

Pressure-temperature range of reactions between liquid iron in the outer core and mantle silicates

Xi Song and Thomas J. Ahrens

Division of Geological and Planetary Sciences, California Institute of Technology

Abstract. The possibility of reaction between the liquid iron of the Earth's outer core and crystalline silicates ((Mg, Fe)SiO₃) of the mantle, Mg_{0.9}Fe_{0.1}SiO₃(pv) + 0.15Fe(ε) = 0.9MgSiO₃(pv) + 0.2FeO(hpp) + 0.05FeSi(ε) + 0.05SiO₂(st), was proposed by Knittle and Jeanloz (1989, 1991) on the basis of exploratory experiments. We calculate Gibbs free-energies for the reactants and the products of the above reaction in order to constrain the pressure-temperature range. Upon application of thermal expansion, equation of state and heat capacity data, we demonstrate that this reaction can occur at pressures as low as 30 GPa at 3500 K, and at temperatures as low as 900 K at the 130 GPa pressure of the present core-mantle boundary. Furthermore, we propose a modified equation of reaction at the core-mantle boundary: Mg_{0.9}Fe_{0.1}SiO₃(pv) + 0.3Fe(ε) = 0.9MgSiO₃(pv) + 0.3FeO(hpp) + 0.1FeSi. Our results imply that similar reactions may occur during the early accretion history of the Earth.

Introduction

The lowest 200 km of the mantle is designated as the D'' layer. The complex properties of this region have received much detailed study. For example, seismologists inferred lateral heterogeneity in the D'' layer due to regional variation in seismic scattering at the base of the mantle (e.g. Lay, 1989). To interpret D'' in terms of chemical composition and physical state, Knittle and Jeanloz (1989) conducted pioneering reaction experiments. In their experiments, iron foils, embedded in a silicate perovskite matrix of a composition representative of the Earth's lower mantle, were laser heated to > 3500 K and the occurrence of reaction between perovskite and iron was inferred from electron microprobe scanning across the silicate-metal interface. However, the high pressures achieved in their experiments were limited to 75 GPa, substantially lower than the 133 GPa pressure at the core-mantle boundary (CMB). To extrapolate their results to the conditions at the CMB, it is important to place their work in a theoretical framework. In this paper, we examine the pressures and temperatures required to induce several related possible reactions which may occur at the present CMB, the CMB of the earlier (hotter) Earth and at the CMB of the accreting Earth.

Method

Gibbs free energy of a single phase along an isotherm can be expressed as (e.g. Kern and Weisbrod, 1967),

$$G(P, T) = H(0, T) - TS(0, T) + \int_0^P V(T, P) dP \quad (1)$$

where

$$H(0, T) = \Delta H_{298}^0 + \int_{298}^T C_p dT \quad (2)$$

$$S(0, T) = \Delta S_{298}^0 + \int_{298}^T \frac{C_p}{T} dT \quad (3)$$

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ΔS_{298}^0 and ΔH_{298}^0 are standard entropy of formation and enthalpy of formation from elements at 298.5 K. V and C_p are molar volume and heat capacity at constant pressure of the phase of interest, while T and P are temperature and pressure of the system, respectively. Integration of V is done along the isotherm at the given temperature and those of C_p and $\frac{C_p}{T}$ are along the isobar at $P=1$ bar.

An empirical form for C_p for use at temperatures as high as 3000 K is (Berman and Brown, 1985),

$$C_p(T) = (K_0 + K_1 T^{-0.5} + K_2 T^{-2} + K_3 T^{-3}) + l_1 T + l_2 T^2 + l_3 T^3 \quad (4)$$

and Fei *et al.* (1990) presents another expression for heat capacity at constant pressure,

$$C_p(T) = 3nR(1 + k_1 T^{-1} + k_2 T^{-2} + k_3 T^{-3}) + (A + BT) + C_p' \quad (5)$$

where k_i and K_i are determined by fitting the measured intermediate temperature (50-1000K) heat capacity data, l_i are used for phases undergoing lambda transitions, A and B are calculated from thermal expansion coefficient, isothermal bulk modulus, and molar volume data, and C_p' is due to cation disordering and is neglected as suggested by Fei *et al.* (1990).

For minerals in the reactions given by equations 9-10 in the paper, we employ thermodynamic data presented by Fei *et al.* (1990). For other minerals discussed in this paper, thermodynamic data are from Fei and Saxena (1986). With equations 2-5, we calculate the free-energy of a single phase at atmospheric pressure as a function of temperature. In order to evaluate the integral in equation (1), we construct isothermal equations of state for several relevant minerals at high temperatures, starting from the Birch-Murnaghan equation of state. An empirical expression for the thermal expansion coefficient at ambient pressure is (Fei *et al.*, 1990),

$$\alpha(T) = a_0 + a_1 T + a_2 T^{-2} \quad (6)$$

Thermal expansion data for many materials are available (Fei and Saxena, 1986) to evaluate the parameters in equation (6) to temperatures up to 1600K (Mao *et al.*, 1991). We will assume that equation (6) is valid at the higher temperatures relevant to the CMB.

The effect of pressure on the thermal expansion coefficient is (Birch, 1952),

$$\alpha = \alpha_0 \left(\frac{V}{V_0} \right)^{\delta_T} \quad (7)$$

where δ_T is the second Gruneisen parameter which is assumed to be independent of temperature and pressure above Debye temperature (e.g. Anderson *et al.* 1991). V_0 and α_0 are molar volume and thermal expansion coefficient at some reference state. Although Fei (1993) collects some δ_T values, we have to estimate δ_T for some minerals using compositionally or structurally similar ones. The values of δ_T we used, which are not given by Fei (1993), are: FeO(hpp), 4.0; FeSi(ε), 4.0; SiO₂(st), 6.0.

Equations of state at high temperature are generated as follows: We construct a grid in the P - T plane (temperature intervals of 1K, pressure intervals of 1 bar), and first consider the 298 K isotherm centered at $P=1$ bar. Molar volume of a mineral along this isotherm is calculated using a third order Birch-Murnaghan equation of state (Birch,

1952). The molar volumes at $P = 1$ bar and a higher temperature T , are calculated using equation (6) together with the definition of the thermal expansion coefficient,

$$V = V_0 \exp \left(\int_{T_0}^T \alpha(T) dT \right) \quad (8)$$

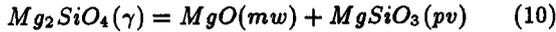
We then calculate the thermal expansion coefficient at higher temperatures and pressures with equation (7) along an isotherm and calculate the molar volume at higher temperatures and pressures with equation (8) along an isobar. Upon the completion of these extrapolations, the equation of state at a given high temperature T is obtained in the form $V_i = V_i(P_i, T)$.

To examine the validity of this method, we compared our calculations with experimental high temperature and high pressure equations of state for perovskite(pv). On the basis of high temperature (up to 1150 K) and high pressure (up to 30 GPa) experiments on $(Mg, Fe)SiO_3$ perovskite, Mao *et al.* (1991) gave two fits for the V - T - P equation of state, specified as fit A and fit B. Fei *et al.* (1992) conducted similar study on $(Mg_{0.6}, Fe_{0.4})O$ magnesiowustite and gave the V - T - P equation of state as their equation (8). In figure 1, we compare isotherms at 1100K, 1500K and 2000K calculated from our extrapolations with the equations of state from Mao *et al.* (1991) and Fei *et al.* (1992). There is excellent agreement between the two methods.

Using our extrapolation method and the heat capacity formulae (4) and (5), we study two known reactions of geophysical interest. Firstly, we study



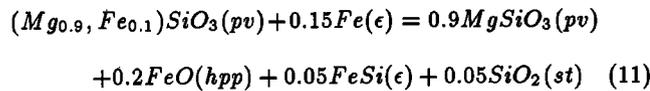
by calculating the Gibbs free energies of β -spinel and γ -spinel along the 1600K isotherm. At lower pressure, β -spinel has a Gibbs free energy that is lower than that of γ -spinel. With the increasing pressure, the difference between the Gibbs free energies of these two phases decreases. At pressure $P=17.5$ GPa, these two phases coexist and are in equilibrium. This result agrees with Akaogi *et al.*'s experiments (1989) which gave the transition pressure at 1600K to be 16-18 GPa. Secondly, we study



The calculation shows the transition pressure for the post-spinel at 1600K is 23.7 GPa, which is in agreement with experimentally determined transition pressure 23.1 GPa (Ito *et al.*, 1989).

Prediction on the Possible Reactions at the Core-Mantle Boundary

Knittle and Jeanloz (1991) proposed that the following reaction occurred in their experiments and it may be representative of reactions between lower mantle silicates and liquid iron at the CMB,



To calculate the pressure and temperature conditions required for this reaction, we assumed that equation (4) and (5) are valid even at high temperatures of the CMB. Moreover, we make a few assumptions for iron, the low and high pressure phases of FeO and FeSi.

ϵ -Iron

According to Brown and McQueen (1982), The high pressure phase of iron stable at the pressures of the CMB may be ϵ -iron. Huang and Bassett (1987) studied the equations of state of α - and ϵ -iron and gave the elastic parameters. Thermal expansion data for ϵ -iron are not available, but our tests of using α -iron data (Fei *et al.*, 1986) and γ -iron data (Boehler *et al.*, 1990) as an approximation show that the free-energy of reaction (11) is relatively insensitive to the thermal expansion model. Thermal expansion data for

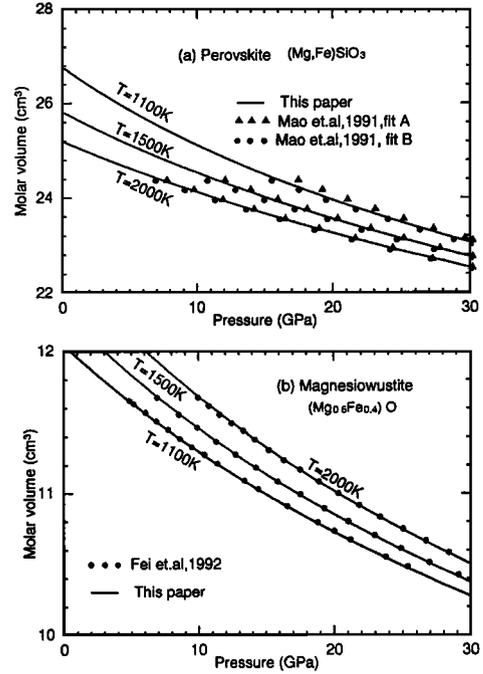


Fig. 1. Isothermal equations of state at 1100 K, 1500 K and 2000 K, for (a) perovskite($(Mg, Fe)SiO_3$) and (b) magnesiowustite($(Mg_{0.6}Fe_{0.4})O$).

α -iron are used in this paper for the liquid phase of iron in the outer core. Specific heats for ϵ -iron are not available either but that for α -iron is given by Fei *et al.* (1986). Moreover, Andrews (1973) calculated the Gibbs potential difference between ϵ -iron and α -iron at atmospheric pressure and various temperature up to 800K. Their difference, decrease linearly with increasing temperature, do not exceed 5KJ/mol and can be fit with

$$G_\epsilon - G_\alpha = 1232.067 - 0.5043T \quad (12)$$

We adopt these values to calculate the Gibbs free energy at 1 atm pressure for ϵ -iron from that of α -iron.

Iron-Silicon Alloy

Thermal expansion data of iron-silicon alloys are not available and we adopted thermal expansion data of α -iron. Chart (1970) studied the thermodynamic properties of the system Fe-Si and presented thermodynamic data for the ϵ phase of $FeSi(\epsilon)$. Heat capacities at atmospheric pressure and temperature lower than 1683K, the melting point, as presented in Chart (1970), are fitted by formula (4) with the coefficients: $k_0 = 113.453$, $k_1 = -1.963 \times 10^3$, $k_2 = 9.6 \times 10^6$, $k_3 = -1.599 \times 10^9$. In this paper, heat capacities of this phase at atmospheric pressure and temperatures higher than 1683K are assumed to be constant and equal to 87.78 J/mol.K, as indicated by Chart's data. Using high temperature heat capacity data that are extrapolated from those at lower temperatures will lower the transition pressures and temperatures of reaction (11), but will not alter our conclusions.

High pressure phase of FeO

At the CMB, the FeO formed via equation (11) presumably occurs in a high pressure phase (Jeanloz and Ahrens, 1980). Although a bulk modulus and molar volume of this high pressure phase of FeO is reported by Jeanloz and Ahrens (1980), the thermal expansion data for this phase is still not available, and we resort to using thermal expansion coefficient of the low pressure phase of FeO for the high pressure phase. Heat capacities calculated from equation (4) with the coefficients for the low pressure phase (Fei and Saxena, 1986), do not appear appropriate for the high pressure phase of FeO. Instead, we adopt the expression

$$C_p = 3nR + \alpha^2 VTk_T \quad (13)$$

derived from the Dulong Petit value for this high pressure phase of FeO. Here n is the number of atoms per formula unit, α is thermal expansion coefficient expressed in equation (6), V is the molar volume in equation (8), and k_T is the bulk modulus. Again we assume that the product αk_T is constant and independent of temperature (Birch, 1952).

On the basis of these assumptions, and neglecting the possible effect of solid solution, we calculated the total Gibbs free-energies at atmospheric pressure and various temperatures for the reactants and the products of the proposed reaction (11). In figure 2, the differences of the total Gibbs free energies between the reactants and products are plotted along 2000K, 3000 and 3500 K isotherms. The same procedure was applied to other isotherms and we derived a P-T diagram for reaction (11) in figure 3. The breaks in slope of the curves in this figure are due to the use of the heat capacity data of FeSi at atmospheric pressure and temperatures higher than 1683 K.

Discussion and Conclusions

Figures 2-3 have a large formal uncertainty. As shown in figure 2, the difference between the energies of the products and the reactants does not exceed 15 KJ per mole atoms, but the uncertainty of ΔH , as indicated in some of the references (e.g. Fei *et al.*, 1990), can be as great as 1 KJ per mole. This in turn may result in a large uncertainty of transition pressure on the order of 100 GPa. Besides, we do not have a clear idea about how much uncertainty is involved by extrapolating isotherms from lower temperature-pressure condition to extremely high temperatures and pressures. A possible mitigating circumstance would be if the error in the measurements of ΔH for individual reactants and products cancel out for the reaction, as we tried to use a self-consistent data set for each reaction. Nevertheless, within the uncertainty, the results of figure 3 are in excellent agreement with the experimental results of Knittle and Jeanloz (1991).

Of importance is that, as pressure increases along the isotherm, the difference in free energies between the reactants and the products increases, and the products become more and more stable relative to the reactants, as shown in figure 2. Also it should be noted that, as temperature increases, the transition pressure decreases. Therefore, to some extent, this result extends the conclusion of Knittle and Jeanloz (1991) to high pressure-temperature conditions relevant to the CMB.

Moreover, our results suggest that reaction between iron and silicates could even occur at lower temperatures and lower pressures than those at the CMB, provided perovskite, the high pressure phase of FeO and stishovite can exist stably. These conditions could be achieved in the center of the present Mars, and could have been achieved within Venus and Earth much earlier during their accretion history. Thus, our results could explain the compositional difference in iron content between the Martian mantle and the Earth's mantle.

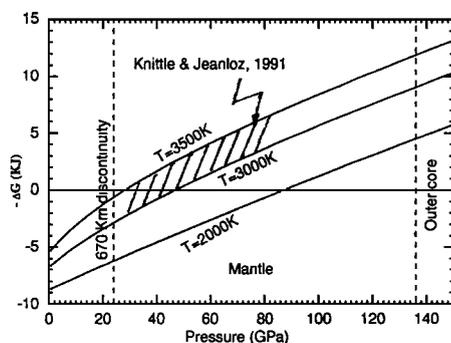


Fig. 2. Gibbs free energy of reaction for Knittle and Jeanloz's (1991) proposed equilibrium (equation (11)), along three isotherms, in KJ. Uncertainties are discussed in the text.

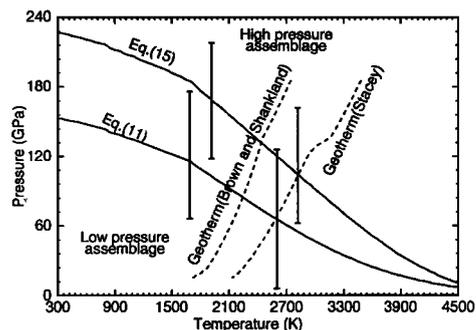
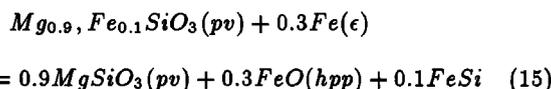


Fig. 3. P-T diagram showing stability field for reactant and product phase assemblages, in equation (11) and (15); Error bars show estimated uncertainties. Also shown are two mantle geotherms derived from the thermal models of Stacey (1977) and Brown and Shankland (1981), with pressures given by PREM (Dziewonski *et al.*, 1981).

The same approach can be applied to another reaction

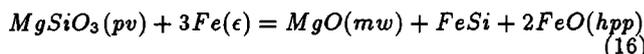


We find there is also a possibility that SiO_2 reacts with ϵ -iron at conditions at the CMB. This is in accord with Knittle and Jeanloz's observation that little stishovite appeared as a product. In fact, our calculations suggest a modified equation of reaction in the form



The P-T diagram for this reaction is also shown in figure 3. In terms of Gibbs free energy, reaction (15) occurs at higher pressure than the reaction originally proposed by Knittle and Jeanloz (1991).

The reactions discussed above are essentially concerned with the partitioning of iron in $FeSiO_3$ and iron alloys. What these calculations tell us is that, at the CMB, iron will react with lower mantle silicates to form Fe-Si alloy, in order to minimize the Gibbs free-energy. Since the composition of the lower-most mantle is not yet well understood and all these reactions may occur at lower pressures during Earth accretion, our discussion about the possible reactions at the CMB will not be complete if we do not also consider other reactions involving different phases of mantle silicates (e.g. $MgSiO_3$ and Mg_2SiO_4). Therefore, with the same approach, we studied the equation



It turns out that this reaction (16) has a very positive free-energy of formation and is therefore unlikely to occur in terrestrial planets even at very high temperatures (> 4500 K) and pressures (> 300 GPa). This suggests that the reaction between $Mg_{0.9}Fe_{0.1}SiO_3$ and iron will slow down as it proceeds, due to the increasing dominance of $MgSiO_3$

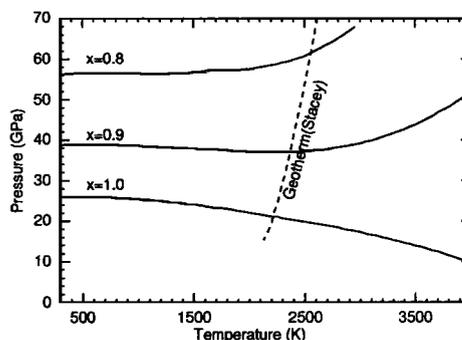
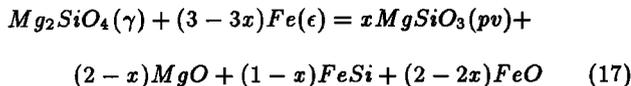


Fig. 4. P-T diagram similar to figure 3 but for the reaction between $Fe(\epsilon)$ and $Mg_2SiO_4(\gamma)$. $(3-3x)$ is the coefficient of Fe in equation (17) for this reaction.

in the composition of the lower-most mantle, unless a dynamic mechanism exists sweeping away the reaction zone and exposing fresh mantle material to the core.

Other equations examined in this study include



and similar reactions with various phases of olivine and iron. These reactions, if possible, can only occur under certain conditions with much lower temperatures and pressures than those of the present CMB, due to the transformation of the Mg_2SiO_4 polymorphs; But these temperature-pressure conditions may still be achieved within the earlier, smaller proto-Earth or Venus. However, our calculations show that, among these reactions, those with $x=1.0$, which denote transforms of the Mg_2SiO_4 polymorphs, may occur at lower temperatures and lower pressures than those with $x < 1.0$ and thus involve iron (see figure 4), indicating that the available data does not suggest the reaction between iron and pure iron-free Mg_2SiO_4 .

In conclusion, we developed a series of high temperature equations of state to calculate Gibbs free-energies for several minerals of interest. Our calculations of the temperature-pressure range of the reaction between iron and $Mg_{0.9}Fe_{0.1}SiO_3$ are consistent with the experimental results of Knittle and Jeanloz (1989, 1991). If $SiO_2(st)$ is not involved in reactions at the CMB, we propose an occurrence of reaction between Fe and $Mg_{0.9}Fe_{0.1}SiO_3$, producing $MgSiO_3$, FeO and $FeSi$. These two reactions have the effect of making the D'' layer and the outer core rich in FeSi and FeO. Our calculations imply that reactions (11) and (15) may occur under the lower temperature-pressure conditions at the proto-Earth's CMB during its accretion history. Moreover, the result that core iron does not tend to react with pure iron-free polymorphs of Mg_2SiO_4 and $MgSiO_3$ suggests that iron is drained via reactions (11) or (15) from the lowermost mantle into the core, which would have been a mechanism for core formation and core-mantle segregation.

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- T. J. Ahrens and Xi Song, Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena, CA 91125.

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