

Extreme isotope variation of microbe-related minerals at great depth in fractured granite

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Precipitation of ¹³C-depleted authigenic carbonate is a tracer of sulphate-dependent anaerobic oxidation of methane (AOM), particularly in marine sediments ($\delta^{13}\text{C}$ of c. -65 to -45‰, inherited from the CH₄-signature [1]). The related bacterial sulphate-reduction (BSR) involves large S-isotope fractionation [2]. Here we present new microanalytical data (SIMS) from Paleozoic carbonate ($\delta^{13}\text{C}_{\text{calcite}}$: -69‰ to +33‰) and pyrite ($\delta^{34}\text{S}_{\text{pyrite}}$: -25 to +66‰) in energy-poor fractured deep granitoid rocks from several sites in Sweden, revealing that sulphate reducers, methanogens and methane oxidisers are present, and have been so for several hundred million years. These results, together with other recently published studies, suggest that AOM, methanogenesis, and BSR are widespread processes in the deep biosphere and feature extreme, previously unseen isotopic variability in the minerals. The isotopic variability detected so far in the deep biosphere of the Baltic shield can be summarized accordingly. Calcite with anticipated Cenozoic age from SE Sweden has $\delta^{13}\text{C}_{\text{calcite}}$ of -125‰ to +5‰ [3]. The latter value is related to methane formed at shallower depth and the former to AOM at the transition to a deep-seated, -300 to -750 m, sulphate-rich water, i.e. reverse to sedimentary AOM. Variation within single calcite crystals of up to 109‰ suggests episodic AOM and micro-scale isotope distillation. Co-genetic BSR-related pyrite has a $\delta^{34}\text{S}$ -range indicating both closed-system distillation and extreme fractionation (-50 to +91‰ in Sweden and Finland [4,5]). Studies of ongoing precipitation in boreholes show that isotope distillation occurs in micro-environments (>60‰ increase over 50 μm pyrite growth) without affecting the bulk $\delta^{34}\text{S}_{\text{SO}_4}$ value [6]. Exploration of the deep subsurface thus gives novel insights to microbe-related isotope systematics in general and to micro-scale variability in energy-poor systems in particular.

[1] Aloisi et al. (2002), *EPSL* **203**, 195-203 [2] Deusner et al. (2014), *EPSL* **399**, 61-73 [3] Drake et al. (2015), *Nature Comm.* [4] Drake et al. (2013) *Geochim Cosmochim Acta* **102**, 143-161 [5] Sahlstedt et al., (2013) *Appl. Geochem.* **32**, 52-69. [6] Drake et al., (in press) *Geochim Cosmochim Acta*.