In situ X-ray diffraction study of aluminous phase in MORB under high pressure and temperature.

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Phase relations in MORB composition show that an Al-rich phase (or aluminous phase) should be stable under lower mantle conditions (e.g. Ono et al., 2001). However, the exact composition and structure of that aluminous phase in the lower mantle is still a matter of debate. Irifune and Ringwood (1993) attempted to synthesize aluminous phase and pointed out the structural similarity between their run product and orthorhombic calcium ferrite. However, presence of glassy material in the run product, led the authors to suggest that the aluminous phase might be unquenchable and that a calcium ferrite type phase, together with other minor phases, is recovered instead. On the other hand, Akaogi et al., (1999) synthesized an aluminous phase with a hexagonal unit cell in the $MgAl_2O_4$-$CaAl_2O_4$ system where both Mg and Ca end member compositions display a calcium ferrite type structure under high P and T. This strongly suggests that the crystal structure of aluminous phase has a compositional dependence.

In this study, we conducted in situ X-ray experiments at 22 GPa, 1873 K in order to constrain the crystal structure of a synthetic aluminous phase with a composition consistent with high-pressure and high-temperature phase equilibria in MORB.

Cell assembly with truncated edge length of 3 mm was used in high pressure run with a combination of synchrotron radiation and SPEED-1500 in SPring-8. Pressure medium was composed of (Mg, Co)O, ZrO_2 and a $LaCrO_3$ heater was used. The sample chamber and window were made of graphite to minimize X-ray absorption. Starting material was a oxide mixture of the aluminous phase composition found in Irifune and Ringwood (1993). Pressure marker was a mixture of MgO, Au, and NaCl, (50 : 1 : 50 volume ratio) also enclosed in graphite. Pressure was derived from the Au equation-of-state (Anderson et al., 1989). The press load was first increased to the target value and then temperature was increased up to 1873 K. Heating duration was 5 hours.

X-ray diffraction data were collected using an energy dispersive detector and were processed using PC-GSAS. XRD pattern indexation and refinement were attempted using both hexagonal $CaMg_2Al_6O_{12}$ structure and calcium-ferrite structure, atomic parameters and space group data were taken from Miura et al., (2000) and, Decker and Kasper (1957), respectively. X-ray diffraction data collected at ambient condition were compared with data obtained at high P and T. Finally, the recovered sample was polished and characterized by SEM-EDS.

At 22 GPa, 1873 K, aluminous phase and majorite were observed. XRD pattern is best fit to the hexagonal $CaMg_2Al_6O_{12}$ structure (Miura et al., 2000) and shows only very poor agreement with the calcium-ferrite type structure. Refinement of the hexagonal lattice parameters at 22 GPa, and 1873 K yielded a = 8.550 (1), c = 2.732 (1), V = 172.96 (3) and D = 4.130 (6) using the composition given hereafter. At ambient condition, X-ray diffraction pattern suggests that no phase transformation occurred during decompression. Hexagonal lattice parameters were also refined at ambient condition and yielded a = 8.747 (1), c = 2.782 (1), V_0 = 184.32 (4) and D_0 = 3.876 (5). Although small grain-size precludes any accurate chemical determination using SEM (EDS), Random point analysis on the hexagonal phase shows the hexagonal phase composition is approximately $(Mg_{0.67}, Na_{0.23}, Ca_{0.07}, Fe_{0.06})(Al_{1.43}, Si_{0.46}, Ti_{0.01})O_4$.

Ono et al., (2001) reported an aluminous phase of calcium-ferrite structure in MORB, and also P-V-T data were collected on that phase (Ono et al., 2002). The difference between (The relative stability of both) calcium ferrite type aluminous phase and hexagonal one is still unclear. In addition to pressure and temperature, we believe that Na, Mg and Ca content plays an important role in stabilizing one or the other structure. Additional quench experiments at higher pressure are in progress, the result of which, will also be discussed.