

## Molecular Dynamics Study of Cement-Aqueous Solution Interfacial System: Cesium Ion Fixation

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Cs<sup>+</sup> ion is one of radioactive species generated by nuclear electric power. It is one of the most problematic ions because of its long half-life and high mobility. Cement material is considered as a candidate for the solid fixation of Cs<sup>+</sup> ions, and the engineered barrier for the geological disposal of such radioactive species. The structures of the cement is complicated, and considered as nano-crystalline aggregation phase with two distinct local structures, tobermorite and jennite, by the difference of Ca/Si ratio and the silica-chain length. The goal of this research is to detect which structural or compositional feature is essential to ionic adsorption into cement matrix.

By using molecular dynamics simulations, we have studied the aqueous solution-mineral (cement) interfacial systems for two different cement local structures (tobermorite and jennite) and two different solutions (NaCl and CsCl). It was found that Na<sup>+</sup> ion could form both inner-sphere complex and outer-sphere complex, without full hydration shell and with full hydration shell at the time of adsorption, respectively. In contrast, Cs<sup>+</sup> ion could only form inner-sphere complex for both mineral cases. This finding is in good correspondence with previous NMR studies[1]. Furthermore, we found that the inner-sphere complex Na<sup>+</sup> is tightly binded with the deprotonated oxygen. More importantly, it was found that tobermorite presents better binding property than that of jennite. The fact that differences in cement structure and ion species may cause these differences in adsorption state and binding property will enhance our understanding on cement materials in the case of the solid fixation and the geological disposal.

[1] Viallis *et al.* (1999) *J. Phys. Chem. B* **103**, 5212-5219

## Subducted halogens and noble gases in the mantle wedge peridotites

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Halogen and noble gas compositions are complementary tracers of H<sub>2</sub>O (or aqueous fluids) in the mantle. Via subduction of sedimentary pore-fluids, halogens and noble gases are carried into the mantle [1, 2]. Here, we present the halogen and noble gas compositions of mantle peridotites from subduction zones (the Avacha volcano in Kamchatka, the Pinatubo volcano in Philippines, and the Horoman massif in Japan) to investigate how far the influence of subducted pore fluids extends in the mantle wedge. H<sub>2</sub>O-rich fluid inclusions are present in the studied peridotites as previously described [3–5]. To determine noble gas and halogen compositions of the fluid inclusions and bulk peridotites, we converted halogens (Cl, Br and I) to Ar, Kr and Xe isotopes by neutron irradiation, and extracted the noble gases by *in vacuo* crushing or heating.

The Br/Cl and I/Cl values of the fluid inclusions obtained by crushing show a sedimentary pore-fluid signature with some variation between localities. The halogen ratios obtained by heating are slightly lower than crushing suggesting the presence of additional Cl in minerals such as amphibole and/or silicate glass [3] in the peridotites. Slab-derived, seawater-like noble gases are also dominant in fluid inclusions as previously reported [6, 7].

The composition of subducted halogens and noble gases in the mantle peridotites demonstrates that sedimentary pore-fluid signatures are carried beneath the island arcs through subduction and survive in the mantle wedge. Deeper subduction of pore-fluid like noble gases into the deep mantle accounts for the same signature of the convecting mantle [2].

[1] Sumino *et al.* (2010) *EPSL* **294**, 163-172. [2] Holland & Ballentine (2006) *Nature* **441**, 186-191. [3] Ishimaru *et al.* (2007) *J. Petrol.* **48**, 395-433. [4] Kumagai *et al.* (2011) *JpGU Meeting 2011*, SCG060-P07. [5] Hirai & Arai (1987) *EPSL* **85**, 311-318. [6] Hopp & Ionov (2011) *EPSL* **302**, 121-131. [7] Matsumoto *et al.* (2001) *EPSL* **185**, 35-47.