Geochemistry and nano-structure of putative filamentous microbes from the 3.24 Ga Sulfur Springs Group, Pilbara, Western Australia

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Pyritic filaments from one of Earth's oldest volcanic hosted massive sulfide (VHMS) deposits within the 3.24Ga Sulfur Springs Group, Western Australia, have been interpreted as thermophilic chemotrophic micro-organisms [1]. This interpretation [1] was based upon textural, morphological and inferred behavorial characteristics of the filaments. However, no geochemical evidence for biology has yet been reported, so an alternative explanation as abiotic mineral filaments remains to be discounted.

Here we revisit these putative filamentous micro-organisms, using a suite of high-spatial resolution techniques to investigate their geochemistry and nano-structure.

NanoSIMS elemental mapping reveals occassional enrichments of carbon within some of the pyritic filaments. Similar patterns of carbon enrichment are seen in *bona fide* pyritic filamentous microfossils from the 1.9 Ga Gunflint chert that were also pyritised by hydrothermal fluids.

In situ SIMS multiple sulfur isotope data show small but significant $+\Delta^{33}S$ (and $-\Delta^{36}S$) anomalies, consistent with previous bulk data from this VHMS deposit [2], indicating mixing of a hydrothermal fluid containing sulfur of magmatic origin ($\Delta^{33}S=0$) with circulating seawater containing reduced sulfur derived from atmospheric elemental sulfur ($+\Delta^{33}S$).

The nano-structure of the filaments was investigated in the TEM using focused ion beam (FIB)-milled ultrathin sections, and by 3D FIB-SEM nanotomography. Notable features include circular to elliptical filament cross sections mostly comprising single pyrite crystals, clustering of filaments in pairs and triplets, and a common preferred orientation of many filaments.

These data provide new insights into one of Earth's oldest black-smoker-type environments and potential associated life. The strength of evidence for the biogenicity of the filaments will be discussed.

[1] Rasmussen (2000) *Nature* **405**, 676-679. [2] Golding *et al.* (2011) in *Earliest Life on Earth: Habitats, Environments and Methods of Detection*, pp. 15-49.

Clumped isotopes, $\delta^{18}O$, $\delta^{13}C$, $\delta^{11}B$, $^{87}Sr/^{86}Sr$: A multiproxy approach applied to Silurian brachiopod shells

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The geochemical composition of fossil brachiopod shells reveals information about physical and chemical conditions of the paleo-ocean. We studied different stable isotopic systems on Silurian brachiopod shells from Gotland/Sweden to test their resistance against diagenesis and their use for paleoreconstructions.

In general, preanalyses (CL, SEM and trace element concentrations) of more than 60 shells indicate very good preservation. However, SEM investigations show that partial recrystallization occurred resulting in a patchwork of pristine and altered structures. $\delta^{18}O$ and $\delta^{13}C$, clumped isotope (Δ_{47}), as well as high resolution (LA-(MC)-ICP-MS) $\delta^{11}B$ and $^{87}Sr/^{86}Sr$ data of several brachiopod shells and their inner fillings (mudstones and sparitic cements) were measured. Clumped isotope temperatures range from 30°C to 70°C, indicating, that Δ_{47} values were partly reset during diagenesis. Because highest shell alteration temperatures correspond to those measured for the cements, we propose that ^{13}C-^{18}O clumps were reset during cement formation. Since no correlation between Δ_{47} and $\delta^{18}O$ values is obtained, we conclude that the bulk oxygen isotopic composition was not altered concurrently. Furthermore, $\delta^{11}B$ and $^{87}Sr/^{86}Sr$ values of the brachiopods seem to reflect pristine marine signatures. Therefore we suggest that the alteration of clumped isotope values occurred at low water-rock ratios, not influencing $\delta^{18}O$, $\delta^{13}C$, $\delta^{11}B$ and $^{87}Sr/^{86}Sr$ signals.

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