Is the oxygen isotope composition of zircon robust against aqueous alteration?

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The oxygen isotope composition of zircon is often used to unravel its (pre-)magmatic history, including the presence of liquid water on the surface of the Hadean Earth [1]. However, it has recently been questioned whether zircons retain their primary oxygen isotope signature during alteration and metamorphism [2], and experimental studies are likely to be most valuable in assesing this assumption. Here we report results from oxygen isotope hydrothermal tracer experiments with a heavily radiation-damaged zircon crystal from Sri Lanka. The experiments were conducted in ^{18}O-enriched water and in an enriched 0.1M HCl solution, as well as in milliQ water at temperatures between 100 and 700°C and pressures ranging from 1 to 1.6 kbar for 1 to 140 days. Preliminary SIMS analyses of altered zones formed at 400°C in milliQ water, known to have a negative δ^{18}O, yielded a weighted average δ^{18}O of -6.46 ± 0.22 ‰ (2σ, $n = 7$) which is significantly different to the δ^{18}O of 6.68 ± 0.15 ‰ ($n = 9$) obtained from unaltered zircon areas. Furthermore, Raman spectroscopic measurements from altered zones formed in the ^{18}O-enriched solutions reveal a significant red-shift of the ν_3 (SiO_4) band when compared to altered zones that formed in milliQ water at the same temperature, indicating a mass-related frequency shift of the ν_3 (SiO_4) band due to the incorporation of significant amounts of ^{18}O from solution. The Raman measurements also indicate temperature-dependent structural recovery processes inside the altered areas which are accompanied by partial loss of radiogenic Pb, as revealed by SHRIMP analyses. Our preliminary data clearly show that, in contrast to the Hf isotope system [3], the oxygen isotope composition of radiation-damaged zircon can be altered signifcantly by the interaction with an external fluid, even during weathering. This has to be kept in mind when using the oxygen isotope composition of zircon to infer its (pre-) magmatic history.

[1] Wilde *et al.* (2001) *Nature* **409**, 175–178 [2] Nemchin *et al.* (2006) *Geochim Cosmochim Ac* **70**, 1864–1872 [3] Lenting *et al.* (2010) *Am Mineral* **95**, 1343–1348

The impact of Fe(III) oxide structure on shaping metal respiring microbial communities and carbon oxidation

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The importance of dissimilatory iron (III)-reducing microorganisms (DIRMs) in the iron (Fe) geochemical cycle has long been recognized. Their ability to reduce and thereby dissolve solid Fe (III) phases plays an important role in the cycling of trace nutrient and contaminants. In addition, metal oxide respiration plays a significant role in controlling organic matter mineralization in metal-rich environments. Despite this importance, our understnading of the role that Fe (III) (hydr)oxide mineralogy plays in controlling microbial Fe (III) respiration is poorly understood. For instance, while current model DIRMs in culture show the ability to greatly reduce ferrihydrite, these DIRMs show diminished abilities to reduce more crystalline phases (goethite and hematite), only reducing a small percent [1].

Through enrichment experiments, we found that both the Fe (III) mineral and carbon source provided specilized ecological niches for micrrooganisms. In fact, while acetate enrichments could support the reduction of ferrhydrite, the reduction of goehtite and hematite was not detected. However, with lactate and glucose as the carbon source, the reduction of these more crystalline phases was significant (30-70%). Clone library (16S rRNA) results indicated that a model Fe (III)-reducing microoganism, *Geobacter*, was prevalent on the ferrihydrite and acetate enrichments but did not occur on the hematite-acetate or goethite-acetate enrichments. Instead, in enrichments where goethite and hemtatie showed significant reduction, lactate and glucose supported the growth of less traditional Fe (III) reducers, *Desulfovibrio* and members of the family *Enterobacteriaceae*. Fe (III) reduction by these organisms is likely driven by indirect Fe (III) reduction coupled to sulfur cycling or fermentation.

Interstingly, our results also suggest that Fe (III) mineralogy will dictate competitive advantages between metal respiration and fermentation, possibly including acetategensis. These findings suggest that the oxidation of carbon and reduction of Fe (III) will be constrained by the host Fe (III) mineralogy of sediments/soils.

[1] C. M. Hansel, S. G. Benner, P. Nico *et al.* (2004) *Geochemica et Cosmochimica Acta* **68** (15), 3217