

Microbial utilization of the products of serpentinization at the Lost City hydrothermal field

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The Lost City vent field (30°N, Mid-Atlantic Ridge) is characterized by extreme conditions: venting of pH 9-11, <90°C, metal-poor and hydrogen-rich fluids and formation of carbonate-brucite hydrothermal structures that reach up to 60 m high. Fluid-rock reactions in the underlying ultramafic rocks result in high concentrations of a number of chemical species proposed to be of abiological origin (hydrogen, methane, C₂⁺ alkanes, formate) [1, 2]. Lost City is a possible analog to Early Earth or Martian environments and is potentially important to understanding the origin of life. For these reasons, a primary research focus has been to investigate the microbial communities that are sustained in this environment and examine their potential link with abiotically produced carbon species. We demonstrate here that in locations where microbial sulfate reduction is believed to be important, up to 50% of the microbial biomass in the carbonate chimneys is derived from mantle carbon. Conversely, mantle carbon contributes only ~10% of the biomass in locations that are minimally impacted by sulfate reduction. We argue that the difference can be attributed to the ability of sulfate reducing bacteria to convert formate to dissolved inorganic carbon which is then accessible by other microbial species such as the more abundant *Methanosarcinales* [3, 4].

[1] Proskurowski, G. *et al.* (2008) *Science* **319**, 604–607. [2] Lang, S. Q. *et al.* (2010) *Geochimica et Cosmochimica Acta* **74**, 941–952. [3] Schrenk *et al.* (2004) *Environmental Microbiology* **6**, 1086–1095 [4] Brazelton *et al.* (2006) *Applied & Environmental Microbiology* **72**, 6257–6270.

Natural organic matter as major sorbent for arsenic in a peatland

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Arsenic (As) is a potentially toxic trace element, which is typically associated with metal-(hydr)oxides, silicates or sulfides in organic-rich soils and sediments. Natural organic matter (NOM) has also been suggested as important sorbent for As [1, 2] but the binding mechanisms are still elusive. In order to investigate the importance of NOM relative to reactive Fe species for As binding, we studied the solid-phase speciation of As and Fe in a minerotrophic peatland in Switzerland that contains high natural concentrations of As.

Anoxic peat samples were analyzed by bulk As and Fe K-edge X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) spectroscopy at ~80 K. The EXAFS spectra were analyzed by means of principal component analysis and target testing followed by linear combination fitting. We focused our speciation analysis on shallow (<0.4 m) peat layers with 358–1810 mg As kg⁻¹ and peat layers from greater depth (1.5–2.6 m) with 106–469 mg As kg⁻¹. Both depth intervals differed significantly in the molar S/Fe ratio of the peat: 0–1 at depths <0.4 m and 2–7 for 1.5–2.6 m depth.

Speciation analysis of As revealed that close to the peat surface As was mainly present as realgar (As₄S₄), As(III)-NOM complexes, and As(III)/As(V) sorbed to Fe(III)-(hydr)oxides. In the deep peat layers, however, As was entirely in its trivalent oxidation state and mostly coordinated to 2–3 S atoms of NOM ($R_{As-S} = 2.26 \text{ \AA}$). The Fe speciation in the upper peat layers was dominated by Fe(III)-(hydr)oxides, chlorite, and Fe(III)-NOM complexes, indicating the presence of low-Fe/high-S microenvironments with high As activities. In the deep peat layers Fe(III)-NOM complexes and pyrite (FeS₂) were detected as main Fe species. Although these phases were shown or hypothesized to immobilize As(III), nearly all As was bound to sulfhydryl groups of NOM.

Our results suggest that As binding to sulfhydryl groups of NOM is the major As-NOM interaction scheme under sulfate-reducing conditions. This mechanism seems to impair As sequestration pathways involving Fe species such as the formation of As-bearing pyrite, the precipitation of arsenopyrite (FeAsS), or the formation of ternary As(III)-Fe(III)-NOM complexes.

[1] Buschmann *et al.* (2006) *Environ. Sci. Technol.* **40**, 6015.

[2] Rothwell *et al.* (2010) *Environ. Sci. Technol.* **44**, 8497.