

Fe³⁺ and Al partitioning between silicate perovskites in the lower mantle condition

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Introduction

ABO₃ perovskites with MgSiO₃ (Mg-Pv) and CaSiO₃ (Ca-Pv) are thought to be the most major silicate minerals in the Earth's lower mantle. Usually, an A site in silicate perovskites is occupied by a divalent ion. However, recent experimental studies indicated that Mg-Pv incorporates significant amount of Fe³⁺ in the lower mantle conditions [1, 2]. Furthermore, it was suggested that the presence of Al in Mg-Pv favors the incorporation of Fe³⁺ as Fe³⁺AlO₃ component [3]. Therefore, taking into consideration of the MgSiO₃-CaSiO₃-Fe³⁺AlO₃ system is fundamental to understand the behaviour of trivalent ions in major portions of the Earth's lower mantle. Especially, Fe³⁺ and Al partitioning between Mg-Pv and Ca-Pv is an important indicator to understand the distribution of Fe³⁺ and Al in the lower mantle. Here, we report the partitioning of Fe³⁺ and Al between Mg-Pv and Ca-Pv at corresponding to the Earth's lower mantle condition by using the combination methods of a laser heating diamond anvil cell (LHDAC), high pressure *in-situ* synchrotron X-ray experiments, and an analytical transmission electron microscopy (ATEM).

Experiments

A gel with a composition of CaMgSi₂O₆ : Fe³⁺AlO₃ = 85 : 15 (85CM) was prepared by a conventional sol-gel method and was used as the starting materials. High pressure and temperature experiments at 27-106 GPa and 1600-2500 K were conducted by using a LHDAC. After each high pressure and high temperature experiment, temperature was quenched to room temperature and pressure was kept loading in the DAC.

In order to identify mineral assemblages at *in-situ* high pressure and those of recovered samples, synchrotron X-ray diffraction measurements were carried out at high pressure and room temperature in the beam line 13A and 18C, Photon Factory. X-ray diffraction spectra were recorded with an imaging plate. Two dimensional X-ray diffraction images were integrated as a function of two-theta in order to give a conventional one-dimensional diffraction profile.

In addition, since it is also important to know chemical compositions of coexisting minerals quantitatively, after synchrotron X-ray diffraction measurements, ATEM observation was performed for recovered samples from high pressure and temperature.

Results and discussion

In-situ X-ray experiments at high pressure above 30 GPa revealed the two-phase assemblage of Mg-Pv and Ca-Pv is stable. On the other hand, small amount of

stishovite coexists with Mg-Pv and Ca-Pv below 30 GPa. Ca-Pv cannot be observed in X-ray diffraction pattern obtained at ambient conditions recovered from 27-100 GPa, because it is well known that Ca-Pv is unstable at ambient conditions. The cell volumes of (Fe³⁺, Al)-bearing Mg-Pv at ambient condition are almost constant in spite of their synthesized conditions and larger than that of pure Mg-Pv.

ATEM observation also showed that the product phases in 85CM are Mg-Pv, Ca-Pv and small amount of stishovite below 30 GPa, and two phases of Mg-Pv and Ca-Pv above 30 GPa. Fe³⁺/Al ratio in Mg-Pv was almost 1.0 in all conditions and this evidence suggests that most Fe³⁺ is incorporated into Mg-Pv with Al as Fe³⁺AlO₃ component. Since (Mg+Ca)/Si ratio in Mg-Pv is also constant at 1.0 in all conditions, the coupled substitution (Fe³⁺Al → MgSi) in Mg-Pv seems to be the dominant substitution mechanism. However, the presence of stishovite in the run products obtained below 30 GPa suggests that oxygen vacancy forming substitution (Fe³⁺Al → 2Si) partly occurs at such pressure-temperature conditions. These evidences indicate that the oxygen vacancy forming substitution is possibly important mechanism at pressures corresponding to the uppermost part of the lower mantle. However, the coupled substitution mechanism seems to be increasingly favored in the most part of the lower mantle.

ATEM observation also showed that Ca-Pv is almost Fe³⁺-free and Al-free. The partitioning coefficient (K^D) of Fe³⁺ and Al between Mg-Pv and Ca-Pv can be defined as the concentration ratio as $K^D = X_{FA}^{Ca-Pv} / X_{FA}^{Mg-Pv}$, where X_{FA}^{Ca-Pv} and X_{FA}^{Mg-Pv} mean Fe³⁺ + Al concentration in Ca-Pv and Mg-Pv, respectively. The partitioning coefficients vary in low values (0.1-0.2) in all conditions and show no significant dependence on pressure and temperature conditions. This means that Fe³⁺ and Al are likely to be preferentially incorporated into Mg-Pv as Fe³⁺AlO₃ component, when Mg-Pv coexists with Ca-Pv at lower mantle conditions.

References

- [1] D.J. Frost et al, nature, 428, 409-412 (2004).
- [2] C.A. McCammon, science, 308, 807-808 (2005).
- [3] C.B. Vanpeteghem et al, Phys. Earth Planet. Inter, 155, 96-103 (2006)

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