

Interactions between As(V), Fe(III) and natural organic matter

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As is naturally occurring mainly as solid $\text{FeAs}_x\text{S}_{2-x}$ and as adsorbed species on Fe and Al hydroxides, but it is also found associated with natural organic matter (NOM) [1]. Under oxic conditions, it has been hypothesized that, ternary complexes of As(V), Fe(III) and NOM are formed and that these play a key role in As biogeochemistry. Recently, spectroscopic evidence for the formation of these complexes in peat humic substances was published [2]. We have further investigated the fundamental properties of the interactions between As(V), Fe(III) and NOM. The experimental range covers different kinds of NOM, concentrations between 6485 and 67 243 ppm Fe, pH 3-7 and Fe(III) to As(V) ratios between 0.5 and 100. Synchrotron based Fe and As K-edge extended X-ray absorption fine structure (EXAFS) spectroscopy in combination with infrared (IR) spectroscopy have been used as molecular probes.

Results and Discussion

The NOM suppressive effect on Fe precipitation [3] is reduced in the presence of As(V). At low pH and Fe concentration, the Fe EXAFS spectrum resembles Fe-NOM reference samples (see Figure 1). At higher Fe concentrations, i.e. 22 916 ppm Fe (or 0.085 mol Fe per mol of carboxylic functional groups), Fe(III):As(V) 1:1 quantitative Fe EXAFS results indicate a precipitated FeAsO_4 phase. As EXAFS and IR data provide further support for these findings. They indicate precipitated FeAsO_4 at high pH and fractions of soluble, unbound H_2AsO_4^- at low pH.

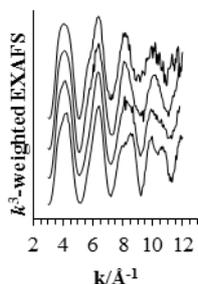


Figure 1. Fe EXAFS data for Suwannee River NOM samples, a) 6489 ppm Fe, pH 5.0, b) 6485 ppm Fe, Fe(III):As(V) 1:1, pH 5.0, c) 22 916 ppm Fe, Fe(III):As(V) 1:1, pH 5.3 and d) precipitated FeAsO_4 .

[1] Redman *et al.* (2002) *Environ. Sci. Technol.* **36**, 2889-2896. [2] Mikutta & Kretzschmar (2011), *Environ. Sci. Technol.* **45**, 9550-9557. [3] Karlsson & Persson (2012), *Chem. Geol.* **322-323**, 19-27.

Coupled radiogenic and stable Sr isotope variations in oceanic basalts

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The formation of basaltic crust at mid-ocean ridges and ocean islands provides a window into the compositional variations in Earth's upper mantle. If basalts are in equilibrium with their mantle source, then the composition of long-lived radiogenic isotopes should be identical and unaffected by partial melting or magmatic processes. Consequently, variations in the isotope composition of Sr, Nd and Pb of oceanic basalts are usually attributed to the existence of compositional heterogeneity in the mantle. In contrast, stable isotope variations can arise from mass dependent processes including partial melting, diffusional exchange or fractional crystallisation [1]. Taken together, radiogenic and stable isotopes can be used to unravel source variations from melting and magmatic processes [2].

Radiogenic Sr ($^{87}\text{Sr}/^{86}\text{Sr}$) is a widely used tracer of mantle chemistry and when paired with stable Sr ($^{88}\text{Sr}/^{86}\text{Sr}$) offers a unique opportunity to trace melt compositions. Moreover, using the double spike-TIMS technique, both radiogenic and stable isotopes can be measured to a high precision. However, to date there is little precise data for the stable $^{88}\text{Sr}/^{86}\text{Sr}$ composition of mantle melts and variations cannot be detected at the precisions of existing studies [3]. This study presents high precision DS-TIMS $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{88}\text{Sr}/^{86}\text{Sr}$ data for a geographically widespread suite of young MORBs and OIBs, including MORBs from the FAMOUS ridge section. Resolvable variations in $\delta^{88}\text{Sr}$ of $\sim 0.14\%$ are found for MORB and within the FAMOUS segment. In contrast, OIB possess a relatively restricted range of compositions from $\delta^{88}\text{Sr} = +0.224 \pm 0.008$ to $+0.280 \pm 0.008 \%$. The extent to which coupled $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{88}\text{Sr}/^{86}\text{Sr}$ data can be used to disentangle source heterogeneity from variations due to the effects of partial melting and magmatic processes will be discussed, as well as reasons accounting for differences in the trends seen between MORB and OIB.

[1] Teng *et al.* (2013) *Geochim. Cosmochim.* **107**, 12-26 [2] Elliott *et al.*, (2006) *Nature*, **443**, 565-568. [3] Charlier *et al.*, (2012) *EPSL*, **329**, 31-40.