

# THE SOLUBILITY OF CALCIUM CARBONATE IN TROPICAL SEA WATER

By C. L. Smith, Ph.D.

*Late* Bahamas Sponge Fishery Investigations Department

## INTRODUCTION

In a previous paper (Smith, 1940*b*) the chemical changes observed in ocean sea water flowing across the shallow banks on the west coast of Andros Island (Bahamas) were reported. High salinities were produced by evaporation and calcium carbonate was precipitated. From the data obtained under natural conditions a maximum value of the solubility product constant of calcium carbonate in sea water was suggested. There was no reason to believe, however, that this value of the constant represented the true equilibrium conditions, and experiments have since been made in the laboratory with a view to bringing water from these banks into equilibrium with solid calcium carbonate.

Before describing this work it is necessary to point out two errors in the calculation of the ionic product,  $\text{Ca}^{++} \times \text{CO}_3^{--}$ , in the previous paper (Smith, 1940*b*). In the first place, the calcium contents there given are uncorrected for strontium, which is usually included in the analysis as calcium. Assuming a calcium/strontium ratio of 30/1 (Lyman & Fleming, 1940), the true calcium content of the water may be found. Secondly, the quantities, carbonate alkalinity, total carbon dioxide, and carbonate ion, were found by reference to Buch's tables (1933). These tables are based on a constant relation between chlorinity and titration alkalinity (Titr. Alk. 0.123 Cl<sup>0/100</sup>), a relation which holds for most open-ocean sea waters. On the Bahama Bank, however, a marked increase in chlorinity may be associated with a considerable decrease in titration alkalinity. For this reason Buch's tables are not applicable to such water, as different values of  $pK_B'$ ,  $pK_1'$  and  $pK_2'$  must be used in the calculations. When these errors are corrected for, the value of the ionic product,  $\text{Ca}^{++} \times \text{CO}_3^{--}$ , becomes  $1.62 \times 10^{-6}$  at 30° C. and 36 ‰ instead of  $1.27 \times 10^{-6}$  as previously reported. Similarly, at 20° C. and 36 ‰,  $\text{Ca}^{++} \times \text{CO}_3^{--}$  becomes  $1.87 \times 10^{-6}$  instead of  $1.77 \times 10^{-6}$ .

## EXPERIMENTAL METHOD

The principle adopted for attaining equilibrium was that of shaking sea water in sealed bottles with a quantity of the naturally precipitated bottom deposit, which was washed with distilled water and dried at 120° C.; about 1 g. was added to each bottle. Standard sampling bottles of 500 ml. capacity were used, leaving about 100 ml. air space. The bottles with solid, but without water, were sterilized in an autoclave. Save for four bottles in the first experiment, the sea water was filtered into the bottles through Berkefeld

filters. It had previously been ascertained that there was no change in the titration alkalinity of a sample on filtering (cf. Gee, 1932), although the  $pH$  increased slightly, owing to the escape of carbon dioxide from solution under reduced pressure.

The bottles were then mounted in a constant temperature shaking apparatus, which was maintained at above or below air temperature, constant to  $\pm 0.2^\circ$  C. Bottles were removed from time to time and estimations of the  $pH$  exponent, titration alkalinity, calcium content, and chlorinity, were made. On removing a bottle from the shaker, it was left in the thermostat for 24 hr. to settle; 10 ml. was then run into a test-tube, and the  $pH$  estimated colorimetrically in the usual way with cresol red. The remainder of the sample was filtered, and the titration alkalinity, calcium content and chlorinity then estimated. In the calculations which were necessary to obtain these values use was made of various constants, such as  $K_1'$ ,  $K_2'$  and  $K_B'$ . The constants  $K_1'$  and  $K_2'$  represent the stoichiometric dissociation constants of carbonic acid in sea water, and they are defined by Wattenberg (1933).  $K_B'$  represents the stoichiometric dissociation constant of boric acid in sea water as defined by Buch (1933). The relation between  $pH$  and the activity of the hydrogen ions ( $a_H$ ) is also defined by the same two authors.

The following analytical methods were employed:

(1) *Hydrogen-ion concentration.* Palitzsch boric acid-borate buffers were used for making up the standard buffer tubes, which covered the range at  $pH$  0.02 interval. The  $pH$  in situ ( $pH_W$ ) was obtained by applying the corrections given by Buch (1937).

(2) *Titration alkalinity* was estimated in duplicate by Wattenberg's (1930) method.

(3) *Calcium content.* Kirk and Schmidt's double precipitation method as adapted for sea water by Kirk & Moberg (1933) was used. More reliable results could thus be obtained than by Gripenberg's (1937) single precipitation method. Estimations were made in duplicate, and the maximum deviation from the mean was 2.0 mg./l., or 0.05 m. mol./l.

(4) *Chlorinity* was determined by Knudsen's standard method.

(5) *Carbonate alkalinity* was calculated directly from the titration alkalinity and  $pH$  by means of the equations

$$\text{Carb. Alk.} = \text{Titr. Alk.} \frac{K_B' C_{\Sigma H_3BO_3}}{a_{H^+} + K_B'}, \quad (i)$$

$$C_{\Sigma H_3BO_3} = 0.0225 \text{ Cl } \text{‰} \text{ (m. mol.) (Buch, 1933).} \quad (ii)$$

Values of  $pK_B'$  were taken from the table given by Buch (1933).

(6) *Total carbon dioxide*,  $\Sigma CO_2$ , was calculated from the equation derived by Moberg *et al.* (1934) from the equilibria equations for the carbonic acid system:

$$\Sigma CO_2 = \frac{\text{Carb. Alk.}}{1 + (2K_2'/a_{H^+})} \left( 1 + \frac{a_{H^+}}{K_1'} + \frac{K_2'}{a_{H^+}} \right).$$

Values of  $K_2'$  were taken from Buch (1933), and of  $K_1'$  from Wattenberg (1933).

(7) Carbonate ion,  $C_{CO_3''}$ , was similarly calculated directly from the equation

$$C_{CO_3''} = \frac{K_2' \text{ Carb. Alk.}}{a_{H^+} I + (2K_2'/a_{H^+})}$$

#### EXPERIMENTAL RESULTS

The first experiment was made with water collected 22 miles due north from Williams Cay on the central part of the Bank (cf. Smith (1940a) for general description of the Great Bahama Bank). Ten bottles of water were collected together with a sample of the bottom deposit. Four of these were prepared as described above, while a second four were placed in the shaker without previous filtration through Berkefeld filters. These were subsequently removed in pairs, one unfiltered and one filtered sample, at intervals of 11, 24, 33 and 38 days. The temperature was  $29.7 \pm 0.2^\circ \text{C}$ . One sample of sea water was analysed as an initial control, while a second was allowed to stand for 19 days before analysis. The analyses are shown in Table I.

The most striking feature of these results is the continuous increase in titration alkalinity, calcium content and total carbon dioxide in all the bottles. Closer inspection of these figures, however, reveals that while the gain in calcium and titration alkalinity is practically identical (within the limits of error of the calcium estimation), the total carbon dioxide content has increased more rapidly. One must conclude, therefore, that carbon dioxide has been produced in the bottles by biological activity. Owing to the fact that there was only a slight gain in total carbon dioxide content when sea water alone was allowed to stand for 19 days, it is more probable that the source of the marked increase in the shaken bottles was due to the added solid. The effect of this increasing carbon dioxide content was to depress the pH and consequently the carbonate-ion content to such an extent that the water became unsaturated with respect to calcium carbonate. This caused calcium carbonate to be dissolved from the solid phase as shown by the increasing carbonate alkalinity and calcium content. As each analysis is based on a separate bottle of water, the results cannot be regarded as a progressive series, and considerable variation in the final state is to be expected. The column in Table I showing values of the ionic product,  $\text{Ca}^{++} \times \text{CO}_3''$ , corrected to 36 ‰ S, shows that, despite considerable variation in pH and carbonate alkalinity, this quantity is practically a constant. The fact that the calcium carbonate in solution has increased in all bottles precludes the possibility of this value of the ionic product representing an over-saturated condition, while its constancy within such narrow limits is indicative of conditions close to the true equilibrium between the solid and liquid phases. This experiment shows, also, that there is no systematic difference in the behaviour of the filtered and unfiltered water, and in subsequent experiments filtered water only was used.

TABLE I. EXPERIMENT I. THE SOLUBILITY PRODUCT CONSTANT,  $K'_{\text{CaCO}_3}$  IN SEA WATER. WATER FROM THE GREAT BAHAMA BANK, 22 MILES N.N.W. FROM WILLIAMS CAY, SHAKEN WITH THE NATURAL BOTTOM DEPOSIT.  
TEMPERATURE =  $29.7 \pm 0.2^\circ \text{C}$ .

No.	Date of analysis	Description	S ‰	pH <sub>w</sub>	Tit. Alk. m. eq./l.	C <sub>Ca<sup>++</sup></sub> m. mol./l.	Carb. Alk. m. eq./l.	ΣCO <sub>2</sub> m. mol./l.	C <sub>CO<sub>3</sub><sup>''</sup></sub> m. mol./l.	Ca <sup>++</sup> × CO <sub>3</sub> <sup>''</sup> × 10 <sup>-6</sup> at 36 ‰
10	18. vii. 40	Experiment started not shaken, no solid added	36.18	8.15	1.781	10.35	1.671	1.445	0.221	2.27
12	6. viii. 40	Not shaken, no solid added, stored 19 days	36.26	8.08	1.779	10.36	1.682	1.489	0.198	2.03
1	30. vii. 40	Unfiltered. Shaken with solid 11 days	36.22	7.79	1.786	10.48	1.729	1.648	0.120	1.24
2	13. viii. 40	Unfiltered. Shaken with solid 24 days	36.37	7.70	1.921	10.41	1.875	1.808	0.108	1.09
3	21. viii. 40	Unfiltered. Shaken with solid 33 days	36.43	7.69	2.022	10.42	1.977	1.905	0.111	1.13
4	26. viii. 40	Unfiltered. Shaken with solid 38 days	36.42	7.69	1.943	10.45	1.898	1.829	0.107	1.09
5	30. vii. 40	Filtered. Shaken with solid 11 days	35.88	7.73	1.905	10.40	1.856	1.775	0.113	1.18
6	13. viii. 40	Filtered. Shaken with solid 24 days	36.32	7.65	2.269	10.56	2.230	2.164	0.115	1.19
7	21. viii. 40	Filtered. Shaken with solid 33 days	36.29	7.72	2.048	10.43	2.000	1.919	0.120	1.23
8	26. viii. 40	Filtered. Shaken with solid 38 days	36.08	7.72	1.880	10.35	1.832	1.758	0.110	1.14

TABLE II. EXPERIMENT II. THE SOLUBILITY PRODUCT CONSTANT,  $K'_{CaCO_3}$  IN SEA WATER. COMPOSITE WATER SAMPLE FROM THE GREAT BAHAMA BANK, SHAKEN WITH THE NATURAL BOTTOM DEPOSIT.  
TEMPERATURE =  $29.7 \pm 0.2^\circ C.$

No.	Date of analysis	Description	S ‰	pH <sub>w</sub>	Tit. Alk. m. eq./l.	C <sub>Ca++</sub> m. mol./l.	Carb. Alk. m. eq./l.	ΣCO <sub>2</sub> m. mol./l.	C <sub>CO<sub>3</sub>''</sub> m. mol./l.	Ca <sup>++</sup> × CO <sub>3</sub> '' × 10 <sup>-6</sup> at 36 ‰
C	6. viii. 40	Not shaken and no solid added	38.22	8.05	2.105	11.01	2.003	1.781	0.228	2.25
A	19. viii. 40	Filtered. Shaken with 1 g. solid 14 days	37.79	7.71	1.946	10.84	1.895	1.816	0.113	1.12
B	19. viii. 40	Filtered. Shaken with 1 g. solid 14 days	37.83	7.73	1.957	10.80	1.903	1.821	0.119	1.17

TABLE III. EXPERIMENT III. OPEN-OCEAN SEA WATER SHAKEN WITH BOTTOM DEPOSIT FROM THE GREAT BAHAMA BANK.  
TEMPERATURE =  $29.7 \pm 0.2^\circ C.$

No.	Date of analysis	Description	S ‰	pH <sub>w</sub>	Tit. Alk. m. eq./l.	C <sub>Ca++</sub> m. mol./l.	Carb. Alk. m. eq./l.	ΣCO <sub>2</sub> m. mol./l.	C <sub>CO<sub>3</sub>''</sub> m. mol./l.	Ca <sup>++</sup> × CO <sub>3</sub> '' × 10 <sup>-6</sup> at 36 ‰
F	4. ix. 40	Open-ocean water. Not shaken and no solid added	36.33	8.24	2.495	10.67	2.367	1.989	0.362	3.80
A	9. ix. 40	Filtered. Shaken with 1 g. solid 5 days	36.20	7.88	2.120	10.41	2.053	1.919	0.168	1.74
B	9. ix. 40	Filtered. Shaken with 1 g. solid 5 days	36.22	7.90	2.136	10.44	2.067	1.905	0.175	1.82
C	19. ix. 40	Filtered. Shaken with 1 g. solid 12 days	36.13	7.80	2.065	10.40	2.008	1.901	0.141	1.46
D	21. ix. 40	Filtered. Shaken with 1 g. solid 16 days	36.17	7.79	2.022	10.39	1.966	1.872	0.136	1.40
E	21. ix. 40	Unfiltered. Shaken without solid 16 days	36.17	8.22	2.491	10.61	2.369	2.002	0.351	3.70

The second experiment was carried out on a small composite sample made up from a number of water samples taken at several different places on the Bahama Bank (Table II). The initial titration alkalinity was higher and the  $pH$  lower than that of the water in Experiment I. After 14 days' shaking with solid there was a fall in titration alkalinity and  $pH$ , although as in the previous series the total carbon dioxide content increased. In these samples, therefore, the predominant process has been precipitation of calcium carbonate despite the liberation of carbon dioxide by some other agency. At the end of the experiment the value of the product,  $Ca^{++} \times CO_3''$ , lies well within the limits of variation found in Experiment I. The average value of the ionic product based on the ten observations made in these two experiments is  $1.16 \pm 0.05 \times 10^{-6}$ . This figure is put forward as a new value for the solubility product constant ( $K'_{CaCO_3}$ ) of calcium carbonate in sea water at  $30^\circ C.$  and 36 ‰.

A third experiment in which open-ocean sea water was shaken with added solid was made to check the previous results. The data (Table III) show that at the start of the experiment the water had the normal characteristics of ocean water in these latitudes. On shaking with solid there was a marked fall in titration alkalinity,  $pH$ , and total carbon dioxide content, which was continuous to the end of the experiment. Comparison of the amounts of calcium carbonate precipitated as shown by the reduction in carbonate alkalinity and calcium content, and the associated decrease in total carbon dioxide again show that there has been a slight carbon dioxide production by biological activity. After 16 days' shaking the ionic product,  $Ca^{++} \times CO_3''$ , had fallen to  $1.40 \times 10^{-6}$ , indicating that final equilibrium had probably not been attained, though the water at that point is only 20 % supersaturated. From this experiment it is apparent that equilibrium is more readily attained when sea water is used which has precipitated the greater part of its excess calcium carbonate under natural conditions. The two samples F and E in Table III show the effect of shaking sea water for 16 days with no solid phase present. On correcting for the slight difference in chlorinity, it can be seen that the carbonate alkalinity and total carbon dioxide have increased slightly. At least a part of the rise in carbonate alkalinity may be attributed to the solvent action of the water on the glass bottle, but the increase is so small that it would have no significant effect on the product  $Ca^{++} \times CO_3''$ .

#### DISCUSSION

The behaviour of the open-ocean water on shaking with the calcareous bottom deposit in Experiment III follows very closely the pattern observed under natural conditions when ocean water flowed across the shallow banks (Smith, 1940*b*). Owing to the continuous diffusion of carbon dioxide from the water on the bank, however, the  $pH$  does not fall to the same extent as in the sealed bottles, and consequently more calcium carbonate must be precipitated before equilibrium is attained. It is therefore to be expected that

a steady state would only be reached under natural conditions after prolonged contact with the solid phase.

Values for the solubility product constant of calcium carbonate in sea water have previously been put forward by Revelle & Fleming (1934) and Wattenberg & Timmermann (1936). Revelle & Fleming concluded that tropical sea water could only be slightly supersaturated with calcium carbonate. This view has already been shown by the writer to be untenable by direct observations on the Bahama Bank, and the present work confirms this view. Wattenberg & Timmermann, however, found a value of  $0.52 \times 10^{-6}$  for  $K'_{\text{CaCO}_3}$  at  $30^\circ \text{C}$ . and  $36 \text{‰}$ . Such a value would suggest that tropical ocean water is as much as  $700 \text{‰}$  saturated with calcium carbonate. Even the lowest values observed on the Bahama Bank after extensive precipitation has taken place would represent approximately  $300 \text{‰}$  saturation. Considering the conditions under which the present experiments were conducted, it is difficult to see how the value of  $K'_{\text{CaCO}_3}$  can lie below  $1.16 \times 10^{-6}$ . Owing to the fortuitous production of carbon dioxide in the bottles, the water in Experiment I became unsaturated with respect to calcium carbonate, and it was in fact being dissolved from the solid phase. In this case if the average value from these observations does not represent the equilibrium, it should be too low and not too high. In Experiment III, however, the ocean water was still slowly depositing calcium carbonate when the ionic product,  $\text{Ca}^{++} \times \text{CO}_3^{--}$ , had fallen to the neighbourhood of  $1.40 \times 10^{-6}$ . On this evidence it is suggested that the true value of the solubility product lies very close to  $1.16 \times 10^{-6}$  under the given conditions of salinity and temperature. Combining such a value with the observations made on the Great Bahama Bank in 1939 shows that the water was in some cases only  $140 \text{‰}$  saturated with calcium carbonate, which is a more probable figure than  $300 \text{‰}$ . It is possible that differences in the material used as the solid phase may account for some of the discrepancies in the recorded values of  $K'_{\text{CaCO}_3}$ . The material used in the present work contains large numbers of minute aragonite needles. Mechanical analyses of similar bottom samples made by Vaughan (1918) show that these deposits contain up to  $57.6 \text{‰}$  of clay and silt-sized particles ( $0.05\text{--}0$  mm. diameter).

It is interesting to note that Gee *et al.* (1932) carried out experiments in which sea water was shaken with solid calcium carbonate in sealed bottles. Calcium content,  $p\text{H}$ , and total carbon dioxide content were estimated after periods of shaking up to 17 days. A very marked fall in  $p\text{H}$  was observed, associated with a reduction of total carbon dioxide and a slight fall in calcium content. From the total carbon dioxide and  $p\text{H}$  values observed by these authors it is possible to compute the carbonate alkalinity and hence the carbonate-ion content by the following equation:

$$\text{Carb. Alk.} = \frac{\Sigma \text{CO}_2 \cdot \text{I} + (2K_2'/a_{\text{H}^+})}{\text{I} + (a_{\text{H}^+}/K_1') + (K_2'/a_{\text{H}^+})}$$

In one experiment the results for five bottles which had been shaken for periods of from 5 to 17 days give an average value for  $K'_{\text{CaCO}_3}$  of  $1.10 \times 10^{-6}$  at  $30^\circ \text{C}$ . and  $36\text{‰}$  when recalculated in this way. Thus this work may be regarded as providing close confirmation of the value found by the writer.

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