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PRODUCTS IN SOILS

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ABSTRACT

Soils often show supersaturation with respect to calcite. This study was undertaken to test alternative methods of measuring Ca^{2+} and CO_3^{2-} activities to assess their effects on measured ion-activity products (IAP) of calcite in soils. Soils were reacted with atmospheric $CO_2(g)$ and distilled H_2O for 1, 3, and 7 d. The soil extracts were analyzed for pH, electrical conductivity (EC), cations, anions, and dissolved organic carbon (DOC). Carbonate activities in soil extracts were obtained by two methods. The first consisted of titrating the soil extracts with standard HCl to pH 4.0 (direct-titration method). The second method consisted of acidifying soil extracts to pH 4.0 and trapping the evolved CO_2 gas in a $NaOH + BaCl_2$ solution (CO_2 gas release method). The IAP values for calcite were calculated in two ways. First, Ca^{2+} activity was obtained by speciating total soluble Ca while CO_3^{2-} activity was obtained from the direct titration of soil extracts. This method gave mean log IAP values of calcite ranging from -7.90 to -7.78 compared with a log K^o $(Ca^{2+})(CO_3^{2-})$ (equilibrium constant) of -8.48 for calcite. These results suggest supersaturation with respect to calcite. Secondly, when Ca^{2+} activity was measured with a Ca^{2+}-specific ion electrode and CO_3^{2-} activity was estimated by the CO_2 gas release method, the mean log IAP values of calcite ranged from -8.45 to -8.35, which is very near equilibrium with calcite. The apparent supersaturation in the first case was probably caused by DOC, which both complexed Ca^{2+} and contributed to titratable alkalinity over that of carbonate and bicarbonate alone.

C ALCITE ($CaCO_3$) strongly buffers soils near pH 8 and affects the equilibrium relationships of many other elements (Lindsay, 1979). Therefore, calcite solubility relationships in soils need to be clearly defined.

Several researchers have examined calcite solubility in soils and have reported supersaturation (Cole, 1956; Olsen and Watanabe, 1959; and Levy, 1981). Suarez (1977) examined the relationships among pH, Ca^{2+}, and HCO_3^- concentrations in waters below the root zone and reported that attainment of calcite equilibrium in soil waters was very slow. Suarez and Rhoades (1982) attributed calcite supersaturation in soils to silicate minerals such as anorthite, which are more soluble than calcite. Inskeep and Bloom (1986) suggested that supersaturation of calcite in soils occurs as a result of inhibition of calcite precipitation due to soluble organic components.

Recently, Amrhein and Suarez (1987) attributed calcite supersaturation to organic-matter mineralization. These authors use a double-titration method to determine alkalinity: once in the presence of CO_2 and once in its absence. They showed that calcite-organic systems showed supersaturation to calcite, but they did not extend their studies to include soils. In all of these studies except Amrhein and Suarez (1987), Ca^{2+}

activity was calculated from the Ca concentration measured by atomic absorption (AA) or ICP, and CO_3^{2-} activity was calculated from total alkalinity. It is hypothesized that most methods overestimate Ca^{2+} and CO_3^{2-} activities because dissolved organic species form complexes with Ca, and also contribute to total alkalinity in soil extracts.

The objective of the present study was to test other methods of measuring Ca^{2+} and CO_3^{2-} activities in soil and to determine their effect on the measured IAP of calcite in soils. The method makes use of CO_2-gas release from soil extracts as a measure of total carbonate species in solution, which are then speciated to give CO_3^{2-} activity. In addition, the specific Ca-ion electrode was used to measure Ca^{2+} activity in soil extracts.

MATERIALS AND METHODS

Three soils were used in this study. Soil 1 was collected at Fort Collins, CO; Soil 2 at Loveland, CO; and Soil 3 at Laramie Range, WY. Soil 1 is classified as Otero, a coarse-loamy, mixed (calcareous), mesic Ustic Torriorthent. Soil 2 is classified as Nunn, a fine, montmorillonitic, mesic Aridic Argiustoll. Soil 3 is classified as a fine-loamy over sandy or sandy-skeletal Borollic Haplargid. These soils were analyzed for selected properties including texture (Soil Conservation Service, 1984, p. 15–17), $CaCO_3$ equivalent (Workman et al., 1988), and organic C (Snyder and Trofymow, 1984). Selected properties of these soils are presented in Table 1. Samples were air dried and ground to pass a 0.25-mm sieve. The sieved samples were used for x-ray diffraction analysis and for the equilibrium studies. For x-ray diffraction analysis, the soil samples were powdered finely by grinding under acetone and x-rayed using Cu $K\alpha$ radiation at 2° 2θ per minute. Calcite was identified by the presence of a sharp peak at 29.50° 2θ.

Duplicate 25-g samples of soil were suspended in 250-mL flasks with 100 mL of distilled deionized H_2O. Laboratory air was moisturized by passing it through distilled deionized H_2O, which was then bubbled through the soil suspensions. All samples were shaken at 25 °C on a mechanical shaker at 100 oscillations per minute. Three drops of toluene were added to the soil suspensions to suppress microbial activity. After reacting for 1, 3, and 7 d, the soil suspensions were centrifuged. The supernatant solutions were filtered using 0.45-μm Millipore filters. The clear filtrates were measured immediately for pH, EC and total carbonates, and later the same day for cations, anions, and DOC.

The pH was measured with a combination glass-calomel electrode, and EC was measured with a conductivity meter. Measurements of Ca, Mg, Al, Sr, Ba, Na, K, Si, B, and Mo were made by inductively coupled plasma optical-emission spectrometry (ICP-OES). Specific-ion electrodes were used to measure Cl^- and F^- activities, while SO_4 was measured by the turbidometric $BaCl_2$-precipitate method, NO_3 by ion

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Table 1. Selected properties of the soils used in the study.†

Property	Soil 1	Soil 2	Soil 3
Texture	Sandy loam	Clay	Sandy clay loam
$CaCO_3$ equivalent, %	4.80	11.60	6.5
Organic C, %	0.92	1.47	0.42

† Soil 1 is Otero series (a Ustic Torriorthent), Soil 2 is Nunn series (an Aridic Argiustoll), and Soil 3 is a Borollic Haplargid.

chromatography, and P with ascorbic acid molybdotartrate. Dissolved organic C was measured with an organic C analyzer. Boron, Mo, and P were found to be <0.01 mg/kg in all soil solutions. Calcium activity in soil solutions was measured with an Orion specific-ion electrode (Model 93-20; Orion Laboratories Group, Cambridge, MA). The electrode was calibrated with a $CaCl_2$ standard (provided by Orion). Several studies (Lindsay and Elrashidi, 1985; Amrhein and Suarez, 1989) successfully used the specific-ion electrode to measure Ca^{2+} activities in media containing organics.

Carbonate species in soil extracts were measured by two methods. The first method consisted of titrating the soil extracts with standard HCl to pH 8.3 (carbonate) and to pH 4.0 (bicarbonate) using a pH electrode (direct-titration method). The second method is represented in Fig. 1. An Ar tank was connected through a flow meter to an ascarite flask used to remove any traces of $CO_2(g)$ from the Ar. The ascarite flask was connected to the sample chamber through a peristaltic pump. An acid burette was inserted into the sample chamber to deliver acid to the sample. The sample chamber was connected to a $CO_2(g)$-trapping chamber.

Argon gas was passed through the system to purge other gases. Ten mL of soil extract was then placed in the sample chamber. Ten mL of NaOH (0.01–0.001 M depending on the amount of carbonates present), 1.0 mL of 0.05 M $BaCl_2$ solution, and three drops of phenolphthalein were placed in the $CO_2(g)$-trapping chamber. A combination pH electrode (calibrated with pH 8.0 and 12.0 buffers) and an acid burette were inserted into the $CO_2(g)$-trapping chamber. The pH electrode was connected to an Orion pH meter to monitor pH of the NaOH + $BaCl_2$ solution. One magnetic stirrer was placed under the sample chamber, and a second stirrer was placed under the $CO_2(g)$-trapping chamber to keep both solutions well mixed. At the start of each measurement, the plastic tube was disconnected at A and connected to the gas outlet (10). The soil extract in the sample chamber was acidified to pH 4.0 with standard dilute HCl. The evolved $CO_2(g)$ from the sample was circulated through the NaOH + $BaCl_2$ solution for 1 h by the peristaltic pump. The $CO_2(g)$ entering into the NaOH + $BaCl_2$ trap precipitated as $BaCO_3$ and released 2 moles of H^+ per mole of entering $CO_2(g)$. The released H^+ was neutralized by the NaOH, and the excess NaOH was back titrated with standardized HCl to pH 8.3. From this measurement, and a blank treated in the same manner, total carbonate species in the initial soil extracts were calculated.
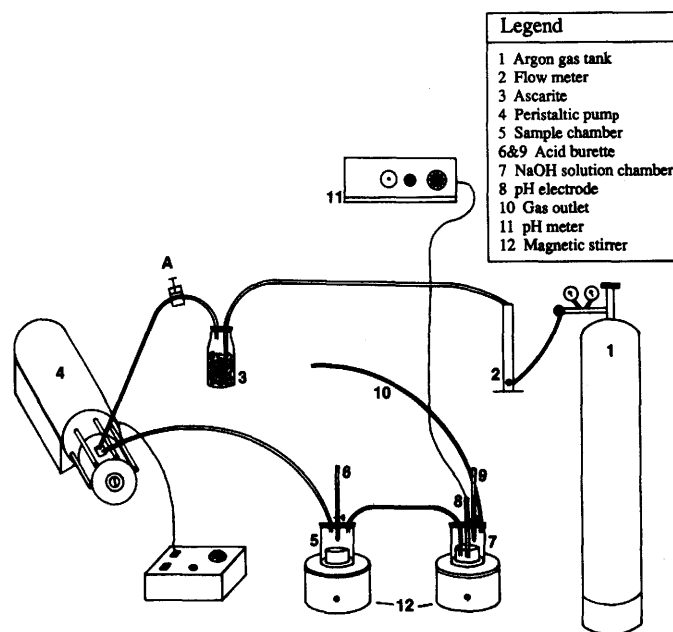

Fig. 1. Experimental setup to measure carbonate species in soil solutions.

Legend
1 Argon gas tank
2 Flow meter
3 Ascarite
4 Peristaltic pump
5 Sample chamber
6&9 Acid burette
7 NaOH solution chamber
8 pH electrode
10 Gas outlet
11 pH meter
12 Magnetic stirrer

Standards consisting of 0.50, 1.00, 5.0, and 10.0 mM $NaHCO_3$ solutions showed excellent recoveries ($r^2 = 0.999$) using this method (hereafter referred to as the $CO_2(g)$-release method). The SOILEQ computer model (Reddy, 1986) was used for the speciation calculations. This program utilizes total elemental concentrations, pH, and EC to calculate equilibrium activities and $CO_2(g)$ partial pressure. All solution species reported by Lindsay (1979) that contribute greater than 1% of the elemental concentrations in soil extracts were included in the speciation model.

RESULTS AND DISCUSSION

Selected properties of the soils used in this study are given in Table 1. The soils differed in organic C, texture, and $CaCO_3$ equivalent. Partial analytical data for the soil extracts from these soils are presented in Table 2. The results show that total carbonates measured by

Table 2. Partial analytical data of soil solution extracts†

| Soil sample‡ | pH | Ca | Mg | Na | K | Total Carbonates | | SO₄ | NO₃ | Cl | DOC§ |
						Titration	CO₂ release				
						–log mol L⁻¹					
						1-d reaction					
1	8.34	3.32	3.95	5.70	3.66	2.88	3.07	5.68	<5.15	4.27	2.91
2	8.33	2.89	3.21	2.69	3.09	2.65	3.00	3.23	3.85	3.02	2.69
3	8.30	2.26	3.05	1.76	3.13	2.65	2.95	1.97	2.31	3.74	2.19
						3-d reaction					
1	8.28	3.15	3.52	3.77	3.54	2.84	3.10	<6.00	3.44	3.97	2.80
2	8.20	2.88	3.24	2.80	3.32	2.76	3.10	3.30	3.37	3.14	2.71
3	8.35	2.25	3.08	1.70	3.11	2.56	3.00	1.96	2.27	3.74	2.19
						7-d reaction					
1	8.30	3.04	3.60	4.70	3.35	2.86	3.07	<6.00	3.00	3.97	2.86
2	8.30	2.90	3.23	2.96	3.22	2.76	3.10	3.22	3.15	3.18	2.65
3	8.35	2.16	3.00	1.79	3.21	2.51	3.20	1.97	3.19	3.64	2.14

† Average of duplicate analysis.
‡ Defined in Table 1.
§ Total dissolved organic C.

Table 3. Comparison of Ca^{2+} and CO_3^{2-} activities in soil extracts obtained by different methods.†

| Sample‡ | Ca^{2+} | | CO_3^{2-} | | |
	Speciation of total Ca	Electrode	Direct-titration method	CO_2 (g)-release method	Dissolved organic C
			($-\log$ mol L^{-1})		
Soil 1	3.27	3.38	4.91	5.13	2.85
Soil 2	3.09	3.24	4.83	5.18	2.67
Soil 3	2.70	3.11	4.71	5.18	2.16

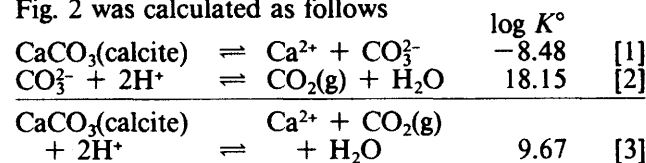† Average of 1-, 3-, and 7-d reaction time and duplicate analysis.
‡ See Table 1 for description.

the direct-titration method were consistently higher than those measured by the CO_2(g)-release method. Soil extracts having the higher levels of DOC showed higher levels of carbonates when measured by the direct-titration method ($r^2 = 0.829$). When measured by the CO_2(g)-release method, there was no correlation ($r^2 = 0.014$). The latter method should provide a more accurate estimate of carbonates in soil extracts than the direct-titration method. Furthermore, as DOC in the soil extracts increased, Ca concentrations measured by ICP also increased ($r^2 = 0.975$).

The Ca^{2+} and CO_3^{2-} activities in the soil extracts obtained by the different methods are presented in Table 3. When DOC in the soil extracts was low, the Ca^{2+} activity obtained by speciating total soluble Ca was only slightly greater than that from the Ca^{2+} electrode. As DOC increased, the difference between the two methods increased. Similarly, when DOC increased, the activity of CO_3^{2-} measured by the direct-titration method increased over that measured by the CO_2(g)-release method. The CO_2(g) calculated for the CO_2(g)-release method ($10^{-4.6}$ MPa) was near atmospheric CO_2 ($10^{-4.52}$ MPa), whereas the CO_2(g), calculated using the direct-titration method ($10^{-4.26}$ MPa), was higher than the expected atmospheric CO_2. These results suggest errors in the measurements of both Ca^{2+} and CO_3^{2-} activities with increasing DOC in the extracts, unless appropriate methods are used to measure ion activities.

The IAP of calcite calculated from Ca^{2+} and CO_3^{2-} activities estimated from different methods are presented in Table 4. These findings show that the mean log IAP values of calcite in soil extracts calculated from Ca^{2+} activity based on total Ca concentration measured by ICP, and from CO_3^{2-} activity based on carbonate species measured by the direct-titration method, ranged from -7.90 to -7.78. The mean log IAP values of calcite in soil extracts calculated from Ca^{2+}-ion-electrode measurements and CO_3^{2-} activity from the CO_2(g)-release method ranged from -8.35 to -8.45.

The equilibrium constant for calcite used to develop Fig. 2 was calculated as follows

			$\log K°$	
$CaCO_3$(calcite)	$\rightleftharpoons$	$Ca^{2+} + CO_3^{2-}$	-8.48	[1]
$CO_3^{2-} + 2H^+$	$\rightleftharpoons$	$CO_2(g) + H_2O$	18.15	[2]
$CaCO_3$(calcite) + $2H^+$	$\rightleftharpoons$	$Ca^{2+} + CO_2(g) + H_2O$	9.67	[3]

The $K°$ for Reactions [1] and [2] were taken from Plummer and Busenberg (1982) and Lindsay (1979), respectively.

Table 4. Comparison of ion activity product (IAP)† of calcite in soils calculated from Ca^{2+} and CO_3^{2-} activities measured by different methods.‡

Reaction time	Soil 1§	Soil 2	Soil 3	Mean
d				
	log IAP calculated using Ca^+ from speciation and CO_3^{2-} from direct-titration method			
1	-8.31	-7.85	-7.56	-7.90
3	-8.16	-7.99	-7.43	-7.86
7	-8.07	-7.99	-7.29	-7.78
	log IAP calculated using Ca^{2+} from electrode and CO_3^{2-} from CO_2 (g)-release method			
1	-8.49	-8.32	-8.22	-8.35
3	-8.58	-8.53	-8.23	-8.44
7	-8.48	-8.45	-8.43	-8.45

† Mean of duplicate analysis, log IAP = log Ca^{2+} + log CO_3^{2-} compared to log equilibrium constant ($K°$) = -8.48 (Plummer and Busenberg, 1982).
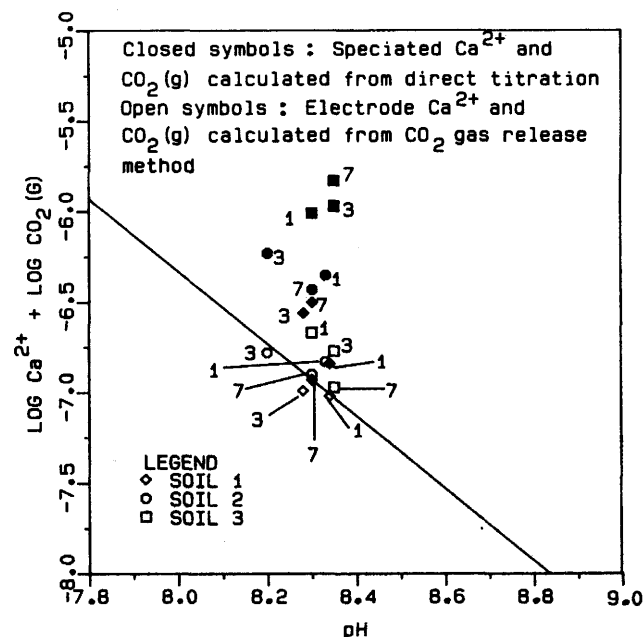‡ Average of duplicate analyses.
§ Soils described in Table 1.

Fig. 2. The relationship between log Ca^{2+} and log CO_2(g) vs. pH for calcite solubility in soils. The numbers identifying the experimental points represent the equilibration period in days.

The results show that speciation of Ca^{2+} in soil extracts based on Ca concentrations measured by ICP and calculation of CO_2(g) partial pressure based on the direct-titration method resulted in apparent supersaturation with respect to calcite. On the other hand, Ca^{2+} activities in soil extracts measured with the Ca^{2+}-specific-ion electrode and calculation of CO_2(g) partial pressure based on the CO_2(g)-release method lie very near the calcite-solubility line, suggesting that calcite is probably controlling the activities of Ca^{2+} and CO_3^{2-} in these soils. All of the 7-d points are almost exactly on the calcite line.

A plot of log IAP vs. pH shown in Fig. 3 summarizes the findings of several workers. Included in this figure are IAP values of calcite in groundwater reported by Suarez (1977) and in soil extracts reported by Inskeep and Bloom (1986), as well as the IAP val-
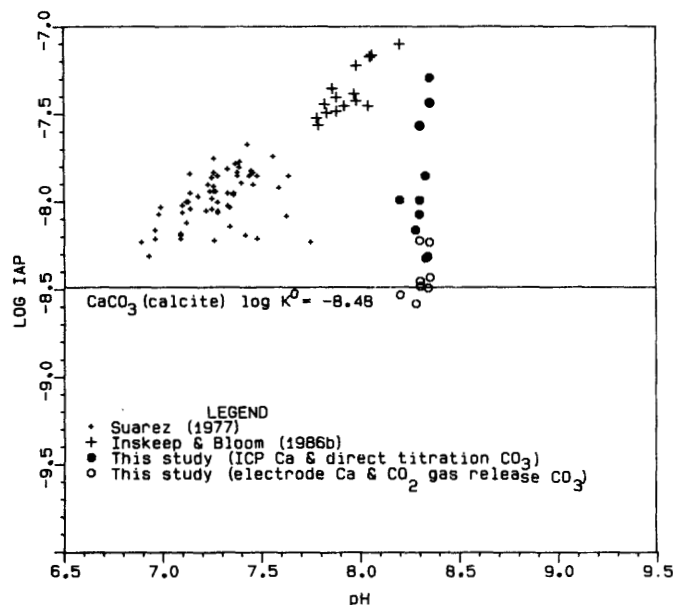
Fig. 3. The log ion-activity products (IAP) vs. pH for calcite solubility in soils.

ues of calcite reported in this study. The IAP values reported by Suarez (1977), Inskeep and Boom (1986), and those from this study shown by closed symbols are based on Ca^{2+} activities calculated from Ca concentrations measured by AA or ICP, and on CO_3^{2-} activities calculated from the direct-titration method. These measurements all show supersaturation of calcite. The open symbols in this figure represent IAP values of calcite obtained in this study when Ca^{2+} activity was measured with a Ca^{2+}-specific-ion electrode and CO_3^{2-} activity was calculated from the $CO_2(g)$-release method. Only the latter IAP value lies near the calcite-solubility line, suggesting equilibrium with calcite.

Two reasons are proposed for the widely reported calcite supersaturation in soils: First, dissolved organic matter in the soil solution complexes Ca^{2+} and leads to an overestimation of Ca^{2+} activity. Since AA and ICP-OES measure total soluble Ca, this measurement includes both organic and inorganic forms. Secondly, during direct titration of soil extracts to determine carbonate species, dissolved organic matter may also adsorb some protons, which results in an overestimation of CO_3^{2-} activity. Use of pH 4.0 instead of 4.4 for the estimation of total alkalinity of soil extracts in this study is expected to be of minor significance. Certainly all carbonates are removed in the pH range of 4.0 to 4.4 and poor buffering capacity of the extracts observed during the titrations suggest very little proton acceptance by soluble organics.

Moreno et al. (1960) showed that Ca-organic complexes occur in soils near granules of dissolving $CaHPO_4 \cdot 2H_2O$. When total Ca in solution was used to calculate Ca^{2+} activity, the soils appeared to be oversaturated with $CaHPO_4 \cdot 2H_2O$. When activated C was added to the soil-fertilizer suspension prior to filtration, the organic complexes were adsorbed by the activated C and were retained on the solid matrix during filtration. Speciation of Ca in the resulting filtrate then showed equilibrium with $CaHPO_4 \cdot 2H_2O$. These workers concluded that the activated C removed Ca-organic complexes and thereby eliminated the apparent supersaturation.

Antweiler and Drever (1983) studied the role of organic solutes in the weathering of volcanic ash by examining the chemistry of waters passing through the soil zone. These workers reported that organic compounds, largely humic acids derived from vegetation, significantly complex metal cations including Ca^{2+}.

Nightingale and Smith (1967) also presented evidence of Ca organic complexes in sodic soils. Willey et al. (1975) reported that some short chain aliphatic anions (acetate and propionate) in oil field waters contributed to the titratable alkalinity above that of carbonate and bicarbonate. The observed supersaturation with respect to calcite could be due to overestimation of carbonate concentrations. Hem (1985) reported that during the direct titration of solutions to measure carbonate species, dissolved organic compounds can adsorb protons and contribute to an overestimation of carbonate species.

Several factors may contribute to the often-observed supersaturation of soils with respect to calcite. These may include high production of CO_2, organic-matter mineralization, slow precipitation of calcite, inhibition of precipitation by organic-matter absorption, and incorporation of other ions in crystal lattices. The most striking feature demonstrated in this study is that IAPs reported in the literature are very similar to those found in this study when total soluble Ca and total titratable alkalinity are used to calculate activities, but when special precautions are taken to eliminate the effects of organic-matter complexation of Ca^{2+}, and the use of released CO_2 as a measure of carbonates in solution, then the resulting ionic activities of Ca^{2+} and CO_3^{2-} are almost identical to those expected for equilibrium with calcite.

CONCLUSIONS

Dissolved organic matter in soils contributes to apparent calcite supersaturation in two ways: First, dissolved organic matter complexes Ca in soil solutions, which leads to an overestimation of Ca^{2+} activity because both organic and inorganic Ca species are included when AA and ICP methods are used to determine total Ca in soil extracts. Chemical speciation programs commonly ignore complexation of cations by natural DOC. Secondly, the direct titration of soil solutions to estimate CO_3^{2-} includes dissolved organic matter, which also adsorbs protons, and leads to an overestimation of CO_3^{2-} activity. The mean log (IAP) of calcite obtained when Ca^{2+} activities were measured with a Ca^{2+} electrode and CO_3^{2-} activities were estimated from the $CO_2(g)$-release method ranged from -8.35 to -8.45, which is very close to the reported log $K°$ value of -8.48 for calcite.

The $CO_2(g)$-release method appears to be a better method of estimating CO_3^{2-} activity in soil solutions. When Ca^{2+} and CO_3^{2-} activities are appropriately measured, IAPs for calcite correspond very closely to equilibrium with calcite.

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.

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

Hem, J.D. 1985. Study and interpretation of the chemical characteristics of natural water. U.S. Geol. Surv. Water-Supply Pap. no. 2254. U.S. Gov. Print. Office, Washington, DC.

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

Levy, R. 1981. Effect of dissolution of alumino-silicates and carbonates on ionic activity products of calcium carbonate in soil extracts. Soil Sci. Soc. Am. J. 45:250–255.

Lindsay, W.L. 1979. Chemical equilibria in soils. Wiley-Interscience, New York.

Lindsay, W.L., and M.A. Elrashidi. 1985. Experimental measurements of soil Ca solubility relationships in soils. p. 149. *In* Agronomy abstracts. ASA, Madison, WI.

Moreno, E.C., W.L. Lindsay, and G. Osborn. 1960. Reactions of dicalcium phosphate dihydrate in soils. Soil Sci. 90:58–68.

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

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. 1986. The solubility, mobility, and plant uptake of toxic elements in retorted oil shales as affected by recarbonation. Ph.D. thesis. Colorado State Univ., Fort Collins (Diss. Abstr. 87–05479).

Snyder, J.D., and J.A. Trofymow. 1984. A rapid accurate wet oxidation diffusion procedure for determining organic and inorganic carbon in plant and soil samples. Commun. Soil Sci. Plant Anal. 15:587–597.

Soil Conservation Service. 1984. Procedures for collecting soil samples and methods of analysis of soil survey. USDA, Soil Survey Investig. Rep. no. 1. U.S. Gov. Print. Office, Washington, DC.

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

Willey, L.M., Y.K. Kharaka, T.S. Presser, J.B. Rapp, and I. Barnes. 1975. Short chain aliphatic acid anions in oil field waters and their contribution to the measured alkalinity. Geochim. Cosmochim. Acta 39:1707–1711.

Workman, S.M., P.N. Soltanpour, and R.H. Follett. 1988. Soil testing methods used at Colorado State University for the evaluation of fertility, salinity, and trace element toxicity. Tech. Bull. no. LTB88–2. Colorado State Univ., Fort Collins.