The Apparent Solubility of Calcium Carbonate in Soils[1]

D. L. Suarez and J. D. Rhoades[2]

ABSTRACT

Soils in the laboratory were reacted with agricultural drainage- and distilled waters at various carbon dioxide (CO_2) levels. The soil water solutions yielded different ion activity product (IAP) values than that of calcite, depending on experimental technique and whether calcite "equilibrium" is approached from supersaturation or undersaturation. Sample storage conditions affected IAP values as did partial pressure of CO_2 and soil/water ratio. With sufficient reaction time all soil waters became supersaturated with respect to calcite—but to different degrees. The only calcium carbonate ($CaCO_3$) phase detected in these soils was low Mg calcite. Calcium carbonate particles isolated from the soils gave IAP values expected for calcite ($10^{-8.45}$ to $10^{-8.49}$). The calcite supersaturation in soil appears to be due to the presence of silicates in the soil more soluble than calcite, and is not the result of unstable $CaCO_3$ phases. It thus appears inappropriate to try to determine the solubility of soil $CaCO_3$ by reacting soil containing $CaCO_3$ and water in the laboratory. Since soil- and drainage waters are not in equilibrium with calcite (or any other $CaCO_3$ phase), calcite solubility is inappropriate for arid land soil-water models. It is likely that the kinetic factors controlling soil solution composition under field conditions are not simulated by conventional types of laboratory experiments.

Additional Index Words: calcite, supersaturation, feldspar dissolution.

$\mathbf{V}$ARIOUS investigators have reported higher solubilities for soil calcium carbonate ($CaCO_3$) than that of calcite. Among these, Cole (1957) noted that calcium concentrations and pH values increased as the soil/distilled water ratio increased in solutions at fixed carbon dioxide (CO_2) pressures. Part of the reported "supersaturation" resulted from activity coefficients and complexation effects, since the soils must have contained residual salts. Olsen and Watanabe (1959) also reported that the apparent calculated $CaCO_3$ solubility increased as the Pierre clay/distilled water ratio increased. They concluded that clay in the soil increased $CaCO_3$ solubility and that the soils contained small amounts of some $CaCO_3$ material more soluble than calcite. Complete analyses were omitted so their findings cannot be reevaluated by correction for complexing. Doner and Pratt (1968) found no interaction between montmorillonite and $CaCO_3$ solubility. The soil-water ratio effect of $CaCO_3$ solubility might be partially accounted for by formation of $CaSO_4^0$ (Clark, 1964) or other complexes. However, Levy (1981) found calcite supersaturation in soil extracts and decreasing apparent solubility with dilution, even after correction for complexes. Despite speculation that an unstable $CaCO_3$ phase might be present in soils, no special precautions were taken in any of the above studies to allow for its effects.

In almost all of these experiments calcium carbonate was dissolved from the soil; i.e., equilibrium was approached from undersaturation. Using such data to predict the composition of the solution phase resulting from irrigation implicitly assumes (i) that the soil solution resulting from concentration of the irrigation water (by evapotranspiration) equilibrates with the soil solid-phase present, and (ii) that the "freshly" precipitated $CaCO_3$ has the same solubility as the bulk of the soil $CaCO_3$. Neither assumption need be valid. This study was undertaken to investigate these reported anomalous soil $CaCO_3$ solubilities and the appropriateness of using them in predictive soil water models. We also evaluate the potential of Ca silicates to affect Ca and HCO_3 in solution and thus the apparent solubility of $CaCO_3$ in soils.

EXPERIMENTAL PROCEDURES

Subsamples of a variety of soils were air-dried, and various size fractions of each soil were settled on glass slides and x-rayed. Samples were scanned with a Philips diffractometer at 1/8° min from 27° to 37° for the calcite peak (to determine degree of Mg substitution). Soil subsamples were then treated with high CO_2 distilled water until all the calcite was removed and then x-rayed again.

Solution experiments were undertaken to achieve soil water equilibrations from both undersaturation and supersaturation to determine if a reversible equilibrium with a solid phase existed and, if so, to determine its solubility product. To determine if the ion activity product (IAP) values obtained were independent of the amount of dissolution or precipitation, we varied soil water ratios, CO_2 partial pressures, composition of reacting waters, and soil sample pretreatment conditions.

Soil samples (mostly from the 0.90- to 1.20-m depth) were collected from major irrigated valleys along the Colorado River and stored at field moisture content until used (2 to 12 months). The water used to react with their corresponding soils was collected from either a tile-drainage line beneath the soil sampling site or from a soil water extractor placed in the soil at the site. Collected soil and water samples were stored at 4°C. Soil samples were reacted in either Pyrex or polyethylene flasks with their corresponding irrigation drainage water, soil water, or distilled water. The CO_2–air gas mixtures were presaturated with water vapor (distilled water). Additional reactions consisted of calcite and distilled water. For some reactions the CO_2–air mixture was passed through $0.1M$ KCl. Reactant mixtures were stirred only intermittently to avoid grinding of the solid phase which may enhance solubility (Chave and Schmaltz, 1966). The supernatant pH and solute species were periodically determined. Measurements of pH in the clear supernatant (taken after stirring and settling of soil) were buffer-calibrated to within 0.01 units. The pH electrode was inserted into the flask through an access hole in the flask-stopper. Carbon dioxide pressure was calculated from determined solution compositions and measured pH in soil water, calcite water, and KCl water reactions to check for liquid junction potential or suspension errors in the pH measurements. Inclusion of the pure calcite reaction provided a check for systematic errors.

Filtered solutions were analyzed for Ca, Mg, Na, and K by atomic absorption (Ca and Mg after acidification and addition of $LaCl_3$). Alkalinity was determined by titration with acid, chloride by titration with Ag, sulfate by the $BaSO_4$

turbidometric method, and nitrate with a specific ion electrode. Ion activities, complexing, and IAPs were calculated as described earlier (Suarez, 1977).

Experimental conditions for the various experiments are given in Table 1. Some additional experiments are described in the appropriate sequence under "Results and Discussion."

RESULTS AND DISCUSSION

The calcite peaks for all soils fell between 29.42 and 29.52° (2θ). This corresponds to 1 to 3% Mg calcite (Goldsmith et al., 1961). Using the data of Thorstenson and Plummer (1977) and the pure calcite pK of Jacobson and Langmuir (1974), the expected solubility of these low Mg calcites (pK values of 8.47 to 8.53) is lower than that for pure calcite. Peaks found in the regions from 29.8 to 31.0° (Cu K_α 2θ) were attributed to feldspars since they did not disappear upon reaction with CO_2-charged water as did the peaks from 29.42 to 29.52°. Magnesium substitution in the calcite crystal lattice *reduces* the expected solubility of these soil calcites.

Experiment 1a—Drainage and Distilled Water—Low Soil/Water Ratio—Low P_{CO_2}

Partial solution analyses for Experiment *1a* are presented in Table 2.[3] Calculated P_{CO_2}'s were somewhat higher than the CO_2–air mixture (5.07 × 10⁻⁴ atm). This was not due to pH liquid junction or suspension errors, as the distilled water, 0.1*M* KCl, and calcite

treatments all showed this same effect. Also the calcite dissolution experiments yielded pIAPs of around 8.44, close to that for calcite (8.47). Thus it appears that the pHs and calculated P_{CO_2}s are correct. The determined pIAPs for soil $CaCO_3$ reacted with drainage

Table 1—Conditions used in various experiments.

Experiment	Soil	Water	Soil/ water	P_{CO_2}	Reaction time
1a	air-dried	drainage or distilled	0.08	5.07 × 10⁻⁴ atm	2 months
1b	air-dried	drainage or distilled	0.08	2.05 × 10⁻¹ atm	2 months
2	wet†	distilled	2.5	8 × 10⁻² atm	2 weeks
3	wet†	distilled + Ca-HCO₃	1.0	9 × 10⁻¹ atm	2 weeks
4	fresh;† untreated	distilled + Ca-HCO₃	1.0	9 × 10⁻¹ atm	2 weeks
5	fresh;‡ untreated; air-dried; oven-dried	distilled + Ca-HCO₃	1.0	9.65 × 10⁻¹ atm	2 weeks
6	wet	variable-distilled to Ca-HCO₃ water	1.0	9.65 × 10⁻¹ atm	2 weeks
7	fresh; untreated	distilled	1.0	9.65 × 10⁻¹ atm	2 months

† Indicates soils previously stored at 5°C near field-capacity water content.
‡ Indicates collection of soil sample near field-capacity water content and reacted with solution within 48 hours of collection.

Table 2—Partial compositions of supernatants and determined ion activity products obtained in Experiment 1—reaction of drainage and distilled water—low soil/water ratio—low P_{CO_2},† and intermediate P_{CO_2}.

Soil and sample depth	Water	Low CO₂				Intermediate P_{CO_2}			
		pH	Ca	Alkalinity HCO₃	pIAP CaCO₃	pH	Ca	Alkalinity HCO₃	pIAP CaCO₃
			meq/L				meq/L		
Indio,§ 1.2 m	Distilled	8.21	1.86	2.53	8.00	6.48	8.84	12.1	8.48
	Drainage	8.16	18.3	2.66	7.50	6.46	25.9	13.7	8.32
Indio§ (repeat), 1.2 m	Distilled	8.30	1.74	2.40	7.97	6.495	11.1	12.4	8.37
	Drainage	8.19	17.8	3.03	7.41	6.486	25.5	13.8	8.29
Dateland,¶ 0.6 m	Distilled	8.255	1.23	1.65	8.27	6.485	8.55	11.4	8.49
	Drainage	8.33	17.3	2.54	7.37	6.46	26.2	13.3	8.33
Dateland,¶ 1.2 m	Distilled	8.31	1.53	1.88	8.09	6.50	10.0	10.9	8.44
	Drainage	8.113	16.8	1.49	7.77	6.477	26.4	11.4	8.34
Ravola,# 1.2 m	Distilled	8.118	1.38	1.54	8.37	6.435	8.85	10.34	8.56
	Drainage	8.011	34.1	1.34	7.62	6.305	39.7	9.30	8.42
Imperial clay,†† 1.2m	Distilled	8.246	1.64	2.22	8.02	6.488	9.40	11.3	8.45
	Drainage	8.157	6.85	1.77	7.90	6.455	15.2	11.3	8.48
Rositas,‡‡ 1.2 m	Distilled	8.137	1.38	1.56	8.33	6.443	8.80	9.65	8.57
	Drainage	8.350	4.82	2.72	7.60	6.426	11.8	10.30	8.59
Holtville clay,§§ 1.2 m	Distilled	8.350	1.25	2.44	8.03	6.550	8.20	12.6	8.42
	Drainage	8.336	4.10	2.66	7.73	6.580	11.3	14.1	8.37
Rositas,‡‡ 1.2 m	Distilled	8.085	22.2	1.36	7.78	6.452	30.2	10.9	8.38
	Drainage	9.20	8.90	1.64	7.93	6.547	17.5	13.5	8.31
1 g calcite, <140 mesh 1 g Baker reagent CaCO₃	Distilled	8.12	1.25	1.27	8.44	6.443	10.18	10.23	8.48
	Distilled	8.123	1.32	1.32	8.44	6.464	10.4	10.4	8.45
1 g calcite, <140 mesh 1 g Baker reagent CaCO₃	Distilled	8.070	1.31	1.28	8.47	6.445	10.2	10.23	8.48
	Distilled	--	--	--	–	6.456	10.3	10.28	8.46
Indio CaCO₃ nodule	Distilled	--	--	--	–	6.457	10.0	10.17	8.48

† 20 g of soil reacted with 250 ml of water (either drainage water or distilled).
‡ Alkalinity expressed as meq/L HCO₃.
§ Coarse, silty, mixed, hyperthermic Typic Torrifluvent.
¶ Coarse, loamy, mixed, hyperthermic Duric Haplargids.
# Fine, silty, mixed (carcareous), mesic Typic Torrifluvent.
†† Clayey over loamy, montmorillonitic (carcareous), hyperthermic Vertic Torrifluvents.
‡‡ Mixed, hyperthermic Typic Torripsamments.
§§ Clayey over loamy, montmorillonitic (carcareous), hyperthermic Typic Torrifluvents.

water ranged from 7.4 for Indio to 7.9 for Imperial clay. These results indicate very high calcite supersaturation. Analyses of Ca in filtered and unfiltered subsamples indicated that no suspended $CaCO_3$ was present in the supernatent when the solutions were sampled.

Soils reacted for up to 2 months showed slight changes in their pIAPs from those reacted for 1 week. These values obtained from initially calcite-supersaturated solutions did not represent the solubility of the bulk soil calcium carbonates because precipitation or dissolution did not occur. The degree of supersaturation was related to the initial drainage water compositions which were themselves calcite-supersaturated to varying degrees when they were collected (data not shown). Evidently contamination of crystal surfaces prevented heterogeneous nucleation and impeded calcite crystal growth.

Reaction of the soil samples with distilled water also resulted in calcite-supersaturated solutions. Experimentally determined pIAP values ranged from 7.78 for Rositas soil to 8.37 for Ravola, with a mean value of 8.18. The more fine-grained soils exhibited a greater degree of supersaturation. The solutions approached these saturation levels from calcite undersaturation since they were reacted at a lower P_{CO_2} but much higher water content than is typical for field conditions. Soil water dilution with distilled water and subsequent dissolution of calcium carbonate should result in Ca uptake by the exchange phase and Na release to solution. As expected from these processes, the HCO_3 concentration (in meq/L) was greater than Ca in solution (see Table 2) with one exception (Rositas, which contains some gypsum). It is concluded that $CaCO_3$ dissolved when these samples were reacted with distilled water, but calcite supersaturation still resulted.

Experiment 1b—Drainage and Distilled Water—Low Soil/Water Ratio—Intermediate P_{CO_2}

Experiment *1b* was carried out by raising the P_{CO_2} to 0.2 atm for the reactions reported in Experiment *1a*. The P_{CO_2} was raised to insure initial calcite undersaturation. Under higher CO_2 the agreement between determined and calculated CO_2 was reasonable. The data in Table 3 indicates that Ca and alkalinity increased with the increase in P_{CO_2}; thus a Ca-containing phase must have dissolved from the soils in Experiment *1b*. The apparent stabilities of the soil $CaCO_3$ obtained upon equilibration with the drainage

waters ranged from pIAP 8.29 to 8.50 with a mean pIAP of 8.36. (We omitted one noncalcareous sandy soil which did not release additional Ca and HCO_3 upon reaction at the higher P_{CO_2} even after further dilution of this soil in water). Despite large amounts of dissolution, the soil drainage-water solutions at higher CO_2 (Table 2) are still calcite-supersaturated.

The results obtained upon equilibration of the soils with distilled water corresponded to pIAP values from 8.31 to 8.50 with a mean value of 8.44 (Table 2). This is near the calcite pK of 8.47. In Experiment *1b* an average increase of from 8 to 10 meq/L of Ca and HCO_3 occurred upon reaction (relative to Experiment *1a*). This amount of dissolution represents 0.5% of the total soil weight, or 10 to 100% of the total $CaCO_3$ present in these soils. These data show that even large amounts of soil $CaCO_3$ dissolution result in calcite supersaturation though the pIAP values are much closer to equilibrium than results from experiments with small amounts of dissolution.

Table 2 also shows the solution composition and pIAP for a soil $CaCO_3$ nodule reacted with distilled water. The nodule was in excess of 50% $CaCO_3$ by weight. The pIAP value determined was 8.48 which is that expected for low Mg calcite. Less than 5% of the nodule was dissolved during the reaction. The low Mg in solution (0.15 meq/L) is consistent with dissolution of a low Mg calcite, as confirmed by x-ray analysis. The pIAP values obtained when other individual particles of soil $CaCO_3$ (determined to be calcite by x-ray diffraction) were reacted with distilled water ranged between 8.46 and 8.48 (data not given). Thus calcite aggregates removed from the soil do not yield the same apparent IAPs as they do in the presence of the soil. This suggests that other, noncarbonate minerals are influencing the IAP of $CaCO_3$ in soil.

Experiment 2—Distilled Water–High Soil/Water Ratio—Intermediate P_{CO_2}

Supersaturated solutions were also obtained when 100 g of undried soil samples were reacted with 40 ml of distilled water and equilibrated at low CO_2. Since the P_{CO_2} was near that existing in the field, the addition of distilled water insured initially undersaturated conditions. The calculated pIAP values (7.91 to 8.34) varied, with finer-texture soils resulting in greater supersaturation.

Results of Experiments 1 and 2 show that an approach to $CaCO_3$ equilibria from supersaturation is

Table 3—Compositions of supernatants and determined calcite activity products obtained in Experiment 3— Ca-HCO₃ water—high soil/water ratio—high P_{CO_2}.†

Soil and sample depth	pH	Ca	Mg	Alkalinity (as HCO₃)	Calculated P_{CO_2}	pIAP	SiO₂
			meq/L		atm		ppm
Indio, 1.2 m	6.164	16.5	8.75	26.4	0.907	8.33	53.5
Ravola, 0.9 m	6.148	20.3	8.85	24.4	0.865	8.30	46.1
Ravola, 0.9 m	6.153	18.1	7.80	25.2	0.890	8.30	45.6
Holtville, 1.2 m	6.145	16.7	7.60	24.6	0.895	8.35	44.3
Imperial, 1.2 m	6.258	23.1	21.2	30.3	0.712	8.36	39.2
Imperial (within 24 hours of collection), 1.2 m	6.142	17.2	6.85	24.5	0.90	8.33	39.1

† 100 g of soil reacted with 50 ml of calcite-saturated water and 50 ml of distilled water.

likely to yield higher apparent solubilities than from undersaturation, presumably due to slow precipitation kinetics. In addition, it appears undesirable to carry out soil $CaCO_3$ solubility experiments at low P_{CO_2} and high dilution. Not only is pH control more difficult under the latter conditions (and thus IAP values less accurate) but also Ca hydrolysis from montmorillonite may be more important under such conditions (Frenkel and Suarez, 1977).

Nightingale and Smith (1967) presented evidence of Ca organic complexes in sodic soils. To determine whether the high apparent solubility values from Experiments 1 and 2 were due to such Ca complexes: samples of the drainage waters were reacted with Baker calcite at 0.20 atm CO_2. Within 48 hours all samples initially undersaturated were at calcite equilibrium and no supersaturation was found (data not given). Calcium-organic complexes are not significant in these equilibrations as they would have caused apparent calcite supersaturation. The lack of equilibrium must be the result of unstable solid phases in the soil.

Experiment 3—Ca–HCO₃ Water—High Soil/Water Ratio—High P_{CO₂}

In this experiment 100-g samples of soil at field water content were reacted with a mixture of 50 ml of $CaCO_3$-saturated solution and 50 ml of distilled water at 0.9 atm P_{CO_2}. The mixtures were gently agitated for 2 weeks while being constantly bubbled with CO_2. Results given in Table 3 indicate a relatively consistent pIAP value, ranging between 8.30 to 8.36. Although these soils were run at high P_{CO_2} for optimum control of pH, only a small percentage of $CaCO_3$ dissolved from the soils. Assuming dissolution of 10 meq/liter of $CaCO_3$, only 0.05% of the soil by weight would be dissolved. A far smaller percentage of $CaCO_3$ was dissolved in this experiment then in the intermediate P_{CO_2}, Experiment 1, because the soil/water ratio was higher and Ca–HCO₃ waters rather than distilled water were used. Correspondingly, the apparent solubility was higher in these experiments. A consistent pattern emerges in the data obtained in the various Experiments 1, 2, and 3, i.e., the apparent solubility of soil

$CaCO_3$ decreases with increasing dissolution from the soil during reaction.

Experiment 4—Ca–HCO₃ Water—High Soil/Water Ratio—High P_{CO₂}—"Fresh" Soil

The preceding determinations and previously published experiments implicitly assume that soil storage did not affect the soil $CaCO_3$ solubility. Air-dried soils were usually used in past studies. Experiments 2 and 3 (above) used refrigerated samples kept at field capacity. The effects of sample handling and storage effects on IAP determinations were evaluated as follows: soils were collected from one of the earlier field sites (Indio, 1.2 m). Soil water–CO_2 "equilibrations" were carried out under conditions similar to Experiment 3, except that the soils were immediately sealed, refrigerated, and subsamples reacted within 48 hours of sampling. Results given in Table 4 show pIAP values considerably lower than those obtained in Experiment 3 (see Table 3). This implies that sample storage may result in recrystallization of soil $CaCO_3$, rendering it more stable (less soluble), or that it reduces the dissolution rate of silicates (as discussed later).

Fresh precipitates are continually formed and crystallized into calcite in semi-arid regions as a result of evapotranspiration. When a soil sample is collected, it is likely that further precipitation is prevented if the water content and P_{CO_2} are maintained, but recrystallization might continue during storage. Surface coatings formed during storage (bacterial activity) may limit the dissolution reaction rate. This may not be important for carbonates but it would be substantial for silicates which have much slower dissolution rates.

Experiment 5—Soil Storage and Drying Effects

To further examine the effect of storage on soil $CaCO_3$ IAPs, we repeated Experiment 4 using subsamples stored for 2 months. A mean IAP of 8.28 was obtained (data not shown) which again indicates lower apparent solubility with storage. In another experiment, 100-g samples of stored wet Indio soil were reacted with 100 g of distilled water, another 100 g of the same soil was air-dried and then reacted with distilled water, and a third 100-g sample of wet soil was oven-dried overnight at 105°C and then reacted with distilled water. The determined pIAP values were 8.17, 8.11, and 7.93, respectively. The test was repeated with an Imperial Valley soil. The results for the latter are given in Table 5. The field water, air-dried, and oven-dried soils had pIAP values of 8.13, 8.10, and 8.01, respectively. These results suggest that

Table 4—Compositions of supernatants and determined calcite ion activity products obtained in Experiment 4—Ca–HCO₃ water—high soil/water ratio—high P_{CO₂}—"fresh" soil.†

Soil and replication	pH	Ca	Mg	Alkalinity (as HCO₃)	Calculated P_{CO₂}	pIAP CaCO₃
			meq/L		atm	
Indio, 1.2 m						
1	6.237	17.7	10.3	31.6	0.90	8.20
2	6.259	19.6	13.2	31.5	0.84	8.13
3	6.264	21.3	16.1	32.4	0.83	8.14
4	6.204	23.4	13.7	28.9	0.85	8.22
5	6.211	22.9	18.1	29.1	0.84	8.20
6	6.204	25.7	22.7	29.4	0.84	8.17
7	6.197	37.0	18.7	29.1	0.84	8.09
8	6.220	30.0	27.3	30.6	0.82	8.13

† 100 g of soil were added to 50 ml of saturated-CaCO₃ solution and 50 ml of distilled water. Samples were collected from an alfalfa field within a 40-foot radius (uniform texture), immediately sealed in plastic bags, and placed in a refrigerator. Samples were reacted with solution 2 days later.

Table 5—Compositions of supernatants and determined calcite ion activity products obtained in Experiment 5—soil storage and drying effects.

Soil preparation	pH	Ca	Mg	Alkalinity (as HCO₃)	Al	SiO₂	P_{CO₂}	pIAP
				meq/L			atm	
Field moisture	6.15	42.7	28.8	33.9	0.0048	0.91	0.964	8.13
Air-dried	6.17	43.6	29.6	34.2	0.0048	0.85	0.925	8.10
Oven-dried	6.16	60.2	31.7	35.3	0.0057	0.84	0.953	8.00

rapid drying of the soil results in precipitation of poorly crystallized material which yields an enhanced solubility value. Heating may result in conversion to a phase that is less stable at 25°C; for example, Kitano et al. (1963) reported the conversion of aragonite to vaterite at 100°C.

Experiment 6—Variable Distilled/Ca-HCO₃ Water Ratio—High Soil/Water Ratio

The effect of amount of soil $CaCO_3$ dissolution on pIAP was evaluated by changing the distilled/saturated water ratio (ranging from 100/1 to 1/9) used in the equilibration. Dissolution ranged between 0.2 to 1% of the soil carbonate present. No trend was found in the pIAP as a function of amount of soil $CaCO_3$ dissolution over this range (data not giverí). When dissolution amounted to >10% of the soil $CaCO_3$ present, as reported earlier in Experiment 1b, pIAP values near those expected for calcite were obtained.

Experiment 7—Dissolution Rate

Rather than consider that soils contain varying amounts of several carbonates of high solubility, it seems likely that equilibrium was not achieved in such laboratory experiments. An additional long-term dissolution reaction was carried out to test this possibility. A Twisselman soil (fine, mixed, calcareous Thermic Torriothent) was collected and reacted at field water content within 24 hours of collection with water at 0.97 atm P_{CO_2}. It was shaken intermittently for several hours each day (100 g of soil and 100 g of water) and analyzed periodically. The alkalinity shown in Fig. 1 indicates a rapid dissolution of $CaCO_3$ for about 1 day, at which time the solution was calcite-saturated. For the next 0.5 months alkalinity in solution increased linearly, then alkalinity became constant. Next, calcite precipitated on the container walls between the soil-solution and solution-gas interfaces. The pIAP remained essentially constant after this time despite additional precipitation. This IAP value of 7.90 is near the average pIAP of 8.0 found beneath irrigated arid lands (Suarez, 1977).

Cause of Apparent Supersaturation

Once precipitation of a more stable phase occurs it is impossible to determine the stability of any less stable phase present. The solution composition is then controlled by kinetic factors. If precipitation does not occur by crystal growth, the solution increases in saturation until heterogeneous nucleation occurs. Laboratory experiments are not likely to simulate $CaCO_3$ kinetic reactions in the natural system since the conditions for heterogeneous nucleation are different. Organic contaminants generated during the reaction which may coat the crystals, the presence of dust and nuclei, the container composition, and stirring rate all affect precipitation rates. The fact that in our earlier experiments we were able to maintain pIAP values as low as 7.4 with drainage water (compared to 7.9 in this experiment) indicates that heterogeneous nucleation of calcite was highly variable even within our own experiments. The more soluble $CaCO_3$ minerals such as vaterite, aragonite, or $CaCO_3$ hydrates are not commonly found in soils or observed to form pedogenically. Also, $CaCO_3$ minerals dissolve readily and do not produce dissolution curves like that in Fig. 1. The varying IAPs of soils might be explained by the presence of small quantities of poorly crystallized calcite; this has not, however, been reported in the literature despite many studies of calcite precipitation. Also, supersaturation was not observed for $CaCO_3$ separated from the soil.

A more likely explanation for calcite supersaturation in soils is that Ca-containing silicates are a source of additional Ca and HCO_3. A variety of silicate minerals such as plagioclase exist in arid land soils which are more soluble than calcite. Rhoades et al. (1968)
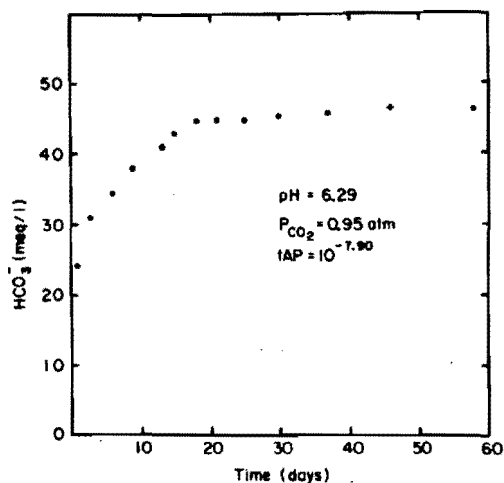
Fig. 1—Alkalinity release (as HCO₃⁻) from Twisselman soil water suspensions vs. time for 100 g of soil reacted with 100 g of distilled water at 0.97 atm CO₂.
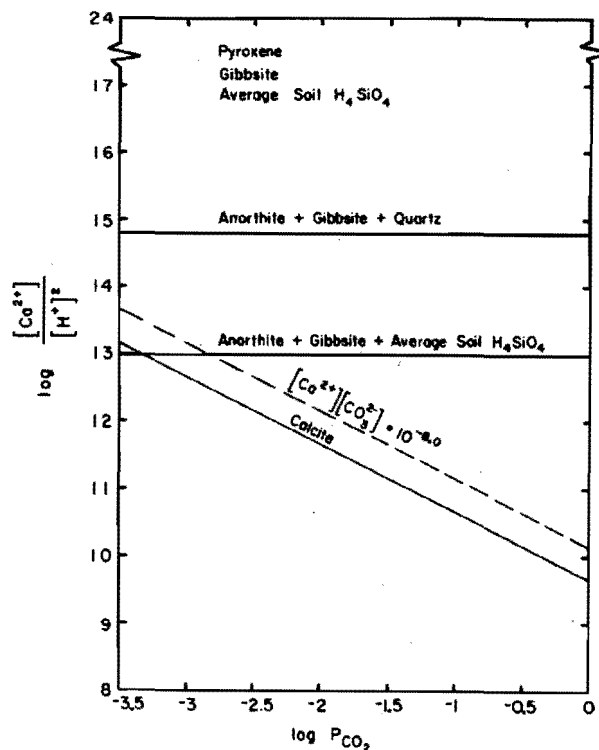
Fig. 2—Stability fields for calcite, anorthite, Ca and pyroxene under typical Si and Al levels in soil water.

found that the unstable Ca, Mg silicates in relatively unweathered arid-zone soils released significant amounts of Ca, Mg, and HCO_3 to solution upon leaching. The weathering of feldspars and precipitation of pedogenic calcite is well documented for arid land soils. For example, Nettleton et al. (1968) showed that, in a noncalcareous igneous parent material, feldspar weathered to montmorillonite and calcite formed.

Since field evidence indicates that the reaction feldspar → calcite occurs during weathering, it seems worthwhile to examine what thermodynamic conditions are needed. Plagioclases found in soils are usually intermediate between anorthite and albite, but the thermodynamic data for intermediate composition plagioclases have not been established. In the following section we compare the stability of calcite, anorthite, and pyroxene phases for which good thermodynamic data exists.

The dissolution of anorthite can be written as Ca $Al_2Si_2O_8 + 8H_2O = Ca^{2+} + 2Al(OH)_4^- + H_4SiO_4$. A reasonable assumption is that $Al(OH)_4^-$ levels in solution are controlled by gibbsite solubility since it precipitates readily (May et al., 1979). Soil solution silica levels are typically quartz-supersaturated. A typical silica concentration in soils is $H_4SiO_4 = 10^{-3.1}$ (Lindsay, 1979). The lines drawn in Fig. 2 show activity ratios $[Ca^{2+}]/[H^+]^2$ for different mineral systems plotted as a function of P_{CO_2}. The lines drawn for anorthite are based on the thermodynamic data of Robie et al. (1978), the gibbsite data of May et al. (1979), and the value of H_4SiO_4 at quartz equilibrium (Robie et al., 1978) or $10^{-3.1}$ (Lindsay, 1979). The calcite line is below the anorthite line—except at very low P_{CO_2} and high silica concentrations. Anorthite is thus unstable relative to calcite under most soil conditions. We need not consider the reactions involving montmorillonite and kaolinite since they decrease Si and Al levels in solution and make anorthite even more unstable relative to calcite. The result of these reactions is Ca (and HCO_3) levels higher than those predicted for calcite. As a test of the Si and Al assumptions made above, the activities of Al species were determined by using the Al dissociation constants determined by May et al. (1979) and the data given in Table 5. The solutions were slightly gibbsite-supersaturated and H_4SiO_4 levels ($10^{-3.02} - 10^{-3.05}$) were near that used by Lindsay (1979). The solutions were anorthite- and pyroxene-undersaturated and montmorillonite-supersaturated. Figure 2 thus provides a reasonable explanation of our laboratory conditions. Also shown in Fig. 2 is a line for pyroxene + gibbsite + quartz obtained using the Ca pyroxene data (reported by Robie et al., 1978). This assemblage is also unstable relative to calcite and could also contribute to calcite supersaturation in soils.

The mixture of various unstable phases in soils means that the solution might not achieve calcite equilibrium. The solution composition should depend on the kinetics of the various precipitation and dissolution reactions and, hence, on the relative surface areas of the various mineral phases. Calcite equilibrium can be achieved only if the calcite precipitation reaction is very fast relative to silicate dissolution. Although silicate dissolution is relatively slow and

calcite dissolution relatively fast, calcite precipitation can be very slow. Due to contamination of crystal surfaces, solutions can remain almost indefinitely calcite-supersaturated. Suarez (in preparation) estimates the Ca precipitation rate in the lower Colorado River to be between 0 and 0.05 meq/L per month despite high levels of supersaturation (pIAPs of 7.5 to 7.8). Also (in preparation) calcite supersaturation can be predicted using the published kinetic data for calcite and anorthite even without considering precipitation inhibitors. The steady-state condition represents the concentrations at which the calcite precipitation rate equals the anorthite dissolution rate. Thus it is not unexpected that the IAP values for $CaCO_3$ found in this study are intermediate between those for calcite and anorthite. For actual prediction of field $CaCO_3$ IAP values we need to know the surface areas and reaction rates of soil mineral phases. This information is not available at present. The measured IAP value of $10^{-8.0}$ for waters beneath irrigated lands (Suarez, 1977) may represent a typical steady-state value. However, in the rootzone with wetting and drying and CO_2 fluctuations, the reaction rates may not be equal and IAP values could be different. The value IAP $= 10^{-8.0}$ is drawn on Fig. 2 for comparison to the solid phase stabilities. That Ca levels in solution are kinetically controlled does not imply that a steady state cannot be achieved. An analogy can be made with Al and Si concentrations. Montmorillonite or kaolinite are the observed feldspar weathering products, as predicted thermodynamically, but the observed levels of Al and Si in soil waters are above those expected by these minerals. These phases do not come to equilibrium because other silicates (such as feldspars) are continually supplying Al and Si to solution. Silica levels found in soils may fluctuate about a given value ($10^{-3.1}$), but this does not indicate the existence of a specific Si phase. Analogously, Ca values in soil solutions are also intermediate between calcite and silicates, suggesting kinetic controls.

CONCLUSION

In laboratory studies of soil $CaCO_3$ solubility it is concluded that (i) initially calcite-supersaturated soil water solutions do not equilibrate to the same IAP values that are obtained if solutions are initially undersaturated; (ii) IAP values obtained depend on the amount of $CaCO_3$ dissolution that occurs in the reaction; (iii) fresh soil samples yield lower apparent stabilities than stored, air-, or oven-dried soils; (iv) despite long reaction times, calcite equilibrium is not achieved in soils; (v) carbonate minerals separated from soils display solubilities identical to thermodynamically stable calcite; (vi) calcite supersaturation in soils can be explained by the simultaneous dissolution of silicates minerals and the unpredictable heterogeneous nucleation of precipitating calcite. Steady state (not equilibrium) is achieved when the calcite precipitation rate is exactly balanced by the Ca silicate dissolution rate. Finally, (vii) a distinction must be made between the stability of individual soil minerals (such as calcite) and the IAP values from mixtures of mineral phases in soils. The solution composition

in soils should not be expected to correspond to the stability of any $CaCO_3$ solid phase.

REFERENCES

1. Chave, K. E., and R. F. Schmaltz. 1966. Carbonate-sea water interactions. Geochim. Cosmochim. Acta 30:1037–1048.
2. Clark, J. S. 1964. An examination of the pH of calcareous soils. Soil Sci. 98:145–151.
3. Cole, C. V. 1957. Hydrogen and calcium relationships of calcareous soils. Soil Sci. 83:141–150.
4. Doner, H. E., and P. F. Pratt. 1968. Solubility of calcium carbonate precipitated in montmorillonite suspensions. Soil Sci. Soc. Am. Proc. 32:743–744.
5. Frenkel, H., and D. L. Suarez. 1977. Hydrolysis and decomposition of calcium montmorillonite by leaching. Soil Sci. Soc. Am. J. 41:887–891.
6. Goldsmith, J. R., D. L. Graf, and H. C. Heard. 1961. Lattice constants of the calcium-magnesium carbonates. Am. Mineral. 46:453–457.
7. Jacobson, R., and D. Langmuir. 1974. Dissociation constants of calcite and $CaHCO_3^+$ from 0 to 50°C. Geochim. Cosmochim. Acta 38:301–318.
8. Kitano, Y., K. Park, and D. Hood. 1963. Pure aragonite synthesis. J. Geophys. Res. 67:4873–4874.
9. Levy, Rachel. 1981. Effect of dissolution of aluminosilicates and carbonates on ionic activity products of calcium carbonate in soil extracts. Soil Sci. Soc. Am. J. 45:250–255.
10. Lindsay, W. L. 1979. Chemical equilibria in soils. John Wiley & Sons, New York.
11. May, H. M., P. A. Helmke, and M. L. Jackson. 1979. Gibbsite solubility and thermodynamic properties of hydroxy-aluminum ions in aqueous solution at 25°C. Geochim. Cosmochim. Acta 43:861–868.
12. Nettleton, W. D., K. W. Flach, and G. Borst. 1968. A toposequence of soils in tonalite grus in the southern California peninsular range. Soil Surv. Investigation Report no. 21, USDA. U.S. Government Printing Office, Washington, DC.
13. Nightingale, H. I., and R. L. Smith. 1967. Evidence for the presence of calcium-organic complexes in sodic soil. Soil Sci. 103:261–264.
14. Olsen, S. R., and F. S. Watanabe. 1959. Solubility of calcium carbonate in calcareous soils. Soil Sci. 88:123–129.
15. Rhoades, J. D., D. B. Krueger, and M. J. Reed. 1968. The effect of soil-mineral weathering on the sodium hazard of irrigation waters. Soil Sci. Soc. Am. Proc. 32:643–647.
16. Robie, R. A., B. S. Hemingway, and J. R. Fisher. 1978. Thermodynamic properties of minerals and related substances at 298.15 K and 1 Bar (10^5 Pascals) pressure and at higher temperatures. Geological Survey Bulletin no. 1432. U. S. Government Printing Office, Washington, DC.
17. Suarez, D. L. 1977. Ion activity products of calcium carbonate in waters below the rootzone. Soil Sci. Soc. Am. J. 41:310–315.
18. Thorstenson, D. C., and L. N. Plummer. 1977. Equilibrium criteria for two component solids reacting with fixed composition in an aqueous phase-example: the Mg calcites. Am. J. Sci. 277:1203–1223.