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

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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: HCO₃ 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 m²L⁻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 R values between 1 and 50 and a CO₂ 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:

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

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 $\geq$0.05 mM.

$R_{HN}$ was related to $\Omega$ 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 $\Omega$ 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 $\leq$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 HCO₃ and Ca in soils probably were not due to a more soluble CaCO₃ 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-
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 (1985, 1986b), Busenberg and Plummer (1986), Compton et al. (1989), Compton and Unwin (1990), Compton and Pritchard (1990), and Brown et al. (1993). Second-

**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).

**Fig. 2.** Relationship between DOC concentration and Ca complexed by DOC, for Swannee river fulvic acid reference and DOC from Pachappa soil.
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 \( P_{\text{CO}_2} < 1.01 \text{kPa} \) the equation that best described the precipitation of calcite was:

\[
R = k_f s \gamma_2^2 ((\text{Ca}^{2+})(\text{CO}_3^{2-}) - K_{\text{sp}} \gamma_2^2),
\]

where \( R \) is the rate of calcite precipitation, \( k_f \) is the precipitation rate constant, \( s \) is the surface area of the calcite seeds, \( \gamma_2 \) is the divalent ion activity coefficient calculated from the Davies equation (Davies, 1962), parentheses represent concentration, and \( K_{\text{sp}} \) 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.

<table>
<thead>
<tr>
<th>Time (days)</th>
<th>Calcite precipitation rates (mmol, L(^{-1})s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>DOC=0.02 mM</td>
</tr>
<tr>
<td>0.04</td>
<td>3.89 x 10^4</td>
</tr>
<tr>
<td>0.21</td>
<td>2.78 x 10^4</td>
</tr>
<tr>
<td>1.00</td>
<td>4.39 x 10^4</td>
</tr>
<tr>
<td>2.00</td>
<td>2.89 x 10^4</td>
</tr>
<tr>
<td>3.00</td>
<td>4.28 x 10^4</td>
</tr>
<tr>
<td>4.00</td>
<td>5.41 x 10^4</td>
</tr>
<tr>
<td>5.00</td>
<td>4.63 x 10^4</td>
</tr>
<tr>
<td>6.00</td>
<td>4.98 x 10^4</td>
</tr>
</tbody>
</table>
Bloom, 1986b; Dove and Hochella, 1993; Gratz and Hillner, 1993; Katz et al., 1993; Paquette et al., 1995). Inkeep and Bloom (1986b), in a seeded crystal growth experiment, found that the precipitation rate constant decreased to zero, at $\Omega = 8.9$ ($\Omega = IAP/K_sp$, 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 $\Omega$ 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 $\mu$m) 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 $<2 \mu$m fraction was collected by sedimentation. Quartz sand and Silver Hill illite ($<2 \mu$m) 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

$^\dagger$Trade names are provided for the benefit of the reader and do not imply any endorsement by the USDA.

![Fig. 3. Calcite precipitation rate in the presence of 2 $\text{m}^2\text{L}^{-1}$ of calcite seeds and $\Omega = 1.9$ as a function of DOC adsorbed on the calcite surfaces (Suwanee river fulvic acid reference).](image1)

![Fig. 4. Langmuir adsorption isotherm for DOC (Swannee river fulvic acid reference) adsorbed on calcite.](image2)
dried. The equilibration with the Ca-HCO₃ solution was carried out as a pretreatment to: (1) saturate exchange sites with Ca, (2) maintain a constant Ca:HCO₃ 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 HCO₃⁻ solutions used in this study were prepared by dissolving 53 µm particle size calcite (Mal- linckrodt) for at least 24 h in DIW with magnetic stirring under an atmosphere of 98 % Pa CO₂. 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 N₂ adsorption with a Quantachrome Quantasorb Jr. surface area analyzer (Quantachrome Corp., Syosset, NY). The surface area of the crystals was 0.96 ± 0.01 m² 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 mM, L⁻¹ Ca-HCO₃, 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 Barbara, 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 triglycerine sulfate (DTGS) detector. The sample holder was a horizontal PLC-1 1M prism liquid cell with a 45° 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 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.

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 pressurized 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 CO₂ = 38-40 Pa) and the P CO₂ 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 CO₂ levels below 100 Pa and to sweep out the CO₂ 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-HCO₃ 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 HCO₃⁻. 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 mM L⁻¹ 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 mM 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 CaCO₃ was determined at constant P CO₂ and temperature at different DOC concentrations. Both Suwannee river fulvic acid reference and soil DOC were used in this experiment. Every suspension was covered by a 0.1 pm filter, diluted with DIW to avoid further precipitation, and analyzed for P CO₂. 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 0.1 µm filters, diluted 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 KH₂O₃ (National Bureau of Standards primary acid standard). The sample was titrated down to pH 4.4, after which N₂ was bubbled into the vial for 5 min to sweep out the dissolved CO₂ gas built up from conversion of HCO₃⁻, 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 (Suarcez et al., 1992). The detection limit with this experimental procedure and our analytical methods corresponds to a calcite precipitation rate of 10⁻² m² m⁻³ s⁻¹; we will refer to this value as the threshold detection level.

The saturation level for CaCO₃ 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 CO₂ 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.

<table>
<thead>
<tr>
<th>Sample #</th>
<th>Control</th>
<th>Initial Concentration (mM)</th>
<th>Complex</th>
<th>Initial</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>PH</td>
<td>DOC</td>
<td>Ca</td>
<td>Total</td>
</tr>
<tr>
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<tr>
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</tr>
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</tr>
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<td>0.87</td>
<td>1.29</td>
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<td>8.38</td>
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<td>0.72</td>
<td>1.48</td>
</tr>
<tr>
<td>Control</td>
<td>8.25</td>
<td>0.01</td>
<td>0.48</td>
<td>1.92</td>
</tr>
</tbody>
</table>

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.

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Calcite precipitation rates were calculated after 1, 5, and 24 h.
Effect of DOM on nucleation kinetics of calcite

Reference Suwannee fulvic acid 0.87 mM DOC

Samples 11 to 20 in Table 3

Fig. 6. Calcium concentration with time in the supernatant 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 $\frac{1}{3}$ 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.
3.4. 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 $\Omega = 1.9$ as the adsorbed DOC increased (Fig. 3). Precipitation was not detectable ($<5.3 \times 10^{-8}$ m$^{-1}$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.

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

Within the first 24 h there was a dominance of crystals $<2 \mu m$, 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 $<2 \mu m$ particles decreased and the percentage of large particles increased, some particles were as large as 100 $\mu m$. Table 1 shows the mean and standard deviation of the number of crystals grouped in three different particle sizes, $\approx 2 \mu m$, 2-10 $\mu m$, and >10 $\mu m$.

In the presence of 0.15 mM DOC, the filters collected after filtration showed $\frac{1}{2}$ to $\frac{1}{2}$ 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.

3.2. 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 precipitation continued in the suspension with DOC 0.3 mM. This corresponds to a precipitation rate of $\approx 1 \times 10^{-7}$ m$^3$M s$^{-1}$. The $\Omega$ 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 $\Omega$ of 9, and a DOC of 2.78 mM, the rate slowed to a 13% of the rate at 0.28 mM.

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 extent 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$^{-1}$ 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 acid and 3.96 mM humic acids). Based on these values, Pachappa soil DOC contains 9.24 $\mu$mol, carboxyl mg$^{-1}$ C vs. 31.33 $\mu$mol, carboxyl mg$^{-1}$ C for Suwannee fulvic acid reference. This indicates that Pachappa soil DOC has approximately $\tfrac{1}{2}$ 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 $\Omega$, 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
Effect of DOM on nucleation kinetics of calcite

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

Measurements of Ca and HCO₃ 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 m² 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 m² 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 m². These values agree with Inskeep and Bloom (1986b), who found a capacity factor of 0.17 mmol m² and a calcite precipitation rate equal to zero at 0.15 mmol m².

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 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 \( \mu \)m (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 \( \mu \)m 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 \( \mu \)m 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.

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

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.
precipitation stopped at DOC 0.87 mM while, for the same $\Omega$, 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 $\text{CaCO}_3$ 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 $\Omega \approx 3.0$ for the sand system when DOC ranged from 0.02-0.3 mM.

![Crystal growth](image)

**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 ($3.9 \times 10^{-4}$mM s$^{-1}$) at similar experimental conditions.

![Heterogeneous nucleation](image)

**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 ($4.45 \times 10^{-4}$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 expression:

\[ R_T = R_{CG} + R_{HN} \]  (2)

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

\[ \frac{\text{DOC}}{C_{ads}} = 0.22 + 5.32 \times \text{DOC}, \]  (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:

\[ R_{CG} = s k_{CG} ([\text{Ca}^{2+}] [\text{CO}_3^{2-}] - K_{sp}) f(DOC)_{CG}, \]  (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\(^{-5}\) mM s\(^{-1}\). For this range, \( c_{DP} \) is the calcite precipitation data obtained in the presence of DOC, given in Fig. 3. We express the results in terms of DOC using the \( C_{ads} \) relation given in Fig. 4. The expression given in Fig. 9:

\[ f(DOC)_{CG} = -0.14 - 0.11 \log \text{DOC}. \]  (5)

is used in the \( f(DOC)_{CG} \) range from 1 to 0, developed from experiments with Suwannee fulvic acid, and 2 m\(^3\)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 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 \( \geq 0.05 \) mM.

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

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

where \( k_{HN} \) is the precipitation rate constant, \( f(SA) \) is \( \leq 0 \) and is the term for the active sites of the particles in suspension, \( f(SA) = 1 \) when there are no 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 \( \Omega \) value below which no further calcite precipitation by nucleation was found in our experiments. The expression \( f(DOC)_{HN} \) 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 \( f(DOC)_{CG} \), we developed a function relating precip-

itation by nucleation to DOC. We combined the calcite precipitation rate of 3.11 \( \times \) 10\(^{-4}\) 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:

\[ f(DOC)_{HN} = 3.37 \times 10^{-4} \text{DOC}^{-1.14}, \]  (7)

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

The surface area of the Silver Hill illite used in the present study is 45 \( \pm \) 0.01 m\(^2\)g\(^{-1}\); thus, the illite surface area in our reaction vessels was 3375 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 m\(^3\)L\(^{-1}\) of calcite crystals and \( \Omega = 1.9 \), calcite precipitation ceased when DOC adsorbed on the calcite surface >0.11 mmol m\(^{-2}\). The adsorption value of 0.11 mmol C \( \cdot \) 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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