Reaction between magnesiowüstite of lower mantle composition and core-forming Fe-Ni alloy at 1–40 GPa

S. Kesson, A.E. Ringwood,[†] W. Hibberson, J. Fitz Gerald, and N. Ware

Research School of Earth Sciences, Australian National University, Canberra ACT 0200, Australia

Abstract

One class of models for the early history of the Earth requires the present-day inventory of siderophile elements in the mantle to have been established by equilibrium partitioning between core-forming metal and mantle minerals at high pressures and temperatures deep inside the Earth. We have accordingly carried out reconnaissance experiments on the partitioning of nickel between model lower mantle magnesiowüstite (Mg′ = 85 and 1.3 wt% NiO) and a model core-forming alloy, $Fe_{94}Ni_6$ (~7 wt% Ni) at pressures between 1–40 GPa and temperatures ranging from 1200 °C to >2000 °C. Reversal experiments were also attempted. Our results highlight the difficulty of attaining equilibrium partitioning in this system and imply that partition coefficients derived from unreversed experiments should accordingly be viewed with reservation. Our data nevertheless imply that the concentration of NiO in lower mantle magnesiowüstite in equilibrium with core-forming metal with ~7 wt% Ni would be extremely low, e.g., about 0.2 wt% NiO. Moreover, equilibrium seems to be fairly insensitive to the effects of either pressure or temperature, and so it is unlikely that magnesiowüstite could acquire 1.3 wt% NiO simply by equilibrating with core-forming metal under special high *P-T* conditions early in Earth history. Alternative hypotheses for the present-day siderophile element inventory of the mantle are accordingly preferred.

Introduction

The upper-mantle inventory of siderophile elements places important boundary conditions on the early history of the Earth and the formation of its metallic core. Absolute abundances of elements such as Ni are much higher than would be expected if the upper mantle had equilibrated with an Fe-rich metal phase during core formation at moderately high temperatures, e.g., ~2000 °C. The highly siderophile elements (Re, Os, Ir, Ru, Rh, Pt, Pd, and Au) are likewise overabundant, being present in the upper mantle at concentrations corresponding to about 0.4% of C1 abundances (Chou 1978). These are much higher than would be expected on the basis of low pressure iron-silicate partition equilibria. Moreover, the coherence within this highly siderophile group, namely their chondritic relative abundances, similarly precludes any low-pressure history of metal-silicate equilibration (Ringwood 1989; O'Neill 1991).

These considerations have led to three general classes of hypothesis for the early history of the Earth. One class of model recognizes that the chondritic relative abundances of highly siderophile elements require that metal-silicate equilibration be prevented in some manner at a late stage of accretion. The preferred model of Ringwood (1989) invoked kinetic effects, with some of the oxidized carbonaceous chondritic component in the proto-Earth being prevented from equilibration with core-forming

metal so that its siderophile inventory was later redistributed homogeneously throughout the mantle. Other workers (Turekian and Clark 1969; Wänke 1981; O'Neill 1991) appealed to the late accretion of oxidized chondritic material onto the newly formed Earth after the core had segregated. Metal-silicate equilibration thus ceases late in the accretion process and does not occur thereafter. In most of these hypotheses, however, the observed overabundance of nickel oxide in the upper mantle is established by complex, multistage processes (e.g., O'Neill and Palme 1997).

A second class of models calls upon inefficient metal extraction during the core-forming process (Arculus and Delano 1981; Jones and Drake 1986). O'Neill (1991) succinctly addressed the fatal weakness of such scenarios. Implausibly large quantities of H_2O (or CO_2) must somehow be introduced into the mantle to convert the metallic residues into their present-day form of oxidized species.

A third class of hypotheses usually skirts the issue of chondritic relative abundances of highly siderophile elements and simply advocates that metal-silicate equilibration at high pressures and temperatures is substantially different from that observed at low pressures. The observed concentration of nickel oxide in the upper mantle is thus attributed to equilibration between core-forming metal and mantle minerals deep inside the Earth (Urakawa et al. 1987; Urakawa 1991). Some models even invoke ultrahigh temperatures arising from (postulated) global melting of the early Earth to alter the partition

[†] Deceased November 12, 1993.

behavior of siderophile elements to the necessary degree (Rama Murthy 1991). The essence of this third class of models is that there is, or was, a *P-T* window in which equilibrium partitioning between a core-forming alloy and mantle minerals established the present Ni inventory of the mantle.

Our experimental study of the partitioning of a typical siderophile element, Ni, focuses on this last category of hypotheses. However, if we are to assess any model invoking high-pressure, high-temperature equilibration, we must first establish the chemical composition and siderophile element inventory of the lower mantle. One line of evidence comes from rare examples of lower mantle minerals that have been trapped as syngenetic inclusions within diamonds (cf. Kesson and Fitz Gerald 1992). Enstatite represents the retrogressive transformation product of former magnesium silicate perovskite, while magnesiowüstite possesses Mg' [100MgO/(MgO + FeO) molar] of 85 and contains 1.3 wt% NiO. (The NiO inventory of the lower mantle is accommodated by magnesiowüstite, rather than perovskite). The phase chemistry of these inclusions can be recombined to show that the bulk composition and NiO inventory of the lower mantle is much the same as that of the upper mantle. Complementary arguments based on thermoelastic properties (e.g., Jackson and Rigden 1997) substantiate this important conclusion.

The objective of the reconnaissance experiments described herein was to see if there were any *P-T* conditions where a typical lower mantle magnesiowüstite with Mg' = 85 and 1.3% NiO might ever have been in equilibrium with a model core-forming Fe-Ni alloy containing 7 wt% Ni. For the sake of simplicity we have not attempted to incorporate any of the candidate light element such as S or O that are thought to be present in the outer core; however, small amounts of O will have dissolved in molten metal in all experiments at or above 15 GPa.

PREVIOUS INVESTIGATIONS

The pioneering studies have limited comparative value. Ohtani et al. (1992) report a disequilibrium assemblage of perovskite with Mg' = 91, magnesiowüstite with Mg' = 30 and ~0.2% NiO, and an alloy 2.4 wt% Ni. The experiments of Urakawa (1991) involve starting chemistry and minerals that differ so much from our own that comparison is difficult.

However a substantive experimental study of magnesiowüstite-metal partitioning behavior has just been completed (O'Neill et al. unpublished manuscript). The distribution of a suite of key elements including Ni and Fe between Fe-rich metal and magnesiowüstite was determined at 5–25 GPa and temperatures to 2500 °C. There is minimal correlation of Ni partitioning with temperature, but there is a modest shift with pressure such that the NiO content of magnesiowüstite increased. It nevertheless remained well below the mantle value. Unlike some of the earlier workers in the field, O'Neill and colleagues refrained from linear extrapolation of this trend

TABLE 1. Starting materials

Magnes-iowüstite	1.3 wt% NiO	0.4 wt% NiO	No NiO
FeO	21.92 ± 0.67	20.52 ± 0.71	24.04 ± 0.25
NiO	1.34 ± 0.04	0.40 ± 0.04	—
MgO	77.90 ± 0.72	79.70 ± 0.54	74.62 ± 0.05
Sum wt%	101.2	100.8	98.7
Mg'	86.4	87.4	84.7
Alloy	**7 wt% Ni**	**9 wt% Ni**	**23 wt% Ni**
Fe	93.03 ± 0.64	90.14 ± 0.73	76.70 ± 0.46
Ni	6.70 ± 0.46	9.17 ± 0.50	23.02 ± 0.34
Sum wt%	99.7	99.3	99.7
Ni mol%	6.4	8.9	22.4

to ultrahigh pressures, and reassuring independent evidence that Ni is still siderophile even at core-mantle boundary pressures can be found in an abstract by Guyot et al. (1992).

EXPERIMENTAL PROCEDURES

Starting materials

Oxide precursors for metallic alloys were prepared by sol-gel techniques and reduced to <5 μm metallic powder by sintering at 675 °C for 2.5 h in an evacuated silica glass tube that also contained a Ti sponge "oxygen getter." Magnesiowüstite was synthesized from finely ground mixtures of ferric, nickel and magnesium oxides plus ~1 μm iron powder fired at 1000 °C for 3 hours. To keep Ni in the oxidized state during the subsequent synthesis procedure, the amount of Fe powder was reduced to 99% of that required for total conversion of ferric oxide to "FeO." Our synthetic magnesiowüstite therefore contains a small ferric component in solid solution (about 0.8 mol%). Homogeneity and compositions of all starting materials were confirmed by XRD and electron probe microanalysis (Table 1). Starting mixtures for all experiments comprised metal and magnesiowüstite in 20:80 wt proportions.

High-pressure experiments

All experiments in a piston-cylinder apparatus were conducted at 1 GPa, except for a high-temperature experiment at 2250 °C that was carried out at 3 GPa for technical reasons. Experiment times ranged from 24 h (at 1200 °C) to 5 min at T ≥ 2000 °C. Samples were contained in Ni metal capsules. No attempt was made to monitor or control f_{O_2}, so all samples were therefore subjected to the ambient f_{O_2} inside our pressure cell, near Ni-NiO. Samples were encapsulated in MgO for multi-anvil runs at 16 Gpa for durations ranging from 30 to 5 min. The ambient oxygen fugacity conditions imposed on the sample by W-Re thermocouples and lanthanum chromate furnace have not been established. Experiments in the laser-heated diamond-anvil cell at 15, 25, and 40 GPa used techniques and characterization procedures described by us elsewhere (Kesson and Fitz Gerald 1992). Diamond-cell heating times are brief, but temperatures may well reach several thousand degrees celsius in places

TABLE 2. Experiments at 1 GPa, with $Fe_{94}Ni_6$ alloy + magnesiowüstite

	1200 °C	1400 °C	1600 °C	1800 °C	2000 °C	2250 °C*
			Alloy initially 7 wt% Ni			
Fe	90.08 ± 0.19	89.92 ± 0.19	90.42 ± 0.11	90.08 ± 0.24	89.97 ± 0.44	92.47 ± 2.31
Ni	9.98 ± 0.27	10.04 ± 0.21	9.68 ± 0.02	10.05 ± 0.19	9.69 ± 0.58	7.15 ± 2.04
Sum wt%	100.1	100.0	100.2	100.2	99.7	99.6
			Magnesiowüstite initially 1.3 wt% NiO			
FeO	24.84 ± 0.18	24.96 ± 0.33	24.44 ± 0.05	20.52 ± 0.78	22.57 ± 0.29	7.97 ± 0.32
NiO	0.22 ± 0.03	0.28 ± 0.06	0.36 ± 0.25	0.19 ± 0.03	0.29 ± 0.02	0.12 ± 0.01
MgO	74.71 ± 0.24	74.82 ± 0.37	75.00 ± 0.26	78.66 ± 0.56	76.98 ± 0.58	91.55 ± 0.29
Sum wt%	99.8	100.1	99.8	99.4	99.8	99.6
Mg′	84.3	84.2	84.5	87.2	85.9	95.3
K_D	12.3	9.9	7.2	12.2	8.2	5.1
ln K_D	2.51	2.29	1.98	2.50	2.10	1.63
			Alloy initially 7 wt% Ni			
Fe	93.45 ± 0.40	94.85 ± 0.18	94.18 ± 0.91	94.33 ± 0.14		93.45 ± 0.40
Ni	6.24 ± 0.29	5.12 ± 0.17	5.89 ± 0.53	5.53 ± 0.08		6.24 ± 0.29
Sum wt%	99.7	100.0	100.1	99.9		99.7
			Magnesiowüstite initially no NiO			
FeO	26.29 ± 0.17	25.66 ± 0.46	25.89	23.25 ± 0.22		23.61 ± 0.08
NiO	0.03 ± 0.00	0.04 ± 0.01	0.05 ± 0.01	0.04 ± 0.01		0.04 ± 0.01
MgO	72.28 ± 0.19	72.81 ± 0.30	72.82 ± 0.45	75.12 ± 0.18		74.71 ± 0.20
Sum wt%	98.6	98.5	98.8	98.4		98.4
Mg′	83.1	83.5	83.4	85.2		84.9
K_D	54.8	37.4	34.3	33.7		37.4
ln K_D	4.00	3.62	3.54	3.52		3.62

*The experiment at 2250 °C was conducted at 3 GPa.

(Heinz and Jeanloz 1987). It was not possible to reverse any of these last experiments by starting with NiO-free magnesiowüstite because the resultant concentrations of NiO in the oxide phase proved to be below TEM detection limits. Ambient oxygen fugacity conditions inside the diamond cell at high *P-T* are unknown.

The first series of experiments involved reacting magnesiowüstite (Mg′ = 85, NiO = 1.3 wt%) with $Fe_{94}Ni_6$. In some piston-cylinder and multi-anvil experiments we attempted reversals by reacting an otherwise identical magnesiowüstite but with zero NiO with the same alloy. In addition, at 1 GPa, magnesiowüstite was reacted with two more-nickeliferous metal alloys $Fe_{91}Ni_9$ and $Fe_{78}Ni_{22}$. Finally, in a few experiments, magnesium borate + lithium carbonate fluxes were used in an attempt to promote equilibration between magnesiowüstite with a lower initial NiO content (0.4 wt%) and metal, with varying degrees of success.

Characterization of experimental products

Piston-cylinder and multi-anvil experiment products were characterized by electron probe microanalysis. Diamond-cell experimental products were characterized by energy-dispersive microanalysis combined with transmission electron microscopy as documented by Kesson and Fitz Gerald (1992). Compositional data presented in Tables 2–4 correspond to the mean of 5 or 6 microprobe analyses. Because both metal and oxide products exhibited compositional zoning, measurements were made as close as possible to their common contact. This proved challenging. We were able to reject analyses of alloys that were in error because of beam overlap onto neighboring

oxides, using the presence of MgO as a criterion. However there is no analogous test for beam overlap in oxide analyses. Data indicating unusually high NiO contents in magnesiowüstite may be suspect for this reason.

Another complication arises from the tendency of nickeliferous magnesiowüstite to exsolve submicron Ni-rich metal blebs at grain boundaries, which sometimes contribute to artificially high NiO contents in the analyses of oxide phases. This was a common problem in many multi-anvil runs, and its implications are addressed in the discussion that follows.

Diamond-cell experiments presented an additional set of experimental difficulties. In our past experience, only phases that are in direct contact with one another can be assumed to have equilibrated to some degree. Accordingly we report data only for metal-oxide pairs in direct contact. Unfortunately, selective erosion of oxide relative to metal during ion-beam thinning meant that such pairs were few indeed. Interpretation of diamond-cell experiments is further complicated by extraction of FeO from magnesiowüstite into molten metal at high pressures and its partial exsolution and back-diffusion into oxide during quenching. [Gourant et al. (1992) appear to have encountered similar phenomena.]

INTERPRETATION OF EXPERIMENTAL RESULTS

It should be emphasized from the beginning that our results define only the direction of equilibration; they do not measure the equilibrium partitioning of Ni between metal and magnesiowüstite. This is illustrated by the fact that the NiO contents of magnesiowüstite in our experimental products often differ by as much as an order of

TABLE 3. Experiments at 1 GPa with $Fe_{91}Ni_9$ alloy + magnesiowüstite

	1200 °C	1400 °C	1600 °C	1800 °C	2000 °C
Alloy initially 9 wt% Ni					
Fe	84.69 ± 1.49	85.14 ± 0.79	84.98 ± 0.29	84.81 ± 0.76	85.37 ± 0.36
Ni	14.98 ± 1.43	14.42 ± 1.16	14.90 ± 0.39	14.60 ± 0.26	14.37 ± 0.18
Sum wt%	99.7	99.6	99.9	99.5	99.8
Magnesiowüstite initially 1.3 wt% NiO					
FeO	23.71 ± 0.68	22.83 ± 0.42	23.14 ± 1.06	20.99	21.60 ± 0.42
NiO	0.25 ± 0.06	0.40 ± 0.20	0.26 ± 0.06	0.27 ± 0.09	0.24 ± 0.05
MgO	75.92 ± 0.53	76.23 ± 0.57	76.23 ± 0.99	77.84 ± 0.65	77.86 ± 0.34
Sum wt%	99.9	99.5	99.6	99.1	99.7
Mg′	85.1	85.6	85.4	86.9	86.5
K_D	15.7	19.2	15.7	13.5	15.2
ln K_D	2.75	2.95	2.76	2.60	2.72
Alloy initially 9 wt% Ni					
Fe	89.5 ± 0.33	90.16 ± 0.08	89.61 ± 0.67	90.22 ± 0.31	
Ni	10.26 ± 0.08	9.65 ± 0.16	10.11 ± 0.27	9.56 ± 0.19	
Sum wt%	99.9	99.9	99.8	99.8	
Magnesiowüstite initially no NiO					
FeO	25.17 ± 0.67	24.69 ± 0.29	24.89 ± 0.37	22.83 ± 0.28	
NiO	0.06 ± 0.01	0.06 ± 0.01	0.06 ± 0.01	0.07 ± 0.00	
MgO	73.40 ± 0.57	73.88 ± 0.29	73.67 ± 0.36	75.80 ± 0.59	
Sum wt%	98.6	98.6	98.6	98.7	
Mg′	83.9	84.2	84.1	85.5	
K_D	55.4	44.8	45.0	32.6	
ln K_D	4.01	3.80	3.81	3.48	

magnitude in cases where we have attempted experimental reversals. Consider for example the first data set of Table 2, where Ni has migrated from magnesiowüstite to metal, leaving ~0.2 wt% NiO in the former phase. This contrasts with only ~0.04 wt% NiO in magnesiowüstite in equivalent reversal experiments where Ni has been transferred from metal to magnesiowüstite.

These results provide a salutary reminder that attempts to measure the partitioning of Ni between metal and oxide phases may be far removed from thermodynamic equilibrium. It follows that extrapolation of unreversed experimental data to higher pressures and temperatures should be viewed with some reservations.

Partition behavior at 1 GPa

In all experiments at 1 GPa, Ni migrates from nickeliferous magnesiowüstite to alloy, and, in reversals, from alloy to magnesiowüstite. The NiO content of magne-

TABLE 4. Experiments at 1 GPa with $Fe_{88}Ni_{22}$ alloy + magnesiowüstite

	1200 °C	1400 °C	1600 °C	1800 °C	2000 °C
Alloy initially 23 wt% Ni					
Fe	74.49 ± 0.53	74.56 ± 0.29	73.44 ± 0.35	74.13 ± 2.42	75.50 ± 0.46
Ni	25.13 ± 0.58	25.34 ± 0.20	26.27 ± 0.25	25.67 ± 2.56	24.14 ± 0.34
Sum wt%	99.7	100.0	99.8	99.8	99.7
Magnesiowüstite initally 1.3 wt% NiO					
FeO	23.49 ± 0.47	22.83 ± 0.42	22.61 ± 0.55	21.28 ± 0.36	20.23 ± 0.29
NiO	0.26 ± 0.06	0.40 ± 0.20	0.26 ± 0.06	0.19 ± 0.04	0.38 ± 0.06
MgO	76.27 ± 0.61	76.23 ± 0.57	77.05 ± 0.32	77.69 ± 0.47	79.27 ± 0.26
Sum wt%	100.0	99.5	99.9	99.2	99.9
Mg′	85.3	85.6	85.9	86.7	87.5
K_D	30.4	19.2	31.2	37.6	17.1
ln K_D	3.41	2.95	3.44	3.63	2.84
Alloy initially 23 wt% Ni					
Fe	79.29 ± 0.31	79.49 ± 0.27	79.64 ± 0.40	80.06 ± 0.15	
Ni	20.64 ± 0.43	20.37 ± 0.32	20.43 ± 0.41	19.69 ± 0.26	
Sum wt%	100.0	99.9	100.1	99.8	
Magnesiowüstite initially no NiO					
FeO	25.97 ± 0.22	25.68 ± 0.31	24.59 ± 0.92	22.30 ± 0.18	
NiO	0.15 ± 0.02	0.13 ± 0.01	0.16 ± 0.03	0.17 ± 0.01	
MgO	72.48 ± 0.39	72.96 ± 0.34	73.40 ± 1.10	76.60 ± 0.16	
Sum wt%	98.6	98.8	98.1	99.1	
Mg′	83.3	83.5	84.2	86.0	
K_D	48.0	51.4	39.8	31.6	
ln K_D	3.87	3.94	3.68	3.45	

TABLE 5. Experiments at 1 GPa with fluxes

	1200 °C	1400 °C	1600 °C
Alloy initially 7 wt% Ni			
Fe	92.80 ± 1.00	93.07 ± 0.64	91.08 ± 0.75
Ni	7.12 ± 0.91	6.53 ± 0.25	8.65 ± 0.16
Sum wt%	99.91	99.60	99.72
Magnesiowüstite initially 0.4 wt% NiO			
FeO	23.75 ± 1.61	16.88 ± 4.10	15.25 ± 0.27
NiO	0.45 ± 0.22	0.07 ± 0.01	0.08 ± 0.01
MgO	75.10 ± 1.59	80.45 ± 0.46	83.61 ± 0.11
Sum wt%	99.30	97.40	98.94
Mg′	84.92	89.52	90.72
K_D	4.75	17.51	18.66
ln K_D	1.48	2.84	2.92
Alloy initially 7 wt% Ni			
Fe	95.24 ± 0.24	95.72 ± 0.27	94.91 ± 0.25
Ni	4.57 ± 0.09	4.10 ± 0.10	4.69 ± 0.15
Sum wt%	99.82	99.82	99.60
Magnesiowüstite initially no NiO			
FeO	24.27 ± 0.62	17.71 ± 0.36	22.66 ± 0.39
NiO	0.03 ± 0.01	0.03 ± 0.01	0.06 ± 0.01
MgO	74.37 ± 0.57	81.16 ± 0.50	76.22 ± 0.24
Sum wt%	98.67	98.90	98.93
Mg′	84.52	89.09	85.70
K_D	36.40	26.46	19.58
ln K_D	3.59	3.28	2.97

FIGURE 1. Compositional gradients in alloy (left side of figure) in contact with magnesiowüstite (right side) are very similar irrespective of whether Ni has migrated from oxide to metal (downward-pointing symbols) or vice versa (upward-pointing symbols). Unfortunately, this means that we cannot select one particular data set for these reversal experiments at 1 GPa, 1800 °C as being more representative of equilibrium than the other.

siowüstite in equilibrium with alloy containing 7 wt% Ni is very low, in the vicinity of 0.1 wt%, similar for equilibration with alloy containing ~9 wt% Ni. Indeed, even if the alloy is comparatively Ni-rich (~23 wt%), the equilibrium content of NiO in magnesiowüstite remains extremely low, with our data bracketing a value of ~0.2 wt%. There is no dependence on temperature.

Once we had realized how low the equilibrium NiO contents of magnesiowüstite would be, we carried out a further experimental campaign with nickeliferous magnesiowüstite initially containing only 0.4 wt% NiO, with the use of carbonate-borate fluxes in the hope that they might accelerate equilibration. These experiments bracket a value of ~0.1 wt% NiO in the oxide phase for equilibration with alloy containing ~7 wt% Ni (Table 5).

We attempted to determine whether the higher or lower levels of NiO in magnesiowüstite were more likely to be representative of the equilibrium value by examination of diffusion profiles. Unfortunately, this exercise was not rewarding. A typical data set obtained in an experiment for 0.5 hours at 1 GPa and 1800 °C is illustrated in Figure 1. It can be seen that the concentration profiles of FeO and NiO in oxide, and Fe and Ni in metal do not indicate whether one metal-oxide pair is any better equilibrated than the other.

Partitioning behavior at 15–40 GPa

The compositional brackets in multi-anvil runs at 16 GPa (Table 6) around the equilibrium contents of NiO are rather wide. Nevertheless, a value of <0.2 wt% might be appropriate for equilibrium with alloy containing 7 wt% Ni. This same pattern of migration of Ni from magnesiowüstite to metal was observed in analogous experiments utilizing alloys with either 9 wt% or 23 wt% Ni.

The exsolution of submicron grains of nickeliferous alloy at the grain boundaries of magnesiowüstite during some runs at 1 GPa and many experiments at 16 GPa calls for further comment. These grains are much too small for quantitative analysis but qualitatively are Ni-rich, perhaps ~50 wt% Ni. Because they are so small and have nucleated during the course of experiments we believe that they may closely approach the equilibrium Ni content of metal in contact with magnesiowüstite containing about 0.1–0.2 wt% NiO. Naturally, this is of some considerable significance in terms of the ultimate objectives of this study.

Initially we assumed that this intergranular alloy had been formed by a reduction reaction that released O among its products. However this may not be correct. O'Neill and McCammon (1993) demonstrated that magnesiowüstite with Mg′ = 80 synthesized at f_{O_2} as low as the iron-wüstite buffer contains about 3% of its total Fe inventory in the ferric rather than the ferrous state. By way of comparison, our synthetic magnesiowüstite used in all high pressure experiments contained only about 0.8 mol% of its Fe in the ferric state. Although our multi-anvil product assemblages were probably subjected to f_{O_2} conditions that were fundamentally different from those under which the original synthesis of magnesiowüstite was carried out, we do not attribute the exsolution of intergranular nickeliferous alloy to this factor. Instead we propose that it involves internal readjustment of the relative proportions of Fe^{2+}, Fe^{3+}, and Ni^{2+} according to

$$5Fe^{2+} + Ni^{2+} = FeNi + 4Fe^{3+} + FeNi\text{-alloy}.$$
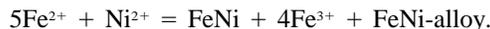
Data obtained in diamond-anvil cell experiments are presented in Table 7. Despite their uncertain temperature history, these experiments at 15, 25, and 40 GPa all define the same general trend of migration of nickel from magnesiowüstite to metal, thereby indicating the direction of equilibration. Unfortunately dissolution of O in molten

TABLE 6. Multi-anvil experiments at 16 GPa—compositions of magnesiowüstite and alloys in contact

	1800 °C	1800 °C	1800 °C	2000 °C	2300 °C
Alloy initially	7 wt% Ni	9 wt% Ni	23 wt% Ni	7 wt% Ni	7 wt% Ni
Fe	87.70 ± 0.22	89.78 ± 0.29	75.39 ± 0.56	92.89 ± 1.68	92.18 ± 0.50
Ni	12.48 ± 0.20	9.98 ± 0.29	24.35 ± 0.22	6.63 ± 1.64	7.50 ± 0.40
Sum wt%	100.2	99.8	99.7	99.5	99.7
Magnesiowüstite initially 1.3 wt% NiO					
FeO	25.22 ± 1.32	25.19 ± 0.90	20.03 ± 0.69	21.86 ± 1.18	21.11 ± 0.54
NiO	0.35 ± 0.04	0.51 ± 0.03	0.62 ± 0.10	0.46 ± 0.11	0.18 ± 0.02
MgO	73.44 ± 1.23	72.85 ± 0.64	78.19 ± 0.41	77.34 ± 1.01	77.54 ± 0.46
Sum wt%	99.0	98.5	98.9	82.0	98.8
Mg′	83.9	83.8	87.4	70.1	86.8
K_D	9.46	5.5	10.3	5.8	9.4
ln K_D	2.25	1.70	2.3	1.7	2.2
Alloy initially 7 wt% Ni					
Fe				95.41 ± 0.47	
Ni				4.55 ± 0.13	
Sum wt%				100.0	
Magnesiowüstite initially no NiO					
FeO				24.07 ± 1.50	
NiO				0.02 ± 0.01	
MgO				74.69 ± 1.24	
Sum wt%				81.8	
Mg′				68.8	
K_D				44.94	
ln K_D				3.81	

iron at high pressures (e.g., Ringwood and Hibberson 1991) introduces additional complexities in the interpretation of diamond-cell experiments. In some experiments, particularly at 25 and 40 GPa, the presence of modest amounts of dissolved O in formerly molten alloy is revealed by composite diffraction patterns that not only contain reflections attributable to α iron, but also reflections for wüstite. Similar observations have been made by Gourant et al. (1992). The O that dissolves in molten alloy at high pressures is provided by the extraction of FeO from neighboring magnesiowüstite. Thus in regions of common contact we sometimes find that the Mg′ of magnesiowüstite has increased to ~90, while the NiO contents fall to ~0.4 wt%. However this simple and self-explanatory trend is comparatively rare.

More commonly we observe that although the NiO content of magnesiowüstite decreases near a common contact with alloy, so does its Mg′. In other words its FeO content increases. We propose that this compositional trend develops because FeO formerly dissolved in molten metal exsolves when the metal solidifies and diffuses outward into neighboring oxide. Indeed this phenomenon is probably unavoidable on the scale of diamond anvil cell experiments (O'Neill et al. unpublished manuscript).

DISCUSSION

A comprehensive thermodynamic and thermochemical appraisal of the partitioning of Ni between alloy and magnesiowüstite can be found in O'Neill et al. (unpublished manuscript). We observe compositional exchange between both phases in our own experiments, and accordingly illustrate our results in terms of these authors' two-

TABLE 7. Diamond-anvil experiments at 15, 25, and 40 GPa— compositions of magnesiowüstites and alloys in contact

Experiments at ~15 GPa							
Alloy							
Fe	84.8	89.3	89.4	89.6	86.7	90.1	83.2
Ni	9.4	10.2	10.9	10.4	13.7	9.9	11.6
Magnesiowüstite							
FeO	30.4	43.3	22.8	24.7	16.4	19.0	16.7
NiO	1.1	0.7	0.4	0.7	0.3	0.9	0.3
MgO	68.4	56.0	76.8	74.6	83.3	80.1	83.0
Mg′	76	70	86	84	90	88	90
K_D	3.7	2.5	8.2	4.2	9.1	24.0	8.5
ln K_D	1.3	0.9	2.1	1.4	2.2	3.2	2.1
Experiments at ~25 GPa							
Alloy							
Fe	87.0	88.4	86.3				
Ni	13.0	11.6	13.5				
Magnesiowüstite							
FeO	80.1	80.0	91.6				
NiO	0.2	0.2	0.1				
MgO	19.2	19.1	8.4				
Mg′	30	30	14				

K_D and ln K_D not calculated because of quench modification of magnesiowüstite

Experiments at ~40 GPa							
Alloy							
Fe	91.1	86.5	87.4				
Ni	7.8	13.2	11.9				
Magnesiowüstite							
FeO	23.5	24.8	25.4				
NiO	1.2	1.0	0.9				
MgO	75.1	74.2	73.8				
Mg′	85	84	84				
K_D	1.4	4.0	4.0				
ln K_D	0.4	1.4	1.4				

Note: Starting assemblage is magnesiowüstite with 1.3 wt% NiO + FeNi alloy 7.0 wt% Ni. Temperatures are unknown.
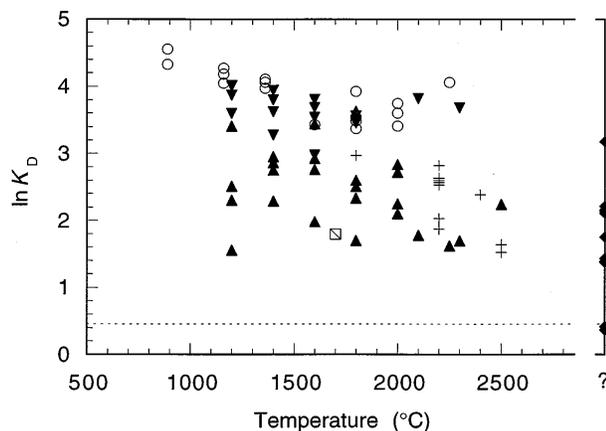
FIGURE 2. Temperature has no significant effect on the partitioning of Ni between alloy and magnesiowüstite. Solid symbols are from this study; downward arrowheads correspond to experiments in which Ni migrated from alloy to magnesiowüstite; upward arrowheads correspond to the reverse. The former data set constitute upper limits while the latter provide lower limits. Diamond-cell data (*T* unknown) are shown as solid diamond symbols on the right axis and provide lower limits only. Literature values provide upper limits only. Urakawa (1991) open circles; Ohtani et al. (1992) are open square; O'Neill et al. (1996) are crosses. The dashed line corresponds to the value of K_D required for equilibrium partitioning to have established the present-day mantle inventory of Ni.

FIGURE 3. Pressure does not appear to exert a significant influence on the partitioning of nickel between alloy and magnesiowüstite. Symbols as for Figure 2.

element partition coefficient. This parameter is the equilibrium constant K_D for the reaction:

$$Fe(alloy) + NiO(magnesiowüstite) =$$
$$FeO(magnesiowüstite) + Ni(alloy)$$

which is defined by the molar ratio of Ni/Fe in alloy, divided by its counterpart for the corresponding oxides in magnesiowüstite such that:

$$K_D = \text{Ni/Fe (alloy)} \div \text{NiO/FeO (magnesiowüstite)}.$$

Partition coefficients calculated from our experimental data are listed in Table 2–7. Because the complementary experiments define only the direction of equilibration, values of K_D derived therefrom correspond to either upper or lower limits that bracket the true equilibrium values for this parameter. Figure 2 combines our new results with unreversed data from Urakawa (1991), Ohtani et al. (1992) and O'Neill et al. (unpublished manuscript). Our diamond-cell data, for which temperatures are unknown, are plotted on the right axis for comparative purposes. These last results constitute lower limits for K_D because they involve migration of Ni from magnesiowüstite to metal. By way of corollary, the aforementioned studies provide only upper limits. In both Figures 2 and 3, the dashed line corresponds to the value of ln K_D required to establish the present-day NiO inventory of the mantle by metal/magnesiowüstite equilibration. The lack of correlation between ln K_D and *T,* and the implausibility of high-temperature equilibrium are self evident. Analo-

gous arguments discourage appealing to pressure-induced equilibration (Figure 3). In conclusion we reiterate the salient point made by O'Neill et al. (1996). Our understanding of the accretion of the Earth and formation of its core cannot rest on the partition behavior of any one siderophile element considered in isolation. Even if Ni were to become less siderophile with increasing pressure, temperature, or both, there is no unique *P-T* window wherein the partitioning of Ni and Co and Fe simultaneously match up with present-day mantle inventories.

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