

## Effect of sediment mineralogy on microbiologically induced (DMRB) changes in divalent metal speciation

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Dissimilatory metal reducing bacteria (DMRB) can either directly mediate or indirectly induce geochemical processes that alter the speciation and lability of metallic contaminants within natural environments. Most investigations into the effect of DMRB on metal speciation utilise synthetic iron oxyhydroxide minerals as the Fe(III) source, thereby allowing well-controlled experiments. However, this technique does not emulate the actual mineralogical composition of natural systems – and does not account for the small-scale heterogeneity that may control metal geochemistry within these systems. Our experiments with a divalent metal that is subject to both surface complexation and ion exchange reactions ( $Zn^{2+}$ ) indicate that clay minerals place an important control on DMRB-induced changes in metal speciation.

Our data demonstrates that microbial Fe(III) reduction alters the proportion of Zn-aq in slurries containing goethite and hydrous ferric oxide (HFO), but has little effect in parallel slurries containing selected iron-bearing natural sediments. These data also indicate that microbial goethite and HFO reduction increases the proportion of HCl-insoluble Zn while microbial reduction of Fe(III) in natural sediments has virtually no effect on HCl-insoluble Zn. Geochemical modelling indicates that Zn may be released from surface complexes (via Fe-reduction) and then react with ion exchange sites on clay mineral surfaces in natural sediments. This process can prevent net solubilization of Zn, and prevent Zn from participating in the surface reactions that occur in the corollary experiments with pure iron oxyhydroxide minerals.

The Zn-speciation changes in the goethite system have been previously reported by these investigators, and may indicate that DMRB are inducing processes that enhance iron-oxyhydroxide recrystallization rates – thus incorporating Zn into less soluble iron oxide minerals. Mössbauer analyses support this hypothesis. XAS data indicate the Zn-O bonding environment is initially similar in both sediments. However, the Zn-O co-ordination number shifts during natural sediment reduction but remains constant during goethite reduction. Although alternate explanations are possible, this shift could represent Zn changing from an iron-oxide surface complex to an ion exchange site. Scanning surface mass spectroscopy analyses of elemental abundance associated with adsorbed Zn in these systems are underway and will be discussed. These results indicate that metal mobility predictions based on microbial experiments with synthetic Fe-oxide minerals may have limited applicability to “real world” systems.

## Oxygen-isotope evidence for altered oceanic crust in the Atlantic MORB source

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A long-wavelength geochemical gradient in Mid-Atlantic Ridge (MAR) samples collected between 33 and 41°N has previously been attributed to mixing of material from depleted and enriched (EMII-type) mantle components. Enriched mantle domains are principally identified using isotopes of incompatible trace elements, which can be dominated by small mass fractions of enriched material. Oxygen, by contrast, occurs in roughly constant abundance in most mantle and crustal minerals and deviations from mantle  $\delta^{18}O$  reflect near-surface processes; thus variations in  $\delta^{18}O$  can be used to constrain the percentage of recycled near-surface materials within a given source region. We present here high-precision oxygen-isotope analyses of MAR glasses and discuss the implications for the nature and percentage of the regional enriched component.

We measured  $\delta^{18}O$  in ~50 MAR glass samples by laser-fluorination techniques at Caltech. The  $\delta^{18}O$  within the suite ranges from 5.3-5.6‰ (<0.05‰ 1 $\sigma$ ), similar to that found in a global survey of normal MORB (5.4-5.8‰<sup>1</sup>). Because the expected magnitude of change in oxygen-isotope composition with fractional crystallization (~0.1‰) is a significant fraction of the observed range, we have quantitatively modelled changes in  $\delta^{18}O$  of the liquid with differentiation. Corrected (primary liquid)  $\delta^{18}O$  values are an average of 0.075‰ lower than those in the measured glasses. Variations in  $\delta^{18}O$  due to different degrees of partial melting are unlikely to explain these data because  $\delta^{18}O$  is not correlated with indices of extent of melting (e.g., Na8 or axial ridge depth).

Relatively high  $\delta^{18}O$  in the MAR suite is correlated with the enriched component (elevated  $^{87}Sr/^{86}Sr$ , La/Sm, and Ce/Pb and low  $^{143}Nd/^{144}Nd$ ). This association suggests that this component was near the Earth's surface at some point in its history and thus supports previous interpretations of EMII-type sources as recycled crustal material. On the other hand, high Ce/Pb indicates that this component cannot be dominated by continent-derived sediment (whether by bulk incorporation, as partial melts or as sediment-derived hydrous fluid) but instead is likely to be composed primarily of subduction-processed altered oceanic crust. The percentage of crustal material required to explain the variations in oxygen isotope composition within this dataset (0-6%) is similar to that required to explain the variations in  $\delta^{18}O$  within the global NMORB suite (0-7%<sup>1</sup>), which may suggest a similar percentage of surface material distributed throughout the upper mantle at a variety of length scales.

<sup>1</sup>Eiler, J.M. et al. (2000), *Nature* **403**, 530-534