

## Fluorine and chlorine fractionation during magma ocean solidification: Implications for the origin and abundance of terrestrial halogens

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The isotopic compositions of terrestrial volatiles, such as hydrogen, nitrogen, and chlorine, are very similar to that of volatile-rich CI-CM type carbonaceous chondrites [e.g., 1, 2], suggesting that terrestrial volatile elements may have been mainly derived from these types of asteroids during the formation of the Earth. However, the abundance pattern of volatiles in the silicate Earth is different from carbonaceous chondrites [e.g., 1]. More specifically, super-chondritic H/N, Ar/Xe, and F/Cl ratios of the Earth have been reported [e.g., 1]. The simplest explanation for these observations is that terrestrial volatiles were delivered and fractionated during the main accretion phase. If this is the case, elucidating the fractional processes of volatiles in terrestrial planets is a key to understanding the origin of volatiles in terrestrial planets.

In this study, we focus on the super-chondritic F/Cl ratio of the Earth. The super-chondritic F/Cl ratio of the Earth indicates the selective loss of chlorine and the preferential retention of fluorine. Previous experimental studies have shown that fluorine and chlorine are moderately to highly lithophile under high pressure and high temperature conditions [3, 4, 5]. This indicates that fluorine and chlorine would have been partitioned into mantle during core-mantle separation. Thus, fluorine and chlorine fractionation would have occurred during magma ocean solidification and/or subsequent degassing processes. In order to test the former case, we experimentally investigate the solubility of fluorine and chlorine in mantle minerals at the transition zone and lower mantle conditions.

Starting materials were composed of high-purity oxides ( $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{CaO}$ ,  $\text{MgO}$ ,  $\text{FeO}$ ) and iron metal (Fe) with enstatite chondritic proportion [e.g., 6]. Fluorine and chlorine were added to the mixture as  $\text{CaF}_2$  and  $\text{FeCl}_2$ , respectively. The starting materials were encapsulated into a graphite capsule. The experiments were performed at 18-25 GPa and 2123-2273 K using the multi-anvil press at Ehime University. The elemental compositions and phase assemblages of recovered samples were determined by raman spectroscopy, microfocused X-ray diffractometry, and electron microprobe analyzer. The abundances of fluorine and chlorine in minerals were determined by nano-scale secondary ion mass spectrometry at Atmosphere and Ocean Research Institute.

The preliminary experimental results show that the solubility of fluorine in  $\text{MgSiO}_3$  majorite is approximately one order of magnitude higher than that of chlorine. Although we did not investigate the mineral-melt partition coefficients for fluorine and chlorine, the experimental results show that the crystallization of majorite in a deep magma ocean might have increased F/Cl ratios of the solid mantle. If the compatibility of fluorine and chlorine with other mantle minerals is similar to the case of majorite, the degassing of volatiles with high F/Cl ratios from the mantle after the escape of chlorine-rich primordial atmospheres might have yielded the current abundance pattern of terrestrial halogens. This hypothesis is consistent with the recent proposed scenario for explaining terrestrial super-chondritic Ar/Xe ratio [7].

[1] Marty, B. (2012) *Earth Planet. Sci. Lett.* 313-314, 56-66.

[2] Sharp, Z. D. et al. (2007) *Nature* 446, 1062-1065.

[3] Mungall, J. E. & Brenan, J. M. (2003) *Can. Mineral.* 41, 207-220.

[4] Sharp, Z. D. & Draper, D. S. (2013) *Earth Planet. Sci. Lett.* 369-370, 71-77.

- [5] Kuwahara et al. *submitted*.
- [6] Javoy, M. et al. (2010) *Earth Planet. Sci. Lett.* 293, 259-268.
- [7] Shcheka, S. S. & Keppler, H. (2012) *Nature* 490, 531-534.

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