Hydration effects on crystal structures and equations of state for silicate minerals in the subducting slabs and mantle transition zone

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Abstract: There are potentially huge amounts of water stored in Earth’s mantle, and the water solubilities in the silicate minerals range from tens to thousands of part per million (ppm, part per million). Exploring water in the mantle has attracted much attention from the societies of mineralogy and geophysics in recent years. In the subducting slab, serpentine breaks down at high temperature, generating a series of dense hydrous magnesium silicate (DHMS) phases, such as phase A, chondrodite, clinohumite, etc. These phases may serve as carriers of water as hydroxyl into the upper mantle and the mantle transition zone (MTZ). On the other hand, wadsleyite and ringwoodite, polymorphs of olivine, are most the abundant minerals in the MTZ, and able to absorb significant amount of water (up to about 3 wt.% H$_2$O). Hence, the MTZ becomes a very important layer for water storage in the mantle, and hydration plays important roles in physics and chemistry of the MTZ. In this paper, we will discuss two aspects of hydrous silicate minerals: (1) crystal structures and (2) equations of state (EoS).

Keywords: Hydrous silicate mineral, Crystal structure, Equation of state (EoS), Mantle transition zone (MTZ), Wadsleyite, Ringwoodite

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1. Introduction

More than 70% of the Earth’s surface is covered by water, and water is very important to human life and society. Due to the bulk volume of the mantle and the significant water solubilities of the minerals in the mantle, the potential water storage deep inside the Earth may be far larger than that on the surface (Smyth, 1987, 1994; Smyth et al., 2003, 2004, 2006; Smyth and Jacobsen, 2006; Williams and Hemley, 2001; Ohtani et al., 2001; Ohtani, 2005; Inoue et al., 2004; Bolfan-Casanova, 2005; Hirschmann and Kohlstedt, 2012). There are several forms for water existing in the mantle: (1) molecules in a fluid, while molecules or hydroxyl (OH$^-$) in the melt, which could be converted to each other (i.e. Stolper, 1982; Zhang and Stolper, 1991; Zhang et al., 1991; Shen and Keplpl, 1995; Ni et al., 2009, 2013; Germán et al., 2015). (2) protons (H$^+$) incorporated into the crystal structures of the minerals, by substituting cations in the lattices (i.e. Bell and Rossman, 1992; Smyth, 1994; Smyth et al., 2006; Ohtani et al., 2001; Smyth and Jacobsen, 2006); (3) molecules around the particle boundaries or in the bulk defects (i.e. Xu et al., 2006; Fu et al., 2001; Su et al., 2002; Liu and Xu, 2004; Zheng, 2009; Kawamoto et al., 2013). Water has important effects on the physical and chemical properties of both minerals and melts in the crust and mantle, as well as evolution of the Earth. Water plays key roles in many geodynamical processes: such as formation of granite, plate kinetics on the Earth’s surface, interaction between the crust and mantle, deformation of the lithosphere; materials exchanging in the subduction slab; evolution of the upwelling plume; earthquake, volcano, and so on.
In this paper, we will focus on water effects on crystal structures and EoSs of the silicate minerals in the subduction slab and MTZ.

Plate subduction is the only potential process, which could bring water down into the upper mantle (Zheng, 2012). Serpentine (containing 13 wt.% H2O) would break up at high temperatures during the subduction process, and generate a series of DHMS phases, like the ones on the brucite (Br, 31 wt.% H2O)–forsterite (Fo, ≤ 0.9 wt.% H2O) (Wunder, 1998; Berry and James, 2001; Smyth et al., 2006); Phase A (2Fo+3Br, 12 wt.% H2O), norbergite (1Fo+1Br, 9 wt.% H2O), chondrodite (2Fo+1Br, 5 wt.% H2O), humite (3Fo+1Br, 4 wt.% H2O), and clinohumite (4Fo+1Br, 3 wt.% H2O). These hydrous phases in subducting slabs may serve as carriers of water into the upper mantle and MTZ (Faust and Knittle, 1994; Wunder et al., 1995). The compositions of hydrous silicate phases in the peridotite system are shown in Figure 1 (MgO-SiO2-Mg(OH)2). Ringwood and Major (1967) firstly synthesized phase A (Mg2SiO4(OH)2), phase B (Mg2SiO4(OH)2) and phase C (Mg2SiO4(OH)2) in MgO-SiO2-H2O system, and it is noted that super hydrous phase B is identical to phase C. Later, phase D (Yamamoto and Akimoto, 1997; Liu, 1986), phase E (Kanzaki, 1989, 1991), phase F (Kudoh et al., 1995) and phase G (Ohtani et al., 1997) were discovered in the following experiments at high pressure and high temperature. The compositions of phases D and E are varied with Mg/Si ratio ranges of 0.55–0.8, 1.8–2.1, respectively. Phases D, F, G are the same phases, sharing the identical space group (Ohtani et al., 2001).

The mantle transition zone is a special and important mineral zone in the mantle (e.g. Weidner and Wang, 2000; Wang and Shen, 2014), with three important seismic discontinuities: (1) at 410-km discontinuity, olivine (α–phase) transits into wadsleyite (β–phase); (2) at 520-km discontinuity, wadsleyite transits into ringwoodite (γ–phase); (3) at the 660-km discontinuity, ringwoodite break down to bridgmanite ((Mg, Fe)SiO3, Tsačauner et al., 2014) plus ferropericlase (Mg, Fe)O), which is also known as the post-spinel phase transition, and 660-km discontinuity also serves as the boundary between the upper mantle and lower mantle. Hence, wadsleyite and ringwoodite, as the high-pressure polymorphs of olivine, play important roles in the physics and chemistry of the MTZ and the storage of water in planetary interiors.

On the other hand, wadsleyite and ringwoodite are nominally anhydrous minerals (NAMs), while could be hydrated up to 3 wt.% H2O by H+ substituting (Smyth, 1987, 1994; Inoue et al., 1995; Kohltedt et al., 1996), which makes MTZ the most important layer for water storage in the mantle. Since wadsleyite and ringwoodite constitute 60–70 vol.% of MTZ (410–660 km), the solubility of the MTZ is 7 to 8 times of the total amount of water on the Earth’s surface. It should be noted that Pearson et al. (2014) recently reported a water content of 1–1.5 wt.% in natural ringwoodite sample, included in a diamond from the MTZ (Juina, Brazil). In addition, Schmandt et al. (2014) demonstrated that hydrous ringwoodite would dehydrate at 660-km discontinuity, due to the postspinel phase transition, yielding partial melting at the top of the lower mantle, and slowing down the seismic velocities at that depth.

Hence, studies on the crystal structures of hydrous silicate minerals would give us a microscope view of how water exists deep inside the Earth; while constraints on equations of state by experiments would support important parameters for the mantle dynamics modeling.

2. Crystal structures

The crystal structures of the DHMS phases on the brucite-forsterite join, as well as forsterite, wadsleyite and ringwoodite are shown in Figure 2. Phase A (Figure 2a) is hexagonal; norbergite (Figure 2b) and humite (Figure 2d) are orthorhombic; while chondrodite (Figure 2c) and clinohumite (Figure 2e) are monoclinic. Forsterite (Figure 2f) and wadsleyite (Figure 2g) are orthorhombic; while ringwoodite (Figure 2h) is cubic. In the following discussion, we will introduce the crystal chemistry studies on these DHMS and hydrous NAMs phases in detail.

In the crystal structures of the silicate phases in the upper mantle and MTZ, Mg2+ and Si4+ cations are generally coordinated with 6 and 4 O2− anions, and forming octahedron and tetrahedron, respectively, while in most cases, O2− anion is coordinated with 4 Mg2+ and 1 Si4+ cations.

2.1 Chondrodite and clinohumite

For the crystal structures of DHMS on the brucite-forsterite joint: (1) Phase A (P63) has three different M2+ octahedral sites and two Si4+ tetrahedral sites. (2) Norbergite and humite share the same space group (Pbnm), and the structure of humite is more complicated. There are two M2+ sites and

![Figure 1](image-url)