Stability and transformations of monomeric U(IV) species at the Rifle, Colorado IFRC field site

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Strategies for the *in situ* immobilization of uranium aim to reduce oxidized and mobile U(VI) to relatively insoluble U(IV), a process long thought to result in the precipitation of the U(IV) mineral uraninite [$UO_{2(s)}$]. However, recent research indicates that non-crystalline products named monomeric U(IV) may form during the *in situ* reduction of U(VI)[1,2]. These products may form via uranium reduction by microbes, by Fe(II) minerals of biogenic origin[3], and in biostimulated natural sediments[4]. Monomeric U(IV) has garnered recent study because it is likely to be more susceptible to reoxidation and remobilization in the environment than uraninite.

To test its stability and possible transformations, two types of materials containing monomeric U(IV) were fixed in agarose gel pucks: (1) monomeric U(IV) produced via U(VI) reduction by *Shewanella sp.* CO-9, and (2) monomeric U(IV) produced by the reduction of U(VI) by phosphate-treated nanoparticulate magnetite of biogenic origin. These gel pucks were deployed in two groundwater wells at the Rifle, Colorado IFRC site for recovery after 1, 2, and 3 months. Digestions of the gels reveal that uranium is lost more rapidly from gels containing monomeric U(IV) than those containing biogenic uraninite. The monomeric U(IV) associated with biomass is more stable than that associated with magnetite. Uranium L_{III}-edge X-ray absorption spectroscopy (XAS) data point to a relative enrichment of uraninite in the gels as monomeric U(IV) species are selectively removed by the groundwater over time. Our results provide the first direct evidence of the *in situ* instability of monomeric U(IV) species relative to uraninite. Thus, the identification and quantification of these species at field remediation sites is likely to be critical in devising accurate uranium transport and fate models.

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The origin of water in asteroids and the terrestrial planets

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Introduction

Determining the source(s) of the volatile elements H, C and N in the terrestrial planet region is important not only for understanding the origin of life on Earth, as well as dynamical processes in the solar nebula and during planet formation. For instance, a massive influx of water ice from the outer Solar System is thought to have altered the O isotopic composition of the inner Solar System early in its history [1,2]. The bulk and secondary mineral O isotopic compositions of chondrites exhibit behavior that is at least consistent with this. It has also been proposed that C, D and P type asteroids, to which carbonaceous chondrites have been linked, were injected into the asteroid belt from the comet-forming regions prior to formation of Mars [3] and during the late heavy bombardment [4]. Equilibrium and kinetic factors should produce increasingly D-rich water with increasing radial distance from the Sun. In support of this, the water in all but one of the measured comets is significantly ($\delta D \approx 1000$ ‰) more D-rich than Earth. Here, we use the H, C and N elemental and isotopic compositions of chondritic water to determine its provenance(s).

Results

The bulk H abundances and isotopic compositions of CM and CR chondrites are produced by variable mixtures of a common organic component ($\delta D \approx 3500$ ‰) and water with δD values of about -450 ‰ and 100 ‰, respectively. After subtracting this common organic component from bulk analyses of the most primitive CIs, COs and CVs, as well as Tagish Lake, their estimated water δD values are in the same range as for the CMs. In contrast, the water in the ordinary chondrite Semarkona has a δD value of >800 ‰.

Discussion and Conclusions

The estimated H isotopic compositions of the water described above should all probably be regarded as upper limits since they may have been D enriched by oxidation of Fe by water during aqueous alteration [5]. Even the current estimates show that, with the possible exception of the CRs, the carbonaceous chondrites did not form in the same regions as known comets. This calls into question both the ice influx and dynamical models described above. Comparison of the H and N isotopic compositions of chondrites and Earth suggests that the Earth's composition is most simply explained as a mixture of CI and a small amount of solar material.

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