

The effect of S on the partitioning of Ni between olivine and silicate melt in MORB

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Abstract

The partitioning behavior of Ni between olivine and silicate melt in S-bearing systems has been investigated using mid-ocean ridge basalts (MORBs). The Nernst Ni partition coefficient between olivine and silicate melt (D^{Ni}) derived from the MORB samples varies between 4 and 9, values that are up to 50% lower than those derived from S-free experimental systems of similar composition. The MORB samples yield lower D^{Ni} values because Ni^{2+} and S^{2-} interact to form a Ni–S complex in the silicate melt. Since the Ni present as NiS contributes to the melt concentration but is not available for sequestration by olivine, the overall effect is a reduction in the D^{Ni} value calculated from the total concentration of Ni in the silicate melt. This hypothesis is supported by the negative correlation between the $\ln K_{\text{D}}^{\text{Ni-Mg}}$ ($K_{\text{D}}^{\text{Ni-Mg}} = [\text{MgO}^{\text{melt}}/\text{MgO}^{\text{Ol}}]/[\text{NiO}^{\text{melt}}/\text{NiO}^{\text{Ol}}]$) values and the contents of S in the silicate melts of the MORB samples.

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1. Introduction

Experimentally derived Nernst partition coefficients for Ni between olivine and silicate melt have been used to infer the compositional evolution of sulfide-bearing mafic intrusions (Li and Naldrett, 1999; Li et al., 2000, 2002, 2003), to deduce the compositions of primary terrestrial and extraterrestrial magmas (Hart and Davis, 1978; Clarke and O'Hara, 1979; Seifert et al., 1988; Korenaga and Kelemen,

2000), as a geothermometer in basaltic rocks (Leeman and Scheidegger, 1977), and to model early planetary differentiation processes (Schmidt et al., 1989; Gaetani and Grove, 1997). Except for those of Gaetani and Grove (1997), all the experiments conducted to determine how Ni partitions between olivine and silicate melt have been performed in S-free systems (Irvine and Kushiro, 1976; Mysen and Kushiro, 1976; Duke, 1976; Hart and Davis, 1978; Leeman and Lindstrom, 1978; Takahashi, 1978; Nabelek, 1980; Kinzler et al., 1990; Snyder and Carmichael, 1992; Ehlers et al., 1992). These studies indicate a significant effect of silicate melt composition, particularly MgO content, on partitioning behavior, and have led to several empirical models relating melt composition

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to D^{Ni} (Arndt, 1977; Hart and Davis, 1978; Nielsen, 1985; Colson et al., 1988; Kinzler et al., 1990; Hirschmann, 1991; Beatie et al., 1991; Hirschmann and Ghiorso, 1994; Li et al., 2001). These models typically reproduce experimentally determined values of D^{Ni} with a precision of 10–25%.

Despite the consistency among the various experiments on S-free systems and apparent success of these models, they do not appear to be consistent with values of D^{Ni} estimated from natural systems. Thus, those derived from olivine and bulk-rock analyses for the Kiglapait intrusion and Mauna Loa picrites are less than half of the model values (Morse et al., 1991). One suggestion to account for the disparity is that Ni dissolved in silicate melt exists as both Ni^{2+} and Ni^0 (Morse et al., 1991). The idea is that since analyzed values reflect total Ni rather than Ni^{2+} , D^{Ni} values derived from more reduced natural systems in which the proportion of Ni as Ni^0 is relatively high are less than those derived from relatively oxidized experiments in which the proportion of Ni as Ni^0 is less. The notion that there is significant Ni^0 dissolved in silicate melts under reducing conditions (near and below the iron–wüstite [IW] buffer) is based on experiments by Colson (1990, 1992). Colson observed an increase in Ni content of glass in the vicinity of Ni wire. He interpreted this to indicate the presence of real concentration gradients in the glass caused by evaporation of Ni from the silicate melt. This interpretation has been disputed by Capobianco and Amelin (1994), who argued that the gradients are not real but due to a poor analytical spatial resolution and that no evidence exists for Ni volatility in the experiments. Subsequent experiments over ranges in oxygen fugacity extending to three orders below IW (i.e., Capobianco and Amelin, 1994; Dingwell et al., 1994; Holzheid and Palme, 1996; Holzheid et al., 1994, 1997) have not found evidence for species other than Ni^{2+} in silicate melts.

Another possibility is that in natural mafic magmas, which all contain S, a proportion of the dissolved Ni exists as NiS, as indicated by the experiments of Peach and Mathez (1993) and Gaetani and Grove (1997). This would also account for the disparity between D^{Ni} values derived from experiments and nature. In order to investigate this matter further, we determined the partitioning of Ni between coexisting olivine and glass (melt) of basalts recovered from the

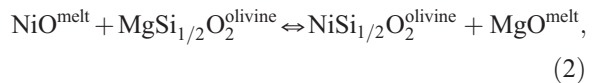
deep ocean using the set of samples originally studied by Mathez (1976, 1979). Because of the high confining pressures, these lavas only partially degassed, were saturated or nearly saturated in an immiscible sulfide liquid at the time of eruption, and retain nearly all of their original S. For these reasons and also because rapid quenching preserved near-liquidus relations, submarine basalts are the best natural samples available for the study of magmatic equilibria involving S and elements that combine with it.

2. Controls on Ni partitioning between olivine and silicate melt

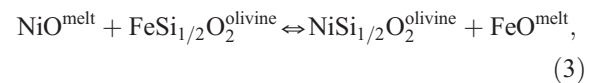
It is common to discuss the partitioning of Ni between olivine and a silicate melt in terms of the Nernst partition coefficient, or D^{Ni} , which is defined as:

$$D^{\text{Ni}} = \frac{\text{wt.\% of Ni in olivine}}{\text{wt.\% of Ni in silicate melt}} \quad (1)$$

Ni in a silicate melt may partition into olivine according to a reaction such as:



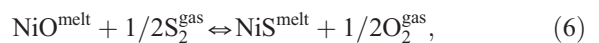
or



where NiO, FeO and MgO refer to hypothetical species in the silicate melt, and $\text{FeSi}_{1/2}\text{O}_2$, $\text{MgSi}_{1/2}\text{O}_2$ and $\text{NiSi}_{1/2}\text{O}_2$ are the appropriate components in the olivine solid solution. The equilibrium constant of reaction (3) is defined as:

$$K_3 = (a\text{FeO}/a\text{NiO}) \times (a\text{NiSi}_{1/2}\text{O}_2/a\text{FeSi}_{1/2}\text{O}_2). \quad (4)$$

In the presence of S, each of the melt species may form their oxide equivalents by the reactions:



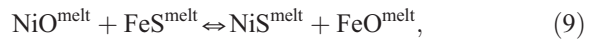
where the equilibrium constants are defined as:

$$K_5 = (a_{\text{FeS}}/a_{\text{FeO}}) \times (f_{\text{O}_2}/f_{\text{S}_2})^{1/2}, \quad (7)$$

$$K_6 = (a_{\text{NiS}}/a_{\text{NiO}}) \times (f_{\text{O}_2}/f_{\text{S}_2})^{1/2}. \quad (8)$$

Thus, the relative proportions of the reactants or products in reaction (3) are expected to vary with f_{O_2} and f_{S_2} .

Reactions (5) and (6) can be combined to express the exchange reaction between NiO and FeS in the melt:



where the equilibrium exchange constant K_9 is defined as:

$$K_9 = (a_{\text{NiS}}/a_{\text{NiO}}) \times (a_{\text{FeS}}/a_{\text{FeO}}), \quad (10)$$

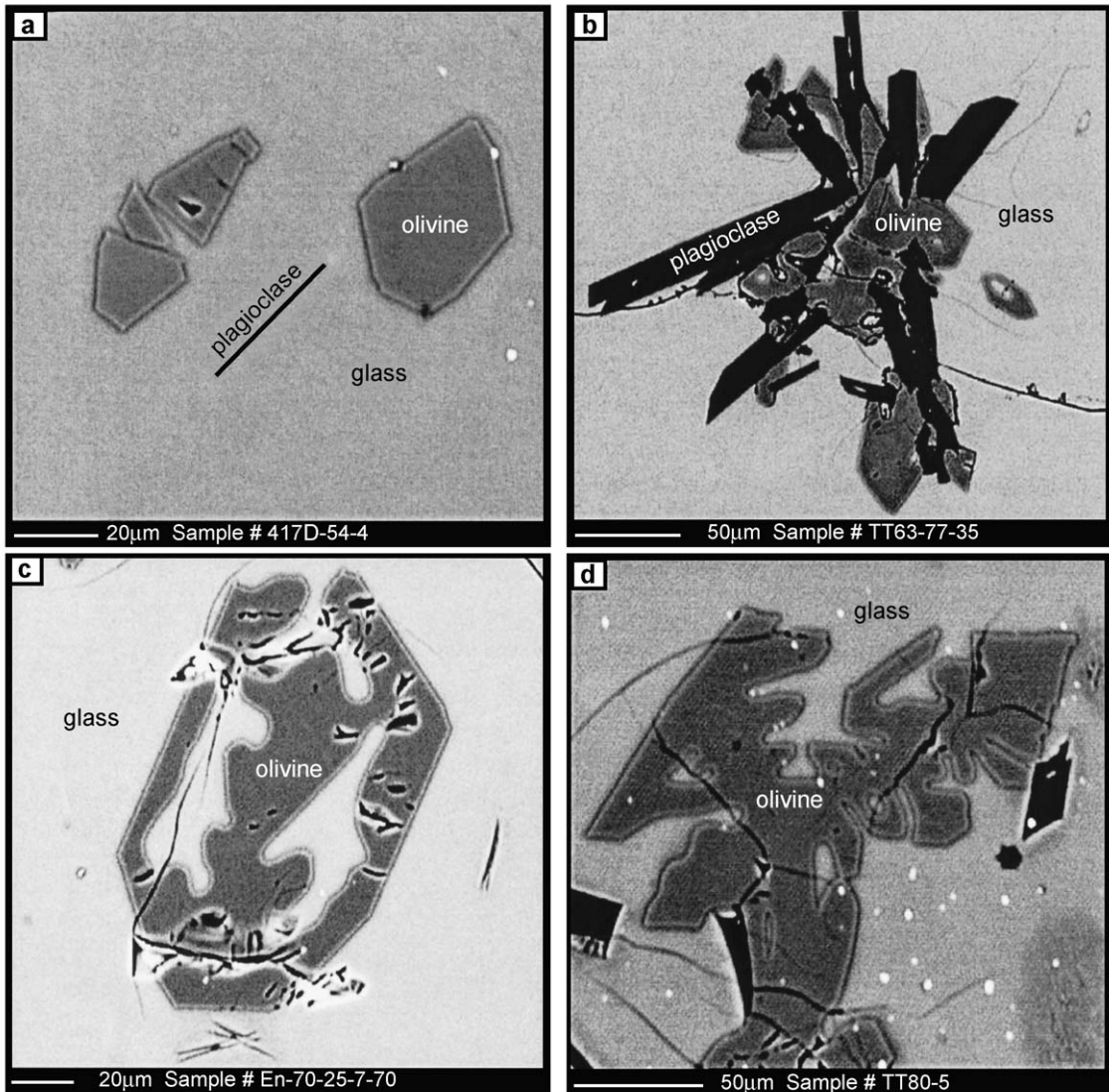


Fig. 1. Back-scattered electron images of representative olivine phenocrysts from mid-ocean ridge basalts (MORBs).

Table 1
Electron microprobe analyses of olivine and glass, and calculated variables

Location sample #	Paul Revere Ridge	Dellwood Smt. Area				Bermuda Rise, Atlantic Ocean						Nazca plate
	En-70-25-6-70 ^a	En-70- 25-16-1	En-70- 25-4	En-70- 25-7-70	En-70- 25-9	417D- 54-4	418A- 46-1	418A- 52-4	418A55-2	418A- 57-5	418A- 75-5	34-320B 4-1
<i>Glass composition (wt. %)</i>												
SiO ₂	48.16 (0.44)	48.46	47.82	49.28	49.66	50.65	50.19	50.58	50.57	50.33	51.32	50.67
TiO ₂	1.12 (0.04)	1.25	1.00	1.47	1.71	1.75	1.22	1.31	1.73	1.64	1.44	1.52
Al ₂ O ₃	17.09 (0.12)	17.11	17.82	16.60	14.64	13.78	15.15	14.74	13.71	14.02	14.03	15.23
Cr ₂ O ₃	0.04 (0.01)	0.04	0.03	0.05	0.04	0.03	0.05	0.05	0.03	0.04	0.02	0.05
FeO ^{total}	9.58 (0.15)	8.98	9.65	8.72	10.71	11.54	9.91	10.10	11.69	11.29	10.54	9.61
MnO	0.18 (0.04)	0.15	0.17	0.16	0.19	0.21	0.18	0.18	0.21	0.20	0.19	0.16
MgO	8.89 (0.06)	9.05	9.00	8.32	7.16	7.10	8.31	7.95	6.99	7.29	7.45	7.70
CaO	11.44 (0.09)	12.09	11.81	12.02	12.01	11.51	12.37	12.22	11.49	11.85	11.80	11.70
Na ₂ O	2.70 (0.05)	2.59	2.50	2.80	2.81	2.45	2.16	2.31	2.37	2.41	2.40	2.72
K ₂ O	0.05 (0.02)	0.10	0.05	0.24	0.15	0.08	0.06	0.07	0.09	0.10	0.10	0.08
P ₂ O ₅	0.09 (0.05)	0.10	0.06	0.18	0.19	0.14	0.10	0.10	0.18	0.16	0.11	0.13
NiO	0.035 (0.006)	0.031	0.027	0.027	0.019	0.026	0.029	0.025	0.026	0.022	0.022	0.028
S	0.109 (0.005)	0.106	0.107	0.101	0.130	0.144	0.116	0.120	0.145	0.138	0.130	0.120
Total	99.48 (0.48)	100.06	100.04	99.96	99.42	99.41	99.84	99.76	99.23	99.49	99.55	99.72
<i>Olivine composition (wt. %)</i>												
SiO ₂	40.24 (0.30)	40.43	40.36	40.46	39.83	39.44	39.90	40.05	39.44	39.49	39.97	40.32
MgO	46.31 (0.16)	47.27	46.91	46.93	43.55	42.04	45.28	44.62	41.62	42.83	43.60	45.02
FeO	12.83 (0.17)	11.81	12.25	12.12	15.60	17.02	13.65	14.51	17.26	16.30	15.58	13.76
MnO	0.19 (0.02)	0.18	0.18	0.18	0.26	0.29	0.23	0.24	0.27	0.26	0.27	0.23
CaO	0.30 (0.02)	0.30	0.32	0.38	0.42	0.36	0.34	0.35	0.37	0.34	0.32	0.34
Cr ₂ O ₃	0.05 (0.01)	0.051	0.049	0.053	0.050	0.028	0.046	0.037	0.024	0.035	0.014	0.045
NiO	0.29 (0.01)	0.280	0.253	0.202	0.128	0.145	0.202	0.166	0.143	0.157	0.148	0.208
Total	100.21 (0.32)	100.33	100.32	100.32	99.84	99.32	99.65	99.97	99.12	99.41	99.90	99.92
Fo	86.74 (0.19)	87.90	87.44	87.63	83.51	81.65	85.72	84.75	81.30	82.56	83.42	85.55
D ^{Ni}	8.3 (0.1)	8.9	9.3	7.6	6.6	5.6	7.1	6.6	5.5	7.1	6.7	7.3
<i>Values calculated using the MELTS program of Ghiorso and Sack (1995) for QFM, 0.25 wt.% H₂O and pressure calculated from collection depth of sea water</i>												
P (bar)	160	200	220	200	160	550	550	550	550	550	550	450
T (°C)	1208	1215	1215	1199	1185	1176	1196	1190	1174	1180	1184	1190
FeO	8.14	7.60	8.22	7.34	9.01	9.80	8.40	8.55	9.93	9.57	8.93	8.12
Fe ₂ O ₃	1.60	1.53	1.59	1.53	1.89	1.94	1.67	1.72	1.95	1.91	1.79	1.65
K _D ^{Fe-Mg}	0.30	0.30	0.29	0.29	0.28	0.29	0.30	0.30	0.29	0.29	0.32	0.29

Location sample #	E. Pacific rise	Explorer Smt.			Gulf of California		Juan de Fuca Ridge				Warwick Smt.
	TT65-2	TT63-72-30	TT63-76-34	TT63-77-35	TT99-1-1	TT99-2-2	TT29-12-7	TT29-15-1	TT29-14-1	TT40-1-1	TT80-5
<i>Glass composition (wt. %)</i>											
SiO ₂	49.15	48.27	47.82	48.13	49.99	50.65	49.77	50.73	49.70	50.67	50.01
TiO ₂	2.47	1.32	1.34	1.01	1.46	1.73	2.27	1.35	1.80	1.88	2.08
Al ₂ O ₃	16.23	17.05	17.46	16.84	14.75	14.27	13.66	14.33	14.07	13.65	14.30
Cr ₂ O ₃	0.03	0.03	0.04	0.04	0.05	0.04	0.01	0.04	0.02	0.02	0.02
FeO ^{total}	9.55	9.77	9.84	10.72	9.88	10.54	12.69	10.68	11.88	11.91	11.14
MnO	0.17	0.18	0.17	0.19	0.18	0.19	0.22	0.20	0.22	0.19	0.20
MgO	6.91	8.42	8.71	8.37	8.18	7.52	5.89	7.53	6.60	6.89	6.38
CaO	9.29	11.45	11.42	11.71	12.47	11.85	10.74	12.33	11.59	11.24	11.34
Na ₂ O	3.65	2.88	2.83	2.59	2.11	2.55	3.34	2.56	3.08	2.59	3.25
K ₂ O	1.06	0.04	0.15	0.04	0.05	0.06	0.30	0.07	0.22	0.12	0.33
P ₂ O ₅	0.53	0.11	0.14	0.09	0.14	0.15	0.24	0.08	0.21	0.20	0.25
NiO	0.026	0.029	0.034	0.026	0.022	0.025	0.018	0.021	0.019	0.022	0.018
S	0.119	0.114	0.116	0.118	0.131	0.135	0.172	0.130	0.155	0.150	0.142
Total	99.18	99.67	100.07	99.87	99.41	99.70	99.32	100.05	99.56	99.53	99.45
<i>Olivine composition (wt. %)</i>											
SiO ₂	39.70	40.33	40.53	40.10	40.16	39.71	38.71	39.81	39.03	39.40	39.64
MgO	43.61	45.43	45.97	45.02	45.46	44.09	39.89	43.79	42.10	41.58	41.68
FeO	15.86	13.27	13.03	14.10	13.56	15.01	20.02	15.45	17.83	17.83	17.75
MnO	0.25	0.22	0.20	0.21	0.21	0.23	0.34	0.29	0.31	0.27	0.29
CaO	0.33	0.39	0.35	0.34	0.33	0.34	0.39	0.39	0.37	0.35	0.39
Cr ₂ O ₃	0.052	0.049	0.051	0.056	0.048	0.035	0.005	0.034	0.016	0.008	0.012
NiO	0.220	0.235	0.269	0.222	0.166	0.163	0.080	0.126	0.112	0.120	0.094
Total	100.02	99.91	100.40	100.05	99.94	99.59	99.44	99.89	99.77	99.56	99.86
Fo	83.21	86.18	86.50	85.26	85.86	84.14	78.17	83.66	80.94	80.76	80.90
D ^{Ni}	8.6	8.2	7.9	8.5	7.6	6.6	4.4	6.0	5.8	5.6	5.3
<i>Values calculated using the MELTS program of Ghiorso and Sack (1995) for QFM, 0.25 wt.% H₂O and pressure calculated from collection depth of sea water</i>											
P (bar)	290	240	230	150	280	280	260	260	210	250	190
T (°C)	1190	1206	1205	1209	1189	1179	1164	1185	1175	1168	1172
FeO	8.06	8.29	8.36	9.12	8.35	8.90	10.71	9.00	10.00	10.09	9.35
Fe ₂ O ₃	1.66	1.65	1.65	1.78	1.70	1.82	2.21	1.87	2.09	2.03	1.99
K _D ^{Fe-Mg}	0.31	0.30	0.30	0.29	0.29	0.29	0.28	0.30	0.28	0.29	0.29

^a The values in parentheses are standard deviations of 10 spot/grain analyses. The deviations of this sample are typical of others.

and thus the relative proportions of NiO and NiS are expected to vary with the content of FeS in the melt.

In the presence of other metals (Me) that may be bonded with S^{2-} , reaction (9) can be modified to express the general exchange reaction between NiO and any of the sulfide species (MeS) in the melt:



where the equilibrium exchange constant K_{11} is defined as:

$$K_{11} = (a\text{NiS}/a\text{NiO}) \times (a\text{MeS}/a\text{MeO}), \quad (12)$$

and thus the relative proportions of NiO and NiS are expected to vary with the contents of all sulfide species in the melt.

From comparison of Eqs. (1), (4), (8) and (12), one expects D^{Ni} to be a function of f_{O_2} and f_{S_2} , or the contents of all sulfide species in the melt, in addition to temperature, pressure and the compositions of the two phases in question.

3. Samples and analytical methods

Petrographic descriptions of the samples used in this study have been given previously by Mathez (1976, 1979). Minerals commonly present in addition to olivine are plagioclase, spinel and clinopyroxene. Olivine phenocrysts vary in size between 20 and 200 μm in diameter, and occur as free-floating crystals (Fig. 1a) and glomeroplastic aggregates with microlites of plagioclase (Fig. 1b). They display a variety of shapes in a single sample, but most frequently occur as euhedral to subhedral (Fig. 1a and b) and, to a lesser extent, as skeletal (Fig. 1c) to hopper-shaped (Fig. 1d) crystals. Most olivine phenocrysts, regardless of morphology, are homogeneous and have similar compositions in the same sample. Zoned crystals are rare and usually normally zoned, with rim compositions similar to coexisting unzoned, small crystals.

The compositions of olivine were determined by wavelength dispersive electron microprobe analysis using the CAMECA SX50 instrument at Indiana University. Back-scattered electron images were used to select small, homogeneous olivine and regions of glass free of sub-micron sulfide inclusions for quantitative analysis. Accelerating voltage, beam current and

counting time for major elements were 15 kV, 20 nA and 20 s, respectively. A 15- μm -diameter beam was used to minimize loss of alkalis during the analysis of glass. Ni and S were analyzed at a beam current of 100 nA and a counting time of 100 s. The minimum detection limits under such conditions were ~ 60 ppm for each element. Synthetic oxide, sulfide and silicate standards were used for calibrations. The accuracies of glass and olivine analyses were determined by analysis of materials with known amounts of Ni, in this case Indian Ocean basaltic glass (USNM 113716) and San Carlos olivine (USNM 1113122/444).

4. Results

The compositions of coexisting olivine and glass are listed in Table 1. The compositions represent the average of at least 10 individual spot or grain analyses for glass and olivine, respectively. The variability among individual analyses of glass and olivine in a typical sample (i.e., En-70-25-6-70) is illustrated in Fig. 2. It can be seen that the respective variations in olivine forsterite (Fo) and Ni contents are 0.3% and 5% of the amount present. For the glass, MgO and $\text{FeO}^{\text{total}}$ vary by 2% and 3% of the amount present, and S and Ni vary by 12% and 30% of the amount present. The propagated uncertainty for D^{Ni} are calculated according to the conventional error propagation formula

$$\left(\frac{S_c}{c}\right)^2 = \left(\frac{S_a}{a}\right)^2 + \left(\frac{S_b}{b}\right)^2, \quad (13)$$

where S_a , S_b , and S_c are the standard deviations, respectively, of D^{Ni} (c), Ni concentration in olivine (a), and Ni concentration in glass (b).

For clarity, only the standard deviations for one representative sample are listed in Table 1, but these are typical of the others. Other listed variables in Table 1 are calculated from the results of original electron microprobe analysis using the MELTS program of Ghiorso and Sack (1995). The FeO and Fe_2O_3 contents are calculated for the conditions of an f_{O_2} equivalent to the quartz–fayalite–magnetite (QFM) buffer, a liquidus temperature that is in turn calculated assuming a water content of 0.25 wt.%, and a total

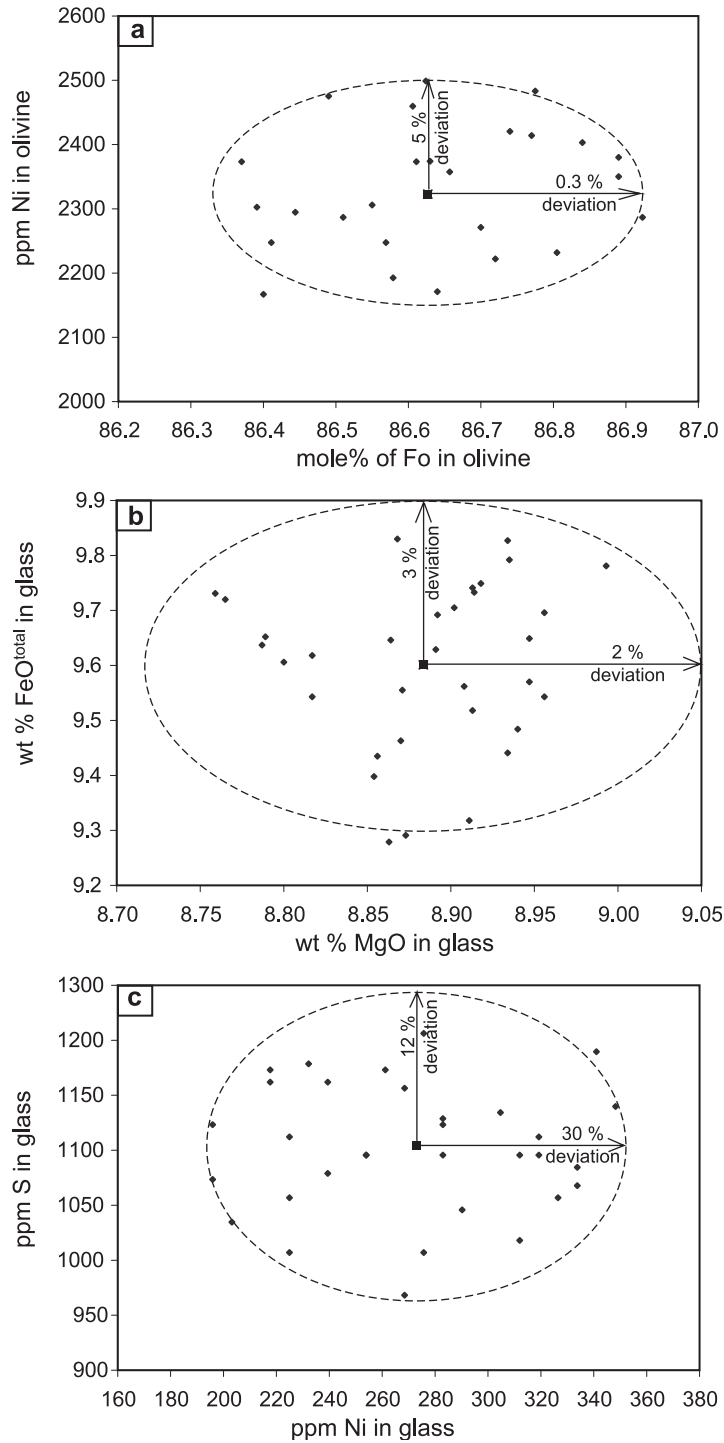


Fig. 2. Typical ranges of compositional variations in a representative MORB sample (# En-70-25-6-70). (a) Fo and Ni contents in olivines. (b) MgO and FeO^{total} contents in glass. (c) Ni and S contents in glass.

pressure corresponding to the water depth at which the samples were collected.

Fig. 3 illustrates the correlation of FeO/MgO ratio in olivine and coexisting glass. The corresponding olivine–melt Fe–Mg exchange $K_D^{\text{Fe–Mg}}$, $(\text{FeO}/\text{MgO})^{\text{olivine}}/(\text{FeO}/\text{MgO})^{\text{glass}}$, calculated from all the samples is 0.29 ± 0.02 , which is similar to the experimentally determined value of 0.3 ± 0.03 for basaltic systems (Roeder and Emslie, 1970). The $K_D^{\text{Fe–Mg}}$ values of individual samples are listed in Table 1. They vary between 0.28 and 0.32. The calculated $K_D^{\text{Fe–Mg}}$ values will vary slightly depending on the assumed oxidation state. For example, a decrease in oxygen fugacity of one log unit from QFM results in a decrease in $K_D^{\text{Fe–Mg}}$ of ~ 0.02 . The typical f_{O_2} at which MORBs erupt has been estimated to be equivalent to QFM based on the Fe–Ni exchange between olivine and coexisting sulfide liquid (Brenan and Caciagli, 2000) and to QFM-1 and QFM-2 based on the glass FeO/Fe₂O₃ ratios (Christie et al., 1986). On the other hand, higher H₂O content results in a lower liquidus temperature, which in turn results in a higher FeO/Fe₂O₃ ratio at the same oxidation state and leads to an increase in the inferred $K_D^{\text{Fe–Mg}}$ of about 0.01 for an increase of 0.2 wt.% H₂O. The contents of H₂O in oceanic basalts

range from ~ 0.25 wt.% in tholeiitic basalts to 0.75 wt.% in alkaline basalts (Moore, 1970). Variations in both H₂O content and oxygen fugacity cannot be precisely estimated for the MORB samples. However, the effects of such variations on the liquidus temperatures and FeO/Fe₂O₃ ratios are small. Thus, we use a constant oxidation state and a uniform H₂O content in our calculations and conclude that small variations in these variables have no significant influence on $K_D^{\text{Fe–Mg}}$.

5. Discussion

5.1. Comparison with S-free experiments

A comparison of the MORB data with the results of S-free experiments conducted at 1 atm pressure is shown in Fig. 4. The results of the experiments of Seifert et al. (1988) conducted at 500 MPa are also shown. The starting materials used in some of the experiments (Arndt, 1977; Leeman and Lindstrom, 1978; Nabelek, 1980; Snyder and Carmichael, 1992) are natural lava samples that may have originally contained trace amounts of S. However, the S would have been very rapidly lost in S-free gas mixtures.

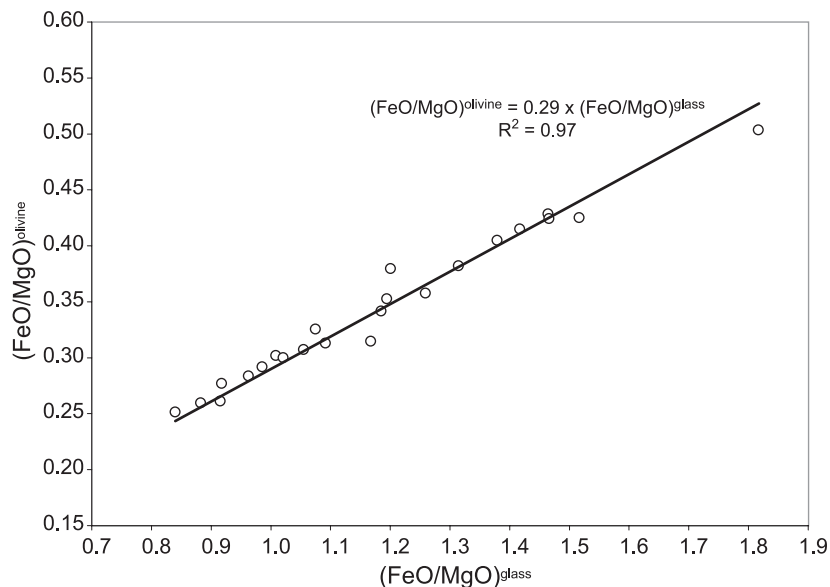


Fig. 3. Correlation of $(\text{FeO}/\text{MgO})^{\text{olivine}}$ with $(\text{FeO}/\text{MgO})^{\text{glass}}$. The values of FeO have been adjusted to account for Fe₂O₃ at the assumed QFM and the liquidus temperatures calculated using the MELTS program of Ghiorso and Sack (1995). Error bars are smaller than symbols.

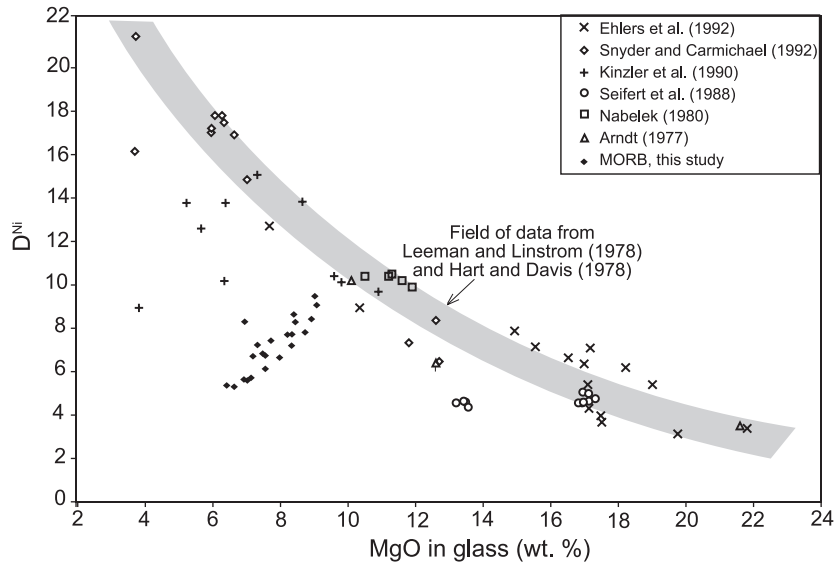


Fig. 4. Comparison of the MORB data with the data of S-free experimental systems. Except for the experiments of Seifert et al. (1988) that were conducted at 500 MPa, all other experiments were conducted at one atmosphere pressure. Error bars for the MORB samples are smaller than symbols.

As represented by the experiments of Hart and Davis (1978) and Leeman and Lindstrom (1978), the values of D^{Ni} exhibit a strong negative dependence on MgO content in S-free silicate melts (Fig. 4). For clarity, the experiments of Caley (1970), Bird (1971), Irvine and Kushiro (1976) and Takahashi (1978) are not shown in the plot, but they generally fall in or close to the field defined by the data of Leeman and Lindstrom (1978) and Hart and Davis (1978). The data of Duke (1976) are also not plotted because they are inconsistent with other data, possibly because equilibrium had not been attained (Irving, 1978). Finally, it should be noted that some of the data from Seifert et al. (1988) and Kinzler et al. (1990) are for relatively reduced compositions.

There are two obvious differences between D^{Ni} values obtained from analysis of the submarine basalts and those from experiments on S-free systems. First, the D^{Ni} values of the MORB samples are up to 50% lower than those of S-free systems at corresponding MgO contents. Second, the D^{Ni} values of the MORB samples are positively correlated with melt MgO content instead of the negative correlation that characterizes the S-free experimental systems.

Possible causes for the lower D^{Ni} values in the submarine basalts compared with the S-free experiments include (1) the presence in the glass of sulfide inclusions, which would yield incorrectly high glass Ni contents, (2) lack of equilibrium between olivine and glass, possibly because some olivine crystals are xenocrystic, and (3) the solution of some of the Ni in the melt as NiS. Great care was taken to avoid sub-micron sulfide inclusions in the glass. The presence of randomly distributed micron-size sulfide inclusions in the glass is ruled out in any case because of the similarity of glass analyses obtained using 15- and 1- μm -diameter electron beams. With regard to the matter of equilibrium, the consistency of the $K_D^{\text{Fe-Mg}}$ for coexisting olivine and glass in different samples and their similarity with the equilibrium $K_D^{\text{Fe-Mg}}$ determined from experiments suggest the olivine and glass represent equilibrium pairs. In any case, xenocrystic olivine crystals would have crystallized before eruption in a more primitive system and if anything should contain more Ni, which would yield an apparent D^{Ni} higher, rather than lower, than the true value. Also, the analyzed glasses are unrelated to each other, yet the population shows a consistent trend that should not exist in a set of disequilibrium compositions.

The third possibility, that some Ni^{2+} may be complexed in the silicate melt with S^{2-} , is indicated by experiments in S-bearing systems (Peach and Mathez, 1993; Gaetani and Grove, 1997) and is thus a more plausible explanation for the lower D^{Ni} values of the submarine basalt samples. This is supported by the correlation between $\ln K_D^{\text{Ni-Mg}}$ ($K_D^{\text{Ni-Mg}} = [\text{MgO}^{\text{melt}}/\text{MgO}^{\text{Ol}}]/[\text{NiO}^{\text{melt}}/\text{NiO}^{\text{Ol}}]$) and S shown in Fig. 5. In this formulation, the NiO content of the melt is computed from its total Ni content, which obviously assumes that it all exists as NiO. The correlation exists because as melt S content increases, more and more of the melt Ni is unaccounted for in the equilibrium. The two-element distribution coefficient is particularly useful in this context because it eliminates most apparent effects due to non-ideality of the melt (see O'Neill and Eggins, 2002). This firmly establishes the positive dependency of $\ln K_D^{\text{Ni-Mg}}$ on melt S content.

The S-free experimental systems most similar in compositions and conditions of solidification to the MORB samples are those of Nabelek (1980) and Snyder and Carmichael (1992), which were conducted at 1 atm pressure, f_{O_2} 's of QFM-1 to QFM-3 and temperatures between 1267 and 1468 °C. The $\ln K_D^{\text{Ni-Mg}}$ values obtained from these experiments are positively correlated with MgO content and increase

from 0.82 to 1. These values are more than double those obtained from the MORB samples at equivalent MgO contents, suggesting that S has an important influence on $\ln K_D^{\text{Ni-Mg}}$.

5.2. Comparison with S-bearing experiments

The only experiments on S-bearing systems to date are those of Gaetani and Grove (1997). These experiments were sulfide-saturated and performed at 1350 °C, 1 atm pressure on a synthetic Munro Township komatiite composition (KOM) and on a CaO–MgO– Al_2O_3 – SiO_2 –FeO– Na_2O barred olivine chondrule analog composition (Fo86). The starting compositions for each series of the experiments (KOM or Fo86) were the same, but the final silicate melt compositions varied significantly due to the formation of variable amounts of olivine and Fe sulfide liquids in response to changing f_{O_2} and f_{S_2} . In addition to the 2 wt.% Ni in the starting compositions, the KOM experiments were also doped with 2 wt.% each of other chalcophile or weakly chalcophile elements. The large range in chalcophile element concentrations does not permit a straightforward evaluation of the effect of S on Ni partitioning in the KOM experiments. S-free experiments with melt composition, temperature and f_{O_2} that are similar to

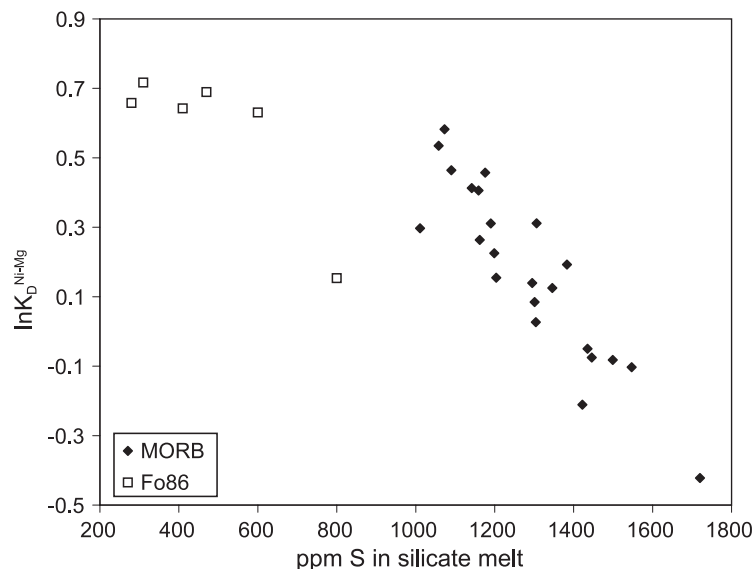


Fig. 5. Correlation between the $\ln K_D^{\text{Ni-Mg}}$ and melt S content for the MORBs and the Fo86 experiments of Gaetani and Grove (1997).

those of the sulfide-saturated KOM experiments are also not available. The Fo86 experiments allow the partitioning behavior of Ni in a sulfide-saturated system to be directly compared with the results of Ehlers et al. (1992), who performed Ni-partitioning experiments in a S-free system using the Fo86 composition at the same temperature. The $\ln K_D^{\text{Ni-Mg}}$ values of the two alloy-free experiments (Fo86-37k and Fo86-48k) of Ehlers et al. (1992) that are most comparable to the sulfide-saturated Fo86 experiments of Gaetani and Grove (1997) in terms of melt composition and f_{O_2} are 0.82 and 0.92. The $\ln K_D^{\text{Ni-Mg}}$ values of the sulfide-saturated Fo86 experiments of Gaetani and Grove (1997) are notably lower, varying between 0.15 and 0.72, with a dramatic decrease at the highest melt S content in the experiments (Fig. 5). Again, this suggests that S exerts a significant effect on $\ln K_D^{\text{Ni-Mg}}$.

6. Conclusions

The MORB data illustrate that olivine-melt D^{Ni} values of 4.4–9.3 characterize these S-bearing basaltic systems. These D^{Ni} values are up to 50% lower than those of the S-free experimental systems of similar compositions. The lower D^{Ni} values of the MORBs are consistent with the hypothesis that in S-bearing systems a portion of Ni dissolved in the melt is present as a Ni–S complex. Ni dissolved in this manner does not enter equilibria involving olivine. This overall effect is a reduction in the D^{Ni} value calculated from the total concentration of Ni in the silicate melt. This hypothesis is supported by the negative correlation between the $\ln K_D^{\text{Ni-Mg}}$ values and melt S contents displayed by the MORB samples. The discrepancy between the MORB data and the results of experiments performed on S-free basaltic compositions illustrates the need for caution in directly using the experimental D^{Ni} to model natural systems that contain S.

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