$(FeH)_{1-x}Ti_xO_2$: a new water carrier to the mantle transition zone

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Abstract

It is now widely accepted that Earth's transition zone, located at depth between 410 km to 670 km is most likely hydrated. However, a definite conclusion has yet to be reached regarding the nature of the hydrous phase or phases that have the capacity to efficiently transport water down to such depths. In their study, Nishihara and Matsukage (2016) show that $(FeH)_{1-x}Ti_xO_2$ can be stable in wet basalts and sediments in high pressure and high temperature conditions. These phases allow the subducting lithosphere to transport far more water to the mantle transition zone than previously thought possible.

Hydrous minerals are stable in subducting lithospheres composed of sediments, basalts and peridotite (Figure1). During subducting paths, most hydrous minerals become unstable at high pressures and dehydrate to liberate aqueous fluids, thus producing the serpentinized forearc mantle and arc magmatism (Kawamoto et al., 1996; Tatsumi, 1989). Serpentine and lawsonite are capable of transferring significant amounts of water into the mantle, but may only do so to depth of about 250 km even in the coldest subduction zones (Figure 1, Poli and Schmidt, 1995; Ulmer and Trommsdorff, 1995). At temperature conditions colder than 500°C at 200 km, corresponding to a very cold mantle, the water released from the dehydrating serpentine may be taken up by dense hydrous magnesium silicates such as clinohumite, chondrodite, and hydrous phase A and be transported further down (Figure 1). Beyond the sub-arc depths greater than 200 km in warm subduction zones, K-richterite can accommodate the water from dehydrating phlogopite in the subducting lithosphere at H/K atomic ratio of 1, meaning that peridotite or basalt having 0.1 weight % K_2O can accommodate 0.02 weight % H_2O (Sudo and Tatsumi, 1990). Still, the water transporting capacities of these phases do not sufficiently explain the potential abundance of water in the transition zone.

As for the high-pressure phases that may retain water in the transition zone, it is known that there are no truly anhydrous minerals in the Earth and that all minerals contain water in their structure to some extent (Bell and Rossman, 1992; Hirschmann et al., 2005). In natural mantle xenoliths, such nominally anhydrous minerals are found to possess < 0.03 weight % H_2O in relatively wet garnet peridotites beneath the Siberian craton (Doucet et al., 2014) and < 0.0135 weight % H_2O at the bottom of the relatively dry Kaapvaal craton at depth of 200 km (Peslier et al., 2012). Below the upper mantle, the transition zone may possibly be wetter (Bercovici and Karato, 2003; Hirschmann et al., 2005; Inoue et al., 1995; Kawamoto et al., 1996; Young et al., 1993). Among the nominally anhydrous minerals, wadsleyite was the first to be theoretically proposed to be hydrated (Smyth, 1987) and then experimentally demonstrated to possess up to 3.3 weight % water in MgO-SiO_2-H_2O and hydrous peridotite systems (Inoue et al., 1995; Kawamoto et al., 1996; Kohlstedt et al., 1996). In addition to wadsleyite, ringwoodite was coincidentally found to have up to 2.7 weight % water (Kawamoto et al., 1996; Kohlstedt et al., 1996). Recent finding of 1.5 weight % water-bearing ringwoodite in a natural diamond supports the possibility of a hydrous mantle transition zone (Pearson et al., 2014). Diamonds are transferred to the surface by kimberlite magmas, which can be produced only through partial melting of a deep-seated mantle source anomalously rich in H_2O-CO_2 fluids, or which may even represent fluids or supercritical fluids themselves exsolved from such mantle sources (Kawamoto and Holloway, 1997; Mibe et al., 2007). While the extent of hydration of the transition zone is still under debate, the transition zone may be quite hydrous, and the mechanism of its hydration is another issue that must be resolved (Kawamoto et al., 1996).

In their study, Nishihara and Matsukage (2016) show that $(FeH)_{1-x}Ti_xO_2$ can be stable in wet basalts and sediments in high pressure and high temperature conditions. They conducted high-pressure experiments in the $FeOOH$-TiO_2 system at 16 GPa and confirmed the existence of two stable hydrous phases: an Fe-rich solid solution ($x < 0.23$) with ε-FeOOH type crystal structure and a Ti-rich solid solution ($x > 0.35$) with α-PbO_2 type structure. The Fe-rich phase is stable up to ~1100°C, whereas the Ti-rich phase is stable up to 1500°C. These iron-titanium-rich phases may correspond to those whose existence were inferred in some previous experimental studies conducted in basalt + H_2O and sediment-H_2O systems. Ono (1998) described FeTi oxides at 9 GPa, 1200°C and at 15 GPa, 1400°C in a sediment-H_2O system, and at 6 GPa, 900°C, and at 9 GPa and 15 GPa, 1200°C in a basalt + H_2O system, but refrained from presenting their chemical compositions because the grain sizes were too small for accurate analysis. Such Fe- and Ti-rich phases having chemical compositions similar to those found in Nishihara and Matsukage (2016) have also been reported by Okamoto and Maruyama (2004). The total sum of oxides in the latter study was 83-92%, and in Table 2 of their paper they were conservatively labeled as an unknown FeTi oxide phase.

Ono (1998) showed that this FeTi oxide is stable at higher temperature than lawsonite, which decomposes at 900°C, 7 GPa and 800°C, 9 GPa (Figure 1). Thus, this $(FeH)_{1-x}Ti_xO_2$ phase can take in and transfer water from the dehydrating lawsonite down to the transition zone. The water retaining capacity of the $(FeH)_{1-x}Ti_xO_2$ phase can be calculated as a function of the whole-rock TiO_2 concentrations of the subducting basalt or sediment. According to Nishihara and Matsukage (2016), the Fe-rich and Ti-rich phases have compositions close to $Fe_{0.8}H_{0.8}Ti_{0.2}O_2$ and $Fe_{0.5}H_{0.5}Ti_{0.5}O_2$, respectively. If we assume that the subducting oceanic crusts has 2 weight % TiO_2, the Fe-rich and Ti-rich phases in the crust can transfer 0.9 weight % H_2O and 0.23 weight % H_2O, respectively. The amount of water transported by these phases exceeds the amount that nominally anhydrous minerals are thought to be capable of possessing in upper mantle conditions (Hirschmann et al., 2005). The two phases found in Nishihara and Matsukage (2016) allow the subducting lithosphere to transport far more water to the mantle transition zone than previously thought possible.

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Figure caption

Figure 1

Pressure and temperature diagram showing stability of lawsonite (Lws) in basalt and hydrous minerals/phases in peridotite: pargasite (Par), chlorite (Chl), orthopyroxene (Opx), antigorite (Atg), phlogopite (Phl), clinopyroxene (Cpx), K-richiterite (K-ric), clinohumite (Chm), chondrodite (Chn), phase A (A), phase E (E), superhydrous B (sB), phase D (D), hydrous wadsleyite (Hy-wd), hydrous ringwoodite (Hy-rg), bridgmanite (Bgm), magnesium wüstite (Mw), along with water-saturated peridotite solidus and mantle adiabat. Simplified after Kawamoto et al. (2006).

Kawamoto Figure1