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CALCITE SUPERSATURATION IN SOIL SUSPENSIONS

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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, 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_2O_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 and b).

In the second case, a soil is brought into the laboratory and equilibrated with H_2O under controlled CO, 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, 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

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observation of calcite supersaturation in laboratory equilibrations to two factors. First, the Ca^{2+} activity may be overestimated because Ca + organic matter complexes are usually not accounted for in speciation calculations. Secondly, the titration for 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 CO_2, which resulted in low alkalinities and relatively high pH values. Under these conditions it is difficult to be assured of CO_2 equilibrium because CO, production from microbial activity may exceed the gas transfer rate. Amrhein et al. (1985) showed that the $CO_2(aq) \leftrightarrow CO_2(g)$ reaction kinetics were sufficiently slow that equilibrium with atmospheric CO, 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 Ca^{2+} activities calculated using a speciation program and 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 Ca^{2+} and $CO_3{}^{2-}$ activities in suspensions of soil + water + organic matter under controlled 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, gypsiferous 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 for alkalinity that corrected for non-carbonate alkalinity and by a CO, outgassing 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 PCO_2 and temperature (21°C ± 0.1) for up to 20 days. Compressed air was mixed with CO_2 using mass flow controllers to give a PCO_2 of 3.0 kPa CO_2, which is typical for a soil atmosphere (Buyanovsky and Wagner 1983). The composition of the air + CO, mixture was checked by gas chromatography. The air + CO, 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% $CaCO_3$, 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% $CaCO_3$, 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% $CaCO_3$, 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 ***satiua*** 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% H_2O_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 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*** CO_2

Treatment	Suspension composition
1	600 ml d.w. + 2 g calcite
2	600 ml d.w. + 2 g calcite + 2 g gypsum
3	200 ml d.w. + 100 g Holtville soil
4	600 ml d.w. + 300 g Lansing soil
5	600 ml d.w. + 300 g Shiprock soil
6	200 ml d.w. + 100 g Holtville soil + 1.0 g alfalfa
	200 ml d.w. + 100 g Holtville soil treated w/H_2O_2
8	200 ml d.w. + 100 g Holtville soil + 20 ml toluene
9	200 ml d.w. + toluene + I g alfalfa
10	200 ml d.w. + toluene
11	200 ml d.w. + 1 g alfalfa
12	200 ml Holtville soil extract
13	200 ml Holtville soil extract treated w/ H_2O_2 + $CaCO_3$
14	200 ml Holtville soil extract + 1 g calcium oxalate
15	200 ml d.w. + 1 g $CaCO_3$ + 1 g calcium oxalate

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 (#l0) was run to check the possible effects of the toluene on the DOC determination. Based on the DOC values from sample #l0, a small correction was applied to the DOC values measured on suspensions #8 and 9. Control suspensions of 2 g calcite + 0.6 L H_2O and 2 g calcite + 2 g gypsum in 0.60 L H_2O were equilibrated under the same PCO_2 and temperature (#l 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 H_2O_2 (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-pm 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 $BaCl_2$ (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 $CaCl_2$ activity standards.

Dissolved inorganic carbon ($CO_2(aq) + H_2CO_3 + HCO_3^- + CO_3^{2-}$ + ion pairs of HCO_3^- and CO_3^{2-}) was determined by two methods using the Dohrmann carbon analyzer. In this procedure, dissolved C is converted into CO_2 using either an acid solution (DIC only) or an acidic solution of potassium persulfate ($K_2S_2O_8$) plus ultraviolet light, which measures DIC plus DOC. In the Dohrmann carbon analyzer, the CO, produced in the acid reaction or in the acid + oxidant reaction is swept from the reaction vessel with O_2 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 CO_2 loss) using the acidic, oxidizing solution. Dissolved inorganic carbon was determined on the same solutions, but the reacting solution was 0.01 *M* H_3PO_4 (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 CO, 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* H_2SO_4) 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 $CO_2(aq)$. 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_2CO_3, and $KC_8H_5O_4$ (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_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^{++} 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.

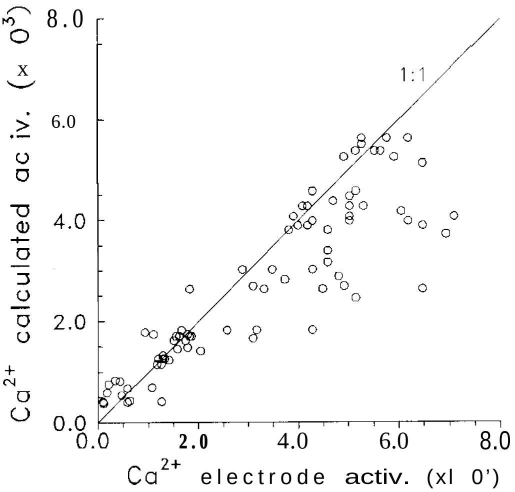

FIG. 1. Calcium activity as measured by an ion specific electrode and as calculated with an ion speciation program that includes corrections for Ca-organic matter complexation.

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% ± 3% of the total alkalinity for the three soils studied over the entire reaction period. Thus, the overestimates of 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 Ca^{2+} activity by specific ion electrode times the CO_3^{2-} activity, as calculated from GEOCHEM with pH and DIC as inputs. The "IAP calculated" values are Ca^{2+} and 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 Ca^{2+} and CO_3^{2-} activities.

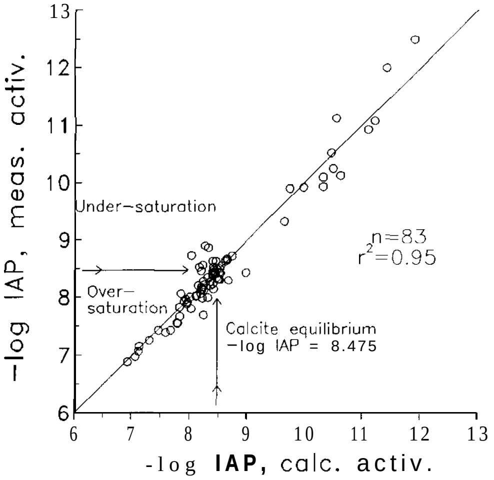

FIG. 3. Ion activity products for calcium carbonate as determined by "calculation" (total Ca, titrated alkalinity, and pH input to SOILSOLN) and by "measurement" (specific ion electrode for Ca^{2+} and CO_3^{2-} by GEOCHEM with pH and DIC as inputs).

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).

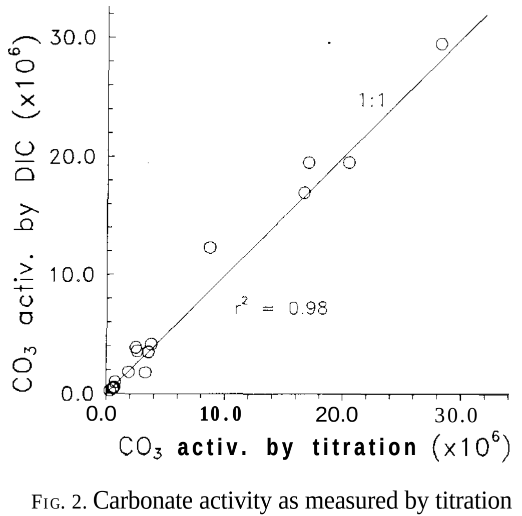

FIG. 2. Carbonate activity as measured by titration and by acidification and outgassing of the dissolved inorganic carbon (DIC).

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 l-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 (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

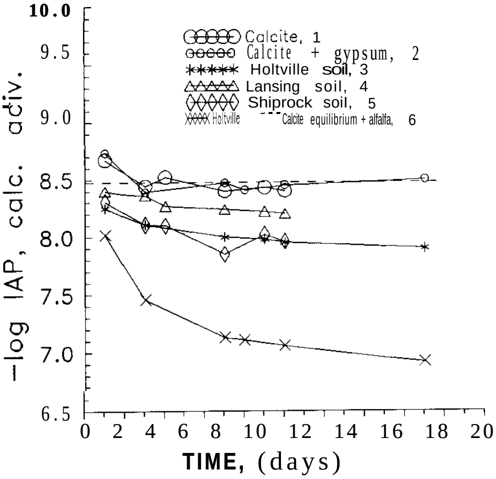

FIG. 4. Changes in $CaCO_3$ ion activity products over time for suspensions #1, 2, 3, 4, 5, and 6.

of reaction, we wondered if organic matter mineralization was fast enough to account for this observation. The following experiments were designed to suppress microbial activity and/or remove readily oxidizable organic matter to see if calcite equilibrium might then be reached.

Plotted in Fig. 5 are the IAP values over time for the untreated Holtville soil, the Holtville soil treated with H_2O_2 to remove organic matter, the Holtville soil treated with toluene to suppress microbial activity, and deionized water + alfalfa, with and without toluene. Attempting to remove the organic matter from the soil and poisoning the soil with toluene initially reduced the level of saturation with respect to calcite, but over time, supersaturation still resulted. After 17 days, the IAP values of the toluene treated and untreated soil were nearly the same ($10^{-7.94}$ and $10^{-7.90}$, respectively). Two possible explanations are possible: 1) microbial activity was suppressed but not eliminated or 2) a mineral phase more soluble than calcite is present in the soil. The H_2O_2-treated soil was repeatedly washed with H_2O_2 and H_2O, and any soluble mineral phases would have been washed out by this treatment. The toluene treated soil was not washed, and the IAP values were lower than the untreated soil at early times. This suggests that rapid microbial activity in the air-dried untreated soil could explain the elevated IAP values observed after one day. The decomposition of alfalfa in water (no soil) also resulted in a 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 H_2O_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:

$$CaC_2O_4 + 0.5\ O_2 + H_2O \rightarrow Ca^{2+} + 2\ HCO_3^-$$

This hypothesis was tested in suspensions #14 and 15. The addition of CaC_2O_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 + CaC_2O_4 + $CaCO_3$ 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 HCO_3

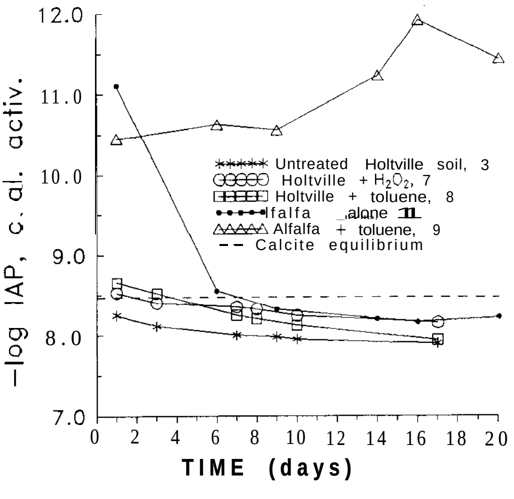

FIG. 5. Changes in $CaCO_3$ ion activity products over time for suspensions #3, 7, 8, 9, and 11.

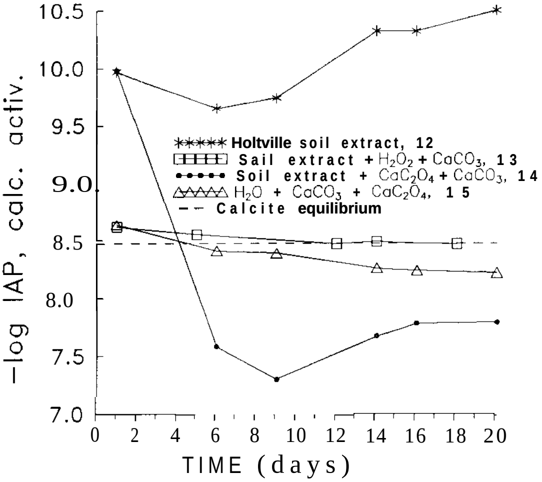

FIG. 6. Changes in $CaCO_3$ ion activity products over time for suspensions #12, 13, 14, and 15.

were very low because the extraction was made under atmospheric CO_2. When the extract was placed under 3.0 kPa CO_2, the pH dropped, CO_3^{2-} shifted to HCO_3^-, and the calcite IAP decreased to about 10^{-10}. This value fluctuated from $10^{-9.7}$ to $10^{-10.5}$ over the 3-week incubation. There was no change in the Ca concentration over this time period, but there was a small loss of alkalinity. Some acidification reaction such as nitrification must have occurred during this time. Treatment of the soil extract with H_2O_2 and addition of solid calcite produced calcite saturation (Fig. 6).

CONCLUSIONS

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_2O_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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