

## Uranyl on Mg-rich minerals: Polarisation Dependent EXAFS

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In the UK, large quantities of intermediate level waste pose complex radiological remediation challenges. Chemical understanding of uranium in these Mg-rich sludges is vital. By applying two EXAFS techniques, we determined: (1) where uranyl ( $\text{UO}_2^{2+}$ ) is adsorbed, and (2) how uranyl attaches to the mineral surface. Powder experiments with U(VI) were performed with magnesite [ $\text{MgCO}_3$ ], brucite [ $\text{Mg}(\text{OH})_2$ ], nesquehonite [ $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$ ] and hydromagnesite [ $\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 4\text{H}_2\text{O}$ ] Kd values for the Mg-carbonate powders were comparable to or exceeded published results for Ca-carbonates. A second set of experiments (GIXAFS) used single crystals of magnesite (10.4) and brucite (0001). Single crystals were reacted under ambient and reduced  $\text{PCO}_2 \sim -4.5$  for 48 hrs. with concentrations of U(VI)-chloride above and below the solubility of schoepite [ $\text{UO}_2(\text{OH})_2 \cdot \text{H}_2\text{O}$ ] (ca. 40% U(VI) adsorbed). GIXAFS measurements were made at  $\chi = 0^\circ$  and  $\chi = 90^\circ$  relative to the synchrotron beam polarisation. GIXAFS results clearly showed polarisation dependence for both ambient and reduced  $\text{PCO}_2$ . XANES results showed uranyl is oriented with the axial oxygens perpendicular to the mineral surface. The EXAFS structural model corroborates an uranyl-triscarbonate. This implies local rutherfordine-like [ $\text{UO}_2(\text{CO}_3)_3$ ] regions which may polymerise at high uranyl activities into a thin film. These results are useful for predicting uranium behaviour during disposal and remediation. The development of *in-situ* measurements is currently in progress.

## Mass-independent sulfur isotope signature in spherule beds of the 3.4-3.2 Ga Barberton Greenstone Belt, South Africa

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Theoretical and experimental studies have shown that atmospheric  $\text{SO}_2$  isotopologue self-shielding effects in the 190-220 nm region of the solar spectrum are the likely cause for mass independent fractionation of sulfur isotopes (S-MIF). The main products of this photochemical reaction –  $\text{SO}_3$  and  $\text{S}_0$  – typically define a compositional array of ca.  $\delta^{33}\text{S} = 0.6 \delta^{34}\text{S}$ . This is at odds with the generally observed trend in Archean sulfides, which broadly defines an array of  $\delta^{33}\text{S} = 1.4 \delta^{34}\text{S}$ . Various explanations have been proposed, including a diminution of  $\delta^{34}\text{S}$  caused by chemical and biogenic mass-dependent fractionation of sulfur isotopes (S-MDF), mixing with photolytic products produced during felsic volcanic events, or partial blocking of the low-wavelength part of the spectrum due to the presence of reduced atmospheric gases or an organic haze.

Early in Earth's history large meteorite impacts would have ejected dust and gas clouds into the atmosphere that shielded solar radiation and affected global climate. It is thus likely that at certain time intervals of high meteorite flux the atmosphere was significantly perturbed, possibly leaving anomalous sulfur isotopic signatures in the rock record. Here we describe the sulfur-MIF and -MDF signatures in sulfides of spherule beds S2, S3 and S4 of the Barberton Greenstone Belt, South Africa. In particular in spherule bed S3 – and to a lesser extent S4 – a trend of  $\delta^{33}\text{S}/\delta^{34}\text{S} = 0.7$  is observed that closely follows the expected trend for  $\text{SO}_2$ -photolysis in the 190-220 nm spectral range. This suggests that an impact dust cloud (deposited as spherule beds), which sampled the higher region of the atmosphere, specifically incorporated products of  $\text{SO}_2$  photolysis in the 190-220 nm range, and blocked photochemical reactions at higher wavelengths (250-330 nm band). By implication, the generally observed Archean trend indeed appears to be the result of additional photochemical reactions that took place in the lower part of the atmosphere.