



Controls of Spherical Crystal Morphology in Ca-/Mg-Carbonates: Results from Culture Experiments and Field Studies

P. Meister, K.H. Nealson, O. Johnson and F. Corsetti

Earth Sciences, University of Southern California (pmeister@usc.edu)

The formation of spherical carbonate crystal aggregates has been observed in different precipitation experiments, and is well known from naturally formed Ca/Mg-carbonates such as ooids and peloids. Microbial activity is often invoked to explain the rounded versus rhombic shape of carbonate crystals (e.g., sulfate reducing bacteria producing round/dumbbell shaped crystals [SRB; Vasconcelos et al., 1995] and the roll of extracellular polymeric substances [EPS] and amino acids in carbonate precipitation [Cölfen and Qi, 2001 and Braissant et al., 2003]). However, the latter studies only considered the pure Ca-carbonate system and did not take into account mixed Mg-/Ca-solutions, more akin to natural systems.

Round carbonate spheres consisting of aggregated crystal needles were precipitated on agar plates with a normal marine concentration of Mg and Ca (50 mM and 10 mM, respectively) in bacteria-absent (control) and bacteria-present media inoculated with different strains of the bacterial genus *Shewanella*. X-ray diffraction analysis indicated poorly ordered crystal structure. However, a broad x-ray diffraction peak occurred in the range of high-Mg calcite. In a few cases, aragonite crystals were detected, however, no indications of dolomite precipitation could be found in any of the cultures, even though the same Ca and Mg concentrations were used as in the experiments with SRB. When no Mg was added, small well-defined rhombs, rather than round carbonate spheres, developed in both inoculated and control experiments. We conclude that addition of Mg appears to be responsible for the round shape of the crystals. The spherical shape is likely the result of lattice defects through kinetic “poisoning” and is not necessarily indicative of microbial activity.

Crystal aggregates were also studied in an ultrabasic spring complex in northern Cal-

ifornia for comparison to our laboratory results. The water derived from serpentinization is extremely basic ($\text{pH} > 11$), and contains up to $100 \mu\text{M}$ Ca, but no Mg. Fast-growing sinter terraces directly at the springs consist of well-defined calcite rhombs. In contrast to the fast growing carbonates, friable carbonate was found in different pools where spring water was mixed with water from the nearby creek. The friable carbonate consists of perfectly spherical aragonite crystal aggregates encrusting algal filaments. Since the algae are not able to grow under the hostile conditions of high pH, we must conclude that the algae grew during a time when the pH was more hospitable. In fact, during the wet season (winter) the source water is diluted by creek water. Meteoric water leaches Mg from the ultrabasic rock, which results in a Mg concentration of up to 1.5 mM. Variation in the Ca/Mg ratio throughout the year may also be responsible for the alteration of spherical and blocky laminae in the carbonate cementing the riverbed.

The findings from the natural springs reinforce our laboratory results that spherical morphology of carbonate crystals is mostly dependent on Mg-poisoning and is not necessarily indicative of microbial activity. In any case, round crystal shape expresses a kinetic inhibition effect of the Mg rather than a precipitation promotion effect of the bacteria. This process should be taken into account for the interpretation of ooids and peloids in the geological record, which show different degree of kinetic poisoning due to the variation of the Mg/Ca ratio in seawater, the so called calcite and aragonite seas.

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