

CALCITE CRYSTAL GROWTH RATE INHIBITION BY AQUATIC HUMIC SUBSTANCES

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ABSTRACT

Calcium carbonate crystallization is an important process in numerous terrestrial and aquatic ecosystems. Moreover, calcium carbonate scale formation on heat transfer surfaces is an important industrial problem. Humic substances, which are ubiquitous in natural waters, often reduce or inhibit calcite crystal growth and may, therefore, have application in scale prevention. This study quantifies and interprets calcite crystal growth rate reduction due to humic substance fractions isolated from surface water. We conducted calcite growth experiments at constant pH (8.5), temperature (25°C), supersaturation ($\Sigma = 4.5$), P_{CO_2} ($10^{-3.5}$ atm), and ionic strength (0.1 M KNO_3) with various concentrations of natural organic acid isolates. Plant-derived aquatic hydrophobic acids from the Everglades were effective growth inhibitors. Organic acid molecular weight correlated with growth inhibition as did aromaticity, aliphatic content and heteroatom content; however, carboxyl content did not. Growth inhibition over a range of organic inhibitor concentrations for Everglades' samples is consistent with a Langmuir adsorption mechanism blocking growth sites on the calcite surface.

INTRODUCTION

Crystal growth on heat transfer surfaces, leading to scale formation and reduced heat transfer efficiency, is an important industrial problem. For example, calcium carbonate scale formation occurs in cooling water technology, desalination processes, and oil

production. Moreover, an important aspect of carbonate mineral formation in current water management strategies in South Florida and elsewhere is surface water storage in unsaturated carbonate aquifers. In this situation, carbonate minerals formed after injection will alter aquifer porosity and permeability.

Calcium carbonate minerals are ubiquitous in the environment. Fresh water lakes and ocean waters are frequently supersaturated with respect to calcite with no observed mineral precipitation.^{1,2,3} Where inorganic carbonate precipitation is thermodynamically favored, natural kinetic inhibitors may prevent carbonate mineral nucleation and crystal growth.^{2,4,5}

Calcite crystal growth mechanisms have been examined extensively,^{6,7} and it is generally agreed that calcite grows by a surface reaction mechanism.^{8,9} Calcium carbonate growth is inhibited by common inorganic ions, such as magnesium ion,^{1,10} phosphate ion,^{9,11} and simple organic compounds.^{2,12,13,14,15}

Nancollas and others¹⁶ discuss crystal growth inhibition mechanisms and show that slightly different compounds may have different effects on calcite growth rates depending on how these compounds interact with growth sites on calcite surfaces. Compounds that bind strongly to active growth sites are efficient growth inhibitors at low concentrations. Several classes of chemical additives, known as "threshold inhibitors", have been found to reduce or eliminate scale by inhibiting calcium carbonate formation at very low solution additive concentrations. Nancollas,¹⁷ summarizing recognized aspects of threshold inhibition, notes that effective inhibitors are usually also good sequestering agents for lattice cations. However, not all good sequestering ligands are good threshold inhibitors because the inhibition mechanism is an adsorption process at growth sites on the crystal surface. Adsorption affinity is favored by low solubility of salts involving the lattice cations and the inhibiting anion.

Model compound studies examining the molecular relationship to growth inhibition have yielded interesting results in precipitation reactions. Miura et al.¹⁸ reported that phosphates adsorbed to calcium carbonate, but pyrophosphate and triphosphate were better inhibitors than orthophosphate and trimetaphosphate. Berner et al.¹⁴ concluded that aragonite growth can be inhibited by the presence of benzenecarboxyl groups. Amjad¹⁹ examined calcite growth inhibition in the presence of benzenepolycarboxylic acid and reported that more highly carboxylated benzenes are better inhibitors (at the same solution concentration) than less carboxylated benzenes.

Strong calcite growth rate inhibitors are effective at concentrations less than one milligram per liter. Important functional groups for crystal growth rate inhibition contain phosphorus, nitrogen or carboxylate groups.^{11,15,16,17} However, threshold inhibitors may pose water quality problems because they contribute to nutrient loading. Perez and Zidovec²⁰ stress environmental advantages of using nonphosphorus containing compounds in scale inhibition applications. Recent publications have shown natural organic acids markedly reduce calcium carbonate crystal growth rates.^{21,22,23}

Humic substances, including fulvic acid, humic acid and humin, are biogenic, refractory organic matter ubiquitous in terrestrial and aquatic environments.²⁴ Some of these substances are effective crystal growth inhibitors.^{14,15,21,22,25} In the past, recognition of humic substances as growth inhibitors has focused on comparing inhibition effects of model compounds with one or two poorly characterized or uncharacterized humic substance samples^{15,26} or comparing the effects of a few unrelated and less well-characterized soil humic extracts.²⁵ The chemistry of aquatic humic substances may vary with regard to molecular weight, functional group content and acidity. It is the goal of this study to examine the effectiveness of well-characterized dissolved organic material (DOM) isolates from the Florida Everglades and Lake Fryxell, Antarctica, in inhibiting

calcite growth. An additional goal is to identify those chemical and structural features of these natural materials that may have application as threshold inhibitors.

MATERIALS AND METHODS

Experimental details appear elsewhere²⁷ and are briefly summarized here. We utilized a constant composition experimental apparatus²⁸ in which solution pH and chemical composition were kept constant to fix calcite supersaturation (Fig. 1). Experiments were done at constant pH of 8.5, temperature (25°C), supersaturation (Ω) of 4.5, solution carbon dioxide partial pressure of $10^{-3.5}$ atmosphere and ionic strength of 0.1 M. Solution supersaturation is regulated by the potentiometrically-controlled addition of solutions containing calcium and carbonate ions. This approach enables measurement of calcite growth rate inhibition with high precision and avoids complications due to changing solution supersaturation. The calcite growth reaction at a pH of 8.5 can be written as:

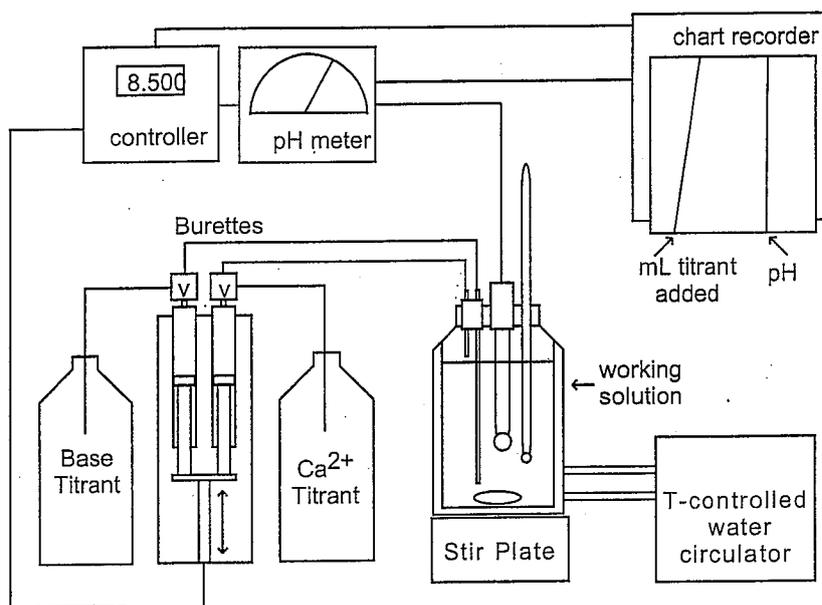


Figure 1. Diagram of constant composition experimental apparatus.

During calcite growth a pH-stat apparatus senses decreasing pH and causes the double burette system (Fig. 1) to respond by adding calcium chloride and sodium carbonate titrant solutions replacing calcium and carbonate ions lost to crystal growth, keeping pH and solution composition constant. Titrant solutions also contained electrolyte (potassium nitrate) to maintain constant ionic strength (Table 1). Constant composition was verified

by measuring total dissolved calcium ion concentration and alkalinity before and after all experiments. Solution pH and volume of titrant added over time were recorded on a dual-pen chart recorder. All experiments were run for 100 minutes.

Table 1. – Inorganic Compositions of solutions used in all experiments

Reagent	Working Solutions (M)			Titrant Solutions (M)		
	A.calcium stock solution	B.carbonate stock solution	A+B reactor working solution	A.calcium titrant solution	B.carbonate titrant solution	A+B net composition of titrant added
CaCl ₂ • 2H ₂ O	0.004		0.002	0.053		0.026
NaHCO ₃		0.004	0.002		0.004	0.002
Na ₂ CO ₃					0.049	0.024
KNO ₃		0.185	0.093	0.038	0.046	0.042

Metastable working solutions were prepared by adding calcium ion containing solutions dropwise to carbonate solution in the thermostatted growth reaction cell. The pH was then adjusted to 8.5 using a few drops of 0.05 M KOH and metastability verified by monitoring constant pH for an hour prior to the experiments. Total working solution volumes were 400 milliliters and 100 milligrams of dry calcite seed were added to metastable solutions to initiate growth. Calcite seed was analyzed using a Siemens X-ray diffractometer to verify mineral purity. The specific surface area of the seed (SA_{seed}) material was $0.256 \pm 0.008 \text{ m}^2/\text{g}$ (determined by BET gas absorption measurement.²⁷

Stock solutions containing organic acids were prepared in base working solutions. Organic acid containing solutions were refrigerated in dark glass bottles. Prior to each experiment, stock solutions were added to base working solutions to obtain the desired organic acid concentrations and then filtered through 0.1 μm Millipore cellulose nitrate filters.

Organic acids used as growth inhibitors in this study were the hydrophobic organic acid fraction of DOM from three Florida Everglades' sites, F1, U3 and 2BS.^{29,30} A fulvic acid sample from Lake Fryxell, Antarctica, was also used in the calcite growth inhibition experiments.³¹ The hydrophobic organic acids are 96% to 97% fulvic acid with the balance being humic acid. Weight averaged (M_w) and number averaged (M_n) molecular weights were determined by high pressure size exclusion chromatography (HPSEC), carboxyl acidity was determined by titration with a base to an endpoint of pH = 8.5; functional group abundances and aromaticity were estimated from ¹³C-NMR spectra.^{30,32}

The slope of the line corresponding to titrant addition due to calcite growth (reciprocal minutes) is proportional to the calcite growth rate and is converted to crystal growth rates by the following equation:

$$\text{Rate } ((\text{mol}/\text{m}^2)/\text{min}) = \text{slope } (\text{l}/\text{min}) * M_{\text{titrant}} (\text{mol}/\text{l}) / (\text{mass}_{\text{seed}}(\text{g}) * SA_{\text{seed}}(\text{m}^2/\text{g})) \quad (2)$$

Most experiments yielded straight lines for titrant addition over time except for experiments with higher organic acid isolate concentrations. These experiments initially exhibited higher rates, but quickly (< 5 min) slowed to a steady rate of growth as the organic acid isolate reached adsorption equilibrium with the calcite surface. For these experiments, rates were calculated using the slope starting at 10 minutes. Calcite growth rate inhibition by organic acids is expressed as reduced rates R/R_0 for each experiment: R is the rate in the presence of inhibitor and R_0 is the rate in the absence of inhibitor. Thus, a smaller reduced rate indicates greater growth inhibition.

RESULTS

Dissolved calcium ion speciation calculations were performed for experiments in the presence and absence of organic acids. There are uncertainties concerning DOM complexation reactions with calcium ion in solution. Here we assume (as an upper limit) that all carboxyl groups of DOM form one-to-one complexes with calcium ion in solution. In this situation, complexes of calcium were small compared with the free calcium ion concentration. Ion pair formation did not significantly reduce calcite supersaturation.

For each organic acid isolate studied a series of experiments were performed at concentrations of 0.2 to 5.0 mg/L DOM. Examples of calcite growth rate data for experiments using hydrophobic organic acids from site F1 are shown in Figure 2. For the organic acid isolate from site F1, measurable rate reduction was observed at the lowest experimental organic acid isolate concentrations and calcite growth was almost completely inhibited at concentrations of 5.0 mg/L.

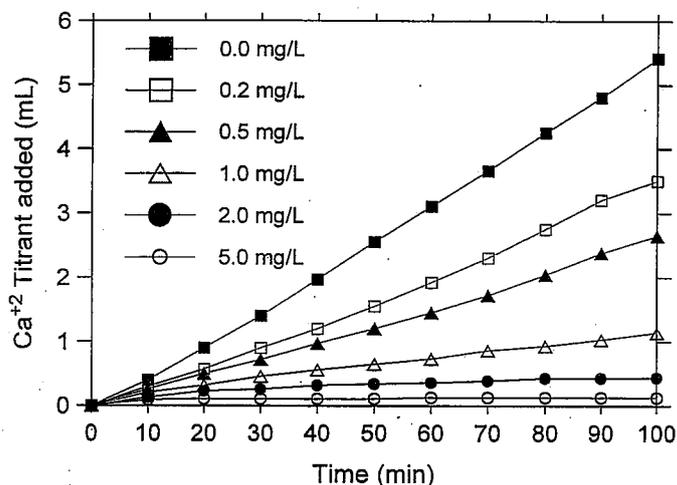


Figure 2. Crystal growth of calcite at constant supersaturation in the presence of varying concentrations of F1 hydrophobic organic acid (slope is proportional to rate).

The marked effect of organic acid isolates in reducing the calcite growth rate is illustrated in Figure 3 where reduced growth rate is plotted versus DOM concentration (expressed in units of milligrams of carbon per liter). Different organic acid isolates had different effects on calcite crystal growth rates. Hydrophobic acid from the F1 site was the strongest inhibitor at all concentrations, followed by U3 hydrophobic acid and 2BS hydrophobic acid. The isolate from site F1 reduced calcite growth rates by more than 50% at concentrations as low as 0.5 milligrams per liter. Fulvic acid from Lake Fryxell was the weakest growth inhibitor of all compounds studied.

Reacted and unreacted crystals were examined by scanning electron microscopy to visualize morphological changes that occurred during growth with and without added organic acids (Fig. 4). Unreacted crystals (Fig. 4A) were well-formed sharp-edged rhombohedra. Crystals that grew for 100 minutes in the absence of organic inhibitors

(Fig. 4B) increased their mass by about 25% and exhibited smooth planes of growth with step features on the face perimeters. Crystal morphology produced by growth in the presence of organic acid isolates is different than in the control experiments. For example, in the 0.5 mg/L F1 isolate experiments the growth rate was reduced by more

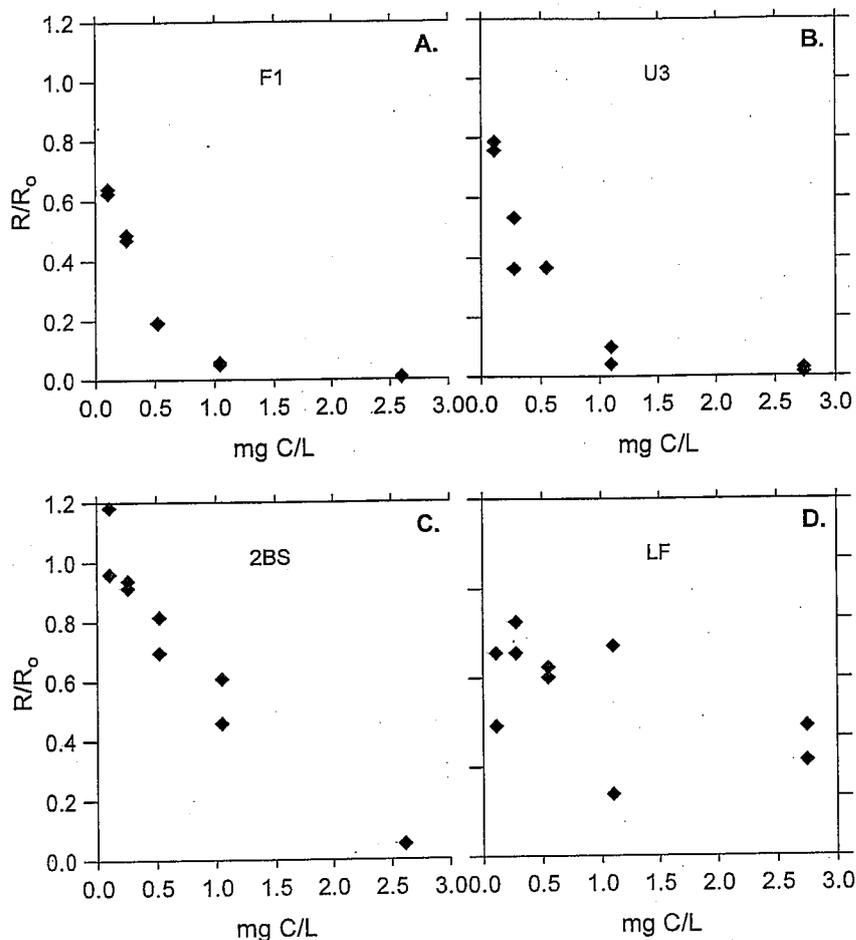


Figure 3. Reduced calcite growth rates (R/R_0) at constant supersaturation at varying concentrations of DOM (milligrams of carbon per liter) isolates from Florida Everglades sites A) F1, B) U3 and C) 2BS and from Lake Fryxell, Antarctica, D) LF.

than 50% compared with control experiments; crystal mass increased by only 12% and crystal surfaces did not exhibit smooth planes of growth but planes in which growth had been interrupted, resulting in a broken or discontinuous appearance (Fig. 4C). Crystals reacted at higher organic acid isolate concentrations showed even smaller "islands" of growth or no growth at all.

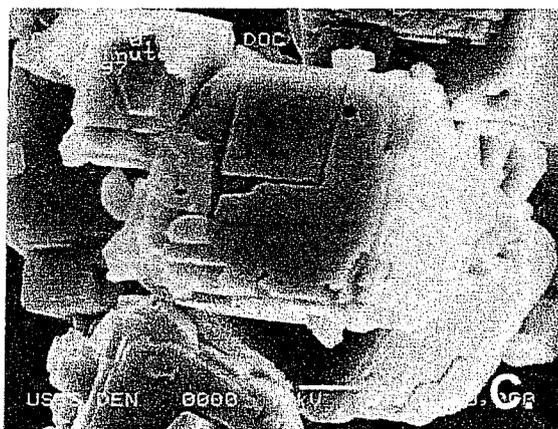
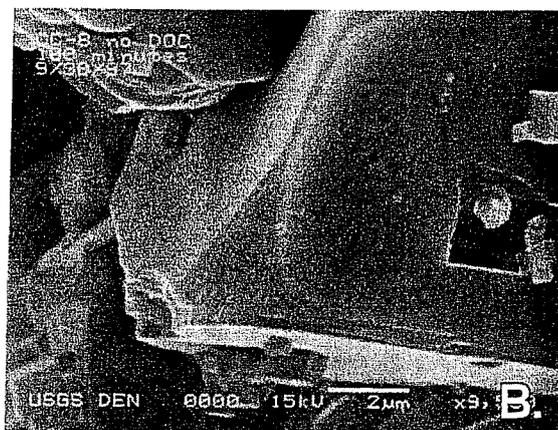
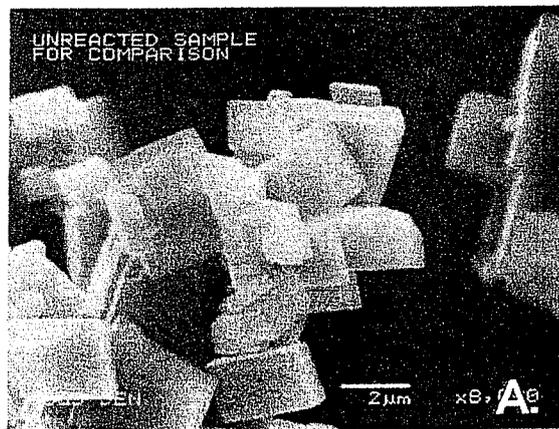


Figure 4. SEM photomicrographs of calcite seed material before and after crystal growth experiments. A) unreacted calcite seed; B) Calcite seed after 100 minutes growth in an experiment with no added organic materials; C) Calcite seed after growing for 100 minutes in a solution containing 0.5 mg/L F1 hydrophobic acid; added mass was about 50% of that observed in control experiment (B).

DISCUSSION

Chin et al.³³ observed that there is a direct relationship between DOM molecular weight and degree of aromaticity in aquatic fulvic acids. Weight average molecular weight (M_w) and number average molecular weight (M_n) for the Everglades' organic acids vary by as much as 65% for the organic acid isolates. Perez and Zidovec²⁰ reported that calcium carbonate growth inhibition in the presence of low-molecular weight polyacrylic acids (PAA) (2000 to 5000 daltons) is proportional to molecular weight. Although the molecular weights of the organic acids used here are slightly below this range (1100 to 1900 weight average molecular weight), higher molecular weight Everglades' organic acid isolates produced greater rate reduction than the lighter organic acids at all concentrations (Fig. 5). These results (Fig. 5) support the influence of organic acid molecular weight in

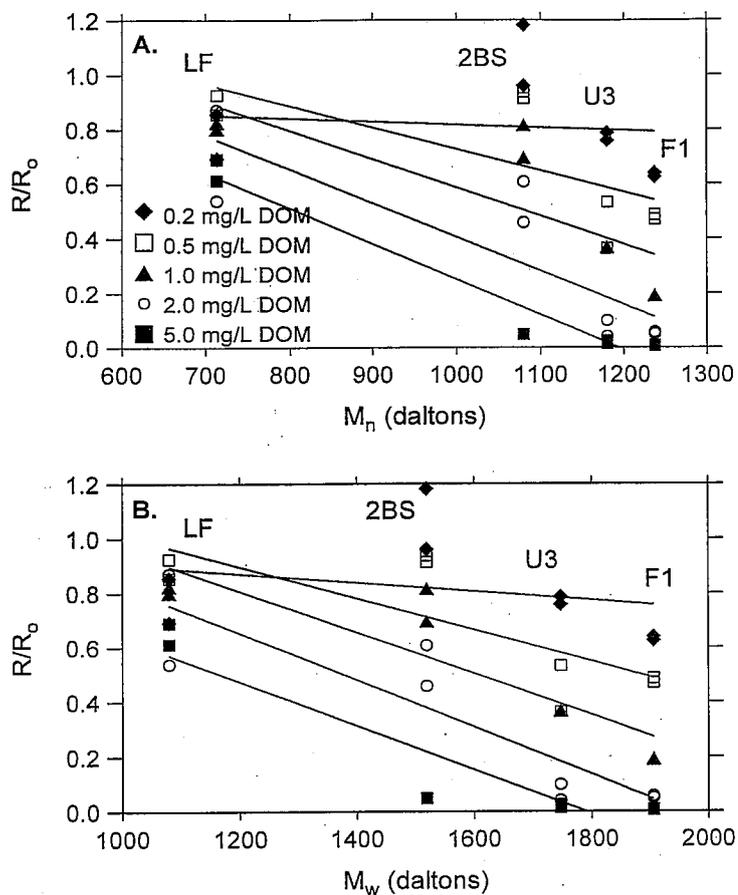


Figure 5. Plots of all experimentally-determined reduced rates R/R_0 versus: A) number-average molecular weights and B) weight-average molecular weight for DOM isolates used in experiments. Each symbol type represents a given concentration of organic acid. Sets of symbols at given molecular weights represent suite of experiments run in the presence of a given organic acid, noted on the figure.

the inhibition mechanism. However, Everglades' organic acid isolates have greater functional group heterogeneity (Table 2) than the PAAs of Perez and Zidovec,²⁰ and this may confound the molecular weight/inhibition relationship. At all concentrations less than 5 mg/L DOM the rate reduction for Lake Fryxell acid is approximately equal to that from site 2BS. This is an exception to the influence of molecular weight. It is noteworthy that the organic acid that is least effective as a growth rate inhibitor (Lake Fryxell, Table 2) has the lowest molecular weight.

Table 2. Acidity and molecular weight data for organic acids

Sample/date collected	Description	MOLECULAR WEIGHT* (Daltons)			ACIDITY**	
		M _w	M _n	M _w /M _n	COOH (meq/g)	OH (meq/g)
Everglades U3, 3/95	Hydrophobic Fraction	1747	1180	1.48	5.99	0.735
Everglades F1, 4/96	Hydrophobic Fraction	1907	1238	1.54	5.14	1.35
Everglades 2BS, 4/96	Hydrophobic fraction	1519	1080	1.41	4.74	1.03
Lake Fryxell - 5.5m	Fulvic acid	1080	713	1.51	5.26	1.06

*Everglades' high pressure size exclusion chromatography (HPSEC) molecular weight data from Aiken and Reddy (1997); Lake Fryxell HPSEC data is from Chin et al.³³

** All acidity data are from Ravichandran.³⁰

Humic substances vary in chemical functionality and molecular structure.²⁴ We have used ¹³C NMR (Table 3) to identify bonding environments of the ¹³C isotope in Everglades' organic acid isolates.³⁴ The ¹³C NMR data is used to estimate average carbon atoms in given bonding environments as follows:

$$C_i \text{ (daltons)} = M.W. \text{ (daltons)} * f_C * f_i \quad (3)$$

where C_i is the average total mass of carbon in functional group i in an organic acid isolate, $M.W.$ is the weight-averaged or number-averaged molecular weight of the organic acid isolate, f_C is the fraction of carbon in the organic acid isolate (Table 4), and f_i is the fraction of carbon in that functional group i (Table 3).

Aliphatic I carbons (carbon-carbon single bond) are the most abundant functional groups (Table 3). Figure 6A shows the relationship between rate reduction and aliphatic I carbon content. Zullig and Morse³⁶ found that fatty acids with longer carbon chains (which would be represented by aliphatic I carbon signal) adsorb to calcite surfaces. The aliphatic II region signal represents C-O, C-N and C-S heteroatom single bonds; most aliphatic II content is C-O bonds (Table 4). Aliphatic II moieties contribute to the hydrophilic nature of the organic acid isolates and are expected to preferentially bind to calcite surfaces. This affinity enhances organic acid crystal growth inhibition. Greater aliphatic II carbon content coincides with greater rate reduction (Fig. 6B). In summary, data presented in Figure 6 show that the only moiety which does not correlate with rate reduction is carboxyl (6D). All others exhibit rate reduction with increasing average

Table 3. Functional character of organic acids as determined by ^{13}C NMR analysis

Sample/date collected	Description	^{13}C NMR – percent C in functional groups (ppm chemical shift)					
		Aliphatic I (0-62)	Aliphatic II (62-90)	Acetal (90-110)	Aromatic (110-169)	Carboxyl (160-190)	Ketone (190-230)
Everglades U3, 3/95*	Hydrophobic fraction	42.3	15.0	7.4	19.0	14.4	4.1
Everglades F1, 4/96*	Hydrophobic fraction	45.0	17.0	5.3	18.2	11.6	2.7
Everglades 2BS, 4/96*	Hydrophobic fraction	48.5	14.9	4.1	15.4	15.4	1.8
Lake Fryxell – 5.5m **	Fulvic acid	46.4	14.5	4.4	15.2	19.6	0.0

* Everglades NMR data from Aiken and Reddy.³⁵

** Lake Fryxell NMR data from Aiken et al.³¹

Table 4. Chemical composition of organic acids as weight percent constituent; standard deviations are given in parentheses

Sample	C (± 0.5)	H (± 0.05)	O (± 0.6)	N (± 0.04)	S (± 0.05)	Ash (± 0.2)
F1*	52.2	4.64	39.9	1.53	1.73	5.8
U3*	54.7	4.79	37.5	1.88	1.15	4.6
2BS*	52.3	4.79	40.2	1.58	1.23	7.3
LF-5.5m**	54.9	5.5	34.9	3.3	1.2	2.3

* Everglades' data from Aiken and Reddy.³⁵

** Lake Fryxell data from Aiken et al.³¹

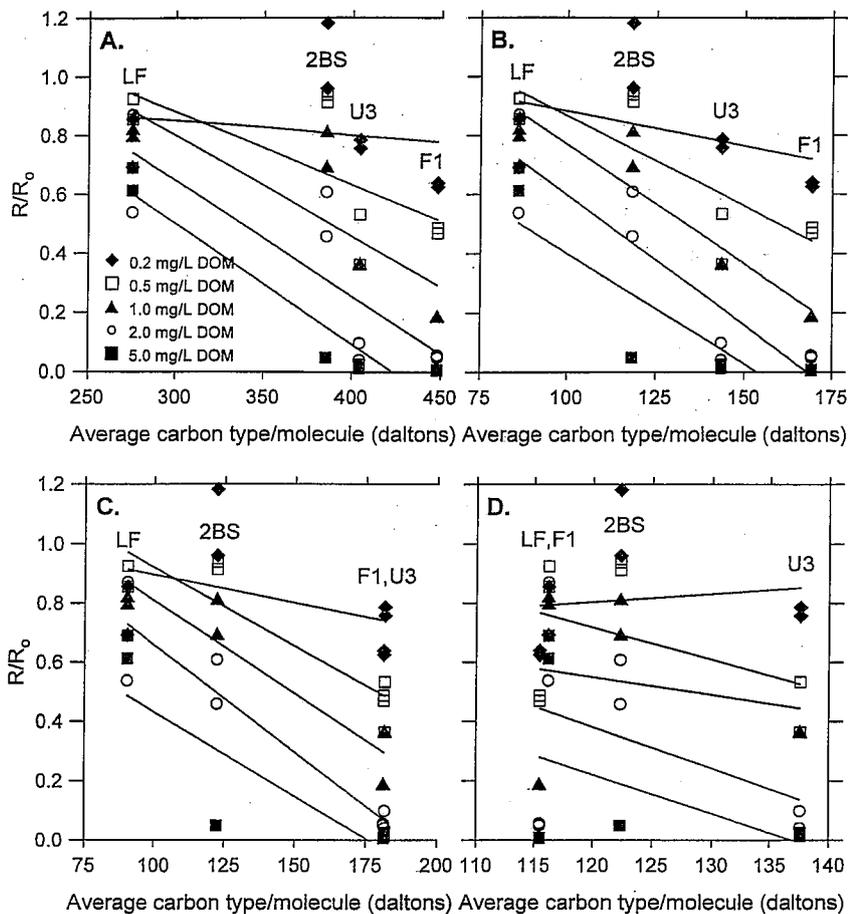


Figure 6. Plots of all experimentally-determined reduced rates R/R_0 versus functional group: A) aliphatic I carbon (C-C single bond); B) aliphatic II carbon (primarily C-O single bond); C) aromatic carbon; and D) carboxyl carbon.

moiety carbon mass/molecule. The patterns of plots 6A, 6B and 6C are remarkably similar suggesting that aromaticity may not be central in determining DOM inhibition effectiveness.

The most efficient growth inhibitors (F1 and U3) contained more aliphatic and aromatic carbon/total carbon than the weaker inhibitors (Fig. 6). Reynolds² reported calcite precipitation rates decreased with increasing aromatic humic substance (polyphenol) concentrations in Lake Powell waters. Berner et al.¹⁴ studied the effects of four sets of model compounds (amino acids/proteins, fatty acids, aliphatic/polycarboxylic acids and aromatic acids) on aragonite precipitation. Of these four classes of compounds, only the aromatic acids were found to be strong inhibitors. Stereochemical reasons were invoked for the strong interaction of the more aromatic acids with the active growth sites on carbonate surfaces.

Scanning Force Microscopy imaging demonstrates that calcite growth on seed crystals at moderate supersaturation is initiated by multiple surface nucleation events, followed by spiral growth.⁹ In inhibitor-free solutions, smaller growth spirals coalesce forming smooth mineral surfaces that grow in straight steps. In solutions containing

solutes that sorb to mineral surfaces, the smooth steps are blocked, producing a jagged, discontinuous appearance as shown in Figure 4C.

If growth inhibition is caused by DOM adsorption at active growth sites on crystal surfaces, an adsorption isotherm should describe the rate reduction with changing inhibitor concentration. Here we consider Langmuir-type adsorption³⁷ at active growth sites on the seed surfaces to cause growth inhibition as found for calcite growth rate inhibition by other ions.^{10,11,15} If we assume α is the fraction of sites blocked by organic inhibitors, the rate in the absence of inhibitor, R_o , is reduced to a slower rate, R , according to the relationship:

$$R = R_o (1-\alpha) \quad (4)$$

which may be rewritten as:

$$\alpha = (R_o - R)/R_o \quad (5)$$

In a given system, DOM adsorption and desorption rates at the growth sites may be expressed as follows:

$$\text{adsorption rate} = k_{ads} [DOM] (1-\alpha) \quad (6)$$

$$\text{desorption rate} = k_{des} \alpha \quad (7)$$

and, at DOM adsorption equilibrium:

$$k_{ads} [DOM] (1-\alpha) = k_{des} \alpha \quad (8)$$

Solving equation 8 for α , and substituting into equation 5 we obtain:

$$R_o/(R_o - R) = (k_{ads}/k_{des})(1/[DOM]) + 1 \quad (9)$$

which is the equation for a line with the slope defined by the adsorption/desorption rates and an intercept of 1. Using our reduced rate notation, a plot of $1/(1-R/R_o)$ versus the reciprocal of the organic acid isolate concentration reveals excellent linear relationships for experiments utilizing hydrophobic acids isolated from Everglades' DOM (Fig. 7A-C). These data plots are consistent with adsorption of organic acid isolates at active growth sites; plots of the Everglades' isolates are linear with an intercept near unity. Agreement of transformed experimental calcite growth rate data with that expected for the Langmuir adsorption model supports a mechanism of growth rate inhibition through attachment of inhibitor ions at growth sites on the crystal surface. Linearity of best fit lines is consistent with growth inhibition as a result of monolayer adsorption at active growth sites. Everglades' DOM best-fit correlation coefficients are significant at the 99% confidence level. The Langmuir plot for Lake Fryxell DOM (Fig. 7D) is not significant at the 90% confidence level. Absence of strong inhibitors in the Lake Fryxell DOM sample may explain the larger experimental scatter in the dataset.

CONCLUSIONS

Aquatic hydrophobic acids isolated from Florida Everglades' DOM are effective calcite growth rate inhibitors. The most effective inhibitors reduced calcite growth rates by more than 50% at concentrations as low as 0.5 milligrams per liter. Molecular weight

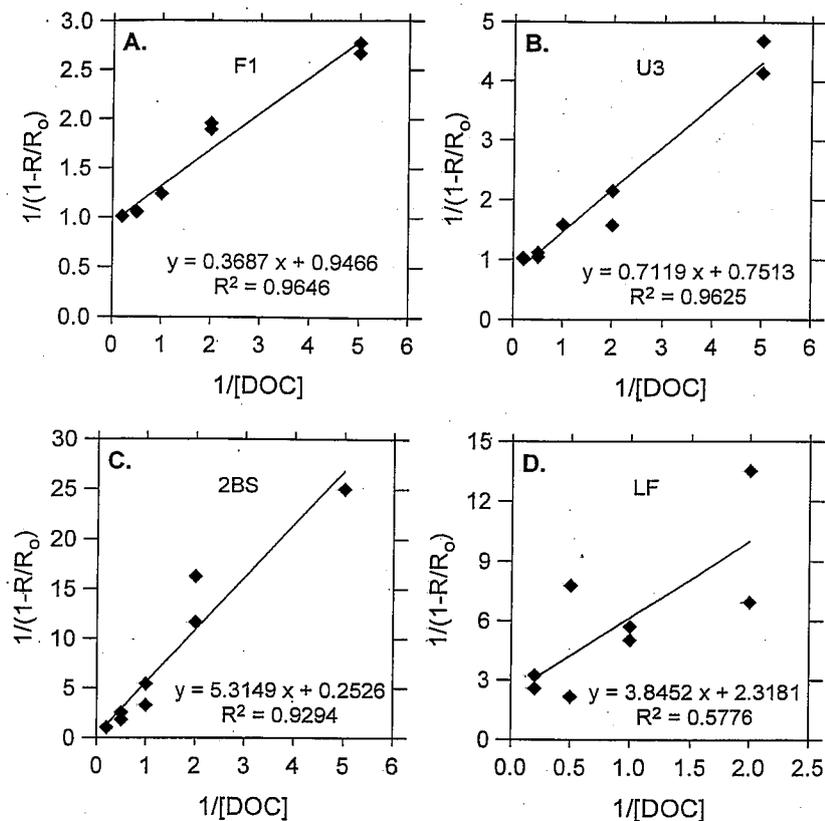


Figure 7. Langmuir isotherm type plots for rate reduction in the presence of organic inhibitors at varying concentrations of DOM isolated from Florida Everglades sites A) F1, B) U3 and C) 2BS and from Lake Fryxell, Antarctica, D) LF.

of Everglades' DOM isolates correlated with growth inhibition. Carboxyl carbon content is less important in identifying an organic acid isolate as an effective inhibitor. The morphology of crystals grown in the presence of organic acids suggests that surface growth sites are blocked by adsorbing organic acid isolates, as demonstrated in other studies using atomic force microscopy. Calcite growth inhibition by Everglades' hydrophobic organic acid isolates, over a range of concentrations, is consistent with a mechanism of Langmuir adsorption of organic ligands to calcite surfaces, blocking growth sites. Our results quantitatively show the significance and variability of the inhibitory effects of natural hydrophobic organic acids when considering kinetics of calcite growth and its control on natural water chemistry. In natural systems DOM concentrations may be an order of magnitude greater than those examined in this study, indicating the importance of time and/or localized areas of increased pH (such as in algal mats) for achieving significant inorganic calcite mineralization.

ACKNOWLEDGEMENTS

This paper benefited from discussions with George Aiken, Greg Brown, Jerry Leenheer, and M. Ravichandran regarding the chemical character of humic substances. Review comments by Z. Amjad, R. Antweiler and G. Brown helped improve the manuscript. A. R. Hoch acknowledges the National Research Council associateship program and the USGS, Water Resources Division, National Research Program for

financial support of his work at the U.S. Geological Survey. Humic isolates supplied by George Aiken and co-workers is gratefully acknowledged. Assistance in revision of several figures by Micaela Beth Reddy is appreciated. Pat La Tour and Charmaine Gunther provided invaluable assistance in the preparation of the camera-ready manuscript. The use of trade names in this report is for identification purposes only and does not constitute endorsement by the USGS.

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