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The stability of hydrous silicates in Earth's lower mantle: Experimental constraints from the systems MgO–SiO$_2$–H$_2$O and MgO–Al$_2$O$_3$–SiO$_2$–H$_2$O

M.J. Walter $^{a,b}$, A.R. Thomson $^a$, W. Wang $^{a,b}$, O.T. Lord $^a$, J. Ross $^a$, S.C. McMahon $^a$, M.A. Baron $^a$, E. Melekhova $^a$, A.K. Kleppe $^c$, S.C. Kohn $^a$

$^a$ School of Earth Sciences, University of Bristol, Queen's Road, Bristol BS8 1RJ, United Kingdom
$^b$ Department of Earth Sciences, University College London, Gower Street, London WC1E 6BT, United Kingdom
$^c$ DIAMOND Light Source Ltd, Chilton, Didcot OX11 0QX, Oxfordshire, United Kingdom

**Abstract**

We performed laser-heated diamond anvil cell experiments on bulk compositions in the systems MgO–SiO$_2$–H$_2$O (MSH) and MgO–Al$_2$O$_3$–SiO$_2$–H$_2$O (MASH) that constrain the stability of hydrous phases in Earth's lower mantle. Phase identification by synchrotron powder diffraction reveals a consistent set of stability relations for the high-pressure, dense hydrous silicate phases D and H. In the MSH system phase D is stable to ~50 GPa, independent of temperature from ~1300 to 1700 K. Phase H becomes stable between 35 and 40 GPa, and the phase H out reaction occurs at ~55 GPa at 1600 K with a negative dT/dP slope of ~75 K/GPa. Between ~30 and 50 GPa dehydration melting occurs at ~1800 K with a flat dT/dP slope. A cusp along the solidus at ~50 GPa corresponds with the intersection of the subsolidus phase H out reaction, and the dT/dP melting slope steepens to ~15 K/GPa up to ~85 GPa. In the MASH system phase H is stable in experiments between ~45 and 115 GPa in all bulk compositions studied, and we expect aluminaous phase H to be stable throughout the lower mantle depth range beneath ~1200 km in both periodotitic and basaltic lithologies. In the subsolidus, alumina phase D is stable to ~55 GPa, whereas at higher pressures alumina phase H is the stable hydrous phase. The presence of hydrogen may sharpen the bridgmanite to post-perovskite transition. The ambient unit cell volume of bridgmanite increases systematically with pressure above ~55 GPa, possibly representing an increase in alumina content, and potentially hydrogen content, with depth. Bridgmanite in equilibrium with phases D and H has a relatively low alumina content, and alumina partitions preferentially into the hydrous phases. The melting curves of MASH compositions are shallower than in the MSH system, with dT/dP of ~6 K/GPa. Phase D and H solid solutions are stable in cold, hydrated subducting slabs and can deliver water to the deepest lower mantle. However, hydrated lithologies in the lower mantle are likely to be partially molten at all depths along an ambient mantle geotherm.

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1. Introduction

The lower mantle is the most massive potential hydrogen-bearing reservoir in Earth. There are several mechanisms whereby hydrous components may have been delivered to the deep mantle over geologic time, creating a long-lived hydrogen reservoir. As the planet accreted and grew in size, primordial volatiles may have become isolated in the deepest parts of the mantle. Primordial hydrogen could have been retained in a primitive lower mantle reservoir along with other volatile elements, and such a reservoir is supported by the isotopic composition of noble gases from mantle-derived samples (Marty, 2012; Mukhopadhyay, 2012; Halliday, 2013). Modest solubility of hydrous species in a global magma ocean may have allowed the mantle to retain significant hydrogen, especially if outgassing were inefficient, or if a relatively small fraction of late incoming metal in a giant impact equilibrated with the magma ocean (Mookherjee et al., 2008; Mysen et al., 2009; Hirschmann et al., 2012). The possibility that magma ocean crystallization occurred from the mid-lower mantle outward may have resulted in a deep basal magma body (Stixrude and Karki, 2005; Labrosse et al., 2007; Mosenfelder et al., 2007), which would be expected to concentrate incompatible elements like hydrogen. It is also possible that mantle overturn after crystallization delivered an unknown quantity of water and other volatiles into the deep mantle (Elkins-Tanton, 2008). And perhaps most importantly, billions of years of plate tectonics will have recycled lithosphere into the deep mantle with the potential to deliver hydrous components (Ohtani et al., 2001b; Komabayashi et al., 2004; Ohtani, 2005; Ohira et al., 2014). Indeed, melting at the top of the lower mantle, possibly related to subduction of hydrous components, has recently been suggested on the basis of a combination of experimental and seismic observations (Schmandt et al., 2014).
There are limited phase equilibrium data at the extreme P-T conditions of the lower mantle in volatile-bearing systems. The amount of water that can be stored in silicate bridgmanite may be small, although the issue is not entirely resolved, with estimated solubility ranging over several orders of magnitude (Meade et al., 1994; Bolfan-Casanova et al., 2000; Murakami et al., 2002; Litavský et al., 2003; Bolfan-Casanova, 2005). If the water content of nominally anhydrous lower mantle phases is very low, then water might be stored in solid hydrous silicate phases, molten hydrous silicate, or possibly even as water–ice (Bina and Navrotsky, 2000; Schwager et al., 2004). Fundamental to modeling the behavior of hydrogen in the deep Earth is knowledge of the phase relations of the solids and liquids that can potentially host hydrogen at the extreme conditions of the lower mantle.

There is a rich diversity of dense hydrous silicates that are stable in mafic and ultramafic assemblages at upper mantle pressures and low to moderate temperatures (Ohtani et al., 2000; Ohtani et al., 2001b; Komabayashi et al., 2004; Ohtani et al., 2004; Ohtani, 2005). Water transport from the transition zone into the lower mantle is primarily by the stability of phase D, an orthorhombic mineral with the ideal formula MgSi₆H₁₄O₁₆, which according to available data has a stability limited to about 45 GPa and, depending especially on its alumina content, possibly to temperatures exceeding 2000 K (Shieh et al., 1998; Shinn et al., 2008; Ghosh and Schmidt, 2014; Pamato et al., 2015). It is also known that a high-pressure form of diaspore (α-AlOOH), called δ-AlOOH, and with an orthorhombic symmetry very close to that of stishovite in the CaCl₂-type structure, is stable throughout the mantle depth range and may be present in suitably aluminous and hydrated lherzolites (Suzuki et al., 2000; Ohtani et al., 2001a; Tsuchiya et al., 2002; Sano et al., 2008). Mg and Si can substitute into the δ-AlOOH structure, causing subtle symmetry changes probably related to disorder of hydrogen (Suzuki et al., 2000; Komatsu et al., 2011).

Recently, the discovery of a new phase closely related to δ-AlOOH, with the stoichiometric composition Mg₅H₅O₄, was predicted by ab initio methods with a calculated stability limit of ~50 GPa (Tsuchiya, 2013), potentially extending the depth range to which hydrous magnesium silicates can deliver water into the lower mantle. This new phase has now been observed in experiments up to 50 GPa in the MgO-SiO₂-H₂O (MSH) system, although an upper pressure limit has yet to be determined, and has been given the name phase H (Nishi et al., 2014). The structure of phase H has recently been shown to have orthorhombic pnmn symmetry (Bindi et al., 2014; Nishi et al., 2014). Given the similarity in crystal structures, and because it has already been shown that Mg and Si dissolve into δ-AlOOH, it may be that a considerable or complete solid solution exists between these phases, and that (Mg,Al)OOH phase may be stable throughout much or all of the mantle depth range in common mantle lithologies. Indeed, aluminous phase H has been found to be stable to the base of the mantle in a composition with ~30 mol% Al₂O₃ in mon mantle lithologies. Indeed, aluminous phase H has been found to be stable throughout much or all of the mantle depth range and that an (Mg,Si,Al)OOH phase exists between these phases, and that an (Mg,Si,Al)OOH phase in crystal structures, and because it has already been shown that Mg and Si can substitute into the δ-AlOOH structure, causing subtle symmetry changes probably related to disorder of hydrogen.

### 2. Experimental and analytical methods

#### 2.1. Starting compositions

| Composition | MgO | Al₂O₃ | SiO₂ | H₂O |
|-------------|-----|-------|------|------|
| MSH1        | 0.500 | -     | 0.372 | 0.128 |
| MSH2        | 0.320 | -     | 0.590 | 0.090 |
| MASH1       | 0.487 | 0.025 | 0.450 | 0.038 |
| MASH2       | 0.477 | 0.046 | 0.418 | 0.059 |
| MASH3       | 0.443 | 0.022 | 0.497 | 0.038 |
| MASH6       | 0.452 | 0.096 | 0.386 | 0.066 |
| MASH7       | 0.405 | 0.085 | 0.445 | 0.065 |

Table 1 and are shown on Fig. 1. In each system we investigate both MgO-rich and SiO₂-rich compositions in order to explore differences between model peridotitic and basaltic systems, respectively. In the MSH system, compositions have ~9 to 13 mol% H₂O, while in the MASH system compositions have ~4 to 7 mol% H₂O. Al₂O₃ contents in the MASH system range from ~2 to 10 mol%, again to emulate differences between peridotitic and basaltic bulk compositions.

Starting compositions are synthesized as mixtures of anhydrous silicate glass and brucite. In the MSH system, MgSiO₃ glass was synthesized by fusing an ~1 g stoichiometric mixture of reagent grade MgO and SiO₂ powders in a Pt capsule inserted into a 1 atm furnace at ~1680 °C. Crystal-free glass forms upon quenching into water. Glass mixtures in the MAS system are the same as those used in previous work (Walter et al., 2004), and were synthesized under similar conditions. Quenched glasses were ground and refused once, and then reground to a fine powder under alcohol. Glass powders were mixed with natural brucite (Mg(OH)₂), the phase purity of which was confirmed by X-ray diffraction that showed only brucite reflections and no indication of carbonate that can form by reaction with air (Ghosh and Schmidt, 2014). Mixtures were ground typically for 2 h in an agate mortar. Pt black was added (10% by weight), and samples reground under acetone until the average Pt grain size was ~1 μm or less.

#### 2.2. Diamond anvil cell experiments

##### 2.2.1. High pressure

Experiments were made in ‘Princeton-type’ symmetric diamond anvil cells, incorporating Type Ia diamonds with culet diameters ranging from 120 to 250 μm. Samples are held in Re gaskets pre-indented to a thickness of ~50 μm. Chambers ~30 μm in diameter are laser-drilled in the indentation. The chamber size is purposefully designed in order to match the laser focal size in order to heat as much of the sample as uniformly as possible, so as to minimize the amount of un-reacted or partially reacted material that can complicate interpretation of diffraction measurements. An added benefit of a small chamber size is that multiple chambers can be used in experiments with culet sizes of 200 (3-holes) or 250 μm (4-holes), as shown in Fig. 2. This multiple chamber design allows a range of temperatures and pressures to be investigated in a single run. Samples are loaded as powders directly into the sample chambers. We chose not to use a thermally insulating pressure medium in this study in order to avoid the possibility of sample contamination, partial reactivity with insulating material, or H₂O loss from the heated sample environment.

Pressure is measured using the Raman shift of the singlet peak of the diamond anvil at the culet surface that is related to stress in the (001) direction (Hanfland et al., 1986). In this way we avoid putting ruby (Al₂O₃) grains in the sample chamber for a pressure marker, and unlike ruby, the signal from this peak remains strong and highly resolvable even to the Mbar range. Raman measurements are made with a Jobin-Yvon T64000 Raman spectrometer in either single- or triple-additive mode and using a confocal aperture of 200 μm. Previous workers have used the high frequency edge of the entire Raman signal to construct a pressure scale (Akahama and Kawamura, 2010). However, we find that the singlet peak is a robust feature in most cases when making highly confocal measurements that can be precisely fitted, typically consistent.
The Raman shift itself is calibrated relative to the ruby scale (Mao et al., 1986). We find that the calibration is sample material dependent, so the calibration was made with the same starting materials as used in this study. The Raman shift is calibrated against the R1 fluorescence shift of ruby, and a Raman shift versus pressure calibration curve constructed as shown in Fig. 2. The straight line fit to the data yields a slope of 0.501. The precision to which pressure can be measured with the Raman peak is about 0.1 GPa, although the accuracy is poorer, ~2 GPa due to uncertainty in measuring the ruby pressure. This potentially can be much improved via calibration using EoS measurements of internal standards. We measured the unit cell volume of Pt at high pressure in experiments at 116 and 123 GPa, and based on the EoS of Pt (Dorogokupets and Dewaele, 2007) there is good agreement with extrapolation of the ruby-based calibration curve (Fig. 3). Pressures are measured before and after heating. Typically post-heating pressures are within 5% of the pre-heating pressure. All reported pressures are post-heating measurements, and no correction has been made for thermal pressure during heating, which at the relatively modest temperatures of these experiments may be of the order 10% or less of the measured pressure (Heinz, 1990; Belonoshko and Dubrovinsky, 1997).

2.2.2. High temperature

Laser heating in a double-sided geometry produces high-temperatures. The system at Bristol comprises two 100 W fiber lasers (1070 nm, SPI Red Laser) operating in a Gaussian output mode. The laser beams are modified by a combination of beam shaping lenses (pi-Shaper) and beam expanders to a flat-top profile of a size to match the dimensions of the sample chamber (~20–30 μm). In this way the energy density can be manipulated to minimize radial temperature gradients. Water-cooled Mitutoyo (10×) NIR long working distance apochromatic lenses are used to focus the lasers onto the sample. Two heating styles were used, ‘isothermal’ and ‘ramped’. In isothermal experiments samples are heated to a target maximum temperature and held for between 5 and 120 min before quenching by shutting off the laser power. In ramped experiments laser power is continually incremented by 0.2 W on each side every 4 s until quenching. Ramp experiments are used to detect thermal perturbations that typically manifest as a temperature ‘plateau’, i.e., relatively constant temperature.

Fig. 1. Starting compositions in the (a) MSH and (b) MASH systems used in this study. Compositions in the MASH system are projected from H2O. Figure (c) shows the MASH quaternary with the compositions of hydrous and anhydrous phases relevant to the deep mantle. Per = periclase; Brd = bridgmanite; St = stishovite; Bru = brucite; D = phase D; Dss = phase D solid solution; H = phase H; Hss = phase H solid solution; IceX = high pressure form of water ice. Shown on (a) are some possible relevant tie lines between phases in the MSH system.

Fig. 2. Calibration of the Raman shift of the diamond singlet mode as measured at the culet surface. The singlet peak is related to stress along the (001) axis. The Raman shift is calibrated relative to the ruby scale, as shown by the red circles. The fitted curve, which is forced through the origin, yields a slope of 0.501. The large blue circles show in situ pressure measurements using the EoS of Pt, and are not included in the fit. The inset shows a Re gasket with four sample chambers filled with starting material.
with increasing power. The interpretation of these perturbations is discussed below.

Temperature is measured using spectroradiometric techniques that have been described in detail elsewhere (Walter and Koga, 2004). In short, incandescent emission from the heated spot is focused (50× magnification) onto the vertical entrance slit of an imaging spectrometer. The slit has a width of 100 μm, which corresponds to an ~2 μm strip across the heated sample at the object plane. The system optical resolution has been measured to be ~2 μm, although the CCD-resolution provides temperatures calculated at ~0.5 μm intervals. The intensity of the thermal emission is normalized with a NIST-calibrated W-lamp of spectral radiance, and fitted with a Wien function over a wavelength range of 570–830 nm. Precision in measured temperatures based on the goodness of the linear fits is typically 2 to 4 K, indicating that chromatic dispersion is minimal in the optical system (Walter and Koga, 2004). The laser heating and temperature measurement systems are described in more detail in Lord et al. (2014).

Fig. 3a shows a typical example of an isothermal heating measurement in which a maximum temperature of 1560 K is achieved. However, the radial gradient indicates temperatures of ~1350 K at the edge of the sample, and this range of ~200 K (±100 K) is typical of the experiments reported here. Fig. 3a also illustrates our ability to maintain stable heating conditions for extended duration, with temperature variation at a given position on the sample of the order ±25 K. In Table 2 (MSH system) and Table 3 (MASH system) we report run conditions, and both maximum temperatures and mean temperatures are provided for all isothermal experiments. Mean temperature is calculated as the average of all temperatures measured across a 20–25 μm strip across the sample and throughout the duration of the experiment as shown in Fig. 3a, and uncertainty estimated as ±2σ of the mean. Here we will refer to mean temperatures when discussing experimental conditions, and all subsolidus data points are plotted on the basis of mean temperatures. Fig. 3b shows a typical temperature vs. laser power ramp, with an unambiguous thermal perturbation at ~1850 K. We determine the temperature on this heating plateau by averaging temperatures on both sides starting from a selected power at which we estimate the plateau to begin. We also note that typically there is a change in the radial temperature distribution (Fig. 3b inset) corresponding to the temperature plateau, often resulting in a central minimum surrounded by an annulus of higher temperature material. Movement apparent visually within the sample frequently accompanies the plateau and change in profile, particularly in the MSH system. As discussed below, we attribute these thermal perturbations to melting.

### 2.2. Synchrotron X-ray diffraction

Powder X-ray diffraction measurements were made on P–T quenched and high-P samples at beamline I15 of the Diamond Light Source, UK. Monochromatic X-rays with wavelengths of either 0.4133 or 0.4246 Å were focused to 65 × 65 μm and further collimated by a tungsten pinhole to give a 20 μm beam diameter. Diffraction X-rays were detected with a MAR345 image plate (MarResearch), with the sample to detector distance calibrated to within ±10 μm using a silicon standard. Diffraction patterns are reduced to 1D profiles using the FIT2D software (Hammersley et al., 1995). Profiles are analyzed using MacDiff software for phase identification. Full profile fitting for the calculation of unit cell volumes was performed using the Le Bail method (Le Bail et al., 1988), as implemented in the GSAS suite of programs (Lazor et al., 1993; Toby, 2001).

### 3. Results

Table 2 (MSH) and Table 3 (MASH) list run conditions and phases identified by X-ray diffraction. In addition to the silicate and oxide phases, all patterns contain diffraction lines from the Pt black absorber as well as a variable contribution from the Re gasket. Interference from these lines does not preclude identification of phases since no peaks from these materials exist at d-spacing greater than 2.4 Å (1 at), and all phases reported on here, with the exception of periclase, have major peaks at larger d-spacing. Some experiments contain traces...
| Experiment | Hole | T max (K) | Mean T (K) | σ Time (min) | Phases |
|------------|------|-----------|------------|-------------|--------|
| MSH1-1     | A    | 1840      | 1700       | 100         | 6      |
|            | B    | 1900      | 1770       | 120         | 6      |
|            | C    | 1780      | 1700       | 100         | 6      |
|            | D    | 1890      | 80         | 80          | Ramp   |
| MSH1-3     | A    | 1930      | –          | 50          | Ramp   |
|            | B    | 2100      | –          | 50          | Ramp   |
|            | C    | 1840      | 1750       | 100         | 6      |
|            | D    | 1900      | 1800       | 100         | 5      |
| MSH1-4     | B    | 1650      | 1550       | 100         | 7      |
|            | C    | 1840      | –          | 40          | Ramp   |
|            | D    | 1720      | 1615       | 100         | 7      |
| MSH1-5     | A    | 1850      | –          | 60          | Ramp   |
|            | B    | 1640      | 1590       | 80          | 15     |
|            | C    | 1600      | 1490       | 100         | 30     |
|            | D    | 1500      | 1400       | 60          | Ramp   |
| MSH1-6     | B    | 1800      | 1660       | 100         | 17     |
|            | C    | 1600      | 1525       | 120         | 22     |
|            | D    | 1600      | 1450       | 100         | 30     |
| MSH1-7     | A    | 1780      | 1635       | 100         | 20     |
|            | B    | 1720      | 1590       | 120         | 20     |
|            | C    | 1640      | 1505       | 80          | 60     |
|            | D    | 1490      | 1400       | 60          | Ramp   |
| MSH1-8     | B    | 1710      | 1610       | 90          | 20     |
|            | C    | 1480      | 1350       | 120         | 120    |
|            | D    | 1560      | 1480       | 100         | 30     |
| MSH1-9     | A    | 1880      | 1590       | 160         | 15     |
|            | B    | 1660      | 1520       | 120         | 20     |
|            | C    | 1620      | 1450       | 100         | 40     |
|            | D    | 1450      | 1350       | 120         | 90     |
| MSH1-10    | A    | 1865      | –          | 60          | Ramp   |
|            | B    | 1720      | 1600       | 120         | 20     |
|            | C    | 1550      | 1460       | 100         | 45     |
|            | D    | 1500      | 1350       | 120         | 55     |
| MSH1-11    | A    | 1550      | 1450       | 100         | 20     |
|            | B    | 1410      | 1350       | 100         | 30     |
|            | C    | 1700      | 1575       | 100         | 10     |
|            | D    | 1790      | 1650       | 140         | 6      |
| MSH1-12    | B    | 1950      | 1810       | 100         | 7      |
|            | C    | 2220      | –          | 100         | Ramp   |
| MSH2-1     | A    | 1840      | 1715       | 100         | 5      |
|            | B    | 1820      | 1720       | 100         | 4      |
|            | C    | 1750      | 1650       | 100         | 15     |
|            | D    | 1905      | –          | 50          | Ramp   |
| MSH2-2     | A    | 1720      | 1600       | 120         | 20     |
|            | B    | 1550      | 1460       | 100         | 45     |
|            | C    | 1500      | 1350       | 120         | 55     |
| MSH2-3     | A    | 1835      | –          | 30          | Ramp   |
|            | B    | 1800      | 1710       | 50          | 5      |
|            | C    | 1950      | 1730       | 130         | 5      |
|            | D    | 1810      | 1690       | 100         | 7      |
| MSH2-4     | B    | 1780      | –          | 70          | Ramp   |
|            | D    | 1990      | –          | 80          | Ramp   |
| MSH2-5     | A    | 1825      | –          | 35          | Ramp   |
|            | B    | 1600      | 1505       | 80          | 15     |
|            | C    | 1530      | 1440       | 80          | 30     |
|            | D    | 1350      | 1300       | 100         | 40     |
| MSH2-6     | A    | 1660      | 1535       | 80          | 12     |
|            | C    | 1620      | 1535       | 60          | 25     |
|            | D    | 1520      | 1450       | 60          | 60     |
| MSH2-7     | A    | 1885      | –          | 50          | Ramp   |
|            | B    | 1760      | 1660       | 80          | 12     |
|            | C    | 1530      | 1440       | 80          | 30     |
|            | D    | 1350      | 1300       | 100         | 120    |
| MSH2-8     | A    | 1760      | 1610       | 100         | 20     |
|            | B    | 1660      | 1520       | 80          | 50     |
|            | C    | 1460      | 1350       | 80          | 60     |
|            | D    | 1350      | 1300       | 100         | 120    |
| MSH2-9     | A    | 1730      | 1630       | 100         | 20     |
|            | B    | 1700      | 1585       | 80          | 25     |
|            | C    | 1550      | 1450       | 100         | 60     |
|            | D    | 1400      | 1350       | 100         | 120    |
| MSH2-10    | A    | 1800      | 1600       | 140         | 14     |
|            | B    | 1570      | 1450       | 80          | 25     |
|            | C    | 1450      | 1350       | 100         | 90     |
|            | D    | 2090      | –          | 50          | Ramp   |
| MSH2-11    | A    | 2200      | –          | 60          | Ramp   |
|            | B    | 2175      | –          | 100         | Ramp   |
|            | C    | 1970      | 1875       | 80          | 10     |
### Table 3
Experimental conditions and results in the system MASH.

| Experiment | Hole | P (GPa) | Max T (K) | Mean T (K) | $\sigma$ | Time (m) | Phases          |
|------------|------|---------|-----------|------------|---------|----------|----------------|
| MASH1-1    | A    | 68      | 1750      | 1670       | 70      | 10       | Brd + H + Per  |
|            | B    | 69      | 2230      | 2230       | 60      | Ramp     | Brd + H + Per  |
|            | C    | 70      | 2000      | 1850       | 100     | 7        | Brd + H + Per  |
| MASH1-2    | A    | 56      | 1850      | 1620       | 150     | 12       | Brd + H + Per + D |
|            | B    | 53      | 1780      | 1605       | 75      | 12       | Brd + H + Per + St + D |
|            | C    | 54      | 2110      | 2000       | 50      | Ramp     | Brd + D + St + Per |
| MASH1-3    | A    | 96      | 1980      | 1700       | 90      | 10       | Brd + H + Per  |
| MASH1-4    | A    | 114     | 1960      | 1720       | 130     | 10       | Brd + H + Per  |
| MASH1-5    | A    | 96      | 1980      | 1780       | 90      | 10       | Brd + H + Per  |
| MASH1-6    | A    | 93      | 1900      | 1650       | 20      | 10       | Brd + H + Per  |
| MASH1-7    | A    | 92      | 1890      | 1750       | 100     | 10       | Brd + H + Per  |
| MASH1-8    | A    | 91      | 1890      | 1750       | 100     | 10       | Brd + H + Per  |
| MASH1-9    | A    | 93      | 2300      | 2000       | 20      | 10       | Brd + H + Per  |
| MASH2-1    | A    | 58      | 1850      | 1550       | 100     | 10       | Brd + H + Per  |
| MASH2-2    | A    | 65      | 1850      | 1500       | 120     | 20       | Brd + H + Per  |
| MASH2-3    | A    | 70      | 1810      | 1670       | 120     | 15       | Brd + D + Per + St |
| MASH2-4    | A    | 70      | 1810      | 1670       | 120     | 15       | Brd + D + Per + St |
| MASH2-5    | A    | 49      | 2110      | 1900       | 20      | 10       | Brd + D + Per + cor |
| MASH2-6    | A    | 47      | 2100      | 1900       | 20      | 10       | Brd + D + Per + cor |
| MASH3-1    | A    | 72      | 2145      | 1800       | 130     | 13       | Brd + H + St  |
| MASH3-2    | A    | 70      | 1900      | 1700       | 100     | 10       | Brd + H + St  |
| MASH3-3    | A    | 55      | 1850      | 1500       | 120     | 12       | Brd + H + St + D |
| MASH3-4    | A    | 60      | 1850      | 1500       | 120     | 12       | Brd + H + St + D |
| MASH3-5    | A    | 49      | 1890      | 1670       | 120     | 15       | Brd + H + St + D |
| MASH3-6    | A    | 47      | 2100      | 1900       | 20      | 10       | Brd + D + Per + cor |
| MASH3-7    | A    | 40      | 2120      | 1900       | 20      | 10       | Brd + D + Per + cor |
| MASH3-8    | A    | 40      | 2120      | 1900       | 20      | 10       | Brd + D + Per + cor |
| MASH3-9    | A    | 40      | 2120      | 1900       | 20      | 10       | Brd + D + Per + cor |
| MASH6-1    | A    | 92      | 1900      | 1750       | 100     | 10       | Brd + H + Per  |
| MASH6-2    | A    | 91      | 1900      | 1750       | 100     | 10       | Brd + H + Per  |
| MASH6-3    | A    | 91      | 1900      | 1750       | 100     | 10       | Brd + H + Per  |
| MASH6-4    | A    | 91      | 1900      | 1750       | 100     | 10       | Brd + H + Per  |
| MASH7-1    | A    | 81      | 1900      | 1700       | 130     | 10       | Brd + H + Per + D + St |
| MASH7-2    | A    | 78      | 1900      | 1750       | 100     | 15       | Brd + H + St  |
| MASH7-3    | A    | 73      | 1900      | 1750       | 100     | 15       | Brd + H + St  |
| MASH7-4    | A    | 70      | 1900      | 1750       | 100     | 15       | Brd + H + St  |
| MASH7-5    | A    | 66      | 1900      | 1750       | 100     | 15       | Brd + H + St  |
| MASH7-6    | A    | 61      | 1900      | 1750       | 100     | 15       | Brd + H + St  |
| MASH7-7    | A    | 60      | 1900      | 1750       | 100     | 15       | Brd + H + St  |
| MASH7-8    | A    | 60      | 1900      | 1750       | 100     | 15       | Brd + H + St  |
| MASH7-9    | A    | 60      | 1900      | 1750       | 100     | 15       | Brd + H + St  |
| MASH7-10   | A    | 91      | 1900      | 1750       | 100     | 15       | Brd + H + St  |

Mean T and $\sigma$ as error as described in text; Ramp = ramped heating experiment.

Brd = bridgmanite; PPv = post-perovskite; Per = periclase; St = stishovite; Sf = seifertite; D = Phase D; H = Phase H; Cor = corundum.

Phases are listed according to estimated order of abundance based on the relative intensity of major diffraction peaks.

* Diffraction taken at high pressure and room temperature.
of brucite, which we interpret as unreacted starting material, likely at the edge of the chamber. We use the following abbreviations in discussing phase relations: Brd = bridgmanite; PPv = post perovskite phase; Per = periclase; St = stishovite; Sf = seifertite; H = phase H; D = phase D; Bru = brucite; Cor = corundum; IceX = high pressure form of water ice; Liq = liquid phase (melt or high density fluid).

3.1. Phase relations in the system MSH

Fig. 4 shows P–T plots illustrating the phase assemblages observed in diffraction measurements of quenched samples for the two bulk compositions in the MSH system. In the experiments in this system we expect no more than four phases to be present (isobaric invariance), with 3-phase assemblages most likely (isobaric univariance). The assemblages may all be solids, and potential 3-phase fields involving candidate solids are depicted in Fig. 1. Alternatively, phase relations may involve a liquid phase. At pressures of 50 GPa and above, in 24 of 25 experiments we observe either 2- or 3-phase solid assemblages. Conversely, at pressures below 50 GPa, only 11 of 49 experiments contained a 3-phase assemblage, while 18 have a 4-phase assemblage and 20 a 5-phase assemblage. We will consider the higher-pressure phase relations first.

3.1.1. Experiments at \( P > 50 \) GPa

Two boundaries have been located at high pressure, which produce sensible ternary phase relations. In isothermal experiments at \( T = 1800 \) K and below, we bracket a boundary assemblages containing phase H on the low-pressure side, to a phase H absent assemblage on the high-pressure side. On the low-pressure side of the boundary assemblages are Brd + H + Per (MSH1) or Brd + H + St (MSH2). On the high pressure side phase H disappears, and we observe 2-phase assemblages of Brd + Per or Brd + St. Diffraction spectra documenting this boundary are shown in Fig. 5, where it is clear that phase H coexists with Brd and St at 53 GPa, but is absent at 55 GPa. Mass balance requires the addition of a third, hydrous phase, and we assume that at the run conditions the H2O component exists as phase Ice X, which on the basis of some experiments and theory, may be stable at these conditions (Schwager et al., 2004; Schwager and Boehler, 2008; Schwegler et al., 2008); when quenched to room pressure the ice phase would melt and vaporize. Three-phase triangles depicting these sub-solidus equilibria are shown as insets on Fig. 4. The phase H-out boundary occurs between 55 and 60 GPa and apparently has a negative \( dT/dP \) slope. This boundary is very close to the H-out boundary of 52 GPa predicted for \( \text{MgSi}_2\text{O}_6\text{H}_2 \) composition in first principles molecular dynamics calculations (Tsuchiya, 2013) (Fig. 1), and is generally consistent with recent multi-anvil results (Nishi et al., 2014), where phase H stable was found to be stable in both \( \text{MgSiH}_2\text{O}_4 \) and \( \text{Mg}_2\text{Si}_3\text{O}_5\text{H}_2 \) compositions at 50 GPa and 1273 K.

As shown on Fig. 4, the ramped experiments produce a curve with a positive \( dT/dP \) slope at pressures above 50 GPa, and the assemblages lack a hydrous phase. We and other workers have found temperature–laser power plateaux to be extremely robust indicators of melting in several metal and silicate systems (Shen and Lazor, 1995; Dewaele et al., 2007; Lord et al., 2009; Lord et al., 2010; Anzellini et al., 2013; Fischer et al., 2013; Lord et al., 2014; Thomson et al., 2014), with melting curves constrained in this way comparing well with melt detection by independent techniques, most significantly the detection of liquid diffuse scattering during in situ XRD (Dewaele et al., 2007; Anzellini et al., 2013).
et al., 2013; Lord et al., 2014). For a more complete discussion of the evidence for the use of plateaux in power vs. temperature functions as a melting criterion, see Lord et al. (2014). Corroborating textural evidence for melting is provided below. Thus, our preliminary interpretation is that the thermal perturbations are indicative of eutectic melting in the Brd + Per + IceX and Brd + St + IceX ternaries. Our boundary falls about 200 K below the melting curve of Ice X of Schwager et al. (2004) that has been corroborated by theory (Schwegler et al., 2008), but above the lower temperature experimental determinations of two other diamond anvil cell studies (Goncharov et al., 2005; Lin et al., 2005). In contrast to our results, Nishi et al. (2014) report breakdown of phase H to an assemblage of Brd + St + fluid or Brd + fluid in experiments at 1373 K, suggesting that this represents the dehydration/melting temperature of phase H. This is hard to reconcile with our observations of phase H present to temperatures of the order 1600 K at 54 GPa.

3.1.2. Experiments at < 50 GPa
At pressures less than 50 GPa phase relations in MSH are more challenging to interpret. However, several boundaries are apparent in the data that are consistent in both starting compositions. The first appearance of phase H in MSH1 composition is tightly bracketed at ~ 40 GPa, and in composition MSH2 phase H appears at somewhat lower pressures, in the range of 35 to 40 GPa. Fig. 5 shows diffraction data that clearly indicate the emergence of phase H at 40 GPa in composition MSH2, whereas it is absent in the experiment at 33 GPa. These results are generally consistent with those of Nishi et al. (2014) who found phase H present in the endmember composition at pressures as low as 35 GPa. The next obvious boundary in our experiments is a phase D-out boundary that occurs at ~48 GPa in both compositions. This boundary is very close to the phase-D out boundary found by Nishi et al. (2014) in multi-anvil experiments at 1273 K, which is generally consistent with the DAC observations of Shieh et al. (1998) on a natural lizardite composition, and is close to the boundary based on molecular dynamics calculations (Tsuchiya, 2013). We note that phase H and phase D coexist in most of our experiments between the H-in and D-out boundaries, and that these experiments tend of have 4 to 5 phases (Brd + H + D ± Per ± St). A five-phase assemblage would require P-T invariance, and because we observe this over a range of conditions we interpret this violation of the phase rule as disequilibrium. This might be explained as a consequence of the bulk compositions being relatively close to 3-phase triangles involving D + H + Per and Brd + H + D (Fig. 2). Another possibility is that a liquid phase is present, and that thermally induced chemical segregation, either Soret or saturation gradient diffusion (Lesher and Walker, 1988; Sinmyo and Hirose, 2010), leads to complex dis-equilibrium assemblages. This effect could be significant especially in regions of the phase diagram where multiple reactions occur over a relatively narrow P-T-X range. However, the observed consistency of our phase-in and phase-out boundaries, combined with results from other independent methods, lends credence to these multi-phase assemblages in locating primary phase boundaries.

In isothermal experiments at pressures less than ~35 to 40 GPa, we consistently produce the univariant assemblage D + St + Per in both starting compositions. Fig. 5 shows an example of an unequivocal diffraction pattern from an MSH2 experiment at 33 GPa, 1350 K, showing phase D and stishovite but no bridgmanite. Fig. 5a shows a false-color X-ray map of a polished MSH2 sample from an experiment at 36 GPa and 1710 K, which exhibits a generally uniform and well-crystallized mixture of phase D, stishovite and periclase. We can identify a Brd-in boundary at ~35 GPa and 1600 K, best constrained in MSH1 composition. The absence of bridgmanite was also observed in the DAC experiments of Shieh et al. (1998) on a lizardite composition at similar conditions, although those workers observed Brd-in at somewhat higher pressures. In contrast, Nishi et al. (2014) produce a Brd + St + Liq assemblage at 1673 K in a phase D bulk composition at 25 GPa. Recently, Ghosh and Schmidt (2014) found that phase D coexists with Brd + St + Mg-rich hydrous melt at 24 GPa, 1623 and 1648 K, in a Si-rich bulk composition in the MSH system; they interpreted this four-phase assemblage to represent spanning of a phase boundary in a temperature gradient, rather than isobaric invariance, and place the solidus at ~1623 to 1648 K. At 32 GPa, 1673 K, these workers find that a Mg-rich hydrous melt coexists with Brd + St, and their results are generally consistent with the phase relations predicted by Komabayashi et al. (2004) at these conditions.

Taken at face value, the assemblage D + St + Per could be stable if a 3-phase triangle exists between periclase, phase D and stishovite. This could arise if stishovite becomes sufficiently hydrated (Spektor et al., 2011) such that a tie-line emerges between periclase and stishovite that occludes anhydrous Brd (Fig. 1), and would explain the repeated appearance of this assemblage in both Mg-rich (MSH1) and Si-rich (MSH2) compositions. Another possibility is that the assemblage occurs due to the involvement of a liquid phase, for example in the reaction:

\[
\text{D + Brd} = \text{St + MgO-rich liquid.}
\]

As noted above, Ghosh and Schmidt (2014) found that an MgO-rich hydrous liquid coexists with bridgmanite ± phase D in the MSH system at pressures of 24 and 32 GPa. Further, first principles molecular dynamics calculations indicate complete miscibility of water and silicate melt throughout almost the entire mantle pressure regime, and note a strong preference for water molecules to bond with Mg cations (Mookherjee et al., 2008). However, why bridgmanite should be absent in our bulk
compositions is unclear, as chemography indicates that bridgmanite should not be the first phase exhausted in such a reaction (Fig. 1).

The ramped experiments at pressures between about 30 and 50 GPa produce relatively flat curves in both starting compositions at ~1800 K. Fig. 6b shows a false-color X-ray map of a ramp experiment at 39 GPa that exhibited a clear temperature plateau at ~1835 K. Compared to the uniform texture observed in the isothermal experiment at 1710 K (Fig. 6a), a distinctly non-uniform, 'bulls-eye' texture developed in this experiment. We commonly observe this kind of texture in ramp-type experiments in MSH, typically showing a concentration of stishovite in the center. This might represent the reaction given above where stishovite crystallizes upon melting due to a very Mg-rich hydrous melt. The periclase-rich annulus surrounding the mixed D + St region in Fig. 6b could represent quenched Mg-rich hydrous melt, and further analyses are required to test this hypothesis.

When combined with the curve derived from the ramped experiments at higher pressures, an inflection is apparent that correlates well with the intersection of the H-out boundary (Fig. 4), and such an inflection is expected where a subsolidus reaction intersects a melting curve. As with the higher-pressure experiments, our current interpretation based on the temperature plateaus and textural evidence is that this curve represents dehydration melting, and above this curve only anhydrous phases plus a hydrous silicate melt are present. The ramp experiments contain hydrous phases, which likely is a consequence of the relatively large temperature gradient. However, we note that in an experiment taken to several hundred degrees above the melting curve (red star in Fig. 4), an entirely anhydrous solid assemblage was produced.

3.2. Phase relations in the system MASH

Fig. 7 is a P–T plot showing the phase assemblages observed in diffraction measurements from quenched samples for the five bulk compositions in the MASH system. The addition of alumina to the MSH system creates solid solutions in bridgmanite, phase D and phase H, and to a minor extent in stishovite. A complete solid solution between endmember MgSiH2O4 and AlOOH may exist (Fig. 1). However, for convenience we will continue to refer to the [Mg, Si, Al] OOH solid solution as phase H. Because of the solid solutions in the MASH system, three-phase equilibria are expected to dominate sub-solidus phase relations, and of the 56 experiments on which diffraction data were collected, 31 have three phases, 17 have four phases and 3 have 5 phases.

3.2.1. Subsolidus phase relations

In contrast to the results in the MSH system, we find that bridgmanite is stable in all experiments in the MASH system, with the exception of one at 123 GPa where it is replaced by post-perovskite. At pressures less than ~45 GPa the subsolidus assemblage is Brd + D + St or Per, depending on the bulk composition, although minor corundum was apparent in a few of the lower pressure run products. The first appearance of phase H occurs at ~45 GPa, and most of the experiments with 4 or 5 phases occur between ~45 and 55 GPa and define a region wherein aluminous phase D and phase H solid solutions coexist. As shown by the diffraction patterns in Fig. 8, an experiment at 49 GPa and 1755 K produced an assemblage of Brd + D + H + St in composition MASH3, but by 62 GPa phase D is absent. A phase D-out boundary is constrained by all compositions at ~55 to 60 GPa, or about 5 to 10 GPa higher than observed in the MSH system. The data indicate that phase D is stabilized in the alumina-bearing system to higher pressures than in the MSH system. Above ~60 GPa phase H solid solution is the stable hydrous phase, coexisting with bridgmanite and a free silica phase in SiO2-rich compositions, or with bridgmanite plus periclase in MgO-rich compositions. Our data show phase H stable in the quenched products of all experiments up to 116 GPa. Thus, even the addition of as little as ~2.5 mol% alumina...
to the MSH system appears to stabilize a phase H solid solution to the base of the lower mantle. In experiment MASH2-4 we observe an assemblage of bridgmanite, post-perovskite and periclase in a diffraction pattern taken at 116 GPa (300 K). The post-perovskite diffraction lines are well fitted, but are weak relative to the bridgmanite lines. In contrast, in MASH7-5 at 123 GPa the post-perovskite lines are strong relative to weaker bridgmanite lines. These observations indicate that at ~1800 K post-perovskite stabilizes in the region of 115 GPa in a composition with ~5 mol% Al₂O₃, and that in a composition with ~10 mol% Al₂O₃ bridgmanite-out will occur in the region of 130 GPa. Bridgmanite and post-perovskite will coexist in a two-phase loop with the addition of alumina to the MgSiO₃ system. Previous experimental results indicate that bridgmanite is stabilized to higher pressures with addition of alumina, and that the two-phase region is large for the composition MgSiO₃–25 mol% Al₂O₃, extending to greater than ~150 GPa (Tateno et al., 2005). First principles calculations confirm that bridgmanite is stabilized relative to post-perovskite, and for compositions in the range of 5–10 mol% Al₂O₃, 2-phase loops of ~10–20 GPa width are predicted (Akber-Knutson et al., 2005). We tentatively put the position of the post-bridgetmanite in boundary at ~115 GPa based on experiment MASH2-4 with ~5 mol% Al₂O₃. This is close to the boundary predicted for pure MgSiO₃ (Murakami et al., 2004; Ono and Oganov, 2005); however, as our pressures do not include a thermal term, we likely underestimate pressure of the phase boundary, perhaps by as much as 10%, and so the boundary is more likely to occur at ~125–130 GPa at high temperature. Our data indicate a relatively narrow two-phase region, of the order 10–20 GPa, which is close to the ab initio predictions but considerably narrower than previous experimental results in the MAS system. We note that phase H was not unambiguously identified in the high pressure patterns, but was clearly present in the quenched pattern from 115 GPa. With the exception of Pt and Re, no diffraction lines were evident in the quench product of the 123 GPa experiment, indicating that all phases became amorphous upon pressure release.

At pressures above ~90 GPa, we no longer observe the presence of stishovite in the quenched diffraction patterns in Si-rich bulk compositions (Fig. 8); all peaks can be indexed with bridgmanite plus phase H. Chemographically, excess silica must be balanced by a silica-rich phase. However, we note that in the high pressure pattern on sample MASH7-5 at 123 GPa (300 K), a full profile fit is achieved with a combination of post-bridgmanite, bridgmanite and seifertite, a high-pressure form of SiO₂ known to be stable in this pressure range (Grocholski et al., 2013). It may be that hydrous and aluminous seifertite is not quenchable, in which case it could be present in all of the apparently stishovite-free experiments above 90 GPa in SiO₂-rich compositions. This is generally consistent with the stishovite to seifertite phase boundary observed by Grocholski et al. (2013).

3.2.2. Melting systematics

The ramped experiments in the MASH system produce a curve with a positive dT/dP slope (~6 K/GPa). Within uncertainty we cannot detect a difference in the melting temperatures related to bulk composition. We suggest that this curve represents the upper temperature limit of hydrous phase stability of phases D or H depending on pressure. Because solid solutions are involved, these phases may persist above the solids over some temperature range, in which case our method of melt detection may overestimate the solids temperatures. Indeed, in all the ramped experiments where we have diffraction data, either phase D or H are present. However, as these experiments were quenched while on a temperature plateau, and experimental temperature gradients certainly spanned solids temperatures, the presence of a hydrous phase in the diffraction pattern is not unexpected. Similar to the MSH system, we typically observe uniform textures in sub-solidus experiments, which we find readily amenable to mechanical polishing. However, melting experiments commonly exhibit a friable, difficult to polish core region, which we interpret as the partially melted region. When compared to the melting curve in the MSH system, we find that the MASH curve is several hundred degrees above the MASH curve at less than ~60 GPa. In the MASH system the melting curve has a shallower slope than in MSH at higher pressures, apparently due to the high pressure stability of phase H, and the two curves are close in temperature at ~90 to 100 GPa. Our observed position of the solidus temperature in the MASH system at ~30 GPa, and the increase in the solidus by ~200 K relative to MSH, are generally consistent with the multi-anvil results of Ghosh and Schmidt (2014), and indicate that addition of alumina to phase D significantly increases the melting temperature (Pamato et al., 2015).

3.3. Unit cell volumes, phase compositions and mass balance

Bridgmanite and phases D and H can all exhibit considerable alumina solution, with more than 25 mol% Al₂O₃ stable in the bridgmanite structure in MAS at lower mantle pressures (Walter et al., 2004; Walter et al., 2006), and potentially complete solid solutions between MgSi- and Al-end-members in phases D and H (Ohira et al., 2014; Pamato et al., 2015). Our attempts to measure crystal compositions directly in experiments in the MASH system with the field emission gun electron microprobe yielded analyses of phase mixtures due to their sub-micron size, which is consistent with the crystal sizes observed in the experiments of Ohira et al. (2014). Unit cell volumes of a P–T quenched phase can in some cases be used to estimate phase compositions at the experimental synthesis conditions (Mao et al., 1991; Walter et al., 2004). A relatively simple linear relationship between ambient unit cell volume and composition is apparent for alumina-bearing bridgmanite in the MAS system (Walter et al., 2004; Walter et al., 2006), and so may be useful to estimate bridgmanite compositions in our experiments.

We calculated unit cell volumes for bridgmanite in experiments in both the MASH and MASH system throughout the covered pressure range, and the results are provided in Table 4 and shown in Fig. 9. We were typically able to use a dozen or more reflections for volume calculations, resulting in reasonably high precision, but unfortunately, uncertainty in the volumes of phases D, H and stishovite are too large for meaningful attempts to estimate compositions, as we typically had 5 or fewer usable reflections for these phases.

Fig. 9 indicates that at pressures below about 55 GPa in the MASH system, where phase D is stable, bridgmanite has a relatively low alumina content, perhaps about 2 mol% Al₂O₃ when cast in the system MgSiO₃–Al₂O₃. At higher pressures where phase H replaces phase D as the hydrous phase, there is a continuous increase in the unit cell volume of bridgmanite with synthesis pressure, suggesting that the amount of alumina in bridgmanite coexisting with phase H increases with pressure. For example, on the basis of this interpretation we would predict that at 70 GPa bridgmanite contains about 6–7 mol% alumina, and at 100 GPa about 10 mol% alumina. Unit cell volumes do not appear to systematically vary with bulk composition as expected, which could mean the dependence is small relative to the uncertainty in the cell volumes.

Estimating bridgmanite alumina content on the basis of Fig. 9 permits mass balance calculations against system bulk compositions. For three-phase sub-solidus equilibrium among Brd + D + (Per, St) at lower pressures, or Brd + H + (Per, St) at higher pressures, the composition of phases D and H can be uniquely defined if the compositions of the coexisting phases are fixed. Using compositions MASH1 (Mg-rich, Al-poor) and MASH7 (Si-rich, Al-rich) as examples, we made mass balance calculations on the basis of the inferred bridgmanite compositions from Fig. 9.

For MASH1 composition at low pressures, and estimating 2 mol% Al₂O₃ in bridgmanite, mass balance yields 78% brd + 14% D + 8% per, with phase D containing ~12 mol% Al₂O₃. This indicates that Al partitions strongly into phase D relative to bridgmanite. The same calculation for MASH7 does not yield a three-phase solution involving Brd + D + St, but requires excess Al₂O₃ for mass balance. Indeed,
The average d-spacing of this reflection in our MASH experiments is 3.15 ± 0.01 Å. Literature data shows that highly aluminous phase H and endmember \( \text{SiO}_2 \) have (110) d-spacings in the range of 3.14–3.15 Å, whereas the d-spacing in endmember MgSiH\(_2\)O\(_4\) in our MSH experiments is 3.176 ± 0.002 Å, and was measured to be 3.19 Å by Bindi et al. (2014).

While perfectly reasonable 3-phase mass balance can be achieved for a range of bridgmanite compositions, as in the examples above, 3-phase mass balance cannot be achieved in bulk compositions MASH1 and MASH3 if bridgmanite contains more than ~5 mol% Al\(_2\)O\(_3\) (MgSiO\(_3\)–Al\(_2\)O\(_3\)), above ~8 mol% Al\(_2\)O\(_3\) for composition MASH2, and above ~10 mol% Al\(_2\)O\(_3\) for compositions MASH6 and MASH7. Thus, at the highest pressures the observed unit cell volumes indicate alumina contents in bridgmanite that are too high for successful mass balance with the system bulk compositions; a fourth, alumina-poor phase is required for mass balance, which is not observed.

The failure in mass balance at high pressures requires an alternative explanation for the observed positive correlation between cell volume and synthesis pressure in Fig. 9. One possibility is that the volume increase with pressure is a quench phenomenon related to decompression. We find this unlikely, as the ambient unit cell volume of bridgmanite in the MSH experiments shows no correlation with pressure, with an average value of 162.3 ± 0.2 Å\(^3\).

A second possibility is that the increase in cell volume is not related to alumina incorporation alone, but also reflects addition of hydrogen into the bridgmanite structure. Measurements of hydrogen in bridgmanite synthesized experimentally in hydrous systems, using both infrared spectroscopy and secondary ion mass spectrometry, have yielded a puzzling range of values from undetectable to several thousand ppm (Bolfan-Casanova et al., 2000; Murakami et al., 2002; Litaso et al., 2003; Bolfan-Casanova, 2005). Recent ab initio calculations in which the partition coefficient of hydrogen between hydrous ringwoodite and bridgmanite in MgSiO\(_3\) was determined indicate as much as a thousand ppm H in bridgmanite (Hernandez et al., 2013).


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Substitution of hydrogen into bridgmanite may be enhanced by coupled substitution of Al\(^{3+}\) on the octahedral site through charge balance: Si\(^{4+}\) = Al\(^{3+}\) + H\(^+\). This can occur in a variety of ways, one of which is through the formation of an oxygen vacancy and subsequent protonation: V\(^o\) + O\(^2-\) + H\(_2\)O = 2OH\(^-\) (Navrotsky, 1999; Brodholt, 2000; Navrotsky et al., 2003). However, oxygen vacancy formation of this sort has been shown to be generally unfavorable in bridgmanite at lower mantle pressures, and should become less favorable with increase in pressure (Brodholt, 2000; Walter et al., 2006).
mechanism would be direct incorporation of an MgAlH₂O₃ component, with protonation of oxygen near to Al³⁺ on the octahedral site. Addition of hydrogen to the bridgmanite structure is expected to increase the unit cell volume, perhaps at a higher rate than for Al³⁺ alone, and this is a possible explanation for the trend observed in Fig. 9. If this interpretation were correct, then the alumina content may remain relatively low in bridgmanite throughout the lower mantle, with alumina preferentially partitioning into phase H. This might also indicate the potential for substantial hydrogen solution in bridgmanite, with important implications for the water storage capacity of the lower mantle. Further investigation is needed to test this hypothesis.

4. Discussion

Our results show that in the MASH system, a stable hydrous solid phase can be stable in the subsolids of model peridotitic and basaltic compositions throughout the lower mantle pressure range; phase D in the shallow lower mantle and phase H from the mid-lower mantle to the mantle–core boundary. In the MSH system, phase D is stable to about 45 GPa, where it is replaced by the endmember phase H, MgSiH₂O₄, and phase H has a high-pressure stability limit of ~55 GPa. In the MASH system an aluminous (Mg,Si,Al)OOH solid solution appears at ~45 GPa in both model peridotitic and basaltic bulk compositions, and remains stable in the subsolids throughout the lower mantle pressure range. Thus, depending on temperature, phase H is potentially an important host for water in the deep lower mantle (Ohira et al., 2014).

Fig. 10 shows a P–T diagram summarizing our results relative to the trajectories of model ambient mantle and cold subduction geotherms. Geotherms for lithosphere subducted into the lower mantle are poorly constrained, and extrapolation of thermal models made for the upper mantle yield a wide range of possible trajectories (Kirby et al., 1996; Eberle et al., 2002; Syracuse et al., 2010). The slab geotherm shown on Fig. 10 represents the coldest portion of the slab in the model of Kirby et al. (1996), extrapolated to the base of the mantle, and this profile probably represents a minimum. Along this model subduction geotherm we expect an aluminous hydrous phase, either D or H, to be stable in hydrated, subducted lithosphere throughout the lower mantle depth range (Ohira et al., 2014). We also plot a model ambient mantle geotherm on Fig. 10 for the lower mantle, assuming a temperature of 1900 K at 660 km (Brown and Shankland, 1981; Ito and Katsura, 1989).

Ghosh and Schmidt (2014) observed a high temperature stability limit for aluminous phase D coexisting with bridgmanite of ~1900 K at 24 GPa in the MASH system, although a hydrous Mg-rich melt is also present at temperatures as low as ~1600 K. This is generally consistent with the results of Schmandt et al. (2014), who found melt present upon heating of hydrous ringwoodite to ~1900 K at 30 GPa. Ghosh and Schmidt (2014) suggest that heating of slabs that stall at the base of the transition zone or in the shallow lower mantle should lead to melting and release from the slab of a Mg-rich hydrous melt. Schmandt et al. (2014) suggest that the observed decreases in seismic velocities in regions of downwelling mantle are consistent with the presence of partial melt. Both these studies suggest that hydration of the transition zone may occur by hydrous slab melting in this depth range. Thus, it would seem that transport of water into the deep lower mantle requires either direct slab penetration into the lower mantle along a cold slab geotherm, or that aluminous phase D remains stable in the presence of hydrous melting around the 660 km discontinuity, such that some hydrous component can be delivered to the lower mantle upon further subduction. Ohira et al. (2014) suggest that hydrous melts might become trapped in subducting material due to their poor wetting properties, and be delivered to the lower mantle where the hydrous component would be stored in phase H.

The curve that we interpret as dehydration melting in the MASH system is very close to the model mantle geotherm on Fig. 10. However, because the mantle will have other components that will lower the melting temperature relative to the MASH system (e.g., Fe, Ca, Na, K), we predict that a solid hydrous phase will not be stable in the ambient lower mantle, and that when the storage capacity for hydrogen in bridgmanite is exceeded, a hydrous silicate liquid will be stable throughout the lower mantle along an adiabatic geotherm. If a subducting slab carries hydrogen in phase H to the deep lower mantle, perhaps all the way to the core–mantle boundary region, and then heats up toward ambient mantle temperatures, it will eventually melt and a hydrous silicate liquid will be stable. Likewise, any primordial hydrogen in the deep lower mantle after accretion would be expected to lead to melting. The calculations of Mookherjee et al. (2008) are suggestive that melts at these deep lower mantle conditions may be neutrally or negatively buoyant relative to solid mantle, and so could become trapped. The expected small volume fraction of hydrous melt would not likely have a detectable effect on observed isotropic seismic velocity in the lower mantle. However, the lowermost mantle has a strong, heterogeneous seismic anisotropy, and the anisotropic signature of large low shear-velocity provinces, especially in the D’ region, appears to be distinct from that of other parts of the lowermost mantle, for example beneath subduction zones (Nowacki et al., 2010; Cottaar and Romanowicz, 2013; Nowacki et al., 2013). A candidate for producing seismic anisotropy is the presence of aligned melts, as these can have a strong anisotropic signature even in small volume fractions (Kendall and Silver, 1996). This possibility should be considered in seismic models of deep mantle anisotropy as our results suggest that along a mantle geotherm a hydrous silicate melt will be stable, and is likely to be the host for hydrogen in the deep lower mantle.

5. Conclusions

Experimentally determined phase relations in the systems MSH and MASH constrain the high-pressure stability of hydrous silicates. At ~1700 K, the recently discovered phase H appears at ~40 GPa in the MSH system, but it has a narrow stability range as predicted by ab initio calculations, with Phase H–out by ~50 GPa. However, the addition of alumina to the system vastly increases the stability of phase H, and an aluminous phase H coexisting with relatively Al-poor bridgmanite can be stable to the base of Earth’s lower mantle. We suggest that the high temperature stability of lower mantle solid hydrous silicates (D and H) is defined by dehydration melting curves, which we deduce from
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