Abstract

Water as one of the most important volatile components plays an important role on Earth's interior. It influences the physical and chemical properties of minerals and melts, which further effects the evolution of the Earth. Water can be transported into the deep Earth as form of hydrous phases in subducting slabs,espeically those of dense hydrous magnesium silicate phases (DHMSs), such as phase A (PhA), phase E (PhE), superhydrous phase B (SUB), phase D (PhD) phase H (PhH), which have been suggested as potential water carriers to transition zone and even to the lower mantle under the conditions presented in the cold subducting slabs (Kanzaki, 1991; Kawamoto et al., 1996; Ulmer and Trommsdorff, 1999; Irifune et al., 1998; Litasov and Ohtani, 2002; Ohtani et al., 2001; Ohtani et al., 2004; Komabayashi et al., 2005, Komabayashi and Omori, 2006; Nishi, 2015). Among the DHMSs, phase H was reported to exist even up to the deepest part of the lower mantle (Nishi et al., 2014). These DHMSs contain 3-18wt% H_2O are also regarded as important storage sites for water in Earth's interior.

Therefore, it is of great importance to illustrate the stability of DHMSs. Recent studies have shown that Al hugely increases the stability region of DHMSs (Ghosh and Schmidt, 2014; Pamato et al., 2015; Kakizawa et al., 2018). To systematically ascertain the effect of Al on stability of DHMSs from various aspects, we have conducted several high pressure and high temperature experiments and found that

1. Al-bearing PhE, SUB and PhD were observed with P-T increasing in serpentine+Al_2O_3 system. Following the P-T path of cold subduction, the phase assemblage PhE + PhD was stable at 14-23 GPa, and even a trace of PhE was identified at 900°C and 25 GPa coexisting with PhD. The phase SUB was stable between 16 and 22 GPa coexisting with PhE + PhD. Following the P-T path of hot subduction, the phase assemblage PhE + Gt was observed at 14-18 GPa coexisting with melt. The phase assemblage SUB + PhD was stable at 18-25 GPa, which was expected to survive at higher P-T condition. Some amount of SUB was even stable at normal mantle geotherm at transition zone pressure. It was obvious that Al enhanced the stabilities of these DHMSs, and the water content drastically increased. Our results may indicate that the wide stabilities of Al-bearing DHMSs increase the chance of obtaining water after antigorite (serpentine) decomposes at the shallow region of the subduction zone and transporting water to the deep lower mantle even in hydrous peridotite and MORB composition.

2. Al-rich PhD has a very wide stability region from 900 ºC and 14 GPa to at least 1500 ºC and 25 GPa. With pressure increasing, Al-rich PhD decomposes to phase Egg and then to δ at above hot subduction at transition zone in MgO-Al_2O_3-SiO_2-H_2O (MASH) system between14 and 25 GPa at 900-1500 ºC. The wide stability region determined in this study makes Al-bearing PhD an important storage site for water in transition zone, suggesting that it can deliver a certain amount of water into the lower mantle along hot subduction and even the normal mantle geotherm P-T condition.

3. Fe slightly decreased the stability region of PhD in FeOOH-PhD system, however, Although Fe decreases the stability region of PhD, Al, Fe-bearing PhD drastically shift to

higher temperatures in both MORB and pyrolite type compositions compared to pure Mg-PhD. Therefore, Al, Fe-bearing PhD could act as long water reservoir along subduction to the deep lower mantle.

4. PhE coexisting with wadsleyite or ringwoodite is at least stable at 15-16.5 GPa and below 1050 °C. PhD coexisting with ringwoodite at pressure higher than 16.5 GPa and temperature below 1100 °C in Fe-rich $MgO-Al_2O_3-FeO-SiO_2-H_2O$ (MAFSH) system between 15 and 21 GPa at 900-1500 °C. We also noticed that transition pressure of the loop in wadsleyite-ringwoodite boundary shifted towards lower pressure in iron-rich system compared with hydrous pyrolite model on Earth

5. Al is strongly partitioned into PhD than coexisting Brg, and partition coefficient of Al (KD) between PhD and Brg slightly decreases with increasing temperature. Al-bearing PhD totally decomposes around 28 GPa and 1350°C, in which Brg is found to be coexisting with a large amount of melt. At 31 GPa and 1350°C, Brg coexists with trace amount of melt and Al-rich phase H, which means some amount of water might be transported into the lower mantle.

6. A binary eutectic diagram is formed without dehydration or melting below 1200 °C at 20 GPa in AlOOH and FeOOH system. We also observe that maximum solubilities of Al and Fe in the solid solutions were more strongly influenced by temperature than by pressure. Our results suggest that $CaCl_2$-type hydroxides subducted in to the deep mantle form a solid solution over a wide composition ranges. As AlOOH and FeOOH are present in hydrous crust, these phases may be subducted into the deep interior, transporting a significant amount of hydrogen to deeper regions. Therefore, a greater understanding of this binary system may

help to elucidate the model geodynamic processes associated with the deep water cycles of the Earth.

7. Modeled velocities of Al-bearing PhD in hydrous pyrolite along normal mantle geotherm shows that Al-bearing PhD generates high velocity anomalies compared with dry pyrolite in mantle transition zone, however, it is seismically invisible due to the small anisotropy. Once Al-bearing PhD is transported to the uppermost lower mantle, it shows a lower signature than dry pyrolite or higher velocities within the slab region. Thus the observed velocity anomalies at the uppermost lower mantle may be considered as the presence of water in subduction zone. Due to its high thermal stability region, Al-bearing PhD is expected to transport water to the Earth's lower mantle, elucidating model geodynamic processes associated with the deep water cycles.