

STABILITY OF (Mg,Fe)SiO<sub>3</sub> PEROVSKITE AND THE STRUCTURE OF THE LOWERMOST MANTLELars Stixrude<sup>1</sup> and M. S. T. Bukowinski

Dept. of Geology and Geophysics, University of California at Berkeley

**Abstract.** Thermodynamic analysis shows that (Mg,Fe)SiO<sub>3</sub> perovskite is stable throughout the likely pressure, temperature and compositional regime of the Earth's mantle. The breakdown of perovskite to its constituent oxides appears unlikely, even under the extreme conditions of the core-mantle boundary. This reaction had been proposed to reconcile estimates of silicate melting with seismic observation and proposed geotherms.

## Introduction

The D'' layer is a few hundred kilometer thick region of anomalous seismic properties at the base of the mantle. It is distinguished by strong lateral heterogeneity, small, often negative, seismic velocity gradients, and velocity discontinuities over much of its upper boundary [Young and Lay, 1987; Weber and Körnig, 1990]. The mineralogical or compositional changes responsible for these unusual properties remain unknown.

(Mg,Fe)SiO<sub>3</sub> perovskite is generally accepted as the most abundant mineral in the lower mantle. Perovskite dominated assemblages readily account for the seismic properties of the bulk of the lower mantle and phase equilibrium studies over most of the mantle's pressure-temperature regime confirm its stability [Knittle and Jeanloz, 1987]. However, the stability of perovskite at pressure-temperature conditions characteristic of D'' has not yet been experimentally addressed.

A comparison of recently proposed geotherms [Jeanloz, 1990] with silicate melting curves in the deep mantle indicates that perovskite cannot be a constituent of D'' [Stixrude and Bukowinski, 1990]. Near the core-mantle boundary, its melting point falls more than a thousand degrees below estimated temperatures in the Earth. The proposed core-mantle boundary temperature is primarily determined by the measured melting temperature of iron under shock-loading [Williams et al., 1987] which is found to be significantly higher than model calculations of the iron hugoniot had predicted [Brown and McQueen, 1982]. If the shock wave measurements and the predicted perovskite melting curve are approximately correct, the constitution of D'' must differ substantially from the rest of the mantle, since seismic observations rule out significant amounts of partial melt. Assuming that the region's bulk chemistry is dominated, like the rest of the mantle, by Mg, Fe and Si oxide components, perovskite must undergo a transformation to a high pressure phase or assemblage under D'' conditions. A proposed breakdown of perovskite to its

constituent oxides permits a solid D'', since oxides are expected to be more refractory than their compounds, and provides a possible explanation of the region's distinctive seismic properties [Stixrude and Bukowinski, 1990].

Here we show that the breakdown of perovskite to its constituent oxides is unlikely in the Earth. The reaction does occur at appropriate pressure-temperature conditions but only for iron contents so high that the products disagree severely with the density and bulk modulus of the lowermost mantle. We discuss other possible resolutions of the apparent discrepancy between the perovskite melting curve, the geotherm and seismic observations.

## Thermodynamic Formalism

Our results are based on semi-empirical thermodynamic potentials [Stixrude and Bukowinski, 1990]. The Gibbs free energy,  $G$ , of a phase consisting of a solid solution of  $N$  species as a function of pressure,  $P$ , and temperature,  $T$ , is:

$$G(P, T) = \sum_{i=1}^N x_i G_i(P, T) + RT \sum_{i=1}^N x_i \ln a_i \quad (1)$$

where  $x_i$ ,  $G_i$  and  $a_i$  are the mole fraction, Gibbs free energy and activity of species  $i$ . The latter is approximated by regular solution theory. We write the free energy as:  $G_i(P, T) = F_i(V, T) + PV_i$ , where  $V$  is the molar volume and assume that the Helmholtz free energy,  $F_i$ , can be divided into a reference term, a purely volume dependent part given by Birch-Murnaghan finite strain theory, a thermal part, given by Debye theory and an electronic contribution:

$$F_i(V, T) = F_0 + F_C(V, T_0) + [F_{TH}(V, T) - F_{TH}(V, T_0)] + [F_{EL}(V, T) - F_{EL}(V, T_0)] \quad (2)$$

where  $F_0$  is the value at  $P=0$  and  $T=T_0$ . The parameters are either directly measured or constrained by experimental data or first principles calculations (Table 1). Reference free energies and interaction parameters,  $W$ , are constrained by phase equilibria measurements. The remaining parameters, including  $V_0$ , the isothermal bulk modulus,  $K_0$ , and its pressure derivative,  $K_0'$ , the Debye temperature,  $\theta_0$ , and its logarithmic volume derivative,  $\gamma_0$ , are determined by inverting compression, thermal expansion and calorimetric data. The electronic term appears only for the metallic high pressure phase of FeO and is given by free electron theory.

Eq. 2, often seen in the form of its volume derivative - the Mie-Grüneisen equation of state - describes a wide variety of thermodynamic properties of mantle minerals at high pressures and temperatures, including their equations of state, phase equilibria and melting behavior. To the extent that anharmonic terms are negligible, the potentials remain sufficiently accurate for our purposes at the extreme pressure-temperature conditions of interest here. The cold part remains well constrained by experimental measurements for most of the

<sup>1</sup>Now at: Geophysical Laboratory and Center for High Pressure Research, Carnegie Institution of Washington

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TABLE 1. Parameters of the thermodynamic potentials. Global parameter set. High and low temperature parameters are identical except:  $F_O$  of Mg-Sp (-98.0, -88.6), Fe-Sp (-97.6, -90.9), Mg-Pv (-0.4, 6.6), Fe-Pv (45.5, 35.2) and  $W$  of Sp (3.6, 4.1) and Mw (13.5, 12.6). Parentheses contain estimated uncertainties in the last digits.

Phase	Formula	$F_O$ , kJ/mol	$V_O$ , cm <sup>3</sup> /mol	$K_O$ , GPa	$K_O'$	$\theta_O$ , K	$\gamma_O$	$W$ , kJ/mol
Spinel (Sp)	Mg <sub>2</sub> SiO <sub>4</sub>	-92.4	39.65	183(3)	4.1(5)	1017(10)	1.21(10)	2.8
	Fe <sub>2</sub> SiO <sub>4</sub>	-94.1	42.02	192(3)	4.1(5)	781(10)	1.21(10)	2.8
Perovskite (Pv)	MgSiO <sub>3</sub>	3.4	24.46	263(7)	3.9(5)	1017(10)	1.96(10)	0
	FeSiO <sub>3</sub>	40.5	25.49	263(7)	3.9(5)	749(50)	1.96(10)	0
Magnesio-wüstite (Mw)	MgO	0	11.25	160(2)	4.1(2)	776(10)	1.45(10)	13.1
	FeO	0	12.25	152(2)	4.9(2)	434(50)	1.45(10)	13.1
Magnesio-wüstiteII(MwII)	MgO	139.7	10.79	161(10)	4.1(1.0)	698(50)	1.36(20)	13.1
	FeO	55.9	10.84	205(10)	6(1)	630(50)	1.45(20)	13.1
Stishovite (St)	SiO <sub>2</sub>	0	14.01	314(8)	8.8(8)	1152(10)	1.35(10)	0

Properties of Pe II are from *Bukowski* [1985]; those of Wu II from *Jackson* [1990].  $q=2.5(1.7)$  for perovskite [*Hemley et al.*, 1992] and is assumed to be 1(2) for all other phases. Inversion of experimental data for all other parameters will be discussed in a forthcoming publication.

relevant phases, while the thermal part closely approaches its high temperature limiting behavior ( $T/\theta > 4$ ). In this limit, results are insensitive to the detailed form of the vibrational density of states which is approximately represented in the Debye model. The adequacy of the regular solution model and the assumed volume dependence of  $\gamma$  is more difficult to evaluate. We ensure that our results are insensitive to wide variations in  $W$  and  $q$ , the second logarithmic volume derivative of  $\theta$ .

### Results

Calculated pseudobinary orthosilicate phase equilibria are compared with the low and high temperature experimental results of *Ito and Takahashi* [1989] in Figure 1. By inverting low and high temperature data separately for the reference free energies of the relevant species (Table 1), we obtained excellent fits to the observations. However, it proved impossible to reproduce both experiments with a single set of reference free energies. Parameters which give the best global fit reproduce the general topology but the calculated coexistence loops shift towards more iron rich compositions with decreasing temperature while the reverse is observed experimentally. The more complex thermodynamic model of *Fei et al.* [1991] produces very similar results and is also unable to fit the data. The reason for this discrepancy is unclear. Barring severe deficiencies in two very different thermodynamic formulations, insufficient equilibration or an unquenchable phase transition in one or more of the relevant species may be responsible.

Considering the discrepancies apparent in Figure 1 to be an additional source of uncertainty, the resulting errors in our calculated phase diagrams at D'' pressure-temperature conditions are small and will not affect our basic conclusions (Figure 2). Differences between the predictions of high temperature and global parameter sets are reduced by increasing pressure. The stability field of perovskite is very wide at pressures greater than 60 GPa (1500 km depth), regardless of the parameter set used in the calculations; the low temperature parameters produce an even wider stability field of perovskite.

The predicted high pressure phase diagrams satisfy experimental constraints, including the transition of wüstite to

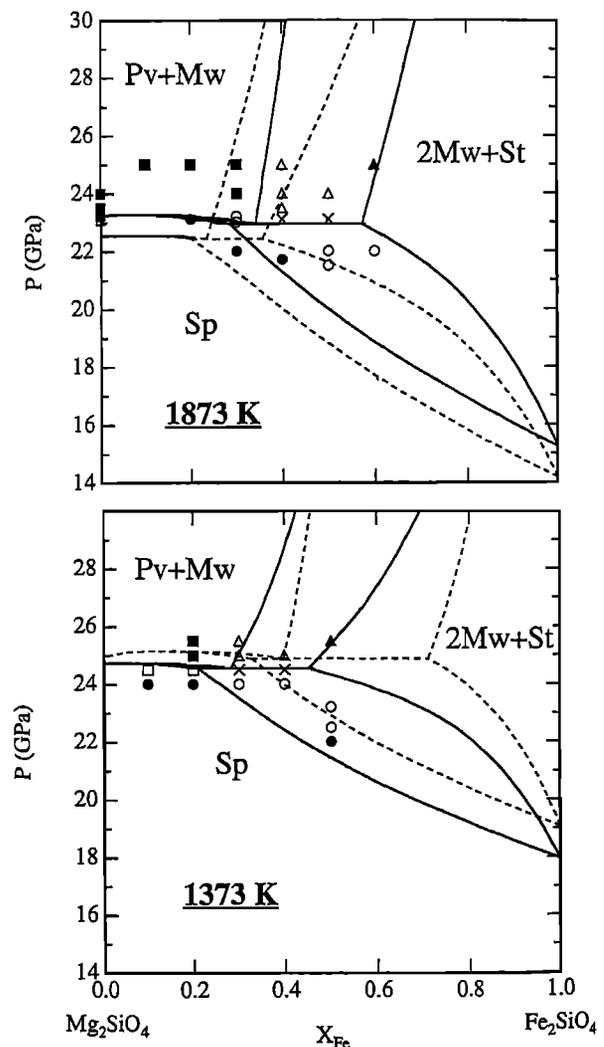


Fig. 1. Pressure-composition phase diagram at two temperatures.  $X_{Fe}=Fe/(Mg+Fe)$ . Experimental observations of pseudo-unary, -binary and -ternary coexistence are indicated by open and closed symbols and crosses, respectively. The solid lines are calculations based on high and low temperature parameter sets. Dashed lines are based on the best fit global parameter set.

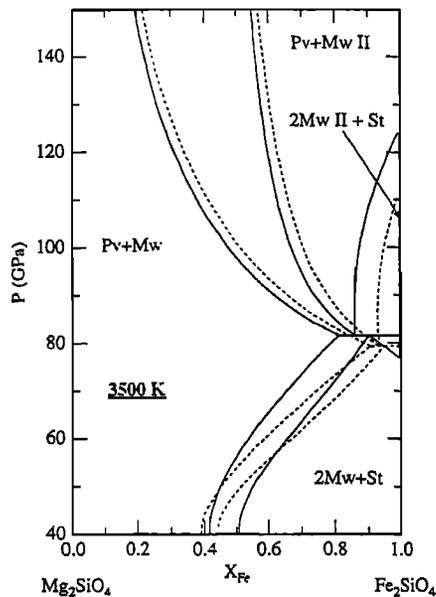


Fig. 2. High pressure  $\text{Mg}_2\text{SiO}_4$ - $\text{Fe}_2\text{SiO}_4$  phase diagram at 3500 K. Solid and dashed curves are calculated with the high temperature and global parameter sets respectively.

a metallic form, observed near 70 GPa in diamond cell [ $T=4000$  K] and shock wave [ $T=1000$  K] experiments [see *Jeanloz, 1990*] and perovskite syntheses up to 127 GPa and approximately 2500 K [*Knittle and Jeanloz, 1987*]. Our results closely resemble the predictions of *Jeanloz and Thompson [1983]* below 80 GPa. At higher pressures, our calculations show two pseudobinary coexistence loops, as required by the phase rule, in place of their four-phase field.

The ternary  $\text{MgO}$ - $\text{FeO}$ - $\text{SiO}_2$  diagram summarizes the important results (Figure 3). To obtain a conservative estimate of the stability of perovskite in D'', we have chosen an extreme temperature (5000 K) since lower values widen the perovskite stability field. Superimposed on the phase diagram are contours of density and acoustic velocity calculated with the same thermodynamic potential formalism and the same parameters used to determine the phase diagram. The intersection of the contours corresponding to the observed density and acoustic velocity at the base of the mantle [e.g. *Dziewonski and Anderson, 1981*], which represent the location of the Earth at this pressure, lies well within the stability field of perovskite.

The uncertainties in seismic properties near the core mantle boundary are larger than those in the rest of the mantle but correspond to an area of the phase diagram much smaller than that of the perovskite stability field. Uncertainties in the calculations are also much too small to substantially alter the phase diagram. Variations in experimentally constrained parameters within their uncertainties and in  $W$ 's from 0 to three times their nominal values move the phase boundaries by  $<0.4 X_{\text{Fe}}$  units. For all parameters but  $q$  of perovskite, the changes are  $<0.2$ . Extreme variations in  $F_o$ 's, obtained by extrapolating their apparent temperature dependence (difference between low- $T$  and high- $T$  parameter sets) to 5000 K also fails to exclude the Earth from the perovskite stability field. Alternative values of  $K_o$  and  $K_o'$  for perovskite (246 GPa, 4.5) or the transformation of stishovite to its recently

discovered high pressure form [*Tsuchida and Yagi, 1989*] have a much smaller effect on the location of the Earth and the position of phase boundaries on the diagram. Perhaps the largest uncertainty lies in the pressure of the assumed phase transition in periclase. The first principles calculations of *Bukowinski [1985]* provide a probable lower bound on the transition pressure of 205 GPa at 300 K, much lower than the value adopted here from more recent results [500 GPa; *Mehl et al., 1988*]. Adopting the lower value expands the Mw II+St field somewhat but not enough to encompass the Earth.

### Discussion and Conclusions

Our results indicate that the breakdown of  $(\text{Mg,Fe})\text{SiO}_3$  perovskite to its constituent oxides is unlikely in the Earth. If core-mantle boundary temperatures are much lower than those derived from shock wave experiments, several alternative explanations for the seismic reflectors at the base of the mantle are possible. Small amounts of stishovite may be responsible, from silica enrichment relative to metasilicate stoichiometry

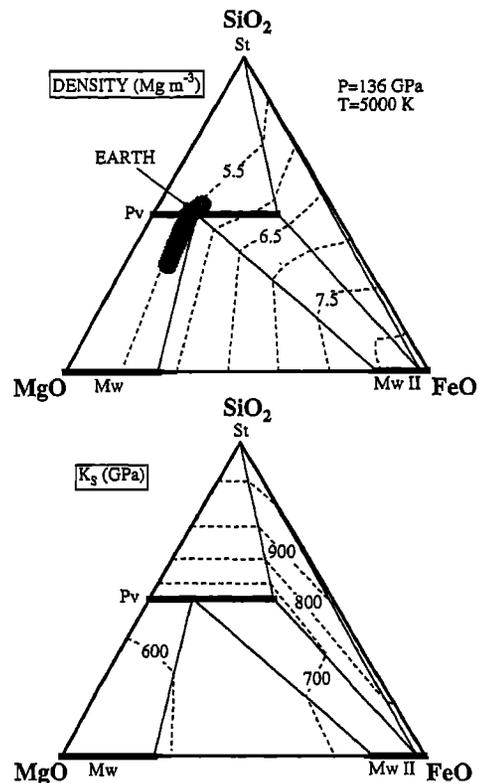


Fig. 3. Ternary  $\text{MgO}$ - $\text{FeO}$ - $\text{SiO}_2$  phase diagram at 136 GPa and 5000 K calculated with the high temperature parameter set. Contours of density (upper figure) and adiabatic bulk modulus (lower figure) are superimposed (dotted lines). The shading, shown only in the upper figure for clarity, indicates the field of possible intersections of the contours corresponding to the observed density and adiabatic bulk modulus of the Earth allowed by uncertainties in calculated and seismically observed densities and bulk moduli. Adopting a value of 205 GPa for the room temperature phase transition in periclase eliminates Mw from the diagram and shifts the Pv+Mw II+St coexistence field towards lower iron contents ( $X_{\text{Fe}}(\text{Pv})=0.58$ ,  $X_{\text{Fe}}(\text{Mw II})=0.83$ ).

(Figure 3). The phase transition of magnesiowüstite to its high pressure form may produce anomalous velocity gradients near the core-mantle boundary, although it appears much too diffuse to produce a seismic discontinuity (Figure 2). Still unobserved phase transitions in calcic, diopside or (Mg,Fe)SiO<sub>3</sub> perovskite, including the predicted orthorhombic to cubic transition in the latter, may produce velocity discontinuities at the appropriate pressures [see Hemley and Cohen, 1992]. Partial reaction of Mg-rich perovskite with iron alloys, similar to that observed at lower pressures [Knittle and Jeanloz, 1991], may also produce seismic reflectors.

All of these explanations rely on perovskite dominated assemblages and thus cannot reconcile geotherms based on shock wave experiments with the lack of partial melt in D''. The melting point of iron under shock loading and in static compression experiments at lower pressures is currently a matter of active debate [Ross *et al.*, 1990; Boehler *et al.*, 1990]. However, if the shock wave data and the predicted perovskite melting curve are approximately correct, they require either the absence of Mg-rich perovskite from D'' or a substantial change in its properties, probably much greater than that associated with the predicted orthorhombic to cubic phase transformation. An exotic bulk composition in D'', perhaps dominated by Ca and Al oxide components [Ruff and Anderson, 1980], may be required. Alternatively, a breakdown or transformation of (Mg,Fe)SiO<sub>3</sub> perovskite to a more diverse assemblage than those considered here remains a possible explanation of the seismic reflectors and the absence of melt in D''. Consideration of other chemical components may lower the free energy of the non-perovskite assemblage, inducing a complete breakdown to a mixture of oxides and metallic alloys (Fe, FeSi). Though speculative, a metal-oxide layer may be heterogeneous on many length scales because of the disparate physical properties of the two components [see also Knittle and Jeanloz, 1991]. This provides a possible explanation for observed heterogeneity in D'' on length scales ranging from the smallest observable with seismic probes (100 km, the size of a seismic wave) to nearly the diameter of the core [Lively *et al.*, 1986; Young and Lay, 1987].

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M.S.T. Bukowinski, Dept. of Geology and Geophysics, University of California, Berkeley, CA 94720.

Lars Stixrude, Geophysical Laboratory, 5251 Broad Branch Rd. NW, Washington, DC 20015.

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