In situ boron isotopic measurements in cultured foraminifera: Implications for δ^{11}B vital effects

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The boron isotope composition of marine carbonates is considered to be a seawater *p*H proxy. Nevertheless, the use of δ^{11}B has some limitations such as the knowledge of the fractionation factor ($\alpha_{4\text{-}3}$) between boric acid and the borate ion and the amplitude of 'vital effects' on this proxy that are not well constrained. Using secondary ion mass spectrometry (SIMS) we have examined the internal variability of the boron isotope ratio in the shallow water, symbionts bearing foraminiferan *Amphistegina lobifera*. Specimens were cultured at constant temperature (24±0.1 °C) in seawater with *p*H ranging between 7.90 and 8.45. Intra-shell boron isotopes showed large variability with an upper limit value of ≈30 ‰. Our results suggest that the fractionation factor $\alpha_{4\text{-}3}$ of about 0.974 (Klochko *et al.* 2006) is in better agreement with our experiments and with direct pH measurements in seawater vacuoles associated with the biomineralization process in these foraminifera. Despite the large variability of the skeletal *p*H values in each cultured specimen, it is possible to link the lowest calculated *p*H values to the experimental culture *p*H values while the upper pH limit is slightly below 9. This variability can be interpreted as follows: foraminifera variably increase the *p*H at the biomineralization site to about 9, as it is measured by micro-electrode. This increase above ambient seawater pH leads to a range in δ^{11}B (Δ^{11}B) for each seawater pH. This Δ^{11}B is linearly correlated with the culture seawater pH with a slope of -12.9 per *p*H unit, and is independent of the fractionation factor $\alpha_{4\text{-}3}$, or the $\delta^{11}B_{sw}$ through time. It may also be independent of the pK_B (the dissociation constant of boric acid) value. Therefore, Δ^{11}B in foraminifera can potentially reconstruct paleo-*p*H of seawater.

Sorption of Pu onto hematite colloids at various total sorbate concentrations

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Introduction

Molecular level understanding of radionuclide/colloid interactions under different geochemical conditions is necessary for prediction of their migration in the enviroment. Most of the laboratory scale experiments were done at the total concentrations of Pu that were significanlty higher than values typical even for contaminated environments, i. e. 10^{-12} – 10^{-16} M. At this concentration interval, no spectroscopic methods exist for direct Pu speciation. The redox speciation could be done only after acid leaching by further application of solvent extraction, co-precipitaton or other separation techniques. At the same time the examination of features like position of pH sorption edges, kinetics of sorption and desorption, leaching behavior could be used to derive mechanisms of sorption.

The purpose of this investigation was to define the mechanisms of plutonium sorption onto hematite colloids at total concentration of < 10^{-13} M and to compare with Pu sorption behavior at total concentration higer than 10^{-10} M.

Experiment

Synthesized hematite colloids were used in all sorption experiments. To study plutonium sorption at different total concentrations, isotopes with different specific activities were used – ^{237}Pu ($T_{1/2}$ = 45.2 d.) and ^{239}Pu ($T_{1/2}$ = $2.41 \cdot 10^4$ y.). In this study Pu (IV) and Pu (VI) pH sorption edges, kinetics and redox speiation were examined at three radionuclide concentration ranges, i. e. femtomolar (~10^{-14} M), nanomolar (~$10^{-1\circ}$ M) and micromolar (~10^{-6} M).

Discussion of results

It was established that Pu in high valence states was reduced to Pu (IV) upon sorption onto hematite at all examined radionuclide concentrations. In case of Pu (IV) at very low total concentration, e.g. ~10^{-14} M, the fast sorption of monomeric Pu $(OH)_n^{(4-n)+}$ species occurred, while in case of Pu (VI), the sorption was kinetically controlled by slow reduction on the surface. Other mechanisms of sorption were proposed for Pu at total concentration of ~10^{-10} - 10^{-9} M and 10^{-6} M. We suppose that upon sorption and reduction Pu (IV) could polymerize as a resuts of increase of its concentration near the surface, that could strongly affected both kinetics of sorption and leaching behavior.