Mineralized microbial mats with extreme lanthanum enrichments in the tunnel of Äspö, Sweden

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Microbial mats precipitating iron oxides and thereby accumulating trace and rare earth elements (REE) are widely recognized [1, 2, 3]. A key role in that biomineralization process is assigned to negatively charged organic surfaces (cell surfaces and extracellular polymeric substances, EPS) binding cations and forming complexes [2,3,4]. Depending on the nature of these surfaces, a fractionation of specific cations may occur, thus giving the resulting minerals an inorganic "biosignature". Bacteriogenic iron oxides covering granitic surfaces in the 450m deep Äspö Hard Rock Laboratory (Sweden) were analysed for inorganic biosignatures using LA-ICPMS. The study revealed an extreme enrichment (about 1000fold) in lanthanum (La) compared the other REE (Fig. 1). According to the similar chemical behaviour of the light REE (La - Nd), this phenomenon cannot be explained by an inorganic precipitation of REE. Likewise, the REE concentration of the water supplying the microbial mat did not show a positive La anomaly. This points to a biologically driven, selective fractionation of La by the bacterial community involved. The resulting biosignature may help to build a better understanding of modern and fossil microbially induced minerals and rocks, even in the absence of fossil remains and organic molecular indicators.

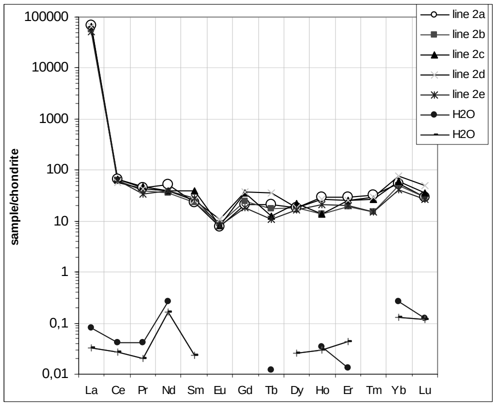

Figure 1: REE plot of mineral precipitates (line 2a-2e on the mineralized microbial mat), and the supplying water (H_2O).

References

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[4] Takahashi *et al*. 2005 *Chemical Geology* **219**, 53–67

Fe isotopes in siliceous igneous rocks: Evidence for fluid-rock interaction in plutons

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The average δ^{56}Fe value of bulk plutonic rocks (PR) with >70wt% SiO_2 is 0.18±0.08‰ (1-SD; n=19; data from Poitrasson and Freydier 2005 CG; Poitrasson 2006 EPSL; this study). In contrast, the average δ^{56}Fe value of bulk volcanic rocks (VR) with >70wt% SiO_2 is 0.02±0.07‰ (1-SD; n=6; data from Beard *et al*., 2003 CG; Beard and Johnson, 2004 GCA; this study). We have conducted a detailed study of minerals and bulk PR and VR samples using high-precision Fe isotope analysis (±0.06‰, 2SD) to evaluate the origin of these differences.

Magnetite in PR has consistently higher δ^{56}Fe values (δ^{56}Fe= +0.13 to +0.51‰) than its host rock, whereas VR magnetite has lower δ^{56}Fe values (-0.05 to +0.27‰). Silicates in both PR and VR have δ^{56}Fe values that fall within the range for mafic VR (δ^{56}Fe= -0.14 to +0.10‰). Fractionation factors between magnetite and silicates are larger for magnetite-biotite pairs in PR ($\Delta^{56}Fe_{mag\text{-}bt}$= +0.15 to +0.58‰) than for magnetite-silicate pairs in VR ($\Delta^{56}Fe_{mag\text{-}sil}$= -0.02 to +0.19‰, one at +0.34‰). Both are positively correlated with the δ^{56}Fe values of magnetite and show a weak negative correlation with those of silicates, but in PR they are also correlated with δ^{56}Fe of the host rock. The positive correlation between $\Delta^{56}Fe_{mag\text{-}bt}$ and bulk δ^{56}Fe in PR indicates that magnetite and bulk PR underwent open-system Fe exchange; the near-zero δ^{56}Fe values in VR indicate that high δ^{56}Fe values in silicic igneous rocks do not reflect crystal fractionation.

Open-system Fe isotope exchange in PR is influenced by cooling rates, Fe content, crystallization temperatures, fO_2 conditions, Fe diffusion rates in minerals, and interaction with late-stage exsolved fluids and/or saline hydrothermal fluids. There is no correlation between δ^{56}Fe and δ^{18}O values for PR, indicating that Fe was not mobilized by dilute meteoric fluids; the largest range in δ^{56}Fe values of minerals and bulk samples occurs in PR that have been mineralized. Fe isotope shifts likely occurred during exsolution of Fe-rich brines during solidification and deuteric alteration. The relatively high δ^{56}Fe values of magnetite from PR probably reflect sub-solidus isotopic equilibration upon cooling and the high Fe diffusion rates in this mineral relative to silicates. Exsolved Fe-chloride solutions will have low δ^{56}Fe values as compared to silicates or magnetite based on theory (Polyakov and Mineev, 2000 GCA; Schauble *et al*., 2001 GCA), suggesting that the remaining pluton will increase in its δ^{56}Fe value; this effect will be most significant in low-Fe, high-SiO_2 rocks, matching the observation that δ^{56}Fe values for bulk samples and magnetite in PR are higher at higher SiO_2 contents.