

The mechanism of uranium isotope fractionation during adsorption to Mn oxyhydroxide

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Recent studies have reported natural variations in the ratio of $^{238}\text{U}/^{235}\text{U}$ due to 'stable' isotope fractionation [1-3]. The largest observed fractionations are apparently associated with redox reactions, but a small fractionation between seawater and marine ferromanganese sediments suggested that adsorption of U (VI) from solution onto Mn and/or Fe oxyhydroxides also causes an isotope effect. Because adsorption to these substrates has critically important implications for U transport, understanding U isotope systematics during adsorption could lead to a useful new tool for monitoring this process in the environment.

Previously we conducted simple U adsorption experiments with synthetic K-birnessite. We reported a fractionation matching that observed between seawater and natural ferromanganese sediments: $\delta^{238}\text{U}/^{235}\text{U}$ of adsorbed U was 0.2‰ lighter than $\delta^{238}\text{U}/^{235}\text{U}$ of dissolved U [4].

Because there is no redox reaction in this system, a difference in uranium's coordination environment between dissolved and adsorbed U is likely responsible for isotope fractionation. We analyzed adsorbed U from our experimental study with extended X-ray absorption fine structure (EXAFS) spectroscopy. Comparison of our EXAFS spectrum with those for abundant aqueous U species reveals subtle, but important differences in the U-O coordination shell between dissolved and adsorbed U, specifically an increase in disorder in the bond distances to equatorial oxygens in the adsorbed complex.

We hypothesize that these differences are responsible for the fractionation observed in our experiments and likely in nature, as well.

[1] Weyer *et al.* (2008) *GCA* **72**, 345. [2] Stirling *et al.* (2007) *EPSL* **264**, 208. [3] Bopp *et al.* (2009) *Geology*, **37**, 611. [4] Brennecka *et al.* (2008) *GCA* **72**(12) *Suppl.* A114.

Evidence for the presence of cyanobacteria and thermophilic methanogens in a 3.46 Ga sea, Western Australia

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The 3.46 Ga Marble Bar Chert/Jasper Formation (MBC) in the Pilbara Craton, Western Australia is a low-grade Algoma-type banded iron formation (BIF). It formed by mixing of submarine hydrothermal fluids ($T < 250^\circ\text{C}$) and local seawater at depth $>200\text{m}$ in a large ($\sim 30\text{ km}$ diameter) submarine caldera (Hoashi *et al.* 2009). The changes in paragenesis and abundances of Fe-bearing minerals (siderite, hematite, magnetite, pyrite) in a 160m-long MBC drill core suggest that the redox state of bottom water in the submarine caldera changed from anoxic during the major siderite precipitation stage to oxic (O_2 content $> 10\ \mu\text{M}$) during intensive hydrothermal activity that caused primary hematite precipitation. O_2 in the deep water was most likely produced by oxygenic photoautotrophs (cyanobacteria) in the surface water.

We have analyzed C/H/N/S ratios and $\delta^{13}\text{C}$ values of bulk rocks, extracted kerogens, and carbonates. The results indicate general trends from the anoxic to oxic (and increased hydrothermal activity) stages of: (1) decreasing organic C contents, from 0.7 to $<0.1\ \text{wt}\%$; (2) increasing $\delta^{13}\text{C}_{\text{org}}$ values from $-27\pm 5\text{‰}$ to $-20\pm 5\text{‰}$; (3) decreasing carbonate (siderite) contents from 3.7 to $<0.1\ \text{wt}\%$ in C_{carb} ; (4) increasing $\delta^{13}\text{C}_{\text{carb}}$ values from -2.4 to $+5.8\text{‰}$; and (5) increasing $\Delta^{13}\text{C}_{\text{carb-org}}$ values from 30 to 15‰. These data suggest that: (A) Organic matter accumulated on the seafloor during the anoxic stage was mostly remnant of cyanobacteria ($\delta^{13}\text{C} = -27\pm 5\text{‰}$); and (B) During the oxic (and intensive hydrothermal) stage, remnants of cyanobacteria were decomposed within unconsolidated sediments to CH_4 and CO_2 by heterotrophic methanogens; and this CO_2 , together with H_2 from hydrothermal fluids, were used by thermophilic chemolithoautotrophic methanogens to produce isotopically heavy organic matter. A variety of organisms that thrived in different chemical and thermal conditions (aerobes and anaerobes; photoautotrophs and chemolithoautotrophs; mesophilic and thermophilic) already existed 3.46 Ga ago.