# The stability of dense hydrous magnesium silicates in Earth's transition zone and lower mantle

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**Abstract**—The presence of $H_2O$ can dramatically influence the chemical and physical properties of minerals that comprise Earth's mantle. In order to understand these effects it is important to identify the phases in which $H_2O$ may exist under mantle conditions. In high pressure experimental studies a number of hydrated magnesium silicate phases have been produced which may be important hosts for $H_2O$. To date, however, the stability fields of such phases were poorly constrained and their ability to exist in mantle compositions has remained essentially untested.

To determine the role of dense hydrous magnesium silicate phases (DHMS) as hosts for $H_2O$ in the mantle the available phase equilibria data are reviewed here at pressures above 10 GPa. New results from multianvil experiments performed on a hydrated natural harzburgite composition are also reported. These data are used to constrain the conditions where DHMS phases could exist in a plausible mantle composition.

Between 10 and 25 GPa there is evidence for the existence of five so-called DHMS alphabet phases, these being phases A, B, superhydrous phase B, D and E. The phases which have previously been described as C and superhydrous phase B appear to be identical and phases D, F and G are similarly a single phase. Due to their limited thermal stability DHMS phases could only exist in the cool interior of a subducting slab and their composition would limit them to Mg-rich ultramafic rocks. A potential mechanism exists, however, by which DHMS phases may be important in transporting $H_2O$ into Earth's transition zone and lower mantle.

Building on the evidence presented in the previous chapter it would appear that along cool subduction geotherms antigorite (serpentine) might persist to pressures greater than 6 GPa. At temperatures below 600°C at 6 GPa antigorite would be replaced by an assemblage containing phase A and 3.7 wt % $H_2O$ could be stored in the solid phases of the slab. With increasing pressure a series of $H_2O$ conserving reactions can occur that preserve this $H_2O$ content within hydrous phases. At 13 GPa phase A will break down to an assemblage containing phase E and hydrous wadsleyite. At approximately 19 GPa phase E will breakdown to superhydrous phase B and stishovite. A continual network of hydrous phases could transport water within the cool, ultramafic regions of subducting slabs to depths corresponding to the base of transition zone. Slabs entering the lower mantle at temperatures below 1300°C could host water in the form of hydrous phase D.

## INTRODUCTION

THERE IS evidence from mantle xenoliths (BELL and ROSSMAN, 1992) and primitive basalt glasses (SOBOLEV and CHAUSSIDON, 1996) for the presence of trace quantities of $H_2O$ in Earth's interior. Estimates for the $H_2O$ content of MORB source mantle range between 100-500 ppm and enriched plume-source mantle may contain up to 3-4 times more (MICHAEL, 1988; JAVOY and PINEAU, 1991; JAMBON, 1994; SOBOLEV and CHAUSSIDON, 1996). Studies have shown that the presence of small quantities of $H_2O$ can have significant effects on such properties of rock forming minerals as rheology, elasticity, electrical conductivity and melting temperature. Dehydration of minerals at high pressure is linked to the petrogenesis of island arc volcanics and may also have implications for the origin of deep focus earthquakes (MEAD and JEANLOZ, 1991).

To fully understand the mantle $H_2O$ budget requires knowledge of the flux of $H_2O$ into and out of Earth's interior and an important step is to evaluate the depth to which $H_2O$ could be returned to Earth's mantle via subduction. If subducting oceanic lithosphere is entirely dehydrated beneath island arcs then $H_2O$ will be recycled back to the overlying crust and mantle on a relatively short time scale ($\sim$15 MY). If, on the other hand, hydrous minerals could persist in slabs to greater depths, $H_2O$ could be recycled into the transition zone or lower mantle. The extent to which $H_2O$ is transported into the mantle and the effects that $H_2O$ might have throughout the mantle will depend largely on the phases in which $H_2O$ is stabilised under various mantle conditions.

The search for minerals that may host $H_2O$ in Earth's interior has motivated many high pressure studies in the simplified $MgO$-$SiO_2$-$H_2O$ (MSH) system. Such studies have identified a number of dense hydrous magnesium silicate (DHMS) phases at pressures above 3 GPa which, to date, have not been found to occur naturally. The so-called alphabet phases comprise phases A, B, C (RINGWOOD and MAJOR, 1967), D (LIU, 1987), E, F (KANZAKI, 1991), G (OHTANI et al., 1997) and superhydrous phase B (GASPARIK, 1993). Two further high pressure hydrous phases have been named after prom-

inent lines in their X-ray diffraction patterns, these being 10 Å phase (SCLAR *et al.*, 1965) and 3.65 Å phase (RICE *et al.*, 1989). Humite minerals such as chondrodite and clinohumite have similarly been produced in high pressure MSH experiments (YAMAMOTO and AKIMOTO, 1977; WUNDER *et al.*, 1995). A significant number of studies have been performed in order to determine the structure, stability and physical properties of these phases, however, very little concerted effort has been made in order to asses the possible presence of these minerals under some conditions in Earth's mantle.

There are three major features of the dense hydrous magnesium silicate phases that would seem to exclude them from existing in the mantle. These phases have limited thermal stability, they require high water concentrations (5-18 wt % $H_2O$), and many appear to be too magnesium-rich for them to coexist with minerals that are known to comprise the bulk of the mantle. In recent years it has also been recognised that some nominally anhydrous minerals, such as garnet, olivine and wadsleyite, can also dissolve significant quantities of OH into their structure (AINES and ROSSMAN, 1984; SMYTH, 1987; KOHLSTEDT *et al.*, 1996). The mantle water budget may be entirely hosted by such minerals without there being residual water to stabilise DHMS. Given these considerations, however, many studies still report the relevance of DHMS to the cool regions of subducting lithosphere (OHTANI *et al.*, 1995;1997; FROST and FEI, 1998; IRIFUNE *et al.*, 1998) and it has been proposed that these phases may be important in returning water to the mantle during subduction (THOMPSON, 1992).

In order to determine the role that DHMS phase might play in the recycling of $H_2O$ into the mantle the current literature on the stability of these phases has been examined at pressures above 10 GPa. New high-pressure experiments on a natural hydrated harzburgite composition are also reported. These data will be used to assess which of the DHMS phases could be stable in Earth's mantle and whether DHMS phases stable in the cool regions of subducting lithosphere could transport water into the transition zone or lower mantle. As the aim of this work is to asses hydrous phase stability above 10 GPa discussion will be generally limited to the alphabet phases as the humite minerals and 10 Å phase have only limited stability above this pressure. Phase relations of hydrous systems below 10 GPa are discussed in this volume by P. ULMER and V. TROMMSDORFF.

## DENSE HYDROUS MAGNESIUM SILICATES

The compositions of the dense hydrous magnesium silicates produced at pressures above 10 GPa are shown in Fig. 1. The phases cover a range of $H_2O$
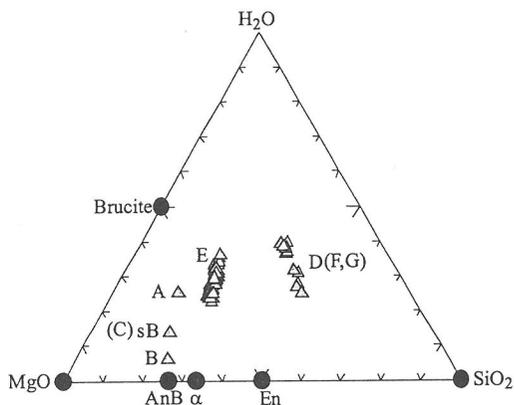


FIG. 1. Molar ternary diagram showing the compositions of the dense hydrous magnesium silicate alphabet phases. The composition of anhydrous phase B (AnB) is also shown. Phases F and G are identical to phase D and phase C is most likely identical to superhydrous phase B (sB). Phases D and E are variable in composition. $H_2O$ contents of phases D and E are estimated from the loss in electron microprobe analysis totals with an uncertainty of at leased 2 wt. %.

contents, from 2.4 wt. % (phase B) to over 20 wt. % (phase E) and two of the phases (E and D) are variable in composition. As will be described later, there is evidence that the phases previously referred to as D, F and G are identical and that phase C is the same as superhydrous phase B. Table 1 lists some of the properties of DHMS phases. In most cases the $H_2O$ contents of these phases have been estimated using the deficit in electron microprobe analysis totals. This method results in uncertainties of at least 2 wt. % in the determined $H_2O$ content.

By far the majority of studies on these phases have been performed using an $Mg_2SiO_4$ + 20 wt. % $H_2O$ starting composition which arises from the combination of brucite and silica in molecular proportions of 2:1. Figure 2 shows the synthesis conditions for DHMS phases using such a starting composition. This diagram summarises the multianvil experiments of KANZAKI (1991), INOUE (1994), OHTANI *et al.* (1995), LUTH (1995) and FROST and FEI (1998). Figure 2 covers a large pressure and temperature range with few experimental points. Due to the poor data coverage and the fact that these were mainly synthesis experiments and only LUTH (1995) performed any reversal experiments, only tentative stability fields are indicated on the diagram. Uncertainties in the experimental pressure and temperature measurements are considered to be at least 1 GPa and 100°C.

At pressures above 10 GPa the melting point in this composition becomes difficult to recognise in quench experiments. The solubilities of MgO and

Table 1. Properties of dense hydrous magnesium silicates

| Name | Formula | Pressure range (GPa) | Mg/Si | $H_2O$ wt. % | Density $(gcm^{-1})$ | Space Group | $K^0$ (GPa) |
|---|---|---|---|---|---|---|---|
| Phase A | $Mg_7Si_2O_8(OH)_6$ | 3-18 | 3.5 | 11.9 | 2.96 | $P6_3$ | $145^1$ |
| Phase B | $Mg_{12}Si_4O_{19}(OH)_2$ | 11-17 | 3.0 | 2.4 | 3.368 | $P2_1/c$ | ........ |
| Anhydrous B | $Mg_{14}Si_5O_{24}$ | 11-20 | 2.8 | ---- | 3.435 | $Pmcb$ | $151.5^2$ |
| Superhydrous B | $Mg_{10}Si_3O_{14}(OH)_4$ | -14-27 | 3.3 | 6 | 3.327 | $Pnnm$ or $P2_1nm$ | $142.6^2$ |
| Phase D/F/G | $MgSi_2O_4(OH)_2$ | 15-50+ | 0.55-0.75 | 10-20 | 3.5 | $P31m$ | $166^3$ |
| Phase E | $Mg_{2.08}Si_{1.16}O_{2.8}(OH)_{3.2}$ | 10-17 | 1.8-2.1 | 6-18 | 2.88 | $R3m$ | $112^4$ |

[1]PAWLEY *et al.* (1995)
[2]CRICHTON *et al.* (1998)
[3]FROST and FEI (unpublished data)
[4]BASS *et al.* (1991)

$SiO_2$ in an $H_2O$ fluid phase are high at high pressures and the quenched textures of hydrous fluids and silicate melts appear very similar. At 20 GPa for example FROST and FEI (1998) observed evidence for a quenched Mg-rich fluid phase at temperatures above the breakdown of brucite (~900°C) as shown in Fig. 2. With increasing temperature, however, we found no further textural evidence for a melting point being reached. This may indicate that the melting point is very low at this pressure or that the difference in quenched textures between fluids and melts is too subtle to tell apart. An alternative explanation, however, could be that a critical end point is reached at some pressure above 10 GPa in the forsterite-$H_2O$ system. Due to the uncertainty in the interpretation all quench textures above 10 GPa are denoted as fluid in Fig. 2.

Figure 2 shows that, at least for this simplified composition, no DHMS phases have been found at temperatures compatible with an average mantle adiabat. It is therefore most unlikely that these phases could exist within the bulk of the mantle, unless significant stabilisation occurs from the addition of components such as $Al_2O_3$ and FeO. What is more likely, however, is that in the absence of an $H_2O$-rich fluid the stability fields of the hydrous phases will be reduced from those shown in Fig. 2.

Much cooler geotherms are predicted, however, for the interior of subducting oceanic lithosphere, the upper regions of which are known to be extensively hydrated from interaction with sea-water. Many hydrous minerals that form in both mafic and ultramafic components of the oceanic lithosphere have significant high-pressure stability. In experimental studies performed on mafic compositions lawsonite, talc, phlogopite and phengite (PAWLEY, 1994; PAWLEY and WOOD, 1995; SCHMIDT, 1995; DOMANIK and HOLLO-

WAY, 1996; SATO *et al.*, 1997) have been found to be stable to pressures above 5 GPa. Although not rigorously tested, the low MgO content of mafic compositions probably excludes DHMS phase formation. However, the ultramafic portion of the oceanic lithosphere, and in particular the depleted mantle compo-
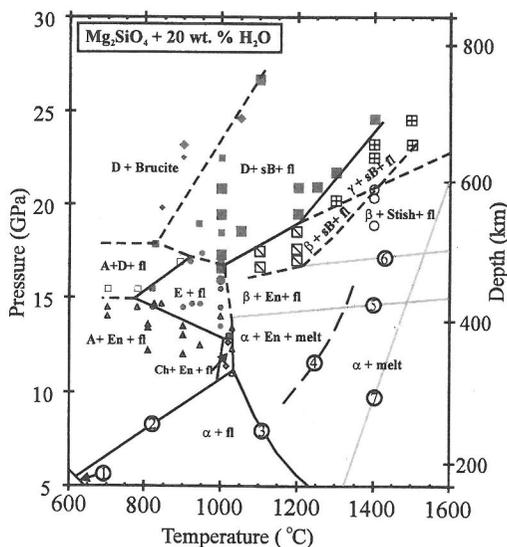


FIG. 2. The synthesis conditions of high pressure hydrous phases in the system $MgO-SiO_2-H_2O$. All experiments shown were performed using a $Mg_2SiO_4$ + 20 wt. % $H_2O$ starting composition. Large symbols are from FROST and FEI (1998), small symbols are from KANZAKI (1991) and OHTANI *et al.* (1995). The line labelled 1 is the breakdown curve of antigorite determined by ULMER and TROMMSDORFF (1995), line 2 (A+En=$\alpha$+fl) is from LUTH (1995), line 3 (melting curve) and line 4 (En out curve) are from INOUE (1994), line 5 ($\alpha$–$\beta$ $Mg_2SiO_4$ transition) and line 6 (En= $\beta$ + st) are from FEI *et al.* (1990). Line 7 is an average mantle adiabat JEANLOZ and MORRIS (1986).

nent, is much closer in composition to the DHMS phases.

The serpentine mineral antigorite is a major alteration product of ultramafic regions of the oceanic lithosphere and it has been shown to have significant high-pressure stability (ULMER and TROMMSDORFF, 1995; WUNDER and SCHREYER, 1997). ULMER and TROMMSDORFF (1995) found that phase A is produced from the breakdown of antigorite at 6 GPa and 600°C by the reaction:-

$$5Mg_{48}Si_{34}O_{85}(OH)_{62}$$
      antigorite
   [12.4 wt % $H_2O$]

$$= 14Mg_7Si_2O_8(OH)_6 + 142MgSiO_3 + 113H_2O$$
         phase A          enstatite          fluid
      [3.7 wt % $H_2O$]
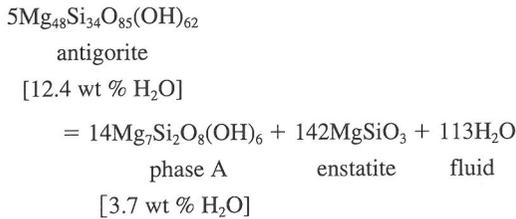
Most of the $H_2O$ bound up in antigorite would be lost from the slab as a free fluid, however, 3.7 wt. % $H_2O$ could be preserved in the solid phases. At temperatures greater than 600°C antigorite dehydrates to produce olivine, enstatite and fluid and only the relatively small concentrations ($\approx$1000 ppm) dissolved in the nominally anhydrous phases would remain in the slab. The formation of phase A could only occur along relatively cold subduction geotherms. Many thermal models, however, predict such cool environments in the top portions of subducting slabs with high plate velocities (DAVIS and STEVENSON, 1992; FURUKAWA, 1993; STEIN and STEIN, 1996). The breakdown of antigorite to produce an essentially harzburgitic bulk composition containing 3.7 wt. % $H_2O$, is probably the only plausible mechanism by which enough water is preserved within the slab to stabilise DHMS phases at high pressure. The capacity of nominally anhydrous minerals such as olivine to store $H_2O$ seems to increase with pressure (KOHLSTEDT et al., 1996). It is, therefore, unlikely that such minerals would become $H_2O$-saturated in the interior of a slab during subduction.

In a first step to understanding the stability of these phases the current compositional and phase equilibria data for each DHMS phase will first be reviewed.

## PHASE A

RINGWOOD and MAJOR (1967) and SCLAR et al. (1967) both reported X-ray diffraction patterns for a new phase synthesised in the MgO-SiO$_2$-H$_2$O system at high pressures and temperatures. The phase was referred to as "A" by RINGWOOD and MAJOR (1967) who observed it in the pressure range 10-15 GPa and at temperatures between 600-1100°C. The composition of phase A was determined by YAMAMOTO and

AKIMOTO (1974) to be $Mg_7Si_2O_8(OH)_6$ and the structure was solved by HORIUCHI et al. (1979). The composition falls along a brucite-fosterite tie line, as do the pure OH end members of the humite series of minerals, clinohumite and chondrodite. Although there are similarities HORIUCHI et al. (1979) point out a number of structural differences that make phase A distinct from minerals of the humite group. Mg octahedra in humites, for example, are linked in chains, while in phase A, layers of Mg octahedra occur.

The stability field of pure phase A extends from approximately 3 to 17 GPa and reaches a maximum temperature of approximately 1100°C at 11 GPa (YAMAMOTO and AKIMOTO, 1974; BURNLEY and NAVROTSKY, 1996; PAWELY and WOOD, 1996). In more Si-rich bulk compositions phase A has been observed as a product of the decomposition of antigorite at 6 GPa (ULMER and TROMMSDORFF, 1995) and coexists with enstatite in the $Mg_2SiO_4$ + 20 wt. % $H_2O$ composition, at conditions shown in Fig. 2 (LUTH, 1995). The high temperature breakdown of phase A above 10 GPa in the $Mg_2SiO_4$-$H_2O$ composition is poorly constrained. Both KANZAKI (1991) and LUTH (1995) recognised clinohumite as forming above 900°C between 9 and 14 GPa and OHTANI et al. (1995) observed forsterite, enstatite and melt at similar pressures above 1000°C. The coexistence of phases A, E, clinohumite, enstatite, melt and fluid in Fig. 2 at approximately 13 GPa and 1000°C apparently breaks the phase rule, however, this may be due to the incorrect definition of fluid and melt under these conditions. Between 13 and 15 GPa in the forsterite-$H_2O$ composition, phase A is replaced by an assemblage containing phase E. The available synthesis data from KANZAKI (1991), OHTANI et al. (1995) and IRIFUNE et al. (1998) suggests that this reaction has a negative P-T slope.

For cool subduction geotherms that result in temperatures of approximately 600°C at 6 GPa, $H_2O$ could pass from antigorite to phase A and then be carried into the stability field of phase E or $\beta$-$Mg_2SiO_4$ (wadsleyite). KAWAMOTO et al. (1995) found that phase A can contain up to 13 wt. % FeO (all Fe was analysed as FeO) which might expand the stability field of phase A in Fe-bearing systems compared to that shown in Fig. 2. LUTH (1995), however, showed that for a range of additional components (CaO, $Al_2O_3$, FeO, $CO_2$) the dehydration curve of phase A changed little from that shown in Fig. 2.

## PHASE B

Phase B was first identified by RINGWOOD and MAJOR (1967) at pressures above 11 GPa. The chemical formula, first proposed by AKIMOTO and AKAOGI

(1980), was confirmed by FINGER et al. (1989) as $Mg_{12}Si_4O_{19}(OH)_2$. Phase B possess a complex structure, the solution of which was possible only after a structurally similar anhydrous phase B had been analysed (FINGER et al., 1989). Both phase B and anhydrous phase B contain silicon in tetrahedral and octahedral coordination.

The stability field of pure phase B extends from approximately 11 to 17 GPa and from 700-1400°C (AKIMOTO and AKAOGI, 1980; KATO and KUMAZAW, 1985; BURNLEY and NAVROTSKY, 1996). Phase B is not, however, observed within $SiO_2$-rich bulk compositions such as the $Mg_2SiO_4$ + 20 wt. % $H_2O$ composition. Over the range of phase B stability more $H_2O$-rich hydrous phases, such as phases A, E and superhydrous phase B, can coexist with forsterite and enstatite (BURNLEY and NAVROTSKY, 1996). Tie lines, that could be drawn on Fig. 1, between forsterite and these more $H_2O$-rich hydrous phases shield phase B from mantle type bulk compositions. Phase B is therefore the least likely of the DHMS phases to be present in the mantle.

## SUPERHYDROUS PHASE B

Superhydrous phase B was first recognised by GASPARIK (1990) as an $H_2O$-rich analogue of phase B, with the formula $Mg_{10}Si_3O_{14}(OH)_4$. The structure was solved by PACALO and PARISE (1992) who determined the space group to be *Pnnm*. KUDOH et al. (1993a) in a subsequent study assigned a lower symmetry of *P2$_1$nm*. CYNN et al. (1996) argued that the existence of two OH sites and the total number of lattice modes observed in the infra red spectra of superhydrous phase B were consistent with the lower symmetry. Both structural variations may exist, however, as no detailed phase equilibria studies have been performed for superhydrous phase B composition.

GASPARIK (1993) found superhydrous phase B coexisting with stishovite between 16 and 24 GPa and 800 to 1400°C for a starting composition of Mg/Si = 1.5 and with 3.6 wt. % $H_2O$. Superhydrous phase B was also observed in more $H_2O$-rich experiments (forsterite + 20 wt. % $H_2O$) to coexist with phase D between 16 and 24 GPa 900-1500°C, (KANZAKI, 1991; OHTANI et al., 1995; FROST and FEI, 1998).

Although Mg-rich, superhydrous phase B is stable within ranges of bulk Mg:Si ratio applicable to mantle assemblages. It could, therefore, be stable within subducting slabs at the base of the transition zone. In Fig. 2 superhydrous phase B is encountered at temperatures up to 1500°C at 25 GPa and the final decomposition temperature may be even higher. In laser heated diamond anvil experiments on serpentine starting material

SHIEH et al. (1998) synthesised superhydrous phase B up to pressures of 27 GPa. Little is known about the partitioning of other components such as FeO and $Al_2O_3$ into superhydrous phase B, which may have important bearings on its stability field.

## PHASE C

Phase C was recognised by RINGWOOD and MAJOR (1967) in powder X-ray diffraction patterns of run products from their exploratory MSH experiments. The exact conditions under which phase C was produced were not stated but it was always found as a minor secondary phase in $H_2O$-rich compositions and in mixtures with Mg/Si between 3 and 5.

From a close examination of the X-ray diffraction lines reported for phase C by RINGWOOD and MAJOR (1967), KANZAKI (1993) proposed that this phase may be the same as superhydrous phase B. The X-ray diffraction lines reported for the two phases are certainly very similar and the lines missing from the phase C pattern may have been assigned to phase B by RINGWOOD and MAJOR (1967). The available phase equilibria data on superhydrous phase B are from experiments performed using Si-rich bulk compositions (atomic Mg/Si<2). In such compositions superhydrous phase B is only produced at pressures above 16 GPa where tie lines between $Mg_2SiO_4$ and phases A or E become unstable. These pressures would have been at the very limit of what RINGWOOD and MAJOR (1967) achieved in their study. The actual stability field of superhydrous phase B, however, is undetermined but given that it has a lower density than phase B it may form at similar or lower pressure conditions ($\approx$11 GPa). In experiment HZ6 reported in Table 2 superhydrous phase B was synthesised at 14 GPa and 950°C, 2 GPa lower than the stability field in more Si-rich compositions shown in Fig. 2. It was not produced, however, at 10 GPa and 850°C in experiment HZ10.

Superhydrous phase B may be stable over similar ranges of pressure as phase B and is therefore quite likely to have been produced by RINGWOOD and MAJOR (1967). RINGWOOD and MAJOR (1967) found phase C in $H_2O$-rich compositions coexisting with MgO and phase B between 10 and 18 GPa. Figure 1 shows that compositions which plot to the $H_2O$-rich side of an MgO-phase B tie line should result in the formation of superhydrous phase B. The conclusion, therefore, from both X-ray diffraction and phase equilibria evidence is that phase C is probably identical to superhydrous phase B.

Table 2. Run products from multianvil experiments

| Exp No | Starting Composition | Pressure (GPa) | Temperature (°C) | Run Duration (min) | Run Products |
|---|---|---|---|---|---|
| HZ 1 | Hartzburgite | 22 | 1300 | 120 | γ, St, sB |
| HZ 2 | Hartzburgite | 25 | 1400 | 20 | Pv, MW |
| HZ 3 | Hartzburgite Phase A comp. | 13 | 1200 | 180 | β, En, Qu An B |
| HZ 4 | Hartzburgite Phase A comp. | 9.5 | 1100 | 120 | α , En, Qu A, Ch |
| HZ 10 | Harzburgite Super B comp. | 10 | 850 | 600 | A, En A |
| HZ 6 | Harzburgite Super B comp. | 14 | 955 | 120 | β, E sB |
| HZ 7 | Harzburgite in Fe Harzburgite in Re | 17 | 1250 | 150 | β,γ β, En,Gt |
| HZ 8 | Harzburgite | 25 | 1000 | 120 | Pv, MW, D |
| HZ 9 | Harzburgite | 25 | 1300 | 120 | Pv,MW |
| HZ11 | Harzburgite | 22 | 1400 | 240 | γ, St,sB |
| HZ13 | Harzburgite | 24 | 1200 | 360 | Pv,sB, γ |

The starting composition comprised a mixture of natural olivine, orthopyroxene and synthetic brucite to give the composition in wt. %, 45.86 MgO, 7.13 FeO, 42.11 $SiO_2$, 0.68 $Al_2O_3$, 4.03 $H_2O$. Phases identified in the run productes were α–$(Mg,Fe)_2SiO_4$ (α), β–$(Mg,Fe)_2SiO_4$ (β), γ–$(Mg,Fe)_2SiO_4$ (γ), $(Mg,Fe)SiO_3$-perovskite (Pv), (Mg,Fe)O (MW), low clinoenstatite (En), chondrodite (Ch), Stishovite (St), garnet (Gt), phase A (A), phase E (E), phase D (D), superhydrous phase B (sB), and quenched material (Qu).

## PHASE D-F-G

The terms D, F and G have been used to describe hydrous phases forming at pressures above 15 GPa. The similarity in both chemistry and crystal structure reported for these phases, however, infers that they all describe a single phase.

The name phase D was first applied by YAMAMOTO and AKIMOTO (1974) to describe a phase with an X-ray diffraction pattern similar to that of the humite mineral chondrodite. A further re-examination of this phase (YAMAMOTO and AKIMOTO, 1977) revealed it to be the pure hydroxyl end member of chondrodite (hydroxyl-chondrodite).

In laser heated diamond-anvil cell (DAC) experiments performed on samples of natural serpentine, LIU (1986) identified a new hydrous phase coexisting with periclase at pressures above 22 GPa and temperatures of approximately 1000°C. LIU (1987) reapplied the name phase D to describe this new phase as he considered that this term would no longer be associated with hydroxyl chondrodite. LIU (1987) reported eight X-ray diffraction lines for phase D, the most characteristic being a low angle reflection at 9.5 Å. LI and JEANLOZ (1987), in similar DAC experiments using a hydrated enstatite starting material, also recognised diffraction lines for phase D coexisting with silicate perovskite at approximately 60 GPa and 1750°C.

YANG et al. (1997) reported a detailed powder X-ray diffraction pattern for phase D that shows all but three of the lines reported by LIU (1987). The characteristic 9.5 Å line and two further reflections at 3.37 Å and 2.53 Å were not observed by YANG et al. (1997). FROST and FEI (1998), KURODA and IRIFUNE (1998) and SHIEH et al. (1998) similarly reported the occurrence of phase D with an identical diffraction profile to YANG et al. (1997). Phase D was found to have a variable composition with Mg/Si ratio between 0.55 and 0.7 and a variable $H_2O$ content (12-18 wt %). YANG et al. (1997) solved the structure of phase D from a single crystal analysis. Si in phase D exists solely in octahedral coordination.

Two other hydrous phases, F (KANZAKI, 1991) and G (OHTANI et al., 1997; KUDOH et al., 1997a), have been proposed based on multianvil experiments. Both of these phases seem to show similar synthesis conditions, range in chemistry and structure as reported for phase D. KANZAKI (1991) recognised that the X-ray diffraction pattern reported for phase D by LIU (1987) contains additional lines that do not exist in the pattern for phase F. OHTANI et al. (1997) also recognised this point but inferred a difference between phase F and phase G based on an erroneous diffraction pattern generated from a crystal structure refinement of phase F by KUDOH et al. (1995). KUDOH et al.

(1997b) later withdrew this refinement as the crystal used was in fact superhydrous phase B.

All the evidence suggests that the phases referred to as D by YANG et al. (1997), KURODA and IRIFUNE (1998), and FROST and FEI (1998), F by KANZAKI (1991) and OHTANI et al. (1995), and G by OHTANI et al. (1997) and KUDOH et al. (1997a) are the same phase. Some doubt remains, however, as to whether this phase is then the same as that originally described by LIU (1987) and LI and JEONLOZ (1987), as these two studies report extra diffraction lines for phase D. These extra lines could arise from some structural variation in phase D at high pressure or high non-hydrostatic pressure. The additional line at 9.5 Å, for example, may indicate that phase D possesses a superstructure at high pressure. However, such additional lines could also be due to some second phase in the run products of LIU (1986) and LI and JEANLOZ (1987), although it is not clear what this phase might be. Both these studies, however, report lower quality diffraction data for phase D. Studies reporting higher quality data performed at almost identical pressures and temperatures have failed to reproduce these additional lines (KURODA and IRIFUNE, 1998; SHIEH et al., 1998; FROST and FEI, 1998). Until good quality diffraction patterns appear to the contrary it seems reasonable to assume that there is only a single phase which hence forth in this report will be referred to as phase D.

*The composition and stability of phase D*

Figure 3 shows a correlation between the Mg/Si ratio and the water content of phase D. Three plausible substitution mechanisms are shown for comparison, however, the compositional trend cannot result from a single mechanism. FROST and FEI (1998) reported that the $SiO_2$ and $H_2O$ contents of phase D are inversely correlated, where as the MgO content remains constant throughout the range of composition. This implies that the $Si^{4+}=4H^+$ mechanism ($MgSi_{2-x}H_{2+4x}O_6$) may be important. The single crystal analysis of YANG et al. (1997), however, assigns 8% of Mg to Si sites, which supports the substitution mechanism $Si^{4+} = 2H^+ + Mg^{2+}$ ($Mg_{1+x}Si_{2-x}H_{2+2x}O_6$). The compositional range may arise from a combination of these two substitution mechanisms.

Figure 2 shows data from OHTANI et al. (1995) and FROST and FEI (1998) for the synthesis conditions of phase D for the $Mg_2SiO_4$ + 20 wt. % $H_2O$ composition. At low temperature phase D coexists with brucite and at higher temperature with superhydrous phase B and a fluid phase. In the higher temperature field phase D is consumed with increasing temperature by a melting/dissolution reaction. The coexisting fluid, which is predominantly $H_2O$ and MgO at low temperature, evolves to become Si-rich as phase D dissolves into it. The partitioning of $H_2O$ between phase D and the liquid phase is temperature dependent, resulting in a decrease in the $H_2O$ content of phase D with increasing temperature (Fig. 4a). The opposite effect is observed with increasing pressure (Fig. 4b).

Using a starting composition of $MgSiO_3$ + 4 wt. % $H_2O$ OHTANI et al. (1997) observed phase D coexisting with superhydrous phase B and stishovite be-
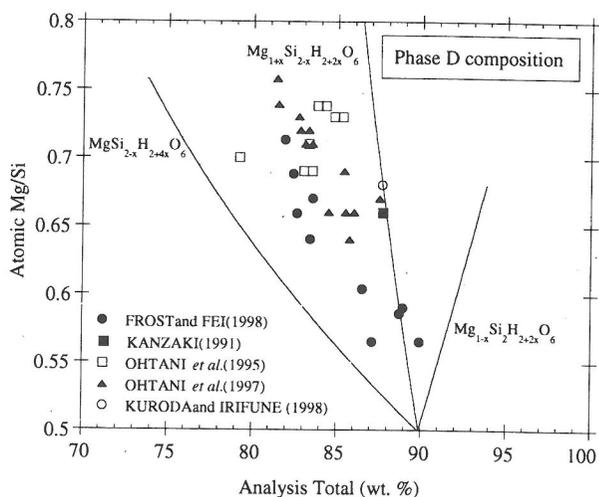
FIG. 3. The composition of phase D. Three proposed substitution mechanisms are shown for comparison. The low analysis totals give an approximation of the $H_2O$ content.
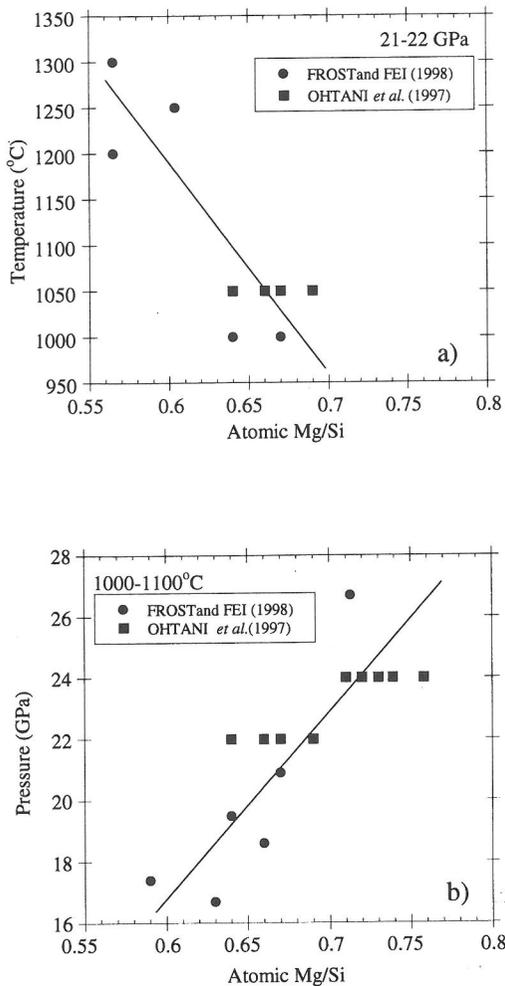
FIG. 4. The composition of phase D as a function of a) temperature, at pressures between 21-22 GPa and b) pressure, at temperatures between 1000 and 1100°C.

tween 20 and 22 GPa, 1000°-1100°C. Using a slightly more Mg-rich composition GASPARIK (1993) found only superhydrous phase B and stishovite within this pressure range. Figure 5 is consistent with these phase equilibria observations for the MSH system between 19 and 23 GPa and approximately 1100°C. A tie line between superhydrous phase B and stishovite excludes phase D from $H_2O$-poor compositions within this pressure range. For realistic slab $H_2O$ contents (<3.7 wt %) phase D is therefore unlikely to be stable within ultramafic compositions in the transition zone.

At a pressure of 24 GPa and 1300°C, however, OHTANI et al. (1997) observed phase D coexisting with $MgSiO_3$-perovskite and stishovite for the starting composition labelled as 3 in Fig. 5. This obser-

vation infers that at these conditions a phase D-perovskite tie line exists. For higher $H_2O$ concentrations OHTANI et al. (1997) also observed phase D coexisting with periclase, confirming the coexistence originally observed by LIU (1986). At temperatures below 1300°C phase D could coexist with (Mg,Fe)-$SiO_3$-perovskite and magnesiowüstite in slabs entering the lower mantle.

From crystal chemical evidence alone it would seem that phase D is a more viable host for $H_2O$ in the lower mantle than superhydrous phase B. Superhydrous phase B contains $SiO_2$ in tetrahedral coordination and is, therefore, unlikely to be stable to significant pressure in the lower mantle. Phase D on the other hand has Si solely in octahedral coordination and was shown by FROST and FEI (1998) in externally heated DAC experiments to be stable to at least 50 GPa at 950°C. The laser heated DAC experiments of SHIEH et al. (1998) produced phase D from serpentine up to pressures of approximately 50 GPa.

## PHASE E

Phase E was first produced in experiments performed between 13 and 17 GPa, 800-1000°C in a $Mg_2SiO_4$ + 20 wt. % $H_2O$ composition (KANZAKI, 1991). KUDOH et al. (1993b) solved the structure of phase E and found it to comprise brucite-like layers that are cross linked by magnesia octahedra and silica tetrahedra. KUDOH et al. (1993b) reasoned that there must be cation vacancies in the brucite layers adjacent to cross linking Si tetrahedra but found no evi-
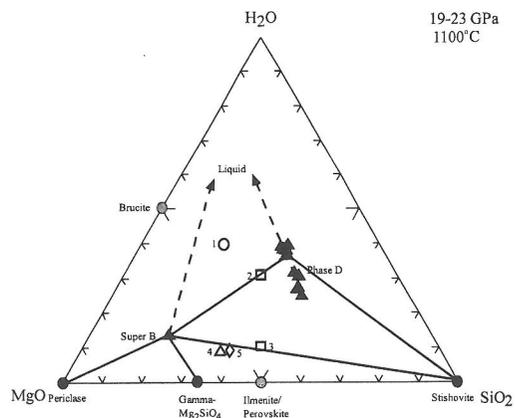


FIG. 5. Phase relations in the MSH system between approximately 19 and 23 GPa and 1100°C. Bulk starting compositions are shown as open symbols. Composition 1 was used by FROST and FEI (1998), 2 and 3 by OHTANI et al., (1997) and 4 by GASPARIK (1993). The diamond symbol marked 5 shows the composition resulting from the breakdown of antigorite to produce phase A and enstatite at 6 GPa and 600°C.

dence for long range ordering of this association. Cation disorder may also account for the broad Raman spectra reported for phase E by FROST and FEI (1998) which resembles spectra of amorphous materials. There is no evidence that phase E contains silicon in octahedral coordination.

The composition of phase E falls approximately along a forsterite-water tie line, as indicated in Fig. 1. Figure 6 shows that there is no apparent coupling between the Mg:Si ratio and $H_2O$ content for phase E and there is no obvious trend in the composition with increasing pressure or temperature. Phase E composition is variable within a single experiment and displays wide ranges over very narrow pressure intervals, although there may be a weak trend of increasing Mg/Si with pressure. Measurements of $H_2O$ using the deficit in microprobe analysis totals are unsatisfactory and it is possible that the range in $H_2O$ contents occurs due to damage from the electron microprobe beam. Such a range in $H_2O$ contents within a single sample, however, is not observed for measurements of phase D which appears to be more easily damaged in the electron beam than phase E. Although further more detailed work is required, the lack of compositional trends for phase E and the disordered crystal structure may indicate that this phase is either a quench product from a hydrous fluid or is significantly modified during quenching by interaction with a hydrous fluid.

There is inconstancy in the reported synthesis conditions of phase E. LUTH (1993) reported phase E between 10 and 12 GPa, 1100-1300°C but INOUE (1994) and OHTANI et al. (1995) reported the occurrence of forsterite, enstatite and melt under similar conditions. Such inconsistencies may also imply
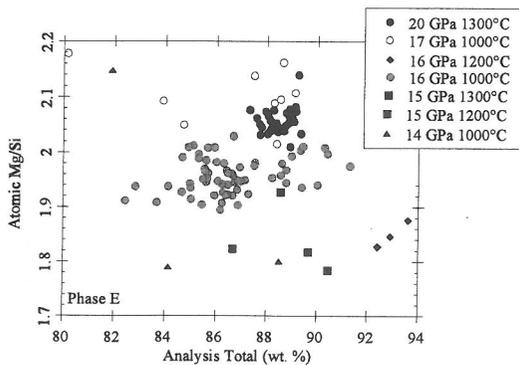
phase E is produced during quenching where quenching rates are more likely to govern the phase formation.

KAWAMOTO et al. (1995) showed that phase E can containing up to 10 wt % FeO and 9 wt % $Al_2O_3$. These additional components may significantly stabilise phase E to higher temperatures, as KAWAMOTO et al. (1995) reported the occurrence of phase E within $H_2O$-saturated peridotite bulk compositions to temperatures of 1400°C at 15.5 GPa. If phase E is a stable phase at the conditions of synthesis and not a quenched product, then the experiments of KAWAMOTO et al. (1995) suggest that phase E can coexist with transition zone minerals at temperatures compatible with subducting slabs. An important consideration for $H_2O$ transport, however, is that over much of the range in conditions where phase E has been synthesised $\beta$-$(Mg,Fe)_2SiO_4$ wadsleyite is also stable. It has been reported that wadsleyite can contain approximately 3 wt. % $H_2O$ in its structure (INOUE et al., 1995). Wadsleyite would make up a significant portion of the slab and phase E is only likely to form once wadsleyite is $H_2O$-saturated. The high water contents required for this mean that only very minor amounts of phase E could exist in the mantle, if at all.

## DHMS PHASES IN SUBDUCTING SLABS

To summarise, DHMS are unlikely to form along a typical mantle adiabat due to their thermal stability and therefore could only be applicable to the cooler regions of subducting slabs. Given the large water contents and the general Mg-rich nature of DHMS the most plausible scenario for their formation is as high pressure products from the break down of antigorite within ultramafic portions of subducting slabs.

Antigorite (serpentine) breaks down at 6 GPa and 600°C to produce an essentially Fe-poor harzburgitic composition (Mg/Si≈1.4), which preserves approximately 3.7 weight % $H_2O$ in an assemblage of phase A and enstatite. Using evidence from the previous summary of hydrous phase stability, it would seem that at higher pressures this assemblage may be replaced by one containing phase E, hydrous wadsleyite and enstatite at approximately 13 GPa (KAWAMOTO et al., 1995), then superhydrous phase B with ringwoodite and stishovite at 16 GPa (GASPARIK, 1993), and possibly phase D with perovskite and magnesiowüstite under lower mantle conditions. For lower $H_2O$ contents (i.e. <4 wt. %) the stability fields of the DHMS phases may be significantly reduced from those shown in Fig. 2.

In order to test this hypothesis a series of experi-

FIG. 6. The composition of phase E in the MSH system. The data are from FROST and FEI (UNPUBLISHED DATA; circles), KUDOH et al., (1993b; triangles), GASPARIK (1993; diamonds), INOUE (1994; squares). Numbers refer to pressure and temperature of synthesis. Circles are individual analyses from a single experiment.

ments were performed using a harzburgitic composition with approximately 3.7 wt. % $H_2O$. This composition is slightly more Mg-rich (Mg+Fe/Si≈1.75) than that produced from the breakdown of antigorite, but is representative of the depleted upper mantle component of the oceanic lithosphere in which antigorite is likely to form.

### Experimental details

Natural orthopyroxene and olivine were combined with synthetic MgO, $SiO_2$ and brucite to derive the composition reported in Table 2. The oxides and natural minerals were ground together under alcohol in an agate mortar. Samples were welded into platinum capsules that were lined with Re foil, in order to minimise Fe loss to the Pt. In several experiments two or three capsules were placed inside an outer rhenium foil capsule that was packed with either a pressure calibrant ($SiO_2$ or $Mg_2SiO_4$) or more starting material. The experiments were performed in a multianvil apparatus at the Bayerishes Geoinstitut. Details of the 14/8, 10/5 and 7/3 MgO octaherdal pressure assemblies used are given by Bussod et al. (1993), Canil (1994) and McFarlane et al. (1994). A cylindrical $LaCrO_3$ heater was employed in all experiments except HZ1 where a Re foil heater was used. The temperature was monitored using a W3%Re/W25%Re thermocouple. Quenched experiments were mounted in epoxy resin and analysed using electron microprobe, X-ray diffraction and Micro Raman spectroscopy.

### Results

The experimental run products are reported in Table 2. Phase A was observed with low-clinoenstatite ($P2_1/c$) at 10

GPa and 850°C, however, at 1100°C only olivine and low-clinoenstatite remained with some evidence of a quenched fluid. At 13 GPa and 955°C wadsleyite was produced with minor amounts of phase E and at 22 GPa and 1300°C superhydrous phase B was observed with stishovite and ringwoodite. At 1400°C and 22 GPa (HZ11) superhydrous phase B was only observed in the lower end of the capsule where temperatures could have been over 100°C lower than at the thermocouple junction. At 22 GPa the limit of superhydrous phase B stability is, therefore, considered to be between 1300 and 1400°C. At 1000°C under lower mantle conditions an assemblage of perovskite, magnesiowüstite and phase D was observed, however, at 1300°C only perovskite and magnesiowüstite remained.

In Table 3 electron microprobe analyses of phases in the experimental charges are reported. In some cases the existence of a fluid phase was inferred by the presence of a fine mass of highly porous quenched crystals. This phase was not analysed with the electron microprobe, however, due to the difficulty in rendering a suitable surface.

Microprobe analyses provide information on the partitioning of Fe and Al between the hydrous phases and typical mantle minerals. Phase E, for example, from experiment HZ6 is much richer in $Al_2O_3$ but is poorer in FeO compared with coexisting wadsleyite. Phase D in experiment HZ8 is the only major $Al_2O_3$ bearing phase and is more FeO-rich than coexisting magnesium silicate perovskite. In experiment HZ1 blobs of metallic Fe were found throughout the sample. This was the only experiment where such reduction occurred and was the only incidence where a metal Re furnace was used. If the metal furnace imposes a low oxygen fugacity inside the assembly then $H_2$ entering the experimental capsule may be responsible for FeO reduction. Superhydrous phase B from this experiment is FeO-rich in comparison to ringwoodite.

Table 3. Electron micro-probe analyses of phases from high-pressure experiments

| Exp. No. | Phase | MgO | $Al_2O_3$ | FeO | $SiO_2$ | Total | $\frac{Fe}{Fe+Mg}$ | $\frac{Mg+Fe}{Si}$ |
|---|---|---|---|---|---|---|---|---|
| HZ1 | γ | 54.4 (6) | 0.06 (3) | 1.7 (3) | 42.4 (3) | 99.1 (7) | 0.02 | 1.94 |
| | sB | 56.7 (7) | 0.4 (1) | 6.4 (5) | 28.5 (8) | 92.8 (4) | 0.06 | 3.10 |
| HZ2 | Pv | 37.4 (7) | 0.8 (4) | 3.4 (4) | 57.2 (3) | 98.8 (6) | 0.05 | 1.00 |
| | MW | 77.6 | | 19.4 | | 97 | 0.12 | |
| HZ3 | β | 48.6 (4) | 0.8 (1) | 8.2 (5) | 40.8 (3) | 98.4 (6) | 0.09 | 1.90 |
| | En | 38.6 (1) | 0.31 (2) | 2.09 (2) | 58.2 (3) | 99.4 (3) | 0.03 | 1.01 |
| HZ4 | α | 51.2 (2) | 0.02 (2) | 7.1 (1) | 40.9 (3) | 99.3 (5) | 0.07 | 2.02 |
| HZ6 | E | 45.3 (4) | 1.9 (1) | 4.6 (2) | 38.8 (2) | 91.2 (2) | 0.05 | 1.74 |
| | β | 48.5 (6) | 0.12 (2) | 7.7 (4) | 43.1 (5) | 99.6 (9) | 0.08 | 1.82 |
| HZ7 | β | 49.3 (1) | 0.28 (1) | 4.8 (2) | 42.5 (1) | 97.3 (1) | 0.05 | 1.81 |
| | En | 39.1(3) | 0.1(1) | 2.1 (4) | 57.7(2) | 99.2(2) | 0.03 | 1.04 |
| | Gt | 31.2 (6) | 10.6 (2) | 4.8 (1) | 51.2 (1) | 98.4 (2) | 0.08 | 0.79 |
| HZ8 | D | 26.6 (4) | 3.1 (1) | 3.5 (2) | 54.2 (6) | 87.9 (6) | 0.07 | 0.73 |
| | Pv | 40.0(7) | 0.07(1) | 2.83(5) | 59.9(8) | 102.8(5) | 0.04 | 1.03 |
| | MW | 82.6 | | 16.5 | | 99.1 | 0.10 | |
| HZ9 | Pv | 38.5(5) | 0.86(5) | 3.06(3) | 59.88(7) | 102.4(8) | 0.04 | 0.98 |
| | MW | 78.5 | | 20.3 | | 99.5 | 0.13 | |

Analyses were performed with a Cameca SX-50 electron microprobe operating at 15kV and 15nA. Data were reduced using the PAP correction routine. Figure in brackets is one standard deviation from at leased 5 analyses in terms of least units cited. Abbreviations are as in table 2. Magnesiowüstite grains in experiments HZ2, HZ8 and HZ9 were too small to analyse individually so a number of measurements were extrapolated to zero $SiO_2$ to determine the FeO and MgO contents.

In FeO bearing experiments low analysis totals give an even poorer approximation of the $H_2O$ content due to the potential for $Fe_2O_3$ also being present. Wadsleyite crystals from experiments HZ6 and HZ7 have $(Mg+Fe)/Si$ of approximately 1.8. This is consistent with the proposed hydration mechanism of wadsleyite $(Mg_{(2-x/2)}SiH_xO_4)$ and, using the results of INOUE et al. (1995), the wadsleyite crystals can be estimated to contain between 2 and 3 wt % $H_2O$.

## DISCUSSION

Several studies have reported the products of the breakdown of serpentine (antigorite) at pressures corresponding to the transition zone and lower mantle (LIU, 1987; IRIFUNE et al., 1996;1998; SHIEH et al., 1998), however, if antigorite were preserved in a subducting slab it would react at approximately 6 GPa and 600°C to produce phase A and enstatite as discussed by ULMER and TROMMSDORFF (THIS VOLUME). Most of the 12 wt. % $H_2O$ content of antigorite would be lost from the slab, as either a fluid or melt, and only 3.7 wt. % $H_2O$ at maximum could be preserved in the solid phases to be subducted to higher pressures. Consequently, studies performed above 6 GPa which use serpentine as a starting material overestimate the plausible $H_2O$ content of the slab. When $H_2O$ contents are reduced important differences occur. For example, the existence of a superhydrous phase B-stishovite tie line excludes phase D from being produced under transition zone conditions.

The experiments reported here on a harzburgitic composition, summarised in Fig. 7, indicate that between 6 GPa and 600°C and 22 GPa at 1300°C the 3.7 wt. % $H_2O$ content could be preserved in an assemblage that with increasing pressure contains phase A, hydrous wadsleyite with minor phase E, and superhydrous phase B. Subducting slabs following such a cool geotherm could therefore transport water into the base of the transition zone. Slabs which may stagnate at the 660 km mantle discontinuity could store $H_2O$ in the form of superhydrous phase B until temperatures exceed 1300°C. Due to the existence of a superhydrous phase B-stishovite tie line, phase D is not stable within such an assemblage in the transition zone. These results are in good agreement with those of GASPARIK (1993) and KAWAMOTO et al. (1995).

Phase D may be produced in slabs entering the lower mantle and possibly transport $H_2O$ to even greater depths. The experiments reported here, however, indicate that $H_2O$ can only be stored in a hydrous phase at temperatures below 1300°C at the top of the lower mantle. Between the transition zone and the lower mantle a decrease of at least 100° seems to
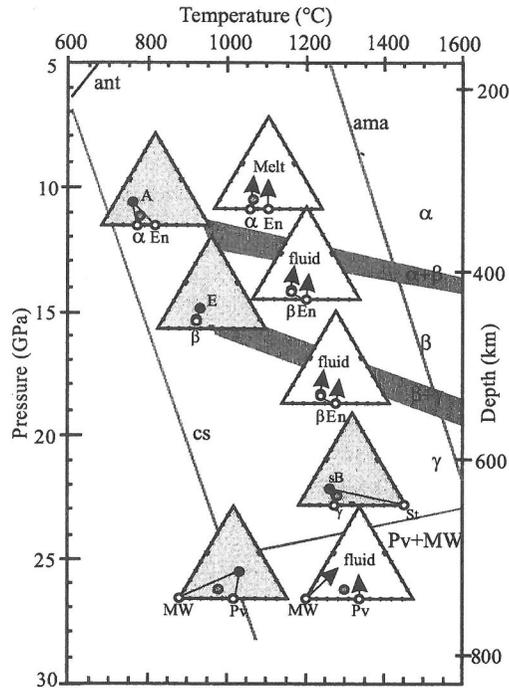


FIG. 7. Ternary MSH diagrams show the composition of run products from multianvil experiments performed on a hydrated harzburgite composition between 10 and 25 GPa. MgO and FeO are on the left-hand axes, $H_2O$ at the top and $SiO_2$ on the right. Solid circles denote hydrous phases, grey symbols show the starting composition and white circles are nominally anhydrous phases. Arrows denote the presence of a fluid or melt, the composition of which was not analysed. Ternary diagrams are shaded grey where hydrous phases were produced. Abbreviations are the same as in Table 2. Positions of the $\alpha-\beta$, $\beta-\gamma$ and $\gamma$-Pv+MW transformations for $(Mg_{1.8}Fe_{0.2})SiO_4$ are shown in grey (ITO and TAKAHASHI, 1989; KATSURA and ITO, 1989). An average mantle adiabat (ama), an estimate of the minimum temperature in a subducting slab (cs), and the antigorite breakdown curve (ant) are also shown (JEANLOZ and MORRIS, 1986; ULMER and TROMMSDORFF, 1995; IRIFUNE et al., 1996; STEIN and STEIN, 1996).

occur in the maximum temperature stability of hydrous phases.

These experiments place some constraints on the temperatures where DHMS phases can form in a depleted mantle bulk composition. In more fertile mantle compositions DHMS phases may be stable to higher temperatures due to increased $Al_2O_3$ or $Fe_2O_3$ contents. LUTH (1995) found no evidence, however, that the dehydration of phase A was perturbed to higher temperatures by the addition of either CaO, FeO, $Al_2O_3$ or $CO_2$.

The deep subduction of $H_2O$ via DHMS phases would require the stability of antigorite to depths where phase A can form and this can only happen if

temperatures in the slab are below 600°C at 6 GPa. Some studies indicate that such low temperature conditions may exist in the interiors of fast moving slabs (DAVIS and STEVENSON, 1992; FURUKAWA, 1993; STEIN and STEIN, 1996). The depth to which serpentinization occurs will also be a key factor in its preservation, as temperatures at the base of the oceanic crust may be 100-200° lower than the top during subduction (PEACOCK, 1993). It is thought, however, that the most pervasively serpentinized areas of the lithosphere, which may be to depths of 10 km, occur at slow spreading ridges (ESCARTIN et al., 1997; FRANCIS, 1981; KONG et al., 1992) but during subduction slower moving slabs will follow warmer P-T profiles. The deep subduction of water via DHMS phases is only viable, therefore, if a balance can exist between the plate velocity and the depth and extent of hydration of the lithosphere.

Serpentine is often localised around faults in the oceanic lithosphere (FRANCIS, 1981). Some faults extend from the surface to great depths (>30 km), particularly those at the outer rise where the oceanic lithosphere bends to underthrust the overriding plate (LYNNES and LAY, 1988). Deep hydrated faults may not account for large concentrations of $H_2O$ in the slab but would follow cooler geotherms during subduction that could result in the formation of DHMS phases. A plausible trigger mechanism for deep focus earthquakes is that $H_2O$ released from DHMS phases might reduce the local friction and remobilize such a fault deep in the mantle (SILVER et al., 1995).

## CONCLUSIONS

From examination of the available structural and phase equilibria data it seems that there are 5 distinct dense hydrous magnesium silicate alphabet phases, A, B, superhydrous B, D and E. The phases previously referred to as D, F and G are identical and phase C is almost certainly the same as superhydrous phase B.

Due to the thermal stability of DHMS phases they could only be produced in very cool regions of subducting lithosphere. If antigorite (serpentine) can persist to 6 GPa at 600°C then it will breakdown to an assemblage of phase A and enstatite and preserve 3.7 wt. % $H_2O$ in solid phases. Further subduction will produce phase E with wadsleyite at 13 GPa and superhydrous phase B with ringwoodite and stishovite above 16 GPa. The water content of 3.7 wt. % could thus be preserved during subduction to conditions of at least 22 GPa and 1300°C. The experiments performed show that slabs entering the lower mantle may host water in the form of phase D but only at temperatures below 1300°C.

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