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Stability field of Mg14Si5O24 anhydrous phase B determined by high-pressure high-temperature experiments and calorimetry

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Anhydrous phase B (Anh-B:$Mg_{14}Si_5O_{24}$) is a high-pressure magunesium silicate possible stable in the upper mantle and transition zone (Ganguly and Frost, 2006). Finger et al.(1991) analysed the crystal structure of Anh-B. Ganguly and Frost (2006) determined the equilibrium boundary of the reaction, 5forsterite (Fo) + 4periclase(Per) = Anh-B, at 9.0-12.5 GPa and 1173-1873 K. However, the upper stability limit of Anh-B has not yet been examined. In this study, we determined stability relations of Anh-B by high pressure experiments and calorimetry, and inferred possible stability in the mantle.

High-pressure high-temperature experiments were performed with a Kawai-type 6-8 multianvil high pressure apparatus. The starting material was a mixture of Per and Fo with 4:5 molor ratio. The experimental conditions were 12-23GPa and 1673 -2073 K for 3 hour. Samples recovered after quenching were analyzed with powder X-ray diffraction method and SEM-EDS. Calorimetry was performed with a Calvet-type calorimeter which was kept at temperature of 978 K. Drop-solution enthalpy of Anh-B was measured with Ar bubbling technique, using lead borate as the solvent. Anh-B was synthesized from 14:5 mixture of Per and quartz by keeping at 15 GPa and 14 50 C for 3 hours, and was recovered after quenching.

Results by the high-pressure and high-temperature experiments that indicated that the equilibrium boundaries of 5 Fo+ 4 Per = Anh-B and of Anh-B=5 Wadsleyite(Wads)+ 4 Per are located at 12-1 3.5 GPa and at 18-21 GPa, respectively at 1673-2073 K. From these boundaries, enthalpies and entropies for the two relations were constrained. The measured drop-solution enthalpy of Anh-B was 867.5(233) kJ/mol. The drop-solution enthalpy of Fo was 168.2(9) kJ/mol, and that of Per was 33.7(10) kJ/mol (H. Kojitani unpublished data), and that of Wads was 142.2(27) kJ/mol (Akaogi et.ai., 2007). Therefore, the enthalpy for the reaction 5 Fo+ 4 Per = Anh-B was obtained as 108.5(241) kJ/mol, and Anh-B = 5 Wads + 4 Per 21.7(235) kJ/mol. From the results of high-pressure high-temperature experiments and calorimetry, best values of enthalpy and entropy for the two reactions were determined. For the reaction of 5Fo+4Per=Anh-B, enthalpy is 110.9 kJ/mol, and entropy was -17 J/(mol.K). For the reaction of Anh-B= 5Wads+4Per, enthalpy was 37.8 kJ/mol, entropy was -24 J/(mol.K). The two equilibrium boundaries were calculated with these values. The boundary of 5 Fo + 4 Per = Anh-B was expressed as P(GPa)=0.0015 T(K)+9.87, and that of Anh-B= 5 Wads + 4Per as P(GPa)=0.0056 T(K)+9.00. This study showed that Anh-B decomposes into Wads and Per, and Anh-B is stabe in magnesium-rich upper mantle and transition zone in the depth range of about 370 - 550 km.