The origin of the inhibitory effect of Mg to (Ca,Mg)CO₃ crystallization

H. HENRY TENG AND MINA HONG

Deptartment of Chemistry, the George Washington University, 800 22nd St., NW, Washington DC 20052, hteng@gwu.edu

Magnesium ocurrs widely at Earth surface in the form of dolomite [(Ca,Mg)CO₃], but ambient condition synthesis of this mineral has proven virtually imporssible. Contradictory to the long held hypothesis that the difficulty in dolomite mineralization arises from the stronger hydration of Mg²⁺ relative to that of Ca²⁺, our test experiment in the absence of water showed that crystalline (Mg,Ca)CO₃ cannot form if the Mg content exceeds ~37%, beyond which the precipitate becomes amorphous. These observations indicate that additonal retardation forces other than cation hydration may be the primary cause for the failed room-temperature dolomite crystallization. We hypothesize that the lattice strain resultant from the size mismatch between Mg and Ca and that between the interstitial spaces amongest Mg-O octahedra and the CO_3 groups may be the critical factor.

To test this hypothesis, we investigated calcite growth morphology deformation in the presence of Mg and attempted to determine the maximal Mg content in the lattice before complete growth inhibition occurs. We found that the inherent rhombohedral morphology evolves elastically at low Mg-containing solutions but eventually gives in to plastic deformation when Mg presence becomes strong. When either Mg to Ca ratio or calcite supersaturation is low, reversible step rounding occurs exclusively in the acute side; increases of the two parameters first engender reversible morphological changes in both the acute and obtuse directions, but ultimately lead to the development of monolayer buckling and step aggregation in the original cleavage directions, resulting in irreversible deformation and complete stoppage of step growth. We propose that the point defects generated by Mg for Ca substitution in the lattice diffuse and align themselves in the cleavage (i.e low energy crystallographic) directions to form a linear stress field which, upon plastic deformation, is responsible for the release of lattice stress in the form of plastic deformation. Calculations show that the Mg content needed to generate a lattice stress exceeding the elastic limit of calcite is around ~ 40%, consistent with the experimental results acquired in nonaqueous solvent and supporting the view that the excessive lattice stress rising from the size difference of the constituent cations may be a fundamental retardation force for Mg^{2+} to enter calcite lattice extensively to form dolomite.