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Molecular insights into formation of bacterial intracellular amorphous calcium carbonate (ACC) by X-ray absorption spectroscopy

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Biomineralization of intracellular amorphous calcium carbonate (ACC) is a fascinating example of how organisms structure their biominerals to obtain a function that otherwise would not have been possible abiotically. Recent studies have shown that ACC is widespread in diverse bacteria (e.g. [1], [2]). Detection of biogenic ACC in cyanobacteria was particularly interesting because they are the only known ACC-forming bacteria that are culturable in the laboratory. While formation of ACC in bacteria has a wide range of biogeochemical implications [1], little is understood about the structural aspects of bacterial ACC. Pure abiogenic ACC is highly unstable, transforming within minutes to crystalline calcium carbonate polymorphs such as calcite, or aragonite. However, ACC found in bacteria remains relatively stable intracellularly with no obvious spontaneous transformation to crystalline phases such as calcite. Numerous organic and inorganic additives have been shown to promote this stabilization, but the specific interactions that inhibit crystallization of ACC over a time scale necessary for its utilization in bacteria remain largely unknown.

One of the main limitations in understanding properties and behavior of cyanobacterial ACC is the lack of knowledge of its structure. This is in part because ACC in bacteria is prone to loss during sample preparation or once exposed to extracellular solutions, and therefore requires the use of in-situ techniques that could probe ACC within intact cell at atomic scale. One such tool for the study of relatively disordered mineral phases such as ACC is X-ray absorption spectroscopy (XAS) comprising X-ray absorption near-edge spectroscopy-extended X-ray absorption fine structure (XANES-EXAFS). Here, using Ca-K edge XANES, we present an approach to detect ACC in intact cyanobacteria cells. Further, we will discuss these findings in the context of quantifying ACC-forming cyanobacteria in the environment. Secondly, we characterized short-range order of cyanobacterial ACC using Ca-K edge EXAFS and discuss the results in the framework of ACC polymorphism. Altogether, findings of this work will provide new perspectives on the formation, occurrence and stability of ACC in bacteria in the environments.

[1] Monteil C et al (2020). ISME J, https://doi.org/10.1038/s41396-020-00747-3

[2] Benzerara K et al (2022), GBE, https://doi.org/10.1093/gbe/evac026