

Formation and transformation of Fe- and S phases by an acid-tolerant sulfate reducing *Desulfosporosinus* species

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Fe²⁺ may be removed from acid mine drainage (AMD) by the activities of Fe (II) oxidizing bacteria that mediate the aerobic oxidation of Fe (II) to Fe (III) and subsequent precipitation of Fe (III) (hydr)oxide phases [1]. The stability of these phases after oxidative precipitation of Fe has been achieved is unclear, particularly under anaerobic conditions. Activities of Fe (III) and/or sulfate reducing bacteria may lead to 1) 'futile redox cycling' [2] of Fe via reduction and subsequent re-solubilization of Fe (III) (hydr)oxide phases and 2) accumulation of iron-sulfide phases near the terrestrial surface via the activities of sulfate reducing bacteria. We examined how the sulfate and Fe (III) reducing activities of *Desulfosporosinus* sp. GBSRB4.2 [3] affected the speciation of iron under anoxic conditions at Fe (II):Fe (III) ratios of 40 mM Fe (II):0 mM Fe (III), 30 mM Fe (II):10 mM Fe (III), 10 mM Fe (II) :30 mM Fe (III), and 0 mM Fe (II):40 mM Fe (III). In incubations containing Fe (III), it was provided as poorly crystalline Fe (III) (hydr)oxide. The presence of Fe (III) had little impact on sulfide production, suggesting that GBSRB4.2 did not reduce Fe (III) in preference to sulfate. Acid-extractable (0.5 M HCl) Fe (II) decreased in incubations containing 40 mM Fe (II):0 mM Fe (III) as sulfate reduction proceeded. Similarly, in incubations containing 0 mM Fe (II):40 mM Fe (III), after an initial increase in Fe (II) concentration due to Fe (III) reduction, acid-extractable Fe (II) concentrations decreased in the incubations, suggesting the transformation of biogenic FeS phases to more stable forms as the incubations proceeded. X-ray diffraction (XRD) revealed the presence of greigite (Fe₃S₄) and mackinawite (FeS) in incubations amended with 40 mM Fe (II):0 mM Fe (III). In incubations amended with Fe (III), the activities of GBSRB4.2 led to the transformation of poorly crystalline Fe (III) (hydr)oxide phases to goethite (α -FeOOH).

[1] Senko *et al.* (2008) *ISME J* **2**, 1134–1145. [2] Johnson & Hallberg (2002) *Re/Views Environ Sci Bio/Technol* **1**, 335–343. [3] Senko *et al.* (2009) *Geomicrobiol J* **26**, 71–82.

U-Pb & O-isotope depth-profiling coupled with REE on zircon: Evidence for Cycladic anatexis

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In order to obtain timing constraints of a crustal-scale mylonitic orthogneiss on Serifos, western Cyclades (Greece), six samples were analyzed for zircon U-Pb ages and O-isotope signatures. REE analyses were performed on zircon from an orthogneiss with co-existing garnet to determine if zircon grew before or in the presence of Grt-Hd skarn veins which are parallel to and cross-cut mylonitic foliation. Imaging of the zircon reveals internal sector and oscillatory zoning and some zircon contain a thin rim overgrowth. We employed the Cameca ims1270 ion microprobe (UCLA) to perform depth-profiling analysis on unpolished grains in an attempt to resolve the age of the zircon rim overgrowth. For the unpolished grains, 76 ion-drilling analyses were conducted typically with one analysis per grain; 20 of the analyses were obtained by subsequent ion-drilling into the same analytical pit to produce a rim-core age profile. Regression of the youngest subset of 32 ages from concordant or near concordant analyses yields an intercept age of 43.3 ± 1.6 Ma (MSWD: 2.2); a weighted average ²⁰⁶Pb/²³⁸U age is within error at 41.2 ± 3.2 Ma (MSWD: 2.6). In addition to the geochronology, 53 O-isotope analyses were conducted on the same zircon following similar ion-drilling methods (reported as $\pm 0.5\%$). Single spot $\delta^{18}\text{O}$ analyses display a moderate bimodal population at 4.1‰ and 7.3‰; there is no apparent correlation between age and $\delta^{18}\text{O}$ values. Trace element concentrations were obtained with LA-ICPMS (Laurentian University); 35 analyses were performed on 12 zircon grains, primarily on rims, and 25 analyses were performed on garnet cores and rims. Chondrite normalised REE patterns in zircon exhibit low values and flat HREE patterns, suggesting crystallization in the presence of garnet. However, chondrite normalised REE profiles on garnet are depleted overall with low LREE values, weak and flat HREE enrichment in the rims and strong HREE depletion in the cores with a positive Eu anomaly. Furthermore, a negative Eu anomaly in zircon suggests crystallization in the presence of a melt, confirmed in thin section with the presence of magmatic relicts (perthitic K-feldspar and zoned plagioclase). We therefore suggest that zircon growth occurred during Eocene exhumation and anatexis in the presence of REE depleted fluids.