Low-Temperature Dolomite Formation: Microbes and other mechanisms

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The prevalence of massive dolomites in the ancient rock record cannot be reconciled with their striking absence from modern environments. This irregularity is compounded by the experimental difficulties in synthesizing primary dolomite (precipitation of the mineral phase directly from aqueous solution) at low–temperatures (less than 50°C). These difficulties have been attributed to reduced reaction kinetics by inhibitors including low Mg:Ca ratio, ion complexing, hydration spheres and the formation of neutral complexes with sulfate (e.g., Baker and Kastner, 1981; Hardie, 1987; Zhong and Mucci, 1989).

Recent studies have demonstrated that microorganisms play a significant role in the formation of dolomite at low-temperatures. The majority of this research has targeted bacterial metabolisms, surfaces and their extra-cellular polysaccharides (EPS). Principle among these include sulfate-reducing bacteria (SRBs) (Vasconcelos et al., 1995; Vasconcelos and McKenzie, 1997; Warthmann et al., 2000; Van Lith et al., 2003; Wright and Wacey, 2005), sulfide oxidizers (Moreira et al., 2004), and moderately halophilic aerobic heterotrophs (Sánchez-Román et al., 2008). Many of these studies observe disordered or ferroan dolomite forming on cell or EPS surfaces, raising the possibility that the nucleation mechanism is surface-mediated and not driven by metabolic processes.

Our work to date has successfully precipitated ordered phases of dolomite in as few as 40 days in the presence of mixed consortia and pure cultures of Archaeal methanogens (Roberts et al., 2004; Kenward et al., 2009). We also observe ordered dolomite forming in the presence of non-metabolizing Archaeal cells, with precipitates forming on cell surfaces (Figure 1). No dolomite formed in the absence Archaeal biomass, including those experiments containing Bacterial biomass, suggesting that these surfaces have characteristics that are key to overcoming kinetic barriers. Measurement of carboxyl group density of all cells, Archaeal and Bacterial, utilized show that the Archaeal

Figure 1: TEM micrograph of negatively stained, whole mounted Methanobacterium formicicum. Selected area diffraction pattern for attached mineral is shown (insert). Looking from the c axis the a, b plane is 4.9 Å and the angle γ being 120° corresponds to dolomite (a, b = 4.84 Å, γ =120°).
biomass had one higher order of magnitude density of carboxyl groups than the bacterial biomass (~10^-3 v. ~10^-4 moles g^-1). Literature values for carboxyl group density are not available for all bacteria involved in dolomite formation, however Braissant et al. (2007) demonstrated disordered dolomite phases forming in the presence of the EPS of sulfate reducing bacteria with a carboxyl group density of ~10^-3 moles g^-1, similar to our values. We suggest that these carboxyl groups promote desolvation of the Mg ion, known to be a kinetic inhibitor in dolomite precipitation (Wright and Wacey, 2004), but are needed in a high density for nucleation to commence.

We propose, therefore, a surface nucleation model for dolomite precipitation based on surface functional group character that accounts for previous observations of dolomite formation in the presence of a variety of microorganisms and their EPS. We hypothesize that precipitation is not based on metabolic constraints, although supersaturated conditions may be related to microbial activity, but rather is controlled by the surface character of microbial cells or potentially other organic carbon in the system. Functional group density of organic matter and microorganisms provides a unifying model for how, when, and where dolomite nuclei form and may provide clues to de-convolute microbial, organogenic and perhaps abiotic sources of dolomite.

References


