

THE ROLE OF IRON PARTITIONING IN MANTLE COMPOSITION,  
EVOLUTION, AND SCALE OF CONVECTIONJ. Peter Watt<sup>1</sup> and Thomas J. AhrensSeismological Laboratory, California Institute of Technology,  
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**Abstract.** The effect on composition and evolution of the mantle of the recently-observed strong concentration of iron in (Mg, Fe)O-magnesiowüstite (mw) at the expense of (Mg, Fe)SiO<sub>3</sub>-perovskite (pv) structure is studied by calculating a temperature- and pressure-dependent iron partitioning coefficient for the lower mantle. The value of the standard entropy for MgSiO<sub>3</sub>-perovskite is found to be  $69.4 \pm 10.3$  J/mole deg from the recently determined phase diagram of forsterite. Iron remains concentrated in (Mg, Fe)O throughout the entire lower mantle if account is taken of an FeO phase change, with the partitioning coefficient  $(x_{Fe}^{pv}/x_{Mg}^{pv})/(x_{Fe}^{mw}/x_{Mg}^{mw})$  increasing from 0.04 to 0.8 between 670 km and the core-mantle boundary. Partitioning has negligible effect on gross density and elastic properties of the lower mantle. By using recent shock wave and static compression results for FeO and MgSiO<sub>3</sub>-perovskite, we find that the lower mantle is more pyroxene-rich than the upper mantle and as iron-rich, or somewhat less so, than the upper mantle.  $Mg/(Mg + Fe) = 0.93-0.95$  for the lower mantle compared with  $0.85-0.90$  for the uppermost mantle. The lower mantle Mg/Si ratio is closer to chondritic values ( $0.99 \pm 0.03$ ) than is the upper mantle ( $\approx 1.5$  for a peridotite with  $px/ol = 0.4$  (molar)), thus supporting the idea of a chemically layered mantle with implications for the style of mantle convection. While partitioning of iron has no significant effect on gross lower mantle density, we find that the (Mg, Fe)O and perovskite components of the lower mantle have essentially the same densities. Mantles with higher bulk iron contents have (Mg, Fe)O denser than the perovskite component; for a bulk magnesium mole fraction of 0.80, the density difference is  $0.7-0.8$  g/cm<sup>3</sup>. We investigate the feasibility of the Mao, Bell, and Yagi gravitational separation hypothesis of mantle evolution in which a mantle more iron-rich than present loses iron through gravitational sinking of the denser (Mg, Fe)O, and we conclude that the process cannot successfully compete with solid state convection unless implausibly large grain sizes or unacceptably low viscosities are invoked. A likely explanation for removal of iron from an initially iron rich lower mantle is upward extraction of FeO-enriched basalts or picrites and concentration of iron in upper mantle garnets during accretion of the earth or subsequent

convection with the entire mantle passing through the partial melt zone. Thus the lower mantle was depleted of iron relative to both the upper mantle and the mantles of the small terrestrial planets and satellites, which do not have mantle pressures sufficient to form perovskite-structure silicates, or which had lower accretional temperatures and less extensive melting. On this basis, Venus would be expected to have a mantle similarly depleted in iron.

## Introduction

One of the major issues in the study of the earth's interior is the question of the radial chemical homogeneity of the mantle, the solution of which has important implications for the evolution of the earth and for the style of mantle convection. A chemical boundary at 670 km, say, would either restrict convection to the upper mantle or require two-layer circulation. The present state of the convection problem has recently been reviewed by Stevenson and Turner [1979]. Arguments in favor of whole-mantle convection have been presented by Ringwood [1975], Davies [1977], O'Connell [1977], Sammis et al. [1977], Hager and O'Connell [1978], Sharpe and Peltier [1979], and Davies [1981], among others. The idea of layered convection has been supported by studies such as those of Richter and Johnson [1974], Anderson [1979], Wasserburg and DePaolo [1979], Jeanloz and Richter [1979], Christensen [1981], and Richter and McKenzie [1981], for example.

In this paper, we investigate the effects of the high-pressure behavior of olivines and pyroxenes on mantle composition, evolution, and scale of convection.

Ringwood [1962] suggested that the 670 km seismic discontinuity is caused by a phase transformation to perovskite-structure silicates. In recent years, both experimental evidence for mantle minerals-see, for example, Liu [1979] for a review of high-pressure products of olivines, pyroxenes, and garnets-and studies of analog materials, summarized by Liebermann [1979], have given strong support to the perovskite (pv) hypothesis. Although there is evidence for additional minor discontinuities below 670 km, the properties of the lower mantle from 670 km to the core-mantle boundary appear to be dominated by the perovskite transformation. Anderson [1977] has argued that a pyrolite mantle transforming to perovskite-structure silicates and (Mg, Fe)O cannot explain the 670 km discontinuity. It has been proposed that the lower mantle is mainly FeO-poor perovskites [Sawamoto, 1977; Butler and Anderson, 1978]. Seismic data for the lower mantle appear to be consistent with a mainly pyroxene stoichiometry [Anderson, 1970; Anderson et al., 1971; Gaffney and Anderson, 1973; Burdick

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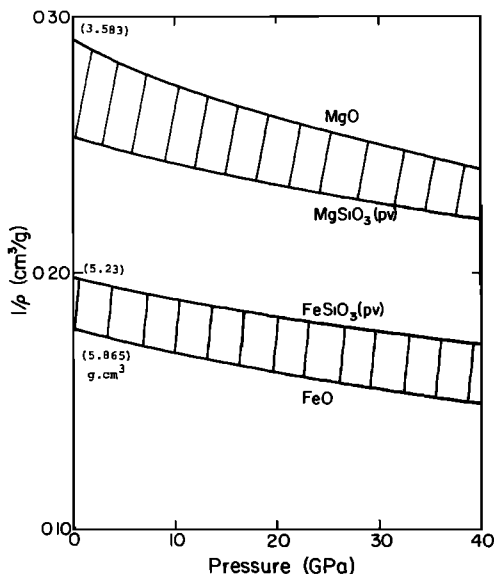
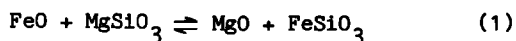


Fig 1. Reciprocal density for MgO, FeO, MgSiO<sub>3</sub>(pv), and FeSiO<sub>3</sub>(pv) vs. pressure calculated from third-order finite strain theory and the equation of state parameters in Table 1. Zero-pressure density values are given in parentheses. Relative densities are unchanged with increasing pressure. The hatched regions enter the partitioning coefficient via equation (5), where  $\Delta V$  is proportional to  $1/\rho$ .

and Anderson, 1975]. Of these studies, only the work of Sawamoto [1977] included experimental data on perovskite-structure silicates; the density of MgSiO<sub>3</sub>-pv was 2.5% lower than the most recent results described below, which now make possible a more detailed study of the relation of seismic models of the lower mantle to specific compositional models.

Data reported by Yagi et al. [1979a] for the lattice parameters of (Mg, Fe)SiO<sub>3</sub>(pv) indicated that the iron-magnesium solid solution extends only from 0.0 to 0.2 mole fraction FeSiO<sub>3</sub>, confirming the results of Liu [1976] who found a maximum Fe mole fraction of 0.3 in the perovskite-structure phase. For more iron-rich orthopyroxenes, (Mg<sub>0.8</sub>Fe<sub>0.2</sub>)SiO<sub>3</sub>(pv) and a mixture of stishovite and magnesiowüstite- (Mg, Fe)O - were formed. Ito and Yamada [1982] reported that perovskites were stable over an even smaller range of 0.0-0.1 mole fraction FeSiO<sub>3</sub>. Thus for realistic Mg mole fractions in the mantle ( $x_{Mg} > 0.85$ ), oxide mixtures may also occur, as well as perovskite-structure silicates. The bulk modulus of MgSiO<sub>3</sub> was determined to be  $260 \pm 20$  GPa [Yagi et al., 1979b], in accord with the estimate of Liebermann et al. [1977] based on elasticity systematic relationships.

The most important result of these studies is the very strong segregation of iron into the magnesiowüstite (mw) phase [Bell et al., 1979]. For the exchange of iron between mw and pv,



the partition coefficient  $K$  is defined as

$$K = \left( \frac{x_{\text{Fe}}^{\text{pv}}}{x_{\text{Mg}}^{\text{pv}}} \right) \cdot \left( \frac{x_{\text{Fe}}^{\text{mw}}}{x_{\text{Mg}}^{\text{mw}}} \right)^{-1} \quad (2)$$

where  $x_a^b$  is the mole fraction of element  $a$  in phase  $b$ . Bell et al. report  $K = 0.08$  for pressures between 25 and 45 GPa and temperatures around 1000°C, indicating strong depletion of iron in pv with respect to mw. This segregation of iron is much more dramatic than that which occurs for upper mantle phases and pressure and temperature conditions; theoretical estimates appear in the work of Ahrens [1972, 1973], while experimental results are given by Akimoto et al. [1976] and Akaogi and Akimoto [1979].

Since the density difference between the mw iron and magnesium end members ( $\rho(\text{FeO}) = 5.865$  g/cm<sup>3</sup>,  $\rho(\text{MgO}) = 3.583$  g/cm<sup>3</sup>,  $\Delta\rho = 2.28$  g/cm<sup>3</sup>) is double that of the pv end members ( $\rho(\text{FeSiO}_3\text{-pv}) = 5.23$  g/cm<sup>3</sup> extrapolated from the lattice parameter data of Yagi et al. [1979a],  $\rho(\text{MgSiO}_3) = 4.10$  g/cm<sup>3</sup>,  $\Delta\rho = 1.13$  g/cm<sup>3</sup>), one might expect that for a given initial unpartitioned composition, the concentration of iron in mw upon partitioning would yield a higher mw + pv density than for an unpartitioned mw + pv assemblage. Figure 1 shows that the relative densities of MgO, FeO, Mg-pv, and Fe-pv persist at depth. Conversely, to produce a given gross density in the lower mantle, one might expect the partitioned mw + pv assemblage to require a lower overall iron content than an unpartitioned mixture. One of the aims of this paper is to investigate this possibility.

Mao et al. [1979] found that for olivine with a bulk iron mole fraction of 0.1, which satisfies the density of the Parametric Earth Model (PEM) [Dziewonski et al., 1975], the densities of the mw and pv components in the lower mantle are essentially equal, assuming that the experimental value of  $K (= 0.08)$  holds throughout the lower mantle. For higher bulk iron contents,  $\rho_{\text{mw}} > \rho_{\text{pv}}$ . They speculated that if the mantle were more iron-rich in the past, gravitational sinking of the denser mw could occur. Near the core-mantle boundary, the iron-rich mw could lose some iron to the core by processes such as chemical reduction, direct solution of FeO in the core, [Ringwood 1977a], or chemical disproportionation [Mao and Bell, 1977]. The remaining mw, somewhat depleted in iron, could float or convect to be reequilibrated with the pv. Repeated operation of this cycle could lead to the present situation where  $\rho_{\text{mw}} \approx \rho_{\text{pv}}$ , and the process would cease. A similar suggestion of separation of FeO because of density differences in a flotive Fe-Si-O mantle was made by Shimazu [1956].

We find this hypothesis appealing. It could explain the fact that the earth, the largest terrestrial planet, has its mantle depleted in iron relative to the mantles of other bodies such as the moon, Mars, and the eucrite parent body (EPB). An overview of planetary compositions has been given by Smith [1979]. Figure 2 shows Mg/(Mg + Fe) estimates for these bodies versus pressures at the base of their mantles. If the earth's mantle had a similarly high iron content at some earlier time, the gravitational settling mechanism could explain an evolution to its present iron content. Such a process would not occur on the moon, the EPB, or Mars (except perhaps near the bottom of the Martian mantle) because pressures required for formation of mw + pv from olivines and pyroxenes (>20 GPa) are higher than those at the bases of the mantles of

these bodies. On the other hand, internal pressures and accretional heating in Venus are similar to the earth. Thus if gravitational separation of  $m_w$  is feasible for the earth, then it should also occur on Venus, making the composition of the Venusian mantle more similar to that of the earth than has previously been supposed [Ringwood and Anderson, 1977], a conclusion reached by Anderson [1980] on petrologic and tectonic grounds and by Morgan and Anders [1980] from a study of fractionation processes in the solar nebula.

We estimate that gravitational sinking of  $m_w$  in a terrestrial mantle with initial  $x_{Mg} = 0.75$  would account for between 10 and 20% of the mass of the present core, assuming maximum efficiency for the process. Thus this mechanism, while not the dominant means of core formation, could still produce an appreciable portion of the core. Accordingly, a second aim of this paper is to investigate the feasibility of the gravitational settling of  $m_w$  hypothesis.

#### Calculated Lower Mantle Partitioning of Iron

In order to explore the geophysical consequences of iron partitioning between  $m_w$  and  $p_v$ , we calculate the variation of  $K$  with pressure and temperature, in a manner similar to the studies of Ahrens [1972, 1973] for iron partitioning among upper mantle olivines, pyroxenes, and garnets.

For an ideal solution, equation (2) can be written as [Kern and Weisbrod, 1967]

$$K = \exp [-(\Delta G)_T^P / RT] \quad (3)$$

where  $(\Delta G)_T^P$  is the net change ( $\Sigma$  products -  $\Sigma$  reactants) in Gibbs free energy for reaction (1) at pressure  $P$  and temperature  $T$ ,  $R$  is the gas constant, and  $T$  is the absolute temperature. Simple thermodynamics allows  $(\Delta G)_T^P$  to be expressed as

$$\begin{aligned} (\Delta G)_T^P &= (\Delta H)_{298}^0 - T(\Delta S)_{298}^0 + \int_{298}^T (\Delta C_p)^0 dT' \\ &\quad - T \int_{298}^T [(\Delta C_p)^0 / T'] dT' + \int_1^P (\Delta V)_T dP' \quad (4) \end{aligned}$$

where  $(\Delta H)_{298}^0$  and  $(\Delta S)_{298}^0$  are the net changes in standard enthalpy and entropy, respectively, for reaction (1),  $(\Delta C_p)^0$  is the net change in specific heat at  $P^0 = 1$  atm, and  $(\Delta V)_T$  is the net change in molar volume at temperature  $T$ . Evidence for ideality of magnesioferrites comes from the lattice parameter-composition studies of Hahn and Muan [1962], Hentschel [1970], Jackson et al. [1978], Rosenhauer et al. [1976], and Bonczar and Graham [1982]. The situation is complicated by departures from a linear lattice parameter-composition relationship at the iron-rich end of the series, caused by the presence of  $Fe^{3+}$  and associated vacancy concentrations [Simons, 1980]. The careful sample characterization of Bonczar and Graham [1981] reveals a nearly perfect correlation between deviation from linear behavior and degree of nonstoichiometry, indicating that  $m_w$  'nonideality' is not caused by imperfect mixing. The limited data on perovskite-structure silicates [Liu, 1976; Yagi et al., 1979a] show no significant departures from ideality.

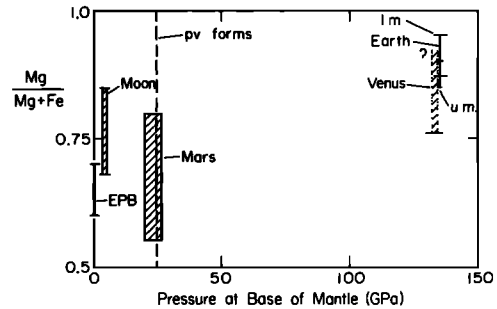


Fig. 2.  $Mg/(Mg + Fe)$  for the earth, Mars, the moon, the eucrite parent body (EPB), and Venus vs. pressure at the base of the mantles of these bodies. Composition estimates for the earth are from Ringwood [1975] (upper mantle) and present work (lower mantle), for Mars from Arvidsen et al. [1980] and Anderson and Baumgardner [1980], for the moon from Ringwood [1977b], Goins et al. [1978], Binder [1980], and Buck and Toksöz [1980], for the eucrite parent body from Stolper [1977], and for Venus from Ringwood and Anderson [1977] Anderson [1980], and present work.

We ignore the  $(\Delta C_p)^0$  integrals in (4), thus assuming either that the four phases in (1) have the same temperature variation of specific heat, or that temperatures are close to, or higher than, the Debye temperatures of the phases. Acoustic Debye temperatures are  $665^\circ C$  for  $MgO$  [Anderson et al., 1968],  $217^\circ C$  for  $FeO$  [Jackson et al., 1978],  $722^\circ C$  for  $MgSiO_3(pv)$  (Yagi et al. [1979b]; elasticity systematics of Liebermann et al. [1977]), and  $599^\circ C$  (systematics estimates) for  $FeSiO_3(pv)$ . Thus for the temperatures of the partitioning experiments [Bell et al., 1979], or for temperatures in the lower mantle, this is an excellent assumption and equation (4) becomes

$$(\Delta G)_T^P = (\Delta H)_{298}^0 - T(\Delta S)_{298}^0 + \int_1^P (\Delta V)_T dP' \quad (5)$$

The  $(\Delta V)_T$  term in (5) requires a knowledge of the variation of molar volume (or density) with pressure. We use a third-order Birch-Murnaghan equation of state with the zero-pressure density  $\rho_0$ , bulk modulus  $K_0$ , and first pressure derivative of the bulk modulus  $K_0'$  specified for each phase, adjusted for temperature effects by using the thermal expansion coefficient  $\alpha$  and the first temperature derivative of the bulk modulus  $\partial K/\partial T$ , as in the work of Watt and O'Connell [1978]. Third-order finite strain is adequate for calculation of densities, and hence molar volumes, to pressures at the core-mantle boundary-see, for example, Banerdt and Sammis [1980]; however fourth-order terms must be included to adequately represent elastic properties. The parameters used for the phases in (1) are collected in Table 1. The bulk modulus of  $FeSiO_3(pv)$  is estimated from elasticity systematics [Liebermann et al., 1977]. The  $MgSiO_3(pv)$  value of  $\partial K/\partial T$  is estimated from data on other perovskite-structure compounds, while the value of  $\alpha(pv)$  is estimated from the proportionality of  $\alpha$  to the product of the cation and anion charge valence [Jones, 1976]. The estimates for a high-pressure phase of  $FeO$  are derived from shock wave experiments of Jeanloz and Ahrens [1980]. A phase transformation in  $FeO$  has been confirmed by Zou

TABLE 1. Equation of State Parameters

	MgO	FeO	MgSiO <sub>3</sub> (pv) <sup>3</sup>	FeSiO <sub>3</sub> (pv) <sup>3</sup>
$\rho_0$ , g/cm <sup>3</sup>	3.583 <sup>a</sup>	5.865 <sup>d</sup> (6.05) <sup>e</sup>	4.10 <sup>i</sup>	5.23 <sup>k</sup>
$K_0$ , GPa	163. <sup>a</sup>	182. <sup>d</sup> (195.) <sup>e</sup>	260. <sup>j</sup>	250. <sup>g</sup>
$\partial K_0/\partial P$ , dimensionless	3.9 <sup>a</sup>	3.2 <sup>f</sup> (3.4) <sup>e</sup>	4.0 <sup>j</sup>	4.0 <sup>g</sup>
$\partial K_0/\partial T$ , GPa/ <sup>o</sup> C	-0.016 <sup>b</sup>	-0.016 <sup>g</sup>	-0.025 <sup>g</sup>	-0.025 <sup>g</sup>
$\alpha$ , 10 <sup>-6</sup> / <sup>o</sup> C	31.5 <sup>c</sup>	37.5 <sup>h</sup>	35. <sup>g</sup>	35. <sup>g</sup>

<sup>a</sup>Spetzler [1970].<sup>b</sup>Anderson and Andreatch [1966].<sup>c</sup>White and Anderson [1966].<sup>d</sup>Jackson et al. [1978].<sup>e</sup>High-pressure phase [Jeanloz and Ahrens, 1980].<sup>f</sup>Jeanloz and Ahrens [1980].<sup>g</sup>Estimated.<sup>h</sup>Calculated from data in Clark [1966].<sup>i</sup>Calculated from lattice parameters of Yagi et al. [1979a].<sup>j</sup>Yagi et al. [1979b].<sup>k</sup>Extrapolated from lattice parameters of Yagi et al. [1979a].

et al. [1980]; however, it is not clear what the structure of the high-pressure phase is [Jackson and Ringwood, 1981; Navrotsky and Davies, 1981].

The standard enthalpies and entropies of the four phases in (1) are needed for the  $(\Delta H)_{298}^0$  and  $(\Delta S)_{298}^0$  terms in (5). These are available for MgO and FeO [Robie et al., 1978] and are listed in Table 2; however, these data do not exist for perovskite-structure silicates and must be estimated.

Various empirical methods exist for estimating  $S_{298}^0$  values for minerals, summarized by Helgeson et al. [1978], but while they can yield good approximations for certain groups of minerals, none of them are of universal applicability. Additional complications, the effects of which on the empirical relations are unknown, arise because of the change of phase to the perovskite structure with its attendant change in coordination. Accordingly, we estimate  $S_{298}^0$ (MgSiO<sub>3</sub>-pv) from the P-T diagram of forsterite and fix  $(\Delta H)_{298}^0$ (MgSiO<sub>3</sub>-pv) from the experimental K value determined by Bell et al. [1979]. Similar approaches have been used by Ahrens and Syono [1967] for the reactions forsterite → oxides and enstatite → oxides and Mao et al. [1969] for the reaction fayalite (α) → fayalite (spinel).

For a given phase transformation occurring at pressure P and 298°C, the net Gibbs free energy for the reaction vanishes:

$$0 = (\Delta G)_{298}^P = (\Delta G)_{298}^0 + \int_1^P (\Delta V)_{298} dP \quad (6)$$

The P-ρ curves for the four phases can be used to calculate the pressure integral in (6) and the  $(\Delta G)_{298}^0$  term is given by

$$(\Delta G)_{298}^0 = (\Delta H)_{298}^0 - 298(\Delta S)_{298}^0 \quad (7)$$

The slope of the equilibrium line in P-T space is given by the Clausius-Clapeyron equation:

$$dP/dT = (\Delta S)_{298}^P / (\Delta V)_{298}^P \quad (8)$$

and  $S_{298}^0$  can then be obtained from

$$S_{298}^P - S_{298}^0 = - \int_1^P (\gamma C_V / K) dP \quad (9)$$

where  $\gamma$  is Grüneisen's constant and  $C_V$  is the specific heat at constant volume. We assume that  $\gamma/v$  is constant.  $(\Delta H)_{298}^0$  is then calculated from equation (7).

Figure 3 shows the P-T diagram for forsterite (Mg<sub>2</sub>SiO<sub>4</sub>). The α → β and β → γ phase boundaries are from Suito [1977]; the γ → MgO + MgSiO<sub>3</sub>(pv) boundary is the recent determination of Ito<sup>3</sup> and Yamada [1982].  $S_{298}^0$  and  $(\Delta H)_{298}^0$  values are computed from the phase boundaries successively for fo(β), fo(γ), and MgSiO<sub>3</sub>(pv). The necessary equation of state data are given in Table 3.

Table 4 shows results for the calculation of  $S_{298}^0$  and  $\Delta H_{298}^0$  for the β and γ phases of forsterite and for MgSiO<sub>3</sub>(pv). Ahrens and Syono [1967] estimated the thermochemical properties of γ-forsterite, assuming formation directly from the phase, and found  $S_{298}^0 = 75.3$  J/mole deg from density-entropy systematics for normal spinels and  $\Delta H_{298}^0 = 2144.3 (+3.3)$  kJ/mole assuming that γ-forsterite has the same P-ρ behavior as MgO. These estimates are in good agreement with our results based on more complete data for γ-Mg<sub>2</sub>SiO<sub>4</sub>. The value of  $S_{298}^0$  for MgSiO<sub>3</sub>(pv) is somewhat higher than that of MgSiO<sub>3</sub>(enstatite) (67.8 J/mole deg [Helgeson, 1978]), although the uncertainty is large. Navrotsky [1980] predicted a larger entropy for MgSiO<sub>3</sub>(pv) compared to the low-pressure phase based on metal-oxygen distance and coordination change arguments. Similar behavior has been observed in the ilmenite-perovskite transformation in CdTiO<sub>3</sub> [Neil et al., 1971]. Since the errors in entropies obtained from P-T diagrams are fairly large, calorimetric investigations of MgSiO<sub>3</sub>(pv) will be of great interest.

Since FeSiO<sub>3</sub>(pv) is not thermodynamically stable with respect to FeO and SiO<sub>2</sub> (stishovite) [Yagi et al., 1979a; Ito and Yamada, 1982], we must estimate  $S_{298}^0$  and  $\Delta H_{298}^0$  in Table 2. The first values have been determined assuming that  $\Delta H_{1273}^0$ (FeO + FeSiO<sub>3</sub>-pv) =  $\Delta G_{1273}^0$ (FeO + FeSiO<sub>3</sub>-

TABLE 2.  $S^0$  and  $\Delta H^0$  (With Respect to Elements)

	$S_{298}^0$ , J/mole °K	$\Delta H_{298}^0$ , kJ/mole
MgO	26.94	-601.49
FeO	59.80	-272.04 <sup>3</sup>
MgSiO <sub>3</sub> -pv	69.4 <sup>a</sup>	-1430.1 <sup>a</sup>
FeSiO <sub>3</sub> -pv(estimated)	61.0 <sup>b</sup>	-1118.4 <sup>b</sup>
	96.7 <sup>c</sup>	-1073.6 <sup>c</sup>

<sup>a</sup>Calculated from Mg<sub>2</sub>SiO<sub>4</sub> P-T diagram and experimental partitioning coefficient.<sup>b</sup> $S_{298}^0$  fixed by experimental partitioning coefficient.<sup>c</sup> $S_{298}^0$  fixed by analogy with MgSiO<sub>3</sub>-pv.

pv) =  $-\int_1^P (\Delta V)_{1273} dP'$ , and taking  $P(\gamma \rightarrow \text{FeO} + \text{FeSiO}_3\text{-pv})$  as 15.5 GPa (Yagi et al. [1979b] for  $\gamma \rightarrow \text{FeO} + \text{stishovite}$ ) and then fixing  $S_{298}^{\circ}$  ( $\text{FeSiO}_3\text{-pv}$ ) from the experimental partitioning coefficient. The second set of values was estimated by taking  $S_{298}^{\circ}$  ( $\text{FeSiO}_3\text{-pv}$ ) as 2.4% higher than  $\text{FeSiO}_3$  (ferrosillite),<sup>3</sup> the same amount that  $S_{298}^{\circ}$  ( $\text{MgSiO}_3\text{-pv}$ ) is larger than  $S_{298}^{\circ}$  ( $\text{MgSiO}_3\text{-enstatite}$ ),<sup>3</sup> and calculating  $(\Delta H)_{298}^{\circ}$  ( $\text{FeSiO}_3\text{-pv}$ ) from the partitioning coefficient. We prefer the first approach as being less artificial. The second set of values leads to a more rapid increase of the computed partitioning coefficient with depth for mantle pressures and temperatures.

Figure 4 shows the calculated lower mantle partitioning coefficient as a function of pressure to the core-mantle boundary. We assume an adiabatic temperature profile and plot results for adiabats initiated at surface temperatures of 1000 and 1400°C, corresponding to temperatures of about 1550 and 2250°C respectively, at 120 GPa ( $\approx 2600$  km depth). The solid curves were calculated assuming no phase change in FeO and indicate that the segregation of iron in mw decreases rapidly with depth until at about 80 GPa ( $\approx 1900$  km),  $K \approx 1$ . At greater depths, iron is segregated into the perovskite phase. The segregation decreases with increasing adiabat

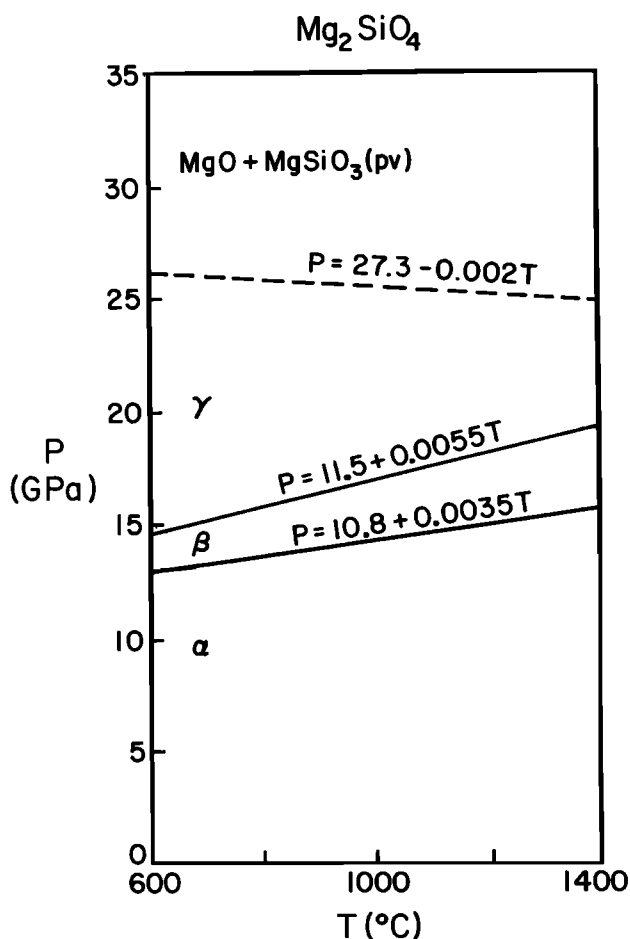


Fig. 3. Pressure-temperature diagram for forsterite. The  $\alpha \rightarrow \beta$  and  $\beta \rightarrow \gamma$  phase boundaries are from Suito [1977], while the  $\gamma \rightarrow \text{MgO} + \text{MgSiO}_3(\text{pv})$  boundary is from Ito et al. [1982].

TABLE 3. Equation of State Data for Forsterite Phases

	Fo( $\alpha$ )	Fo( $\beta$ )	Fo( $\gamma$ )	MgO	MgSiO <sub>3</sub> (pv)
$\rho_0$ , g/cm <sup>3</sup>	3.222 <sup>a</sup>	3.467 <sup>c</sup>	3.549 <sup>c</sup>	3.584 <sup>f</sup>	4.10 <sup>h</sup>
$K_0$ , GPa	129. <sup>a</sup>	166. <sup>c</sup>	213. <sup>c</sup>	163. <sup>f</sup>	260. <sup>i</sup>
$\partial K / \partial P$ , dimensionless	5.2 <sup>a</sup>	4.5 <sup>d</sup>	4.5 <sup>d</sup>	3.9 <sup>f</sup>	4.0 <sup>i</sup>
$\gamma$ , dimensionless	1.13 <sup>a</sup>	1.13 <sup>d</sup>	1.27 <sup>e</sup>	1.54 <sup>g</sup>	1.5 <sup>d</sup>
$C_v$ , J/mole <sup>o</sup> K	118. <sup>b</sup>	120. <sup>d</sup>	120. <sup>d</sup>	37.3 <sup>b</sup>	120. <sup>j</sup>

<sup>a</sup>Graham and Barsch [1969] and Kumazawa and Anderson [1969].

<sup>b</sup>Robie et al. [1978].

<sup>c</sup>Mizukami et al. [1975].

<sup>d</sup>Estimated.

<sup>e</sup>Suzuki et al. [1979].

<sup>f</sup>Spetzler [1970].

<sup>g</sup>Anderson and Andreatch [1969].

<sup>h</sup>Calculated from lattice parameters of Yagi et al. [1979a].

<sup>i</sup>Yagi et al. [1979b].

<sup>j</sup>Helgeson et al. [1978] value for enstatite.

initial temperature. If the phase change in FeO is included, the dashed curves result, with  $K < 1$  throughout the entire lower mantle, indicating that iron remains concentrated in mw at all depths, although less markedly so with increasing depth. The segregation decreases with increasing adiabat initial temperature.

Thus the concentration of iron in mw at the expense of pv decreases with depth in the lower mantle, with the high-pressure phase of FeO having a major influence on whether or not iron becomes concentrated in the pv phase in the lowermost mantle.

#### Effect of Partitioning on Lower Mantle Composition

We investigate the effect of iron partitioning on composition of the lower mantle by considering three simple chemical models: olivine, pyroxene, and a model peridotite (2 ol:1 px) that approximates the composition of the upper mantle [Nokolds, 1954; Graham and Dobrzykowski, 1976].

In Figure 5, we examine the effect of partitioning on the gross zero-pressure density of our model peridotite. We plot the magnesium mole fractions for coexisting partitioned mw and pv phases versus bulk unpartitioned magnesium mole fraction for two values of  $K$  ( $= 0.1$  and  $0.01$ ). We also plot the density of the mixed-oxide ( $\text{Mg}_{1-x}\text{Fe}_x\text{O}$ ) + stishovite assemblage. It is apparent that partitioning has only a very small effect on gross density, and for plausible mantle bulk magnesium mole fractions,  $x_{\text{Mg}} > 0.80$ , the effect is negligible.

We follow the approach of Watt and O'Connell [1978] for both mixed-oxide and mw + pv assemblages, varying  $x_{\text{Mg}}$ , the bulk magnesium mole

TABLE 4.  $S_{298}^{\circ}$  and  $\Delta H_{298}^{\circ}$  Values Calculated for High-Pressure Phases of  $Mg_2SiO_4$

	$S_{298}^{\circ}$ , J/mole $^{\circ}K$	$\Delta H_{298}^{\circ}$ , kJ/mole <sup>a</sup>
Fo( $\alpha$ )	95.19 <sup>b</sup> (+0.84)	-2170.37 <sup>b</sup> (+1.32)
Fo( $\beta$ )	85.3 (+3.5)	-2143.2 (+4.1)
Fo( $\gamma$ )	82.3 (+5.7)	-2135.9 (+5.4)
MgSiO <sub>3</sub> (pv)	69.4 (+10.3)	-1430.1 (+15.1)

<sup>a</sup>With respect to elements.

<sup>b</sup>Robie et al. [1978].

fraction, and  $T_0$ , the adiabat initial temperature, for the models until density and bulk modulus profiles for PEM and C2 [Anderson and Hart, 1976] are matched below 670 km. The differences between PEM and the most recent standard earth model—Preliminary Reference Earth Model (PREM) [Dziewonski and Anderson, 1981] are not significant for our purposes. Since we do not model the shear modulus, we cannot use the Hashin-Shtrikman bounds for the bulk modulus; instead, we use the Voigt-Reuss-Hill average. The resulting theoretical uncertainty is at most +6 GPa. Although the finite-strain equations are coupled in  $x_{Mg}$  and  $T_0$ , the coupling is very weak for the range of parameters used here:  $x_{Mg}$  basically controls the density, while  $T_0$  controls the bulk modulus. We use the data of Table 1 and assume linear variation of density, bulk modulus, and  $\partial K/\partial P$  with  $x_{Mg}$ , a good assumption for mw given the errors and scatter in the experimental data (see, for example, Bonczar and Graham [1982]) and also for pv where compositions are confined to the Mg-rich end of the solid solution. For stishovite, we take  $\rho = 4.29$  g/cm<sup>3</sup>,  $K = 280$  GPa and  $\partial K/\partial P = 5.0$  [Liebermann et al., 1976],  $\alpha = 18 \cdot 10^{-6}/^{\circ}C$  [Weaver et al., 1973], and  $\partial K/\partial T = -0.035$  GPa/ $^{\circ}C$  [Graham, 1973].

Figure 6 shows  $\rho$  versus  $P$  plots for the peridotite model with  $x_{Mg} = 0.94$  to match the mw + pv density to the PEM and C2 values. The solid line is the result for both partitioned and unpartitioned cases, so that the effect of partitioning is negligible, given the assumptions stated above.

Figure 7 shows the bulk modulus versus  $P$  results for the same model with  $T_0 = 900^{\circ}C$  to match PEM and C2. Again, the partitioning effect is negligible. Third-order finite strain is clearly inadequate to account for the seismic model bulk modulus throughout the entire lower mantle. In accord with the results of Banerdt and Sammis [1980], significant deviations begin to occur when  $P \approx 0.15K$  and at lower pressures for more olivine-rich models. Fourth-order finite strain is needed to fit the seismic models adequately, with values of  $\partial^2 K/\partial P^2$  between  $-0.02$  and  $-0.05$  GPa<sup>-1</sup>, in agreement with the estimates of Davies and Dziewonski [1975], but larger than the value of  $-0.10$  GPa<sup>-1</sup> suggested by Graham and Justice [1980]. Addition of fourth-order terms

has essentially no effect on  $T_0$ . Fourth-order finite strain still fails to fit the lowermost 200–300 km mantle (region D<sup>n</sup>), where strong velocity gradients or lateral variations in properties have been proposed by Lay and Helmberger [1981] from studies of SH waves.

Table 5 summarizes the  $x_{Mg}$  and  $T_0$  values required in the three models to fit PEM and C2  $\rho$  and  $K$  profiles. It can be seen that the mw + pv models require less iron than the mixed oxides, and that there are not large differences between olivine and pyroxene  $x_{Mg}$  values. Significant differences arise in the temperatures at which mantle adiabats must be initiated, with pyroxene-rich lower mantles requiring hotter geotherms than olivine-rich lower mantles.

We test the plausibility of these  $T_0$  values, and hence of the chemical models, by computing adiabats for the lower mantle as in the work of Watt and O'Connell [1978]. In Figure 8, we compare the calculated profiles with two recent literature lower mantle geotherms which make no compositional assumptions—Stacey [1977a] and Brown and Shankland [1981]; however, these geotherms assume a homogeneous mantle with no thermal boundary layers. We note that geotherms derived by Jeanloz and Richter [1979] and Anderson and Baumgardner [1980] using specific compositions lie between these two profiles. We estimate uncertainties in the calculated model temperature profiles by considering the effect of errors in the equation of state parameters in Table 1. The chief uncertainties for mw + pv occur in the  $\partial K/\partial P$  and  $\partial K/\partial T$  values for the pv component and contribute an error of about  $\pm 800^{\circ}C$  at the core-mantle boundary. Obviously, experimental determination of these quantities is of great interest. The effect of a phase change in FeO or changes in the value of  $\alpha$  for the pv component have only a small effect ( $\approx 50^{\circ}C$ ). Thus it appears that an mw + pv lower mantle more pyroxene-rich than the upper mantle is needed to yield sufficiently high temperatures for compatibility with composition-independent geotherms.

In order to produce the same temperatures in a mixed-oxide lower mantle, we would require a higher stishovite  $\partial K/\partial P$  than used here; we estimate 7 or higher. The final Brillouin scattering

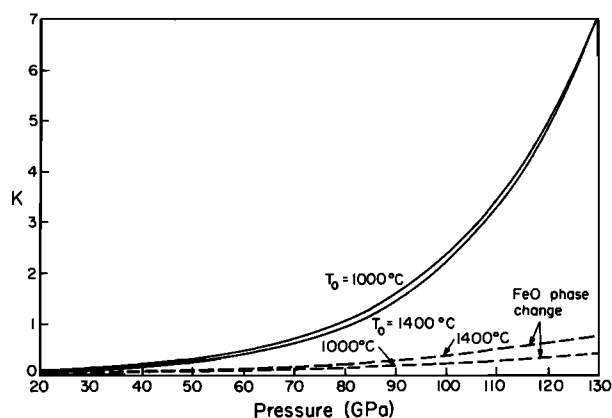


Fig. 4. Calculated iron partitioning coefficient for reaction (1) for adiabats initiated at the surface at temperatures of 1000 $^{\circ}$  and 1400 $^{\circ}$ C. The dashed curves include the phase change in FeO observed by Jeanloz and Ahrens [1980].

data of Weidner et al. [1980] on single-crystal stishovite, combined with existing static compression measurements, should provide the data necessary to resolve this question.

We estimate that uncertainties in the equation of state parameters could decrease the magnesium mole fractions in Table 5 by up to 0.08, so that the iron content of the lower mantle could be similar to, or lower than, that of the upper mantle; however, the preferred solutions have  $x_{Mg}$  values between 0.93 and 0.95 indicating that the lower mantle is more magnesium-rich than the upper mantle. The effect of an FeO phase change is very small (an increase of at most 0.01), as would be expected at the magnesium-rich end of the solid solution.

Recent shock wave studies on  $(Mg_{0.6}Fe_{0.4})O$  by Vassiliou and Ahrens [1981] suggest that intermediate composition magnesiowüstites may be less compressible at high temperatures than would be inferred from a linear interpolation between the end members. By using equation of state parameters from the shock wave experiments, we find that the  $T_0$  values in Table 5 are increased by 500°C at most for mixed oxides and 300°C for mw + pv, while the  $x_{Mg}$  values are reduced by at most 0.02— a slightly more iron-rich lower mantle results.

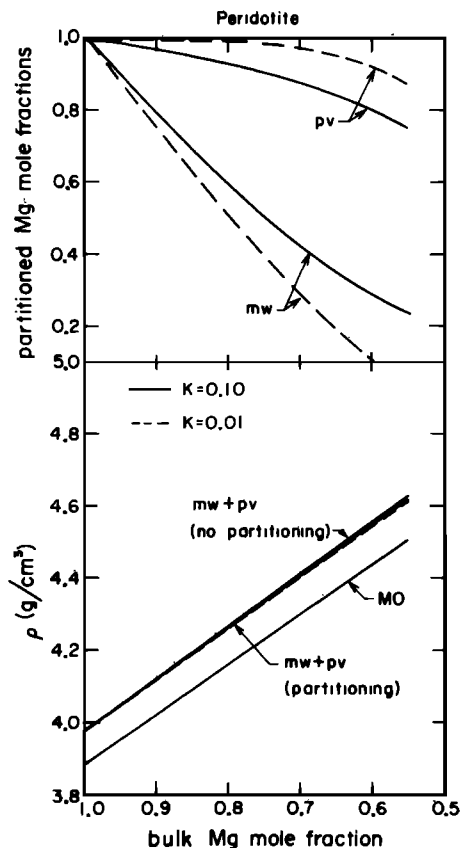


Fig. 5. Magnesium mole fractions in coexisting mw and pv of peridotite stoichiometry (2 ol:1 px) as a function of bulk unpartitioned magnesium mole fraction for values of 0.10 and 0.01 for the iron partition coefficient. Also plotted are the gross densities of the mw + pv assemblages with and without partitioning, as well as the densities of simple mixed-oxide (MO) assemblages.

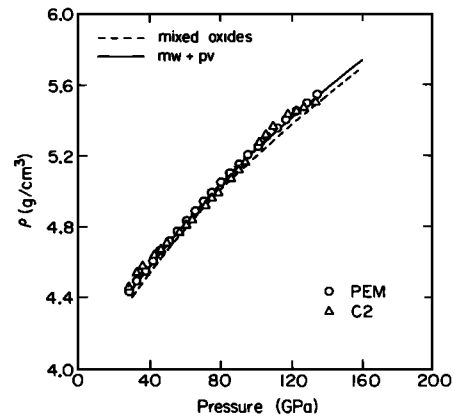


Fig. 6. Density versus pressure for mixed-oxide and mw + pv lower mantles of peridotite (2 ol:1 px) stoichiometry. A bulk magnesium mole fraction of 0.94 is used to match the mw + pv curve to PEM and C2 profiles. The mw + pv curve is for both partitioned and unpartitioned cases.

Pyroxene-rich lower mantles were excluded in the study of Watt and O'Connell [1978] because even iron-free  $MgSiO_3$  under lower mantle conditions was denser than seismic model values. The estimate of  $\alpha(pv)$  described above is the linear thermal expansion, and this value was incorrectly used by Watt and O'Connell rather than the volume thermal expansion given in Table 1. Additionally, the recent improved elasticity data of Jackson et al. [1978], Jeanloz and Ahrens [1980], and Bonczar and Graham [1982] for FeO differ considerably from that of Mizutani et al. [1972] used by Watt and O'Connell.

We can conclude that, within the uncertainties in our knowledge of mechanical and thermal properties, iron segregation in mw has no detectable effect on gross density and elastic properties of the lower mantle. A magnesiowüstite + perovskite lower mantle appears to be more pyroxene-rich (lower Mg/Si ratio) than the upper mantle and as iron-rich, or somewhat less so, than the upper mantle. A pyroxene-rich lower mantle has been proposed earlier by Anderson [1970], Anderson et al. [1971], Gaffney and Anderson [1973], Burdick and Anderson [1975], and Butler and Anderson [1978]. Thus the Mg/Si ratio in the lower mantle is closer to the chondritic value of  $0.99 \pm 0.03$  [Ross and Aller, 1976], corresponding to pure pyroxene, than to the upper mantle, where  $Mg/Si \approx 1.5$  for a peridotite with  $px/ol = 0.4$  (molar) and  $x_{Mg} = 0.88$ , as suggested by Anderson [1977]. These differences in Mg and Si contents would present a chemical barrier to single-cell convection extending deep into the lower mantle, a barrier that does not necessarily appear if only Mg and Fe contents of the upper and lower mantles are considered [e.g., Mao, 1974; Watt et al., 1975].

The above arguments apply to a lower mantle modelled in terms of (Mg, Fe) silicates. Jackson and Ahrens [1979] have considered the effect of calcium and aluminum (11 weight % total) in a pyrolite mantle and used 120 GPa shock compression data to estimate Hugoniot densities in the lowermost mantle. By using their analysis, we calculate that including calcium and aluminum

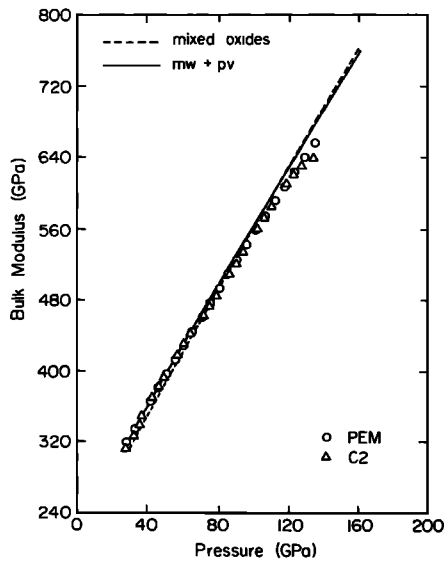


Fig. 7. Bulk modulus versus pressure for mixed-oxide and mw + pv lower mantles of peridotite (2 ol:1 px) stoichiometry. An adiabat initial temperature of 900°C is used to match the mw + pv curve to PEM and C2 below 700 km. The mw + pv curve is for both partitioned and unpartitioned cases. Note that third-order finite strain lacks sufficient curvature to match the bulk modulus in the lowermost mantle.

should increase the density of an (Mg, Fe) silicate lower mantle by at most 0.2%, so that our results for  $x_{Mg}$  in the lower mantle are slightly low, and a more realistic chemical model would only reinforce our present conclusions.

#### Feasibility of Gravitational Separation of mw and pv

Concentration of iron in mw at the expense of pv appears not to affect the overall density of an mw + pv assemblage under lower mantle conditions. In order to investigate the plausibility of the gravitational separation of mw hypothesis, we must consider the densities of mw and pv individually.

In Figure 9, we plot the individual densities for mw and pv in a peridotite lower mantle with  $T_o = 900^\circ\text{C}$ , the value needed to match PEM and C2 bulk modulus profiles, by using a calculated partitioning coefficient including an FeO phase change (Figure 2). The solid curves are for  $x_{Mg} = 0.95$ , the value matching PEM and C2 densities. We see that the two phases have essentially equal densities throughout the lower mantle. The fine-dashed curves are for  $x_{Mg} = 1.0$ , an iron-free lower mantle. In this case, the pv density is about 0.3 g/cm<sup>3</sup> higher than that of mw. For  $x_{Mg} = 0.90$ , more iron rich than the present lower mantle, the long-dashed curves indicate that the mw density is about 0.2 g/cm<sup>3</sup> greater than that of pv. Thus the present lower mantle has an iron content such that  $\rho_{mw} \approx \rho_{pv}$ , in accord with the end point of the gravitational separation cycle. If an FeO phase change is not included in the partitioning calculation (Figure 2), for iron contents satisfying PEM and C2,  $\rho_{mw} \approx \rho_{pv}$  just below 670 km, then  $\rho_{pv} > \rho_{mw}$  for the remainder of

the lower mantle. For higher iron contents ( $x_{Mg} = 0.80$ ),  $\rho_{mw} > \rho_{pv}$  from 670 to about 1800 km, and  $\rho_{pv} > \rho_{mw}$  to the core-mantle boundary. Thus while the FeO phase change plays only a small role in determining the lower mantle iron content, it has a major influence on the relative densities of lower mantle mw and pv.

In order to see whether the denser mw in a mantle more iron rich than present can sink to the core-mantle boundary in sufficiently short times for the gravitational separation cycle to function over geologic time, we require an estimate of mw settling velocity. We use the results of the modified Stokes problem of a spherical drop of fluid of radius  $r$ , density  $\rho'$ , and viscosity  $\eta'$  moving under gravity in a fluid of density  $\rho$  and viscosity  $\eta$  [Landau and Lifshitz, 1959]. The velocity of the particle is given by

$$v = 2r^2g(\rho - \rho')(\eta + \eta')/[3\eta(2\eta + 3\eta')] \quad (10)$$

where  $g$  is the acceleration of gravity. We assume that  $\eta = \eta'$  and ignore effects such as departures from sphericity [McNown and Malaika, 1950] and the influence of unequal particle sizes and suspensions of mineral grains on viscosity [Walker et al., 1976, 1978]. We estimate that these effects could alter the calculated velocities by no more than a factor of 2.

For a peridotite model with  $x_{Mg} = 0.8$ ,  $\rho_{mw} - \rho_{pv} = 0.8 \text{ g/cm}^3$ , and  $g = 1000 \text{ cm/sec}^2$  (700 km value), we find that mw settling times would be unacceptably long ( $\approx 10^{22}$  Gy) for the present mantle viscosity ( $10^{22}$  poise) and for reasonable grain sizes (1 mm). In order to compete successfully with convection, with net vertical velocities of a few centimeters per year [Davies, 1977; Hager and O'Connell, 1979], mw grain sizes of about 12 km would be required, an unrealistic value given the fact that mw and pv form as an intimate mixture on the microscopic level. If we suppose mw separation was completed early in mantle evolution and use Schubert et al.'s [1978] viscosity estimates of  $10^{14}$ - $10^{16}$  poise at the end of Earth accretion and Stevenson's [1982] estimate of net vertical convective velocity of about 4.5 m/yr, we still require mw grain sizes of at least 25-250 m. Thus it is unlikely that gravitational separation of mw could compete successfully with solid state convection.

A more likely mechanism for removal of iron from an initially iron-rich lower mantle is melting during accretion or subsequent convection with the entire mantle passing through the melting zone. FeO will become concentrated in the

TABLE 5. Magnesium Mole Fractions and Adiabat Initial Temperatures Inferred for Chemical Models of the Lower Mantle

Model	mixed oxides		mw + pv	
	$T_o, ^\circ\text{C}$	$x_{Mg}$	$T_o, ^\circ\text{C}$	$x_{Mg}$
olivine	100	0.93	700	0.93
peridotite	600	0.91	900	0.94
pyroxene	1200	0.92	1500	0.95



low density melt [Stolper and Walker, 1980], and also in upper mantle garnets [Akaogi and Akimoto, 1979]. Thus FeO will be preferentially removed upward in basaltic-picritic melts. Additionally, picritic melts are SiO<sub>2</sub>-poor compared with the primitive mantle. Accordingly, the residual mantle would be SiO<sub>2</sub>-rich and FeO-poor.

Another possible mechanism for gravitational separation is partial melting of iron-rich mw in the lower mantle. The partial melt could percolate along pv grain boundaries to the core-mantle boundary. This process would require mw to have a lower melting point than pv and would require the mw melt to be denser than the remaining solid. Jackson [1977a, b] reviewed various approaches to the variation of mineral melting points with pressure and concluded that an expansion of melting temperature (T<sub>m</sub>) in a polynomial in pressure is probably best. Because of the lack of T<sub>m</sub>-P data for the materials of interest here, we adopt the Lindemann melting law, as advocated by Stacey [1977b]:

$$\frac{\partial \ln T_m}{\partial \ln} = 2(\gamma - 1/3) \quad (11)$$

We use a third-order finite strain equation of state and assume that  $\gamma\rho = \text{constant}$  ( $= \gamma_0 \rho_0$ ). In Figure 10, we plot our estimated melting curves for MgO, FeO, and MgSiO<sub>3</sub> (pv). We take T<sub>0</sub> for MgO from Johnson and Muan [1965] and for FeO from Lindsley [1965], and  $\gamma_0$  for MgO from Anderson and Andreatch [1969] and for FeO from Jeanloz and Ahrens [1980]. The hatched region represents T-P behavior for magnesiowüstite compositions between (Mg<sub>0.7</sub>Fe<sub>0.3</sub>)O and (Mg<sub>0.55</sub>Fe<sub>0.45</sub>)O, the values for a partitioned peridotite lower mantle with bulk

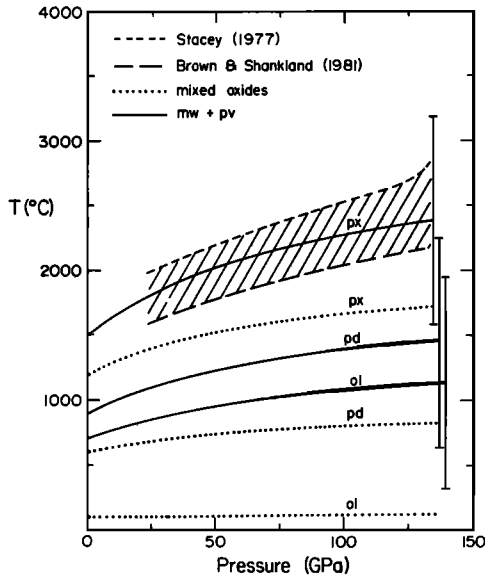


Fig. 8. Adiabatic temperature profiles calculated from the  $x_{Mg}$  and T<sub>0</sub> values of Table 5 (which allow the  $x_{Mg}$  chemical models to satisfy PEM and C2 density and bulk modulus profiles) for olivine (ol), pyroxene (px), and peridotite (pd) stoichiometries. Included for comparison are the geotherms of Stacey [1977] and Brown and Shankland [1981] which were derived without assuming specific compositions.

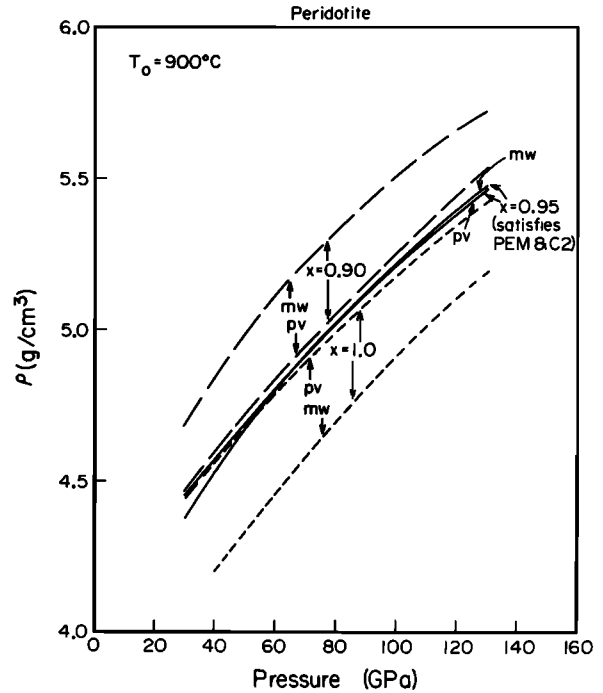


Fig. 9. Individual mw and pv densities versus pressure in a peridotite lower mantle for  $x_{Mg} = 0.95$  (which satisfies PEM and C2 densities,  $\rho_{mw}$  and  $\rho_{pv}$ ) and for more iron-rich ( $x_{Mg} = 0.90$ ) and iron-free ( $x_{Mg} = 1.0$ ) lower mantles. These results include the FeO phase change of Jeanloz and Ahrens [1980].

$x_{Mg} = 0.80$ , assuming congruent melting. Also given is an MgSiO<sub>3</sub> (enstatite) T<sub>m</sub>-P curve based on the 0-5.0 GPa melting data of Boyd et al. [1964], using a fit to Simon's law extrapolated to 670 km; below this depth, we use Lindemann's law for MgSiO<sub>3</sub> (pv). The error bars represent the uncertainty introduced by an error of  $\pm 0.5$  in  $\gamma_0$ . The estimated melting behaviors of mw and pv are very similar, so that partial melting of mw is not implausible. Below 670 km, mw and pv appear to melt at temperatures 500-1000°C above those of present lower mantle, so that partial melting and gravitational settling of mw and removal of iron at the core-mantle boundary would have to be completed considerably before the lower mantle had cooled to its present state. On the other hand, such elevated temperatures may be higher than one might expect for a mantle cooling by convection; see, for example, Sharpe and Peltier, [1979], Cook and Turcotte [1981], Arkani-Hamad et al. [1981]. Accordingly, the relative melting points of mw and pv and the density of molten mw compared to pv are problems ripe for experimental investigation. Stolper et al. [1981] considered the analogous problem of segregation of basaltic melts.

Conclusions

We have investigated the effect of the strong segregation of iron into magnesiowüstite at the expense of perovskite-structure silicates on the composition and evolution of the lower mantle. In calculating the variation of the iron partitioning coefficient with mantle pressures and temperatures, we required the standard entropy of

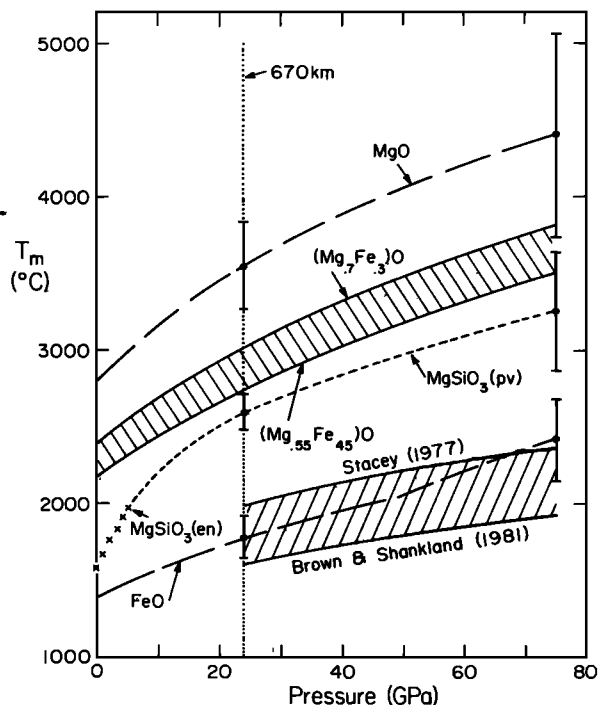


Fig. 10. Speculated melting curves for *mw* and magnesium-rich  $\text{MgSiO}_3$  (perovskite) calculated by using Lindemann's law.<sup>3</sup> The enstatite curve (above 670 km) is based on a Simon's law fit to the 0-5.0 GPa melting data of Boyd et al. [1964], shown as crosses. The hatched region is for *mw* compositions in a partitioned peridotite lower mantle. The error bars represent an uncertainty of  $\pm 0.5$  in the zero-pressure Grüneisen constant. The Stacey [1977a] and Brown and Shankland [1981] temperature curves are included for comparison.

$\text{MgSiO}_3(\text{pv})$ , which we have determined from the P-T diagram of forsterite, including the recently determined  $\gamma\text{-Mg}_2\text{SiO}_4 \rightarrow (\text{Mg}, \text{Fe})\text{O} + \text{MgSiO}_3(\text{pv})$  phase boundary.<sup>2</sup> The value of  $S_{298}^0$  of 69.4 ( $\pm 10.3$ ) J/mole deg for  $\text{MgSiO}_3(\text{pv})$  is about 2.5% larger than that of  $\text{MgSiO}_3(\text{enstatite})$ , in agreement with the prediction of Navrotsky.

The iron partitioning coefficient increases with depth in the lower mantle, from 0.06 at 670 km to about 6 at the core-mantle boundary, but if the recently discovered FeO phase change is included, the partitioning coefficient remains less than unity throughout the lower mantle ( $\approx 0.8$  at the base of the mantle), indicating that iron remains concentrated in magnesiowüstite to the core-mantle boundary. Our calculations demonstrate that the partitioning is not sufficient to produce a lower mantle of essentially pure FeO in equilibrium with essentially pure  $\text{MgSiO}_3(\text{pv})$ .

We find that partitioning of iron has no detectable effect on lower mantle gross density and elastic properties, so that its presence is most likely transparent to seismic studies. We assume simple chemical models, third-order finite strain, an adiabatic lower mantle, a linear variation of density and elastic properties within *mw* and *pv* solid solutions, and by using recent ultrasonic, shock wave, and static compression results for FeO and  $\text{MgSiO}_3(\text{pv})$ , we

conclude that a pyroxene-rich lower mantle is about 1000°C hotter than an olivine-rich lower mantle. For compatibility with geotherms based on other independent approaches, the lower mantle appears to be more pyroxene-rich than the upper mantle and as iron rich, or somewhat less so, than the upper mantle, but not more iron rich. Our preferred values for the lower mantle magnesium mole fraction are 0.93-0.95, compared with 0.85-0.90 for the upper mantle. Thus the Mg/Si ratio in the lower mantle is closer to chondritic values ( $0.99 \pm 0.03$ ) than to the upper mantle—a peridotite upper mantle with  $\text{px/ol} = 0.4$  (molar) and  $x_{\text{Mg}} = 0.88$  has  $\text{Mg/Si} \approx 1.5$ . This difference in Mg and Si content between upper and lower mantles would pose a barrier to single-cell whole mantle circulation, as would a lower mantle somewhat depleted in Fe relative to the upper mantle. Some previous arguments for major element chemical homogeneity of the mantle, for example, those of Watt et al. [1975], were based on differences in Fe content and were not sensitive to variations in Mg and Si content. The present study strengthens the arguments for a pyroxene-rich lower mantle and hence for layered mantle convection.

We have studied the feasibility of the gravitational settling of *mw* mechanism for mantle evolution in which an iron rich lower mantle would lose iron at the core-mantle boundary because of sinking of denser magnesiowüstite and cycle to its present state where the densities of the magnesiowüstite and perovskite phases were hypothesized to be essentially equal. We find that the present lower mantle does have  $\rho_{\text{mw}} \approx \rho_{\text{pv}}$  and that for a more iron-rich mantle,  $\rho_{\text{mw}} > \rho_{\text{pv}}$  throughout the entire lower mantle; for example,<sup>3</sup> for a bulk  $x_{\text{Mg}}$  of 0.80,  $\rho_{\text{mw}} - \rho_{\text{pv}} = 0.7\text{-}0.8 \text{ g/cm}^3$ , but only if an FeO phase change is included.

Investigation of the sinking velocities of denser magnesiowüstite through the lower mantle indicates that implausibly large grain sizes and unacceptably low viscosities are necessary for the gravitational separation hypothesis to compete successfully with convection in the solid state over geologic time to a state of *mw* and *pv* density equality. The likely mechanism for depletion of iron in an initially iron rich lower mantle is upward extraction of FeO-rich melts during accretion and subsequent convection. If *mw* were to partially melt in the lower mantle, the gravitational separation process could perhaps operate, but we estimate only at temperatures at least 500 to 1000°C higher than those in the present lower mantle. If partial melting occurred early in Earth history, the combination of a lower melting point for (Mg, Fe)O enriched in iron, and the higher density of this phase, which results from equilibrium with perovskite-structure silicates, could perhaps give rise to this lower mantle differentiation. Since the elevated temperatures estimated for this process to occur are higher than those calculated in parameterized convection studies, investigation of the relative melting temperatures of *mw* and *pv* and of the effect of partial melting on relative densities and iron partitioning in *mw* and *pv* is needed to test the viability of the partial melting hypothesis.

The concentration of iron in the *mw* component

of the high-pressure products of mantle silicates could explain the depletion of iron in the earth's mantle with respect to the upper mantle and the mantles of other planetary bodies for which we have estimates of composition. In the earth, mw and pv will form from silicates and removal of iron from the iron-enriched mw phase could occur either in the upper mantle by upward extraction of FeO-rich melts or at the base of the mantle after gravitational settling of mw as a consequence of partial melting, leaving the mantle depleted in iron relative to the mantles of smaller bodies, which have internal pressures too low for formation of perovskite-structure silicates or lower accretional temperatures and less extensive melting. Accordingly, we propose that the mantle of Venus has an iron content much more similar to the earth's mantle than to that of other terrestrial planets and satellites.

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