Iron-titanium oxyhydroxides as water carriers in the Earth’s deep mantle

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ABSTRACT

We experimentally explored phase relations in the system FeOOH-TiO₂ at pressures of 16 GPa and temperatures of 1000–1600 °C, which corresponds to conditions of the Earth’s mantle transition zone. Analyses of the recovered samples revealed that, in the studied conditions, there are two stable iron-titanium oxyhydroxide phases whose estimated composition is expressed by (FeH)ₓTi₂O₇. One is the Fe-rich solid solution (x < 0.23) with ε-FeOOH type crystal structure (orthorhombic, P2₁nm), and the other is the more Ti-rich solid solution (x > 0.35) with α-PbO₂ type structure (orthorhombic, Pbcn). The ε-FeOOH phase is stable up to ~1100 °C irrespective of chemical composition, whereas the α-PbO₂ type phase is stable up to 1300 °C for a composition of x = 0.5 and at least to 1600 °C for x = 0.75, and thus the α-PbO₂ type phase is stable at average mantle temperature in the Earth’s mantle transition zone. Iron-titanium-rich phases found previously in basalt + H₂O system are estimated to be the ε-FeOOH and α-PbO₂ type phases where the phase with iron-rich composition found at relatively low temperature (~1100 °C) is ε-FeOOH phase and the phase with titanium-rich composition is α-PbO₂ type phase. The α-PbO₂ type and ε-FeOOH phases may be stable in the subducted basaltic crust at pressures in the mantle transition zone under water-rich conditions.

Keywords: Mantle transition zone, water, titanium, hydrous mineral, basaltic crust

INTRODUCTION

In the high-pressure and high-temperature environments of the Earth’s mantle, water (or hydrogen) is considered to exist either as H₂O-rich fluids (or hydrous melts) or in minerals containing hydroxyl (OH) either as part of stoichiometric formulas or as a substantial defect in nominally anhydrous mineral formulas. These hydroxyl-containing minerals may be transported by large-scale mantle convection to deeper parts of the mantle such as the mantle transition zone and the lower mantle, whereas the H₂O-rich fluids are thought to rise quickly to shallower parts (e.g., Ikemoto and Iwamori 2014). Due to the importance of water in the chemical and physical evolution of the mantle, the stability and water storage capacity of the H₂O-bearing minerals in mantle rocks (peridotite) and subducted oceanic crusts (basalt) have been studied extensively (e.g., Kawamoto 2004; Okamoto and Maruyama 2004; Komabayashi and Omori 2006). Previous studies have revealed that the stability of hydrous minerals (e.g., antigorite, lawsonite, dense hydrous magnesium silicates) in these rock compositions is mostly restricted to temperatures lower than the average mantle temperature (e.g., Litasov and Ohtani 2005; Nishi et al. 2014). Although wadsleyite, which is the most abundant nominally anhydrous mineral in peridotitic mantle composition in the upper half of mantle transition zone, can incorporate up to 3.3 wt% water in its crystal structure at relatively low temperatures (~1200 °C), its water content decreases to 0.4–0.5 wt% or less at average mantle temperature of ~1500 °C (Litasov et al. 2011). Lawsonite, which is the water-carrying phase in subducted basaltic crust, decomposes at depths exceeding 300 km (e.g., Schmidt and Poli 1998; Okamoto and Maruyama 2004). Thus, at the conditions in the mantle transition zone, the water storage capacity of the basaltic crust is thought to be restricted by water solubility of nominally anhydrous minerals such as clinoxyroxene and garnet, which is lower than ~0.1 wt% (e.g., Bromiley et al. 2004a; Mookherjee and Karato 2010). However, in most previous studies, the high-pressure and high-temperature experiments were carried out on simple systems where minor elements (such as Ti) were omitted.

In a recent experimental study on the connectivity of H₂O-rich fluids in a basalt + 3.5 wt% H₂O system with multiple component at pressure (P) of 10–12 GPa and temperature (T) of 1000 °C (Matsukage et al. in review; Hashimoto and Matsukage 2013), we identified an iron-titanium-rich phase (FeTi-phase) whose weight total determined by chemical analyses using scanning electron microscope equipped with energy-dispersive spectrometer (SEM-EDS) turned out to be significantly lower than 100%, suggesting high water content of the phase (Fig. 1a, Table A1). While the presence of similar FeTi-phases has been reported in experiments on similar systems by previous studies, they were assumed to be anhydrous; Ono (1998) reported the presence of an unknown FeTi-phase at P = 9–15 GPa and T = 700–1200 °C in basalt + 6 wt% H₂O and sediment + 6 wt% H₂O systems and Okamoto and Maruyama (2004) reported the presence of a similar phase at P = 10–19 GPa and T = 700–1400 °C in a basalt + 2 wt% H₂O system. From the chemical data available, it would seem that these phases are previously unknown hydrous phases having chemical compositions in the Fe-Ti-O-H system, and that their stability field may possibly encompass a wide pressure and temperature range corresponding to the deeper part of the upper mantle and the mantle transition zone. However, their small grain

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