Reprinted from

DEEP-SEA RESEARCH
and Oceanographic Abstracts

UNIVERSITY OF WASHINGTON
DEPARTMENT OF OCEANOGRAPHY
TECHNICAL REPORT NO. 109

7p

PERGAMON PRESS
OXFORD · LONDON · NEW YORK · PARIS

Deep-Sea Research, 1963, Vol. 10, pp. 633 to 638. Pergamon Press Ltd. Printed in Great Britain.

Calcium carbonate and the *in situ* pH

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(*Received* 13 *May* 1963)

Abstract—The effect of hydrostatic pressure on the dissociation constants of carbonic acid and on the solubility product of calcium carbonate are used for estimating the effect of depth and of calcareous sediments on the *in situ* pH.

INTRODUCTION

IN THIS work the combined effects of hydrostatic pressure on the dissociation of carbonic acid and on the solubility of calcium carbonate are evaluated. The values are then used to calculate the *in situ* pH at depths in the oceans.

When a solution in which various ionic and molecular species are in equilibrium is subjected to increasing pressure, the concentrations of those species with the smaller partial molal volumes will increase at the expense of the others, in accordance with Le Chatelier's principle. The pressure, or depth effect is expressed by the pressure coefficient of the equilibrium constant (KIRKWOOD and OPPENHEIM, 1961) which, when integrated between two pressure levels yields :

$$K_z = K_o \exp\left[\frac{1}{RT}\int_{P_o}^{P_z} \Sigma(\bar{v}_R - \bar{v}_P)\,dP\right] \tag{1}$$

In natural systems, the pressure difference between the surface and at depth may be large and is approximately proportional to the depth. The subscripts o and z refer to the surface and the depth z, K is the equilibrium constant (which may be a dissociation constant or a solubility product), R is the gas constant, T the absolute temperature, P the pressure, $\bar{v}_R$ and $\bar{v}_P$ the partial molal volumes of the reactants and products, respectively.

BRANDER (1932) measured the pressure coefficients for the first dissociation constant of carbonic acid and that of acetic acid in pure water, and BUCH and GRIPENBERG (1932) adopted his values of the pressure coefficient for the first dissociation constant of carbonic acid and of acetic acid for the second dissociation constant of carbonic acid. They used these coefficients to calculate the effect of depth on the *in situ* pH.

REVELLE and FAIRBRIDGE (1957) used an equation similar to (1) to calculate the change in the solubility product of calcium carbonate with depth from the thermodynamic data of OWEN and BRINKLEY (1941). They predicted an increase in the solubility product with depth. WATTENBERG observed an increase in the concentrations of calcium and carbonate ions with depth (DEFANT, 1961).

If calcium carbonate should dissolve at depth because of high pressure, carbon dioxide and carbonate ions would combine to form bicarbonate ions, and the total carbon dioxide, alkalinity, and pH would increase. The increase in pH is compensated for in part by the increased dissociation of carbonic acid. These changes cannot be rigorously calculated for several reasons :

(1) The effect of calcium and magnesium carbonate ion complexes (GREENWALD, 1941) on the equilibrium constants will be neglected because it cannot now be evaluated but is probably small (WEYL, 1961).
(2) The presence of other buffer systems such as the clay minerals suggested by SILLÉN (1961) will not be included because their buffering capacity is not known.
(3) Although the *in situ* biological oxidation of organic matter may increase the carbon dioxide by up to 20 per cent of its total amount (F. A. RICHARDS, personal communication), these increments vary in time and space and will not be treated.
(4) BUCH and GRIPENBERG (1932) use pressure data measured in pure water and adapt results for acetic acid to the second dissociation of carbonic acid; therefore the accuracy of their calculations for sea water is unknown.
(5) REVELLE and FAIRBRIDGE (1957) consider their estimates of the effect of pressure on the solubility product of calcite to be approximations that should eventually be replaced by measured data.

With these limitations, the effect of pressure changes on the alkalinity, carbon dioxide-carbonate components, calcite solubility and pH will be calculated for an isothermal system at 16°C.

THE EQUATIONS FOR THE CARBONATE SYSTEM

BUCH and GRIPENBERG (1932) derived :

$$(a_{H^+})^2_z - K^1_{1z}(A-1)(a_{H^+})_z - K^1_{1z}K^1_{2z}(2A-1) = 0 \qquad (2)$$

where K^1_{1z} and K^1_{2z} are the first and the second, apparent dissociation constants of carbonic acid at depth z, a_{H^+} is the activity of the hydrogen ions, and A is the ratio of the total carbon dioxide : carbonate alkalinity. These authors assume that A remains constant with depth and can be calculated from the pH measured at the surface. The pH at any depth is obtained from the value of A, K^1_{1z} and K^1_{2z}. By examining the dependence of the total carbon dioxide and of the carbonate alkalinity on the concentrations of carbon dioxide and calcium carbonate it will be shown that this procedure is valid only if these compounds do not transfer into or out of the water sample.

The condition of electrical neutrality is :

$$\sum_i c_i (C_i^{+c_i}) + (H^+) + 2(Ca^{++}) = \sum_j b_j (B_j^{-b_j}) + (\mathrm{OH}^-) + (\mathrm{HCO_3}^-) + 2(\mathrm{CO_3}^=) \qquad (3)$$

where C_i represents all the cations except calcium and hydrogen ions, and B_j represents the anions not shown explicitly. Because the major ions of sea water occur in constant ratio to each other, $(C_i^{+c_i})$ and $(B_j^{-b_j})$ are proportional to the chlorosity and equation (3) can be written in the form used by WATTENBERG (1936) :

$$\text{Titr. Alkal.} = 2\,(Ca^{++}) - 0{\cdot}93 \times \text{chlorosity} \tag{4}$$

This equation can be rewritten by setting the total calcium concentration $(Ca^{++})_z$ as the sum of two terms; $(Ca^{++})_o$ the calcium concentration prior to exposure to sediments or settling calcareous shells, and $\Delta\,(Ca^{++})_z$, the increment resulting from the solution of calcium at great depths. Then

$$\text{Titr. Alkal.} = 2\,(Ca^{++})_o + 2\,\Delta\,(Ca^{++})_z - 0{\cdot}93 \times \text{chlorosity} \tag{5}$$

Equal numbers of calcium and of carbonate ions must leave the sediments; therefore the increase in total carbon dioxide must equal the increase in calcium. This is expressed by :

$$\Sigma(CO_2)_z = \Sigma(CO_2)_o + \Delta\,(Ca^{++})_z \tag{6}$$

where the subscripts o and z represent concentrations before and after exposure to calcium carbonate such as shells, sediments, or limestone out-crops.

From the definition of A, and equations 5 and 6 :

$$A = [\Sigma(CO_2)_o + \Delta\,(Ca^{++})_z]/[2\,(Ca^{++})_o + 2\,\Delta\,(Ca^{++})_z - 0{\cdot}93 \times \text{chlorosity}] \tag{7}$$

Upon solution of calcium carbonate, the following reactions occur :

$$CaCO_3\,(s) = Ca^{++} + CO_3^{=} \tag{8}$$

$$H_2CO_3 + CO_3^{=} = 2HCO_3^{-} \quad \text{or} \quad H_2O + CO_2 + CO_3^{=} = 2HCO_3^{-} \tag{9}$$

for which the equilibrium constants are :

$$(Ca^{++})_z\,.\,(CO_3^{=})_z = (K^1{}_{sp})_z \tag{10}$$

$$(HCO_3^{-})^2 = \frac{K^1{}_{1z}}{K^1{}_{2z}}\,(CO_3^{=})\,.\,(CO_2) \tag{11}$$

where $K^1{}_{sp}$ is the apparent solubility product.

If $2x$ represents the increase in bicarbonate ion concentration resulting from $\Delta\,(Ca^{++})_z$, equations 10 and 11 can be rewritten as :

$$[(Ca^{++})_o + \Delta\,(Ca^{++})_z]\,.\,[(CO_3^{=})_o + \Delta\,(Ca^{++})_z - x] = (K^1{}_{sp})_z \tag{12}$$

and :

$$[(HCO_3^{-})_o + 2x]^2 = K^1{}_{1z}/K^1{}_{2z}\,[(CO_3^{=})_o + \Delta\,(Ca^{++})_z - x]\,.\,[(CO_2)_o - x] \tag{13}$$

These equations will be used for the calculation of the effects of pressure on the carbon dioxide and calcium carbonate components.

pH AND CALCIUM CARBONATE RELATIONSHIPS AT THE SURFACE

The concentrations of calcium that correspond to given pH values for surface waters are presented in Table 1 for Cl = 19·5‰ and $T = 16°$. These results will be compared with the values at a depth of 5000 m in the next section. The data of Table 1 were calculated in the following way :

(a) pH values were selected arbitrarily, from within the range in which they may occur in natural environments.

(b) carbon dioxide was assumed to be at equilibrium with an atmosphere in which its partial pressure was $3 \cdot 3 \times 10^{-4}$ atmospheres. Tables equivalent to 1 can be obtained for any desired values of the carbon dioxide concentration.

(c) the bicarbonate ion concentration was determined from the first dissociation constant, the pH, and the activity of carbonic acid corresponding to the carbon dioxide present in solution (HARVEY, 1955).

(d) the carbonate ion concentration was obtained from the second dissociation constant of carbonic acid.

(e) the total carbon dioxide, the carbonate alkalinity, and the titration alkalinity were obtained from steps, *b*, *c* and *d*.

(f) the pH was calculated from *A* and compared with the value selected originally as a check on the correctness of the results.

(g) the calcium concentration was calculated from equation 4.

Table 1. *The components of carbonate system at equilibrium with the atmosphere. Chlorinity* = 19·5‰ 16°. $(CO_2) + (H_2CO_3) = 1 \cdot 25 \times 10^{-5}$ mol/l. *Concentrations in* mol/l. (Ca^{++}) g atoms/l.

pH	$(HCO_3^-)_o$ $\times 10^3$	$(CO_3^=)_o$ $\times 10^4$	$\Sigma(CO_2)_o$ $\times 10^3$	(Titr. Alk.)$_o$ $\times 10^3$	$(Ca^{++})_o$ $\times 10^2$	$(Ca^{++})_o \cdot (CO_3^=)_o$ $\times 10^6$
7·00	0·126	0·011	0·140	0·128	0·931	0·010
7·80	0·796	0·444	0·853	0·883	0·969	0·430
7·88	0·952	0·635	1·028	1·119	0·981	0·625
7·89	1·006	0·708	1·089	1·188	0·984	0·695
7·90	1·000	0·798	1·092	1·200	0·985	0·775
8·00	1·260	1·110	1·383	1·532	1·001	1·11
8·06	1·431	1·453	1·590	1·770	1·012	1·46
8·15	1·825	2·322	2·067	2·324	1·040	2·42
8·20	2·003	2·793	2·292	2·618	1·060	2·96

For Cl = 19·5‰ and 16°, WATTENBERG and TIMMERMANN (1936) measured an apparent solubility product of calcite = $0 \cdot 66 \times 10^{-6}$. The data in Table 1 show that if this is the true, apparent solubility product, seawater of the given chlorinity and temperature and at equilibrium with the atmosphere will be saturated with calcium carbonate at pH 7·89, and supersaturated at higher values. However, the data of REVELLE and FLEMING (1934) for aragonite would indicate under-saturation at least up to pH 8·16 because $(K^1{}_{sp})_o = 2 \cdot 4 \times 10^{-6}$ at 30 C and would be higher at 16°.

The large difference in solubility products measured by those authors cannot be explained by the different crystal forms, and further measurements are needed to determine the correct value. The data of WATTENBERG and TIMMERMANN will be used here because calcite is the stable form at 16°.

THE EFFECT OF DEPTH

BUCH and GRIPENBERG (1932) calculate an increase in pH when a water sample is raised from great depths, and a decrease when it sinks, because of the effect of changing pressure on the dissociation constants of carbonic acid. These changes in pH are correct if no calcium carbonate or carbon dioxide enters or leaves the system.

Table 2. Effects of depth and exposure to calcareous sediments on the carbonate system.

Depth, m	pH	(CO_2) × 10^5	$\Sigma(CO_2)$ × 10^3	Carb. Alk. × 10^3	(Ca^{++}) × 10^2	$(Ca^{++}).(CO_3^{=})$ × 10^6
0	7·89	1·25	1·089	1·148	0·984	0·695
↓ Sinking and Saturation						
5000	8·16	0·45	1·189	1·348	0·994	1·620
↓ Raising						
0	8·26	0·45	1·189	1·348	0·994	1·620
↓ Equilibration						
0	7·95	1·25	1·225	1·300	0·994	0·870

Table 2 presents an example of what happens to the pH if, in addition to the pressure effect on the dissociation, the sample exchanges calcium carbonate and carbon dioxide with its surroundings.

The sample from Table 1, at pH 7·89, is assumed to sink to 5000 m where it becomes saturated by sedimented calcite. The ion product $(Ca^{++})_z$. $(CO_3^{=})_z$ increases because of the increase in the apparent solubility product with pressure. Then, the sample is raised and two alternatives are considered : (1) there is no equilibration of carbon dioxide with the atmosphere, or (2) equilibration occurs. Results are presented in Table 2 and were determined as follows :

(a) Equations 12 and 13 were used to calculate the effects of the increase in pressure and saturation on the concentrations of calcium, carbonate, and bicarbonate in going from the surface to 5000 m. An approximate solution was obtained by successive approximations. K'_{1z}, K'_{2z} and $(K'_{sp})_z$ were determined from the data of BUCH and GRIPENBERG (1932) and REVELLE and FAIRBRIDGE (1957). The small effect of compression on molar concentrations was neglected.

(b) In raising the sample without exchange with the atmosphere equation 2 was used.

(c) After equilibration with the atmosphere, the pH corresponding to the new calcium concentration was determined by the methods of Table 1.

Thus, the pH would increase with sinking and the concentrations of molecular carbon dioxide and carbonic acid would decrease as a result of Reaction 9. Upon return to the surface the sample is under-saturated in molecular carbon dioxide and would become more alkaline or acid, depending on the amount of carbon dioxide that it absorbs from the atmosphere. Thus, wave and wind action or vigorous laboratory manipulations should decrease the pH, and a pH between 7·95 and 8·26 would be observed. The results presented in Table 1 show that, if a water sample was exposed to sedimented calcite, the concentrations of calcium ions and molecular carbon dioxide and the surface pH are needed for the calculation of the *in situ* pH at the depth where the sample was collected.

Renewed sinkings should cause further increases in calcium and alkalinity until a pH around 8·1–8·2 is reached. At this point, unless calcium carbonate precipitates at the surface, further exposures to sediments at 5000 m should not alter the sample because the ion product, $(Ca^{++})\,.\,(CO_3^{-})$ is equal to the saturation value at that depth. Because the average depth of the ocean is of the order of 4000 m, it is possible that such a cycling of waters between the surface and the bottom controls the surface pH. However, a test of this mechanism will require much further data to check the assumptions made here.

Acknowledgements—Contribution No. 295, Department of Oceanography, University of Washington. Supported by Office of Naval Research contract No. Nonr 477 (10). The author acknowledges the helpful comments of Professors C. A. BARNES, F. A. RICHARDS and M. G. GROSS, University of Washington, and the fruitful discussions with Dr. JOHN LYMAN, National Science Foundation.

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