The reduction of elemental sulfur by metal-reducing bacteria under alkaline conditions

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Metal-reducing bacteria such as *Shewanella*, *Desulfuromonas*, and *Geobacter* are abundant in many terrestrial environments, where their respiration is often linked to the reduction of ferric iron (Fe^{III}). Under alkaline conditions, however, the reduction of Fe^{III} ceases to be energetically favorable and suggests that under these conditions, metal reducers must utilize alternate electron acceptors. One possible alternative is elemental sulfur (S^0), which is produced when ferric minerals react with dissolved sulfide such as that created by microbial sulfate reduction. Using geochemical modeling, we show that unlike the reduction of ferric minerals, the reduction of S^0 becomes more energetically favorable as pH increases. We also show experimentally that, under alkaline conditions, *Shewanella oneidensis* is capable of reducing S^0 to sulfide, which then reacts with ferric minerals to form Fe^{II}. We suggest that in slightly alkaline environments where both sulfate and Fe^{III} are available, metal-reducing bacteria may survive primarily by respiring the S^0 created by sulfate-reducing bacteria.

Global variation in Fe-isotopic composition of arc basalts indicate a variably oxidised and metasomatised mantle wedge source?

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New Fe-isotope data on basaltic samples from the global network of subduction arcs is used to investigate whether there is systematic variation in Fe isotopic compositions resulting from varying source oxidation. This in turn may reflect variation in slab-derived water flux.

Global arc magmas have elevated $Fe^{3+}/\Sigma Fe$ values in the range >0.1 to 0.5 (our data set has a mean of ~ 0.35), compared to MORB with values in the range 0.1-0.2. [1,2]. For lavas, our $\delta^{57}Fe$ data (vs.IRMM-014) span a range from -0.2 to +0.2 (± 0.04), with a mean around +0.05. This is significantly lighter than the mean for MORB and BABBs (~+0.10) [3], though the arc data sets clearly trend towards heavier values for more fractionated samples. Light $\delta^{57}Fe$ values in arcs may reflect that the mantle wedge in many arcs is more depleted than MORB source [4]. Our $\delta^{57}Fe$ values show moderate positive correlation with $Fe^{3+}/\Sigma Fe$.

Using the subduction thermal parameter (ϕ) [5] which is a proxy for the thermal structure of the down going slab, we find a positive correlation of $\delta^{57}Fe$ where $\phi/100 > 50$, but for values < 50 there seems to be a negative correlation. Interestingly we find that mineral separates from some ultramafic xenolith suites have very light $\delta^{57}Fe$ values (CPX as low as -0.79 & Ol at -0.66) apparently reflecting metasomatism [6] and extending the negative ϕ - $\delta^{57}Fe$ trend.

A possible explaination is that the iron isotopic values and trends of primitive arc basalts reflect three influences; 1. source oxidation, 2. fraction of melting and 3. impact of metasomatism.

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