Iron and sulfur speciation in the Arvadi Spring, a model habitat for the Proterozoic ocean

E. KOEKSOY, A. SUNDMAN, AND A. KAPPLER

Geomicrobiology, Center for Applied Geoscience, University of Tuebingen, Sigwartstrasse 10, 72074 Tuebingen, Germany (*correspondance: elif.koeksoy@uni-tuebingen.de)

The Arvadi Spring in Switzerland is an unique model environment for ocean biogeochemistry in the Proterozoic eon (~2.5 to 0.543 Ga) [1]. The pH-neutral, highly mineralized spring links the iron and sulfur biogeochemical cycles as it contains oxidized and reduced iron and sulfur species at the same time. While the spring water contains μM concentrations of sulfide and dissolved Fe(II), it is enriched in bicarbonate and sulfate. The spring sediment is covered by red, iron-rich mineral precipitates and white, sulfur-rich flocks probably originating from abiotic/microbial sulfide oxidation and/or microbial sulfate reduction [2]. Cultivation-based microbial studies showed that iron- and sulfur-metabolizing bacteria co-exist in this environment. The presence of reduced redox-sensitive S- and Fe-species under highly oxic conditions may represent conditions in the oxic surface waters of the late Proterozoic ocean. [1]. Hence, determining the exact speciation of iron and sulfur in the Arvadi Spring, will provide knowledge about substrates, intermediates and end products that could have been present in the (Neo-)Proterozoic ocean.

Red and white flocks were collected under anoxic conditions, frozen and freeze-dried prior to chemical characterization and spectroscopic analysis by synchrotron based X-ray absorption spectroscopy and ^{57}Fe Mössbauer spectroscopy. The samples showed great heterogeneity at the m, cm, mm and μm scale. Based on linear-combination-fitting, we found that the red precipitates consisted of a variety of Fe-species, e.g. organically complexed Fe(III) and different Fe(III) oxyhydroxide minerals including ferrihydrite, lepidocrocite and goethite. The white flocks mainly consisted of elemental sulfur, i.e. in accordance with previous studies [2]. This speciation study will be used to extend current models on Proterozoic Fe-S biogeochemistry in order to better understand how biotic and abiotic processes influenced the ancient iron and sulfur cycles.

[1] Koeksoy *et al*. (2016) *Int. J. Astrobiol*., in press.
[2] Strauss *et al*. (2016) *Isot. Environ. Health Stud*., in press.