

Calcite growth-rate inhibition by fulvic acid and magnesium ion—Possible influence on biogenic calcite formation

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ABSTRACT

Increases in ocean surface water dissolved carbon dioxide (CO_2) concentrations retard biocalcification by reducing calcite supersaturation (Ω_c). Reduced calcification rates may influence growth-rate dependent magnesium ion (Mg) incorporation into biogenic calcite modifying the use of calcifying organisms as paleoclimate proxies. Fulvic acid (FA) at biocalcification sites may further reduce calcification rates. Calcite growth-rate inhibition by FA and Mg, two common constituents of seawater and soil water involved in the formation of biogenic calcite, was measured separately and in combination under identical, highly reproducible experimental conditions. Calcite growth rates ($\text{pH}=8.5$ and $\Omega_c=4.5$) are reduced by FA (0.5 mg/L) to 47% and by Mg (10^{-4} M) to 38%, compared to control experiments containing no added growth-rate inhibitor. Humic acid (HA) is twice as effective a calcite growth-rate inhibitor as FA. Calcite growth rate in the presence of both FA (0.5 mg/L) and Mg (10^{-4} M) is reduced to 5% of the control rate. Mg inhibits calcite growth rates by substitution for calcium ion at the growth site. In contrast, FA inhibits calcite growth rates by binding multiple carboxylate groups on the calcite surface. FA and Mg together have an increased affinity for the calcite growth sites reducing calcite growth rates.

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1. Introduction

Over the past decade, the importance of calcium carbonate formation in the global carbon cycle has stimulated research concerning calcium carbonate crystal growth kinetics [1]. For example, increasing ocean water CO_2 concentrations retard biogenic calcite formation by reducing calcite supersaturation (Ω_c) [2–4]. Fulvic acid (FA), a large reactive global carbon reservoir, reduces calcite growth rates [5] and may reduce biocalcification rates, affecting ocean uptake of CO_2 . Reduced biocalcification rates may influence growth-rate dependent Mg incorporation into biogenic calcite, an indicator for past sea surface temperatures, and may thereby modify the use of calcifying organisms as paleoclimate proxies. In terrestrial ecosystems carbonate mineral formation in soils has important biogeochemical consequences for the global carbon cycle and sequestration of anthropogenic carbon dioxide emissions, because carbonate mineral crystallization influences CO_2 transfer between soils and the atmosphere [6]. Pedogenic calcite in desert soils, an important indicator of paleoclimate and landscape age, is not simply the result of inorganic precipitation of calcium

carbonate; biomineralization by soil microorganisms also leads to carbonate mineral formation [7].

Despite the importance of calcium carbonate formation in the global carbon cycle, the effects of multiple calcite crystal-growth rate inhibitors mediating carbonate mineralization have not been examined. Multiple mineral formation pathways are susceptible to growth rate inhibition by a range of aqueous acidic organic species [1]. One model of calcite crystal growth is the spiral crystal-growth theory developed by Burton, Cabrera, and Frank (BCF) [8]. Other mechanisms, including polynuclear growth mechanisms have been reported in the literature for the crystal growth of calcite from solutions both in the absence and in the presence of inhibitors [9]. Calcite forms by terrace-ledge-kink nucleation and growth processes, and the rate-determining step in calcite formation is incorporation of a calcium ion (Ca) at growth sites. Calcite growth-rate inhibition occurs when FA and/or Mg reduce Ca incorporation.

At present, it is unclear that the BCF or the polynuclear model of crystal growth applies to biocalcification or biogenic calcite formation. For example, during the past decade amorphous calcium carbonate (ACC), stabilized by acidic biomolecules, has been identified as an intermediate in calcite biomineralization. Carboxylic acids influence ACC Mg content and the Mg content of biogenic calcite formed from ACC [1]. However, the molecular basis for the relation between ACC Mg content and acidic

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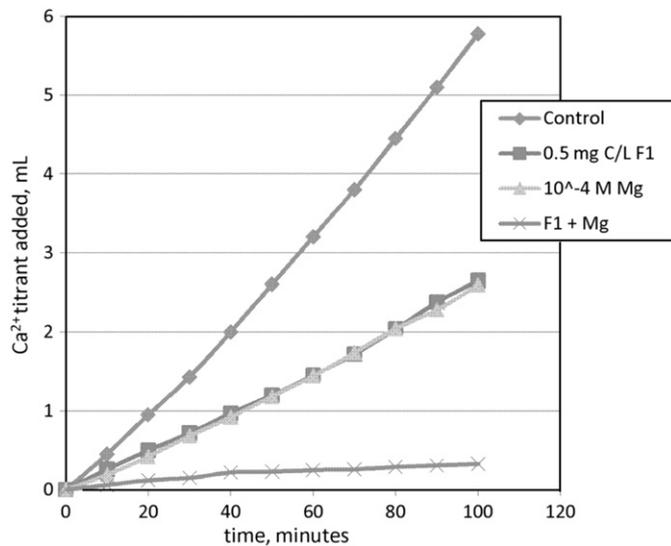


Fig. 1. Calcite crystal growth at constant Ω_c in the presence of FA (0.5 mg/L), Mg (10^{-4} M), and FA (0.5 mg/L) with Mg (10^{-4} M).

dissolved organic matter is unclear. Biogenic calcite Mg content increases the mineral solubility. Thus, biogenic Mg calcites are “first responders” to ocean acidification. As oceans acidify, biogenic Mg calcites will dissolve based on their solubility, with the most soluble minerals (that is those with the highest Mg content) dissolving first.

This paper addresses an aspect of calcite formation that may be important in biogenic calcite formation. Calcite growth-rate inhibition was examined in the presence of FA and Mg separately and in combination under identical, highly reproducible experimental conditions using a calcite seeded growth procedure at constant $\Omega_c=4.5$ [10–13]. The growth rate inhibition effectiveness of HA is also examined.

2. Fulvic acid description

Fulvic acid used here was obtained at site F1 (26°21'35"N, 80°22'14"W) along a 40-mile transect in the Florida Everglades in Water Conservation Area 2A, discharging into Florida Bay and the Atlantic Ocean [14], using procedures and techniques developed in the US Geological Survey over the past 30 years [15]. Dissolved organic matter in surface water at site F1 is from cattail (*Typha domingensis*) and sawgrass (*Cladium jamaicense*) aquatic decomposition products [14,16–18]. FA isolated at site F1, operationally defined as organic material adsorbed by Amberlite[®]XAD-8 resin at pH=2 and eluted from the resin with a 0.1 N sodium hydroxide solution, comprises approximately 96 to 97% FA with the balance being HA [16]. Two calcite growth-rate measurements were done with HA (isolated at site F1 at the same time as the FA sample) to evaluate its growth rate inhibition effectiveness in comparison with FA.

3. Materials and methods

3.1. Seeded constant composition calcite growth-rate experiments

Experimental details and solution preparation are given elsewhere [5]. Briefly, solutions prepared using doubly distilled water and American Chemical Society (ACS) reagent-grade chemical reagents were filtered through a 0.1- μ m Whatman filter before use. Grade A glassware was used for all experiments.

Growth-rate measurements, at fixed solution pH, calcite supersaturation, and chemical composition, employed a constant composition system [19]. Experimental solutions contain total calcium concentration of 0.0019 M, total carbonate concentration of 0.0019 M, pH~8.5, ionic strength of 0.1 M maintained with KNO₃ background electrolyte, carbon dioxide partial pressure of $10^{-3.55}$ atm, and Ω_c of 4.5. After seed addition, experiments were conducted in a sealed reactor closed system to the atmosphere. Reactor dead volume above the supersaturated solution was kept to a minimum during the experiments.

Potentiometrically controlled addition of lattice ions fixed calcite supersaturation during seeded growth and ensured accurate determination of calcite growth rates during the experiment.

The calcite growth reaction can be written as:



During calcite growth the pH-stat apparatus senses decreasing pH and causes the double-buret, constant-composition system to respond by adding CaCl₂ and Na₂CO₃ titrant solutions (at 5-times reactor solution concentration) to replace solute lost to crystal growth, keeping pH and solution composition constant. Titrant solutions also contained KNO₃ electrolyte to maintain constant ionic strength. Titrant volume added over the 100-min experiment length is recorded, along with pH, on a computer and dual-pen chart recorder (Fig. 1).

The slope of the line plotted for titrant volume added versus time yields a calcite growth rate using the following equation:

$$\text{Rate}(\text{mol}/((\text{m}^2) * (\text{min}))) =$$

$$\text{slope}(\text{L}/\text{min}) * M_{\text{titrant}}(\text{mol}/\text{L}) / (\text{mass}_{\text{seed}}(\text{g}) * \text{SA}_{\text{seed}}(\text{m}^2/\text{g})) \quad (2)$$

where M_{titrant} is the molar concentration of the titrant solution, $\text{mass}_{\text{seed}}$ is the mass of the seed crystal added at the start of the experiment in grams, and SA_{seed} is the specific surface area of the added seed crystal in units of square meters per gram of seed (determined using the BET procedure [20]). Titrant addition over time plots were straight lines ($r^2 > 0.995$ for the control experiments (without any added FA or Mg) and > 0.94 for experiments with FA). Relative growth rate inhibition by FA, Mg, or FA+Mg, in comparison to calcite growth rates in solutions without added organic material, are expressed as reduced rates R/R_0 for each experiment:

$$R/R_0 = \text{rate in presence of inhibitor} / \text{rate in absence of inhibitor} \quad (3)$$

Thus, a smaller reduced rate indicates greater growth inhibition. FA and Mg concentrations used in this study reduce the additive-free calcite growth rate by about half. Nine control experiments without added FA or Mg, five calcite growth-rate measurements in the presence of FA, two experiments with 10^{-4} M Mg and one experiment in the presence of FA (0.5 mg/L) plus 10^{-4} M Mg were done. Two experiments at solution concentrations of 1 mg/L were performed with FA and two with HA to assess the differences between FA and HA.

3.2. Solution supersaturation

Solution Ω_c values describe calcium carbonate mineral formation tendency and are defined as:

$$\Omega_c = [\text{Ca}^{+2}][\text{CO}_3^{-2}] / K_{\text{sp}} \quad (4)$$

where brackets refer to calcium and carbonate ion activities in solution, and K_{sp} is the calcite thermodynamic solubility product at 25 °C. Solution speciation and Ω_c are calculated with the WATEQ4F program of Ball and Nordstrom [21].

4. Results

4.1. Calcite growth rates in the presence FA and Mg separately and together

Supersaturated solutions, prior to the addition of seed crystals, are stable and do not nucleate calcium carbonate minerals for at least several hours. Calcite growth-rate inhibiting substances do not initiate calcium carbonate nucleation or growth in the reaction vessel in the absence of added seed crystals.

Calcite growth begins immediately after the addition of seed crystals—growth is not preceded by an induction period. Solution pH is maintained at a constant value of 8.5 as crystal growth proceeds by titrant addition. Calcium concentration and alkalinity are determined before and after each experiment and demonstrate constant solution composition during the experiment. Titrant addition with time, and measured calcite growth rates, are linear and uniform during each experiment (Fig. 1).

Control experiments have a mean calcite growth rate, standard deviation, and relative standard deviation of 11.0×10^{-5} mol/(m² min), 1.6×10^{-5} mol/(m² min), and 14% ($n=9$), respectively. Experiments in the presence of FA (0.5 mg/L) have a mean calcite growth rate, standard deviation, and relative standard deviation of 5.2×10^{-5} mol/(m² min), 2.3×10^{-6} mol/(m² min), and 15% ($n=5$), respectively. Growth-rate measurements in solutions containing FA are reproducible, and the reduced rate in the presence of FA (0.5 mg/L) is 0.47 (Table 1).

Experiments in the presence of 10^{-4} M magnesium have a mean calcite growth rate and a mean rate difference for two samples of 4.2×10^{-5} mol/(m² min) and 0.8×10^{-5} mol/(m² min), respectively (Table 1). The reduced rate in the presence of 10^{-4} M magnesium is 0.38. Experiments in the presence of FA (0.5 mg/L) and 10^{-4} M magnesium have a calcite growth rate of 0.6×10^{-5} mol/(m² min) and a reduced rate of 0.054.

4.2. Calcite growth rates in the presence HA

Experiments in the presence of higher FA concentrations (1 mg/L) have a mean calcite growth rate of 2.03×10^{-5} mol/(m² min). Growth-rate measurements in solutions containing FA are reproducible, and the rate in the presence of FA (1 mg/L) is about half that of experiments with 0.5 mg/L FA. In contrast, experiments in the presence of HA (1 mg/L) have a mean calcite growth rate of 0.97×10^{-5} mol/(m² min). Duplicate growth-rate measurements in solutions containing HA have a mean rate difference of 0.34×10^{-5} mol/(m² min). At 1 mg/L R/R_0 for HA is 0.09 in comparison to the R/R_0 value of FA of 0.18. Therefore, HA is twice as effective as a calcite growth-rate inhibitor as FA at a concentration of 1 mg/L.

5. Discussion

FA and Mg reduce calcite growth rates substantially, and in combination cause a synergistic decrease in the calcite growth rate (Table 1) through interactions at growth sites on calcite

surfaces [19,22]. Calcite growth-rate inhibition by FA and Mg separately, and together, occurs at low solution concentrations of FA and Mg, consistent with blockage of growth and/or surface nucleation sites on calcite seed crystals. During calcite growth at low supersaturations Mg inhibits the growth rate by substitution for Ca at growth sites with a concomitant decrease in solution magnesium ion concentration [10,22]. In contrast, FA inhibits calcite growth rates by binding multiple carboxylate groups at or near growth sites on the calcite surface, FA is not substantially incorporated in the growing crystals, and solution FA concentrations do not change [5]. At high Ω , natural organic matter incorporates into calcium carbonate formed in an alkaline lake [15,23].

FA and Mg reduce calcite biocalcification rates at sub part per million concentration levels (Table 1). FA adsorbed at calcite growth sites may be charged or uncharged. Calcite growth in the absence and presence of FA and/or Mg likely involves incorporation of a hydrated Ca or Mg ion, or carbonate ion pair, and Ca solution speciation will influence the growth mechanisms. Ca is the predominant cation in solution and FA complexes are predominately CaFA.

FA and Mg interaction at the calcite-growth site influences biogenic calcite formation by calcite growth-rate reduction. Biogenic calcite formation is facilitated by a precursor (i.e. amorphous calcium carbonate (ACC)) [1]. Acidic (carboxylated) proteins and other polycarboxylic molecules mediate ACC Mg content and subsequent calcite morphology [1]. High molecular weight (MW) and high charge density (CD) enhance polycarboxylic interaction with growth sites on calcite surfaces [5,19,24]. MW influences polycarboxylic acid solubility and adsorption affinity for calcite surfaces. Carboxylic acid aqueous solubility trends are similar to the solubility trends for alcohols, that is, low molecular weight carboxylic acids are more soluble in water, and solubility decreases as the carboxylic acid molecular weight increases. A solubility–molecular weight relation is expected to apply to the solubility of HA and FA in aqueous solution. Supersaturated solution divalent ion content influences FA CD. Ca and/or Mg reduce dissociated FA charge and the FA CD by complex formation. Ca–FA binding, incorporating monodentate and bidentate complex formation, shows an effective charge on FA (i.e., the resulting FA charge after FA–Ca complex formation) between 0.7 and 0.8 at pH values of 6 to 7 [25].

Calcite crystal-growth rates and FA adsorption are influenced by calcite surface charge. Coating calcite with cationic polymers (increasing the calcite surface positive surface charge) enhances adsorption of negatively charged FA [26]. However, differences in calcite growth-rate inhibition between HA and FA reflects molecular weight differences not differences in CD. FA molecular weight is 850 Da and that of HA is 1162 Da [27]. Higher molecular weight HA has greater calcite surface affinity than FA. This is because of the lower solubility of HA in comparison to FA. At the same solution concentration, HA is about twice as effective in reducing calcite growth rates as FA. FA equivalent weight is 179 g/equ and that of HA is 262 g/equ [27]. FA and HA have 4.6 \pm 0.2 ionized carboxyl groups per average molecule. Ionized carboxylate groups per average

Table 1
Summary of results.

Experiment	Inhibitor concentration, mg/L or M	Number of samples	Mean rate, mol/((m ²)(min))	Standard deviation mol/((m ²)(min))	R/R_0
Control	0.0	9	11.0×10^{-5}	1.5×10^{-5}	
FA	0.5 mg DOC/L	5	5.2×10^{-5}	2.3×10^{-5}	0.47
Magnesium	10^{-4} M	2	4.2×10^{-5}	–	0.38
FA+Magnesium	0.5 mg DOC/L+ 10^{-4} Mg	1	0.6×10^{-5}	–	0.054

–: not applicable.

molecule and molecular CD differences are insufficient to cause the observed differences in calcite growth rates between HA and FA.

HA and FA calcite growth rate differences may arise because HA contains FA molecular aggregates particularly effective in reducing calcite growth rates (Jerry, Leenheer, 2011, personal communication). Alternatively, greater calcite growth rate inhibition by HA in comparison to FA may be due to complex formation differences between FA and HA. Increased calcite growth rate inhibition by HA reflects the greater metal ion binding ability of HA than for FA, if formation of surface complexes is favored over the formation of aqueous complexes [28]. Multiple carboxylate groups are not sufficient for significant calcite growth-rate reduction. For example, citric acid (10 mg/L) [19] and Lake Fryxell, Antarctica FA (5 mg/L) [5] have only slight calcite growth-rate inhibition (R/R_0 values of about 0.6). A minimum number of available carboxylate groups per inhibitor molecule, appropriate carboxyl group orientation, and a minimum molecular charge density are required for optimum calcite growth-rate inhibition and influence on calcite biocalcification rates [19,24].

6. Conclusions

FA and Mg inhibit calcite growth rates by blocking growth sites on the calcite surface. Synergistic calcite growth-rate reduction in a solution containing both FA and Mg suggests that a FA–Mg interaction enhances calcite growth site adsorption affinity of both FA and Mg. Differences in HA and FA calcite growth rate reduction reflect differences in HA and FA molecular weight and corresponding lower solubility of the (higher molecular weight) HA inhibiting species at the calcite growth site although other processes cannot be ruled out. Inhibition of calcite growth rates by FA and Mg together involve enhanced adsorption affinity of a FA–Mg species and/or a less soluble FA–Mg species on the calcite surface as the agent for the synergistic rate reduction.

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