Experimental investigation of antigorite stability to 80 kbar

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Introduction

The high pressure stability of antigorite is fundamental for the understanding of H_2O storage and recycling during subduction of oceanic lithosphere. Antigorite contains approximately 13 wt% H_2O (28 mol%) and often constitutes 90% of hydrated peridotites. Natural examples of ultramafic complexes, subjected to eclogite-facies metamorphism (Zermatt-Zone, Switzerland; Erro-Tobbio, Liguria, Italy) indicate that antigorite is stable in excess of 600°C and 25 kbar.

High pressure experimental studies on the stability of serpentine have been performed with two different starting materials: Kitahara *et al.* (1966) and Yamamoto and; Akimoto (1977) used synthetic starting materials in the system MgO–SiO_2–H_2O; they did not specify their serpentine minerals. Evans *et al* (1976) used natural antigorite. Experiments with synthetic (MSH) starting material resulted a very limited high pressure stability of serpentine ($\leqslant$ 550°C at 10–50 kbar), but large stability fields of hydromagnesium-silicate phases A and D were encountered at high pressures ($\geqslant$ 30 kbar). The experiments of Evans *et al.* (1976) up to 15 kbar using natural antigorite (X_{Mg} = 0.98, Al_2O_3 = 1.28) resulted in a much higher temperature stability for antigorite (660°C at 15 kbar). This apparent discrepancy can most probably be attributed to the difference in starting material. Calculations using internally consistent data bases result in notable backbending of the equilibrium:

$$tc + fo = 5 en + H_2O$$
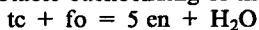
and intersection with the equilibrium

$$ant = 18fo + 4tc + 27H_2O$$
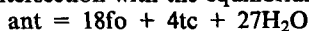
at 16 kbar.

Experimental methods

In the present study a natural, well characterised antigorite (no variation in periodicity, m = 17, Mellini *et al.*, 1987; composition: X_{Mg} = 0.96, Fe^{3+}/Fe_{tot} = 0.15, Al_2O_3 = 1.30) from a serpentinite of the Malenco ultramafic unit was used as starting material. The separated sample consists of 80% antigorite and 20% brucite. The starting mixture was made from 90% of the separate and 10% high temperature products (forsterite - enstatite) obtained by reacting the original material at 10 kbar, 900°C for 48 hours. This arrangement is similar to the one used by Evans *et al.* (1976). H_2O saturation was achieved through the presence of brucite which reacts at low temperatures with antigorite to form forsterite and H_2O

Experiments up to 35 kbar were performed in piston cylinder apparatus using NaCl assemblies. The samples were encapsulated in 2.3mm $Ag_{75}Pd_{25}$-containers and welded shut. Experiments from 35 to 80 kbar were performed in a Wacker-type multi-anvil apparatus using 12 mm truncation (TEL) WC-anvils and a MgO-based pressure medium. The pressure was calibrated against various high pressure phase transitions in the range 30 to 90 kbar and 1000–1200°C. Temperatures were measured with 2 Pt–$Pt_{10}Rh$ (type S) thermocouples placed at the bottom and the centre of the capsules. Temperature gradients from bottom to the centre of the capsules are less than 10°C at 700°C and 25°C at 1000°C. The starting material was contained in 1.6mm OD $Ag_{50}Pd_{50}$ capsules (2.5–3.5 mm long). Run duration varied from 12 hours at high pressures to 120 hours at 15 kbar. The recovered charges were analysed by powder X-ray diffraction and electron microprobe. Brucite, present in the starting material, was never observed in the run products, but forsterite, not present in the starting material, was always present in appreciable amounts ($\geqslant$ 15%), demonstrating that the low temperature reaction of

$$ant + 20 bru = 34 fo + 51 H_2O$$

always went to completion.

Results

Figure 1 summarises the preliminary results on antigorite stability. Brackets below 18 kbar were taken from Evans *et al.* (1976). Antigorite is stable to at least 62 kbar. At 77 kbar and 500°C no
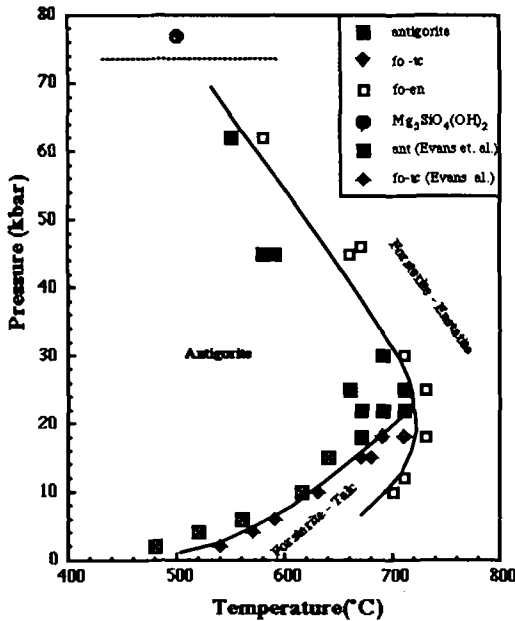
FIG. 1 Pressure–temperature diagram showing the experimentally determined reaction curves for ant = 18fo + 4tc + 27 H_2O, ant = 14fo + 20en + 31H_2O (brackets below 18 kbar taken from Evans et al., 1976), and fo + tc = 5en + H_2O

antigorite was found, but norbergite (Mg$_3$SiO$_4$(OH)$_2$), overgrown (quench from fluid) by an unknown phase with the composition Mg$_4$Si$_3$O$_9$(OH)$_2$ was observed. At 62 kbar 10-A-phase (Mg$_3$Si$_4$O$_{10}$·2H_2O, metastable, quench?) was observed. The reaction

ant = 18fo + 4tc + 27H_2O
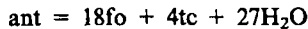
has a positive slope, and is consistent with the results of Evans et al. (1976). The assemblage forsterite + talc has a larger stability field than the calculated phase equilibria. The invariant point (in the system MSH) is located at approximately 22 kbar and 720°C, instead of 640°C/16 kbar in the calculated phase diagrams. The reaction ant = 14fo + 20enstatite + 31H_2O has a negative PT-slope. Refinement of thermodynamic data from the experiments is, however, inappropriate at the present state of knowledge.

Conclusions

The experimental results presented above show that antigorite is a stable phase in peridotite bulk compositions at low temperatures to at least 62 kbar (200 km). Antigorite breaks down to forsterite + talc + H_2O at pressures less than 22 kbar. At higher pressures antigorite breaks down directly to the hydrate free assemblage forsterite + enstatite + H_2O. This implies that the release of H_2O from deeply subducted, serpentinised peridotites could be either stepwise (in 'hot subduction environment'; slow subduction, young oceanic lithosphere) with intermediate talc, or single step ('cold subduction'; fast subduction, old oceanic lithosphere). Thus, there is a considerable potential of antigorite to store and transport H_2O deeply into the upper mantle, where its breakdown can lead to mantle metasomatism and generation of arc-type magmas in the overlying mantle wedge.

References

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