LATTICE ENERGIES, PHASE TRANSFORMATIONS AND VOLATILES IN THE MANTLE

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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 cm^3 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 cm^3/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

about -2 cm^3/mol and if diamond was to be impossible in the mantle, the bond energy of graphite would need to be 80 kcal greater than diamond. Even if diamond had never been seen, data on the energies and lengths of carbon bonds as seen in organic molecules would certainly lead us to expect diamond at quite moderate pressures. In fact quantum mechanical calculations would be adequate in this case.

The problem of predicting the possibility of a phase change over the mantle P–T range thus resolves itself into two questions (if we assume that T and S are rather unimportant to a first approximation). First, can the volume change be guessed? Second, can the bond energies or lattice energies be guessed with any degree of significance? It is normally the latter question that involves difficulty; but less so if we do not require an accurate transition pressure. For a long time to come experimental methods will be required, but at least some guidance for experiment seems possible. The limited success of Fersman's approach to bond energies (see MASON, 1966, p. 85) from which it follows that

$$\sum \Delta H_f \text{ oxides} \approx \sum \Delta H_f \text{ compound}$$

emphasizes the difficulty of finding energy differences between structural states as these are often small differences between very large values (e.g. compare the lattice energies of quartz and cristobalite).

2. Changes in coordination

Phase changes induced by high pressures most frequently involve changes in coordination numbers. There are important exceptions (e.g. the olivine–spinel transition discussed by KAMB, 1968). Most of the discussion that follows is involved with examples where changes in coordination occur.

A typical simple example is illustrated by KCl. This is known to change from the NaCl structure (6-coordination) to the CsCl structure (8-coordination) at moderate pressures. The ratio of the radii of K$^+$ and Cl$^-$ (0.734) is almost exactly on the theoretical crossover from 6- to 8-coordination. Without any change in bond lengths ΔV would be about -8 cm^3/mol. For the transition to occur in the mantle pressure range, the ΔH of transition must not exceed 280 kcal/mol, and as this figure is greater than the lattice energy of the 6-coordinated form (163 kcal) the transition must be considered feasible.

If we consider the simple Born lattice energy equation:

$$U = \frac{NAe^2 z_1 z_2}{R} \left(1 - \frac{1}{n}\right),$$

and assume that both R and n are similar, then the lattice energies of the two forms are given by

$$\frac{U_1}{U_2} = \frac{A_1}{A_2},$$

where U is the lattice energy and A the Madelung constant for the structure concerned. In this case, on account of the small value of the U's, a reasonable prediction can be made of the energy barrier (see FYFE et al., 1958).

Another such simple case is shown by the rather high pressure transition of ZnO from the four coordinated sphalerite structure to the halite structure. Again, assuming no change in bond lengths, ΔV is about -2.5 cm^3/mol. In this case a rather good lattice energy for the NaCl structure can be obtained from analogous transition metal oxides allowing for crystal-field terms (FYFE, 1963). The transition is feasible and the transition pressure can be estimated with significance.

An interesting case is provided by magnesium oxide. This oxide is certainly a possible mantle phase, particularly where silicates are replaced by oxides including stishovite. It has been suggested that MgO may change from the halite to the CsCl structure. Simple spherical ions such as Mg^{2+} and O^{2-} are rather incompressible. In this case, unless large repulsive oxygen overlap is to be introduced, the Mg–O bond length in periclase must lengthen in an 8 coordinate structure. If the volume of the latter is calculated assuming that O–O penetration does not occur, it will be larger than in the periclase structure. If the volume is made smaller, ΔV will still be small and a large barrier introduced. Thus, from present data, MgO in the CsCl structure does not appear easily accessible at least not till such pressures are achieved that the ionic model ceases to be relevant.

Magnesium does occur in 8-coordination in some silicate structures, for example pyrope. But in this case, oxygen atoms linked to magnesium are also linked to either aluminium or silicon with quite covalent bonds. These linkages all reduce the ionic charge on oxygen and can remove the spherical symmetry of the charge cloud. Such influences are unlikely with the simple oxide.

That the stishovite transition in SiO_2 is feasible is also easily shown but in this case, on account of the large lattice energies involved, calculation of the barrier with significant accuracy is difficult. First, SiO_2 in the rutile structure, even with the same cell volume as TiO_2, would have a smaller volume than quartz, by about 4 cm³/mol. The lattice energies of rutile and quartz differ by about 240 kcal (experimental values) so that given the true volume of stishovite this barrier can be overcome and the real barrier must be less. A reasonable guess of both cell volume and barrier can be derived by consideration of bond distances and energies involved in the formation of TiF_6^{2-} and SiF_6^{2-} in aqueous solution (FYFE, 1963). We may note, that once pressures are high enough that SiO_2 in the rutile structure is favoured, we may then expect a large array of silicates with 6-coordinated silicon to also be in the realms of possibility; the heats of formation of most compounds from the oxides in the appropriate structural state being rather small (cf. $FeO + SiO_2 \rightarrow FeSiO_3$ and $FeO + TiO_2 \rightarrow FeTiO_3$). Thus phases such as $KAl Si_3O_8$ (orthoclase) in a dense structure should be possible in the stishovite stability field as suggested by KUME et al. (1966).

The high-spin–low-spin transition in FeO and hence in all iron oxygen compounds has been discussed by FYFE (1960) and more recently by STRENS (1969). This transition, which seems feasible in the mantle, has considerable bearing on iron-magnesium geochemistry in the deep mantle and on the optical properties of this region. While it must lead to denser iron compounds (the diamagnetic ferrous ion being small) it may also lead to iron compounds with rather different compressibilities than those with which we are familiar. The transition in octahedrally coordinated iron oxygen compounds has not been observed. The calculations of the transition region in the mantle both by Fyfe and Strens seem inadequate as neither have taken into account all the factors involved, but at least Strens calculations show it to be feasible (more detailed work is in progress by Fyfe and McLellan).

3. Phases containing volatiles

While phase changes in rather simple compounds can often be rationalized and predicted, as soon as we come to consider multi-atom compounds, problems increase. In the lower crust and upper mantle, most water

is contained in rather complex structures such as micas and amphiboles while in some regions, serpentine minerals may be significant. With our present knowledge, carbon dioxide is mainly found in rather simple carbonates. RUBEY (1951) in his classic essay on sea water discussed the evolution of the hydrosphere, and showed convincingly that water and other volatiles have been slowly added to the surface from the mantle. It is of some importance to understand how volatiles may be trapped in the deep mantle for this has bearing on many geochemical problems including evolution of the oceans, atmosphere and life.
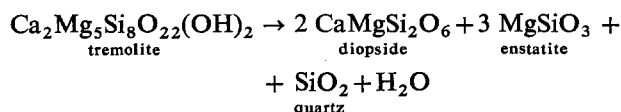
It is a striking fact, that most of the complex hydrate minerals with which we are familiar cannot persist far into the mantle. First we may consider the serpentine minerals. BOWEN and TUTTLE (1949) showed that at low water pressure (1–2 kb) serpentine breaks down to less hydrous phases at temperatures near 500 °C. Let us consider the simplified reaction

$$Mg_3Si_2O_5(OH)_4 \rightarrow MgSiO_3 + Mg_2SiO_4 + 2H_2O.$$
serpentine   enstatite   forsterite

The ΔV_0 of this reaction is about 5 cm³/mol. As breakdown occurs in the region 5–600 °C, we would anticipate maximum thermal stability where ΔV tends to zero. From data in SHARP's (1962) tables we would expect this inflection to occur near 30 kb. KITAHARA et al. (1966) have observed such inflection in the vapour pressure curve. The general form of the phase diagram is shown in fig. 1.

The form of vapour pressure curve of fig. 1 is not normally observed in low pressure studies, but once the mantle pressure range is considered, most curves will follow such a pattern. Two types of mineral are of particular interest in deep water retention; the micas (in particular phlogopite) and amphiboles (in particular hornblendes). Not much data is available for hornblendes as yet, but tremolite provides a model.

For the reaction

$$Ca_2Mg_5Si_8O_{22}(OH)_2 \rightarrow 2 CaMgSi_2O_6 + 3 MgSiO_3 +$$
tremolite   diopside   enstatite

$$+ SiO_2 + H_2O$$
quartz

$$\Delta G_0 = 18 \text{ kcal} \qquad \Delta V_0 = -5.5 \text{ cm}^3.$$

From the available data (CLARK, 1966) it would be expected that tremolite would have a maximum thermal stability at about 1000 °C, and after about 10 kb the
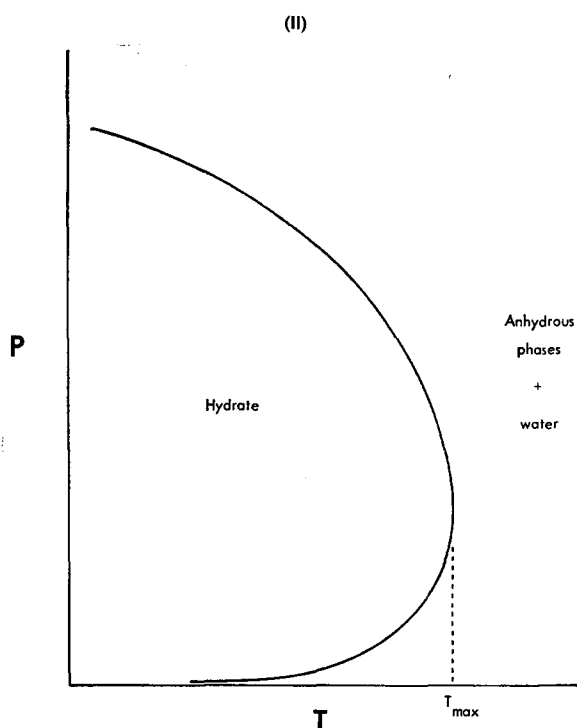
(II)

Fig. 1. General form of the stability field of most hydrates. T_{max} occurs near 600 °C for serpentine, 1000 °C for amphiboles, and rather higher for phlogopite.

vapour pressure curve will become negative and reach about 100 kb at room temperature.
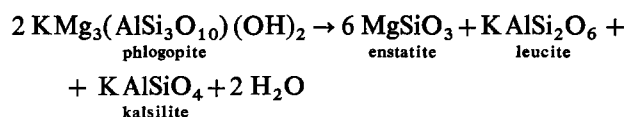
We would anticipate a similar curve for the transition

$$\text{amphibolite} \rightarrow \text{eclogite} + \text{vapour}.$$

Previously, ESSENE and FYFE (1967) suggested that this curve could have positive slope on account of the large negative ΔV of the reaction

$$\text{amphibolite} \rightarrow \text{eclogite} + \text{water},$$
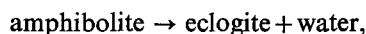
and the small amount of water. Essene and Fyfe suggested that ΔS could also be negative. It seems however that this is inconsistent with all data on the reaction and with the anomalously low entropy of amphiboles as compared with pyroxenes. In fact, the limits of hornblende may be similar to that indicated for tremolite. It seems that YODER and TILLEY's (1962) statement that eclogite cannot exist stably in the crust with excess water is probably correct (this point will be discussed separately by the writer in a paper in press).

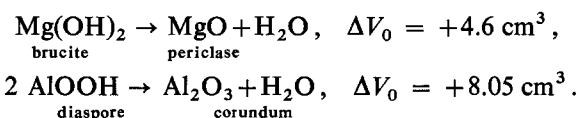Of all micas studied, phlogopite has the greatest thermal stability. The reaction

$$2\,\text{KMg}_3(\text{AlSi}_3\text{O}_{10})\,(\text{OH})_2 \rightarrow 6\,\text{MgSiO}_3 + \text{KAlSi}_2\text{O}_6 +$$
$$\text{phlogopite} \qquad\qquad \text{enstatite} \qquad \text{leucite}$$
$$+\,\text{KAlSiO}_4 + 2\,\text{H}_2\text{O}$$
$$\text{kalsilite}$$

occurs in quartz free systems and the vapour pressure reaches 5 kb only over 1000 °C. The ΔV_0 of the reaction is 73.5 cm^3 on account of the low densities of leucite and kalsilite. There is no way of changing the slope of the vapour pressure curve unless it is changed by melting of phlogopite or unless phase changes occur in the K-Al silicates. In this connection the possible phase change of $KAlSi_3O_8$ to a dense phase suggested by KUME et al. (1966) is of considerable interest. If this occurs in the region of stishovite stability we may then have the reaction

$$\text{KMg}_3(\text{AlSi}_3\text{O}_{10})\,(\text{OH})_2 \rightarrow \text{dense KAlSi}_3\text{O}_8 +$$
$$+\,3\,\text{MgO} + \text{H}_2\text{O}.$$
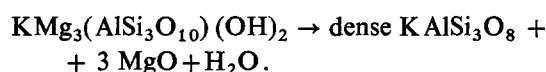
If the molar volume of dense $KAlSi_3O_8$ is placed at the same value as the germanate $KAlGe_3O_8$ (and it must be less), the reaction now has a large negative ΔV and the reaction must reach a thermal maximum. Other changes in leucite and kalsilite may occur and cause reversal even sooner.

It is of considerable interest to note that hydrates which can show surprising thermal stability at high pressures are simple ones. Thus

$$\text{Mg(OH)}_2 \rightarrow \text{MgO} + \text{H}_2\text{O}, \quad \Delta V_0 = +4.6\ \text{cm}^3,$$
$$\text{brucite} \qquad \text{periclase}$$

$$2\,\text{AlOOH} \rightarrow \text{Al}_2\text{O}_3 + \text{H}_2\text{O}, \quad \Delta V_0 = +8.05\ \text{cm}^3.$$
$$\text{diaspore} \qquad\quad \text{corundum}$$

To reverse the sign of these reactions (it has already been stated that it is unlikely that a major phase change can occur with MgO) water will have to be compressed to very large densities, about two in the case of the diaspore reaction. For example, at 1000 °C the entropy of this reaction and the ΔV will probably still be positive at 100 kb (SHARP, 1962). KENNEDY (1959) has studied diaspore stability to 50 kb and shows a linear relation of log P with T. But even in this case the geothermal gradient is probably too steep to allow persistence to great depths.

In summary, it seems that few known hydrated silicates are likely to remain stable below a few hundred kilometers in the mantle of the earth. Phlogopite stability will exceed amphibole stability unless unknown phase changes in K-Al silicates occur at rather low

pressures. This conclusion poses the question: are terrestrial processes concerned with water restricted only to the upper mantle or is water still present at much deeper levels?

## 4. Hydro-silicates and related compounds

To increase the stability of hydrates at high pressures, much denser hydroxy compounds are required, or phases must form which will readily mix with common phases in the mantle leading to lower chemical potentials. In this connection phases which may be of interest are hydroxy silicates such as the hydrogarnets. In these phases $(OH)^{4-}$ replaces SiO^{4-}, the best known case being the hydrogarnets. YODER (1950) showed that these can have considerable thermal stability.

Volume data for the grossularite–hydrogrossular series (YODER, 1950) indicate that along the series

$$Ca_3Al_2(SiO_4)_3 \rightarrow Ca_3Al_2(OH)_{12}$$
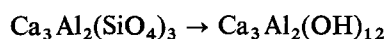
replacement of one SiO_4 by $(OH)_4$ leads to a ΔV of 8 cm^3. The structure of the $(OH)_4$ group has been studied by neutron diffraction and indicates that the structure contains unsymmetrical hydrogen bonds and that the O–O distances of the $(OH)_4$ group are much longer (3.17–3.39 Å) compared to the O–O distances in the normal SiO_4 group (2.7 Å). Nevertheless, even with this large O_4 group some processes of interest appear almost possible.

Thus a reaction such as

$$\underset{\text{brucite}}{2\,Mg(OH)_2} \rightarrow \underset{\text{olivine}}{Mg_2(OH)_4}$$
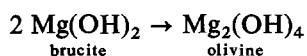
would have a ΔV of only $+2$ cm^3 (we should perhaps note that brucite may well change to a rutile structure like MgF_2 at high pressures).

It seems to this author that the $(OH)_4$ grouping might show abnormal compressibility. If the hydrogen bonds were to become symmetrical, considerable shortening of O–O distances would follow. Such shortening

is observed in the F–H–F distances in the bifluoride ion HF_2^- as compared with polymerized HF. A symmetrical O–H–O bridge might have an O–O distance of as little as 2.5 Å. In this case a hydrogarnet might well be denser than a normal garnet. Overlap calculations (FYFE, 1953) show that changes from unsymmetrical to symmetrical hydrogen bonds are probable as bond distances shorten. The state of our knowledge on the structures of hydroxy compounds at high pressures is so meagre that one hesitates to predict, but it appears that more work on hydroxysilicates is needed. Unless denser compounds can be produced, it seems unlikely that much water will occur in deep mantle phases. The situation with carbonates is equally tantalizing. Are there spinels such as Mg_2CO_4 based on CO_4 groups? Reactions such as

$$MgCO_3 + MgO \rightarrow Mg_2CO_4 \text{ (spinel)}$$
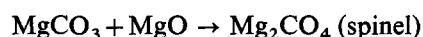
would certainly have negative volume changes.

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