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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.

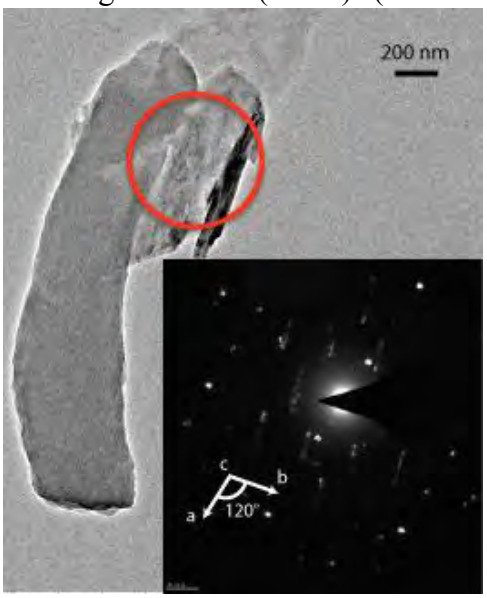

Figure 1: TEM micrograph of negatively stained, whole mounted *Methanobacterium formicicum*. Selected area diffraction pattern for attached mineral is shown (insert). Looking from the c axis the a, b plane is 4.9 Å and the angle γ being 120° corresponds to dolomite (a, b = 4.84 Å, γ =120°).

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*

biomass had one higher order of magnitude density of carboxyl groups than the bacterial biomass ($\sim10^{-3}$ v. $\sim10^{-4}$ 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 $\sim10^{-3}$ 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

Baker, P.A., and Kastner, M., 1981, Constraints on the formation of sedimentary dolomite: Science, v. 213, p. 214–216.

Braissant, O., Decho, W., Dupraz, C., Glunk, C., Przekop, K.M. and Visscher, P.T., 2007, Exopolymeric substances of sulfate-reducing bacteria: Interactions with calcium at alkaline pH and implication for formation of carbonate minerals: Geobiology, v. 5, p. 401-411.

Hardie, L.A., 1987, Dolomitization: a critical view of some current views: Journal of Sedimentary Petrology, v. 57, p.166–183.

Kenward, P.A., Goldstein, R.G., Gonzalez, L.A. and Roberts, J.A., 2009, Precipitation of low temperature dolomite from an anaerobic microbial consortium: the role of methanogenic Archaea: Geobiology, v. 7, p. 556-565.

Moreira, N.F., Walter, L.M., Vasconcelos, C., McKenzie, J.A. and McCall, P.J., 2004, Role of sulfide oxidation in dolomitization: sediment and pore-water geochemistry of a modern hypersaline lagoon system: Geology, v. 32, p. 701–704.

Roberts, J.A., Bennett, P.C., Gonzalez, L.A., Macpherson, G.L., and Milliken, K.L., 2004, Microbial precipitation of dolomite in methanogenic groundwater: Geology, v. 32, p. 277–280.

Sánchez-Román, M., Vasconcelos, C., Schmid, T., Dittrich, M., McKenzie, J.A., Zenobi, R.,Rivadeneyra, M.A., 2008, Aerobic microbial dolomite at the nanometer scale: implications for the geologic record: Geology, v.36, p. 879–882.

van Lith, Y., Warthmann, R., Vasconcelos, C., and McKenzie, J.A., 2003, Sulphate-reducing bacteria induce low-temperature Ca-dolomite and high Mg-calcite formation: Geobiology, v. 1, p. 71-79.

Vasconcelos, C. and McKenzie, J.A., 1997, Microbial mediation of modern dolomite precipitation and diagenesis under anoxic conditions, Lagoa Vermelha, Rio de Janeiro, Brazil: Journal of Sedimentary Research, v. 67, p. 378–390.

Vasconcelos, C., McKenzie, J.A., Bernasconi, S., Grujic, D., and Tien, A.J., 1995, Microbial mediation as a possible mechanism for natural dolomite formation at low temperatures: Nature, v. 377, p. 220–222.

Warthmann, R., van Lith, Y., Vasconcelos, C., McKenzie, J.A. and Karpoff, A.M., 2000, Bacterially induced dolomite precipitation in anoxic culture experiments. Geology, v. 28, p. 1091–1094.

Wright, D.T. and Wacey, D., 2004, Sedimentary dolomite – a reality check. In The Geometry and Petrogenesis of Dolomite Hydrocarbon Reservoirs (eds. Braithwaite, C.J.R., Rizzi, G. and Darke G): Geological Society Special Publication, v. 235, p. 65–74.

Wright D.T. and Wacey, D., 2005, Precipitation of dolomite using sulphate-reducing bacteria from the Coorong Region, South Australia: significance and implications: Sedimentology, v. 28, p. 987–1008

Zhong, S. and Mucci, A., 1989, Calcite and aragonite precipitation from seawater solutions of various salinities: precipitation rates and overgrowth compositions: Chemical Geology, v.78, p. 283-299.