THE PROCESSES CONTRIBUTING TO THE VERTICAL DISTRIBUTION OF APPARENT pH IN THE NORTHEASTERN PACIFIC OCEAN

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ABSTRACT

Two major processes that affect the vertical distribution of apparent pH in the Subarctic region of the Northeastern Pacific Ocean are (1) apparent oxygen utilization by marine organisms and (2) carbonate dissolution. Simplified mathematical approximations show that, in the pH range of 7.2 to 8.3, the utilization of 0.1 mM of oxygen (2.24 ml/liter) lowers the pH by 0.20 units and 0.1 mM of carbonate dissolution increases the pH by 0.25 units. Since oxygen utilization exceeds 0.3 mM while the carbonate dissolution, with respect to the surface, is about 0.05 mM, the effect of oxygen utilization is much greater than the dissolution effect of carbonate on the pH of seawater.

INTRODUCTION

Since the time of the *Meteor* Expedition, 1925-1927, the similarity between the distribution of dissolved oxygen and apparent pH has become well known (Harvey, 1960, pp. 32-37)(Fig. 1). This observation has been used to formulate a theory in which the pH of seawater is primarily controlled by the carbon dioxide and carbonate cycle in the ocean.

During the First International Oceanographic Congress in 1959, Sillén (1961) presented an equilibrium model of the chemical composition of seawater. His analysis on the model suggested that contrary to the traditional view of the carbonate buffer system, the heterogeneous equilibria of silicate minerals are the principal pH buffering systems in the oceanic water. Garrels (1965) and Mackenzie and Garrels (1965) experimented to support Sillén's theory. However, Pytkowicz (1967) pointed out that within the mixing time of seawater, in the order of 1,000 years, the carbonate buffer system, rather than the silicate buffer system, is the primary buffering agent in the ocean,

Presently Sillén (1967) pointed out that there are at least three different definitions of pH. Since there are some discords among the definitions, the pH of seawater samples measured using glass and calomel electrodes will be defined as apparent pH in this paper. However, here, I should point out that the reproducibility rather than accuracy of the pH measurement is important in oceanographic applications (Pytkowicz et al., 1966).

Apart from the long range, large scale pH governing system, there still remains a quantitative problem to be solved on the relationship between the observed oxygen concentration and apparent pH distribution in the ocean. This report shows mathematically that the apparent oxygen utilization (AOU) by marine organisms is the major factor controlling the vertical distribution of pH in the ocean. Carbonate dissolution affects it to a lesser extent.

THEORETICAL CONSIDERATION

In nature it is very difficult to observe separately the effects of various processes that affect the pH of seawater. Here, we will separately examine the

AOU-pH and the carbonate dissolution-pH relationships. The hydrostatic pressure effect (Culberson et al., 1967), the temperature and salinity effects (Harvey, 1960, pp. 155-182) are not discussed.

AOU-pH relationship

To derive a mathematical expression relating AOU and pH we start with:

$$\Sigma CO_2 = \frac{H^2 + HK'_1 + K'_1 K'_2}{(H + 2K'_2)K'_1} \, \text{Alk}$$

$$= f(p\text{H})\text{Alk} \qquad (1)$$

The above equation is derived from the definitions of the first and second apparent dissociation constants of carbonic acid, K'_1 and K'_2, carbonate alkalinity, Alk, and total carbon dioxide, ΣCO_2, in seawater. Its derivation is given in my previous report (Park, 1965). The term H is apparent hydrogen in concentration measurable by glass and calomel electrodes (Pytkowicz et al., 1966; Park, 1966). The apparent dissociation constants, K'_1 and K'_2, are determined previously by Buch (1951, cited from Harvey, 1960, p. 167) and Lyman (1956).

The term $f(p\text{H})$ in equation (1) is a function of pH only under constant temperature, salinity, and pressure. Such conditions can be found at an equal depth in the deep ocean where temperature and salinity ranges are very small. In addition, if we use the pH values measured under one atmosphere (shipboard), then high latitude water, where the vertical variations of temperature and salinity are small, can satisfy in first approximation the conditions set for $f(p\text{H})$ being a function of pH only (Fig. 1).

Let us consider the biochemical oxidation of organic matter taking place in this seawater. The oxidation increases the carbon dioxide content by ΔCO_2, but it does not affect carbonate alkalinity. Even if we consider the effects of borate and possible organic alkalinities (Gripenberg, 1960) on carbonate alkalinity by the lowering of pH during biochemical oxidation, its magnitude can be neglected from our simplified calculation. From the Richards' (1965, p. 624) stoichiometric model of biochemical oxidation of organic matter in the ocean of:

$$(CH_2O)_{106}(NH_3)_{16} \, H_3PO_4 + 138 \, O_2$$
$$= 106 \, CO_2 + 122 \, H_2O + 16 \, HNO_3 + H_3PO_4$$
$$\qquad (2)$$
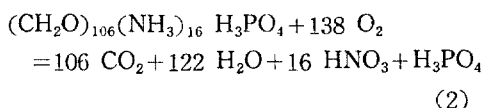
We note that 138 molecules of oxygen depletion is accompanied by the release of 106 molecules of carbon dioxide. Therefore, after some biochemical oxidation of organic matter in seawater, the equation (1) becomes:

$$\Sigma CO_2 + \Delta CO_2 = \Sigma CO_2 + \frac{106}{138} \text{AOU}$$

$$= f(p\text{H}) \, \text{Alk} \qquad (3)$$

By rearranging equation (3) we obtain:

$$\text{AOU} = 1.30 \, \text{Alk} \, f(p\text{H}) - 1.30 \, \Sigma CO_2 \quad (4)$$

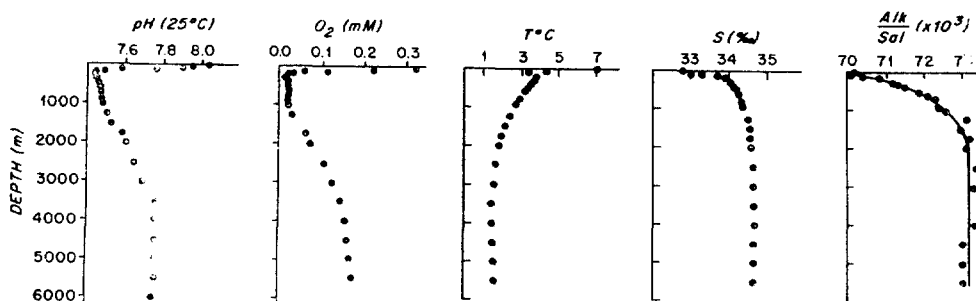Fig. 1. Vertical profiles of pH, oxygen, temperature, salinity, total alkalinity /salinity ratio at 53°46'N, 158°35'W on 7 July 1966 (Hydrographic station AKH-16 of YALOC-66 cruise on R/V YAQUINA).

Equation (4) indicates that if carbonate alkalinity is constant there is a linear relationship between AOU and f(pH) with a slope of 1.30 Alk and with an intercept of -1.30 ΣCO_2. The term ΣCO_2 in equation (4) is the preformed total CO_2 at zero AOU. The AOU value in mM is calculated by subtracting the measured oxygen concentration from a 100% saturation value (Redfield et al., 1963).

To obtain a direct relationship between AOU and pH, it is necessary to express the term f(pH) by pH. The relationship between f(pH) and pH is not linear. However, in seawater in the pH range of 7.2 to 8.3, the relationship is almost linear. By the use of Buch's (1951) constants for K'_1, 1.01×10^{-6}, and K'_2, 1.02×10^{-9}, at 34 ‰ salinity and 25°C, f(pH) can be expressed as:

$$f(pH) = -0.160 \ pH + 2.20$$
$$7.2 < pH < 8.3 \qquad (5)$$

The maximum error arising from the above simplification is 0.03 pH unit. By combining equations (4) and (5), we obtain:

$$AOU = -0.208 \ Alk \ pH + 2.86 \ Alk$$
$$-1.30 \ \Sigma CO_2 \qquad (6)$$

Any changes in AOU are, therefore:

$$(AOU)_1 - (AOU)_2 = -0.208 \ Alk \ (pH_1 - pH_2)$$
$$or \ \Delta AOU = -0.208 \ Alk \ \Delta pH \qquad (7)$$

Since an average value for the carbonate alkalinity of the hydrographic station used in this report (Fig. 1) is approximately 2.4 milliequivalent/liter, the AOU change can be expressed by:

$$\Delta AOU = -0.50 \ \Delta pH \quad 7.2 < pH < 8.3 \quad (8)$$

Equation (8) indicates that an increase in AOU of 0.1 mM (equivalent to 2.24 ml/liter of dissolved oxygen at STP) corresponds to a pH drop of 0.20 unit. It agrees fairly well with the field data (Fig. 2). From the sea surface to the oxygen minimum zone (250 m depth) the calculated slope coincides with the field data. Also, in the deep water, below 1,250 m, the relationship between AOU and pH follows the calculated slope.
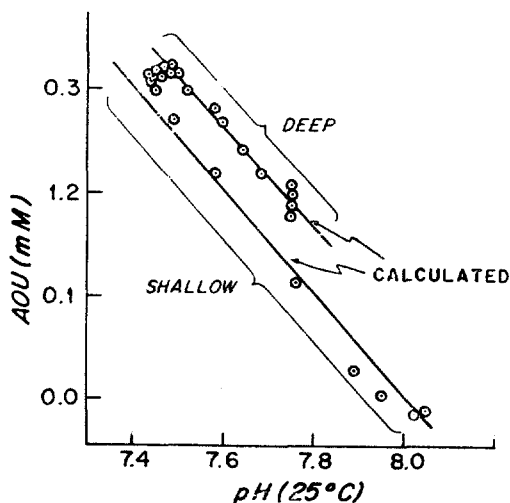

Fig. 2. Apparent oxygen utilization (AOU) vs. pH for the hydrographic station AKH-16. Apparent pH was measured aboard R/V YAQUINA under one atmosphere at 25°C. Calculated slope of -0.50 is from equation (9): Upper slope follows deep water of the depth greater than 1,250 m and the lower slope for the water shallower than 250 m. Negative AOU is observable near the surface.

At a given AOU value, there is about 0.1 pH unit difference between shallow and deep waters (Fig. 2). I attribute this mainly to the difference in the extent of carbonate dissolution in this column of seawater.

Carbonate dissolution-pH relationship

In the open ocean, it is difficult to separate the effects of carbonate dissolution and biochemical oxidation on the pH of seawater, for both go on concurrently. A unique opportunity to separate them was presented to us in 1966 during the YALOC 66 cruise of R/V YAQUINA in the Northeastern Pacific Ocean. On 7 July 1966, at the hydrographic station AKH-16, 600 km southwest of the Kodiak Island over the Aleutian trench, we observed a column of seawater that had essentially the same AOU (approximately 0.31 mM) in the water from 250 to 1,250 m (Fig. 3). The pH measured on shipboard at 25°C showed a steady
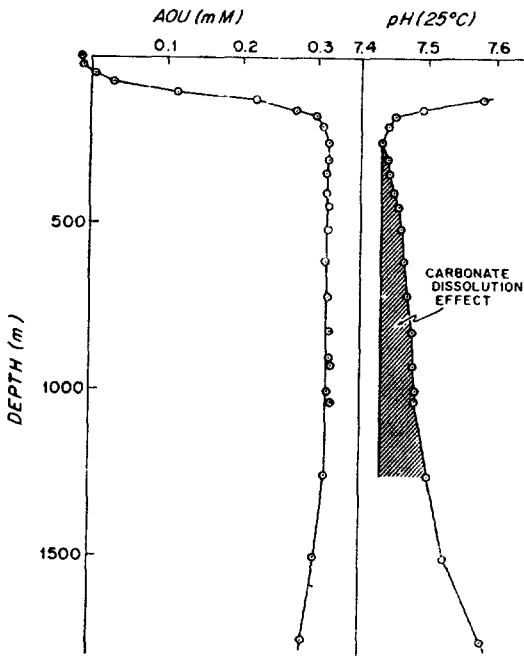
Fig. 3. Comparison of the vertical profiles of AOU and pH in the upper 1,800 m. Note the almost constant AOU between the depths of 250 and 1,250 m. The increase in apparent pH in the same depths (shown by the shaded area) is mainly due to the carbonate dissolution.

increase from 7.43 at 250 m to 7.50 at 1,250 m. As there was no appreciable AOU difference (Fig. 3) but the alkalinity/salinity ratio increased steadily (Fig. 1) in these depths, the observed pH increase was primarily due to the difference in carbonate dissolution. Below 1,250 m, the changes in AOU essentially decide the pH value (Fig. 2).

A quantitative estimation of the pH change due to carbonate dissolution can be made by the use of equation (1). Since one unit of carbonate dissolution results in the increase of dissolved carbon dioxide and alkalinity by one and two units respectively, equation (1) is modified to:

$$\frac{\Sigma CO_2 + CO_3}{Alk + 2CO_3} = f(pH) \qquad (9)$$

Here, ΣCO_2 and Alk are total carbon dioxide in mM and carbonate alkalinity in milliequivalent/

liter at a given AOU, and CO_3 denotes the magnitude of carbonate dissolution. The extent of the carbonate dissolution in deep water with respect to the surface seawater in the Northeastern Pacific Ocean does not exceed 0.1mM, as the alkalinity/salinity ratio is 0.068 at sea surface and 0.073 near the sea floor. In such a small range, the left-hand side of equation (9) can be expressed as a linear function of the magnitude of carbonate dissolution.

Any change in the magnitude of carbonate dissolution is:

$$\frac{\Sigma CO_2(CO_3)_1}{Alk\,2\,(CO_3)_1} - \frac{\Sigma CO_2(CO_3)_2}{Alk\,2\,(CO_3)_2}$$
$$= -0.160\ (pH_1 - pH_2) \qquad (10)$$

Since an average value for the total CO_2 was approximately 2.4 mM, and carbonate alkalinity was 2.4 milliequivalent, the left-hand side of equation (10) can be graphically transformed into $-0.40\ [(CO_3)_1 - (CO_3)_2]$. Therefore, equation (10) can be reexpressed as:

$$\Delta CO_3 = 0.40\ \Delta pH \qquad (11)$$

Equation (11) shows that 0.1 mM dissolution of carbonate mineral increases the seawater pH by 0.25 units, which would be the maximum carbonate dissolution effect, with respect to the surface, for the Northeastern Pacific Ocean. This effect is about 2.5 times smaller than the maximum AOU (0.31 mM) effect of –0.63 pH units.

A conventional way to assess the net carbonate dissolution, with respect to surface, is by the examination of alkalinity/salinity ratio as shown by:

$$\Delta CO_3 = \frac{Sal_{(z)}}{2}\left[\frac{TA_{(z)}}{Sal_{(z)}} - \frac{TA_{(sfc)}}{Sal_{(sfc)}}\right]$$

Where Sal denotes salinity, TA is an abbreviation for total alkalinity, subscripts z is the depth under study and sfc is surface. At my hydrographic station, the total alkalinity/salinity ratio is about 0.070 at sea surface and below a depth of 1,250 m it is about 0.073 (Fig. 1). Therefore, the net carbonate dissolution in the deep water, with
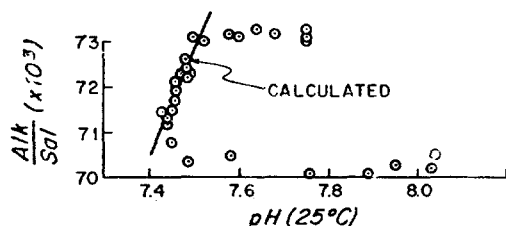
Fig. 4. Total alkalinity/ salinity ratio vs. pH for the hydrographic station AKH-16. The calculated slope of 0.025 is from equations (11) and (12). The field data agree with the slope in the depth range of 250 m to 1,250 m where AOU is essentially invariant.

respect to the surface, is approximatlye 0. 5 mM. Substituting 0.05 mM for the carbonate dissolution in equation (11) a pH increase of 0.13 units is obtained.

The oceanographic carbonate-dissolution parameter, total alkalinity/salinity ratio, and observed pH for my hydrographic station are correlated in Fig. 4. The calculated line in Fig. 4 is obtained by combining equations (11) and (12): It agrees with the observed data at depths between 250 and 1,250 m, where AOU essentially does not change. To be more specific, we can test the validity of equations (11) and (12) by the examination of data presented in Fig. 3. Here, the increase in the carbonate dissolution at 1,250 m depth with respect to 250 m is:

$$\Delta CO_3 = \frac{34.5}{2}(0.0731-0.0713)=0.031 \text{ mM}$$

Substituting 0.031 mM carbonate dissolution into equation (11) we obtain a pH increase of 0.08, which agrees well with the observed pH increase of 0.07 (Fig. 3).

SILICATE CONSIDERATION

Dissolved reactive silicate determination for the hydrographic station under study gives 0.02 mM at surface, 0.10 mM at 250 m depth, 0.14 mM at 1,250 m, and over 0.15 mM below 2,000 m depth. The vertical difference is almost 3 times greater than that of net carbonate dissolution. Since the

first dissociation constant of silicic acid is in the order of 10^{-10} (Armstrong, 1965, p. 411) the direct contribution of silicic acid on the alkalinity of seawater is very small, less than 0.01 millieq-uivalent/liter.

However it must be remembered that not all forms of silica in solution would react to give the silicomolybdate complex that is determined colorimetrically (Strickland and Parsons, 1965, p. 67).

Since the hydrographic station under scrutiny is away from the inputs of silicate minerals (major river mouths), I cannot suspect that we have a substantial differential silicate mineral effect with depth on the pH I measured. The uptake and release of silicic acid by marine organisms (mainly diatom) is the main process of giving a vertical reactive silicate distribution. If silicic acid dynamics between the seawater and the biomass is a simple transportation of the acid between them without releasing or uptaking hydrogen ion, then the biological input and output of silicic acid will not affect the pH of seawater.

The effect of siliceous sediments on the apparent pH of seawater overlying them has to work against the vertical density stability of seawater. Therefore its effect would be confined to only near the bottom.

THE SUM OF THE EFFECTS OF AOU AND CARBONATE DISSOLUTION ON pH

If two major processes that alter the vertical distribution of pH are AOU and carbonate dissolution, then the profile of apparent pH should be approximated by the results of these two processes, provided there exists no appreciable interdependency of the variables. Since I have treated that both the AOU and the carbonate dissolution affect pH linearly, the additivity of these two effects holds in first approximation. The AOU effect lowers the apparent pH, and in turn favors the

dissolution of carbonate minerals. Thus it is probable that the initial process is oxygen utilization by animals followed by carbonate dissolution. Here. I stress the following simplification I made. In my original calculations shown by equations (7) and (10) I have assumed the constancy of preformed CO_2 and carbonate alkalinity, while the extent of either AOU or carbonate dissolution changes. Since both AOU and carbonate dissolution processes are quite active in the upper 250 m, strictly speaking, I have to take into consideration these processes simultaneously in the upper layers. However, for the sake of simplicity I have ignored the interdependency of the variables in my crude approximation.

The extent of the AOU effect, along with the carbonate effect, is plotted in Fig. 5. These two effects work against each other and the net effect is shown by the central curve. It agrees well with the pH data. The magnitude of the AOU effect increases with depth to the oxygen minimum zone (approximately -0.6 pH unit), and it decreases at depths deeper than the oxygen minimum zone with depth. The carbonate effect increases with
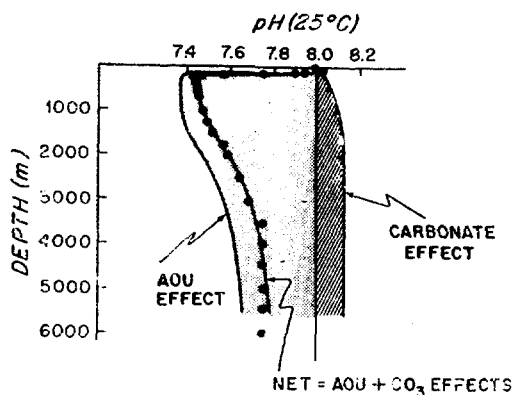

pH (25°C)

Fig. 5. Vertical profiles of the AOU effect (left), the carbonate dissolution effect (right) and the net effect on pH for the hydrographic station AKH-16. The net effect is obtained by summing both the AOU and carbonate dissolution effects. The dots are pH 1 measured at 25°C.

depth down to 1,250 m (approximately 0.1 pH unit) but no further increase is seen at greater depths. Throughout the water column the AOU effect is always greater than the carbonate effect.

Based on my analysis, the vertical pH distribution essentially can be explained by the apparent oxygen utilization of marinn organisms and by the carbonate dissolution to a lesser extent. My interpretation does not oppose the silicate buffering mechanism advanced by Sillén (1961, 1967). The silicate buffer appears to be a coarse control on the seawater pH, while the carbon dioxide-carbonate buffer controls the fine structure of the oceanic pH profile. These two buffering systems supplement, rather than oppose, each other.

The prediction of the vertical distribution of apparent pH by the summation of the AOU and the carbonate dissolution effects is applicable in a water column consisting of similar water mass in which both temperature and salinity variations are normally small. When one water mass overlies a distinctly different water mass, my calculation does not always approximate the measured pH of the entire water column. The approximation is only close in the lower water mass where variation of temperature and salinity are small. For instance, at approximately 1,000 km north of the Hawaiian Islands, the Subtropic water is in the upper 400 m, but near 600 m the cold and less saline Subarctic water intrudes to the south. If the apparent pH at 600 m is used as a reference level, the pH distribution in the lower water mass can be explained by the AOU and the carbonate dissolution effects but the pH of the upper water mass cannot be explained in this manner. In the Subtropic water, the steep temperature gradient, from 10°C to 22°C, within this water body and possible differences in the exchange of oxygen and carbon dioxide across the air-sea interface necessitate an additional factor to make the calculated pH and measured pH agree. Since

AOU is a temperature dependent quantity, the apparent pH at *in situ* temperature rather than at a constant temperature may give a better correlation between AOU and pH when the temperature gradient is steep.

In summary, the vertical distribution of apparent pH in the Subarctic region of the Northeastern Pacific Ocean can be explained by the consideration of AOU and carbonate dissolution in first approximation. The AOU effect has a maximum pH change of −0.63 while the carbonate effect is 0.13 units.

ACKNOWLEDGMENTS

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