

## Evaluation of calcium binding and carbonate precipitation by cyanobacteria in aquatic and terrestrial habitats by XAFS

C.R. OMELON\*, I.M. POWER AND G. SOUTHAM

Department of Earth Sciences, The University of Western Ontario, London, Ontario, N6A-5B7, Canada  
(\*correspondence: comelon@uwo.ca)

Bacteria are known to play a major role in geochemical cycling of metals and biosorption of metals, however there is little understanding of these processes in the context of cyanobacteria. Prokaryotic phototrophs are widespread in terrestrial and aquatic habitats, and contribute significantly to primary production in all ecosystems. An interesting aspect for autotrophic metabolism is the presence of CO<sub>2</sub> concentrating mechanisms (CCMs) to maintain high rates of CO<sub>2</sub> fixation for photosynthesis under conditions of low [CO<sub>2</sub>], which enables them to survive under a wide range of environmental conditions [1]. CCMs consist of active transport systems to accumulate inorganic carbon (Ci) within the cell, with Ci uptake as either HCO<sub>3</sub><sup>-</sup> or CO<sub>2</sub> by transporters. Activation of HCO<sub>3</sub><sup>-</sup> transporters leads to production of OH<sup>-</sup> that is expelled from the cell, leading to cyanobacterial biomineralization observed as whiting events [2], and may also be instrumental in the formation of carbonate microbialites in habitats such as Pavilion Lake, Canada [3].

Cyanobacteria associated with Pavilion Lake microbialites as well as from a range of terrestrial habitats were examined for evidence of calcium binding and carbonate precipitation by XAFS. Preliminary examination of the Ca K-edge of these cyanobacteria exposed to high dissolved calcium concentrations revealed immediate binding to cell surfaces in all cases. In addition, cyanobacterial cultures exposed to high [Ca<sup>2+</sup>] for ~6 months produced carbonate precipitates and distinct XAFS spectra: cultures isolated from Pavilion Lake are similar to that of calcite, whereas those from terrestrial habitats appear unrelated to carbonate mineral standards examined in this study. This suggests that calcium bound to cyanobacterial cell surfaces can produce distinctive XAFS spectra that may or may not relate to observed carbonate precipitates.

[1] Badger *et al.* (2006) *Journal of Experimental Botany* **57**, 249–265. [2] Thompson & Ferris (1990) *Geology* **18**, 995–998. [3] Laval *et al.* (2000) *Nature* **407**, 626–629.

## Multiple sulfur isotope evidence for deep biosphere in altered oceanic basalt and peridotite basement rocks

SHUHEI ONO<sup>1</sup>, NICOLE KELLER<sup>1</sup>, OLIVIER ROUXEL<sup>2</sup>  
AND JEFF ALT<sup>3</sup>

<sup>1</sup>Department of Earth, Atmospheric, and Planetary Sciences, Massachusetts Institute of Technology, 77 Massachusetts Avenue, Cambridge, MA 02139, (sono@mit.edu, nkeller@whoi.edu)

<sup>2</sup>Marine Chemistry & Geochemistry Department, Woods Hole Oceanographic Institution, Woods Hole, MA 02543, USA, (orouxel@whoi.edu)

<sup>3</sup>Department of Geological Sciences, University of Michigan, Ann Arbor, MI 48109, USA, (jalt@umich.edu)

We present new high-precision multiple sulfur isotope data of altered oceanic basaltic and serpentinized ultramafic basement rocks. Bulk-rock sulfur analyses yield a wide range of δ<sup>34</sup>S<sub>CDT</sub> values (–44 to +15 ‰) but yield distinct Δ<sup>33</sup>S\* values depending upon their host rock types; sulfides from serpentinite sites (ODP sites 897 and 895) are characterized by excess <sup>33</sup>S relative to seawater sulfate (Δ<sup>33</sup>S +0.16 to +0.05 ‰, analytical precision ± 0.01 ‰), whereas sulfides from basaltic basement sites (801C and 1301B) are depleted in <sup>33</sup>S (Δ<sup>33</sup>S - 0.06 to 0.05 ‰). We propose that enriched Δ<sup>33</sup>S values in serpentinites are linked to the formation of secondary sulfide through closed-system microbial sulfate reduction, where 10 to 90 % of sea-water sulfate are reduced with a large isotope fractionation factor of 40 - 70 ‰. In contrast, the depleted Δ<sup>33</sup>S values for secondary sulfides from basaltic sites suggest open-system sulfate reduction, also with a large fractionation factor of up to 80 ‰ consistent with microbial sulfate reduction. These large isotope fractionation factors are required to account for the measured range of Δ<sup>33</sup>S values. A group of samples from 1301B and 895 shows near-zero Δ<sup>33</sup>S values (± 0.02 ‰), suggesting these could have been formed by high temperature water-rock reactions during the early stages of oceanic crust alteration. The closed- versus open-system behavior of sulfur alteration is related to the higher H<sub>2</sub> production capacity of ultramafic compared to basaltic basement rocks. These new multiple sulfur isotope data add a new dimension that is critically needed to constrain the temperature, water-rock ratios as well as the extent and mechanisms of sulfate reduction during high to low temperature alteration of oceanic basement rocks, thus offering a unique tool to trace the extent and activity of the putative deep sulfur biosphere in the oceanic lithosphere.

\* Δ<sup>33</sup>S = ln (δ<sup>33</sup>S+1) – 0.515 × ln (δ<sup>34</sup>S+1)