# Fluorine sink in Earth’s lower mantle: solubility and substitution mechanism in bridgmanite

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Volatile elements degassed from the mantle throughout the Earth’s history. The halogens are key tracers of accretionary processes owing to their high volatility and incompatibility. Among halogens fluorine substitute for OH in hydrous mantle minerals and could extend their stability field. The experimental results demonstrated that F is less incompatible than $OH^-$ in olivine and orthopyroxene. The F concentrations of the model bulk silicate Earth (BSE) have been estimated to be 25 ppm, which is too high to satisfy a volatile-rich chondrite origin for late veneer model unlike the heavy halogens (Cl, Br and I). Recent high-pressure experiments suggested that nominally anhydrous minerals such as olivine, wadsleyite and ringwoodite can incorporate significant amount of fluorine even if water is absent in the system. The lower mantle would be one of candidate for F budget in the BSE. However, the F solubility in bridgmanite, which is the most dominant constituent mineral in the lower mantle, has not been determined.

In the present study, high-pressure experiments were performed in the system $MgO\text{-}SiO_2 + MgF_2$ ($\pm Al_2O_3 \pm H_2O$) at 2073 K and 25 GPa to determine the F solubility in bridgmanite. Electron microprobe measurements show that F concentrations in bridgmanite occasionally exceed 1 wt%, although the F content in the Al- and $H_2O$-free system is below detection limit (50 ppm). F solubility in bridgmanite is higher than that in wadsleyite. The solubility of F in bridgmanite shows a strong compositional dependence with a positive correlation between $Al^{3+}$ and $F^-$, suggesting a coupled substitution of $Al^{3+}$ and $F^-$ with $Si^{4+}$ and $O^{2-}$ to incorporate F in bridgmanite. When the system contains $H_2O$, bridgmanite can incorporate larger amounts of F even for the Al-free system. In this case, F substitution mechanism would be similar to the water incorporation mechanism. Since the concentration of hydrated Si vacancies is extremely low at all water concentrations (Muir & Brodholt, 2018), F may incorporate into Mg site. Our experiments show that nominally fluorine-free bridgmanite has ability as the entire fluorine budget of the lower mantle.

Keywords: fluorine, bridgmanite, substitution mechanism

 