Reevaluation of Calcite Supersaturation in Soils

D. L. Suarez,* J. D. Wood, and I. Ibrahim

ABSTRACT

The calcite saturation status of soil–water systems in semiarid regions was reexamined taking into consideration organic ligand alkalinity and Ca–organic complexation. These factors have been forwarded as the reason for earlier reports of calcite supersaturation in soil–water systems. We examined groundwaters beneath irrigated lands, soil–water suspensions in the laboratory using four soils and two levels of CO_2, and soil water extracted from the root zone of an irrigated, cropped field. Total alkalinity and net inorganic C alkalinity were determined by titration. Calcium activity values calculated from total concentrations using the speciation program WATEQ4F were compared with Ca^{2+} activity values measured with an ion-specific electrode. In all our systems, total alkalinity and inorganic C alkalinity were almost equivalent and thus organic C alkalinity was negligible. Calculated Ca^{2+} activity was generally 5 to 25% greater than Ca^{2+} activity determined with an ion-specific electrode. Although these data suggest the presence of additional Ca complexes not included in the speciation routines, the determined dissolved organic C values are too low for Ca–organic complexes to be the cause of these differences in Ca^{2+} activity. Ion activity products based on either measured Ca^{2+} activity values or calculated Ca^{2+} activities indicated that all systems were supersaturated, with saturation ratios of two to three.

THE SATURATION STATUS of calcite in soil–water systems has been the subject of numerous studies, often with apparently conflicting results and different conclusions. Past studies may not be as conflicting as a first examination might indicate because experimental conditions often differed. Also, differences in past studies are at least in part due to an examination of different problems. For example, early reports of calcite supersaturation in soil–water reactions (Cole, 1957; Olsen and Watanabe, 1959) can be questioned because these studies did not correct for ion activity coefficient and complexation effects. Many studies have also been conducted that assumed soil–water reactions could be represented by solution studies without a solid phase or only by solution clay reactions. We do not examine these studies here because they do not directly relate to the questions formulated below.

In order to properly interpret the published research on soil $CaCO_3$ and its effect on soil solution composition, we considered two distinct questions. First, what is the thermodynamic stability of the $CaCO_3$ phase present in soils? Secondly, what is the $CaCO_3$ ion activity product, $(Ca^{2+})(CO_3^{2-})$, in soil water? The former question is best answered by isolating the $CaCO_3$ phase, if possible, and reacting it under controlled laboratory conditions of fixed temperature and CO_2 partial pressure. The latter question is best resolved by direct examination of the natural system. Laboratory soil–water equilibrations have been by far the most common experiments reported, but provide only a limited evaluation of the natural system. Within this

framework, a distinction should be made among systems in which relevant ions may be released or removed from sources other than the carbonate phase and those in which this does not occur. Since we are dealing with a system also involving kinetic considerations, a distinction needs to be made between conditions where saturation is approached from undersaturated or supersaturated conditions.

Calcite supersaturation under field conditions was reported by Suarez (1977) for groundwaters below irrigated lands in two different hydrologic systems. All of the 62 well waters sampled were supersaturated with respect to calcite. This supersaturation could be the result of either deviations of the ΔG_f° of soil $CaCO_3$ from that of pure well-crystallized calcite, or from kinetic factors that prevent solution equilibrium with the existing solid phase. Determination of the cause of apparent supersaturation requires examination of the solid phase.

Suarez and Rhoades (1982) extracted pedogenic $CaCO_3$ from soils and identified it by XRD as low-Mg calcite. This material, when reacted with deionized water, gave the same ion activity product as pure calcite. This appears to be the only study in which the stability of the $CaCO_3$ solid phase present in a soil was determined directly, in the absence of other mineral phases and organic matter.

Suarez and Rhoades (1982) also reacted soils containing calcite (including the soil from which the pedogenic calcite was isolated and reacted) in the laboratory with various solutions including deionized water and soil water extracts. All reactions resulted in calcite supersaturation including those under controlled, high CO_2 partial pressures. The degree of supersaturation depended on the extent of calcite dissolution, suggesting nonequilibrium conditions. Increases in supersaturation with time implied that Ca or alkalinity were released from other sources, and that there was also inhibition of calcite precipitation. These results suggest that well-crystallized calcite, with a solubility comparable to specimen samples, is formed in these soils, and that the supersaturation observed for soil water reactions may be due to other sources of Ca and alkalinity and slow precipitation kinetics.

Additional experiments, conducted under ambient CO_2 conditions, have also demonstrated supersaturation. Marion and Babcock (1977) observed calcite supersaturation for two out of three soils reacted with distilled water in the laboratory. Their data show increasing alkalinity with time through 40 d of reaction. Inskeep and Bloom (1986a) found high degrees of supersaturation in soil–water suspensions measured in the laboratory. Their calculations indicate that their samples were also supersaturated under field conditions. They related the persistence of supersaturation to the inhibition of precipitation due to the presence of soluble organic C.

Inhibition of calciteprecipitation by soluble organ-

D.L. Suarez and J.D. Wood, USDA-ARS, U.S. Salinity Lab., 4500 Glenwood Dr., Riverside, CA 92501; and I. Ibrahim, Soil Salinity and Alkalinity Lab., Bacos, Alexandria, Egypt. Contribution from the U.S. Salinity Lab., Riverside, CA. Received 18 July 1991. *Corresponding author.

ics has been demonstrated by Reynolds (1978) and Inskeep and Bloom (1986b). In addition to inhibiting precipitation, organic matter may decompose and release alkalinity (Amrhein and Suarez, 1987). Increases in bicarbonate alkalinity in suspensions of calcite, organic matter, and deionized water produced high levels of calcite supersaturation despite the use of well-crystallized specimen calcite (Amrhein and Suarez, 1987). These experiments indicate that, even when using soil–water suspensions at fixed partial pressure of CO_2 and approaching equilibrium from initial undersaturation, results are not indicative of the true solid-phase stability.

More recently, Reddy et al. (1990) measured calcite ion activity products in soil–water suspensions at ambient CO_2. They indicated that measurements with a Ca^{2+} electrode and determination of total dissolved inorganic C gave calcite equilibrium. Reddy et al. (1990) also indicated that traditional alkalinity determinations and calculation of Ca^{2+} activity from total concentration gave highly supersaturated IAP values, comparable to those reported by Inskeep and Bloom (1986a) and Suarez (1977). Reddy et al. (1990) proposed two reasons for the widely reported calcite supersaturation in soils: (i) overestimation of Ca^{2+} activity because of failure to correct for Ca–organic complexation, and (ii) overestimation of CO_3^{2-} activity due to proton adsorption by dissolved organic matter during alkalinity titrations.

In this study, we determined the degree of Ca–organic complexation and organic ligand contributions to alkalinity in the following systems: groundwaters beneath irrigated lands, soil–water suspensions reacted in the laboratory under controlled conditions of CO_2, and soil water extracted from the unsaturated root zone of an irrigated, cropped field. We also reevaluated the calcite saturation status in these systems and examined the quantities of dissolved organic matter necessary to produce errors in the calculated IAP values for calcite.

MATERIALS AND METHODS

Groundwaters

All groundwater samples were collected at the pump outlets from drainage wells in the Wellton–Mohawk Irrigation District of southwestern Arizona. Field pH was measured

with a Sargent-Welch 4090[1] portable pH meter (Sargent-Welch Scientific, Skokie, IL). The electrode and nominal pH 4.01 and 6.86 buffers were equilibrated at groundwater temperatures and the meter was calibrated to within 0.01 pH units. Samples for metal analyses were filtered through prerinsed 0.10-μm Millipore filters (Millipore Corp., Bedford, MA) and acidified with four drops of 6 M HCl in 50-mL, acid washed, prerinsed polyethylene bottles. Another subsample from each well was placed in a 100-mL prerinsed polyethylene bottle, filled to the top, capped, and placed on ice for 24 to 48 h before determination of alkalinity. Acidified samples were analyzed for Ca, Mg, Na, K, and S by ICP and for NO_3 with a Technicon Autoanalyzer II (Technicon Instrument Corp., Tarrytown, NY). Unacidified samples were used for analyses of alkalinity, inorganic C alkalinity, Cl, and Ca^{2+} activity using an ion-specific electrode (Orion, 93-20 Orion Research, Boston, MA). Total alkalinity was determined by titration to pH 4.40 with 0.01 M $KH(IO_3)_2$ (National Bureau of Standards primary acid standard). A magnetic stirrer was used and N_2 continuously bubbled into the sample to remove CO_2 and obtain a fixed titration endpoint (independent of initial alkalinity). To determine inorganic C alkalinity, the pH of the samples was next further lowered to <3.0. The solutions were then vigorously bubbled with N_2 to remove all carbonate species. Samples were next adjusted back to the original pH values with CO_2-free 0.025 M NaOH and then retitrated to pH 4.40 with 0.01 M $KH(IO_3)_2$. Distilled water and various concentrations of $NaHCO_3$ solution were analyzed to verify the suitability of the procedure. After correction for the blank, the second acid titration values were taken as measures of noncarbonate alkalinity. These values represent the sum of weak inorganic acid ligands (P, B, Al, and Si) and proton-accepting organic ligands or colloids. Inorganic carbonate alkalinity was calculated from the difference between the two titrations. We attempted to analyze total dissolved carbonate using a modification of the method described by Reddy et al. (1990). We do not report values obtained with this method because recovery for the standards was low and variable.

Dissolved organic carbon was analyzed with a Technicon Autoanalyzer II using Technicon Method no. 451-76W. The precision was 4% and the detection limit was 0.01 mmol L^{-1}. Data were analyzed with three different chemical speciation programs: a carbonate model with equilibrium constants listed in Suarez (1977) using an extended Debye–Huckel expression for calculation of activity coefficients; the program WATEQ4F (Ball et al., 1987), which

---

[1] The citation of particular products is for the convenience of the reader and does not imply any particular endorsement by the USDA or its agents.

Table 1. Selected soil properties and classification.

Surface soil	Texture				Carbon	
	<2 μm	2–50 μm	50–250 μm	250–2000 μm	Inorganic	Organic
	%					
Holtville silty clay (clayey over loamy, montmorillonitic [calcareous], hyperthermic Typic Torrifluvent)	39	30	22	8	0.99	0.93
Imperial silty clay (fine, montmorillonitic [calcareous], hyperthermic Vertic Torrifluvent)	57	37	5	1	1.38	0.55
Indio loam (coarse-silty, mixed [calcareous], hyperthermic Typic Torrifluvent)	27	39	22	11	1.21	0.63
Vint very fine sandy loam (sandy, mixed, hyperthermic Typic Torrifluvent)	13	16	31	39	0.73	0.52

Table 2. Chemical analyses of groundwater sampled from drainage wells in the Wellton–Mohawk Irrigation District, Arizona.

Well	pH	Ca	Mg	Na	K	Cl	Total alkalinity	Inorganic C alkalinity	SO$_4$	NO$_3$	Dissolved organic C
						mmol L^{-1}					
21A	7.47	2.74	1.90	25.81	0.18	11.78	7.87	7.85	7.31	0.68	0.19
43B	7.45	1.41	1.13	21.98	0.15	6.27	8.01	7.98	6.12	0.55	0.16
43C	7.50	3.38	2.15	20.56	0.17	11.28	7.09	7.09	6.22	0.21	0.19
61A	7.15	5.62	3.16	16.22	0.23	10.92	8.05	8.05	7.44	0.25	0.29
23A	7.47	2.63	1.71	22.38	0.23	9.57	7.75	7.74	6.57	0.96	0.22
53B	7.21	6.68	3.86	15.16	0.21	15.15	7.33	7.33	6.89	0.48	0.25
33	7.34	4.78	3.97	40.33	0.23	23.96	11.88	11.88	11.35	0.14	0.29
28A	7.40	6.55	3.81	19.25	0.21	15.56	7.50	7.48	8.56	0.17	0.25
38A	7.20	6.46	3.91	20.10	0.29	17.07	6.73	6.72	8.59	0.02	0.23
47	7.39	4.59	2.84	25.60	0.13	13.30	9.52	9.48	8.87	0.07	0.27
612	7.41	2.95	2.37	35.34	0.18	18.36	7.92	7.88	9.60	0.42	0.18
611	7.20	5.98	4.16	33.00	0.20	18.38	10.57	10.53	11.81	0.26	0.30
608	7.36	5.68	3.81	43.33	0.24	25.54	9.19	9.13	13.31	0.21	0.35
39	7.19	7.05	5.69	57.04	0.16	41.66	11.24	11.18	15.45	0.06	0.36
30A	7.27	4.99	4.31	62.36	0.23	46.64	8.22	8.14	12.13	0.09	0.32
20A	7.45	4.67	2.98	16.62	0.31	9.90	7.45	7.42	7.38	0.08	0.23
53A	7.55	2.86	2.20	32.07	0.28	16.66	7.96	7.93	8.12	0.08	0.18
37	7.15	7.95	5.47	26.54	0.18	20.03	9.30		9.25	11.80	0.09	0.24

also uses an extended Debye–Huckel expression; and GEO-CHEM (Sposito and Mattigod, 1979), which uses the Davies equation for calculation of activity coefficients.

Laboratory Soil–Water Equilibrations

Samples of Imperial silty clay, Holtville silty clay, Indio loam, and Vint very fine sandy loam were collected from cropped fields and cooled to 4 °C. Texture and soil classification data are provided in Table 1. Soil water content and soil texture were determined on subsamples. Total C and organic C in soils were determined with a U.I.C. coulometric C analyzer (UIC, Joliet, IL). Various amounts of wet soil, sufficient to yield 100 g of dry soil, were placed in 500-mL flasks. Deionized water was added until each flask contained 150 mL of water. The soil–water suspensions were mixed thoroughly, capped, and shaken gently on a reciprocating shaker table. Two CO$_2$ levels were used: (i) 10 kPa (10%) CO$_2$ delivered from an air–CO$_2$ mixture and previously saturated with water, and (ii) ambient laboratory air, whose CO$_2$ partial pressure is variable and always greater than the quoted value of 35 Pa. The air-equilibrated samples remained capped and were opened daily when all samples were hand mixed. Samples were reacted for a total of 26 d at 26 °C (±0.5). A Fisher Accumet 520 pH meter (Fisher Scientific Co., Pittsburgh, PA) and Thomas 4094 pH electrode (Thomas Scientific, Swedesboro, NJ), calibrated as described above, were used to determine the pH of the suspensions in the flasks. Samples (35 mL) were removed on Days 12, 19, and 26 and centrifuged at 2000 $\times$ g for 5 min. They were then filtered through prerinsed 0.1-μm Millipore filters. All samples were run in duplicate. Solutions were analyzed as described above for the water samples.

**Unsaturated Zone Soil Waters**

Soil water samples were taken from the root zone of a field (Pachappa sandy loam) previously cropped to wheat (*Triticum aestivam* L.). The samples were obtained using the vacuum extractors described by Suarez (1986), operated at a vacuum of 20 kPa. Under these conditions, this extractor design produces negligible pH changes during sampling. Solutions were analyzed as described above for the water samples.

RESULTS AND DISCUSSION

Groundwaters

Chemical analyses of the 18 well waters, given in Table 2, indicate that an accurate cation–anion bal-

ance was achieved (all samples were within 3%). Figure 1 provides a comparison of the Ca^{2+} activity measured with the electrode and the activity calculated from the analytical data and the WATEQ4F chemical speciation program (Ball et al., 1987). Most of the data points fall below the 1:1 dashed line, indicating that measured Ca^{2+} values are smaller than the calculated values. In all cases the differences are $\leq13\%$. Most differences are within the 7% reproducibility of the electrode determinations. Nonetheless, assuming that these differences could be attributed to Ca–organic complexes, which are not considered by the computer program, then up to 0.3 mmol L^{-1} Ca would be complexed. If these relatively small differences in Ca^{2+} activity were caused by the presence of Ca–organic complexes, we would expect the following behavior: (i) a greater fraction of total Ca complexed at low than at high Ca concentration, and (ii) a correlation between the quantity of apparent Ca complexation and DOC. Neither of these relationships was observed. In addition, even such low levels of potential Ca–organic complexation are incompatible with the DOC levels found in these waters. Inskeep and Baham (1983) determined the value of 10 mol C mol$_c^{-1}$ for water-soluble organic matter. If we use this
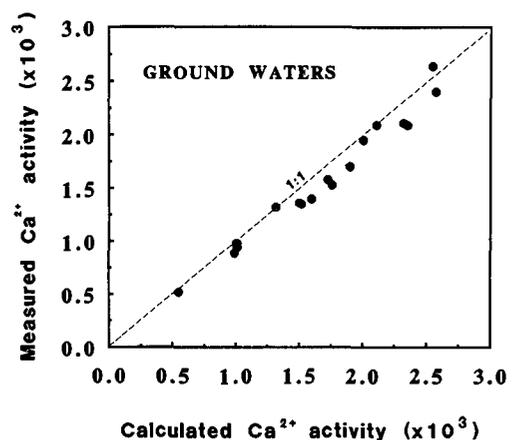
Fig. 1. Groundwater Ca^{2+} activities measured with an electrode vs. activities calculated using the analytical data and a speciation program.
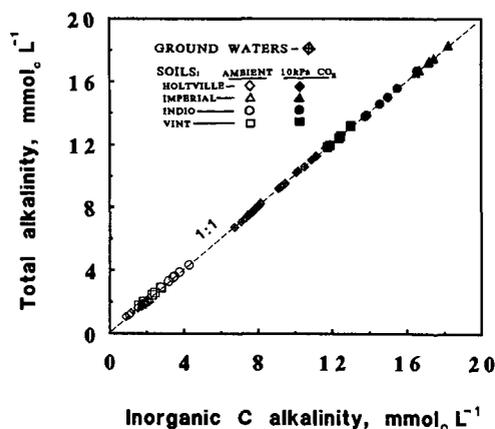
Fig. 2. Total alkalinity vs. inorganic C alkalinity for groundwater and laboratory equilibrations. Data include two replicates for all three sampling days.

pIAP (with measured Ca^{2+} activity)

Fig. 3. Groundwater ion activity products (IAP) of $(Ca^{2+})(CO_3^{2-})$ calculated using the analytical data along with Ca concentration and total alkalinity in a speciation program vs. IAP calculated using inorganic C alkalinity in the speciation program and Ca activities measured with an electrode.

value and our mean DOC value of 0.25 mmol L^{-1}, and assume complete complexation with Ca, Ca–organic complexes would constitute a mean concentration of only 0.0125 mmol L^{-1} for these waters.

The relationship between total alkalinity and inorganic C alkalinity for the groundwaters is presented in Fig. 2. The data lie almost directly on the dashed 1:1 line. Differences are <1% in all instances. The calculated differences between the two procedures result in a mean value of only 0.03 mmol L^{-1} of alkalinity, potentially attributable to organic C alkalinity.

A further check on the accuracy of the inorganic C alkalinity determinations is provided by an examination of the DOC values for these waters. These data can be converted into estimates of alkalinity by the method of Oliver et al. (1983). These authors determined a mean value of 10 μmol_c mg^{-1} organic C for a variety of water samples taken from different climatic and geologic environments. The amount of dissociated organic matter at any pH can be calculated by the following relations (Oliver et al., 1983):

$$pK = 0.96 + 0.90\ pH - 0.039\ (pH)^2 \quad [1]$$

$$K/(K + H^+) = \alpha \quad [2]$$

where pK is the negative log of the mass action quotient, α is the dissociated fraction of the organic material, and concentrations are expressed in moles of charge per liter. The organic matter should be essentially (98%) completely dissociated at pH values >7.0 (Oliver et al., 1983). For our data, at the titration endpoint of pH 4.40, pK = 4.43 and α = 0.63. These values indicate that 37% of the total charges, most likely from carboxyl groups, are neutralized when the pH is lowered from >7 to 4.40. The mean DOC value for our well waters is 0.25 mmol L^{-1} or 3 mg L^{-1} C. Based on the method of Oliver et al. (1983) described above, we calculated a mean value of 30 μmol_c L^{-1} for the concentration of proton-accepting groups and a proton consumption of 11 μmol_c L^{-1} for the titrations. This small calculated value of 11 μmol_c L^{-1} is consistent with our measured value of 30 μmol_c L^{-1} organic alkalinity, obtained the the titration method. Based on both the titration data and the calculations from the measured DOC values, we concluded that
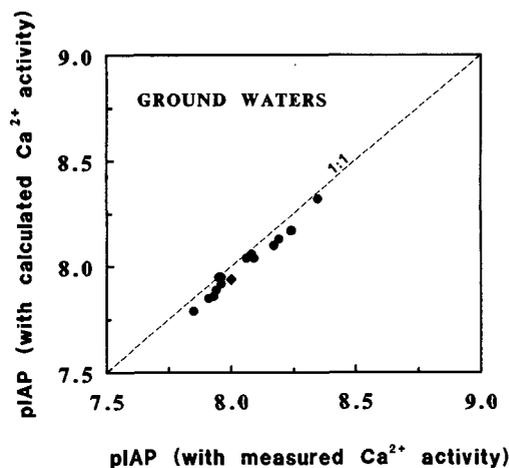
organic anions provide a negligible contribution to our alkalinity values.

The IAP of $(Ca^{2+})(CO_3^{2-})$ for these well waters were calculated in two ways: (i) using ion-specific electrode determinations of Ca^{2+} activity and calculation of CO_3^{2-} activity from inorganic C alkalinity values using the speciation program WATEQ4F, and (ii) using the total analytical values (Table 2) and calculating activities from WATEQ4F assuming no Ca–organic complexation and no organic anion alkalinity. As can be seen by the data points in Fig. 3, the pIAP values using Method 1 are only slightly larger than the values calculated using Method 2. All values are clearly calcite supersaturated (pIAP = 8.48 at calcite equilibrium at 25 °C, according to Plummer and Busenberg, 1982).

If Ca–organic complexation and organic alkalinity had an important effect on pIAP values, we would expect a strong correlation between DOC and pIAP. As shown in Fig. 4, a relation between the degree of supersaturation and DOC is not apparent, except possibly for the three samples with the lowest DOC. This relationship at very low DOC values is expected since small amounts of DOC can act as surface poisons and reduce calcite precipitation rates via crystal growth. At higher DOC levels, the calcite surfaces have already been poisoned and no crystal growth should occur. Thus, further increases in DOC values should have no additional effect on pIAP values. Inskeep and Bloom (1986b) determined that complete inhibition of calcite crystal growth was obtained for DOC values >0.15 mmol L^{-1} for an aqueous soil extract, consistent with our data.

Laboratory Soil–Water Equilibrations

All soils contained substantial amounts of inorganic C (Table 1), with XRD confirmation of the presence of calcite. The chemical analyses of the laboratory soil–water equilibrations are presented in Table 3 for both atmospheric CO_2 levels and the 10 kPa (10%) CO_2 conditions following 26 d of reaction. The data
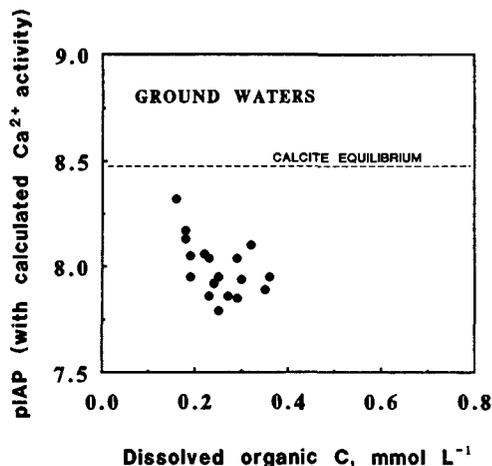
Fig. 4. Groundwater ion activity products (IAP) of $(Ca^{2+})(CO_3^{2-})$ calculated using the analytical data along with Ca concentration and total alkalinity in a speciation program vs. dissolved organic C in solution. The line indicates the pIAP value of 8.48 for equilibrium with pure calcite.
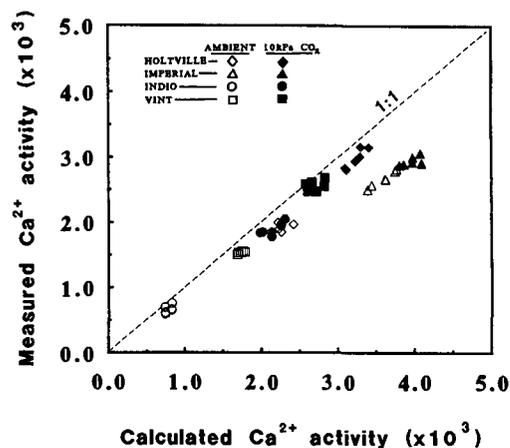

Fig. 5. Calcium activity of the laboratory equilibrations measured with an electrode vs. activity calculated using the analytical data and a speciation program. Data include two replicates and three sampling days.

in Table 3 also indicate good agreement between replicates. Samples collected after 12 and 19 d contained slightly lower Ca and alkalinity values (data not shown). Comparisons of the computed and electrode-determined Ca^{2+} activities are provided in Fig. 5 for all three sampling dates. All data points fall below the 1:1 line, indicating that the computed Ca^{2+} values are greater than the measured values. With the exception of the Imperial soil–waters, all differences in sample Ca^{2+} activity are <21%.

Consistent differences between calculated and electrode-measured Ca^{2+} activity were found for reactions with the Imperial soil, with the electrode values averaging 25% lower than calculated values. An additional evaluation of Ca^{2+} activity values is available for the Imperial samples, since the soils contain gypsum. Using the electrode Ca^{2+} activity values and calculated SO_4^{2-} activity values, these soil waters, on average, are gypsum saturated (pIAP = 4.57). In contrast, use of computed Ca^{2+} activities results in slight gypsum supersaturation (pIAP = 4.45 vs. 4.62 for

gypsum saturation). Similar slightly supersaturated results were obtained from the program with the Suarez (1977) constants as well as with GEOCHEM (Sposito and Mattigod, 1979). Such results suggest that the electrode values may be more reliable than the computed values.

High Ca–organic complexation is unlikely for the Imperial soil samples, because reactions with Holtville and Vint soils show much smaller differences between calculated and measured Ca^{2+} (Fig. 5) despite approximately twice the DOC values. In addition, the Indio soil, having comparable DOC values, does not show high apparent complexation. The major difference between the Imperial soil and the other samples is that the Ca and SO_4 concentrations are much higher, resulting in relatively high ionic strengths (Table 3). At constant organic ligand concentration, increased Ca values should result in smaller percentages of organic Ca complexation. These results suggest that the differences in Ca^{2+} activity are not due to Ca–organic complexation. Further support for this

Table 3. Chemical analyses of soil equilibrations at two CO_2 partial pressures and a soil water ratio of 2:3, after 26 d of reaction.

| Soil	pCO_2	pH	Ca	Mg	Na	K	Cl	Total alkalinity	Inorganic C alkalinity	SO_4	NO_3	Dissolved organic C
	kPa							mmol L⁻¹				
Holtville	10	6.73	7.73	4.54	9.16	0.32	1.75	11.79	11.66	2.30	17.40	1.93
	10	6.75	7.99	4.64	9.20	0.28	1.81	12.01	11.91	2.19	17.19	1.73
	air	7.61	4.62	2.61	8.02	0.22	1.69	1.29	1.15	2.13	16.40	1.54
	air	7.68	4.63	2.59	8.17	0.25	1.67	1.07	0.89	2.13	17.00	1.43
Imperial	10	6.90	18.97	12.05	45.90	0.56	13.02	18.34	18.22	38.27	0.94	1.13
	10	6.91	18.23	11.41	43.97	0.59	12.52	17.51	17.46	36.77	0.87	1.12
	air	7.87	17.37	9.25	41.92	0.65	12.96	2.04	1.90	40.66	0.81	1.08
	air	7.89	17.31	9.26	42.53	0.50	12.58	1.88	1.72	40.00	0.83	1.01
Indio	10	6.89	4.70	2.83	4.58	0.64	0.71	15.58	15.51	1.01	1.74	0.96
	10	6.91	4.87	2.92	4.60	0.66	0.74	16.68	16.55	1.03	1.57	0.90
	air	8.04	1.40	0.82	3.54	0.37	0.76	3.55	3.41	1.13	1.60	0.99
	air	8.17	1.25	0.72	3.35	0.39	0.70	2.94	2.76	1.11	1.63	1.20
Vint	10	6.81	7.62	4.67	14.48	0.61	8.68	13.16	13.01	6.69	3.73	1.93
	10	6.82	7.63	4.65	14.53	0.60	8.68	13.19	13.03	6.81	3.77	1.90
	air	8.02	4.42	2.72	13.59	0.39	8.44	1.99	1.82	6.58	3.81	1.84
	air	8.04	4.37	2.67	13.42	0.40	8.66	1.76	1.58	6.75	3.60	1.78
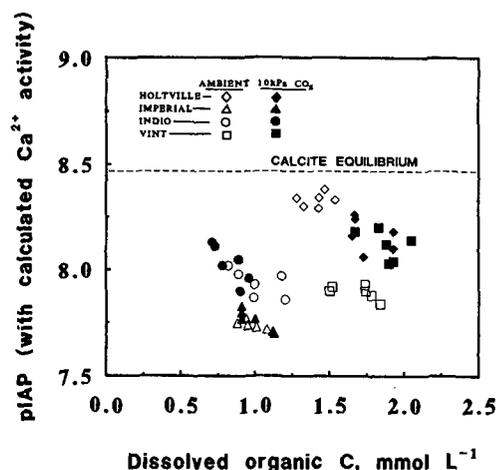
Fig. 6. Ion activity products (IAP) of $(Ca^{2+})(CO_3^{2-})$ in the laboratory equilibrations calculated using the analytical data along with Ca concentration and total alkalinity in a speciation program vs. dissolved organic C in solution. The line indicates the pIAP value of 8.48 for equilibrium with pure calcite. Data include two replicates and three sampling days.
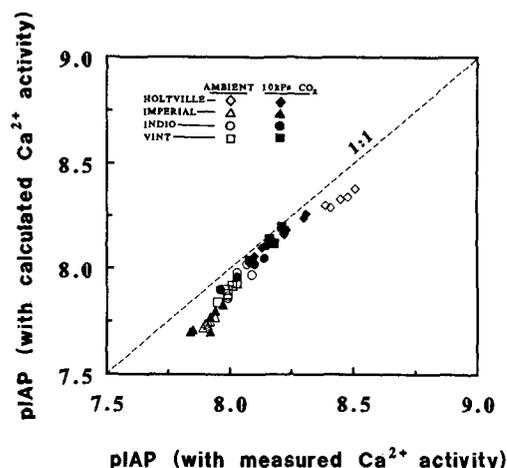

Fig. 7. Ion activity products (IAP) of $(Ca^{2+})(CO_3^{2-}$ in the laboratory equilibrations calculated using the analytical data along with Ca concentration and total alkalinity vs. IAP calculated from inorganic C alkalinity in the speciation program and activity of Ca measured with an electrode. Data include two replicates and three sampling days.

conclusion is provided by the DOC values. Since each mole of charge requires 10 mol C, even assuming that all potential sites are Ca complexed, the analyzed DOC values (mean of 1.2 mmol L^{-1}) allow only a maximum of 0.12 mmol L^{-1} of Ca–organic complexes, which would be almost undetectable in our systems.

In contrast to the differences in Ca^{2+} activity, the total alkalinity and inorganic C alkalinity values are in excellent agreement (Fig. 2). These data indicate that organic C alkalinities are negligible despite relatively high DOC values (Fig. 6). The mean analyzed value of organic C alkalinity from the titration data was 0.138 $mmol_c$ L^{-1}. The mean DOC value for these samples is 1.20 mmol L^{-1}. With the calculation method described above, this number corresponds to a calculated concentration of 144 μmol_c L^{-1} for the proton-accepting organic sites. The corresponding calculated proton consumption during the titration would be 53 μmol_c L^{-1}. Again, within the uncertainties of the titration methods, the calculated value of 0.053 $mmol_c$ L^{-1} organic anion alkalinity based on DOC values is in good agreement with the measured value

of 0.138 $mmol_c$ L^{-1} based on titration (which also includes non-C proton-accepting ligands such as HPO_4^{2-}).

Comparison of the two methods of pIAP calculation is provided in Fig. 7 for the laboratory reactions of soil and deionized water. With one exception, all values are calcite supersaturated when evaluated using the Ca^{2+} electrode measurements and inorganic C alkalinity. All values are supersaturated based on calculated Ca^{2+} activities. The differences in pIAP values with the two calculation methods are generally < 0.1. The degree of calcite supersaturation for these waters is only slightly reduced by correcting for possible organic complexation. As shown in Fig. 6, there is no significant correlation between the amount of DOC present and the pIAP values calculated from total concentrations using the computer model speciation. This result is not surprising, since these waters contain ≈ 10 times more DOC than the groundwaters described above. All of the soil waters therefore contain sufficient organic matter to inhibit calcite crystal growth. The lack of a relation between increasing DOC and

Table 4. Chemical analyses of soil water obtained with an extractor from a field previously cropped to wheat.

| Soil water sample	pH	Ca	Mg	Na	K	Cl	Total alkalinity	Inorganic C alkalinity	SO_4	NO_3	Dissolved organic C
							mmol L^{-1}				
1 N 06	7.27	2.48	2.11	17.71	0.07	9.20	9.00	8.93	2.98	2.79	1.24
1 N 09	6.92	5.68	5.41	10.61	0.17	16.39	8.80	8.75	3.34	0.73	0.94
1 N 12	6.72	7.42	5.89	15.17	0.12	29.72	7.18	7.14	2.13	0.74	0.53
1 S 06	7.23	2.20	1.90	12.09	0.06	5.88	8.25	8.19	2.39	1.69	1.02
1 S 09	7.04	3.55	2.91	9.65	0.11	6.41	9.80	9.75	2.63	1.03	0.84
1 S 12	6.88	3.74	3.07	9.99	0.12	10.18	8.90	8.82	2.01	1.10	0.72
2 S 06	6.94	7.98	4.31	11.65	0.05	14.06	6.30	6.28	5.73	4.77	0.92
2 S 09	6.88	6.20	2.75	8.66	0.10	13.59	7.60	7.53	2.17	1.10	0.43
2 S 12	6.82	4.41	2.02	11.44	0.08	11.47	8.60	8.51	1.54	1.16	0.53
2 N 06	6.92	8.89	4.81	13.14	0.03	20.41	5.68	5.62	5.50	3.51	0.90
2 N 09	6.85	8.04	3.45	13.53	0.12	25.98	6.45	6.38	1.53	1.30	0.45
2 N 12	6.99	3.86	2.05	13.48	0.10	8.19	9.68	9.63	2.42	2.01	0.73
6 S 12	7.08	3.37	2.93	16.93	0.13	12.67	10.58	10.54	2.36	1.52	0.95
6 N 12	6.87	4.74	4.07	13.79	0.17	18.82	7.53	7.49	1.74	1.00	0.63
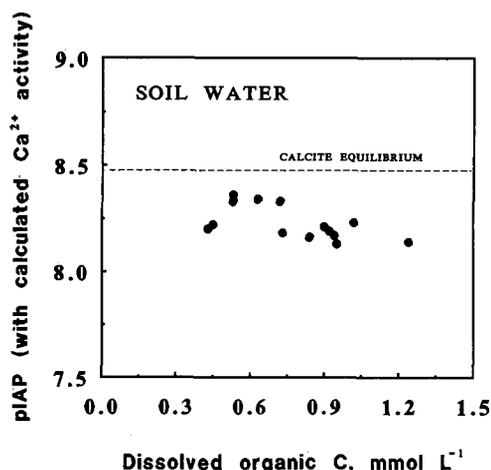
Fig. 8. Ion activity products (IAP) of $(Ca^{2+})(CO_3^{2-})$ in unsaturated-zone field samples calculated using the analytical data with Ca concentration and total alkalinity vs. dissolved organic C in solution. The line indicates a pIAP value of 8.48 for equilibrium with pure calcite.

decreasing pIAP (Fig. 6) suggests that organic complexation is not the cause of the relatively small discrepancies between pIAP values calculated from Ca^{2+} electrode values vs. calculated Ca^{2+} activities. Based on analysis of variance of pIAP data for all soils, treatments and replicates, only 1.4% of the total variance is due to replicates and associated analytical errors and 98.6% is caused by treatment or soil differences.

Unsaturated Zone Soil Waters

The analyses in Table 4 represent soil waters collected from the field with extractors. Calculated Ca^{2+} activities are between 0 and 26% higher than values measured by electrode (data not shown). Again, it is unlikely that these values are due to Ca–organic complexation, since the DOC values indicate a maximum of 77 μmol L^{-1} of Ca–organic complexation. This represents only $\approx 1\%$ of the total Ca in solution. Total alkalinity and inorganic C alkalinity values are almost identical, with only 0.056 $mmol_c$ L^{-1} attributed to organic C alkalinity. This value is in agreement with the value of 0.028 $mmol_c$ L^{-1} organic alkalinity, calculated from the mean DOC value of 0.77 $mmol$ L^{-1}. As shown in Fig. 8, all extractor waters are calcite

supersaturated and differences in pIAP values are relatively small between the two calculation methods.

DISCUSSION

The mean pIAP values for $(Ca^{2+})(CO_3^{2-})$ are presented in Table 5. Measurement of Ca^{2+} activity by electrode and correction of alkalinity for organic anions shifted the mean pIAP value of the groundwaters only from 7.98 to 8.01. Thus the solutions are still calcite supersaturated with a saturation ratio $(IAP/K_{calcite})$ ≈ 3. The mean pIAP value of 8.01 in this study compares very closely with the mean value of 7.97 reported by Suarez for different well waters from the same region. This result indicates that earlier reported values were in fact highly supersaturated, and that a mean pIAP around 8.0 apparently represents a metastable state for calcite precipitating from groundwaters in the presence of organic inhibitors. A comparison of calculations using the WATEQ4F program and the speciation program used by Suarez (1977) indicated that pIAP values were only 0.01 to 0.02 higher using the WATEQ4F model.

The mean calculated pIAP value for laboratory soil–water reactions at laboratory CO_2 concentrations is 8.11 based on measured Ca^{2+} activity and inorganic C alkalinity, and the value is 8.00 based on the calculated Ca^{2+} activity and total alkalinity. The pIAP values at 10 kPa CO_2 are 8.10 and 8.04, respectively (Table 5). If Ca–organic complexation and organic anion alkalinity are responsible for these differences, the differences in pIAP values would be expected to be much greater at low CO_2. Given constant amounts of organic matter and assuming strong Ca–organic complexes, a greater percentage of Ca would be complexed and a greater percentage of the alkalinity would be present as organic C alkalinity at lower CO_2 levels. Since differences in pIAP were not greater at low CO_2 this suggests that the small differences in pIAP are caused by factors other than Ca–organic complexation.

The pIAP values for the laboratory reactions from this study indicate a greater degree of supersaturation than for other arid land soils also reacted under initially undersaturated conditions (Suarez and Rhoades, 1982). We consider these differences to be due to increased amounts of inorganic C alkalinity resulting from decomposition of solid-phase soil organic matter during the 26-d reaction time. This process was de-

Table 5. Statistics for the negative log of the ion activity product (pIAP) values of (Ca^{2+}) (CO_3^{2-}) calculated two different ways.

	Computation method aCa²⁺/Alkalinity	Mean	Standard error	Min.	Max.	n
Groundwater						
	Electrode/inorganic	8.01	0.03	7.84	8.34	18
	Calculated/total	7.98	0.03	7.79	8.32	18
Suarez, 1977	Calculated/total	7.97	0.03	7.77	8.23	28
Lab reactions						
Air	Electrode/inorganic	8.11	0.04	7.90	8.53	24
Air	Calculated/total	8.00	0.04	7.74	8.40	24
10 kPa CO₂	Electrode/inorganic	8.10	0.03	7.83	8.32	24
10 kPa CO₂	Calculated/total	8.04	0.04	7.71	8.28	24
Soil water (field)						
	Electrode/inorganic	8.26	0.02	8.11	8.38	14
	Calculated/total	8.24	0.02	8.14	8.37	14

scribed by Amrhein and Suarez (1987). The soils used here are expected to have greater amounts of organic matter decomposition than those used by Suarez and Rhoades (1982) because, for this study, we specifically selected soils from sites recently cropped and abundant in fresh organic matter. This was done in an attempt to get the maximum possible DOC values and Ca–organic complexation. Assuming that the calcite present in each soil is thermodynamically stable, we would ordinarily expect a reaction approached from undersaturation to equilibrate to the pIAP value for calcite. In these experiments, however, additional inputs of alkalinity during the equilibration process (from decomposition of solid-phase organic matter) results in calcite supersaturation.

The mean pIAP values for soil waters obtained directly from the field with extractors in the unsaturated zone are comparable for both computation methods (with a mean value of 8.26 for values based on measured Ca^{2+} activity vs. a mean of 8.24 for calculated values of Ca^{2+} activity). Note that the groundwater and laboratory equilibrations are less supersaturated than the field soil water data. We attribute these lower levels of supersaturation from the field system to the fact that the Pachappa soil is noncalcareous and that the waters had not yet reached a level of supersaturation sufficient for calcite precipitation at these soil CO_2 partial pressures.

We investigated the sensitivity of the saturation calculations to potential errors in temperature and pH by the following simulations. Using the analyses of well water sample no. 21a (Table 2), we ran simulations at various temperatures and pH using WATEQ4F. Changing the temperature from 25 to 20 and 30 °C changed the pIAP by only 0.04 and -0.03, respectively. Similarly, changing the pH from 7.47 to 7.37 and 7.57 changed the pIAP by 0.10 and -0.10, respectively. Based on these calculations, we consider that the maximum likely temperature errors of ± 1 °C and pH errors of ± 0.05 would produce minor changes in the saturation studies of any of these waters.

The DOC data reported by Reddy et al. (1990) can be used to obtain an estimate of Ca–organic complexation and organic C alkalinity. The DOC values reported by Reddy et al. (1990) ranged from 1.23 to 7.24 mmol L^{-1}, with a mean value of 3.4 mmol L^{-1}. Although their DOC values are somewhat larger than the values reported by us, they still appear to be much too low to be consistent with the organic anion alkalinity values reported in the same study. The differences between values obtained by conventional titration and total carbonates based on CO_2 release ranged from 0.46 to 2.46 mmol L^{-1} with a mean of 1.14 mmol L^{-1} noncarbonate alkalinity (calculated from the data of Reddy et al., 1990, Table 2). Using the model of Oliver et al. (1983) to calculate organic alkalinity from DOC, we would expect the mean DOC value of 3.4 mmol L^{-1} from Reddy et al. (1990) to produce only 0.19 mmol$_c$ L^{-1} of organic C alkalinity. By using this value of 0.19 mmol$_c$ L^{-1} to correct the total alkalinity values, one also obtains calcite supersaturation of the samples investigated by Reddy et al. (1990).

Corrections of organic C alkalinity to total alkalinity tend to be insignificant for soil waters under field conditions. These waters are typically at much greater CO_2 levels than atmospheric CO_2, and thus, under field conditions, typically contain more inorganic C than the 0.87 mmol total C reported by Reddy et al. (1990). Further, as noted by Reddy et al. (1990), Nightingale and Smith (1967) found high Ca–organic complexation in extracts from sodic soils of high pH. Since the samples had not been filtered, it is likely that the majority of the organic material characterized as dispersed was present as a suspended solid phase. Adsorption of Ca by organic matter probably results in formation of a stable precipitate that remains as part of the soil solid phase in the pH range of 6 to 8.5. Stumm and Morgan (1981) postulated that this coagulation process explains why surface waters with Ca^{2+} and Mg^{2+} concentrations $>10^{-3}$ M contain almost no humic substances (<1 mg C L^{-1}). This process also explains the high DOC values of 50 mg L^{-1} or 4 mmol L^{-1} reported by Antweiler and Drever (1983). These DOC values are consistent with the low pH (5.2) and low Ca values (0.1 mmol L^{-1}) reported by these authors. Even when using these values, one obtains calculated organic alkalinity values of only 0.11 mmol$_c$ L^{-1} for titration to pH 4.4 and a maximum potential Ca complexation of 0.25 mmol L^{-1}. Such values are much too low to explain calcite supersaturation in our systems.

Organic C alkalinity is an insignificant component of total alkalinity for the soil–water systems we examined. The low values of organic C alkalinity are consistent with the measured DOC values for these waters. Although measured Ca^{2+} activities were lower than calculated values, we do not consider this observation to be the result of Ca–organic complexation. Such a hypothesis is incompatible with the DOC values determined. Calcite supersaturation in these systems gives saturation ratios of two to three using either calculated or measured values of Ca^{2+} activity. We consider that calcite supersaturation results from concentration via evapotranspiration combined with additional sources of inorganic C alkalinity and inhibition of calcite crystal growth by low concentrations of dissolved organic matter. The analyzed DOC concentrations are at levels sufficient to completely inhibit calcite crystal growth and thus maintain metastable calcite supersaturation. Additional research is needed to determine why computed Ca^{2+} activities are higher than electrode determinations of Ca^{2+} activity.

REFERENCES

Amrhein, C., and D.L. Suarez. 1987. Calcite supersaturation in soils as a result of organic matter mineralization. Soil Sci. Soc. Am. J. 51:932–937.

Antweiler, R.C., and J.I. Drever. 1983. The weathering of a late Tertiary volcanic ash: Importance of organic solutes. Geochim. Cosmochim. Acta 47:623–629.

Ball, J.W., D.K. Nordstrom, and D.W. Zachmann. 1987. WATEQ4F—A personal computer fortran translation of the geochemical model WATEQ2 with revised data base. U.S. Geol. Surv. Open-File Rep. 87-50. USGS, Menlo Park, CA.

Cole, C.V. 1957. Hydrogen and calcium relationships of calcareous soils. Soil Sci. 83:141–150.

Inskeep, W.P., and J. Baham. 1983. Competitive complexation of Cd(II) and Cu(II) by water-soluble organic ligands and Na-montmorillonite. Soil Sci. Soc. Am. J. 47:1109–1115.

Inskeep, W.P., and P.R. Bloom. 1986a. Calcium carbonate supersaturation in soil solutions of Calciaquolls. Soil Sci. Soc. Am. J. 50:1431–1437.

Inskeep, W.P., and P.R. Bloom. 1986b. Kinetics of calcite precipitation in the presence of water soluble organic ligands. Soil Sci. Am. J. 50:1167–1172.

Nightingale, H.I., and R.L. Smith. 1967. Evidence for the presence of calcium–organic complexes in sodic soil. Soil Sci. 103:261–264.

Marion, G.M., and K.L. Babcock. 1977. The solubilities of carbonates and phosphates in calcareous soil suspensions. Soil Sci. Soc. Am. J. 41:724–728.

Oliver, B.G., E.M. Thurman, and R.L. Malcolm. 1983. The contribution of humic substances to the acidity of colored natural waters. Geochim. Cosmochim. Acta 47:2031–2035.

Olsen, S.R., and F.S. Watanabe. 1959. Solubility of calcium carbonate in calcareous soils. Soil Sci. 88:123–129.

Plummer, L.N., and E. Busenberg. 1982. The solubilities of calcite, aragonite and vaterite in CO_2–H_2O solutions between 0 and 90 °C, and an evaluation of the aqueous model for the system $CaCO_3$–CO_2–H_2O. Geochim. Cosmochim. Acta 46:1011–1040.

Reddy, K.J., W.L. Lindsay, S.M. Workman, and J.I. Drever. 1990. Measurement of calcite ion activity products in soils. Soil Sci. Soc. Am. J. 54:67–71.

Reynolds, R.C., Jr. 1978. Polyphenol inhibition of calcite precipitation in Lake Powell. Limnol. Oceanogr. 23:585–597.

Sposito, G., and S.V. Mattigod. 1979. GEOCHEM: A computer program for the calculation of chemical equilibria in soil solutions and other natural water systems. Kearny Found. of Soil Sci., Univ. of California, Riverside.

Suarez, D.L. 1977. Ion activity products of calcium carbonate in waters below the root zone. Soil Sci. Soc. Am. J. 41:310–315.

Suarez, D.L. 1986. A soil water extractor that minimizes CO_2 degassing and pH errors. Water Resour. Res. 22:876–880.

Suarez, D.L., and J.D. Rhoades. 1982. The apparent solubility of calcium carbonate in soils. Soil Sci. Soc. Am. J. 46:716–722.

Stumm, W., and J.J. Morgan. 1981. Aquatic chemistry. 2nd ed. John Wiley & Sons, New York.