Strontium Sequestration in Biominerals: From Cellular Dynamics to Probing Local Structure Evolution

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In many organisms, the chemical similarity of calcium, strontium, and barium leads to uptake of the latter two *via* Ca-transport proteins. This can be beneficial, as in Sr-ranelate therapy of osteoporosis, but can lead to serious consequences when we are exposed to radioactive ^{90}Sr, a "bone-seeker" with a half-life of ~30 years. The safe, selective removal of ^{90}Sr from spent reactor fuels is thus critical for sustainable use of nuclear power, one of the few current and scalable technologies for energy production that is independent of fossil fuels. In addition, accidental release of radioactive Sr isotopes, with the latest example being the ongoing Fukushima incident, creates an acute need for environmental remediation. Inspiration to overcome this technological hurdle may come from a small number of highly unusual organisms that separate Ca^{2+}, Sr^{2+}, and Ba^{2+} during biomineralization [1]. We report here on the intracellular ion trafficking dynamics in a desmid green alga, *Closterium moniliferum*, which deposits strontium-substituted barite $(Sr,Ba)SO_4$ crystals. We take snapshots (by cryo-fixation, freeze-drying, and SXRF microscopy) of the intracellular distribution of all relevant elements during pulse-chase experiments and correlate them to the cellular ultrastructure gleaned from cryo-SEM. Based on this multidimensional data and S-edge XANES for speciation of sulfur, we develop a model of Ba/Sr sequestration in *C. moniliferum* that we then use to engineer culture conditions to optimize Sr-incorporation into the biomineral.

In a different context, non-selective uptake of Sr in calcium carbonate ($CaCO_3$) mineralizing organisms can be used to probe the evolution of mineral local structure. In particular, we are interested in understanding the mechanism of the disorder-to-order transition from amorphous calcium carbonate to calcite in sea urchin embryo spicules and in liposome-based model systems. This transformation has been suggested to be at the heart of the ability of many different organisms to create smoothly curving, even branching, yet single crystralline skeletal elements. We report on our first steps using Sredge XAS in combination with Sr-SXRF-microscopy to follow the phase transformation with much improved spatial and temporal resolution.

[1] M. R. Krejci, L. Finney, S. Vogt, D. Joester, ChemSusChem **2011**. Selective Sequestration of Strontium in Desmid Green Algae by Biogenic Co-precipitation with Barite.