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

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**INTRODUCTION**

Although abundant in ancient rocks, dolomite is uncommon in modern sedimentary environments. Present-day low-temperature dolomite formation is usually observed in association with marine and other saline environments (Jones 1961; Zenger et al. 1980; Machel and Mounjoy 1986; Hardie 1987; Mazzullo 2000; Warren 2000). Freshwater dolomite has also been documented, but its occurrence is rare (El-Sayed et al. 1991; Colson and Cojan 1996; Capo et al. 2000; Whipkey et al. 2002; Roberts et al. 2004; Kenward et al. 2009). The rarity of modern dolomite is largely consistent with the notorious difficulty in reproducing dolomite crystallization under ambient conditions (Lippmann 1973; Oomori and Kitano 1987; Land 1998; Higgins and Hu 2005), contributing to the long-existing controversy over the formation mechanism of sedimentary dolomite, i.e., the “dolomite problem” (Zenger et al. 1980; Machel and Mounjoy 1986; Hardie 1987; Burns et al. 2000; Mazzullo 2000; Warren 2000).

While there is no simple abiotic recipe for dolomite precipitation, recent studies suggest that microbes are paramount to overcoming kinetic barriers to dolomite crystallization. Several metabolic pathways have been implicated in catalyzing dolomite precipitation, including both bacterial sulfate reduction (BSR) and methanogenesis (Baker and Kastner 1981; Baker and Burns 1985; Hardie 1987; Compton 1988; Vasconcelos and McKenzie 1997; Wright 1999; Burdige et al. 2000; Mazzullo 2000; Warren 2000; Van Lith et al. 2003b; Roberts et al. 2004; Kenward et al. 2009). Many carbonate precipitation studies have been performed exploring the poorly constrained role of sulfate-reducing bacteria (SRB) in promoting dolomite precipitation (Vasconcelos et al. 1995; Nielsen and Jahn 1999; Warthmann et al. 2000; Van Lith et al. 2003b; Wright and Wacey 2005; Zhang et al. 2012a, 2013; Xu et al. 2013). For example, Zhang et al. (2012a) demonstrated the catalytic role of dissolved sulfide, one of the major products of BSR, in dolomite precipitation. However, fewer studies have been devoted to methanogens, although there may exist some physiochemical rules that are common to dolomite induced by SRB and methanogens. Roberts et al. (2004) and Kenward et al. (2009) conducted Ca-Mg carbonate precipitation experiments in natural environment and culture media, respectively, with the involvement of methanogens and showed dolomite precipitation in the natural environment. Recent molecular dynamics modeling also proves that polysaccharides (main components in EPS) can lower the dehydration energy barrier (Shen et al. 2015).

In natural environments, the vast majorities of microor-