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pH BUFFERING OF PORE WATER OF RECENT ANOXIC MARINE SEDIMENTS¹

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ABSTRACT

A model is proposed to explain the relative pH stability in pore water of recent anoxic marine sediments. Oceanic data are not inconsistent with a model which assumes that the pH of the pore waters is controlled by the byproducts of organic decomposition, sulfate reduction, and precipitation of sulfide and carbonate. The model predicts that the pH of pore waters should remain in the range 6.9 to 8.3, which is in agreement with measured values.

Anoxic marine sediments generally contain active sulfate-reducing bacteria (ZoBell and Rittenberg 1948) which oxidize organic matter through the reduction of sulfate to sulfide. This process consumes sulfate from the pore water and produces a variety of protolytic species, such as H₂S and NH₃, whose amount is large in comparison to their amount in the original seawater. For example, Presley (1969) has found that the concentration of dissolved CO₂ in pore water of recent sediments (e.g. Saanich Inlet, B.C.) may reach the value of 60 mmole kg⁻¹, about 30 times the total CO₂ concentration in the overlying waters.

Despite the vast amount of protolytic species added to the pore waters during decomposition of organic matter, the pH of pore water of recent marine sediments is fairly constant and rarely exceeds the limits pH 7.0 to 8.2. This stability can better be exemplified, perhaps, if one considers the buffer capacity of seawater with respect to dissolved CO₂. This parameter (β_{CO_2}) is defined here as the incremental change in total dissolved inorganic CO₂ required to shift the pH of a solution by one pH unit. The buffer capacity of average seawater was calculated using the method of Ben-Yaakov (1970a) for seawater with total

alkalinity of 2.2 mmole kg⁻¹ (Fig. 1). Maximum buffer capacity is reached at low pH values below the first apparent dissociation constant of carbonic acid (pK_1) which is about 6.0 (Lyman 1957), but the buffer capacity around the pH of ocean and pore waters is very low and does not exceed 0.5 mmole kg⁻¹ pH⁻¹. That is, an addition of 0.5 mmole kg⁻¹ of CO₂ will reduce the pH of seawater by more than a pH unit. It is therefore surprising that the concentration of CO₂ in pore water of marine sediments may reach values of 60 mmole kg⁻¹, and yet show pH shifts less than one unit. It is evident that the increase in CO₂ must be counter balanced by other processes that tend to increase the pH of seawater (such as the production of ammonia and increase in total alkalinity) so that the net balance results in a fairly constant pH.

The purpose of this study is to examine the chemistry of pore water of anoxic marine sediments and to propose a model that many explain mechanisms controlling its pH. The derived relationships will then be compared to field data. The pH buffering model presented here differs from the model of Thorstenson (1970) in that it considers the roles of diffusion and chemical equilibria with solid phases and does not assume thermodynamic equilibria between all the species.

A METHOD FOR pH CALCULATION

It is convenient to divide the ions in a complex system, such as seawater, into protolytic and nonprotolytic species. Protolytic

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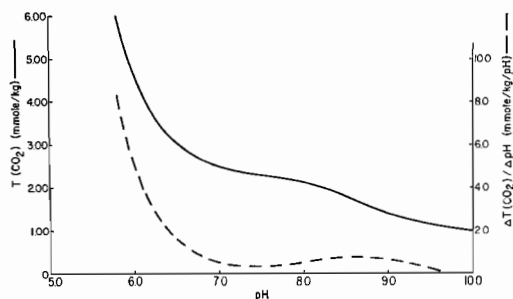


Fig. 1. Buffer capacity of seawater with respect to total dissolved CO₂ (broken line). Solid line represents the concentration of total dissolved CO₂ at any given pH. Curves are for TA = 2.2 meq kg⁻¹ (based on data in Ben-Yaakov 1970b).

ions are defined as ions of weak acids or weak bases; a “weak acid” (“weak base”) is defined here as one whose total anionic (cationic) charge changes appreciably over the pH range of interest. The principle of charge neutrality requires that the net total charge (i.e. the difference between the total charge of the cation and the total charge of the anions) held by the protolytic ions (Q_P) be balanced against the net total charge held by the nonprotolytic ions (Q_{NP}). Namely:

$$Q_P + Q_{NP} = 0 \quad (1)$$

The value Q_P (or Q_{NP}) is closely related to the parameter “alkalinity” or “titration alkalinity” (Anderson and Robinson 1946) which is often used in chemical oceanography. However, this equivalency breaks down when the sample water contains weak bases such as ammonia. Total alkalinity (TA) of a given solution is equal to the charge held by ions of weak acids (HCO₃⁻, CO₃²⁻, etc.) plus the concentration of the undissociated bases such as NH₄OH, but does not include the concentration of NH₄⁺. These differences may result in some confusion and the term alkalinity will not be used here in conjunction with pore waters. In open ocean waters:

$$TA = |Q_{NP}| = |Q_P|. \quad (2)$$

The total charge held by each part of the solution (Q_P and Q_{NP}) is invariant with

respect to addition (or removal) of weak acids, weak bases, or gases to the solution. This is so because the addition of a weak acid, for example, does not add any net charge to Q_P since the charges of the added anions are balanced against the charge of the added hydronium ions.

The total charge held by a weak monobasic acid (Q_{A1}) can be calculated from:

$$Q_{A1} = -T(\text{acid}) \frac{K'_1}{K'_1 + aH^+}, \quad (3)$$

where $T(\text{acid})$ is the total concentration (dissociated plus undissociated species) of the acid in the solution, K'_1 is the apparent dissociation constant of the acid and aH^+ is the activity of the hydronium ion. Apparent dissociation constants rather than thermodynamic constants are used to permit analysis in terms of concentration rather than activities. The error in applying the apparent constant (which can be defined only for solutions of constant composition) to pore water is probably insignificantly small, because the ionic strength of interstitial water of unlithified sediment is similar to that of the overlying seawater.

The total charge held by the ions of a dibasic acid can be calculated from:

$$Q_{A2} = -T(\text{acid}) \frac{K'_1 aH^+ + 2K'_1 K'_2}{[aH^+]^2 + K_1 aH^+ + K'_1 K'_2}, \quad (4)$$

where K'_1 and K'_2 are the first and second apparent dissociation constants of the acid. Similarly, the total charge held by the cation of a monoacidic base can be calculated from the expression:

$$Q_{B1} = T(\text{base}) \frac{K'}{K' + (aH_2O \cdot K_w / aH^+)}, \quad (5)$$

where K_w is the thermodynamic dissociation constant of water and aH_2O is the activity of water at the given ionic strength.

The apparent dissociation constant of a weak acid is related to the thermodynamic constant by:

$$K' = \frac{K \cdot \gamma_{B_{OH}}}{\gamma_{B^+}}, \quad (6)$$

where $\gamma_{B_{OH}}$ and γ_{B^+} are the activity coefficients of the base and its cation, respectively.

The pH of a solution containing both weak acids and weak bases can now be calculated from the expression:

$$Q_P = \Sigma Q_B + \Sigma Q_A + [H^+] - [OH^-], \quad (7)$$

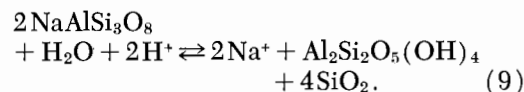
where Q_P is the total charge held by the protolytic ions, ΣQ_B and ΣQ_A are the total charges held by the weak acids and weak bases, and $[OH^-]$ and $[H^+]$ are the concentrations of the hydroxyl and hydronium ions in solution. The right side of equation 7 is a function of the total concentrations of the weak acids and weak bases, their apparent dissociation constant and aH^+ . If the concentrations, the apparent dissociation constants, and Q_P are known, one can solve the last equation for pH defined by:

$$pH = -\log(aH^+). \quad (8)$$

The concentrations of $[H^+]$ and $[OH^-]$, over the pH range of natural waters, are extremely small when compared to the total charge, Q_P . These species can, therefore, be eliminated from equation 7 without introducing an appreciable error in the results.

Equation 7 is a high order equation in aH^+ as Q_A and Q_B can be calculated from equations similar to equations 3, 4, and 5. It can be solved by an iteration procedure similar to the one proposed by Ben-Yaakov (1970b), in which pH is incremented until the magnitudes of the two sides of the equation approach each other to within the required precision.

Examination of equation 7 reveals that a given reaction can change the pH of a solution either by changing Q_P (which must be accompanied by a corresponding change in Q_{NP}) or by adding (or removing) a weak acid or base. An example of the first condition is pH buffering due to silicate reaction, as proposed by Garrels (1965):

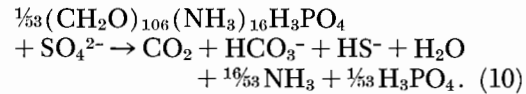


In this reaction, H^+ is replaced by Na^+ in solution, which has the net effect of transferring charge from Q_P to Q_{NP} .

DEVELOPMENT OF A MODEL

The equilibrium pH of a parcel of pore water depends on the chemical reaction within it as well as on diffusive gain or loss of various components. To simplify the discussion, a closed system model will first be developed, and the effects of diffusion will be considered at a later stage.

Using the concept of average composition of marine organic matter (Fleming 1940), one can write a generalized reaction for decomposition of organic matter in marine sediments through bacterial sulfate reduction (Richards 1965) as:



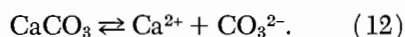
When writing this general reaction, one assumes that the ratio of C:N:P in average organic matter is 106:16:1 as proposed by Redfield et al. (1963). It should be emphasized, however, that slight variations in this ratio will not affect the results presented here. Equation 10 demonstrates that bacterial sulfate reduction should shift the pH of pore waters, as it involves the two reactions mentioned above. There is a net transfer of charge from Q_{NP} to Q_P (SO_4^{2-} is replaced by HS^- and HCO_3^-) and both weak acids (CO_2 , H_3PO_4) and a weak base (NH_4OH) are added to the waters. If the original alkalinity of the seawater (TA_0) is given, one can calculate the pH of the pore waters by solving equation 7 for these conditions. Namely,

$$\begin{aligned} 2\Delta\text{SO}_4^{2-} - \text{TA}_0 = \text{TC} \cdot F(\text{CO}_2) + \text{TS} \cdot F(\text{H}_2\text{S}) \\ + \text{TP} \cdot F(\text{H}_3\text{PO}_4) \\ + \text{TN} \cdot F(\text{NH}_4\text{OH}) \\ + \text{TB} \cdot F(\text{H}_3\text{BO}_3) \\ - [\text{OH}^-] + [\text{H}^+]; \quad (11) \end{aligned}$$

ΔSO_4^{2-} (negative value) is the amount of sulfate removed; TC, TS, and TP are the concentrations of total dissolved CO_2 , total dissolved H_2S , and total dissolved H_3PO_4 ; TB is the total dissolved borate and TN the

total dissolved ammonium, respectively. The functions (F) are the expressions in equations 3, 4, and 5 which incorporate aH^+ and the apparent dissociation constants of the weak acids and bases.

Two additional reactions may shift the pH of the pore water: carbonate and silicate reaction. Solution or precipitation of calcium carbonate both changes the concentration of TC, and also removes (or adds) charges to Q_P .



If such a reaction has taken place, one can calculate the equilibrium pH by correcting TC by the value ΔCa^{2+} and adding the charge $-2 \Delta Ca^{2+}$ to the left side of equation 11. Similarly, one can take into account a silicate reaction by correcting for the charge added or removed (the net change in charge can be traced by examining the concentration of the cations).

An additional reaction that should be considered here is the precipitation of sulfides from the water, mainly in the form of iron sulfides (Berner et al. 1970). The net result of this reaction is to remove the weak acid H_2S from the system, which will therefore shift the pH of the waters (equation 11). Note that this reaction does not change Q_P if the iron enters the system as a weak base (an oxide) and the reaction, therefore, does not involve a charge transfer between the protolytic and nonprotolytic species.

Consider now a parcel of pore water (assumed to be a closed system) in which organic matter is decomposed through sulfate reduction. Using the ratios from equation 10, one can rewrite equation 12 as a function of the amount of sulfate reduced (ΔSO_4^{2-}) and the initial composition of the water:

$$2\Delta SO_4^{2-} - TA_0 = (TC_0 - 2\Delta SO_4^{2-}) \cdot F(CO_2) - \Delta SO_4^{2-} \cdot F(H_2S) + \frac{1}{3}\Delta SO_4^{2-} \cdot F(NH_4OH) + (TP_0 - \frac{1}{3}\Delta SO_4^{2-}) \cdot F(H_3PO_4) + TB \cdot F(H_3BO_3) - [OH^-] + [H^+]. \quad (13)$$

This equation can now be solved for any

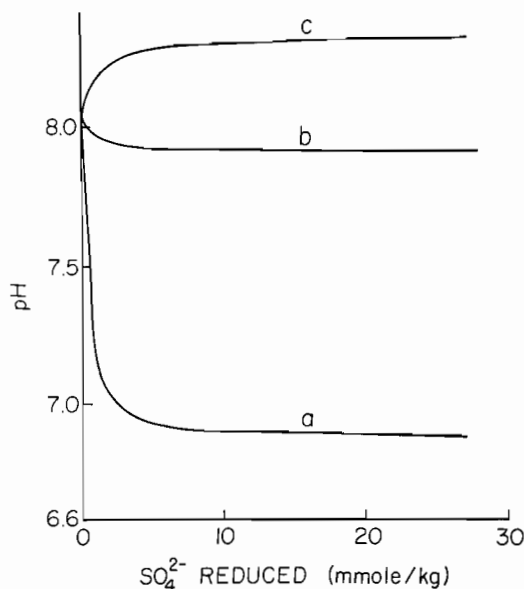


Fig. 2. Predicted pH of pore water of anoxic marine sediments as a function of the amount of sulfate reduced, for different sulfide concentrations: $TS = -\Delta SO_4^{2-}$ (curve a), $TS = 0.2 \Delta SO_4^{2-}$ (curve b), $TS = 0$ (curve c).

stage in the process. The expected pH variation as a function of sulfate reduced was calculated (Fig. 2, curve a) for normal seawater of 35‰ salinity at 25°C, $TA_0 = 2.2 \text{ meq kg}^{-1}$, $TC_0 = 2 \text{ mmole kg}^{-1}$, $TP_0 = 0$ (the original concentration of phosphate in seawater is negligibly small in comparison to that due to the decomposition of organic matter), and $TB = 0.414 \text{ mmole kg}^{-1}$. The apparent dissociation constants of carbonic acid are Lyman's (1957), the apparent dissociation constants of phosphoric acid were taken from Kester (1966), and the apparent constant of H_2S and NH_4OH are after Presley (1969). It should be emphasized that the accurate value of the various constants is unimportant if only a rough estimation of pH is desired. A variation of 25% in the constants will change the equilibrium pH by no more than 0.1 pH unit.

It is evident from Fig. 2 that the pH of the pore water under anoxic conditions is essentially buffered around a pH value of about 6.9, if a closed system is considered. The buffering effect results from

the fact that the various components enter the system in a constant proportion, when the initial concentration of weak acids and bases is small in comparison to the by-products of decomposition. In this calculation (curve a) it was assumed that all the sulfide produced remains in solution. In reality, however, sulfide will precipitate, and the amount of sulfide to be removed will depend on the pH, pE, the concentration of the precipitating metal, and the solubility of the precipitate.

To examine this case, the calculation has been repeated for different concentrations of TS. Curve b in Fig. 2 summarizes the results for the model $TS = -0.2 \Delta SO_4^{2-}$, whereas curve c represents the case in which all the sulfide disappeared from solution. The removal of sulfide from solution has the effect of increasing the pH of the pore waters, and the maximum pH to be expected is about 8.3. Curve b, which resembles the conditions found in anoxic marine sediments, predicts that the pH of these sediments should be around 7.9. It should be noted that although the concentrations of the various species are changed drastically during the sulfate reduction process, the maximum calculated shift is smaller than 1.5 pH units, and if precipitation of sulfide occurs, a pH change < 0.5 unit takes place. This range should be even narrower if one considers that $CaCO_3$ might precipitate at the higher pH range due to the increase of CO_3^{2-} in the solution. Shifts in pH may also result from silicate reactions similar to the reaction of equation 9. The equilibrium pH can be calculated in this case by correcting the left side of equation 12 by the total charge transfer, which will be equivalent to the net change in concentration of the nonprotolytic cations.

The closed-system model, presented above, predicts that the maximum pH shift in pore water of anoxic sediment should be in the range pH 6.9–8.3. However, the real equilibrium condition depends not only on in situ chemical reactions (both in solution and between solution and solid phases), but

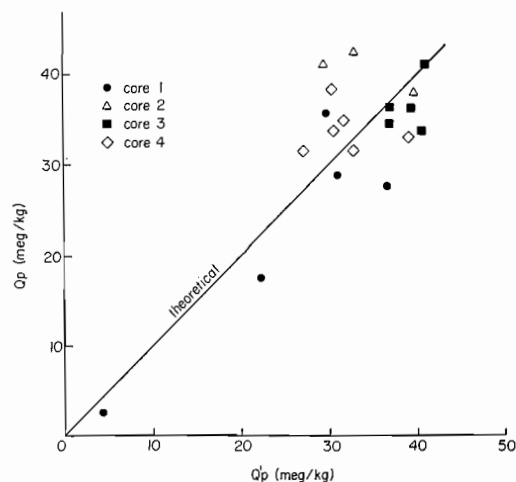


Fig. 3. Actual (Q_p) and predicted (Q'_p) charge held by the protolytic species in pore water of anoxic sediments. Q_p was calculated by equation 8 and Q'_p was calculated from: $2 \Delta SO_4^{2-} - TA_0 - 2 \Delta Ca^{2+}$. (Raw data are from Nissenbaum et al. 1972).

also on ionic diffusion to and from the interstitial waters.

The diffusion process has, in general, the reverse effect of the sulfate reduction process and would tend, therefore, to restore the pH of the pore water to its original value. However, ionic migration in marine sediment is a complex function of many variables such as ionic mobility in seawater, chemical reaction between ions and sediment (Kemper and Van Schaik 1966), and ionic interaction (Ben-Yaakov 1972). Since virtually no experimental data of ionic diffusion in marine sediment are yet available, it is not possible to estimate the pH shift due to diffusion. Nonetheless, equation 7 can be used to calculate the pH of pore waters irrespective of the diffusion process because it expresses the charge condition that must be maintained at all times.

TEST OF THE MODEL

The data to be studied here were obtained by Nissenbaum et al. (1972) during a comprehensive study of pore water of sediments from Saanich Inlet (British Columbia), a fjord characterized by a high rate of deposition ($4 \text{ m } 1,000 \text{ yr}^{-1}$) and high

Table 1. Major ion concentration in pore water of Saanich Inlet cores (from Nissenbaum et al. 1972)

| Depth (cm) | Cl ⁻ | Na ⁺ | K ⁺ | Ca ²⁺ | Mg ²⁺ | Sr ²⁺ | pH | Eh (mv) | CO ₂ | S ²⁻ | SO ₄ ²⁻ | NH ₃ | PO ₄ ²⁻ |
|---------------|-----------------|-----------------|----------------|------------------|------------------|------------------|-----|------------|-----------------|-----------------|-------------------------------|-----------------|-------------------------------|
| | moles/liter | | | | | | | | mM/liter | | | | mM/liter |
| Core 1 | | | | | | | | | | | | | |
| 0-15 | 0.49 | 0.38 | 0.0117 | 0.0077 | 0.044 | 0.064 | 7.6 | +330 | 02.7 | 0.0 | 22.9 | 0.15 | 0.042 |
| 40-50 | 0.49 | 0.39 | 0.0122 | 0.0057 | 0.044 | 0.042 | 8.0 | -120 | 13.6 | 3.8 | 11.5 | 0.53 | 0.035 |
| 85-100 | 0.50 | 0.40 | 0.0117 | 0.0032 | 0.042 | 0.056 | 7.9 | -140 | 23.7 | 5.0 | 00.3 | 2.05 | 0.155 |
| 135-150 | 0.50 | 0.40 | 0.0143 | 0.0022 | 0.047 | 0.032 | 8.0 | -130 | 29.7 | 0.6 | 00.7 | 3.50 | 0.073 |
| 175-185 | 0.50 | 0.42 | 0.0125 | 0.0019 | 0.051 | 0.052 | 8.0 | -120 | 36.2 | 1.2 | 00.3 | 4.26 | 0.122 |
| Core 2 | | | | | | | | | | | | | |
| 0-15 | 0.50 | 0.41 | 0.0125 | 0.0077 | 0.043 | 0.078 | 7.8 | -060 | 40.6 | 0.0 | 01.3 | 4.05 | 0.120 |
| 75-85 | 0.50 | 0.41 | 0.0125 | 0.0077 | 0.050 | 0.081 | 7.8 | +260 | 49.2 | 0.0 | 00.2 | 8.58 | 0.115 |
| 150-165 | 0.50 | 0.41 | 0.0130 | 0.0077 | 0.051 | 0.082 | 7.7 | +250 | 50.0 | 0.0 | 00.6 | 10.0 | 0.091 |
| 225-235 | 0.50 | 0.41 | 0.0130 | 0.0074 | 0.052 | 0.080 | 7.7 | +260 | 51.2 | 0.0 | 00.0 | 14.0 | 0.136 |
| Core 3 | | | | | | | | | | | | | |
| 0-10 | 0.52 | 0.41 | 0.0115 | 0.0077 | 0.050 | 0.079 | 8.0 | -100 | 30.2 | 5.3 | 01.4 | 3.71 | 0.195 |
| 50-60 | 0.52 | 0.41 | 0.0115 | 0.0072 | 0.050 | 0.078 | 7.6 | -140 | 40.6 | 4.4 | 00.3 | 4.00 | 0.280 |
| 100-110 | 0.52 | 0.41 | 0.0115 | 0.0077 | 0.050 | 0.078 | 7.6 | -130 | 38.0 | 3.1 | 00.3 | 5.24 | 0.325 |
| 150-160 | 0.52 | 0.41 | 0.0115 | 0.0074 | 0.050 | 0.078 | 7.8 | -110 | 36.2 | 3.1 | 00.0 | 6.41 | 0.420 |
| 190-200 | 0.51 | 0.40 | 0.0117 | 0.0077 | 0.050 | 0.075 | 7.7 | -100 | 39.1 | 2.8 | 00.0 | 6.71 | 0.375 |
| Core 4 | | | | | | | | | | | | | |
| 0-15 | 0.50 | 0.41 | 0.0115 | 0.0084 | 0.050 | 0.082 | 7.7 | -120 | 32.4 | 4.1 | 02.2 | 4.26 | 0.383 |
| 50-65 | 0.51 | 0.41 | 0.0122 | 0.0084 | 0.050 | 0.082 | 7.7 | -110 | 34.6 | 4.1 | 01.9 | 7.92 | 0.358 |
| 100-110 | 0.51 | 0.42 | 0.0122 | 0.0077 | 0.050 | 0.079 | 7.8 | -120 | 36.8 | 3.8 | 01.2 | 10.4 | 0.333 |
| 150-160 | 0.51 | 0.41 | 0.0122 | 0.0084 | 0.051 | 0.079 | 7.7 | -135 | 39.7 | 3.8 | 00.0 | 10.6 | 0.320 |
| 200-210 | 0.51 | 0.41 | 0.0120 | 0.0077 | 0.050 | 0.080 | 7.9 | -110 | 42.4 | 3.4 | 00.2 | 9.8 | 0.363 |
| 240-250 | 0.51 | 0.40 | 0.0117 | 0.0074 | 0.050 | 0.078 | 7.7 | -110 | 40.1 | 3.1 | 00.2 | 9.1 | 0.291 |

concentrations of organic matter in the sediment (1-5% organic C). The sediment is anoxic, and sulfate is reduced by bacterial activity.

Table 1 shows some of the data of Nissenbaum et al. (1972). The concentrations of total dissolved carbon dioxide, phosphate, ammonia, and sulfide are extremely high in the interstitial water compared to those in seawater. Sulfate is depleted in all cores and completely disappears in some cases. The negative *Eh* value measured in three cores clearly indicates that the environment is highly reducing. Concentrations of major ions are fairly constant except for calcium and strontium, which are depleted in two cores (1 and 2), probably because CaCO₃ precipitated from the interstitial water and strontium coprecipitated with it (Kinsman and Holland 1969).

Equation 11 will be used as an idealized model for pH control in the sediment. The pH value, obtained by direct measurement, can be used to calculate the total net charge held by the protolytic ions (*see* equation 7) and compared to the expected Q_P :

$$Q_P = 2\Delta\text{SO}_4^{2-} - \text{TA}_0 - 2\Delta\text{Ca}^{2+}. \quad (14)$$

Figure 3 compares the calculated and predicted values for the data given by Nissenbaum et al. (1972). The scatter of the calculated points around the theoretical line is probably due to the uncertainties in the concentration of the protolytic species. The partial pressures of the gases CO₂ and H₂S are fairly high in the solution, and some of the gases may have escaped during handling. Nevertheless, the plot of Fig. 3 demonstrates, at least in a statistical

Table 2. Comparison of pH, CO_3^{2-} , and IP:K'sp (calcite) before and after CaCO_3 precipitated from the pore water of core 1 of Saanich Inlet (raw data from Presley 1969)

| Depth (cm) | pH | pH* | CO_3^{2-} (mmole/kg) | CO_3^{2-*} (mmole/kg) | IP:K'sp | IP:K'sp* |
|------------|-----|------|-------------------------------|--------------------------------|---------|----------|
| 0-15 | 7.6 | 7.82 | 0.083 | 0.12 | 1.18 | 2.1 |
| 40-50 | 8.0 | 8.46 | 1.16 | 2.68 | 12.27 | 47.15 |
| 85-100 | 7.9 | 8.60 | 1.70 | 6.27 | 10.20 | 110.3 |
| 135-150 | 8.0 | 8.71 | 2.623 | 9.43 | 10.68 | 165.90 |
| 175-185 | 8.0 | 8.67 | 3.129 | 10.60 | 11.01 | 186.48 |

*Calculated condition before precipitation took place.

sense, that the data are not inconsistent with the model presented here.

The data of Table 1 also indicate that the concentration of sulfide is lower than expected by the model of equation 10. This may be explained by the fact that the concentration of sulfide is controlled by the solubility product of the precipitated metal sulfide. Such precipitation is responsible for the pH observed in the Saanich Inlet cores since, in its absence, the pH should have been around pH 6.9 (Fig. 2). However, pH 6.9 would be reached if the sediment is depleted in iron; data on interstitial water of carbonate sediment (Berner 1966) show that such pore water may reach this value.

It should be emphasized that the pH calculations presented here are for 25°C, as all the pH measurements were made at room temperature. The actual in situ pH values can be calculated from equation 11 by using the values of the constants at in situ temperatures. However, the temperature dependence should be small (Ben-Yaakov 1970b) and the maximum shift will probably be 0.2 pH units.

Berner et al. (1970) suggested that CaCO_3 precipitation from pore water of anoxic sediments is probably taking place in the laboratory after the waters have been squeezed from the sediments. Using equation 11, one can calculate the pH of the waters before precipitation by correcting Q_P and TC by $-2\Delta\text{Ca}^{2+}$ and ΔCa^{2+} , and one

can estimate the ionic product ($\text{IP} = [\text{Ca}^{2+}][\text{CO}_3^{2-}]$) before and after precipitation. These calculations are summarized in Table 2 in which the ratio IP:K'sp for calcite is also given. The value of the apparent solubility product, K'sp, is after McIntyre (1965). It is evident from Table 2 that the IP of calcium and carbonate would have been extremely high before precipitation took place. Although seawater may sustain supersaturation with respect to calcite (Ben-Yaakov 1970a; Suess 1970) it is likely that the carbonate will precipitate at such high IP values. The in situ values for the ratio IP:K'sp are somewhat lower than the value given in Table 2 owing to increase of solubility at low temperatures. One should also correct the ratio for pH at in situ temperatures. Accurate correction cannot be made, because the temperature coefficients of the various dissociation constants are not accurately known. However, even when temperature and pH effects are included, the calcite saturation ratio would be at least 20-30 times that of surface seawater. One may therefore expect that calcium carbonate will precipitate in situ under these conditions.

Apart from consideration of protolytic ions, sulfate, and calcium, a change in the concentration of one of the major dissolved ions will result in the proportional change in Q_{NP} and will therefore affect Q_P (equation 1). This, in turn, will result in a pH shift. Changes in the concentrations of

major ions can be a result of chemical reaction and selective diffusion. In selective diffusion, one should distinguish between $Q_{NP}-Q_{NP}$ diffusion and $Q_{NP}-Q_P$ or Q_P-Q_P diffusion. The first type will not cause a pH shift, whereas the others might (equation 7).

The results of the charge calculation presented above (Fig. 3) suggest that silicate reaction (such as the one of equation 9) and $Q_{NP}-Q_P$ diffusion are probably limited in this environment. Maximum scatter is 10 meq kg^{-1} which sets the limit to the magnitude of silicate reaction and protolytic-nonprotolytic diffusion that might have taken place. The contribution of dissolved SiO_2 to pH buffering is also very small, as the maximum concentration of dissolved silica was about $2.7 \text{ mmol liter}^{-1}$ (Presley 1969).

CONCLUSIONS

From the model, we can derive that the pH of interstitial water of recent anoxic marine sediments is controlled by four processes: 1) the presence of high concentrations of weak acids and bases which are byproducts of organic decomposition; 2) transfer of charge from the nonprotolytic species to the protolytic ions ($\text{SO}_4^{2-} \rightarrow \text{HS}^-$); 3) precipitation of metal sulfides; 4) precipitation of calcium carbonate. The first two (which are dependent on bacterial sulfate reduction) will tend to shift the pH of pore waters toward 6.9. Precipitation of sulfide will increase the pH toward 8.3. Additional changes may result from selective diffusion of various ions as the diffusion of the ions is electrically coupled. However, the upper limit of pH is controlled by precipitation of calcium carbonate, as the concentration of CO_3^{2-} increases manifold at the higher pH range. Hence, the lower limit of pH in pore water, under these conditions, is controlled by sulfide precipitation, and the upper limit is probably controlled by CaCO_3 precipitation. This model predicts that the pH value of interstitial water of anoxic sediment will generally lie between 7.0 and 8.0. Silicate reaction may cause a further

shift in pH, but the data given by Nissenbaum et al. (1972) do not support the assumption that this reaction is important in this area. The presence of organic acids in the pore water of anoxic sediments also probably has only a minor effect on the pH of the waters, since the measured pH values can be accounted for by the model without taking these compounds into consideration.

REFERENCES

- ANDERSON, D. H., AND R. J. ROBINSON. 1946. Rapid determination of the alkalinity of seawater. *Anal. Chem.* **18**: 767-769.
- BEN-YAAKOV, S. 1970a. An oceanographic instrumentation system for in situ measurements. Ph.D. thesis, Univ. Calif., Los Angeles. 343 p.
- . 1970b. A method for calculating the in situ pH of seawater. *Limnol. Oceanogr.* **15**: 326-328.
- . 1972. Diffusion of sea water ions. 1. *Geochim. Cosmochim. Acta* **36**: 1395-1406.
- BERNER, R. A. 1966. Chemical diagenesis of modern carbonate sediments. *Amer. J. Sci.* **264**: 1-36.
- , M. R. SCOTT, AND C. THOMLINSON. 1970. Carbonate alkalinity in pore water of anoxic marine sediments. *Limnol. Oceanogr.* **15**: 544-549.
- FLEMING, R. A. 1940. The composition of plankton and units for reporting population and production. *Proc. Pac. Sci. Congr.* 6th, 1939 **3**: 534-540.
- GARRELS, R. M. 1965. Silica: Role in buffering of natural waters. *Science* **148**: 69.
- KEMPER, W. D., AND J. C. VAN SCHAİK. 1966. Diffusion of salts in clay-water systems. *Soil Sci. Soc. Amer. Proc.* **30**: 534-540.
- KESTER, D. R. 1966. Determination of the apparent dissociation constant of phosphoric acid in seawater. M.S. thesis, Oregon State Univ. 55 p.
- KINSMAN, D. J. J., AND H. D. HOLLAND. 1969. The co-precipitation of cations with CaCO_3 . 4. *Geochim. Cosmochim. Acta* **33**: 1-17.
- LYMAN, J. 1957. Buffer mechanisms of seawater. Ph.D. thesis, Univ. Calif., Los Angeles. 196 p.
- MCINTYRE, W. G. 1965. The temperature variation of the solubility product of calcium carbonate in sea water. *Fish. Res. Bd. Can., Ms. Rep. Ser.* 200. 153 p.
- NISSENBAUM, A., B. J. PRESLEY, AND I. R. KAPLAN. 1972. Early diagenesis in a reducing fjord, Saanich Inlet, British Columbia. Part 1. *Geochim. Cosmochim. Acta* **36**: 1007-1027.
- PRESLEY, B. J. 1969. Chemistry of interstitial water from marine sediments. Ph.D. thesis, Univ. Calif., Los Angeles. 225 p.

- REDFIELD, A. C., B. J. KETCHUM, AND F. A. RICHARDS. 1963. The influence of organisms on the composition of seawater, p. 26-77. In M. N. Hill [ed.], *The sea*, v. 2. Interscience.
- RICHARDS, F. A. 1965. Anoxic basins and fjords, p. 611-645. In J. P. Riley and G. Skirrow [eds.], *A treatise on chemical oceanography*, v. 1. Academic.
- SUESS, E. 1970. Interaction of organic compounds with calcium carbonate. 1. *Geochim. Cosmochim. Acta* **34**: 157-168.
- THORSTENSON, D. C. 1970. Equilibria distribution of small organic molecules in natural waters. *Geochim. Cosmochim. Acta* **34**: 745-770.
- ZOBELL, C. E., AND S. C. RITTENBERG. 1948. Sulfate reducing bacteria in marine sediments. *J. Mar. Res.* **7**: 602-617.

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