

## CARBON DIOXIDE SYSTEM IN SEAWATER

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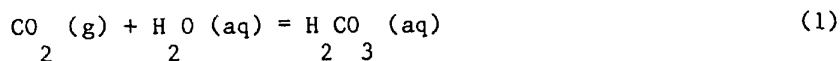
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Carbon is one of the key components of life on the earth. Its biogeochemical cycle is mostly maintained through global tectonic processes in the long run but its short term changes are brought by biological processes. In the oceans, organic matter produced through carbon fixation plays a very important role in influencing the processes of many other elements.

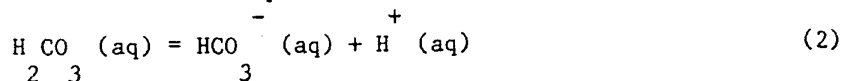
Carbon is added to seawater through rivers, atmosphere, sediment-water exchange, submarine volcanic inputs and icemelting. In seawater carbon is present in dissolved, particulate and gaseous forms. Inorganically it is mostly present as carbonate and bicarbonate ions in dissolved form while as skeletal carbonates in particulate form. Dissolved organic carbon exists as labile and refractory fractions, including humic substances, while particulate organic carbon occurs as living and dead organisms. Carbon dioxide is the gaseous form, which might mostly be present as carbonic acid.

### Carbonate Equilibria

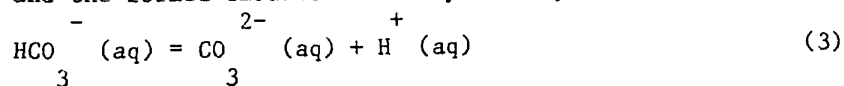
Dissolved inorganic carbon is present in seawater as carbon dioxide and carbonate ions, wherein carbon dioxide reacts with a water molecule thus giving rise to carbonic acid as



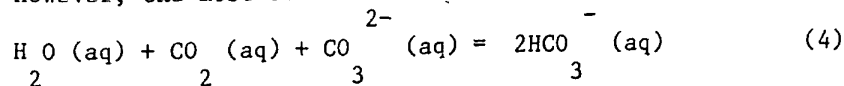
which in turn decomposes into



and the formed bicarbonate ion yields by dissociation

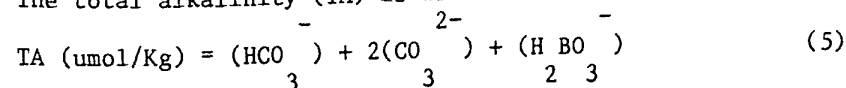


However, the most common reaction in seawater is



In seawater these components regulate the alkalinity and acidity. The alkalinity is generally defined as the number of protons required to neutralise the anions present in seawater. However, the dissolved borate ions also contribute to the same to some extent but not so significant as that of carbon components.

The total alkalinity (TA) is written as



and the carbonate alkalinity (CA) is

$$CA \text{ (umol/Kg)} = (\text{HCO}_3^-) + 2(\text{CO}_3^{2-}) \quad (6)$$

The acidity of seawater is measured in terms of hydrogen ion concentration which is generally expressed as

$$pH = -\log (H^+) \quad (7)$$

On short time scales the pH of seawater is maintained by carbonate equilibria while it is maintained by equilibrium with siliceous minerals on geological time scales. Hence, siliceous minerals are responsible for buffering mechanism of seawater. The reaction responsible for short term change is reaction (2), and hence hydrogen ion concentration can be written as

$$[H^+] = 10^{-pH} = K_2 \cdot (\text{HCO}_3^-) / (\text{CO}_3^{2-}) \quad (8)$$

where  $K_2$  is the second dissociation constant of the carbonic acid. The partial pressure of carbon dioxide can be calculated from total carbonate ion content, alkalinity and carbon dioxide solubility ( $a$ ) in seawater.

$$pCO_2 = \frac{1}{aK_2} \frac{(2(TCO_3) - (TA))^2}{((TA) - (TCO_3))} \quad (9)$$

where

$$K_2 = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]} \quad (10)$$

Since, all carbonate contents are interrelated all these species can be estimated just by measuring any two of these components. The dissolved organic carbon is very significant most of it being considered to be refractory and not available for biological decomposition. However, its concentration is much less compared to inorganic carbonate species.

#### Analysis of Carbon components

Hydrogen ion concentration measurements are performed by electrometric measurements with glass and reference electrodes calibrated by standard buffers. Alkalinity is done by potentiometric titration of seawater. Since, the bicarbonate and carbonate equilibrium is near seawater pH, the titration is to be controlled by computer in order to detect the inflection point accurately. Carbon dioxide gas is measured by gas chromatograph. Dissolved organic carbon is estimated by oxidising the sample and the liberated carbon dioxide will be measured. Particulate inorganic and organic carbon are estimated through oxidative or titrimetric procedures.

## Carbon dioxide cycle

Carbon dioxide is fixed as organic carbon by phytoplankton in surface seawater. The fixation is done both as soft tissue and for some organisms as hard skeletal parts. Thus produced organic and skeletal parts sink to the deeper layers of the ocean, after the death of organisms, where these will be decomposed. This decomposition is effected by bacteria and changes in temperature and pressure for organic and skeletal parts, respectively. The dissolved carbon dioxide thus increases in the deep ocean compared to the surface values. Dissolved organic carbon is produced mostly in surface layers of the ocean due to excretion and exudates of the organisms apart from the rupturing of biological cells. A part of this DOC can be decomposed by bacteria and ultraviolet radiation, resulting in its back entry into inorganic carbon pool.

The extent of skeletal calcium carbonate dissolution varies spatially due to changes in nature of organisms, carbonate mineralogy and changes in temperature and pressure. The degree of carbonate saturation of seawater is defined as

$$D = \frac{((Ca^{2+})_3(CO_3^{2-})_{sw})}{((Ca^{2+})_3(CO_3^{2-})_{swsc})} \quad (10)$$

where  $sw$  is for seawater sample and  $swsc$  is for seawater saturated with carbonate mineral. The surface seawater, in general, is supersaturated ( $D > 1$ ) while the deep ocean is undersaturated ( $D < 1$ ). The saturation horizon normally occurs between 400 and 1000m depth range in the ocean.

The carbon dioxide in surface seawater is in constant exchange with the atmospheric counterpart through the molecular diffusion across air-sea interface. The gas flux ( $F$ ) can be calculated by measuring the gas concentration near the interface ( $if$ ) and that of bulk seawater ( $bs$ ), according to the equation

$$F = D \cdot ((CO_2)_{if} - (CO_2)_{bs}) / Z \quad (11)$$

where  $D$  is the diffusivity at a particular temperature and  $Z$  is the thickness of the boundary layer. The sign of  $F$  indicates the flux direction.

The transport of carbon in the ocean is by circulation as in the case of other dissolved constituents. The atmospheric carbon dioxide will find its way into the deep oceans through its increased dissolution in surface seawater and its subsequent sinking near cold polar regions. The thus sank carbon dioxide is carried on to the other parts of the oceans predominantly by Antarctic Bottom water. The carbon dioxide is ultimately transported to the surface ocean and back to the atmosphere by vertical advection and ventilation near equatorial and tropical latitudes.

#### REFERENCES

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2. Skirrow, G. (1975) The Dissolved Gases - Carbon Dioxide. In : Chemical Oceanography, vol.2, second edn., (J. P. Riley and G. Skirrow, editors), Academic Press, London, p. 1-192.