CALCITE GROWTH – RATE INHIBITION BY FULVIC ACIDS ISOLATED FROM BIG SODA LAKE, NEVADA, USA, THE SUWANNEE RIVER, GEORGIA, USA AND BY POLYCARBOXYLIC ACIDS

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ABSTRACT

Calcite crystallization rates are characterized using a constant solution composition at 25° C, pH=8.5, and calcite supersaturation (Ω) of 4.5 in the absence and presence of fulvic acids isolated from Big Soda Lake, Nevada (BSLFA), and a fulvic acid from the Suwannee River, Georgia (SRFA). Rates are also measured in the presence and absence of low-molar mass, aliphatic-alicyclic polycarboxylic acids (PCA). BSLFA inhibits calcite crystal-growth rates with increasing BSLFA concentration, suggesting that BSLFA adsorbs at growth sites on the calcite crystal surface. Calcite growth morphology in the presence of BSLFA differed from growth in its absence, supporting an adsorption mechanism of calcite-growth inhibition by BSLFA. Calcite growth-rate inhibition by BSLFA is consistent with a model indicating that polycarboxylic acid molecules present in BSLFA adsorb at growth sites on the calcite crystal surface. In contrast to published results for an unfractionated SRFA, there is dramatic calcite growth inhibition (at a concentration of 1 mg/L) by a SRFA fraction eluted by pH 5 solution from XAD-8 resin, indicating that calcite growth-rate inhibition is related to specific SRFA component fractions. A cyclic PCA, 1, 2, 3, 4, 5, 6-cyclohexane hexacarboxylic acid (CHXHCA) is a strong calcite growth-rate inhibitor at concentrations less than 0.1 mg/L. Two other cyclic PCAs, 1, 1 cyclopentanedicarboxylic acid (CPDCA) and 1, 1 cyclobutanedicarboxylic acid (CBDCA) with the carboxylic acid groups attached to the same ring carbon atom, have no effect on calcite growth rates up to concentrations of 10 mg/L. Organic matter adsorbed from the air onto the seed crystals has no effect on the measured calcite crystal-growth rates.

Keywords: Calcium carbonate (calcite) growth-rate inhibition, fulvic acid, Big Soda Lake, Nevada, Suwannee River, Georgia, polycarboxylic acids.

1. INTRODUCTION

Understanding calcium carbonate mineral formation in alkaline lakes and other locations such as arid soils, geological formations and the deep-sea sediment-water interface [1] requires knowledge of mineral formation factors [2]: mineral solution supersaturation (Ω) mineral nucleation inhibition of mineral nucleation and growth by specific chemical substances crystal growth and mineral aggregation and transformation. Calcium carbonate polymorphs calcite, and aragonite occur widely at the earth surface; other polymorphs and hydrates such as vaterite, monohydrocalcite [3], hexahydrocalcite (ikaite) [4], and amorphous calcium carbonate [5] occur less frequently. Calcite growth-rate inhibitors facilitate unstable calcium carbonate polymorph formation (for example, aragonite, monohydrocalcite, and ikaite [3, 4]) by reducing the stable polymorph (calcite) crystal growth rates.

Investigators [6-16] have studied aqueous carbonate mineral growth kinetics in natural waters. For example, Cloud [14] summarizes early experiments dealing with calcium carbonate precipitation from seawater. Chave and Suess [15] discuss the influence of dissolved organic matter on calcium carbonate precipitation from seawater. Calcium carbonate formation and organic carbon production rates in surface ocean water are key marine variables influencing ocean carbon cycling [16].

Natural polycarboxylic acids (PCAs) (for example, aquatic and soil fulvic acids) often are effective calcite growth-rate inhibitors at part per million solution concentrations [17-20]. Aquatic fulvic acids present in lakes, rivers, oceans and sediments influence lake eutrophication [8, 21-23], carbon sequestration [16], organic and inorganic pollutant distribution [24] and radionuclide speciation [25].

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Carbonate formation in lacustrine environments is an active research area [3-4, 11, 26-27]. For example, McConnaughey *et al.* [11], examined the importance of biological processes in lake water calcium carbonate formation and hypothesize that algae alter water pH adjacent to algal cells, shifting Ω during photosynthesis and leading to calcium carbonate formation. Recently, carbonate mineral reactions in a variety of geological settings have been proposed for anthropogenic carbon dioxide sequestration [28].

Calcite growth-rate inhibition in the presence of benzene PCAs (rigid, planar, cyclic structures) demonstrates that more carboxylated benzenes are better calcite growth-rate inhibitors than less carboxylated benzenes [29]. The distance between carboxyl groups across a benzene ring is similar to the 2- to 5-chain carbons suggested by Kuntze as optimum for crystallization rate reduction [30]. Because the organic acids in BSLFA and SRFA are mixtures in contrast to pure PCAs, the details of atomic distances between functional groups and their orientations for BSLFA and SRFA are unknown.

Dissolved organic substances mediate and/or modify calcium carbonate reaction rates in surface water and groundwater, and reduce calcite growth rates at low concentrations (milligram to microgram per liter concentrations) [18, 21-23, 31-33]. Plummer *et al.* [13] report calcite growth-rate reduction associated with dissolved organic carbon (DOC). Recently, De Yoreo and Dove [34] proposed that interactions between organic growth-rate modifiers and step edges on existing crystal faces modify growth morphology.

Calcium carbonate formation in lakes may lead to mineral assemblages mediated by DOM [3-4, 12, 35]. Calcite growth-rate reduction may be significant for modeling carbon sequestration by lakes and organic matter preservation leading to fossil fuel formation. For example, Big Soda Lake sediments contain only low-magnesian calcite (Michael Rosen, personal communication, 2010). Monohydrocalcite, which forms at the lakeshore, is absent in the sediments, and calcite is only a small part of the Big Soda Lake sediment. Fulvic acid may reduce calcite precipitated in Big Soda Lake, causing monohydrocalcite to form in the tufa towers along the shore [3]. Alternatively, the tufa towers may reflect a change in ground water inputs associated with changing irrigation practices over the past one hundred years.

The purpose of this work is to characterize calcite crystal-growth rates in pure solution, in the presence of fulvic acids isolated from Big Soda Lake, Nevada, and from the Suwannee River, Georgia. Calcite crystal-growth rates are also determined in the presence of several aliphatic-alicyclic polycarboxylic acids. The influence of atmospheric organic matter adsorbed on calcite growth surfaces is also examined. We seek to identify and characterize the relationship between BSLFA/SRFA/PCA structure and calcite growth-rate inhibition.

2. STUDY AREAS

Big Soda Lake, Nevada, USA is a groundwater-fed, closed-basin lake studied by numerous investigators over the past 70 years. Hutchinson [36] describes Big Soda Lake as a small crater lake near Fallon, Nevada, discusses early exploration of Big Soda Lake by Russell [37] and documents changes in the lake morphology and volume up to the 1930s. Recently, Rosen *et al.* [3] described rapid formation of calcium carbonate monohydrate in the alkaline surface water at groundwater seeps at the margins of Big Soda Lake.

The Suwannee River is a major river of southern Georgia and northern Florida in the United States. Averett *et al.* [38] characterize the Suwannee River, and describe the isolation and characterization of fulvic acids from the river.

3. MATERIALS AND METHODS

3.1. Seeded Constant Composition Calcite Growth-Rate Experiments

Experimental details and solution preparation are described in detail elsewhere [18, 33, 39]. Briefly, solutions prepared using doubly distilled water and American Chemical Society (ACS) reagent-grade chemicals were filtered through a 0.1-μm Whatman filter before use. 1, 2, 3, 4, 5, 6-cyclohexane-hexacarboxylic acid (CHXHCA); 1, 1-cyclopentane-dicarboxylic acid (CPDCA), and 1, 1-cyclobutane-dicarboxylic acid (CBDCA) purchased from TCI America (Portland, Oregon) were used as received. Grade A glassware was used for all experiments.

Growth-rate measurements at fixed solution pH and chemical composition employ a constant composition system [40]. Experimental solutions contain a total calcium concentration of 0.0019 M, total carbonate concentration of 0.0019 M, pH ~ 8.52±0.01, ionic strength 0.1 M maintained with KNO_3 background electrolyte, carbon dioxide partial

pressure of $10^{-3.55}$ atm, and Ω of 4.5 at 25.0±0.1°C. Aragonite supersaturation is 3.2, vaterite supersaturation is 1.2, and other calcium carbonate hydrated phases and an amorphous phase are subsaturated in the calcite seeded growth solution.

Atmospheric carbon dioxide exchange with reactor solutions was minimized by keeping all reactor openings sealed during experiments. The working volume of the experimental solution is sufficient to minimize the dead volume over the supersaturated solutions. Isolation from atmospheric carbon dioxide was verified by demonstrating a stable supersaturated solution pH over a 24-hour test period. Seed addition and reactor sampling were done rapidly -- solution carbon dioxide exchange with atmospheric carbon dioxide during opening the reaction vessel was minimal and was very slow compared to the time needed to add seed material or remove samples for chemical analysis.

Potentiometrically-controlled addition of lattice ions during seeded growth ensured accurate determination of calcite growth rates at a fixed calcite supersaturation during the experiment. The constant composition procedure avoids complications due to changing solution supersaturation encountered in more conventional seeded-growth experiments.

The calcite growth reaction can be written as Eq. 1,

$$Ca^{2+}(aq) + HCO_3^-(aq) \Leftrightarrow CaCO_3(s) + H^+(aq) \qquad (1)$$

Eq. 1 occurs during each experiment and the pH-stat apparatus, sensing decreasing pH, causes the double-burette system to respond by adding $CaCl_2$ and Na_2CO_3 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 KNO_3 electrolyte to maintain constant ionic strength. Constant solution composition during each experiment is verified by measuring total calcium concentration and alkalinity before and after all experiments. Total calcium ion concentration is measured with a complexometric titration procedure; free calcium ion concentration is calculated from the measured solution composition using the WATEQ4F program. Titrant volume added over the 100-minute experiment length was recorded along with pH on a computer and dual-pen chart recorder.

Before each seeded-growth experiment, calcite supersaturated solutions are prepared by adding carbonate solution to the thermostated, jacketed reaction vessel, then adding calcium solutions dropwise to reduce the possibility of nucleation. After calcium solution addition to the carbonate solution is completed, the supersaturated solution pH is adjusted to 8.5 using a few drops of 0.05 M KOH. Supersaturated solution metastability is verified by monitoring solution pH for an hour prior to the experiment and verifying that the pH value remains constant, demonstrating that there is no calcite growth or nucleation prior to the addition of seed crystals. Total solution volume in the reaction vessel is 400 mL and experiments start by addition of dry calcite seed (100 mg) to the supersaturated solution.

Calcite seed (Baker Chemical Company, ACS reagent grade, Lot 26832) was verified as pure calcite with a scanning electron microscopy and a Siemens D5000 X-ray diffractometer. Seed crystal contained only calcite. Calcite seed crystal had a specific surface area of 0.256 ± 0.008 m^2/g, as determined by a three-point nitrogen adsorption technique on eight replicate samples [41]. Seed crystals have a lognormal size distribution [39]. Some experiments used calcite seed crystals heated in an oven at 450° C for two 4-hour cycles, removing any adsorbed organic material prior to use in the growth-rate experiment. Baked seed crystals were stored in a glass container baked at the same temperature.

Solutions containing organic acids, prepared in matrices identical to the carbonate solutions, were filtered through 0.1-μm Millipore cellulose nitrate filters and used within 36 hours of preparation.

The slope of the titrant volume added vs. time line, a measure of calcite growth rate, is converted to a growth rate by the following Eq. 2,

$$\text{Rate } (mol/m^2min) = \text{slope } (L/min)M_{titrant} \ (mol/L) \ / \ (mass_{seed} \ (g)SA_{seed} \ (m^2/g)) \qquad (2)$$

where $M_{titrant}$ is the molar concentration of the titrant solution, $mass_{seed}$ 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. A strip chart recorder recorded titrant addition as a function of time during each experiment, and values for milliliters of titrant added were entered into a spreadsheet with 0.02 mL precision. The slope of the best-fit line over the 100-minute experiment interval was used to calculate the calcite crystal growth rate. Experiments yielded straight lines for titrant addition over time ($r^2 > 0.995$ for the control experiments and >0.94 for experiments with BSLFA). Relative growth rate inhibition by organic acids in comparison to calcite growth rates in solutions without added organic material are expressed as reduced rates R/R_o for each experiment Eq. 3,

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

Thus, a lower reduced rate indicates greater growth inhibition. Calcite crystal-growth experiments were performed with a range of inhibitor concentrations for several PCAs, at two concentrations for BSLFA and at one concentration for SRFA. Fulvic acid isolated from Big Soda Lake concentrations in the supersaturated solutions were 1 and 5 mg/L and for SRFA were 1 mg/L. Control experiments and calcite growth-rate measurements in the presence of BSLFA and a SRFA fraction were done at least in duplicate.

3.2 Solution Supersaturation

Solution Ω values describe calcium carbonate mineral formation tendency and are defined in Eq. 4,

$$\Omega = [Ca^{2+}(aq)][CO_3^{2-}(aq)]/K_{sp} \quad (4)$$

where brackets refer to calcium and carbonate ion activities in solution and K_{sp} is the calcite thermodynamic solubility product at the sample temperature. Solution speciation and Ω are calculated with the WATEQ4F program of Ball and Nordstrom [42].

3.3 Isolation of Big Soda Lake and Suwannee River Fulvic Acids

Big Soda Lake is alkaline (pH~9.7) and chemically stratified, containing dissolved organic carbon (DOC) concentrations as high as 60 mg/L and dissolved salt concentrations as high as 88,000 mg/L [3, 43]. Big Soda Lake surface water is moderately saline and oxygenated, whereas water below the chemocline is hypersaline and anoxic [43]. Fulvic acid was isolated from the surface water (the chemocline of Big Soda Lake is at 34 m depth) by adsorption chromatography (Amberlite ^{R} XAD-8 resin) [44-47]. The number average molar mass of the BSLFA is estimated to be 550 Daltons (determined by equilibrium ultracentrifugation) [45].

A specific fraction of fulvic acid from the Suwannee River, Georgia, was obtained by a large-scale isolation in November 1983 employing methods described previously [44]. This isolation procedure differed from the method used to isolate the Suwannee River Reference Sample for the International Humic Substances Society [38]. Briefly, a pH-gradient fractionation of 40 gm of unfractionated SRFA was conducted on an Amberlite ^{R} XAD-8 resin. This pH-gradient fractionation yielded 19 different elution-pH fractions. Selected fractions were measured for a range of physical and chemical characteristics. The fraction of SRFA eluted by pH 5.0 solution (the second most abundant fraction comprising about 12 % of the initial 40 gm of unfractionated SRFA), was used in the calcite-seeded crystallization experiments reported here.

This fractionation procedure, larger in scale than the fractionation reported previously [44], isolated sufficient SRFA sub-fractions to allow a detailed study of the acidity characteristics of fulvic acid from the Suwannee River [46,47]. This large-scale fractionation of SRFA required significant field and laboratory resources to obtain sufficient SRFA isolate mass for the growth-rate inhibition studies and other investigations [46].

3.4 DOC Concentration Measurements in Calcite Growth Experiments

DOC measurements in calcite growth solutions were conducted before and after selected calcite growth rate experiments with fulvic acid. Solutions were sampled for DOC before the addition of seed crystals and at the end of the growth rate experiment. DOC measurements made at the USGS Laboratory in Boulder, CO employed the persulfate wet-oxidation method (Oceanographic International Model 700 instrument). The standard automated analytical conditions for the instrument were used and sample volume was constrained to assure analytes were within the linear response of the instrument.

3.5 Solution Analysis

Solution calcium concentration before and after growth-rate measurement experiments is determined with the ethylenediaminetetraacetic acid (EDTA)-calcein complexometric method [48]. Alkalinity is determined before and after calcite-seeded growth experiments using a Radiometer model ABU 91 automatic titrator. Sample pH is recorded continuously during each experiment and temperature was regulated at 25.0±0.1°C with a jacketed Pyrex reaction flask with constant temperature circulating water from a temperature-controlled bath [33].

3.6 $CaCO_3$ Examination by Scanning Electron Microscopy (SEM) and X-ray Diffractometry

Scanning electron microscopy (SEM) was used to examine fresh calcite growth following experiments in

the absence and presence of BSLFA. Calcium carbonate particles from selected growth-rate experiments were isolated on filters and characterized with a JEOL SEM at the Denver Federal Center, Lakewood, Colorado, under a 20-kV, 64-μA beam with magnifications up to about 20,000x. A Siemens D5000 X-ray diffractometer using Cu(k_α) x-rays in the US Geological Survey Laboratory in Boulder, Colorado, was employed to measure the intensity of diffracted x-ray radiation from the seed crystal material. Seed crystal was scanned from 2θ = 20-80°.

4. RESULTS

4.1 Supersaturated Solutions

Supersaturated solutions are stable (i.e., 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.

4.2 Calcite Growth Rates in the Presence of Big Soda Lake Fulvic Acid

Crystal growth begins with addition of seed crystals. Growth is not preceded by an induction period. Solution pH, controlled by titrant addition, is constant as crystal growth proceeds. Solution calcium concentration and alkalinity, determined before and after each experiment, demonstrate constant calcite supersaturation during the experiment. Titrant addition with time and measured calcite growth rates are linear and uniform during each experiment (Figure 1).

Growth-rate measurements in solutions containing BSLFA are reproducible and identify effective BSLFA concentrations for calcite growth-rate reduction (Table 1). Slope values of titrant addition versus time plots, proportional to the calcite growth rates, decrease with increasing BSLFA concentration (Figure 1). Calcite-reduced growth rates (Eq. 3) decrease with increasing fulvic acid concentration (Figure 2). The calcite growth rate is about 52% of the control experiment growth rate at BSLFA concentrations of 1 mg/L and about 8% of the control experiment growth rate at BSLFA concentrations of 5 mg/L. Calcite reduced growth rates, expressed as the ratio R/R_0 (Eq. 3, Table 1) show a regular, statistically significant (R^2=0.9939, n=3) decrease with increasing BSLFA concentration (Figure 2).

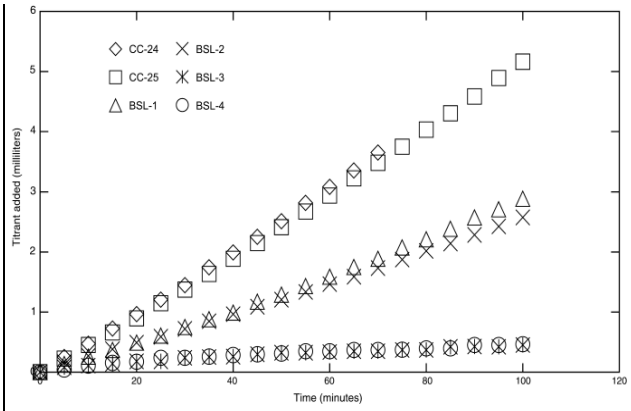

Figure 1 Calcite growth onto seed crystals at constant solution composition, 25°C, pH 8.5, and calcite supersaturation Ω 4.5, expressed as the amount of calcite growth (proportional to the titrant added) vs. time in the absence and presence of BSLFA. Calcite growth rates are calculated from the slopes of the best-fit curves. Growth rates decrease with increasing BSLFA concentration (mg/L). Control experiments have no added BSLFA (CC-24 and CC-25) other experiments shown have added BSLFA (1 mg/L BSL-1 and BSL-2; 5 mg/L BSL-3 and BSL-4).

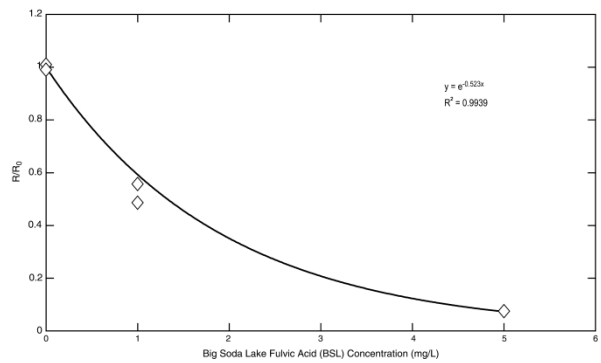

Figure 2 Calcite reduced growth rates onto seed crystals at constant solution composition, pH 8.5, and calcite supersaturation 4.5 expressed as the ratio R/R_0 where R_0 in the growth rate in the absence of added organic matter, and R is the rate in solutions with varying concentrations of fulvic acid isolated from Big Soda Lake, Nevada.

The best-fit curve slopes for each 100- minute experiment determine values of R. Calcite growth rates in the presence of fulvic acid are constant over the 100-minute experiments, indicating that fulvic acid adsorption is rapid. If fulvic acid adsorption was slow, calcite growth rate would decrease during the

experiment as more fulvic acid adsorbed onto the growing seed crystals. This was not observed for 47 calcite growth rate measurements with a range of fulvic acids and fulvic acid concentrations. Particle diffusion of the fulvic acid into the calcite seed crystal does not occur because the crystals are all well-formed calcite rhombs without significant internal structure.

4.3 Calcite Growth Rates in the Presence of Suwannee River Fulvic Acid fraction Eluted from XAD-8 Resin at pH 5

The pH 5 eluted SRFA (1.0 mg/L) dramatically inhibited calcite growth during the 100-minute growth experiment (Table 1). Control experiments with no organic matter (CC-21 and CC-22, Table 1) have an average calcite growth rate of $(9.9 \times 10^{-5} \pm 0.1) \times 10^{-5}$ mol/(m^{2}min). The SRFA pH 5 eluted-fraction replicate experiments have a calcite growth rate of 0.04×10^{-5} mol/(m^{2}min) (Table 1). The marked calcite growth rate reduction of this SRFA fraction at concentration of 1 mg/L (R/R_0= 0.006) contrasts with the un-fractionated SRFA which had R/R_0 values (1.0 mg/L) of 0.4 to 0.08 [20]. The number-average molar mass was 515 Daltons for the SRFA fraction eluted from XAD-8 resin at pH 2.5 and 645 Daltons for the SRFA fraction eluted from XAD-8 resin at pH 5.5. The number of carboxyl groups per average molecule was 3.5 for the SRFA fraction eluted at pH 2.5 and 3.6 for the SRFA fraction eluted at pH 5.5. Values for the number average molar mass and the number of carboxyl groups per average molecule for the pH 5 fraction are unavailable but are presumed to be similar to the values of the pH 2.5 and pH 5.5 fractions. The percent aromatic character of the average molecule for the SRFA fraction eluted at pH 5 is about 25%. Pronounced calcite growth-rate inhibiting properties of the SRFA fraction eluted from XAD-8 resin at pH 5.0 emphasizes the calcite growth-rate inhibition effectiveness of a SRFA component fraction with a high carboxyl group content.

Table 1 Summary of experiments and results[a].

Exp ID	Compound	Inhibitor conc. (mg/L)	10^5 Rate (mol/(m^{2}min))	r^2
CC-24	Control	0	9.97	0.9990
CC-25	Control	0	9.78	0.9993
CC BSL-1	Big Soda Lake fulvic acid	1.0	5.5	0.9965
CC BSL-2	Big Soda Lake fulvic acid	1.0	4.8	0.9979
CC BSL-3	Big Soda Lake fulvic acid	5.0	0.74	0.9403
CC BSL-4	Big Soda Lake fulvic acid	5.0	0.74	0.9403
CC 8	Control	0	10.1	0.999
CC 9	Control	0	9.57	0.996
CC 11	Control	0	12.1	0.997
CC 18	Control	0	13.8	0.999
CC 19	Control	0	11.9	0.999
CC BC-2	Baked seed control	0	9.49	0.999
CC BC-3	Baked seed control	0	11.9	0.997
CC F1-3	Everglades site F1	0.5	5.15	0.995
CC F1-4	Everglades site F1	0.5	4.98	0.996
CC F1-12	Everglades site F1	0.5	5.35	0.997
CCF1BC1	Baked seed Everglades site F1	0.5	5.44	0.996
CCF1BC2	Baked seed Everglades site F1	0.5	4.91	0.998
CC-21	Control	0	6.56	0.998
CC-22	Control	0	7.55	0.998
CC GB5-1	SRFA pH5 fraction	1.0	0.04	0.223
CC GR5-2	SRFA pH5 fraction	1.0	0.04	0.185

[a] Experimental solutions contain a total calcium concentration of 0.0019 M, a total carbonate concentration of 0.0019 M, pH ~ 8.5, ionic strength 0.1 M maintained with KNO_3, carbon dioxide partial pressure $10^{-3.55}$ atm, and calcite supersaturation (Ω) 4.5.

4.4 Calcite Growth Rates in the Presence of Polycarboxylic Acids

Calcite growth rates measured for several cyclic PCAs include CHXHCA, a cyclic molecule with six carboxyl groups per molecule. Carboxyl groups attached to each carbon atom of the CHXHCA ring will change depending on the configuration of the cyclohexane ring, and adjacent carboxyl groups may interact to form hydrogen-bonded moieties.

Calcite growth rates are very low over the CHXHCA concentration range of 1 mg/L to 0.03 mg/L. In experiments with CHXHCA concentrations of 0.1 mg/L, initial growth stopped shortly after the start of the experiment, and at CHXHCA concentrations of 0.01 mg/L the growth rate varied. Thus, CHXHCA is an effective calcite growth-rate inhibitor, supporting the previous assessment [18] that carboxyl groups attached to cyclic aliphatic carbon atoms are effective calcite growth rate inhibiting entities. Higher molar mass PCAs such as humic acids and high molar mass fulvic acids [23] may not reach adsorption equilibrium in the calcite growth-rate experiments described here. In contrast to CHXHCA, four experiments done with CDDCA (1 to 10 mg/L) and ten experiments with CPDCA (1 to 10 mg/L) demonstrated that these molecules have no effect on the calcite growth rate.

4.5 Effect of Adsorbed Organic Compounds on Calcite Crystal-Growth Rates

Further examination of organic matter influence on the calcite crystal-growth rate was made by measuring growth rates with seed crystals heated to remove adsorbed atmospheric carbon compounds. Calcite seed crystal when washed with distilled water yielded a solution containing measurable DOC. The seed crystal baking experiments were conducted to remove seed crystal DOC prior to the start of a growth experiment. The baking process lowered, but did not eliminate, organic material on the seed crystal surface -- additional organic material readsorbed onto the baked seed from the atmosphere. Seven control experiments, conducted with unbaked seed crystal in the absence of added organic matter have a mean calcite growth rate and standard deviation of 11.0 x 10^{-5} M/(m^2min) and 1.6 x 10^{-5} M/(m^2min), respectively. Two control experiments with baked seed crystals have a mean calcite growth rate and standard deviation of 10.7 x 10^{-5} M/(m^2min) and 1.7 x 10^{-5} M/(m^2min), respectively. The difference in the calcite growth rate between the unbaked seed crystals and the baked seed crystals is not significant at the 95% confidence level.

Five calcite growth-rate experiments were conducted in the presence of 0.5 mg/L dissolved organic matter from site F1 in the Florida Everglades [17]. Three experiments used conventional seed crystals and two experiments used seed crystals baked prior to the experiment. The experiments in the presence of F1 fulvic acid with unbaked seed crystals have a mean calcite growth rate and standard deviation of 5.2 x 10^{-5} M/(m^2min) and 0.2 x 10^{-5} M/(m^2min), respectively. The experiments in the presence of F1 fulvic acid with baked seed crystals have a mean calcite growth rate and standard deviation of 5.2 x 10^{-5} M/(m^2min) and 0.4 x 10^{-5} M/(m^2min), respectively. The difference between calcite seeded crystal-growth rates in solutions containing dissolved organic matter with unbaked and baked seed crystals was not significant at the 95% confidence level. This lack of a statistical difference between measured calcite growth rates demonstrates that organic matter present in the air that adsorbs onto calcite surfaces has no influence on the measured calcite seeded growth rates in pure solutions and in solutions containing a calcite growth-rate inhibitor. The chemical nature of the small amount of organic material on the calcite seed prior to the seeded growth experiment is unknown; however, this adsorbed organic material had no effect on the measured growth rate in the presence or absence of fulvic acid.

4.6 Morphological Changes Accompanying Calcite Growth in the Presence of BSLFA

Examination of calcite seed crystals by SEM following calcite growth-rate experiments illustrates calcite growth morphological changes in solutions containing BSLFA compared to growth in solutions not containing added organic material. Seed crystals prior to addition to supersaturated solution are well-formed, sharp-edged calcite rhombohedra with smooth, flat crystal faces having a lognormal size distribution [39]. Growth surfaces on seed crystals after addition to supersaturated solutions without added BSLFA exhibit smooth steps of uniform thickness (Figure 3 A). Seed faces exhibited smooth planes of growth with regular step features on the face perimeters and crystal edges rounded with uniform calcite growth on all faces (Figure 3 A). Growth occurs in regular layers spreading uniformly to the edge of the growing crystal face without formation of irregular particles, breaks in growth faces, or pits in the fresh surface (Figure 3 A).

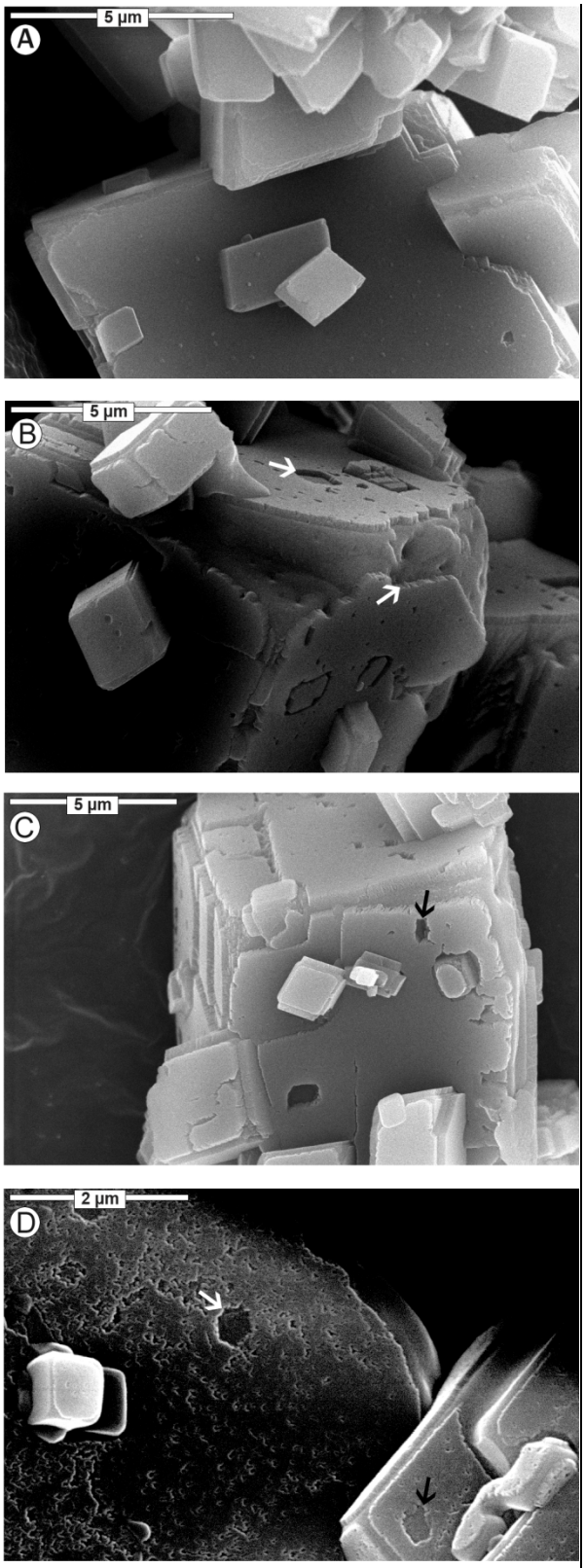

Figure 3 SEM images of calcite seed crystals after growth experiments in the presence and absence of fulvic acid isolated from Big Soda Lake, Nevada (magnification is shown as a bar marker on each panel): (A) Calcite seed crystals grown for 100 minutes at Ω 4.5 in solutions without added organic matter. Note the laterally continuous plane of calcite growth on the seed crystal surface; (B) Calcite seed crystal after growing for 100 minutes in solutions containing 1 mg/L BSLFA. Laterally discontinuous calcite growth on the seed crystal surface is indicated at two locations by arrows; (C) Calcite seed crystal after growing for 100 minutes in solutions containing 1 mg/L BSLFA. Discontinuous calcite growth on the seed crystal surface at one location is indicated by an arrow; (D) Calcite seed crystal after growing for 100 minutes in solutions containing 5 mg/L BSLFA. Arrows indicate calcite growth-surface pits at two locations.

These observations indicate that nucleation in solution did not occur during the experiments. Calcite growth-rate constants are independent of the amount of seed crystals for the seed concentration used in the experiments reported here [49].

In contrast to calcite growth in solutions without added organic inhibitors, calcite growth onto seed crystals in the presence of BSLFA produced laterally discontinuous planes of calcite growth at BSLFA concentrations of 1 mg/L (Figure 3 B and C), and pits in newly formed calcite growth planes on the seed crystal surface at BSLFA concentrations 5 mg/L (Figure 3 D). Crystal mass increases 25% for 100-minute growth in control experiments and increased seed surface area for this growth amount is less than 10%. Experiments in the presence of rate inhibitors have a smaller increase in crystal mass and surface area. Moreover, a change in the seed surface area is not observed in the rate plots (Figure 1); data points lie on a straight line without upward curvature, demonstrating that the seed surface area is not increasing substantially during the experiment.

5.0 DISCUSSION

5.1 Calcite Growth-Rate Reduction Mechanism

Growth-rate reduction mechanisms depend on aqueous-solution phase or crystal-surface processes. For example, growth-rate reduction will occur if BSLFA forms significant calcium-fulvate complexes in solution reducing calcite supersaturation by

reducing calcium ion activity in solution [25]. Complexation does not alter the calcite saturation state because the fulvic acid molar concentration is about 0.5% of the total calcium ion concentration in solution. Calcium BSLFA complex concentrations in calcite growth-rate experiments are a maximum of 2% of the solution total calcium concentration corresponding to a small decrease in the calcite supersaturation [17] and calcium-BSLFA complex formation does not decrease the rate of crystallization.

Carboxylate structures proposed for SRFA calcite growth-rate inhibition may also be present in BSLFA. An unfractionated SRFA model structure (Leenheer [45], Structure 1, page 199) differs from a structural model of the most acidic fraction of SRFA (Leenheer *et al*., [46], Figure 4). In contrast to the unfractionated SRFA, the acidic fraction has cyclic ether structures such as substituted tetrahydrofurans [18] that contribute to its strong acid characteristics and enhanced (relative to the unfractionated SRFA) calcite growth-rate inhibition. An important feature of this SRFA acidic fraction is enhanced acidity due to intramolecular hydrogen bonding by ionized carboxyl groups. More efficient carboxyl group ionization of this SRFA fraction due to this intermolecular hydrogen bonding enhances carboxylate interaction with growth sites on the calcite crystal surface.

Calcite growth-rate reduction is a significant function of BSLFA concentration: there is an abrupt change in growth rate over a narrow range of solution concentration from 1 mg/L to 5 mg/L (Figure 2). Previous studies indicate that calcite growth-rate inhibition mechanisms involve adsorption of an inhibiting molecule at sites on the seed surface [18, 33], and that, for example, a Langmuir-type adsorption [24] holds for growth-rate inhibition in the presence of phosphonate ions [31]. If calcite growth-rate reduction by BSLFA is due to adsorption at growth sites on the calcite surface, then an adsorption isotherm should characterize the growth-rate reduction process. Calcite crystal-growth rate reduction in the presence of BSLFA may follow a Langmuir-type isotherm represented by Eq. 5,

$$R_0 / (R_0 - R) = 1 + (K_a C)^{-1} \quad (5)$$

where R_0 and R are the growth rates in the absence and presence of BSLFA, respectively, K_a is the adsorption affinity constant of the calcite growth surface for BSLFA and C is the BSLFA concentration, mg/L [33]. Two BSLFA concentrations (each experiment done in duplicate) give a linear relation with an intercept of near unity (the best-fit intercept is 0.468) for Eq. 5. The available data suggests that a Langmuir isotherm may describe the inhibitory effect of BSLFA in terms of a monomolecular blocking layer of active molecules at the growth sites on the crystal surface. Calcite growth-rate measurements at additional BSLFA concentrations are needed to verify this assessment. There is not an induction period prior to calcite formation, which is unlike calcium sulfate dihydrate growth from supersaturated solutions [50].

Calcite growth-rate reduction by BSLFA is similar to that found in solutions containing fulvic acids from the Florida Everglades and other locations [17, 33], although the concentration range for calcite growth-rate reduction varies among fulvic acid isolates from different locations depending on the chemical composition of each sample isolate [17]. For example, fulvic acid concentrations reducing the calcite growth rate by 50% are lower for some Florida Everglades fulvic acids than for BSLFA. In addition, several cyclic PCAs reduce the calcite growth rate by 50% at concentrations well below 1 mg/L [18].

Calcite growth morphology in the presence of BSLFA (Figure 3) exhibits broken or discontinuous growth plains that are similar to morphological changes associated with dissolved organic carbon in calcite growth from seawater reported by Zuddas *et al*. [51]. Growth morphology differences in solutions containing BSLFA are also similar to growth morphology in solutions containing aliphatic-alicyclic PCAs (at much lower concentrations) (cyclopentane-tetracarboxylic acid and tetrahydrofurantetracarboxylic acid [18]).

High-resolution imaging techniques, such as Atomic Force Microscopy (AFM), examine calcite growth at the atomic (nanometer) level. In the experiments reported here, calcite crystal growth occurs by a uniform advance of macro-steps across the major calcite low index crystal faces. Macro-step discontinuities occur at a larger (micrometer) scale than atomic scale discontinuities observed by AFM. Macro-step morphology changes between the control experiments and those experiments containing fulvic acid are due to adsorbed fulvic acid pinning growth terraces and ledges on the crystal surface in addition to blocking the kink growth sites on the crystal surface. Fulvic acid pinning growth steps prevent lateral growth while allowing continued vertical growth, causing the observed pits and other irregular calcite growth surfaces.

Growth-rate inhibition depends on the interaction of inhibitor molecules with active growth sites on calcite surfaces [52]. For example, synthetic organic compounds that bind strongly to calcite

growth sites are efficient growth inhibitors [53]. Effective growth-rate inhibiting compounds are usually also good sequestering agents for lattice cations [54]. However, not all good sequestering ligands (EDTA, for example) are good inhibitors. Inhibitors typically have a strong affinity for the mineral surface and adsorb at growth sites and other locations on the crystal surface; low solubility of salts involving the lattice ions and the inhibiting anion favors adsorption. Nancollas [54] describes carboxylate growth-rate inhibition effectiveness in terms of the match of the distance between carboxyl groups and the calcium ions in the mineral lattice; inhibitors with less flexible structures (for example, aliphatic-alicyclic compounds) are more specific inhibitors than more flexible molecules. Our results suggest that only a fraction of PCAs present in fulvic acids have these structural requirements necessary for effective calcite growth-rate inhibition.

Calcite growth-rate inhibition is due to one or several components of the BSLFA and SRFA isolates capable of adsorbing to growth sites on the calcite mineral surface [55]. Adsorption on crystal faces away from active growth sites will act as a blocking site when a growing surface reaches the location of adsorption. Didymus *et al*. [56] observed that the influence of monofunctional additives on calcium carbonate growth morphology increased with overall charge. For the same charge, the change in morphology decreased with decreasing partial charge on the ligand oxygen atoms. Additional inhibitor effectiveness factors for multifunctional molecules discussed by Didymus *et al*. [56] include distance between ligands and ligand conformation.

Growth-rate inhibitors usually adsorb on all crystal faces and when inhibitor adsorption occurs only on selective faces, morphology of the growing crystal changes [55]. Adsorption on crystal faces, as opposed to adsorption at kink growth sites, increases step height and requires more inhibitor adsorption per unit area of crystal surface (and correspondingly higher solution concentrations for effective reduction of calcite growth rates) than for blockage of kink sites. Growth rate inhibitors cause mineral polymorphic alteration by preventing nucleation and crystal growth of more thermodynamically stable phases. Calcite surface adsorption of one or more inhibiting components of BSLFA and SRFA, the mechanism proposed for the concentration dependent reduction in the calcite growth rate in the presence of BSLFA, may be further evaluated by measuring the amount of FA adsorbed on 100 mg of calcite seed in solution. FA adsorption onto calcite seed crystals is small and FA solution concentrations do not change substantially during the growth experiments. Moreover, the presence of organic carbon adsorbed to the seed crystals prior to the growth experiments confounded the adsorption measurements because seed crystals released small amounts of DOC to the reacting solution.

5.2 Polycarboxylic Acids Influence on Calcium Carbonate Formation

Substituted succinic acids (formed by oxidative bacterial degradation of aromatic rings in lignin) are abundant, clustered carboxyl-group structures in aquatic fulvic acids. These structures are present in the proposed average structure model for BSLFA discussed previously by Leenheer [45] (Figure 2, and pp. 202-204). Lignin contains tetrahydrofuran structures. Cleaving aromatic rings in lignin produces substituted succinic acids, and carboxylated tetrahydrofuran structures [45] identified as strong calcite crystal-growth inhibitors [18].

In contrast to substituted succinic acids and CHXHCA, cyclic PCAs such as CPDCA, and CBDCA, which are aliphatic alicyclic structures with two carboxyl groups attached to one ring carbon atom, are ineffective calcite growth-rate inhibitors. The molecular configurations of these dicarboxylic acids give little flexibility to adsorbed carboxylate groups at the calcite surface. Experiments with CDDCA (1 to 10 mg/L) and CPDCA (1 to 10 mg/L) demonstrated that these molecules have no effect on the calcite growth rate. This result demonstrates that a rigid orientation of two-carboxylate groups (attached to a small rigid ring) is not a sufficient condition for a successful calcite growth-rate inhibitor.

Small cyclic, inflexible molecules reduce multiple-carboxyl group interactions with a calcite surface. Moreover, interactions through hydrogen bonding between adjacent carboxyl groups on cyclic structures may also influence carboxyl group mobility and adsorption strength on calcite surfaces. Formation of carboxylic acid dimer or trimers (by hydrogen bonding) may also contribute to differences in calcium carbonate growth rate inhibition. In particular, molecular dynamic simulations of carboxylate containing molecules adsorbing to mineral surfaces demonstrates that crystal growth rate inhibition requires molecular flexibility allowing multiple carboxylate group surface attachment (Dr. Graeme Hunter, 2011, personal communication).

6. CONCLUSIONS

BSLFA (1 and 5 mg/L), SRFA (1 mg/L), and CHXHCA (at concentrations below 0.1 mg/L) markedly reduce calcite crystal-growth rates. Fulvic acid isolated from BSLFA inhibits calcite crystal-growth rates with increasing BSLFA concentration suggesting that BSLFA adsorbs at growth sites on the calcite crystal surface. A Langmuir adsorption isotherm is consistent with the inhibition effect of BSLFA on the calcite crystal-growth rate in terms of a monolayer of active molecules adsorbed at growth sites on the calcite crystal surface. Calcite growth morphology in the presence of BSLFA differs from growth in its absence, supporting an adsorption mechanism of calcite-growth inhibition by BSLFA.

Dramatic calcite growth-rate inhibition at 1 mg/L of a SRFA fraction contrasts with the unfractionated SRFA and emphasizes calcite growth-rate inhibition by one SRFA component fraction rich in carboxylate groups. CHXHCA, with each carboxyl group attached to a different ring carbon atom, is a strong calcite growth-rate inhibitor at concentrations less than 0.1 mg/L. CPDCA and CBDCA, with the carboxyl groups attached to the same ring carbon atom, have no effect on calcite growth rates at concentrations up to 10 mg/L. Organic matter adsorbed from the air onto the seed crystals has no influence on the measured calcite crystal-growth rates. Calcite growth-rate experiments suggest that BSLFA and SRFA contain inhibitor components consisting of aliphatic-alicyclic molecules containing multiple carboxylate groups attached to different carbon atoms. Identification of multiple-carboxylate groups attached to different aliphatic-alicyclic carbon atoms with effective calcite growth-rate inhibition identifies a specific functionality present in aquatic fulvic acids that influences calcium carbonate formation rates in natural systems.

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