Constraining the fidelity of sulfate-oxygen in the geological record

VICTORIA RENNIE* AND ALEXANDRA V. TURCHYN

Dept. Earth Sciences, University of Cambridge
(*correspondence: vcr22@cam.ac.uk)

The oxygen isotope composition of aqueous sulfate ($\delta^{18}O_{SO4}$) in natural environments reflects microbially-mediated oxygen isotope exchange with water during bacterial sulfate reduction, as well as oxygen isotope fractionation during sulfide oxidation. When the $\delta^{18}O_{SO4}$ is preserved in the geological record, it is a potentially powerful tool for reconstructing these key microbial metabolisms (sulfate reduction and sulfide reoxidation) over time. This may be of critical importance in the NeoProterozoic, when the existence and evolution of these metabolisms is intimately related to the redox evolution of the Earth's surface environment.

The viability of using the $\delta^{18}O_{SO4}$ to elucidate these processes in both modern and ancient environments rests on the assumption that there is minimal abiotic exchange between sulfate-oxygen and water-oxygen during the variety of conditions imposed by sample storage, mineral extraction, and laboratory processing. Previous work has shown that oxygen isotope exchange between sulfate and water occurs readily at very low pH (<1) and/or at high temperatures (>100°C). Aqueous samples are routinely acidifed prior to analysis, but current estimates for timescales of exchange under these conditions rely on extrapolation from highly dissimilar solutions.

We present results from exchange experiments mimicking pore fluids under a variety of conditions. These rule out short and medium-term exchange of sulfate-oxygen with water during sample treatment over a range of acidic conditions. Additionally, the presence of aqueous sulfide in sedimentary pore fluids may facilitate sulfate-oxygen exchange with water-oxygen via the transient formation of thiosulfite complexes. Our experiments constrain the range of pore fluid (and natural) conditions over which $\delta^{18}O_{SO4}$ will remain stable. Finally, in contrast with aqueous sulfate, results from extracted carbonate-associated-sulfate (CAS) show that mineral bound $\delta^{18}O_{SO4}$ is not solely a function of the oxygen isotope composition of the aqueous sulfate during carbonate crystallization. This points towards further controls on $\delta^{18}O_{SO4}$ in CAS possibly imposed by the presence of the carbonate lattice.

Investigating the transport of strontium through biogenic hydroxyapatite Barriers

J.C. RENSHAW*, S. HANDLEY-SIDHU,
F. SINCLAIR SMITH, Q. GRAIL, M. CUTHBERT, M RILEY
AND L.E. MACASKIE

University of Birmingham, Edgbaston, Birmingham B15 2TT, UK (*correspondence: j.c.renshaw@bham.ac.uk)

Hydroxyapatite (HAp) has potential as a material for the remediation of metal contaminated waters [1] and in reactive barriers [2]. *Serratia* sp. cells bio-manufacture nanophase hydroxyapatite (Bio-HAp) from the substrates glycerol 2-phosphate and Ca^{2+} [3]. This Bio-HAp has properties that increase metal uptake (e.g. decreasing crystallite size, increasing specific surface area and organic content).

Column experiments were conducted to investigate the transport of Sr^{2+} (0.5 mg) through Drigg sand (sampled near low level waste repository) and Drigg sand containing either 0.25% commercial (Com-HAp) or Bio-HAp. Figure 1 shows the elution of Sr^{2+} through columns containing groundwaters (GW) with high levels of competing ions (100 and 50 mg L^{-1} of Ca^{2+} and Mg^{2+}, respectively). The Com-HAp and Bio-HAp retained 2.5 and 3.7 mg of Sr^{2+} per 1 g of HAp, respectively. Work is now been undertaken with GW containing lower cation concentrations. Numerical modelling is also being carried out to test various hypotheses regarding Sr^{2+} transport processes.
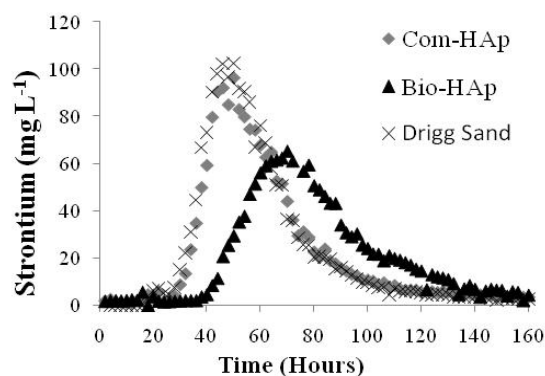

Figure 1: The Transport of Sr^{2+} through Drigg Sand (x), with Com-HAP (♦) and Bio-HAp (▲)

[1] Handley-Sidhu (2011) *Biotechnol. Lett.* **33**, 79–87.
[2] Simon (2004) *Sci. Total Environ..* **326**, 249–256.
[3] Thackray (2004) *J. Mater. Sci. Mater. Med.* **15**, 403–406.