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The effect of carboxylates on the Mg content of calcites that transform from ACC

N. Han[a], C.R. Blue[a], J.J. De Yoreo[b], P.M. Dove[a]

[a]*Department of Geosciences, Virginia Polytechnic Institute & State University, Blacksburg, Virginia 24060, USA*
[b]*Molecular Foundry, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA*

Abstract

In some skeletal-forming and sedimentary environments, calcite and other $CaCO_3$ polymorphs are produced from an amorphous calcium carbonate (ACC) phase. This experimental study determined the Mg content of calcites that grew in the presence of ACC with/without carboxylated biomolecules. The Mg content of the initial ACC obeys a simple fractionation for all conditions except in the presence of oxydiacetate. For all solution compositions, this ACC transforms into calcite crystallites that contain zero to 38 mole %$MgCO_3$, without evidence of secondary polymorphs (Mg/Ca = 0-15). Mg is in the calcite structure within the resolution of the XRD method. The biomolecules slow the ACC to calcite transformation in proportion to their selectivity for Ca over Mg. Citrate, tartarate, and oxydiacetate increase the amount of Mg in both ACC and the resulting calcite. When the Mg^{2+}/Ca^{2+} ratios of initial solutions are less than ~5-8, the Mg content of the ACC and calcite products are similar.

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Keywords: ACC; Mg-calcite; carboxylate; biomineralization.

1. INTRODUCTION

An understanding of the processes by which high magnesium calcites form in biogenic and sedimentary settings is critical to accurately reconstructing modern and ancient environmental conditions. Observations of natural calcites with Mg contents of up to 44 mole% $MgCO_3$ [1] contrast with the maximum of a few percent that forms when calcite is experimentally grown by the classical process of ion-by-ion attachment [2, 3]. The realization that some skeletal calcites form via a precursor phase of amorphous calcium carbonate (ACC) [4, 5] suggest a pathway to understanding anomalous compositions that are observed; thus motivating efforts to revisit underlying processes and inorganic/organic factors that control composition and isotopic signatures. There is also the question of whether the ACC to calcite transformation occurs by classical or non-classical processes in these complex organic-rich environments

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[6]. Using a simple model system, this study determines the effect of the ACC to calcite transformation on the Mg content of calcite in an inorganic (Control) and carboxyl-rich (organic acids) environment.

2. METHODS

The inorganic control experiments were conducted by synthesizing ACC using 1) 100 ml solutions with Mg/Ca ratios = 0.5 to 10.0 (prepared from $CaCl_2•2H_2O$ and $MgCl_2•6H_2O$), and a fixed Ca^{2+} concentration of 50 mM; and 2) 200 mM $NaHCO_3$ solutions adjusted to pH = 9.5 by NaOH. Upon mixing, these immediately produced ACC. After two minutes of continuous stirring, a 10 ml aliquot was collected and filtered for phase characterization and Mg and Ca analyses of solid and solution. The remaining ACC was allowed to transform within the parent solution. Upon crystallization, the products were separated from parent solution by centrifugation, rinsed with ethanol, and dried prior to further analysis. Experiments with the organic acids (aspartic, citric, oxydiacetic, tartaric) were selected for their ability to complex Ca^{2+} and Mg^{2+}. A 1.0 M stock solution of each organic acid was adjusted to a pH ~8.5 with NaOH. 5 ml of each stock solution was added to the Mg-Ca solution and brought to 100 ml. Synthesis of ACC then proceeded as described for the controls.

Compositions of solutions and solids were characterized by measuring molar concentrations of Mg and Ca by ICP-OES (CirOS VISION). Morphologies of ACC and Mg-calcite crystallites were imaged using SEM (FEI 600 FEG) with a thin layer of Au-Pd applied before imaging. The MiniFlex II XRD (Rigaku) was used to identify calcium carbonate phases. Raman spectra (JY Horiba LabRam 800mm) were also obtained using a 632.8 nm He-Ne laser for both amorphous and crystalline phases.

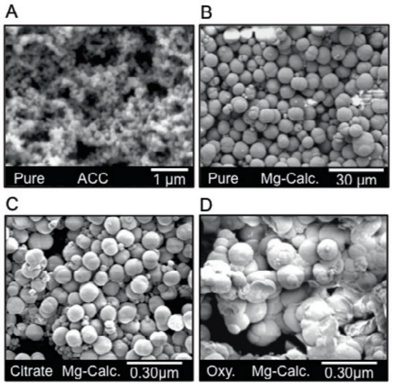
3. RESULTS

3.1. Transformation of Mg-ACC into Mg-calcite in the absence of carboxylated molecules

The ACC is comprised of spherical particles of <50 nm (Fig. 1A) for all Mg contents. Raman spectra are absent of lattice and internal vibrations except the symmetric stretch of the CO_3 group (ν_1), that shifts from 1083 cm^{-1} and 1094 cm^{-1} with increasing Mg/Ca ratios as reported previously [7]. In contrast to studies that produce a mixture of calcite–aragonite or calcite–vaterite [8, 9, 10], the ACC formed by this process transforms into calcite without evidence of secondary phases for all Mg/Ca conditions (to the extent that additional phases can be detected by SEM, XRD, and Raman). The calcite, regardless of Mg content, is comprised of ~8–10 μm spherulites whose external surfaces are rhombic microfacets (e.g., Fig. 1B). XRD spectra show peak broadening and a reduction in the d-spacing for all reflections as expected for Mg incorporation into the crystallites [11,12]. Fig 2 shows the (104) d-spacing correlates with $MgCO_3$ concentrations, suggesting that Mg^{2+} is located within the crystal lattice rather than adsorbed on surfaces. Raman spectra support this interpretation with four prominent bands in all the synthetic Mg-calcites that are attributable to shifts of external (lattice) and internal (CO_3 group) vibrations to higher frequencies with increasing solution Mg/Ca ratio. For solutions with initial Mg/Ca = 2 the ACC to calcite transformation occurred in approximately ~5 hours.

3.2. *Transformation of Mg-ACC into Mg-calcite in the presence of carboxylates*

For the conditions of these experiments, organic acids have little effect on Mg-ACC morphology (Fig. 3A). Again, ACC transforms to Mg-calcite without evidence of other polymorphs or differences in morphology for aspartate, citric and tartarate (Fig. 1C). In the presence of oxydiacetate, calcite forms as botyroids (Fig. 1D) similar to a previous report [13]. Raman and XRD show shifts in peak positions and broadenings, respectively, similar to the organic-free crystallites. However, organic molecules (except aspartate) significantly slow the rate of the ACC to calcite transformation. For example, at initial Mg/Ca = 2, the transformation requires 43, 48, and 100 hours, respectively. Fig. 3B shows the Mg content of the resulting calcites are biomolecule-specific with compositions that correlate with the Mg levels in the corresponding ACC.



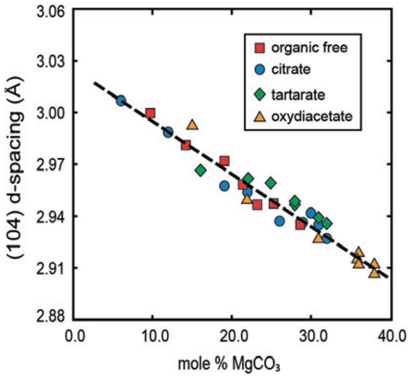


Fig. 1 (left). SEM images of ACC and Mg-Calcite formed in 5:1 Mg/Ca solutions illustrate typical morphologies. (A) ACC produced in the absence of organics. (B) Mg-Calcite formed in the absence of organics. (C) Mg-Calcite formed in the presence of 25 mM of citrate. (D) Mg-Calcite formed in the presence of 25 mM of oxydiacetate.

Fig. 2 (right). Calcite (104) d-spacing correlates with the mole% $MgCO_3$, as analyzed by ICP-OES.

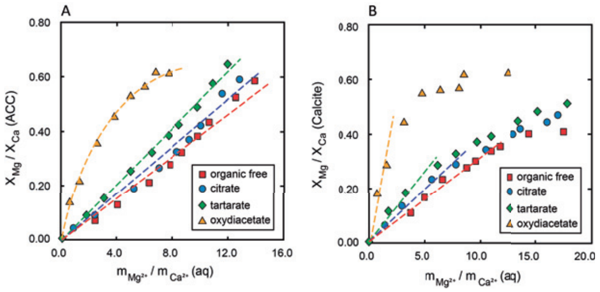


Figure 3. Mg partitioning into (A) ACC; and (B) calcite. (A) The X_{Mg} / X_{Ca} (ACC) is linearly dependent upon the ratio of Mg^{2+} /Ca^{2+} ions in solution, except for oxydiacetate. (B) In calcite, the linear relationship only occurs at low Mg^{2+}/Ca^{2+} ratios. Oxydiacetate significantly modifies the partition coefficient of Mg by a factor of 4x.

4. DISCUSSION

The Mg content of calcite that transforms from ACC displays a pattern that shifts with the initial Mg/Ca ratio of the solution. For an initial solution Mg/Ca <5, the Mg content of calcite is slightly enhanced relative to the original ACC for all control and all biomolecule-containing experiments (Fig. 4A). Compositions of ACC and transformed calcite are similar for conditions where Mg/Ca ~5 (~3 for oxydiacetate) (Fig. 4B). At higher initial Mg/Ca, the transformation produces Mg-deplete calcite compositions with respect to the precursor ACC (Fig. 4C).

We focus on conditions relevant to most natural environments by evaluating the region where Mg/Ca levels are 0 to ~8. Assuming Mg partitioning into ACC is governed by equilibrium thermodynamics, one can write:

$$\left(\frac{\chi_{Mg}^{ACC}}{\chi_{Ca}^{ACC}}\right) = D_{Mg^{2+}}^{ACC}\left(\frac{m_{Mg^{2+}}^{aq}}{m_{Ca^{2+}}^{aq}}\right) \tag{1}$$

where χ_{Mg}^{ACC} and χ_{Ca}^{ACC} = mole fraction of $MgCO_3$ and $CaCO_3$ in ACC, respectively, $m_{Mg^{2+}}^{aq}$ and $m_{Ca^{2+}}^{aq}$ = molar concentration of ions in solution, and D_{Mg2+} = distribution coefficient for ACC [14]. ACC compositions obey the linear trend predicted by Eqn. (1) for Control and all organic-bearing experiments except for oxydiacetate at higher Mg levels (Fig. 3A). At lower Mg levels, the calcite that transforms from ACC also obeys this linear dependence (Fig. 3B) with similar, but small enhancements in the values of $D_{Mg^{2+}}^{ACC}$ and $D_{Mg2+\ calcite}$ over the linear segments (compare Fig. 3AB). Thus, the Mg content of calcite is similar, but slightly higher, than the Mg content of the ACC from which it forms. Moreover, compositions are biomolecule-specific with the strongly electronegative ions correlated with calcites that have the highest Mg content. While an equilibrium model appears to describe the calcite compositions seen here, previous studies provide evidence that the Mg content of calcite is more likely controlled by a combination of kinetic and thermodynamic factors [15, 16].

The shift in the Mg fractionation pattern at higher Mg contents (Fig 3B, 4C) likely reflects a combination of effects that arise from 1) slower rates of calcite growth in the progressively higher Mg solutions; and 2) shifts in solution chemistry during precipitation as Mg/Ca ratios increase. By slowing the rate of calcite growth, a progressively larger amount of Mg can be excluded from the calcite that forms [8]. This explanation is also consistent with the observation that the threshold for departure from the linear trend (Fig 3B) is inversely related to the increasing time to transformation of control and organic-acid experiments. These observations support evidence that the ACC to calcite transformation occurs by a classical dissolution/reprecipitation process [15].

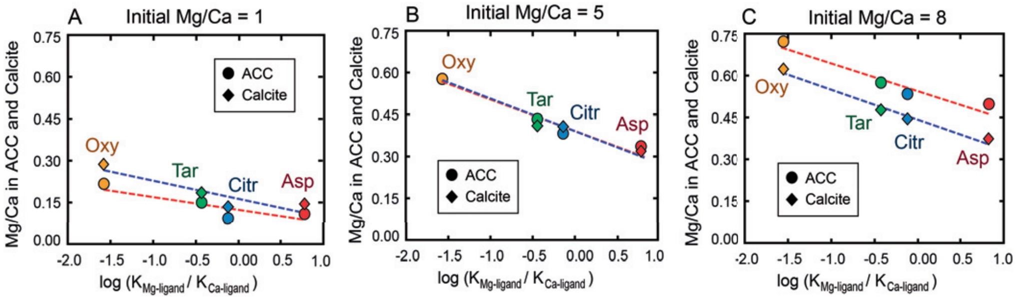


Figure 4. Mg/Ca ratio in ACC and calcite formed in the presence of organics as a function of $log\left(\frac{K_{Mg-ligand}}{K_{Ca-ligand}}\right)$ for conditions: (A) Initial Mg/Ca ratio of 1.0. (B) Initial Mg/Ca ratio of 5.0. (C) Initial Mg/Ca ratio of 8.0.

Consistent with Wang et al. [13], ACC composition is regulated by a systematic relationship to the ability of the organic acids to complex free Ca^{2+} and Mg^{2+}. Fig. 4 quantifies this dependence and shows 1) the highly electronegative oxydiacetate promotes the highest Mg levels for all Mg/Ca ratios; and 2) the

ACC that forms from the highest initial Mg levels transforms (slowly) to a calcite with a relatively depleted level of Mg (Fig 4C), also by a systematic dependence upon ligand chemistry.

In conclusion, the findings demonstrate a pathway to forming very high Mg calcite that contains up to 42 mol% $MgCO_3$ without evidence of other polymorphs. The calcite compositions formed by this process are similar to the ACC intermediate phase and Mg content increases by a systematic relationship to the chemistry of the organic acids.

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