

Nickel partitioning between olivine and silicate melt: Henry's law revisited

BJØRN O. MYSEN

*Geophysical Laboratory, Carnegie Institution of Washington
Washington, D. C. 20008*

Abstract

Partition coefficients for nickel between olivine and an aluminous anhydrous silicate melt have been determined as a function of nickel content under isothermal conditions (1300°C) at pressures between 1 atm and 20 kbar. The partition coefficients are independent of nickel content until 1000 ppm Ni is dissolved in the forsterite. No pressure-dependence of this concentration limit was observed. It is concluded that a maximum of about 1000 ppm Ni can dissolve in forsterite according to Henry's law. The partition coefficients are pressure-dependent at both higher and lower nickel concentration. The pressure-dependence is less pronounced in the olivine with nickel content above 1000 ppm because the activity coefficient of nickel in the coexisting liquid varies with pressure, presumably as a consequence of pressure-induced structural changes of the silicate melt.

Fractional crystallization of olivine results in a lowering of the nickel content of the magma, but the extent to which such fractionation results in a lowered nickel content depends on both the nickel content of the silicate magma and the confining pressure. It is concluded that the nickel content of natural magma derived from the upper mantle is commonly controlled by fractional crystallization that involves minerals other than the major rock-forming minerals.

Introduction

The nickel content of olivine-bearing natural magmas is considered a sensitive petrogenetic indicator (e.g. Häkli and Wright, 1967; Leeman, 1974; Hart and Davis, 1978; O'Hara *et al.*, 1975) because of the importance of olivine in igneous processes and because of the large values of olivine-liquid partition coefficients for nickel ($D_{\text{Ni}}^{\text{ol-liq}}$). Recently, the interpretation of nickel partitioning data when applied to such problems has been questioned (Mysen, 1978a) because of the apparent dependence of $D_{\text{Ni}}^{\text{ol-liq}}$ on temperature (Häkli and Wright, 1967; Leeman, 1974), bulk composition (Hart and Davis, 1978; Arndt, 1977), and pressure (Mysen and Kushiro, 1979), and because of the possibility that $D_{\text{Ni}}^{\text{ol-liq}}$ is a function of the nickel content of olivine in the natural abundance range of nickel in magmatic olivine (Mysen, 1976a, 1978a). There is little agreement about the quantitative values of any of these functional relationships.

One of the least well defined variables is the dependence of $D_{\text{Ni}}^{\text{ol-liq}}$ on the nickel content of olivine. It has been suggested that nickel dissolves according to

Henry's law only at or below about 1000 ppm Ni in olivine (Mysen, 1976a, 1978a). Hart and Davis (1978) worked at 1 atm in the nickel concentration range measurable with the electron microprobe and reported no dependence of $D_{\text{Ni}}^{\text{ol-liq}}$ on nickel concentration. On the basis of their results, they suggested that previous data (Mysen, 1976a, 1978a) obtained at lower nickel concentration and at higher pressure might need reinterpretation. Lindstrom and Weill (1978), using a technique similar to that of Hart and Davis (1978), also argued that the data of Mysen (1976a, 1978a) might need reevaluation. Finally, Shaw (1977), summarizing some pertinent experimental data on element partitioning, concluded that the data of Mysen (1978a) were open to question but did not attempt to explain how he reached this conclusion.

Experiments involving nickel partitioning are complicated because of the extensive solubility of nickel in most of the sample containers used. This problem existed in all the published work on nickel partitioning summarized above, although the extent of the problem depended on the experimental conditions.

In view of the above arguments, it was decided to conduct experiments where at least some of the experimental problems could be avoided. Experiments were conducted at pressures ranging from 1 atm to 20 kbar, because all previous data reporting concentration dependence of $D_{\text{Ni}}^{\text{ol-liq}}$ were at high pressure, whereas all those claiming no dependence of the nickel partition coefficients on the nickel concentration were at 1 atm. The present data would therefore help rectify the lack of overlap between the published data sets.

Experimental technique

The starting composition ($\text{Fo}_{20}\text{Jd}_{80}$, by weight) was chosen because at 1300°C (the experimental temperature) the liquidus of this composition does not change within experimental uncertainty with pressure up to 20 kbar (Schairer and Yoder, 1961; Mysen and Kushiro, 1979). The uncertainty of the melt composition with this technique corresponds to ± 1.5 percent forsterite component. Electron microprobe analysis of the melt was not employed because of problems with loss of Na by volatilization even with 0.01 μA beam current at 15 kV acceleration potential. Significant broadening of the electron beam to lower the temperature on the surface during analysis could not be done with confidence because of interference from neighboring forsterite crystals. Only a small percentage (10 percent) of pure, quite small ($\sim 10 \mu\text{m}$) forsterite crystals is formed, thus making attainment of equilibrium less cumbersome than in previous experiments (e.g. Mysen, 1978a). The experimental conditions were the same as those of Mysen and Kushiro (1979), with the exception that 1-atm experiments were added to the program and a range of nickel concentrations was employed (2–3200 ppm Ni).

Two sets of starting materials were used. For forward experiments, the starting material was a glass of $\text{Fo}_{20}\text{Jd}_{80}$ composition with 10 ppm ^{63}Ni and various amounts of nonradioactive nickel. This glass was made by fusing oxide mixtures, thoroughly ground, for 2 hr at 1450°C in air. The material was checked for homogeneity of all elements prior to the experiments. For the reversal experiments, 20 weight percent crystalline forsterite with 10–16,000 ppm Ni in solution was mixed with 80 weight percent nickel-free glass of $\text{NaAlSi}_2\text{O}_6$ composition (10–16,000 ppm Ni in forsterite corresponds to 2–3200 ppm in forsterite glass mixture). The forsterite was synthesized from an oxide mixture at 20 kbar and 1650°C for 1 hr and checked for homogeneity. In all experiments,

the forsterite contained 10 ppm ^{63}Ni and different amounts of nonradioactive nickel to make up the total nickel concentration.

The experiments at 10 and 20 kbar were conducted in the solid-media, high-pressure apparatus (Boyd and England, 1960), whereas the 1-kbar experiments were carried out in the gas-media, high-pressure apparatus (Yoder, 1950). The sample containers were BN capsules sealed inside Pt capsules. The BN capsules had been fired at 1000°C and stored at 110°C before use to decompose the reducing ammonia-based binder of the BN and to avoid adsorption of H_2O from the moisture of the air before the experiments. With this sample-container configuration, the experimental charges were never in physical contact with the outside platinum capsule; thus the problem of Ni loss from the experimental charge to the container was eliminated. At the same time, no reducing agent was present that could cause reduction of Ni^{2+} to metallic Ni. Mass-balance calculations were conducted on a routine basis to assess the extent to which this experimental design was successful. The results of these calculations are shown in the run tables. The uncertainty ($\pm 1\sigma$) of the mass-balanced nickel values includes all analytical uncertainties (about 3 percent of the individual analyses), weighing errors (negligible), and other experimental errors (± 1 kbar and $\pm 10^\circ\text{C}$ at $P \geq 10$ kbar, negligible pressure uncertainty and $\pm 5^\circ\text{C}$ at $P = 1$ kbar).

The 1-atm experiments were conducted in a vertical quench furnace in air with a temperature uncertainty of $\pm 2^\circ\text{C}$ using 0.1 mm Pt loops as sample holders. The high air pressure inside the BN–Pt capsules at 1300°C and 1 atm resulted in rupture of the capsule during the experiment. With open capsules, the sample migrated out of the capsule during the experiment. The technique was therefore not used in 1-atm experiments.

About 20 mg of sample was used in these experiments. Larger samples tended to fall off the loop because of the low viscosity of the melt. Theoretically, there is a small nickel loss to the Pt loop during the 1-atm experiments. The absolute amount of Ni thus lost appears to have been so small, however, that it did not appear in the mass-balance calculations within the quoted uncertainty. It should also be noted that because there may have been some Na loss by volatilization, the proportions of phases may be slightly different from the theoretical value. At the same time the liquid composition may have been slightly off the join. This problem is not considered

serious, however, in the light of experimental data relevant to the problem by Seifert *et al.* (1979).

The nickel analyses were carried out with the beta-track mapping technique (Mysen and Seitz, 1975), using ^{63}Ni as the source of beta particles and Ilford K-5 nuclear emulsions as detectors. The applicability and accuracy of this technique for nickel analysis of experimental run products have previously been demonstrated (Mysen and Seitz, 1975; Mysen, 1978a).

Reversal experiments were conducted at all pressures and with three different nickel concentrations in olivine to ensure that $D_{\text{Ni}}^{\text{ol-liq}}$ at low, intermediate, and high nickel concentration represented equilibrium values. The low nickel concentration chosen was well within the range where results of forward experiments had indicated that $D_{\text{Ni}}^{\text{ol-liq}}$ was independent of nickel content. An intermediate concentration (1000–3000 ppm Ni in olivine) was chosen because this was the range where forward experiments had indicated the most rapid change of $D_{\text{Ni}}^{\text{ol-liq}}$ with nickel concentration. The third reversal experiment at each pressure was carried out in the high nickel concentration range ($\geq 10,000$ ppm Ni in olivine), where the value of $D_{\text{Ni}}^{\text{ol-liq}}$ reached a minimum level and was relatively insensitive to changing nickel concentration.

The agreement between forward and reversal experiments within experimental and analytical uncertainty is taken to indicate that equilibrium was closely approximated in all the experiments. According to Clark and Long (1971), the nickel diffusion coefficient in olivine at 1300°C is about 6×10^{-11} cm^2/sec . Using the simple relationship (Hofmann and Magaritz, 1977)

$$\chi = \sqrt{Dt} \quad (1)$$

where χ is the distance, D is the diffusion coefficient, and t is the time, χ equals about $10 \mu\text{m}$ in 4 hr. With crystals of about $5 \mu\text{m}$ radius, the transport distance is about $5 \mu\text{m}$, indicating that a run duration of 4 hr is more than sufficient to attain equilibrium. This conclusion is also substantiated by the homogeneity of the phases and the small analytical uncertainty of the partition coefficients (near the theoretical uncertainty, Mysen and Seitz, 1975).

Results

All experimental data are shown in Table 1, and the results are plotted as partition coefficients against the nickel content of forsterite ($C_{\text{Ni}}^{\text{ol}}$) in Figure 1, in which reversal experiments are shown with open

symbols. The size of the symbols reflects the uncertainty of the data ($\pm 1\sigma$).

Two features of these data warrant comment. First, there is a limited nickel concentration range where the value of $D_{\text{Ni}}^{\text{ol-liq}}$ is independent of nickel concentration (≤ 1000 ppm Ni in forsterite). Second, the value of the partition coefficient in the concentration range used by Mysen and Kushiro (1979) (≤ 100 ppm Ni) shows the same dependence on pressure observed by them. The limited concentration range of constant $D_{\text{Ni}}^{\text{ol-liq}}$ occurs at all pressures studied (including 1 atm). There is no pressure-dependence of the width of this concentration range. This conclusion contrasts with that of Mysen (1978a), who suggested that the nickel concentration range of constant partition coefficient may expand with decreasing pressure in the system plagioclase ($\text{An}_{50}\text{Ab}_{50}$)–forsterite–silica–water in the range 10–20 kbar at $1025^\circ\text{--}1075^\circ\text{C}$. It should be remembered, however, that Mysen (1978a) did not have a close bracket on the absolute extent of this concentration range. Furthermore, those data (Mysen, 1978a) were acquired in a hydrous system, whereas the results reported here are in the absence of H_2O .

There is only a limited concentration range of constant $D_{\text{Ni}}^{\text{ol-liq}}$ even at 1 atm pressure. At this pressure, previous results (Leeman, 1974; Hart and Davis, 1978; Lindstrom and Weill, 1978) in the concentration range attainable with the electron microprobe indicated that the olivine–liquid partition coefficient remained constant until several weight percent Ni had dissolved in the olivine. None of those data was extended significantly below a concentration of 1000 ppm. As can be seen from the data in Figure 1, approximately 1000 ppm Ni can dissolve in forsterite before the partition coefficients become dependent on the nickel content even at 1 atm pressure.

The extent of the change of $D_{\text{Ni}}^{\text{ol-liq}}$ with nickel content varies with pressure (Table 2). This change is likely to reflect the structural change of the liquid coexisting with forsterite, resulting in varying activity coefficients of nickel in the melt (Mysen and Kushiro, 1979). From Nernst's distribution law, it can be shown that

$$D_{\text{Ni}}^{\text{ol-liq}} = (a_{\text{Ni}}^{\text{ol}}/a_{\text{Ni}}^{\text{liq}})/(\gamma_{\text{Ni}}^{\text{ol}}/\gamma_{\text{Ni}}^{\text{liq}}) \quad (2)$$

where $a_{\text{Ni}}^{\text{ol}}$ and $a_{\text{Ni}}^{\text{liq}}$ are activities of nickel in olivine and liquid, and $\gamma_{\text{Ni}}^{\text{ol}}$ and $\gamma_{\text{Ni}}^{\text{liq}}$, respectively, are the activity coefficients of nickel in olivine and liquid. According to the data of Mysen and Kushiro (1979), the activity coefficient of nickel in silicate melt such as

Table 1. Experimental results*

Run No.	<i>P</i> (kbar)	Ni added (ppm)	Ni in olivine (ppm)	Ni in liquid (ppm)	D_{Ni}^{ol-liq}	Ni by mass balance (ppm)
950**	0.001	2.7	17.4 ± 0.08	0.96 ± 0.05	18.1 ± 1.3	3.1 ± 0.3
926	0.001	10	55 ± 2	3.19 ± 0.17	17.2 ± 1.0	9.9 ± 0.9
925	0.001	50	276 ± 10	15.9 ± 0.9	17.4 ± 1.1	50 ± 4
943**	0.001	200	1370 ± 40	79 ± 4	17.3 ± 1.0	247 ± 25
934	0.001	300	1710 ± 39	111 ± 4	15.4 ± 0.7	319 ± 22
952	0.001	500	2092 ± 101	144 ± 4	14.5 ± 0.8	400 ± 35
935	0.001	1000	5050 ± 300	427 ± 21	11.8 ± 0.9	1028 ± 103
933	0.001	3000	13980 ± 500	1232 ± 44	11.3 ± 0.6	2890 ± 2890
954**	0.001	3200	17853 ± 706	1497 ± 85	11.9 ± 0.8	3600 ± 400
915**	1	2	11.7 ± 0.4	0.53 ± 0.02	22.1 ± 1.1	2.0 ± 0.2
859	1	10	57.6 ± 1.8	2.63 ± 0.08	21.9 ± 1.0	9.5 ± 0.9
858	1	50	290 ± 10	11.7 ± 0.4	24.8 ± 1.2	46 ± 5
857	1	100	607 ± 22	25.5 ± 1.0	23.8 ± 1.3	98 ± 9
916**	1	200	1127 ± 36	59 ± 1	19.1 ± 0.7	198 ± 16
927	1	300	1815 ± 31	100.1 ± 1.8	18.2 ± 0.4	323 ± 27
856	1	500	2727 ± 101	148 ± 6	18.4 ± 1.0	470 ± 42
855	1	1000	5913 ± 257	429 ± 14	13.8 ± 0.8	1115 ± 110
928	1	3000	16210 ± 550	1480 ± 71	11.0 ± 0.7	3400 ± 300
907**	10	2	10.5 ± 3	0.50 ± 0.02	21.0 ± 1.0	1.8 ± 0.2
854	10	10	47.6 ± 1.3	2.34 ± 0.06	20.3 ± 0.8	8.2 ± 0.8
852	10	50	242 ± 8	12.0 ± 0.3	20.2 ± 0.8	42 ± 4
917	10	100	576 ± 15	28.2 ± 1.9	20.4 ± 1.5	99 ± 8
880**	10	200	1127 ± 36	59 ± 1	19.1 ± 0.7	198 ± 16
929	10	300	1529 ± 67	85 ± 2	18.0 ± 0.9	273 ± 22
848	10	500	2496 ± 81	145 ± 5	17.2 ± 0.8	2451 ± 40
931	10	3000	11011 ± 511	1187 ± 36	9.3 ± 0.5	2464 ± 222
949**	10	3200	12400 ± 419	1578 ± 51	7.9 ± 0.4	2985 ± 269
875**	20	2	8.9 ± 0.3	0.88 ± 0.03	10.1 ± 0.5	1.9 ± 0.2
853	20	10	55.1 ± 1.6	5.21 ± 0.14	10.6 ± 0.4	11 ± 1
851	20	50	273 ± 10	27.2 ± 0.7	10.0 ± 0.4	57 ± 5
849	20	100	536 ± 20	51.1 ± 1.8	10.5 ± 0.5	111 ± 10
879	20	200	854 ± 32	101 ± 3	8.5 ± 0.4	199 ± 20
930	20	300	1141 ± 36	137 ± 6	8.3 ± 0.6	268 ± 24
847	20	500	1791 ± 53	246 ± 7	7.3 ± 0.3	440 ± 40
845	20	1000	2595 ± 130	519 ± 16	6.9 ± 0.4	904 ± 90
932	20	3000	9800 ± 400	1397 ± 36	7.0 ± 0.4	2489 ± 200
948**	20	3200	10800 ± 316	1769 ± 81	6.1 ± 0.3	2940 ± 260

* $T = 1300^{\circ}\text{C}$ and time = 4 hr in all experiments.

**Reversal run.

that used here increases with pressure up to about 5–10 kbar before it decreases with further pressure increase. If it is assumed that γ_{liq}^{ol} shows the same dependence on nickel composition at all pressures, equation 2 shows that the degree of alteration of D_{Ni}^{ol-liq} with changing nickel concentration would increase with increasing pressure until about 10 kbar and then begin to decrease as the pressure is increased further. This prediction is in accordance with observation (Table 2). If it is assumed that the expression of Hart and Davis (1978) relating MgO contents of melts to D_{Ni}^{ol-liq} ,

$$D_{Ni}^{ol-liq} = \frac{124}{MgO} - 0.9 \quad (3)$$

is valid for the present compositions, the uncertainty in MgO content (± 0.9 weight percent, derived from ± 1.5 weight percent uncertainty of Fo content of the melt) over this pressure interval results in about a 20 percent uncertainty of the pressure-dependence of D_{Ni}^{ol-liq} . The data in Figure 1 show that the pressure effects discussed here are greater than 20 percent. Consequently, the variations cannot be explained in terms of analytical uncertainty.

Because the rate of change of D_{Ni}^{ol-liq} as a function of nickel concentration is also a function of pressure at constant temperature (1300°C) and liquid bulk composition, the pressure-dependence of D_{Ni}^{ol-liq} depends on the nickel content of the system (Fig. 2). Note that the maximum D values occur at lower

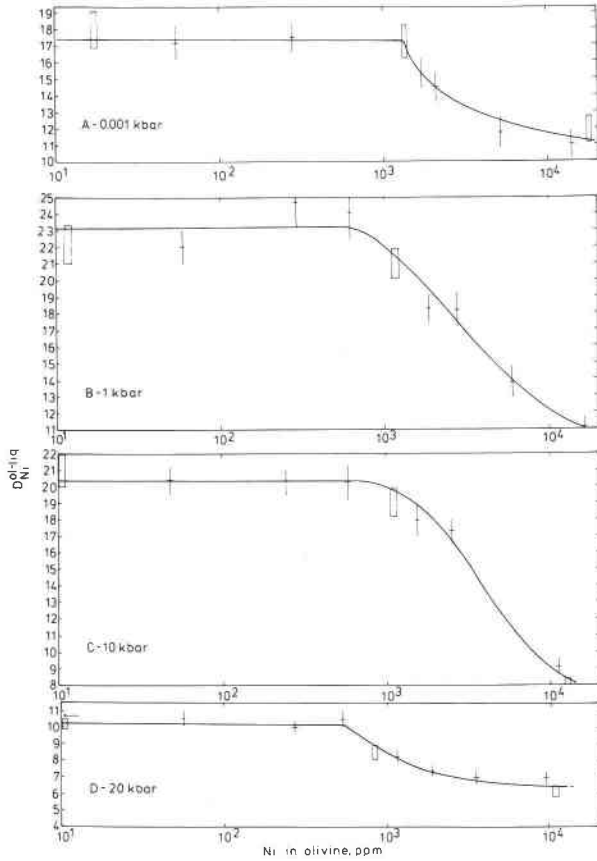


Fig. 1. Partition coefficient D_{Ni}^{ol-liq} as a function of nickel content in olivine at pressures from 1 atm to 20 kbar and a temperature of 1300°C.

pressure the higher the nickel content. This shift may relate to the structural role of Ni in the melt. No data are available, however, for further discussion of this point. The data points in Figure 2 have been connected with smooth, dashed lines. Mysen and Kushiro (1979) showed a discontinuous curve with increasing pressure at $C_{Ni}^{ol} \leq 100$ ppm based on more closely bracketed data. The main discontinuity was between 15 and 20 kbar. Such a discontinuity is in accord with other data involving pressure-induced structural changes in $NaAlSi_2O_6$ -rich liquids (Mysen,

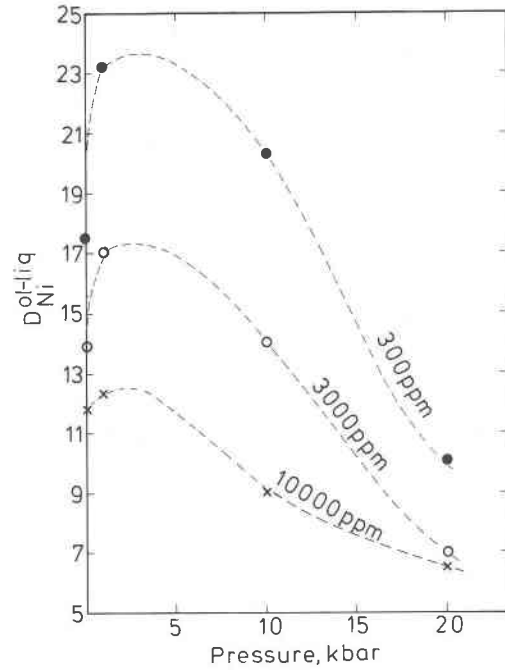


Fig. 2. Partition coefficient D_{Ni}^{ol-liq} as a function of pressure at 300, 3000, and 10,000 ppm Ni in olivine.

1976b; Kushiro, 1976; Mysen and Virgo, 1978; Sharma *et al.*, 1978). The present data can also be fitted to such a curve, but in the absence of a closer bracket such a fit was not attempted.

Discussion

In view of the somewhat surprising observation that D_{Ni}^{ol-liq} appears to depend on nickel concentration at much lower levels than previously expected, it is useful first to discuss the present data in the light of previous considerations of experimental problems that could have affected the results.

Lindstrom and Weill (1978) argued that nickel loss to the container could be a problem in experiments such as these, as also discussed by Mysen (1978a). Mysen (1978a) suggested that nickel loss would most likely cause the partition coefficients to increase with increasing nickel content, whereas D_{Ni}^{ol-liq} , in fact, showed a decrease. Hart and Davis (1978) commented, however, that Pt containers effectively become Ni-saturated at relatively low nickel concentration. They suggested that this apparent nickel saturation resulted from the formation of a surface layer of nickel-saturated platinum, making the remaining platinum unavailable as a Ni sink. According to the hypothesis of Hart and Davis (1978), the effective nickel loss to the container from the experi-

Table 2. Percentage of change of D_{Ni}^{ol-liq} between 1000 and 10,000 ppm Ni in forsterite as a function of pressure

P (kbar)	Percentage of change relative to value at 1000 ppm Ni
0.001	-33
1	-47
10	-55
20	-36

mental charges would decrease with increasing nickel content of the system. In view of the more rapid diffusion of nickel in liquid than in crystals (Clark and Long, 1971; Hofmann and Magaritz, 1977), Hart and Davis plausibly argued that the relative nickel loss is reduced as total nickel content of the system is increased. As a result, the apparent $D_{\text{Ni}}^{\text{ol-liq}}$ would be lowered with increasing nickel content. However plausible the arguments may sound, they are moot points in view of the present experiments, because these results were obtained without the complication of nickel loss to the container (Table 1), and the dependence of $D_{\text{Ni}}^{\text{ol-liq}}$ on nickel content of the system remained (Fig. 1). On the basis of these new data, the suggestion that nickel loss to the sample container is the cause of the apparent variations of the partition coefficient (Hart and Davis, 1978; Lindstrom and Weill, 1978) must be ruled out.

Lindstrom and Weill (1978) also suggested that the effects seen by Mysen (1976a, 1978a) could reflect the lack of isotopic equilibrium, because in those experiments stable nickel was added mostly as NiO whereas ^{63}Ni was added as a dilute chloride solution. Mysen (1978a) conducted two experiments with all nickel in dilute chloride solution to attain a total nickel content similar to that of some of the experiments with NiO and chloride where dependence of $D_{\text{Ni}}^{\text{ol-liq}}$ on nickel concentration was observed. The two new experiments gave the same results as those with NiO and Ni^{2+} in chloride solution. In the present experiments the starting materials were homogenized either in the glass or in the synthetic forsterite prior to the experiment itself. Consequently, the potential problem of equilibrating ^{63}Ni in solution with stable NiO during the experiment is eliminated. The effect of nickel concentration on $D_{\text{Ni}}^{\text{ol-liq}}$ remained, however. Consequently, the suggestion by Lindstrom and Weill (1978) must be ruled out.

Navrotsky (1978) suggested that the use of radioactive ^{63}Ni or the growth conditions of forsterite in the experiments by Mysen (1976a, 1978a) may result in formation of metastable defects in the olivine structure. She argued that the distribution curves of Mysen resembled those observed for solution of gaseous N_2 in cold-pressed steel, where the presence of metastable defects had been demonstrated (Wriedt and Darken, 1965). Mysen (1978b) commented that the $\gamma_{\text{N}_2}^{\text{steel}}$ in the experiments by Wriedt and Darken changed continuously with nitrogen pressure (concentration), whereas in the results of Mysen (1976a, 1978a) the activity coefficient of nickel in olivine and

liquid remained constant over extensive concentration intervals. Furthermore, Mysen (1978b) pointed out that growth-induced metastable defects would anneal with time. The results of time studies by Mysen (1978a) indicated that the sites on which nickel substituted remained during the time studies. There were no signs of metastable defects. Mysen (1978b) concluded that such structural features could not explain the variation of $D_{\text{Ni}}^{\text{ol-liq}}$ with nickel concentration. The present experimental results lend further credence to this conclusion. First, the effects were observed whether forsterite was grown in the solid-media, high-pressure apparatus, in the gas-media, high-pressure apparatus, or in the 1-atm vertical quench furnace (Fig. 1). Second, in the reversal experiments the forsterite was first grown in the solid-media, high-pressure apparatus from an oxide mixture. These forsterite crystals were then equilibrated with the rest of the system in all the different experimental equipment. Growth rates and growth mechanisms are likely to be different in these apparatus; however, the variable $D_{\text{Ni}}^{\text{ol-liq}}$ remained.

Mysen (1978b) concluded that if transmutation of ^{63}Ni was the cause of the variation of $D_{\text{Ni}}^{\text{ol-liq}}$ (Navrotsky, 1978), different specific activities of ^{63}Ni in the crystals should result in a systematic change of $D_{\text{Ni}}^{\text{ol-liq}}$. Mysen (1978b), in summarizing the available data, showed that no such effects were observed when the specific activity of ^{63}Ni was varied by a factor of 6. In the present experiments the specific activity of ^{63}Ni in the reversal experiments was only 20 percent of that in the forward experiments. The specific activity of the present experiments was as much as 20 times greater than that of some of the experiments by Mysen and Kushiro (1979). No relation between the specific activity of ^{63}Ni and the value of $D_{\text{Ni}}^{\text{ol-liq}}$ has been discerned. I conclude, therefore, that defects in forsterite crystals induced by the radioactivity of ^{63}Ni are not the cause of the variable $D_{\text{Ni}}^{\text{ol-liq}}$.

Hart and Davis (1978) suggested that the presence of H_2O in the experiments by Mysen (1976a, 1978a) could be the cause of the variable $D_{\text{Ni}}^{\text{ol-liq}}$. The present experiments were conducted under anhydrous conditions, and the effect remained.

It is appreciated that the similar ionic radius and electrical charge of Ni^{2+} and Mg^{2+} could indicate that (Ni,Mg) solid solutions behave as Raoult's or at least Henry's law type solutions. Such similarity is no proof that the activity coefficients are constant, however. Despite the similarity of Mg^{2+} and Fe^{2+} , for example, thermodynamic data on (Fe,Mg)

solid solutions in olivine (Nafziger, 1973; Olsen and Bunch, 1970) indicated deviations from ideality.

Observations that olivine-liquid partition coefficients for nickel appear relatively constant at high nickel concentration (within the range attainable with the electron microprobe), such as reported by Leeman (1974), Hart and Davis (1978), and Lindstrom and Weill (1978), does not rule out different behavior at lower nickel concentration. Furthermore, observations that a partition coefficient is nearly constant at high nickel concentration do not constitute proof of behavior according to Henry's law at lower Ni concentration (see Iiyama, 1974, for a discussion of the behavior of elements in mineral solutions according to Henry's law).

In summary, the results reported here (Table 1, Fig. 1) and elsewhere (Mysen, 1976a, 1978a) are not artifacts of experimental problems. They represent equilibrium partition coefficients for nickel between olivine and liquid.

Mysen (1976a, 1978a) presented arguments in favor of the variations of $D_{\text{Ni}}^{\text{ol-liq}}$ resulting from the solubility behavior of nickel in forsterite. Paul (1975) has shown that $\gamma_{\text{Ni}}^{\text{liq}}$ may depend on nickel concentration at low Ni content of borate melts. The observations and discussion of Mysen (1978a) indicate that the activity coefficient of nickel becomes a function of nickel concentration at lower Ni content of olivine than coexisting liquid. The present data cannot be used to rule out an effect of the liquid structure.

Variations of $D_{\text{Ni}}^{\text{ol-liq}}$ with Ni content may be expected from the phase equilibria in the system Mg-olivine-Ni-olivine (Ringwood, 1956). In the concentration region close to pure forsterite, the solidus and liquidus curves approach linear asymptotes, in which case $D_{\text{Ni}}^{\text{ol-liq}}$ approaches a constant value. This is the concentration region where Henry's law is approximately obeyed. A similar reasoning may explain the present data.

Petrological implications

The role of nickel in igneous processes is governed by a complex function of intensive and extensive variables, as discussed above. The present data were obtained in a simplified system, and quantitative application of the data to rock-forming processes should be exercised with care. Some principles can be derived.

Mysen (1977) and Mysen and Popp (1978) commented that primary partial melts from a peridotite source containing 1500–2000 ppm Ni (Fisher *et al.*,

1969) would contain 500–700 ppm Ni, depending on the modal composition of the source, the mechanisms of melting, and the bulk composition of the partial melt. This primary melt is unlikely to be more basic than that of an olivine tholeiite (Yoder, 1976, p. 128–131). Tholeiites containing more than 350–400 ppm Ni are not common. Andesitic melts contain even less nickel than olivine tholeiite. Hart and Davis (1978) suggested that nickel partition coefficients between olivine and andesitic melts were so great that their nickel content is that of primary partial melts from peridotite. Mysen and Kushiro (1979) observed, however, that the partition coefficients at pressures corresponding to the depth of partial melting in the upper mantle are much lower than indicated by 1-atm experiments. This reduction of $D_{\text{Ni}}^{\text{ol-liq}}$ is due to structural changes of the silicate melt as a result of the increased pressure (Mysen and Kushiro, 1979). Consequently, the primary melts are likely to have precipitated minerals that also act as sinks for nickel before the magma reaches the earth's surface.

Acknowledgments

Critical reviews by W. Harrison, S. R. Hart, and H. S. Yoder, Jr. are appreciated.

References

- Arndt, N. T. (1977) The partitioning of nickel between olivine and ultrabasic and basic komatiite liquids. *Carnegie Inst. Wash. Year Book*, 76, 553–557.
- Boyd, F. R. and J. L. England (1960) Apparatus for phase equilibrium measurements at pressures up to 50 kilobars and temperatures up to 1750°C. *J. Geophys. Res.*, 65, 741–748.
- Clark, A. M. and J. V. P. Long (1971) The anisotropic diffusion of nickel in olivine. In *Thomas Graham Memorial Symposium on Diffusion Processes*, p. 511–521. Gordon and Breach, London.
- Fisher, D. E., O. Joensuu and K. Bostrom (1969) Elemental abundances in ultramafic rocks and their relation to the upper mantle. *J. Geophys. Res.*, 74, 3865–3873.
- Häkli, T. A. and T. L. Wright (1967) The fractionation of nickel between olivine and augite as geothermometer. *Geochim. Cosmochim. Acta*, 31, 877–884.
- Hart, S. R. and K. E. Davis (1978) Nickel partitioning between olivine and silicate melt. *Earth Planet. Sci. Lett.*, 40, 203–219.
- Hofmann, A. W. and M. Magaritz (1977) Diffusion of Ca, Sr, Ba and Co in a basalt melt: implications for the geochemistry of the mantle. *J. Geophys. Res.*, 38, 5432–5441.
- Iiyama, J. T. (1974) Behavior of trace elements in feldspars under hydrothermal conditions. In W. S. MacKenzie and J. Zussman, Eds., *The Feldspars*, p. 552–573. Manchester University Press, Manchester, England.
- Kushiro, I. (1976) Changes in viscosity and structure of melt of NaAlSi₃O₈ composition at high pressure. *J. Geophys. Res.*, 81, 6347–6350.
- Leeman, W. P. (1974) *Experimental Determination of Partitioning*

- of Divalent Cations between Olivine and Basaltic Liquid. Part II of Ph.D. Thesis, University of Oregon.
- Lindstrom, D. J. and D. F. Weill (1978) Partitioning of transition metals between diopside and coexisting silicate liquids. I. Nickel, cobalt, and manganese. *Geochim. Cosmochim. Acta*, 42, 817-833.
- Mysen, B. O. (1976a) Partitioning of samarium and nickel between olivine, orthopyroxene and liquid: preliminary data at 20 kbar and 1025°C. *Earth Planet. Sci. Lett.*, 31, 1-7.
- (1976b) The role of volatiles in silicate melts: solubility of carbon dioxide and water in feldspar, pyroxene and feldspathoid melts to 30 kb and 1625°C. *Am. J. Sci.*, 276, 969-996.
- (1977) Magma genesis in peridotite upper mantle in the light of experimental data on partitioning of trace elements between garnet peridotite minerals and partial melts. *Carnegie Inst. Wash. Year Book*, 76, 545-550.
- (1978a) Experimental determination of nickel partition coefficients between liquid, pargasite and garnet peridotite minerals and concentration limits of behavior according to Henry's law at high temperature and pressure. *Am. J. Sci.*, 278, 217-243.
- (1978b) Limits of solution of trace elements in minerals according to Henry's law: review of experimental data. *Geochim. Cosmochim. Acta*, 42, 871-885.
- and I. Kushiro (1979) The effect of pressure on the partitioning of nickel between olivine and aluminous silicate melt. *Earth Planet. Sci. Lett.*, 42, 383-389.
- and R. K. Popp (1978) Solubility of sulfur in silicate melts as a function of f_{S_2} and silicate melt composition at high pressures. *Carnegie Inst. Wash. Year Book*, 77, 709-713.
- and M. G. Seitz (1975) Trace element partitioning determined with beta-track mapping—an experimental study using carbon and samarium as examples. *J. Geophys. Res.*, 80, 2627-2635.
- and D. Virgo (1978) Influence of pressure, temperature and bulk composition on melt structures in the system $NaAlSi_2O_6-NaFe^{3+}Si_2O_6$. *Am. J. Sci.*, 278, 1307-1322.
- Nafziger, R. H. (1973) High-temperature activity-composition relations of equilibrium spinels, olivines and pyroxenes in the system Mg-Fe-O-SiO₂. *Am. Mineral.*, 58, 457-465.
- Navrotsky, A. (1978) Thermodynamics of element partitioning: (1) systematics of transition metals in crystalline and molten silicates and (2) defect chemistry and "the Henry's law problem." *Geochim. Cosmochim. Acta*, 42, 887-903.
- O'Hara, M. J., M. J. Saunders and E. L. P. Mercy (1975) Garnet peridotite, primary ultrabasic magma and eclogite: interpretation of upper mantle processes in kimberlite. *Phys. Chem. Earth*, 9, 571-604.
- Olsen, E. and T. E. Bunch (1970) Empirical derivation of activity coefficients for the magnesium-rich portion of the olivine solid solution. *Am. Mineral.*, 55, 1829-1842.
- Paul, A. (1975) Activity of nickel in alkali borate melts. *J. Mater. Sci.*, 10, 422-426.
- Ringwood, A. E. (1956) Melting relationships in Ni-Mg olivines and some geochemical implications. *Geochim. Cosmochim. Acta*, 10, 297-303.
- Schairer, J. F. and H. S. Yoder, Jr. (1961) Crystallization in the system nepheline-forsterite-silica at one atmosphere pressure. *Carnegie Inst. Wash. Year Book*, 60, 141-144.
- Seifert, F., D. Virgo and B. O. Mysen (1979) Sodium metasilicate melts in CO₂ and CO atmospheres. *Carnegie Inst. Wash. Year Book*, 78, in press.
- Sharma, S. K., D. Virgo and B. O. Mysen (1978) Raman study of structure and coordination of Al in $NaAlSi_2O_6$ glasses synthesized at high pressures. *Carnegie Inst. Wash. Year Book*, 77, 655-662.
- Shaw, D. M. (1977) Trace element behavior during anatexis. In H. F. B. Dick, Ed., *Proceedings of the Chapman Conference on Partial Melting in the Earth's Upper Mantle*, p. 189-215. American Geophysical Union, Washington, D. C.
- Wriedt, H. A. and L. S. Darken (1965) Lattice defects and the solution of nitrogen in a deformed ferritic steel: Part I. Experimental data and thermodynamic analysis. *Trans. AIME*, 233, 111-133.
- Yoder, H. S., Jr. (1950) High-low quartz inversion to 10,000 bars. *Trans. Am. Geophys. Union*, 31, 827-835.
- (1976) *Generation of Basaltic Magma*. National Academy of Sciences, Washington, D. C.

Manuscript received, November 13, 1978;
accepted for publication, June 2, 1979.