Calcite supersaturation in soil solutions has been attributed to errors in measuring Ca\(^{2+}\) and CO\(_3^{2-}\) activities, metastable forms of CaCO\(_3\), or soluble silicates, and organic matter mineralization. Laboratory batch suspensions of soils under controlled CO\(_2\), and temperature were studied to clarify the mechanism producing calcite supersaturation. Treatments included the addition and removal of organic matter prior to reaction and the use of toluene to suppress microbial activity. The soil solutions were sampled over time and analyzed for Ca\(^{2+}\) and CO\(_3^{2-}\) activity. Carbonate activity was determined by two methods: 1) a double titration procedure that separates non-carbonate alkalinity from carbonate alkalinity and 2) acidification and outgassing of dissolved inorganic carbon species as CO\(_2\). Calcium activity was determined by two methods: 1) specific ion electrode and 2) total Ca analysis plus ion speciation modeling. Calcium-organic matter complexation was taken into account in the speciation calculations. It was found that calcite supersaturation in soil suspensions was not an artifact of inaccurate Ca\(^{2+}\) or CO\(_3^{2-}\) activity values. Rather, calcite supersaturation occurred because rapid organic matter mineralization increased the Ca and HCO\(_3^-\) concentrations. These elevated Ca and HCO\(_3^-\) concentrations persisted because of the slow precipitation kinetics of calcite. Attempts to block organic matter mineralization with toluene only slowed down the reaction in the soils. Removal of organic matter with H\(_2\)O\(_2\) resulted in Ca-oxalate formation, and oxidation of the oxalate to HCO\(_3^-\) produced elevated CO\(_3^{2-}\) activities.

Calcite supersaturation in natural waters and soil solutions has been reported and studied by many researchers (Olsen and Watanabe 1959; Berner et al. 1978; Suarez 1977; Levy 1981; Suarez and Rhoades 1982; Inskeep and Bloom 1986b; Baker et al. 1987; Al-Kanani et al. 1989; Reddy et al. 1990; Miyamoto and Pingitore 1992; Suarez et al. 1992). Observations of calcite supersaturation can be separated into two categories. In the first case, supersaturation is observed in field-collected waters and soil solutions where evaporation and transpiration have concentrated the water. When this increase in concentration is coupled with slow calcite precipitation kinetics, supersaturation results. Calcite precipitation kinetics may be retarded as a result of the blockage of precipitation sites or the presence of precipitation inhibitors such as Mg, P, and organic matter (Doner and Pratt 1968; Berner et al. 1978; Suarez 1977; Levy 1981; Inskeep and Bloom 1986a

In the second case, a soil is brought into the laboratory and equilibrated with H\(_2\)O under controlled CO\(_2\) conditions. After a day or two, supersaturation with calcite is observed (Olsen and Watanabe 1959; Levy 1981; Suarez and Rhoades 1982). In this case the system reaches supersaturation with no increase in concentration because of evaporation. Supersaturation can only occur under these conditions if there is a source of Ca or CO\(_3\) that is more soluble than calcite and the precipitation of calcite is kinetically inhibited. Several sources of Ca and CO\(_3\) have been suggested, including the presence of metastable CaCO\(_3\) phases such as aragonite (Olsen and Watanabe 1959), Mg-substituted CaCO\(_3\) (Marion and Babcock 1977; Miyamoto and Pingitore 1992), the dissolution of Ca-containing silicate minerals such as anorthite (Suarez and Rhoades 1982), and microcrystalline calcite (Suarez 1977; Inskeep and Bloom 1986b).

Amrhein and Suarez (1987) showed that the mineralization of organic matter can produce an increase in Ca and CO\(_3\) that may explain the observed supersaturation seen in laboratory equilibrated soil suspensions. However, this study has been criticized for not including soil + water + organic matter equilibrations (Reddy et al. 1990). Reddy et al. (1990) attributed the
observation of calcite supersaturation in laboratory equilibrations to two factors. First, the \( \text{Ca}^{2+} \) activity may be overestimated because Ca + organic matter complexes are usually not accounted for in speciation calculations. Secondly, the titration for \( \text{CO}_3^- \) may be in error due to the inclusion of non-carbonate alkalinity. In the study by Reddy et al. (1990), soil + water suspensions were reacted with atmospheric \( \text{CO}_2 \), which resulted in low alkalinities and relatively high pH values. Under these conditions it is difficult to be assured of \( \text{CO}_2 \) equilibrium because \( \text{CO} \) production from microbial activity may exceed the gas transfer rate. Amrhein et al. (1985) showed that the \( \text{CO}_2(\text{aq}) \rightleftharpoons \text{CO}_2(\text{g}) \) reaction kinetics were sufficiently slow that equilibrium with atmospheric \( \text{CO}_2 \) in a soil + water suspension or saturation paste is not likely to be achieved. In addition, Amrhein and Suarez (1987) and Suarez et al. (1992) showed that Ca-organic complexes were insignificant based on a comparison of \( \text{Ca}^{2+} \) activities calculated using a speciation program and \( \text{Ca}^{2+} \) activities measured using a specific ion electrode.

Miyamoto and Pingitore (1992) evaporated synthetic irrigation waters in the laboratory and attributed the extensive oversaturation of the resulting solutions to Mg-substituted calcite. However, considering the rapid evaporation rate, it is possible that an equilibrium situation did not exist in their study, and supersaturation may be explained by the slow precipitation of calcite.

The objective of this present study was to examine the effects of organic matter on the \( \text{Ca}^{2+} \) and \( \text{CO}_3^- \) activities in suspensions of soil + water + organic matter under controlled \( \text{CO}_2 \) conditions. We hypothesized that calcite equilibrium in soil + water suspensions could be achieved if organic matter was removed from the soil or organic matter mineralization was blocked. In this study, organic matter was both added and removed from a calcareous, gypseriferous soil, and, in some cases, toluene was used to inhibit microbial activity. In order to address some of the above stated concerns, calcium activities were determined both by total analysis coupled with speciation calculations, which took into account Ca-organic matter complexes, and by specific ion electrode. Carbonate activities were determined using a double titration procedure that was able to distinguish between dissolved inorganic carbon (DIC) and dissolved organic carbon (DOC).

**MATERIALS AND METHODS**

Laboratory batch equilibrations were carried out on suspensions of soil plus deionized water under controlled \( \text{PCO}_2 \) and temperature (21°C ± 0.1) for up to 20 days. Compressed air was mixed with \( \text{CO}_2 \), using mass flow controllers to give a \( \text{PCO}_2 \) of 3.0 kPa \( \text{CO}_2 \), which is typical for a soil atmosphere (Buyanovsky and Wagner 1983). The composition of the air + \( \text{CO}_2 \) mixture was checked by gas chromatography. The air + \( \text{CO}_2 \) mixture was saturated with water vapor by bubbling the gas mixture through deionized water before it was bubbled through the soil suspensions.

Three soils were used in these studies. The Holtville soil was a surface sample collected from the Imperial Valley, CA from an area mapped as Holtville series (clayey over loamy, montomorillonitic (calcareous), hyperthermic Typic Torrifluvent). This soil had 8.2% \( \text{CaCO}_3 \), 0.84% organic carbon, and a trace amount of gypsum (<0.5%). The Lansing soil was a surface sample collected from an area near Lansing, MI mapped as Capac series (fine-loamy, mixed mesic, Aeric Ochraqualf). This soil contained 9.5% \( \text{CaCO}_3 \), 2.0% organic carbon, and no gypsum. The Shiprock soil was a surface sample collected from an unmapped area on the Navajo Indian reservation near Shiprock, NM. Tentative classification at the time of sampling was mesic Torriorthent (possibly Shalet or Fruitland series). This soil contained 11.3% \( \text{CaCO}_3 \), 0.7% organic carbon, and 9.3% gypsum.

The soil samples were air dried and ground to pass a 2-mm sieve and reacted with water at soil:water ratios of 1:2 kg L\(^{-1}\). Table 1 lists the various combinations of soil, organic matter, soil water extracts, and toluene that were used. Dried alfalfa shoots (Medicago \textit{sativa} L.) with a C content of 38.9%, were added to the suspensions numbered 6, 9, and 11. In the suspension #7, the soil was repeatedly treated with 30% \text{H}_2\text{O}_2 to remove native organic matter. In suspensions numbered 8, 9, and 10, toluene was added to suppress microbial activity. In the toluene treated suspensions, the air plus \( \text{CO}_2 \) gas mixture was saturated with both water vapor and toluene vapor before being bubbled through the suspensions. In the toluene treated suspen-
TABLE 1
Batch equilibrations under 3.0 kPa CO₂

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Suspension composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>600 ml d.w. + 2 g calcite</td>
</tr>
<tr>
<td>2</td>
<td>600 ml d.w. + 2 g calcite + 2 g gypsum</td>
</tr>
<tr>
<td>3</td>
<td>200 ml d.w. + 100 g Holtville soil</td>
</tr>
<tr>
<td>4</td>
<td>600 ml d.w. + 300 g Lansing soil</td>
</tr>
<tr>
<td>5</td>
<td>600 ml d.w. + 300 g Shiprock soil</td>
</tr>
<tr>
<td>6</td>
<td>200 ml d.w. + 100 g Holtville soil + 1.0 g alfalfa</td>
</tr>
<tr>
<td>7</td>
<td>200 ml d.w. + 100 g Holtville soil + 20 ml toluene</td>
</tr>
<tr>
<td>8</td>
<td>200 ml d.w. + 100 g Holtville soil + 20 ml toluene</td>
</tr>
<tr>
<td>9</td>
<td>200 ml d.w. + toluene + 1 g alfalfa</td>
</tr>
<tr>
<td>10</td>
<td>200 ml d.w. + toluene</td>
</tr>
<tr>
<td>11</td>
<td>200 ml d.w. + 1 g alfalfa</td>
</tr>
<tr>
<td>12</td>
<td>200 ml Holtville soil extract</td>
</tr>
<tr>
<td>13</td>
<td>200 ml Holtville soil extract treated w/ H₂O₂</td>
</tr>
<tr>
<td>14</td>
<td>200 ml Holtville soil extract + 1 g calcium oxalate</td>
</tr>
<tr>
<td>15</td>
<td>200 ml d.w. + 1 g CaCO₃ + 1 g calcium oxalate</td>
</tr>
</tbody>
</table>

d.w. = deionized water.
The Holtville soil extracts were prepared by extracting a 1:2 soil/water suspension after shaking for 30 minutes.

sions, the toluene was added at a rate equal to 10% of the solution volume. A blank of water + toluene (#10) was run to check the possible effects of the toluene on the DOC determination. Based on the DOC values from sample #10, a small correction was applied to the DOC values measured on suspensions #8 and 9. Control suspensions of 2 g calcite + 0.6 L H₂O and 2 g calcite + 2 g gypsum in 0.60 L H₂O were equilibrated under the same PCO₂ and temperature (#1 and #2). In order to determine if soluble organic matter might be contributing to the observed calcite supersaturation, (either due to Ca complexation or mineralization of the organic matter), 1:2 soil:water extracts of the Holtville soil were studied (#12,13, and 14). Because calcium oxalate can form in calcareous soils treated with H₂O₂ (Martin 1954), a suspension of Holtville soil extract plus calcium oxalate and a suspension of calcite and calcium oxalate in deionized water were studied (#14 and 15).

The suspensions were sampled periodically for up to 20 days. The total reaction time and time of sampling varied because the suspensions were not all run simultaneously. The suspensions were stirred daily and allowed to settle prior to sampling.

The pH of the water above the settled soil was measured in situ at the time of sampling. A 10-ml aliquot of the solution was sampled by syringe and immediately filtered through a 0.45-μm membrane filter using the syringe to press the solution through the filter. The filtered solutions were analyzed for Ca and Mg by atomic absorption spectrophotometry after the addition of 1000 mg L⁻¹ La. Sodium and K were measured by atomic emission spectrophotometry, sulfate by the turbidimetric method using BaCl₂ (Rhoades 1982), chloride by titration with a digital chloridometer from Haake Buchler Instruments (Saddlebrook, NJ), nitrate by Technicon Auto Analyzer (Method 353.2), and total dissolved carbon (TC), DIC and DOC on a Dohrmann carbon analyzer (Xertex Corp., Santa Clara, CA).

Calcium activity was also measured using an Orion calcium ion electrode (Model 92-20), calibrated daily with CaCl₂ activity standards.

Dissolved inorganic carbon (CO₃(aq) + H₂CO₃ + HCO₃⁻ + CO₃²⁻ + ion pairs of HCO₃⁻ and CO₃²⁻) was determined by two methods using the Dohrmann carbon analyzer. In this procedure, dissolved C is converted into CO₂ using either an acid solution (DIC only) or an acidic solution of potassium persulfate (K₂S₂O₈) plus ultraviolet light, which measures DIC plus DOC. In the Dohrmann carbon analyzer, the CO₂ produced in the acid reaction or in the acid + oxidant reaction is swept from the reaction vessel with O₂ and is measured with an infrared detector and signal integrator. Total dissolved carbon (organic + inorganic) was determined on the freshly sampled solutions (taking care to prevent CO₂ loss) using the acidic, oxidizing solution. Dissolved inorganic carbon was determined on the same solutions, but the reacting solution was 0.01 M H₃PO₄ (no oxidation of organics). In addition, an aliquot of the sample was acidified to pH 3, placed under vacuum, and stirred for 20 min to accelerate CO₂ outgassing. This sample, with the DIC removed, was then injected into the Dohrmann carbon analyzer for determination of DOC. Thus, DIC was determined directly and by difference using the TC minus the DOC.

The bicarbonate + carbonate alkalinity was determined by acid titration using a modification of the procedure previously discussed in Amrhein and Suarez (1987). In this procedure, the sample solution was titrated to pH 4.4 under air using standard acid (5 mM H₂SO₄) and the titrant volume used to calculate the total alkalinity. The sample pH was then lowered to <3.0
and the sample placed in a vacuum chamber for 20-30 min to outgas all CO$_3^{(aq)}$. The sample was stirred by magnetic stirrer while under vacuum. Following outgassing, the sample was placed under N$_2$ gas and the pH raised to the pH of the original sample using 0.10 or 0.05 M NaOH. This sample was titrated again to pH 4.4 and the titrant volume used to calculate non-carbonate alkalinity. The volume of acid used in the first titration minus the volume of acid required in the second titration is a measure of the HCO$_3^-$ and CO$_3^-$ alkalinity in the sample.

Freshly prepared solutions of NaHCO$_3$, Na$_2$CO$_3$, and KCaH$_5$O$_4$ (potassium hydrogen phthalate, organic C standard) were used to standardize all procedures. Bicarbonate and carbonate standards were also prepared in solutions of sodium acetate, sodium oxalate, sodium citrate, sodium salicylate, and boric acid to check for possible interferences from organic ligands and non-carbonate alkalinity. The double titration procedure accurately measured carbonate alkalinity in all of these test solutions.

The total chemical analysis for each sample was input to three ion speciation models. The first program was an extensively modified ion speciation program called SOILSOLN (Wolt 1989). This program takes into account Ca-organic matter complexation using the method of Sposito et al. (1981). In addition, the program was modified to accept either pH + alkalinity, or pH + DIC, or PCO$_2$ + alkalinity, or PCO$_2$ + DIC. All of the dissociation and ion pair constants were corrected to those given in MINTEQA2, version 3.00 (U.S. Environmental Protection Agency 1990). The other two programs were GEOCHEM (Parker et al. 1987) and MINTEQAB, version 3.00 (U. S. Environmental Protection Agency 1990). Neither of these programs were run with dissolved organic carbon as an input, and thus, Ca-organic matter complexes were not taken into account.

RESULTS AND DISCUSSION

Shown in Fig. 1 is the comparison of Ca$_{2+}$ activities for all of the suspensions (except #10) as determined by specific ion electrode and as calculated using the ion speciation program SOILSOLN with CO$_3$$_2$ carbonate alkalinity, and DOC as input data. Based on the speciation program, 3% of the total dissolved Ca was complexed with organic matter in the untreated Holtville soil and 11% in the alfalfa-amended soil. The relationship between these two procedures was fair ($r^2 = 0.78$, $n = 83$), and the electrode activity was often higher than the calculated activity. This is contrary to the findings of Suarez et al. (1992), who found Ca$_{2+}$ activities were generally higher calculated by ion speciation than when measured by electrode. Suarez et al. (1992) decided that the Ca$_{2+}$ activities measured by electrode were better because the calculated Ca activities yielded gypsum supersaturation in their gypsiferous soils. In our gypsiferous soils, the ion activity products (IAP) for gypsum, using calculated Ca activities, averaged 10$^{-4.73}$, which is slightly undersaturated with respect to gypsum (K$_{sp}$ = 10$^{-4.64}$). The average gypsum IAP value for suspension #2 (calcite + gypsum) was 10$^{-4.61}$, which is very close to gypsum equilibrium.

When the data were input to the programs SOILSOLN, GEOCHEM, and MINTEQAB, the log (IAP) values for calcite varied 0.02 units on average, with a maximum difference of 0.05 log units. Organic carbon was not included in the data in this comparison. The small differences among these values can be attributed to differences in thermodynamic stability constants and whether the Davies or the extended Debye-Huckel equation was used. Plotted in Fig. 2 is a comparison of CO$_3$$_2$- activity as calculated using the double titration data and the DIC data from
the Dohrmann carbon analyzer for suspensions #2, #3, and #6. The relationship between these two methods was excellent ($r^2 = 0.98$), which is contrary to the findings of Reddy et al. (1990) who reported significantly lower DIC concentrations by an acidification and outgassing procedure. The non-carbonate alkalinity from the double titration procedure averaged $5\% \pm 3\%$ of the total alkalinity for the three soils studied over the entire reaction period. Thus, the overestimates of $\text{CO}_3^{2-}$ by the traditional, single titration procedure are insufficient to explain the high levels of supersaturation.

Plotted in Fig. 3 is a comparison of the calcite ion activity products for all of the suspensions as determined by “measurement” and by “calculation.” The “IAP measured” values are $\text{Ca}^{2+}$ activity by specific ion electrode times the $\text{CO}_3^{2-}$ activity, as calculated from GEOCHEM with pH and DIC as inputs. The “IAP calculated” values are $\text{Ca}^{2+}$ and $\text{CO}_3^{2-}$ activities from SOILSOLN with pH, total Ca (by atomic absorption), and alkalinity by titration as inputs. The agreement between the IAP values was very good ($r^2 = 0.95$ for $n = 83$), demonstrating that all of these procedures are reasonably accurate for determining $\text{Ca}^{2+}$ and $\text{CO}_3^{2-}$ activities.

In Fig. 3, the solutions highly oversaturated with respect to calcite (-log IAP < 8.475, Plummer and Busenberg 1982) were measured in the Holtville soil amended with alfalfa (#6), and the highly undersaturated solutions were the soil extract and the alfalfa + toluene treatment (#9 and #12).

Plotted in Fig. 4 are the -log IAP values for calcium carbonate for the three soils, the Holtville soil + alfalfa, and the two controls over time. Both control suspensions reached calcite equilibrium, even though the calcite + gypsum suspension had a six times higher Ca concentration than the calcite alone system. In all of the soils, oversaturation with respect to calcite was observed after 1-day reaction time, and the degree of oversaturation tended to increase with time. After about a week the IAP values for the Holtville and Shiprock soils leveled off at $10^{-8.0}$. This is the same IAP value that has been reported previously for soil solutions extracted from fields and in laboratory equilibrations of soils (Olsen and Watanabe 1959; Suarez 1977; Suarez and Rhoades 1982; Inskeep and Bloom 1986; Suarez et al. 1992). The addition of readily decomposable organic matter (#6) greatly increased the level of supersaturation ($\text{IAP} = 10^{-7.0}$), confirming the observations reported earlier that organic matter mineralization can result in high carbonate alkalinity (Amrhein and Suarez 1987).

Because calcite supersaturation was observed in the soil + water suspension even after 1 day...
solution that was supersaturated with respect to calcite after several days. This reaction is clearly microbial-mediated because the alfalfa + toluene treatment stayed more than two orders of magnitude undersaturated for 17 days (Fig. 5). The decreasing IAP values in the alfalfa + toluene system are due to a decrease in the titratable alkalinity and pH over time. It is not clear why the alkalinity was decreasing in this system except that some acid producing reaction, like nitrification, was occurring.

It has been reported that $\text{H}_2\text{O}_2$ treatment of soils leaves 40 to 60% of the organic carbon unoxidized (Bartlett et al. 1937), and significant amounts of calcium oxalate can be formed in calcareous soils (Martin 1954). We hypothesized that the microbial decomposition of oxalate to bicarbonate could yield calcite supersaturation as follows:

$$\text{CaC}_2\text{O}_4 + 0.5 \ O_2 + \text{H}_2\text{O} \rightarrow \text{Ca}^{2+} + 2 \ \text{HCO}_3^-$$

This hypothesis was tested in suspensions #14 and 15. The addition of $\text{CaC}_2\text{O}_4$ to a soil extract resulted in very high levels of calcite supersaturation (IAP $> 10^{-7.5}$) after 6 days (Fig. 6). In a deionized water + $\text{CaC}_2\text{O}_4 + \text{CaCO}_3$ suspension (#15), slight oversaturation was observed (IAP = $10^{-8.22}$), probably due to the lack of microbes and nutrients. In the Holtville soil extract (#12), the concentration of Ca and $\text{HCO}_3^-$
Calcite supersaturation in laboratory equilibrated soil suspensions could not be attributed to an overestimation of Ca$^{2+}$ and CO$_3^{2-}$ activities. Calcium activities as measured by specific ion electrode were reasonably close to the calculated activities, and discrepancies are attributed to vagaries in the specific ion electrode. There was excellent agreement between the CO$_3^{2-}$ activity as determined by acid titration and by outgassing the dissolved inorganic carbon. Calcite supersaturation was observed in suspensions of all three soils and appeared to be due to the production of HCO$_3^-$ from organic matter decomposition. Attempting to stop organic matter mineralization with toluene only slowed the reaction. The IAP values of the toluene-treated soil were lower than the untreated soil, suggesting that a mineral phase more soluble than calcite was not present in the soil. Removal of the organic matter with H$_2$O$_2$ resulted in Ca-oxalate formation. Mineralization of the oxalate produced elevated concentrations of HCO$_3^-$ and CO$_3^{2-}$ and calcite supersaturation.

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