

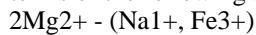
## Phase relations of aegirine at high pressures and temperatures: Na behavior in the compounds bearing ferric iron

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### INTRODUCTION

The behavior of sodium and its host minerals in the main part of lower mantle have not been clarified sufficiently. The estimated Na<sub>2</sub>O content of a pyrolite mantle is ~0.4 wt%, which is much lower than the 1.6 wt % in a chondritic silicate mantle, and the reason for this difference is still controversial. High-pressure laboratory experiments on constituent materials in subducting slabs indicate that two-type Na-rich phases can form under lower mantle conditions: the hexagonal NAL phase and calcium ferrite-type phase. On the other hand, in the main part of mantle, Na<sub>2</sub>O component must exist as main content in the Na-rich phases of the accessory mineral or as a minor content in dominant minerals. In most of above-mentioned studies, it was considered that total iron was ferrous iron, because ferrous iron is by far the more dominant than ferric iron in the upper mantle. However, it has been reported that the aluminous magnesium silicate perovskite has an Fe<sup>3+</sup>/total Fe ratio of at least 0.6 (McCammon et al., 1997; Frost et al., 2004). The solution of Na with Fe<sup>3+</sup> to the MgSiO<sub>3</sub>-perovskite structure can be described in terms of the following substitution:



This substitution leads to the NaFeSi<sub>2</sub>O<sub>6</sub> composition. This is the chemical formula of aegirine. Here, we have investigated that the phase relation of aegirine at high-pressure and high-temperature, expecting that perovskite structure containing Na and Fe<sup>3+</sup> exists at lower mantle conditions.

### EXPERIMENTAL METHODS

The high-pressure X-ray diffraction experiments were performed using a LHDAC high-pressure apparatus. Natural aegirine was used as the starting material. Fine powdered sample was loaded with fine Al<sub>2</sub>O<sub>3</sub>, KCl or NaCl powder, which works not only as a pressure-transmitting medium but also as a thermal insulator. Pressure was determined from ruby fluorescence method. The sample was heated with a Nd:YAG laser for 0.5-1 h. The samples were probed using an angle-dispersive X-ray diffraction technique at the synchrotron beamline BL13A and BL18C, KEK-PF and BL10XU, SPring-8. Transmission electron images, qualitative chemical compositions, and selected area electron diffraction (SAED) patterns of the recovered samples were examined by using a 200 kV JEOL JEM-2010 (ATEM) attached with an energy-dispersive analytical system (EDS).

### RESULTS AND DISCUSSION

At 31 and 52 GPa and 300K before heating, the diffraction peaks of aegirine and corundum (used for the pressure medium) were observed, indicating that aegirine still maintained its original form. At high pressures quenching from 1300-1500K, the aegirine peaks disappeared while the diffraction peaks of SiO<sub>2</sub> stishovite appeared, proving that aegirine was decomposed. However, the peaks of other phases consisted of residual components, Na<sub>2</sub>O and Fe<sub>2</sub>O<sub>3</sub>, were not observed. TEM observation and EDS analyses of the recovered samples confirmed that NaFeO<sub>2</sub> phase exists with SiO<sub>2</sub> stishovite. SAED patterns taken from the same grain show that the NaFeO<sub>2</sub> phase has a cubic system with space group Fd-3m or Fd3, having the unit cell parameter of 9.3 Å. This phase is a new high-pressure phase. The NaFeO<sub>2</sub> phase may be of incoherent crystallite size against incident X-ray wavelength (0.4216 Å at BL13A, KEK-PF), because the grain size of observed NaFeO<sub>2</sub> phase was very small (less than 50 nm) compared with the unit cell. On the other hand, ATEM analyses of another recovered sample from 30 GPa and 2000K indicated that aegirine was decomposed into SiO<sub>2</sub> stishovite, iron oxide and sodium oxide. At this moment the structure of these oxides remains to be seen. These experimental results showed that NaFeSi<sub>2</sub>O<sub>6</sub> perovskite did not exist even at high pressure at least 50 GPa while the NaFeO<sub>2</sub> phase formed. However, the NaFeO<sub>2</sub> phase was stable only under relatively lower temperature condition than 1500K and was decomposed into two oxides at higher temperature.