## 論文の内容の要旨

### 論文題目

# Nitrogen solubilities in the lower-mantle minerals:

### implications for the formation process of nitrogen reservoir

#### in the deep Earth

(下部マントル鉱物への窒素溶解度:

地球深部における窒素貯蔵庫形成過程の考察)

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Molecular nitrogen (N<sub>2</sub>) constitutes approximately 78% of the Earth's atmosphere. Nitrogen is an essential element for sustaining life, and it plays a vital role in the biogeochemical cycle. Molecular nitrogen (N<sub>2</sub>) is fixed as ammonium ions (NH<sub>4</sub><sup>+</sup>) by microorganisms on the Earth's surface. Past variations in the atmospheric content of nitrogen, which are still under debate, may have played an essential role in regulating the early Earth's climate (e.g., Goldblatt et al., 2009; Wordsworth and Pierrehumbert, 2013). Therefore, nitrogen is an important volatile element in geoscience, but the geochemical behavior of nitrogen in the deep Earth remains controversial. Compared to other volatile elements, the amount of nitrogen in the bulk Earth, including the atmosphere, is one order of magnitude less (Marty et al., 2012). This constitutes the so-called "missing" nitrogen. However, the causes of nitrogen depletion have not been identified.

One of the hypotheses explaining this "missing" nitrogen is the existence of a nitrogen reservoir in the deep Earth. High-pressure and high-temperature experiments conducted by Watenphul et al. (2009) and Mallik et al. (2018) suggested that a deep nitrogen reservoir can be formed via subducting slabs. Li et al. (2013) and Yoshioka et al. (2018) also experimentally examined the possibility of nitrogen storage in the deep mantle through the solidification of a magma ocean. However, a nitrogen carrier in the lower mantle, which has the largest storage capacity in the Earth's interior, has not been discovered and its nitrogen storage mechanism has not been clarified.

Furthermore, nitrogen solubility in ferropericlase, which is the secondary most abundant mineral in the lower mantle (e.g., Hirose et al., 2017), has not been reported.

In this thesis, I experimentally examined how much nitrogen is incorporated into lowermantle minerals such as bridgmanite and periclase, including stishovite. In the high-pressure and hightemperature experiments, I used multi-anvil apparatus installed at the Geodynamics Research Center, Ehime University, under 28 GPa and 1400 °C–1700 °C. In all the experiments, Fe-FeO buffer was used to reproduce the redox state of the lower mantle. Nitrogen in recovered samples was analyzed using NanoSIMS installed at the Atmospheric Ocean Research Institute, The University of Tokyo and high-resolution SIMS (1280 HR2, CAMECA) installed at Centre de Recherches Pétrographiques et Géochimiques (CRPG). Nitrogen standard samples for NanoSIMS analysis were prepared by implanting <sup>14</sup>N<sup>+</sup> into MgO single crystal plates and quartz glass plates at the National Institute for Materials Science (NIMS).

In the samples quenched from the lower mantle *P-T* conditions, bridgmanite, stishovite, and periclase were present in the solid phase, and hydrous melt (now, quenched crystals) coexisted in the liquid phase. A series of experimental results revealed that stishovite can incorporate more nitrogen than bridgmanite (MgSiO<sub>3</sub>) and periclase (MgO). Nitrogen solubility in bridgmanite and periclase (MgO) increased with an increase in the FeO content. The nitrogen solubility in bridgmanite increased with increasing experimental temperature. I suggest that bridgmanite and ferropericlase, the major minerals in the lower mantle, can form a nitrogen reservoir through the solidification of the SiO<sub>2</sub>-rich oceanic crustal sedimentary rocks, can transport nitrogen to the lower mantle via the subducting slab. This thesis suggests that nitrogen was supplied to the lower mantle in the subduction zone approximately 4 billion years ago with the beginning of tectonic plate tectonics, forming a "hidden nitrogen" reservoir in the lower mantle.