

Degree of Saturation of CaCO_3 in the Oceans¹

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The degree of saturation of CaCO_3 in the Pacific and Atlantic oceans has been calculated from measurements of the partial pressure of CO_2 gas and of the total content of dissolved inorganic CO_2 . Lyman's apparent dissociation constants for carbonic and boric acid at 1 bar, MacIntyre's apparent solubility product of CaCO_3 in sea water at 1 bar, and the Disteches' determinations of the pressure dependence of these parameters were used for the calculation. The results indicate that the crossover from supersaturation to undersaturation for CaCO_3 occurs at a water depth between 500 and 3000 meters for calcite and at about 300 meters for aragonite in the Pacific, and between 4000 and 5000 meters for calcite and between 1000 and 2500 meters for aragonite in the North Atlantic Ocean. This difference between the Pacific and Atlantic oceans may be attributed to a difference in the amount of CO_2 dissolved in these waters. Such a difference may, in turn, be caused by a difference in the residence times in these waters. The marked decrease of CaCO_3 content in the ocean bottom sediments observed at water depths greater than 3500 meters in the Pacific and 4500 meters in the Atlantic appears to reflect a transition of the sea water from saturation to undersaturation with respect to calcite.

INTRODUCTION

Alkalinity and pH measurements have been utilized by many investigators for estimation of the degree of saturation of CaCO_3 dissolved in sea water; however, uncertainties in pH measurements made on shipboard are often too great to yield meaningful estimates of carbonate ion concentrations. Since the development of the infrared gas analyzer, it has become possible to measure the partial pressure of CO_2 with an accuracy of 1×10^{-6} bar. Since a change of 0.01 pH unit in sea water corresponds to a change of $15\text{--}20 \times 10^{-6}$ bar in partial pressure of CO_2 , the resolution of the infrared method is better by

an order of magnitude than is obtained with the conventional glass electrode method.

The purpose of this work is to study the degree of saturation of CaCO_3 in the Pacific and Atlantic waters by direct measurements of total content and partial pressure of CO_2 by means of an infrared gas analyzer on shipboard. The results will be used to explain the distribution of CaCO_3 in the ocean bottom sediments.

Review of the sea water chemistry for the $\text{CO}_2\text{--CaCO}_3$ system. Measurements of total content of inorganic CO_2 , ΣCO_2 , and partial pressure of CO_2 , $p\text{CO}_2$, at temperature T and 1 bar pressure, can be used for the calculation of pH, the carbonate alkalinity $[A]$, and the alkalinity $[Alk]$ of sea water by the following relationships:

$$a_{\text{H}^+} = \alpha \cdot p \text{CO}_2 \cdot K_1 [1 + (a_{\text{H}^+}/K_1) + (K_2/a_{\text{H}^+})] / \Sigma \text{CO}_2 \quad (1)$$

$$[A] = \Sigma \text{CO}_2 [1 + (2K_2/a_{\text{H}^+})]$$

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$$\div [1 + (a_{H^+}/K_1) + (K_2/a_{H^+})] \quad (2)$$

$$[Alk] = [A] + K_B \cdot \Sigma B / (K_B + a_{H^+}) \quad (3)$$

where

a_{H^+} = activity of hydrogen ions ($-\log a_{H^+} = pH$).

α = $[CO_2]_{tot}/pCO_2$, solubility coefficient of CO_2 gas.

K_1 = $a_{H^+} \cdot [HCO_3^-]_{tot}/[CO_2]_{tot}$, first apparent dissociation constant of carbonic acid.

K_2 = $a_{H^+} \cdot [CO_3^{2-}]_{tot}/[HCO_3^-]_{tot}$, second apparent dissociation constant of carbonic acid.

K_B = $a_{H^+} \cdot [H_2BO_3^-]_{tot}/[H_3BO_3^0]_{tot}$, apparent dissociation constant of boric acid.

ΣB = $[H_2BO_3^0]_{tot} + [H_2BO_3^-]_{tot} = 2.2 \times 10^{-5} \times Cl\%$.

$[HCO_3^-]_{tot}$ and $[CO_3^{2-}]_{tot}$ are total concentrations including both free ion and ion-pair forms. $[CO_2]_{tot}$ includes both dissolved CO_2 and undissociated carbonic acid.

The solubility coefficients of CO_2 in water and in NaCl solutions have been well studied by Bohr [1899], Markham and Kobe [1941], and Harned and Davis [1943]. Indirect measurements of the solubility coefficient of CO_2 in sea water [Krogh, 1904; Li, 1967] confirm Buch's [1951] estimation. Buch estimated α from Bohr's NaCl solution data, assuming that the salt in sea water is all NaCl (by weight). In the range of $0^\circ \leq T \leq 35^\circ C$ and $0 \leq Cl\% \leq 25$, Buch's α can be well represented by the Setschenow equation

$$\log \alpha_0/\alpha = (0.0806 - 0.00074T) \times (Cl\%/20) \quad (4a)$$

where α_0 is the solubility coefficient of CO_2 in distilled water at temperature T °C and is

$$\alpha_0 = (770 - 29.5T + 0.685T^2 - 0.0075T^3) \times 10^{-4} \text{ mole/bar} \quad (4b)$$

The apparent dissociation constants of carbonic acid K_1 and K_2 and boric acid K_B in sea water were determined by Buch [1933a, b, 1938, 1951] and by Lyman [1956] and have been widely used for oceanographic studies. Since Lyman's constants cover a wide range of tem-

peratures and are based on the National Bureau of Standards pH scale, they have been adopted for this study. Furthermore, the recent determinations of K_1 , K_2 , and K_B in sea water (19% Cl) at $22^\circ C$ by Disteche and Disteche [1967] are consistent with Lyman's values. Lyman's constants are expressed by the following relationships in the range of $0^\circ \leq T \leq 25^\circ C$ and $16 \leq Cl\% \leq 21$:

$$-\log K_1 = 6.34 - 0.01 Cl\% - (0.008 - 0.00008 T)T \quad (5a)$$

$$-\log K_2 = 9.78 - 0.02 Cl\% - 0.012 T \quad (5b)$$

$$-\log K_B = 9.26 - 0.016 Cl\% - 0.010 T \quad (5c)$$

for both molal and molar units.

In the present work, the pCO_2 exerted by sea water was determined from the measurements of the CO_2 gas concentration in the air equilibrated with sea water sample at a temperature, T_{eq} and a pressure of approximately 1 bar. The values of pH and $[Alk]$ at the equilibrium temperature can be obtained for the values of pCO_2 and ΣCO_2 from (1), (2), and (3). Since $[Alk]$ and ΣCO_2 are both conservative quantities, the pH values for the in situ temperature $T_{in situ}$ can be directly obtained from Figure 1 or from (1), (2), and (3). In the range of oceanographic interests, the relationship between the values of pH at T_{eq} and that at $T_{in situ}$ may be simply expressed by

$$pH(at T_{in situ}) = pH(at T_{eq}) + 0.011(T_{eq} - T_{in situ}) \quad (6)$$

The pH at in situ pressure can be estimated directly from the data of Disteche and Disteche [1967], for $7.5 \leq pH^{(a)} \leq 8.1$,

$$pH^{(P)} = pH^{(1)} - (1.042 - 0.1 pH^{(1)})P \times 10^{-3} \quad (7a)$$

and for $pH^{(a)} \geq 8.1$,

$$pH^{(P)} = pH^{(1)} - 0.232 P \times 10^{-3} \quad (7b)$$

where superscripts indicate the pressure in bars.

The $pH^{(P)}$ also can be calculated by solving (2) and (3), since K_1 , K_2 , and K_B are given

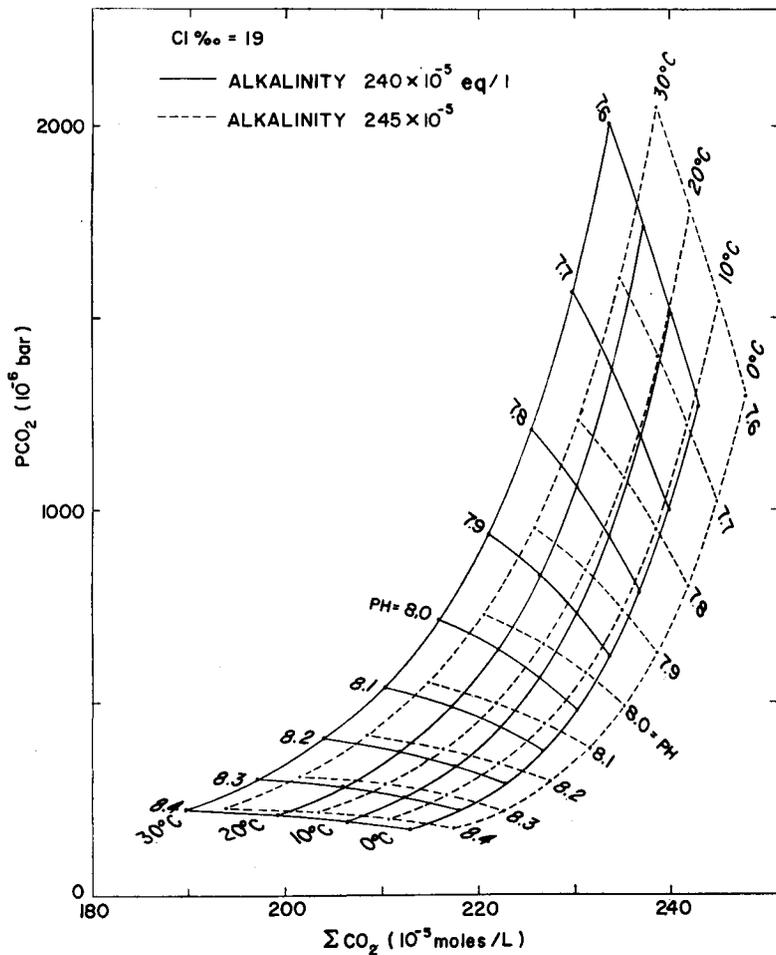


Fig. 1. The relationship between $p\text{CO}_2$, pH , ΣCO_2 , and temperature for the two alkalinity values, 240 and 245×10^{-5} eq/liter, for sea water with a chlorinity of 19.0% .

as functions of pressure by *Disteche and Disteche* [1967]. The results are essentially the same no matter which method is used.

Once the hydrogen ion activity at pressure P , $a_{\text{H}^+}^{(P)}$ is known, the in situ $[\text{HCO}_3^-]_{\text{tot}}^{(P)}$ and $[\text{CO}_3^{2-}]_{\text{tot}}^{(P)}$ concentrations can be calculated from the equations

$$[\text{HCO}_3^-]_{\text{tot}}^{(P)} = \frac{\Sigma \text{CO}_2}{[1 + (a_{\text{H}^+}^{(P)}/K_1^{(P)}) + (K_2^{(P)}/a_{\text{H}^+}^{(P)})]} \quad (8)$$

$$[\text{CO}_3^{2-}]_{\text{tot}}^{(P)} = K_2^{(P)} \cdot \Sigma \text{CO}_2 / a_{\text{H}^+}^{(P)} \cdot [1 + (a_{\text{H}^+}^{(P)}/K_1^{(P)}) + (K_2^{(P)}/a_{\text{H}^+}^{(P)})] \quad (9)$$

The pressure dependence of K_1 , K_2 , and K_B can be estimated from the relationship

$$(\partial \ln K_i / \partial P) = -\Delta \bar{V}_i / RT \quad (10a)$$

where $\Delta \bar{V}_i$ is the change in partial molar volume for the reaction occurring in sea water. *Disteche and Disteche* [1967] have shown that $\Delta \bar{V}_i$ for carbonic and for boric acids are independent of pressure up to 1000 bars; therefore

$$\log (K_i^{(P)} / K_i^{(1)}) = -\Delta \bar{V}_i (P - 1) / 2.30 RT \quad (10b)$$

Disteche and Disteche [1967] give the following for sea water of $20 \text{ Cl}\%$ at 22°C :

$$\begin{aligned}\Delta \bar{V}_1 &= \bar{V}_{\text{HCO}_3^-} + \bar{V}_{\text{H}^+} - \bar{V}_{\text{CO}_3} - \bar{V}_{\text{H}_2\text{O}} \\ &= -19.0 \text{ cm}^3/\text{mole}\end{aligned}$$

$$\begin{aligned}\Delta \bar{V}_2 &= \bar{V}_{\text{CO}_3} + \bar{V}_{\text{H}^+} - \bar{V}_{\text{HCO}_3} \\ &= -10.7 \text{ cm}^3/\text{mole}\end{aligned}$$

$$\begin{aligned}\Delta \bar{V}_B &= \bar{V}_{\text{H}_2\text{BO}_3} + \bar{V}_{\text{H}^+} - \bar{V}_{\text{H}_2\text{BO}_4} \\ &= -23.1 \text{ cm}^3/\text{mole}\end{aligned}$$

where \bar{V} denotes a partial molar volume for a simple ionic species specified by the subscript and \bar{V}^* denotes a partial molar volume for simple ion plus complex ion-pair species. The precision for these measurements has been estimated to be $\pm 0.05 \text{ cm}^3/\text{mole}$.

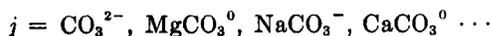
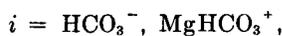
Assume that the partial molar volume of CO_2 in sea water is equal to $34.8 \pm 0.5 \text{ cm}^3/\text{mole}$, as determined for pure water by *Enns et al.* [1965] (which is the case for O_2), and select $\bar{V}_{\text{H}^+} (= 0)$ as a reference state at all temperatures and pressures, then

$$\begin{aligned}\bar{V}_{\text{HCO}_3^-} &= 34.0 \quad \text{and} \quad \bar{V}_{\text{CO}_3} \\ &= 23.3 \text{ cm}^3/\text{mole}.\end{aligned}$$

The values $\bar{V}_{\text{HCO}_3^-} = 34.0 \text{ cm}^3/\text{mole}$ and especially $\bar{V}_{\text{CO}_3} = 23.3 \text{ cm}^3/\text{mole}$ in sea water are higher than the values $\bar{V}_{\text{HCO}_3} = 26 \text{ cm}^3/\text{mole}$ and $\bar{V}_{\text{CO}_3} = 2.7 \text{ cm}^3/\text{mole}$ in 0.725 *N* NaCl solution given by *Owen and Brinkley* [1941]. This discrepancy may be accounted for by the formation of complex ion pairs in sea water. The values of \bar{V}_{HCO_3} and \bar{V}_{CO_3} are related to the partial molar volumes of existing molecular species by

$$\begin{aligned}\bar{V}_{\text{HCO}_3} &= \sum f_i \bar{V}_i \quad \text{and} \quad \bar{V}_{\text{CO}_3} \\ &= \sum f_j \bar{V}_j \quad (11)\end{aligned}$$

where f_i and f_j are the statistical weights of ion and ion-pair species k and j , and $\sum f_i = \sum f_j = 1$, and



According to *Garrels and Thompson* [1962], 31% of the bicarbonate and 91% of the carbonate ions are bonded in ion pairs.

Hepler [1957] has shown that the partial

molar volumes of simple ions in aqueous solutions are related to the radius of the ions in the crystal, r_i , and the charge, Z_i ,

$$\bar{V}_i = Ar_i^3 - BZ_i^2/r_i \quad (12)$$

where A and B are constants. If this relationship holds for complex ion-pairs, the partial molar volumes for ion pairs should be greater than those for simple ions as a result of greater r_i and smaller Z_i values for ion pairs. *Spiro et al.* [1968] prove it is the case.

The formation of bicarbonate and carbonate ion pairs in sea water, therefore, would cause

$\bar{V}_{\text{HCO}_3^-} > \bar{V}_{\text{HCO}_3}$ and $\bar{V}_{\text{CO}_3} > \bar{V}_{\text{CO}_3}$. *Duedall* [1968] gives $\bar{V}_{\text{HCO}_3^-} = 28 \text{ cm}^3/\text{mole}$ in sea water ($S = 34.8\%$) at 25°C , but it is hard to compare with *Disteche's* data, since *Duedall's* value for $\bar{V}_{\text{HCO}_3^-}$ is actually a mixture of $\bar{V}_{\text{HCO}_3^-}$ and \bar{V}_{CO_3} . In the absence of experimental data at different temperatures, $\bar{V}_{\text{HCO}_3^-}$ and \bar{V}_{CO_3} as well as $\Delta \bar{V}_1$ and $\Delta \bar{V}_2$ have been assumed here to be temperature independent.

The degree of saturation of calcium carbonate in a solution is expressed as the ratio of the activity product of calcium and carbonate to the equilibrium solubility product of calcium carbonate, i.e.,

$$\begin{aligned}D.S. &= (a_{\text{Ca}^{2+}})^{(P)} \cdot (a_{\text{CO}_3^{2-}})^{(P)} / k^{(P)} \\ &= [\text{Ca}^{2+}]_{\text{tot}} \cdot [\text{CO}_3^{2-}]_{\text{tot}}^{(P)} / K_{sp}^{(P)} \quad (13)\end{aligned}$$

where $k^{(P)}$ and $K_{sp}^{(P)}$ are, respectively, a thermodynamic and apparent dissociation constant, and the superscript (P) indicates pressure condition. If

$$\begin{aligned}D.S. > 1 &\text{ supersaturation} \\ &= 1 \text{ saturation} \\ &< 1 \text{ undersaturation}\end{aligned}$$

in the above equation, $[\text{Ca}^{2+}]_{\text{tot}}$ can be obtained by *Wattenberg's* relationship

$$\begin{aligned}[\text{Ca}^{2+}]_{\text{tot}} &\approx \frac{1}{2}[A] + 0.000477 \text{ Cl}\% \\ &\quad \cdot (\text{moles/liter}) \quad (14)\end{aligned}$$

The apparent solubility product of calcium carbonate, K_{sp} , in sea water at 1 bar pressure has been studied by *Wattenberg* [1933, 1936], *Wattenberg and Timmerman* [1936], *Hindman* [1942], *MacIntyre* [1965], and some others as

a function of temperature and chlorinity. Since MacIntyre used Lyman's constants for his calculations of K_{sp} , whereas all previous workers used Buch's, it was necessary to recalculate them with the same set of dissociation constants in order to compare all the K_{sp} values. Because the older papers lack the information necessary for recalculation with Lyman's constants, MacIntyre's data were recalculated with Buch's constants (Figure 2a). Although the recalculated MacIntyre K_{sp} values for calcite differ by as much as 20% from the K_{sp} values for calcite obtained by Wattenberg at temperatures between 25° and 40°C, they are consistent with the linearly extrapolated values of Wattenberg at lower temperatures (Figure 2b). Since MacIntyre measured K_{sp} values for both calcite and aragonite over a temperature range of 0° and 40°C, his values were adopted in this paper. These K_{sp} values can be expressed as a function of temperature and chlorinity

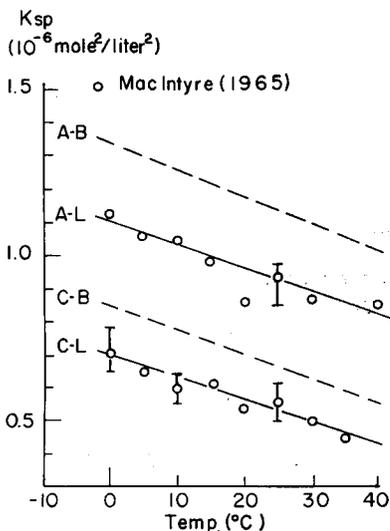


Fig. 2a. The solubility products for calcite and aragonite which were determined by MacIntyre [1965] in sea water with a chlorinity of 19.0‰ are shown as a function of temperature. The open circles indicate the experimental points which were obtained with the Lyman's dissociation constants for carbonic acid, and the lines A-L and C-L are, respectively, the best fit lines for the experimental data for aragonite and calcite. The lines A-B and C-B indicate the solubility products of aragonite and calcite that were calculated from the MacIntyre's data with the Buch's constants for carbonic acid.

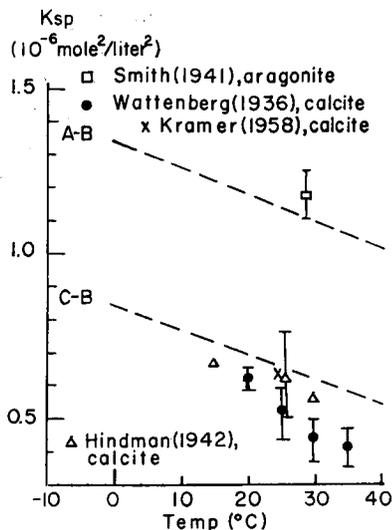


Fig. 2b. A comparison of the results obtained by Smith [1941] for aragonite in sea water with a chlorinity of 20‰, by Wattenberg and Timmermann [1936] for calcite in sea water with a chlorinity of 17.6‰, by Hindman [1942] for calcite in sea water with a chlorinity of 18.5‰, and by Kramer [1958] for calcite in sea water with a chlorinity of 19.0‰. These solubility product values are all based on the Buch's constants for carbonic acid. The lines A-B and C-B are based upon the experimental data of MacIntyre [1965] and the dissociation constants of Buch. Since MacIntyre's experiments cover a wider range of temperatures than the previous investigators, and appear to be internally consistent, his solubility product values were adopted in the present investigation.

by the equations

$$K_{sp} = (0.69 - 0.0063 T) \times 10^{-6} \cdot (Cl\%_o/19) \text{ moles}^2/\text{liter}^2$$

for calcite, and

$$K_{sp} = (1.09 - 0.0078 T) \times 10^{-6} \cdot (Cl\%_o/19) \text{ moles}^2/\text{liter}^2$$

for aragonite, where the effect of chlorinity was estimated on the basis of measurements of Wattenberg [1936].

The pressure dependence of K_{sp} can be calculated from (10a) or (10b) if the value of $\Delta\bar{V}$ is known. This $\Delta\bar{V}$ value can be calculated from the equation

$$\Delta\bar{V} = \bar{V}_{Ca^{2+}} + \bar{V}_{CO_3^{2-}} - V_{CaCO_3}$$

Since about 90% of the calcium in sea water is in free ion form [Garrels and Thompson, 1962] $\bar{V}_{Ca^{2+}}$ should be approximately equal to $\bar{V}_{Ca^{++}}$. Owen and Brinkley [1941] reported a value for $\bar{V}_{Ca^{2+}}$ of -16.1 cm³/mole. The value of $\bar{V}_{CO_3^{2-}}$ has already been shown to be 23.3 cm³/mole. The value for V_{CaCO_3} is 36.9 cm³/mole for calcite and 33.9 cm³/mole for aragonite [Clark, 1966]; therefore, the value for $\Delta\bar{V}$ is -29.7 cm³/mole for calcite and -27.0 cm³/mole for aragonite.

If $\Delta\bar{V}$ is independent of pressure and temperature, then the effect of pressure on the solubility products for calcite and aragonite can be calculated with (10b). The results of these calculations for a temperature of 25°C are summarized in Table 1 and are plotted in Figure 3. These values closely agree with the values determined experimentally by Pytkowicz and Fowler [1967] for calcitic Foraminifera and aragonitic oolites as shown in Figure 3; therefore, the magnitude of uncertainty in $\Delta\bar{V}$ is probably ± 1 cm³/mole. The uncertainty in the values listed in Table 1 was calculated on the basis of this uncertainty value for $\Delta\bar{V}$. There are no experimental data available for estimating $\Delta\bar{V}$ at lower temperature, but Pytkowicz and Connors [1964] show that there is no difference for high pressure solubility of aragonitic oolites at 22°C and 6°C within experimental uncertainty; therefore, the temperature dependence of $\Delta\bar{V}$ may be small.

Water sampling and ΣCO_2 and pCO_2 measurements on shipboard. A 200-liter water sampler designed by Gerard and Ewing [1961] was used to collect the sea water samples. About

TABLE 1. The Effect of Pressure on the K_{sp} Values Calculated with Equation 10b for Calcite and Aragonite at 25°C

The uncertainty was estimated on the basis of an uncertainty of ± 1 cm³/mole in the value of $\Delta\bar{V}$.

Pressure, bars	$K_{sp}^{(P)}/K_{sp}^{(1)}$	
	Calcite	Aragonite
1	1.00	1.00
100	1.13 \pm 0.03	1.11 \pm 0.03
250	1.35 \pm 0.04	1.31 \pm 0.04
500	1.82 \pm 0.06	1.72 \pm 0.06
750	2.45 \pm 0.08	2.26 \pm 0.08
1000	3.31 \pm 0.10	2.97 \pm 0.11

19 liters of sea water sample were introduced into an evacuated 20-liter jar for pCO_2 equilibration soon after the sampler reached the deck. Samples for ΣCO_2 analyses were stored in 250-ml airtight glass cylinders and in ordinary salinity bottles.

It is necessary that no loss of dissolved gases, including CO_2 , occurs from water samples brought up from depth. It is quite unlikely that such a loss has occurred, since the sum of partial pressures of gases dissolved in deep water was always on the order of one atmosphere when the water was brought to the surface. Even if a slight tendency to outgas existed, it would have been prevented because the door of the sampler had a tight O-ring seal.

Some of the water samples were analyzed for ΣCO_2 on shipboard immediately after they were brought up to the surface; others were analyzed as long as one month after sampling. There is no measurable change, however, in ΣCO_2 of water samples kept in salinity bottles even after one month storage.

The ΣCO_2 content dissolved in the water sample was determined by the infrared absorption method described by Broecker and Takahashi [1966]. Briefly, a sample of known volume (25-50 ml) was placed into an extraction

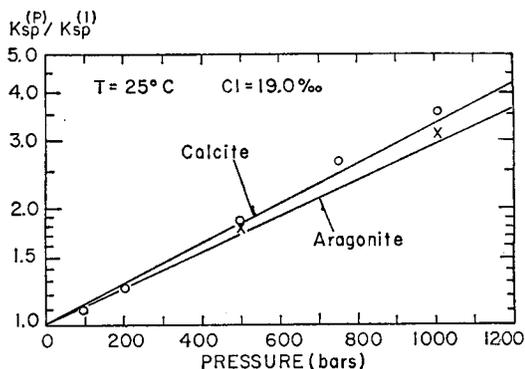


Fig. 3. The effect of pressure on the apparent solubility product for calcite and aragonite in sea water with a chlorinity of 19.0‰ at 25°C. The lines were calculated from (10b) using a $\Delta\bar{V}$ value of -29.7 cm³/mole for calcite and -27.0 cm³/mole for aragonite, and are represented by $\log(K_{sp}^{(P)}/K_{sp}^{(1)}) = 5.20(P - 1) \times 10^{-4}$ for calcite, and $\log(K_{sp}^{(P)}/K_{sp}^{(1)}) = 4.73(P - 1) \times 10^{-4}$ for aragonite. The results of the experiments by Pytkowicz and Fowler [1967] for calcite and aragonite are indicated respectively by open circles and crosses.

chamber filled with pure nitrogen gas. The sample was acidified with sulfuric acid. Pure nitrogen was swept through the acidified sample, dried over P_2O_5 , and collected in an evacuated 5000-ml flask. The CO_2 concentration in this known amount of nitrogen was then determined by using an infrared gas analyzer. The ΣCO_2 in sea water can be determined with an accuracy of $\pm 0.5\%$.

The partial pressure of CO_2 in sea water, $p\text{CO}_2$, was determined from the measurements of the CO_2 concentration in a sample of air equilibrated with sea water at a known temperature and pressure. Two to three liters of air and 19 liters of sea water were contained in a closed system equilibrator. The air was circulated at a rate of 5 liters/minute through a gas disperser immersed in the water sample using a diaphragm pump. A one-liter sampling flask was inserted into the system in series with the gas pump. After 40 min of equilibration, the sampling flask was transferred to the infrared analyzer for CO_2 determination. The temperature of the water sample was recorded before and after the equilibration. The temperature increment during the run ranged from 0° to 2°C depending on the temperature difference between the water sample and the surroundings. Since the rate of CO_2 equilibration is faster than the rate of change in temperature, the temperature of the water sample at the end of the equilibration was taken as the equilibration temperature. The pressure above the water sample inside the equilibration system was determined from the barometric pressure and from the pressure difference between the atmosphere and the system as measured by a U-tube manometer. Several standard gas tanks containing known concentrations of CO_2 gas (250–1000 ppm CO_2 in dry air) were used for CO_2 determinations. The over-all uncertainty in $p\text{CO}_2$ determinations is about $\pm 1\%$, which is mainly due to a correction for a change in the total dissolved CO_2 occurred during the equilibration process.

DISCUSSION

Experimental data and derived quantities.

The analytical results for ΣCO_2 and $p\text{CO}_2$ are tabulated in Table 2 along with the sample locations, depths, water temperatures, and salinities. The ship's tracks for the *Conrad 10*,

Vema 21, and *Vema 22* cruises, during which the samples were collected, are shown in Figure 4.

The values listed in the tenth column of Table 2 are the $p\text{CO}_2$ values obtained at the equilibration temperature; the values in the eleventh are those at the in situ temperature. These latter values were obtained by correcting for the difference between the equilibration temperature and the in situ temperature by means of (1). The $p\text{H}$ at the in situ temperature and pressure was calculated from (6) and (7).

The values of carbonate alkalinity $[A]$, and total alkalinity $[Alk]$ were calculated from (2) and (3) with the ΣCO_2 and the $p\text{H}$ values at T_{in} . If $[A]$ were calculated for the in situ T or at in situ T and P , it agrees with the value of $[A]$ for T_{in} within 0.5×10^{-5} eq/liter as shown in Table 3. The uncertainty of about $\pm 1 \times 10^{-5}$ eq/liter stems mainly from the uncertainty in the ΣCO_2 determination.

The $[\text{CO}_3^{2-}]_{\text{tot}}$ values at the in situ T and P were calculated from (9) with the ΣCO_2 value and the $p\text{H}$ value calculated for the in situ T and P . The value of $[\text{CO}_3^{2-}]_{\text{tot}}$ calculated for the in situ T and P differs from that for T_{in} and 1 bar no more than 0.5×10^{-6} mole even at a 5000-meter depth (Table 3). Because of the charge balance restriction, the $[\text{CO}_3^{2-}]_{\text{tot}}$ value cannot change appreciably with changes in P and T . Instead, the $p\text{H}$ value shifts in response to the change in K_1 , K_2 , and K_B induced by pressure and temperature change. The uncertainty in the $[\text{CO}_3^{2-}]_{\text{tot}}$ is less than 0.5×10^{-6} mole/liter.

The value of $[\text{Ca}^{2+}]_{\text{tot}}$ necessary for the calculation of the ion product of calcium carbonate was calculated from (14). The uncertainty in this value is small compared to that of the $[\text{CO}_3^{2-}]_{\text{tot}}$ value, and may be neglected. The degree of saturation of calcium carbonate in sea water was then calculated by dividing the concentration product by the equilibrium solubility product, K_{sp} . Since Lyman's dissociation constants for carbonic acid were used for the calculation of both the concentration product and K_{sp} values, the uncertainty in Lyman's constants cancels out in the calculation of the degree of saturation; therefore, the uncertainty in the degree of saturation is mainly due to that of the $[\text{CO}_3^{2-}]_{\text{tot}}$ value and the

TABLE 2. Analytical Data and Derived Quantities

T^* indicates the ocean water temperature *in situ*; T_{eq} , the temperature at which the partial pressure of CO_2 was determined by the gas equilibration technique; S , salinity; ΣCO_2 , the total CO_2 dissolved in water; $[\Sigma CO_2]_N$, the value of ΣCO_2 normalized to a salinity of 35.0‰; pCO_2 , the partial pressure of CO_2 at T_{eq} and 1 bar total pressure; pCO_2^* , the partial pressure of CO_2 at the *in situ* temperature and 1 bar total pressure; pH^* , the value of pH at the *in situ* temperature and pressure; $[A]$, carbonate alkalinity at *in situ* temperature and 1 bar total pressure; $[Alk]$ and $[Alk]_N$, respectively, the alkalinity of sample water and the alkalinity value normalized to a salinity of 35.0‰; $[CO_3^{2-}]_{tot}$, the total concentration of the carbonate ion species at *in situ* temperature and pressure; and $C.P.$, the concentration product, $[Ca^{2+}]_{tot}[CO_3^{2-}]_{tot}$, at *in situ* temperature and pressure. The letter (B) following a sample number denotes that the sample was taken at or near the floor of the ocean.

Sample	Depth m	Lat.	Long.	T^* , T_{eq} °C	S , ‰	$[\Sigma CO_2]$, $[\Sigma CO_2]_N$ 10 ⁻³ M/l	pCO_2 , pCO_2^* 10 ⁻³ bar	pH^*	$[Al]$, $[Alk]$, $[Alk]_N$ 10 ⁻³ eq/l	$[CO_3^{2-}]_{tot}$ 10 ⁻³ M/l	$C.P.$ 10 ⁻⁷ M ² /l ²	Degree of Saturation		
												Calcite	Aragonite	
Northwest Atlantic (Nov.-Dec., 1965; BMD sample, May, 1968)														
9S	0	21°47'N	54°00'W	24.8	36.5	218	209	8.31	262	251	31.6	34.5	6.5	3.9
BMD2-7	0	32°14'N	64°39'W	21.7	36.7	217	208	8.26	242	254	26.7	29.1	5.2	3.1
BMD2-8	0	32°15'N	64°46'W	21.6	36.5	219	209	8.27	245	257	27.6	30.2	5.4	3.2
BMD2-3	100	32°14'N	64°39'W	20.0	36.6	217	207	8.29	238	245	27.4	30.0	5.2	3.1
BMD2-5	200	32°14'N	64°39'W	18.5	36.6	220	210	8.28	245	256	26.5	29.0	4.9	3.0
9	200	24°47'N	54°60'W	18.2	36.3	216	207	8.24	238	249	25.4	25.4	4.3	2.6
BMD2-4	300	32°14'N	64°39'W	18.0	36.5	219	209	8.27	243	254	23.4	27.7	4.6	2.8
8	500	25°32'N	55°15'W	16.3	36.1	218	211	8.21	238	248	21.1	22.7	3.6	2.2
BMD2-6	700	32°14'N	64°39'W	13.0	35.6	225	221	8.10	239	246	16.0	17.0	2.5	1.5
7	1070	25°11'N	56°07'W	6.4	35.0	227	227	8.03	236	242	11.6	12.2	1.6	1.0
11	2250	21°44'N	61°28'W	3.4	34.9	226	227	8.10	238	244	13.2	13.8	1.5	0.99
10	3290	22°50'N	57°52'W	2.7	34.9	228	229	8.05	240	246	13.1	13.7	1.3	0.88
6	4170	26°56'N	55°02'W	2.1	34.9	231	232	8.02	242	249	12.7	13.2	1.1	0.75
3	4820	29°46'N	62°26'W	2.2	34.9	228	229	8.08	239	245	12.3	12.8	0.98	0.67
12	5600	21°44'N	61°28'W	2.1	34.9	229	230	7.99	239	244	11.5	12.0	0.84	0.57
Northeast Atlantic (Sept. 1966, Sampled by Willard Moore)														
V22-57	300	37°55'N	43°38'W	16.9	36.2	215	208	8.25	236	247	22.8	24.6	4.0	2.5
V22-56	710	27°55'N	43°55'W	10.6	35.4	225	222	8.01	234	240	11.9	12.6	1.8	1.2
V22-55	1700	23°02'N	34°29'W	4.1	35.0	230	230							
V22-54	4100	19°02'N	29°09'W	2.3	35.0	231	231	7.97	239	244	10.5	11.0	0.96	0.64
Caribbean Sea (Dec. 1965-Jan. 1966)														
B03-24	0	25°25'N	79°12'W	28.7	36.4	201	193	8.22	227	239	230	29.5	5.7	3.1
51S	0	16°34'N	79°32'W	27.3	37.2	208	199	8.26	236	249	238	31.6	6.1	3.6
33	530	18°58'N	81°37'W	12.6	35.5	223	220	8.04	235	241	238	14.6	2.2	1.4
16	1300	17°50'N	69°36'W	5.1	35.0	228	228	8.06	238	244	244	12.6	1.6	1.0
29	2090	17°21'N	86°14'W	4.1	35.0	228	228	8.10	240	246	246	14.1	1.6	1.0
31	2920	16°52'N	86°50'W	3.4	35.0	228	228	8.06	239	245	245	13.1	1.3	0.87
36	3120	10°39'N	81°20'W	4.1	35.0	230	230	8.02	240	245	245	12.3	1.2	0.80
32	3770	17°36'N	86°58'W	4.2	35.0	228	228	8.05	240	246	246	13.6	1.2	0.83
26	4280	19°40'N	78°10'W	3.9	35.0	226	226	8.02	238	244	244	13.5	1.1	0.77
34	4690	18°58'N	81°37'W	4.3	35.0	224	224	8.02	235	241	241	13.2	1.0	0.69
35	5400	18°57'N	81°15'W	4.5	35.0	223	223	7.99	233	240	240	12.7	0.92	0.63
24	6600	19°42'N	76°42'W	4.7	35.0	225	225	8.00	237	243	243	13.6	0.87	0.59

TABLE 2 (continued)

Sample	Depth m	Lat.	Long.	$T^* T_{eq}$ °C	S, σ_t ‰	$[\Sigma CO_2] / [\Sigma CO_2]_N$ 10 ⁻³ M/l	pCO_2, pCO_2^* 10 ⁻⁶ bar	pH*	$[Al]/[Al]_N$ 10 ⁻³ eq/l	$[CO_3^{*2-}]_{tot}$ 10 ⁻³ M/l	C.F. 10 ⁻⁷ M ² /l ³	Degree of Saturation						
												Calcite	Aragonite					
Central Equatorial Pacific (Mar.-Apr. 1966, sampled by Teh-Lung Ku)																		
56S	0	02°53'S	136°47'W	27.9	28.2	35.1	206	205	398	394	8.18	229	240	239	24.4	25.8	5.0	3.0
65S	0	04°18'S	146°27'W	29.4	29.4	35.1	205	204	388	387	8.19	229	241	240	25.7	27.2	5.4	3.2
66	100	08°10'S	147°15'W	27.6	28.2	35.0	208	208	350	342	8.24	234	246	246	27.3	28.6	5.4	3.2
65	300	04°18'S	146°26'W	11.4	17.4	35.0	230	230	810	635	7.95	238	243	243	10.9	11.3	1.7	1.1
64	500	01°46'N	146°05'W	7.7	22.5	34.5	235	238	1210	665	7.91	241	245	249	9.6	9.6	1.4	0.87
61	720	03°35'N	140°46'W	5.6	27.1	34.5	241	244	1560	659	7.90	246	250	254	8.8	9.2	1.2	0.80
57	1000	03°30'N	129°43'W	4.6	14.0	34.5	240	243	1250	831	7.79	242	245	249	6.6	6.9	0.91	0.58
56	1500	05°39'N	127°22'W	3.4	22.5	34.5	245	248	1480	673	7.86	249	253	257	8.0	8.3	1.0	0.56
55	2000	09°55'N	122°30'W	2.1	14.4	34.6	248	251	1186	698	7.83	251	255	258	7.5	7.8	0.87	0.56
53	2500	16°39'N	110°14'W	1.8	14.2	34.6	247	250	1057	619	7.87	251	255	258	8.2	8.5	0.89	0.58
60	3430	00°35'N	138°56'W	1.5	13.0	34.6	240	243	836	508	7.91	246	251	254	9.1	9.5	0.88	0.58
54(B)	3830	15°08'N	113°30'W	1.5	16.5	34.6	246	249	1020	539	7.89	252	256	259	9.0	9.4	0.82	0.54
63(B)	4860	04°33'N	144°13'W	1.4	26.7	34.6	243	246	1210	433	7.95	251	256	259	10.7	11.2	0.85	0.57
Western Equatorial Pacific (Apr.-May 1966, sampled by Teh-Lung Ku)																		
129S	0	08°58'S	176°03'E	29.5	29.5	35.1	202	201	346	346	8.24	229	240	239	33.1	28.6	5.7	3.3
150S	0	04°39'N	149°34'E	29.0	29.0	35.1	203	202	324	324	8.26	230	243	242	28.6	30.0	5.9	3.5
99	200	01°16'N	149°12'E	16.4	17.9	35.1	222	221	513	484	8.08	236	243	242	15.9	16.7	2.8	1.7
97	300	00°21'S	153°59'E	11.3	14.6	34.8	234	235	852	743	7.89	240	245	246	9.7	10.0	1.6	0.97
96	400	01°08'S	156°18'E	9.4	19.7	34.7	238	240	1350	888	7.81	241	245	247	7.7	8.0	1.2	0.75
77	400	04°54'N	171°25'W	8.3	15.9	34.6	238	241	1126	818	7.84	242	245	248	8.0	8.2	1.2	0.77
75	500	00°31'S	168°47'W	8.1	15.1	34.6	239	242	1110	825	7.83	243	246	249	7.9	8.2	1.2	0.75
88	1500	14°32'S	157°58'E	2.8	16.2	34.6	245	248	1064	600	7.91	250	254	257	8.8	9.1	1.1	0.72
95(B)	1650	02°39'S	156°59'E	2.7	16.5	34.6	244	247	1124	624	7.89	249	252	255	8.3	8.7	1.0	0.67
70	2000	13°50'S	161°43'W	2.1	14.1	34.6	245	248	950	566	7.92	252	256	259	9.0	9.4	1.1	0.70
90(B)	2650	15°22'S	151°32'E	2.0	17.7	34.6	244	247	970	499	7.96	251	256	259	9.9	10.3	1.1	0.70
68	3000	15°42'S	158°49'W	1.7	15.9	34.6	246	249	923	503	7.94	253	257	260	9.8	10.3	1.0	0.67
67	4500	16°32'S	156°04'W	1.4	16.8	34.6	244	247	938	486	7.91	251	256	259	9.8	10.2	0.83	0.56
91(B)	4500	13°17'S	153°07'E	1.9	19.4	34.6	245	248	990	475	7.93	252	256	259	10.2	10.7	0.88	0.59
93(B)	5600	07°09'S	154°20'E	2.2	18.4	34.6	245	248	1017	513	7.88	252	256	259	9.5	9.9	0.71	0.48
78	5600	07°31'N	172°50'W	1.4	17.9	34.6	243	246	1040	517	7.86	249	254	257	9.0	9.3	0.66	0.45

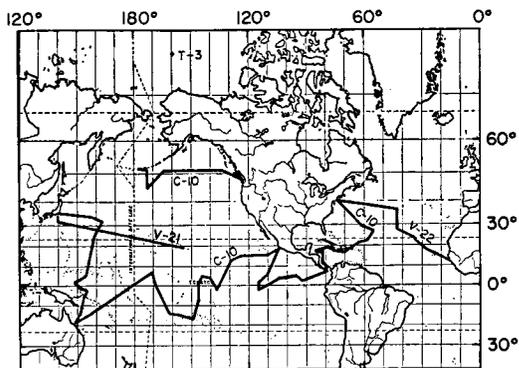


Fig. 4. The tracks of the oceanographic expeditions and the position of a sampling station in the Arctic Ocean. The tenth cruise of the R. V. *Conrad* is indicated by C-10, and the 21st and 22nd cruises of the R. V. *Vema* are indicated by V-21 and V-22.

K_{sp} value. MacIntyre reported an uncertainty of 0.05×10^{-6} mole²/liter² in his determination of K_{sp} at 1 bar pressure. The uncertainty in the calculation of the effect of pressure on K_{sp} is presumably about 3%; hence, the overall uncertainty in the degree of saturation reported here has been estimated to be about $\pm 10\%$.

Distribution of ΣCO_2 . As shown in Figure 5, the surface water in both oceans has a total dissolved CO_2 content of about 205×10^{-5} mole/liter (normalized at a salinity of 35.00‰). In the North Atlantic and Caribbean, the CO_2 content increases with depth to about 228×10^{-5} mole/liter at 100 meters and then remains nearly constant down to the bottom. In the Pacific, an increase to 245×10^{-5} mole/liter occurs in the first 1000 meters, and the concentration remains the same below 1000 meters. The values of ΣCO_2 in the Arctic Ocean samples collected at the T-3 station (Figure 4)

increase rapidly with depth to about 222×10^{-5} mole/liter at 1500 meters, and remain nearly constant down to 4000 meters. The ΣCO_2 content in the Arctic deep water is about 6×10^{-5} mole/liter lower than that for the North Atlantic deep water. The northern North Pacific water at depths between 500 meters and 3000 meters contains about 4% more CO_2 than the waters from other areas of the Pacific. A value of as high as 252×10^{-5} mole/liter has been observed; however, the ΣCO_2 contents in water from the same area at depths greater than 4000 meters do not differ significantly from those in the central and south Pacific Ocean waters.

Distribution of $p\text{CO}_2$. As shown in Figure 6, with an exception of a depth range between 500 and 1500 meters, the partial pressure of CO_2 at in situ temperature for waters in the Atlantic and Caribbean is remarkably constant with depth and only slightly higher than that in the atmosphere. On the other hand, the $p\text{CO}_2$ values of the Pacific waters are far higher than the atmospheric values. The high $p\text{CO}_2$ values up to 1044×10^{-6} bar were observed at depths comparable to those where the oxygen minimum exists in the main thermocline. Below 1500 meters, the $p\text{CO}_2$ values decrease from 700×10^{-6} bar at 1500 meters to 400×10^{-6} bar at 5000 meters. This trend appears to persist across the Pacific.

Comparison with previous measurements. The ΣCO_2 values determined by *Moberg et al.* [1934] off southern California and by *Hamm and Thompson* [1941] at $48^\circ 24' \text{N}$, $127^\circ 02' \text{W}$ and $54^\circ 10' \text{N}$, $134^\circ 10' \text{W}$ in the Pacific with the Van Slyke method agree well with the results of this investigation. Similarly, the values of $p\text{CO}_2$ obtained by *Wattenberg* [1933] with the Van Slyke method for the samples taken in the Atlantic agree well with the $p\text{CO}_2$ values

TABLE 3. The Effect of Pressure and Temperature on the Carbonate Chemistry of a Sea Water Sample Having $\text{Cl} = 19.0 \text{‰}$, $\Sigma\text{CO}_2 = 241 \times 10^{-5} \text{ M/l}$ and $\text{Alk} = 255 \times 10^{-5} \text{ eq/l}$

$T, P,$ °C bar	pH	$[\text{HCO}_3^-]$ 10^{-5} M/l	$[A]$ 10^{-5} eq/l	$[\text{CO}_2]_{\text{tot}}$ 10^{-5} M/l	$[\text{HCO}_3^-]_{\text{tot}}$ 10^{-5} M/l	$[\text{CO}_3^{2-}]_{\text{tot}}$ 10^{-5} M/l	$K_{sp}^{(P)}$ $10^{-7} \text{ M}^2/\text{l}^2$	$\frac{[\text{Ca}^{2+}]_{\text{tot}} \cdot [\text{CO}_3^{2-}]_{\text{tot}}}{K_{sp}^{(P)}}$
25	1 7.79	6.5	248.5	3.7	226.1	11.2	5.3	2.2
0	1 8.07	6.0	249.0	2.7	227.6	10.7	6.9	1.6
0	250 8.01	6.0	249.0	2.5	228.0	10.5	9.6	1.1
0	500 7.95	5.9	249.1	2.2	228.5	10.3	13.4	0.8

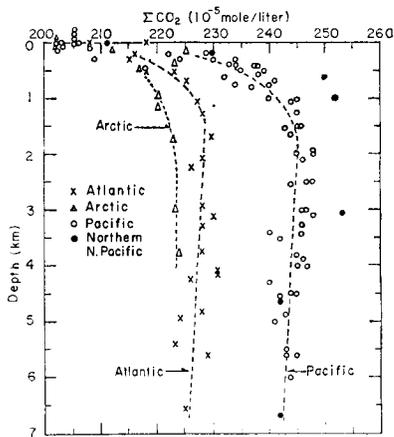


Fig. 5. The distribution of ΣCO_2 in the Atlantic and Pacific oceans and in the Arctic Ocean as a function of depth.

obtained in this work. For example, a $p\text{CO}_2$ value of about 350×10^{-6} bar was obtained by both investigators for the North Atlantic deep water.

The alkalinity values calculated from the ΣCO_2 and $p\text{CO}_2$ data (Figure 7) agree with the direct alkalinity determinations made by Bruneau *et al.* [1950]. The average value of the calculated specific alkalinity ($\text{Alk}/\text{Cl}\%$) values for the deep Pacific water is $(0.134 \pm 0.001) \times 10^{-3}$, a value in good agreement with Park's [1966] determinations of 0.133×10^{-3} . If the alkalinity values are also calculated with Buch's K_1 and K_2 , the results are systematically 3×10^{-5} eq/liter greater than those calculated with Lyman's K_1 and K_2 values, and no longer agree with the direct alkalinity measurements. This again suggests that Lyman's constants are more reliable than Buch's.

Degree of saturation of calcite and aragonite in the oceans. The concentration products, $[\text{Ca}^{2+}]_{\text{tot}} \cdot [\text{CO}_3^{2-}]_{\text{tot}}$, at in situ T and P conditions, and the $K_{sp}^{(P)}$ values for calcite and aragonite in sea water ($\text{Cl} = 19\%$, $T = 0^\circ$ and 25°C) are plotted as a function of depth in Figure 8. The values of the degree of saturation for calcite and aragonite at the conditions of in situ T and P are plotted in Figures 9 and 10, respectively.

As shown in Figures 8 and 9, the Pacific water is supersaturated, with respect to calcite, down to a depth of about 500 meters. At the depth of about 1000 meters, where the $p\text{CO}_2$ maximum

occurs (Figure 6), the sea water is undersaturated. At depths between 1000 and 3000 meters, the water appears, within the experimental uncertainty, to be saturated. Below 3000 meters, the sea water is undersaturated with respect to calcite. In the North Atlantic, the water is supersaturated with calcite from the surface down to about 4000 meters. From 4000 to 5000 meters, the sea water is, within the experimental uncertainty, saturated. Below about 5000 meters, the sea water appears to be undersaturated with respect to calcite.

In contrast to the findings of the present work, Berner [1965] found that both the Pacific and Atlantic Ocean waters are undersaturated with respect to calcite below a depth of 500 meters; however, he assumed the effect of pressure on the activity coefficients of calcium and carbonate ion species

$$(\gamma_{\text{Ca}^{2+}} \cdot \gamma_{\text{CO}_3^{2-}})^{(P)} / (\gamma_{\text{Ca}^{2+}} \cdot \gamma_{\text{CO}_3^{2-}})^{(1)}$$

to be 1.2 at pressure of 500 bars instead of 1.57, which has been calculated on the basis of the experiments by Disteché and Disteché [1967]. In addition, the values of $p\text{H}$ and alkalinity for his average ocean differ from the values determined in the present work; therefore, his results are not specifically applicable to the region of the oceans studied in the present work.

On the basis of the measurements for alka-

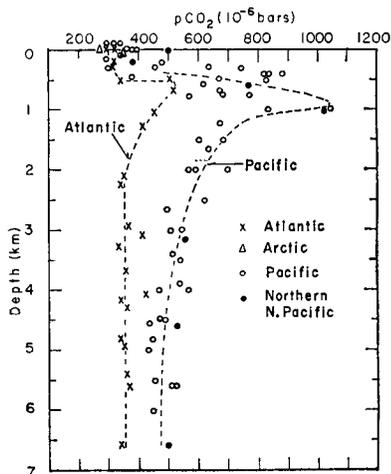


Fig. 6. The distribution of $p\text{CO}_2$ at the in situ temperature and 1 bar total pressure in the Atlantic and Pacific oceans and in the Arctic Ocean as a function of depth.

linity and pH obtained during the USNA *Eltanin 3* cruise, *Pytkowicz* [1965] concluded that the southeast Pacific Ocean water is undersaturated with respect to calcite below 100 meters, and that the degree of saturation existing at the bottom is about 0.3. Later work by *Pytkowicz and Fowler* [1967] has reached essentially the same conclusion. Further work is needed in order to resolve the discrepancy between the results of this work and that of *Pytkowicz*.

Peterson [1966] determined the rate of dissolution of calcite as a function of water depth in the central Pacific by means of weight loss of optical grade calcite crystals suspended in the ocean. He found that the weight loss is virtually zero in the water between the surface and several hundred meters, and is consistently small from several hundred meters down to 3300 meters. A sharp increase in the dissolution rate was observed at a depth of about 3700 meters. Similarly, *Berger* [1967] determined the weight loss of the calcite shells of Foraminifera as a function of depth in the central Pacific. He observed a weight loss of several per cent below 1000 meters and a greater rate of weight loss below about 3000 meters. The

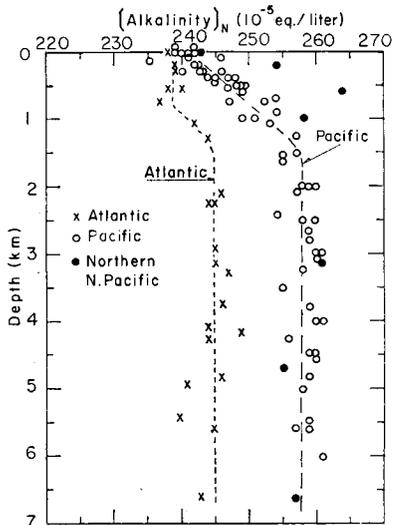


Fig. 7. The distribution of the calculated alkalinity values in the Atlantic and Pacific oceans as a function of depth. The abscissa, $[Alk]_N$, indicates the alkalinity values which were calculated with (3) and then normalized to a salinity of 35.0‰.

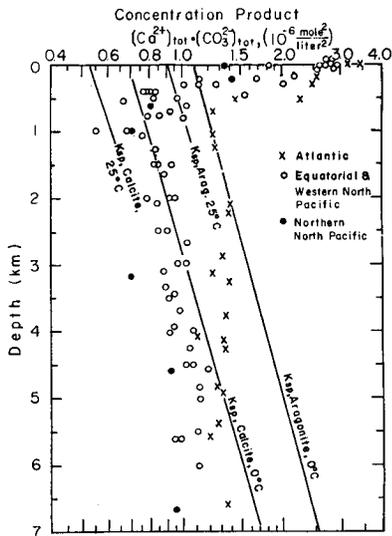


Fig. 8. The concentration products as a function of depth. The observed values are indicated respectively by crosses, open circles, and solid circles for the Atlantic, Pacific and northern North Pacific oceans. The solid lines indicate the equilibrium solubility products for calcite and aragonite at temperatures of 0° and 25°C and at the pressure corresponding to the hydrostatic pressure at depth.

rapid rate of dissolution of calcite observed by these investigators in the Pacific water at depths greater than 3000–3700 meters may be accounted for by the finding of the present investigation that the Pacific water becomes distinctly undersaturated with respect to calcite at depths below about 3000 meters. If the Pacific water is undersaturated with respect to calcite below 100–500 meters as concluded by *Pytkowicz* [1965] and *Berner* [1965], such a sharp increase in the dissolution rate of calcite at 3700 meters can only be explained in terms of solution kinetics as suggested by *Peterson* [1966]. The findings of the present investigation appear to offer a simpler explanation for the observed sharp increase in the dissolution rate of calcite.

As shown in Figures 9 and 10, the Pacific water is supersaturated with respect to aragonite from the surface down to a depth of about 200 meters. The northwest Atlantic water is supersaturated with aragonite from the surface down to a depth of about 1000 meters. From 1000 to 2300 meters, the sea water is

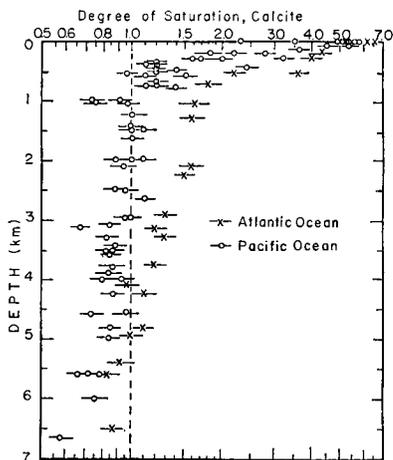


Fig. 9. Degree of saturation of calcite in sea water as a function of depth in the Atlantic (X) and Pacific (O) oceans. The values for the degree of saturation were obtained by dividing a concentration product, $[Ca^{2+}]_{tot} \cdot [CO_3^{2-}]_{tot}$, with an equilibrium solubility product for calcite at temperature and pressure corresponding to the temperature and depth of the sample; thus, the values greater than unity indicate supersaturation, and those smaller than unity indicate undersaturation.

essentially saturated. Below 2300 meters, the sea water is undersaturated with respect to aragonite. *Murray and Chumley* [1924] found that the aragonitic shells of pteropods occur in the bottom sediments deposited at a water depth of less than 2100 meters in the Atlantic Ocean. Their observations are consistent with the finding of the present investigation that the Atlantic water is undersaturated with aragonite below a depth of about 2300 meters; therefore, aragonitic shells should be dissolved in the water below this depth.

The CaCO₃ content in deep sea sediments has been studied as a function of water depth by *Murray and Renard* [1891], *Revelle* [1944], *Pia* [1933], *Bramlette* [1961], *Turekian* [1964, 1965], and others. All these results are essentially in agreement. In the Pacific, the abrupt decrease in the CaCO₃ content in the sediments starts between 3000 and 4000 meters, and in the Atlantic between 4000 and 5000 meters.

Revelle and Fairbridge [1957] and *Turekian* [1964] suggested that this abrupt change in the CaCO₃ content in the sediments may be due to the transition from saturation to undersaturation of the water above the sediments.

Their explanation is supported by the results of this work.

Sources of the excess CO₂ in deep water. Both the Atlantic and Pacific surface waters contain about 205×10^{-6} mole/liter of CO₂. As shown in Figure 5, the deep Atlantic water below a depth of 1000 meters contains about 10% more dissolved CO₂, and the deep Pacific water contains about 20% more dissolved CO₂, than the surface water. This excess CO₂ in the deep water may have been derived from the dissolution of skeletal CaCO₃, and from the oxidation of organic matter. The addition of CO₂ into sea water by the solution of CaCO₃ is accompanied by an increase in the Ca content in sea water. This increase shows up as a change in alkalinity. For each mole of CaCO₃ dissolved, the alkalinity will rise by two equivalents. The oxidation of suspended organic matter should account for the remaining amount of the excess CO₂ found in the deep water. Table 4 shows these quantities calculated from the present data. About 80% of the excess CO₂ in the deep waters is derived from the oxidation of organic debris.

Sverdrup et al. [1942] have shown that the concentrations of phosphate and nitrate in sea water increase with depth from the surface

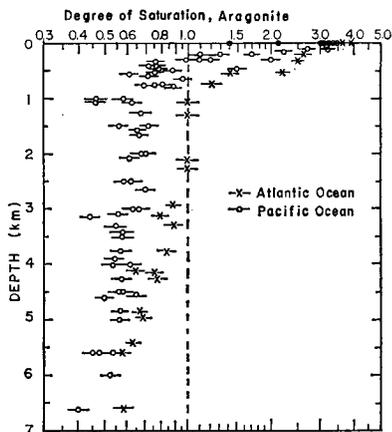


Fig. 10. Degree of saturation of aragonite in sea water as a function of depth in the Atlantic (crosses) and Pacific (open circles) oceans. The values for the degree of saturation were obtained by dividing a concentration product with an equilibrium solubility product for aragonite at temperature and pressure corresponding to the temperature and depth of the sample.

TABLE 4. The Sources of the Excess CO₂ and Calcium in Deep Water of the Oceans

	$[\Sigma\text{CO}_2]_N$, 10 ⁻⁴ M/l	$[\text{Alk}]_N$, 10 ⁻⁵ eq/l	Excess CO ₂ , 10 ⁻⁵ M/l	Solution* of CaCO ₃ , 10 ⁻⁵ M/l	Oxidation† of Organic Debris, 10 ⁻⁵ M/l	Excess‡ PO ₄ , 10 ⁻⁵ M/l	Excess‡ NO ₃ , 10 ⁻⁵ M/l	P : N : C
Atlantic surface water	204	238						
Atlantic deep water	227	245	23	4	19	0.17	2.1	1 : 12.5 : 112
Pacific surface water	206	241						
Pacific deep water	248	258	42	9	33	0.25	3.3	1 : 13.2 : 132

* Solution of CaCO₃ = $\frac{1}{2} \{([\text{Alk}]_N \text{ in the deep water}) - ([\text{Alk}]_N \text{ in the surface water})\}$

† CO₂ produced by oxidation of organic debris = (excess CO₂) - (CO₂ from the solution of CaCO₃)

‡ The data are from *Sverdrup et al.* [1942]. The excess PO₄ and NO₃ values indicate the difference between the concentrations in the surface and deep waters.

down to 1000 meters and are nearly constant below 1000 meters. Since both phosphorus and nitrogen are biogenic elements, the excess of these elements in deep water should represent the decomposition of organisms. The ratio of excess CO₂ derived from organic debris to nitrogen to phosphorus in deep water should then be the same as that in plankton (i.e., P:N:C = 1:16:106). The atomic ratios of these excesses have been calculated for the deep waters of the Atlantic and Pacific (Table 4). The calculated ratios are as expected.

Ca cycle in the world's ocean. If the formation of calcareous parts of planktonic organisms is the major mechanism for the removal of calcium from the oceans, and if the calcium cycle in the ocean is at steady state, then the rate of accumulation of the biogenic CaCO₃ in deep-sea sediments should be equal to the rate at which calcium is supplied by rivers. *Turekian* [1964] has computed the rate of CaCO₃ accumulation from sediment distribution and sedimentation rate data and has shown that, within the uncertainty of such calculations, this is indeed the case. *Livingstone* [1963] has estimated that 1×10^{13} moles of Ca are supplied to the sea each year by river inflow; therefore, the annual rate at which CaCO₃ is accumulating in deep-sea sediments should be 1×10^{13} moles calcium.

The rate at which CaCO₃ is being dissolved in the deep sea can be obtained from the data for the alkalinity excess in deep water and from

the deep water residence times calculated on the basis of C¹⁴ measurements. The excess calcium in deep water must average close to 6×10^{-5} mole/liter as shown in Table 4. The volume of the deep water mass may be assumed to be 1×10^{21} liters, about 75% of the volume of the entire ocean. Thus a total of 6×10^{16} moles of excess calcium is stored in the deep sea. Radiocarbon data indicate that the average deep water molecule returns to the surface once each 1000 ± 300 years [*Broecker*, 1963]. The excess dissolved calcium must then be replaced with this frequency. The production rate of CaCO₃ destined to be redissolved must then be $(6 \pm 2) \times 10^{13}$ moles/yr.

The total production rate of CaCO₃ can be obtained to be $(7 \pm 2) \times 10^{13}$ moles/yr or 2 ± 0.5 g/cm²·1000 years by summing these two components. Of this, roughly 15% accumulates and the remainder redissolves. This 5 to 1 ratio may be compared with the ratio of ocean bottom bathed in water undersaturated with CaCO₃ to that in water supersaturated with CaCO₃. As given by *Sverdrup et al.* [1942], 85% of the floor of the Pacific and Indian Oceans lies below 2000 meters and 35% of the Atlantic Ocean floor lies below 4500 meters. Since the area of the Pacific and Indian Oceans is three times larger than that of the Atlantic, about 80% of the ocean floor lies below the compensation level of calcite. Almost the entire ocean floor lies below the compensation level for aragonite. Thus the ratio of 5 units CaCO₃

dissolved per 1 unit preserved is not inconsistent with the ratio of red clay to calcareous ooze sediments on the ocean floor. In other words, the data on river inputs, sediment accumulation, deep water residence times, deep water alkalinity excesses, and observed and calculated compensation levels are internally consistent.

Factors controlling the oceanic CaCO_3 compensation levels. If the oceanic system is actually in a steady-state mode of operation, then the fraction of the ocean floor covered by CaCO_3 -free sediments is controlled by material balance. If, as shown above, organisms precipitate CaCO_3 from sea water five times as fast as Ca is being supplied to the oceans by rivers, then the material balance restriction requires that the chemistry of the ocean adjust to the state where 5/6 of the biogenic CaCO_3 fall into undersaturated water and redissolve. The fraction of the ocean floor bathed in undersaturated water is thus fixed by the ratio of the rate of calcium supply by weathering to the rate of calcium fixation by organisms.

The areal distribution of sediments bathed in undersaturated water depends on topography of the ocean floor (other factors being equal, the higher the pressure, the lower the degree of saturation) and on the amount of CO_2 gas released into the deep water through oxidation of organic debris (as shown in Table 4, this excess is about twice as great in the deep Pacific as in the deep North Atlantic). As the temperature is uniform to $\pm 2^\circ\text{C}$ throughout the deep ocean, the temperature dependence of CaCO_3 solubility currently has little effect on the geographical distribution of undersaturated water.

Material balance thus determines the proportion of the ocean floor bathed in water undersaturated with CaCO_3 . The increase in CaCO_3 solubility with pressure dictates that resolution will preferentially take place in the deepest regions of the ocean. Since the present mode of mixing favors an enrichment of the deep Pacific relative to the deep Atlantic in organically derived CO_2 , the level of compensation is not the same in the two oceans; it lies at shallower depths in the Pacific.

Paleocompensation levels reconstructed by studying the calcite and aragonite distribution in Cenozoic deep sea sediments will then reflect

some combination of paleotopography, temperature structure, mixing pattern, productivity, and weathering rate. Since so many factors are involved, doubt is cast on geological conclusions that have been drawn from such data.

SUMMARY AND CONCLUSIONS

Approximately 100 determinations of the partial pressure of CO_2 and the total CO_2 dissolved in the water samples collected in the Atlantic and Pacific oceans were made by means of an infrared gas analyzer installed on shipboard.

The values of the partial pressure of CO_2 in the Atlantic deep water below a depth of 1500 meters are nearly constant at 350×10^{-6} bar, whereas those in the deep Pacific water below a depth of 1200 meters decrease monotonically from 700×10^{-6} bar at 1200 meters to 420×10^{-6} bar at 5000 meters.

The amount of CO_2 dissolved in the water increases with depth from 206×10^{-5} mole/liter at the surface in both oceans to 228×10^{-5} mole/liter at a depth of 1000 meters in the Atlantic and to 245×10^{-5} mole/liter at the same depth in the Pacific. Below this depth, the CO_2 content remains almost constant in the Atlantic, but decreases slowly to 240×10^{-5} mole/liter at a depth of 5000 meters in the Pacific. The excess of CO_2 found in the deep waters is attributed mainly to the CO_2 produced by oxidation of organic matter suspended in the water.

On the basis of these measurements, the degree of saturation of CaCO_3 in sea water was calculated for the in situ temperature and pressure conditions. Lyman's apparent dissociation constants for carbonic and boric acids, MacIntyre's apparent solubility products for calcite and aragonite, and the effect of pressure on these constants which was determined by *Disteche and Disteche* [1967] were used for the calculation. It was found that the Atlantic water becomes undersaturated with respect to calcite below a water depth of 4000–5000 meters, and the Pacific water below a water depth of 1500–3000 meters. It was also found that the Atlantic water becomes undersaturated with respect to aragonite below a water depth of about 2300 meters, and the Pacific water, below about 300 meters. The change in the degree of saturation for calcite from saturation to

undersaturation accounts for the decrease of CaCO_3 content in the ocean sediments observed at water depths greater than 4000 meters in the Atlantic and 3000 meters in the Pacific.

Since the distribution of temperature, salinity, and pressure are similar in the deep waters of both oceans, the difference in the water depths at which the water becomes undersaturated with respect to calcite in the two oceans is due mainly to the difference in the CO_2 contents. This difference in the CO_2 content is controlled by the pattern of deep circulation in the oceans.

The annual production of calcium carbonate in the surface water of the world oceans is estimated to be 6×10^{16} grams. This corresponds to 2 grams $\text{CaCO}_3/\text{cm}^2 10^8$ yr; of this roughly 20% accumulates on the floor of the oceans, and the remainder is dissolved in the deep water.

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