

Ion Activity Products of Calcium Carbonate in Waters Below the Root Zone¹

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ABSTRACT

The pH, Ca²⁺, and HCO₃⁻ relations were investigated in 28 well waters obtained from beneath irrigated fields in Arizona. The mean [Ca] [CO₃] ion activity product (IAP) was 11.3×10^{-9} (pIAP = 7.95) with a standard error of 0.7×10^{-9} based on field measurements of pH. As indicated by ionic strength the residence time of the waters in the soil vary widely. The lack of a trend in pIAP vs. ionic strength indicates the kinetics of calcite equilibration (from supersaturation) is quite slow in soil-water systems. This conclusion was supported by an average pIAP of 7.97 calculated from 35 water analyses obtained from wells in the Grand Valley of Colorado and by a pIAP value of 7.96 obtained from a soil water sample in a lysimeter study. Since these pIAP values are quite consistent and were obtained under a wide variety of conditions, a pIAP value of 7.95 is recommended for use in predictive models when CaCO₃ precipitation occurs.

Additional Index Words: CaCO₃ solubility, soil waters, precipitation of CaCO₃

IN MOST INVESTIGATIONS of the solubility of soil calcium carbonate, calcareous soils were equilibrated with distilled water at various soil-water ratios. The determined ion activity products varied from values similar to that for calcite (Cole, 1957) (without consideration of ion pairs) to values 10 times greater. As a result, solid phases including calcite, aragonite, dolomite, calcium carbonate monohydrate,

vaterite, and huntite among others, were proposed to be the controlling phase. Enhanced solubility due to Mg substitution into soil calcites has also been proposed—but without consideration of ion pairs. Studies by Suarez³ (1976) indicate that a range of solubility products exists for the CaCO₃ solid phase in any soil, and the values obtained depend on the experimental conditions. If equilibrium is approached from undersaturation, the activity product depends on how much material was dissolved, since there is a variation in the stability of the solid, probably due to slow recrystallization of the fresh precipitate. As the most unstable material dissolves first (the fresh precipitate) its solubility cannot be readily obtained if it constitutes a small percentage of the dissolved soil carbonate material. Experiments from supersaturation yield very soluble apparent stability constants, especially if stirring is minimized.

The present investigation was undertaken to directly determine the [Ca] [CO₃] ion activity product of waters under irrigated lands which contain calcite, rather than assume equilibrium with the soil CaCO₃. The Wellton-Mohawk Irrigation District of Arizona was chosen because of the ex-

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tensive network of shallow drainage wells available for sampling. These wells are pumped continuously at rates of 1,000 to 4,000 liters/min, thus CO₂ degassing would not be expected, and was demonstrated as not significant. Determining the activity product of CaCO₃ in soil drainage waters obtained by pumping from the saturated zone prevents degassing and yields a direct determination of the desired predictive value (in contrast to laboratory studies which give variable results depending on experimental conditions.)

PROCEDURES

Water samples were collected from the pump outlets. Wells from which a fresh sample could not be immediately obtained or those which did not have immediate access (before degassing in a drain line) were avoided. Since accurate determination of pH must be made at the sampling site (Back and Barnes, 1961), immediate and repeated pH measurements were taken with an Orion Model 407 Ionalyzer on the expanded pH scale with a Thomas pH combination electrode.⁴ The electrode was calibrated with nominal pH buffers 5.00, 6.86, and 8.00 at sample temperatures. The measurements are considered accurate to ± 0.02 pH units.

Samples were collected in polyethylene bottles that had been washed with HCl and thoroughly rinsed with $< 1 \mu\text{ohm}$ water. One sample was filled to the top, capped, and stored in an ice chest to prevent precipitation of CO₃. Alkalinity titrations (HCO₃⁻ + CO₃²⁻) were performed within 8 hours of collection. A second sample was immediately filtered in the field through a 0.1 μm Millipore filter pad with a pressure filtration unit using a 6.0% CO₂-air mixture. This procedure prevented precipitation of Ca during filtration because it was sufficiently fast (< 5 min) and the composition of the air mixture was near that of the soil so that any suspended carbonate material did not have time to dissolve. This portion was then acidified to pH 2 with concentrated reagent grade HCl and subsequently analyzed for Ca, Mg, Na, and K by atomic absorption. Lanthanum chloride was added for Ca and Mg determinations (Brown et al., 1970). The unfiltered samples were analyzed for alkalinity, Cl, SO₄, and NO₃, Ca, Mg, Na, and K. The similarity of Ca in the unfiltered acidified and filtered, acidified samples indicated that suspended CaCO₃ was not present in the waters. Chloride was analyzed by an American Instrument Company chloride titrator, and sulfate was analyzed by the turbidimetric method (Am. Public Health Assoc., 1971). Nitrate was analyzed with an Orion nitrate electrode. Some of the filter pads were rinsed with distilled water and examined with a JM-16 scanning electron microscope for suspended material. None was found.

The activities of all species including ion pairs were calculated from the analytical data with an IBM 360/50 computer and appropriate algorithm. P_{CO₂} was calculated from pH, temperature and [HCO₃⁻]. Table 1 lists the temperature dependent thermodynamic constants used in the calculations.

RESULTS

Chemical analyses of the well waters from the Wellton-Mohawk Irrigation District are listed in Table 2, as are the calculated Ca²⁺ ion activities, pIAP of CaCO₃, and calculated P_{CO₂}. The determined values ranged from 17.0×10^{-9} (pIAP 7.77) to 5.9×10^{-9} (pIAP 8.23) with a mean value of 11.3×10^{-9} (pIAP 7.95) standard error of 0.7×10^{-9} at field water temperatures of about 25°C.

The Wellton-Mohawk District is underlain by a relatively shallow alluvial aquifer, over an impermeable clay layer. The recharge water is about evenly divided between re-

charge from orchard irrigation on the mesa (leaching fraction of 0.65) and irrigation in the valley (leaching fraction of 0.32). Annual recharge is approximately one-tenth the total aquifer capacity. Wells near the mesa thus pump more dilute and younger water, whereas those further away pump more saline water. In addition to the increased travel time for the more saline waters to reach the aquifer, they are likely to be older because of the selective pumping of wells. Until 1974, low quality wells were only pumped when downstream users were not receiving water. Selective extraction of higher quality waters resulted, further increasing the residence time of the more saline waters. Seepage of ground water from the Gila River alluvium appears to be minor.

In Fig. 1, the plot of pIAP CaCO₃ vs. P_{CO₂} shows no apparent or significant trend. Thus degassing of the well waters which would have increased pIAP, did not occur and cannot be used to explain the deviation of pIAP from that for calcite (8.47).

A plot of pIAP CaCO₃ vs. ionic strength (Fig. 2) for the Wellton-Mohawk water samples, showed no significant trend. Since waters of higher ionic strength or salinity underwent relatively higher evapotranspiration losses during transit to the ground water and thus move through the soil profile at a slower rate, the ionic strength is related to soil residence time; i.e., the higher the ionic strength, the longer the residence time. Since pIAP's appear independent of residence time, the data suggests that the water compositions have achieved a metastable equilibrium (supersaturated with respect to calcite).

During transit through the soil evapotranspiration losses and CO₂ fluctuations occur resulting in CaCO₃ precipitation and occasional dissolution. Recrystallization of the fresh CaCO₃ precipitate into calcite undoubtedly occurs in the soil with aging; however, the solubility product of calcite is not achieved—probably because precipitation continues until the soil water leaves the root zone (and may even continue in the aquifer if the CO₂ pressure is lower there than in

Table 1—Dissociation and Debye-Hückel constants used in activity calculations.

Constants	References
$\text{p}K \text{ CO}_2 = +13.417 - (2299.6/T) - 0.01422 T$	Harned & Davis (1943)
$\text{p}K \text{ H}_2\text{CO}_3^* = -14.8435 + (3404.71/T) + 0.03279 T$	Harned & Davis (1943)
$\text{p}K_2 \text{ H}_2\text{CO}_3 = -6.498 + (2902.39/T) + 0.02379 T$	Harned & Scholes (1941)
$\text{p}K \text{ CaHCO}_3^+ = -2.95 + 0.0133 T$	Jacobson & Langmuir (1974)
$\text{p}K \text{ CaCO}_3^0 = -27.393 + 4114/T + 0.05617 T$	Reardon & Langmuir (1974)
$\text{p}K \text{ CaSO}_4^0 = +1.24 + 0.0036 T$	Bell & George (1953)
$\text{p}K \text{ MgSO}_4^0 = 0.95 + 0.011 T$	Jacobson (1973)†
$\text{p}K \text{ MgCO}_3^0 = -21.39 + 3265/T + 0.04467 T$	Reardon & Langmuir (1974)
$\text{p}K \text{ MgHCO}_3^+ = -76.344 + (11132/T) + 0.1338 T$	Reardon (1974)‡
$\text{p}K \text{ NaCO}_3^+ = 0.550 (25^\circ\text{C})$	Nakayama (1970)
$\text{p}K \text{ NaSO}_4^- = 0.718 (25^\circ\text{C})$	Tanji (1969)
$\text{p}K \text{ NaHCO}_3^0 = 0.169 (25^\circ\text{C})$	Nakayama (1970)
$\text{p}K \text{ KSO}_4^- = 0.85 (25^\circ\text{C})$	Reardon (1974)
$\log A = -1.15083 + 93.642/T + 1.8298 \times 10^{-3} \times T$	Robinson & Stokes (1965)
$\log B = -0.766445 + 30.7702/T + 6.05749 \times 10^{-4} T$	Robinson & Stokes (1965)

† R. Jacobson. 1973. Controls on the quality of some carbonate ground waters: dissociation constants of calcite and CaHCO₃⁺ from 0 to 50°C. Ph.D. Thesis. Pennsylvania State Univ. 131 p.

‡ E. J. Reardon. 1974. Thermodynamic properties of some sulfate, carbonate and bicarbonate ion pairs. Ph.D. Thesis. Pennsylvania State Univ. 85 p.

⁴Trade names are provided for the benefit of the reader and do not imply any endorsement by the USDA.

Table 2—Chemical analyses and calculated αCa^{2+} , P_{CO_2} , and pIAP CaCO_3 values of drainage well waters from Wellton-Mohawk Irrigation District, Arizona.

Sample	pH	ΣCa	ΣMg	ΣNa	ΣK	ΣCl	ΣHCO_3	ΣSO_4	ΣNO_3	αCa^{2+}	Calculated P_{CO_2}	pIAP CaCO_3
											mM/liter	
15	7.48	12.2	9.66	37.5	0.270	31.1	6.50	19.5	1.07	2.11	1.02×10^{-2}	7.85
20	7.36	9.70	6.66	20.3	0.212	14.4	7.24	14.6	0.71	1.86	1.59×10^{-2}	7.95
28	7.26	20.2	13.6	33.5	0.314	40.9	7.07	19.2	1.23	3.46	1.78×10^{-2}	7.83
32	7.28	20.5	19.5	99.8	0.438	96.7	8.57	30.9	1.90	2.89	1.82×10^{-2}	7.85
34	7.35	8.45	8.38	61.2	0.248	38.6	8.82	28.8	1.62	1.27	1.81×10^{-2}	8.08
35	7.25	14.0	10.5	41.0	0.300	29.5	10.15	24.7	1.09	2.24	2.67×10^{-2}	7.86
37	7.23	13.9	9.69	27.3	0.255	19.2	8.98	21.5	1.05	2.37	2.55×10^{-2}	7.90
38	7.13	17.7	11.4	26.2	0.295	25.3	7.26	22.6	0.98	3.00	2.55×10^{-2}	8.00
41	7.26	12.6	7.30	19.0	0.255	13.1	7.63	17.7	0.86	2.31	2.09×10^{-2}	7.94
46	7.28	10.9	6.49	18.2	0.240	16.1	5.99	14.2	0.84	2.12	1.58×10^{-2}	8.06
49A	7.46	4.50	3.46	29.2	0.179	14.0	6.91	15.0	1.45	0.841	1.22×10^{-2}	8.21
53A	7.63	3.75	2.85	28.2	0.193	10.8	7.67	15.8	0.85	0.689	9.22×10^{-3}	8.08
56	7.75	2.82	2.30	25.5	0.165	10.5	5.19	14.2	0.86	0.541	4.80×10^{-3}	8.23
60	7.39	11.7	6.87	16.8	0.235	9.87	8.65	16.4	0.61	2.18	1.78×10^{-2}	7.77
61	7.39	14.8	8.36	19.5	0.283	17.4	6.81	18.2	0.82	2.69	1.36×10^{-2}	7.80
64	7.45	13.7	7.30	67.2	0.268	57.6	7.34	24.0	1.69	2.14	1.16×10^{-2}	7.84
65	7.24	17.3	10.1	59.8	0.396	52.3	7.59	24.9	1.64	2.70	1.95×10^{-2}	7.94
65A	7.25	12.6	11.6	69.8	0.294	52.1	8.47	30.0	1.18	1.86	2.11×10^{-2}	8.04
67	7.22	22.5	11.0	114.	0.388	101.	5.90	38.0	2.03	3.02	1.44×10^{-2}	8.05
69	7.34	7.45	4.48	15.0	0.187	7.90	5.78	11.9	0.75	1.54	1.38×10^{-2}	8.14
601	7.26	7.60	3.80	15.5	0.185	8.69	5.60	12.5	0.67	1.55	1.61×10^{-2}	8.22
603	7.09	19.2	21.8	100.	0.295	97.3	6.66	32.7	2.36	2.70	2.19×10^{-2}	8.18
605	7.38	11.6	7.68	40.5	0.306	29.8	8.61	18.7	0.87	1.99	1.71×10^{-2}	7.85
606	7.45	10.5	6.34	17.2	0.243	11.3	7.18	15.0	0.80	2.03	1.29×10^{-2}	7.82
616	7.42	5.05	3.12	20.7	0.158	10.16	6.36	11.6	1.05	1.03	1.26×10^{-2}	8.19
619	7.37	15.5	14.0	69.2	0.305	63.7	9.49	25.0	1.65	2.36	1.76×10^{-2}	7.78
620	7.33	17.7	13.1	48.3	0.330	50.9	7.59	19.4	1.55	2.94	1.59×10^{-2}	7.81
621	7.27	19.0	14.8	90.5	0.406	87.3	7.32	28.2	1.90	2.77	1.64×10^{-2}	7.94

the soil). Ground waters should show a long-term trend in pIAP (towards calcite) with time after leaving the root zone however the continuous input of supersaturated water may balance the tendency for pIAP to approach the calcite value. The metastable IAP's obtained are more soluble than calcite ($\text{pK} = 8.47$) or aragonite ($\text{pK} = 8.30$) and less soluble than calcium carbonate monohydrate ($\text{pK} = 7.60$, Hull and Turnbull, 1973). This latter value is for an aged, well-characterized natural specimen, and freshly precipitated material would be expected to be even more soluble. The pIAP data in Table 2 indicate that soil waters are not equilibrated with any known, well-crystallized CaCO_3 phase.

The average (pIAP CaCO_3) value determined in the Wellton-Mohawk drainage waters equals the value found in an examination of 35 waters pumped from observation wells in Grand Valley, Colorado (data listed in Table 3). The calculated mean pIAP CaCO_3 was 7.97. (IAP of 10.8×10^{-9} with a standard error of 0.6×10^{-9}), As in the

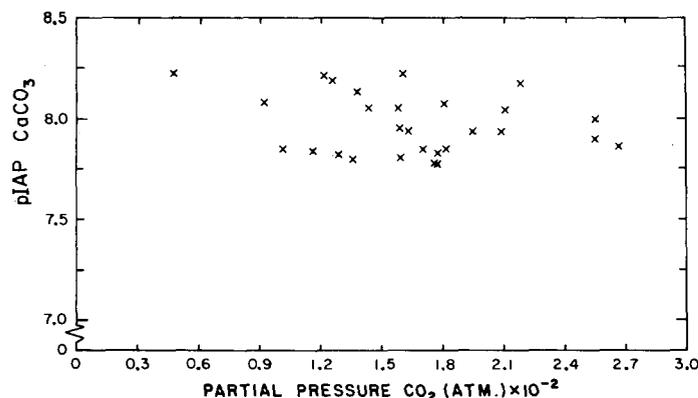


Fig. 1—Solubility of CaCO_3 (pIAP CaCO_3) vs. CO_2 partial pressure in well waters from Wellton-Mohawk Irrigation District, Arizona.

Wellton-Mohawk waters, IAP values were not related to P_{CO_2} or ionic strength.

The Grand Valley irrigated lands are underlain by alluvial deposits and the Mancos Shale. Contact of irrigation drainage waters with the weathered shale results in dissolution of soluble salts—mostly Na_2SO_4 , MgSO_4 and gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$). Thus, the ionic strength of the water is not necessarily related to the residence time of the water in the subsurface.

Water temperatures in Grand Valley were around 15°C . Although the solubility of calcite increases with decreasing temperatures, this effect is substantially less than the commonly reported data of Frear and Johnston (1929). Jacobson and Langmuir (1974) indicate that calcite $\text{pK} = 8.42$ at 15°C . The temperature effect on solubility is thus relatively minor compared to the differences in solubility observed in this study. It cannot explain the enhanced CaCO_3 solubility of soil waters.

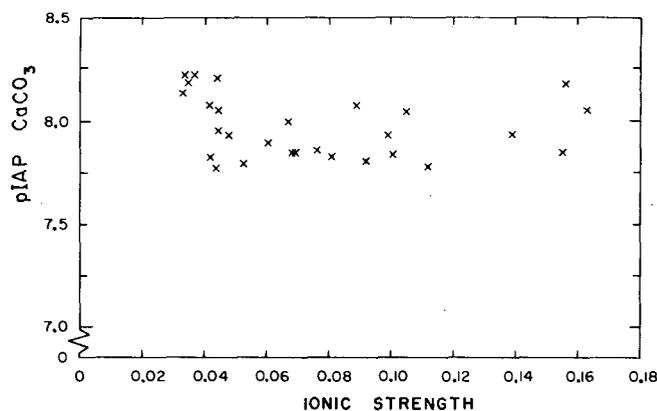


Fig. 2—Solubility of CaCO_3 (pIAP CaCO_3) vs. ionic strength of well waters from the Wellton-Mohawk Irrigation District, Arizona. Note: Increasing pIAP values correspond to decreasing solubility of CaCO_3 or increasing stability of solid phase.

Table 3—Chemical analyses and calculated αCa^{2+} , P_{CO_2} , and pIAP CaCO₃ values of well waters from Grand Valley, Colorado.

Sample	pH	ΣCa	ΣMg	ΣNa	ΣK	ΣCl	ΣHCO ₃	ΣSO ₄	ΣNO ₃	αCa^{2+}	Calculated P_{CO_2}		pIAP CaCO ₃
											meq/liter	mM/liter	
1	7.46	22.6	200.	253.	0.792	42.9	16.4	405.	10.3	1.38	1.47×10^{-2}	7.90	
2	7.46	23.2	30.5	42.6	0.242	8.21	6.97	75.1	1.08	2.72	9.53×10^{-3}	7.83	
3	7.10	25.7	33.5	15.1	1.40	8.23	7.47	58.1	0.95	3.43	2.36×10^{-2}	8.02	
5	7.12	28.2	24.4	13.5	0.362	8.97	6.77	50.2	0.69	3.95	2.15×10^{-2}	8.00	
6A	7.25	26.6	27.8	8.25	0.348	5.08	5.86	48.8	0.68	3.83	1.33×10^{-2}	7.98	
7	6.96	27.4	22.0	8.75	0.322	6.24	6.70	44.1	0.61	4.05	3.08×10^{-2}	8.16	
8	7.10	27.0	16.4	15.7	0.318	5.54	6.50	45.5	0.63	3.91	2.15×10^{-2}	8.06	
9	7.09	27.5	17.6	6.20	0.218	4.77	4.49	41.2	0.66	4.19	1.55×10^{-2}	8.19	
11	7.56	24.3	124.	208.	0.328	48.5	14.0	284.	5.26	1.68	1.11×10^{-2}	7.74	
13	7.26	27.2	24.9	21.0	0.182	9.32	6.62	57.0	0.60	3.59	1.52×10^{-2}	7.91	
20	7.38	26.3	20.6	13.7	0.248	6.24	5.92	44.5	1.78	3.86	1.02×10^{-2}	7.83	
21	7.26	31.5	18.8	14.1	0.465	13.2	6.85	42.9	0.50	4.61	1.65×10^{-2}	7.75	
23	7.18	27.9	15.7	9.90	0.282	6.24	6.10	40.0	0.45	4.26	1.69×10^{-2}	7.97	
27	7.14	30.1	9.45	10.0	0.162	5.46	6.15	36.4	0.57	4.74	1.90×10^{-2}	7.95	
28	6.96	27.4	17.8	10.8	0.300	6.51	6.40	43.2	0.46	4.08	2.87×10^{-2}	8.21	
29	7.33	28.0	35.5	15.6	0.418	15.5	5.17	58.2	0.62	3.75	9.69×10^{-3}	7.95	
31	7.43	23.9	164.	151.	0.465	27.2	19.7	290.0	0.92	1.63	2.37×10^{-2}	7.67	
32	7.44	26.8	24.6	7.70	0.120	4.39	4.72	49.7	0.31	3.81	7.21×10^{-3}	7.85	
33	7.34	24.6	19.1	17.3	0.48	2.67	4.24	54.7	0.48	3.28	8.50×10^{-3}	8.03	
34	7.40	22.8	53.4	344.	1.10	57.1	19.0	351.	1.43	1.38	2.03×10^{-2}	7.89	
35	7.64	22.5	193.	370.	0.462	32.1	14.1	532.	10.1	1.19	7.92×10^{-3}	7.85	
36	6.99	30.6	9.05	5.87	0.442	38.4	6.62	34.4	0.42	4.91	2.98×10^{-2}	8.03	
37	7.09	24.3	58.5	29.0	5.28	12.1	7.50	88.1	2.68	2.79	2.22×10^{-2}	8.21	
40	7.36	21.7	35.4	50.4	0.492	7.06	7.64	92.8	0.71	2.31	1.31×10^{-2}	7.96	
44	6.89	27.0	25.8	8.55	0.198	4.64	6.50	48.9	0.051	3.83	3.65×10^{-2}	8.23	
46	7.12	27.8	9.6	7.70	0.492	2.20	4.45	37.5	0.34	4.34	1.50×10^{-2}	8.12	
48	7.59	21.3	107.	320.	0.535	39.8	12.5	396.	2.41	1.25	8.56×10^{-3}	7.92	
49	6.93	25.8	34.3	24.4	0.565	7.54	7.02	66.3	3.27	3.26	3.19×10^{-2}	8.31	
51	6.98	34.2	16.1	10.2	0.640	12.8	5.90	38.0	2.46	5.30	2.60×10^{-2}	8.07	
52	7.14	25.4	29.1	34.4	0.525	11.8	11.9	66.0	0.86	3.11	3.50×10^{-2}	7.84	
55	7.14	28.8	10.7	4.32	0.235	2.71	5.07	35.7	0.30	4.62	1.59×10^{-2}	8.04	
56	7.33	21.4	61.3	103.	0.628	11.3	10.6	156.	5.17	1.86	1.66×10^{-2}	8.02	
61	7.28	20.2	69.5	206.	0.902	7.81	15.6	269.	3.30	1.36	2.52×10^{-2}	8.05	
61A	7.28	20.6	91.3	246.	0.905	12.4	19.1	324.	4.93	1.29	2.94×10^{-2}	8.00	

Inhibition of calcite precipitation by Mg due to surface poisoning (Lippman, 1973) or enhanced solubility of Mg calcite (Berner, 1975) was investigated. There is no statistically significant trend in the $[\text{Mg}^{2+}]/[\text{Ca}^{2+}]$ ratio vs. pIAP plot given in Fig. 3 for waters from the Grand Valley; however, waters with a $[\text{Mg}^{2+}]/[\text{Ca}^{2+}]$ ratio > 5 appear to have a lower pIAP. Since the ionic strengths, μ , of these solutions were > 0.3 (outside the range of the extended Debye-Hückel equation) ion activities were recalculated using the model of Truesdell and Jones (1974) (an extended Debye-Hückel equation with *A* and *B* and additional “*a* and *b* parameters calculated from experimental mean salt single ion activity coefficients”). The resulting activities were not substantially changed. The Wellton-Mohawk waters, with lower $[\text{Mg}^{2+}]/[\text{Ca}^{2+}]$ ratios also showed no significant trend between pIAP and $[\text{Mg}^{2+}]/[\text{Ca}^{2+}]$, as shown in Fig. 4.

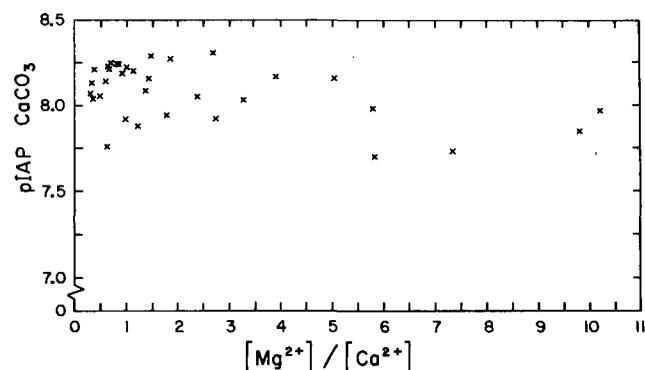


Fig. 3—Solubility of CaCO₃ (pIAP CaCO₃) vs. $[\text{Mg}^{2+}]/[\text{Ca}^{2+}]$ activity ratio in well waters from Grand Valley, Colorado.

Consequently, Mg interference with precipitation cannot account for the higher solubilities obtained in this study.

The applicability of a single nonequilibrium value requires that it be constant over the time frame of interest. A lysimeter study with daily irrigation, a leaching fraction of 0.20 and a calculated travel time of water through the lysimeter of 57 days⁵ was utilized for the following experiment. Soil water was extracted out of the bottom of the 108-cm lysimeter and collected in a sealed 125-ml flask connected to a large reservoir connected in turn to a 235-mbar suction. Soil water pH from an unsaturated profile cannot be accurately analyzed without special precautions to minimize the CO₂ loss from the vacuum extractor. The pH of the soil

⁵S. D. Merrill 1976. Distribution and growth of sorghum roots in response to irrigation frequency. Ph.D. Thesis. Univ. of California, Riverside. 210 p.

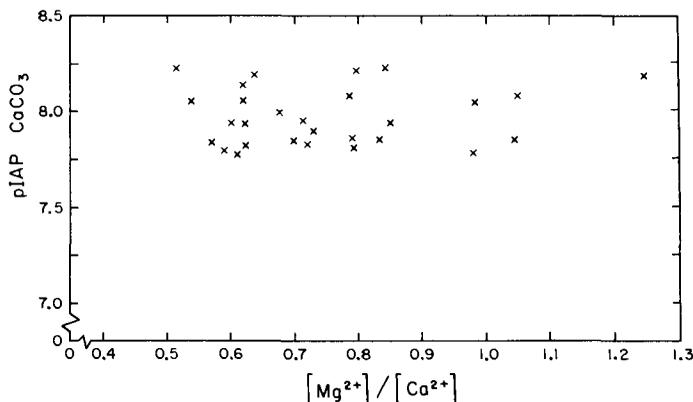


Fig. 4—Solubility of CaCO₃ (pIAP CaCO₃) vs. $[\text{Mg}^{2+}]/[\text{Ca}^{2+}]$ ratios in well waters from the Wellton-Mohawk Irrigation District, Arizona.

water was measured in situ by insertion of the electrode into the flask and the drainage composition was also determined. Calculated P_{CO_2} values from pH and solution composition (2.05×10^{-2} atm) corresponded very closely to those measured by gas chromatography on soil-air, extracted from the lysimeter through septum-sealed sampling tubes (2.00×10^{-2} atm CO_2), if at least 2 volumes of drainage water passed through the flask (the exit tube was at the top of the flask to minimize the volume of the gas phase). The calculated pIAP CaCO_3 of the drainage water was 7.96.

Based on a Ca + Mg fit of their data, Oster and Rhoades (1975) recommended the use of the aragonite value, however they listed an apparent solubility product of 15.4×10^{-9} (pK of 7.82) for soil CaCO_3 . This value indicates a higher solubility (lower pIAP) than that found in the present study. Correction for degassing, expected to have occurred during drainage from the lysimeters, would decrease their apparent solubility toward those found in this study.

DISCUSSION

Various reasons for enhanced CaCO_3 solubility are given in the literature, including mineralogy (Mg substitution), particle size and abrasion-induced strain, Chave and Schmaltz (1966), as well as Mg, PO_4 and organic matter inhibition of precipitation.

A decrease in calcite particle size can cause an enhanced CaCO_3 solubility. The particle size effect can be expressed by the following relationship,

$$G \text{ mol} = G^\circ + (r\bar{v}\bar{\tau}/x) \quad [1]$$

where $G \text{ mol}$ is the molar free energy of the crystal, G° is the standard state free energy of formation, r is the shape factor, \bar{v} is the molar volume, $\bar{\tau}$ is the mean surface energy of the exposed faces, and x is a linear dimension of the particles, (Chave and Schmaltz, 1966). These authors obtained an average value of 244 ergs/cm² for the surface energy of CaCO_3 using particles from 10^{-4} cm to 2×10^{-5} cm. Using the relationship

$$\Delta G_r^\circ = -1.364 \log \frac{[\text{Ca}^{2+}][\text{CO}_3^{2-}]}{a\text{CaCO}_{3(s)}} \quad [2]$$

we can determine the "apparent" activity of our CaCO_3 solid phase relative to pure calcite. Using ΔG_r° of 11.55 kcalories from Jacobson and Langmuir (1974) and $[\text{Ca}^{2+}][\text{CO}_3^{2-}]$ of $10^{-7.95}$ from this study yields an $a\text{CaCO}_{3(s)}$ value of 3.3 for the soil carbonates. On the basis of Eq. [1], the calculated particle size is 1.8×10^{-6} cm or 0.018 μm . This calculation does not consider edge and corner contributions which become increasingly important as the particle size decreases. Although $< 2 \mu\text{m}$ sized calcite is sometimes observed in soils, the author could not obtain any information on the $< 2 \mu\text{m}$ particle-size distribution of soils. X-ray analyses were made on numerous soil samples from various depths in the Wellton-Mohawk Valley. Filtration of dispersed soils through a Millipore filter system produced filtrates of 0.1 to 0.5 μm and 0.45 to 1.0 μm material. X-ray identifiable minerals were montmorillonite, kaolinite, feldspar, and quartz. Scanning electron microscope examination of the filters used to separate different size fractions

revealed that when carbonate material was present, it existed in sizes $> 1 \mu\text{m}$ (usually $> 5 \mu\text{m}$), thus particle size cannot account for the high solubilities observed. Crystal surfaces were not smooth, but rather very irregular. Although this cannot be quantified, it does indicate a decrease in crystal stability which would enhance solubility.

Magnesium substitution into the calcite structure has been proposed as a possible explanation for enhanced solubility of soil carbonates (Akin and Lagerwerff, 1965, and Doner and Pratt, 1969); however they did not account for ion-pair formation.

Katz (1973) demonstrated that if the Mg/Ca ratio in solution is sufficiently low, Mg^{2+} does not prevent calcite crystallization, even at levels approaching that of the oceans (108 meq/liter). That true inhibition of the crystallization process does not occur is shown by Berner (1975), for sea water, who found that increasing supersaturation at a Mg/Ca ratio of 5 can bring about (magnesian) calcite precipitation which does not occur at lower levels of supersaturation. This effect—which is one of destabilization of the calcite structure—requires the Mg/Ca ratio in solution to be somewhat higher than one. Few soil waters have Mg concentrations greatly in excess of Ca. That Mg levels are not sufficiently high to destabilize calcite is also evident by the abundance of precipitated calcite in the soil, and the pIAP CaCO_3 vs. $[\text{Mg}^{2+}]/[\text{Ca}^{2+}]$ plots (Fig. 3 and 4.) Only at $[\text{Mg}^{2+}]/[\text{Ca}^{2+}]$ ratios > 5 is there any decrease in pIAP.

The possibility that Mg substitution into the calcite lattice of the Wellton-Mohawk soil carbonates was responsible for the observed high CaCO_3 IAP's was also investigated. Based on shifts in the X-ray determined d (211) spacing in the calcite structure (Goldsmith and Graf, 1958) the amount of Mg^{2+} substitution in the calcite lattice was determined on soil carbonates obtained from the Wellton-Mohawk Irrigation District. A substitution of 2 to 3% Mg in the calcite structure was found. The solubility of calcites is minimal at 2% Mg substitution, (pK = 8.50) and only at 10% Mg substitution does pK CaCO_3 reach 8.00. (Plummer and MacKenzie, 1974). Recalculated data from Chave et al. (1962) indicate that approximately 20 mole % MgCO_3 in calcite would be necessary to enhance the solubility to pK = 8.00. Calcites with such large Mg substitutions are very unstable relative to low Mg calcites even when Mg/Ca ratios in solution exceed 10. High Mg calcite would not be expected to form in irrigated land even at extremely low leaching fractions. Drainage waters commonly have a Mg/Ca ratio of about 1/5 to 1/2 and should precipitate an equilibrium magnesian calcite of about 3.0 mole % MgCO_3 , which is the value determined in the Wellton-Mohawk soils. In addition these drainage waters are all supersaturated with respect to aragonite. Aragonite is not destabilized by Mg^{2+} (Berner, 1975) and should precipitate.

Phosphate (PO_4 reactive) levels in the waters were below 1×10^{-6} molar. Thus, a surface-poisoning effect would not likely explain the observed enhanced solubilities. Griffin and Jurinak (1973) reported a monolayer capacity of 8.43 $\mu\text{g PO}_4/\text{g CaCO}_3$. A comparison with the experimentally determined specific-surface area of the calcite they examined indicated that only about 5% of the surface was involved in phosphate adsorption. Further sorption occurs as lateral interaction of adsorbed ions. Filling of the monolayer

specific sites requires 0.6 ppm PO_4 ($6 \times 10^{-6} M$) in solution, much higher than seen in our waters.

The lack of equilibrium with respect to coarse-grain calcite may, nevertheless, be due to surface poisoning. Under high degrees of supersaturation, heterogeneous nucleation of calcite occurs. As precipitation occurs, a point is reached where nucleation is no longer important and further precipitation must be by crystal growth. Polysaccharides secreted by microorganisms or plants are undoubtedly present in soils, and they can inhibit CaCO_3 precipitation by coating crystal surfaces as shown by Suess (1970). Orderly crystal growth can be prevented by blocking of "critical sites" of higher energy—such as edges and corners. This might also explain the very irregular surfaces seen in the scanning electron microscope photomicrographs of the suspended material. Surface poisoning and subsequent slow crystal growth might also explain why these waters do not equilibrate with aragonite.

Kinetic studies of CaCO_3 precipitation of both aragonite and calcite indicate that, as expected, precipitation is drastically reduced when the solution approaches IAP's similar to that in equilibrium with the solid. Continuous fluctuation in soil-air CO_2 due to wetting and drying cycles with subsequent constant precipitation and dissolution of the highly soluble CaCO_3 fraction may also prevent equilibrium with calcite in soils. The nonequilibrium situation found could also be the result of the increasing Ca and HCO_3^- levels due to concentration by evapotranspiration. The rate of precipitation, greatly retarded by organic poisoning of existing surfaces, is further reduced as equilibrium is approached.

The nonequilibrium value described in this study may be the point at which the rate of precipitation for natural systems drops to negligible values for the short time spans examined here. The variety of natural conditions encountered in these waters suggest the applicability of this value to drainage waters where precipitation has occurred. Waters undergoing rapid CO_2 degassing (such as surface exposure of drainage waters) would be expected to have higher IAP values and measurable rates of precipitation.

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