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Effect of water in depleted mantle on post-spinel transition and implication for 660 km seismic discontinuity

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ABSTRACT

We have determined the post-spinel transition boundary in anhydrous and hydrous Mg_2SiO_4 in a temperature range from 1173 to 2023 K at 19.3–25.4 GPa using synchrotron *in situ* X-ray diffraction measurements. The phase boundary in Mg_2SiO_4 is located at 22 GPa and 1800 K and 22.1 GPa and 1500 K, which is slightly lower ($\sim$0.3–0.5 GPa) than that determined in the previous *in situ* measurements using the same pressure scale [*e.g.* Katsura et al., 2003, Post-spinel transition in Mg_2SiO_4 determined by high *P*–*T in situ* X-ray diffractometry. Phys. Earth Planet. Inter. 136, 11–24]. The Clapeyron slope of Mg_2SiO_4 was found to be gentle *i.e.* between −0.4 and −0.7 MPa/K, which is also consistent with previous *in situ* measurements, but inconsistent with diamond anvil cell experiments and theoretical estimations. The phase boundary in Mg_2SiO_4+2 wt% H_2O which is relevant to Fe free-depleted harzburgitic composition is located between 23.4 and 23.6 GPa and 1500 K, which shifts the hydrous boundary to the higher pressures relative to anhydrous Mg_2SiO_4 from 1.3 to 1.0 GPa. The result for hydrous Mg_2SiO_4 shows steeper Clapeyron slope between −3.2 and −3.1 MPa/K compared with anhydrous Mg_2SiO_4 and hydrous pyrolite system. The present data suggest that water has a strong influence on 660 km discontinuity and the depressions observed at this boundary in several regions, especially related to subduction zones, can be explained by the presence of water in depleted harzburgite component.

1. Introduction

Water plays an important role in the Earth's evolution and dynamics. The amount of water, even at ppm level, can strongly modify the physical and chemical properties of mantle minerals and rocks. Water can enhance melting (Hirschmann, 2006), affect rheological and transport properties (Chen et al., 1998; Karato, 2006), and also change the phase relations of mantle minerals and rocks and shift their phase boundaries (*e.g.* Wood, 1995; Ohtani et al., 2004). Subducting slabs can transport significant amount of water into the Earth's interior and much of the subducted water can be stored in the mantle transition zone according to recent tomography observations, which suggest that most of the subducted oceanic lithosphere is stagnant above 660 km depth (*e.g.* Fukao et al., 2001, 2009).

The 660 km discontinuity is one of the most important structural boundaries in the Earth's interior and it has been widely accepted to be due to a phase transition in $(Mg,Fe)_2SiO_4$ system (*e.g.*, Green and Ringwood, 1967; Liu, 1976; Ito and Takahashi, 1989). At this boundary, $(Mg,Fe)_2SiO_4$ (γ-spinel or ringwoodite; hereafter Rw) transforms to a mixture of $(Mg,Fe)SiO_3$ (Mg-perovskite; hereafter Pv) and (Mg,Fe)O (ferropericlase). According to seismic observations this boundary is placed at a depth corresponding to a pressure of about 23.6 GPa at 1873 K (Dziewonski and Anderson, 1981; Ita and Stixrude, 1992). This phase boundary is endothermic (Christensen, 1995; Akaogi et al., 1998) and is often called the post-spinel transition (hereafter PST). The 660 km discontinuity is a global feature, but seismological studies suggest that its depth varies considerably in different regions. Short period and vertical waveform data from Fiji–Tonga region and beneath Indian Ocean suggest that the 660-km discontinuity is sharp and flat (*e.g.* Benz and Vidale, 1993;

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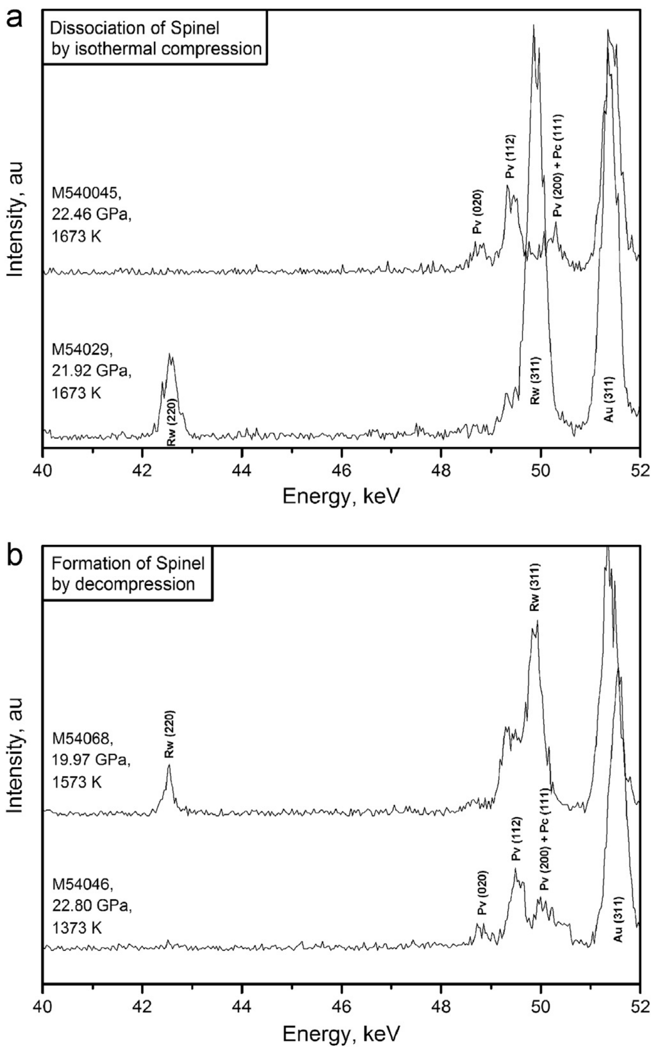

Fig. 1. Representative X-ray diffraction patterns of Mg_2SiO_4 showing (a) dissociation of Rw to Pv+Pc by compression. New Pv peaks e.g. (020), (112) and (200) appear and some Rw peaks *e.g.* (220) and (311) diminish or disappear. (b) Formation of Rw from Pv+Pc by decompression. New Rw peak (220) appears and some Pv peaks *e.g.* (020) diminish or disappear. *Abbreviations:* Rw—ringwoodite; Pv—perovskite; Pc—periclase; Au—gold.

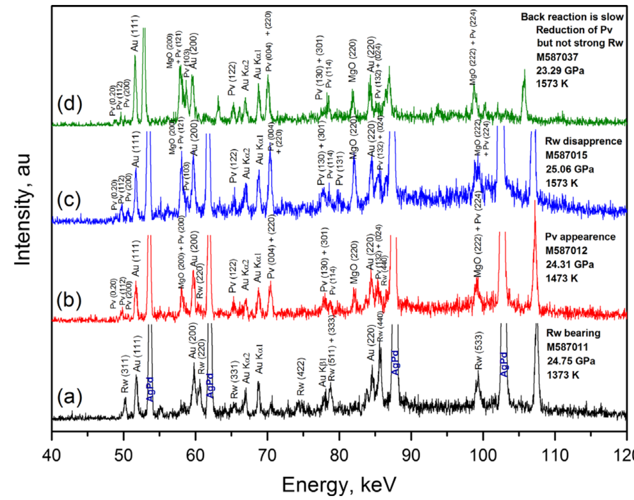

Fig. 2. Representative X-ray diffraction patterns of Mg_2SiO_4+2 wt% H_2O at the indicated *P–T* conditions. Abbreviations are the same as in Fig. 1. Backward transformation of Rw from Pv+Pc is very sluggish and it can be even more sluggish than in dry system either due to growth of large Pv and Pc grains or release of water from the capsule during the experiment.

Yamazaki and Hirahara, 1994). However, comprehensive SS precursor and receiver functions studies in Central Europe and NE China propose that the discontinuity is depressed by 30–70 km or shows significant variations over short spatial wavelengths (*e.g.* Petersen et al., 1993; Flanagan and Shearer, 1998; Helffrich, 2000; Gu and Dziewonski, 2002; Li and Yuan, 2003; Hetényi et al., 2009; Lombardi et al., 2009; Wang and Niu, 2010; Cornwell et al., 2011). The most often mentioned effect to explain these seismic observations is the lateral variation or gradient in temperature (*e.g.* Shearer, 2000) beneath 660 km (Helffrich, 2000), and only a few studies evoke chemical changes as well (*e.g.* Cornwell et al., 2011 and references therein).

To correlate 660 km seismic discontinuity, it is important to know the precise pressure–temperature conditions for the PST (see Ohtani and Litasov (2006) for review). Recent *in situ* X-ray diffraction measurements on pure Mg_2SiO_4 (Irifune et al., 1998; Katsura et al., 2003; Fei et al., 2004b) and a pyrolitic composition (Litasov et al., 2005a) using multianvil technique suggest that the boundary is located at lower pressures than the actual pressure of 660 km discontinuity (~23.6 GPa) and shows a gentle negative Clapeyron slope ranging from −0.4 to −1.3 MPa/K (*e.g.* Katsura et al., 2003; Fei et al., 2004b; Litasov et al., 2005a) such that large variations in the depth of 660 km discontinuity cannot be explained by a temperature effect only. Conversely, laser heating diamond anvil cell (LHDAC) experiments (Chudinovskikh and Boehler, 2001; Shim et al., 2001) and first-principles estimations for Mg_2SiO_4 (Yu et al., 2007), in which the density function theory (DFT) was adopted, show reasonable agreement with pressure and expected Clapeyron slope of the 660 km discontinuity. These latter data support original determination of the depth and Clapeyron slope for the post-spinel transition by Ito and Takahashi (1989) using laboratory multianvil experiments. However, it is important to note that LHDAC experiments may give a large uncertainty in temperature measurements and be influenced by kinetic effects (Li and Jeanloz, 1987). Furthermore, DFT simulations tend to have relatively large errors in transition pressures for non-isochemical transitions at finite temperature.

It was shown that water and other compositional variations might affect the depth and thickness of the 660 km discontinuity (*e.g.* Litasov et al., 2005b). Rw is the most important phase at the lower part of the transition zone from 520 to 660 km depth (Ringwood, 1975). It can incorporate a large amount of hydrogen in its structure (up to 3.0 wt% H_2O) (*e.g.* Kohlstedt et al., 1996; Bolfan-Casanova et al., 2000; Ohtani et al., 2000). In contrast, the most relevant results to date suggest that Mg-Pv and periclase (hereafter Pc) have very low hydrogen solubility (*e.g.* Bolfan-Casanova et al., 2002, 2003; Litasov et al., 2003; Litasov, 2010). Based on thermodynamic relations, hydrogen incorporation into Rw can expand its stability field to higher pressures relative to anhydrous system (Higo et al., 2001; Litasov et al., 2005b; Ohtani, 2005; Ohtani and Litasov, 2006).

The effect of water on the 660 km discontinuity has not been studied extensively. Higo et al. (2001) first noted the shift of the post-spinel phase boundary in Mg_2SiO_4 under hydrous condition based on laboratory experiments and thereafter Litasov et al. (2005b) have studied the post-spinel transition in a hydrous pyrolite system using *in situ* technique and observed the shift of this boundary ~0.6 GPa toward higher pressure compared to anhydrous pyrolite at 1473 K. However, the Clayperon slope was poorly constrained due to restricted temperature interval of measurements. Besides, it is difficult to distinguish the effect of water from a combined effect of other components in the system, such as Al, Fe, and Ca. Therefore, to distinguish the effect of water