

Modern chemistry and chemical technology applied to the ocean and its resources Introduction

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INTRODUCTION

MARINE chemistry became a sub-discipline of chemistry during the early decades of the twentieth century. Chemists could be identified during this period who spent their entire research activity studying the oceans and who trained colleagues for advanced degrees in this pursuit. Now, half a century or more later, the field encompasses chemists from all parts of the mother science itself; it possesses its own journal; an encyclopaedic work of eight volumes; and curricula leading to doctorates in marine departments throughout the world.

As a consequence of this blossoming, contact with pure chemists diminished. The prevailing concepts and technologies of the pure chemists reach the marine chemists years after their formulation. This assemblage of representatives of both groups of scientists is dedicated to reducing this time period.

The ocean and ocean chemistry play a central role in processes involved in the evolution of the Earth, in processes affecting its habitability and in the distribution of its living and mineral resources. The utilization and exploitation of the marine environment for its resources demands a continuing improvement in our knowledge of the chemistry of the oceans—its intimate composition and its chemical reactions. Some scientists have argued that the most important uses of the oceans for the next decades will be as space to accommodate the material and energy wastes of the world society. A knowledge of the fates of such materials is crucial to an understanding of whether or not they will impact upon other resources of the sea or, in any way, affect the utilization of the ocean realm. Coastal waters are increasingly being used for the culture of fish and shellfish. How can one alter the composition of the waters, either deliberately or inadvertently, and maintain economically successful populations? Also, the oceans may

become more and more important as a source of chemicals, both organic and inorganic. At the present time NaCl, Mg and Br are the substances recovered from seawaters. With improvements in extractive chemistries and in the handling of large volumes of water, perhaps other materials will join this short list.

Additionally, there are increasing concerns about protecting the oceans from inadvertent entry of toxic substances that can endanger public health through exposure or consumption of food products or can disrupt communities of marine organisms.

Thus, there are a variety of practical reasons to extend, continually, our knowledge of marine chemistry. The advances in chemistry over the past decade have been extensive. Exposure of this information to the younger group of marine chemists, educated in oceanographic institutions, and to the older group of marine chemists divorced from these new concepts and technologies, is one mechanism to enhance substantially researches in ocean chemistry.

GLOBAL CHANGE: AN URGENT ISSUE

In recent years, scientific research has yielded new knowledge of the Earth at an ever increasing rate. Studies of the continents, oceans, atmosphere, biosphere and cryosphere have delineated, with greater clarity, the complex interactions among the Earth's components and the profound effects of these interactions, not only upon Earth history and evolution but, also, upon the Earth's environment and resources whose qualities are critical to the welfare of mankind. Our knowledge has provided a deeper insight into the Earth as a system and has set the stage for a complete and unified approach to its study by systematic pursuit of its key components.

Investigations in Earth science, in the past, have been motivated by an innate curiosity about our

planet and also by the search for practical benefits to improve the quality of human life. More human beings, today, enjoy greater abundance from the Earth than at any time in our history. Future advances in weather prediction, agriculture and forestry, navigation and ocean resource management, will provide a still better understanding of Earth processes. But, a third and urgent factor has emerged. Humans are no longer simple spectators to the drama of Earth evolution but have become active participants on a worldwide scale, contributing to processes of global change that will significantly alter our habitat within a few generations.

In some cases, such as the depletion of Earth's energy and mineral resources, the effects of human activity are obvious and irreversible. In other cases, such as the alteration of atmospheric and oceanic chemical composition, the processes of change are much more difficult to document, and their consequences are harder to foresee. Moreover, the global effects of many man-induced changes cannot be readily distinguished at this time from the results of natural change on the same time scale.

Changes on a planetary scale can arise from three causes:

- (1) External forces, such as that provided by variations in the Earth's orbit around the sun.
- (2) Internal oscillations and instabilities, such as those inherent in the non-linearity of the system of those induced by biological evolution, volcanic eruption or continental rearrangement.
- (3) Perturbations generated by human activity.

Earth processes can be viewed as a related set of interacting processes operating over time scales from fractions of seconds to billions of years and spatial

scales from molecular dimensions to the circumference of the Earth. Important interactions connect many of these processes and thus bridge widely separated spatial and temporal regions. Once change is introduced it can propagate through the entire Earth system. Further, the future wise management of Earth resources is dependent upon our understanding of these complex interactions.

The hydrosphere and biosphere are highly sensitive to the external environment, being driven extensively by the energy of solar radiation. Diurnal and annual variations in insolation play a central role. Some of the complexity of the resulting events and motions in the fluid atmosphere and ocean, at least on short time scales, have been subject to direct observation and are now becoming understood.

But longer term processes, particularly those involving interactions between several processes, are not understood and research attention must now be directed to these components. Studies of the past 30 a have led to the development of a conceptual model of the fluid and biological Earth, shown schematically in Fig. 1, that describes factors likely to be active in controlling global change on a times-scale of decades to centuries. A notable feature is the presence of human activity as a major inducer of change. Human society must understand these factors and their interactions if it is to adjust and live with the results of change from both anthropogenic and natural factors.

The processes of global change on this time-scale fall into two basic groups, (1) the climate system and (2) the biogeochemical cycles; they are woven together with the ubiquitous presence of water in the forms of vapor, liquid and ice.

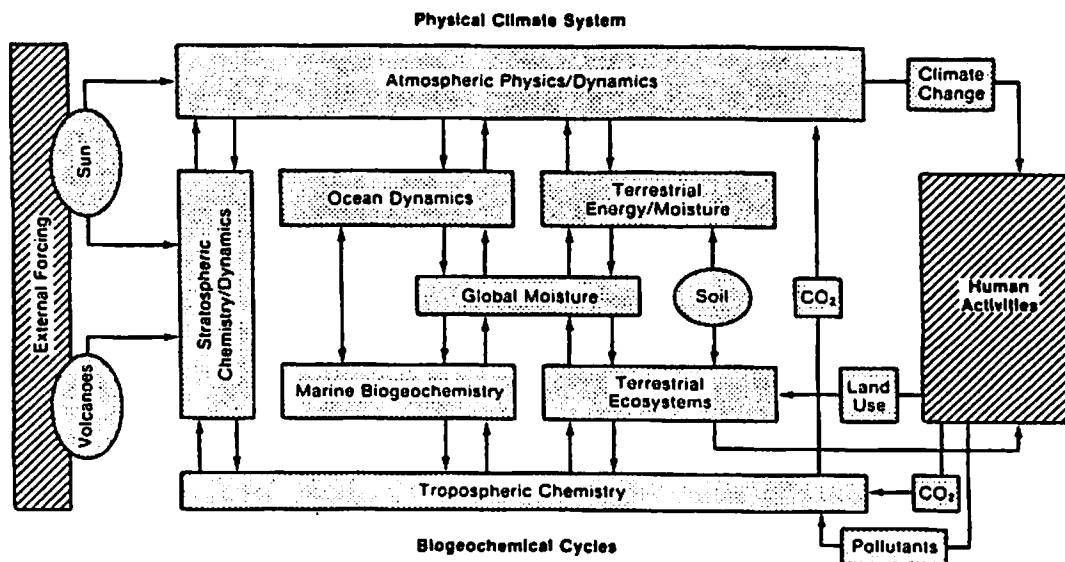


FIG. 1. Biogeochemical cycle. Adapted from a report *Earth System Science: A Program for Global Change* prepared by the Earth System Science Committee, NASA Advisory Council (Chairman F. BRETHERTON), NASA, Washington DC 20546, 1986.

THE OCEAN AND OCEAN CHEMISTRY IN THE EARTH SYSTEM

Resolution of many of the future problems and major progress toward the development of an understanding of the Earth as a system, clearly depend on the integrated contributions of many disciplines, but it is evident from Fig. 1 that ocean biogeochemistry occupies a central position in both the spatial and temporal frames.

The ocean, with its many reservoirs of energy and materials, may be thought of as "the flywheel" of the Earth system. It is critical that we develop a much more detailed understanding of the exchanges of energy, momentum and materials among the ocean reservoirs and between the ocean, the atmosphere and the land, for these are the components that are likely to be intimately involved with the internal instabilities that may be most affected by change.

The biogeochemical cycles, movements by key chemical constituents through the Earth system, are essential to the maintenance of life on our planet. Carbon, N, S and O play primary roles, cycling in various forms through the atmosphere, the hydrosphere and the lithosphere, and interacting with other essential elements.

In addition to the sustenance of life, the biogeochemical cycles play a major role in determining the atmospheric concentrations of radiatively active gases that influence the Earth's energy budget. The most prominent of these, CO_2 , is of special interest because of the human role in perturbing the global C cycle through the burning of fossil fuels. Also, CH_4 , N_2O and chlorofluoromethanes are entering the

atmosphere at accelerating rates and are additional "greenhouse gases".

The biogeochemical cycles impact on longer time scales by establishing environmental conditions leading to the production of oil and mineral resources. Chemical fluxes and reactions in the ocean form the basis for a major control of the global biogeochemical cycles, particularly over short and intermediate terms (seconds to hundreds of years). Over these time scales, there is a clear and strong interaction with ocean living resources. The role that the cycling of nutrients in the ocean plays in ocean biological productivity is understood in principle even though our current observational base is too poor to have effective predictive capability and the nature of many nonlinear interactions that seem to be involved in the whole-scale regional replacement of dominant food species, are not at all clear (e.g. anchovy/sardines in west-coast fisheries).

However, as illustrated in Fig. 2, the cascade of influence from the short and intermediate time and spatial-scale ocean processes to the large spatial scale processes in weather and climate and the longer time scale Earth mineral resource problems are of even greater significance to the habitability of the planet and the social and economic welfare of mankind.

Much of our current understanding of the Earth as a system has derived from our abilities to measure the chemical and physical properties of the ocean, to understand the observed variability in terms of basic biological, physical and chemical principles and to verify and extrapolate the results in multicomponent, conceptual and numerical models. Moreover, developments in basic measurement technology have

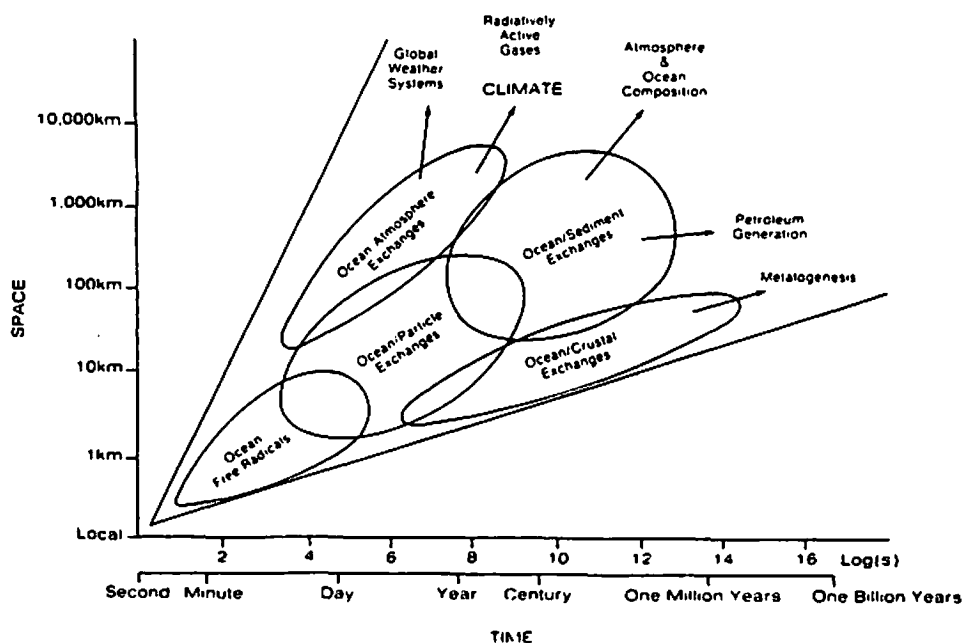


FIG. 2. Time/space phenomena in the environment.

supplied many of the tools that have been instrumental in allowing us to observe the ocean with new and fresh perspectives. In particular, basic chemistry has had significant impacts in the past and must play a major role in the future in our abilities to measure and conceptualize Earth processes.

In the development of our understanding of global change some very real and specific challenges lie ahead. How are the important measurements to be made? What new tools will be needed? How firm is our grasp of the fundamental processes?

For ocean chemists the challenge is particularly acute. The spectrum of oceanic processes is typically "red" so that measurements over long time periods are essential for the observation of change. In some cases, superb development of technique has been achieved (e.g. low level radiochemistry and mass spectrometry) so that critical observations are made. In other areas, the parent field of chemistry has developed somewhat separately (e.g. laser probes, IR spectroscopy, electrochemistry and sensor development) so that a significant gap exists in the development of modern observational systems and chemical theory and their application to ocean problems.

Many chemists are unaware of the major problems in ocean chemistry and many ocean scientists are frustrated in their quest for new chemical tools. For these reasons it is timely to bring together distinguished ocean scientists and chemists to examine these challenges and to propose approaches for their solution.

ADVANCES IN THE CHEMICAL DESCRIPTIONS OF THE OCEANS

The nature of seawater throughout the past two centuries, since the scientific revolution, has developed on the basis of the conventional chemical wisdom of the day. Antoine Lavoisier, the father of modern chemistry, carried out environmental studies in the normal course of his work. His chemical description of seawater (LAVOISIER, 1776) was based upon the salts that precipitated out under evaporation and those salts that could be extracted from the dried saline mass recovered from seawater. About this time TOBERN BORGMAN (1778), one of the first analytical chemists, independently developed a similar technique. Both investigators determined that seawater contained in solution NaCl, CaSO₄ and MgCl₂ as well as mixed chlorides and sulphates.

JOHN MURRAY (1818) formulated the modern methods of water analysis by advocating the determination of the "acids and bases" in solution rather than the minerals left by the removal of the water. He argued that the previous methods reflected more the chemical operations than the actual make-up of seawater. He thus described seawater in terms of the amounts of dissolved Ca, Mg, Na, SO₄ and Cl.

The nineteenth and first part of the twentieth

centuries witnessed a remarkable expansion in our knowledge of the elements (it should be noted that the studies of LAVOISIER and BORGMAN preceded the identification of water as a compound and not as an element). As new elements were found, their concentrations were rapidly sought in seawaters. Two elements were initially discovered in the marine environment: I in the ash of marine algae (COURTOIS, 1813) and Br in the bittern from deposits of marine salts (BALARD, 1826). Still, valid seawater values were a long time in coming: 81 a for I and 47 a for Br. All stable elements have been measured in seawater up to the present time (1987) with the exception of Rh and Os.

During the first half of the twentieth century, a primary concern of marine chemists was the analysis for the plant nutrients, phosphate, nitrate and silicate. Questions as to how the living organisms of the sea were distributed in relation to these inorganic species governed the activities of the scientists.

The phenomenal growth of marine chemistry began just after World War II in the late 1940s. The expansion paralleled that of oceanography itself and in part began as an extension of the wartime activities of scientists and their institutions. The explosive activity began slowly. Young chemists entered the marine field bringing with them mass spectrometers, low level radioactive counting equipment and sensitive analytical techniques. Isotopic analyses of elements in seawater, such as H, O, S, N and Sr, brought a fine detail into the composition of seawaters. Naturally occurring radionuclides were assayed. The analyses of substances went from the micromolar to the nanomolar to the femtomolar concentration ranges. Organic chemists were able to identify specific compounds among the thousands existing in ocean waters; sometimes they were restricted to analyses of collectives of ill-defined substances like the fulvic and humic acids. New sources of oceanic compounds were added to those from river inputs: wind transfer from the continents and both positive and negative entries from the spreading centers. But there was also an unnatural provider of marine components.

It was in the early 1950s that scientists recognized that materials of societal origin not only would enter the oceans but could jeopardize its resources. The nuclear age brought the realization that fission and fusion bomb debris and discharges from nuclear energy facilities were building up in the sediments, water and organisms of the oceans at readily measurable levels. Some marine chemists dedicated their activities during this period to an understanding of the fate of these novel radionuclides in the marine environment and the potential fluxes back to human society. The maximum levels of artificial radionuclides in waters and organisms of the sea that would pose no public health impact were ascertained and appropriate emission controls at nuclear facilities were put into place. The study of these contaminants

markedly increased our knowledge about the processes governing the compositions of waters and sediments.

Perhaps an even more insidious human invasion of the marine environment has resulted from the widespread utilization of chlorinated hydrocarbons such as the pesticide DDT and the industrial chemicals, the polychlorinated biphenyls. These substances were transported, to a large extent, by the winds and had a profound impact upon marine organisms. Higher trophic levels of the organisms suffered morbidities and mortalities through ingestion of these substances. Their regulation, primarily in the northern hemisphere, was based not upon public health concerns but upon the consequent disruptions of the marine community of organisms.

Still, a number of questions about the composition of seawater and the reactions therein haunt the marine science community: (1) the nature of the dissolved organic matter; (2) the speciation of the elements; (3) the appropriate thermodynamic approaches to equilibria, especially at the high temperatures found in hydrothermal vents; and (4) kinetic problems. These problems pervade most of the following presentations. In many cases new avenues of attack have been proposed by the authors.

THE BACKGROUND FOR CHEMRAWN IV

In the 1960s and 1970s some marine chemists voiced concerns that the field was drifting too far from the mainstream of chemistry itself. Remedies were sought at the first Dahlem Conference held in Berlin, Germany in 1975 with the goal to "seek out from the information base of present day chemistry those novel techniques and concepts that deepen our knowledge of the nature of seawater and of the chemical reactions occurring with the marine environment". The meeting brought together about 60 chemists and marine chemists who deliberated in five groups: speciation in seawater; physicochemical conventions; kinetics; colloidal state and surface phenomena; marine organic chemistry. The strategy to initiate discussion involved the preparation of articles by the participating chemists with descriptions of recent advances in their fields, advances whose applications might yield a better understanding of seawater chemistries. These presentations were circulated as preprints before the meeting and provided stepping stones for discussion. These articles, along with the deliberations of the chemists and marine chemists at the Conference, were recorded in the volume *The Nature of Seawater* (GOLDBERG, 1975).

It might appear that the marine chemists had the most to gain from such a gathering through discussions with leaders in the field of chemistry. On the contrary, it turned out that non-marine chemists, upon exposure to challenging problems in the "real

world" of the marine environment, responded with vigor. Some even subsequently pursued researches in marine science. This situation somewhat recalls the entry of Professor LARS GUNNAR SILLEN, the distinguished Swedish inorganic chemist to oceanography, following a presentation on his views of marine chemistry in 1959 at the First Oceanographic Congress in New York. It is somewhat of an understatement to point out that this inelastic collision and his subsequent studies of oceanic chemistry revolutionized the field.

About a decade after the Dahlem Conference there developed a swell of opinion by marine chemists that a second gathering of chemists and marine chemists was in order. During this period a remarkable development of concepts and instrumentation took place in chemistry; also, there was an increasing frustration among marine chemists relating to the rather slow development in their understanding of seawater. Further, there was a growing despair over the deterioration of the marine environment as a result of technological, agricultural and social changes. This provided a sense of urgency to gain a deeper insight into what governs the compositions and chemical reactions of our oceans. Thus, CHEMRAWN IV provided an appropriate outlet—the collation of prevailing wisdom in marine chemistry to better manage our environment.

The Woods Hole Oceanographic Institution was the lead group in CHEMRAWN IV under the direction of its Associate Director, Dr Derek W. Spencer. The program co-chairmen, Dr Allen Bard of the University of Texas and Dr Edward D. Goldberg of the Scripps Institution of Oceanography, through organizing committees invited chemists and marine chemists to participate in CHEMRAWN IV through five panels:

- Panel 1: Oceanic reactive chemical transients
Donald T. Sawyer (Texas A&M University)
Oliver C. Zafriou (Woods Hole Oceanographic Institution)
- Panel 2: The nature of reactions on marine particle surfaces
Arthur W. Adamson (University of Southern California)
James W. Murray (University of Washington)
- Panel 3: Chemical models of sea water systems
Harold L. Friedman (SUNY)
Frank J. Millero (University of Miami/RSMAS)
- Panel 4: Chemistry at the air-sea interface
Peter G. Brewer (Woods Hole Oceanographic Institution)
F. Sherwood Rowland (University of California, Irvine)
- Panel 5: Chemical processes at the ocean bottom
Stephen R. Emerson (University of Washington)
Charles Lochmuller (Duke University).

As a spring board to the deliberations, each of the fifty marine chemists attending the conference were asked to prepare a single page description of their opinion of the most important unresolved problems in marine chemistry. These fifty presentations were then sent to all participants before the meeting and accompany the panel deliberations in the following pages. The Conference was held 4-9 October 1987 at Keystone, Colorado, U.S.A.

Although the panels were constituted in a somewhat different way than that of the Dahlem Conference, the overlap in topics and in concerns is considerable. This gives a sense of the minimum time scale for the resolution of significant environmental problems today.

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