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STABILITY OF SOME CARBONATES AT 25°C AND ONE ATMOSPHERE TOTAL PRESSURE*

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ABSTRACT. The stabilities of a number of carbonates, both minerals and synthetic compounds, were determined by dissolving them in water saturated with one atmosphere carbon dioxide at 25°C and one atmosphere total pressure. The pH of the solution was monitored continuously and the equilibrium value determined by extrapolating the pH-time data to infinite time. This equilibrium pH value was used to obtain the standard free energies of formation of the carbonates. The values obtained are listed below, and are compared, where data are available, with values listed in U. S. Bureau of Standards Circular 500 or in Latimer's "Oxidation Potentials."

Carbonate	$\Delta F_{f\,25^\circ C.}$ This work	U. S. Bureau of Standards
Calcite, natural and synthetic	-269.8_6	-269.78
Magnesite		-246.
Dolomite	-520.0_0	
Huntite	-1007.7_0	
Hydromagnesite	-1108.3_0	
Rhodochrosite, natural	-195.7	-195.4[1]
Rhodochrosite, synthetic pptd.	-194.7	-194.3 (Latimer)
Kutnahorite	-466.2	
Aragonite	-269.6_1	-269.53
Witherite	-272.0_1	-272.2
Alstonite	-543.0_0	
Barytocalcite	-542.9_1	
Strontianite, natural and synthetic	-272.0_2	-271.9

The value obtained for dolomite indicates that dolomite is stable with respect to calcite plus magnesite; conflicting experimental results by previous workers apparently are explained by the greatly increased solubility of dolomite that results from prolonged grinding.

INTRODUCTION

One of the oldest methods of determining the solubility of a carbonate is to dissolve it in a water solution under a fixed pressure of carbon dioxide. The justification for reporting the present work comes from the use of continuous recording of pH of the solution, which provides data that can be used to obtain accurate equilibrium values by appropriate extropolation. Equilibrium was approached at 25°C. and one atmosphere pressure only from undersaturation; but the values we obtained agree well with previous determinations in which equilibrium was approached from both sides. If the approach to equilibrium from undersaturation alone is valid, the stability of a number of species such as dolomite and huntite can be determined, even though these compounds have not yet been synthesized at room temperature and pressure.

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[1] Natural or synthetic not specified.

The method used has the additional virtue of being rapid and simple; 24 hours is usually sufficient to obtain data for determination of an equilibrium constant.

EXPERIMENTAL

Materials.—Water was prepared by distillation in a Barnstead still, and yielded a pH of 7.0 ± 0.1 after washing with nitrogen. Carbon dioxide was obtained from a commercial tank, and was bubbled through a gas-washing bottle containing distilled water to presaturate it with water before it entered the experimental container. Nitrogen, used for removing other gases from the water, was obtained from commercial tanks, and was passed through a carbon dioxide absorbent and through distilled water before use. The carbonate compounds were either mineral specimens of good quality or *Reagent Grade* commercial products (table 1). We are indebted to C. Frondel and C. Hurlbut of the Department of Mineralogy, Harvard University, for most of the specimens, Jun Ito, of the same Department, for analyses of magnesite, huntite, and dolo-

TABLE 1

Data on carbonate specimens studied

Specimen	Identification*	Analysis sample	Locality
Calcite Natural	H.M. 87189		Iceland
Calcite** Synthetic	Baker# Lot No. 11246	Same lot	
Dolomite	H.M. 105064	Same sample	Oberdorf, Styria, Austria
Huntite**	H.M. 106304	Same locality	Tea Tree Gully, S. Australia
Huntite**	H.M. 106589	Same locality	Crestmore, California
Magnesite	H.M. 105090	Same sample	Oberdorf, Styria, Austria
Hydromagnesite**		None	Soda Springs, Idaho
Rhodochrosite Natural	H.M. 96030	Same locality	John Reed Mine, Alicante, Colo.
Rhodochrosite Natural	H.M. 89794	Same specimen	Franklin, N. J.
Rhodochrosite** Synthetic	Baker Lot No. 90504	Same lot	
Rhodochrosite** Synthetic		Made from analytical grade reagents	
Kutnahorite	H.M. 85670	Same sample	Franklin, N. J.
Aragonite	H.M. 84357		Bilin, Bohemia
Alstonite	H.M. 76361	Same locality	Alston Moor, England
Barytocalcite	H.M. 80399		Alston Moor, England
Witherite	H.M. 88199		Northumberland, England
Strontianite Natural	H.M. 93448		Ahlen, Westphalia
Strontianite Synthetic	Baker Lot No. 8040	Same lot	

* H.M. = Harvard Museum

\# Baker Chemical Company, Phillipsburg, New Jersey

** Less than 2 microns

mite. 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	kutnahorite H.M. 85670 Frondel, 1955
CaO	30.43	0.10	0.28	2.08	27.44
MgO	21.78	47.34	0.33	0.69	2.21
MnO	0.02	0.05	59.11	58.27	28.31
FeO	0.08	0.52	1.16	0.27	0.50
CO_2	47.37	51.88	37.89	38.71	41.80
insol.	0.44		0.82		
Total	100.12	99.89	99.59	100.02	100.26

	huntite Australia Skinner, 1958	huntite Australia Skinner, 1958	huntite H.M. 106589 anal: J. Ito		alstonite Alston, Eng. Kreutz, 1905
CaO	16.0	15.6	15.84	CaO	17.60
MgO	34.4	33.2	33.42	SrO	4.25
ign. loss			46.37	BaO	48.54
CO_2	50.4	48.9		CO_2	29.41
Cl_2	tr	N.D.			
Fe, Al			small		
insol.	nil	N.D.	3.95		
Total	100.8	97.7	99.58	Total	99.80

	Synthetic Calcite Baker Lot #11246	Synthetic Rhodochrosite Baker Lot #90504	Synthetic Strontianite Baker Lot #8040
insoluble in HCl		0.010	
chloride		0.010	0.002
sulfate		0.003	0.003
nitrate			0.010
iron		0.002	0.001
other heavy metals (as Pb)		0.005	
barium	<0.01		0.002
zinc		0.05	
Mg and alkali salts (as SO_4)	0.052	0.12	0.022

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 $\pm$ 0.02 pH units. The temperature of the water bath was controlled at 25 $\pm$ 0.1°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 CO_2 gas) pH was to be measured, the water was washed with N_2 to a pH of 7.0 $\pm$ 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 CO_2 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 CO_2, 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 CO_2 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.

After a given pair of samples had run long enough to give a satisfactory approach to equilibrium, stirring was stopped, and the supernatant solution and suspended carbonate removed by decanting. Fresh water was added, and the run repeated. This procedure was used to avoid the possibility of a significant contribution to the solubility from material so fine grained as to have a significantly higher surface energy than bulk material.

Most runs required 12 to 18 hours under these experimental conditions. When some of the more slowly soluble carbonates required more time, we tried to bring them back into the 12 to 18 hour range by using larger samples or finer grinding, or both. If the runs lasted 3 or 4 days, contamination of the solution and of the calomel electrode resulted, and there was difficulty in obtaining checks on buffer solutions. Also, diffusion of KCl from the calomel electrode caused an unknown increase in ionic strength of the solution.

Analyses of solutions that had approached equilibrium were made from time to time to check calculated values. The concentration of bicarbonate ion was determined by titrating the filtered solution with standard HCl under one atmosphere CO_2 to an endpoint at pH 3.91. Calcium was determined by precipitation as the oxalate, or calcium and magnesium were determined by titration with Versene, according to the procedure outlined by Shapiro and Brannock (Shapiro and Brannock, 1956). Barium was determined gravimetrically as the sulfate, and manganese colorimetrically after oxidation to permanganate. The results are discussed under the sections devoted to the behavior of the individual carbonates.

RESULTS

General.—Typical results of the experiments are shown in figure 1. Figure 1a shows curves for huntite and calcite. The similarity in behavior indicates that a similar solution mechanism is involved, despite the fact that huntite contains two different essential cations. Complete equilibrium was seldom achieved, but figure 1b, which shows data for synthetic $SrCO_3$, il-

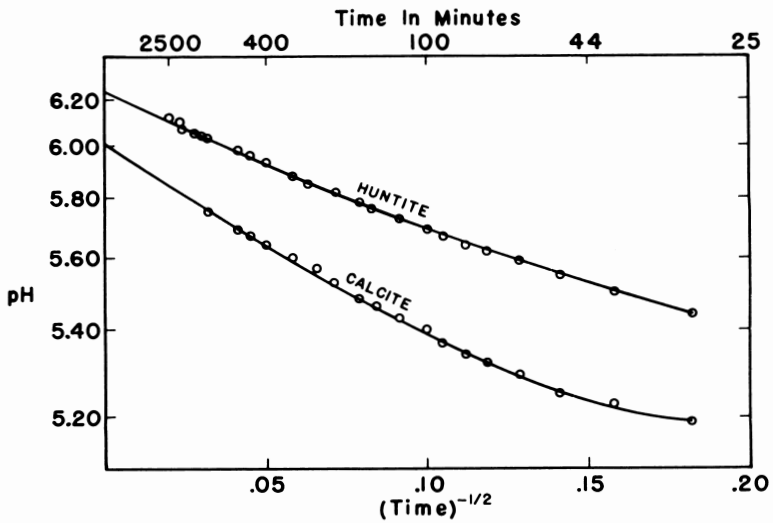

Fig 1. A. Log pH versus time$^{-1/2}$ for runs of huntite and calcite.

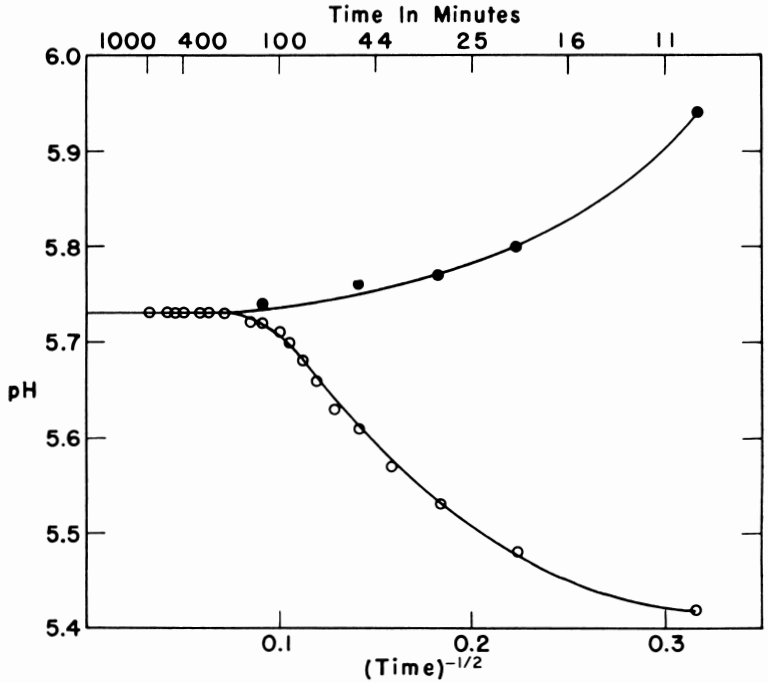

Fig. 1. B. pH versus time$^{-1/2}$ for two runs of synthetic strontianite.

lustrates achievement of equilibrium during the experiment. It would be expected, therefore, that our extrapolated equilibrium values from runs of the type shown in figure 1a would give a pH that is too high, and from this a lower than actual stability. However, our experimental points are sufficiently close to the ordinate to preclude the possibility of a serious error. Also, comparison of our results with those of previous investigators shows that our deviation from them is in the direction of greater, rather than lesser, stability.

Calcite.—Both natural and synthetic calcites were run. The natural material was large clear rhombic cleavage fragments of Iceland spar. Synthetic calcite, obtained from D. Stewart of the U. S. Geological Survey, was a specimen of reagent grade material produced by J. T. Baker Chemical Company. Both the natural and synthetic calcite dissolved very rapidly, and a value for the equilibrium pH accurate within 0.01 or 0.02 pH units could be taken from the highest pH achieved in most of the runs. The filtered solution from some of the runs, left open to the room so that the CO_2 might pass off, precipitated a mixture of calcite and aragonite. Equilibrium pH is 6.02.

Magnesite.—The magnesite used was unusually pure material, as shown by the analysis in table 2, but a reliable extrapolation to equilibrium pH was not obtained because the mineral dissolved so slowly that the curves approached the "infinity axis" much too steeply. Numerous runs, using up to 30 grams of finely ground magnesite, were made, with inconclusive results. The filtered outgassed solutions formed no precipitate for months, until, because of evaporation, nesquehoneite, $MgCO_3.3H_2O$ formed. A cleavage fragment of magnesite,

suspended in one such solution for 18 days, showed no gain or loss of weight. No satisfactory equilibrium pH was obtained.

Dolomite.—The dolomite specimen used was also of very pure material (see analysis in table 2). Unlike the magnesite from the same locality, however, dolomite behaved very well when subjected to our standard procedure. Good duplication of results was obtained, even from the earliest runs, made outside the water bath. However, if a run was allowed to approach to within about 0.1 pH units of the extrapolated equilibrium value (fig. 2), and then subjected to the addition of several grams of dolomite that had been ground for 12 hours or more, the pH rose rapidly, and leveled off to give an extrapolated value appropriate to aragonite. When this experiment was re-run, after

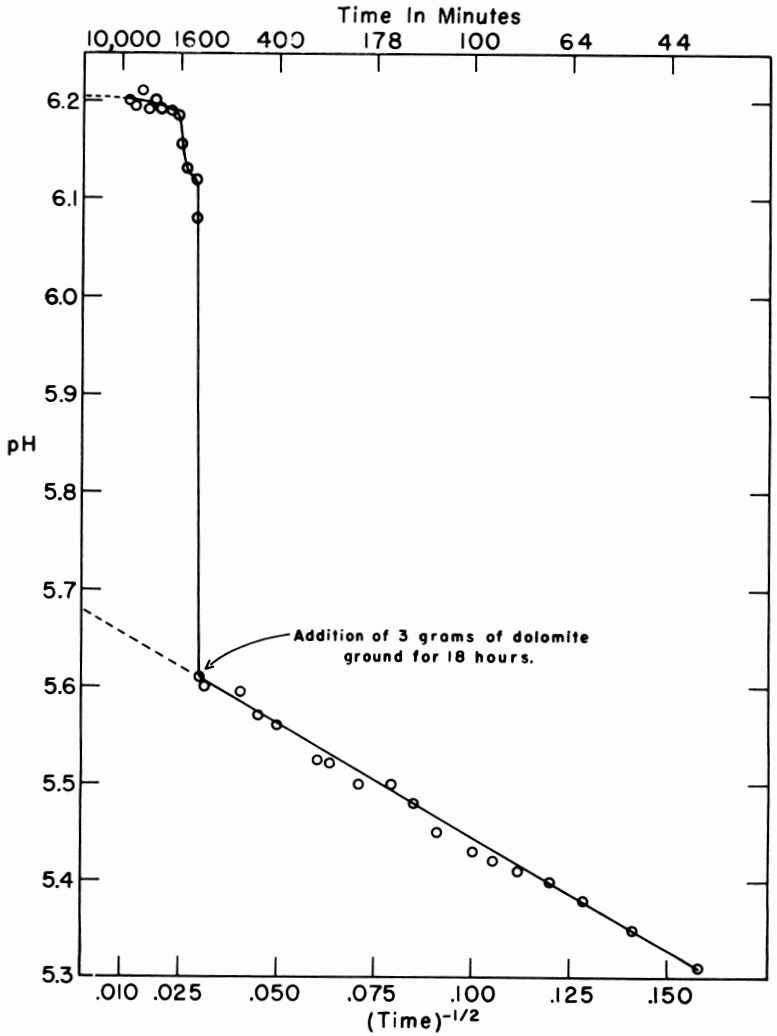

Fig. 2. Effect of adding finely ground dolomite to a solution approaching saturation with coarser material.

removing the supernatant liquid and its accompanying fine particles, an extrapolation to the usual pH was obtained. Equilibrium pH (coarse material) is 5.68.

Huntite.—Two specimens of huntite were run, but that from Crestmore was found to be a mixture of about equal proportions of aragonite and huntite. That from Australia was a single phase, however, and good duplication of results was obtained from it. Moreover, analyses of some of the solutions showed that the mineral dissolved essentially congruently. However, we cannot be sure that huntite is as stable as calculated; it is possible that it dissolved congruently until calcite started to precipitate, and then ceased reacting. The precipitate that formed when some of the filtered solution was left open to the room was calcite.

The runs of the Crestmore aragonite-huntite showed an interesting break in slope, from which two extrapolations might be made—the lower one to approximately the equilibrium pH of aragonite, and the upper to about the equilibrium pH of huntite. Equilibrium pH is 6.24.

Hydromagnesite.—The hydromagnesite specimen, from near Soda Springs, Idaho, was not analyzed chemically, but the x-ray diffractometer chart showed it to consist essentially of hydromagnesite, with no other carbonates present, but with 10 or 15 percent of silt and clay. Two runs of this material gave duplicate results, but the standard HCl titrations of the solutions did not confirm the measured pH's. It may be that at pH's of 6 or higher, the Mg^{++} ion is partially complexed, and the measured pH does not give a true measure of the cation concentration. Comparison of a series of calculated versus measured bicarbonate molalities for magnesium bicarbonate solutions indicate the presence of a minor amount of associated $Mg(HCO_3)_2$ or $Mg(HCO_3)^+$. We regard the equilibrium constant value for hydromagnesite as the least reliable of the listed values. Equilibrium pH value is 6.71.

Rhodochrosite.—Two mineral specimens of rhodochrosite were run; both contained about 5 mole percent of other cations in diadochic substitution. Good extrapolations to an equilibrium pH were not easily obtained from either rhodochrosite, so the average result of a number of runs is presented. Precipitated $MnCO_3$, prepared from Reagent Grade reagents, was shown by the x-ray diffractometer to have the structure of rhodochrosite, though the reflections were broad. This material was found to be more soluble than the mineral rhodochrosites. As differences in solubility were not found between other mineral and synthetic carbonate pairs, it may be that the difference found for $MnCO_3$ is due to the presence of about 5 mole percent of other cations in the natural rhodochrosites. A small amount of better crystallized synthetic rhodochrosite was made by using an electric current to cause reaction of Mn^{++} and HCO_3^- ions in a salt bridge. The rate of precipitation was necessarily slow, and only about 100 mg were obtained. (The reaction between Mn^{++} and HCO_3^- produces CO_2 as well as $MnCO_3$, but the side effect of oxidation of Mn^{++} is less at the lower pH of the HCO_3^- solution than at that of the higher pH of a CO_3^{--} solution.) One equilibrium pH run only was made with this material because so little was available, and a projected equilibrium pH value of 5.73 was obtained. Equilibrium pH of natural rhodochrosite is 5.09; of fine grained precipitated $MnCO_3$ is 5.35.

Kutnahorite.—Our sample of kutnahorite was part of an analyzed specimen from Franklin, New Jersey. The x-ray diffractometer chart of our sample showed only kutnahorite peaks, but the solution behavior suggested that it might be contaminated with a little calcite, or perhaps the grinding involved in the preparation of the sample tended to disorder the cations. The first few runs projected to and reached considerably higher pH's than later runs. The filtered solution from one of the later runs was titrated with standard acid, and confirmed the measured pH exactly. The colorimetric analysis showed that Mn was 49.5 mole percent of the total cations. Equilibrium pH is 5.58.

Aragonite.—The aragonite sample was prepared from beautifully crystallized material from Bilin, Czechoslovakia. Two runs were made, giving good duplication of results, and checking the Bureau of Standards value very closely. Equilibrium pH is 6.08.

Witherite.—The sample of witherite was prepared from one large crystal. Two runs were made, giving good duplication, and titration of the solution for HCO_3^- and precipitation of Ba as the sulfate both confirmed the measured pH. Witherite precipitated again from the filtered solution. Equilibrium pH is 5.93.

Alstonite.—The alstonite sample was prepared by handpicking to separate it from the associated calcite and witherite. Most of the fragments of alstonite were recognized by their distinctive crystal habit, as well as by distinctive luster. The x-ray diffractometer chart showed no extra peaks. Three runs were made, giving reasonably good duplication. Titration of one of the solutions for HCO_3^- confirmed the measured pH. The phase that precipitated out of one of the filtered solutions was a barian calcite. Equilibrium pH is 5.93.

Barytocalcite.—This sample was also prepared by handpicking from the associated barite and calcite. The barytocalcite was recognized by a difference in luster. The x-ray diffractometer chart showed no extra peaks. Two runs were made, giving reasonably good duplication.

The precipitate that formed in a filtered solution of barytocalcite was a barian calcite that was found by analysis to contain 40 mol percent $BaCO_3$. Equilibrium pH is 5.95.

Strontianite.—Both natural and synthetic strontianites were run, and good agreement was obtained between the coarsely crystallized mineral and the fine grained synthetic precipitate. Titrations for HCO_3^- confirmed the measured pH's, and the phase that precipitated from the filtered solution was again strontianite. Equilibrium pH is 5.73.

Summary.—The equilibrium pH values for the carbonates, as well as their dissociation constants, are summarized in table 3 and figure 3. In the figure, equilibrium constants for all carbonates are shown on the basis of dissociation to a single carbonate ion (e.g. k dolomite $= a^{1/2}_{Mg^{++}} a^{1/2}_{Ca^{++}} a_{CO_3^{--}}$). The position of a given carbonate in the table is a criterion of its stability in aqueous solution in the absence of complexing agents.

DISCUSSION OF RESULTS

Standard free energy values.—The equilibrium constants for the ionization of the carbonates, and hence their standard free energies of formation from the elements at 25°C and 1 atmosphere total pressure can be obtained

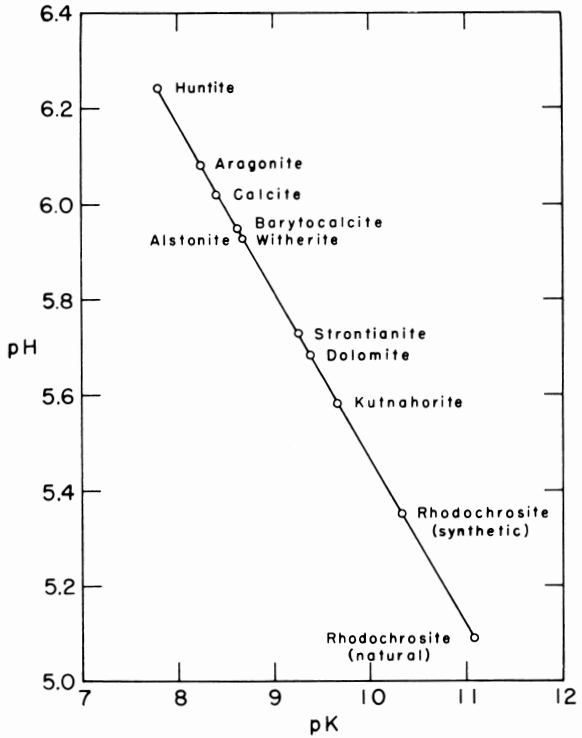

Fig. 3. Equilibrium pH for solutions saturated in carbonate compounds versus dissociation constant of solid carbonate. 25°C and 1 atmosphere CO_2 pressure.

from the equilibrium pH values. The calculations depend upon ΔF_f° values already available in the literature for various ionic and molecular species. so that the values obtained for the carbonates are no better than the other data used.

TABLE 3

Equilibrium pH values for carbonate species

Equilibrium pH	Species
5.09	rhodochrosite, Colo.
5.09	rhodochrosite, N. J.
5.35	syn. $MnCO_3$
5.58	kutnahorite
5.70	dolomite
5.73	strontianite
5.73	syn. $SrCO_3$
5.93	witherite
5.93	alstonite
5.95	barytocalcite
6.02	calcite
6.02	syn. $CaCO_3$
6.08	aragonite
6.24	huntite, Australia
6.71	hydromagnesite

A sample calculation for dolomite should suffice to show the procedure used in obtaining ΔF_f° values.

For the dissociation of dolomite, $CaMg(CO_3)_2 = Ca^{++} + Mg^{++} + 2CO_3^{--}$, the equation for the solubility product, K, is:

$$K = a_{Ca^{++}} a_{Mg^{++}} a^2_{CO_3^{--}} \quad (1)$$

The value for $a_{CO_3^{--}}$ is obtained from the equilibrium pH through the following relationships from the equilibrium for carbonic acid (Harned and Owen, 1958).

$$P_{CO_2} / a_{H_2CO_3} = 10^{+1.47} \quad (2)$$

$$a_{H^+} a_{HCO_3^-} / a_{H_2CO_3} = 10^{-6.35} \quad (3)$$

$$a_{H^+} a_{CO_3^{--}} / a_{HCO_3^-} = 10^{-10.33} \quad (4)$$

Combining equations #2 and #3, and setting $P_{CO_2} = 1$:

$$a_{HCO_3^-} = 10^{-6.35} \times 10^{-1.47}/a_{H^+} = 10^{-7.82}/a_{H^+} \quad (5)$$

The values for $a_{Ca^{++}}$ and $a_{Mg^{++}}$ are also obtained from the equilibrium pH, though less directly. When dolomite dissolves to equilibrium in water saturated with CO_2 at one atmosphere pressure:

$$CaMg(CO_3)_2 + 2H_2O + 2CO_2 = Ca^{++} + Mg^{++} + 4HCO_3^- \quad (6)$$

At the pH values (5-7) found experimentally[2], no dissolved ionic species other than Ca^{++}, Mg^{++}, and HCO_3^- need be considered as being of quantitative importance in the mass balance, hence a close approximation is:

$$2m_{Ca^{++}} + 2m_{Mg^{++}} = m_{HCO_3^-} \quad (7)$$

Because dolomite apparently dissolves congruently (the ion products of Ca^{++} or Mg^{++} times CO_3^{--} are less than those for any other known solid carbonate species):

$$m_{Ca^{++}} = m_{Mg^{++}} = 1/4 m_{HCO_3^-} \quad (8)$$

If the ionic strength is known, then ionic activity coefficients (γ) may be calculated and the value for $a_{HCO_3^-}$ from equation #5 may be converted to $m_{HCO_3^-} \cdot m_{HCO_3^-}$, in equation #8, yields values for $m_{Ca^{++}}$ and $m_{Mg^{++}}$, which are in turn converted to $a_{Ca^{++}}$ and $a_{Mg^{++}}$. The equation for ionic strength is:

$$\mu = 1/2 \, \Sigma m_i z_i^2 \quad (9)$$

Again, the only quantitatively important species in the solution are the dissolved cations and HCO_3^-. Therefore, in the case of dolomite:

$$\mu = 1/2 \, (4m_{Ca^{++}} + 4m_{Mg^{++}} + m_{HCO_3^-}) \quad (10)$$

In general, for doubly charged cations, the expression for μ is reducible to:

$$\mu = 1/2 \, (3m_{HCO_3^-}) \quad (11)$$

Using the value for μ in the Debye-Hückel equation, (Klotz, 1950)

$$-\log \gamma_i = A z_i^2 \sqrt{\mu}/(1 + a^\circ B\sqrt{\mu}) \quad (12)$$

values for $\gamma_{HCO_3^-}$, $\gamma_{Ca^{++}}$, and $\gamma_{Mg^{++}}$ are obtained.

An analytical determination of $m_{HCO_3^-}$ may be made by titrating the solution with a standard acid, but in general $m_{HCO_3^-}$ was calculated from $a_{HCO_3^-}$

[2] At higher pH values the approximation given by (7) is not so close.

$$19.52 = -132.18 - 108.99 - 561.24 - \Delta F_f^\circ{}_{CaMg(CO_3)_2} + 113.4 + 188.52$$

$$\Delta F_f^\circ{}_{CaMg(CO_3)_2} = -520.0_1 \text{ kilocalories}$$

Our estimate of the accuracy of the free energy values, based on the checks against known values where available, the consistency of values obtained by various calculation routes, the generally good agreement between analyzed solutions and values calculated for them and the probable error in determining the extrapolated equilibrium pH value, is that they are generally accurate to about ± 0.2 kilocalorie. This assumes no error in the Bureau of Standards values for various species used in calculating ΔF_f° of a given carbonate from the standard free energy of the dissociation reaction.

Relations among the Ca-Mg carbonates.—Relations among the Ca-Mg carbonates, although not entirely definitive because of our inability to get a satisfactory free energy value for magnesite, indicate that calcite and magnesite are unstable with respect to dolomite at 1 atmosphere total pressure and 25°C. Using the U. S. Bureau of Standards value for magnesite:

$$CaCO_3 + MgCO_3 = CaMg(CO_3)_2;\ \Delta F_R^\circ \cong -4 \text{ kilocalories}$$

Huntite apparently is not stable with respect to dolomite and magnesite:

$$CaMg(CO_3)_2 + 2MgCO_3 = CaMg_3(CO_3)_4;\ \Delta F_R^\circ = +5.1 \text{ kilocalories}$$

Nesquehonite is markedly unstable (Latimer, 1952). Even in the presence of pure water:

$$MgCO_3.3H_2O = MgCO_3 + 3H_2O;\ \Delta F_R^\circ = -4.5 \text{ kilocalories}$$

Thus in the composition triangle $CaCO_3$–$MgCO_3$–H_2O, relations among the species studied are shown in figure 4.

The solubility of the carbonates in water is so small that the composition of the solutions in equilibrium with the solids cannot be shown well on figure 4. A more graphic illustration of the relations in this system is obtained by plotting stability of the solids as a function of the activities of the Ca^{++} and Mg^{++} ions in solution, and as a function of P_{CO_2}. This permits inclusion of hydromagnesite, which falls outside the triangle $CaCO_3$–$MgCO_3$–H_2O.

All the reactions of interest can be written in terms of the three variables $a_{Ca^{++}}$, $a_{Mg^{++}}$, and P_{CO_2}, always assuming water in excess. For example, for equilibrium between calcite and dolomite:

$$2\,CaCO_3 + Mg^{++} = CaMg(CO_3)_2 + Ca^{++} \qquad (14)$$

$$K = \frac{a_{Ca^{++}}}{a_{Mg^{++}}}$$

For equilibrium between calcite and hydromagnesite:

$$4\,CaCO_3 + 4\,Mg^{++} + H_2O = Mg_4(CO_3)_3(OH)_2.3H_2O + 4Ca^{++} + CO_2$$

$$K = \frac{a^4_{Ca^{++}} P_{CO_2}}{a^4_{Mg^{++}}}$$

Consequently a logarithmic plot of the variables provides linear boundaries among species.

The summary diagram is shown in figure 5. Note that hydromagnesite is not stable under earth surface conditions ($P_{CO_2} = 10^{-3.5}$). Moreover, if the ratios of the molalities of Ca^{++} and Mg^{++} in sea water are used as criteria of their activities, the stable carbonate in sea water should be dolomite. In other words, the implication is that the oceans are supersaturated with respect

by a method of successive approximations. For the first approximation $a_{HCO_3^-}$ is assumed to be equal to $m_{HCO_3^-}$. From this, ionic strength and $\gamma_{HCO_3^-}$ are calculated. Then $\gamma_{HCO_3^-}$ is used to correct $a_{HCO_3^-}$ and new values for ionic strength and $\gamma_{HCO_3^-}$ are calculated. In most cases it is necessary to repeat this cycling only two or three times. An example of the calculation for dolomite is given. To simplify the calculations γ's are read from a previously prepared graph of γ_i versus μ taken from a table in Klotz (p. 332).

Sample calculation.—Equilibrium pH for dolomite = 5.68 (table 3).

$a_{HCO_3^-} = 10^{-7.82}/a_{H^+} = 10^{-7.82}/10^{-5.68} = 10^{-2.14} = 0.00724$

$m_{HCO_3^-} = a_{HCO_3^-} = 0.00724$ (First approximation)

$\mu = 3/2\ (0.00724) = 0.01084$

$\gamma_{HCO_3^-} = 0.902$

$m_{HCO_3^-} = a_{HCO_3^-}/.902 = 0.00724/.902 = 0.00802$ (Second approximation)

$\mu = 3/2\ (0.00802) = 0.01202$

$\gamma_{HCO_3^-} = 0.898$

$m_{HCO_3^-} = 0.00724/.898 = 0.00805$ (Third approximation)

$\mu = 3/2\ (0.00805) = 0.01208$

$\gamma_{HCO_3} = 0.898$

$m_{Ca^{++}} = m_{Mg^{++}} = 1/4\ m_{HCO_3^-} = 0.00201$

$\gamma_{Ca^{++}} = 0.654$

$\gamma_{Mg^{++}} = 0.665$

$a_{Ca^{++}} = (0.00201)\ .654 = 0.00131 = 10^{-2.88}$

$a_{Mg^{++}} = (0.00201)\ .665 = 0.00135 = 10^{-2.87}$

$$a_{CO_3^{--}} = \frac{10^{-10.33} \times 10^{-2.14}}{10^{-5.68}} = 10^{-6.79}$$

$K = (10^{-2.88})\,(10^{-2.87})\,(10^{-6.79})^2 = 10^{-19.33}$

From the relation $\Delta F_R^\circ = -RT \ln K = -1.364 \log k$ at 25°C and 1 atmosphere pressure, the standard free energy of reaction 9 is:

$$\Delta F_R^\circ = -1.364 \times -19.33 = 26.37 \text{ kilocalories} \qquad (13$$

Then we can write:

$$\Delta F_R^\circ = \Delta F_f^\circ{}_{Ca^{++}} + \Delta F_f^\circ{}_{Mg^{++}} + 2\Delta F_f^\circ{}_{CO_3^{--}} - \Delta F_f^\circ{}_{CaMg(CO_3)_2}$$

Substituting the value for ΔF_R° obtained in equation 13, and values for the ions from U. S. Bureau of Standards Circular 500:

$$+26.37 = -132.18 - 108.99 - 252.44 - \Delta F_f^\circ{}_{CaMg(CO_3)_2}$$

$$\Delta F_f^\circ{}_{CaMg(CO_3)_2} = -519.9_8 \text{ kilocalories}$$

A check on the consistency of the free energy values from the literature can be obtained by calculating ΔF_f° dolomite from the initial reaction with CO_2:

$$CaMg(CO_3)_2 + 2H_2O + 2CO_2 = Ca^{++} + Mg^{++} + 4HCO_3^-$$

$$K = 10^{-14.31}$$

$$\Delta F_R^\circ = +19.52 \text{ kcal.}$$

$$+19.52 = \Delta F_f^\circ{}_{Ca^{++}} + \Delta F_f^\circ{}_{Mg^{++}} + 4\Delta F_f^\circ{}_{HCO_3^-} - \Delta F_f^\circ{}_{CaMg(CO_3)_2} - 2\Delta F_f^\circ{}_{H_2O} - 2\Delta F_f^\circ{}_{CO_2}$$

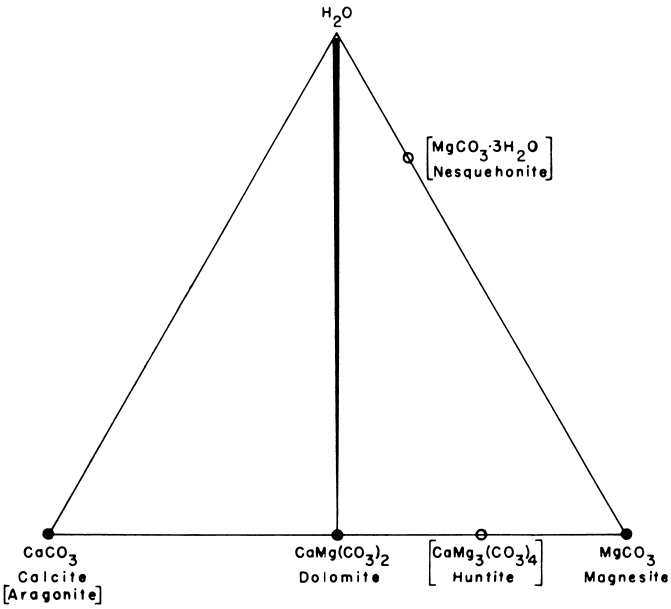

Fig. 4. Some stability relations in the system $CaCO_3$–$MgCO_3$–H_2O.

to dolomite, and calcite or aragonite on the floor of the sea should react with the sea water to form dolomite until the ratio of the activity of Ca^{++} to Mg^{++} is equal to $10^{+2.48}$.

There appear to be two alternatives to this conclusion. First, our value for the free energy of formation of dolomite may be in error. Second, the concentration of magnesium ion in sea water may be vastly different from its activity. The approximate activity of calcium ion in sea water is not in serious question,[3] therefore any large anomalies between concentrations and activities must be attributed to the magnesium ion. The small amount of indirect evidence available now suggests that the value we have obtained for the free energy of formation of dolomite is approximately correct, and that the near-absence of dolomite as a primary marine precipitate results from supersaturation.

Robie (personal communication) has summarized all the data available for calcite, magnesite, and dolomite, and has determined values for their free energies of formation that are in essential agreement with ours.

The solubility data of Yanat'eva (1954) on calcite, magnesite, and dolomite, as determined at 25°C and 1 atmosphere P_{CO_2}, show dolomite as a stable phase. On the other hand her data at 25°C, 1 atmosphere total pressure but with $P_{CO_2} = 10^{-3.5}$ (that of the present atmosphere), indicate that dolomite dissolves incongruently to yield calcite plus solution. As shown in figure 5 or in equation number 14, the stability of dolomite relative to calcite is not a function of P_{CO_2}, so the inference is that her experiments at lower P_{CO_2} and hence higher pH, somehow caused dolomite to increase its relative solubility drastically.

[3] The activity coefficient for Ca^{++} in sea water is of the order of 0.24, as shown by various studies of the solubility of calcite. (c.f. Garrels and Dreyer, 1952, p. 334.)

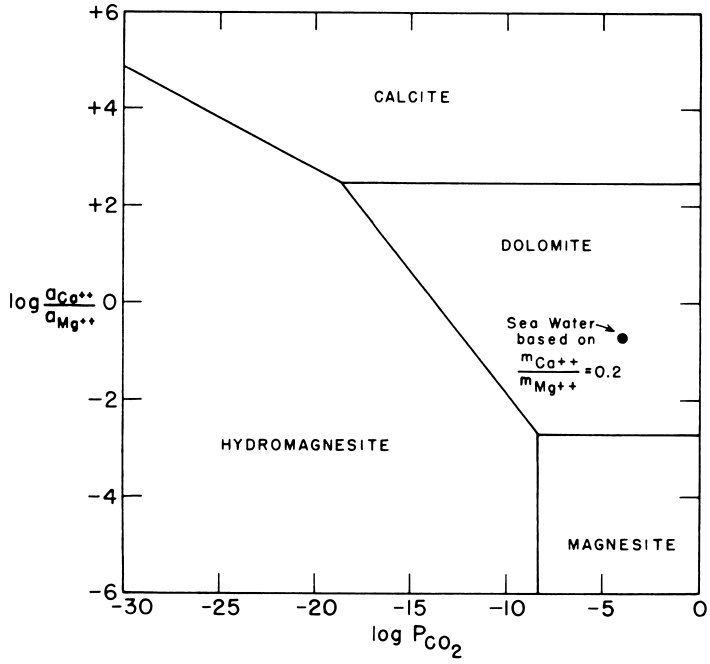

Fig. 5. Stability of some Ca-Mg carbonates in aqueous solution at 25°C. and one atmosphere total pressure, as a function of calcium-magnesium ion ratio and partial pressure of carbon dioxide.

One possible explanation of this peculiar phenomenon is that the behavior of dolomite is analogous to that of quartz. When quartz solubility is determined by experiments during which the quartz is tumbled or otherwise ground, the solubility increases by 10 to 15 times and approaches that of amorphous silica (Van Lier, 1959). This increased solubility is considered to result from the disordering of the quartz surface during grinding, so that a layer of amorphous silica is produced. Because dolomite has two structurally nonequivalent cations it is susceptible to disordering effects from grinding. This disordering has been reported by Bradley, Burst, and Graf (1953). These effects would be especially noticeable in experiments in which the dolomite would be continuously stirred or tumbled for long periods of time. The effects of a very slight disordering produced during the preparation of the sample would be noticed especially in experiments where the solubility is small, as under low CO_2 partial pressures.

To test this hypothesis we permitted dolomite to react with water saturated with CO_2 under one atmosphere pressure, until the pH of the solution was within 0.1 pH unit of the extrapolated equilibrium value. (Note that under these conditions dolomite is soluble enough so that if any small portion of it has been disordered by the original preparation of the sample it will all be dissolved before the solution is saturated.) Then three grams of the same dolomite, that had been ground continuously for 18 hours, were added to the system. The effect was immediate and striking. Within minutes the pH had

risen nearly 0.5 pH units, and after a few hundred minutes a new extrapolated equilibrium pH was obtained (fig. 2). Calculations based on the higher value (pH 6.2) show that the product $a_{Ca^{++}} \times a_{CO_3^{--}}$ is $10^{-8.22}$, exactly the value we had previously determined as the equilibrium constant for aragonite. Apparently the prolonged grinding had so increased dolomite solubility that it dissolved incongruently to yield $CaCO_3$ plus magnesium-rich solution.

It was also found that when the first solution was decanted and replaced with more distilled water and the solution experiment repeated that the dolomite had reverted to its original solubility. In other words, the material responsible for the increased solubility had all been dissolved during the first run or was carried off by the decanting, and by the time the solution approached saturation the second time, we were again measuring the solubility of relatively coarse-grained, ordered dolomite.

The anomalously high solubility was measured again by addition of more of the well-ground dolomite to the new solution, with the same results.

It is concluded that our usual procedure measures the stability of dolomite accurately, and that the higher solubilities reported by other investigators result from grinding, either during sample preparation or from the stirring or tumbling during the measurement itself.

Our experiments are too preliminary in nature to explain this phenomenon completely. One possibility is that the surfaces of the grains are disordered during prolonged grinding; another possibility is that a small amount of the sample is ground so fine that its solubility is enhanced. Ordinarily, when a supersaturated solution is in contact with the appropriate solid, the supersaturation is relieved by precipitation on the less soluble larger grains, but because of the extremely slow rate of precipitation of dolomite, this effect is probably not seen in the usual experiments. X-ray diffractometer charts of the dolomite before and after grinding showed that the prolonged grinding tended to produce line broadening due to decreased particle size. There was no apparent relative intensity decrease of the ordering reflections.

Similarly, well-ground calcite was added to a calcite run near the equilibrium pH. After the first addition the solution attained the equilibrium pH and successive additions of finely ground material raised the pH by no more than 0.01 pH units.

Within 5 minutes of each addition, the pH was again at the equilibrium value. The effect in this case is so slight that we cannot definitely say whether the small increase in pH was due to excess solubility of the finely ground material, or whether it was due to a slight loss of CO_2 atmosphere as a result of the necessary opening of the container.

Furthermore, our whole experience with magnesium ion in solution has impressed us with its reluctance to form solids from saturated solution. When solutions partly saturated with magnesite at $P_{CO_2} = 1$ atmosphere were allowed to stand open, so that the P_{CO_2} approached that of the laboratory, no precipitate formed over a period of several months. These solutions were highly supersaturated with respect to magnesite. If precipitation was finally forced by permitting the solutions to evaporate, the product was nesquehonite, which is many times as soluble as magnesite.

Perhaps the clue to the reluctance of magnesian carbonates to precipitate lies in some peculiar characteristic of the magnesium ion; it may be abnormally firmly hydrated, or it may form a stable ion pair $(MgCO_3)^\circ$.

Calcium-barium carbonates.—The data on the calcium-barium carbonate system indicates that the ordered intermediate phases barytocalcite and alstonite have approximately the same solubility, and that they are slightly more stable than an ideal solid solution of the same composition. Our data are not good enough to permit us to determine which of the dimorphs is more stable, but the free energy of the reaction

$$BaCa(CO_3)_2 \text{ (Barytocalcite)} = BaCa(CO_3)_2 \text{ (Alstonite)}$$

is probably not more than $\pm$ 100 calories. In harmony with our other attempts to form ordered intermediate phases, the precipitate resulting from loss of CO_2 from a nearly saturated CO_2-rich solution yielded a high (40 mol %) barian calcite, rather than the initial barytocalcite or alstonite.

Ca-Mn carbonates.—Results of experiments involving kutnahorite indicate that this ordered intermediate phase is stable at the conditions of the experiment. Also, we observed a marked difference in the stability of precipitated and natural $MnCO_3$. The difference we found is about the same as that reported by Latimer (Latimer, 1952, p. 235).

Sr.-carbonate.—Our value for strontianite agrees closely with that of the Bureau of Standards. No anomalies in behavior were observed.

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