

CHEMISTRY OF THE OCEANS

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Summary

The oceans are filled with seawater which is mainly composed of water, a chemical compound composed of one oxygen and two hydrogen atoms. The polar nature of a water molecular, induced by a positive charge on the hydrogen side and a negative charge on the oxygen side, produces some unusual properties, one of the most important being water's remarkable ability to dissolve more substances than any other solvent. Although most solids and gases are soluble in water, the oceans are essentially in chemical equilibrium with as much material removed as that which enters every year. Each kilogram of typical seawater contains about 965 g water (857.8 g oxygen and 107.2 g hydrogen). The major ions are chloride (18.98 g), sodium (10.56 g), sulfate (2.65 g), magnesium (1.27 g), calcium (0.40 g), potassium (0.38 g) and bicarbonate (0.14 g). These few elements alone constitute over 99.9 per cent of seawater.

Three of the minor elements, namely nitrogen (but not dissolved N_2), phosphorus and silicon, are essential for the growth of phytoplankton. As these elements are utilized in the surface ocean by phytoplankton, their concentrations decrease to the extent that they are almost undetectable in the subtropical gyres. It follows, then, that productivity is low there. Only when these nutrients are released back into seawater due to respiration or decomposition can a new cycle of production begin.

Once the phytoplankton die (the phytoplankton biomass is far larger than the zooplankton and fish combined), they start to sink and are decomposed by bacteria, thus releasing nutrients back into the seawater. In the meantime, oxygen is consumed by

bacteria and carbon dioxide is released. In the open oceans because of their great depths, most of the nutrients are released at depths much greater than the euphotic zone. As a result, these nutrients are not available for plants until they are recycled back up to the euphotic zone, most likely in the polar regions or in regions with strong upwelling. On the shelves, however, nutrients are recycled back to the euphotic zone more readily because of the shallow water depth. The mixing of surface and bottom water occurs there because of winds, tides and winter cooling. In short, the cycling of nutrients is much more efficient on the shelves.

The cycling of carbon in the oceans, the atmosphere, the terrestrial biosphere and the lithosphere is an essential process that controls the environmental conditions on the surface of the planet. Inorganic carbon mainly in the form of carbon dioxide (CO₂) exists in the atmosphere where CO₂ moves about rather quickly, making the concentration spatially more or less uniform. CO₂ dissolves in seawater with relative ease and is fixed by phytoplankton during photosynthesis. In this process, the inorganic carbon is converted to organic carbon, mostly carbohydrates. Over 99 per cent of the organic carbon is decomposed in the top 1000 m of the water column as organisms die and sink. This process releases inorganic carbon back to the seawater just like that process which releases nutrients. The small amount of organic carbon that is not decomposed remains on the seafloor, and over geological time, it forms deposits of fossil fuels. The burning of fossil fuels since industrialization has been returning this buried store of carbon to the atmosphere in the form of CO₂, a greenhouse gas.

As a gas, CO₂ is chemically very stable, yet when dissolved in seawater, it is highly reactive, serving as a key player in a complex series of reactions with other seawater constituents. The time taken for such reactions to achieve equilibrium, their effects on pH, on alkalinity and on the mixing rates near the surface film provide first-order controls over CO₂ exchanges across the air-sea boundary layer. While excess CO₂ in the atmosphere enhances physico-chemical uptake, such a relationship is non-linear, with uptake becoming progressively weaker at higher CO₂ levels. The oceans now take up about 3×10⁹ tons of carbon yearly in the form of CO₂, mainly in the polar regions. Aside from the anthropogenic CO₂ that invades the oceans, wastes discharged by ships, and by offshore accidents, as well as effluents from urban, agricultural and industrial land sources all contribute to a reduction in the health and quality of the marine environment.

Human disposal of sewage, detergents and other domestic and industrial wastes along with the runoff of agricultural fertilizers increases the availability of nutrients and hence productivity in the coastal waters. The increased productivity, however, may not necessarily be to human's advantage as sometimes a large quantity of nutrients may lead to bursts of primary production in the form of algal blooms, some even toxic.

The release of artificial radionuclides, mainly from coastal nuclear power plants, thermal effluents from most coastal power plants, nuclear or otherwise, and extensive reclamation of coastal swamps and lagoons may have been damaging the marine environment as much as the domestic and industrial effluents. Humankind's fingerprints are now found everywhere in the ocean. Chemical contamination and litter can be found from the poles to the tropics and from beaches to the abyssal depths. Marine life has not

been spared: of particular note, for example, is mercury, a highly toxic trace metal, found in tuna, an important commercial fish.

Still, all-in-all the open oceans are relatively clean thanks to the vast capacity of seawater to dilute and assimilate pollutants. The greatest problems due to pollution and contamination are found in coastal and shelf areas, especially in estuaries. Many coastal marine habitats are being lost irretrievably to the construction of harbors, marinas and airports, the development of coastal communities and settlements as well as to an increase in mariculture.

The international community has long recognized that land-based pollution is the major source of pollution in the marine environment and has recently started to take measures to counteract the problem. The 1982 United Nations Convention on the Law of the Sea contains a major part dealing with the protection and preservation of the marine environment. Agenda 21, approved by the governments attending the United Nations Conference on Environment and Development held in Rio de Janeiro in 1992, has also made a call for all coastal states to develop integrated coastal zone management plans by the year 2000. Indeed, many nations did make that deadline.

1. Introduction

'From a drop of water, a logician could infer the possibility an Atlantic or a Niagara, without having seen or heard of one or the other'. Sherlock Holmes, in a *Scarlet*, by Sir Arthur Conan Doyle.

Producing salt from seawater probably dates back before written history. In fact, the Kingdom of Qi in China (221 to 475 BC) prospered because of its production and sale. People, therefore, obviously had a desire to measure salinity, and to this effect the first salinometer was probably introduced in the Song Dynasty of China (1023-1063 AD) and it made use of lotus seeds. Interest in salinity did not stop there. Around 1670, R. Boyle studied the relation between salinity and seawater density in his article, 'Observations and experiment about the saltness of the sea'. Later, in 1819, A.M. Marcet pointed out that although the concentrations of Mg^{2+} , Ca^{2+} , Na^+ , Cl^- and SO_4^{2-} vary in seawater, the ratios remain constant.

The oceans obtain much of their constituents from rivers, but in terms of chemical properties, ocean water is markedly different from river water. In seawater the ratios between the principal cations is $Na^+ > Mg^{2+} > Ca^{2+}$, whereas in river water it is $Ca^{2+} > Na^+ > Mg^{2+}$. The ratios among the principal anions in seawater are $Cl^- > SO_4^{2-} > CO_3^{2-}$, but in river water, the ratios are $CO_3^{2-} > SO_4^{2-} > Cl^-$. The natural conclusion is that Ca^{2+} , Mg^{2+} and CO_3^{2-} are preferentially removed from seawater to form carbonate or Mg-containing carbonate sediments. Then, over geological time, part of this carbonate-containing oceanic crust is uplifted to form land. The easy-to-dissolve carbonates then return Ca^{2+} , Mg^{2+} and CO_3^{2-} to the oceans via the rivers.

Every year around $3.3 \times 10^5 \text{ km}^3$ of water evaporates from the surface of the oceans and about two thirds of this returns to the oceans. The remaining one third falls on landmass in the form of rain, snow or sleet, which induces the weathering of rocks by way of the

tremendous dissolution power of water, especially after it has been slightly acidified by the dissolution of CO_2 in the atmosphere. This chemical action, combined with changes in temperature and the physical abrasion of particles moved by wind and water, gradually erodes the surface of the land. Erosion products are then carried in solution or in suspension through streams, rivers, runoffs and groundwater into the oceans. Over time, seawater has become a moderately concentrated aqueous electrolyte solution. The bursting of bubbles at the ocean surface ejects salt into the atmosphere, and some of the salt is blown back to the land.

The substances contained in seawater may be categorized into two: dissolved substances, including salts, organic compounds and dissolved gases; and undissolved substances, such as gas bubbles as well as organic and inorganic solids ranging in size from colloidal to particulate forms.

The most abundant substance in seawater is, of course, water. As a result, seawater still keeps many of the unique properties of water, like high surface tension and heat capacity. The most obvious dissolved substances in seawater are the salts. The chemical composition of seawater is examined in detail in 6.18.3.1, General Chemistry of Seawater. Nevertheless, it will suffice to say that a typical 1 kg of seawater that contains 35 grams of salt has about 19 g of chlorine as chloride ion, 11 g of sodium ion, 1.3 g of magnesium ion and 0.9 g of sulfur as sulfate ion. Roughly speaking, artificial seawater, i.e. one which is 92 per cent real, can be prepared by simply mixing 0.5 M NaCl and 0.05 M MgSO_4 solutions. The remaining 8 per cent, under natural conditions, would contain a little bit of almost everything imaginable.

Marine chemistry, i.e., the study of the properties and interactions of the substances present in the marine environment, occupies a central position in oceanography. For instance, in the field of physical oceanography, our knowledge of the water masses of the oceans and deep sea currents as well as of their origins is largely based on the measurements of such chemical parameters as salinity and oxygen. Determinations of the essential micro-nutrients of nitrogen, phosphorus and silicon are of great value to marine biologists concerned with the fertility of the seas. The drawdown of CO_2 by marine biota and the subsequent removal of particulate organic carbon constitute the biological pump which helps to delay the build-up of CO_2 in the atmosphere and, hence, the greenhouse effect.

In cases where rates or ages are needed, be it of the air-sea gas transfer velocity or the speed of water mass movement, or even the ages of a particular water mass, radionuclides probably provide the most readily-available answer. Studies concerning radionuclides benefited, quite accidentally from the initiation of nuclear weapons testing in the Pacific Ocean in the 1950s by the United States, and elsewhere by other members of the nuclear weapons 'club'. There was a concern for the fate and effects of radioactive elements which led to an intensification of research concerned with biogeochemical cycling in the oceans. There were major concerns about the ultimate exposure of marine organisms and the critical pathways for lethal radionuclides to come back to Humans through the sea. The introduction of radionuclides and other pollutants also provided transient tracers that have been used to verify oceanic circulation and our understanding of oceanic processes.

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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 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.