

High resolution synchrotron-based imaging of sulphur oxidation states in individual microfossils and contemporary microbial filaments

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Putative fossilized microorganisms are complex object which biogenicity is often difficult to establish unequivocally. Here, we present a combined use of μm -scale chemical imaging techniques as an attempt to obtain reliable biogenic signatures from prokaryote microfossils. For relevance to some of the earliest known microfossils, analyzed samples came from hydrothermal sites and emphasis was put on the study of sulfur behavior. We analyzed iron-oxide silicified fossil filaments of suspected biogenic origin from a fragment of an inactive hydrothermal chimney of the East Pacific Rise and, as possible living analogues, filamentous bacteria (most likely ϵ -Proteobacteria) collected from substrates exposed to a hydrothermal fluid vent at the Mid-Atlantic Ridge. Proton-induced X-ray emission mapping showed silicification has preserved the original composition of the microfossil from latter contamination. For both filament types, synchrotron X-ray micro-fluorescence analysis allowed to establish the major and trace elements composition, which is dominated by elements commonly involved in biological processes (such as Fe, S, Zn and Se). Synchrotron IR studies revealed the presence of amides and CH-radicals similar in the living and the fossilized filaments, which further confirms the biogenicity of the latest. Three species of sulfur (sulfide, SH-radicals and sulfate) were identified by X-ray absorption near-edge structure and their μm -scale spatial distribution (different for each species, outlining individual cells in the living bacteria) suggests that sulfur metabolism occurred in the living bacteria as well as in the microfossil. These results suggest that co-occurrence of different sulfur oxidation states within single microfossils can be preserved and could constitute a biogenic metabolic marker indicating S-metabolizing activities in antique hydrothermal systems.

Nitrogen quest in Archean metasediments of Pilbara, Australia

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Nitrogen can be a reliable biomarker in ancient sediments where all other evidences of former life have been destroyed. However, the interpretation of the N isotopic signal in terms of metabolic activity of ancient forms of life is rather difficult. Here, we present new N isotopic data measured in 3.2-3.5 Ga cherts from North Pole, Pilbara craton, Western Australia. Sediments and hydrothermal-derived rocks from this area show different forms of possible ancient life: stromatolites and "bacteria-like" filamentous structures. Samples analyzed include: a silicified stromatolite from the Trendal Formation (Pi-02-47), a brechified hydrothermal chert from the Apex Formation (Pi-02-07); a barite vein (Pi-II-08-00) and two black chert veins (Pi-85-00 and Pi-47-00) from the North Pole Chert-Barite hydrothermal system. Sample Pi-47-00 is intrusive into pillow-basalts underlying the Chert-Barite system. Samples were analyzed for N and Ar isotopes and C and H₂O total amounts. Analyses were done by combustion steps (25-100°C) to discriminate the N components. Nitrogen in stromatolites is dominated by an atmospheric component ($\delta^{15}\text{N}$ of -1.4 to -0.3‰ and $^{40}\text{Ar}/^{36}\text{Ar} = 300-303$) which is likely fractionated modern-air included in carbonates. Apex Chert shows a high $\delta^{15}\text{N}$ component ($\delta^{15}\text{N} = +25\text{‰}$) released at 650 °C together with C, that could be related to alteration. At high temperature, a second component shows $\delta^{15}\text{N}$ close to 0‰, accompanied by radiogenic argon. Depleted- ^{15}N components released at high temperature occur in barite Pi-II-08-00 ($\delta^{15}\text{N} = -1.7 \pm 0.8 \text{‰}$), accompanied by large amounts of H₂O and C. The negative N signature in barite, though small, is an indigenous one, unlike the stromatolite case, and it could be related to micrometric fluid inclusions in sulfur-iron minerals. The most intriguing result is the ^{15}N -depleted component ($\delta^{15}\text{N} = -8.0 \pm 0.5\text{‰}$), accompanied by large amounts of ^{40}Ar * ($^{40}\text{Ar}/^{36}\text{Ar} = 33,000 \pm 1000$) and a C/N ratio of 83 ± 26 . These ratios are close to those found in the mantle (MORBs), suggesting the occurrence of mantle fluids as a source of inorganic N, possibly metabolized by chemoautotrophic bacteria (Pinti and Hashizume, 2001).

Reference

Pinti, D. L. and Hashizume, K. (2001) *Precambrian Res.* **105**, 85-88.