

## Geochemical behavior of (thio)arsenates with Fe-minerals

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Under microbially-mediated sulfate (SO<sub>4</sub>) reducing conditions, the mobility of arsenic (As) in iron (Fe) rich sediments is influenced by the transformations of Fe minerals and changes in aqueous As speciation. Hence, to predict As mobility in complex biogeochemical systems, the sorption of aqueous As species to various Fe mineral phases should be fully understood. However, despite the accumulating evidence that thioarsenates dominate As speciation under a variety of environmental conditions, their sorption behaviour in sediments is poorly known. We used batch experiments to measure sorption of six individual As species in suspensions of 2-lines ferrihydrite (2L-Fh), hematite, goethite, mackinawite (FeS<sub>m(s)</sub>) and pyrite. The table below shows the results for FeS<sub>m(s)</sub> and 2L-Fh. As can be seen, there are marked differences in the partition coefficients of the different soluble As species.

	FeS <sub>m(s)</sub>	2L-Fh
Arsenate	5	1600
Arsenite	3	50
Mono-thioarsenate	0.1	12
Di-thioarsenate	310	70
Tri-thioarsenate	0.2	150
Tetra-thioarsenate	1.5	120

**Table:** Partition coefficients (K<sub>d</sub>; L g<sup>-1</sup>) for As sorption to selected Fe-minerals at pH 7 and ionic strength = 0.05M.

We also used flow-through reactors (FTRs) to look at the formation and sequestration of thioarsenates in Fe-rich and Fe-poor lake sediments run under SO<sub>4</sub> reducing conditions. The FTRs were supplied with either soluble arsenate or soluble arsenite. We monitored SO<sub>4</sub>, total sulfide, zero-valent sulfur, Fe as well as pH and E<sub>h</sub> in the outflow of the FTRs. The results indicate that arsenate is first reduced to arsenite, which is then sulfidized to thioarsenates. Thioarsenates only dominated As speciation in the FTR outflow of the Fe-rich sediments. In addition, As was released as mono-thioarsenate, in line with the observation that mono-thioarsenate is the least strongly bound to Fe-minerals (see Table). These preliminary observations are currently being used to improve existing reactive-transport models for the fate of As under sulfate reducing conditions.

## Metatranscriptomics of the green sulfur bacteria in a meromictic Swiss lake (Lago di Cadagno)

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Lake Cadagno in the Swiss Alps is a potential modern analog of the early ocean. The lake is permanently stratified with anoxic water containing sulfate (1.5 - 2.0 mM) and sulfide below the chemocline. The sulfidic water column contains high concentrations of phototrophic sulfur bacteria (peak concentrations more than 250 µg/L BChl *e*). We have previously shown that the bacterial community in this layer is dominated by the green sulfur bacterium *Chlorobium clathratiforme* (up to 70% of recovered bacterial 16S rRNA gene sequences in a clone library [1]). Several lines of molecular sequence evidence suggest that this population is clonal and has replaced the previously dominant purple sulfur bacteria over the last decade [1]. This feature makes the lake a highly suitable site for metatranscriptomic studies of natural populations.

Samples were collected at the top of the chemocline during the day (1) and at night (2) and at a depth where light intensity precludes active photosynthesis (3). The mRNA was converted to cDNA and subjected to high-throughput sequencing. As expected from previous results [1,2] a high proportion of the sequences could be matched to the genome of *Chlorobium clathratiforme* BU-1 which was isolated from a lake in Southern Germany. There were relatively small differences in the normalised transcript levels between the 3 samples. The highest transcript levels were observed for the major protein of the light-harvesting chlorosomes, *csmA*, and the gas vesicle protein *gvpA*.

[1] Gregersen *et al.* (2009) *FEMS Microbiol. Ecol.* **70**, 30-41.

[2] Habicht *et al.* (2011) *Environ. Microbiol.* **13**, 203-21