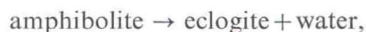


Fig. 1. General form of the stability field of most hydrates. T_{max} occurs near 600 °C for serpentine, 1000 °C for amphiboles, and rather higher for phlogopite.

vapour pressure curve will become negative and reach about 100 kb at room temperature.

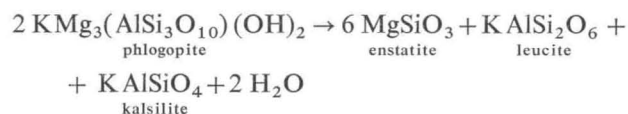
We would anticipate a similar curve for the transition
amphibolite \rightarrow eclogite + vapour.

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

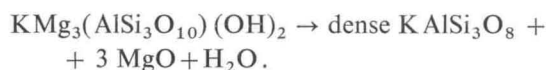


and the small amount of water. Essene and Fyfe suggested that ΔS could also be negative. It seems however that this is inconsistent with all data on the reaction and with the anomalously low entropy of amphiboles as compared with pyroxenes. In fact, the limits of hornblende may be similar to that indicated 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

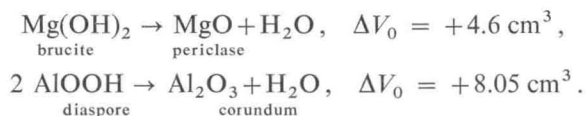


occurs in quartz free systems and the vapour pressure reaches 5 kb only over 1000 °C. The ΔV_0 of the reaction is 73.5 cm³ on account of the low densities of leucite and kalsilite. There is no way of changing the slope of the vapour pressure curve unless it is changed by melting of phlogopite or unless 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



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



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.

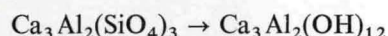
In summary, it seems that few known hydrated silicates are likely to remain stable below a few hundred kilometers in the mantle of the earth. Phlogopite stability will exceed amphibole stability unless unknown phase changes in K-Al silicates occur at rather low

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

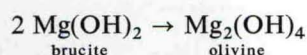
To increase the stability of hydrates at high pressures, much denser hydroxy compounds are required, or phases must form which will readily mix with common phases in the mantle leading to lower chemical potentials. In this connection phases which may be of interest are hydroxy silicates such as the hydrogarnets. In these phases $(\text{OH})^{4-}$ replaces SiO_4^{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



replacement of one SiO_4 by $(\text{OH})_4$ leads to a ΔV of 8 cm^3 . The structure of the $(\text{OH})_4$ group has been studied by neutron diffraction and indicates that the structure contains unsymmetrical hydrogen bonds and that the O-O distances of the $(\text{OH})_4$ 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.

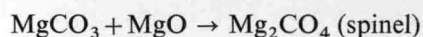
Thus a reaction such as



would have a ΔV of only $+2 \text{ cm}^3$ (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 $(\text{OH})_4$ 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



would certainly have negative volume changes.

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