

Geochemical correlations of low-temperature calcite and groundwater in subsurface granite fractures

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Studies of calcite precipitated in bedrock fractures can reveal past groundwater conditions (e.g. [1]). Studies of low-temperature fracture calcite in Proterozoic or Archaean crystalline rocks are, however, very limited, mainly because this calcite usually is very fine-grained or forms rims on older, much more abundant, hydrothermal calcite and is thus difficult to distinguish. Knowledge of chemical characteristics and the correlation with groundwater chemistry is thus scarce for low-temperature calcite in these settings.

In the Proterozoic rock setting at Laxemar, SE Sweden, Quaternary glaciations and related marine transgressions and land uplift, have favoured calcite formation in the bedrock fractures due to repeated introduction and mixing of different waters [2]. We have sampled very fine-grained euhedral low-temperature calcite from these fractures from drill cores (~50 samples, down to 1 km depth) and analysed them for trace elements (using ICP-MS, LA-ICP-MS, WDS) and $\delta^{13}\text{C}$, $\delta^{18}\text{O}$, $^{87}\text{Sr}/^{86}\text{Sr}$, following detailed SEM-studies (e.g. CL) of crystal zonations. Existing groundwater data from the same borehole sections [2] enabled detailed direct calcite-groundwater comparison in terms of both geochemistry and isotopic ratios, e.g. depth-variations. Thereby we tested the utilisation of low-temperature fracture calcite in terms of understanding the groundwater history, also giving input to the understanding of trace element incorporation into calcite in natural systems.

Calcite $^{87}\text{Sr}/^{86}\text{Sr}$ -ratios correlated with the groundwater in all sections and ~50% of the sections showed $\delta^{18}\text{O}$ calcite-groundwater equilibria at ambient temperatures, which suggests potential scattered recent precipitation, e.g. indicated for intruding marine and meteoric water. Calcite isotope signatures also differ considerably from Proterozoic and Paleozoic calcite [3]. The calcite generally showed Me/Ca depth trends consistent with the groundwater for Mn, Mg and Sr. However, only Mn incorporation was in the range expected from experiments [4], which shows the difficulty of applying experimental data onto natural systems, and that $^{87}\text{Sr}/^{86}\text{Sr}$, $\delta^{18}\text{O}$, and Mn are the most representative proxies for low-temperature calcite-groundwater interaction.

[1] Tullborg *et al.* (2008) *Appl Geochem* **23**, 1881–1897. [2] Laaksoharju *et al.* (2009) *SKB report R-08-93*. [3] Drake & Tullborg (2009) *Appl Geochem* **23**, 715–732. [4] Curti (1999) *Appl Geochem* **14**, 433–445.

Recent and fossil chemosynthetic endosymbioses

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Metazoans with chemosynthetic endosymbionts are widespread in marine habitats and respective endosymbioses are known from seven recent animal phyla. However, very little is known about endosymbioses in fossil settings and, hence, ecological significance as well as evolution of endosymbioses in earth history. In the presented project, we investigate the ancient and recent bivalve fauna living at marine sedimentary oxic/anoxic interfaces. Two bivalve species collected from the same benthic environment a Mediterranean lagoon- were studied in detail. The diet of *Loripes lacteus* is based on thiotrophic gill symbionts. *Venerupis aureus* is a filter feeding bivalve without symbionts. Analysis of 16S rDNA and fluorescence-*in situ* hybridisation confirmed the presence of symbionts in *Loripes* gill tissue. In addition, the presence of one key enzyme of sulfur oxidation (APS-reductase) could be detected by immunofluorescence.

In search of biosignatures associated with thiotrophic chemosymbionts that could also be detected in fossil bivalves, we analysed the isotopic composition of shell lipids ($\delta^{13}\text{C}$) and the shell matrix protein conchiolin ($\delta^{13}\text{C}$, $\delta^{15}\text{N}$, $\delta^{34}\text{S}$). In recent shells and in gill tissue the stable isotopic ratio of carbon is more depleted in the thiotrophic *Loripes*: e.g., $\delta^{13}\text{C}_{\text{lipid}(18:1\text{FA})} - 32.2\%$, $\delta^{13}\text{C}_{\text{conchiolin}} - 25.4\%$ than in the filterfeeding *Venerupis*: $\delta^{13}\text{C}_{\text{lipid}(18:1\text{FA})} - 28.2\%$, $\Delta^{13}\text{C}_{\text{conchiolin}} - 21.8\%$. The isotopic ratios of nitrogen and sulfur are also more depleted in the chemosynthetic *Loripes* ($\delta^{15}\text{N}_{\text{conchiolin}} + 3\%$, $\delta^{34}\text{S}_{\text{conchiolin}} - 18.5\%$ in contrast to filter feeding *Venerupis*: $\delta^{15}\text{N}_{\text{conchiolin}} + 10.1\%$, $\delta^{34}\text{S}_{\text{conchiolin}} + 13.6\%$). Our results give evidence for a major influence of sulfide-oxidizing symbionts on the isotopic composition of organic matter of the host bivalve and are compared with respective data from fossil samples.