Intracellular calcification by cyanobacteria: a significant controlled biomineralization process

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Cyanobacteria had a pivotal role on several global geochemical cycles throughout Earth's history in particular, by biomineralizing $CaCO_3$. Calcification by cyanobacteria has so far been considered exclusively as an induced extracellular biomineralization process. However, we recently discovered deep-branching cyanobacteria that form intracellular amorphous Ca-Mg-Sr-Ba carbonates [1]. The existence of such intracellularly calcifying cyanobacteria may modify significantly our view on the past and modern role of cyanobacteria in the formation of carbonate deposits and the degree of control they achieve on this geochemically important process. However, several questions remain open: is this biomineralization process widespread phylogenetically or restricted to one single species? Does it occur under specific or diverse environmental conditions? To what extent do phases formed intracellularly by these cyanobacteria differ from abiotically-formed carbonates?

We will address these questions using diverse approaches including high spatial and spectral resolution spectromicroscopies and molecular biology.

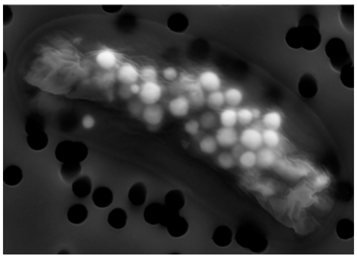

Figure 1: SEM image of *Candidatus* Gloeomargarita lithophora.

[1] Couradeau, Benzerara, Gérard, Moreira, Bernard, Brown Jr.., López-García (2012), Science **336**, 459-462.

Polysulfides as intermediates in the bacterial metabolism of stored sulfur

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Zero-valent sulfur is a key intermediate in the microbial oxidation of sulfide to sulfate. Many sulfide-oxidizing bacteria therefore produce and store large amounts of sulfur intra- or extracellularly. It is still not well understood how the stored sulfur is metabolized as the most stable form of S^0 under standard biological conditions – orthorhombic α-sulfur – can most likely not be utilized by bacterial enzymes.

In this study, the speciation of sulfur in single cells of living bacteria was investigated by Raman spectroscopy. Four different strains of *Beggiatoa* were used to compare the chemical nature of sulfur under various ecological and physiological conditions. Results showed that in microaerobic cultures at circumneutral pH, stored intracellular sulfur consisted of S_8 rings and inorganic polysulfides (S_n^{2-}). Linear sulfur chains were detected during both the oxidation and reduction of stored sulfur suggesting that S_n^{2-} species comprise a pool of activated sulfur utilized by bacteria. The formation of S_n^{2-} results from the cleavage of sulfur rings, either biologically by membrane-bound thiol groups and glutathione or chemically by the strong nucleophile HS^-. It is likely that *Beggiatoa* in the environment utilize both of these mechanisms to generate S_n^{2-} intermediates as they migrate vertically between oxic and sulfidic sediment zones.

With Raman spectroscopy it was possible to further track the fate of sulfur during its oxidation to sulfate. Unexpectedly high concentrations (up to ~2 M) of internal sulfate were detected in *Beggiatoa* sp. Although the reason for the intracellular accumulation of sulfate remains unknown we could show for the first time that *Beggiatoa* contain sulfate in concentrations 100-1,000-fold higher than that of the external environment.

DOI:10.1180/minmag.2013.077.5.2
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