Dissolved silica-catalyzed disordered dolomite precipitation

YIHANG FANG1† and HUIFANG XU1,*

1NASA Astrobiology Institute, Department of Geoscience, University of Wisconsin–Madison, 1215 West Dayton Street, Madison, Wisconsin 53706, U.S.A.

ABSTRACT

There is a great abundance of sedimentary dolomite in the Proterozoic and Lower Paleozoic, but examples of primary dolomite are scarce in the Cenozoic. This discrepancy suggests a poorly understood but dramatic shift in the geochemical system that inhibited dolomite formation. Previous research on microbial-mediated dolomite formation demonstrated that microbial activity could promote disordered dolomite precipitation through the catalytic role of polysaccharides. However, the microbial-mediated model cannot explain some of the Precambrian dolomite for which there is no evidence of microbial origin. Here, we present an abiotic mechanism with dissolved silica catalyzed dolomite precipitation that provides new insight into this long-lasting “dolomite problem.” In this study, we demonstrate that the presence of 1–2 mM of aqueous Si(OH)₄ in high Mg:Ca ratio solutions at room temperature will promote disordered dolomite precipitation (with up to 48.7 mol% MgCO₃) and inhibit aragonite formation. Dissolved silica in solution also promotes Mg incorporation into the Ca-Mg carbonates. Dissolved silica possesses low-dipole moment and dielectric constant similar to hydrogen sulfide, dioxane, polysaccharide, and exopolymeric substances (EPS), which are catalysts in previously established room-temperature dolomite synthesis. The molecules with low-dipole moment adsorbed on the dolomite surface can lower the dehydration energy barrier of a surface Mg²⁺-water complex and promote dolomite nucleation and growth. This study provides a new model for abiotic sedimentary dolomite formation, which is likely to be responsible for the significant amount of primary dolomite in Earth history.

Keywords: Disordered dolomite, dolomite problem, sedimentary dolomite, dissolved silica

INTRODUCTION

In spite of extensive research, dilemmas and puzzles surrounding the formation mechanism of dolomite linger on. Although dolomite is the thermodynamically favored product in seawater and many other natural saline/hypersaline bodies of water, dolomite is rarely found in the modern environment. The difficulty in understanding sedimentary dolomite formation comes from the scarcity of modern examples and the inability to precipitate dolomite from seawater at surface temperature. Although modern seawater is supersaturated with respect to dolomite, primary dolomite has mostly been reported in limited settings such as alkaline lakes (Peterson et al. 1963; Rosen et al. 1988; Last 1990), deep marine carbonate pavements associated with methane seeps (Lumsden 1988; Gregg and Frank 2009; Xu 2010; Lu et al. 2018) and shallow marine environments with microbial mats (Curtis et al. 1963; Kendall and Skipwith 1968; Vasconcelos and McKenzie 1997; Meister et al. 2007; Zhang et al. 2015). Land (1998) concluded after a 32-year experiment with a thousandfold oversaturated solution at room temperature, which failed to precipitate dolomite, that the “dolomite problem” results from the kinetic inhibition of dolomite crystallization. One of the main issues is that the Mg²⁺ cation possesses a high affinity for water and forms a hydration layer that inhibits dolomite growth (Lippmann 1973; Berner 1975). Therefore, dolomite formation at low temperature requires the presence of a catalyst to destabilize the surface Mg²⁺-water complex (Shen et al. 2015).

Most of the Ca-Mg carbonate that approaches the stoichiometric composition of dolomite found in recent sediments displays little to no ordering (Land 1980; Fang and Xu 2019). Cation ordering in dolomite refers to alternating calcium and magnesium layers along the c axis that results in a reduced R3c symmetry relative to the R3c symmetry of calcite. Although thermodynamics favors the ordered dolomite structure, the ordering process is kinetically inhibited at low temperatures. Partially ordered “protodolomite,” a term proposed by Graf and Goldsmith (1956), with weak or absent ordering, is believed to be the precursor to sedimentary dolomite (Zhang et al. 2012b; Gregg et al. 2015; Kaczmarek et al. 2017). Gregg et al. (2015) refer to Ca-Mg carbonates without ordering as “very high-magnesium calcite” (VHMC), and Sibley et al. (1994) suggest VHMC has a composition of 35–40 mol% MgCO₃. In this study, we use the term “disordered dolomite” to refer to Ca-Mg carbonates containing over 36 mol% MgCO₃ with no cation ordering, whereas materials described as “protodolomite” display weak to moderate ordering. The composition range of “disordered dolomite” is determined by the extent of cation ordering observed in natural samples (Fang and Xu 2019).

Previously published disordered dolomite synthesis experiments usually require the presence of low-dipole moment catalysts such as hydrogen sulfide (Zhang et al. 2012a, 2013), dioxane...