

Specific sorption of Th(IV), Np(V) and U(VI) on biogenic Mn oxide

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Introduction

Sorption of radioactive elements on mineral surfaces is one of important processes which retard their migration in natural environments. Manganese(IV) oxide has attracted much attention because of its strong sorption property. Recently, it is accepted that the formation of Mn oxide is microbially mediated in most of Mn oxide deposits. Therefore, we investigated the sorption behavior of actinides on biogenic Mn oxide.

Methods

Sorption experiments of Th(IV), Np(V) and U(VI) on biogenic and synthetic Mn oxides were carried out in 10 mmol/L NaCl solution. We used *Acremonium* sp. strain KR21-2, a Mn-oxidizing fungus, to prepare biogenic Mn oxide [1]. Abitic Mn oxide (δ -MnO₂) was synthesized according to Villalobos *et al.* [2]. The biogenic or synthetic Mn oxide was put into 10 mmol/L NaCl solution. Then, stock solution containing ²³²Th(IV), ²³⁷Np(V) and ²³⁸U(VI) was added to the NaCl solution. Solutions after sorption experiments were sampled by filtration with a 0.2 μ m filter to measure actinide concentrations using an ICP-MS.

Results and Discussion

Sorption experiments showed that Th(IV) and U(VI) were strongly sorbed on synthetic Mn oxide. Neptunium(V) was also strongly sorbed on synthetic Mn oxide. In contrast, Np(V) was not sorbed on biogenic Mn oxide at all. Uranium(VI) was sorbed less on biogenic Mn oxide than on synthetic Mn oxide. Difference of the sorption behavior of Np(V) and U(VI) between biogenic and synthetic Mn oxides may be caused by the difference of their sorption properties. Sorption of Th(IV) on biogenic Mn oxide decreased with increasing pH. Thorium(IV) sorbed on biogenic Mn oxide was desorbed into solution phase with increasing time. This is possibly due to complexation of Th(IV) with organic ligands released from fungal cells.

[1] Tanaka *et al.* (2010) *GCA* **74**, 5463–5477. [2] Villalobos *et al.* (2003) *GCA* **67**, 2649–2662.

Re-evaluation of the B isotopic fractionation between B(OH)₃ and B(OH)₄⁻ using methods beyond harmonic level

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Since Hemming and Hanson (1992), B isotopic signature of carbonates has been used as a proxy to indicate the paleo-pH value of seawater and paleo-pCO₂ up to at least 13 Ma. This largely depends on the isotopic fractionation factor between B(OH)₃ and B(OH)₄⁻ (e.g. Spivack *et al.* 1993; Sanyal *et al.* 1995; Palmer *et al.* 1998; Pearson and Palmer, 1999; Sanyal *et al.* 2000; Palmer and Pearson, 2003). However, the B isotope proxy was questioned recently for the unclear mechanisms of B incorporation into carbonates especially using NMR techniques (e.g. Klochko *et al.* 2009). Furthermore, the fractionation factor between B(OH)₃ and B(OH)₄⁻ is not completely established. Kakihana and Kotaka (1977) suggested 1.019 at 25 °C, but subsequent theoretical studies suggested a larger value (e.g. Liu and Tossell, 2005; Zeebe, 2005; Rustad and Bylaska, 2007). Klochko *et al.* (2006) measured the fractionation factor between B(OH)₃ and B(OH)₄⁻ using pH-shift method. Their new value is 1.0272 ± 0.0006 in seawater at 25 °C. Their pure water result contains much larger uncertainty (2 per mil at 25 °C and about 5 per mil at 40 °C). Rustad *et al.* (2010) investigated the fractionation factor in pure water through a series of computational quantum chemistry methods. They found DFT methods could not produce a fractionation factor close to the experimental value (1.031), and extrapolated MP2 results were also significantly different. Their results raised questions about the suitability of DFT methods to deal with B species in solution.

In this study, we use theoretical methods beyond harmonic approximations to study B isotope fractionation. Large anharmonic effects are found for some B-bearing compounds. This is the first study to show that B isotope fractionation is affected significantly by its anharmonicity. B isotope system hence becomes another which requires theoretical treatments beyond harmonic approximations. Unfortunately, all the previous studies including our previous work (Liu and Tossell, 2005) used Bigeleisen-Mayer equation which is purely based on harmonic approximations to deal with B isotope fractionation. Those previous results therefore need to be re-evaluated.