American Mineralogist, Volume 101, pages 1021–1022, 2016

HIGHLIGHTS AND BREAKTHROUGHS

$(FeH)_{1-x}Ti_xO_2$: 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 and 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 the April issue of *American Mineralogist*, Nishihara and Matsukage (2016) show that $(FeH)_{1-x}Ti_xO_2$ can be stable in wet basalts and sediments at high pressures and temperatures. These phases allow subducting lithosphere to transport far more water to the mantle transition zone than previously thought possible. **Keywords:** Nominally anhydrous mineral, hydrous mineral, subduction zone, H_2O, wadsleyite, ringwoodite, water recycling

INTRODUCTION

Hydrous minerals are stable in subducting lithospheres composed of sediments, basalts, and peridotite (Fig. 1). Along the *P-T* trajectories of subducting paths, most hydrous minerals become unstable and dehydrate to liberate aqueous fluids, thus producing the serpentinized forearc mantle and arc magmatism (Kawamoto et al. 1996; Tatsumi 1989). Thus, minerals such as serpentine and lawsonite are capable of transferring significant amounts of water into the mantle, but may only do so to depths of about 250 km, even in the coldest subduction zones (Fig. 1, Poli and Schmidt 1995; Ulmer and Trommsdorff 1995). At temperature conditions colder than 500 °C at depths of 200 km, the water released from dehydrating serpentine may be taken up by dense hydrous magnesium silicates such as clinohumite, chondrodite, and hydrous phase A and be transported further down in a subduction zone (Fig. 1). Beyond sub-arc depths, greater than 200 km in warm subduction zones, K-richterite can accommodate water from dehydrating phlogopite in the subducting lithosphere at H/K atomic ratio of 1, meaning that peridotite or basalt having 0.1 wt% K_2O can accommodate 0.02 wt% 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.

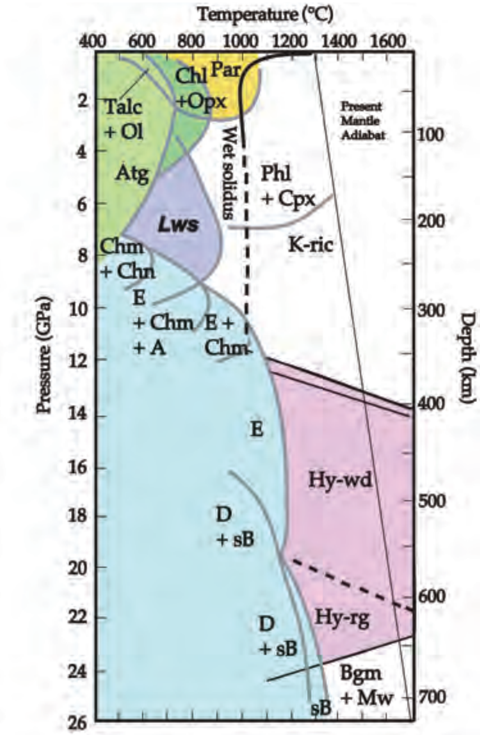

FIGURE 1. Pressure and temperature diagram showing stability of lawsonite (Lws) in basalt and hydrous minerals/phases in peridotite: pargasite (Par), chlorite (Chl), orthopyroxene (Opx), olivine (Ol), antigorite (Atg), phlogopite (Phl), clinopyroxene (Cpx), K-richiterite (K-ric), clinohumite (Chm), chondrodite (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 (2006). (Color online.)

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 wt% H_2O in relatively wet garnet peridotites beneath the Siberian craton (Doucet et al. 2014) and <0.0135 wt% 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 was later experimentally demonstrated to possess up to 3.3 wt% 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 wt% water (Kawamoto et al. 1996; Kohlstedt et al. 1996). Recent findings of 1.5 wt% water-bearing ringwoodite in a natu-

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0003-004X/16/0005–1021$05.00/DOI: http://dx.doi.org/10.2138/am-2016-5643

ral diamond support 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; the fluids involved may represent 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 must be resolved (Kawamoto et al. 1996).

A NEW WATER CARRIER

In their study, Nishihara and Matsukage (2016) show that $(FeH)_{1-x}Ti_xO_2$ can be stable in wet basalts and sediments at high pressures and high temperatures. They conducted 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 was 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 chemical compositions because 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 (Fig. 1). Thus, this $(FeH)_{1-x}Ti_xO_2$ phase can take in and transfer water from 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 have 2 wt% TiO_2, Fe-rich and Ti-rich phases in such crusts can transfer 0.9 wt% H_2O and 0.23 wt% 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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MANUSCRIPT RECEIVED DECEMBER 4, 2015
MANUSCRIPT ACCEPTED DECEMBER 24, 2015
MANUSCRIPT HANDLED BY KEITH PUTIRKA