Impact of diurnal cycles on intracellular precipitation of carbonates by cyanobacteria

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Diverse and ubiquist species of cyanobacteria have been shown to biomineralize intracellular amorphous carbonates [1,2]. In order to evaluate the importance of this process in the Ca and C biogeochemical cycles, it is crucial to assess the environmental parameters (i.e. pH, pCO_2, pO_2) impacting the rates of this process. For this purpose, we studied intracellular amorphous Ca-carbonate formation by *Gloeomargarita lithophora*. This cyanobacterium hyperaccumulates alkaline earth metals and shows selective uptake of Ba>Sr>Ca [3,4]. The first set of experiments was performed in batch reactors open to atmosphere, under an initial Ca exposure of 250 µmol L^{-1} at 30 °C during 120 h under a 6:6 h light (30 µmol s^{-1} m^{-2}):dark circadian cycle. The impact of diurnal variations was monitored by *in situ* measurements of aCa^{2+}, pH, pO_2, pCO_2, and conductivity using selective probes at a high temporal resolution (<1min). Other physicochemical parameters such as alkalinity, DOC and elemental concentrations were analysed after one-off sampling. Exposure to Sr at 250 µmol L^{-1} for 24 h under continous dark or continuous light was also performed to detect the potential formation of new intracellular carbonates using a combination of bulk chemical measurements on the solutions and observations of the cells by STEM-HAADF coupled with EDX mapping. As a result, we obtained an unprecedented record of the chemical variations of the solutions upon cell growth and evidenced specific day and night trends as shown consistently by bulk and microscopy analyses. Coupled with geochemical models, elemental and microscopy analyses stress out the complexity of alkali-earth metals biomineralization, questions its connection with photosynthesis and open new insights on its impact on Ca and C cycling in the environment.

[1] Couradeau et al. (2012) *Science* **336**, 459-462. [2] Benzerara et al. (2014) *PNAS* **111**, 10933-10938. [3] Cam et al. (2015) *Geochim. Cosmochim. Acta* **161**, 36-49. [4] Blondeau et al. (2018) *Chem. Geol.* **483**, 88-97.