Biogeochemical Cycling of Carbon in Oceans and Climate Change

Covering more than 70% of Earth, the world's oceans cycle carbon rapidly and exert strong, complex feedbacks on both contemporary geochemistry and ongoing climate change. Understanding the global carbon cycle will require a more refined accounting of processes and interchanges between total marine biota and relevant biogeochemical processes.

In climate change scenarios, potential impacts on ocean processes include suppression of nutrient fluxes resulting from increased stratification of water layers; acidification of surface waters driven by rising atmospheric CO_2 levels; and perturbations in the availability of nutrients, such as phosphorus and iron, that limit growth of planktonic communities. To predict shifts in marine biogeochemical cycling and carbon biosequestration resulting from climate change variables, new methods and research are needed to inform oceanic components of various Earth System Models.

Oceanic systems and processes span the full spectrum of biological and physical scales, from genomes to biogeochemical cycling. However, most current efforts to model ecosystem-scale biogeochemical processes in oceans lack the necessary level of spatial or temporal resolution to represent potentially important factors, including (1) functional variation of different phytoplankton classes, (2) heterotrophic bacteria, (3) grazers and higher trophic levels, (4) the chemistry of trace elements and their oxidation states, and (5) points of integration with atmospheric processes. For each of these areas, new research approaches are needed to assess the functional capabilities of marine communities, connect these functions to biogeochemical processes, determine turnover and transformation rates of relevant nutrients, and integrate resulting information into models across multiple scales of resolution.

Marine Carbon "Pumps" and Potential Consequences of Climate Change

Oceans are massive reservoirs for inorganic carbon, containing about 50 times as much CO_2 as the atmosphere. Oceans absorb atmospheric CO_2 by two fundamental processes—the so-called biological and solubility pumps. The biological pump operates via the action of surface-water photosynthetic microbes that transform dissolved CO_2 into organic carbon. Some of this organic carbon subsequently sinks into deeper waters and is effectively sequestered from the active carbon cycle (see sidebar, Marine Food Web and the Carbon Cycle, pp. 80–81). In contrast, the solubility pump is driven by a combination of physical and chemical processes. CO_2 has increased solubility in cooler waters, which are denser than warmer waters. As ocean currents circulate tropical waters to higher latitudes, cooling CO_2-laden water sinks, resulting in a net transport of CO_2 into the deep ocean (see sidebar, CO_2 Absorption and Ocean Acidification, pp. 90–91).

The vertical gradient of nutrients and carbon observed in ocean waters is determined by the coupled action of the biological and solubility pumps, with *(text continued on p. 82)*

Marine Food Web and the Carbon Cycle

Microscopic plants and other photosynthetic organisms that drift with ocean currents lie at the heart of the marine carbon cycle (see figure, Oceanic Food Web, p. 81). Sunlit surface waters teem with phytoplankton that convert inorganic carbon dissolved in surface waters to organic carbon—which forms the basis of the marine food web—and account for about half of all primary production on Earth (Field et al. 1998; Falkowski, Barber, and Smetacek 1998). In contrast to terrestrial carbon-turnover times that may take months to years, carbon cycles rapidly in oceans, with the entire phytoplankton population in some environments replacing itself weekly (Falkowski 2002).

Major Primary Producers

Coccolithophores (5 to 10 µm in diameter), single-celled algae prevalent in tropical oceans.

Diatoms (about 30 µm in diameter), prevalent in temperate and polar oceans.

Dinoflagellates (30 to 2000 µm in diameter), prevalent in the subtropics and tropics, as well as in temperate oceans in late summer.

Cyanobacteria (about 1 µm in diameter), the world's most abundant phytoplankton.

Phytoplankton, such as those described above, are grazed upon by marine heterotrophs known as zooplankton. These grazer species range from microscopic protozoa and copepods to worms, krill, crabs, jellyfish, and the larvae of fish and other organisms. Comprising most of the animal mass in the ocean, zooplankton serve as the crucial link between primary producers and the rest of the marine food web. Viruses, which act as predators in oceanic food chains by infecting and lysing marine bacteria, also play an important but still poorly understood role in marine carbon turnover.

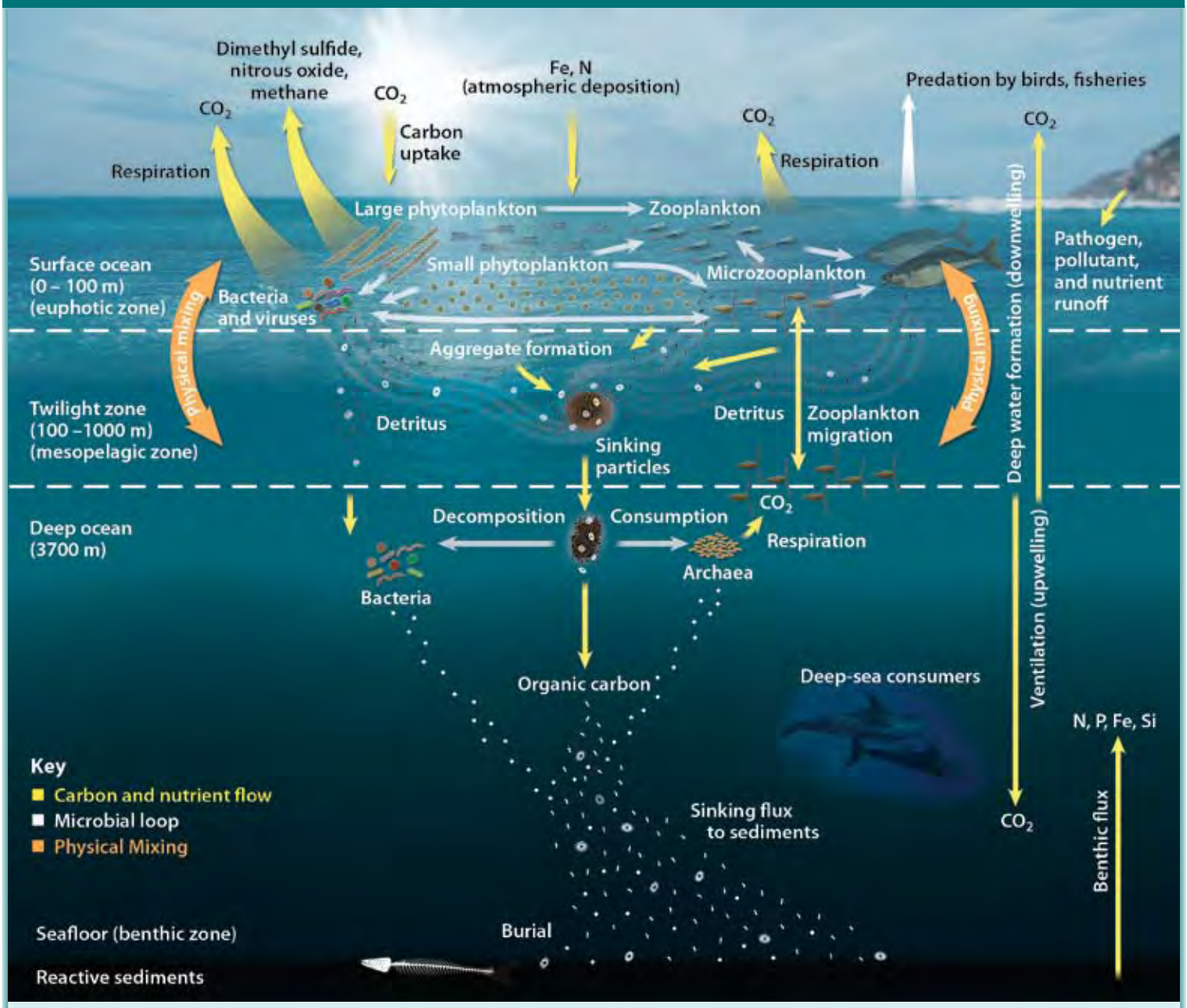
The overall efficiency with which organic carbon is exported to the deep ocean depends on the type of photoautotrophic cells that create the organic material and the efficiency with which heterotrophic organisms respire it.

Carbon Flow and Fate

Carbon fixed in phytoplankton eventually enters the water column as either particulate or dissolved organic carbon through direct exudation, consumption by grazing zooplankton, viral lysis, or cell death. Subsequently, most of this carbon material is degraded by heterotrophic bacteria, resulting in particulate solubilization and conversion of organic carbon back to CO_2. Some of the organic matter, however, sinks intact to the underlying twilight zone (the ocean's barely lit middle layer) and beyond, where lower temperatures, lack of oxygen, and other factors significantly slow degradation.

CO_2 fixed during photosynthesis by phytoplankton in the upper ocean can be transferred to the depths via three major processes: passive sinking of particles, physical mixing of particulates and dissolved organic matter through currents, and active transport by zooplankton migrating to deeper waters. Detrital particles and organic matter associated with mineral structures from phytoplankton, for example, may resist rapid microbial degradation and sift down as flakes, also called marine snow, becoming platforms for microbes to live on. As this particulate organic matter falls deeper, it can cluster with other small particles, such as zooplankton fecal pellets, molts, and larvacean houses, to form larger, heavier aggregates held together by a polysaccharide matrix. The carbon in these particles can be isolated from exchange with the atmosphere for centuries to millennia before upwelling currents return it and other nutrients from the deep ocean to warm surface waters. Some carbon is lost at each step of the way, however, as the organisms involved consume or degrade the organic carbon and remineralize it to CO_2 through respiration.

However, if climate change and ocean acidification significantly alter marine ecosystems' functions, the efficiency of this biologically mediated ocean carbon export may change, leading to an indirect effect on the net annual uptake of carbon.



Oceanic Food Web.

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Key Research Questions

1. **What are the potential impacts of climate change on carbon cycle pathways and fluxes mediated by microbes and the remainder of the marine food web?**
2. **What are the uncertainties associated with these predictions?**

biological processes carrying out more than 80% of the pumping (Gruber and Sarmiento 2002; Sarmiento and Gruber 2006). Atmospheric concentrations of CO_2 would be much higher in the absence of these ocean processes, and climate-driven changes in ocean circulation, chemical properties, or biological rates could thus result in strong feedbacks to the atmosphere. Moreover, records from ice cores indicate these processes are highly sensitive to shifts in atmospheric CO_2 concentration.

The biological pump is driven by phytoplankton inhabiting sunlit surface waters (see sidebar, Marine Food Web and the Carbon Cycle, with figure, Oceanic Food Web, pp. 80–81), and shifts in microbial community composition and function can have large impacts on the ultimate fate of carbon. Most organic matter produced by photosynthesis in surface waters is consumed for respiratory processes (either by phytoplankton or other organisms) and is returned to the atmosphere as CO_2. However, some fraction of this material sinks to the deep ocean. The ratio of export to primary production depends upon many factors, particularly the physiology and composition of phytoplankton that dominate surface waters, rates of mortality resulting from grazing and predation, and the efficiency of microbial processes that degrade dissolved and particulate organic material. Unlike terrestrial systems, which have a large living biomass with resultant inherent stability amid climate variability, ocean systems have very low resident biomass. The rapid rates and high efficiencies of carbon turnover in marine systems thus make biological processes in the surface ocean highly susceptible to shifting environmental variables. Predicting these potential effects on a global scale requires a better understanding of microbial community structure, function, and dynamics that will lead to more robust and predictive models of biogeochemical cycles in marine systems.

Nitrification and denitrification, two key processes that set the pace of the nitrogen cycle, are carried out by microbes. Researchers estimate that half of all microbially mediated nitrogen fixation occurs in the oceans, with planktonic archaea potentially playing a primary role in subeuphotic zone nitrification (Karl et al. in press). Additionally, greater amounts of wind-blown dust arising from drought-stricken areas are being deposited in oceans. Metals carried in this dust, including iron, are likely to affect marine microbial communities and the cycles they carry out. Marine microbes also may play a role in cloud formation by cycling compounds such as dimethyl sulfide into the atmosphere.

The oceans' future capacity as a carbon sink is uncertain because of potential (and currently uncharacterized) feedbacks among global climate change, ocean circulation, and the microbial communities that actively cycle carbon. These natural ocean carbon biosequestration processes are affected by the amount and availability of organic and inorganic pools of nitrogen, phosphorus, oxygen, and many other chemical species. A better understanding of the mechanisms and pathways governing these biogeochemical processes is critical for determining the magnitude of the oceans' capacity to mitigate changes in atmospheric CO_2 concentrations. Integrating genomics, transcriptomics, and proteomics with ecological, biophysical, and chemical techniques is necessary for delineating fundamental physiological processes, understanding their regulation, and determining how they relate to biogeochemical cycles.

Linking Microbial Community Structure to Biogeochemical Cycling of Carbon in Marine Systems

Many critical biological processes directing oceanic carbon cycling remain poorly understood. Particularly unclear is how these processes contribute to the formation of organic carbon compounds, their chemical character, and the biological and environmental factors governing their subsequent fate. Small perturbations in biological processes controlling the production or consumption of dissolved organic carbon pools in oceans could strongly affect the biological pump's functioning and thus the balance between oceanic and atmospheric CO_2. The uncertainty associated with these disruptions severely complicates efforts to represent many key microbially mediated processes in models of oceanic biogeochemical cycling and to predict potential impacts of climate change.

The phylogenetic composition of marine microbial communities plays an important role in the eventual fate of fixed organic carbon. For example, diatoms and coccolithophores are associated with distinct mineral structures (silicate and calcium carbonate, respectively) that affect the rate at which carbon fixed by these organisms is exported to deeper waters. The detritus from communities dominated by these algal phytoplankton types is expected to sink more rapidly than purely organic particles. Moreover, the mineral matrix of this detritus protects a fraction of the associated organic matter from heterotrophic respiration as the material sinks. Studies of material from sediment traps indicate a stronger association between calcium carbonate and organic matter below 1000 m than between silicate and organic matter at such depths. These findings suggest coccolithophore communities' importance in driving a more efficient biological carbon pump relative to diatoms or purely organic organisms (Klaas and Archer 2002). More research is needed to fully understand how community composition of primary producers influences the relative rates of carbon export from surface waters.

Mortality of primary producers, which may arise from viral lysis, grazers, predation, or simple aggregation and sinking, strongly influences the flow of carbon through the marine food chain. Developing a predictive understanding of these processes is essential for understanding the marine carbon cycle and anticipating potential impacts of climate change. Research has highlighted the specificity of interactions between microbial populations and forces driving mortality, but its magnitude and drivers in the natural environment are poorly understood. In particular, uncertainty surrounds the role of viruses as predators in marine food chains. Very little is known about the rates at which populations are infected, transformed, and lysed by viruses in the natural environment or the effective "epidemiology" behind such events. Combining targeted metagenomics with proteomics-based activity measurements ultimately can reveal the mechanisms directing prey selection or susceptibility to viral mortality.

Bacterial heterotrophs also significantly influence oceanic carbon cycling. These microbes largely govern the final fate of fixed carbon in marine systems and are responsible for most organic-matter transformation, solubilization, and subsequent remineralization occurring in the water column. Despite the crucial role of bacterial heterotrophs in mediating these processes, little is known about

Key Research Questions

1. **How are microbial community metabolic processes in marine habitats linked to the global carbon cycle, and how are these processes integrated across genetic, organismal, community, and ecosystem scales?**
2. **How is the structure of heterotrophic microbial communities in marine systems determined by dissolved organic matter composition and nutrient limitations?**
3. **How do environmental, ecological, and physiological factors interact to dictate pathways and regulate the flows of carbon and other elements through upper-ocean ecosystems?**

their identities, the key genes and proteins involved in organic-matter degradation, relative degradation rates of various types of compounds, and which factors control partitioning of carbon between particulate matter and dissolved organic carbon. The latter is particularly critical because, in some situations, dissolved organic carbon may be exported more efficiently to the deep ocean than particulate matter (Hopkinson and Vallino 2005).

Interactions Between the Marine Carbon Cycle and Other Relevant Biogeochemical Cycles (Nitrogen, Phosphorus, Iron, and Sulfur)

Although primary producers in ocean surface waters have plentiful supplies of water and light, these organisms' growth is limited by the relative scarcity of inorganic nutrients such as nitrate, phosphorus, and iron (see sidebar, Marine Nutrient Cycling, p. 92). Such nutrients become available to surface planktonic communities almost exclusively through upwellings of deeper, nutrient-laden waters or by transfer from terrestrial landmasses via, for example, runoff and atmospheric aerosols. A fundamental discovery in oceanography related to nutrient availability is the relatively constant ratio between carbon, nitrogen, and phosphorus in bulk oceanic particulate matter. This proportion, called the Redfield ratio, is 106C:16N:1P. Dissolved concentrations of these elements exhibit a similar but more variable ratio. Current biogeochemical models tend to use data from one element (typically nitrogen) to determine carbon pools using the Redfield ratio. Very small changes in the Redfield ratio of sinking particulate or dissolved organic matter can have potentially large impacts on estimates of global carbon flux. However, the particular processes and pools that might be most affected by these shifts remain unclear.

Unlike nitrogen and phosphorus, iron is not found in a constant ratio to carbon. In fact, ratios in phytoplankton range from 30,000C:1Fe to 500,000C:1Fe, possibly reflecting the importance of iron as a critical nutrient limiting primary productivity. Determining the factors regulating carbon-iron ratios in planktonic communities under different environmental conditions is essential for understanding carbon flow through these communities. Furthermore, iron availability in the open ocean potentially could undergo significant shifts as a result of global climate change or altered human activities. For example, increasingly arid continental interiors could cause greater quantities of iron to enter the atmosphere as dust aerosol and subsequently be redistributed to ocean surface waters. Such alterations could have profound effects on marine primary productivity and thus require further research to improve predictive capabilities.

In addition to their direct impact on carbon flow and fate, the iron and nitrogen biogeochemical cycles are interlinked with that of sulfur in ways having difficult-to-predict effects on nutrient availability and climate drivers. For example, nitrogen and sulfur may help facilitate the transformation of atmospheric iron into a form readily available to primary producers. Before phytoplankton can use iron within incoming dust aerosol, the element must be shifted from the Fe(III) to Fe(II) form through a combination of complexation and photoreduction chemistry. Mechanisms driving these reactions are poorly understood but seem to be favored under lower-pH, or acidic, conditions. The flow from sea to air of dimethyl sulfide

(DMS) and ammonia (NH_3)—the volatile, reduced gaseous forms of sulfur and nitrogen—controls the acidity of hydrometeors (i.e., atmospheric water particles) over much of the ocean surface and thus influences iron reduction. Shifts in the magnitude of ecological processing resulting from climate change may alter flows of both DMS and NH_3, impacting iron bioavailability from the bottom up.

Understanding the critical couplings between these cycles requires studying carbon cycle interrelationships with nitrogen, phosphorus, iron, and sulfur in the context of coupled physical-biological models. After exploring and refining the contrasting hypotheses in models, results must be used to design more insightful field experiments and observational strategies for marine ecosystems.

Key Research Questions

1. **What are the effects of the availability of nitrogen, phosphorus, iron, and other micronutrients on biogeochemical cycling and biosequestration of carbon by microbial communities?**
2. **How does chemical processing in the troposphere link and affect terrestrial and ocean systems? How do these systems in turn impact tropospheric activity, with the air pollution–iron mobilization interaction as a primary example?**

Omic and Systems Biology Approaches to Understanding the Marine Carbon Cycle

Integrated understanding of biological processes relevant to marine carbon cycling requires ecological approaches to study relationships of both individual organisms and whole communities in an environment. A major limitation in understanding biogeochemical cycling in oceans, as in most environments, is the inability to cultivate microorganisms of interest and study them under laboratory conditions. Even in cases in which physiological processes in cells under isolated conditions can be measured, extrapolation of laboratory results to natural environments can be misleading because of these systems' highly variable physiochemical conditions and complex webs of community interactions. Fortunately, DNA fragments from mixed microbial communities can now be extracted and characterized directly from environmental samples. This approach has provided novel insights into the ecology, evolution, and metabolism of uncultured microorganisms in nature (see sidebar, Marine Metagenomic Studies, p. 93).

Metagenomics, metatranscriptomics, and metaproteomics (collectively referred to as metaomic approaches) provide information on the identity, abundance, and physiology of marine microbes carrying out carbon fixation or degradation processes (see sidebar, Marine Metagenomics and the Discovery of Proteorhodopsin, p. 94). Such approaches also enable linked studies of community structure and function. Moreover, previous research has demonstrated reproducible patterns in marine microbial community structure that is predictive of physical and chemical conditions in the oceans (Morris et al. 2005; Fuhrman et al. 2006). By combining information from both isolated and environmental omic studies, scientists can begin to characterize mechanisms of carbon assimilation and transformation and develop biological indicators to measure these activities in situ.

The necessary integrated research approach for achieving such advances requires continued identification of model organisms that can be cultured and used for whole-genome sequencing; laboratory-based experimentation; and discovery of key genes, proteins, and pathways. Specifically, such studies could reveal which compounds an organism or group of organisms has the potential to use and which ones are being exploited under a defined set of conditions. The effectiveness of these approaches can be enhanced further when combined with rate studies, stable-isotope techniques, and pulse-labeling to measure species- or

lineage-specific contributions to ecosystem function. Identifying target genes, proteins, and pathways can catalyze development of high-throughput omic approaches for new sensors and field experiments. In situ omic information on microbial function is crucial for providing more-accurate data to inform modeling of marine biogeochemical carbon cycling. However, these approaches require improved analytical techniques, such as combining flow cytometric sorting and mass spectrometry of proteins and developing automated devices that can collect high-resolution environmental measurements on microbial community composition and function. By focusing on biogeochemical processes at ocean interfaces and along existing gradients, scientists can use variability within the system to inform experiments and predict ecosystem response to future perturbations.

Integration of Experiments, Observations, and Modeling Efforts

Emerging views of carbon cycling in upper-ocean ecosystems continue to affirm the importance of diverse and multifaceted interactions among marine biota and their environment across all levels of biological, spatial, and temporal complexity. However, characterizing these relationships with traditional approaches is extremely challenging. For example, the spatial scales of interaction between diverse biota and environmental conditions range from molecular to global. This variation demands creative, coordinated approaches to synergistic observational and modeling activities emphasizing the links between models and data derived from environmental observations and experiments (see Fig. 6.1. Modeling Marine Ecosystems: Genomes to Biogeochemical Cycles, p. 88).

Significant observational challenges hamper sustainable long-term monitoring of the genetic, biochemical, and ecological diversity of planktonic communities and their associated rates of carbon and energy transfer. Overcoming these challenges requires development of observational capabilities in conjunction with modeling frameworks readily capable of leveraging or assimilating data to identify strategic ocean and coastal sites for study. These efforts should be coupled with controlled experiments to study links among genetic, physiological, biochemical, and ecological information of important organisms that can be incorporated into models and investigated with hypothesis-driven approaches in natural environments. Ocean observatory facilities will provide critical infrastructure for such investigations. Emerging methods are enabling assessment of genetic and taxonomic diversity at the scales of relevant physical and geochemical forcing—or shifting of the climate system. New omic approaches must be adapted to provide critical links between environmental forcing and ecosystem structure and function. However, efforts to establish such links are in their infancy, requiring further research to connect microbial genetic characterizations, as well as genomic and metagenomic data, to questions on global biogeochemical cycles and climate change. Furthermore, global-scale ecodynamic models, which focus on primary producers, should include more-robust descriptions of marine heterotrophic processes, including predators and heterotrophic microbes, that currently are poorly represented.

New individual channels for modeling geochemical data are required to represent global change feedbacks on key marine microbial processes, including organic-compound recycling in the central ocean, nitrogen cycling by chemoautotrophs,

and biogeochemical functioning of abundant but understudied classes of organisms such as marine crenarchaea. Also needed are systems biology laboratory studies of model organisms and consortia that can improve understanding of environmentally important functional capabilities, resource allocation, and metabolic tradeoffs. Such studies can be followed by various metaomic approaches to characterize distributions, abundances, and in situ activities of related classes of organisms in the environment. Resulting information could then lead to process parameterizations for large-scale climate and biogeochemistry models incorporating stochastic, self-determining ecosystems.

Models representing climate change and carbon cycling rely heavily on observed ecological-response data. These observational data are gathered, processed, and parameterized into new models by various means. The amount and diversity of such data are exploding because of increasingly sophisticated metagenomic studies and development of new sensor technologies, remote-sensing methods, and ever-expanding numbers of networked sensors operating in real time (see Fig. 6.2. Oceanic Measurement Technologies, p. 89). This data explosion extends beyond traditional definitions of ecological observations by including quantitative measurements of how individual and communities of organisms carry out carbon cycling processes in biological and geobiological systems. Incorporating more experimental and observational data into predictive climate change and carbon cycling models will require assimilating information from not only traditional ecological measurements but also those derived from high-throughput biological observations and investigations.

Key Research Questions

1. **What are the physical and biological scales for biota-environment interactions most critical in regulating changes in ocean carbon fluxes over seasonal, interannual, and decadal time frames?**
2. **Which scales must be resolved in space and time and with respect to ecological diversity to better constrain predictions of changes in carbon flux?**
3. **How do we organize the explosion of data from metagenomic studies, place-based and remote-sensing efforts, and other data-intensive investigations? How can this information be used to enhance fidelity and efficiency in large-scale ecodynamic models? To what degree can the data-assimilation process be automated?**

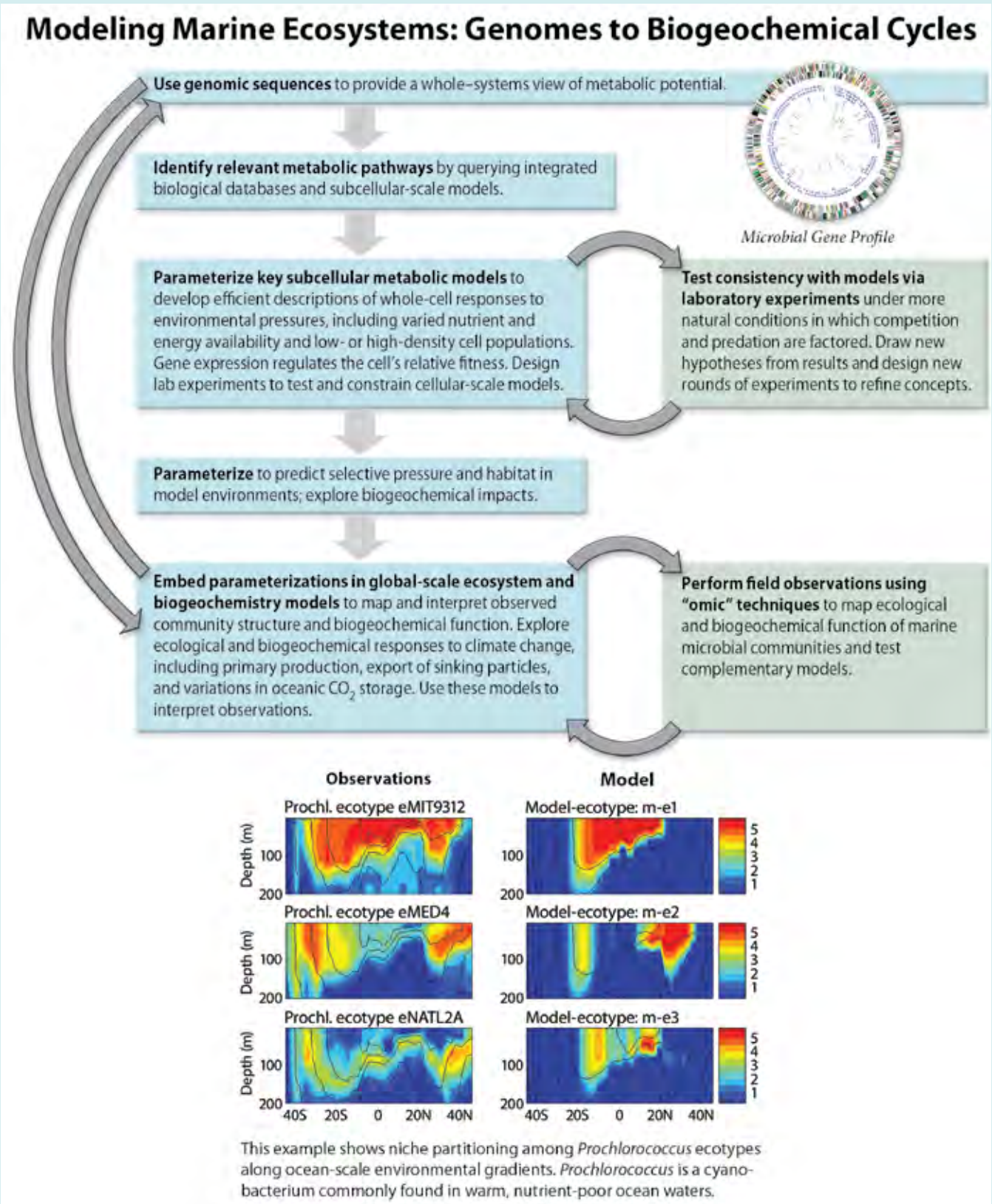


Fig. 6.1. Modeling Marine Ecosystems: Genomes to Biogeochemical Cycles. Depicted are observed and modeled distributions of ecotypes of *Prochlorococcus* [log (cells ml^{-1})] along a meridional transect in the Atlantic Ocean. Black lines indicate isotherms. Observations are from Johnson et al. (2006). Model ecotypes that qualitatively reflected real-world counterparts in terms of *Prochlorococcus* geographic habitat, ranking of abundance, and physiological specialism were emergent in the self-assembling model of global phytoplankton communities (Follows et al. 2007). [Source of Observations and Model graphs: Reprinted with permission from *Science* and AAAS.]

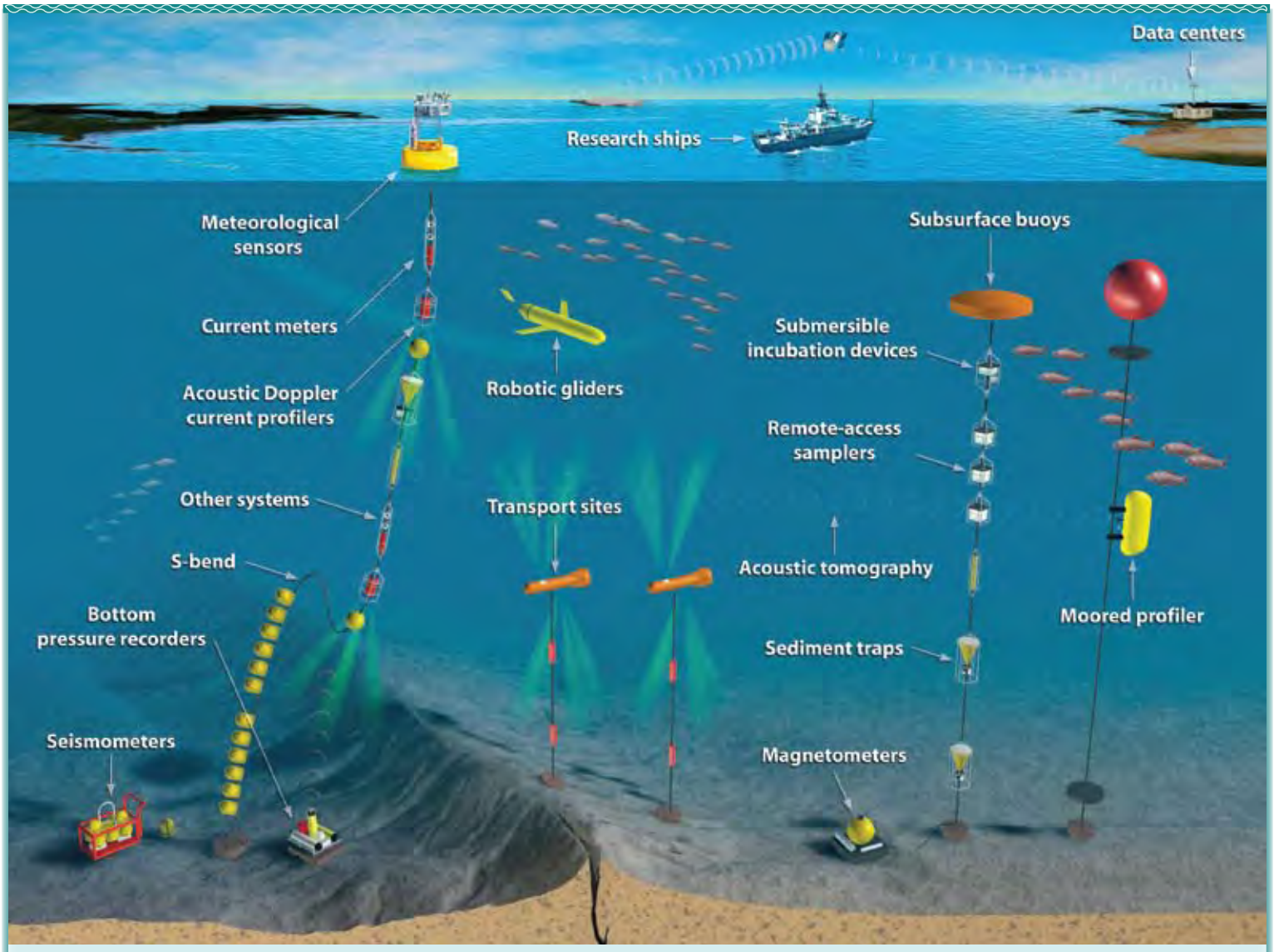


Fig. 6.2. Oceanic Measurement Technologies. A range of different sensors are used to measure meteorology, climate, physical oceanography, water transport, biogeochemistry, carbon cycle, biology, and geophysics. [Source: Cooperative Institute for Climate and Ocean Research, Woods Hole Oceanographic Institution. 2006. "OceanSITES: Taking the Pulse of the Global Ocean," http://www.oceansites.org/documents/oceanSITESbrochure.pdf. Illustration by Jack Cook, Woods Hole Oceanographic Institution.]

Meteorological sensors atop a surface buoy provide data for calculating heat, water, and momentum exchange between air and ocean. The self-reliant buoys carry batteries, solar panels, two satellite transmitters (in case one fails), and a GPS locator. Instruments in the hull record sea temperature, salinity, oxygen content, and carbon dioxide.

Current meters record current speed, direction, temperature, and salinity to produce a motion picture of flow and mixing in the water column.

Acoustic Doppler current profilers emit high-pitched pings and measure their echoes to calculate current speed at regular intervals in the water column.

Other systems record dissolved oxygen, light levels, photosynthetic activity, and nutrients like nitrogen, phosphorus, and silica.

Engineers build an **S-bend** in the mooring line to reduce the tension between anchor and buoy during heavy seas.

Bottom pressure recorders can sense the pressure from a passing tsunami wave, then beam a warning to a surface buoy.

Seismometers measure earthquakes in the seafloor.

Robotic gliders monitor precise locations on the fly, without requiring ship time or mooring hardware.

Transport sites measure water moving in important ocean currents. Rows of buoys placed in the deep ocean measure currents, temperature, and salinity. The data help scientists calculate how much water is moving from one ocean basin to another.

Subsurface buoys are good choices for studying the deep ocean. These moorings are not exposed to surface waves, so they get much less wear and tear than surface buoys.

Submersible incubation devices incubate seawater samples to measure phytoplankton productivity.

Remote-access samplers automatically do routine prep work, like filtering seawater, and then store the samples in individual jars to be analysed for nutrients, phytoplankton, or zooplankton.

Acoustic tomography sends sound waves long distances to calculate temperature and track warming across entire ocean basins.

Sediment traps collect falling "marine snow" (dead organic matter). They provide key data on how carbon cycles in the ocean.

Magnetometers measure changes in the Earth's magnetic field during earthquakes.

Subsurface moorings often are deployed in pairs. One line supports a **moored profiler**, which crawls up and down the cable measuring temperature, salinity, and currents. Instruments on the sister mooring measure different variables at fixed depths.

Research ships sample water for in-depth biogeochemical analyses.

Data centers receive buoy data, check quality, and serve calibrated data to the Internet.

CO_2 Absorption and Ocean Acidification

Rising atmospheric CO_2 concentrations are altering the chemical makeup of ocean waters, making them more acidic. Over the last 200 years, nearly half the CO_2 emitted from the burning of fossil fuels—about 525 billion tons—has dissolved into ocean surface waters (Sabine et al. 2004), lowering their pH by 0.1 units. The figure below shows the water column inventory of anthropogenic CO_2 in the oceans.

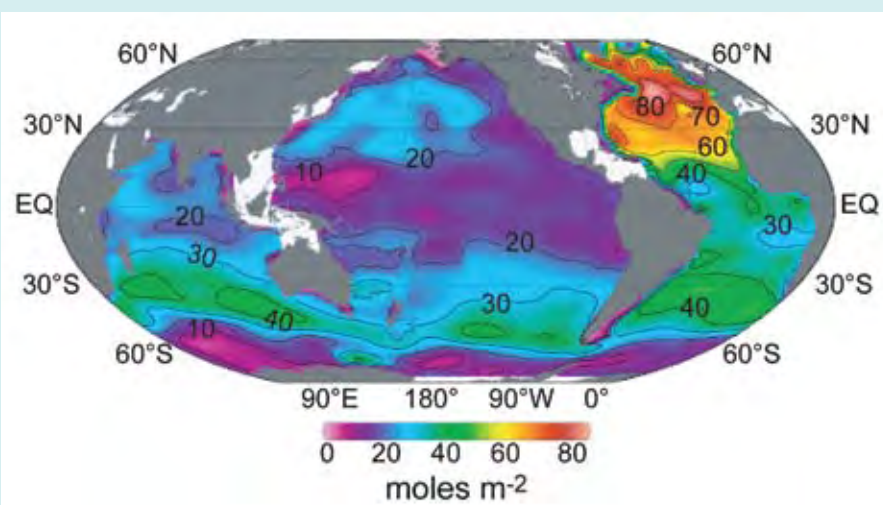
If CO_2 emissions keep rising at current rates, the average surface seawater pH level, which typically ranges from 7.8 to 8.2, could decline another 0.3 to 0.4 units by 2100 (IPCC 2007). Such a level would represent the lowest pH of the upper ocean in many millions of years and would constitute a rate of change 100 times greater than at any time spanning this period (Caldeira and Wickett 2003). The pH drop of 0.1 units observed to date is equivalent to a 30% increase in surface-water acidity. A further decrease of 0.3 to 0.4 pH units would translate to a 100% to 150% increase in acidity.

Oceans remove roughly 30% of the CO_2 emitted annually to the atmosphere. The resulting increasingly acidic waters could threaten a wide range of marine organisms—from microscopic phytoplankton and shellfish to massive coral reefs—as well as the food webs depending on them (see sidebar, Marine Food Web and the Carbon Cycle, pp. 80–81). Consequently, the oceans' capacity to absorb excess CO_2 could decline with alteration in trophic cascades, reducing the oceans' ability to mitigate global warming.

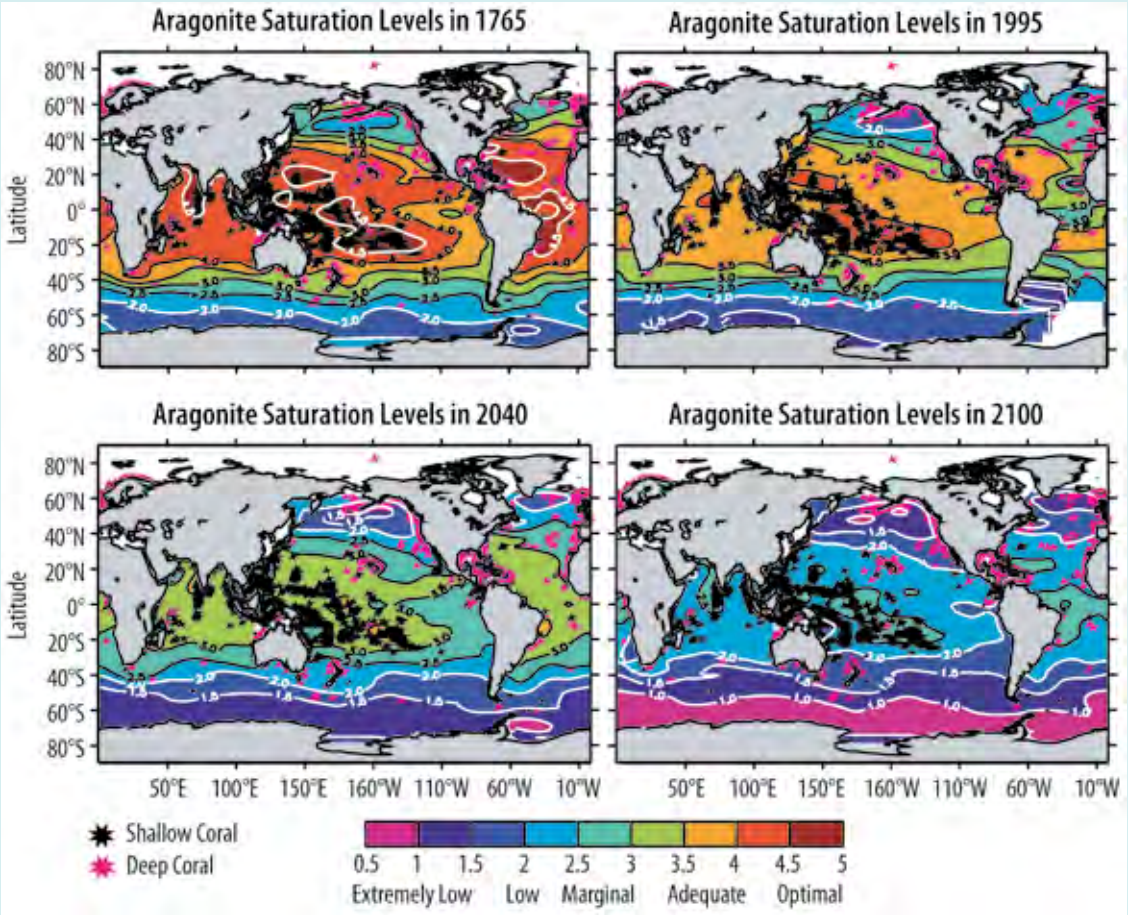
The Nature of Possible Biological Impacts

Calcium carbonate structures important for microorganism formation have two distinct mineral forms—calcite and aragonite. Each form has a different solubility, or tendency to dissolve in seawater, measured by what is known as the saturation rate. This rate, in turn, depends on the oceanic concentration of calcium, carbonate, and depth or pressure. Marine calcium concentrations are relatively constant; thus shifting carbonate concentrations determine rates of calcium carbonate formation.

If the saturation horizon moves closer to the surface, already-formed calcium carbonate could start to dissolve, decreasing concentrations of compounds marine organisms need to maintain shells or build new ones. Especially vulnerable are calcifying organisms that construct aragonite structures [e.g., corals and pteropods (tiny planktonic marine snails)] because this form of calcium carbonate is more soluble than calcite (Orr et al. 2005). Other organisms, including coccolithophores (microscopic algae) and foraminifera (microscopic protozoans), build skeletal structures of the more-resistant calcite. The figure, next page, shows the shifting aragonite saturation levels in the global oceans and the impact on coral formation.



Water Column Inventory of Anthropogenic CO_2 in the Ocean (mol m^{-2}). High inventories of anthropogenic CO_2 are associated with deep-water formation in the North Atlantic and intermediate and mode water formation between 30° and 50°S. Total inventory of shaded regions is 106 ± 17 Pg C for 1994. (Red and green indicate high amounts of carbon storage; purple and blue areas contain less carbon.) [Source: Sabine, C. L., et al. 2004. "The Oceanic Sink for Anthropogenic CO_2," *Science* **305**, 367–71. Reprinted with permission from AAAS.]



Aragonite (Form of Calcium Carbonate) Saturation Levels Shown from Before the Industrial Revolution to 2100, and How These Saturation Levels Affect the Growth of Both Shallow and Deep Corals. Before the Industrial Revolution, large bands of the tropical ocean were optimal for growth. By 2040, these same bands are projected to be only adequate, and by 2100 (in the IS92 business-as-usual scenario, Orr et al. 2005), most areas are only marginal at best. [Source: Ocean Acidification Network FAQs at http://ioc3.unesco.org/oanet/FAQacidity.html. From Feely, R. A., et al. In press. "Present and Future Changes in Seawater Chemistry due to Ocean Acidification," AGU Monograph on *The Science and Technology of Carbon Sequestration*. Eds. B. J. McPherson and E. T. Sundquist.]

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Marine Nutrient Cycling

In the ocean, nutrients fuel the production of organic matter and the sinking of carbon. Microscopic marine phytoplankton transform nitrogen-, iron-, phosphorus-, and sulfur-containing compounds in ways affecting these nutrients' availability for biological production and, consequently, influence on the global climate. Of these four nutrient cycles, nitrogen is the most complex, given the diversity of nitrogen metabolism and its existence in numerous inorganic and organic forms and oxidation states.

Nitrogen cycling consists of five main processes whose descriptions follow.

- **Fixation** through metabolic processes, whereby microbes transform atmospheric nitrogen (N_2) into ammonium, a form useful to organisms.
- **Uptake** via the growth of organisms that assimilate the element into organic matter.
- **Mineralization** or decay, by which much of the nitrogen within dead organisms is converted back to ammonium for use by plants or for further transformation into nitrate via **nitrification**.
- **Denitrification**, which returns nitrate to the atmosphere as N_2 and nitrous oxide, a volatile and highly potent greenhouse gas. This process results in the loss of biologically available nitrogen from the ocean system.

Iron, a scarce micronutrient, limits both primary production (Coale et al. 1996) and nitrogen fixation in many areas of the ocean (Falkowski 1997). Iron is highly reactive and quickly removed from the water column by biological uptake as well as scavenging and desorption onto sinking particles. Inputs from the atmosphere are an important source of iron for marine systems, and some open-ocean regions exhibit enhanced productivity following remote dust events.

Phosphorus is cycled as either inorganic or organic phosphate—with no major gaseous intermediate—making it distinct from other nutrient cycles. During this cycling, the only existing form of inorganic phosphate is transformed into an organic compound and back again. Under natural conditions, phosphorus is the slowest nutrient cycle because of the gradual rate at which phosphate salts are released from rocks and soils through weathering. Consequently, phosphorus often is a limiting agent in plant and algae growth, particularly in freshwater systems. In oceans, phosphorus concentrations can vary significantly with depth, with biologically productive surface layers generally containing less phosphorus than deeper waters.

Sulfur cycling largely parallels the nitrogen cycle, with the exception of sulfur fixation from the atmosphere to land or water. Marine phytoplankton affect the sulfur cycle by producing dimethylsulfoniopropionate (DMSP), a precursor to dimethyl sulfide (DMS) that, when oxidized, becomes sulfate. The flux of DMS from ocean surface waters is the predominant source of sulfur to the atmosphere (Kettle and Andreae 2000). Once there, DMS-derived sulfate aerosol particles may cool the Earth system by reflecting solar radiation back into space and by promoting cloud formation or modifying cloud properties. Additionally, atmospheric sulfur deposition can lead to surface-water acidification, impairing the uptake of other nutrients, especially phosphate.

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Marine Metagenomic Studies

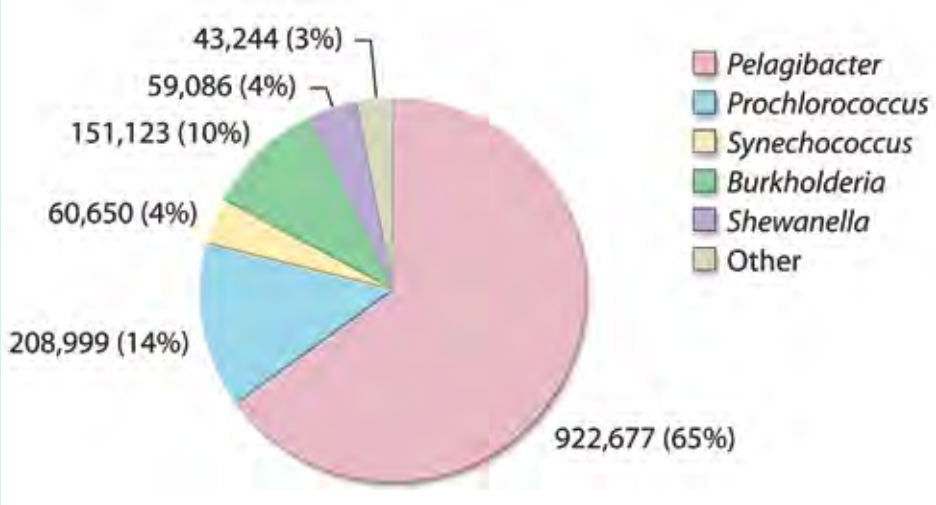
In the largest metagenomic survey to date—the Global Ocean Sampling (GOS) expedition—an enormous amount of genomic diversity was found among upper-ocean microbial communities. High-throughput DNA sequencing and computational genomics produced a massive dataset of more than 6 million new genes and thousands of new protein families that include a wide range of novel metabolic pathways.

This gene catalogue includes and extends the results of an earlier metagenomic pilot project conducted in 2003 to study the genomic diversity of microbes collected from the nutrient-poor Sargasso Sea near Bermuda. That project alone led to the discovery of more than a million new genes and the identification of more than 1800 species in an area thought to be low in diversity. DNA shotgun sequencing also verified both the abundance and variety of a new class of light-harvesting proteins, suggesting they play a potentially important role in energy metabolism under low-nutrient conditions (see sidebar, Marine Metagenomics and the Discovery of Proteorhodopsin, p. 94).

To study the global extent of this genomic diversity, as well as how different environmental pressures might be reflected in organisms and communities residing in heterogeneous ocean biomes, the GOS study covered an 8000-km transect extending from the North Atlantic through the Panama Canal and ending in the South Pacific. Forty-one different samples were collected from a wide variety of surface waters (mostly marine). Major differences were found at almost every site, and researchers could determine from where in the ocean a sample was derived by its DNA sequence alone.

Surprisingly, despite the wealth of diversity and variation found at the gene and protein levels, only five bacterial genera dominate the GOS sequence data: *Pelagibacter*, *Prochlorococcus*, *Synechococcus*, *Burkholderia*, and *Shewanella* (see figure below).

Further studies are expected to help elucidate key biological processes that eventually could offer new solutions to address climate change and other environmental issues.



Dominant Bacterial Genera and Global Ocean Survey Sequences Aligning to Them. Indicated are the numbers and percentages of sequence reads that aligned with the reference genomes from five dominant bacterial genera and all other reference genomes. [Source: Figure adapted by permission from Macmillan Publishers Ltd. From Koonin, E. V. 2007. "Metagenomic Sorcery and the Expanding Protein Universe," *Nature Biotechnology* **25**(5), 540–41.]

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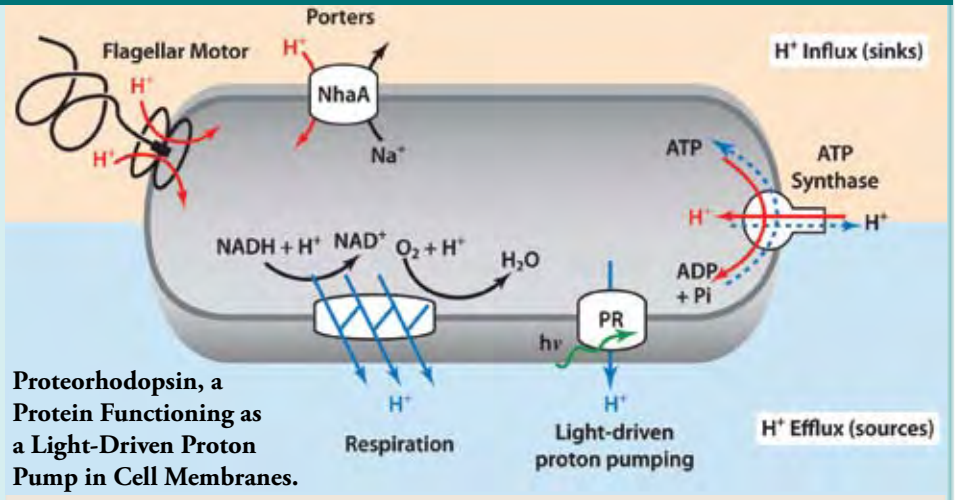
Marine Metagenomics and the Discovery of Proteorhodopsin



Proteorhodopsin, a Protein Functioning as a Light-Driven Proton Pump in Cell Membranes.

[Source: Lawrence Berkeley National Laboratory. 2007. "Research News: Shedding New Light on Proteorhodopsin," http://www.lbl.gov/Science-Articles/Archive/PBD-proteorhodopsin.html. Image used with permission and adapted from original figure in Walter, J. M., et al. 2007. "Light-Powering *Escherichia Coli* with Proteorhodopsin," *Proceedings of the National Academy of Sciences of the USA* **104**(7), 2408–12. doi: 10.1073/pnas.0611035104. Copyright (2007) National Academy of Sciences, USA.]

Although surface waters in the open ocean receive ample sunlight to fuel photosynthetic growth, concentrations of dissolved organic carbon, a photosynthetic byproduct, typically are very low (less than 200 µmol C per liter). Heterotrophic members of the bacterioplankton community thus are forced to contend with severe carbon substrate limitation, yet the specific metabolic strategies employed by these marine oligotrophs to grow under these conditions are just being discovered. As in many environments, the lack of insight arises primarily from difficulties inherent in cultivating relevant organisms in a laboratory setting. New metagenomic approaches, however, are overcoming this challenge by characterizing microbial DNA directly from the environment.

Metagenomic sampling of microbial communities in the open ocean has revealed a surprising new pathway for energy conservation by marine heterotrophs. Proteorhodopsin, a protein functioning as a light-driven proton pump in cell membranes, has been detected in a wide range of ocean habitats. Previously thought to exist only in archaeal extremophiles living in salt ponds, genes encoding these proteins are ubiquitous in marine bacterioplankton such as the SAR cluster, which was originally isolated from samples taken in the Sargasso Sea. In those samples alone, more than 782 rhodopsin-like photoreceptors were identified (Venter et al. 2004). The common occurrence of bacterioplankton harboring this protein in surface waters worldwide suggests a potential mechanism for widespread mixotrophic energy conservation in marine environments. Mixotrophy is a form of growth in which two methods of energy generation are used simultaneously. In this form, bacteria would augment energy derived from the consumption of organic substrates and conserve carbon resources by creating an additional proton gradient using light energy to drive synthesis of ATP, a multifunctional nucleotide responsible for cellular energy transfer and storage (see figure above).

The initial observation of proteorhodopsin in metagenomic samples sparked a series of experiments to test the mixotrophic-growth hypothesis. Expression of the proteorhodopsin gene in *Escherichia coli* confirmed the protein was involved in light-dependent ATP formation. Preparations of bacterial cell membranes collected from ocean surface waters reveal not only high levels of proteorhodopsin, but various types of the protein tuned to absorb different wavelengths of light. This variation suggests ecological specialization for different niches and depths in the water column. Furthermore, experiments using recently cultivated marine heterotrophs equipped with proteorhodopsins have shown that at least some types grow more efficiently under substrate-limited conditions when exposed to light.

Though further field studies are needed to assess the role of proteorhodopsin in marine ecosystems, initial results suggest this novel mode of growth could represent an important new pathway affecting carbon flow and energy conservation in ocean-surface habitats. Proteorhodopsin discovery also represents an important early success story for using metagenomic approaches to detect previously untapped metabolic capabilities, facilitate development of new hypotheses and experiments, and reveal significant components of the global carbon cycle.

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