Report for the Joint Use/Research of the Institute for Planetary Materials, Okayama University

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Category: International Joint Research

Name of the research project: The coupling of water and fluorine in bridgmanite

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Research report:

1) Please write the research report with free format, but include followings: research purpose, actually conducted research, and research outcomes. If necessary, you can add another pages.

H_2O solubility in bridgmanite, the most abundant mineral in the Earth's lower mantle, is still in debate, yet it has far-reaching impacts on the physical behavior of the mantle and our planet's evolution. Previous studies suggested that bridgmanite can contain either low (a few ppm wt, near or less than the detection limit) or high (~2,000 ppm wt) water concentrations at the presence of Fe and Al (e.g. Panero et al., 2014; Fu et al., 2019). Yoshino and Jaseem. (2018) reported that H solubility in bridgmanite correlates with the F solubility (Figure 1), suggests that certain amounts of H_2O (up to 4948 ppm, which is much higher than what we observed before) could be incorporated into the bridgmanite in the presence of F. However, they did not take Fe (the most abundant transition metal in the Earth's mantle) into their account where Fe^{2+} may reduce the solubility of F in minerals (named Fe^{2+}-F acoidance rule) (e.g. Mason, 1992). To explore H_2O, F solubility and the coupling of H_2O and F in the natural Earth's lower mantle, we have synthesized two stishovite and four bridgmanite with different compositions at 24 GPa and 1973 K for 3 hours. Their microstructures were examined by scanning electron microscopy (Figure 2) and their chemical compositions were determined with an electron microprobe analyzer (EMPA) (Table 1). The run product phases were identified by Raman Spectrum (Figure 3) and micro-focused X-ray diffractometer. Stishovite with small grain size of ~50 μm and bridgmanite with small grain size of ~100 μm.

EMPA results show that F solubility in stishovite are under detection limit, but (Al,Fe)-rich bridgmanite (1K3277) can contain a large amount of F (range from 4225 ppm to 9735 ppm). We also found the distinct OH-stretching peak at 3580 cm^{-1} using Raman spectrum, indicating that bridgmanite from Run 1K3277a and b contain H_2O in its structure. The volume of stishovites are 46.891(3) and 46.822(3) $Å^3$ for 1K3277a and b decided by a micro-focused X-ray diffractometer, and they contain ~1.25 wt% H_2O calculated by the equation: C (H_2O, wt %) = 4.64 $\times \mathit{\Delta V}$ from Nisr et al. (2017). Our results show that stishovites can only carry a large amount of H_2O to Earth's lower mantle, and (Al,Fe)-bearing bridgmanite in the uppermost lower mantle may be a reservoir for fluorine and water.

To quantitative analysis H_2O solubility in bridgmanite, we are going to use NanoSIMs by co-operating with Dr. Jing Yang from Carnegie Institution of Washington. Also, Mössbauer Spectroscopy is needed to study the Fe^{2+}/ Fe^{3+} in bridgmanite and the effects of valence state of iron on solubility of F and H. Moreover, high-pressure and high-temperature X-ray diffraction and Brillouin scattering should be carried to studied the effects of F and H on the elastic properties of bridgmanite at lower mantle conditions.

Table 1. Chemical compositions of bridgmanite and stishovite.

Run #	1K3277a	1K3277b	1K3277a	1K3277b	5K3542a	5K3542b
Phase	Stishovite	Stishovite	Bridgmanite	Bridgmanite	Bridgmanite	Bridgmanite
F	0	0	0.9735	0.4225	0.1123	0.075
Al_2O_3	3.6985	4.5645	16.842	15.916	3.2707	6.626
MgO	0.0335	0.028	28.289	27.2635	37.7123	35.0477
SiO_2	95.083	92.871	40.3555	39.8475	55.5877	51.5263
FeO	0.0295	0.097	9.264	12.4115	2.9507	7.641
Total	98.8445	98.1945	95.724	95.861	99.6337	100.916

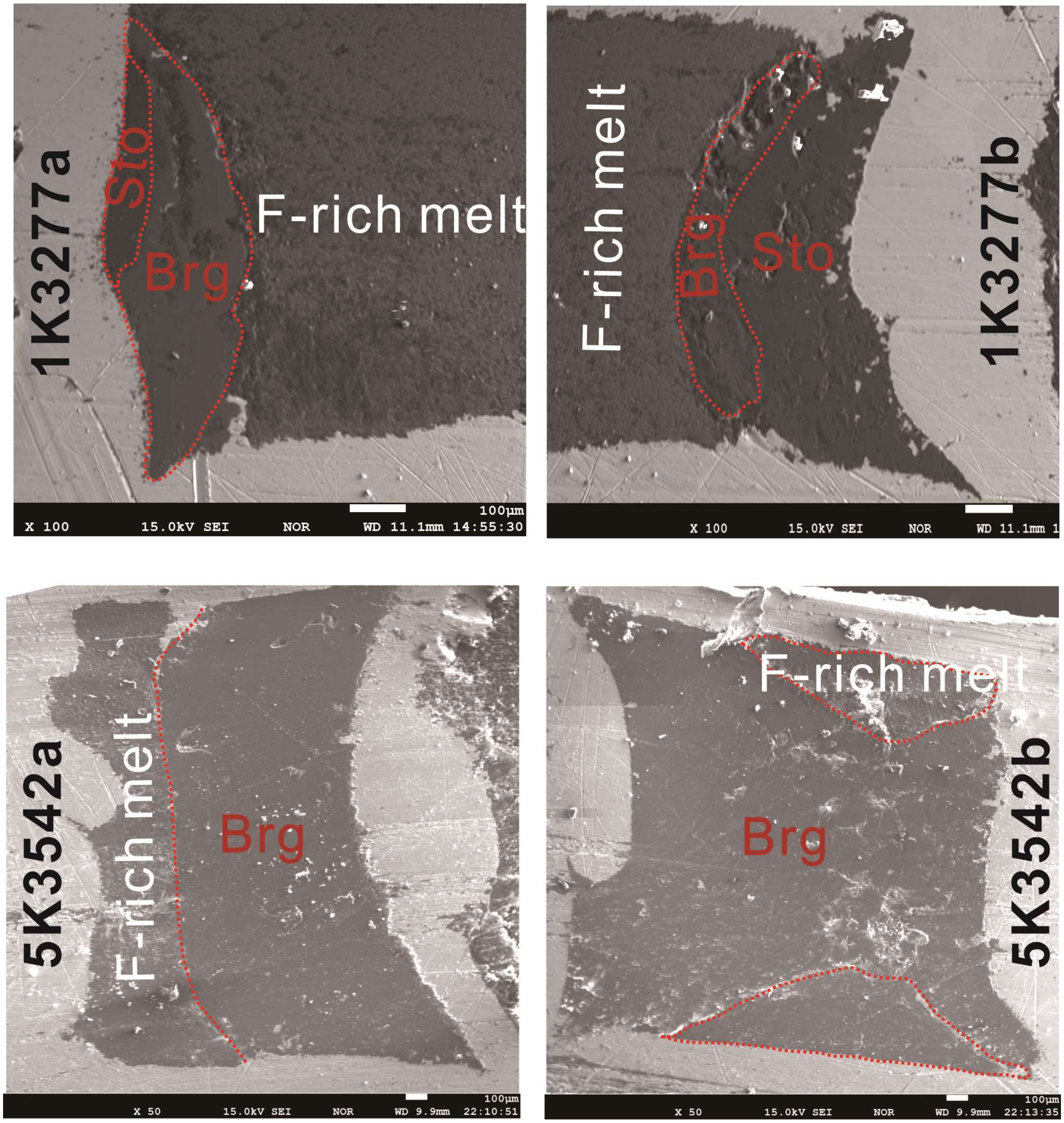

Figure 2. Scanning electron micrographs (SEM) of 1K3277 and 5K3542, Sto = Stishovite, Brg = bridgmanite.

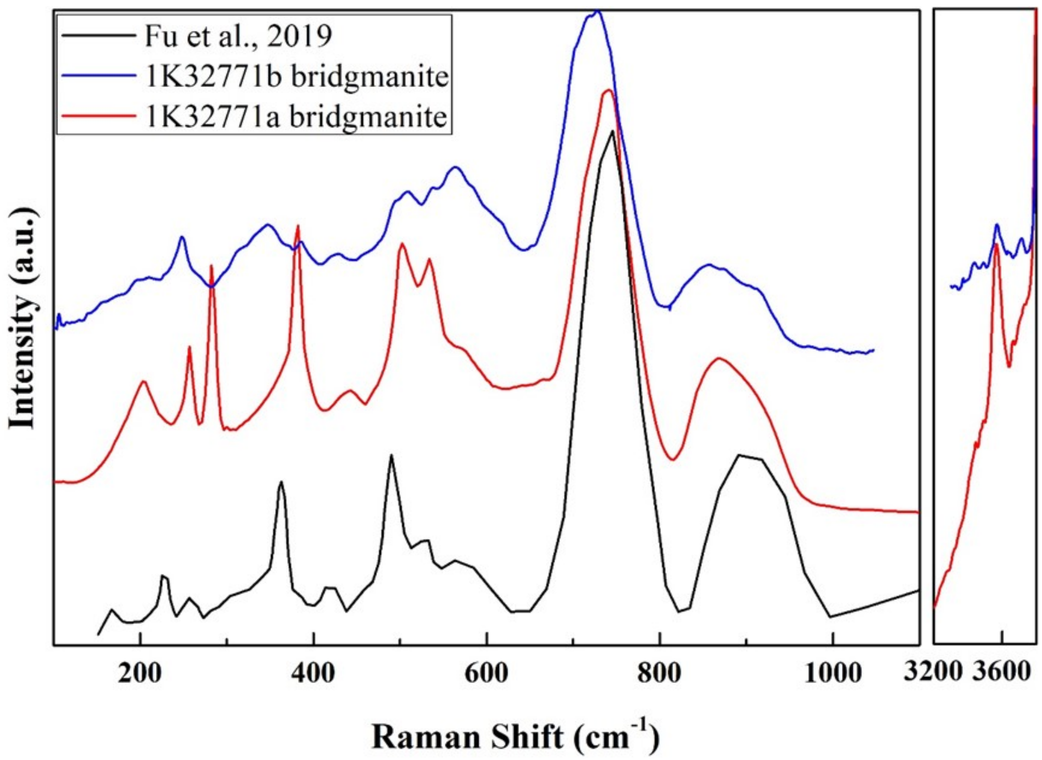

Figure 3. Unpolarized Raman spectra of bridgmanite. The black line represents the dates from Fu et al., 2019 and the red and blue line represent the date from 1K32771a and 1K32771b, respectively. There also have sharp vibrational bands at 3580 cm^{-1}.

References:

Fu, S.Y., Yang, J., Karato, S.-I., Vasiliev, A., Presniakov, M.Y., Gavrilliuk, A.G., et al. (2019). Water Concentration in Single-Crystal (Al,Fe)-Bearing Bridgmanite Grown From the Hydrous Melt: Implications for Dehydration Melting at the Topmost Lower Mantle. *Geophysical Research Letters*, *46*, 10346–10357.

Nisr, C., Shim, S.H., Leinenweber, K., & Chizmeshya, A. (2017). Raman spectroscopy of water-rich stishovite and dense high-pressure silica up to 55 GPa. *American Mineralogist*, *102*, 2180–2189.

Panero, W.R., Pigott, J.S., Reaman, D.M., Kabbes, J.E., Liu, Z.X. (2014). Dry (Mg,Fe)SiO3 perovskite in the Earth's lower mantle. *Journal of Geophysical Research: Solid Earth*, *120*, 894–908.

Yoshino. T., & Jaseem, V. (2018). Solubility in bridgmanite: A potential fluorine reservoir in the Earth's mantle. *Earth and Planetary Science Letters*, *504*, 106–114.

2) For the workshop, please write the report for the workshop. Also, attach the program, abstracts, and list of the participants etc.

3) Please add Collaborator's Name, Affiliated institution and department as needed.

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