Catalysis in low-temperature geochemical process: a key to the sedimentary dolomite enigma

HUIFANG XU

NASA Astrobiology Institute, Department of Geoscience, University of Wisconsin – Madison, Madison, Wisconsin 53706 (hfxu@geology.wisc.edu)

Catalysis may play pivotal role in many lowtemperature geochemical processes. An enigma of sedimentary dolomite problem is a good case for demonstarting calalysis at the dolomite-water interafce. Major role of a catalyst is to lower activation energy and promote chemical reaction, such as, dolomite growth. The dolomite Sedimentary dolomite can be potential hydrocarbon reservoirs. Sedimentary dolomites or dolostones are generally abundant in the geological record, yet scarce or less common in certain geological time periods and Holocene sediments. The main factor inhibiting the nucleation and growth of dolomite is the strong hydration of the aqueous Mg2+ ion. The dehydration of surface Mg^{2+} -water complexes is the key to dolomite crystallization. Recent results from our research group indicate that disordered dolomite can precipitate and growth in normal seawater in presence of dissolved polysaccharides and microbial extracellular polymeric substances or exopolymeric substances (EPS). A positive relationship between concentrations of dissolved polysaccharides and microbial EPS in a solution with fixed Mg/Ca ratio and amount of Mg in the precipitated Ca-Mgcarbonates has been established. Polysaccharides are the main components in the EPS. Molecular dynamics modeling results indicate that the adsorbed polysaccharides will weaken the bonding between water molecule and surface Mg, therefore promote carbonate anion binding and dolomite crystallization. Our results from sedimentary carbonate rocks with oscillatory dolomite and limestone layers (ribbon rocks) and micro-laminations clearly demonstrate preferential dolomitization of the organic-rich (i.e., biomat-rich) carbonate layers. Molecular dynamics modeling results indicate that adsorbed polysaccharide can lower activation energy of surface water removal / dehydration. Polysaccharides associated with the carbonates sediments (calcite, high magnesian calcite, and aragonite) take very important catalytic roles in the dolomitization. The dolomitization could be penecontemporaneous process through interaction with ambient sea water in presence of the catalysts (1). No special "dolomitizing fluids" are required.

(1) Shen, Z., Brown, P. E., Szlufarska, I., and H. Xu, H. (2015) *Langmuir, 31, 10435-10442*.