LATTICE ENERGIES, PHASE TRANSFORMATIONS AND VOLATILES IN THE MANTLE

W. S. FYFE

Manchester University

While an exact calculation of the conditions of a phase transition is yet impossible in most chemically complex materials, it may be possible to show that a given transition is at least likely at some position in the mantle. The necessary conditions for a transition are that the volume change be negative and that the free energy barrier does not exceed 36 kcal for each cm³ of negative volume change. It is this rather large energy change ($\Delta P.\Delta V$) involved over the range of mantle pressures that allows any reasonable prediction. With simple substances with relatively small lattice energies predictions can be made with some degree of certainty; e.g. AB, AB$_2$ compounds such as MgO, SiO$_2$ etc. It is shown that none of the common types of hydrates minerals, amphiboles and micas, can carry water into the deep mantle. If water is trapped, it is more likely to be found in phases such as hydroxy silicates where (OH)$_n$ species replace Si–O groups and are partially stabilized by dilution in solid solutions.

1. Introduction

One of the ultimate and most difficult problems of Earth Science is to deduce the chemical composition and structural states of matter in the inaccessible portions of the earth. It is almost certain that our present views on the composition of the earth (i.e. the mantle and core), so largely influenced by the composition of an unbalanced meteorite sample, will require modification in future years. There are still innumerable problems in rationalizing views on the change in composition with depth with changes to be expected from thermodynamic equilibrium in a gravitational field. This latter problem has received scant attention (e.g. BREWER, 1951) and some calculations on the MgO–FeO–SiO$_2$ system (KERN and WEISBROD, 1967) seem hardly in accord with present proposals concerning the composition of the mantle. Perhaps the earth is still a long way from being in gravitational equilibrium or perhaps our knowledge of phases and their compressibilities at high pressures still leaves something to be desired.

If a given chemical composition is to be in stable equilibrium at a given position in the earths gravitational field it is necessary that the phases formed be of appropriate density. While such perfect equilibrium states may not be achieved, we are continually searching for phase changes and phase chemistry which are feasible and any approach in this test of feasibility can guide experimental approaches. The problem is difficult and I would agree with KAMB's (1968) remark: "In proposing structural explanations for physical properties, one must guard against facile a posteriori rationalizations that are arbitrarily contrived to fit particular facts, and that have no general validity or significance".

If we consider the mantle with its rather small thermal gradient it is clear that in a general way pressure is a more significant thermodynamic variable than temperature. For most phase changes (A→B), entropy and volume changes are sympathetic in sign and to some extent in magnitude. Thus when plotted on P–T coordinates, slopes of phase changes tend to be similar. On average, for a ΔV of -1 cm³/mol, ΔS is near -0.5 cal/mol °C. Given the mantle pressure range of 1.5×10^6 b and temperature range of about 5000 °C, over this range, changes in ΔG of reaction for the above ΔV and ΔS averages will be

$$\left(\frac{\partial \Delta G}{\partial P}\right)_T = \Delta V \approx -36 \text{ kcal},$$

$$\left(\frac{\partial \Delta G}{\partial T}\right)_P = -\Delta S \approx +2.5 \text{ kcal}.$$

The $P\Delta V$ term is comparable to chemical bonding energies and indicates that structures most unlikely at the surface may be easily achieved in the deep mantle. For example the ΔV of the graphite–diamond transition is