

## Technical Report

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**Project title:** Interface Induced Carbonate Mineralization: A Fundamental Geochemical Process Relevant to Carbon Sequestration

**Participants:** Mo Zhou, Fangfu Zhang, Zhizhang Shen, Hiromi Konishi (Department of Geoscience, University of Wisconsin – Madison); Henry Teng (George Washington University)

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**Total Award Amount:** \$ 230,242.

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**Key words:** Mica, biotite, muscovite, diopside, tremolite, ultramafic rock, hematite, Ca-Mg-carbonate, calcite, aragonite, dolomite, crystal nucleation, crystallization, interface, catalysis, EBSD, XRD, TEM

### Summary:

Carbonate mineralization and polymorphic formation are key issues in underground CO<sub>2</sub> storage and biomineralization processes and closely related to mineral substrates. We investigated effects of mineral surfaces, solution chemistry, and anhydrous organic solvent on nucleation and growth of Ca-Mg-carbonate minerals. The effect of substrates of mica, diopside, tremolite, and hematite on calcite nucleation and growth in both experimental and natural environments were investigated using SEM, XRD, and EBSD methods. EBSD analysis can determine orientations between substrates and calcite crystals effectively.

Our results demonstrate a strong controlling effect on the orientation of calcite on mineral substrates of mica (both biotite and muscovite), diopside, tremolite, and hematite (Figs. 1-5). The calcite crystals nucleated on mica and diopside surfaces are commonly twinned due to pseudo-hexagonal symmetry of (001) surface of mica (Figs. 6, 7) and (100) surface of diopside. The calcite crystals nucleated on hematite's (001) surface keep same crystallographic orientation with the hematite substrate due to good lattice match and hexagonal symmetry of (001) surface. The studied minerals surfaces promote stable form calcite nucleation and Mg incorporation (Fig. 8), and inhibit nucleation of meta-stable polymorph aragonite.

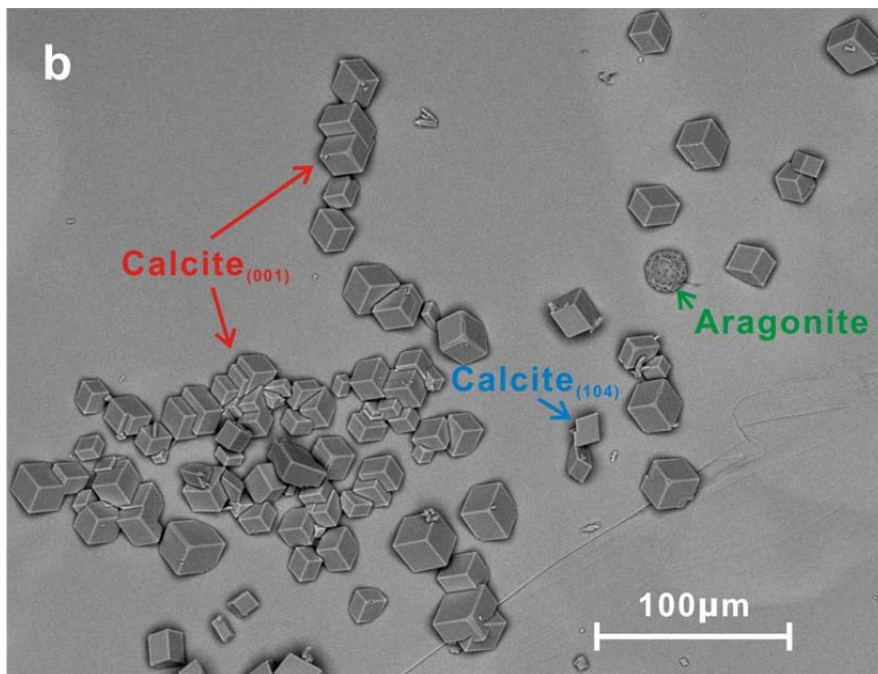


Fig. 1: SEM image of calcium carbonate crystals on biotite substrate.

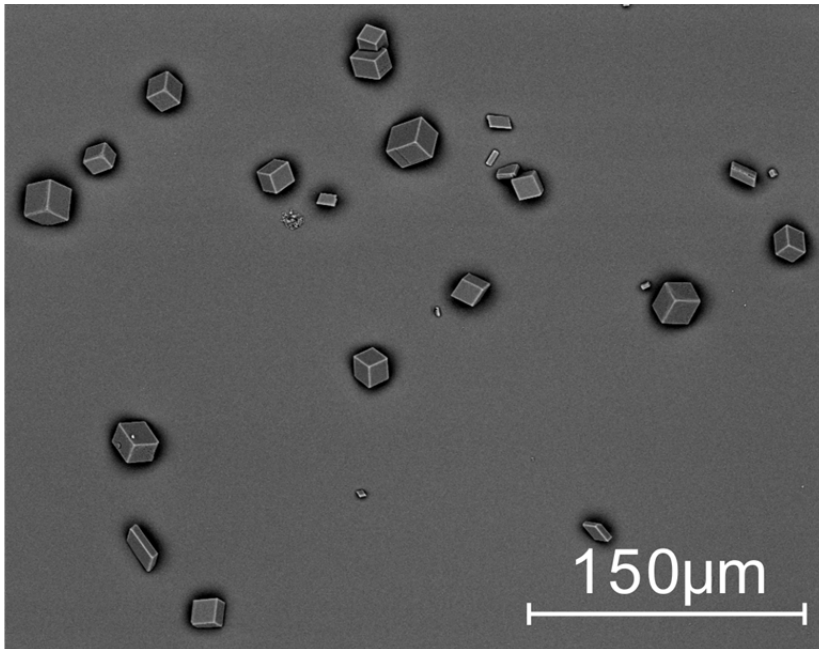


Fig. 2: SEM image of calcium carbonate crystals on muscovite substrate.

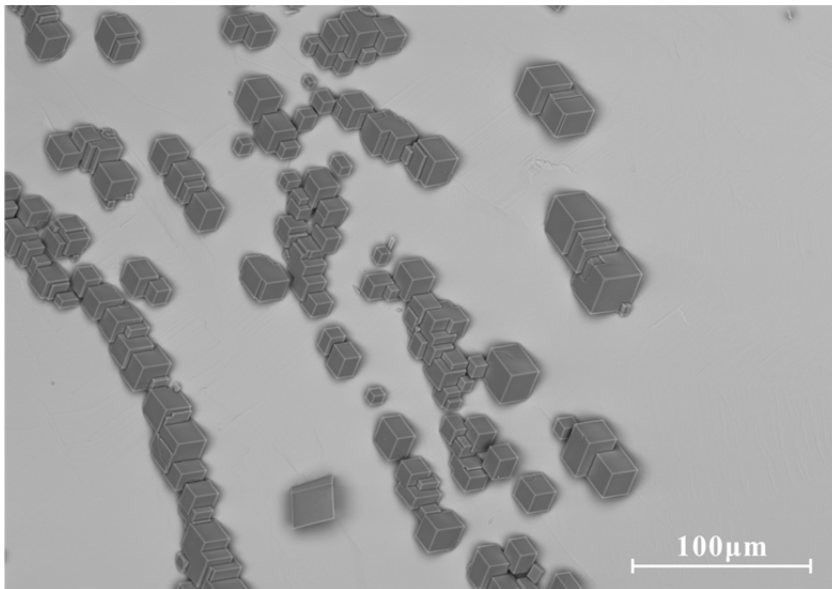


Fig. 3: SEM image of calcium carbonate crystals on (001) surface of hematite.

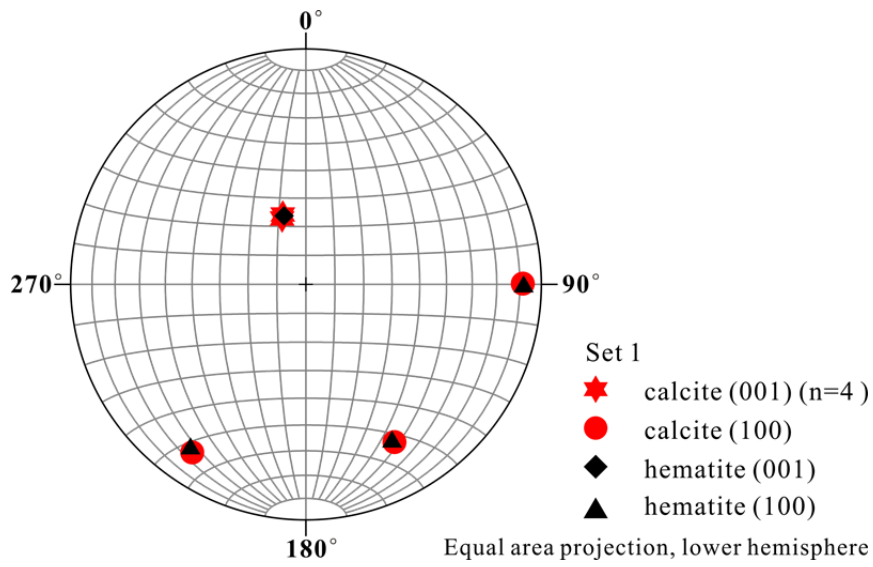


Fig. 4: Stereographic Projection of calcite crystals on hematite substrate.

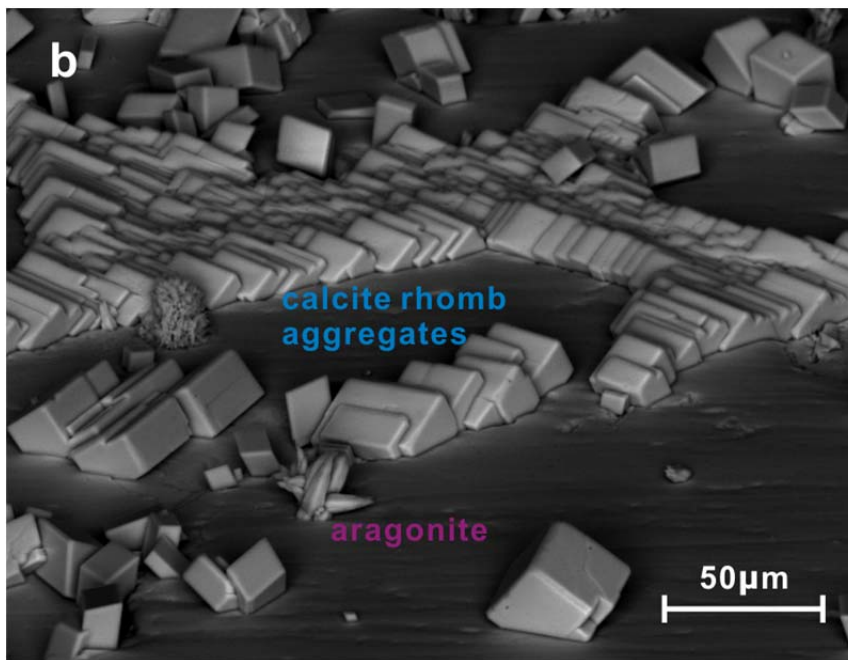


Fig. 5: SEM image of calcium carbonate crystals on diopside substrate.

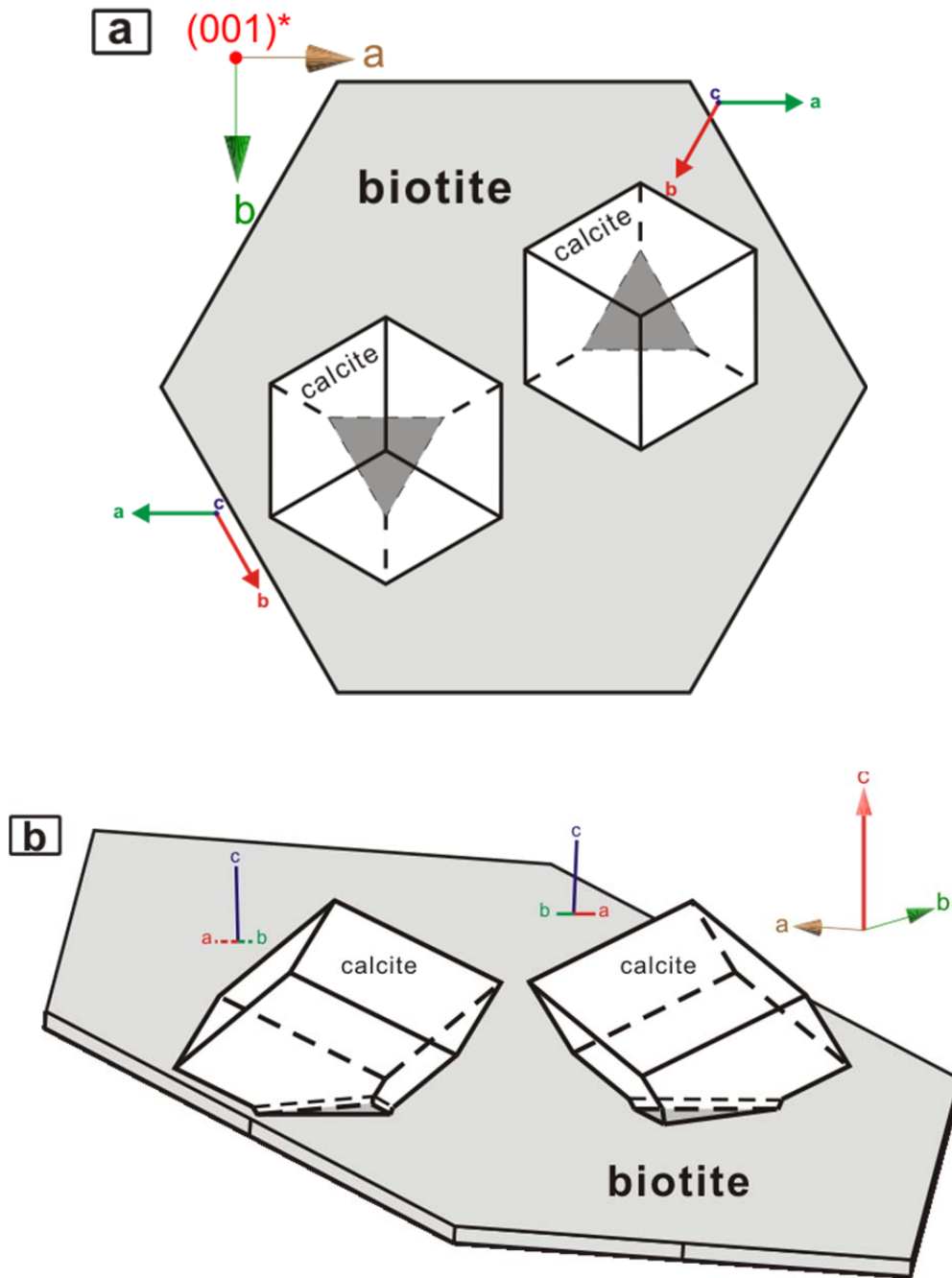


Fig. 6: Schematic diagrams of calcite (001) twinning were also created to give a better view of the calcite twins and their relationships with the biotite substrate .

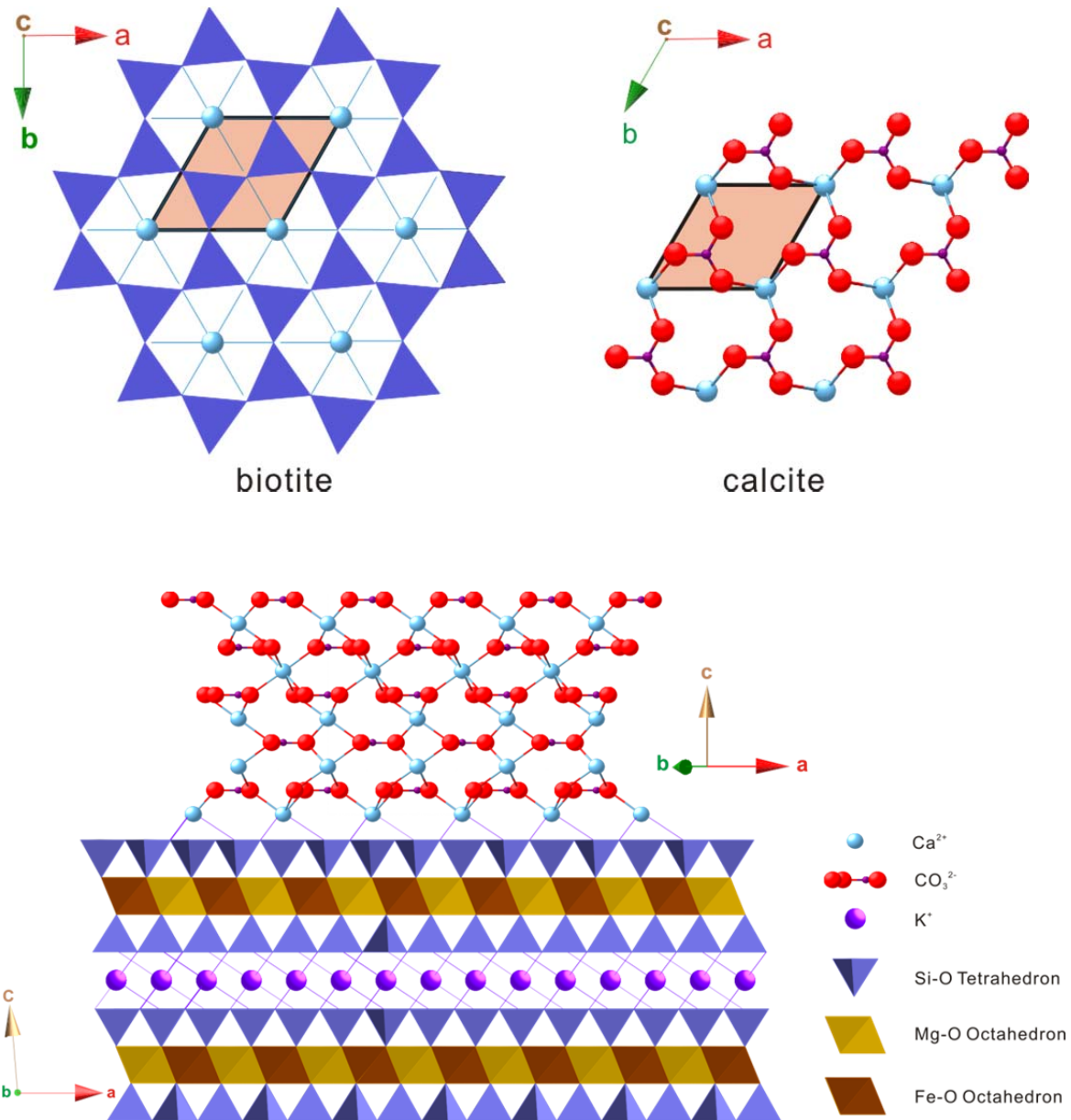


Fig. 7: Diagrams illustrate the interface between calcite and biotite substrate. The shape of calcite-biotite interface is created as a triangle based on the interface morphology derived from SEM studies and the crystal shape of calcite.

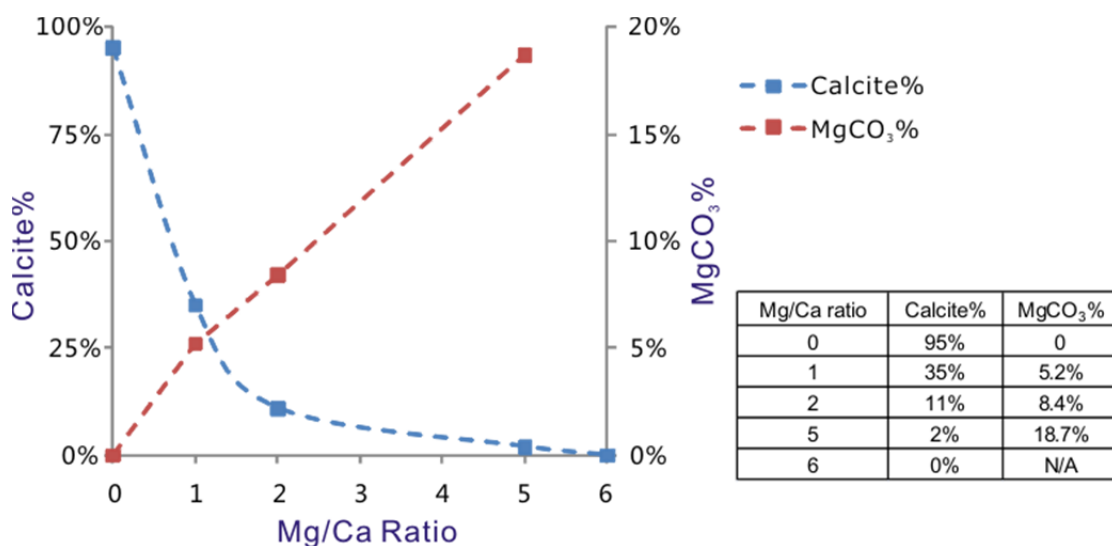


Fig. 8: Calcite percentage and Mg incorporation extent under different Mg/Ca ratios.

One reviewer also suggested use to investigate the effects of solution chemistry on carbonate structure and composition. We observed that small amount of certain dissolved chemicals can enhance selection of Ca-carbonate polymorphs and even incorporation of Mg in anhydrous Ca-Mg-carbonates. We also systematically investigated aqueous solution chemistry on nucleation and growth of Ca-Mg-carbonates. Small amount of dissolved hydrogen sulfide (Fig. 9) and polysaccharides (such as carboxymethyl cellulose, agar) (Fig. 10) can promote dolomite and Ca-Mg-carbonate growth, and inhibit nucleation of meta-stable polymorph aragonite. The dissolved hydrogen sulfide and polysaccharides that adsorbed on surfaces of the Ca-Mg-carbonates serve as catalysts for enhancing removal of surface water and the carbonate growth.

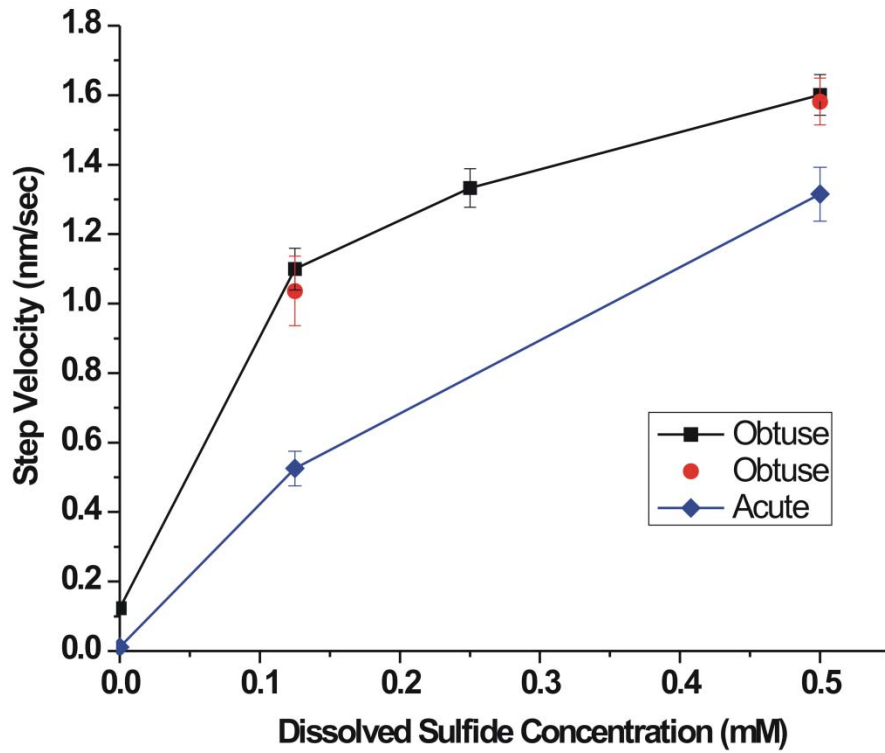


Fig. 9: Kinetic measurements of step propagation rate versus dissolved sulfide concentration. Squares show velocities of obtuse steps from experiments which flowed Mg-bearing control solutions containing no dissolved sulfide first. Circles and diamonds show velocities of obtuse and acute steps, respectively, from experiments which directly flowed dissolved sulfide-bearing solutions.



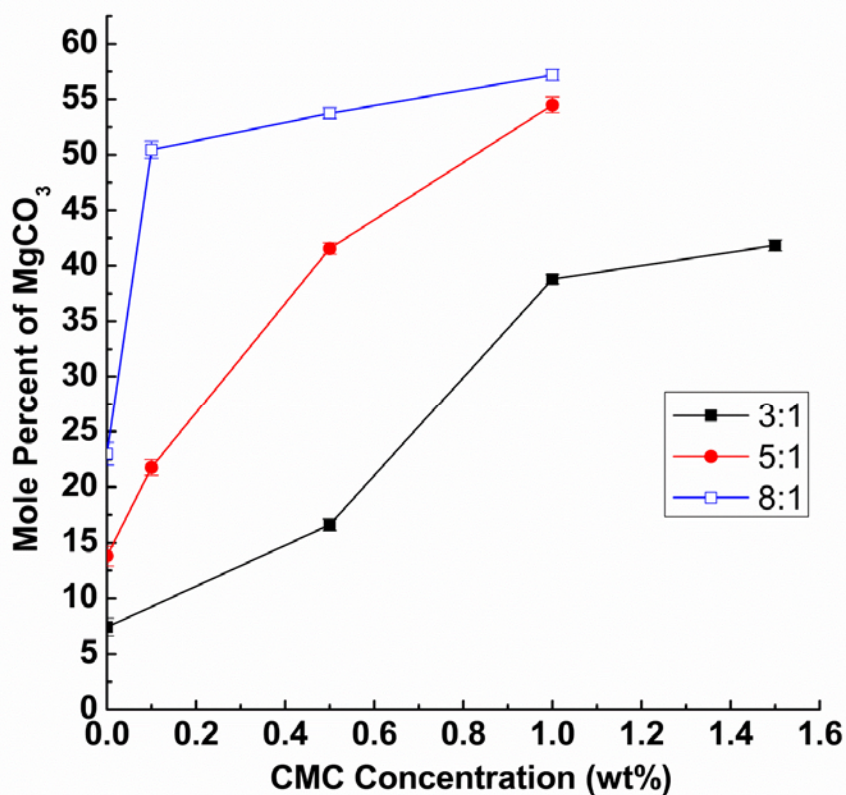


Fig. 10: A plot showing the composition of CMC (carboxymethyl cellulose)-induced Ca-Mg carbonates as a function of CMC concentration and initial Mg:Ca ratios of the solutions. Data from three different Mg:Ca ratios (3:1, 5:1, and 8:1) were plotted here. Error bars represent the standard deviation of MgCO<sub>3</sub> contents of triplicate samples.

In order to further understand crystallization mechanism of the Ca-Mg-carbonates, especially Mg-rich carbonates, we also studied precipitation of Ca-Mg-carbonates in anhydrous organic solvent. Ca-rich disordered dolomite formed in the anhydrous solvent with Mg/Ca ratio of 1:1. High Mg/Ca ratio results amorphous Mg-rich carbonates. Both dehydration and strong bonding between Mg(II) and carbonate affect structure ordering and crystallization in dolomite, magnesite, and Mg-rich carbonates.

This is a collaborative study intending to examine how the surfaces of noncarbonate minerals affect the polymorphic speciation and crystal growth mode of CaCO<sub>3</sub> during carbonate mineralization. Carbonate minerals and their crystallization processes have been an important subject of earth sciences for the past quarter century because of the minerals' wide occurrence and high reactivity. Scientific interests on this subject are rejuvenated in the 21st century due to the emerging threat of global warming resulting from the anthropogenic emission of excessive CO<sub>2</sub>. Past research has led to a solid understanding in the growth mechanisms and kinetics of carbonate mineralization, but limited the effort to either homogeneous systems (i.e. no substrate) or carbonate-seeded crystallization experiments.

Our research directly tackles the mineral-water interface complexity and dynamics through assessing the heterogeneous effect of geological systems. It examines the microscopic basis of macroscopic complexity by investigating surface reactions ranging from atomic (i.e. lattice matching) to bulk scales. Our results will help to understand and design effective and long-term stable mineral forms of sequestered CO<sub>2</sub> in sub-surface geological environments.

### **Products developed under the award**

#### **Publications**

Konishi, H., Xu, H., and Dymek, R. F. (2010) TEM investigation of Jimthompsonite, chesterite, and chain-width disorder in Archaean ultramafic rocks from Isua, Greenland. *American Mineralogist*, 95, 73-80.

This paper reported transmission electron microscopy observations of alteration products of an ultramafic rock from Isua, Greenland. Ca-Mg-carbonate mineral of dolomite is considered as a stable sink for carbon dioxide injected into potential ultramafic rocks. The structural relationship between dolomite and its host Ca-Mg-silicate minerals was observed. Ca-Mg-silicate minerals of pyroxene and amphibole may provide Ca-Mg source and nucleation site.

Zhang, F., Xu, H., Konishi, H., and Roden, E. E (2010): A relationship between d-104 value and composition in the calcite – disordered dolomite solid solution series. *American Mineralogist*, 95, 1650-1656.

This paper is about using different concentrations of dissolved sulfide to synthesize high-Mg calcite and disordered dolomite in the Ca-Mg-carbonate solid solution series. We built a new empirical curve that correlate X-ray diffraction results with composition of the Ca-Mg-carbonate. Several linear relationships were used in carbonate mineralogy community for decades. Our new curve (not linear) integrates composition, Ca-Mg-ordering degree and inter-planar d-spacing together.

Zhang, F., Xu, H., Shelobolina, E. S., Konishi, H., and Roden, E. E (2012): Polysaccharide-catalyzed nucleation and growth of disordered dolomite: A potential precursor of sedimentary dolomite. *American Mineralogist*, 97, 556-567.

This paper is about growing dolomite and even Mg-rich dolomite in presence of certain polysaccharides that could be major components in extracellular polymeric substances (EPS) of anaerobic bacteria like sulfate-reducing bacteria, methanogens and fermenters. This paper lays foundation for us to investigate roles of polysaccharide in governing compositions of Ca-Mg-carbonates and dolomite. Polysacchrides may be used as catalysts for enhancing stable Ca-Mg-carbonate (dolomite) in deep surface environment.

Zhang, F., Xu, H., Konishi, H., Kemp, J. M., Shen, Z., and Roden, E. E. (2012b): Dissolved sulfide-catalyzed crystallization of Ca-Mg carbonates and implications for the formation mechanism of sedimentary dolomite. *Geochimica et Cosmochimica*, 97, 148-165.

This paper is about the effects pH and dissolved sulfate on dolomite growth. Effect of sulfate on dolomite formation has been controversial for decades. Based on synthesis experiments at high temperature, dissolved sulfate inhibits dolomite growth. However, some research groups proposed that sulfate promote dolomitization based on gypsum occurrences in some sedimentary dolomites. According to our results, dolomite can still grow at room

temperature in presence of dissolved sulfate if dissolved sulfide exists. Gypsum and dissolved sulfate indicate presence of sulfate-reducing bacteria for producing hydrogen sulfide.

Zhang, F., Yan, C., Teng, H., Roden, E. E., and Xu, H. (2013): *In situ* AFM observations of Ca-Mg carbonate crystallization catalyzed by dissolved sulfide: Implications for sedimentary dolomite formation. *Geochimica et Cosmochimica*, 105, 44-55.

This paper is about *in situ* AFM observations of Ca-Mg carbonate crystallization catalyzed by dissolved sulfide. We obtained Ca-Mg-carbonate growth rates as function of dissolved hydrogen sulfide in solutions with Mg:Ca ratio of 5:1. We observed a new step nucleation mechanism in presence of dissolved sulfide. Without dissolved catalysts, there is no new step generated. We proposed that adsorbed H<sub>2</sub>S on (104) surface through hydrogen bonding with carbonate anion is the key to for improving surface water removal.

Zhou, M., Xu, H., Teng, H., and Konishi, H.: Effect of mica and hematite (001) surfaces on the precipitation of calcite. (in preparation).

This paper discusses the effect of biotite substrate on the nucleation and crystallization of calcite were using SEM, XRD, and electron backscatter diffraction (EBSD) methods. Our results of Ca<sup>2+</sup>-only system show that biotite has a strong controlling effect on the orientation of calcite. Calcite crystals initially nucleate from Ca<sup>2+</sup>-layers on the biotite surface where Ca<sup>2+</sup> replaces the original K<sup>+</sup> ions. Minor lattice mismatch the geometrical similarity between the host-guest minerals could be the controlling factor for this configuration. The pseudo-hexagonal symmetry on biotite (001) surface also leads to the observed calcite (001) twinning. Results from Mg<sup>2+</sup>-Ca<sup>2+</sup> system with biotite substrate show the substrate can enhance Mg incorporation into calcite even in solutions with Mg/Ca ratio of 5.

Xu, H., Yan, C., Zhang, F., Konishi, H., Xu, H., and Teng, H. (2013) Testing the Cation Hydration Effect on the Crystallization of Ca-Mg-CO<sub>3</sub> Systems. *Proceedings of the National Academy of Sciences*, (accepted).

This paper describes that both nano-crystals Ca-rich proto-dolomite and amorphous phase of Mg-rich  $\text{Mg}_x\text{Ca}_{(1-x)}\text{CO}_3$  were formed at conditions of  $[\text{Mg}^{2+}]/[\text{Ca}^{2+}] = 1$  in anhydrous organic solvent. Magnesian calcite dominated in low  $[\text{Mg}^{2+}]/[\text{Ca}^{2+}] (<1)$  solutions, but amorphous  $\text{Mg}_x\text{Ca}_{(1-x)}\text{CO}_3$  and  $\text{MgCO}_3$  in high- $[\text{Mg}^{2+}]/[\text{Ca}^{2+}]$  ratio ( $>1$ ) and pure-Mg solutions. The results suggested that the long-held belief of cation-hydration inhibition on dolomite and magnesite mineralization needed to be reevaluated. Our study provides significant insight into the longstanding "dolomite problem" in geochemistry and mineralogy, and may promote a better understanding of the fundamental chemistry in biomineralization and mineral-carbonation processes.

#### **Master Thesis:**

Mo Zhou (2011): Investigation on the effect of biotite and diopside on calcite precipitation.

#### **Ph. D. Dissertation**

Fangfu Zhang (2013): The Role of Anaerobic Microorganisms in Sedimentary Dolomite Formation.

#### **Other products**

Lecture materials (such as, interface structures, evolution of crystal sizes and shapes of carbonates, characterization of interface using EBSD method, and effects of mineral substrates on crystal nucleation) developed from this project have been used in teaching "Crystal Chemistry," a course for graduate students and undergraduate seniors.