixing properties of the exchanging phase (oxide or alloy). Thus, a more relevant question is whether the Hirschmann (1991, 1992) model is consistent with the cation exchange data from these studies. Figure 3 demonstrates that this is so for the olivine-oxide data and Figure 4 shows that is so for the Fe-Ni olivine-alloy exchange experiments of Campbell et al. (1979), Seifert et al. (1988), and for some those from Snyder and Carmichael (1992). The model agrees with about half of the data of Snyder and Carmichael (1992), which is not surprising given that their K_D values vary by 20–40% when olivine compositions of nearly identical composition are compared at similar temperatures. Fleet (2000) discounts the significance of all of these predictions because he claims that cation exchange K_D values are insensitive to mixing behavior. On the contrary, there are numerous published studies documenting that cation exchange K_D values are affected significantly by mixing properties (e.g., Sack 1980; Davidson and

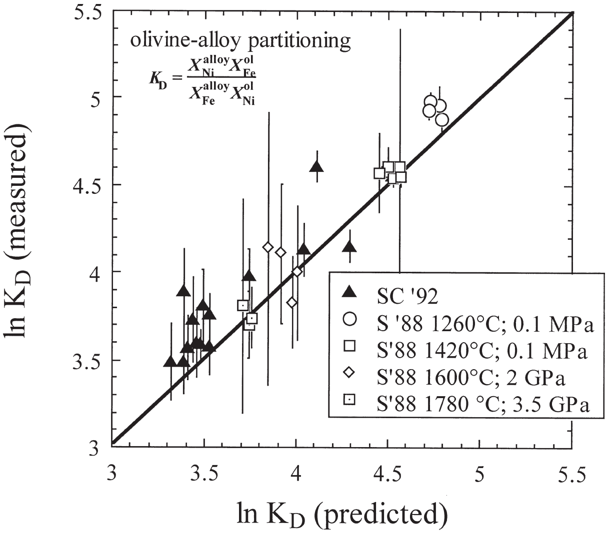

FIGURE 4. Comparison of predicted vs. experimentally determined partitioning between olivine and FeNi alloy. Experimental data of Campbell et al. (1979) (C ’79; 1300 °C, 1 bar), Seifert et al. (1988) (temperatures and pressures indicated on graph), and Snyder and Carmichael (1992) (SC ’92; 1168–1296 °C, 1 bar). Alloys in 1600 and 1780 °C experiments are molten. Experimental error bars are 2σ. Predictions are made using model of Hirschmann (1991) and calibration of Hirschmann (1992), with the preferred olivine mixing parameters as in Figure 1 and standard state properties of olivine and alloy given in Hirschmann (1991) and Hirschmann and Ghiorso (1994).

Lindsley 1989; Sack and Ghiorso 1989, 1991; Wood et al. 1991; von Seckendorff and O’Neill 1993). For example, different assumed mixing parameters for Ni-Mg olivine yield substantially different predictions of olivine-oxide Ni-Mg K_D values (Fig. 3).

PROBLEMS WITH FLEET (1989)

Fleet (1989) extracted activity coefficients of $NiSi_{0.5}O_2$ in $(Ni,Mg,Fe)_2SiO_4$ olivine by examining the systematics of Fe-Ni partitioning between ternary olivine and Fe-Ni oxysulfide liquids. These activity coefficients are surprising in a number of respects, as they indicate strong positive deviations from ideality for $NiSi_{0.5}O_2$ in Mg-rich olivine, in seeming conflict with systematics of mineral mixing properties based on differences in cation radii (Navrotsky 1987) and with the well-known strong long-range ordering of Ni in olivine (e.g., Nord et al. 1982), as ordering has the tendency to reduce macroscopic activity coefficients (e.g., Sack 1980). Also, the activity coefficients extracted by Fleet (1989) indicate strong deviations from Henrian behavior for Ni in olivine, which is in conflict with observed Henrian behavior of Nernst partition coefficients between olivine and silicate liquid (Hart and Davis 1978; Leeman and Lindstrom 1978; Takahashi 1978; Nabelek 1980; Drake and Holloway 1981). Hirschmann (1991) reviewed the methods employed by Fleet (1989) and concluded that Fleet’s (1989) procedure was problematic and that the extracted activity coefficients were probably incorrect.

Fleet (1989, 2000) cites four studies, Campbell and Roeder (1968), Seifert and O’Neill (1987), Boström and Rosén (1988), and Snyder and Carmichael (1992), as being in broad agreement with the large activity coefficients of $NiSi_{0.5}O_2$ derived by Fleet (1989). However, I have shown that these same studies are largely consistent with the model of Hirschmann (1991, 1992), which predicts small activity coefficients for $NiSi_{0.5}O_2$. In the cases of Seifert and O’Neill (1987) and Snyder and Carmichael (1992), this apparent conflict is the result of already discussed ambiguities arising from assumed standard states and mixing properties of equilibrated phases, meaning that the derived activity coefficients are less robust than the cation exchange K_D values. As already noted, all of the Boström and Rosén (1988) data for olivine with <50 mol% Ni_2SiO_4 indicate negative deviations from ideality and so do not, as Fleet asserts, agree with his extracted activities. Thus, most of the supporting evidence cited by Fleet (1989, 2000) for large activity coefficients of $NiSi_{0.5}O_2$ in Mg-rich olivine is equivocal.

Two parts of Fleet’s (1989) procedure were particularly questionable. First, he assumed that activities of olivine components could be related to activities of oxysulfide liquid components by reactions of the form

$$\underset{\text{oxysulfide liquid}}{MS} + \underset{\text{gas}}{1/2\ O_2} + 1/2\ SiO_2 \leftrightarrow \underset{\text{olivine}}{MSi_{0.5}O_2} + \underset{\text{gas}}{1/2\ S_2} \quad (1)$$

where M = Fe or Ni. Second, he calculated FeS and NiS mole fractions by assuming that the oxysulfide liquids approximate the FeS-NiS binary mixtures and that activity coefficients of NiS could be extracted from activity coefficients of FeS by integration of the Gibbs-Duhem equation.

The assumption of constant silica activity

Fleet and MacRae (1988) analyzed the thermodynamics of Ni-Fe exchange between olivine and oxysulfide liquid by examining reactions of the form

$$\underset{\text{oxysulfide liquid}}{MS} + \underset{\text{gas}}{1/2\ O_2} \leftrightarrow \underset{\text{olivine}}{MO} + \underset{\text{gas}}{1/2\ S_2} \quad (2)$$

and by assuming that the activities of FeO and NiO in olivine are equal to the activities of $FeSi_{0.5}O_2$ and $NiSi_{0.5}O_2$. Recognizing that this assumption was invalid, Fleet (1989) instead assumed that a_{SiO_2} was buffered in each experimental series and evaluated the experiments using Equation 1. This assumption was justified by the observation that a spinel scale formed at the contact between the experimental charges and the alumina crucibles. Fleet asserted that a_{SiO_2} remained buffered in the experiments according to the reaction

$$\underset{\text{olivine}}{Mg_2SiO_4} + \underset{\text{crucible}}{Al_2O_3} \leftrightarrow \underset{\text{liquid}}{SiO_2} + \underset{\text{scale}}{MgAl_2O_4.} \quad (3)$$

Now Fleet (2000) acknowledges that spinel and corundum do not buffer silica activity in the experiments in question because the corundum was not in contact with the experimental charge. However, Fleet (2000) maintains that the extrapolations in Fleet (1989) are valid so long as a_{SiO_2} can be assumed to be nearly constant across any given isothermal, constant f_{O_2} and f_{S_2} experimental traverse. He suggests that variations in silica activity are negligible for the five separate data sets examined in Fleet (1989) because the standard deviation of the silica mole fraction for one of those series, A2, is 2.3 mol% and he asserts that the shift in activity may be equal to the shift in mole fraction, which would be true if the activity coefficient for silica were close to unity. However, because Fleet's method requires constant silica activity in extrapolation across the putative (Fe,Ni)S binary, it is not the mean value of the silica activity that is relevant, but the magnitude of systematic variation in this parameter. Additionally, there is reason to suspect that variations in a_{SiO_2} in these experimental series are not negligible.

Fleet and MacRae (1987) noted that compositional variations of silicate liquids are systematic across the FeS-NiS join in their experiments. They reported two liquid compositions, from experiments OT38 and OT44, from the A2 series of experiments and these differ by 4.8 mol% SiO_2. Because these liquids coexist with sulfides with intermediate Ni/(Fe+Ni) ratios (0.156 and 0.688, respectively), the shift in silica mole fraction extrapolated to the pure NiS join should be more than 4.8 mol%. Estimation of the change in silica activity is more difficult, as activity-composition relations are poorly known for the synthetic ferromagnesian peraluminous liquids reported by Fleet and MacRae (1987). However, the activity coefficient of SiO_2 is commonly quite different from unity in simple and complex silicate liquids (Ryerson 1985; Hess 1995; Hirschmann et al. 1998). In general, a_{SiO_2} is believed to be related to the degree of melt polymerization (Hess 1995), a crude indicator of which is the ratio of non-bridging oxygen atoms divided by tetrahedral cations (NBO/T; Mysen et al. 1985). Assuming all Fe as FeO, NBO/T for the silicate liquids in experiments OT38 and OT44 are 0.99 and 0.71, respectively. For comparison, the first value is intermediate between that typical of alkali olivine basalts and olivine nephelinites (NBO/T = 0.83 and 1.17, respectively; Scarfe et al. 1987) and the second is typical of tholeiitic basalts (e.g., NBO/T = 0.66–0.76, Scarfe et al. 1987). For natural silicate liquids, these differences in lava composition correspond to variations in log a_{SiO_2} of about 0.2 (Ghiorso and Carmichael 1987). If such shifts applied linearly to the liquids in Fleet's A2 series, and if they were corrected for in the method depicted in Figure 1 of Fleet (2000), then extracted activity coefficients would range from 0.98 to 1.26, instead of the values (1.12 to 1.79) extracted by assuming constant a_{SiO_2}. Additional shifts would be expected if one accounted for the effect of silica activity variation on extracted activity coefficients of FeS [Eq. 1 of Fleet (2000) and Eq. 13 of Fleet (1989)]. Although the analogy between the thermochemistry of natural lavas and the liquids present in the studies of Fleet and MacRae (1987, 1988) may or may not be accurate, it is likely to be more realistic than the ideal assumption made by Fleet (2000), and it demonstrates that silica activity variations sufficient to influence significantly the activity coefficients extracted by Fleet (1989) are quite plausible. In the absence of more direct information on the compositions and mixing properties of the silicate liquids in the experiments examined by Fleet (1989), it seems unwise to assume otherwise.

Evidence against monosulfide stoichiometry

As acknowledged by Fleet (1989, 2000), the Gibbs-Duhem integration performed by Fleet (1989) requires that the experimental oxysulfide liquid compositions be approximated by the FeS-NiS binary. Fleet (2000) reviews analytical procedures and results from Fleet and MacRae (1987, 1988) that suggest that the oxysulfide liquids approximated monosulfide stoichiometry. However, a large body of literature suggests that under the conditions of these experiments, Fe-Ni oxysulfide liquids depart significantly from the monosulfide binary. Ni-rich liquids have substantial metal excess. Fe-rich liquids are also likely to have a significant oxide component.

The chief problem is that, under the experimental conditions of Fleet and MacRae (1300–1395 °C;$-\log f_{S_2} = 0.91–1.05$), metal excesses are expected for all liquids with Ni/(Ni + Fe)>0.05 (Conard et al. 1987; Hsieh and Chang 1987) and these become progressively larger as Ni/(Ni + Fe) increases. To take a specific example, in the gas-mixing experiments of Conard et al. (1987) at 1403 °C, $-\log f_{S_2} = 1.11$ and Ni/(Fe + Ni) = 0.508, the metal/sulfur ratio is given as 1.19, whereas at 1395 °C, $-\log f_{S_2} = 1.05$ and Ni/(Fe + Ni) = 0.496 (experiment OT40), Fleet and MacRae (1987) report a metal/sulfur ratio of 0.97. High confidence can be placed on the measurements of Conard et al. (1987) because (1) they determined their compositions by bulk metallurgical assay, (2) they corroborated their experiments with Knudsen Cell mass spectrometry, and (3) their results are demonstrably consistent with crystal-liquid phase equilibria in the system Fe-Ni-S and with liquid data on the Fe-S and Ni-S joins (Sharma and Chang 1987). Conard et al. (1987) showed that under the conditions in the experiments of Fleet and MacRae (1987, 1988), Fe-Ni-S liquids follow a trend very close to the FeS-Ni_3S_2 join, which is supported by thermodynamic models in the Fe-Ni-S system (Sharma and Chang 1980; Hsieh and Chang 1987). The same holds true for Fe-Ni-S-O liquids when projected onto the Fe-Ni-S ternary (Yoshiki-Gravelsins and Toguri 1993; Brenan and Caciagli 2000). Thus, for compositions approximated by Fleet as $NiS_y - FeS_{(1-y)}$ liquids, the actual mole fractions of components are more accurately portrayed as $NiS_{0.667y} - Ni_{0.333y} - FeS_{(1-y)}$, meaning Ni-rich liquids considered by Fleet (1989) to be $X_{NiS} = 0.7$ should have mole fractions of NiS and Ni of approximately 0.47 and 0.23, respectively.

Despite this evidence, Fleet (2000) maintains that the oxysulfide liquids of Fleet and MacRae (1987, 1988) approximate near-monosulfide stoichiometry. Unfortunately, departures from this stoichiometry would be most easily detected for the Ni-rich charges, and analyses of the Ni-rich charges were hampered by quench crystallization even after rehomogenization, requiring reconstruction of bulk compositions from visual estimates of quenched sulfide and oxide modes (Fleet and MacRae 1987). Indeed, the observed difference in quenching behavior probably reflects increased metal/sulfide ratio with increasing Ni/(Ni+Fe). Fleet (2000) provides no explanation for the discrepancies between the compositions reported by Fleet and MacRae (1987, 1988) and the evidence cited above.

An additional problem is that the Fe-rich oxysulfide liquids produced by Fleet and MacRae (1987, 1988) are likely to have a significant oxide component. Fleet and MacRae (1988) estimated that the O content of the most Fe-rich liquids of each of their run series ranged from <0.5 to 4 wt%. Fleet (2000) asserts that this small quantity of oxygen can be neglected for the series (A2) with the lowest oxygen content. However, oxygen can have a significant thermodynamic effect even when its weight proportion is small because of its low molecular weight and because it probably resides in a component such as FeO. For example, an oxysulfide liquid with 1 wt% O has about 5 mol% FeO. Also, examination of independent studies of Ni-Fe-S-O liquids for which direct O analyses are given at similar $\log(f_{O_2}/f_{S_2})$ (Yoshiki-Gravelsins and Toguri 1993; Brenan and Caciagali, 2000) suggest that Fleet and MacRae's visual method underestimates O contents.

The oxide component of oxysulfide liquids is generally taken to depend on $\log(f_{O_2}/f_{S_2})$, based on the assumption that the FeO component is controlled by a reaction similar to:

$$\underset{\text{oxysulfide liquid}}{\mathrm{FeO}} + \underset{\text{gas}}{1/2\,\mathrm{S_2}} \leftrightarrow \underset{\text{oxysulfide liquid}}{\mathrm{FeS}} + \underset{\text{gas}}{1/2\,\mathrm{O_2}}. \qquad (4)$$

(Doyle and Naldrett 1987), although some caution is warranted because the liquids of interest are not truly monosulfide-monoxide solutions and because they are not ideal. Examination of the data of Yoshiki-Gravelsins and Toguri (1993) and Brenan and Caciagali (2000) (see Fig. 5) shows that the FeO mole fraction for the most Fe-rich liquids should be at least 15 mol% for 3 out of 5 of the experimental series (C1, C2, and D) considered by Fleet (1989). For conditions similar to the most Fe-rich liquids in the A1 and A2 series, the data conflict. The wet-chemical bulk analyses of Yoshiki-Gravelsins and Toguri (1993) suggest FeO contents >15 mol%, whereas the microprobe analyses of Brenan and Caciagali (2000) indicate between 5 and 10 mol% FeO. As noted by Brenan and Caciagali (2000) and Fleet (2000), microprobe analyses of O in oxysulfide liquids are possibly problematic [except when extreme measures are taken to ensure rapid quench (Kress 1997)], so the results of Yoshiki-Gravelsins and Toguri (1993) are more likely to be correct. Also, studies of O contents of pure Fe-S-O liquids (Fig. 5, see caption for references) are more consistent with the trend of Yoshiki-Gravelsins and Toguri (1993) than that of Brenan and Caciagali (2000). Thus, in the series least-affected by O (A2) the liquid considered by Fleet to be $\mathrm{FeS_{0.844}NiS_{0.156}}$ is better described as $\mathrm{FeO_xFeS_{0.844-x}\ NiS_{0.156}}$, where $x > 0.15$. Even applying the results of Brenan and Caciagali (2000), $x = 0.05$–0.10, which still suggests that the oxide content of the A2 series is a significant energetic factor.

Fleet (2000) notes that the modest to strong positive deviations from ideality for FeS determined by Fleet (1989) conflict with the strong negative deviations from ideality for FeS liquid across the $\mathrm{FeS\text{-}Ni_3S_2}$ join found by Hsieh and Chang (1987), but dismisses this discrepancy because he believes metal excesses are relevant to the latter study and not to the former. Because significant metal excesses are almost certainly present in the Fleet and MacRae (1987,1988) liquids, the comparison between Fleet (1989) and Hseih and Chang (1987) seems quite appropriate.

Henry's Law

An additional reason to question the olivine activity coefficients extracted in Fleet (1989), noted in Hirschmann (1991) but not addressed by Fleet (2000), is that they exhibit sharp deviations from Henry's Law. According to Fleet (1989, 2000), the activity coefficient for $\mathrm{NiSi_{0.5}O_2}$ in $\mathrm{Fo_{90}}$ olivine decreases from >1.8 at ~350 ppm Ni to 1.2 at ~4000 ppm Ni (Fig. 4 of Fleet 1989). In contrast, a large body of data is consistent with Henrian behavior for olivine/liquid partitioning of Ni (e.g., Hart and Davis 1978; Leeman and Lindstrom 1978; Takahashi 1978; Nabelek 1980; Drake and Holloway 1981). Of particular note is the study of Nabelek (1980), who performed reversed experiments on olivine compositions of $\mathrm{Fo_{89}}$ that ranged from 1000 to 3000 ppm Ni. Over this compositional range, the data of Nabelek (1980) require less than 6% deviation from Henry's Law for olivine/liquid partitioning, but the activity coefficients of Fleet (1989) vary by approximately 40%. To reconcile the Henrian behavior observed by Nabelek (1980) for the olivine/liquid system and the non-Henrian behavior for olivine inferred by Fleet (1989), one would have to posit that between 100 to 300 ppm, activity coefficients of Ni in silicate liquid increase in such a way as to cancel ~85% of the changes in activity coefficients of $\mathrm{NiSi_{0.5}O_2}$ in olivine between 1000 and 3000 ppm Ni.

There have been claims that partitioning of Ni between olivine and liquid deviates strongly from Henry's law (e.g., Mysen 1976, 1979). Although these claims conflict with a large number of subsequent studies (see references above), it is interesting to note they suggest decreases in $D_{\mathrm{Ni}}^{\mathrm{ol/liq}}$ with increasing Ni in olivine. This shift is therefore in the opposite sense of the deviations from Henry's Law implied by the activity coefficients derived by Fleet (1989), and are therefore in even greater conflict with the non-Henrian behavior surmised by Fleet (1989) than the coefficients from those studies suggesting Henrian behavior.

FINAL REMARKS

Fleet (2000) highlights discrepancies between the models of Hirschmann (1991, 1992) and certain experimental phase-equilibrium data, but applies this approach selectively and without considering experimental uncertainties in these data. The thermodynamic model for Ni-bearing ferromagnesian olivine employed by Hirschmann (1991, 1992) provides reasonable results when applied to a wide range of mineral exchange equilibria (olivine-alloy, olivine-oxide, olivine-orthopyroxene, olivine-silicate liquid; Hirschmann 1991, 1992; Hirschmann and Ghiorso 1994). It is consistent with much of the data available for calibration, including both order-disorder constraints as well as activity-composition measurements and phase-equilibrium data.

Calibration of thermodynamic mixing models generally requires emphasizing some of the available data relative to others, simply because some of the data cannot be reconciled the collective constraints imposed by the rest of the data. Hirschmann (1991, 1992) discounted the activity coefficients derived by Fleet (1989) because they cannot be reconciled with

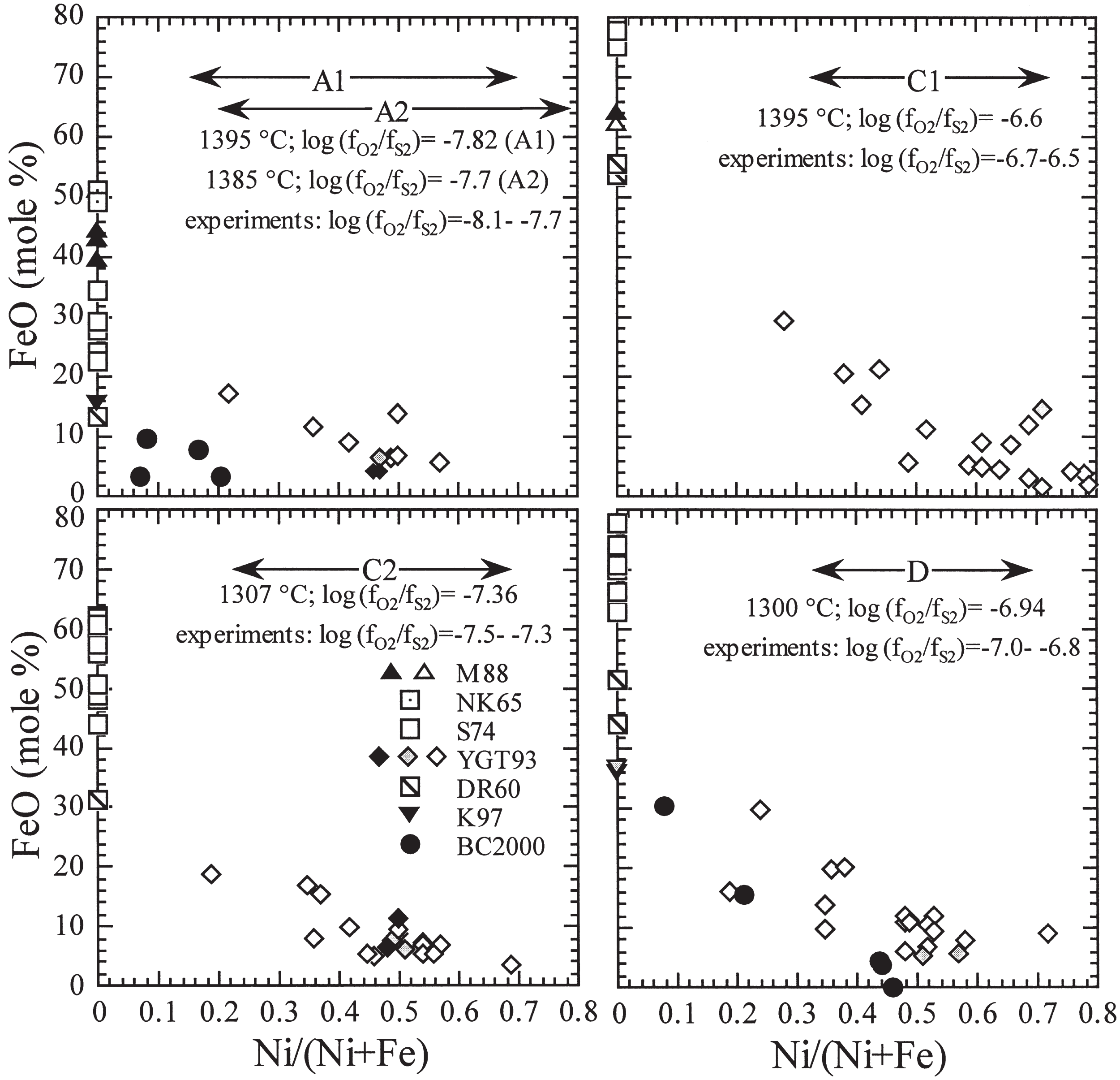

FIGURE 5. Molar FeO content of Ni-Fe-S-O liquids under conditions similar to the experiments of Fleet and Macrae (1987, 1988). Data are from Mintsis et al. (1988) (M88), Nagmori and Kameda (1965) (NK65), Stofko et al. (1974) (S74), Yoshiki-Gravelsins and Toguri (1993) (YGT93), Dewing and Richardson (1960) (DR60), Kress 1997 (K97), and Brenan and Caciagli, 2000 (BC2000). Mole fractions are calculated for FeO-MS-MS_2 or FeO-MS-M (M = Fe,Ni) components, depending on the cation/anion ratio of the liquid. Data in each panel are taken for experiments within the range of $\log(f_{O_2}/f_{S_2})$ indicated. These ranges encompass the value of $\log(f_{O_2}/f_{S_2})$ from the appropriate experimental series examined by Fleet (1989). Arrows indicate the range of liquid Ni/(Ni + Fe) observed for each of these series. The most O-rich liquid expected from these series is in each case expected to be at the Ni-poor end of the arrows. Experimental data are at 1200–1206 °C (open symbols), 1250 °C (shaded symbols) and 1300 °C (closed symbols). These temperatures are close to the range of experimental temperatures (1300–1385 °C) from Fleet and MaCrae (1987, 1988). The higher temperatures of Fleet and MacRae probably reduce slightly the O content of their liquids, but direct studies of the temperature dependence of O solubility of oxysulfide liquids (Mintsis et al. 1988; Yoshiki-Gravelsins and Toguri 1993) suggest that this effect is small.

the collective body of ordering and phase-equilibrium constraints discussed above and because of problems in the methods used by Fleet (1989). The arguments presented by Fleet (2000) do not justify reconsideration of that earlier judgement.

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