

## Barium and Sr isotopic fractionation during their uptake by cyanobacteria forming intracellular carbonates

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The non-essential trace alkaline earth elements Ba and Sr can be hazardous for ecological systems depending on their dissolved concentration and speciation in solution. Their toxicity is increased through their potential substitution with Ca in biogeochemical processes. In order to characterize the mechanisms controlling the uptake of Ba and Sr into cells, their stable isotope fractionation was studied during the growth of *Gloeomargarita lithophora*, a cyanobacterium that selectively hyperaccumulates alkaline earth metals (Ba>Sr>Ca) which are intracellularly precipitated as amorphous carbonates [1, 2]. Experiments were performed in open batch reactors during bacterial growth (700 h) with a non-buffered medium (initial pH  $\approx$  7.5) and an initial Sr, Ba and Ca exposure of *ca* 260  $\mu\text{mol L}^{-1}$ . Temperature and luminosity were kept constant at 30 °C and 30  $\mu\text{mol s}^{-1} \text{m}^{-2}$ , respectively. During the exponential growth of *G. lithophora*, the expected sequence of elemental uptake was observed (Ba before Sr before Ca). Within the cells, both Ba and Sr were principally stored in intracellular carbonates, which were found to be enriched in the lighter isotopes compared to the initial solution, following a Rayleigh distillation trend. The observed fractionation of both Ba and Sr isotopes is larger than for inorganically precipitated carbonates [3,4]. After >97% of Ba and Sr were intracellularly incorporated, the isotopic composition of the ambient solution became lighter, suggesting an isotopic re-equilibration. This is consistent with electronic microscopic observations which show partial dissolution of the carbonate inclusions. However, no elemental net efflux was observed. These unexpected results stress out the complexity of biological uptake of alkali-earth metals, and provide insight into Sr and Ba cycling in nature.

[1] Couradeau *et al.* (2012) *Science* **336**, 459-462. [2] Cam *et al.* (2015) *Geochim. Cosmochim. Acta* **161**, 36-49. [3] Mavromatis *et al.* (2016) *Geochim. Cosmochim. Acta* **190**, 72-84. [4] Böhm *et al.* (2012) *Geochim. Cosmochim. Acta* **93**, 300-314.