

Calcite Supersaturation in Soils as a Result of Organic Matter Mineralization¹

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ABSTRACT

Solutions equilibrated with soils under laboratory conditions often exhibit Ca^{2+} and CO_3^{2-} activities that exceed calcite saturation. This supersaturation has been attributed to various possibilities, none of which have been fully able to explain the phenomenon. In this study we report on the attainment of calcite supersaturation in calcite + water + organic matter systems under controlled CO_2 conditions. The decomposition of alfalfa shoots (*Medicago sativa* L.) and soybean roots (*Glycine max* L. merr.) in batch reactors under CO_2 pressures of 1.0, 10.0, and 99.5 kPa was found to result in HCO_3^- as an end product of aerobic decomposition. The rate of HCO_3^- production from mineralizing organic matter exceeded calcite precipitation rates and, thus, calcite supersaturation resulted. The decomposition of pure organic compounds (dextrose, inositol, glucosamine, glucuronic acid, citric acid, and sodium citrate) was studied to elucidate the mechanism of HCO_3^- production. It was determined that the decomposition of organic anions associated with inorganic cations always results in HCO_3^- as an end product. The rates of calcite dissolution and precipitation were greatly inhibited in the presence of decomposing organic matter.

Additional Index Words: carbon dioxide, alkalinity, organic matter decomposition, mineral weathering, ion activity products, kinetics.

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SUAREZ (1977) found calcite supersaturation (ion activity products three times that of calcite) in waters sampled from below the root zone in both field and lysimeter studies. Inskeep and Bloom (1986b)

found that Calciaquolls in western Minnesota were up to 40-fold oversaturated with respect to pure calcite. Both studies found that these high levels of Ca and carbonate activities in solution could not be explained by Mg substitution in the calcite, calcite particle size, or the presence of a more soluble soil CaCO_3 phase. Suarez (1977) attributed these large supersaturation values to the concentrating effects of evapotranspiration and the kinetic inhibitions of calcite precipitation, and further hypothesized that organic excretions from microorganisms blocked the crystal growth sites on calcite surfaces. Reynolds (1978) and Inskeep and Bloom (1986a) have shown that some organic matter constituents may inhibit calcite precipitation.

Apparent calcite supersaturation in soil/water laboratory equilibrations have been noted by several investigators. In contrast to the field studies, calcite supersaturation in the laboratory equilibrations cannot be attributed to the concentrating effects of evapotranspiration. Cole (1957), Olsen and Watanabe (1959) and Levy (1981) observed that Ca concentrations and calcite supersaturation increased as the soil-to-water ratio increased. Suarez and Rhoades (1982) found that calcareous soils which were reacted with water under controlled CO_2 conditions resulted in calcite supersaturation when equilibrated from initially undersaturated conditions. However, calcite nodules isolated from soil gave CaCO_3 ion activity product (IAP) values of $10^{-8.45}$ to $10^{-8.49}$. Organic complexes with Ca

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Table 1. Composition of each reaction bottle.

Exp.	Solution	Organic material	Calcite, g	pCO ₂ , kPa
1	300 mL 5.0 mM NaCl	None	1.0	1.0, 10.0, 99.5
2	300 mL 5.0 mM NaCl	0.5 g alfalfa	1.0	1.0, 10.0, 99.5
3	300 mL 5.0 mM NaCl	2.0 g alfalfa	1.0	1.0, 10.0, 99.5
4	300 mL 5.0 mM NaCl	2.0 g soybean roots	1.0	1.0, 10.0, 99.5
5	300 mL 5.0 mM NaCl	0.5 g alfalfa	None	1.0, 10.0, 99.5
6	300 mL 5.0 mM NaCl	2.0 g alfalfa	None	1.0, 10.0, 99.5
7	300 mL 5.0 mM NaCl	2.0 g soybean roots	None	1.0, 10.0, 99.5
8	300 mL 5.0 mM NaHCO ₃ + 5.0 mM CaCl ₂	None	None	1.0, 10.0, 99.5
9	300 mL 5.0 mM NaHCO ₃ + 5.0 mM CaCl ₂	2.0 g alfalfa	None	1.0, 10.0, 99.5
10	300 mL 5.0 mM NaCl + 0.1 mM (NH ₄) ₂ HPO ₄	20 mM dextrose	1.0	1.0, 10.0, 99.5
11	300 mL 5.0 mM NaCl + 0.1 mM (NH ₄) ₂ HPO ₄	20 mM inositol	1.0	1.0, 10.0, 99.5
12	300 mL 5.0 mM NaCl + 0.1 mM (NH ₄) ₂ HPO ₄	20 mM glucosamine	1.0	1.0, 10.0, 99.5
13	300 mL 5.0 mM NaCl + 0.1 mM (NH ₄) ₂ HPO ₄	20 mM glucuronic acid	1.0	1.0, 10.0, 99.5
14	300 mL 5.0 mM NaCl + 0.1 mM (NH ₄) ₂ HPO ₄	10 mM citric acid	1.0	1.0, 10.0, 99.5
15	300 mL 5.0 mM NaCl + 0.1 mM (NH ₄) ₂ HPO ₄	10 mM sodium citrate	1.0	1.0, 10.0, 99.5
16	300 mL 5.0 mM NaCl + 0.1 mM (NH ₄) ₂ HPO ₄	None	1.0	1.0, 10.0, 99.5
17	300 mL 5.0 mM NaCl	2.0 g alfalfa	None	99.5
18	300 mL 5.0 mM NaCl	2.0 g alfalfa	1.0	99.5
19	300 mL 5.0 mM NaCl	None	1.0	99.5

were shown to contribute insignificantly to total soluble Ca. Suarez and Rhoades (1982) hypothesized that calcite supersaturation in soils under laboratory conditions would occur if the rate of weathering of more soluble silicate minerals (anorthite) exceeded the precipitation rate of calcite.

While investigating the dissolution of anorthite as a potential source of Ca and alkalinity to soil solutions, we observed (unpublished data) that tile drain water, high in dissolved organics, showed increases in pH and alkalinity after 2 d in closed bottles. The changes in pH and alkalinity appeared to be related to the amount of dissolved organic matter in the water. With this observation we decided to test the hypothesis that organic matter mineralization can contribute substantial amounts of bicarbonate alkalinity to solutions and can result in calcite supersaturation.

MATERIALS AND METHODS

Polyethylene reaction bottles (500 mL) were mounted on a wrist-action shaker modified to shake at 80 cycles per minute. Analyzed mixtures of CO₂ plus air were bubbled through a series of four water saturators before being bubbled into the reaction bottles. The gas flow rate into each of the suspensions was regulated by use of a small hypodermic needle as a bubbler. Microbial activity affected CO₂ levels only during initial rapid decomposition at low CO₂ and high organic matter levels. Table 1 gives the contents of each reaction bottle. The calcite used was powdered Baker reagent grade CaCO₃ with a surface area of 0.17 m² g⁻¹ as measured by single point Kr adsorption. The pure organic materials used were dextrose, inositol, glucosamine, glucuronic acid, citric acid, and sodium citrate. The plant materials used were alfalfa shoots (*Medicago sativa* L.) and soybean roots (*Glycine max* L. merr.) grown hydroponically in a high Mg, Ca deficient solution. Solution 8 was a blank to determine if any evaporation occurred over the course of the reactions. The concentrations of Na, Ca, HCO₃, and Cl in the blank solution varied by no more than 2% during the experiment. All suspensions were inoculated with microorganisms at the start by adding one drop of fresh soil water extract.

The two plant material-to-water ratios used in this study were 1.67 and 6.67 g L⁻¹ (0.5 g in 300 mL and 2.0 g in 300 mL, respectively). Given a hypothetical soil at water saturation (saturation percentage = 20), organic matter to water ratios of 1.67 and 6.67 g L⁻¹ are equal to 0.33 and 1.3 g

Table 2. Chemical composition of plant materials used in the decomposition studies.

	Na	K	Ca	Mg	Cl	S	P	Total N
	mmol kg ⁻¹ dry weight							g kg ⁻¹
Alfalfa shoots	154	995	550	91	330	116	182	42.5
Soybean roots	320	1225	98	518	931	213	415	38.1

organic matter per kg of soil, respectively. For a 1:1 soil/water extract, the two organic to water ratios used in this study were equivalent to 1.7 and 6.7 g of organic matter per kg of soil.

The chemical analyses of the plant materials are given in Table 2. The Ca, Mg, Na, and K concentrations of the plant tissue were analyzed by atomic absorption spectrometry (AAS) of nitric-perchloric acid digests. Chloride was determined by argentometric titration on an American Instrument Company³ chloride titrator. Sulfate in the plant material was determined gravimetrically as barium sulfate (Am. Public Health Assoc., 1976). Total N was determined by Kjeldahl distillation (Bremner and Mulvaney, 1982). Phosphorus was determined colorimetrically by the molybdate blue procedure (Am. Public Health Assoc., 1976).

Organic matter decomposition reactions were studied in a background solution of 5.0 mM NaCl. Solutions 1–16 were continuously bubbled with either 1.0 or 10.0 kPa CO₂ (balance air) or 99.5 kPa CO₂. Ten-milliliter aliquots of solution were withdrawn at various time intervals and filtered through a 0.45-μm cellulose nitrate membrane filter before analysis for Ca, Mg, Na, K, SO₄, Cl, and alkalinity. Calcium, Mg, K, and Na were determined by atomic absorption spectroscopy (AAS). Acidified La₂O₃ was added (5.0 g La L⁻¹) for the Ca and Mg determinations. Sulfate in solution was determined by the turbidimetric method (Am. Public Health Assoc., 1976) and chloride by argentometric titration on an American Instrument Company chloride titrator.

The alkalinity titration consisted of a two-step procedure to determine bicarbonate + carbonate alkalinity and non-carbonate alkalinity. Each sample was titrated to pH 4.40 in the presence of air using 0.010 M KH(IO₃)₂ (NBS primary acid standard). This acid volume was used to calculate total alkalinity. The sample was then acidified to pH < 3.0 and vigorously bubbled with N₂ gas for at least 5 min on a magnetic stirrer to remove all carbonate species. The sample pH was then raised with CO₂-free 0.025 M NaOH to the original pH of the sample and the sample retitrated to pH 4.40. This

³ Trade names are provided for the benefit of the reader and do not imply endorsement by the USDA.

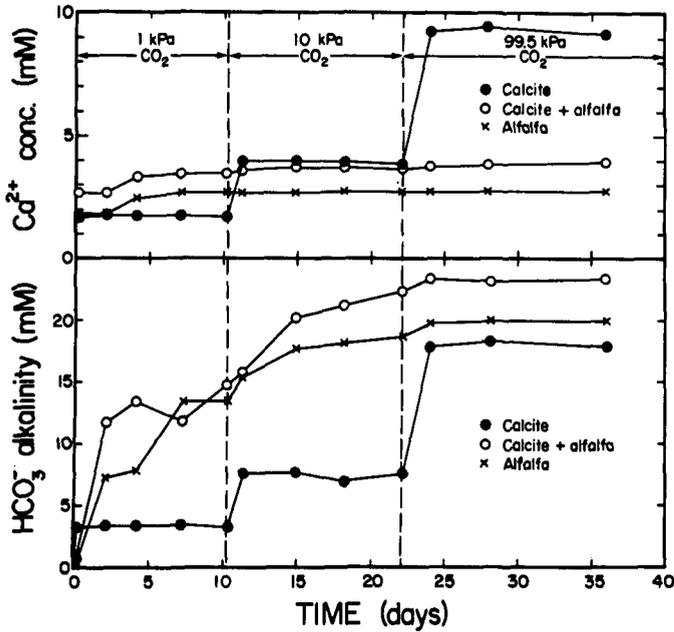


Fig. 1. Concentrations of Ca and bicarbonate alkalinity in solution under controlled CO_2 conditions in Exp. 1, 3, and 6. The $p\text{CO}_2$ was initially maintained at 1.0 kPa for 10 d. The gas was then switched to 10 kPa for 15 more days. Finally, the gas was changed to 99.5 kPa CO_2 for the remainder of the incubation.

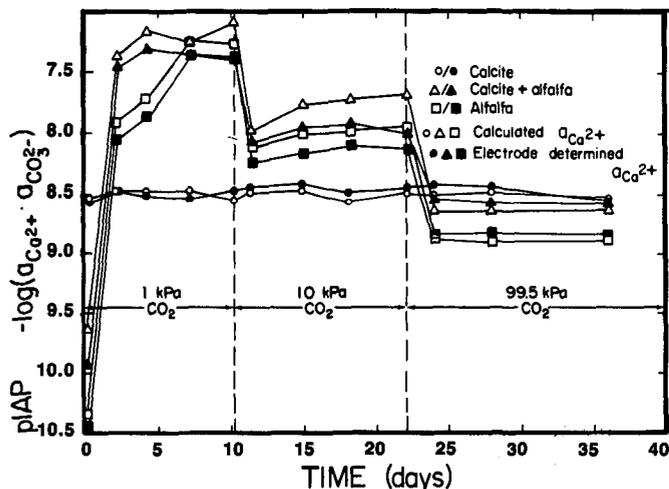


Fig. 2. Values for the negative logarithm of the calcite ion activity product (pIAP) during Exp. 1, 3, and 6. Solid points were calculated using Ca^{2+} activity values measured by ion specific electrode. Open points are pIAP values determined by calculated Ca^{2+} activities using an ion speciation program. Calcite equilibrium occurs at a pIAP of 8.48. Solutions with pIAP values < 8.48 are supersaturated with respect to calcite.

second titration measured noncarbonate alkalinity, which includes phosphate, ammonia, hydroxy-aluminum, and dissociated organic alkalinity. Thus, bicarbonate plus carbonate alkalinity (hereafter, HCO_3^- alkalinity) was determined as the difference between total alkalinity and noncarbonate alkalinity.

Citrate in solution (Exp. 14 and 15) was estimated from the initial citrate minus the citrate that decomposed to HCO_3^- alkalinity. The HCO_3^- alkalinity derived from citrate decomposition was calculated as the difference between $\text{mol}_c \text{L}^{-1}$ HCO_3^- alkalinity and $\text{mol}_c \text{L}^{-1}$ Ca. Carbonate/bicarbonate alkalinity in excess of Ca must be from citrate decomposi-

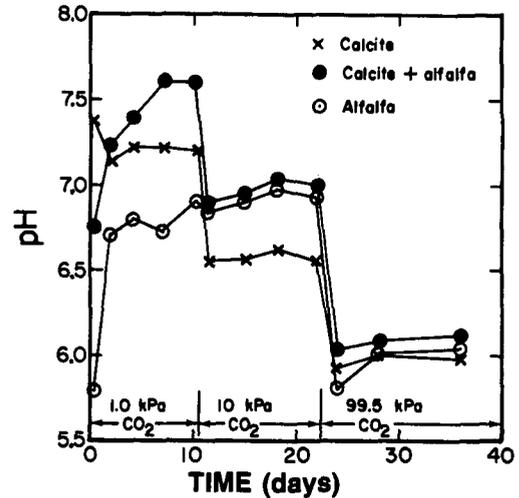


Fig. 3. The pH values during Exp. 1, 3, and 6.

tion since calcite dissolution by itself produces equal mol. Ca and mol. HCO_3^- alkalinity.

Solution pH was measured in situ at the time of sampling and immediately after calibration of the pH meter/electrode with buffers to within ± 0.01 pH units. The difference between total cations and total inorganic anions was attributed to organic anions.

Calcium activity of the solution was measured in situ at the time of sampling with an Orion specific ion electrode (model 92-20, ion exchanger type). The electrode was calibrated for each sampling with CaCl_2 standards of known activity (determined by the chemical speciation program Wateq (Truesdell and Jones, 1974)). The electrode values for Ca^{2+} activity were compared with calculated Ca^{2+} activity values. Some of the samples were treated with activated C (0.1 g mL^{-1}) to remove dissolved organics to evaluate the significance of Ca-organic complexes.

Ion activities were calculated using a speciation program (Suarez, 1977) using the concentrations of Ca, Mg, Na, K, Cl, SO_4 , $\text{CO}_3 + \text{HCO}_3^-$ alkalinity, and citrate. The stability constants for citric acid and citrate ion pairs were taken from Martell and Smith (1977). Organic anions other than citrate were not taken into account in the speciation. The calculated pH values, using CO_2 and alkalinity as inputs, were usually within ± 0.2 pH units of the measured pH values. Ion activity products for calcite were determined from calculated ion activities (Ca^{2+} and CO_3^{2-}) and from electrode measured Ca^{2+} activities.

RESULTS AND DISCUSSION

Figure 1 shows the relationship between Ca concentration in solution and incubation time for the experiments with ground alfalfa, alfalfa plus calcite, and calcite (Exp. 1, 3, and 6, respectively). The system containing only calcite quickly responded to changes in $p\text{CO}_2$ and reached a constant Ca concentration within 1 d. Initially, the alfalfa and alfalfa plus calcite released more Ca than the calcite system, apparently due to soluble Ca in the alfalfa. Upon increasing the $p\text{CO}_2$ to 10 kPa and then to 99.5 kPa, from an initial value of 1.0 kPa, the alfalfa plus calcite showed no substantial change in Ca concentration.

Also shown on Fig. 1 is the HCO_3^- alkalinity data for the same reactions (Exp. 1, 3, and 6). The HCO_3^- concentrations increased rapidly, reaching a constant level in the simple calcite system. The alfalfa and alfalfa plus calcite systems showed a continuous in-

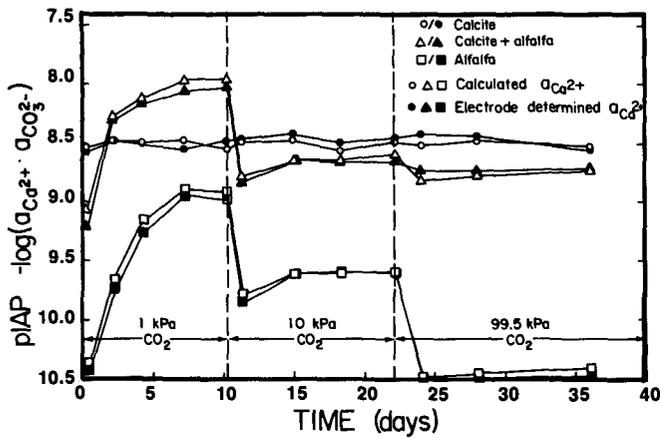


Fig. 4. Calcite pIAP values during Exp. 1, 2, and 5. Solid points were determined using electrode measured Ca^{2+} activities and open points using calculated Ca^{2+} activities. Calcite equilibrium occurs at a pIAP of 8.48.

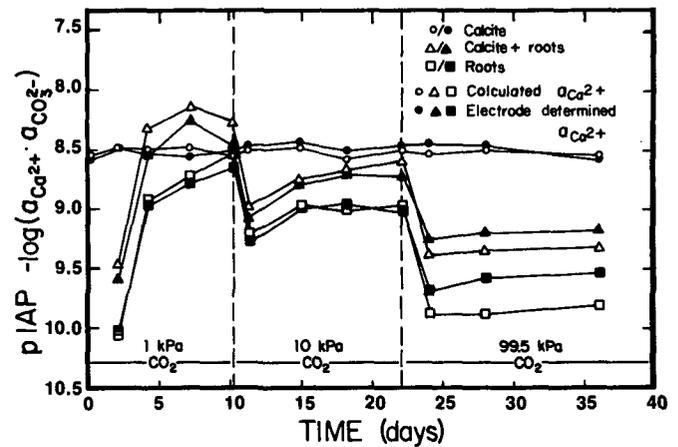


Fig. 6. Calcite pIAP values during Exp. 1, 4, and 7. Solid points were determined using electrode measured Ca^{2+} activities and open points using calculated Ca^{2+} activities. Calcite equilibrium occurs at a pIAP of 8.48.

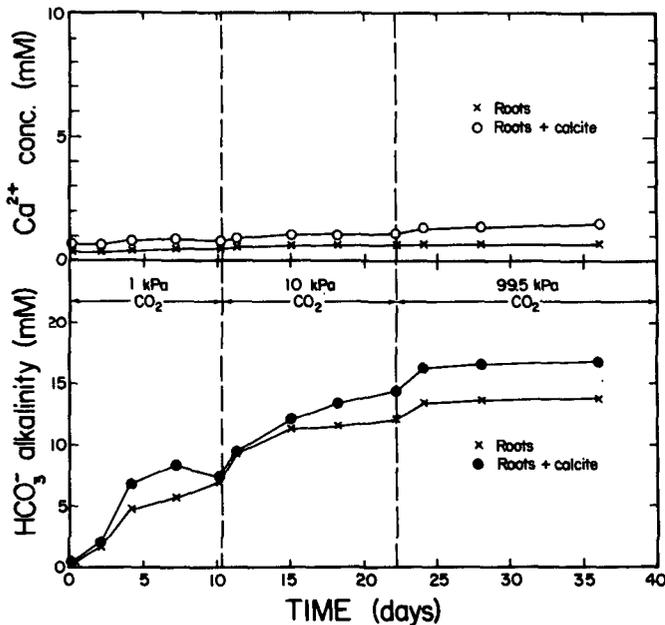


Fig. 5. Concentrations of Ca and bicarbonate alkalinity in solution in Exp. 4 and 7.

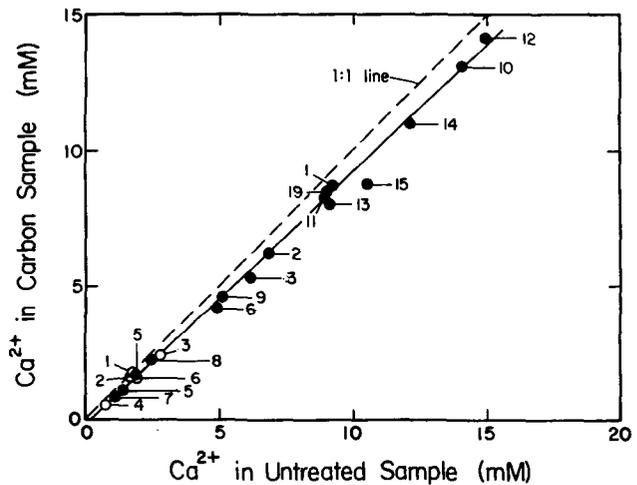


Fig. 7. Calcium concentrations in solutions treated with activated charcoal vs. the Ca concentrations in the untreated samples. Experiment numbers (Table 1) are shown next to each point.

crease (except for one point) in bicarbonate alkalinity with time.

Figure 2 shows that the calcite system reached equilibrium almost immediately (negative common logarithm of the IAP, $\text{pIAP} = 8.475$, Jacobson and Langmuir, 1974). The systems with alfalfa and alfalfa plus calcite quickly became supersaturated with respect to calcite, and pIAP values continued to decrease, reaching values as low as 7.1 at 1 kPa $p\text{CO}_2$. The effect of increasing $p\text{CO}_2$ was to immediately lower the solution pH values and the degree of supersaturation. The pIAP values tended to decrease with time in solutions at CO_2 pressures of 1.0 and 10 kPa, consistent with the increasing HCO_3^- alkalinity (Fig. 1). When 99.5 kPa CO_2 pressure was imposed, the alfalfa system did not reach calcite saturation. The measured pH values during these experiments (1, 3, and 6) are shown in Fig. 3 and are in excellent agreement with calculated pH values (data not shown). Initially there was a rapid release of 2.5 to 3.1 $\text{mmol}_c \text{L}^{-1}$ of noncarbonate al-

kalinity (organic anions). Subsequently, the concentration of noncarbonate alkalinity never exceeded 1.2 $\text{mmol}_c \text{L}^{-1}$ in the two alfalfa experiments. The agreement between calculated Ca^{2+} activities and electrode measured activities was good, demonstrating insignificant Ca-organic complexation.

Figure 4 is a plot of the pIAP vs. time for the experiments with 0.5 g of alfalfa in 300 mL of water. At 1.0 kPa CO_2 pressure, supersaturation was rapidly achieved in a suspension of calcite plus alfalfa, however the levels of supersaturation were not as great as those shown in Fig. 2. This result was consistent with the greater concentrations of alfalfa in the previously described experiments and the subsequent greater alkalinity production. In the system with 0.5 g of alfalfa (Exp. 5; Fig. 4), the total concentrations of Ca and alkalinity produced by organic matter decomposition were not sufficient to achieve calcite saturation. The calcite plus alfalfa system remained undersaturated after increasing the $p\text{CO}_2$ to 10 kPa. Even though calcite was present in suspension, its dissolution was prevented, presumably by contamination of the calcite surfaces by organic materials.

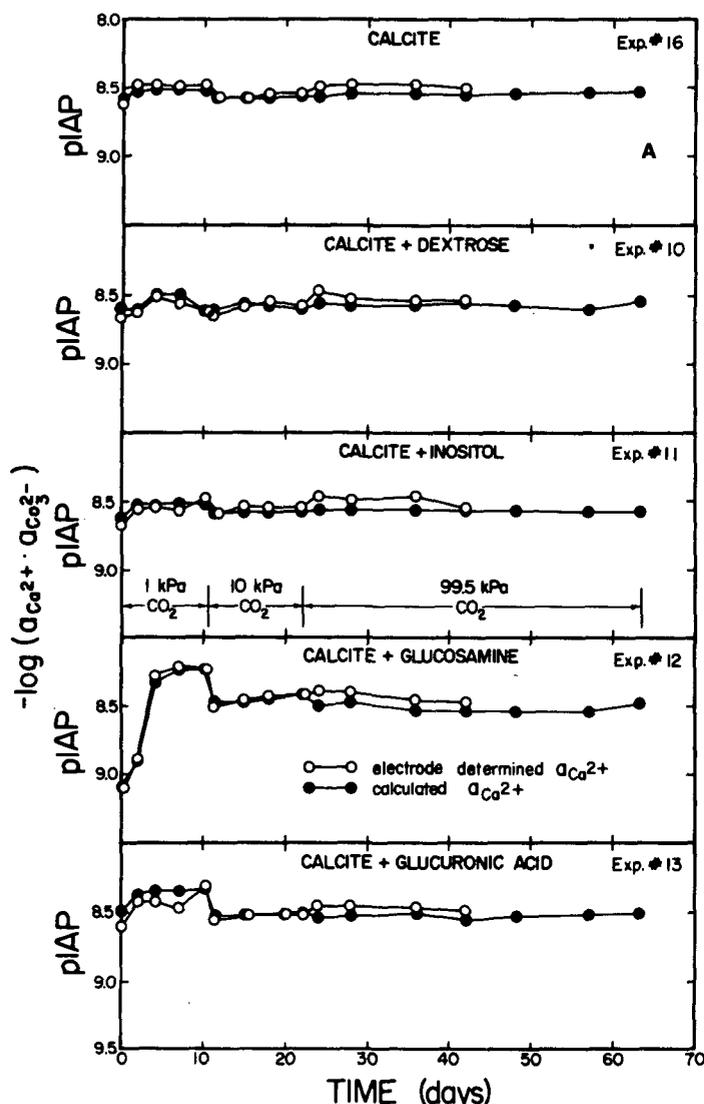
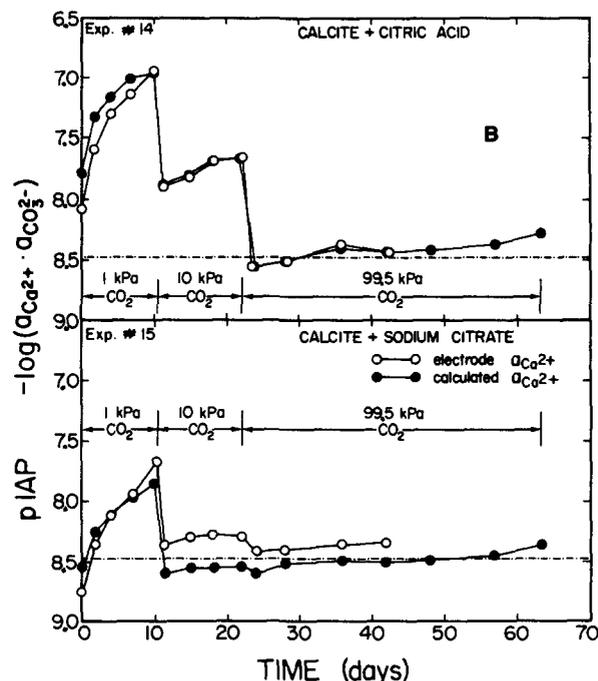


Fig. 8. Calcite pIAP values during the decomposition of pure organics in the presence of calcite under controlled CO_2 conditions. Open points were determined using electrode-measured Ca^{2+} activities and solid points using calculated Ca^{2+} activities. Calcite equilibrium occurs at a pIAP of 8.48.

Figure 5 shows the alkalinity and Ca concentrations as a function of time for the soybean root systems. The root material contained one fifth of the Ca of the alfalfa tissue (Table 1). The aerobic decomposition of this material yielded a steady supply of bicarbonate alkalinity to solution, again resulting in calcite supersaturation (Fig. 6). As in the alfalfa experiments, precipitation was not observed despite the presence of calcite. At 7 d, more calcite (1.0 g) was added to the soybean root plus calcite system. When fresh calcite was added to the supersaturated solution a slight increase in the pIAP occurred, likely due to precipitation of calcite (Fig. 6).

Switching from 1.0 kPa CO_2 to 10 kPa CO_2 initially resulted in calcite undersaturation. The pIAP values subsequently approached saturation (Fig. 6), primarily due to the conversion of organic matter to HCO_3^- alkalinity. The calcite dissolution was very slow, presumably as a result of the blocking of the surface by plant polyphenols (Reynolds, 1978). When the CO_2



was raised to 99.5 kPa the solution of calcite plus roots was nearly 10-fold undersaturated. This undersaturated solution approached calcite equilibrium very slowly and even after 9 weeks (data not shown) was still five fold undersaturated. Apparently, the organic matter blocked the calcite surface, retarding both precipitation and dissolution. It is hypothesized that the reactivity of soil calcite should be lower than laboratory calcite of the same surface area for this reason.

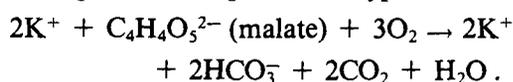
Decomposition studies done under 99.5 kPa CO_2 resulted in only small amounts of bicarbonate alkalinity (Exp. 17, 18; data not shown). Typical end products of anaerobic decomposition are organic acids, alcohols, and methane. Only the aerobic decomposition of organic matter resulted in a significant production of HCO_3^- alkalinity.

As shown in Fig. 2, 4, and 6 the pIAP, $\text{p}(\text{Ca}^{2+})(\text{CO}_3^{2-})$, values calculated using electrode measured Ca^{2+} activities and computed Ca^{2+} activities, agreed quite well, demonstrating that the concentration of Ca-organic complexes were minimal. In order to verify this observation we treated two sets of samples with activated C to remove organics. The Ca concentrations of the C-treated suspensions were all slightly lower than the untreated samples (Fig. 7). However, the lowering was independent of whether or not organic matter was present in the samples. All samples, even the calcite alone and the blank, showed lower Ca concentrations following treatment with activated charcoal. This data suggests that there was little or no Ca-organic complexation in these systems and that Ca losses onto activated C are not all due to the presence of organic compounds.

In order to elucidate the mechanism of HCO_3^- production, additional studies were conducted using pure organic compounds. Figures 8A and 8B show the experimental $(\text{Ca}^{2+})(\text{CO}_3^{2-})$ pIAP values during the decomposition of dextrose, inositol, glucuronic acid, glucosamine, citric acid, and sodium citrate, each in the presence of calcite. No supersaturation was observed

during sugar or inositol decomposition. Both glucuronic acid and glucosamine decomposed, to yield higher HCO_3^- alkalinity and calcite supersaturation at a CO_2 partial pressure of 1.0 kPa. The decomposition of these organics was rapid and essentially complete after a 1 week incubation. Thereafter, changing the $p\text{CO}_2$ to 10 kPa and then to 99.5 kPa resulted in calcite saturation. The decomposition of citric acid and sodium citrate, each in the presence of calcite, resulted in calcite supersaturation (Fig. 8B). In the citric acid plus calcite system, all of the citrate ion was rapidly converted to HCO_3^- . This was known because the $\text{mol}_c \text{HCO}_3^-$ alkalinity minus the $\text{mol}_c \text{Ca}$ was exactly equal to the total mol_c citrate added. In the sodium citrate plus calcite system only one third of the added citrate was converted to HCO_3^- . We have no explanation for this difference. However, the calculated Ca^{2+} activities were lower than the electrode measured activities in Exp. 15, suggesting that the citrate had been partially decomposed, possibly to another organic anion. Inhibition of calcite dissolution was not seen in any of the pure organic studies. This suggests that organics from the plant materials (polyphenols), and not microbial polysaccharides, were responsible for the inhibition. From these results it was deduced that the decomposition of organic anions results in the formation of HCO_3^- alkalinity as an end product. Supersaturation occurred in the presence of organic acids only after decomposition of the organic anion to HCO_3^- .

It is concluded that calcite supersaturation as a result of organic matter mineralization can be produced in two ways. First, the aerobic decomposition of organic anions associated inorganic cations results in HCO_3^- . All plants have an excess of inorganic cations over inorganic anions, the balance being maintained by organic anions, typically malate, citrate, oxalate, quinate, and succinate (Dijkshoorn, 1973). The following is an example of this type of decomposition



Secondly, in poorly mixed systems, such as soil columns or saturation pastes, the rapid decomposition of organic matter can result in elevated partial pressures of CO_2 that will increase the amount of calcite dissolved. When the rate of decomposition slows, the CO_2 will degas, and calcite supersaturation can result due to inhibition of precipitation. In the present study, CO_2 gas was constantly bubbled through the reaction suspensions in steps of increasing CO_2 ; therefore, the observed supersaturation could have resulted only from the aerobic decomposition of organic anions.

These experiments demonstrate that even for readily soluble minerals it is not possible to assume equilibrium between a soil solution and a mineral phase simply because the mineral is found in the soil. Conversely, it can not be assumed that a mineral phase exists in a soil simply because the IAP of a solution happens to equal the K_{sp} (thermodynamic equilibrium product) for a mineral.

CONCLUSION

Calcite supersaturation was achieved under conditions of controlled CO_2 in reactions with organic ma-

terials plus calcite. Organic matter had a dual role in preventing the systems in this study from reaching equilibrium with respect to calcite: (i) the production of bicarbonate alkalinity from the decomposition of organic matter, and (ii) the influence of organic coatings on the retardation of calcite precipitation. Calcite precipitation and dissolution were retarded due to plant derived organic coatings on the calcite. We conclude that the observed increases of HCO_3^- alkalinity, as a result of organic matter decomposition, may also be readily attained under natural conditions and are an important contribution to the alkalinity found in soil solutions. The typical harvest from an alfalfa field is approximately 11 Mg ha^{-1} (5 tons/acre; 3–4 cuttings). The amount of organic matter removed during a single cutting, if incorporated into a soil, is comparable to the amount of organic matter used in these experiments. The discing in of a green manure crop would introduce an enormous source of HCO_3^- alkalinity to soil solutions and ultimately to the ground water.

Calcite supersaturation was observed because the rate of organic matter mineralization was much faster than the rate of calcite precipitation. The enhanced solubility of calcite in soil-water reactions observed in several studies can be explained by the slow calcite precipitation following the production of HCO_3^- via organic matter mineralization.

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