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## 学位論文要旨 Dissertation Summary

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論文名:

(Dissertation Title) Phase relations of Al-bearing dense hydrous phases up to the uppermost lower mantle and sound velocities of Al-bearing phase D

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Part 1, a series of dense hydrous magnesium silicate phases (DHMSs) have been suggested as potential water carriers to transition zone and even to the lower mantle under the conditions present in the cold subducting slabs. Recently, the reported Al-bearing PhD was stable at temperatures up to 2,000 °C at 26 GPa, which indicated Al increases stability region of DHMSs (Pamato et al., 2015). To systematically illustrate the effect of Al on the stability of DHMSs, we performed high pressure and high temperature experiments in FeO-MgO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-H<sub>2</sub>O (FMASH) system, containing about 15 wt% H<sub>2</sub>O and about 14 wt% Al<sub>2</sub>O<sub>3</sub>, up to 25 GPa and 1600 °C by MA8-type (Kawai-type) apparatus. A chemical mixture of clinocllore in MASH was also investigated for comparison.

The Al-bearing PhE, SUB and PhD were observed with *P-T* increasing. 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. DHMSs in MASH had approximately

the same phase assemblage as FMASH, except for SUB was observed at 14-16 GPa.

We noticed that PhE contains 8.5-15 wt%  $\text{Al}_2\text{O}_3$ , SUB contains 3-8.5 wt%  $\text{Al}_2\text{O}_3$  and PhD contains 8-18 wt%  $\text{Al}_2\text{O}_3$  in crystal structures, respectively. It was obvious that Al enhanced the stabilities of these DHMSs, and the water content drastically increased estimated from deficit of total weight percent. On the other hand, the Al substitution mechanism in PhE, SUB and PhD were clarified according to chemical compositional relationship between Mg, Si and Al. 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.

In part 2, first of all, we have investigated the stability of the Al-rich dense hydrous magnesium silicate phase D in  $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$  (MASH) system between 14 and 25 GPa at 900-1500 °C. Al-rich PhD has a very wide stability region from 900 °C and 14 GPa to at least 1500 °C and 25 GPa. With pressure increasing, Al-rich PhD decomposes to phase Egg and then to  $\delta$  at above hot subduction at transition zone. Al-rich PhD is also determined by X-ray diffraction and Raman spectroscopy at ambient condition. Compared with Al-free PhD, unit-cell volume of Al-rich PhD is little larger, but the Raman spectra resemble some of Al-free PhD. The wide stability region determined in this study makes Al-bearing PhD an important storage site for water in transition zone. Therefore, dehydration of Al-bearing PhD may be responsible for a series of observed seismic discontinuities from transition zone to uppermost lower mantle, and even deep earthquakes in some typical places.

Secondly, melting phase relation of Fe-bearing PhD was investigated up to the uppermost lower mantle, since Fe is not only one of the most abundant elements in the Earth, but also in Fe-enriched planetary systems such as Mars. In spite of the importance, few experiment has been conducted so far to clarify the effect of Fe in DHMSs systematically. Therefore we investigated the stability of Fe-bearing phase D (PhD) in  $\text{AlOOH-FeOOH-PhD}$  system between 18 and 25 GPa at 1000-1600 °C.

Fe-bearing PhD was synthesized by using two different iron contents in  $\text{FeOOH-PhD}$  binary system, and the Al, Fe-bearing compositions were like analog materials of MORB and pyrolite in  $\text{AlOOH-FeOOH-PhD}$  ternary system. Compared with Mg-PhD, iron slightly decreased the stability region of PhD in  $\text{FeOOH-PhD}$  system. 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.

Thirdly, in order to ascertain the possible water cycles in iron-rich Mars, we investigated the phase relation of a water-unsaturated (2 wt%) analog of Martian mantle in simplified MgO-Al<sub>2</sub>O<sub>3</sub>-FeO-SiO<sub>2</sub>-H<sub>2</sub>O (MAFSH) system between 15 and 21 GPa at 900-1500 °C using multi-anvil apparatus. We have found that Phase E coexisting with wadsleyite or ringwoodite is at least stable at 15-16.5 GPa and below 1050 °C. Phase D coexisting with ringwoodite at pressure higher than 16.5 GPa and temperature below 1100 °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. As on Fe-rich Mars, some evidence has shown that water once existed on the Martian surface and existing possible plate tectonic activities on ancient Mars. The water present in hydrous crust might be tectonically embedded and subducted into the deep interior. Therefore, water may be transported to the deep Martian interior by hydrous minerals, such as phase E and phase D, in cold subduction plates, and further may be stored in wadsleyite or ringwoodite after those hydrous materials decompose when the plates equilibrate thermally with the surrounding Martian mantle.

Fourthly, partitioning of Al between Brg and PhD was obtained at high pressures, because dense hydrous magnesium silicates (DHMSs) are supposed to be one of the important water carriers to the deep Earth. Phase D (PhD) is the dominant high pressure phase among DHMSs in hydrous pyrolite composition from the shallow parts of the lower mantle to at least middle region, has been shown to coexist with bridgmanite (Brg), which is widely viewed as the most abundant mineral assemblage in the Earth's interior. Therefore, partitioning of Al between Brg and PhD is particularly important to constrain water distribution in the deep mantle, especially because Al<sup>3+</sup>+H<sup>+</sup> substitutes for Si<sup>4+</sup> in PhD greatly enhances its water content.

To systematically illustrate this issue, we performed high pressure and high temperature experiments in MgO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-H<sub>2</sub>O system to investigate the partitioning of Al between pyrolite type Brg and PhD in volume ratio of 4:1 up to 31 GPa by MA8-type (Kawai-type) apparatus. Our result shows that Al is strongly partitioned into PhD than coexisting Brg, and partition coefficient of Al ( $K_D$ ) 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. The decomposition of Al-bearing PhD around 28 GPa may be the second chock point for hydrous minerals and help to explain 770 km LVZ within Japan subduction zone in Western Pacific sand the discontinuity and the low-velocity zones (LVZ) around 800 km beneath European Alp (Liu et al., 2016; 2018).

At last, we investigated Solubility behavior of  $\delta$ -AlOOH -  $\epsilon$ -FeOOH at high pressures. Low-pressure polymorphs of AlOOH and FeOOH are common natural oxyhydroxides at the Earth's surface, which may transport hydrogen to the deep mantle via subduction. At elevated pressures, the low-pressure polymorphs transform into  $\delta$ -AlOOH and  $\epsilon$ -FeOOH with CaCl<sub>2</sub>-type structure, which form a solid solution above 18 GPa. Nevertheless, few studies have examined the solid solution behavior of this binary system in detail. In this study, we ascertain the phase relations in an AlOOH and FeOOH binary system at 15–25 GPa and 700–1200 °C. XRD measurements of quenched samples show that  $\delta$ -AlOOH and  $\epsilon$ -FeOOH partly form solid solutions over wide pressure and temperature ranges. Our results demonstrated that a binary eutectic diagram is formed without dehydration or melting below 1200 °C at 20 GPa. Our results suggest that CaCl<sub>2</sub>-type hydroxides subducted in to the deep mantle form a solid solution over a wide composition ranges.

In part 3, the sound velocities and density of Al-bearing phase D (PhD) was investigated up to 22 GPa and 1300 K by in situ synchrotron X-ray techniques combined with ultrasonic measurements. Modeled velocities of Al-bearing PhD in hydrous pyrolite along normal mantle geotherm shows that Al-bearing phase D 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 phase D 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 phase D is expected to transport water to the Earth's lower mantle, elucidating model geodynamic processes associated with the deep water cycles.