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Calcite nucleation and precipitation kinetics as affected by dissolved organic matter at 25°C and pH > 7.5

I. LEBRON* and D. L. SUAREZ

U.S. Salinity Laboratory, 450 West Big Springs Road, Riverside, CA 92507, USA

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Abstract-We examined the processes of calcite nucleation and crystal growth to determine the dominant mechanism for precipitation of calcite in the presence of dissolved organic carbon (DOC). Our experiments, conducted at 25°C and at a $Ca:HCO_3$ molar ratio of 1:2, were performed with and without calcite seeds. Scanning electron micrograph observations showed that the particle size of calcite crystals in the presence of DOC = 0.02 mM and after 24 h reached values bigger than 100 μm, while at the same saturation value (Ω), when the DOC = 0.15 mM, the size of the crystals were <2 μm for the same period of time. A crystal growth experiment in the presence of different DOC concentrations and 2 $m^2 L^{-1}$ of calcite crystals showed that precipitation was not detectable when 0.11 mmol m^2 of carbon was coating the calcite crystals. This surface coverage corresponds to a DOC in solution of 0.05 mM.

The rate of calcite precipitation was measured at different concentrations of DOC in quartz sand and quartz sand-Silver Hill illite suspensions with calcite Ω values between 1 and 50 and a CO_2 partial pressure of 35 Pa. The precipitation rate of calcite in the sand:solution suspensions decreased eightfold as the DOC increased from 0.02 to 0.15 mM at a Ω value of 9.0. Precipitation was completely inhibited in the Ω range of 1-24 when the DOC was 0.3 mM or greater. In the sand-illite suspensions, a similar eightfold decrease in the precipitation rate of calcite was observed when the DOC increased from 0.28 to 2.78 mM at a Ω value of 9.0. Differences in calcite precipitation rates between sand and sand-clay systems are likely due to differences in the number of potential heterogeneous nucleation sites. Experimental data were described by the equation:

$$R_T = R_{CG} + R_{HN},$$

where R_T is the total precipitation rate of calcite (mM s^{-1}), R_{CG} is the calcite precipitation rate due to crystal growth, and R_{HN} is the precipitation rate due to heterogeneous nucleation.

R_{CG} for natural systems is related to the DOC of the suspension by the expression:

$$R_{CG} = sk_{CG}([Ca^{+2}][CO_3^{-2}] - K_{SP})f(DOC)_{CG},$$

where brackets represent activities, s is the surface area of the calcite crystals, k_{CG} is the precipitation rate constant due to crystal growth, K_{SP} is the solubility of pure calcite at 25°C, and $f(DOC)_{CG}$ is the precipitation rate reduction for crystal growth with DOC. Experimentally we determined that $R_{CG} = 0$ when DOC ≥ 0.05 mM.

R_{HN} was related to Ω with the following expression:

$$R_{HN} = k_{HN}f(SA)(\log \Omega - 2.5)f(DOC)_{HN},$$

where k_{HN} is the precipitation rate constant due to heterogeneous nucleation, f(SA) is a function of the surface area of the particles in suspension, 2.5 is the Ω value at which no further precipitation by nucleation was observed, and f(DOC)$_{HN}$ is the function representing the reduction in precipitation by heterogeneous nucleation due to inhibition of DOC. The above equation, developed for natural environments, predicts that the overall calcite precipitation rate is unaffected by the existing calcite surface area when the DOC in the system is ≥ 0.05 mM.

1. INTRODUCTION

Calcite precipitation in natural waters is a kinetically controlled process. Knowledge of the precipitation rate is required to model mineral-water interactions in natural environments and to predict the fate of other pH dependent processes. Calcite supersaturation has been reported for groundwater in carbonate rocks (Back and Hanshaw, 1970), natural waters (Jacobson and Usdowski, 1975; Reynolds, 1978; Suarez, 1983; Dandurand et al., 1982; Last, 1982; Lorah and Herman, 1988), shallow groundwater beneath irrigated lands (Suarez, 1977), and for laboratory soil-water suspensions (Suarez and Rhoades, 1982; Inskeep and Bloom, 1986a; Suarez et al., 1992). Suarez and Rhoades (1982) showed that supersaturated levels of HCO_3 and Ca in soils probably were not due to a more soluble $CaCO_3$ phase but to kinetic competition between the release of Ca and alkalinity from other sources, including evapoconcentration, and the inhibition of calcite precipitation. Another well-described phenomena that contributes to calcite supersaturation in waters is the degassing of carbonate groundwaters upon pumping to the surface or emergence as springs. Car-

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* Author to whom correspondence should be addressed.

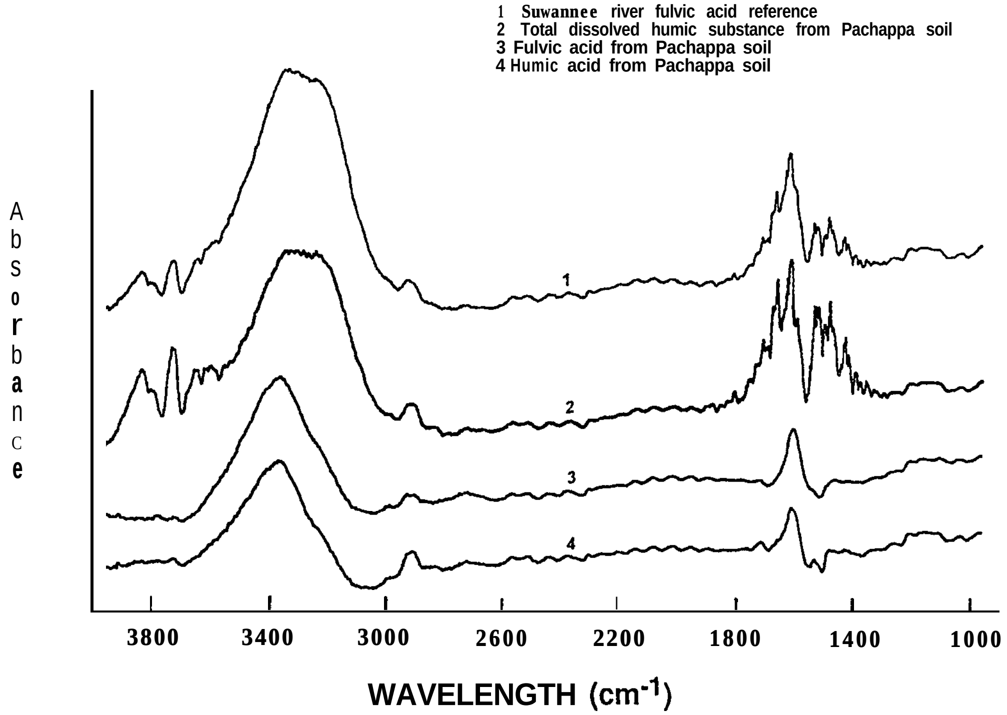

FIG. 1. FTIR absorbance spectra for humic (DOC = 3.96 mM), fulvic (DOC = 1.5 mM), and total humic substances (DOC = 5.65 mM) from soil Pachappa water extract, and for reference Suwannee river fulvic acid (DOC = 1.75 mM).

bonate groundwaters typically have a CO_2 content 10-100 times greater than atmospheric levels (Pearson et al., 1978; Jacobson and Langmuir, 1970).

Photosynthetic and microbial activity also affects the calcite precipitation rate in natural environments. A number of researchers have shown that bacteria, and algae, moss, and other photosynthetic plants take up significant amounts of CO_2 from stream waters (Mathews, 1962; Suarez, 1983; Stumm, 1985).

The kinetics of calcite dissolution and precipitation has been studied and modeled by several researchers; these studies have been performed in clean, crystal seeded systems and have resulted in several different rate equations to describe calcite precipitation. The kinetics of calcite precipitation/dissolution using seeded crystal growth experiments and first-order term equations has been described by Nancollas and Reddy (1971), Plummer et al. (1978), Inskeep and Bloom (198.5, 1986b), Busenberg and Plummer (1986), Compton et al. (1989), Compton and Unwin (1990), Compton and Pritchard (1990), and Brown et al. (1993). Second-

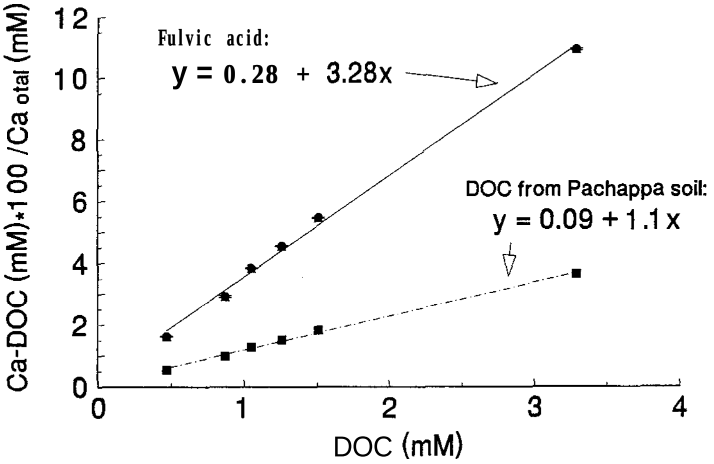

FIG. 2. Relationship between DOC concentration and Ca complexed by DOC, for Swannee river fulvic acid reference and DOC from Pachappa soil.

Table 1. Particle size distribution of calcite crystals with time for $\mathrm{DOC_{soil}} = 0.02$ mM and 0.15 mM. Data from scanning electron microscopy.

CALCITE CRYSTALS

Size (pm)	Mean number of crystals (Std. Dev.)				
	1h	5h	24h	48h	72h
			$\mathrm{DOC_{soil}} = 0.02$ mM		
≤ 2	147 (22)	175 (30)	189 (32)	22 (7)	8 (3)
2- 10	16 (4)	21(6)	23 (9)	7 (1)	3 (1)
> 10	4 (2)	5 (2)	6 (3)	2 (2)	2 (1)
			$\mathrm{DOC_{soil}} = 0.15$ mM		
≤ 2			8 (4)	6 (3)	
2- 10			2 (1)	1(1)	
> 10			0 (0)	0 (0)	

order rate equations (spiral growth mechanism) were described by Reddy and Nancollas (1973), Reddy (1986), Reddy and Gaillard (1981), and Shiraki and Brantley (1995). Higher-order equations (3.0-3.7, surface nucleation mechanism) were used by Mucci and Morse (1983) and Mucci (1986). These different formulations may correspond with different stages in the calcite precipitation process. Different stages of calcite precipitation were initially proposed by Nancollas and Reddy (1971) and have been observed by Dove and Hochella (1993) using atomic force microscopy in a clean and seeded system.

Inskeep and Bloom (1985) reviewed the rate models and reaction mechanisms of Davies and Jones (1955), Nancollas and Reddy (1971), Reddy and Nancollas (1971), and Plummer et al. (1978). They concluded that for pH > 8.0 and $P_{\mathrm{CO_2}} < 1.01$ kPa the equation that best described the precipitation of calcite was:

$$R = k_f s \gamma_2^2((\mathrm{Ca}^{2+})(\mathrm{CO}_3^{2-}) - K_{\mathrm{SP}}\gamma_2^{-2}), \qquad (1)$$

where R is the rate of calcite precipitation, k_f is the precipitation rate constant, s is the surface area of the calcite seeds, γ_2 is the divalent ion activity coefficient calculated from the Davies equation (Davies, 1962), parentheses represent concentration, and K_{SP} is the solubility product of pure calcite at 25°C.

Water-soluble organic ligands and ions such as PO_4^{3-} have been known to act as precipitation inhibitors by blocking crystal growth sites (Kitano and Hood, 1965; Reddy, 1977; Reynolds, 1978; Reddy and Wang, 1980; Inskeep and

TABLE **2.** Calcite precipitation rates for a six day period with dissolved organic carbon 0.02 and 0.15 mM DOC from Pachappa soil.

Time (days)	Calcite precipitation rates (mmol, $L^{-1}s^{-1}$) DOC=0.02mM	DOC=0.15 mM
0.04	3.89×10^{-5}	1.67×10^{-5}
0.21	2.78×10^{-6}	1.20×10^{-6}
1.00	4.39×10^{-7}	3.09×10^{-7}
2.00	2.89×10^{-6}	1.16×10^{-6}
3.00	4.28×10^{-6}	1.50×10^{-6}
4.00	5.41×10^{-6}	1.04×10^{-6}
5.00	4.63×10^{-6}	1.27×10^{-6}
6.00	4.98×10^{-6}	1.04×10^{-6}

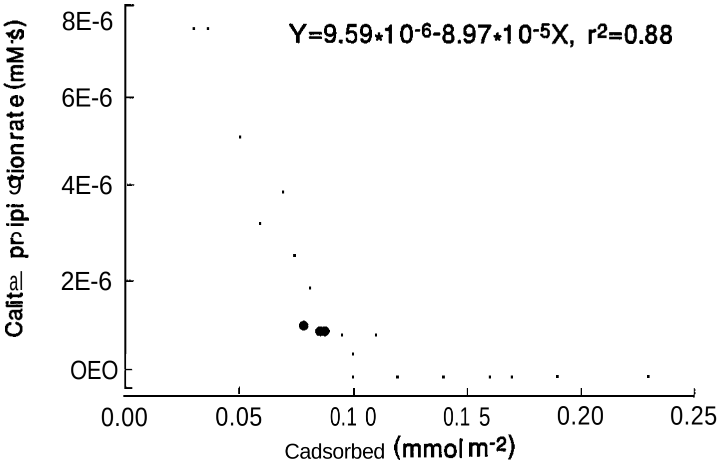

FIG. 3. Calcite precipitation rate in the presence of 2 $m^2 L^{-1}$ of calcite seeds and $\Omega = 1.9$ as a function of DOC adsorbed on the calcite surfaces (Suwannee river fulvic acid reference).

Bloom, 1986b; Dove and Hochella, 1993; Gratz and Hillner, 1993; Katz et al., 1993; Paquette et al., 1995). Inskeep and Bloom (1986b), in a seeded crystal growth experiment, found that the precipitation rate constant decreased to zero, at Ω = 8-9 ($\Omega = IAP/K_{SP}$, where IAP is the ionic activity product) in the presence of 0.15 mM DOC (dissolved organic carbon) from a water-soil extract, and in the presence of only 0.028 mM DOC when the DOC source was a fulvic acid. Levels of DOC in natural environments are comparable to the levels found by Inskeep and Bloom (1986b) to inhibit calcite precipitation, thus, it is reasonable to question whether calcite crystal growth is the dominant precipitation mechanism in most natural environments. In soils, where there is usually sufficient soluble organic matter to inhibit crystal growth, it is not surprising that well-developed pedogenic crystals of calcite are not encountered.

The objectives of the present research were to: (1) evaluate the inhibitor effect of DOC on calcite precipitation by nucleation, (2) quantify the effect of DOC on calcite precipitation at atmospheric P_{CO_2}, pH greater than 7.5, and Ω values between 1 and 50 in the presence of several potential nucleation materials, and (3) develop a rate model for calcite precipitation applicable to natural systems with DOC.

2. MATERIALS AND METHODS

Quartz sand (200-700 μm) and a reference clay mineral (Silver Hill illite) were used in this study. The sand (Paragon Building Products, Inc.[†], City of Industry, CA) was washed first with 0.1 M HCl, and then extensively with deionized water (DIW). Silver Hill illite was obtained from the Source Clay Minerals Repository of the Clay Minerals Society (Columbia, MO), and ground in an agate mortar after which the <2 μm fraction was collected by sedimentation. Quartz sand and Silver Hill illite (<2 μm) were mixed in a 7:3 sand:clay weight ratio, equilibrated three times with a solution of 0.5 mM of Ca and 1 mM HCO_3 in a 1:5 solid:solution ratio, washed once with DIW at the same solid:solution ratio, and air

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[†] Trade names are provided for the benefit of the reader and do not imply any endorsement by the USDA.

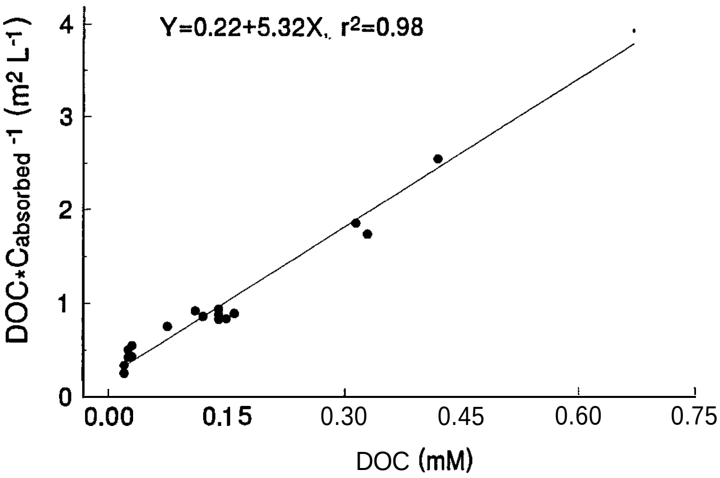

FIG. 4. Langmuir adsorption isotherm for DOC (Swannee river fulvic acid reference) adsorbed on calcite.

dried. The equilibration with the Ca-HCO_3 solution was carried out as a pretreatment to: (1) saturate exchange sites with Ca, (2) maintain a constant Ca:HCO_3 molar ratio, and (3) adjust the pH of the solid to a value close to that of the experiment. Since reaction with the solutions resulted in very undersaturated (with respect to calcite) conditions, preparation did not result in precipitation onto the solid (which was free of carbonates). All HCO_3^- solutions used in this study were prepared by dissolving 53 μm particle size calcite (Mallinckrodt) for at least 24 h in DIW with magnetic stirring under an atmosphere of 98 kPa P_{CO_2}.

Calcite crystals (Baker, Analytical Reagent) were used as seeds to study the effect of calcite surface area on the precipitation rate at different concentrations of DOC. Calcite crystals with a particle size of 2-20 μm were separated by sedimentation. Surface area was analyzed by single-point BET N_2 adsorption with a Quantachrome Quantasorb Jr. surface area analyzer (Quantachrome Corp., Syosset, NY). The surface area of the crystals was 0.96 ± 0.01 $m^2 g^{-1}$.

Suwannee River fulvic acid reference (International Humic Substances Society, Golden, CO) and DOC collected from a water-soil extract were used in the present study. The soil-water extraction was made at a soil:water ratio of 1:5 from a surface sample of Pachappa soil (Mollic Haploxeralf, fine-loamy, mixed thermic) The soil sample was previously equilibrated with a solution of 1 mmol, L^{-1} Ca-HCO_3, washed with DIW, and air-dried. The extract was filtered through a 0.2 μm filter and stored at 4°C. Carbon analyses were performed with a Dohrmann Carbon Analyzer (Dohrmann, Santa Clara, CA). Characterization of the humic, fulvic, and total acids in the soil:water extracts was made by infrared spectroscopy. Humic and fulvic acids from the soil extract were separated by traditional procedures (Stevenson, 1982). The initial soil extract, fulvic, and humic fractions were analyzed for DOC. The fulvic and humic concentrations were calculated from the concentrations of the extracts, taking into account the changes in volume. Infrared spectra of the liquids were recorded with a Bio-Rad FTS-7 FTIR spectrophotometer and a deuterated triglycine sulfate (DTGS) detector. The sample holder was a horizontal PLC-I 1M prism liquid cell with a 45 degree single reflection ZnSe prism and a simple two-mirror transfer optics design for high performance. Attenuated total internal reflectance (ATR) ATR-FTIR spectra were recorded from 4000 to 1000 cm^{-1} at 4 cm^{-1} over sixty-four scans. All final ATR-FTIR spectra were the result of subtracting the spectra of the water from the spectra of the samples.

The calcite precipitation experiments were conducted ‘in 250 mL flasks which were connected to a pressurized air source with a plastic capillary inserted into the flask stoppers. The air was presaturated with water by bubbling through three DIW-filled water towers. The first tower was heated to 45°C and the other two were maintained at 25°C. The composition of the air bubbled into the flasks was similar to atmospheric air (P_{CO_2} = 38-40 Pa) and the P_{CO_2} in the flasks was maintained between 35-50 Pa for the clean systems, and 35-90 Pa for the sand-Silver Hill illite suspensions. Relatively high bubbling rates were required to maintain P_{CO_2} levels below 100 Pa and to sweep out the CO_2 that was generated by the precipitation reaction (and to a much lesser extent the decomposition of DOC). Every flask contained 20 g of either sand, or a sand-illite mixture, and 80 mL of a Ca-HCO, solution with different Ω values. The experiments were performed in a constant temperature room at 25 ± 0.5°C. A flask with Ω = 1 was used in each experiment as a control for possible evaporation.

2.1. Particle Size of Calcite Crystals as Affected by Time and DOC

A duplicated calcite precipitation experiment in a sand-suspension system, without initial seeds, Ω = 9 and DOC (from a soil extract) = 0.02 and 0.15 mM, was performed for a duration of 6 days. Twenty mL of supernatant were filtered through a 0.1 μm pore-size filter at 0.04, 0.21, 1, 2, 3, 4, 5, and 6 days; sand samples were taken at the same intervals. After 24 h the supernatant was decanted and replaced by a fresh supersaturated solution; this replacement procedure was repeated each day for 6 days. The filters and sand samples were observed with a scanning electron microscope (SEM) (Link Analytical Limited, Bucks, England) and the composition of the supernatant was analyzed for Ca and HCO_3. The precipitate was also characterized by X-ray diffraction (XRD) (Norelco, Phillips Electronic Instrument, New York).

A semiquantitative particle size analysis was done with the calcite crystals collected on the filters. We designated ten different regions of equal area in each micrograph. The number of calcite crystals were counted and grouped into three different particle sizes: ≤ 2 μm, 2-10 μm, and > 10 μm. Particle size was determined from filters corresponding to 1, 5, 24, 48, and 72 h at DOC = 0.02 mM and at 24 and 48 h at DOC = 0.15 mM.

2.2. Kinetics of Calcite Precipitation **in the Presence of Calcite Crystals as Affected by DOC**

Calcite precipitation rate was measured in duplicate in a solution of Ω = 1.9 and with 2 $m^2 L^{-1}$ of calcite crystals. Suwannee river fulvic acid reference was added to achieve DOC concentrations from 0.02 to 1 mM. Up to a total of ten different concentrations were used. Ca-DOC complexation was accounted for in order to maintain the same Ω value in all the flasks. Samples from the supernatant were taken at t = 0 and t = 1 h and analyzed for Ca, alkalinity, and DOC. Standard errors of the duplicates for the Ca and alkalinity analysis were within ± 0.02 $mmol_c L^{-1}$ and DOC within ± 0.005 mM. The amount of DOC adsorbed on the surface of the crystals was expressed using a Langmuir adsorption isotherm.

2.3. **Kinetics of Calcite Precipitation in the Absence of Calcite Crystals as Affected by DOC**

The precipitation rate of $CaCO_3$ was determined at constant P_{CO_2} and temperature at different DOC concentrations. Both Suwannee river fulvic acid reference and soil DOC were used in this experiment. Every reaction set contained ten to twenty-four flasks having a range in Ω from 1 to 40 at a fixed DOC concentration. All the reactions were duplicated; standard errors of the duplicates for Ca and alkalinity analysis were within ± 0.02 mM. Precipitation rates were measured in quartz sand suspensions and sand-illite suspensions. The soil DOC levels studied were 0.02, 0.15, and 0.30 mM for the sand suspensions, and 0.28, 0.56, 0.80, and 2.78 mM for the sand-illite suspensions. The reference fulvic acid material was added to sand-illite suspensions to achieve concentrations of 0.47, 0.87, 1.05, 1.26, 1.51, and 3.29 mM DOC. The flasks were shaken on a reciprocating shaker table at ninety cycles per minute during the experiment.

Samples were reacted for a variable period of time (1 day to 9 days) in a constant temperature room at 25°C ± 0.5°C. Solution samples were removed after 1, 5, and 24 h, and several days. Solutions were filtered through prerinsed 0.1 μm filters, diluted fivefold with DIW to avoid further precipitation, and analyzed for Ca, alkalinity, and DOC. The pH of the suspensions was measured at the time of sampling with a Fisher Accumet 520 pH meter (Fisher Scientific Co., Pittsburgh, PA) and a Thomas 4094 combination pH electrode (Thomas Scientific, Swedesboro, NJ) calibrated with buffers pH 4.00 and 6.86 to within 0.01 pH units at 25°C. Calcium was determined by inductively coupled plasma emission spectroscopy; alkalinity was measured by titration with $KH(IO_3)_2$ (National Bureau of Standards primary acid standard). The sample was titrated down to pH 4.4, after which N_2 was bubbled into the vial for 5 min to sweep out the dissolved CO_2 gas built up from conversion of HCO_3, then acid was added again until the pH was 4.4. The *sum* of the volume of acid used in both steps of the titration was used to calculate the alkalinity of our samples (Suarez et al., 1992). The detection limit with this experimental procedure and our analytical methods corresponds to a calcite precipitation rate of 10^{-7} mM s^{-1}; we will refer to this value as the threshold detection level.

The saturation level for $CaCO_3$ was calculated for every sampling; this was necessary because we did not replace the supernatant and consequently Ω changed with time. The calculations were made in two different ways, from P_{CO_2} and solution composition, and from pH and solution composition. In both cases the equilibrium constants used were those given by Suarez (1977). In the experiments with sand only, the differences between the Ω values obtained by

Table 3. Initial composition of the sand-illite **suspensions for the calcite precipitation rate experiment with reference Suwannee River** fulvic acid.

		<---- Initial Concentration (mM) ----						
	Initial	< ----Total---->					**Complex**	**Initial**
Sample #	**PH**	**DOC**	**Ca**	**alk**	**Ca^{2+}**	**HCO_3^-**	**Ca-fulvic**	**Ω**
1	**8.25**	**0.47**	**1.70**	**3.47**	**1.58**	**3.30**	**0.026**	**9.88**
2	**8.29**	**0.47**	1.51	2.95	1.40	2.81	0.023	9.22
3	8.18	0.47	1.38	2.82	1.29	2.70	0.022	6.24
4	8.25	0.47	1.45	2.95	1.35	2.82	0.023	7.67
5	8.39	0.47	1.35	2.69	1.25	2.56	0.021	9.01
6	8.44	0.47	1.29	2.57	1.20	2.45	0.020	9.22
7	8.34	0.47	1.10	2.19	1.03	2.10	0.028	6.09
8	8.28	0.47	1.00	2.04	0.94	1.96	0.017	4.52
9	8.30	0.47	0.85	1.74	0.80	1.67	0.015	3.51
10	8.28	0.47	0.72	1.48	0.69	1.43	0.013	2.60
11	8.35	0.87	1.55	3.09	1.42	2.95	0.044	10.59
12	8.45	0.87	1.45	1.48	1.33	1.41	0.041	11.61
13	8.43	0.87	1.41	2.88	1.31	2.76	0.040	10.59
14	8.43	0.87	1.29	2.57	1.19	2.46	0.038	9.66
15	8.42	0.87	1.18	2.40	1.08	2.29	0.034	7.67
16	8.40	0.87	1.15	2.30	1.06	2.20	0.034	7.50
17	8.52	0.87	1.10	2.19	1.02	2.10	0.033	8.22
18	8.40	0.87	0.93	1.91	0.87	1.83	0.029	5.43
19	8.37	0.87	0.85	1.74	0.80	1.67	0.027	4.03
20	8.38	0.87	0.72	1.48	0.69	1.43	0.023	3.13
Control	8.25	0.01	0.48	1.02				1.0

P_{CO_2}-solution and pH-solution methods were less than 2%. When clay particles were in suspension, differences in calculated Ω values were as high as 10%, and similar differences were found between the measured and calculated pH. These discrepancies are attributed to calculated P_{CO_2} above atmospheric values; the high P_{CO_2} is due to inefficient elimination of the CO_2 produced by $CaCO_3$ precipitation. We utilized measured pH values, rather than assuming a fixed P_{CO_2}, because of the difficulties in removing CO_2 from solution at the same rate at which it is generated by the precipitation of calcite. We initially observed that the P_{CO_2} could increase several orders of magnitude when slow bubbling rates were used. As a result of these preliminary experiments, high bubbling rates were used in the experiments reported, reducing the P_{CO_2} fluctuations to the range 35-90 Pa CO_2. Use of measured pH in the calculations represents the actual conditions in solution during the reaction.

The use of reference Suwannee river fulvic acid allowed us to account for Ca-fulvic complexes using the program GEOCHEM-PC (Parker et al., 1994). GEOCHEM-PC has two different fulvic acids in the thermodynamic data base. The fulvic acid used for our calculations to account for Ca-fulvic complexes was that registered as FUL2- with a pK for the Ca-fulvic acid of 1.7. This choice was based on the similarities of the elemental chemical composition and the infrared spectra of FUL2 (Sposito et al., 1976) and the Suwannee fulvic acid reference used in this study.

We used the arithmetic mean of the Ω value at $t = 0$ and $t = 1$ h as the representative value during the first hour of the precipitation experiment. Arithmetic means were also calculated for the Ω values at $t = 1$ h and $t = 5$ h, and for $t = 5$ h and $t = 24$ h to represent Ω during these respective intervals.

Calcite precipitation rates were calculated after 1, 5, and 24 h

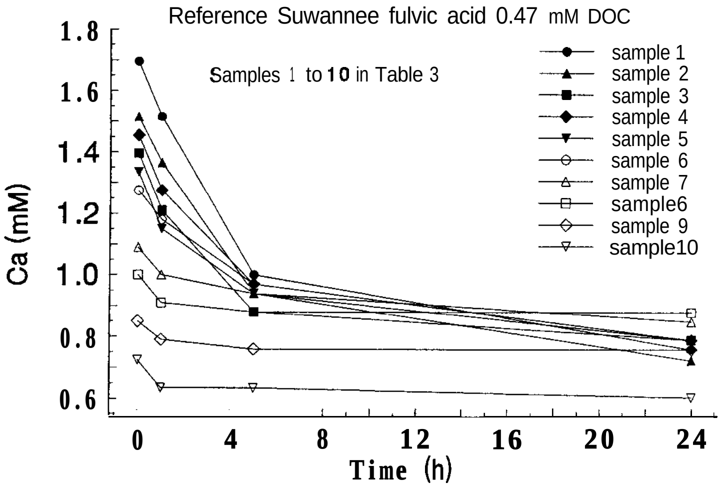

FIG. 5. Calcium concentration with time in the supematant for DOC = 0.47 mM (Suwannee river fulvic acid reference) in a sand-illite system.

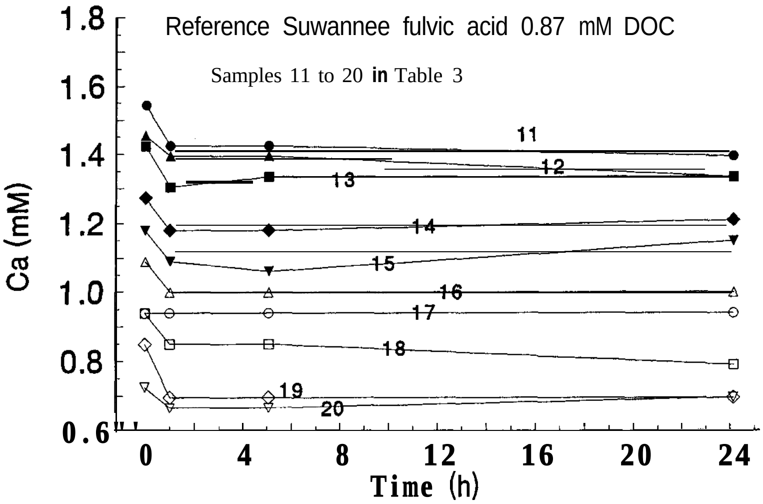

FIG. 6. Calcium concentration with time in the supematant with DOC = 0.87 mM (Suwannee river fulvic acid reference) in a sand-illite system.

based on (1) changes in mass of Ca in solution and (2) changes in mass of HCO_3 in solution. Precipitation rates for calcite, based on Ca or HCO_3 data, showed good agreement, as required, and were not statistically different.

3. RESULTS

3.1. DOC Characterization and Ca-DOC Complexation

After the separation of the humic and fulvic acids from the soil:water extract, we proceeded to characterize each fraction by FTIR. FTIR spectra of the total humic substance (DOC = 5.65 mM), fulvic acid (DOC = 1.5 mM), and humic acid (DOC = 3.96 mM) from the soil:water extracts and the reference Suwannee river fulvic acid (DOC = 1.75 mM) are shown in Fig. 1. The main adsorption bands are in the region of 3300 cm^{-1} (H-bonded OH groups), 2900 cm^{-1} (aliphatic C-H stretching), 1620 cm^{-1} (aromatic C=C and H-bonded C=O), and 1550 cm^{-1} (COO- symmetric stretching). All extracts and reference materials showed similar spectra, as expected.

Based on FTIR spectra, DOC concentration, and literature values of the carboxyl groups for soil humic substances (see discussion), we assumed, as a first approximation, that the soil DOC complexation capacity is $^1/_3$ the complexation capacity of DOC from reference fulvic acid and we calculated the Ca-DOC complexation. Calculations of the Ca-fulvic acid reference complexes were made at 0.47, 0.87, 1.05, 1.26, 1.51, and 3.29 mM of DOC. Figure 2 shows the concentration of the Ca-complexes with increasing DOC in solution for Suwannee fulvic acid reference and Pachappa soil. Every point in Fig. 2 is the average of forty values (ten

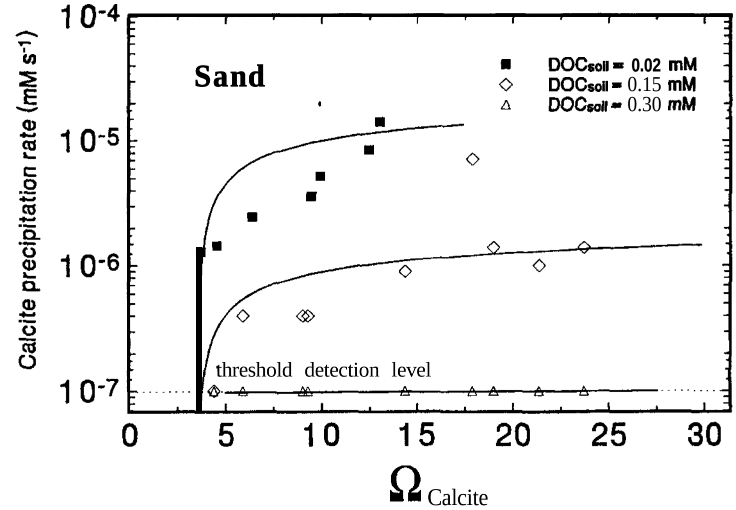

FIG. 7. Calcite precipitation rate, as a function of calcite supersaturation, at three different DOC (from Pachappa soil extract). The rates were measured in a quartz sand:water system, and based on changes in Ca concentration. The solid line represents the predicted precipitation rate using Eqn. 2.

reaction beakers times four samplings of each beaker) ; standard errors, in the DOC range of 0.5 to 4 mM, are within ±0.02.

3.2. Particle Size of Calcite Crystals as Affected by Time and DOC

The characterization of the precipitate by SEM and XRD showed that calcite was the only mineral phase in the seeds or precipitated in our experiments. Also, observations of the filters and sand samples by SEM showed that calcite precipitated in the bulk solution and not on the surfaces of the sand particles.

Within the first 24 h there was a dominance of crystals <2 μm, and there was no significant change in the size distribution of the calcite crystals. After 24 h, at DOC = 0.02 mM, the percentage of <2 μm particles decreased and the percentage of large particles increased, some particles were as large as 100 μm. Table 1 shows the mean and standard deviation of the number of crystals grouped in three different particle sizes, $\leq 2\ \mu$m, 2-10 μm, and $>10\ \mu$m.

In the presence of 0.15 mM DOC, the filters collected after filtration showed ⅕ to ½ of the total number of crystals observed in the systems when DOC = 0.02 mM. No increase in the particle size of the crystals was observed with time when the DOC = 0.15 mM. This observation is also confirmed by the precipitation rates shown in Table 2. Calcite precipitation rate increased with time when the DOC = 0.02 mM, but remained constant when the DOC = 0.15 mM.

3.3. Kinetics of Calcite Precipitation in the Presence of Calcite Crystals as Affected by DOC

The calcite precipitation rate decreased in the presence- of 2 $m^2 L^{-1}$ calcite crystals and initial Ω = 1.9 as the adsorbed DOC increased (Fig. 3). Precipitation was not detectable (<5.3 x 10^{-8} mM L^{-1}) when 0.10 mmol m^{-2} of C was coating the calcite crystals. Expressing the results in terms of the Langmuir adsorption isotherm, we calculated the maximum amount of DOC than can be adsorbed by the calcite crystals. This maximum value is 0.19 mmol m^{-2} and is represented by the inverse of the slope of the line in Fig. 4.

3.4. Kinetics of Calcite Precipitation in the Absence of Calcite Crystals as Affected by DOC

The initial pH, Ca, and HCO_3 concentrations for experiments with two levels of Suwannee river fulvic acid reference (0.47 and 0.87) mM and a sand-illite system are shown in Table 3. The calcite precipitation rate during the first hour of reaction was similar for the two concentrations of DOC, as shown in Figs. 5 and 6. After the first hour, precipitation ceased in the suspensions with DOC 0.87 mM (see Fig. 6) for Ω = 2-9, while precipitation continued in the suspensions with DOC = 0.47 mM, as shown by the decrease in the Ca concentration of the supernatant in Fig. 5.

The effect of soil extract DOC on the precipitation rate of calcite is shown in Fig. 7 for quartz sand suspensions, and in Fig. 8 for sand-illite suspensions. In Fig. 7 the maximum precipitation rate was observed at the lowest level of DOC (0.02 mM). With increasing DOC the rate decreased until precipitation ceased when the DOC was 0.3 mM. No precipitation was observed during nine days of reaction when the DOC was 0.3 mM. This corresponds to a precipitation rate of $\leq 1 \times 10^{-7}$ mM s^{-1}. The Ω was calculated for each sampling from the measured pH and calculated activity of Ca^{2+} and CO_3^{2-}, after correction for Ca-DOC complexation.

Figure 8 shows a reduction in the $CaCO_3$ precipitation rate with increasing DOC in the sand-illite suspensions. For an Ω of 9, and a DOC of 2.78 mM, the rate **slowed to a 13% of the rate at 0.28** DOC.

4. DISCUSSION

4.1. DOC Characterization and Ca-DOC Complexation

We separated and quantified the humic and fulvic acid from the soluble organic fraction of Pachappa soil to estimate the extend of Ca-DOC complexation in our system. The FTIR spectra from fulvic, humic, and total humic substances from Pachappa soil and from reference Suwannee river fulvic acid are shown in Fig. 1. The four samples showed similar spectra, indicating the presence of the same functional groups. Also, the intensities of the peaks were very similar for Pachappa and the fulvic acid reference despite the differences in DOC concentration. Based on the FTIR data we calculate that 1.75 mM of fulvic acid reference contains a similar quantity of functional groups as 5.65 mM of DOC from Pachappa soil. These results are consistent with the observations of Inskeep and Bloom (1986b), in which the fulvic acid used by these authors had approximately 5 times the effectiveness to inhibit calcite precipitation than did a water soil extract. Oliver et al. (1983) quantified the carboxyl content of different fulvic and humic acids and, for soils, they consider a typical value of 6.4 pmol, carboxyl mg -' C for humic acid and 17.9 pmol, carboxyl mg^{-1} C for fulvic acid. Pachappa soil DOC is composed of 70% humic acid (5.65 mM total humic substances gave 1.5 mM fulvic and 3.96 mM humic acids). Based on these values, Pachappa soil DOC contains 9.24 μmol_c carboxyl mg^{-1} C vs. 31.33 μmol_c carboxyl mg^{-1} C for Suwannee fulvic acid reference. This indicates that Pachappa soil DOC has approximately ⅓ of the complexation capacity of Suwannee river fulvic acid. A similar conclusion is obtained on a molar DOC basis and the relative intensities of the IR spectra.

With these results we calculated the complexation capacity of Pachappa DOC soil with Ca, for the Ca concentration range of 0.7-2 mM, and DOC concentrations of 0.5-4 mM (Fig. 2). The concentration of the Ca-fulvic acid complexes is relatively minor and decreases with increasing Ca concentration. In a calcite supersaturated system, considering a typical DOC content in arid soils of 0.43-1.24 mM and using the data in Fig. 2, the error in the calculation of Ω, if we neglected Ca-DOC complexes, is about 1.5%, for Ca concentrations in the range of 0.7-2 mM.

4.2. Particle Size of Calcite Crystals as Affected by Time and DOC

We followed, by SEM, the morphology and evolution with time of the calcite precipitate in the absence of initial

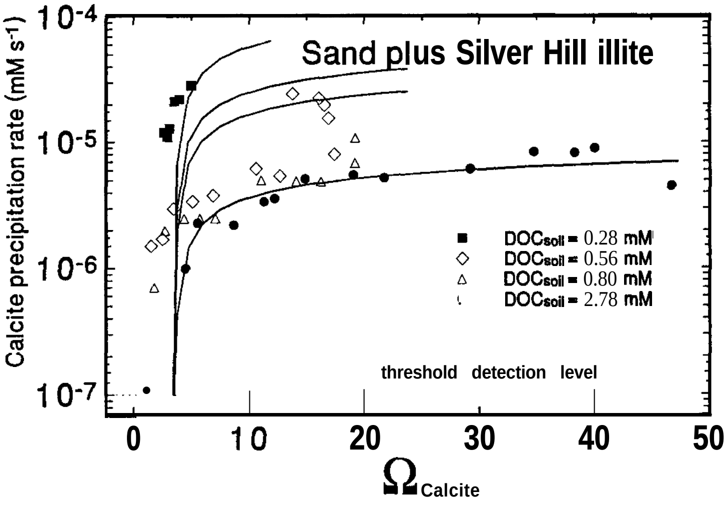

FIG. 8. Calcite precipitation rate, as a function of calcite supersaturation at 4 different DOC concentrations (from Pachappa soil extract). The rates were measured in a sand + Silver Hill illite:water system, and based on changes in Ca concentrations. The solid line represents the predicted precipitation rate using Eqn. 2.

crystals and at two concentrations of DOC. In the system $\Omega = 9$ and soil extract DOC = 0.02 mM, the particle size of the calcite precipitate was predominantly <2 μm (Table 1) after 1 h reaction time. Within 24 h and with the same DOC concentration, the particle size of the precipitate did not change significantly. Only after 24 h did the size of the precipitate become larger, however, these >2 μm particles are clusters of many small particles rather than large single crystals. Our observations agree with those of Dove and Hochella (1993)) who, using scanning force microscopy, describe a coalescence among calcite nuclei after an initial period of nuclei formation.

The size of the crystals was also <2 pm within the first 24 h when the DOC = 0.15 mM. However, the number of calcite crystals was significantly lower when DOC = 0.15 mM than at DOC = 0.02 mM (Table 1). This observation alone indicates that DOC inhibits the initial stages of nucleation, since all the reaction vessels had the same calcite supersaturation level after correction for DOC-Ca complexation. Accordingly, calcite precipitation at DOC = 0.02 mM was faster than when the DOC was 0.15 mM (Table 2).

The size of the calcite crystals when DOC = 0.15 mM did not increase significantly in the six-day period of observation. Also, we observed that calcite precipitation did not increase with time, which was the case for the suspensions where the DOC = 0.02 mM (Table 2). This may indicate that crystal growth is limited in the presence of a DOC concentration of 0.15 mM.

4.3. Kinetics of Calcite Precipitation in the Presence of Calcite Crystals as Affected by DOC

Measurements of Ca and HCO_3 concentrations in the absence of DOC and in calcite supersaturated solutions with $\Omega = 1.9$ indicated no precipitation for several days in the absence of calcite crystals. Precipitation occurred only when calcite crystals were added. This indicates that at $\Omega \approx 2$ and in the presence of crystals, calcite precipitates by crystal growth and no heterogeneous nucleation occurs.

We found that calcite precipitation decreased rapidly as DOC covered the calcite crystals. When the DOC adsorbed was 0.11 mmol per m^2 of calcite crystal, the calcite precipitation dropped below our detection limit (Fig. 3). Using the linear equation in Fig. 4 we calculate that 0.11 mmol m^2 of DOC adsorbed corresponds to an equilibrium concentration of 0.05 mM of DOC in solution. From the same equation in Fig. 4 we also obtained the capacity factor or maximum amount of DOC that can be adsorbed by the calcite crystals which is 0.19 mmol m^2. These values agree with Inskeep and Bloom (1986b), who found a capacity factor of 0.17 mmol m^2 and a calcite precipitation rate equal to zero at 0.15 mmol m^2.

4.4. Kinetics of Calcite Precipitation in the Absence of Calcite Crystals as Affected by DOC

Apparently, the only attempt to quantify the inhibition of calcite precipitation by humic and fulvic substances was that reported by Inskeep and Bloom (1986b). Their experiment was carried out in the presence of calcite seeds. As shown above, calcite crystals are sufficiently coated with DOC that crystal growth is prevented when DOC > 0.05 mM. Consequently, a realistic model formulated to describe the precipitation rate of calcite in natural environments should consider the calcite surface area term only during the period of time from when heterogeneous nucleation occurs until the surface generated by the new crystal is poisoned by the DOC. This period of time, we assume, changes with the DOC concentration, but according to our SEM observations is certainly less than 1 h in a relatively clean system, with DOC concentrations as low as 0.15 mM. Also, comparing the results shown in Figs. 5 and 6, in a sand-illite system, the precipitation of calcite at DOC = 0.47 and 0.87 mM is not substantially different during the first hour. After this time, the calcite

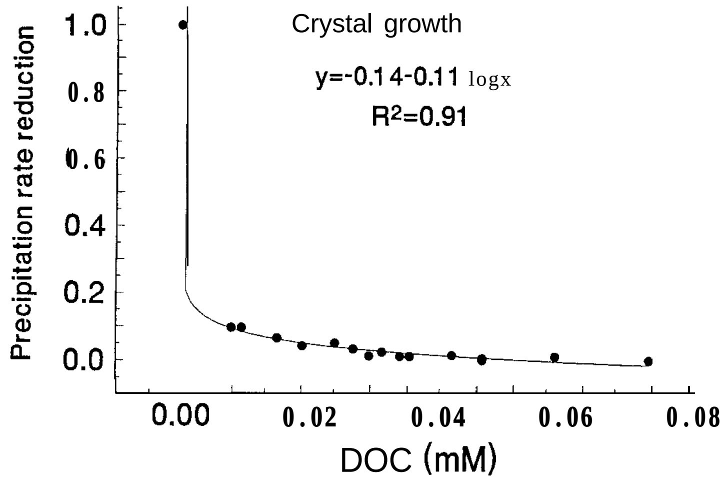

FIG. 9. Reduction in the rate of calcite precipitation by crystal growth as a function of DOC (Suwannee river fulvic acid reference). Calcite precipitation rates were measured in the presence of 2 $m^2 L^{-1}$ of calcite seeds and $\Omega = 1.9$. Calculations were made based on the precipitation rate of calcite in the absence of DOC (3.9×10^{-5} mM s^{-1}) at similar experimental conditions.

precipitation stopped at DOC 0.87 mM while, for the same Ω, the precipitation continued at 0.47 mM.

From Fig. 6 and from SEM observations, we conclude that the poisoning of the surface of the calcite crystals occurs very rapidly in soil environments at DOC concentrations of 0.87 mM, and in aqueous systems at 0.05 mM. Under these conditions, the existing surface of the calcite crystals is not a leading factor affecting the overall precipitation rate, instead, heterogeneous nucleation controls the precipitation of calcite.

Calcite precipitation rates at different soil DOC concentrations in sand:suspensions (Fig. 7) and sand-illite:suspension (Fig. 8) were quantified over a 24 h time period. Calcite precipitation in the sand:solution system occurred mainly in the solution (see above, SEM results), indicating that dust and bacteria were the active sites during the initial nucleation stage. Organisms aid in the precipitation of $CaCO_3$ by trapping microparticulate calcite and by providing a substrate for calcite growth (Golubic, 1969; Pentecost, 1978; Chafetz and Folk, 1984; Dennen and Diecchio, 1984).

The calcite nucleation stage is adversely affected at DOC levels as low as 0.30 mM; this is the DOC concentration at which calcite precipitation is completely inhibited (Fig. 7). When the nucleation sites are more numerous (as in the sand:illite suspensions), higher DOC levels (2.78 or 3.29 mM) reduced the precipitation rate but did not stop it (Fig. 8). No further precipitation for the sand-illite system was observed in the DOC range studied (0.28-2.78 mM) when $\Omega \leq 2.0$. The solution remained supersaturated for up to nine days at $\Omega \leq 3.0$ for the sand system when DOC ranged from 0.02-0.3 mM.

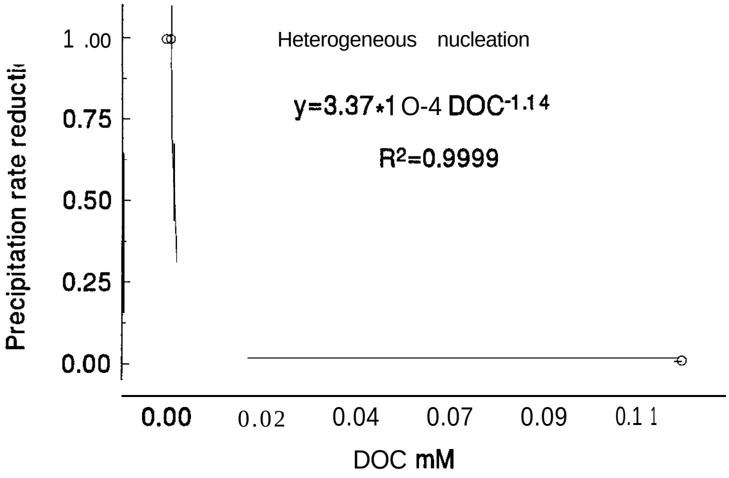

FIG. 10. Reduction in the rate of calcite precipitation by heterogeneous nucleation as a function of DOC (Suwannee river fulvic acid reference). Calcite precipitation rates were measured in the absence of calcite crystals and $\Omega = 5$. Calculations were made based on the precipitation rate of calcite in the absence of DOC (4.45×10^{-4} mM s^{-1}) with similar experimental conditions.

4.5. Precipitation Rate Equation

The calcite precipitation rate in the presence of fulvic and humic substances can be represented by the following the expression:

$$R_T = R_{CG} + R_{HN}, \tag{2}$$

where R_T is the total precipitation rate of calcium carbonate ($\mathrm{mM\,s^{-1}}$), R_{CG} is the calcite precipitation rate due to crystal growth and R_{HN} is the calcite precipitation due to heterogeneous nucleation.

R_{CG} for natural systems decreases when the amount of DOC adsorbed on the calcite surface increases (Fig. 3). Likewise, C_{ads} is related (Fig. 4) to the DOC of the solution by the equation:

$$\frac{\mathrm{DOC}}{C_{ads}} = 0.22 + 5.32\ \mathrm{DOC}, \tag{3}$$

where C_{ads} is the amount of DOC adsorbed on the calcite surface, expressed in mmol m^{-2}. Taking the equation of Inskeep and Bloom (1985) (Eqn. 1) and including the correction factor for the inhibition of DOC we have:

$$R_{CG} = sk_{CG}([\mathrm{Ca}^{2+}][\mathrm{CO}_3^{2-}] - K_{SP})f(\mathrm{DOC})_{CG}, \tag{4}$$

where brackets represent activities. The correction factor f(DOC) is a function representing the reduction of the calcite precipitation rate with increasing DOC (Fig. 9). The results shown in Fig. 9 were obtained from the calcite precipitation rate of $3.9 \times 10^{-5}\ \mathrm{mM\,s^{-1}}$, $\Omega = 1.9$, in the absence of DOC, and the precipitation data obtained in the presence of DOC, given in Fig. 3. We express the results in terms of DOC using the C_{ads} − DOC relation given in Fig. 4. The expression given in Fig. 9:

$$f(\mathrm{DOC})_{CG} = -0.14 - 0.11\ \log\ (\mathrm{DOC}). \tag{5}$$

is used in the $f(\mathrm{DOC})_{CG}$ range from 1 to 0, developed from experiments with Suwannee fulvic acid, and 2 $\mathrm{m^2\,L^{-1}}$ of calcite seeds. The constant k_{CG} in Eqn. 4 was calculated from Eqn. 1 in the absence of DOC. The value for our experimental conditions is $k_{CG} = 64.8$ mmol $\mathrm{s^{-1}m^{-2}}$. Experimentally, we determined that $R_{CG} = 0$ when DOC = 0.05 mM, which is the concentration at which the DOC inhibits precipitation by crystal growth (Fig. 3). Consequently, $R_{CG} = 0$ for values of DOC ≥ 0.05 mM.

R_{HN} was related to the calcite saturation level Ω, for a given value of DOC, with the following expression:

$$R_{HN} = k_{HN}f(\mathrm{SA})(\log[\Omega - 2.5])f(\mathrm{DOC})_{HN}, \tag{6}$$

where k_{HN} is the precipitation rate constant, $f(\mathrm{SA})$ is ≥ 1 and is the term for the active sites of the particles in suspension, f(SA) = 1 when there are not particles suspended. In the absence of specific information on these sites we relate the active sites to the surface area of these particles. The value 2.5 is the Ω value below which no further calcite precipitation by nucleation was found in our experiments. The expression $f(\mathrm{DOC})_{HN}$ is the reduction in calcite precipitation due to the inhibition of the DOC in the absence of calcite seeds (Fig. 10). In a manner similar to that used to develop $f(\mathrm{DOC})_{CG}$, we developed a function relating precipitation by nucleation to DOC. We combined the calcite precipitation rate of $3.11 \times 10^{-4}\ \mathrm{mM\,s^{-1}}$, obtained in the absence of both calcite seeds and Suwannee fulvic acid, at $\Omega = 5$, with the precipitation data in the absence of calcite seeds and in the presence of DOC. We obtained the following expression:

$$f(\mathrm{DOC})_{HN} = 3.37 \times 10^{-4}\,\mathrm{DOC}^{-1.14}, \tag{7}$$

where the k_{HN} constant was found to be 7.82×10^{-4} and DOC > 0.

The surface area of the Silver Hill illite used in the present study is 45 ± 0.01 $\mathrm{m^2\,g^{-1}}$; thus, the illite surface area in our reaction vessels was 3375 $\mathrm{m^2\,L^{-1}}$ We determined that only 2% of the illite surface was active in the calcite precipitation process, using the quartz sand as a reference.

4.6. Prediction of the Calcite Precipitation Rate in Natural Systems

The above model was applied to our experimental data to predict calcite precipitation rates for natural systems with DOC (Figs. 7, 8). In Fig. 7, for the sand system, crystal growth was considered at DOC = 0.02 mM, for DOC = 0.15 mM only heterogeneous nucleation was relevant. Good agreement was found between the data and the predictions at both DOC levels. Figure 8 shows the model predictions for the Silver Hill-sand systems, where there is good agreement with the data at DOC = 0.28 and 2.78 mM. The calcite precipitation rate is poorly predicted at the intermediate DOC levels, which is not surprising if we consider that the experimental data at DOC = 0.56 and 0.80 mM were almost indistinguishable.

5. CONCLUSIONS

In the presence of 2 $\mathrm{m^2\,L^{-1}}$ of calcite crystals and $\Omega = 1.9$, calcite precipitation ceased when DOC adsorbed on the calcite surface >0.11 mmol $\mathrm{m^2}$. The adsorption value of 0.11 mmol C $\mathrm{m^{-2}}$ of calcite corresponds to 0.05 mM of DOC in solution.

SEM observations and measurements of calcite precipitation rates show that the adsorption of DOC on the calcite crystals occurs rapidly. We conclude that crystal growth is not the major mechanism of calcite precipitation in earth surface systems, where almost without exception DOC > 0.05 mM.

Calcite precipitation rates measured under controlled conditions, without initial calcite crystals and at different DOC concentrations, are described by a model in which two terms are included, one for the contribution of crystal growth, in clean systems, and the second for the contribution of heterogeneous nucleation, which is important in both clean and natural systems.

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REFERENCES

Back W. and Hanshaw B. B. (1970) Comparison of chemical hydrogeology of the carbonate peninsulas of Florida and Yucatan. J. ***Hydrology*** **10,** 330-368.

Brown C. A.. Comoton R. G.. and Narramore C. A. (1993) The kinetics of calcite dissolution/precipitation. J. *Colloid Interface Sci. 160, 372-379.*

Busenberg E. and Plummer L. N. (1986) A comparative study of the dissolution and crystal growth kinetics of calcite and aragonite. In *Studies in Diagenesis* (ed. F. A. Mumpton), USGS *Bull.* **1578, 139-168.**

Chafetz H. S. and Folk R. L. (1984) Travertines: Depositional morphology and the bacterially constructed constituents. J. *Sediment. Petrol. 54, 289-316.*

Compton R. G. and Pritchard K. L. (1990) The dissolution of calcite at pH >7: kinetics and mechanism. Phil. *Trans. Roy. Soc. London Series A 330, 47-70.*

Compton R. G. and Unwin P. R. (1990) The dissolution of calcite in aqueous solution at pH < 4: Kinetics and mechanism. *Phil. Trans. Roy. Soc. London Series A 330,* l-46.

Compton R. G., Pritchard K. L., and Unwin P. R. (1989) The dissolution of calcite in acid waters. Mass transport versus surface control. *Freshwater Biology 22, 285-288.*

Dandurand J. L., Gout R., Hoefs J., Menschel G., Schott J., and Usdowski E. (1982) Kinetically controlled variations of major components and carbon isotopes in a calcite-precipitating spring. *Chem. Geol. 36, 299-315.*

Davies C. W. (1962) Ion *Association.* Butterworths, London.

Davies C. W. and Jones A. L. (1955) The precipitation of silver chloride from aqueous solutions. Part 2. Kinetics of growth of seed crystals. *Trans. Faraday Soc.* **51,** 812-817.

Dennen K. 0. and Diecchio R. J. (1984) The Falling Spring, Alleghany County, Virginia. In *Stratigraphy and Structure in the Thermal Spring Area of the Western Anticlines* (ed. E. K. Rader and T. M. Gathright), pp. 17- 19. Virginia Div. Mineral Resources, Charlottesville.

Dove P. M. and Hochella M. F., Jr. (1993) Calcite precipitation mechanisms and inhibition by orthophosphate: In situ observations by scanning force microscopy. *Geochim. Cosmochim. Acta 57, 705-714.*

Golubic S. (1969) Cyclic and noncyclic mechanism in the formation of travertine. *Verh. Int. Ver. Theor. Angew. Limnol. 17,956-N* l.

Gratr A. J. and Hillner P. E. (1993) Poisoning of calcite growth viewed in the atomic force microscope (AFM). J. *Cryst. Growth* **129, 789-793.**

Inskeep W. P. and Bloom P. R. (1985) An evaluation of rate equations for calcite precipitation kinetics at pCO_2 less than 0.01 atm and pH greater than 8. *Grochim. Cosmochim. Acta 49, 2165-2180.*

Inskeep W. P. and Bloom P. R. (1986a) Calcium carbonate supersaturation in soil solutions of Calciaquolls. Soil Sci. Soc. Amer. J. 50, 1431-1437.

Inskeep W. P. and Bloom P. R. (1986b) Kinetics of calcite precipitation in the presence of water soluble organic ligands. *Soil Sci. Soc. Amer. J. 50,* 1167- 1172.

Jacobson R. L. and Langmuir D. (1970) The chemical history of some spring waters in carbonate rocks. *Ground Water 8, 5-9.*

Jacobson R. L. and Usdowski E. (1975) Geochemical controls on a calcite precipitating spring. *Contrib. Mineral. Petrol. 51, 65-74.*

Katz J. L., Reick M. R., Herzog R. E., and Parsiegla K. I. (1993) Calcite growth inhibition by iron. *Langmuir 9, 1423- 1430.*

Kitano Y. and Hood D. W. (1965) The influence of organic material on the polymorphic crystallization of calcium carbonate. *Geochim. Cosmochim. Acta 29, 29-4* 1.

Last W. M. (1982) Holocene carbonate sedimentation in Lake Manitoba, Canada. *Sedimentology 29, 691-704.*

Lorah M. M. and Herman J. S. (1988) The chemical evolution of a travertine-depositing stream: geochemical processes and mass transfer reaction. *Water Resources Res. 24,* 154 1 – 1552.

Mathews H. L. (1962) The formation of calcareous tufa deposits in Montgomery County, Virginia. *Vu. J. Sci.* **13, 283** (abstr.).

Mucci A. (1986) Growth kinetics and composition of magnesian calcite overgrowths precipitated from seawater: Quantitative influence of orthophosphate ions. *Geochim. Cosmuchim. Acta 50, 2255-2265.*

Mucci A. and Morse J. W. (1983) The incorporation of Mg^{2+} and Sr^{2+} into calcite overgrowths: Influences of growth rate and solution composition. *Geochim. Cosmochim. Acta 47, 217-233.*

Nancollas G. H. and Reddy M. M. (197 1) The crystallization of calcium carbonate II. Calcite growth mechanism. J. *Colloid Interface Sci.* **10,** 215-252.

Oliver B. G., Thurman E. M., and Malcolm R. L. (1983) The contribution of humic substances to the acidity of colored natural waters. *Geochim. Cosmochim. Acta 47, 203* l *-2035.*

Paquette J., Vali H., and Mucci A. (1995) Morphology of calcite overgrowths precipitated from strong electrolyte solutions: a TEM study of growth mechanisms. *Abstracts of Papers,* 209th Nat. Mtg. of the ACS.

Parker D. R., Norvell W. A., and Chaney R. L. (1994) GEOCHEM-PC: A chemical speciation program for IBM and compatible personal computers. In *Soil Chemical Equilibrium and Reaction Models, SSSA Spec. Publ. 42, 253-269.*

Pearson F. J., Fisher D. W., and Plummer L. N. (1978) Correction of groundwater chemistry and carbon isotopic composition for effects of CO_2 degassing. *Geochim. Cosmochim. Acta 42,* 1799-*1807.*

Pentecost A. (1978) Blue-green algae and freshwater carbonate deposits *Proc. Roy. Soc. London, Ser. B 200, 43-61.*

Plummer L. N., Wigley T. M. L., and Parkhurst D. L. (1978) The kinetics of calcite dissolution in CO_2:water systems at 5” to 60°C and 0.0 to 1.0 atm CO,. *Amer. J. Sci. 278, 179-216.*

Reddy M. M. (1977) Crystallization of calcium carbonate in the presence of trace concentrations of phosphorous containing anions I. Inhibition by phosphate and glycerophosphate **ions at** pH 8.8 and 25°C. *J. Cryst. Growth 41, 287-295.*

Reddy M. M. (1986) Effect of magnesium ions on calcium carbonate nucleation and crystal growth in the dilute aqueous solutions at 25°C. In *Studies in Diagenesis* (ed. F. A. Mumpton); USGS Bull. 1.578, 169- 182.

Reddy M. M. and Nancollas G. H. (1971) The crystallization of calcium carbonate I. Isotopic exchange and kinetics. J. *Colloid Interface Sci. 36, 166- 172.*

Reddy M. M. and Nancollas G. H. (1973) Calcite crystal growth inhibition by phosphonates. Desalination 12, 61-73.

Reddy M. M. and Wang K. K. (1980) Crystallization of calcium carbonate in the presence of metal ions I. Inhibition by magnesium ion at pH 8.8 and 25°C. J. Cryst. *Growth 50, 470-480.*

Reddy M. M. and Gaillard W. D. (198 1) Kinetics of calcium carbonate (calcite)-seeded crystallization:influence of solid/solution ratio on the reaction rate constant. *J. Colloid Interface Sci. 80,* 17 **1–** 178.

Reynolds R. C., Jr. (1978) Polyphenol inhibition of calcite precipitation in Lake Powell. *Limnol. Oceanogr. 23, 585-597.*

Shiraki R. and Brantley S. (1995) Kinetics of near-equilibrium calcite precipitation at 100°C: An evaluation of elementary reaction-based and affinity-based rate laws. *Geochim. Cosmochim. Acta 59,* 1457-1471.

Sposito G.. Holtzclaw K. M., and Baham J. (1976) Analytical properties of the soluble, metal-complexing fractions in sludge-soil mixtures: II. Comparative structural chemistry of fulvic acid. Soil *Sci. Soc. Amer. J. 40, 69* l-697.

Stevenson F. J. (1982) *Humus Chemistry. Genesis. Composition, Reactions.* Wiley.

Stumm W. (1985) *Chemical Processes in Lakes.* Wiley.

Suarez D. L. (1977) Ion activity products of calcium carbonate in waters below the root zone. Soil Sci. Soc. *Amer. J.* 41. 310-3 1.5.

Suarez D. L. (1983) Calcite supersaturation and precipitation kinetics in the lower Colorado River, All-American Canal and East Highline Canal. *Water Resour. Res.* **19, 653-661.**

Suarez D. L. and Rhoades J. D. (1982) The apparent solubility of calcium carbonate in soils. *Soil Sci. Sci. Amer. J. 46, 716-722.*

Suarez D. L., Wood J. D., and Ibrahim 1. (1992) Reevaluation of calcite supersaturation in soils. Soil *Sci. Soc. Amer. J.* 56, 1776-:784.