

Multivariable Dependence of Fe-Mg Partitioning in the Lower Mantle

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High-pressure diamond-cell experiments indicate that the iron-magnesium partitioning between (Fe,Mg)SiO₃-perovskite and magnesiowüstite in Earth's lower mantle depends on the pressure, temperature, bulk iron/magnesium ratio, and ferric iron content. The perovskite stability field expands with increasing pressure and temperature. The ferric iron component preferentially dissolves in perovskite and raises the apparent total iron content but had little effect on the partitioning of the ferrous iron. The ferrous iron depletes in perovskite at the top of the lower mantle and gradually increases at greater depth. These changes in iron-magnesium composition should affect geochemical and geophysical properties of the deep interior.

At depths greater than 670 km in the lower mantle, olivine and orthopyroxene transform to (Fe,Mg)SiO₃-perovskite (pv) and (Fe,Mg)O-magnesiowüstite (mw) (1), which are likely to form the most abundant mineral assemblage in the Earth (2, 3). The Fe-Mg partition coefficient of pv and mw, $K = (X_{Fe}^{pv}/X_{Mg}^{pv})/(X_{Fe}^{mw}/X_{Mg}^{mw})$, where X is the molar fraction of Fe (Fe²⁺ and Fe³⁺) or Mg in pv or mw, plays a crucial role in determining the composition (4–6) and physical properties (7–10) of the lower mantle, the interaction between the solid oxide mantle and the molten metallic core (11–13), the partitioning of siderophile elements (14–16), and the stability of pv and mw (17). However, reported K values have varied enormously, from 0.08 to 1 (Table 1), rendering lower mantle geochemistry essentially unconstrained. The upper limit of Fe in pv, X_{Fe}^{pv} , has also been a subject of controversy. Yagi *et al.* (18) have reported X_{Fe}^{pv} as high as 0.21 for pv synthesized in diamond cells, whereas $X_{Fe}^{pv} > 0.15$ has never been observed in pv synthesized with multianvil apparatus (17).

Guyot *et al.* (19) have reported that K increased sharply with pressure from 25 to 40 GPa but remained constant above 40 GPa. The constancy of K at higher pressures has generally been accepted and used for models of the deep lower mantle. Multianvil experiments have provided information on the dependence of K on other variables, including the Fe (20) and Al₂O₃ content (21, 22), the presence of a B₂O₃ catalyst (23), the equilibration time (23, 24), and the temperature (24). With the addition of 4% Al₂O₃ (21), the Fe content in pv increases drastically to become equal to that

in mw. The extremely large K value in the presence of Al₂O₃, however, implies (22) an extremely high Fe³⁺/ΣFe fraction (50 to 90%) (25), a composition unlike that expected for the lower mantle. The central issue pertinent to the composition of the lower mantle remains the role of ferrous iron, and the behavior of Fe²⁺ and Fe³⁺ must be evaluated separately.

We used a laser-heated diamond cell and synchrotron x-ray diffraction (26) to determine the K value as a function of pressure (P), temperature (T), and composition (X) at conditions deep into the lower mantle. Starting samples were synthetic olivines (Fo₁₀₀, Fo₈₂, Fo₆₅, Fo₆₀, and Fo₃₅) or orthopyroxenes (En₁₀₀ and En₆₀) with all Fe in ferrous form (27). To investigate the effects of Fe³⁺, we added 4 ± 1 mole percent hematite. The diamond cell is a closed

system, in which the bulk Fe³⁺/Fe²⁺ ratio in the starting material is preserved in the absence of other transition elements (unless metallic Fe is produced). We used the double-sided, multimode laser-heating technique (26) to attain uniform and constant temperatures (±50 K) in heated areas 30 to 50 μm wide (Fig. 1A). Samples were sandwiched between two NaCl thermal insulation layers (26). Temperatures were increased and fixed for at least 5 min at 1500, 1800, and 2000 (±50) K (Fig. 1B), which are sufficiently below the melting point to minimize preferential diffusion (28). Compositional uniformity within the 50-μm heated area was confirmed by x-ray diffraction and electron microprobe. Pressures were calibrated with ruby chips situated near the hot spot; all reported pressures refer to measurements after heating.

A total of 38 experiments were performed at myriad P - T - X conditions within the pv stability field. In each experiment, the sample had transformed to pv + mw whereas the surrounding unheated area remained as the starting phase. A 5-μm synchrotron x-ray beam (29) was used to probe the sample after it was quenched (30). We used the unit-cell parameters of pv and mw to calculate X_{Fe}^{pv} (17) and X_{Fe}^{mw} (31). We tested the effects of variable heating time and found that the value of K did not change significantly (<10%) in heating times lasting 5 to 30 min, indicating that 5 min was sufficient. Equilibrium and reversibility were tested by approaching the same P - T point along different thermodynamic paths.

Table 1. High P - T partition coefficients (K) obtained by multianvil and diamond-cell experiments. The list was selected to highlight extreme values and multivariable dependence; ts, this study. Dashes indicate that temperatures were not measured or reported for that experiment.

K	Samples	T (K)	P (GPa)	Reference
<i>Multianvil</i>				
0.09	Fo ₈₀	1873	26	(20)
0.15	Fo ₉₀	1873	26	(20)
0.16	Fo ₇₀ + B ₂ O ₃	1900	23	(23)
0.35	Fo ₉₁ + B ₂ O ₃	1900	23	(23)
0.26	Fo ₉₁	1573	26	(24)
0.23	Fo ₉₁	1873	26	(24)
0.17	Fo ₈₉	1600	25	(21)
1.0	Fo ₈₉ + Al ₂ O ₃	1600	25	(21)
<i>Diamond cell</i>				
0.08	Fo ₉₃ -Fo ₅₉	–	25–35	(35)
0.16	Fo ₈₃	2500 ± 750	25	(19)
0.29	Fo ₈₃	2500 ± 750	40	(19)
0.13	Fo ₈₅ -Fo ₇₃	~1673	26	(32)
0.12	Fo ₉₀ + Cr, Ni, Mn	–	30	(16)
0.50	Fo ₉₀ + Cr, Ni, Mn	–	25	(16)
0.04	Fo ₆₀	1500 ± 50	32	ts
0.29	Fo ₈₂	2000 ± 50	50	ts
0.09	Fo ₆₅	1500 ± 50	40	ts
0.12	Fo ₆₅ + Fe ₂ O ₃	1500 ± 50	37	ts
0.11	Fo ₈₂	1800 ± 50	31	ts
0.24	Fo ₈₂ + Fe ₂ O ₃	1800 ± 50	29	ts

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The stability limit of Fe in pv increased rapidly with increasing P and T : from $X_{\text{Fe}}^{\text{pv}} = 0.08$ at 26 GPa and 1500 K to $X_{\text{Fe}}^{\text{pv}} = 0.28$ at 50 GPa and 2000 K (Fig. 2). The P - T dependence of K explains the difference between the low value of $X_{\text{Fe}}^{\text{pv}} = 0.12$ (17) obtained with the multianvil apparatus at 26 GPa and 1900 K and the high value of 0.21 (18) obtained with the diamond cell at 25 to 35 GPa. The positive P - T slope of the $\text{pv} = \text{mw} + \text{st}$ (stishovite) boundary is consistent with thermodynamic calculations (32) and implies that the pv becomes more stable relative to $\text{mw} + \text{st}$ (subsidius) at higher P and T . In addition, our experiments with the Fo_{100} and En_{100} (+ platinum black) as starting materials showed the Fe-free pv to be stable to at least 85 GPa and 2000 K. Meade *et al.* (33) have interpreted their observation of breakdown of pv to $\text{mw} + \text{st}$ at 70 GPa as either dissociation or partial melting of pv at high P - T . Our results support the latter alternative. Likewise, our results suggest that the recent report of the breakdown of MgSiO_3 -perovskite (34) was possibly due to incongruent melting and diffusion (28) of pv in a large temperature gradient (1900 to 3200 K), which was avoided in our experiment.

We observed a large dependence of K on P - T - X variables. Examples are listed in Table 1; the lowest K (0.04) is below the previously observed minimum of 0.08 (35). A systematic trend is observed: K increases with increasing P , increasing T , decreasing ferrous iron content, and increasing ferric iron content, and these dependencies are

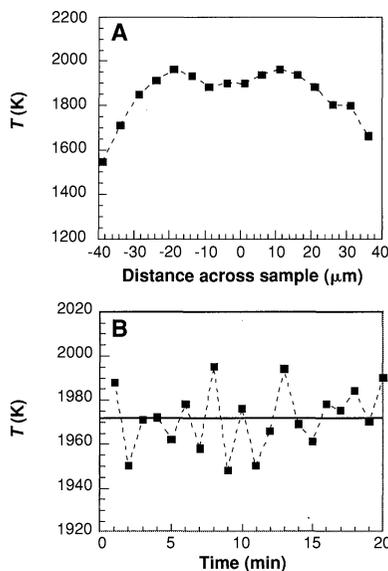


Fig. 1. (A) Temperature profile across a laser-heated sample in a diamond cell. (B) Temperature stability; SD, 14 K. Each point corresponds to spectra collected over 0.5 to 1.0 s, thereby averaging any higher frequency fluctuations in temperature.

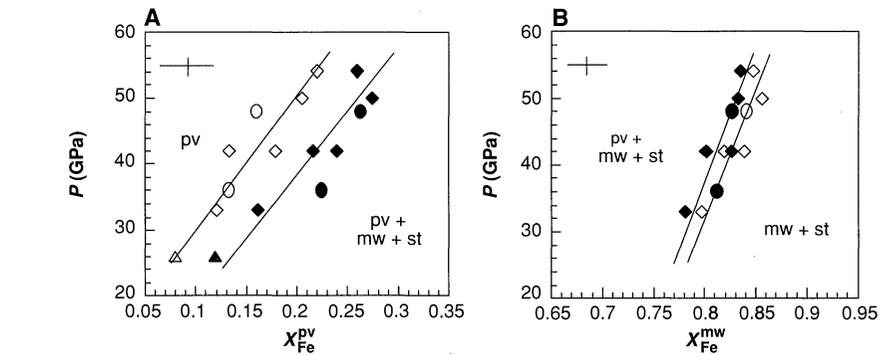


Fig. 2. (A) Maximum Fe composition limit in pv, $X_{\text{Fe}}^{\text{pv}}$, and (B) the coexisting mw composition limit, $X_{\text{Fe}}^{\text{mw}}$, as a function of pressure at 1500 (open symbols) and 2000 K (solid symbols); \blacklozenge , starting composition: En_{60} ; \bullet , starting composition: Fo_{35} ; \blacktriangle , starting composition from (17). The crosses at the upper left corners indicate error bars. The P error was estimated from the pressure variations around the heating spot; the X error is from the uncertainty in lattice parameter refinement (29).

coupled (Fig. 3). The increase in both P and T along the mantle geotherm, therefore, has a compound effect of increasing K . $X_{\text{Fe}}^{\text{mw}}$ and $X_{\text{Fe}}^{\text{pv}}$ could change as much as 30 to 50% (relative to the values at 670 km) within the top one-third of the lower mantle, when a constant bulk composition of $\text{MgO}/(\text{MgO} + \text{FeO}) = 0.88$ (all Fe as Fe^{2+}) is assumed (Fig. 4). $X_{\text{Fe}}^{\text{mw}}$ and $X_{\text{Fe}}^{\text{pv}}$ are also strong functions of the bulk pyroxene/olivine ratio. For a lower mantle with a constant bulk composition, the Fe contents in pv and mw would not be constant; they should reequilibrate and change continuously along the geotherm. Such a change has intriguing consequences for geochemical and geophysical models. For example, at ambient conditions, the $\text{pv} + \text{mw}$ mixture with higher K has higher density than the mixture with lower K (when the same bulk composition is assumed). The density difference, if it persists or increases at high P - T , has an opposite effect to that of thermal expansion.

We observed that ferric iron can be readily added into the pv structure in our

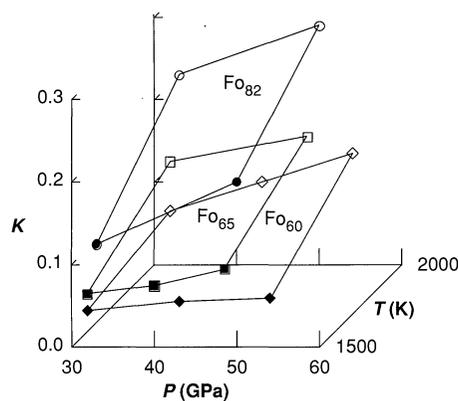


Fig. 3. K of three starting compositions (Fo_{82} , Fo_{65} , and Fo_{60}) as a function of pressure at 1500 and 2000 K; error in K , ± 0.035 .

hematite-containing, ferromagnesian silicate samples free of other trivalent elements. Consequently, the apparent K value (Fe as $\text{Fe}^{2+} + \text{Fe}^{3+}$) increases with increasing Fe_2O_3 . We found that Fe^{2+} is concentrated in mw and Fe^{3+} is concentrated in pv (Table 1). This result is consistent with their crystal chemistry; the ferrous end-member, FeO , has the mw structure, and the ferric Fe end-member, Fe_2O_3 , has the pv structure at high pressures (36, 37). In the closed system, the amount of Fe^{3+} in pv is dictated by the total available Fe^{3+} . In an open system,

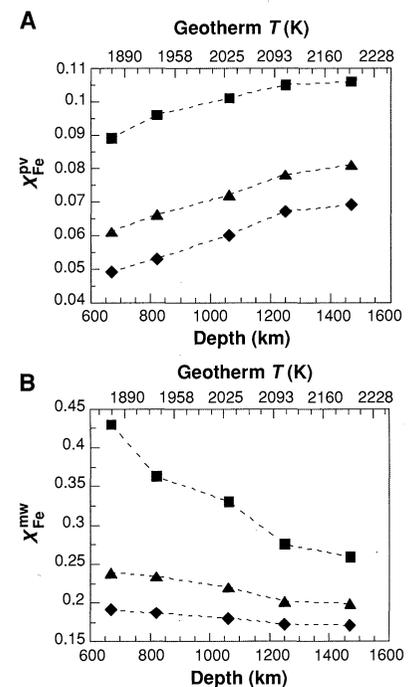


Fig. 4. (A) $X_{\text{Fe}}^{\text{pv}}$ and (B) coexisting $X_{\text{Fe}}^{\text{mw}}$ as functions of depth along the geotherm for bulk pyroxene/olivine composition ratios of 9 (\blacksquare), 1 (\blacktriangle), and 0 (\blacklozenge). All values have a constant bulk composition of $\text{MgO}/(\text{MgO} + \text{FeO}) = 0.88$. Errors, ± 0.03 for $X_{\text{Fe}}^{\text{pv}}$ and ± 0.02 for $X_{\text{Fe}}^{\text{mw}}$.

however, it is conceivable that other trivalent ions, such as Al^{3+} , B^{3+} , and Cr^{3+} , may pair with Fe^{3+} and substitute for the Mg^{2+} - Si^{4+} pair, thus favoring the formation of Fe^{3+} by oxidizing Fe^{2+} . This paired substitution provides an interpretation for the reported increase of the apparent K values in the presence of Al_2O_3 (21), B_2O_3 (23), and a variety of transition-element oxides (such as Ni, Cr, and Mn) (16). Major and trace element partitioning could thus be coupled with ferrous and ferric distributions. The electrical conductivity (8, 10, 38), radiative heat transfer, and melting behavior (9) are all highly dependent on the Fe contents and oxidation states of component phases. Likewise, the density, thermal expansion, and elasticity of the mantle models (4, 7, 39, 40) must be adjusted with variable composition.

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- With regard to oxidation, multianvil presses involve open systems in which the ferric/ferrous ratio is not controlled by the starting samples but varied by a buffering condition specific to the cell assemblage. These experiments demonstrated that adding Al_2O_3 would indirectly assist oxidizing Fe^{2+} to form Fe^{3+} in pv (21, 22). The Al_2O_3 effect, therefore, is a Fe^{3+} effect.
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Impact of Molecular Order in Langmuir-Blodgett Films on Catalysis

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Catalytically active Langmuir-Blodgett films of a rhodium complex were prepared and characterized to determine the possible effect of the molecular order of metal complexes on catalytic activity. The hydrogenation of carbon-oxygen double bonds was used as a model reaction. The complex in solution exhibited low catalytic activity, whereas it was highly active in the film. The catalytic activity was found to be highly dependent on the orientation of the complex within the film. The reactions were also highly selective with regard to the substrate. These observations and the observed rate dependence on temperature strongly implicate the molecular order of a metal complex as an important dimension in catalysis.

Homogeneous catalysis by metal complexes plays a major role in chemical and biological processes and is used for the production of millions of tons of chemicals annually (1). By controlling and modifying the properties of the metal center, the catalytic activity can be optimized and high degrees of efficiency and selectivity can be achieved. Such catalysis generally involves discrete metal complexes that function independently of each other. We are interested in the properties of highly ordered, two-dimensional structures with catalytically active metal complexes. Our approach is based on the generation of Langmuir-Blodgett (LB) films from appropriately modified complexes. This approach allows analysis of the films by well-established analytical methods (2). The catalytic activity

of the film may be controlled by systematic structural modifications. Furthermore, synergistic effects may occur as a result of interactions of molecules in a close-packed LB film.

Recently, an approach to the generation of chemically bound layers of metal complexes, which exhibit catalytic activity quite similar to that of the complexes in solution, was reported (3). We report here on the generation of LB films of a rhodium complex, which show high catalytic activity, whereas the complex exhibits low activity in a homogeneous system. Moreover, the catalyst exhibits remarkably high substrate selectivity and is highly dependent on the order and orientation of the films. The importance of order in the layer is also clearly manifested in the observed dependence of the rate on temperature.

We chose to study the amphiphilic complex 1 (Scheme 1), an analog of the known air- and water-stable hydrogenation catalyst (bipy)rhodium(hexadiene)PF₆ (bipy = bipyridine) (4). This complex was prepared by reaction of the ligand 4,4'-diheptadecyl-2,2'-bipyridine (5) with [Rh(hexadiene)

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