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Letters

Water storage capacity in olivine and pyroxene to 14 GPa: Implications for the water content of the Earth's upper mantle and nature of seismic discontinuities

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ABSTRACT

Experiments were performed under water-saturated conditions in the MFSH ($MgO–FeO–SiO_2–H_2O$) and MFASH ($MgO–FeO–Al_2O_3–SiO_2–H_2O$) systems at 2.5, 5, 7.5 and 9 GPa, at temperatures from 1175 to 1400 °C and H_2O initial abundance of 0.5–5 wt%. One experiment was performed at 13.5 GPa at a temperature of 1400 °C in the MFSH system. Water contents were analyzed by Fourier transform infrared spectroscopy. Results show that Al contents in olivine and pyroxene in equilibrium with an aluminous phase decrease significantly with increasing pressure and decreasing temperature. The incorporation of Al enhances water incorporation in olivine and pyroxene, but only at pressures of 2.5 and 5 GPa. At 7.5 GPa (i.e. 225 km depth) the pyroxene is monoclinic, indicating that in a hydrous mantle the orthoenstatite to clinoenstatite phase transition occurs at shallower depths than previously thought, which is more consistent with the Lehmann discontinuity than with the X discontinuity. The partitioning of water between pyroxene and olivine in the MFASH system decreases from a value of 2 at 2.5 GPa (80 km depth) to 0.9 at 9 GPa (270 km depth). At 13.5 GPa and 1400 °C, the water content of olivine is 1700 ± 300 ppm wt H_2O. The water partition coefficient between coexisting wadsleyite and olivine equals 4.7 ± 0.7. We conclude that the water storage capacity of the upper mantle just above the 410 km discontinuity is of 1500 ± 300 ppm wt H_2O. If we assume that the Low Velocity Layer observed near 350 km is due to mantle melting, we can constrain the water content of the mantle at that depth to be $\sim 850 \pm 150$ ppm wt H_2O. This new value is four times higher than previous estimates for the mantle source of Mid Oceanic Ridge Basalts.

Finally, comparison of the depth ranges of the L and X seismic discontinuities and the water storage capacity of the upper mantle suggests that the L-discontinuity (180–240 km) is concomitant with a kink in the water storage due to the orthorhombic to monoclinic phase transition in enstatite, while the X-discontinuity (240–340 km) coincides with a kink in the water storage capacity due to dehydration of garnet.

1. Introduction

Trace amounts of hydrogen dissolved as point defects in nominally anhydrous minerals (NAMs) are believed to play a key role in physical and chemical processes in the Earth's upper mantle. Indeed, the distribution of water inside the mantle controls global mantle dynamics through the important effect of water on mantle viscosity (Hirth and Kohlstedt, 1996; Mei and Kohlstedt, 2000), solidus temperature (Gaetani and Grove, 1998; Aubaud et al., 2004) or phase diagrams (Frost and Dolejs, 2007; Deon et al., 2011). Hence, it is important to estimate the water storage in mantle phases to constrain the deep water cycle and its effects on mantle melting and seismic signature.

Survey of water concentrations in natural minerals from mantle xenoliths shows that among NAMS, olivine is significantly less hydrous than pyroxenes (Bell and Rossman, 1992; Peslier et al., 2002; Bell et al., 2004). However, the application of measurements of natural olivines on the water content of the source region is questionable because of rapid hydrogen diffusion through olivine at high temperatures (Demouchy et al., 2006; see also Peslier, 2010 and references therein), leading to partial dehydration of olivine in mantle xenoliths during ascent (except apparently in kimberlitic samples). In addition, natural samples generally originate from shallow depths (maximum 250-km depth) and thus the water content in the deep mantle would be only accessible via remote sensing methods such as seismic observations or magneto-telluric measurements. Still, high-pressure and high-temperature experiments can provide information

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on the equilibrium water solubility or water storage capacity of mantle olivine, which constitutes up to 60 vol% of the upper mantle mineralogy. Such data are important in order to constrain the water storage capacity of the upper mantle.

Numerous experimental data on water solubility in NAMs are available for upper mantle minerals, such as olivine (Kohlstedt et al., 1996; Mosenfelder et al., 2006; Zhao et al., 2004), pyroxenes (Rauch and Keppler, 2002; Mierdel and Keppler, 2004) and garnet (Lu and Keppler, 1997; Withers et al., 1998; Mookherjee and Karato, 2010). However, the majority of these studies are based on single phases, and at temperatures or pressures that are too low to be extrapolated to upper mantle conditions. Thus, models of water storage capacity in the mantle based solely on solubilities measured in simple systems and at lower temperatures are likely to be over-estimated (see Bolfan-Casanova, 2005). Indeed, contrary to low-pressure observations made at 0.3 GPa (Zhao et al., 2004), water solubility in olivine at high pressures decreases with increasing temperatures (Smyth et al., 2006; Litasov et al., 2007). With increasing depth silicates dissolve more and more into fluid water until formation of a supercritical fluid or melt (Stalder et al., 2001; Mibe et al., 2007). Thus, at high-pressures, the activity of water in melts decreases with increasing temperature and causes a decrease in water solubility in olivine. This effect was previously constrained (Bali et al., 2008) for melts coexisting with forsterite and enstatite at 2.5, 6 and 9 GPa and explains well the drop of solubility that was observed previously not only in olivine (Smyth et al., 2006; Litasov et al., 2007) and enstatite (Withers and Hirschmann, 2007), but also in wadsleyite (Demouchy et al., 2005) and ringwoodite (Ohtani et al., 2000, see Bolfan-Casanova, 2005 Fig. 2b for a review of existing data). In addition, the changes of composition and structure in pyroxenes should affect water partitioning with olivine and other minerals. Especially, it is expected that the water partitioning between olivine and pyroxenes will increase with depth due to the decrease of aluminum content in pyroxene with depth. However, this has never been constrained experimentally and previous estimates using low-pressure partitioning for the upper mantle may lead to overestimations of the pyroxene water contents.

The aim of this study is to constrain the combined effects of pressure, temperature and composition on water solubility in olivine and pyroxene under upper mantle conditions. Experiments were performed under water-saturated conditions in the MFSH ($MgO–FeO–SiO_2–H_2O$) and MFASH ($MgO–FeO–Al_2O_3–SiO_2–H_2O$) systems at 2.5, 5, 7.5 and 9 GPa, at temperatures from 1175 to 1400 °C and H_2O initial abundance of 0.5–5 wt%. One additional experiment was performed at 13.5 GPa and 1400 °C in the MFSH system.

2. Experimental procedures and analytical techniques

2.1. Starting materials

Water saturated experiments were carried out in the MFSH and MFASH systems. The starting material was made of a mixture of highly pure MgO and SiO_2 with FeO $+/-$ Al_2O_3 powders and H_2O which was added as brucite $Mg(OH)_2$. MgO, SiO_2 and Al_2O_3 powders were annealed at 1000 °C overnight before weighting. FeO was incorporated as mixes of Fe and Fe_2O_3. The initial water content was variable from 0.5 to 5 wt% H_2O, depending on the pressure and temperature conditions and was controlled by incorporating different ratios of $Mg(OH)_2$ and MgO. Indeed, when pressure is increased, the amount of melt increases owing to the fact that it mixes a lot of water. Thus the bulk water content must be decreased to prevent extensive melting of the experimental charge. Olivine to enstatite ratios varied from 0.8 to 2, depending on the pressure and temperature conditions. The mixed powder was homogenized in an agate mortar with ethanol and kept at 120 °C to avoid re-hydration.

2.2. High-pressure experiments

Experiments were performed from 2.5 to 13.5 GPa and 1175 to 1400 °C using the 1000-ton multi-anvil press fitted with a Walker type module at Laboratoire Magmas et Volcans (Clermont-Ferrand, France). The starting material was loaded into a Re folded capsule which in turn is placed into a Pt tube prior to welding. Inner Re capsule avoids iron loss and permits to buffer the oxygen fugacity by adding rhenium oxide at one end of the capsule. The $Re–ReO_2$ buffer is located between the Ni–NiO and magnetite–hematite buffers (Pownceby and O'Neill, 1994) and has the advantage of not reacting with the sample charge. Given that ferric iron solubility in olivine and enstatite is very low (O'Neill et al., 1996), the high oxygen fugacity should not affect the solubility of OH in these NAMs through interaction with Fe^{3+} (as seen in low-pressure olivines by Grant, 2007). Still, varying oxygen fugacity could change the speciation of H in the fluid/melt and hence change the activity of H_2O or OH. However, experiments conducted at 8 GPa and 1400 °C under varying conditions of f_{O_2} (from iron–wüstite to hematite–magnetite) show no systematic variation of water storage in olivine (Withers and Hirschmann, 2008). The capsule was surrounded by MgO, which acts as an insulator from the adjacent $LaCrO_3$ furnace, which in turn is thermally insulated by a ZrO_2 sleeve. In these assemblies, a stepped furnace is used in order to minimize thermal gradients. The pressure transmitting medium was made of MgO-octahedra doped with 5 wt% Cr_2O_3. Experiments at 2.5 and 5 GPa were carried out using 25 mm edge-length octahedra and WC-cube with 17 mm truncation length (25/17, 25M). Experiments at 7.5 and 9 GPa were performed in 18/11 (18M) assembly. Pressure was calibrated for both assemblies using known phase transitions of quartz/coesite and coesite/stishovite in SiO_2 (Zhang et al., 1996; Akaogi et al., 1995), garnet/perovskite in $CaGeO_3$ (Liu et al., 1991) and fayalite/spinel in Fe_2SiO_4 (Morishima et al., 1994). One additional sample was synthesized at 13.5 GPa using the 14/8 assembly (14M). Temperature was measured by $Pt/PtRh_{10}$ thermocouple in the 25M and by $W_5Re/W_{26}Re$ thermocouple in the 18M and 14M assemblies, and monitored by a Eurotherm controller. Heating durations ranged from 5 to 50 h with the lower the temperature, the longer the heating time.

All the experiments were carried out under oxidizing conditions, confirmed by the simultaneous presence of Re and ReO_2 in the recovered capsule. The water saturation conditions were confirmed by the presence of free fluid after piercing the capsules. The capsules were then mounted in a UV light-cured composite to prepare doubly-polished thin sections for Fourier transform infrared (FTIR) spectroscopy analysis.

2.3. Analytical techniques

The textural relations within the capsule were achieved using a JEOL JSM-5910 scanning electron microprobe. The chemical compositions of olivine, pyroxene, aluminous phase and the quenched aqueous melt were recorded using a Cameca SX100 electron microprobe under operating conditions of 15 kV voltage and 15 nA current. 10, 20 and 50 s peak counting time were respectively used for analyzing Si, Mg, Fe and Al. Under such conditions for Al, the detection limit is of 0.015 wt% Al, that is ~0.0005 Al per formula unit. For the minerals, except wadsleyite, only data whose total was between 99 and 101 wt% were kept and normalized to 100 wt% (see Supplementary Tables 1 and 2). At such pressures, melts do not vitrify upon quenching, and thus