

References and Notes

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Seawater Hydrogen-Ion Concentration: Vertical Distribution

Abstract. Two major processes that affect the vertical distribution of hydrogen-ion concentration in the sub-Arctic region of the northeastern Pacific Ocean are the apparent oxygen utilization by marine organisms and, to a lesser extent, carbonate dissolution.

There is a similarity between the vertical distribution of oxygen and pH in the northeastern Pacific Ocean (1). Because the processes that control pH of seawater have been discussed frequently (2), I now suggest that the major process affecting the vertical distribution of pH is due to the apparent oxygen utilization by marine organisms. Carbonate dissolution in the deep ocean affects the pH change much less than the oxygen utilization.

To derive an equation relating pH, apparent oxygen utilization, and carbonate dissolution, we consider, as a first approximation, that oxygen utilization lowers seawater pH initially, and that the elevation of the pH then follows carbonate dissolution. We assume that there is no appreciable interdependency of these two variables on seawater pH (3). The equation we seek is:

$$\Delta pH = \Delta pH_{(a)} + \Delta pH_{(c)} \quad (1)$$

where c denotes the magnitude of carbonate dissolution, and a the apparent oxygen utilization in millimoles per liter.

The relation between $\Delta pH_{(a)}$ and apparent oxygen utilization is obtainable from the following relation (4):

$$\Sigma CO_{2(p)} + 106/138 (a) = f(pH) \cdot (Alk_{(p)}) \quad (2)$$

where $\Sigma CO_{2(p)}$ and $Alk_{(p)}$ denote the total carbon dioxide and carbonate alkalinity formed before the water sank at higher latitudes.

By a graphical approximation in a pH range of 7.2 to 8.3, the term $f(pH)$ can be expressed by $-0.160 pH + 2.20$ (5). An average value for the carbonate alkalinity for the region studied is approximately 2.4 meq/liter. Therefore,

changes in oxygen utilization can be related to pH between 7.2 and 8.3 as follows:

$$\Delta pH_{(a)} = -2.0 (\Delta a) \quad (3)$$

Equation 3 indicates that an increase in a of 0.1 mmole/liter (equivalent to 2.24 ml/liter of dissolved oxygen at standard temperature and pressure) corresponds to a drop in pH of 0.20 unit. The apparent oxygen utilization effect on the vertical pH profile is

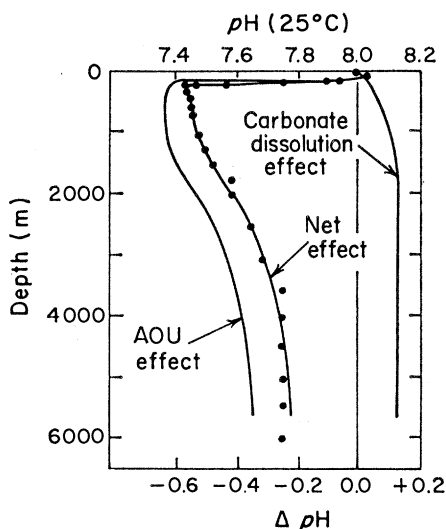


Fig. 1. Vertical profile of pH (shown by dots) at 54°46'N, 158°36'W on 7 July 1966. The pH was measured aboard R.V. *Yaquina*, under 1 atm at a constant temperature of 25°C. The calculated effect of the apparent oxygen utilization by marine organisms on the vertical pH distribution is shown on the left-hand side, while the calculated carbonate dissolution effect is on the right-hand side, and their net effect in the center. The temperature and the salinity of seawater ranged from 7.0°C and 32.8 parts per thousand at sea surface to 1.5°C and 34.7 parts per thousand near the sea floor.

shown at the left-hand side of Fig. 1.

The relation between $\Delta pH_{(c)}$ and the carbonate dissolution can be expressed by

$$\frac{\Sigma CO_{2(p)} + (106/138) (a) + c}{Alk_{(p)} + 2c} = f(pH) = -0.160 pH + 2.20 \quad (4)$$

The extent of the carbonate dissolution in deep water with respect to the surface seawater in the northeastern Pacific Ocean does not exceed 0.1 mmole/liter (6). For such a small range, the left-hand side of Eq. 4 can be expressed as a linear function of the magnitude of the carbonate dissolution. Since total carbon dioxide is 2.4 mmole/liter and carbonate alkalinity is 2.4 meq/liter for the hydrographic station under study, the change in carbonate dissolution is correlated to the change in pH for the 7.2 to 8.3 range by:

$$pH_{(c)} = 2.4 \Delta c \quad (5)$$

The right-hand side of Fig. 1 shows the vertical carbonate dissolution effect with respect to the sea surface. By summing Eqs. 3 and 5, we have

$$\Delta pH = -2.0 (\Delta a) + 2.4 (\Delta c) \quad (6)$$

The combined a and carbonate dissolution effect is plotted in the central part of Fig. 1. Even though my theoretical treatment may be oversimplified, the net curve agrees fairly well with the measured pH at 25°C.

From my analysis, the vertical pH distribution can be attributed to the apparent oxygen utilization of marine organisms and to a lesser extent the carbonate dissolution. My interpretation is not in conflict with the silicate buffering mechanism advanced by Sillén (2). The silicate buffer is a geological coarse control on the seawater pH, whereas the carbon dioxide-carbonate buffer controls the fine structure of the profile of pH in the ocean. These two buffering systems supplement, rather than oppose, each other (7).

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3. The extents of apparent oxygen utilization and carbonate dissolution in the oceans are, generally speaking, less than 0.3 and 0.1 mmole/liter, respectively. Because apparent oxygen utilization is relatively a rapid process, while

carbonate dissolution is slow, and because low pH facilitates carbonate dissolution, it appears logical to suppose that the major part of apparent oxygen utilization takes place first and that in turn favors carbonate dissolution. In addition, R. M. Pytkowicz and D. N. Connors [*Science* **144**, 840 (1964)] showed that high hydrostatic pressure (500 atm) near the sea floor increases the apparent solubility product of calcium carbonate by twice that at sea surface. Their study supports that carbonate dissolution is favored even after seawater sinks down to the depth whereas apparent oxygen utilization goes on while the water is sinking.

4. The fundamental equation used to obtain Eq. 1 is

$$2 \text{CO}_2 = [\text{H}^2 + \text{HK}_1' + \text{K}_1' \text{K}_2' / (\text{H} + \text{K}_2') \text{K}_1'] \text{Alk}$$

where H is hydrogen ion concentration, K_1' and K_2' are the first and second apparent dissociation constants of carbonic acid in seawater. Its derivation is given by K. Park [*J. Oceanogr. Soc. Japan* **21**, 54 (1965)]. The term (106/138) in Eq. 2 is from the model by F. A. Richards [in *Chemical Oceanography*, J. P. Riley and G. Skirrow, Eds. (Academic Press, London, 1965), vol. 1, p. 624] of biochemical oxidation of organic matter; that

is, $(\text{CH}_2\text{O})_{106}(\text{NH}_3)_{10}(\text{H}_3\text{PO}_4) + 138 \text{O}_2 \rightarrow 106 \text{CO}_2 + 122 \text{H}_2\text{O} + 16 \text{HNO}_3 + \text{H}_3\text{PO}_4$. Here, we see that an oxygen depletion of 138 molecules is accompanied by the increase of 106 molecules of carbon dioxide in seawater.

5. The apparent dissociation constants used are those of K. Buch [*Havsforsk. Inst. Skr. Helsing.* **151**, 6 (1951)], at 19 parts per thousand chlorinity and 25°C (shipboard temperature for the pH determination).

6. Changes in specific alkalinity and ratio of alkalinity to chlorinity provide an estimate of the extent of carbonate dissolution. Dissolution of 0.1 mmole/liter of carbonate mineral increases specific alkalinity by 0.1. At my hydrographic station, the surface specific alkalinity was 0.128, while at 4000 m it was 0.133. Therefore, when we take the surface condition as our reference, the deep water dissolution of carbonate is 0.05 mmole/liter.

7. R. M. Pytkowicz [*Geochim. Cosmochim. Acta* **31**, 63 (1967)] pointed out that, within a seawater turnover time of 1000 years, the carbonate cycle rather than the silicate cycle is the primary pH buffering agent in the ocean.

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Orientation of Nuclei Produced under Nonhydrostatic Stress

Abstract. *Recrystallization of a material involves two distinct processes: critical nuclei are produced; these then grow into much larger crystallites. The present theory predicts the distribution of nuclei in orientation and the effect of growth on this initial distribution. The results are in good qualitative agreement with experiments.*

In most cases, the recrystallization of a material occurs through heterogeneous nucleation. The size of the critical nuclei depends on the conditions under which nucleation takes place. In the present report we are concerned with the *orientation* of the nuclei and not with their size and concentration, which are assumed known.

As usual, we assume that the stress in the material has the same value at every point and that the temperature is uniform and constant during nucleation. [It was pointed out by Kamb (1) that for such an imposed stress field, a body of arbitrary shape and orientation and arbitrary elastic properties is always in stable equilibrium.] A nucleus can be considered as a macromolecule; its orientation distribution is then given by a generalized Boltzmann's law (for an ensemble with given temperature and stress field). From a macroscopic point of view the same distribution is easily obtained from fluctuation theory (2). Let us call W the minimum work required to create a nucleus of a given orientation from the host (material within which nucleation occurs). The probability of having such an orientation is proportional to $(2) \exp - W/kT$. In general, W includes a surface term which represents the work of formation of the surface. We neglect the influence of this term on orientation in the pres-

ent theory: we can properly do so if the host is isotropic. (In practice, the host often behaves like an isotropic material if it is composed of many crystals randomly oriented.) Furthermore, we shall see that for *nonhydrostatic* stress, terms proportional to the volume of the nucleus enter W . In that case, the interaction with the host, which is only proportional to the surface of the nucleus, may have a negligible effect on orientation (for large enough nuclei) even if the host is a monocrystal. Notice that for hydrostatic stress the orientation of nuclei must be random if the interaction with the host plays no role. Notice also that, by definition, isotropic nuclei cannot have a preferred orientation.

We define a system of coordinates (S) fixed with respect to the host and call $\overline{\sigma_{mn}}$ the stress tensor measured in this system of coordinates. Since $\overline{\sigma_{mn}}$ has the same value at every point of the material (independently of the nucleus orientation), the principal axes of the stress tensor can always be taken as the (S) axes. Normally the three principal stresses are negative, that is, they are three compressions. We also define another system of coordinates (Σ) attached to each nucleus. The orientation of a nucleus is then defined by the usual Euler angles (3) (θ, ϕ, ψ) of the system (Σ) attached to that nucleus, with respect to the system (S). We call δ_{ijkl} the

fourth-order tensor of the compliance coefficients measured in the (Σ) frame of reference. This tensor is then the same for each nucleus independently of its orientation. We denote by σ_{mn} and e_{mn} the stress and strain tensors also measured in system (Σ) (they depend on the nucleus orientation). If we call u_{ij} the cosine of the angle formed by the i th and j th axes of the (Σ) and (S) systems, respectively, then

$$\sigma_{mn} = u_{mp} \overline{\sigma_{pq}} u_{nq} \quad (1)$$

With these notations the strain energy F , per unit volume of nucleus, is

$$2F = \delta_{ijkl} \sigma_{ij} \sigma_{kl} \quad (2)$$

which can be expressed in terms of the fixed stress tensor $\overline{\sigma_{pq}}$ and the nucleus orientation through Eq. 1. As the molecules, originally part of the host, take the orientation of the nucleus, the corresponding change in strain energy gives a first term contributing to W . A second term represents the work performed by the fixed stress field as the change in orientation takes place (2). If the change in orientation leads to an increase (decrease) in volume this last term is minimum, since W must be minimum, if only the smallest (largest) of the applied compressions performs work. Call $(-\overline{\sigma})$ this compression (in either case) and define the Gibbs potential per unit volume, G

$$2G = e_{ij} [\sigma_{ij} - \overline{\sigma} \delta_{ij}] \quad (3)$$

G is obviously related to one of Kamb's chemical potentials. Notice that $\overline{\sigma}$, which in Kamb's case can be any of the principal stresses, is exactly defined in the present theory. If G_0 is the Gibbs potential per unit volume for the host and V the volume of the nucleus, then

$$W = V [G - G_0] \quad (4)$$

Then the probability density ρ for a nucleus to have the orientation (θ, ϕ, ψ) is

$$\rho(\theta, \phi, \psi) = A [\exp - W/kT] \quad (5)$$

A is a normalization constant given by

$$A^{-1} = \iiint [\exp - W/kT] \sin\theta \, d\theta \, d\phi \, d\psi \quad (6)$$

the element of "volume" in the (θ, ϕ, ψ) space being $\sin\theta \, d\theta \, d\phi \, d\psi$. It is checked at once from the foregoing equations that, as expected, ρ is a constant when the stress is hydrostatic or the embryo isotropic. Notice that the *maxima* of ρ (most probable orientations) correspond