Mineral nucleation and redox transformations of U(VI) and Fe(II) species at a carboxyl surface

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Environmental radionuclide contaminants interact with mineral and bacterial surfaces in a solution matrix of dissolved organic ligands and bacterial metabolic products (e.g. exopolysaccharides, Fe (II), etc.). The complex reaction network representing such interactions needs to be better understood to enable reliable modelling. For uranium in particular, two important sequestration mechanisms are the formation of phosphate minerals and the reduction of soluble U (VI) to less soluble U (IV) species. While these reactions are relatively well studied in homogeneous solution, the presence of charged surface sites creates ion concentration profiles that may result in surface precipitation and other reactions that would not be expected under the bulk solution conditions.

We have studied the reaction of 0.1 mM U (VI) adsorbed to a carboxyl functionalized colloid with dissolved Fe (II) and phosphate ligands. X-ray absorption spectroscopy (uranium and iron edge XANES and EXAFS) and synchrotron XRD were used to determine solid-phase speciation and mineralization. Acid/base titrations were used to monitor surface proton release or hydroxyl consumption. Results show that adsorption of Fe (II) to the surface leads to the formation of edge-sharing Fe (II)-$(OH)_2$-Fe (II) clusters, under solution conditions that do not result in bulk Fe $(OH)_2$ mineral formation. This surface-precipitated Fe (II)-$(OH)_2$-Fe (II) phase was very reactive towards reducing U (VI), resulting in inner-sphere association of U (IV) atoms with the oxidized Fe (II, III) magnetite phase (in addition to the U-U coordination typically observed in nanoparticulate uraninite). Small amounts of dissolved phosphate (0.1 mM) did not inhibit U (VI)-Fe (II) redox, but lead to the formation of mononuclear U (IV) phases (no U-U coordination) and green rust Fe (II, III) phases. Larger amounts of dissolved phosphate lead to the formation of U (VI)-PO_4 and Fe (II)-PO_4 phases (autinite and vivianite), which inhibited U (VI)-Fe (II) redox. Our results provide insight into the reaction products and the factors controlling U (VI) reduction during mineral nucleation, a stage of presumed high reactivity due to the exposed mineral surface and highly strained bonds.

A detailed Sm-Nd investigation of enstatite chondrites

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Ordinary and carbonaceous chondrites are characte-rized by ^{142}Nd/^{144}Nd ratio ranging from -15 to -40 ppm below the value measured for modern terrestrial samples [1-5]. This signature can be explained by a very early global differentiation of the silicate Earth [2] or a super-chondritic Sm/Nd ratio of the Earth [6]. Enstatite chondrites (EC) were formed in a highly reduced part of the solar nebula and under such conditions, rare earth elements are mainly hosted in oldhamite (CaS). Despite of the importance of this chondrite group, only two ECs (type EH4) have been investigated for high precision ^{142}Nd/^{144}Nd so far.

This study presents high precision Nd isotopes data (using the Triton TIMS in Clermont-Ferrand) for 11 enstatite chondrites (both EH and EL from petrographic type 3 to 6). Results obtained on enriched standards with low excesses in ^{142}Nd show that small variations on ^{142}Nd/^{144}Nd ratio are resolvable. Moreover, we have confirmed the ^{142}Nd excesses in Isua samples in agreement with what we have previously measured in DTM. ^{142}Nd/^{144}Nd isotope ratios in ECs range from -24 ppm to the terrestrial value and are not correlated with the ^{147}Sm/^{144}Nd ratios. We note that the four chondrites showing ^{142}Nd/^{144}Nd ratios that are similar to the terrestrial value are amongst the most primitive samples (all from type 3). Other Nd isotope ratios suggest that the ^{142}Nd signature is affected by s- and r- un-mixing process. We will present also Sm and Ba isotope measurements on the same samples in attempt to explore further the role of ^{146}Sm decay in the ^{142}Nd signature. Furthermore, this study shows the difficulty for determining the initial ^{142}Nd/^{144}Nd of the Earth.

[1] Nyquist *et al.* (1995) *GCA* **59**. [2] Boyet & Carlson (2005) *Science* **309**. [3] Andreasen & Sharma (2006) *Science* **314**. [4] Rankenburg *et al.* (2006) *Science* **312**. [5] Carlson *et al.* (2007) *Science* **316**. [6] Caro *et al.* (2008) *Nature* **452**.