PART

The Physical Chemistry of Seawater
1.1 **INTRODUCTION**

The study of marine chemistry encompasses all chemical changes that occur in seawater and the sediments. The ocean is a place where biological, physical, geological, and chemical processes interact, making the study of marine chemistry very interdisciplinary and more appropriately termed **marine biogeochemistry**. Chemical approaches are now commonly used by marine biologists, marine geologists, and physical oceanographers in support of their research efforts. Likewise, oceanographers recognize the interconnectedness of Earth’s hydrosphere with its atmosphere and crust, requiring that a true understanding of the ocean include consideration of its interactions with the rest of the planet. Also important are extraterrestrial forces, such as changes in solar energy and meteorites. For these reasons, this textbook covers topics that range far beyond the margins of the seashore and seafloor, as well as the boundaries of a classical study of chemistry.

1.2 **WHY THE STUDY OF MARINE BIOGEOCHEMISTRY IS IMPORTANT**

Most of the water on Earth’s surface is in the ocean; relatively little is present in the atmosphere or on land. Because of its chemical and physical properties, this water has had a great influence on the continuing biogeochemical evolution of our planet. Most notably, water is an excellent solvent. As such, the oceans contain at least a little bit of almost every substance present on this planet. Reaction probability is enhanced if the reactants are in dissolved form as compared with their gaseous or solid phases. Many of the chemical changes that occur in seawater and the sediments are mediated by marine organisms. In some cases, marine organisms have developed unique biosynthetic pathways to help them survive the environmental conditions found only in the oceans. Some of their metabolic products have proven useful to humans as pharmaceuticals, nutraceuticals, food additives, and cosmeceuticals.
Another important characteristic of water is its ability to absorb a great deal of heat without undergoing much of an increase in temperature. This enables the ocean to act as a huge heat absorber, thereby influencing weather and climate.

Thus through many means, water sustains life, both marine and terrestrial. Scientific evidence supports the hypothesis that on Earth, life first evolved in a wet environment, such as an early ocean or submarine hydrothermal system. In turn, biological activity has had important effects on the chemical evolution of the planet. For example, the photosynthetic metabolism of plants is responsible for the relatively high concentration of oxygen gas ($O_2$) in our present-day atmosphere. Most of this oxygen was originally present as $CO_2$ emitted onto Earth’s surface as part of volcanic gases. Over the millennia, photosynthesizers, such as marine phytoplankton, have converted this $CO_2$ into $O_2$ and organic matter (their biomass). Burial of their dead biomass (organic matter) in marine sediments has enabled $O_2$ to accumulate in the atmosphere. In this way, microscopic organisms have effected a global-scale transformation and transport of chemicals. This is only one example of many in which microscopic organisms serve as global bioengineers.

In studying the ocean, marine biogeochemists focus on exchanges of energy and material between the crust, atmosphere, and ocean. These exchanges exert a central influence on the continuing biogeochemical evolution of Earth. Particular concern is currently focused on the role of the ocean in the uptake and release of greenhouse gases, such as $CO_2$. As part of the atmosphere, these gases influence solar heat retention and, hence, influence important aspects of climate, such as global temperatures, the hydrological cycle, and weather, including tropical storms. Exchanges of material between the land and sea control the distribution of marine life. For example, transport of nutrients from the nearby continents causes marine organisms to grow in greater abundance in coastal waters than in the open ocean. The exchange rates of many substances have been or are being altered by human activities. Thus, the study of marine chemistry has great practical significance in helping us learn how to use the ocean’s vast mineral and biological resources in a sustainable fashion to ensure its health for future generations of humans and other organisms.

### 1.3 THE CRUSTAL-OCEAN-ATMOSPHERE FACTORY AND GLOBAL BIOGEOCHEMICAL CYCLES

As illustrated in Figure 1.1, the planet can be viewed as a giant chemical factory in which elements are transported from one location to another. Along the way, some undergo chemical transformations. These changes are promoted by the ubiquitous presence of liquid water, which is also the most important transporting agent on Earth’s surface. It carries dissolved and particulate chemicals from the land and the inner earth into the ocean via rivers and hydrothermal vents. Chemical changes that occur in the ocean cause most of these materials to eventually become buried as sediments or diffuse across the sea surface to accumulate in the atmosphere. Geological processes uplift marine sediments to locations where terrestrial weathering followed by river transport
returns the chemicals to the ocean. The mobility of chemicals within the crustal-ocean-atmosphere factory is strongly affected by partitioning at interfaces. In the ocean, these include the air-sea and sediment-water interfaces, as well as the contact zone between seawater and suspended or sinking particulate matter. Thus, the ocean acts as a giant stirred flow-through reactor in which solutes and solids are added, transformed, and removed.

The representation of the ocean presented in Figure 1.1 is not a complete description of the ocean but serves to illustrate aspects important to the discussion at hand. Scientists refer to these simplified descriptions as a model. Models are useful ways of summarizing knowledge and identifying avenues for further study. Those that include mathematical information can be used to make quantitative predictions. The model illustrated in Figure 1.1 is a mechanistic one that emphasizes the flow of materials between various reservoirs. Because most material flows appear to follow closed circuits (if observed for long enough periods of time), the entire loop is referred to as a biogeochemical cycle. Such a cycle can be defined for any particular substance, whether it be an element, molecule, or solid. An example of the latter, the rock cycle, is given in Figure 1.2. This type of depiction is called a box model because each reservoir, or form that a substance occurs in, is symbolized by a box (e.g., sedimentary rock). The flow
1.3.1 Steady State, Residence Times, and Turnover Times

If the size of a reservoir remains constant over time, the combined rates of input ($J_{in}$) to each box must equal the combined rates of output ($J_{out}$):

$$-\frac{dM_C}{dt} = 0 = J_{in} - J_{out}$$

(1.1)

where $M_C$ is the amount of material, $C$, in the reservoir, and $J$ has the units of amount per unit time.$^1$ This condition is referred to as steady state. The average period of time

$^1$ Typically, $M_C$ has units of mass.
that a specified unit of a substance spends in a particular reservoir is called its *residence time*. This steady-state residence time is given by

\[
\text{Residence time} = \frac{\text{Total amount of a substance in a reservoir}}{\text{Total rate of supply to or removal of the substance from the reservoir}} = \frac{M_c}{J_{in} \text{ or } J_{out}} \quad (1.2)
\]

In the case of water,

\[
\text{Residence time} = \frac{\text{Total volume of water in the ocean}}{\text{Annual volumetric rate of water input}} = \frac{V_{SW}}{Q_{RW}} \quad (1.3)
\]

As shown in the next chapter, the average molecule of water spends 3800 years in the ocean before being removed, mostly via the process of evaporation.

The steady-state concentration of a chemical with an oceanic residence time much longer than that of water can be predicted if it is assumed that its removal rate is directly proportional to its abundance in seawater, i.e.,

\[
J_{out} = kM = kC_{SSW}V_{SW} \quad (1.4)
\]

where \( k \) is a removal rate constant and \( C_{SSW} \) is the steady-state concentration of \( C \) in seawater. Since river input is the major source of most elements to seawater,

\[
J_{in} = Q_{RW}C_{RW} \quad (1.5)
\]

where \( C_{RW} \) is the concentration of \( C \) in riverwater. Substituting Eqs. 1.3 and 1.4 into Eq. 1.1 and solving for \( C_{SSW} \) yields

\[
[C]_{SSW} = \frac{[C]_{RW}}{RT \times k} \quad (1.6)
\]

where RT is the residence time of water in the ocean. Equation 1.5 indicates that the steady-state concentration of a given chemical is dependent on the relative magnitudes of its \( k \) and \([C]_{RW}\). Steady-state concentrations can shift given a sustained change in \( k \) and/or \([C]_{RW}\). In many biogeochemical cycles, changes in the steady-state concentration are difficult to achieve because natural systems tend to have feedbacks that act to reduce the effects of rate and/or concentration changes and, hence, stabilize biogeochemical cycles against perturbations.

Equation 1.6 is built upon the assumption that each of the removal processes that \( C \) undergoes follows first-order behavior. If these are chemical reactions, a first-order rate law can be written for each (individual) process in which

\[
\text{Rate of change of } C \text{ due to reaction } i = - \left( \frac{d[C]_{SW}}{dt} \right)_i = k_i [C]_{SW} \quad (1.7)
\]

where \( k_i \) is the first-order reaction rate constant that has a positive value if \( C \) is lost from the ocean through chemical reaction. These rate constants are additive so the \( k \) used in Eq. 1.7 can be computed as the sum of the individual reaction rate constants:

\[
k = \sum_{i}^{n} k_i \quad (1.8)
\]

First-order chemical behavior is commonly assumed because reaction rate laws are generally not known. Although this approach is accepted as a reasonable and practical
accommodation, marine scientists are careful to acknowledge any computed results as “first approximations” or “back-of-the-envelope estimates.”

Equation 1.2 assumes that the concentration of $C$ is constant throughout the ocean, i.e., that the rate of water mixing is much faster than the combined effects of any reaction rates. For chemicals that exhibit this behavior, the ocean can be treated as one well-mixed reservoir. This is generally only true for the six most abundant (major) ions in seawater. For the rest of the chemicals, the open ocean is better modeled as a two-reservoir system (surface and deep water) in which the rate of water exchange between these two boxes is explicitly accounted for.

Another useful measure of biogeochemical processing is the fractional residence time or turnover time of a material in a reservoir. Computation of this “time” is similar to that of a residence time except that some subset of the input or output processes is substituted into the denominator of Eq. 1.2. The resulting turnover time represents how long it would take for that subset of processes by itself to either supply or remove all of the material from the reservoir. Turnover times can be calculated for reservoirs that are not in steady state. As will be shown in Chapter 21, the residence time can be computed by summing the reciprocals of the turnover times.

Using the rock cycle as an example, we can compute the turnover time of marine sediments with respect to river input of solid particles from: (1) the mass of solids in the marine sediment reservoir ($1.0 \times 10^{24}$ g) and (2) the annual rate of river input of particles ($1.4 \times 10^{16}$ g/yr). This yields a turnover time of $(1.0 \times 10^{24}$ g)/(1.4 $\times 10^{16}$ g/yr) = $71 \times 10^6$ yr. On a global basis, riverine input is the major source of solids buried in marine sediments; lesser inputs are contributed by atmospheric fallout, glacial ice debris, hydrothermal processes, and in situ production, primarily by marine plankton. As shown in Figure 1.2, sediments are removed from the ocean by deep burial into the seafloor. The resulting sedimentary rock is either uplifted onto land or subducted into the mantle so the ocean basins never fill up with sediment. As discussed in Chapter 21, if all of the fractional residence times of a substance are known, the sum of their reciprocals provides an estimate of the residence time (Equation 21.17).

1.4 CONSIDERATION OF TIME AND SPACE SCALES

Box models are limited in their ability to show temporal and spatial variability. In the case of the former, rates and reservoir sizes are liable to change over time. For example, plankton distributions tend to fluctuate on a seasonal, and even a daily, basis. Climate change appears to be causing rate and abundance changes over longer time periods, such as decades. This temporal variability is difficult to show in the box model format. One approach is to provide a range of values for the rate or reservoir size. Likewise,
spatial variability is also difficult to depict. Reservoirs in box models are assumed to be homogenous, i.e., having uniform composition. In reality, most reservoirs have some degree of heterogeneity or nonuniformity. For example, surface-water concentrations of nutrients tend to be much lower than deep-water concentrations, and coastal waters tend to have much higher concentrations than open-ocean waters.

One approach to dealing with spatial variability is to partition reservoirs into sub-reservoirs, such as into surface, deep-water, and coastal-water boxes. Sediments also tend to exhibit great horizontal and vertical variability. For example, most of the solid particles carried by rivers into the ocean are deposited nearshore on the continental margin. In the open ocean, most of the input of particles to the sediments is from atmospheric fallout of dust particles and in situ production of calcareous hard parts by plankton. Thus, calcareous oozes are common on mid-ocean ridges and rare on continental shelves. These examples of temporal and spatial variability highlight the important role of marine organisms in controlling chemical distributions. In turn, their biological activity and spatial distributions are greatly influenced by physical processes such as water movement, gravity, gas diffusion, and heat exchange. In many cases, chemical distributions can be used to trace the pathways and rates of these physical processes.

As illustrated in Figure 1.3, these biogeochemical and physical phenomena occur over a wide range of time and space scales in the crustal-ocean-atmosphere factory. Some are restricted to short time and space scales, whereas others are important only over long time and/or space scales. This requires that oceanographers sample strategically to ensure that their measurements of rates, concentrations, and amounts are truly representative. Because of the complex nature of variability in the marine environment, statistical techniques are now commonly used to design these strategic sampling plans. The goal of these plans is to most effectively target limited resources by adequately covering the temporal and spatial scales over which the processes of interest operate. In some cases, the best approach is to collect large numbers of small samples. In other cases, it is more cost effective to collect very large samples.

Temporal variability in the crustal-ocean factory can disrupt or prevent attainment of steady-state conditions for a given element. Examples of catastrophic events that can perturb global biogeochemical cycles include: (1) meteorite impacts, (2) changes in the rate and pattern of plate tectonic activity, and (3) climate change induced by fluctuations in delivery of solar radiation. Fortunately, many of the biogeochemical cycles seem to have an inherent structure that drives them back toward a steady-state condition. This stabilizing effect is the result of interactions among the transport processes that constitute the biogeochemical cycles. For example, a perturbation that causes an increase in the rate of supply of some element will be countered by an ensuing increase in the rate of its removal. In this way, the steady state is reestablished, although most likely at a new setpoint concentration. This type of interconnected response is termed a negative feedback loop.

Unfortunately, some perturbations can induce a positive feedback response in which perturbations are amplified. For example, the warming associated with global climate
change is reducing ice cover, which is in turn reducing Earth’s ability to reflect, rather than absorb, incoming solar radiation, thereby enhancing global warming.

Geological evidence documents that Earth has experienced numerous catastrophic changes throughout its history, leading to at least five major extinction events during which a majority of species died off. After each extinction event, a repopulation occurred of life forms that were able to adapt to changed environmental conditions. Over the long term, this has lead to a steady chemical evolution of Earth’s surface from a hot, acidic, rocky, airless place to one with a moderate climate, soils, an atmosphere that absorbs UV radiation, and an oxygenated atmosphere and ocean. Much of this evolution is attributable to the effects of marine microbes and algae, some of which have endured for billions of years. Others, such as the diatoms and coccolithophorids, are relative newcomers whose recent evolution has added important stabilizing structure to many of the global biogeochemical cycles. Some scientists consider that these negative feedback loops have conferred upon Earth self-regulatory functions akin to those exhibited by an organism. In this view, called the Gaia hypothesis, Earth’s biota and its abiotic environment interact so as to maintain the atmosphere, land, and ocean in a
1.5 The History of the Study of Marine Biogeochemistry

Marine chemistry became a formal subdiscipline of chemistry in the early 1900s, with the advent of scientists who focused all their research efforts in this field and with the development of doctoral degree programs. Prior to the 1900s, the study of marine chemistry focused on investigations of the composition of the salts in seawater. The first such work was published in 1674 by the English chemist Robert Boyle, the discoverer of Boyle’s law, which describes the behavior of ideal gases. Many other notable early chemists chose to focus their efforts on seawater and, in so doing, discovered new elements, established important new principles, and developed new investigative techniques. In 1772, the French chemist Antoine Lavoisier published the first analysis of seawater based on a method of evaporation followed by solvent extraction. Twelve years later, the Swedish chemist Olaf Bergman also published results of the analysis of seawater. To make his measurements, Bergman developed the method of weighing precipitated salts. Through their efforts, the field of analytical chemistry was born. Between 1824 and 1836, the technique of volumetric titrimetry was developed by Joseph Louis Gay-Lussac. Using this method of analysis, Gay-Lussac determined that the salt content of open-ocean seawater is nearly geographically constant. This conclusion was confirmed in 1818 by John Murray and in 1819–1822 by Alexander Marcet, who proposed that seawater contained small quantities of all soluble substances and that the relative abundances of some were constant. This hypothesis is now known as Marcet’s principle.

The concept of salinity was introduced by Georg Forchhammer in 1865. From extensive analyses of seawater samples, he was able to demonstrate the validity of Marcet’s principle for the most abundant of the salt ions: chloride, sodium, calcium, potassium, magnesium, and sulfate. Thus, he recognized that the salinity of seawater could be inferred from the easily measurable chloride concentration or chlorinity. The details of this relationship were worked out by Martin Knudsen, Carl Forch, and S. P. L. Sorenson between 1899 and 1902. With the international acceptance of their equation relating salinity to chlorinity ($S‰ = 1.805 \text{ Cl‰} + 0.030$), the standardization necessary for hydrographic research was provided. A slight revision in this equation ($S‰ = 1.80655 \text{ Cl‰}$) was made in 1962 by international agreement.

The modern era of oceanography began in 1876 with the Challenger Expedition. This voyage of exploration was the first undertaken for purely scientific reasons. The results from the analysis of 77 seawater samples collected during this cruise were published by William Dittmar in 1884 and supported Marcet’s principle. During the remainder of the 19th century, progress was made in the development of analytical methods for stead state that favors the survival of life. Although direct evidence for the existence of such a high level of organization has not yet been found, a significant body of data support the existence of various negative feedbacks. Some are discussed in this text.
the measurement of trace constituents, such as dissolved oxygen (O₂) and nutrients. With this information, attention shifted to the investigation of the chemical controls on marine life.

The study of oceanography grew increasingly more sophisticated during the period from 1925 to 1940, with the initiation of systematic and dynamic surveys. The most famous was performed by the R/V *Meteor*, in which echo sounding was first used to map seafloor topography. Oceanography and the field of marine chemistry entered a new era in the 1940s, primarily as a result of submarine activity during World War II. This was a period of rapid development in technology and instrumentation. Analytical methods were developed for the measurement of trace constituents, such as metals, isotopes and organic matter, with detection levels dropping to subnanomolar levels. The salinity and temperature of seawater became recognized as a powerful tracer of large-scale water movements, including surface and deep ocean currents. Salinity and temperature were also employed to determine the density of seawater for the purposes of correcting sonar and computing geostrophic current velocities.

Modern oceanography is presently characterized by multidisciplinary research projects conducted collaboratively by large groups of scientists often from different research institutions. This approach is necessitated by the complexity of studying marine processes, such as ones that involve global scales, like climate change. This current era was initiated in 1958 with the International Geophysical Year, which was organized by the United Nations' UNESCO General Assembly. For marine chemistry, the first multi-investigator, multi-institution project was the Geochemical Ocean Sections Study (GEOSECS) that ran from 1968 to 1978 during the National Science Foundation's International Decade for Ocean Exploration (IDOE). Its goal was to determine the pathway of deep-ocean circulation using radioisotopes, such as radiocarbon, as tracers of water movement. This work was continued in the Transient Tracers in the Ocean (TTO) program, which ran from 1980 to 1983. Both programs sought to take advantage of the global injection of artificial radionuclides into the ocean from fallout generated during the nuclear weapons testing conducted in the 1950s and 1960s.

The Joint Global Ocean Flux Study, which ran from 1987 to 2003, investigated fluxes of chemicals, primarily carbon and other biogenically controlled elements, to better understand linkages to global climate change. This international program was one of the first core projects of the International Geosphere-Biosphere Programme (IGBP) developed by the Scientific Committee on Oceanic Research (SCOR), a committee of the International Council for Science (ICSU). An important component of JGOFS was the establishment of time-series measurements at two sites, HOTS (Hawaii Ocean Time Series) and BATS (Bermuda Atlantic Time Series Study), to provide interannual and seasonal resolution of biogeochemical variability. Sampling at the BATS site was initiated in 1978 by Dr. Werner Deuser at the Woods Hole Oceanographic Institution as part of the Oceanic Flux Program (OFP) and is the longest time series of its kind; recording

[^3]: http://www.uib.no/jgofs/
temporal variability in the delivery of sinking biogenic detritus to the seafloor. JGOFS was also notable in its use of remote sensing data collected by satellites.

Data from GESECS, TTO, BATS, and HOTS and other major oceanographic research projects, such as the WOCE (World Ocean Circulation Experiment) are available online.4 The GESECS, TTO, and WOCE datasets are part of the Java Ocean Atlas, which provides a graphic exploration environment for generating vertical profiles, cross-sections, and property-property plots.5 Many of the data presented in this text were obtained from this source.

The research ships that supported these major projects were largely managed by the University-National Oceanographic Laboratory System (UNOLS),6 a consortium of 64 academic institutions established in 1971. UNOLS now coordinates schedules of 28 research vessels ranging in size from 20 to 85 m that are operated by 20 different member organizations, including universities, research institutions, and federal agencies. Ship time is available to all federally funded oceanographers. Deep-sea submersibles and remotely operated vehicles (ROVs) schedules are also coordinated through UNOLS. This technology has played a major role in the study of hydrothermal vents and cold-water seeps. The vents were first discovered in 1977, providing marine chemists with direct observations of large sources and sinks of materials associated with venting along submarine plate boundaries. It also lead to the discovery of a new food web based on chemosynthetic bacteria.

An increasing focus of ongoing work is directed at understanding anthropogenic impacts on the crustal-ocean-atmosphere factory: not just climate change, but also the long-range transport and fate of pollutants. Of particular interest are processes that occur at interfaces, such as the fate of river input after it mixes with seawater, the effect of sunlight on the photochemistry of surface water, and the role of organisms in the formation and solubilization of particles. Much of the work involving particles and the fate of pollutants relies on research into very small-scale phenomena, namely the role of phytoplankton and microbes, such as bacteria and viruses, in translocating and transforming chemicals.

1.6 NEW TECHNOLOGIES, NEW APPROACHES

The next step in obtaining a true systems-level understanding of the crustal-ocean-atmosphere factory requires establishment and maintenance of a global-scale, long-term observational program. For marine scientists, this requires switching from short-duration, ship-based expeditions in which discrete samples are collected and brought back to shore for lab-based analysis to one that relies on continuous data collection using

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4 http://whpo.ucsd.edu/index.html
5 http://odf.ucsd.edu/joa
6 http://www.unols.org
in situ and remote-sensing technologies. The latter is referred to as operational oceanography. In the United States, implementation of these approaches is being directed through the National Aeronautics and Space Administration (NASA), National Oceanic and Atmospheric Administration (NOAA), the Joint Oceanographic Institutions (JOI), and the Consortium for Oceanographic Research and Education (CORE). In 2004, these groups established the Ocean Research Interactive Observatory Networks (ORION) Program to coordinate development and operation of large-scale ocean observatories.\(^7\) Examples include NOAA’s seafloor observatories, such as the Aquarius, an underwater laboratory moored at 20 m in the Florida Keys National Marine Sanctuary since 1993, and the Long-term Ecosystem Observatory (LEO-15) established in 1996. LEO-15 is located in 15 m of water over a 30 × 30 km\(^2\) area on the inner continental shelf of New Jersey.\(^8\) In 2001, LEO-15 was expanded into the New Jersey Shelf Observing System (NJSOS), which covers a 300 × 300 km\(^2\) area. More than a dozen different sensors have been deployed at this site, carried by autonomous underwater vehicles (AUVs), ROVs, and human-occupied vehicles (HOVs).

Another example of such a comprehensive approach to ocean monitoring is the High Latitude Time Series Observatory, which is located in the NW Pacific. This observatory was established in 2001 by the Joint North Pacific Research Center to study what appears to be a site of major CO\(_2\) uptake. It is a collaborative effort between the Woods Hole Oceanographic Institution and two Japanese groups, Mutsu Institute for Oceanography and the Japan Marine Science and Technology Center. An innovative technology being used at this site is moored geochemical profilers that shuttle 200 times a year between the mixed layer and deep zone, providing in situ measurements of conductivity, temperature, depth, and 3D current velocity.\(^9\) Also deployed are automated samplers that collect experiments conducted on filtered water, sediment and plankton in automated incubators. In the mixed layer, an optical sensor continuously measures fluorescence, chlorophyll, and particles to depths of 35 m. These measurements are being coordinated with remote sensing obtained from the ADEOS-II, a satellite launched by the National Space Development Agency of Japan (NSDA).

Space-based earth observations began in 1960 with NASA’s Television Infrared Observation Satellite (TIROS). In the United States, NOAA and NASA have since developed sensors to measure sea surface temperature, winds, and topography. The first experimental effort to obtain remotely sensed color data was made in 1978 with the launch of the Coastal Zone Color Scanner (CZCS) aboard the Nimbus-7 satellite. The first effort to collect biogeochemical data began in 1997 with NASA’s SEAWIFS (Sea-viewing Wide Field of View Sensor) Project, which relies on an ocean color sensor to provide an estimate of phytoplankton production by estimating in vivo fluorescence from chlorophyll. These data were designed to help assess the oceans’ role in the global carbon cycle, and were by JGOFS. In 1999, NASA began its Earth Observing System (EOS) program.

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\(^7\) http://www.orionprogram.org.  
\(^8\) NURP; http://www.nurp.noaa.gov  
\(^9\) http://jpac.whoi.edu/hilats/strategy/instruments.html
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with the launch of the Terra satellite, which contains an upgraded color sensor called the Moderate Resolution Imaging Spectroradiometer (MODIS). MODIS has 36 spectral channels, as compared to SEAWIFS’ eight, enabling it to collect information on colored dissolved organic matter (CDOM) and detritus at a resolution of 0.25 to 1 km. A second MODIS satellite, Aqua, was launched in 2002. Near real-time imagery from MODIS sensors is available online.\(^\text{10}\) The NOAA Polar Orbiting Environmental Satellites (POES) also carry a multispectral sensor called an Advanced Very High Resolution Radiometer (AVHRR). As shown in Table 1.1, many other countries have launched satellites with ocean color sensors.

Plans have been made to fly a new high-resolution multispectral sensor, Visible/Infrared Imager/Radiometer Suite (VIIRS), aboard the National Polar-Orbiting Operational Environmental Satellite System (NPOESS). The Navy also has plans to send a Coastal Ocean Imaging Spectrometer (COIS) with a resolution of 30 m aboard the Navy Earth Map Observer (NEMO). This sensor is designed to enable detection of oil spills and plankton blooms from spectral signatures. In addition to improving spectral coverage and spatial resolution, future efforts will be directed at increasing temporal resolution. Satellites have been deployed by other countries than the United States. For example, Japan’s Advanced Earth Observing Satellite (ADEOS), launched in 2002, carries a Global Imager (GLI) with resolution of 250 m in some of its 36 spectral channels. An international group, the Committee on Earth Observation Satellites (CEOS), was formed in 1984 to coordinate and enhance productivity of space-related earth observation activities. With 100 new satellites expected to be launched over the next decade, this technology can be expected to play an increasingly important role in oceanographic research.

THE FUTURE OF MARINE BIOGEOCHEMISTRY

Operational oceanography is a first step in the direction of obtaining a systems-level understanding of the crustal-ocean-atmosphere factory. The next step is integrating oceanography with other earth sciences and translating our new understanding into a form that can be used to protect resources and humans. Formal work toward this end began at the First Earth Observation Summit held in July 2003. At its conclusion, thirty countries agreed to support the development of a Global Earth Observation System of Systems (GEOSS). GEOSS currently includes a land-based component, the Global Terrestrial Observing System (GTOS), a satellite-based component (CEOS), and an ocean-based component, the Global Ocean Observing System (GOOS). A systems approach will facilitate integration of data collection with data processing, database management, and data delivery conducted via query-based web pages to provide open access. Forty countries are now participating in GEOSS.

In the United States, GOOS will be implemented through a new Integrated Ocean Observing System (IOOS) run by a new organization, Ocean.US, the National Office

\(^{10}\) http://rapidfire.sci.gsfc.nasa.gov/
Table 1.1 Summary of Recent and Current Satellite Ocean Color Sensors.

<table>
<thead>
<tr>
<th>Sensor</th>
<th>Agency</th>
<th>Satellite</th>
<th>Operating Dates</th>
<th>Resolution (m)</th>
<th>Number of Bands</th>
<th>Spectral Coverage (nm)</th>
<th>Ref.</th>
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<td>NASA (USA)</td>
<td>Nimbus-7 (USA)</td>
<td>24/10/78–22/06/86</td>
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<td>6</td>
<td>433–12500</td>
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<tr>
<td>OCTS</td>
<td>NASDA (Japan)</td>
<td>ADEOS (Japan)</td>
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<td>12</td>
<td>402–12500</td>
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<td>ADEOS (Japan)</td>
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<td>9</td>
<td>443–910</td>
<td>c</td>
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<tr>
<td>MOS</td>
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<td>IRS P3 (India)</td>
<td>Launched 21/03/96</td>
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<td>408–1600</td>
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<td>SeaWIFS</td>
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<td>OrbView-2 (USA)</td>
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<td>8</td>
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c: http://smsc.cnes.fr/POLDER.
g: http://www.isro.org/programmes.htm.
h: http://modis.gsfc.nasa.gov.
j: http://envisat.esa.int/instruments/meris.
k: http://www.cnsa.gov.cn/main_e.asp.

for Integrated and Sustained Ocean Observations. The goals of IOOS are to benefit humans by (1) improving predictions of climate change and weather and their effects on coastal communities and the nation; (2) improving the safety and efficiency of maritime operations; (3) more effectively mitigating the effects of natural hazards; (4) improving national and homeland security; (5) reducing public health risks; (6) more effectively protecting and restoring healthy coastal ecosystems; and (7) enabling the sustained use of ocean and coastal resources. IOOS is split into an ocean and a coastal component. The coastal component is divided into 10 Regional Coastal Ocean Observing Systems (RCOOS), each run by a Regional Association (RA). The National Federation of Regional Associations (NFRA) is charged with producing an integrated network by coordinating efforts of the RCOOSs. One interesting challenge lies in linking the existing freshwater observational framework, such as gaging stations maintained by the U.S. Geological Survey (USGS), to downstream efforts in estuaries. Several RCOOSs have seafloor observatories, such as LEO-15, which will continue to be coordinated through the ORION. One of the important challenges of these initiatives is in developing strategies for coping with large data streams generated by multiple sensors and instruments, including providing power, high-speed data transmission, and two-way, shore-to-seafloor communications. Another important initiative is the development of telepresence at sea in which an advanced type of videoconferencing is used to transmit video and digital data between ship and shore in near real time using satellite links to the Internet. Through telepresence, the science command center for an expedition can be located on land, thereby reducing costs and scheduling problems amongst the lead scientists.

A notable example of a GOOS program is the broad-scale global array of temperature/salinity profiling floats, known as Argo. Deployments began in 2000, with the final array to be composed of 3000 floats that will generate 100,000 vertical profiles of temperature, salinity and velocity measurements per year at an average 3-degree spacing. Sensor technology is improving rapidly, enabling in situ measurement of other parameters such as dissolved oxygen, nitrate, in vivo chlorophyll fluorescence, CDOM, turbidity, pH, photosynthetically active radiation (PAR), and redox potential (ORP). At present, long-term deployments of these sensors are rare because of biofouling and calibration issues. An interesting short-term deployment technique uses towed undulating ROVs. Depth and GPS sensors provide location information used by an onboard computer to produce horizontal maps, cross-sectional depth profiles, and property-property plots. A new generation of in situ sensors using a wet chemistry approach for measuring nutrients and iron in seawater is now commercially available, but the need for a larger variety of in situ sensors for identifying and quantifying a wide range of gases, organic compounds, and plankton, including microbes, is great. Future approaches will likely seek to create instrument packages that carry sophisticated chemical instrumentation such as high-pressure liquid chromatographs (HPLCs), UV-VIS spectrophotometers, mass and Raman spectrometers, and even DNA analyzers.11

Though great progress has been made in the past four decades, many gaps remain in our understanding of the chemical processes that occur in the sea. There are several reasons for this. First, except for water and the six major ions, all the other substances in seawater are present at very low concentrations. The combination of trying to detect low concentrations in the presence of large amounts of salts makes measurement of the trace constituents in seawater very difficult. To make matters even more complicated, most elements are present in several different forms, or species, in seawater. The speciation of an element determines its reactivity. Thus, the concentration of each species of an element must be known to fully understand the chemical behavior of that element.

Another great challenge in furthering our understanding of the ocean lies in improving our theoretical approach to the ocean. Marine chemists have traditionally resorted to assuming that the chemical reactions of interest attain equilibrium. This greatly simplifies computations, but provides limited insight into the wide variety of biogeochemical processes controlled by marine organisms. Since living organisms are themselves not at equilibrium, neither are the reactions they mediate. Some attempts have been made at kinetic descriptions of marine processes, with most relying on an assumption of first-order rate behavior. Higher-order rate laws are more likely to be the rule and are thought to confer stability on biological systems.

Marine chemistry has traditionally been divided into two fields. One seeks to understand the chemistry of organic substances in the ocean. The other investigates inorganic substances. Because of analytical difficulties, more is known about the latter than the former. Continuing methodological advances are causing this gap to close rapidly. Our growing recognition of the ubiquitous influence of marine organisms has also blurred the distinction between the two fields. This has direct impact on how research is now being conducted to elucidate the controls on ocean fertility, namely assessing the role of trace metals, such as iron, in supporting the growth of phytoplankton. Understanding ocean fertility will help better manage fisheries and cope with pollution problems. Related areas of research include (1) establishing the molecular structure and reactivity of dissolved and particulate organic matter; (2) elucidating the role of marine organisms in packaging materials into solids that settle and become buried in marine sediments, and (3) quantifying material inputs to the ocean from the coastal ocean, atmosphere, and hydrothermal vents. Other efforts are directed at exploring the recovery of mineral resources from the seabed and the discovery of marine natural products. Many of these research areas are characterized by multidisciplinary approaches, making it difficult to separate chemical studies from biological, geological, physical, atmospheric, and even aquatic work. As a result, biogeochemists are being increasingly common and can be found working in laboratories and departments of biology, geology, physics, atmospheric, space, and environmental science!

Biogeochemistry has been particularly useful in efforts to study the ocean’s past. This subdiscipline is called *paleoceanography*: Because of the linkages among the crust, ocean, and atmosphere, the field of paleoceanography also provides insight into past climate and terrestrial conditions. Much of the geochemical reconstruction of the ocean’s past has relied on compositional analysis of marine microfossils recovered from long sediment cores. These cores are collected by specialized drill ships. The first of these
was the *Glomar Challenger*, deployed in 1966 as part of the Deep Sea Drilling Project (DSDP). In 1984, DSDP was transformed into the Ocean Drilling Program (ODP) and acquired a new vessel, the *Resolution*, operated by JOIDES (Joint Oceanographic Institutions for Deep Earth Sampling). In 2003 this program was retooled as the Integrated Ocean Drilling Program (IODP) that now involves 22 countries, including the United States, Japan, and the European Union.\(^\text{12}\) IODP has a new drill ship, the Japanese *Chikyu*, and an annual budget of $160 million! IODP’s goals include elucidating the history of global climate change and discovering new energy resources and microbes. The ocean covers most of Earth’s surface, contains half the planet’s biota, and controls our climate. Thus the story of the ocean’s past is truly the story of Earth’s past. Using information about the causes and behavior of such phenomena as ice ages and plate tectonics, paleoceanographers hope to predict the future of our ocean and planet. This goal is of more than academic interest. Humans have greatly accelerated the transport rates of some materials into the atmosphere and ocean. These changes are so profound that they have arguably launched planet Earth into a new geological epoch, dubbed the Anthropocene.\(^\text{13}\) It is critical to our own continued existence on this planet that we predict the effects of our own actions so we can take appropriate actions to protect our home, planet Earth.

\(^\text{12}\) http://www.iodp-usio.org

\(^\text{13}\) Geologists have deemed it necessary to recognize this new epoch because sediments now accumulating on the seafloor are chemically distinct from those whose origins predate human impacts on the crustal-ocean-atmosphere factory.