

Silicon isotopic variability in Proterozoic cherts

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Biological fractionation of Si isotopes in the Phanerozoic marine realm has been well documented (e.g. [1]). In the absence of any known silica-secreting organisms, however, the Si cycle must have been very different in earlier oceans [2]. Cherts, which are common in the rock record of all ages, can provide important clues into states and processes of Earth's early Si cycle. However, the use of cherts as a direct proxy of the composition of Precambrian seawater (e.g. [3]) has its limitations because most cherts have formed during diagenesis of precursor sediments. In addition, while younger Proterozoic cherts are typically found in a peritidal environment, many Late Archean and Paleoproterozoic cherts precipitated along with Fe-bearing minerals in deepwater settings [4].

Keeping in mind the above mentioned complexities, we have analyzed Si-isotopes ($\delta^{29}\text{Si}$ and $\delta^{30}\text{Si}$) in well characterized Proterozoic cherts of varying ages (750-2500 Ma) deposited in different water depths. HF-free sample dissolution was performed using an alkali flux; Si was chemically purified using ion chromatography and isotope ratios were measured using a GV Isoprobe-P MC-ICPMS by sample-standard (NBS28) bracketing in high resolution.

$\delta^{30}\text{Si}$ of the cherts of the present study range from -4.36 to +1.84 ‰ (w.r.t. NBS28). The heaviest values obtained so far are from the 1.5 Ga old peritidal cherts of the Yusmastakh Formation, Siberia, while the lightest values are from Fe-associated basinal cherts from the 1.8 Ga Duck Creek Formation. Cherts associated with BIFs show systematically lighter Si-isotopic compositions consistent with fractionation of Si-isotopes during adsorption of silica on Fe-hydroxide particles [5]. The large range in $\delta^{30}\text{Si}$ (-2.6 to +1.26‰) in peritidal cherts from a single basin (Neoproterozoic Akademikerbreen Group, Spitsbergen) suggests that source variability as well as diagenesis must be taken into account when interpreting the Si isotopic compositions of Proterozoic cherts.

[1] De La Rocha *et al.* (1997) *GCA*, **61**, 5051-5056. [2] Siever (1992) *GCA*, **56**, 3265-3272. [3] Robert & Chaussidon (2006) *Nature*, **443**, 969-972. [4] Fischer & Knoll (2009) *Bull. GSA*, **121**, 222-235. [5] Delstanche *et al.* (2009) *GCA*, **73**, 923-934.

Spectroscopic investigations of uranyl reduction by Fe-bearing clays

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Ferrous iron in clay is a potential natural reductant in anoxic environments. The reduction of U^{VI} by Fe^{II} is an important pathway for the immobilization of uranium in subsurface as well as in high-level nuclear waste (HLW) repositories. In the present study, we employed three dithionite-bicarbonate-citrate (DCB) treated, Ca-exchanged Fe-bearing clays viz. montmorillonite (FeSM), Fe-rich smectite (Swa-1) and nontronite (NAu-2) with varying Fe content and studied the reactivity of structural and readsorbed (surface complexed) Fe(II) species in sorption-reduction of U at pH 6 under CO_2 -free anoxic atmosphere (<1 ppm O_2 (v/v)) by using XPS, EXAFS and ^{57}Fe Mössbauer spectroscopies. The surface complexed Fe(II) species on untreated, Ca-exchanged clays were not found to be reactive in uranyl reduction. All three partially (17-45%) reduced, Ca-exchanged clays remove U from solution with a fast rate (minutes-hours), followed by a slow (in months) reduction step. The EXAFS analysis showed that U forms a mononuclear bidentate surface complex with Fe in the untreated Ca-exchanged clays at near-neutral pH which is the pre-requisite for heterogeneous reduction of U by their analogue in DCB treated clays. The adsorbed U was present as partially reduced mixed valence state (U^{VI} and U^{IV}) in 15 days and 30 days. After 3 months, XANES spectra showed a substantial increase of U^{IV} (20-50%) at the expense of U^{VI} in case of reduced (DCB treated) FeSM, Swa-1 and complete reduction occurred (100%) in case of reduced NAu-2. The $\text{U}4f_{5/2}$ XPS spectra were deconvoluted into two components, a higher binding energy (393.2 ± 0.2 eV) for U^{VI} and a lower binding energy (391.5 ± 0.2 eV) for U^{IV} . Despite the presence of abundant structural Fe(II) species, the slow reduction of U might be due to (1) the stabilization of Ca in the clay interlayer inhibiting the cation release into solution linked to the electron transfer process, (2) the fewer number of potentially reactive Fe(II) in clays are accessible to uranium.

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