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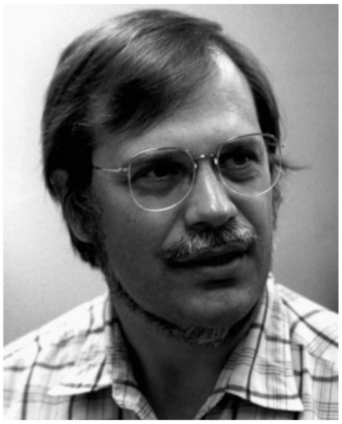
Introduction: Chemical Oceanography

George W. Luther III was born in Philadelphia, PA, in 1947. He attended La Salle College, where he received an ACS certified B.A. degree in 1968. He received a National Defense Education Act Fellowship from the University of Pittsburgh, where he graduated in 1972 with a Ph.D. in Physical-Inorganic Chemistry. His studies included NMR spectroscopy and boron hydride chemistry with Dr. James C. Carter. Upon graduating from the University of Pittsburgh, he became an Assistant Professor at Kean College of New Jersey, where he rose through the ranks and became Department Chair (1976–1984) and helped the program become ACS certified. During this time, he also was active in ACS local section activities and became chair of the New Jersey ACS local section in 1983. In 1986, he moved to the University of Delaware, where he began a research program in marine inorganic chemistry including studies on trace metal, sulfur, and iodine speciation in natural waters and sediments. His work emphasizes the use of physical chemistry to understand environmental problems. Specific examples include the use of chemical kinetics and frontier molecular orbital approaches to understand redox and metal complexation reactions as well as mineral, nanoparticle, and cluster formation and reactivity. In the early 1990s, he began developing *in situ* voltammetric sensors to determine chemical species in sedimentary pore waters and the water column. He has participated on many research expeditions studying the chemistry of the major oceans, the hydrothermal vents, the Black Sea, the Arabian Sea, and the Mediterranean Sea. In 1997 he was elected chair of the ACS Division of Geochemistry, and in 2004 he received the Claire C. Patterson award from the Geochemical Society.



Ed Boyle is Professor of Marine Geochemistry in the Department of Earth, Atmospheric and Planetary Sciences at the Massachusetts Institute of Technology. He obtained his undergraduate degree (Chemistry, 1971) from the University of California, San Diego (Revelle College) and his Ph.D. from the MIT/WHOI Joint Program in Oceanography. His research applies low-level chemical and isotopic analyses of trace elements in the ocean to issues of anthropogenic impact (e.g., Pb and Pb isotopes), biogeochemical cycling (e.g., Fe and Fe and Zn stable isotopes), and paleoclimate (the effect of ice age cycles on ocean and fossil chemistry).

Chemical Oceanography plays a central role in understanding the distribution and reactivity of chemical components within the ocean and at the earth–ocean, sediment–ocean, and atmosphere–ocean interfaces. The oceans cover approximately 70% of the earth's surface, and their average depth is about 3900 meters. The transport of materials to the center of the oceans occurs primarily via atmospheric deposition and to a lesser extent from hydrothermal vent inputs, whereas the coastal ocean is affected primarily by exchange with rivers, atmospheric processes, and groundwater exchange with coastal aquifers. Until recently, the oceanic reservoir appeared to be an expanse that could not be polluted by humans. However, as recently shown in the thematic issue on Atmospheric Chemistry in this journal (Vol. 103, No. 12), humans have altered the earth's atmosphere, so it is not surprising that the oceans have also been altered despite the one thousand year mixing time of the entire ocean.

The origin of the study of the chemistry of the oceans, frequently termed Chemical Oceanography or Marine Chemistry, can be formally traced to the three and a half year expedition of the H.M.S. *Challenger* in 1872. That research cruise collected samples and specimens to study the biology, chemistry, and geology of the water column and sediments around the globe. A major chemical finding was the constancy in the ratio of the major ions (sodium, calcium, magnesium, chloride, and sulfate) to each other throughout the oceanic water column. Since that time, Analytical Chemistry has played a fundamental role in Chemical Oceanography, as method development to determine trace elements at micromolar, nanomolar, and picomolar concentrations is required to understand the distribution and reactivity of chemical components within the ocean and at its interfaces. Reliable results at extremely low concentrations

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require strict sampling protocols or *in situ* techniques so that contamination of the sample does not occur. Also, the protocols for sampling of carbon and its organic compounds are normally different for inorganic elements and compounds. For trace metals and nonmetals, proper analytical and sampling protocols were finally developed in the 1970s and have led to an improved understanding of element cycling in the ocean. Since then, technique development to determine the chemical speciation (redox state as well as specific compounds) of each element has become of paramount importance.

Physical Chemistry has always provided a conceptual framework for the description of oceanic chemistry, and many of the papers in this issue use physical chemical principles to discuss oceanic processes. For inorganic elements and compounds, the thermodynamic approach initially dominated the thinking of marine chemists. Over the last two decades, chemical kinetics and quantum mechanical approaches have enhanced our understanding of chemical transformations via reaction mechanisms at the molecular level for inorganic, organic, and biochemical reactions. In addition to studying chemical transformations via reaction mechanisms at the molecular level, Chemical Oceanography requires studying physical, geological, atmospheric, and biological processes to demonstrate how the elements and their compounds, both natural and anthropogenic, vary over a range of spatial and temporal scales. For example, much effort has been expended on the study of the uptake of chemical species by organisms, as trace amounts of an element are needed for growth but too much of an element can lead to toxicity and death.

In this thematic issue, experts look at oceanic inorganic and organic chemistry to understand the earth's oceans, environment, and global change. We had hoped to have a few more topics reviewed, but author availability limited participation. The collected papers describe a rich variety of oceanic chemistry ranging from atmospheric and surface ocean processes to sediment and hydrothermal vent processes. The range of chemistry under diverse oxygen conditions is also demonstrated—from oxygenated (oxic) to zero oxygen and sulfidic (anoxic).

The chemistry of the surface ocean is dominated by the uptake of CO_2 into phytoplankton. The paper by Millero demonstrates the chemical complexity of the oceanic CO_2 cycle but documents the physical and analytical chemistry of the CO_2 system and how the ocean CO_2 cycle has been perturbed by fossil fuel burning. Morse, Arvidson, and Lüttge continue that topic with a thorough discussion of the thermodynamics and kinetics of $CaCO_3$ formation and dissolution, and how surface and nanoparticulate chemistry are important in understanding reactivity. Both the Millero and Morse et al. papers discuss how the ocean will respond to increased acidification which is occurring. McCollum and Seewald discuss the abiotic syntheses of organic compounds, which are necessary for life, at the elevated temperatures found in deep-sea hydrothermal vent environments. Inorganic minerals are the catalysts for these homogeneous and heterogeneous reactions using CO_2 as the carbon source.

Much of the chemistry of all the elements involves understanding how they are cycled via photosynthetic primary productivity, zooplankton grazing, and the microbial decay of the produced organic matter (OM) both in the water column and in sediments. Coble discusses how colored dissolved organic matter (CDOM) gives the ocean its characteristic color and how it is studied via oceanic and satellite optical instrumentation even though the exact chemical structure(s) of CDOM is not known. Satellite data are also used as a proxy for primary productivity measurements and to track riverine inputs and surface-ocean circulation features. Mopper, Stubbins, Ritchie, Bialk, and Hatcher describe the difficulty in getting structural information on dissolved organic matter (DOM, which accounts for up to 90% of the organic carbon in the ocean) yet demonstrate how mass spectrometry and NMR spectrometry are effectively used to obtain exact chemical structural information on small fractions of the total DOM. McNichol and Aluwihare discuss the use of radiocarbon techniques to track DOM and particulate organic matter (POM) in the ocean. They discuss developments in acceleratory mass spectrometry to accurately measure ^{14}C in water and particulate samples as well as specific compounds in those phases. They then review how CO_2 in the ocean can be controlled by DOM and POM production and decay as well as how organic carbon is transferred between DOM and POM within the ocean water column and how POM is transferred to the sediments. Although POM decomposition to bicarbonate/CO_2 occurs in sediments, Burdige reviews organic matter preservation in marine sediments, which helps sequester CO_2 from the atmosphere. The importance of oxygen concentrations and redox oscillations in sediments has a profound effect on OM preservation.

Reeburgh discusses another greenhouse carbon gas, methane, which is produced in sediments at micromolar concentrations under zero oxygen conditions, and in the surface mixed layer under oxic conditions at (sub)nanomolar concentrations. He discusses oceanic methane clathrate deposits and aptly demonstrates that the ocean is a large chemical reactor that oxidizes CH_4. The thermal reduction of sulfate in seawater and the microbial decomposition of organic matter in marine sediments using sulfate as the electron acceptor both lead to H_2S production. Rickard and Luther review the physical chemistry of the oceanic iron, sulfur, and iron sulfide systems including cluster, nanoparticle, and mineral formation and how these materials may be used as catalysts at hydrothermal vents to form organic carbon using CO_2 as the carbon source.

The nutrient elements (N and P) are essential for the synthesis of proteins, peptides, DNA, and RNA. Paytan and McLaughlin review the phosphorus cycle and provide details on its role in organic chemistry, biochemistry, and the formation of biogenic minerals. They also discuss phosphorus as a limiting reagent for primary productivity and how it can constrain nitrogen fixation. Brandes, Devol, and Deutsch review the dynamics of the marine nitrogen cycle with emphasis on new ways to fix nitrogen and new processes leading to N_2 formation in sediments and suboxic/anoxic waters. They demonstrate that there is still much to be learned about the nitrogen cycle, which appears to be as complicated as the marine carbon cycle.

In situ sensor development is an important component of Chemical Oceanography, and new sensors are still needed for a variety of chemical constituents. Sensors are an important feature of research vessels, submersibles, remotely operated vehicles, autonomous underwater vehicles, benthic landers, and moorings. Observatories are considered to be essential for future ocean science research and will likely be cabled for power and high data throughput. Reimers discusses the use of a variety of microelectrodes in the study of sediment processes including organic matter oxidation, $CaCO_3$ dissolution, and redox processes/kinetics. The use of O_2 sensors is also essential in understanding photosynthesis and respiration in the water column. Ding and Seyfried review the technological challenges in making accurate *in situ* measurements of pH and H_2 in hot hydrothermal vent fluids. These data are essential to constrain the chemistry and evolution of hydrothermal environments, which are among the most dynamic environments known. Johnson, Needoba, Riser, and Showers describe the need for chemical sensor networks that can measure pH, dissolved gases including O_2 and CO_2, nutrients, and other chemical parameters. Coupling chemical measurements with physical, satellite, and biological data should provide a detailed description of seasonal and event driven coastal and oceanic processes.

Trace elements can have their own unique cycling, which may be unrelated to carbon and nutrient chemistry. Fitzgerald, Lamborg, and Hammerschmidt review the cycling of Hg in the marine environment. There is agreement that most Hg enters the ocean via the atmosphere where it can then accumulate in biota. Although we have excellent analytical data on Hg and its chemical species, we lack information on how it is chemically transformed and transported within the water column. In other instances, trace elements can be used to understand global processes as well as their own cycling. Swarzenski describes how the U/Th series of radionuclides can be used as tracers for groundwater along coastal margins (also known as submarine groundwater discharge or the subterranean estuary). This field has erupted over the past decade as chemical oceanographers discovered the magnitude of groundwater flux to and exchange with the coastal ocean. Because there are several isotopes with different half-lives that can be used, it is possible to provide temporal and kinetic information on groundwater−ocean processes and water−rock interactions.

This thematic issue shows how chemistry can be effectively used to understand complex problems at both the molecular scale and the global scale. The authors have made new interpretations to provoke our thinking about coastal and oceanic (bio)chemical processes as well as provided an up-to-date assembly of important information. The authors also showed areas where further research is required. Clearly, advances in chemistry continue to further the field of Chemical Oceanography. The Guest Editors thank all the authors for their timely and worthy contributions.

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