High-Pressure and High-Temperature Experiments on Core-Mantle Segregation in the Accreting Earth

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The abundances of siderophile elements in the Earth's silicate mantle are too high for the mantle to have been in equilibrium with iron in the core if equilibrium occurred at low pressures and temperatures. It has been proposed that this problem may be solved if equilibrium occurred at high pressures and temperatures. Experimental determination of the distribution of siderophile elements between liquid metal and liquid silicate at 100 kilobar and 2000°C demonstrates that it is unlikely that siderophile element abundances were established by simple metal-silicate equilibrium, which indicates that the segregation of the core from the mantle was a complex process.

Siderophile, or metal-loving, elements are expected to have segregated with iron metal into the core of the Earth. Thus, their abundances in the Earth's mantle should give us clues to the processes that occurred early in the history of the Earth when core formation took place. The pattern of siderophile element abundances in the Earth's mantle has been well characterized (*1*, *2*). Comparison of this pattern with the abundances of siderophile elements that would be expected to result from simple equilibrium between segregating metal and mantle silicates at near surface pressures and temperatures (Fig. 1) shows that the more siderophile elements are overabundant in the mantle, and conversely, the less siderophile elements are underabundant. Although it is a misnomer, this apparent disequilibrium is often termed the "excess siderophile element problem."

Several models have been proposed to account for this apparent disequilibrium. Among these models are heterogeneous accretion (*3*, *4*), inefficient core formation (*5*), and homogeneous accretion with continuous core formation (*6*). With each model, however, there are some difficulties in accounting for the siderophile element abundance pattern in its entirety [for review, see (*2*)]. Testing these models has relied on the available metal-silicate partitioning data—partition coefficients that were measured at temperatures ranging from 1260° to 1600°C and at pressures of approximately 1 bar.

Recently, Murthy (*7*) put forth the idea that perhaps simple high-temperature (3000 to 4000 K) equilibrium between metal and silicate liquid in a magma ocean is responsible for the siderophile element pattern in the Earth's mantle. Although this idea has merit, Murthy's method of extrapolation of metal-silicate partition coefficients to the relevant temperatures has been criticized (*8*–*11*). Murthy's extrapolation technique predicts that with increasing temperature the metal-silicate partition coefficients of all siderophile elements will converge on a value of 1. Using more rigorous thermodynamics, other authors (*8*–*11*) have concluded that the metal-silicate partition coefficients could either increase or decrease with temperature, depending on valence state and thermodynamic properties such as the enthalpy and entropy of formation of the oxide species. These authors have further concluded that extrapolations of low-temperature partition coefficients to high temperatures are unreliable because the chemistry occurring at high temperatures and pressures may not be the same as that occurring at low temperatures and pressures. Thus, we began an experimental study of the partitioning behavior of moderately siderophile elements at elevated temperatures and pressures.

High-pressure experiments were conducted in the 1200-ton multi-anvil apparatus at the Bayerisches Geoinstitut. A sample was contained in either MgO or Al_2O_3 capsules within an octahedral assembly (*12*). The starting material consisted of a synthetic basalt we prepared by mixing together reagent-grade oxides in the following proportions by weight: 50% SiO_2, 19% FeO, 13% Al_2O_3, 11% CaO, and 7% MgO. This synthetic basalt was doped with 1.5% each of NiO and CoO or MoO_2 and WO_2 or V_2O_3, Cr_2O_3, and MnO. These mixtures were melted and quenched to a glass and then ground back to a powder. This glass powder and Fe metal filings were mixed together in an approximately 50/50 ratio by mass.

A pressure of 100 kbar was first applied to the sample assembly. After reaching pressure, samples were heated to 1600°C and held at that temperature for 45 to 60 min to sinter the capsule material in order to minimize its subsequent chemical interaction with the sample. The temperature was then raised to 2000°C and held there for 3 min. At this temperature and pressure, both metal and silicate are liquids. The charges were quenched by turning off power to the $LaCrO_3$ furnace, and pressure was gradually released over 10 hours.

Samples were analyzed with a Cameca SX50 electron microprobe. The initially homogeneously distributed metal filings had largely segregated into a single spheroid in the center of the charges (Fig. 2). The silicate liquid did not quench to a glass but

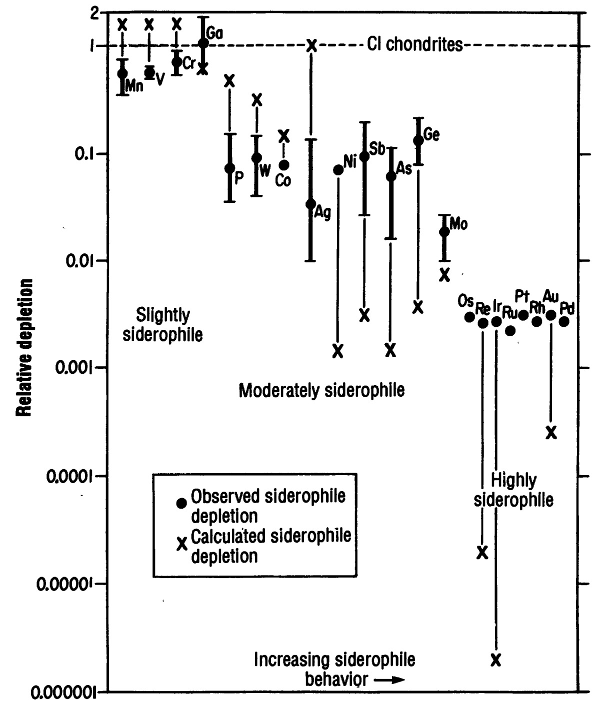

Fig. 1. Observed abundances of siderophile elements in the mantle, compared to abundances expected from simple equilibrium. Filled circles are best estimates of primitive mantle abundances corrected for volatility as described (*2*). The "X" symbols indicate mantle abundances calculated for a simple equilibrium between core and mantle by use of the metal-silicate partition coefficients experimentally determined at low temperature and 1 bar of pressure, as described (*9*).

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segregated into two phases with a dendritic texture. To determine the composition of the silicate liquid before quenching, we rastered the electron beam over an area approximately 20 μm on a side, and 30 to 40 analyses were taken and averaged together. For the metal, a point beam was used. For major elements, a beam current of 30 nA and a counting time of 15 s were used. For the trace elements, beam currents of between 125 and 250 nA and counting times of up to 10 min were used. Traverses across the metal bead showed no compositional gradients, which suggests that equilibrium was attained.

The compositions of the run products are shown in Table 1 and discussed below. The metal-silicate partition coefficients that were determined for Ni, Co, Mo, W, V, Cr, Mn, and Fe are shown in Table 2. The amounts of Mo and W present were below analytic detection in the quenched silicate liquid; thus, only lower limits for their metal-silicate partition coefficients are reported.

Metal-silicate partition coefficients depend strongly on oxygen fugacity [see, for example, (*13*, *14*)]. Thus, in order to decouple the effects of temperature and pressure from those of oxygen fugacity on the partition coefficients, our results must be compared to the results of experiments performed at lower temperatures and pressures but at similar oxygen fugacities. Therefore, we need to ascertain the oxygen fugacity of our experiments. Normally, the oxygen fugacity of such experiments is calculated on the basis of a calibration of the iron-wüstite (IW) buffer, along with the concentrations of FeO in the silicate and of Fe in the metal. However, the IW buffer is not calibrated to 2000°C, so an actual numerical value for the oxygen fugacity cannot be reliably determined. Nevertheless, the oxygen fugacity relative to the IW buffer can still be calculated, because in such calculations the term that gives oxygen fugacity relative to the IW buffer is simply

$$\Delta IW = 2.0 \log \frac{a_{FeO}}{a_{Fe}}$$

where a_{FeO} and a_{Fe} are the activities of FeO in the silicate liquid and of Fe in the metal, respectively. If ideal behavior is assumed (an assumption that is likely to be increasingly valid at progressively higher temperatures), the activities of Fe in the metal and of FeO in the silicate liquid can be estimated as their mole fractions. The results of this calculation indicate that our experiments range from 1.6 to 2.3 log units below the IW buffer.

We compared our results to the metal-silicate experiments of Jones and Drake (*5*) and of Drake *et al.* (*15*), which were performed at 1 bar of pressure and 1260°C and were between 1 and 1.5 log units below the IW buffer. As shown in Fig. 3, the Ni and Co metal-silicate partition coefficients decrease with increasing temperature and pressure. Although the W partition coefficient measured here is only a lower limit, it is larger than its low-temperature and -pressure counterpart, which indicates that W becomes more siderophile as temperature and pressure increase from 1260° to 2000°C and from 1 bar to 100 kbar, respectively. This result is contrary to the prediction of Murthy (*7*). The Mo partition coefficient is also a lower limit, and this lower limit is less than the low-temperature and -pressure partition coefficient by nearly a factor of 10. It is presently unclear whether Mo becomes less siderophile or more siderophile with increasing temperature and pressure. The partition coefficients for V and Mn both increase with increasing temperature and pressure. The Cr partition coefficient appears to decrease slightly with increasing temperature and pressure.

Walker *et al.* (*16*) reported Fe, Ni, and Cr metal-silicate partition coefficients of 6.2, 175, and 0.16, respectively, for a silicate liquid with 10% by weight Fe at 2180°C and 100 kbars. We report values of 12.4 and 247 for Fe and Ni for a silicate liquid with 8% Fe, and values of 6.2, 135, and 0.32 for Fe, Ni, and Cr for a silicate liquid with 16% Fe. The experiments of Walker *et al.* were done under somewhat different conditions (their temperature was higher, they used a carbon capsule, and their metallic liquid contained sulfur). For comparison of our data sets, the oxidation state of the experiments of Walker *et al.* must be ascertained. Walker *et al.* only constrained the oxidation state of their experiments to be less than 1 log unit above the IW buffer. However, the experiments of Walker *et al.* were probably in an oxidation

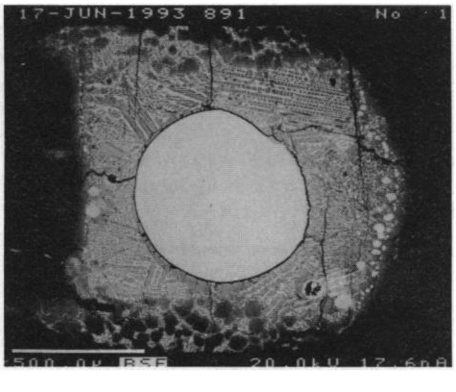


Fig. 2. Back-scattered electron image of experimental run 891. At run conditions, the bright phase was liquid Fe metal and the darker dendritic texture was silicate liquid. The dark euhedral crystals are pieces of the capsule. Scale bar: 500 μm.

Table 1. Composition of run products in percent by weight (uncertainties, ±1σ). For the metal, the uncertainties are the standard deviation among the analyses. Because the dendritic nature of the silicate liquid leads to large variations among individual analyses, the silicate uncertainties are the error of the mean of the analyses. Blank spaces indicate that element was not present in charge.

Element	Run 888 Al_2O_3 capsule	Run 891 MgO capsule	Run 895 Al_2O_3 capsule	Run 912 Al_2O_3 capsule
		Silicate		
Si	16.04 ± 0.48	16.65 ± 0.75	17.01 ± 0.27	17.16 ± 0.14
Mg	3.05 ± 0.10	25.63 ± 1.17	3.18 ± 0.07	2.99 ± 0.03
Ca	4.90 ± 0.17	4.87 ± 0.33	4.54 ± 0.09	4.88 ± 0.05
Al	19.32 ± 1.09	3.80 ± 0.22	16.81 ± 0.64	15.70 ± 0.40
Fe	15.48 ± 0.50	7.78 ± 0.20	16.30 ± 0.31	15.23 ± 0.14
Ni	0.008 ± 0.001	0.005 ± 0.001		
Co	0.016 ± 0.001	0.011 ± 0.001		
Mo			<0.003	
W			<0.01	
V				0.74 ± 0.02
Cr				0.44 ± 0.03
Mn				0.80 ± 0.06
O	43.87 ± 0.21	43.39 ± 0.26	42.90 ± 0.13	42.81 ± 0.18
Total	102.68	102.14	100.74	100.75
		Metal		
Fe	96.10 ± 0.92	98.24 ± 0.43	97.34 ± 0.88	99.44 ± 0.38
Ni	1.06 ± 0.03	1.27 ± 0.03		
Co	0.98 ± 0.02	1.11 ± 0.02		
Mo			1.08 ± 0.09	
W			1.23 ± 0.05	
V				0.066 ± 0.006
Cr				0.14 ± 0.007
Mn				0.013 ± 0.001
Total	98.14	100.62	99.65	99.66

state similar to that of our experiments in Al_2O_3 capsules (*17*). Given the difference in experimental conditions, there appears to be good agreement between the two studies.

This good agreement is particularly satisfying because, during the course of an experimental run, our silicate liquids became contaminated with the capsule material. In the case of the MgO capsule, this resulted in a silicate liquid with a composition close to that of a mantle peridotite such as KLB1 (*18*). However, the silicate liquids resulting from the experiments performed in Al_2O_3 capsules were extremely rich in Al (Table 1). It is of some concern that this odd composition may affect the partitioning behavior of the elements. The effect of adding Al to a silicate melt is to depolymerize the melt (*19*); this could potentially affect partitioning because it could help stabilize metal cations in the melt (*20*). However, we feel that this effect should be minor when compared to the effects of oxygen fugacity, temperature, and pressure on metal-silicate partition coefficients. This assertion is supported by the fact that despite large compositional differences, our results from Al_2O_3 capsules agreed quite well with those of Walker *et al.*, which implies that temperature and pressure, not bulk composition, are principally responsible for the trends we see in Fig. 3.

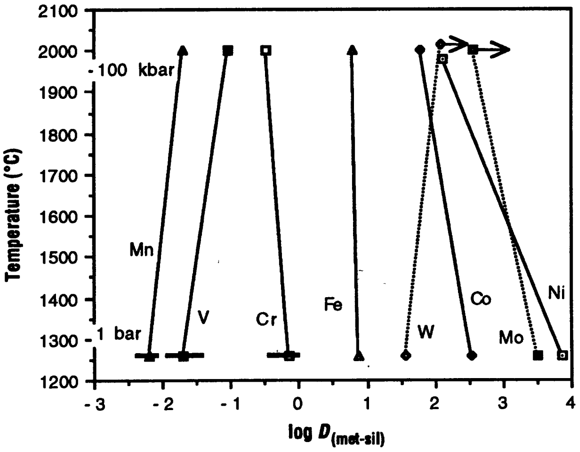
The partition coefficients reported above may be used to evaluate whether simple high-temperature equilibrium between metal and silicate during accretion and core formation in the Earth can account for the abundances of Ni, Co, W, and Mo in the upper mantle of the Earth. In particular, the approximately equal abundances of Ni, Co, and W constitute a powerful test. Simple mass balance between the core and the mantle of the Earth may be used to calculate what metal-silicate partition coefficients are necessary to produce the observed abundances of these elements in the mantle. Mean core-mantle partition coefficients for Ni, Co, and W need to be 40 ± 5 (Table 2). Figure 3 shows that this condition is not satisfied in the pressure range of 1 bar to 100 kbar and in the temperature range of 1260° to 2000°C. Extrapolation of these results to higher temperatures and pressures is uncertain, because with the current experimental results, we cannot resolve the effects of temperature and pressure, and pressure may play a important role in modifying partition coefficients (*21*). However, if the trends observed in Fig. 3 continue (which only further experimentation can tell us), although the Ni and Co partition coefficients are approaching one another, the probability of obtaining core-mantle partition coefficients of 40 ± 5 for Ni, Co, and W simultaneously at any temperature and pressure is low.

The metal-silicate partition coefficients we have reported here do not corroborate the predictions of Murthy (*7*), because the metal-silicate partition coefficients of siderophile elements do not decrease uniformly with increasing temperature. Indeed, the partition coefficient for W increases with increasing temperature and pressure. Our results (particularly the W partition coefficient) indicate that it is unlikely that the excess siderophile element problem in the Earth's mantle can be reconciled with simple high-temperature and -pressure equilibrium between metal and silicate during accretion and core formation. Instead, processes more complex than a simple metal-silicate equilibrium appear to have established the siderophile element pattern in the mantle.

Table 2. Liquid metal–liquid silicate partition coefficients at 100 kbar and 2000°C. Uncertainties are ±1σ, on the basis of the average of the individual analyses of metal and silicate. ΔIW is the redox state relative to the IW buffer at 100 kbar and 2000°C. For each element, ΔIW was −1.6 in run 888, −2.3 in run 891, −1.6 in run 895, and −1.6 in run 912. $D_{(\text{met-sil})}$ is the metal-silicate partition coefficient. Blank spaces indicate that element was not present in charge.

Element	Run 888	Run 891	Run 895	Run 912	$D_{(\text{met-sil})}$ required for core-mantle equilibrium
Fe	6.2 ± 0.2	12.4 ± 0.4	6.0 ± 0.1	6.5 ± 0.5	16
Ni	135 ± 15	247 ± 44			45
Co	60 ± 3	106 ± 16			40
W			>123		35
Mo			>360		160
V				0.089 ± 0.008	4
Cr				0.32 ± 0.03	2
Mn				0.016 ± 0.002	4

Fig. 3. Comparison of partition coefficients of (*5*) and (*15*) at 1260°C, 1 bar, and an oxygen fugacity of 1.0 to 1.5 log units below the IW buffer, with our results at 2000°C, 100 kbar, and an oxygen fugacity estimated to be about 1.6 log units below the IW buffer. The arrows indicate that the partition coefficients for Mo and W are lower limits and that the actual values of these partition coefficients are larger. The dark bars on the low-pressure and -temperature data for V, Cr, and Mn indicate the ranges of these data.



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12. The capsules were surrounded by a MgO sleeve contained in a cylindrical $LaCrO_3$ heater with a geometry designed to minimize thermal gradients across the sample (*22, 24*). The sample assembly consisted of a MgO (with 5% Cr_2O_3 by weight) octahedron with an edge length of 18 mm. Components of the sample assembly were dried by heating at 1000°C, and immediately before each experiment, the complete sample assembly was dried in a vacuum oven at 230°C overnight. This procedure minimizes the H_2O content of the assembly (*23, 24*). Temperature was monitored with a thermocouple, consisting of 0.25-mm–diameter W3%Re/W25%Re wire, that was in contact with the sample capsule. Pressure was calibrated by use of Bi transitions at room temperature and by reversals of phase transformations in SiO_2 (quartz-coesite and coesite-stishovite) and Fe_2SiO_4 (olivine-spinel) at high temperatures (1000° and 1450°C) [see also (*24*)].

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Phase Transitions Between β and γ $(Mg,Fe)_2SiO_4$ in the Earth's Mantle: Mechanisms and Rheological Implications

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The mechanisms of the phase transformations between the spinel (γ) and modified spinel (β) polymorphs of Mg_2SiO_4 have been studied experimentally between 15 and 20 gigapascals and 800° to 950°C. The γ to β transformation occurs by a shear mechanism, whereas the β to γ transformation involves grain-boundary nucleation and interface-controlled growth. These contrasting mechanisms are a consequence of the number of independent slip systems that are available in the respective crystal structures. This result leads to the prediction that in subduction zones and perhaps also rising plumes in the Earth's mantle, the γ to β transformation should be accompanied by a transient reduction in strength.

High-pressure phase transformations are likely to play an important role in several aspects of the dynamic behavior of the Earth's mantle. A detailed understanding of the mechanisms of these transformations is essential for evaluating transformation kinetics in the mantle as well as the effects of phase transitions on mantle rheology and convection. In addition, rheological changes associated with phase transitions may be involved in the triggering of deep focus earthquakes. In the context of rheological changes, the phenomenon known as "transformation plasticity" has considerable potential importance. Metals and ceramics often exhibit a reduction in mechanical strength as they undergo phase transitions (*1*, *2*). Unusually high strains can develop under low differential stress, especially when the temperature is varied in order to cycle the conditions back and forth across the phase transition.

Transformation plasticity may be important during mineralogical phase transformations in the Earth's interior (*3*–*8*). Phase boundaries in the mantle between, for example, the polymorphs of $(Mg,Fe)_2SiO_4$ are obvious locations where this phenomenon might occur. Such phase boundaries are believed to coincide with the seismic discontinuities located at depths of 410 km, possibly 520 km, and 660 km. Theoretical studies have demonstrated that transformation plasticity at such phase boundaries would cause mechanical decoupling and favor layered convection (*8*). In addition, deep focus earthquakes may result from shear instabilities initiated by localized rheological change, associated with phase transformations in subducting slabs (*9*–*13*). We have studied the mechanisms of the β to γ and γ to β transformations in Mg_2SiO_4 at high pressure to understand how these transformations occur and whether they are likely to cause transformation plasticity in the Earth's mantle.

Different mechanisms of transformation plasticity will presumably operate, depending on the mechanism of the phase transition (*1*, *2*, *4*, *14*). Martensitic or shear transformations are particularly likely to result in a reduction in strength. Such transformations occur by the migration on certain slip planes of partial dislocations, each of which changes the stacking sequence and leaves behind a layer of the product phase. In addition to changing the crystal structure, the migration of the partial dislocations also results in plastic deformation. The driving force for the migration of the partial dislocations and the resulting deformation is the change in Gibbs free energy associated with the phase transformation. Thus, while the phase transformation is in progress, the externally applied stress required to deform the material should be much smaller than normal.

It has been demonstrated experimentally that the olivine to spinel transformation can occur by a martensitic-like mechanism involving the synchroshear of cations (*15*, *16*). However, because the differential stress required to produce a small degree of transformation by this mechanism is in excess of 1 GPa (*16*, *17*), the martensitic-like mechanism is unlikely to be of major importance in the Earth's mantle. Theoretically, phase transformations between the high-pressure polymorphs of $(Mg,Fe)_2SiO_4$, modified spinel (β) and spinel (γ), may also occur by a shear mechanism (*18*, *19*). For the β to γ transformation, the mechanism involves the migration of $1/2[\bar{1}01](010)$ partial dislocations, whereas the γ to β transformation occurs by the migration of $1/4[1\bar{1}2](110)$ partial dislocations (*18*). In either case, partial transformation would result in an increase in stacking disorder [either on $(010)_\beta$ or $(110)_\gamma$, respectively] and, at advanced degrees of transformation, lamellar intergrowths of the two phases, crystallographically oriented with $[001]_\beta//[001]_\gamma$ and $[010]_\beta//[110]_\gamma$. Similar stacking faults can also form during crystal growth (*20*), making detailed microstructural stud-

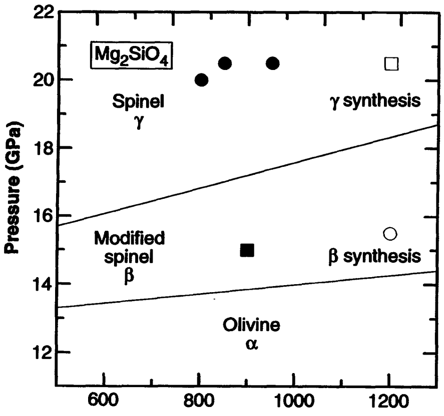

Fig. 1. Phase diagram for Mg_2SiO_4 showing the stability fields of α (olivine), β (modified spinel), and γ (spinel) (*30*). The synthesis conditions for β and γ are shown (open symbols) in addition to the experimental run conditions for the β to γ (filled circles) and γ to β (filled square) transformations.

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