Geochemical variation of fracture carbonates in crystalline bedrock

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The current study is focused on trace and rare earth elements (REE) in carbonates from two fracture mineral generations formed at separate events at very different conditions, but in the same granitoid fracture system. Both generations are well-characterized and separation is based on paragenesis, $\delta^{13}C$, $\delta^{18}O$, $^{87}Sr/^{86}Sr$ and crystal habit [1]. The oldest generation was formed in the Proterozoic era (~1.4 Ga) [2] and the youngest in the Paleozoic era (~440-400 Ma) [2, 3].

In total, 41 calcite samples and 1 dolomite sample from 17 drill cores (up to 1 km depth), originating from the Swedish Nuclear Fuel and Waste Management Co's investigations in the Laxemar-Simpevarp area, SE Sweden, were analysed (with ICP-MS of calcite leachates).

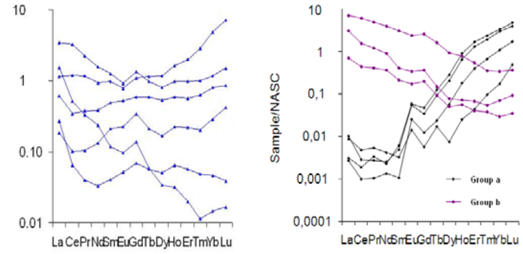

Figure 1: NASC-normalized REE patterns (REE_n) of Proterozoic carbonates (left) and Paleozoic carbonates (right), NASC according to [4].

Proterozoic carbonate shows two groups (a and b) which differ both in REE_n patterns and trace element compositions, accordingly: a) positive Eu_n- and La_n-anomalies, very low light REE concentrations, gradually enriched in REE_n from Gd_n to Lu_n, relatively high amounts of Sr, Mg and Fe; b) no Eu_n- or La_n-anomalies, gradual decrease in REE_n from La_n to Lu_n, depleted in other trace elements.

Paleozoic calcite shows larger REE_n variation including e.g. both slightly enriched heavy or middle REE_n, as well as gradual depletion from La_n to Lu_n. All Paleozoic calcite samples show low trace element concentrations and large Mn and Y variations. Observed trace element variations in different generations are predominantly caused by factors that influenced composition of parental solutions. Intense hydrothermal wall rock alteration in the Proterozoic, and microbial activity and descending organic-rich fluids in the Paleozoic might be these factors.

[1] Drake & Tullborg (2009) *Appl. Geochemistry* **23**, 715-732. [2] Drake *et al.* (2009) *Lithos* **110,** 37-49. [3] Alm *et al.* (2005) *Report* **SKB-R-05-66**. www.skb.se. [4] Haskin *et al.* (1968) *Pergamon* **vol.1**, 889-911.

Microbial sulfur isotope fractionation in littoral sediments: Interpreting $\delta^{34}S$ variability in Archean rocks

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Sulfur isotope variations in Archean rocks have been used to argue for the presence of sulfate reducing mircoorganisms as one of the earliest forms of life in the early Archean, back to 3.49 Ga [1-3]. Extensive laboratory pure culture and incubation studies with modern sediments have been used to support these interpretations with measured and predicted $\delta^{34}S$ values up to 49 ‰ for a single reduction step of sulfate to sulfide (e.g. [4, 5]). Here we expand the available data for isotope fractionation by natural communities of microorganisms, with an extensive laboratory flow through reactor study, that enables sulfate reduction under close to *in situ* conditions. Sediments were collected from a brackish marine estuary (Sheldt estuary, The Netherlands), a hypersaline soda lake (Mono Lake, California), a freshwater river (Scheldt, Belgium) and a shallow marine hydrothermal system (Vulcano, Italy).

Sulfate reduction rates (SRR) varied between 5 and 180 nmol cm^{-3} h^{-1} with corresponding isotope fractionations (ε), calculated as the difference between inflow sulfate and product sulfide, of 5 to 43 ‰. No overall relationship was found between SRR and ε , but weak correlations were found within the individual sites. Isotope fractionation data fall within the range predicted by standard models with lowest values at highest rates, but do not fall towards the smallest values predicted by the Rees model [5]. Our data indicate that relatively small isotope fractionations (<20 ‰) would be typical for sulfate reducing communities, under optimum growth conditions, and in the absence of competition from other metabolisms. Without an oxidative component in the sulfur cycle, widespread microbial sulfate reduction would result in minor $\delta^{34}S$ variations and may be more widespread in the Archean than previously envisaged.

[1] Shen *et al.* (2001) *Nature* **410**, 77–81. [2] Ueno *et al.* (2008) *GCA* **72**, 5675–5691. [3] Shen *et al.* (2009) *EPSL* **279**, 383–391. [4] Detmers *et al.* (2001) *Appl. Env. Microbiol* **67**, 888–894. [5] Rees (1973) *GCA* **37**, 1141–1162.