

THERMODYNAMICS OF THE SYSTEM FeO-MgO AT HIGH PRESSURE

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Introduction Recent shock wave data (1) have established the presence of a phase transformation in $\text{Fe}_{0.94}\text{O}$, occurring at approximately 70 GPa. A recent reassessment of the shock wave data, while conceding the possibility of a B1→B2 transition on which the analysis of (1) is based, has demonstrated that the density difference between low- and high-pressure phases is at least 10-16% and possibly significantly larger, based on a systematic variation of the Hugoniot parameters (2). Recent room temperature compression data of FeO (3) demonstrating the instability of the rocksalt phase at high pressure, and the large density increase associated with the phase transformation of FeO at 70 GPa, suggest that the transformation involves a significant rearrangement of the crystalline lattice. The occurrence of such a transformation in FeO has profound implications for the geophysically important MgO-FeO system at high pressure. Above the transformation pressure, a two-phase region consisting of a magnesian rocksalt (B1) phase and an iron-rich high-pressure phase (hpp) forms. The solubility of a given compound, e.g. MgO (B1), in solid solution with a compound having a denser structure, e.g. FeO (hpp), is a function of the free energy difference between structures and is thus related to the pressure at which the pure compound transforms to the denser structure (4). Assuming ideal behaviour and given that no phase transformation occurs in MgO to at least 200 GPa (5), the solubility of MgO in the high-pressure phase at 1300K and 100 GPa is calculated to be 0.4 mol %. We conclude, therefore, that an increase of pressure in the system (Fe,Mg)O will result in a gradual exsolution of an essentially pure FeO (hpp) phase leaving an iron-depleted (Fe, Mg)O (B1) phase.

Thermodynamics The degree to which FeO (hpp) exsolves with increasing pressure is a function of the trade-off between the decrease in free energy obtained by the volume reduction from the formation of FeO (hpp) and the increase in free energy associated with the loss of configurational entropy of the B1 solid solution. The phase boundary between $\text{Fe}_x\text{Mg}_{1-x}\text{O}(\text{B1})$ and $\text{Fe}_x\text{Mg}_{1-x}\text{O}(\text{B1}) + \text{FeO}(\text{hpp})$ is approximately given by

$$RT \ln x - (P - P_{\text{tr}}) \Delta V + (T - T_{\text{tr}}) \Delta S = 0$$

where ΔV and ΔS refer to the transition $\text{FeO}(\text{B1}) \rightarrow \text{FeO}(\text{hpp})$. The range for ΔV was estimated using the parameters comprising the extremal Hugoniot for the shock wave data of FeO (hpp) (2). The maximum allowed range for ΔV at 70 GPa is 0.54 to 0.99 $\text{cm}^3 \text{mol}^{-1}$ (7% to 11% volume decrease). Estimates of ΔS were more difficult to establish. Accordingly, ΔS was varied between the limits 5JK⁻¹ mol⁻¹ and -5JK⁻¹ mol⁻¹, which represents the range within which the majority of values for phase transformations fall. P_{tr} and T_{tr} , the respective pressure and temperature at which FeO (B1) and FeO (hpp) are in equilibrium, were estimated from the shock wave data as 70 GPa and 1300°K, respectively.

These thermodynamic calculations indicate that the transition pressure at which FeO (hpp) exsolves from $\text{Fe}_x\text{Mg}_{1-x}\text{O}(\text{B1})$ increases asymptotically at a constant temperature from the value at $x = 1$ for the transition $\text{FeO}(\text{B1}) \rightarrow \text{FeO}(\text{hpp})$ to an infinite value at $x = 0$ for $\text{MgO}(\text{B1}) \rightarrow \text{MgO}(\text{hpp})$. The effect of increasing temperature is generally to increase the pressure at which a given composition $\text{Fe}_x\text{Mg}_{1-x}\text{O}(\text{B1})$ exsolves FeO (hpp).

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Implications for the Earth The rocksalt phase (Fe, Mg)O has been proposed by a number of investigators to be an important component of the lower mantle, e.g. (6,7); exsolution of FeO (hpp) from (Fe,Mg)O must be considered therefore as a process which may occur within the earth. For simplicity, we shall assume in the following that the present day lower mantle has a pyrolite bulk composition (6,8) with an Mg/(Mg+Fe) ratio of approximately .90. Partitioning of iron between the dominant iron-bearing phases rocksalt and perovskite (9) will yield approximately Fe_{.02} Mg_{.98} SiO₃ (perovskite) and Fe_{.18} Mg_{.82} O rocksalt. For this composition of the rocksalt phase, exsolution of FeO (hpp), if it does occur in the lower mantle, will only take place in the region immediately overlying the core and will not be a significant factor in the chemistry of the present-day lower mantle.

While exsolution of FeO (hpp) from (Fe,Mg)O may not be an important process in the present-day lower mantle, it may have played a significant role in the development of the early earth. Assuming oxygen as the light alloying element in the core, e.g. (11), the bulk composition of the earth, and by inference, of the material from which the earth accreted, can be estimated as 20 wt% metallic Fe, 32% SiO₂, 28% MgO and 20% FeO. The bulk Mg/(Mg+Fe) ratio is thus approximately 0.7 with partitioning of Fe and Mg between the co-existing magnesio-wüstite phases resulting in the rocksalt phase composition Fe_{.5} Mg_{.5} O. Exsolution of FeO (hpp) from this more iron-rich rocksalt phase will occur at significantly lower pressures corresponding to a depth of order 2000Km. Exsolution of FeO (hpp) from (Fe,Mg)O is therefore a potentially significant process in the development of the earth because it provides a means of decoupling the chemistry of iron from magnesium at high pressure and temperature. Coupled with a model predicting the formation of a low-temperature eutectic in the system Fe-FeO at high pressure (12), it forms the basis for a model describing core segregation within the earth (13).

References: (1) Jeanloz, R. and Ahrens, T. (1980) *Geophys. J.R. astr. Soc.* 62, 505. (2) Jackson, I. and Ringwood, A.E. (1981) *Geophys. J.R. astr. Soc.* 64, 767. (3) Zou, G.T., et al. (1980) *Ann. Rept. Geophys. Lab.* 79, 374. (4) Ringwood, A.E. (1962) *Geochim. Cosmochim. Acta* 26, 457. (5) Vassiliou, M.S. and Ahrens, T.J. (1980) *Trans. Am. Geophys. Union* 61, 378. (6) Ringwood, A.E. (1975) *Composition and Petrology of the Earth's Mantle*, McGraw-Hill. (7) Liu, L.G. (1979) in *The Earth, its Origin, Structure and Evolution* (ed. McElhinny), Academic Press. (8) Green, D.H., et al. (1979) *Ibid.* (9) Bell, P.M. et al. (1979) *Ann. Rept. Geophys. Lab.* 78, 618. (10) Stacey, F.D. (1977) *Physics of the Earth* 2nd ed., John Wiley and Sons. Inc. (11) Ringwood, A.E. (1977) *Geochem. Jour.* 11, 111. (12) McCammon, C.A., et al. (1981) This volume. (13) McCammon, C.A. et al. (1981) This volume.