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Dissertation Summary

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Phase relations and melt compositions in hydrous pyrolite under high temperature and high pressure and the equation of state of hydrous minerals

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This thesis presents the experimental constraints on the phase relations and melt compositions in hydrous pyrolite, as well as on the equation of state of hydrous minerals under high temperature and high pressure.

In part 1, phase relations and melt compositions as well as the density of hydrous melt in 2wt% or 8wt% water bearing pyrolite systems were reported. Quench experiments at pressure range of 12-21 GPa; temperature range of 1200-1600°C were done in MA8-type (Kawai-type) high pressure apparatus, ORANGE-1000 and ORANGE-2000 in Geodynamics Research Center, Ehime University. Water has significant effects on the high pressure phase transition boundaries in both olivine and garnet systems. The phase boundary between olivine and wadsleyite under hydrous conditions changed to lower pressure compared to that in dry condition, while the boundary between wadsleyite and ringwoodite moved to slightly higher pressure; and both of these two phase boundaries became sharper than those in dry condition. The post-garnet transformation occurred at 20GPa, 1400 °C, more than 3GPa lower pressure compared to that in dry condition. Chemical compositions of hydrous melts were much different from the dry melt, with Mg# about 76-86, and the Mg# of coexist olivine was about 93 at 12GPa. Hydrous melt also had higher (Mg + Fe)/Si (1.57-2.58) and Ca/Al (1.65-13.1) ratios, and indicated that the hydrous melt generated in the present pressure range were beyond komatiite compositions. Water content of some minerals with larger grain size (larger than 30 μm) were measured

by the secondary ion mass spectrometry (SIMS), and results showed that the majoritic garnet had large amount of water (~1 wt %), larger than the water solubility reported by the previous study; while the water content of ringwoodite and perovskite were 1.72-1.97wt% and 0.19-0.34wt%, respectively, consistent with the water solubility reported by the previous studies. In the present experiments, all run charges were coexisted with hydrous liquid (fluid); this indicate that the water solubility of the minerals in the present experiments show the maximum solubility in each P-T condition. Water content of the hydrous melt was calculated by the melt fraction and subtracting the water in residue minerals from the bulk composition. The calculated water content of hydrous melt was more than 40wt% at 14GPa, 1400°C, or more than 17wt% at 14GPa, 1527°C, which was higher than the critical value (5-8wt %) for the density crossover between the hydrous melt and the surrounding mantle reported by the previous studies (Jing and Karato, 2009; Matsukage et al., 2005; Sakamaki et al., 2006). This suggested that the density crossover between hydrous melt and solid mantle may not happen at ~14 GPa; the result of our density calculation supported this conclusion.

Part 2 established the equation of state (EoS) of antigorite at high pressure and high temperature. Antigorite contains ~13wt% water in its formula, so it is an important water carrier in subducting slab. The equation of state (EoS) of natural antigorite has been determined up to ~10 GPa and 500°C by *in-situ* x-ray diffraction in a cubic type multi-anvil apparatus, MAX80, located at the Photon Factory-Advanced Ring at the High Energy Accelerator Research Organization (KEK), and the temperature dependence of the bulk modulus was determined, for the first time by high pressure and high temperature x-ray diffraction based on a series of direct measurements. No dehydration occurred during the entire experimental process, and no significant deviatoric stress was observed after heating. The room temperature  $P$ - $V$  data below 7 GPa have been fit to the Birch-Murnaghan EoS, yielding  $V_{0,300K} = 366.9(7)\text{\AA}^3$ , bulk modulus  $K_{0,300K} = 65.2(31)\text{GPa}$ , and the pressure derivative  $K'$  fixed to 6.1. The high pressure phase transition was observed through volume softening behavior at around 7 GPa, and the  $dP/dT$  slope seems to be flat or slightly positive, which is consistent with the recent report by Bezacier et al. (2013). The high temperature Birch-Murnaghan EoS was used to fit the  $P$ - $V$ - $T$  data below 7GPa. Since the present experimental data was obtained by energy dispersive X-ray diffraction at high pressure and temperature and the resolution was slightly lower than that obtained by angle dispersive x-ray method, the bulk modulus  $K_{0,300K}$ , and the pressure derivative were fixed to 62.9 GPa and 6.1, respectively, which was obtained by single

crystal x-ray diffraction in a diamond anvil cell with angle dispersive method (Nestola et al., 2010) during fitting. From the fitting, we obtained  $V_{0, 300K} = 367.3(2)\text{\AA}^3$ ,  $dK/dT = -0.0265(41)$  GPa/K, thermal expansion  $\alpha_0 = 3.92(50) \times 10^{-5}$  /K. The temperature dependence of the bulk modulus was larger than the value calculated empirically (Holland and Powell, 1998). The thermal expansion of antigorite is larger than the results from the previous study. The compression of antigorite is very anisotropic along three axes, with a ratio of 1.15:1.00:3.33 at room temperature. Considering the  $P$ - $T$  condition of the subducting slab, the phase transition of antigorite may occur only in a limited area in the slab.

Phase A,  $\text{Mg}_7\text{Si}_2\text{O}_8(\text{OH})_6$ , is a dehydration product of antigorite, so in Part 3, we investigated the EoS of it at HPHT condition. Phase A was synthesized by using mixture powder of  $\text{MgO}$ ,  $\text{Mg}(\text{OH})_2$  and  $\text{SiO}_2$ , at around 10 GPa and 1000°C. Pressure-volume-temperature ( $P$ - $V$ - $T$ ) data got from the *in-situ* synchrotron x-ray diffraction experiments. These experiments were performed at pressures of 1atm to ~10 GPa, and at temperatures from room temperature to 700°C. 49  $P$ - $V$ - $T$  data were collected successfully, and were fitted to a high temperature Birch-Murnaghan equation of state, yielding  $V_0=511.7(3)$   $\text{\AA}^3$ ,  $K_0=104.4(24)$  GPa,  $K'=4.39(48)$ ,  $dK/dT= -0.027(5)$  GPa/K, and thermal expansion  $\alpha_0 = 2.88(27) \times 10^{-5} + 3.54(68) \times 10^{-8}T$ ; we also fitted the  $P$ - $V$ - $T$  data to Mie-Grüneisen-Debye equation of state, and got  $V_0=511.9(3)$   $\text{\AA}^3$ ,  $K_0=106.7(27)$  GPa,  $K'=3.55(46)$ , Debye temperature  $\theta_0=985(142)$  K, and Grüneisen parameter  $\gamma_0=0.98(4)$ , with the  $q$  value fixed to 0.  $V_0$  is quite consistent with the previous studies, while the bulk modulus obtained here is much smaller than the value of 145(5) GPa reported by Pawley et al. (1995), and consistent with the results from the recent other studies within uncertainties. Temperature derivative of bulk modulus,  $dK/dT$ , and the Mie-Grüneisen-Debye equation of state of Phase A were reported independently for the first time. The compressibility of Phase A is very anisotropic along  $a$ - and  $c$ -axis, and  $a$ -axis is ~25% more compressive than  $c$ -axis, which supported the previous studies (Holl et al., 2006; Crichton and Ross, 2002). Geophysical implication was also discussed. Phase A is a dehydration production of serpentine, and it is the main water storage in the serpentinized subducting slab after the serpentine has dehydrated. Density of subducting slab with different degree of serpentinization was calculated along the cold geotherm up to ~13GPa, and compared with the density of normal mantle. The results show that the serpentinization of subducting slab will significant lower the density of slab at shallower depth, however, this effect become negligible when antigorite dehydrated to Phase A.