Desorption behavior of cesium from smectite by major cations

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The radiocesium released from the Fukushima Daiichi nuclear power plant is retained at the surface soils around the power plant (Tanaka *et al* 2012GJ). The expandable clay minerals such as smectite and vermiculite are thought to be the one of the candidate for the host phases of radiocesium. The sorption behavior of cesium (Cs) on smectite has been widely studied (Cornell, 1993JRNC). On the other hand, the desorption behavior of trace Cs from smectite has not been well understood. The understanding of Cs desorption from the soil clay minerals are essential for the prediction of the migration of Cs in the surface environment. In present study, the desorption behavior of Cs from Cs bearing smectite by major cations (Na^+, K^+, Mg^{2+}, Ca^{2+} and NH_4^+) were systematically examined in laboratory.

The suspension of the Cs bearing smectite was prepared by reaction of 1 g/L smectite with 75 nM Cs^+ solution in NaCl solutions at neutral pH. The desorption of Cs were examined by adding the major cations of which concentrations ranged from 10^{-3} to 10^{-1} N to the smectite suspensions.

All cations except for K^+ lead to the desorption of Cs from smectite when the concentrations of the added cations increased. The order of the ability for the desorption of Cs from smectite by the major cations was summarized as follow: $Ca^{2+} \approx Mg^{2+} > NH_4^+ > Na^+$. The selectivity coefficients based on Gaines-Thomas convention relative to Na^+ were estimated from the macroscopic drsorption results. The estimated selectivity coefficients were almost consistent with previously reported values. This indicates that the exchanges of Na^+, Mg^{2+}, Ca^{2+} and NH_4^+ to Cs^+ in smectite are reversible reactions.

On the other hand, K^+ plays a role for inhibition of Cs desorption from smectite. It is well documented that K^+ lead to the shrinking of the layer space in smectite (Morodome *et al* 2009CCM). The shrinking probably makes the Cs inside the smectite layers undesorbable. Some recent studies indicated that the radiocesium in the soils affected by Fukushima Daiichi nuclear plant accident was merely leached by the high concentrations of cations (Qin *et al* 2012GJ). The effect of K in natural water is thought to be the one of the possible mechanism for the fixation of radiocesium in the soils.

Chromium solubility in chlorite and implications for subduction zone dynamics: an experimental study in the CrMASH system up to 6.5 GPa, 900°C

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Chlorite is known to form nearly monomineralic hybrid rocks at the slab-mantle interface at subduction zones. In hydrated ultramafic systems, chlorite containing 13 wt.% of H_2O represents a good candidate for transferring water beyond the stability field of antigorite, being stable up to 4-6 GPa, 700-800°C. Although pressure-temperature stability of clinochlore has been widely investigated in the system MgO-Al_2O_3-SiO_2-H_2O, the role of Cr in modifying phase relationships is poorly assessed at the low-temperatures characteristic of subducting slabs. Despite chromium is a minor constituent of the Earth Mantle, being incorporated in almost all major mantle phases, it is expected to affect phase equilibria and to extend chlorite stability. This study mainly aims to experimentally investigate the solubility of chromium in chlorite as a function of pressure, temperature and bulk composition and evaluate its effect on phase relations.

Three different compositions with X_{Cr} = Cr/(Cr+Al) = 0.075, 0.25 and 0.5 respectively, have been investigated between 1.5-6.5 GPa, 650-900°C. Cr-chlorite only occurs in bulk with X_{Cr} =0.15. It coexists with enstatite up to 3.5 GPa, 800-850°C, and with forsterite, pyrope and spinel at higher pressure. At P>5 GPa other hydrates occur: a Cr-bearing phase HAPY [1] is stable in assemblage with pyrope, forsterite, and spinel; Mg-sursassite coexist at 6.0 GPa, 650°C with a new Cr-bearing phase, named SAD, forsterite and spinel.

Chromium strongly partitions into spinel (X_{Cr}=0.8806), followed by orthopyroxene (X_{Cr}=0.1428), Cr-chlorite (X_{Cr}=0.0815) and garnet (X_{Cr}= 0.0339).

Cr affects the stability of chlorite by shifting its breakdown reactions towards higher T and P, but Cr solubility at high P results to be reduced as compared with low P occurrence in hydrothermal environments.

[1] Gemmi *et al* (2011) *EPSL* **310**, 422-428.