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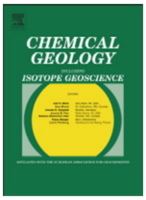

The stability of hydrous silicates in Earth's lower mantle: Experimental constraints from the systems $MgO–SiO_2–H_2O$ and $MgO–Al_2O_3–SiO_2–H_2O$

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ABSTRACT

We performed laser-heated diamond anvil cell experiments on bulk compositions in the systems $MgO–SiO_2–H_2O$ (MSH) and $MgO–Al_2O_3–SiO_2–H_2O$ (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 aluminous phase H to be stable throughout the lower mantle depth range beneath ~1200 km in both peridotitic and basaltic lithologies. In the subsolidus, aluminous phase D is stable to ~55 GPa, whereas at higher pressures aluminous 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.

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).

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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; Litasov 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 controlled primarily by the stability of phase D, an orthorhombic mineral with the ideal formula $MgSi_2H_2O_6$, 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; Shinmei 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 $CaCl_2$-type structure, is stable throughout the mantle depth range and may be present in suitably aluminous and hydrated lithologies (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 $MgSiH_2O_4$, was predicted by ab initio methods with a calculated stability limit of ~50 GPa (Tsuchiya, 2013), potentially extending the depth range to which hydrous magnesian silicates can deliver water into the lower mantle. This new phase has now been observed in experiments up to 50 GPa in the $MgO–SiO_2–H_2O$ (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 *pnnm* 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 an (Mg,Si,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% Al_2O_3 in the system $MgO–Al_2O_3–SiO_2–H_2O$ (MASH) (Ohira et al., 2014).

Here we investigate phase relations in the systems $MgO–Al_2O_3–H_2O$ (MSH) and $MgO–Al_2O_3–SiO_2–H_2O$ (MASH) at lower mantle pressures and high temperatures using the laser-heated diamond anvil cell, with the aim of determining the stability of hydrous phases and constraining melting temperatures of model hydrated mantle lithologies. Synchrotron-based powder diffraction is used to identify phases in run products, constraining the stability of phases D and H in model peridotitic and basaltic lithologies in these systems. We use thermal signal processing and high-resolution imaging to constrain melting temperatures, and evaluate the stability of solid and liquid hydrous phases in these systems at lower mantle conditions.

2. Experimental and analytical methods

2.1. Starting compositions

The compositions of the seven starting mixtures used in this study, two in the MSH system and five in the MASH system, are provided in Table 1 and are shown on Fig. 1. In each system we investigate both MgO-rich and SiO_2-rich compositions in order to explore differences between model peridotitic and basaltic systems, respectively. In the MSH system, compositions have ~9 to 13 mol% H_2O, while in the MASH system compositions have ~4 to 7 mol% H_2O. Al_2O_3 contents in the MASH system range from ~2 to 10 mol%, again to emulate differences between peridotitic and basaltic bulk compositions.

Table 1
Experimental starting compositions (mol fraction).

Composition	MgO	Al_2O_3	SiO_2	H_2O
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

Starting compositions are synthesized as mixtures of anhydrous silicate glass and brucite. In the MSH system, $MgSiO_3$ glass was synthesized by fusing an ~1 g stoichiometric mixture of reagent grade MgO and SiO_2 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 H_2O 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 (Al_2O_3) 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