EFFECT OF PARTITIONING IN DETERMINING THE COMPOSITION OF PLANETARY MANTLES, J. Peter Watt and Thomas J. Ahrens, Seismological Laboratory, Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena, California 91125.

Recent static compression studies ((1)-(4)) of olivines and pyroxenes have confirmed formation of solid solutions of magnesiowüstite (mw)-\((\text{Mg,Fe})\text{O}\) and ferromagnesian silicates having the perovskite structure (pv)-\((\text{Mg,Fe})\text{SiO}_3\). For example, for olivine

\[(\text{Mg}_x\text{Fe}_{1-x})_2\text{SiO}_4 + (\text{Mg}_y\text{Fe}_{1-y})_0 + (\text{Mg}_z\text{Fe}_{1-z})\text{SiO}_3 \quad (1)\]

Iron was found to be strongly concentrated in the mw phase, and led to a low value of the partitioning coefficient, \(K\), for the reaction

\[\text{FeO} + \text{MgSiO}_3 \rightleftharpoons \text{MgO} + \text{FeSiO}_3 \quad (2)\]

\[K = \frac{x_{\text{pv}}^\text{pv}}{x_{\text{pv}}^\text{mw}} = \frac{\text{Fe}}{\text{Mg}} \cdot \frac{1-y}{y} \cdot \frac{z}{1-z} \quad (3)\]

between 20 and 45 GPa at 1000°C, where \(x, y,\) and \(z\) denote mole fractions.

In this paper, we calculate a theoretical partitioning coefficient for the MgZFe exchange in (2) using experimental and estimated equation of state data, and examine the effect of iron segregation on lower mantle composition. We find that the concentration of iron in mw can be calculated theoretically, and that the effect on present lower mantle composition is negligible; however, the partitioning may have important implications for the evolution of the Earth's lower mantle in comparison with those of the moon, Mars, and the eucrite parent body, and may provide an important constraint on the composition of the mantle of Venus.

For an ideal solution, simple thermodynamic considerations allow the partitioning coefficient (3) to be written as a function of pressure and temperature as

\[K_T = \exp \left[\frac{-\Delta G_T^P}{RT}\right] \quad (4)\]

where

\[\Delta G_T^P = (\Delta H)_T^0 - T(\Delta S)_T^0 + \int_0^P (\Delta V)_T dP \quad (5)\]

where \(\Delta G, (\Delta H)_T^0,\) and \((\Delta S)_T^0\) are the net changes in Gibbs free energy, standard enthalpy and entropy respectively for reaction (2), \((\Delta V)_T\) the net change in molar volume, \(R\) the gas constant, and \(T\) the absolute temperature. Equation (5) assumes that either the specific heats of the four materials in (2) all have the same temperature variation, or that the temperature is high compared to the Debye temperatures of the mw and pv endmembers.

We estimate \(S_{98}^2\) and \(H_{98}^2\) for the two perovskites from the linear variation of these quantities with molar volume for iron and magnesium solid solution endmembers for a variety of materials. We find \(S_{98}^2\) values of 56.2 and 85.6 J/mole/deg and \(H_{98}^2\) values of -1097.8 and 718.0 kcal/mole for \((\text{MgSiO}_3)_{(pv)}\) and \((\text{FeSiO}_3)_{(pv)}\) respectively. For third-order finite strain equation of state parameters, we use the data of (5) for MgO, (6) for FeO, (1) and (2) for \((\text{MgSiO}_3)_{(pv)}\) and \((\text{FeSiO}_3)_{(pv)}\), and elasticity systematics estimates for \((\text{FeSiO}_3)_{(pv)}\).

Fig. 1 presents the calculated \(K\) curves for comparison with the experimental result (4). The error bars on the preferred equation of state curve...
are the uncertainties introduced by a 1% variation in the $s_{98}$ and $h_{98}$ estimates for $pv$. Also shown are curves using maximum and minimum values of the first pressure derivative of the perovskite bulk modulus (2) - 5 and 3 respectively, and estimated high-pressure phase equation of state parameters for FeO (6). The effect of an increase in temperature is to raise the calculated $K$ curve. Thus, the strong concentration of iron in $mw$ can be accounted for theoretically.

To calculate the effect of $P$ and $T$ variations within the mantle on $K$, we use the pressure distribution of seismic earth model PEM (7) and the temperature profile of Stacey (8), and find that $K$ increases with depth, so that the degree of iron concentration in $mw$ decreases with depth.

Modelling the lower mantle below 700 km using 3rd- and 4th-order finite strain theory, the method of (9) and (10), olivine (ol), pyroxene (px), and peridotite (2ol:1px) stoichiometries, and $mw + pv$ assemblages, we find that the density, bulk modulus, and bulk velocity throughout the lower mantle are changed by at most 0.2% when partitioning is included, so that the segregation of iron in $mw$ has no significant effect on our understanding of the composition of the present mantle.

Following the suggestion of Mao et al. (11) on the effect of partitioning on mantle evolution, we plot in Fig. 2 the densities of the $mw$ and $pv$ components for a peridotite model with an adiabat initial temperature of 900°C at the surface and overall magnesium mole fractions of 0.80, 0.94, and 1.0. For $x_{Mg}=0.94$ (the value which satisfies seismic earth model densities), the densities of the $mw$ and $pv$ components are essentially equal (within 0.1 g/cm$^3$). If iron partitioning is not considered, $\rho_{mw} > \rho_{pv}$ by 0.1-0.3 g/cm$^3$. For $x_{Mg}=0.80$, $\rho_{mw} > \rho_{pv}$ by up to 0.8 g/cm$^3$, while for $x_{Mg}=1.0$, $\rho_{pv} > \rho_{mw}$ by about 0.4 g/cm$^3$. Thus, the iron content of the lower mantle is that for which the densities of $mw$ and $pv$ are essentially equal.

This observation provides a possible explanation for the fact that the earth's mantle is considerably depleted in iron compared to the mantles of the moon, Mars, and the eucrite parent body, where $x_{Mg}$ values are thought to lie in the range 0.70-0.85 ((12)-(15)). A similarly iron-rich initial terrestrial mantle would have an $mw$ component considerably denser than the $pv$ component, and the $mw$ could gravitationally differentiate, with removal of iron occurring at the core-mantle boundary by chemical reduction, direct solution of FeO in metallic iron, or chemical disproportionation (11). The lighter iron-depleted $mw$ would rise, re-equilibrate, and resink, with the cycle repeating until the $mw$ and $pv$ densities were essentially equal. Treating this as a simple Stokes-type problem (16), we find that for grain sizes of the order of 1 mm, a single separation cycle will occur in a few hundred million years or less if lower mantle viscosities are $10^{15}$ Poise or less. This would require mantle temperatures about twice present values, a not unreasonable requirement. This mechanism would transfer iron from the mantle to the core, without changing the total iron content of the earth. Convection would enable even the upper mantle to be reprocessed by this method.

Such a separation mechanism would not have operated on the moon, Mars, or the eucrite parent body, because internal pressures are too low for the formation of $mw + pv$ assemblages. In Venus, pressures are sufficiently high for $mw + pv$ formation, allowing the removal of iron from the mantle, as in the earth. Thus, the mantle of Venus may be more similar to that of the earth than previously thought (17), a conclusion also reached by Anderson (18) using tectonic arguments.

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Fig. 1 Experimental and calculated partitioning coefficient for exchange of iron between mw and pv (reaction (2)).

Fig. 2 Densities of mw and pv components of a peridotite lower mantle for overall Mg mole fractions of 0.80, 0.94, and 1.0. The mw and pv total density for x_Mg = 0.94 satisfies seismic earth model densities.