

## Spatial distribution of As(V) in cell-mineral aggregates formed by NO<sub>3</sub><sup>-</sup>-reducing Fe(II)-oxidizing bacteria

MARTIN OBST<sup>1\*</sup>, TINA LÖSEKANN-BEHRENS<sup>2</sup>, SEBASTIAN BEHRENS<sup>2</sup>, ANDREAS KAPPLER<sup>2</sup>, CLAUDIA PANTKE<sup>2</sup>, TOLEK TYLISZCZAK<sup>3</sup>, ADAM P. HITCHCOCK<sup>4</sup>

<sup>1</sup>Environmental Analytical Microscopy, ZAG, University of Tuebingen, Germany, martin.obst@uni-tuebingen.de

<sup>2</sup>Geomicrobiology, ZAG, University of Tuebingen, Germany, tina-loesekann-behrens@uni-tuebingen.de, sebastian.behrens@uni-tuebingen.de, andreas.kappler@uni-tuebingen.de

<sup>3</sup>Molecular Environmental Science, Advanced Light Source, LBNL, Berkeley, USA, tolek@lbl.gov

<sup>4</sup>Canada Research Chair in Materials Research, CLS-CCRS, B.I.M.R, McMaster University, Hamilton, Canada, aph@mcmaster.ca

Ground water contamination with As is an environmental problem affecting human health [1]. Sorption of As to Fe(III)-(oxyhydr)oxides, is one of the most efficient mechanisms for immobilizing As in the environment. Fe(II)-oxidizing bacteria have recently been identified as possible contributors to As immobilization [2]. The objective of this study was to map the partitioning of As at various stages of precipitation [3] and to clarify the detoxification mechanisms.

The nitrate-reducing, Fe(II)-oxidizing *Acidovorax* strain BoFeN1 was cultured in presence of 0.2-1 mM arsenate. Samples were prepared anoxically for spectromicroscopic identification and mapping of the cell-mineral aggregates formed during biogenic Fe(II) oxidation. Chemical speciation of As was measured at sub-100 nm spatial resolution by scanning transmission (soft) X-ray microscopy (STXM) using X-ray fluorescence (XRF) detection at beamline 11.0.2, Advanced Light Source (ALS), Berkeley USA.

Biogenic Fe-precipitates formed at different stages of microbial Fe(II) oxidation were found to vary significantly in their affinity for arsenate sorption/coprecipitation. The cytoplasm and the periplasm of cells cultured in the absence of Fe as well as periplasmic Fe(III) precipitates formed when cultivated with Fe(II) were highly depleted in As(V). No reduction of arsenate to arsenite was detected, which would be an essential step in the conventional As-detoxification systems. These results together indicate a yet unknown, efficient mechanism of either hindering As(V) from entering the cytoplasm through the phosphate transport mechanisms, or an arsenate-specific efflux pump. Although present in the genome of BoFeN1, the *arsC*, *arsA* and the *ARR3* genes which are involved in the conventional detoxification, seemed not to play a role in the As depletion of the cells. In contrast, cell-associated extracellular precipitates of mineral-filled cell-residues of late stages of Fe(II) oxidation were enriched in their As(V)-content.

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[1] Smedley (2002) *Appl. Geochem.* **17**, 517-568. [2] Hohmann (2010) *Environ. Sci. Tech.* **44**, 94-101. [3] Hitchcock (2012) *Environ. Sci. Tech.*, DOI: 10.1021/es202238k.

## Origin of Anomalous Isotope Effects in Photo- and Thermo-chemical Reactions of Organosulfur Compounds

HARRY ODURO<sup>1,2\*</sup>, ANDREW WHITEHILL<sup>1</sup>, JAMES FARQUHAR<sup>2</sup>, ROGER E. SUMMONS<sup>1</sup>, AND SHUHEI ONO<sup>1</sup>

<sup>1</sup>Department of Earth, Atmospheric, and Planetary Sciences, Massachusetts Institute of Technology, 77 Massachusetts Avenue, Cambridge, MA 02139-4307, USA, mit.edu.

<sup>2</sup>Department of Geology and Earth System Science Interdisciplinary Center (ESSIC), University of Maryland, College Park, Maryland 20742, USA, umd.edu.

(\*Author Presenting : [Hoduro@mit.edu](mailto:Hoduro@mit.edu))

### 15f. Organic sulfur in the Earth System

There is overwhelming hypothesis about the importance of sulfur mass-independent isotopic (MIF) signatures  $\Delta^{33}\text{S}$ ,  $\delta^{34}\text{S}$ , and  $\Delta^{36}\text{S}$  observed in the early Earth's history<sup>[1]</sup>. The accumulation of MIF signals in ancient rocks has been linked to UV photolysis of SO<sub>2</sub> that penetrated deep in the Earth's atmosphere during the Archean<sup>[2]</sup>. Recently, it has been argued that thermochemical sulfate reduction (TSR) produce anomalous sulfur-33 compositions<sup>[3]</sup>, but the source of this anomalous isotope signature have been suggested to result from a magnetic isotope effects (MIE) and the anomaly is limited to the magnetic isotope <sup>33</sup>S and not on <sup>36</sup>S<sup>[4]</sup>.

In order to elucidate the mechanisms and differentiate between the sulfur isotope anomalies produced by photochemical and thermochemical reactions. We carried out a series of UV photolysis experiments of SO<sub>2</sub> with methane (CH<sub>4</sub>), acetylene (C<sub>2</sub>H<sub>2</sub>), and ethylene (C<sub>2</sub>H<sub>4</sub>). The photolysis produced a number of methylated sulfoxide aerosol species (such as dimethylsulfone - DSO and methanesulfonic acids -MSA). The different isotope patterns are observed for the radiation under 190 to 220 and 250 to 330 nm UV absorption bands. But all shows anomaly in both S-33 and S-36. New thermochemical experiments of model organosulfur compounds demonstrate that thermolysis of terminal thiy (such as glutathionine) and aromatic thiane (1,3,5-trithiane) compounds can also produce significant  $\Delta^{33}\text{S}$  anomalies. These <sup>33</sup>S enrichments are attributed to a magnetic isotope effect (MIE) that affects only odd isotopes via the formation of thiy-disulfide ion-radical pairs.

The findings in this thermal experiment are not consistent with multiple sulfur isotope trends of extracted methylated sulfoxide compounds observed in SO<sub>2</sub>-CH<sub>4</sub>-C<sub>2</sub>H<sub>2</sub>-C<sub>2</sub>H<sub>4</sub> photochemical experiments, which exhibit significant <sup>36</sup>S anomalies and further the assertion that the early Archean record does not reflect this thermally induced radical sulfur chemistry. Detailed reaction mechanisms and processes leading to photochemical and thermochemical S-MIF signals will be presented.

#### References:

- [1] Kaufman A.J. et al., 2007: *Science* **317**, 1900-1903.
- [2] Farquhar J., et al., 2001: *J. Geophys. Res.* **106**, 32829 – 32839.
- [3] Watanabe Y., et al., 2009: *Science* **324**, 370-373.
- [4] Oduro et al., 2011: *PNAS* **108**, 17635-17638.