CARBONATE CHEMISTRY OF THE OCEANS

Chen-Tung Arthur Chen
Institute of Marine Geology and Chemistry, National Sun Yat-sen University, Kaohsiung 804, Taiwan, R.O.C.

Keywords: Alkalinity, aragonite, benthic, bicarbonate, bryozoa, buffer, calcite, carbonate, CCD, DIC, DOC, end point, JGOFS, lysocline, mollusca, pCO_2, pelagic, PIC, POC, pteropods, TA**,** TCO_2.

Contents

1. Introduction
2. Carbon Dioxide and Carbonate System
3. Carbon Cycle
4. Carbonate Sedimentation
Glossary
Bibliography
Biographical Sketch

Summary

One of the most important systems in the oceans is the CO_2-carbonate system, a buffering system that helps to maintain the pH of seawater to within a narrow range. With the sole exception of the chemistry of water itself, this is by far the most complex equilibrium system, and it touches upon every aspect of the Earth sciences-meteorology, geology, oceanography and certainly biology. Within oceanography, it plays an important role in each of the four reactive zones of the oceans: in the air-sea interface, in the chemistry of seawater, in the biogeochemistry and in the deposition and dissolution of marine sediments.

The CO_2-carbonate system has been a major participant in the evolutionary history of the atmosphere, hydrosphere and lithosphere, and it may play a major role in the future by removing anthropogenic CO_2 from the atmosphere. Over 95 per cent of oceanic carbon is in the form of inorganic dissolved carbon; the remainder is comprised of various forms of organic carbon, namely living organic matter as well as particulate and dissolved organic carbon.

1. Introduction

The ocean carbon cycle is one of the most complex planetary phenomena. Chemical and biological processes determine the partial pressure of CO_2 (pCO_2) away from the region where it may be affected by direct atmospheric exchange. Dissolved inorganic carbon (DIC) is divided among CO_2 and the much larger pools of bicarbonate and carbonate, and this takes place by virtue of a reversible reaction. The rates of the reaction in either direction depend on pH, alkalinity and temperature. The half-time for the air-sea exchange and water chemistry equations to approach equilibrium is about 5 months. Another important process is photosynthesis in the well-lit surface layer as far down as

UNESCO – EOLSS SAMPLE CHAPTERS

the depth of 100 m. At certain times of the year, this reaction is so fast that CO_2 is driven far from its state of physical or chemical equilibrium. As a result, pCO_2 in the surface water may at times be far off the corresponding value in the atmosphere.

There is far more carbon in the oceans than nutrients, and the amount of carbon taken up, mostly made up of phytoplankton by marine organisms, depends on inorganic nutrients, like nitrogen, phosphorus and silica. In low-latitude regions, basically all the nutrients are used up in the summer, which means phytoplankton can no longer grow in size to take up more CO_2.

At high latitudes, however, especially in the Southern Ocean around Antarctica, large amounts of nutrients remain in the water all year round because of a limited amount of iron. If they were taken up, then the pCO_2 in the ocean, and subsequently the pCO_2 in the atmosphere, could be drawn down further. There is evidence that this happened during glacial periods. Ice-core records show that changes as large as (though much slower than) the anthropogenic input occurred between glacial and inter-glacial periods.

Much of the biological production of organic matter is quickly recycled back to CO_2 through respiration and, as such, does not represent a net removal. Total primary production in the ocean is about 40 Gt yr^{-1}, and about half of this sinks away from the surface waters downward in the form of particles (plant cells, faecal particles, etc.) while the remaining gets recycled. The amount of recycling of biological production through respiration is difficult to estimate.

There is no way to distinguish 'new' or 'recycled' CO_2 in primary production, and only the 'new' production has any net effect on reducing pCO_2. Nitrogen is also taken up in an almost constant proportion of one nitrogen atom for every seven carbon; one can distinguish 'new' nitrogen (primarily in the form of nitrate) and nitrogen fixation from 'locally regenerated' nitrogen (primarily ammonia or urea). As a result, new and regenerated production of biomass, defined in principal by the kind of nitrogen taken up, are equated with exported and recycled carbon uptake in the open oceans.

The calcium carbonate components of some phytoplankton and zooplankton also contribute to the downward flux of carbon. When shells sink, they are dissolved, causing CO_2 to be regenerated at much greater depths. As carbonate is removed from the water, equilibrium must take place to restore carbonate and therefore increase CO_2, leading to a potential reduction in the oceanic drawdown of atmospheric CO_2.

It is now possible to detect those changes in oceanic CO_2 that have already occurred due to human activities. Observations at the same time on the global scale over at least several decades-frequent enough to determine the dominant scales of variation in terms of space and time-can now be made using satellites in space. Only through the use of such remote observations can the objectives of the Joint Global Ocean Flux Study (JGOFS) on a global scale be achieved.

For the first time, it is possible to estimate wind speed and direction, the fluxes of heat, as well as momentum and material, including carbon dioxide at sea surface. The

UNESCO – EOLSS SAMPLE CHAPTERS

biological production of organic matter and the variability of surface currents on suitable scales can also be estimated.

2. Carbon Dioxide and Carbonate System

Besides the chemistry of water itself, the most important equilibrium system in the oceans is that of carbon dioxide-carbonate. It is largely responsible for controlling the pH of seawater and thus affects many of the chemical states of balance in the sea. Carbon dioxide is far more soluble than many other gases, like N_2, O_2 or Ar because CO_2 (gas) combines with water rather rapidly (in milliseconds) to form carbonic acid (H_2CO_3). Once CO_2 is hydrated, it is involved in a series of even more rapid proton transfer steps (sub-microseconds) to form bicarbonate (HCO_3^-) and carbonate (CO_3^{2-} ions):

$$CO_2\ (\text{gas}) + H_2O = H_2CO_3; \tag{1}$$

$$H_2CO_3 = H^+ + HCO_3^-; \quad \text{and} \tag{2}$$

$$HCO_3^- = H^+ + CO_3^{2-} \tag{3}$$

The sum of these three aqueous carbonate species is defined as total CO_2 or TCO_2. A frequently used property is titration alkalinity (TA), which refers to the amount of acid needed to neutralize all bicarbonate and carbonate ions plus a few minor species.

Because of the large buffer factor of seawater, at equilibrium, a 10 per cent change in the partial CO_2 pressure (pCO_2) results in a mere one per cent change in TCO_2:

$$\Delta TCO_2 / TCO_2 = \alpha\ \Delta\ pCO_2 / pCO_2, \tag{4}$$

where the deltas represent changes in values, and α is almost always constant at 0.1.

With the current pH of seawater at about 8, any excess CO_2 added to the oceans reacts with the carbonate ion to form a bicarbonate ion without utilizing the hydrogen ion (H^+):

$$CO_2 + CO_3^{2-} + H_2O = 2HCO_3^-. \tag{5}$$

Carbonate chemistry is controlled by the chemical behaviour of water as it moves through the hydrological cycle. It picks up salts in solution during weathering on land and precipitates these salts, albeit in different amounts and at different rates, after it reaches the sea again. Rainwater contains dissolved gases, particularly CO_2 and SO_2, along with other trace organic acids, all of which form acidic solutions in water; this means rainwater can be considered a weak acid (pH=5.0). When rain falls on land, the acidity is neutralized by a reaction with the minerals in soils and rocks, such as calcite ($CaCO_3$) and albite ($NaAlSi_3O_8$):

UNESCO – EOLSS SAMPLE CHAPTERS

$$CaCO_3 + CO_2 + H_2O \rightarrow Ca^{2+} + 2HCO_3^-. \quad (6)$$

$$NaAlSi_3O_8 + 2CO_2 + 3H_2O \rightarrow$$
$$Al_2Si_2O_5(OH)_4 + 2Na^+ + \quad (7)$$
$$2HCO_3^- + 4Si_2O_2.$$

The above two representative examples broadly account for the processes by which rainwater is transformed into river water. The exceptionally large increases in the concentrations of Ca^{2+} and HCO_3^- from rainwater to river water arise from the fact that these ions can be produced from the weathering of both carbonates and calcium-bearing silicates.

The concentration of carbonate ions in the oceans is limited by the solubility of calcium carbonate as follows:

$$Ca^{2+} + CO_3^{2-} = CaCO_3. \quad (8)$$

In this reaction, the solubility of $CaCO_3$ increases with pressure but decreases with temperature. The surface layer is usually supersaturated with respect to $CaCO_3$, but except in isolated regions such as the Bahama Banks, spontaneous precipitation does not occur because organic material and magnesium in seawater retard $CaCO_3$ formation. Organic matter forms a film on almost any particle in the oceans rather quickly. As a result, when $CaCO_3$ crystals start to form, an organic film covers the surface such that Ca^{2+} and CO_3^{2-} in seawater do not come in contact with the crystals, and thus they cease to grow. In addition, much of the carbonate is in the form of $MgCO_3^\circ$ ion pairs (General Chemistry of Sea Water, Figure 3). As a result, a relatively small amount of CO_3^{2-} in seawater is actually available for the formation of $CaCO_3$ crystals.

Many marine organisms, however, utilize calcium and carbonate ions to form $CaCO_3$ skeletons, shells, scales and teeth, and they do so mainly on the surface of the ocean. As the organisms die, their shells and skeletons sink to a level where the temperature is low enough or the pressure high enough to make the water undersaturated with respect to $CaCO_3$. It is at that point they start to dissolve. The accumulation of undissolved $CaCO_3$ in the sediments over millions of years makes these sediments a major sink of carbon over geological time. Since calcium and carbon are always in abundant supply, they are not considered nutrients. However, in the 'silica ocean', such as in the Southern Ocean and in the western North Pacific where diatoms prosper, siliceous shells are formed and deposited instead. Unlike calcium and carbon, silicon can be in short supply in the open oceans; this explains the reason that it is considered a nutrient.

Photosynthesis and the subsequent decomposition of organic matter are critical in carbonate chemistry. If we formulate the particulate organic materials as $(CH_2O)_{106}(NH_3)_{16}H_3PO_4$, then the aerobic oxidation of organic material in seawater by oxygen can be represented by an equation which reduces TA:

UNESCO – EOLSS SAMPLE CHAPTERS

$$(CH_2O)_{106}(NH_3)_{16}H_3PO_4 + 138O_2 = 106CO_2 + 122H_2O + 16HNO_3 + H_3PO_4. \quad (9)$$

When the dissolved oxygen is exhausted, the system turns to the next most abundant source for the oxidation of organic material, namely NO_3^-. The overall identification process can be represented by the following equation, which also increases TA:

$$(CH_2O)_{106}(NH_3)_{16}H_3PO_4 + 84.8HNO_3 = 106CO_2 + 42.4N_2 + 148.4H_2O + 16NH_3 + H_3PO_4. \quad (10)$$

In addition, NH_3 can be oxidized:

$$5NH_3 + 3HNO_3 = 4N_2 + 9H_2O. \quad (11)$$

Afterwards, manganese, iron, sulfate and methane reductions occur:

$$(CH_2O)_{106}(NH_3)_{16}(H_3PO_4) + 236MnO_2 + 472H^+ = 106CO_2 + 366H_2O + 236Mn^{+2} + 8N_2 + H_3PO_4. \quad (12)$$

$$(CH_2O)_{106}(NH_3)_{16}(H_3PO_4) + 424FeOOH + 848H^+ = 106CO_2 + 742H_2O + 424Fe^{+2} + 16NH_3 + H_3PO_4. \quad (13)$$

$$(CH_2O)_{106}(NH_3)_{16}(H_3PO_4) + 53SO_4^{-2} + 106H^+ = 106CO_2 + 106H_2O + 53H_2S + 16NH_3 + H_3PO_4. \quad (14)$$

$$(CH_2O)_{106}(NH_3)_{16}(H_3PO_4) = 53CO_2 + 53CH_4 + 16NH_3 + H_3PO_4. \quad (15)$$

Equations (12), (13) and (14) all increase TA, and organic carbon is decomposed in each process. Equation (15) does not change TA except for the small contribution that is by phosphoric acid, but when the NH_3 produced is oxidized to N_2 (Equation 11), the TA increases.

UNESCO – EOLSS SAMPLE CHAPTERS

-
-
-

TO ACCESS ALL THE **15 PAGES** OF THIS CHAPTER,
Visit: http://www.eolss.net/Eolss-sampleAllChapter.aspx

Bibliography

Chen, C.T. and Drake, E.T. (1986). Carbon dioxide increase in the atmosphere and oceans and possible effects on climate. *Annual Review of Earth and Planetary Sciences*, 14, 201-235. [This is a review of the fossil fuel CO_2 increase in the atmosphere and in the oceans, and it looks into the possible effects of this on climate].

Chen, C.T. and Millero, F.J. (1979). Gradual increase in oceanic carbon dioxide. *Nature*, 277, 205-206. [This is the first publication to ever put forward a method to calculate anthropogenic CO_2 anywhere in the Atlantic Ocean].

Chen, C.T. and Pytkowicz, R.M. (1979). On the total CO_2- titration alkalinity-oxygen system in the Pacific Ocean. *Nature*, 281, 362-365. [This is the first publication to provide a method to calculate the anthropogenic CO_2 anywhere in the Pacific Ocean].

Chen, C.T.A., Feely, R.A. and Gendron, J.F. (1988). Lysocline, calcium carbonate compensation depth and calcareous sediments in the North Pacific Ocean. *Pacific Science*, 42, 237-252. [This manuscript describes the relationship between the calcium carbonate compensation depth and the deposits of calcite and aragonite on the surface sediments in the North Pacific].

Handa, N. and Ohsumi, T.(eds) (1995). Direct Ocean Disposal of Carbon Dioxide. *Terrapub*, Tokyo, 274 pp. [This book describes the role of the oceans as a regulator of atmospheric carbon dioxide. Various options for disposal in the oceans are presented].

Lisitzin, A.P. (1996). Oceanic Sedimentation. *American Geophysical Union*. Washington D.C. 400 pp. [This is a monograph describing the delivery of sedimentary material to the ocean; terrigenous and biogenic sedimentation in the oceans; and volcanism].

Wong, C.S. and Hirai, S. (1997). Ocean Storage of Carbon Dioxide: A review of oceanic carbonate and CO_2 hydrate chemistry. *IEA Greenhouse Gas R&D Programme*, 90 pp. [The current state of knowledge is examined, and research needs are determined regarding the direct storage of CO_2 in the deep oceans as a potential greenhouse gas mitigation option].

Biographical Sketch

Born in Changhwa, Taiwan, on 22 April 1949, **Prof. Chen-Tung Arthur Chen**, his wife and two daughters are currently residing in Kaohsiung, where he has been Professor at the Institute of Marine Geology and Chemistry since 1986. After receiving his B.Sc. degree in Chemical Engineering from National Taiwan University in 1970, Prof. Chen was awarded his Ph.D. degree in Chemical Oceanography from the University of Miami in 1977. In the same year, he was appointed Assistant Professor in the College of Marine Sciences of Oregon State University, where he was later promoted to Associate Professor in 1981. He served as visiting professor at National Sun Yat-Sen University (NSYSU) in Kaohsiung, Taiwan, and as Chargé de recherche (CNRS), Université Pierre et Marie Curie in Paris during 1984-1985. During this period, he founded the Institute of Marine Geology at NSYSU, and served as its director until 1989 when he was made Dean of the College of Marine Sciences, a position he held until 1992.

Prof. Chen has sat on numerous international committees, including the Scientific Committee on Oceanic Research and the World Ocean Circulation Experiment. He also served as one of the executives of the

UNESCO – EOLSS SAMPLE CHAPTERS

Scientific Steering Committee of the Joint Global Ocean Flux Study (JGOFS) between 1992-1995. Just prior to that, he had helped to form the Joint JGOFS / LOICZ Marginal Seas Task Team in 1991, and served as its chairman until 1995. Prof. Chen is at present one of the editors of *Oceanography Journal* and associate editor of *Marine Chemistry*. Besides having more than 150 of his own scientific papers published, Professor Chen was awarded the highly-coveted Biowako Prize for Ecology from Japan in 1997.

UNESCO – EOLSS
SAMPLE CHAPTERS