

mie. Donald L. Graf of the Illinois Geological Survey gave us hydromagnesite. Analyses of the other carbonates are quoted from the literature; in a few instances they represent analyses of the same specimen, but some of the quoted analyses are of other specimens from the same locality (table 2). With the exceptions of huntite, hydromagnesite, and the synthetic materials, all of the samples used were selected from good quality, coarsely crystallized specimens. X-ray diffractometer charts were made of all the samples used, and all were found to be pure phases, properly labeled, except for the huntite specimen from Crestmore, California, which was found to be about half huntite and half aragonite.

TABLE 2

	Analyses of minerals and synthetic materials used			
	dolomite H.M. 105064 anal.: J. Ito	magnesite H.M. 105090 anal.: J. Ito	rhodochrosite Colorado Wherry & Larsen, 1917	rhodochrosite H.M. 89794 Frondel, 1955
CaO	30.43	0.10	0.28	2.08
MgO	21.78	47.34	0.33	0.69
MnO	0.02	0.05	59.11	58.27
FeO	0.08	0.52	1.16	0.27
CO ₂	47.37	51.88	37.89	38.71
insol.	0.44		0.82	
Total	100.12	99.89	99.59	100.02

	huntite Australia Skinner, 1958	huntite Australia Skinner, 1958	huntite H.M. 106589 anal.: J. Ito	alstonite Alston, Eng. Krenzl, 1905
	CaO	16.0	15.6	15.84
MgO	34.4	33.2	33.42	4.25
ign. loss		48.9	46.37	48.54
CO ₂	50.4	N.D.		29.41
Cl ₂	tr			
Fe, Al				
insol.	nil	N.D.	small 3.95	
Total	100.8	97.7	99.58	99.80

	Synthetic Calcite Baker Lot #11246	Synthetic Rhodochrosite Baker Lot #90504	Synthetic Strontianite Baker Lot #8040
	insoluble in HCl		
chloride		0.010	0.002
sulfate		0.010	0.003
nitrate		0.003	0.010
iron		0.002	0.001
other heavy metals (as Pb)		0.005	0.002
barium		<0.01	0.002
zinc			0.05
Mg and alkali salts (as SO ₄)		0.052	0.12

Analyses of minerals and synthetic materials used

rhodochrosite
Colorado
Wherry &
Larsen, 1917

dolomite
H.M. 105064
anal.: J. Ito

magnesite
H.M. 105090
anal.: J. Ito

rhodochrosite
H.M. 89794
Frondel, 1955

rhodochrosite
H.M. 85670
Frondel, 1955

Table 1
analysis is
C.M. 215
synthetic
1955

The mineral specimens were ground dry in a motor-driven agate mortar before they were dissolved; most synthetic carbonates were sufficiently fine as obtained to give satisfactorily high solution rates. No attempt was made to size the ground carbonates; in general all material used was less than 0.1 mm.

Apparatus.—Solution of the carbonates was carried out in cylindrical pyrex containers of 600 ml capacity. Covers for the containers were made from 1/4 inch thick plastic plate, cut to fit, and having holes to fit #3 and #1 rubber stoppers. Communication with the solution was established by means of a set of pH-measuring electrodes mounted in rubber stoppers and inserted through the holes in the cover. A resistance thermometer for temperature compensation, a platinum electrode for solution grounding, and a gas inlet tube were also introduced through rubber stoppers firmly seated in the holes in the plastic cover. Leads from the electrodes, thermal compensator, and solution ground were connected to an amplifier and an automatic recorder. In order to use a magnetic stirrer the water bath was set upon the stirring motors and the reaction vessels were wrapped in flexible plastic material and sunk to the bottom of the bath. Thus a seal became unnecessary, because the plastic envelope, which stretched about 12 inches above the top of the container, soon became filled with whatever gas was fed in, and provided the desired pressure of one atmosphere. Most experiments were run in duplicate; the pH of each container was recorded every 18 seconds. The apparatus used is well balanced for measurements of pH to within 0.01 pH units; we estimate the accuracy of individual measurements as about ± 0.02 pH units. The temperature of the water bath was controlled at $25 \pm 0.1^\circ\text{C}$.

Procedure.—The electrodes were first calibrated in pH 7 and pH 4 standard buffer solutions; the check was always within 0.01 pH units. Then the pyrex container and electrodes were carefully cleaned and 500 ml of distilled water added. A teflon coated magnetic bar was used to stir the solution. Then, if the hydrolysis (i.e., carbonate and water with no CO₂ gas) pH was to be measured, the water was washed with N₂ to a pH of 7.0 ± 0.1 . Finally several grams of fine grained carbonate were added. The container was encased in the plastic envelope, weighed down, sunk to the bottom of the water bath, and stirred continuously through the glass bottom of the bath. Then CO₂ was bubbled continuously through the solution. The pH, originally high as a result of the hydrolysis of the carbonate, dropped rapidly to a low value, then started to rise again as the carbonate dissolved. Several runs in the absence of carbonate showed that the water quickly became saturated with CO₂, and gave pH values consistent with equilibrium between gas and solution (pH = 3.91).

No attempts were made to compensate for variations in atmospheric pressure, and hence CO₂ pressure in the solution. Records of barometric pressure during the experiments, obtained from the U. S. Weather Bureau, showed that the variations from one atmosphere were not sufficient to affect our calculations. The pH values obtained during each run were plotted on linear or semi-log paper against time^{-1/2} to obtain an extrapolation to an equilibrium value at infinite time. These plots were empirically chosen because they yielded nearly linear plots as equilibrium was approached.

Calcite

el.	wt % oxide <small>ideal</small>	wt % el. <small>ideal</small>	β <small>ideal</small>	α_{Ca}
CaO	56.030	40.044	1.000	1.0
MgO				
MnO				
FeO				
CO ₂	43.972	C 12.000	1.001	.54262 50.107
		O ₃ 47.955		.54.029 49.992
				.000 .000
			β 1.0008	.001 .001
CaO	56.08			
CO ₂	44.011			

Dolomite, #105064, Styria

el.	wt % oxide <small>ideal</small>	wt % oxide	wt % el.	β	α_{Mg}
CaO	30.4125	30.43	21.819	1.054	1.22
MgO	21.861	21.78	13.178	1.129	1.0
MnO		0.02	0.015	1.180	1.59
FeO		0.08	0.062	1.154	1.67
CO ₂	47.734	47.37	47.522		1.18
insol.		.44	0		
	100.12		100.00		β 1.15

mole %

CaO	56.08	30.412	50.107	CaCO ₃
MgO	40.912	21.861	49.892	MgCO ₃
CO ₂	44.011	47.734	.001	FeCO ₃