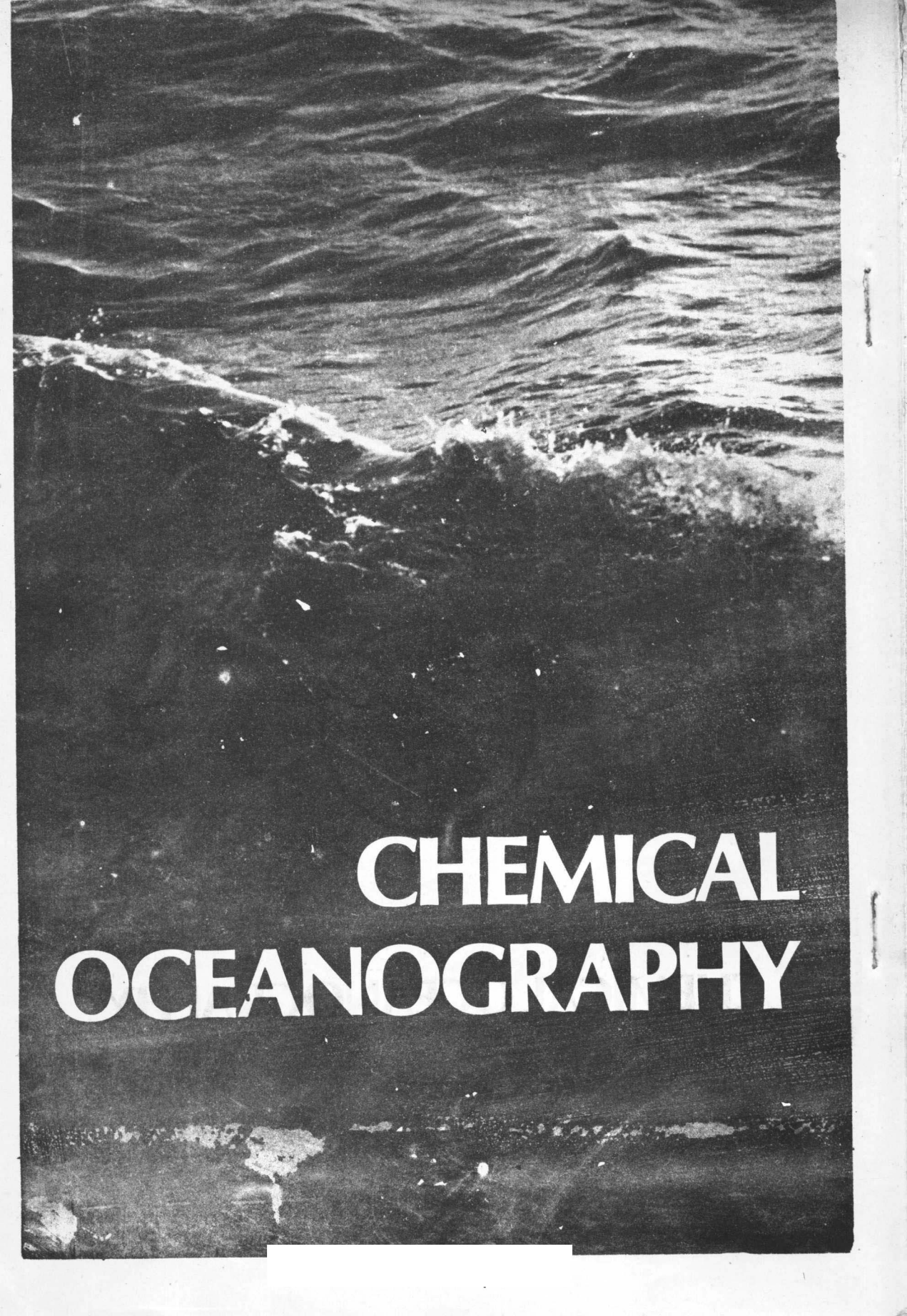


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A black and white photograph of the ocean surface, showing a series of waves. The water is dark, and the white foam of the waves is prominent, especially in the foreground and middle ground. The lighting creates highlights on the crests of the waves.

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Credits and acknowledgments appear on pages 207-209

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FOREWORD

Most information comes to us thirdhand or fourth-hand. This is particularly true of scientific information. Original scientific papers are summarized in review articles, then digested into textbooks, and finally outlined by lecturers. Something is lost in each translation, and it is not entirely the fault of students if their examination papers bear little resemblance to the original scientific data.

Scientists seldom have both the inclination and the skill to explain their work directly to students. Wallace S. Broecker is a fortunate exception. In this book, one of the world's best-known oceanographers gives first-year oceanography students clear and simple access to the way he views and understands the sea.

The book began as a series of tapes of Professor Broecker's lectures to his undergraduate oceanography students at Columbia University. The presence of a student audience automatically minimized the possibility of carelessness or inattentiveness on the part of the author. Subsequently, the lecture tapes were transcribed and reworked, and the author then saw the manuscript through three revisions. But the informality of the original lectures survives here.

In the last several years, beginning oceanography textbooks have explained as little as possible about chemical oceanography. Evidently, some authors and editors feel chemical oceanography is more difficult than biological, geological, or physical oceanography. Professor Broecker's book proves that this is not the case.

Wide and detailed in scope yet simple in presentation, *Chemical Oceanography* is useful as a supplement to the beginning oceanography course or as an independent source for self-education. The highest compliment I can pay this book is to confess that I have relied heavily on its various drafts in preparing my own chemical oceanography course.

Kenneth S. Deffeyes

PREFACE

Prior to 1955, chemical measurements in the ocean were made largely as aids to programs designed by physical or biological oceanographers. Consequently, only a very small fraction of the fantastic potential of chemical and isotopic tracers was realized. During the International Geophysical Year (July 1957–December 1958) the atomic technology boom that occurred during the Second World War finally reached the seas. Since then, the field has seen spectacular growth. Great advances have been made in our understanding of the substances dissolved in the sea and buried in its sediments and their utilization as guides to the nature of both past and present processes within the sea. While this book was being written, a very large program, the Geochemical Ocean Section Study (GEOSECS), was initiated, with the objective of mapping on a global scale the chemical and isotopic properties of the sea. These measurements, when completed, will permit the development of a new generation of ocean models that will be far more sophisticated than those given here. Chemical oceanography has at last attained full status as an integral part of the field. Because chemical studies cross so many traditional disciplinary boundaries, the product of the efforts of the new breed of oceanographer will have a profound impact on our understanding of the sea.

In *Chemical Oceanography*, I attempt to summarize the first order processes taking place within the sea which affect its chemistry. I show that the distribution of chemical species in the water and in the sediment is largely generated by an interaction between mixing cycles and biological cycles. Radioisotope measurements are used to establish the time scale of these processes. The object of this book is to give readers a feeling for the power of the approach rather than to overwhelm them with a mountain of undigested facts.

Despite the great leap forward, for every process within the sea that we think we understand there are dozens for which our knowledge

is extremely sparse. Because of this, my attempt to give an overview of the first-order processes at work in the sea is a mixture of fact, speculation, and frank admission of ignorance. Although I have tried to make it clear where I leave the firm ground paved with observations and enter upon the quicksands of intuition, I regret that there is no sure way to make perfectly clear the precise location of this boundary—it is a fuzzy one. In attempts to maximize the use of the measurements made at sea and in the laboratory, one cannot fully resist the temptation to guess what nature is up to. This is true, in essence, of any frontier field.

Many of the ideas presented here were gleaned from papers written by colleagues in the field and from conversations with them. However, the format of the book does not permit more than a casual recognition of their specific contributions. My own research has been greatly stimulated by a close association with a number of graduate students who have written their doctoral theses under my supervision. Such associations are a key ingredient in scientific discovery. Edwin A. Olson, David L. Thurber, Aaron Kaufman, Teh-Lung Ku, Yuan-Hui Li, Michael Bender, Harry James Simpson, Kenneth Wolgemuth, Tsung-Hung Peng, and Steve Emerson all worked with me on problems dealt with in this book. Since my initial involvement in oceanographic research during the International Geophysical Year, I have worked closely with my friend and colleague Taro Takahashi. Most of the expeditions mounted by my group at the Lamont-Doherty Geological Observatory were organized by Ross Horowitz, whose cheerful enthusiasm, attention to detail, and efforts well beyond the call of duty cannot be forgotten. Finally, my wife, Grace, has provided me with a home and an atmosphere conducive to my work. During both my long trips to sea and my short trips into deep thought, she has covered for me in the many details of raising a family.

In the preparation of this book I am indebted to my secretary, Marylou Zickl, who carried the manuscript from the lecture tapes through its many revisions, and to Eleanor Feltser, who converted the hodgepodge of incomplete and redundant sentences on the original typescript into readable English. Tsung-Hung Peng aided with many of the figures, and Harry James Simpson acted as guinea pig by using various drafts of the book in his chemical oceanography course. The enthusiasm of Kenneth Deffeyes pushed me over the initial brink into tape recording my lectures and also sustained me in the harder jobs of editing, illustrating, and proofreading the manuscript throughout its three revisions.

Wallace S. Broecker

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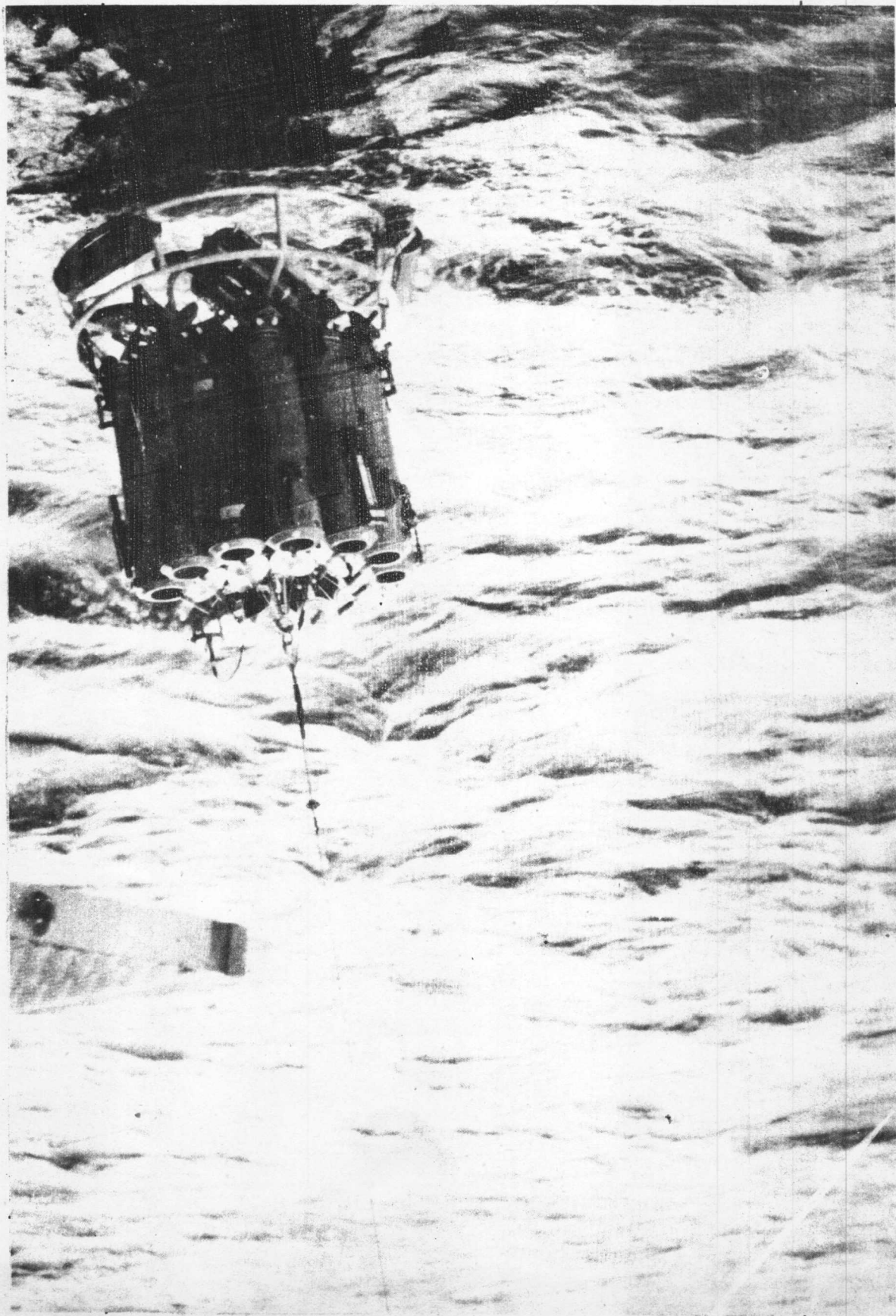
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CHEMICAL OCEANOGRAPHY

1

INTERNAL CYCLING AND THROUGHPUT

The sea is a way station for the products of continental erosion. All substances the sea receives are ultimately passed on to the underlying blanket of sediment. The great tectonic forces that continually alter the geography of the globe eventually bring these sediments above the sea surface and expose them to erosion. Then another trip to the sea begins.

Some of the products of this cycle reach the sea in particulate form. They are dropped by the winds to the sea surface or disgorged by rivers into coastal waters. Within the sea, these rock fragments and soil residues are quite inert. They travel only as far as the currents can carry them before they fall to their burial places on the sea floor.

Of particular interest to us are those products that dissolve during erosion and are carried to the sea in ionic form. They constitute the sea's salt. As long as they remain dissolved, gravity cannot influence them; but other processes at work in the sea ultimately "reprecipitate" the dissolved material delivered from rivers.

The composition of sea salt reflects not only the relative abundance of these dissolved substances in river water but also the difficulty with which they are fixed into sediment forming materials. Sodium, for example, is both abundant in the dissolved matter in rivers and sparingly reactive in the sea. This combination is reflected by its high concentration in sea salt. Calcium, although even more abundant in

river water than sodium, is an important ingredient in the shells of marine organisms. Because of its high reactivity, the abundance of calcium in sea water is far lower than that of sodium.

Many components of sea salt show little variation throughout the sea. Others vary in concentration by one-hundredfold from place to place. As we shall see, these differences are largely the result of cycling by organisms. Plants, for example, live only in surface waters, from which they extract certain elements to construct their tissues. Some plant matter is returned to solution after it has been consumed by animals and bacteria, but insoluble and indigestible plant tissues move downward under the influence of gravity—and so the life cycle leads to chemical segregation. On the average, destruction occurs at greater depth than formation. The interaction of this life cycle with the large-scale water circulation pattern in the sea results in the remarkable distribution of these organically influenced elements, not only within the sea itself but also in the sediments forming on the ocean floor.

The aim of this book is to point out the major factors that influence the average concentrations of the various components of sea salt and the major factors that produce chemical inhomogeneities in the sea and in the sediments. The approach might be termed "inverse chemical engineering". The ocean is a great chemical plant that processes matter fed to it from rivers and dispenses it as sediment. Unlike most chemical plants, the sea has no advance operational blueprint. As chemical oceanographers, we wander through the plant measuring inputs, losses, internal compositions—trying to reconstruct the missing design. As in most other chemical plants, the two critical features of the ocean are the manner in which its ingredients are stirred and the catalysts that accelerate the rate at which its ingredients react with one another. Oceanic mixing is accomplished by a complex system of currents and a host of turbulent eddies. The catalysts are the enzymes in living organisms. Thus any study of the chemistry of sea water is heavily dependent on knowledge derived from physical oceanographic studies and marine biologic studies.

Beyond a desire to understand the chemistry of the ocean, geochemists have a more important goal. Sea salt contains radioisotopes which serve as time clocks. They offer a means of determining the absolute rates of oceanic mixing and of the generation and destruction of plant tissue. However, since the distribution of these time clocks within the sea is controlled by the interaction of physical and biological processes, the influences must be disentangled before the clocks can be read. This difficult task now occupies the attention of many oceanographic researchers.

In this book, we will emphasize the dominant processes operating within the sea. Until these are mastered, it is fruitless to proceed to the less important and much more obscure second-order processes. With

this in mind, we explore our first subject—the grand chemical balance existing in the sea.

The salt dissolved in sea water has remarkably constant major constituents. This fact has greatly simplified the task of the physical oceanographer interested in mapping water density patterns within the sea. He needs only to measure the water temperature and one major property of the sea salt (for example, the chloride ion content or the electrical conductivity) to make a very accurate estimate of the density of a given sample of sea water. This task would be extremely complex if the composition of sea salt were more varied.

Yet it is fortunate, too, that compositional constancy is restricted to the *major* components of sea salt and that it does not extend to all the trace components. If this were not the case, the oceanographer would lose one of his most powerful tools, for variations in the trace constituents of sea water are immediate clues to the mixing, biological, and sedimentary processes taking place within the sea.

The major ion matrix of sea salt consists of the following elements: chlorine in the form of Cl^- ion; sulfur in the form of SO_4^{--} ion; and magnesium, potassium, calcium and sodium in the form of Mg^{++} , K^+ , Ca^{++} , and Na^+ ions, respectively. These six ions dominate sea salt; their ratios, one to another, are very nearly constant. In fact, only calcium has been shown to vary measurably from place to place in its ratio to the other five elements. Although this constancy also extends to many of the lesser components of sea water (boron, bromine, strontium, fluorine, uranium, cesium, and others), it does not extend to all of them.

Excluding the dissolved gases in sea water, all variations in the composition of sea salt, as far as we know, arise from the removal of elements from surface sea water by organisms and the subsequent destruction of organism-produced particles after downward movement. Deep water masses are richer in the elements consumed by organisms than surface water is. If the ocean were sterile, the chemical composition of sea salt would be almost perfectly uniform. Only slight differences in composition resulting from the transfer of gases between the atmosphere and surface waters of differing temperature would exist.

Plants can live *only* in surface water, where there is enough light to permit photosynthesis. By the time the chemical components of their particulate debris are returned to the water as a result of oxidation or dissolution, downward movement under the influence of gravity or migrating animals has occurred. It is not surprising, then, that the primary chemical differences observed in the ocean are all of the type just mentioned: deep water is enriched relative to surface water.

Figure 1-1 shows the distribution with depth of six important oceanic properties at two locations in the Pacific Ocean. In all cases, the most dramatic change occurs in the upper several hundred meters of the water column. This so-called main thermocline separates the

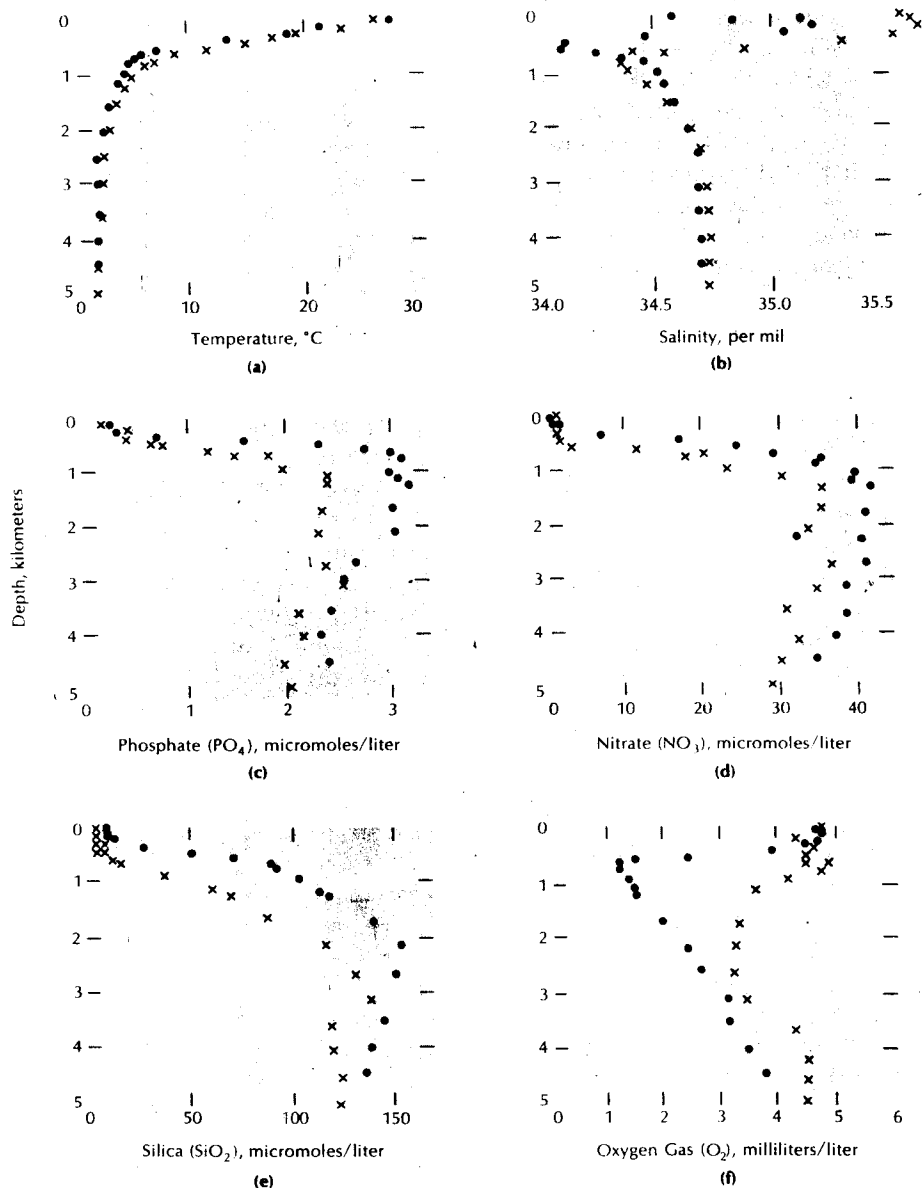


Figure 1-1 The vertical distributions of temperature, salinity, phosphate, nitrate, silica, and oxygen gas for two stations in the Pacific Ocean as determined during the Southern Cross Expedition of the Japanese Research Vessel *Hakuho Maru*. The crosses represent data from a station at 23° S, 170° W; the circles, data from a station at 21° N, 170° W. (Data collected by Yoshio Horibe, Ocean Research Institute, University of Tokyo.)

warm surface waters from the cold underlying waters invading from polar regions. The nutrient elements P, N, and Si show the deep water enrichment mentioned above. Dissolved oxygen gas, by contrast, shows a depletion. Unlike P and N, which are released by respiration, O_2 is consumed. Its pattern is complicated by the fact that cold waters carry with them more dissolved gas than warm waters descending from the surface do. At the southern station, a local excess of evaporation over precipitation gives the surface water a pronounced higher salt content than that found in the underlying cold water. In the northern station, the salinity minimum at about 500 meters depth represents the lateral invasion of Antarctic intermediate water. Keep in mind that these salinity differences are quite small (± 6 per mil* is equivalent to ± 2 percent in salt content) compared to the more than tenfold differences in the concentrations of the three nutrient elements.

Element Classification

About one quarter of the 92 known elements will be considered in this book. They are shown in Table 1-1, grouped as they appear in the periodic table. The first column is comprised of a group of elements known as the alkali metals; they have a valence of +1 (that is, in sea water each atom loses one electron and becomes an ion with a single positive charge). The alkaline earths occupy column (2). These elements have a common valence of +2 (two electrons are given up upon solution in sea water, and the atom becomes a doubly charged ion). The noble gases are in column (8). They do not undergo chemical reactions in sea water, but remain neutral and in gaseous form. Column (7) contains elements with the common property of accepting an extra electron (one of the electrons released by the alkali metal and the alkaline earth metal atoms). These elements are present in sea water with a charge of -1 . The elements in columns (3)–(6) all combine with oxygen, and sometimes with hydrogen, to form multiatom ions. In most cases, they form negatively charged ions; in a few cases, they form neutral groupings. Those dissolved units with negative charges are known as *anions*; those with positive charges, as *cations*. Iron, manganese, nickel, cobalt, copper, uranium, and thorium are the only other elements we will consider in this book in addition to those in Table 1-1.

The elements in the table are divided into three major categories: the *biolimiting* elements (those which are almost totally depleted in surface water); the *biointermediate* elements (those which are partially depleted in surface water); and the *biounlimited* elements (those which show no measurable depletion in surface water).

The three known biolimiting elements are nitrogen (N), phos-

* A per mil (‰) is a part per thousand; a percent is a part per hundred.

Table 1-1 Abbreviated periodic table showing the elements whose marine chemistry will be dealt with in this book. For each, the dominant ionic and molecular forms found in sea water are noted. For those elements whose distribution within the sea is sufficiently well understood, the designations biolimiting, biointermediate, and biounlimited are given. Asterisks denote minor constituents.

(1)							(8)
Hydrogen H_2O H^{+*} Unlimited							Helium He Unlimited
	(2)	(3)	(4)	(5)	(6)	(7)	
Lithium Li^{+} —	Beryllium Be^{++} —	Boron H_3BO_3 $\text{H}_2\text{BO}_3^{-}$ Unlimited	Carbon HCO_3^{-} CO_3^{--} CO_2 Intermediate	Nitrogen N_2 NO_3^{-} Limiting	Oxygen H_2O O_2 Intermediate	Fluorine F^{-} Unlimited	Neon Ne Unlimited
Sodium Na^{+} Unlimited	Magnesium Mg^{++} Unlimited	Aluminum Al^{+} —	Silicon H_4SiO_4 Limiting	Phosphorus $\text{H}_2\text{PO}_4^{--}$ $\text{H}_3\text{PO}_4^{-}$ Limiting	Sulfur SO_4^{--} HS^{-*} H_2S^{*} Unlimited	Chlorine Cl^{-} Unlimited	Argon Ar Unlimited
Potassium K^{+} Unlimited	Calcium Ca^{++} Intermediate					Bromine Br^{-} Unlimited	Krypton Kr Unlimited
Rubidium Rb^{+} Unlimited	Strontium Sr^{++} Unlimited						Xenon Xe Unlimited
Cesium Cs^{+} Unlimited	Barium Ba^{++} Intermediate						Radon Rn Unlimited
	Radium Ra^{++} Intermediate						

† Form in sea water is not known.

phorus (P), and silicon (Si). Plant activity (and, in the case of silicon, animal activity as well) is actually efficient enough to extract these three elements almost totally from surface water. Life in the surface ocean must therefore be limited by the availability of N, P, and Si. Deep water is greatly enriched in these elements in relation to surface water as (c), (d), and (e) in Figure 1-1 indicate. When deep water is returned to the surface, these elements become available to photo-synthetic organisms, are fixed into particulate material, and are then carried by gravity back to the deep sea.