18C/1999G031

Stability and solubility relations of $(Mg,Fe)SiO_3$ and $CaSiO_3$ perovskites

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Introduction

The Earth's lower mantle is generally considered to consist of mainly $(Mg,Fe)SiO_3$ and $CaSiO_3$ perovskites and $(Mg,Fe)O$ magnesiowustite [1]. However, it is still not clear about the stability and solubility relations of $(Mg,Fe)SiO_3$ and $CaSiO_3$ perovskites under the lower mantle conditions [2].

To clarify these points, laser-heated diamond anvil cell (DAC) experiments under the lower mantle conditions were conducted using natural and synthetic $Ca(Mg,Fe)Si_2O_6$ pyroxenes. Run products were analyzed by synchrotron X-ray diffraction at KEK and recovered samples were examined by analytical transmission electron microscopy (ATEM) at Hokkaido University.

Experimental

Natural clinopyroxenes whose compositions are nearly on the join of $CaMgSi_2O_6$ diopside (Di) - $CaFeSi_2O_6$ hedenbergite (Hd) were selected as starting materials for DAC experiments. Some of the starting materials were also synthesized by heating the oxide mixtures of MgO, SiO_2, Fe_2O_3 and $CaCO_3$ at temperatures 1060 – 1300 ^oC under the controlled oxygen fugacity. These powdered pyroxenes were YAG laser-heated in a diamond anvil cell at 20-40 GPa and 1500-2000 ^oC at ISSP, the University of Tokyo.

Synchrotron X-ray powder diffraction experiments of run products were performed at BL-18C at KEK. X-ray diffraction patterns of the run products at high pressures and at atmospheric pressure were collected on an imaging plate detector with the incident beam monochromatized to 20 keV and collimated to 40 μm. The typical exposure time for X-ray diffraction was 30 min.

Most of the recovered samples were Ar-ion thinned or sectioned by an ultramicrotome into ATEM foils. Transmission electron images, selected area electron diffraction patterns and chemical compositions of the foils were obtained using a 200 kV ATEM (JEOL JEM-2010) attached with an energy-dispersive analytical system..

Results and discussion

The X-ray diffraction patterns of the recovered run products of Di_{100} and $Di_{84}Hd_{16}$ at atmospheric pressure showed only $MgSiO_3$ perovskite, while that of $Di_{75}Hd_{25}$ showed $MgSiO_3$ perovskite, stishovite and magnesiowustite, and those of $Di_{50}Hd_{50}$, $Di_{18}Hd_{82}$ and $Di_{02}Hd_{98}$ revealed stishovite and magnesiowustite. Meanwhile high pressure in-situ X-ray diffraction patterns of $Di_{75}Hd_{25}$ and $Di_{18}Hd_{82}$ showed $CaSiO_3$ perovskite in addition to other phases described above. Considering the fact that $CaSiO_3$ perovskite becomes amorphous after decompression, $CaSiO_3$ perovskite would coexist with other phases at high pressures in the whole region of the $CaMgSi_2O_6$ - $CaFeSi_2O_6$ system. By the ATEM ovservation of the $Di_{84}Hd_{16}$ foil magnesiowustite was detected among other phases, although it was not detected by X-ray diffraction, indicating that a very small amount of magnesiowustite coexists with other phases.

Above X-ray and ATEM obervations indicate that at 20-40 GPa and 1500-2000 ^oC $(Mg,Fe)SiO_3$ and $CaSiO_3$ perovskites are stable in the region $Di_{100}Hd_0$ – $Di_{85}Hd_{15}$, while these two perovskites, magnesiowustite and stishovite are stable in the region $Di_{85}Hd_{15}$ – $Di_{55}Hd_{45}$, and in the region $Di_{55}Hd_{45}$ – Di_0Hd_{100} $CaSiO_3$ perovskite, magnesiowustite and stishovite are stable.

The study on the solubility relations between $(Mg,Fe)SiO_3$ and $CaSiO_3$ perovskites are still under way. The Ca solubility into $(Mg,Fe)SiO_3$ perovskite seems to be very low, nearly 1 mole% or less at these conditions. The Fe solubility into $(Mg,Fe)SiO_3$ perovskite would be less than about 15 mole% and increase with pressure. One problem we have met in the ATEM analysis is that some elements tend to be selectively removed from the foil by the irradiation of the convergent electron beam during the characteristic X-ray measurement, although the chemical analysis of high spatial resolution is the big advantage of ATEM for fine-grained high pressure phases [3]. For example in the case of $CaSiO_3$ perovskite the obtained Ca content tends to be too low compared to the ideal chemical formula. The improvement of this point is in progress.

References

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