

CHEMICAL PROPERTIES OF THE WORLD OCEAN

V.V. Sapozhnikov

Russian Federal Research, Institute of Fisheries and Oceanology, Moscow, Russia

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Summary

Main processes that led to formation of the World ocean, chemical composition of the seawater, stability of the macroion relationship, and dissolved seawater gasses are discussed. Role of photosynthesis in oceanic development and accumulation of organic matter and maintenance of acid-alkali balance in the carbonate system is revealed. Special attention is given to chemical peculiarities of inland seas which are marked by their salinity and regional peculiarities of production and destruction processes.

1. Geochemical formation of the World Ocean and its salt composition

Before investigation of the chemical composition of seawater we should first recall how the ocean was formed and how water appeared on our planet.

Differentiation of the Earth into lithosphere and hydrosphere resulted from and was maintained by gravitational compression and radioactive decay of uranium, thorium, and potassium-40. On Earth water is released through continuous degassing and fusing of the mantle substance. Composition of the Earth's mantle is similar to that of aerolites.

If we try to fuse aerolite substance the first released fraction will be the fusibles such as H₂O, HCl, HF, NH₃, and other substances which formed the ocean and atmosphere, as well as alkaline metals which formed the Earth's crust.

Water makes the dominating portion (round 6.7-7%) of the released gases. on cooling and condensing water takes up and dissolves HCl, HF, HBr, HI, B(OH₃), (NH₄)₂CO₂, O₂, CO₂, SO₂, H₂S, and other sulfur compounds, consequently forming the primordial oceanic solution (hydrosphere). The modern ratio of water and volatile gases released in volcanic eruptions is almost the same as during the initial formation of the oceans. If we assume that the ratio remained stable we can see that due to degassing of acid smokes and their neutralization by substances released during rock decay, the primordial seawater already contained dissolved salts in proportions close to those we see today.

Obviously the Earth saw a period when there was little or no H₂O in the liquid state on its surface. Later a small and shallow ocean started to grow and it gradually gained its modern size and outline. For billions of years, there was a certain equilibrium between the oceanic solution and rocks of the oceanic bottom and coasts, as well as between atmospheric gases and the ocean. Definitely, all oceanic anion salts (Cl⁻, F²⁻, SO²⁻⁴, I⁻, Br²⁻, AsO²⁻⁴, PO³⁻⁴, SiO³⁻⁴, etc.) are products by degassing volcanoes, while cation salts (Ca²⁺, Mg²⁺, N⁺, K⁺, Ba²⁺, Sr²⁺, etc.) are released by rock decay.

In the early Archeozoic when there was no life on the Earth volcanoes released vapors of CH₄, CO, CO₂, NH₃, S, H₂S, H₃PO₃, HCl, HF, HBr, HI, and possibly Se, As, and Te, which mixed with water to produce acid solutions. The latter interacted with rocks and released equivalent quantities of alkalis. Eventually acids were neutralized by alkalis and salts were developed.

The high water-solubility of the majority of salts explains the initial formation of the World Ocean as a saline and possibly a slightly acid basin with an acid-alkali equilibrium developed at pH of 6 to 7.

In the primordial seawater the sodium: potassium ratio was higher than now. In the early geological period decaying basic and ultra basic rocks, which were the only rocks on the Earth, contained tenfold more Na than K, whereas the modern Na:K ratio on the Earth surface approaches unity.

During the long history of the biosphere clay, shale, and, finally, granite developed to form a future concentrated source of K⁺.

The initial substrate which underwent decay was favorable for release of significant amounts of Ca²⁺ but not in the modern form of CaHCO₃.

The first organisms which appeared in this anaerobic ocean (i.e. there was no dissolved oxygen in seawater at the end of the Archean period) acquired energy to synthesize organic substances either from the chemical energy of reduced compounds or from the sun. This could be better illustrated by activities of chemolithoforic bacteria which use reduced sulfur compounds (Equation 1)



2. Appearance of photosynthetic organisms and a cardinal change in oceanic geochemistry

A cardinal change in the oceanic salt composition occurred 1.5 to 2.0 billion years ago when life appeared and our biosphere started to form.

The first protozoa appeared in the ocean because life could start and evolve only when protected from the ultraviolet rays of the sun by a layer of seawater. Oxygen was scarce in the atmosphere and seawater (c. 0.1 of the present content) and the ozone protective screen was absent.

The first living organisms were anaerobic microbes which were able to live without free oxygen. The formation of oxygen through seawater radiolysis and other processes permitted the evolution of single-celled organisms. Photosynthetic organisms appeared at a very early stage; these were able to decompose water and to release oxygen (Equation 2)



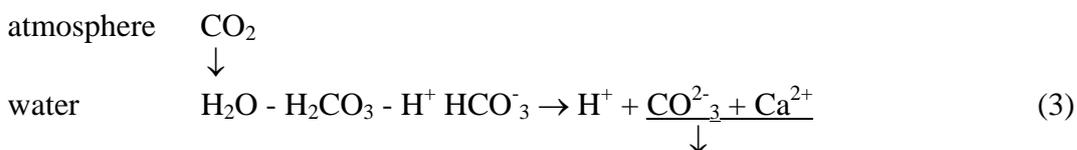
This process and its product, free oxygen, brought about a complete change in geological processes both on land and in the sea. Photosynthesis altered acid-base redox conditions of the medium.

Appearance of free oxygen resulted in oxidation of methane to CO_2 and, consequently, to stabilization of the carbonate-bicarbonate system of the ocean. Atmospheric carbon dioxide (CO_2) was almost completely utilized by photosynthetic organisms; it was the starting point of oceanic deposits of nutrient carbonates. Reduced sulfur compounds such as H_2S , $\text{S}_2\text{O}_3^{2-}$, S, etc. were oxidized to sulfates (SO_4^{2-}). This changed the seawater composition. Obviously ammonium (NH_4^+) was utilized by protozoa and oxidized to elementary nitrogen (N_2). This was the formation of a completely different, nitrogen-oxygen atmosphere.

Atmospheric accumulation of oxygen led to formation of the ozone screen and life was then able to emerge onto the land.

Meanwhile the degassing of mantle substances continued, but now the released products were immediately oxidized to N_2 , SO_2 , CO_2 , etc.

Degradation and oxidation of the oceanic organic matter (OM) produced large amounts of CO_2 and, consequently, led to a carbonate-bicarbonate equilibrium (Equation 3) and development of the seawater buffer properties which allowed maintenance of an acid-base stability in the oceanic surface waters at a pH of 8.2.



bottom sediments

CaCO₃

Since the seawater was saturated with CaCO₃, interaction with aluminosilicates released through decay of the oceanic coasts and bottom lost its importance.

Oxidation of sulfur compounds to sulfates also changed the seawater chemical composition; the World Ocean became mainly a chloride-sulfate basin.

Photosynthetic green plants take 2000 to 3000 years to recycle the whole bulk of atmospheric oxygen, 500 to 600 years to recycle the carbon dioxide stocks (i.e. at the modern level of atmospheric CO₂), and millions of years to recycle the entire water masses of the World Ocean (i.e. all the modern oceans and seas).

We could state that 3.5 billion years ago the chemical composition of the ocean, atmosphere, river discharge, and sediment deposits underwent a complete change.

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Biographical Sketch

Victor V.Sapozhnikov is a Doctor of Science (Geography). He is Head of the Marine Ecology Laboratory of the Russian Federal Research Institute of Fisheries and Oceanography (VNIRO) and Professor of Moscow State University. He is the author of 397 scientific publications. His field of scientific interest is methods of hydrochemical analysis and the hydrochemical basis of biological productivity of the World Ocean. He headed hydrochemical teams in 30 research expeditions to various areas of the World Ocean.

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