Iron isotopes in marine anoxia

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We measured Fe isotopes in dissolved and suspended Fe sampled across the anoxic-oxic boundary of the Gotland Deep, Baltic Sea, with an *in situ* pump-CTD on two cruises in 2005. Dissolved-Fe δ^{56}Fe from -0.7 to -0.4 ‰ in the anoxic zone are in agreement with a diagenetic Fe-source dominated by dissimilatory iron reduction (DIR). Suspended-Fe δ^{56}Fe increased from -0.4 to -0.1 ‰ with depth, similar to sediment profiles of reactive Fe(III) from reducing continental margins [1]. This could indicate some DIR in the water column in addition to reduction of Fe-oxyhydroxides by H_2S. Upwards across the suboxic zone dissolved Fe concentration decreased by an order of magnitude and δ^{56}Fe values increased to +0.3 ‰. Suspended Fe maintained δ^{56}Fe values well below 0 ‰. This trend is the opposite of what can be expected when Fe^{2+}(aq) is oxidized to Fe^{3+}(aq) and rapidly removed by precipitation of Fe(III)-hydroxides, as, for example, has been observed in streams fed by a hydrothermal Fe^{2+}(aq) source [2]. Given the total fractionation factor of the above reaction ($\Delta^{56}Fe_{Fe^{2+}(aq)\text{-}Fe(III)s}$ ~ +1 ‰, [3]), the Baltic Sea trend requires the removal of Fe^{2+}(aq) into a poorly soluble Fe(II) phase prior to oxidation instead of oxidation followed by removal. This would confirm the importance of the much more rapidly oxidised $Fe(OH)^+$ and $Fe(OH)_2^0$ species compared to Fe^{2+}(aq) [4]. In addition, Fe^{3+}(aq) may build up when organic Fe-binding ligands are present, which inhibit the precipitation of Fe(III)-hydroxides at low Fe^{3+}(aq) concentration.

The above results will have some implications for the interpretation of sedimentary Fe isotope trends from the Archean-Proterozoic transition. Banded Iron Formations show a wide range of δ^{56}Fe values from + 1 to -2 ‰ [5]. If the Baltic Sea serves as a modern analog, at least part of the observed variability may reflect whether the Fe removal pathway was by a solid Fe(II) phase or a solid Fe(III) phase. A shift to an alkaline ocean, perhaps also with abundand organic ligands, would at first produce low δ^{56}Fe Fe-hydroxides but with a trend towards higher values as Fe removal progresses.

[1] Staubwasser *et al*. 2006 *Geology* **34**. [2] Bullen *et al*. 2001 *Geology* **29**. [3] Beard & Johnson 2004 *Rev. Mineralogy* **55** [4] Millero 1985 *GCA* **49**. [5] Johnson *et al*. 2008 *GCA* **72.**

Thermodynamic controls on the bioreduction of U, V, and Fe

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The bioreduction of uranium and iron are closely coupled in many environments, either through abiotic pathways, or through their roles as competing electron acceptors. At the Old Rifle bioremediation site in Colorado, the reaction network is further complicated by the presence of the electron acceptors sulfate and vanadium, although these reactants also provide additional information on the overall thermodynamic state of the system. Of particular interest is the effect of the thermodynamic driving force on the rates of the individual bioreduction reaction, a subject of growing interest among researchers focusing on biogeochemical processes in the subsurface [1,2].

In this presentation, we focus on the development of thermodynamic/kinetic models for U(VI), V(V), and Fe(III) bioreduction, with application to a set of column experiments using natural sediments from the uranium bioremediation site at Old Rifle, Colorado. In the experiments, uranium-contaminated groundwater from the site is amended with variable concentrations of acetate to investigate explicitly the thermodynamic controls on the bioreduction of U, V, Fe, along with consideration of sulfate reduction that with time comes to dominate the reaction network. At 3 mM acetate, U and V removal from the groundwater are almost quantitative. However, sulfate reduction begins well before the breakthrough of sulfide from the column, and based on an analysis of the electron balance, most of the acetate (>90%) is used in sulfate reduction. This implies that the sulfide produced must be consumed through abiotic reduction of iron hydroxide in the column, rather than through direct reaction with Fe(II) from bioreduction of Fe(III) phases. Breakthrough of sulfide occurs when the “bioavailable” Fe(III), as defined by a 0.5 N hydroxylamine extraction, is exhausted. In contrast, U decreases only about 40% when 0.5 mM acetate is injected, with Fe reduction initially dominating the reaction network without completely suppressing sulfate reduction. Reactive transport modelling of these dynamics highlight the important role that the solid phase solubilities, along with aqueous complexation, have in determining the system behavior through their effects on the thermodynamic driving force.

[1] Jin, Q. and Bethke, C.M. (2005) *Geochim. Cosmochim. Acta* **69**, 1133-1143. [2] Dale *et al*., *Amer. J. Sci.* **306**, 246-294.