

Influence of dehydration to Cl isotopic fractionations: implication for behavior of hydrophilic Cl during subduction

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Chlorine, which is known as a hydrophilic element, has been used for elucidating mechanisms of the oceanic materials recycling during subduction (Philippot et al., 1998). Since Cl-bearing minerals such as NaCl are highly dissociative in solution, chloride can be a sensitive proxy for fluid mobility in crustal and subduction-related environments (Barnes et al., 2008).

Chlorine isotopic ratio ($d^{37}\text{Cl}/\text{permil}$ vs. SMOC, standard mean ocean chloride) varies in a range of ± 10 permil. The highly positive $d^{37}\text{Cl}$ values were found in the MORB while the negative $d^{37}\text{Cl}$ values were seen in subduction-zone pore fluids. Serpentinized ultramafic rocks from ODP sites showed negative $d^{37}\text{Cl}$, indicating that a result of hydration of the ultramafic rock by infiltrating ^{35}Cl -enriched pore fluids from the overlying sediments (Barnes and Sharp, 2006). The pore fluids having strongly negative $d^{37}\text{Cl}$ values (Ransom et al., 1995) are also consistent with preferential retention or fixation of ^{37}Cl in silicates.

However, the mechanism of Cl isotopic fractionation between two phases occurring phase separation along dehydration and recrystallization at subduction related environments has not been described well. To elucidate an influence of water to the Cl isotope fractionation, we have conducted anion exchange chromatographic experiments. The results showed the heavier isotope, ^{37}Cl , enriched into liquid phase while the lighter, ^{35}Cl , enriched into anion-exchange resin phase (Musashi et al., 2007).

The trend of the heavier isotopic enrichment into liquid phase by the chromatography was agreeable to the theoretical and experimental studies on Li isotope effect: dehydration of the Li hydrate influenced on ^7Li enrichment into the liquid phase (Oi et al., 1991). Controversially, Schauble et al. (2003) theoretically estimated the lighter isotope, ^{35}Cl , enriched into liquid phase by the Cl isotope equilibrium of the anhydrites.

To understand the Cl isotopic fractionation factor (S) experimentally obtained, the reduced partition function ratios (named f value) of several Cl-hydrates were computed after geometrical structures of the Cl-hydrates were optimized by ab initio molecular orbital calculation. Remarkably, the Cl-hydrates were not optimized until hydration number being more than 100, although the number of the primary hydration sphere around a Cl⁻ in aqueous solution was seven. This implied that the extremely dissociative Cl⁻ was negatively hydrous and the hydration structure was unstable. The f value of the Cl-(H₂O) _{n} was calculated and $1000 \cdot \ln f(100) = 1.658$ ($n=100$) (Oi, private comm.). The S value is expressed by the theory of two phases' separation as follows: $\ln S = \ln F(m) - \ln f(n)$ (Eq.1), where $F(m)$ is a RPF of Cl-(H₂O) _{m} adsorbing to resin with the hydration number of m , and $f(n)$ is that of Cl-(H₂O) _{n} dissolved in solution with the number of n . Since the m becomes less than the n by dehydration, symmetry of the molecular structure of the former $F(m)$ is less than that of the latter $f(100)$. We speculate that $F(m) < f(100)$, implying that ^{37}Cl preferably can be enriched into solution phase by dehydration effect.

When we summarize from the above-mentioned things, the thermo-dynamical stability of the primary hydration sphere around Cl⁻ ion is an important factor controlling the tendency of Cl isotope fractionation between liquid and solid phases of geochemical interests. Assuming an anion exchange resin as oceanic sediment, we may say that ^{35}Cl preferentially enriches into the sediment phase while ^{37}Cl enriches into the subduction-zone pore fluid phase. However, only if Cl⁻ incorporated into the solid phase such as oceanic sediment is stable thermo-dynamically, as $F(m) > f(n)$ (Schauble et al., 2003), the ^{37}Cl may enrich into the sediment phase rather than the pore fluid phase. Similarly, in case of the ultimate dehydration such as recrystallization of NaCl from the saturated solution, the ^{37}Cl may enrich into crystal phase (Eggenkamp et al., 1995).

Keywords: chlorine isotope fractionation, hydrophilic, hydration structure, subduction-zone pore fluid, molecular orbital calculation, anion exchange equilibrium