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## 学位論文要旨 Dissertation Summary

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論文名: Discovery of a new Al-bearing high pressure hydrous phase (23 Å phase) and  
(Dissertation Title) some implications to the deep Earth

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Water plays an important role in modifying the chemical and physical properties of the mantle's rocks and minerals. Water is transferred, released and recycled into the deep mantle through the subduction processes, mainly in the form of hydrous phases. Lots of researches have clarified the stability of hydrous phases in the MgO-SiO<sub>2</sub>-H<sub>2</sub>O system, which is the most important system for a pyrolitic mantle. Base on the previous results, hydrous phases, such as antigorite or serpentine, dense hydrous magnesium silicates (DHMS) phase A, 10 Å phase, phase E, superhydrous phase B, phase D, were suggested to be stable along the cold subducting P-T paths. Thus, as the predominant metamorphosed hydrous phase of the peridotite composition, antigorite plays an important role in transporting water into the deep earth.

Chlorite is another important hydrous phase, especially in an Al-bearing subduction zone. Previously lots of experiments were just focusing on the dehydration or decomposition boundaries of chlorite, and the results have shown that all the water will be lost from the chlorite system at the depth greater than ~150 km.

However, the finding of phase HAPY and 23 Å phase at pressures and temperatures beyond the stability of chlorite, may largely extend the thermal stability of hydrous phases in the Al-bearing MSH system. Thus it is important to clarify the physical and chemical properties of 23 Å phase, and also the stability of hydrous phases, especially the 23 Å phase at high pressure and high temperature, in the Al-bearing system.

In this thesis we will discuss about the characterization of this newly found hydrous phase - 23 Å phase. The cell parameters and chemical composition of this 23 Å phase were constrained by means of X-ray diffraction (XRD), transmission electron microscopy (TEM), electron probe microanalysis (EPMA) (energy or wavelength dispersive X-ray spectroscopy, EDS or WDS), and secondary ion mass spectrometry (SIMS). The chemical composition of this new 23 Å phase is Mg<sub>11</sub>Al<sub>2</sub>Si<sub>4</sub>O<sub>16</sub>(OH)<sub>12</sub>, and it contains about 12.1 wt% water. Powder X-ray diffraction and transmission electron diffraction patterns show that this new 23 Å phase has a hexagonal structure,

with  $a = 5.1972(2)$  Å,  $c = 22.991(4)$  Å, and  $V = 537.8(2)$  Å<sup>3</sup>, and the possible space group is  $P\bar{6}c2$ ,  $P6_3cm$ , or  $P6_3/mcm$ . The calculated density is 2.761 g/cm<sup>3</sup> accordingly, which was determined by assuming that the formula unit per cell ( $Z$ ) is 1. This crystal structure is quite unique among mantle minerals in having an extraordinarily long  $c$  axis. Thus we named this phase as 23 Å phase, after its characteristic length of  $c$  axis.

In this thesis we also determined the high temperature and high pressure stability region of 23 Å phase at the  $P$ - $T$  conditions ranging from 5 to 14 GPa and 600 to 1300 °C. The 23 Å phase is stable up to 12 GPa and ~1200 °C. At low pressures we have observed the coexisting of 23 Å phase and forsterite with chlorite, Mg-sursassite or phase HAPY, which may imply the transformation of hydrous phases from chlorite to Mg-sursassite/phase HAPY, and further to this 23 Å phase. Thus 23 Å phase could be a very important water reservoir even along the relatively warm subducting  $P$ - $T$  path, when considering an Al-bearing subducting system.

A series of experiments on the decomposition of a natural and chemically-mixed chlorite were also conducted to examine the hydrous phases in the system MgO-(FeO)-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-H<sub>2</sub>O (MFASH) under 5 - 12 GPa, 700 - 1100 °C. The upper limit of chlorite in the present study is consistent with previous results. Phase HAPY and Mg-sursassite were observed just above the stability region of chlorite. Clinohumite was observed coexisting with phase HAPY at 6 GPa and 800 °C, while with 23 Å phase at 7 GPa and 800 °C, which may suggest the hydrous phase transformation through  $\text{Chl} \rightarrow (\text{HAPY} \rightarrow \text{cHm}) \rightarrow 23 \text{ \AA phase}$  along a relatively warm slab. Besides, 23 Å phase has a larger stability region in the pure MASH system than in the MFASH system.

In this thesis for the first time we determined the equation of state of this new phase up to 10 GPa and 800 °C by angle-dispersive *in situ* X-ray diffraction. Fitting the  $P$ - $V$  data to the room temperature Birch-Murnaghan equation of state yields:  $V_0 = 537.7(2)$  Å<sup>3</sup>,  $K_0 = 112(1)$  GPa,  $K' = 4$ . The high temperature 3<sup>rd</sup> order Birch-Murnaghan equation of state was used to fit the  $P$ - $V$ - $T$  data, and yields:  $V_0 = 538.0(3)$  Å<sup>3</sup>,  $K_0 = 109(1)$  GPa,  $\partial K/\partial T = -0.012(5)$  GPa/K,  $\alpha_0 = 3.0(4) \times 10^{-5}/\text{K}$ ,  $K' = 4$ . No or slight anisotropy was observed, and the compressibility is  $-2.54(2) 10^{-3}/\text{GPa}$  for  $a$  axis and  $-2.68(5) 10^{-3}/\text{GPa}$  for  $c$  axis. This new hydrous phase has a very similar compressibility comparing with phase A (106.3(6) GPa, Yang, 2013) and phase E (112 GPa, Bass et al., 1991), while lower density (2.761 g/cm<sup>3</sup>) than that of phase A (2.96 g/cm<sup>3</sup>, Ross and Crichton, 2000), indicating that this new phase could possibly be stable in the upper mantle condition. The results obtained in this thesis suggest that this 23 Å phase could be thermally stable in the subduction zones, and may play an important role in transporting water into deep earth, even into the mantle transition zone.