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Precipitation of low-temperature disordered dolomite induced by extracellular polymeric substances of methanogenic Archaea *Methanosarcina barkeri*: Implications for sedimentary dolomite formation

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Abstract

A correlation between methanogenesis and dolomite formation has been reported; however, the mechanism underlying this association is not fully understood. In this study, we conducted forced carbonate precipitation experiments at room temperature in calcite-seeded Ca/Mg carbonate solutions containing either purified non-living biomass or bound extracellular polymeric substances (EPS) of the methanogen *Methanosarcina barkeri.* Purified non-living biomass and bound EPS was used so as to avoid the possible influence of the complex components of the growing microbial culture on carbonate crystallization. Our results demonstrated that non-living biomass of *M. Barkeri* can enhance the Mg incorporation into calcitic structure and induce the crystallization of disordered dolomite. In the presence of ~113 mg L^{-1} of non-living biomass, disordered dolomite with ~41 and 45 mol% of $MgCO_3$ was precipitated in solutions with initial Mg:Ca ratios of 5:1 and 8:1, respectively. A systematic increase in the $MgCO_3$ contents of the precipitated Ca-Mg carbonates was also observed with the increased non-living biomass concentration. Bound EPS was shown to be the component of non-living biomass that catalyzed the precipitation of disordered dolomite. At only ~25 mg L^{-1} of bound EPS, disordered dolomite with ~47 and 48 mol% of $MgCO_3$ was precipitated in solutions with initial Mg:Ca ratios of 5:1 and 8:1, respectively. We propose that adsorption of bound EPS to growing carbonate surfaces through hydrogen bonding is the key to catalyzing disordered dolomite crystallization, and that this mechanism is also applicable to natural EPS-induced dolomite formation. This study provides significant insight into the formation mechanism of microbial-induced dolomite with high $\delta^{13}C$ values.

Keywords: Sedimentary dolomite, methanogen, EPS, catalysis, microbial-induced dolomite, high $\delta^{13}C$ value