8.05 Biogeochemistry of Primary Production in the Sea

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As the present condition of nations is the result of many antecedent changes, some extremely remote and others recent, some gradual, others sudden and violent, so the state of the natural world is the result of a long succession of events, and if we would enlarge our experience of the present economy of nature, we must investigate the effects of her operations in former epochs.

Charles Lyell, *Principles of Geology*, 1830

8.05.1 INTRODUCTION

Earth is the only planet in our solar system that contains vast amounts of liquid water on its surface and high concentrations of free molecular oxygen in its atmosphere. These two features are not coincidental. All of the original oxygen on Earth arose from the photobiologically catalyzed splitting of water by unicellular photosynthetic organisms that have inhabited the oceans for at least 3 Gyr. Over that period, these organisms have used the hydrogen atoms from water and other substrates to form organic matter from CO₂ and its hydrated equivalents. This process, the *de novo* formation of organic matter from inorganic carbon, or primary production, is the basis for all life on Earth. In this chapter, we examine the evolution and biogeochemical consequences of primary production in the sea and its relationship to other biogeochemical cycles on Earth.

8.05.1.2 A Primer on Redox Chemistry

The biologically mediated redox reactions cycle carbon through three mobile pools: the atmosphere, the ocean, and the biosphere. Of these, the ocean is by far the largest (Table 1); however, more than 98% of this carbon is found in its oxidized state as CO₂ and its hydrated equivalents, HCO₃⁻ and CO₃²⁻. To form organic molecules, the inorganic carbon must be chemically reduced, a process that requires the addition of hydrogen atoms (not just protons, but protons plus electrons) to the carbon atoms. Broadly speaking, these biologically catalyzed reduction reactions are carried out by two groups of organisms, chemoautotrophs and phototrophs, which are collectively called primary

<table>
<thead>
<tr>
<th>Pools</th>
<th>Quantity (×10¹⁵ g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atmosphere</td>
<td>720</td>
</tr>
<tr>
<td>Oceans</td>
<td>38,400</td>
</tr>
<tr>
<td>Total inorganic</td>
<td>37,400</td>
</tr>
<tr>
<td>Surface layer</td>
<td>670</td>
</tr>
<tr>
<td>Deep layer</td>
<td>36,730</td>
</tr>
<tr>
<td>Dissolved organic</td>
<td>600</td>
</tr>
<tr>
<td>Lithosphere</td>
<td></td>
</tr>
<tr>
<td>Sedimentary carbonates</td>
<td>&gt;60,000,000</td>
</tr>
<tr>
<td>Kerogens</td>
<td>15,000,000</td>
</tr>
<tr>
<td>Terrestrial biosphere</td>
<td></td>
</tr>
<tr>
<td>(total)</td>
<td>2,000</td>
</tr>
<tr>
<td>Living biomass</td>
<td>600–1,000</td>
</tr>
<tr>
<td>Dead biomass</td>
<td>1,200</td>
</tr>
<tr>
<td>Aquatic biosphere</td>
<td></td>
</tr>
<tr>
<td>1–2</td>
<td></td>
</tr>
<tr>
<td>Fossil fuels</td>
<td></td>
</tr>
<tr>
<td>Coal</td>
<td>4,130</td>
</tr>
<tr>
<td>Oil</td>
<td>3,510</td>
</tr>
<tr>
<td>Gas</td>
<td>230</td>
</tr>
<tr>
<td>Other (peat)</td>
<td>140</td>
</tr>
</tbody>
</table>

The second carbon cycle is dependent on the biologically catalyzed reduction of inorganic carbon to form organic matter, the overwhelming majority of which is oxidized back to inorganic carbon by respiratory metabolism (Schlesinger, 1997). This cycle, which is observable on timescales of days to millennia, is driven by reduction—oxidation (redox) reactions that evolved over ~2 Gyr, first in microbes, and subsequently in multicellular organisms (Falkowski *et al.*, 1998). A very small fraction of the reduced carbon escapes respiration and becomes incorporated into the lithosphere. In so doing, some of the organic matter is transferred to the slow carbon cycle. In this chapter, we will focus primarily on this fast, biologically mediated carbon cycle in the sea, and the supporting biogeochemical processes and feedbacks.

8.05.1.1 The Two Carbon Cycles

There are two major carbon cycles on Earth. The two cycles operate in parallel. One cycle is slow and abiotic. Its effects are observed on multimillion-year timescales and are dictated by tectonics and weathering (Berner, 1990). In this cycle, CO₂ is released from the mantle to the atmosphere and oceans via vulcanism and seafloor spreading, and removed from the atmosphere and ocean primarily by reaction with silicates to form carbonates in the latter reservoir. Most of the carbonates are subsequently subducted into the mantle, where they are heated, and their carbon is released as CO₂ to the atmosphere and ocean, to carry out the cycle again. The chemistry of this cycle is dependent on acid–base reactions, and would operate whether or not there was life on the planet (Kasting *et al.*, 1988). This slow carbon cycle is a critical determiate of the concentration of CO₂ in Earth’s atmosphere and oceans on timescales of tens and hundreds of millions of years (Kasting, 1993).

The second carbon cycle is dependent on the biologically catalyzed reduction of inorganic carbon to form organic matter, the overwhelming majority of which is oxidized back to inorganic carbon by respiratory metabolism (Schlesinger, 1997). This cycle, which is observable on timescales of days to millennia, is driven by reduction—oxidation (redox) reactions that evolved over ~2 Gyr, first in microbes, and subsequently in multicellular organisms (Falkowski *et al.*, 1998). A very small fraction of the reduced carbon escapes respiration and becomes incorporated into the lithosphere. In so doing, some of the organic matter is transferred to the slow carbon cycle. In this chapter, we will focus primarily on this fast, biologically mediated carbon cycle in the sea, and the supporting biogeochemical processes and feedbacks.
producers. The organic carbon they synthesize fuels the growth and respiratory demands of the primary producers themselves and all remaining organisms in the ecosystem.

All redox reactions are coupled sequences. Reduction is accomplished by the addition of an electron or hydrogen atom to an atom or molecule. In the process of donating an electron to an acceptor, the donor molecule is oxidized. Hence, redox reactions require pairs of substrates, and can be described by a pair of partial reactions, or half-cells:

$$A_{\text{ox}} + n(e^-) \leftrightarrow A_{\text{re}} \quad (1a)$$

$$B_{\text{red}} - n(e^-) \leftrightarrow B_{\text{ox}} \quad (1b)$$

The tendency for a molecule to accept or release an electron is therefore “relative” to some other molecule being capable of conversely releasing or binding an electron. Chemists scale this tendency, called the redox potential, $E$, relative to the reaction

$$H_2 \leftrightarrow 2\text{H}^+ + 2e^- \quad (2)$$

which is arbitrarily assigned an $E$ of 0 at pH 0, and is designated $E_0$. Biologists define the redox potential at pH 7, 298 K (i.e., room temperature) and 1 atm pressure ($=101.3$ kPa). When so defined, the redox potential is denoted by the symbols $E_0^\circ$ or sometimes $E_{m0}$. The $E_0^\circ$ for a standard hydrogen electrode is $-420$ mV.

### 8.05.2 CHEMOAUTOTROPHY

Organisms capable of reducing sufficient inorganic carbon to grow and reproduce in the dark without an external organic carbon source are called chemoautotrophs (literally, “chemical self-feeders”). Genetic analyses suggest that chemoautotrophy evolved very early in Earth’s history, and is carried out exclusively by prokaryotic organisms in both the Archaea and Bacteria superkingdoms (Figure 1).

Early in Earth’s history, the biological reduction of inorganic carbon may have been directly coupled to the oxidation of H$_2$. At present, however, free H$_2$ is scarce on the planet’s surface. Rather, most of the hydrogen on the surface of Earth is combined with other atoms, such as sulfur or oxygen. Activation energy is required to break these bonds in order to extract the hydrogen. One source of energy is chemical bond energy itself. For example, the ventilation of reduced mantle gases along tectonic plate subduction zones on the seafloor provides hydrogen in the form of H$_2$S. Several types of microbes can couple the oxidation of H$_2$S to the reduction of inorganic carbon, thereby forming organic matter in the absence of light.

Ultimately all chemoautotrophs depend on a nonequilibrium redox gradient, without which there is no thermodynamic driver for carbon fixation. For example, the reaction involving the oxidation of H$_2$S by microbes in deep-sea vents described above is ultimately coupled to oxygen.

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**Figure 1** The distribution of autotrophic metabolic pathways among taxa within the three major domains of life (as inferred from $^{16}$S ribosomal RNA sequences (Pace, 1997)). Specific metabolic pathways are indicated.
in the ocean interior. Hence, this reaction is dependent on the chemical redox gradient between the ventilating mantle plume and the ocean interior that thermodynamically favors oxidation of the plume gases. Maintaining such a gradient requires a supply of energy, either externally, from radiation (solar or otherwise), or internally, via planetary heat and tectonics, or both.

The overall contribution of chemoautotrophy in the contemporary ocean to the formation of organic matter is relatively small, accounting for <1% of the total annual primary production in the sea. However, this process is critical in coupling reduction of carbon to the oxidation of low-energy substrates, and is essential for completion of several biogeochemical cycles.

8.05.3 PHOTOAUTOTROPHY

The oxidation state of the ocean interior is a consequence of a second energy source: light, which drives photosynthesis. Photosynthesis is a redox reaction of the general form:

\[
2H_2A + CO_2 + \text{light} \rightarrow (CH_2O) + H_2O + 2A
\]

where A is an atom, e.g., S. In this formulation, light is specified as a substrate, and a fraction of the light energy is stored as chemical bond energy in the organic matter. Organisms capable of reducing inorganic carbon to organic matter by using light energy to derive the source of reductant or energy are called photoautotrophs. Analyses of genes and metabolic sequences strongly suggest that the machinery for capturing and utilizing light as a source of energy to extract reductants was built on the foundation of chemoautotrophic carbon fixation; i.e., the predecessors of photoautotrophs were chemoautotrophs. The evolution of a photosynthetic process in a chemoautotroph forces consideration of both the selective forces responsible (why) and the mechanism of evolution (how).

8.05.3.1 Selective Forces in the Evolution of Photoautotrophy

Reductants for chemoautotrophs are generally deep in the Earth’s crust. Vent fluids are produced in magma chambers connected to the Athena-sphere. As such, the supply of vent fluids is virtually unlimited. While the chemical disequilibrium between vent fluids and bulk seawater provides a sufficient thermodynamic gradient to continuously support chemoautotrophic metabolism in the contemporary ocean, in the early Earth the oceans would not have had a sufficiently large thermodynamic energy potential to support a pandemic outbreak of chemoautotrophy. Moreover, magma chambers, vulcanism and vent fluid fluxes are tied to tectonic subduction and spreading regions, which are transient features of Earth’s crust and hence only temporary habitats for chemoautotrophs. In the Archean and early Proterozoic oceans, the chemoautotrophs would have already been dispersed throughout the oceans by physical mixing and helping to colonize new vent regions. This same dispersion process would have also helped ancestral chemoautotrophs exploit solar energy near the ocean surface.

Although the processes that selected the photosynthetic reactions as the major energy transduction pathway remain obscure, central hypotheses have emerged based on our understanding of the evolution of Earth’s carbon cycle, the evolution of photosynthesis, biophysics, and molecular phylogeny. Photoautotrophs are found in all three major superkingdoms (Figure 1); however, there are very few known Archea capable of this form of metabolism. Efficient photosynthesis requires harvesting solar radiation, and hence the evolution of a light harvesting system. While some Archea and Bacteria use the pigment-protein rhodopsin, by far, the most efficient and ubiquitous light harvesting systems are based on chlorins. The metabolic pathway for the synthesis of porphyrins and chlorins is one of the oldest in biological evolution, and is found in all chemoautotrophs (Xiong et al., 2000). Mulkidjanian and Junge (1997) proposed that the chlorin-based photosynthetic energy conversion apparatus originally arose from the need to prevent UV radiation from damaging essential macromolecules such as nucleic acids and proteins. The UV excitation energy could be transferred from the aromatic amino acid residues in the macromolecule to a blue absorption band of membrane-bound chlorins to produce a second excited state which subsequently decays to the lower-energy excited singlet. This energy dissipation pathway can be harnessed to metabolism if the photochemically produced, charge-separated, primary products are prevented from undergoing a back-reaction, but rather form a biochemically stable intermediate reductant. This metabolic strategy was selected for the photosynthetic reduction of CO₂ to carbohydrates, using reductants such as S²⁻ or Fe²⁺, which have redox potentials that are too positive to reduce CO₂ directly.

The synthesis of reduced (i.e., organic) carbon and the oxidized form of the electron donor permits a photoautotroph to use “respiratory” metabolism, but operate them in reverse. However, not all of the reduced carbon and oxidants remain accessible to the photoautotrophs. In the oceans, cells tend to sink, carrying with them organic carbon. The oxidation of Fe³⁺ forms insoluble Fe⁵⁺ salts that precipitate. The sedimentation and subsequent burial of organic carbon and Fe³⁺
removes these components from the water column. Without replenishment, the essential reductants for anoxygenic photosynthesis would eventually become depleted in the surface waters. Thus, the necessity to regenerate reductants potentially prevented anoxygenic photoautotrophs from providing the major source of fixed carbon on Earth for eternity. Major net accumulation of reduced organic carbon in Proterozoic sediments implies local depletion of reductants such as S\(^{2-}\) and Fe\(^{2+}\) from the euphotic zone of the ocean. These limitations almost certainly provided the evolutionary selection pressure for an alternative electron donor.

8.05.3.2 Selective Pressure in the Evolution of Oxygenic Photosynthesis

H\(_2\)O is a potentially useful biological reductant with a vast supply on Earth relative to any redox-active solute dissolved in it. Liquid water contains \(\sim 100\) kmol of H atoms per m\(^3\), and, given \(>10^{18}\) m\(^3\) of water in the hydrosphere and cryosphere, \(>10^{20}\) kmol of reductant are potentially accessible. Use of H\(_2\)O as a reductant for CO\(_2\), however, requires a larger energy input than does the use of Fe\(^{2+}\) or S\(^{2-}\). Indeed, to split water by light energy requires 0.82 eV at pH 7 and 298 K. Utilizing light at such high energy levels required the evolution of a new photosynthetic pigment, chlorophyll \(a\), which has a red (lowest singlet) absorption band that is 200–300 nm blue shifted relative to bacteriochlorophylls. Moreover, stabilization of the primary electron acceptor to prevent a back-reaction necessitates thermodynamic inefficiency that ultimately requires two light-driven reactions operating in series. This sequential action of two photochemical reactions is unique to oxygenic photoautotrophs and presumably involved horizontal gene transfer through one or more symbiotic events (Blankenship, 1992).

In all oxygenic photoautotrophs, Equation (3) can be modified to:

\[
2\text{H}_2\text{O} + \text{CO}_2 + \text{light} \rightarrow \text{Chl}^a \text{a} \rightarrow (\text{CH}_2\text{O}) + \text{H}_2\text{O} + \text{O}_2
\]  

(4)

where Chl \(a\) is the pigment chlorophyll \(a\) exclusively utilized in the reaction. Equation (4) implies that somehow chlorophyll \(a\) catalyzes a reaction or a series of reactions whereby light energy is used to oxidize water:

\[
2\text{H}_2\text{O} + \text{light} \rightarrow \text{Chl}^a \rightarrow 4\text{H}^+ + 4\text{e}^- + \text{O}_2
\]

(5)

yielding gaseous, molecular oxygen. Hidden within Equation (5) are complex suites of biological innovations that have heretofore not been successfully mimicked \textit{in vitro} by humans. At the core of the water splitting complex is a quartet of manganese atoms, that sequentially extract electrons, one at a time, from 2H\(_2\)O molecules, releasing gaseous O\(_2\) to the environment, and storing the reductants on biochemical intermediates.

The photochemically produced reductants generated by the reactions schematically outlined in Equation (5) are subsequently used in the fixation (fixation is an archaic term meaning to make non-volatile, as in the chemical conversion of a gas to a solid phase) of CO\(_2\) by a suite of enzymes that can operate \textit{in vitro} in darkness and, hence, the ensemble of these reactions are called the dark reactions. At pH 7 and 25 °C, the formation of glucose from CO\(_2\) requires an investment of 915 cal mol\(^{-1}\). If water is the source of reductant, the overall efficiency for photosynthetic reduction of CO\(_2\) to glucose is \(\sim 30\%\); i.e., 30% of the absorbed solar radiation is stored in the chemical bonds of glucose molecules.

8.05.4 PRIMARY PRODUCTIVITY BY PHOTOCUTROPHS

When we subtract the costs of all other metabolic processes by the chemautotrophs and photoautotrophs, the organic carbon that remains is available for the growth and metabolic costs of heterotrophs. This remaining carbon is called \textit{net} primary production (NPP) (Lindeman, 1942). From biogeochemical and ecological perspectives, NPP provides an upper bound for all other metabolic demands in an ecosystem. If NPP is greater than all respiratory consumption of the ecosystem, the ecosystem is said to be net autotrophic. Conversely, if NPP is less than all respiratory consumption, the system must either import organic matter from outside its bounds, or it will slowly run down—it is net heterotrophic.

It should be noted that NPP and photosynthesis are not synonymous. On a planetary scale, the former includes chemautotrophy, the latter does not. Moreover, photosynthesis \textit{per se} does not include the integrated respiratory term for the photoautotrophs themselves (Williams, 1993). In reality, that term is extremely difficult to measure directly, hence NPP is generally approximated from measurements of photosynthetic rates integrated over some appropriate length of time (a day, month, season, or a year) and respiratory costs are either assumed or neglected.

8.05.4.1 What are Photoautotrophs?

In the oceans, oxygenic photoautotrophs are a taxonomically diverse group of mostly single-celled, photosynthetic organisms that drift
with currents. In the contemporary ocean, these organisms, called phytoplankton (derived from Greek, meaning to wander), are comprised of \( \sim 2 \times 10^4 \) species distributed among at least eight taxonomic divisions or phyla (Table 2). By comparison, higher plants are comprised of \( >2.5 \times 10^5 \) species, almost all of which are contained within one class in one division. Thus, unlike terrestrial plants, phytoplankton are represented by relatively few species but they are

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**Table 2** The taxonomic classification and species abundances of oxygenic photosynthetic organisms in aquatic and terrestrial ecosystems. Note that terrestrial ecosystems are dominated by relatively few taxa that are species rich, while aquatic ecosystems contain many taxa but are relatively species poor.

<table>
<thead>
<tr>
<th>Taxonomic group</th>
<th>Known species</th>
<th>Marine</th>
<th>Freshwater</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Empire: Bacteria (=Prokaryota)</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Kingdom: Eubacteria</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Subdivision: Cyanobacteria (sensu strictu) (=Cyanophytes, blue-green algae)</td>
<td>1,500</td>
<td>150</td>
<td>1,350</td>
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<tr>
<td>Subdivision: Chloroxybacteria (=Prochlorophyceae)</td>
<td>3</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td><strong>Empire: Eukaryota</strong></td>
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<td></td>
</tr>
<tr>
<td>Kingdom: Protozoa</td>
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<td></td>
</tr>
<tr>
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<td>1,050</td>
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<td>1,020</td>
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<td>Class: Euglenophyceae</td>
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<td>Division: Dinophyta (Dinoflagellates)</td>
<td>2,000</td>
<td>1,800</td>
<td>200</td>
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<tr>
<td>Class: Dinophyceae</td>
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<td></td>
</tr>
<tr>
<td>Kingdom: Plantae</td>
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<td></td>
</tr>
<tr>
<td>Subkingdom: Biliphyta</td>
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<tr>
<td>Division: Glaucocystophyta</td>
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<td>Class: Glaucocystophyceae</td>
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<td>Division: Rhodophyta</td>
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<tr>
<td>Class: Rhodophyceae</td>
<td>6,000</td>
<td>5,880</td>
<td>120</td>
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<tr>
<td>Division: Chlorophyta</td>
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<tr>
<td>Class: Chlorophyta</td>
<td>2,500</td>
<td>100</td>
<td>2,400</td>
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<tr>
<td>Prasinophyceae</td>
<td>120</td>
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<td>20</td>
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<tr>
<td>Ulvophyceae</td>
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<td>1,000</td>
<td>100</td>
</tr>
<tr>
<td>Charophyceae</td>
<td>12,500</td>
<td>100</td>
<td>12,400</td>
</tr>
<tr>
<td>Division: Bryophyta (mosses, liverworts)</td>
<td>22,000</td>
<td></td>
<td>1,000</td>
</tr>
<tr>
<td>Division: Lycopsida</td>
<td>1,228</td>
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<td>70</td>
</tr>
<tr>
<td>Division: Filicopsida (ferns)</td>
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<td>94</td>
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<tr>
<td>Division: Magnoliophyta (flowering plants) (240,000)</td>
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<td>0</td>
</tr>
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<td></td>
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</tr>
<tr>
<td>Division: Cryophyta</td>
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<td>200</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Division: Haptophyta</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Class: Prymnesiophyceae</td>
<td>500</td>
<td>100</td>
<td>400</td>
</tr>
<tr>
<td>Division: Heterokonta</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Class: Bacillariophyceae (diatoms)</td>
<td>10,000</td>
<td>5,000</td>
<td>5,000</td>
</tr>
<tr>
<td>Chrysophyceae</td>
<td>1,000</td>
<td>800</td>
<td>200</td>
</tr>
<tr>
<td>Eustigmatophyceae</td>
<td>12</td>
<td>6</td>
<td>6</td>
</tr>
<tr>
<td>Fucoxymophyceae (brown algae)</td>
<td>1,500</td>
<td>1,497</td>
<td>3</td>
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<tr>
<td>Raphidophyceae</td>
<td>27</td>
<td>10</td>
<td>17</td>
</tr>
<tr>
<td>Synurophyceae</td>
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<td>250</td>
</tr>
<tr>
<td>Tribophyceae (Xanthophyceae)</td>
<td>600</td>
<td>50</td>
<td>500</td>
</tr>
<tr>
<td>Kingdom: Fungi</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Division: Ascomycotina (lichens)</td>
<td>13,000</td>
<td>15</td>
<td>20</td>
</tr>
</tbody>
</table>

Primary Productivity by Photoautotrophs

phylogenetically diverse. This deep taxonomic diversity is reflected in their evolutionary history and ecological function (Falkowski, 1997).

Within this diverse group of organisms, three basic evolutionary lineages are discernible (Delwiche, 2000). The first contains all prokaryotic oxygenic phytoplankton, which belong to one class of bacteria, namely, the cyanobacteria. Cyanobacteria are the only known oxygenic photoautotrophs that existed prior to ~2.5 Gyr BP (Ga) (Lips, 1993; Summons et al., 1999). These prokaryotes numerically dominate the photoautotrophic community in contemporary marine ecosystems and their continued success bespeaks an extraordinary adaptive capacity. At any moment in time, there are \( 10^{24} \) cyanobacterial cells in the contemporary oceans. To put that into perspective, the number of cyanobacterial cells in the oceans is two orders of magnitude more than all the stars in the sky.

The evolutionary history of cyanobacteria is obscure. The first microfossils assigned to this group were identified in cherts from 3.1 Ga by Schopf (Schopf, 1993). Macroscopic stromatolites, which are generally of biological (oxygenic photoautotrophic) origin, are first found in strata a few hundred million years younger. However, much of the fossil evidence provided by Schopf (e.g., Schopf, 1993) has been questioned (Brasier et al., 2002), and many researchers believe in a later origin. The origin of this group is critical to establishing when net \( \text{O}_2 \) production (and hence, an oxidized atmosphere) first occurred on the planet. Although photodissociation of \( \text{H}_2\text{O} \) vapor could have provided a source of atmospheric \( \text{O}_2 \) in the Archean, the UV absorption cross-section of \( \text{O}_2 \) constrains the reaction, and theoretical calculations supported by geochemical evidence suggest that prior to ca. 2.4 Ga atmospheric \( \text{O}_2 \) was less than \( 10^{-5} \) of the present level (Holland and Rye, 1998; Pavlov and Kasting, 2002). There was a lag between the first occurrence of oxygenic photosynthesis and a global buildup of \( \text{O}_2 \) possibly due to the presence of alternative electron acceptors, especially \( \text{Fe}^{2+} \) and \( \text{S}^{2-} \) in the ocean. Indeed, the dating of oxidation of Earth’s oceans and atmosphere is, in large measure, based on analysis of the chemical precipitation of oxidized iron in sedimentary rocks (the “Great Rust Event (Holland and Rye, 1998) and the mass-independent (Farquhar et al., 2002) and mass-dependent (Habicht et al., 2002) fractionation of sulfur isotopes. The ensemble of these analyses indicate that atmospheric oxygen rose sharply, from virtually insignificant levels, to between 1% and 10% of the present atmospheric concentration over a 100 Myr period beginning ca. 2.4 Ga. Thus, there may be as much as a 1 Gyr or as little as a 100 Myr gap between the origin of the first oxygenic photoautotrophs and oxygenation of Earth’s oceans and atmosphere.

All other oxygen-producing organisms in the ocean are eukaryotic, i.e., they contain internal organelles, including a nucleus, one or more chloroplasts, one or more mitochondria, and, in some cases, a membrane-bound storage compartment, the vacuole. Within the eukaryotes, we can distinguish two major groups, both of which appear to have descended from a common ancestor thought to be the endosymbiotic appropriation of a cyanobacterium into a heterotrophic host cell (Delwiche, 2000). The appropriated cyanobacterium became a chloroplast.

8.05.4.1.1 The red and green lineages

In one group of eukaryotes, chlorophyll \( b \) was synthesized as a secondary pigment; this group forms the “green lineage,” from which all higher plants have descended. The green lineage played a major role in oceanic food webs and the carbon cycle from ca. 1.6 Ga until the end-Permian extinction, ~250 Ma (Lips, 1993). Since that time however, a second group of eukaryotes has risen to ecological prominence in the oceans; that group is commonly called the “red lineage” (Figure 2). The red lineage is comprised of several major phytoplankton divisions and classes, of which the diatoms, dinoflagellates, haptophytes (including the coccolithophorids), and the chrysophytes are the most important. All of these groups are comparatively modern organisms; indeed, the rise of dinoflagellates and coccolithophorids approximately parallels the rise of dinosaurs on land, while the rise of diatoms approximately parallels the rise of mammals in the Cenozoic. The burial and subsequent diagenesis of organic carbon produced primarily by members of the red lineage in shallow seas in the Mesozoic era provide the carbon source for many of the petroleum reservoirs that have been exploited for the past century by humans.

8.05.4.2 Estimating Chlorophyll Biomass

As implied in Equation (4), given an abundance of the two physical substrates, \( \text{CO}_2 \) and \( \text{H}_2\text{O} \), primary production is, to first order, dependent on the concentration of the catalyst Chl \( a \) and light. The distribution of Chl \( a \) in the upper ocean can be discerned from satellite images of ocean color. The physical basis of the measurement is straightforward; making the measurements is technically challenging. Imagine two small parcels of water that are adjacent to each other. As photons from the sun enter the water column, they are either absorbed or scattered. Water itself absorbs red wavelengths of light, at shorter wavelengths of the visible spectrum, light is not
as efficiently absorbed. However, because water molecules can randomly move from one adjacent parcel to another, there are continuous minor changes in density and hence in the refractive index of the water parcels. These minor changes in refractive index lead to incoherence in the downwelling light stream. The incoherence, in turn, increases the probability of photon scattering (a process called “fluctuation density scattering”), such that light in the shorter wavelengths is more likely to be scattered back to space (Einstein, 1910; Morel, 1974). If the ocean contained sterile,
8.05.4.2.1 Satellite based algorithms for ocean color retrievals

Empirically, satellite sensors that measure ocean color utilize a number of wavelengths. In addition to the blue and green region, red and far-red spectra are determined to derive corrections for scattering and absorption of the outgoing or reflected radiation from the ocean by the atmosphere. In fact, only a very small fraction (~5%) of the light leaving the ocean is observed by a satellite; the vast majority of the photons are scattered or absorbed in the atmosphere. However, based on the ratio of blue-green light that is reflected from the ocean, estimates of photosynthetic pigments are derived. It should be pointed out that the blue-absorbing region of the spectrum is highly congested; it is virtually impossible to derive the fraction of absorption due solely to chlorophyll a as opposed to other photosynthetic pigments that absorb blue light. The estimation of chlorophyll a is based on empirical regression of the concentration of the pigment to the total blue-absorbing pigments (Gordon and Morel, 1983). Water-leaving radiances ($L_W$) at specific wavelengths are corrected for atmospheric scattering and absorption, and the concentration of chlorophyll is calculated from the ratios of blue and green light reflected from the water body. The calibration of the sensors is empirical and specifically derived for individual satellites. Examples of such algorithms for five satellites are given in Table 3.

One limitation of satellite images of ocean chlorophyll is that they do not provide information about the vertical distribution of phytoplankton. The water-leaving radiances visible to an observer outside of the ocean are confined to the upper 20% of the euphotic zone (which is empirically defined as the depth to which 1% of the solar radiation penetrates). In the open ocean there is almost always a subsurface chlorophyll maximum that is not visible to satellite ocean color sensors. A number of numerical models have been developed to estimate the vertical distribution of chlorophyll based on satellite color data (Berthon and Morel, 1992; Platt, 1986). The models rely on statistical parametrizations and require numerous in situ observations to obtain typical profiles for a given area of the world ocean (Morel and Andre, 1991; Platt and Sathyendranath, 1988). In addition, large quantities of phytoplankton associated with the bottom of ice flows in both the Arctic and Antarctic are not visible to satellite sensors but do contribute significantly to the primary production in the polar seas (Smith and Nelson, 1990). Despite these deficiencies, the satellite data allow high-resolution, synoptic observations of the temporal and spatial changes in phytoplankton chlorophyll in relation to the physical circulation of the atmosphere and ocean on a global scale. The global distribution of phytoplankton chlorophyll in the upper ocean for winter and summer, derived from a compilation of satellite images, is shown in Figure 3. To a first order, the images reveal how the horizontal and temporal distribution of phytoplankton is related to the physical circulation of the oceans, especially the major features of the basin-scale gyres. For example, throughout most of the central ocean basins, between 30° N and 30° S, phytoplankton biomass is extremely low, averaging 0.1–0.2 mg chlorophyll a m$^{-3}$ at the sea surface. In these regions the vertical flux of nutrients is generally extremely low, limited by eddy diffusion through the thermocline. Most of the chlorophyll biomass is associated with the thermocline. Because there is no seasonal convective overturn in this latitude band, there is no seasonal variation in

### Table 3

<table>
<thead>
<tr>
<th>Sensor</th>
<th>Equation</th>
<th>$R$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SeaWiFS/OC2</td>
<td>$C = 10\cdot 0^{0.341 - 3.001 R + 2.811 R^2 - 2.041 R^3} - 0.04$</td>
<td>490/555</td>
</tr>
<tr>
<td>OCTS/OC40</td>
<td>$C = 10\cdot 0^{0.405 - 2.909 R + 1.690 R^2 - 0.530 R^3 - 1.144 R^4}$</td>
<td>443 &gt; 490 &gt; 520/565</td>
</tr>
<tr>
<td>MODIS/OC3M</td>
<td>$C = 10\cdot 0^{0.2830 - 2.753 R + 1.457 R^2 - 0.659 R^3 - 1.403 R^4}$</td>
<td>443 &gt; 490/550</td>
</tr>
<tr>
<td>CZCS/OC3</td>
<td>$C = 10\cdot 0^{0.362 - 4.068 R + 5.125 R^2 - 2.645 R^3 - 0.597 R^4}$</td>
<td>443 &gt; 520/550</td>
</tr>
<tr>
<td>MERIS/OC4E</td>
<td>$C = 10\cdot 0^{3.68 - 2.814 R + 1.456 R^2 + 0.768 R^3 - 1.292 R^4}$</td>
<td>443 &gt; 490 &gt; 510/560</td>
</tr>
<tr>
<td>SeaWiFS/OC4v4</td>
<td>$C = 10\cdot 0^{0.366 - 3.067 R + 1.930 R^2 - 0.649 R^3 - 1.532 R^4}$</td>
<td>443 &gt; 490 &gt; 510/555</td>
</tr>
<tr>
<td>SeaWiFS/OC2v4</td>
<td>$C = 10\cdot 0^{0.319 - 2.336 R + 0.879 R^2 - 0.135 R^3}$ - 0.071</td>
<td>490/555</td>
</tr>
</tbody>
</table>
phytoplankton chlorophyll. The chlorophyll concentrations are slightly increased at the equator in the Pacific and Atlantic Oceans, and south of the equator in the Indian Ocean. In the equatorial regions the thermocline shoals laterally as a result of long-range wind stress at the surface (Pickard and Emery, 1990). The wind effectively piles up water along its fetch, thereby inclining the upper mixed layer. This results in increased nutrient fluxes, shallower mixed layers, and higher chlorophyll concentrations on the eastern end of the equatorial band, and decreased nutrient fluxes, deeper mixed layers, and lower chlorophyll concentrations on the western end. This effect is most pronounced in the Pacific. The displacement of the band south of the equator in the Indian Ocean is primarily a consequence of basin scale topography.

At latitudes above ~30°, a seasonal cycle in chlorophyll can occur (Figure 3). In the northern hemisphere, areas of high chlorophyll are found in the open ocean of the North Atlantic in the spring and summer. The southern extent and intensity of the North Atlantic phytoplankton bloom are not found in the North Pacific. The North Atlantic bloom is associated with deep vertical convective mixing, which allows resupply of nutrients to the upper mixed layer of the ocean. This phenomenon does not occur in the Pacific due to a stronger vertical density gradient in that basin (driven by the hydrological cycle). The North Atlantic bloom leads to a flux of organic matter into the ocean interior that is observed even at the seafloor.

In the southern hemisphere, phytoplankton chlorophyll is generally lower at latitudes symmetrical with the northern hemisphere in the corresponding austral seasons. For example, in the austral summer (January–March), phytoplankton chlorophyll is slightly lower between 30°S and the Antarctic ice sheets than in the northern hemisphere in July to September (Yoder et al., 1993).

8.05.4.3 Estimating Net Primary Production

8.05.4.3.1 Global models of net primary production for the ocean

Using satellite data to estimate upper-ocean chlorophyll concentrations, satellite-based
observations of incident solar radiation, atlases of seasonally averaged sea-surface temperature, and models that incorporate a temperature response function for photosynthesis, it is possible to estimate global net photosynthesis in the world oceans (Antoine and Morel, 1996; Behrenfeld and Falkowski, 1997a; Longhurst et al., 1995). Although estimates vary between models, based on how the parameters are derived, for illustrative purposes we use a model based on empirical parametrization of the daily integrated photosynthesis profiles as a function of depth. The physical depth at which 1% of irradiance incident on the sea surface remains is called the euphotic zone. This depth can be calculated from surface chlorophyll concentrations, and defines the base of the water column at which net photosynthesis can be supported. Given such information, net primary production can be calculated following the general equation:

\[ PP_{eu} = C_{sat} \cdot Z_{eu} \cdot P_{opt}^b \cdot DL \cdot F \]  

where \( PP_{eu} \) is daily net primary production integrated over the euphotic zone, \( C_{sat} \) is the satellite-based (upper water column; i.e., derived from Table 3) chlorophyll concentration, \( P_{opt}^b \) is the maximum daily photosynthetic rate within the water column, \( Z_{eu} \) is the depth of the euphotic zone, \( DL \) is the photoperiod (Behrenfeld and Falkowski, 1997a), and \( F \) is a function describing the shape of the photosynthesis depth profile.

This general model can be both expanded (differentiated) and collapsed (integrated) with respect to time and irradiance; however, the global results are fundamentally similar (Behrenfeld and Falkowski, 1997). The models predict that NPP in the world oceans amounts to 40–50 Pg per annum (Figure 3 and Table 4).

In contrast to terrestrial ecosystems, the fundamental limitation of primary production in the ocean is not irradiance per se, but temperature and the concentration of chlorophyll in the upper ocean. The latter is a negative feedback; i.e., the more the chlorophyll in the water column, the shallower is the euphotic zone. Hence, to double NPP requires nearly a fivefold increase in chlorophyll concentration.

### 8.05.4.4 Quantum Efficiency of NPP

The photosynthetically available radiation (400–700 nm) for the world oceans is \( 4.5 \times 10^{18} \) mol of photons per annum, which is \( \approx 9.8 \times 10^{20} \) kJ yr\(^{-1}\). The average energy stored by photosynthetic organisms amounts to \( \approx 39 \) kJ per gram of carbon fixed (Platt and Irwin, 1973). Given an annual net production of 40 Pg C for phytoplankton, and an estimated production of 4 Pg yr\(^{-1}\) by benthic photoautotrophs, the photosynthetically stored radiation is equal to \( \approx 1.7 \times 10^{18} \) kJ yr\(^{-1}\).

The fraction of photosynthetically available solar energy conserved by photosynthetic reactions in

**Table 4** Annual and seasonal net primary production (NPP) of the major units of the biosphere.

<table>
<thead>
<tr>
<th>Seasonal</th>
<th>Ocean NPP</th>
<th>Land NPP</th>
</tr>
</thead>
<tbody>
<tr>
<td>April–June</td>
<td>10.9</td>
<td>15.7</td>
</tr>
<tr>
<td>July–September</td>
<td>13.0</td>
<td>18.0</td>
</tr>
<tr>
<td>October–December</td>
<td>12.3</td>
<td>11.5</td>
</tr>
<tr>
<td>January–March</td>
<td>11.3</td>
<td>11.2</td>
</tr>
<tr>
<td>Biogeographic</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Oligotrophic</td>
<td>11.0</td>
<td>Tropical rainforests 17.8</td>
</tr>
<tr>
<td>Mesotrophic</td>
<td>27.4</td>
<td>Broadleaf deciduous forests 1.5</td>
</tr>
<tr>
<td>Eutrophic</td>
<td>9.1</td>
<td>Broadleaf and needleleaf forests 3.1</td>
</tr>
<tr>
<td>Macrophytes</td>
<td>1.0</td>
<td>Needleleaf evergreen forests 3.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Needleleaf deciduous forest 1.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Savannas 16.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Perennial grasslands 2.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Broadleaf shrubs with bare soil 1.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Tundra 0.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Desert 0.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cultivation 8.0</td>
</tr>
</tbody>
</table>

Total 48.5 56.4

Source: Field et al. (1998). After Field et al. (1998). All values in GtC. Ocean color data are averages from 1978 to 1983. The land vegetation index is from 1982 to 1990. Ocean NPP estimates are binned into three biogeographic categories on the basis of annual average \( C_{sat} \) for each satellite pixel, such that oligotrophic = \( C_{sat} < 0.1 \) mg m\(^{-3}\), mesotrophic = \( 0.1 < C_{sat} < 1 \) mg m\(^{-3}\), and eutrophic = \( C_{sat} > 1 \) mg m\(^{-3}\) (Antoine et al., 1996). This estimate includes a 1 GtC contribution from macroalgae (Smith, 1981). Differences in ocean NPP estimates between Behrenfeld and Falkowski (1997) and those in the global annual NPP for the biosphere and this table result from: (i) addition of Arctic and Antarctic monthly ice masks; (ii) correction of a rounding error in previous calculations of pixel area; and (iii) changes in the designation of the seasons to correspond with Falkowski et al. (1998).
the world oceans amounts to \(1.7 \times 10^{18} \text{ kJ}/9.8 \times 10^{20} = 0.0017\) or 0.17%. Thus, on average, in the oceans, 0.0007 mol C is fixed per mole of incident photons; this is equivalent to an effective quantum requirement of 1,400 quanta per CO\(_2\) fixed. This value is less than 1% of the theoretical maximum quantum efficiency of photosynthesis; the relatively small realized efficiency is due to the fact that photons incident on the ocean surface have a small probability of being absorbed by phytoplankton before they are either absorbed by water or other molecules (e.g., organic matter), or are scattered back to space.

8.05.4.4.1 Comparing efficiencies for oceanic and terrestrial primary production

The average chlorophyll concentration of the world ocean is 0.24 mg m\(^{-3}\) and the average euphotic zone depth is 54 m; thus the average integrated chlorophyll concentration is \(~13\) mg m\(^{-2}\). Carbon to chlorophyll ratios of phytoplankton typically range between 40:1 and 100:1 by weight (Banse, 1977). Given the total area of the ocean of \(3.1 \times 10^{18} \text{ km}^2\), the total carbon biomass in phytoplankton is 0.25–0.65 Pg. If NPP is \(~40\) Pg per annum, and assuming the ocean is in steady state (a condition we will discuss in more detail), the living phytoplankton biomass turns over 60–150 times per year, which is equivalent to a turnover time of 2–6 d. In contrast, terrestrial plant biomass amounts to \(~600–1,000\) Pg C, most of which is in the form of wood (Woodwell et al., 1978). Estimates of terrestrial plant NPP are in the range of 50–65 Pg C per annum, which gives an average turnover time of \(~12–20\) yr (Field et al., 1998). Thus, the flux of carbon through aquatic photosynthetic organisms is about 1,000-fold faster than terrestrial ecosystems, while the storage of carbon in the latter is about 1,000-fold higher than the former. Moreover, the total photon flux to terrestrial environments amounts to \(~2\times 10^{18} \text{ mol yr}^{-1}\), which gives an effective quantum yield of \(~0.002\). In other words, on average one CO\(_2\) molecule is fixed for every 500 incident photons. The results of these calculations suggest that terrestrial vegetation is approximately three times more efficient in utilizing incident solar radiation to fix carbon than are aquatic photoautotrophs. This situation arises primarily from the relative paucity of aquatic photoautotrophs in the ocean and the fact that they must compete with the media (water) for light.

This comparison points out a fundamental difference between the two ecosystems in the context of the global carbon cycle. On timescales of decades to centuries, carbon fixed in terrestrial ecosystems can be temporarily stored in organic matter (e.g., forests), whereas most of the carbon fixed by marine phytoplankton is rapidly consumed by grazers or sinks and is transferred from the surface ocean to the ocean interior. Upon entering the ocean interior, virtually all of the organic matter is oxidized by heterotrophic microbes, and in the process is converted back to inorganic carbon. Elucidating how this transfer occurs, what controls it, how much carbon is transferred via this mechanism, on what timescales, and whether the process is in steady state was a major focus for research in the latter portion of the twentieth century.

8.05.5 EXPORT, NEW AND “TRUE NEW” PRODUCTION

We can imagine that NPP produced by photoautotrophs in the upper, sunlit regions of the ocean (the euphotic zone) is consumed in the same general region by heterotrophs. In such a case, the basic reaction given by Equation (4) is simply balanced in the reverse direction due to respiration by heterotrophic organisms, and no organic matter leaves the ecosystem. This very simple “balanced state” model, also referred to as the microbial loop (e.g., Azam, 1998), accounts for the fate of most of the organic matter in the oceans (and on timescales of decades, terrestrial ecosystems as well).

In marine ecology, this process is sometimes called “regenerated production”; i.e., organic matter produced by photoautotrophs is locally regenerated to inorganic nutrients (CO\(_2\), NH\(_4^+\), PO\(_4^{3-}\)) by heterotrophic respiration. It should be noted here that with the passage of organic matter from one level of a marine food chain to the next (e.g., from primary producer to heterotrophic consumer), a metabolic “tax” must be paid in the form of respiration, such that the net metabolic potential of the heterotrophic biomass is always less than that of the primary producers. This does not mean, \textit{a priori}, that photoautotrophic biomass is always greater, as heterotrophs may grow slowly and accumulate biomass; however, as heterotrophs grow faster, their respiratory rates must invariably increase. The rate of production (i.e., the energy flux) of heterotrophic biomass is always constrained by NPP.

Let us imagine a second scenario. Some fraction of the primary producers and/or heterotrophs sink below a key physical gradient, such as a thermocline, and for whatever reason cannot ascend back into the euphotic zone. If the water column is very deep, sinking organic matter will most likely be consumed by heterotrophic microbes in the ocean interior. The flux of organic carbon from the euphotic zone is often called export production, a term coined by Wolfgang Berger. Export production is an important conduit for the exchange of carbon between the upper ocean and the ocean interior (Berger et al., 1987).
This conduit depletes the upper ocean of inorganic carbon and other nutrients essential for photosynthesis and the biosynthesis of organic matter. In the central ocean basins, export production is a relatively small fraction of total primary production, amounting to 5–10% of the total carbon fixed per annum (Dugdale and Wilkerson, 1992). At high latitudes and in nutrient-rich areas, however, diatoms and other large, heavy cells can form massive blooms and sink rapidly. In such regions, export production can account for 50% of the total carbon fixation (Bienfang, 1992; Campbell and Aarup, 1992; Sancetta et al., 1991; Walsh, 1983). The subsequent oxidation and remineralization of the exported production enriches the ocean interior with inorganic carbon by \( \approx 200 \mu \text{M} \) in excess of that which would be supported solely by air–sea exchange (Figure 4 and Table 5). This enrichment is called the biological pump (Broecker et al., 1980; Sarmiento and Bender, 1994; Volk and Hoffert, 1985). The biological pump is crucial to maintaining the steady-state levels of atmospheric CO\(_2\) (Sarmiento et al., 1992; Siegenthaler and Sarmiento, 1993).

### 8.05.5.1 Steady-state versus Transient State

The concepts of new, regenerated, and export production are central to understanding many aspects of the role of aquatic photosynthetic organisms in biogeochemical cycles in the oceans. In steady state, the globally averaged fluxes of new nutrients must match the loss of the nutrients contained in organic material. If this were not so, there would be a continuous depletion of nutrients in the euphotic zone and photoautotrophic biomass and primary production would slowly decline (Eppley, 1992). Thus, in the steady state, the sinking fluxes of organic nitrogen and the production of N\(_2\) by denitrifying bacteria must equal the sum of the upward fluxes of inorganic nitrogen, nitrogen fixation, and the atmospheric

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**Figure 4** Vertical profiles of total dissolved inorganic carbon (TIC) in the ocean. Curve A corresponds to a theoretical profile that would have been obtained prior to the Industrial Revolution with an atmospheric CO\(_2\) concentration of 280 \( \mu \text{mol mol}^{-1} \). The curve is derived from the solubility coefficients for CO\(_2\) in seawater, using a typical thermal and salinity profile from the central Pacific Ocean, and assumes that when surface water cools and sinks to become deep water it has equilibrated with atmospheric CO\(_2\). Curve B corresponds to the same calculated solubility profile of TIC, but in the year 1995, with an atmospheric CO\(_2\) concentration of 360 \( \mu \text{mol mol}^{-1} \). The difference between these two curves is the integrated oceanic uptake of CO\(_2\) from anthropogenic emissions since the beginning of the Industrial Revolution, with the assumption that biological processes have been in steady state (and hence have not materially affected the net influx of CO\(_2\)). Curve C is a representative profile of measured TIC from the central Pacific Ocean. The difference between curve C and B is the contribution of biological processes to the uptake of CO\(_2\) in the steady state (i.e. the contribution of the “biological pump” to the TIC pool.) (courtesy of Doug Wallace and the World Ocean Circulation Experiment).
deposition of fixed nitrogen in the form of aerosols (the latter is produced largely as a consequence of air pollution and, to a lesser extent, from lightning).

8.05.6 NUTRIENT FLUXES

Primary producers are not simply sacks of organic carbon. They are composed of six major elements, namely, hydrogen, carbon, oxygen, nitrogen, phosphorus, and sulfur, and at least 54 other trace elements and metals (Schlesinger, 1997). In steady state, the export flux of organic matter to the ocean interior must be coupled to the upward flux of several of these essential nutrients. The fluxes of nutrients are related to the elemental stoichiometry of the organic matter that sinks into the ocean interior. This relationship, first pointed out by Alfred Redfield in 1934, was based on the chemistry of four of the major elements in the ocean, namely, carbon, nitrogen, phosphorus, and oxygen.

8.05.6.1 The Redfield Ratio

In the ocean interior, the ratio of fixed inorganic nitrogen (in the form of NO$_3^-$) to PO$_4^{3-}$ in the dissolved phase is remarkably close to the ratios of the two elements in living plankton. Hence, it seemed reasonable to assume that the ratio of the two elements in the dissolved phase was the result of the sinking and subsequent remineralization (i.e., oxidation) of the elements in organic matter produced in the open ocean. Further, as carbon and nitrogen in living organisms are largely found in chemically reduced forms, while remineralized forms are virtually all oxidized, the remineralization of organic matter was coupled to the depletion of oxygen. The relationship could be expressed stoichiometrically as

$$[106(CH_2O)16NH_31PO_4^{2-}] + 138O_2 \rightarrow 106CO_2 + 122H_2O + 16NO_3^- + PO_4^{2-} + 16H^+]$$

(7)

Hidden within this balanced chemical formulation are biochemical redox reactions, which are contained within specific groups of organisms. (In the oxidation of organic matter, there is some ambiguity about the stoichiometry of O$_2$/P. Assuming that the mean oxidation level of organic carbon is that of carbohydrate (as is the case in Equation (9)), then the oxidation of that carbon is equimolar with O. Alternatively, some organic matter may be more or less reduced than carbohydrate, and therefore require more or less O for oxidation. Note also that the oxidation of NH$_3$ to NO$_3^-$ requires four atoms of O, and leads to the formation of one H$_2$O and one H$^+$.) When the reactions primarily occur at depth, Equation (7) is driven to the right, while when the reactions primarily occur in the euphotic zone, they are driven to the left. Note that in addition to reducing CO$_2$ to organic matter, formation of organic matter by photoautotrophs requires reduction of nitrate to the equivalent of ammonia. These two forms of nitrogen are critically important in helping to quantify “new” and export production.

8.05.7 NITRIFICATION

NO$_3^-$ is produced via oxidation of NH$_3$ by a specific group of eubacteria, the nitrifiers, that are obligate aerobes found primarily in the water column. The oxidation of NH$_3$ is coupled to the reduction of inorganic carbon to organic matter; hence nitrification is an example of a chemooautotrophic process that couples the aerobic nitrogen cycle to the carbon cycle. However, because the thermodynamic gradient is very small, the efficiency of carbon fixation by nitrifying bacteria is low and does not provide an ecologically significant source of organic matter in the oceans. In the contemporary ocean, global CO$_2$ fixation by marine nitrifying bacteria only amounts to ~0.2 Pg C per annum, or ~0.5% of marine photoautotrophic carbon fixation.

There are two major sources of nutrients in the euphotic zone. One is the local regeneration of simple forms of combined elements (e.g., NH$_4^+$, HPO$_4^{2-}$, SO$_4^{2-}$) resulting from the metabolic...
activity of metazoan and microbial degradation. The second is the influx of distantly produced, “new” nutrients, imported from the deep ocean, the atmosphere (i.e., nitrogen fixation, atmospheric pollution), or terrestrial runoff from streams, rivers, and estuaries (Dugdale and Goering, 1967). In the open ocean, these two sources can be usefully related to the form of inorganic nitrogen assimilated by phytoplankton. Because biological nitrogen fixation is relatively low in the ocean (see below) and nitrification in the upper mixed layer is sluggish relative to the assimilation of nitrogen by photoautotrophs, nitrogen supplied from local regeneration is assimilated before it has a chance to become oxidized. Hence, regenerated nitrogen is primarily in the form of ammonium or urea. In contrast, the fixed inorganic nitrogen in the deep ocean has sufficient time (hundreds of years) to become oxidized, and hence the major source of new nitrogen is in the form of nitrate. Using \(^{15}\)NH\(_4\) and \(^{15}\)NO\(_3\) as tracers, it is possible to estimate the fraction of new nitrogen that fuels phytoplankton production (Dugdale and Wilkerson, 1992). This approach provides an estimate of both the upward flux of nitrate required to sustain the \(^{15}\)NO\(_3\) pool in \(^{13}\)C, while the organic carbon produced is enriched in \(^{12}\)C.

8.05.7.2 Carbon Isotope Fractionation in Organic Matter and Carbonates

The isotopic fractionation in carbonates mirrors the relative amount of organic carbon buried. It is generally assumed that the source carbon, from vulcanism (the so-called “mantle” carbon) has an isotopic value of approximately \(-5\%e\). As mass balance must constrain the isotopic signatures of carbonate carbon and organic carbon with the mantle carbon, then

\[
\frac{f_{\text{org}}}{\Delta B} = \frac{\delta_w - \delta_{\text{carb}}}{B}
\]

where \(f_{\text{org}}\) is the fraction of organic carbon buried, \(\delta_w\) is the average isotopic content of the carbon weathered, \(\delta_{\text{carb}}\) is the isotopic signature of the carbonate carbon, and \(\Delta B\) is the isotopic difference between organic carbon and carbonate carbon deposited in the ocean. Equation (8) is a steady-state model that presumes the source of carbon from the mantel is constant over geological time. This basic model is the basis of nearly all estimates of organic carbon burial rates (Berner et al., 1983; Kump and Arthur, 1999).

Carbonate isotopic analyses reveal positive excursions (i.e., implying organic carbon burial) in the Proterozoic, and more modest excursions throughout the Phanerozoic (Figure 5). Burial of organic carbon on geological timescales implies that export production must deviate from the steady state on ecological timescales. Such a deviation requires changing one or more of (i) ocean nutrient inventories, (ii) the utilization of unused nutrients in enriched areas, (iii) the average elemental composition of the organic material, or (iv) the “rain” ratios of particulate organic carbon to particulate inorganic carbon to the seafloor.

8.05.7.3 Balance between Net Primary Production and Losses

In the ecological theater of aquatic ecosystems, the observed photoautotrophic biomass at any moment in time represents a balance between the rate of growth and the rate of removal of that trophic level. The burial of organic carbon in
Figure 5  Phanerozoic $\delta^{13}$C$_{\text{carb}}$ record. The Jurassic through the Cenozoic record was generated from bulk sediment carbonates primarily from open ocean Atlantic Deep Sea Drilling Project boreholes; Lower Jurassic samples were used from the Mochras Borehole (Wales) (Katz et al., in review). Dashed intervals indicate data gaps. Singular spectrum analysis was used to generate the Mesozoic–Cenozoic curve. The Paleozoic record was generated from brachiopods (Veizer et al., 1999; note that the timescale has been adjusted from the original reference by interpolating between period boundaries). Data were averaged for each time slice to obtain the Paleozoic curve. The timescales of Berggren et al. (1995; Cenozoic), Gradstein et al. (1995; Mesozoic), and GSA (Paleozoic) were used.
the lithosphere requires that the ecological balance between NPP and respiration diverge; i.e., the global ocean must be net autotrophic. For simplicity, we can express the time-dependent change in photoautotrophic biomass by a linear differential equation:

\[ \frac{dP}{dt} = [P](\mu - m) \quad (9) \]

where \([P]\) is photoautotrophic biomass (e.g., organic carbon), \(\mu\) is the specific growth rate (units of 1/time), and \(m\) is the specific mortality rate (units of 1/time). In this equation, we have lumped all mortality terms, such as grazing and sinking together into one term, although each of these loss processes can be given explicitly (Banse, 1994). Two things should be noted regarding Equation (9). First, \(\mu\) and \(m\) are independent variables; i.e., changes in \(P\) can be independently ascribed to one or the other process. Second, by definition, a steady state exists when \(dP/dt\) is zero.

### 8.05.7.4 Carbon Burial in the Contemporary Ocean

The burial of organic carbon in the modern oceans is primarily confined to a few regions where the supply of sediments from terrestrial sources is extremely high. Such regions include the Amazon outfall and Indonesian mud belts. In contrast, the oxidation of organic matter in the interior of the contemporary ocean is extremely efficient; virtually no carbon is buried in the deep sea. Similarly, on most continental margins, organic carbon that reaches the sediments is consumed by microbes within the sediments, such that very little is actually buried in the sediments, organic carbon that reaches the sediments is consumed by microbes within the sediments, such that very little is actually buried in the contemporary ocean (Aller, 1998). The solution to Equation (9) must be close to zero; and consequently, in the absence of human activities, the oxygen content of Earth’s atmosphere is very close to steady state and has been so for tens, if not hundreds, of millions of years.

### 8.05.7.5 Carbon Burial in the Precambrian Ocean

In contrast, carbon burial in the Proterozoic ocean must have occurred as oxygen increased in the atmosphere; i.e., the global solution to Equation (9) must have been \(>0\). Photoautotrophic biomass could have increased until some element became limiting. Thus, the original feedback between the production of photoautotrophic biomass in the oceans and the atmospheric content of oxygen was determined by an element that limited the crop size of the photoautotrophs in the Archean or Proterozoic ocean. What was that element, and why did it become limiting?

### 8.05.8 LIMITING MACRONUTRIENTS

A general feature of aquatic environments is that because the oxidation of organic nutrients to their inorganic forms occurs below the euphotic zone where the competing processes of assimilation of nutrients by photoautotrophs do not occur, the pools of inorganic nutrients are much higher at depth. As the only natural source of photosynthetically active radiation is the sun, the gradients of light and nutrients are from opposite directions. Thermal or salinity differences in the surface layers produce vertical gradients in density that effectively retard the vertical fluxes of soluble nutrients from depth. Thus, in the surface layers of a stratified water column, nutrients become depleted as the photoautotrophs consume them at rates exceeding their rate of vertical supply. Indeed, throughout most of the world oceans, the concentrations of dissolved inorganic nutrients, especially fixed inorganic nitrogen and phosphate, are exceedingly low, often only a few nM. One or the other of these nutrients can limit primary production. However, the concept of limitation requires some discussion.

#### 8.05.8.1 The Two Concepts of Limitation

The original notion of limitation in ecology was related to the yield of a crop. A limiting factor was the substrate least available relative to the requirement for synthesis of the crop (Liebig, 1840). This concept formed a strong underpinning of agricultural chemistry and was used to design the elemental composition of fertilizers for commercial crops. This concept subsequently was embraced by ecologists and geochemists as a general “law” (Odum, 1971).

Nutrients can also limit the rate of growth of photoautotrophs (Blackman, 1905; Dugdale, 1967). Recall that if organisms are in balanced growth, the rate of uptake of an inorganic nutrient relative to the cellular concentration of the nutrient defines the growth rate (Herbert et al., 1956). The uptake of inorganic nutrients is a hyperbolic function of the nutrient concentration and can be conveniently described by a hyperbolic expression of the general form

\[ V = (V_{\text{max}}(U, ...))/(K_s + (U, ...)) \quad (10) \]

where \(V\) is the instantaneous rate of nutrient uptake, \(V_{\text{max}}\) is the maximum uptake rate, \((U, ...\) represent the substrate concentration of nutrient \(U\), etc., and \(K_s\) is the concentration supporting half the maximum rate of uptake (Dugdale, 1967; Monod, 1942). There can be considerable variation between species with regard to \(K_s\) and \(V_{\text{max}}\) values and these variations are potential
sources of competitive selection (Eppley et al., 1969; Tilman, 1982).

It should be noted that Liebig’s notion of limitation was not related a priori to the intrinsic rate of photosynthesis or growth. For example, photosynthetic rates can be (and often are) limited by light or temperature. The two concepts of limitation (yield and rate) are often not understood correctly: the former is more relevant to biogeochemical cycles, the latter is more critical to selection of species in ecosystems.

8.05.9 THE EVOLUTION OF THE NITROGEN CYCLE

Globally, nitrogen and phosphorus are the two elements that immediately limit, in a Liebig sense, the biologically mediated carbon assimilation in the oceans by photoautotrophs. It is frequently argued that since N₂ is abundant in both the ocean and the atmosphere, and, in principle, can be biologically reduced to the equivalent of NH₃ by N₂-fixing cyanobacteria, nitrogen cannot be limiting on geological timescales (Barber, 1992; Broecker et al., 1980; Redfield, 1958). Therefore, phosphorus, which is supplied to the ocean by the weathering of continental rocks, must ultimately limit biological productivity. The underlying assumptions of these tenets should, however, be considered within the context of the evolution of biogeochemical cycles.

By far, the major source of fixed inorganic nitrogen for the oceans is via biological nitrogen fixation. Although in the Archean atmosphere, electrical discharge or bolide impacts may have promoted NO formation from the reaction between N₂ and CO₂, the yield for these reactions is extremely low. Moreover, atmospheric NH₃ would have photodissociated from UV radiation (Kasting, 1990), while N₂ would have been stable (Kasting, 1990; Warneck, 1988). Biological N₂ fixation is a strictly anaerobic process (Postgate, 1971), and the sequence of the genes encoding the catalytic subunits for nitrogenase is highly conserved in cyanobacteria and other eubacteria, strongly suggesting a common ancestral origin (Zehr et al., 1995). The antiquity and homology of nitrogen fixation capacity also imply that fixed inorganic nitrogen was scarce prior to the evolution of diazotrophic organisms; i.e., there was strong evolutionary selection for nitrogen fixation in the Archean or early Proterozoic periods. In the contemporary ocean, N₂ is still catalyzed solely by prokaryotes, primarily cyanobacteria (Capone and Carpenter, 1982).

While apatite and other calcium-based and substituted solid phases of phosphate minerals precipitated in the primary formation of crustal sediments, secondary reactions of phosphate with aluminum and transition metals such as iron are mediated at either low salinity, low pH, or high oxidation states of the cations (Stumm and Morgan, 1981). Although these reactions would reduce the overall soluble phosphate concentration, the initial condition of the Archean ocean probably had a fixed low N:P ratio in the dissolved inorganic phase. As N₂ fixation proceeded, that ratio would have increased with a buildup of ammonium in the ocean interior. The accumulation of fixed nitrogen in the oceans would continue until the N:P ratio of the inorganic elements reached equilibrium with the N:P ratio of the sedimenting particulate organic matter (POM). Presumably, the latter ratio would approximate that of extant, nitrogen-fixing marine cyanobacteria, which is ~16:1 by atoms (Copin-Montegut and Copin-Montegut, 1983; Redfield, 1958; Quigg et al., 2003) or greater (Letelier et al., 1996) and would ultimately be constrained by the availability of phosphate (Falkowski, 1997; Tyrell, 1999).

The formation of nitrate from ammonium by nitrifying bacteria requires molecular oxygen; hence, nitrification must have evolved following the formation of free molecular oxygen in the oceans by oxygenic photoautotrophs. Therefore, from a geological perspective, the conversion of ammonium to nitrate probably proceeded rapidly and provided a substrate, NO₃⁻, that eventually could serve both as a source of nitrogen for photoautotrophs and as an electron acceptor for a diverse group of heterotrophic, anaerobic bacteria, the denitrifiers.

In the sequence of the three major biological processes that constitute the nitrogen cycle, denitrification must have been the last to emerge. This process, which permits the reduction of NO₃⁻ to (ultimately) N₂, occurs in the modern ocean in three major regions, namely, continental margin sediments, areas of restricted circulation such as fjords, and oxygen minima zones of perennially stratified seas (Christensen et al., 1987; Codispoti and Christensen, 1985; Devol, 1991; Nixon et al., 1996). In all cases, the process requires hypoxic or anoxic environments and is sustained by high sinking fluxes of organic matter. Denitrification appears to have evolved independently several times; the organisms and enzymes responsible for the pathway are highly diverse from a phylogenetic and evolutionary standpoint.

With the emergence of denitrification, the ratio of fixed inorganic nitrogen to dissolved inorganic phosphate in the ocean interior could only be depleted in nitrogen relative to the sinking flux of the two elements in POM. Indeed, in all of the major basins in the contemporary ocean, the N:P ratio of the dissolved inorganic nutrients in the ocean interior is conservatively estimated at 14.7
There are three major conclusions that may be drawn from the foregoing discussion:

(i) Because the ratio of the sinking flux of particulate organic nitrogen and particulate phosphorus exceeds the N:P ratio of the dissolved pool of inorganic nutrients in the ocean interior, the average upward flux of inorganic nutrients must be slightly enriched in phosphorus relative to nitrogen as well as to the elemental requirements of the photoautotrophs (Gruber and Sarmiento, 1997; Redfield, 1958). Hence, although there are some exceptions (Kromer, 1995; Wu et al., 2000), dissolved, inorganic fixed nitrogen generally limits primary production throughout most of the world’s oceans (Barber, 1992; Falkowski et al., 1998).

(ii) The N:P ratio of the dissolved pool of inorganic nutrients in the ocean interior was established by biological processes, not vice versa (Redfield et al., 1963, 1934). The elemental composition of marine photoautotrophs has been conserved since the evolution of the eukaryotic phytoplankton (Lipps, 1993). The Redfield N:P ratio of 16:1 for POM (Codispoti, 1995; Copin-Montegut and Copin-Montegut, 1983; McElroy, 1983; Redfield et al., 1963, 1958) is an upper bound, which is not observed for the two elements in the dissolved inorganic phase in the ocean interior. The deficit in dissolved inorganic fixed nitrogen relative to soluble phosphate in the ocean represents a slight imbalance between nitrogen fixation and denitrification on timescales of $10^3$–$10^4$ yr (Codispoti, 1995).

(iii) If dissolved inorganic nitrogen rather than phosphate limits productivity in the oceans, then it follows that the ratio of nitrogen fixation/denitrification plays a critical role in determining the net biologically mediated exchange of CO$_2$ between the atmosphere and ocean (Codispoti, 1995).

8.05.10 FUNCTIONAL GROUPS

As we have implied throughout the foregoing discussion, the biologically mediated fluxes of...
elements between the upper ocean and the ocean interior are critically dependent upon key groups of organisms. Fluxes between the atmosphere and ocean, as well as between the ocean and the lithosphere, are mediated by organisms that catalyze phase state transitions from either gas to solute/solid or from solute to solid/gas phases. For example, autotrophic carbon fixation converts gaseous CO$_2$ to a wide variety of organic carbon molecules, virtually all of which are solid or dissolved solids at physiological temperatures. Respiration accomplishes the reverse. Nitrogen fixation converts gaseous N$_2$ to ammonium and thence to organic molecules, while denitrification accomplishes the reverse. Calcification converts dissolved inorganic carbon and calcium to solid phase calcite and aragonite, whereas silicification converts soluble silicic acid to solid hydrated amorphous opal. Each of these biologically catalyzed processes is dependent upon specific metabolic sequences (i.e., gene families encoding a suite of enzymes) that evolved over hundreds of millions of years of Earth’s history, and have, over corresponding periods, led to the massive accumulation of oxygen in the atmosphere, andopal, carbonates, and organic matter in the lithosphere. Presumably, because of parallel evolution as well as lateral gene transfer, these metabolic sequences have frequently co-evolved in several groups of organisms that, more often than not, are not closely related from a phylogenetic standpoint (Falkowski, 1997). Based on their biogeochemical metabolism, these homologous sets of organisms are called functional groups or biogeochemical guilds; i.e., organisms that are related through common biogeochemical processes rather than a common evolutionary ancestor affiliation.

8.05.10.1 Siliceous Organisms

In the contemporary ocean, the export of particulate organic carbon from the euphotic zone is highly correlated with the flux of particulate silicate. Most of the silicate flux is a consequence of precipitation of dissolved orthosilicic acid by diatoms to form amorphous opal that makes up the cell walls of these organisms. These hard-shelled cell walls presumably help the organisms avoid predation, or if ingested, increase the likelihood of intact gut passage through some metazoans (Smetacek, 1999). In precipitating silicate, diatoms simultaneously fix carbon. Upon depleting the euphotic zone of nutrients, the organisms frequently sink en masse, and while some are grazed en route, many sink as intact cells. Ultimately, either fate leads to the gravitationally driven export flux of particulate organic carbon into the ocean interior.

Silica is supplied to the oceans from the weathering of continental rocks. Because of precipitation by silicious organisms, however, the ocean is relatively depleted in dissolved silica. Although diatom frustules (their silicified cell walls) tend to dissolve and are relatively poorly preserved in marine sediments, enough silica is buried to keep the seawater undersaturated, throughout the ocean. As the residence time of silica in the oceans is $\sim 10^4$ yr (i.e., about an order of magnitude longer than the mean deep-water circulation), one can get an appreciation for the silicate demands and regeneration rates by following the concentration gradients of dissolved silica along isopycnals. While these demands are generally attributed to diatoms, radiolarians (a group of nonphotosynthetic, heterotrophic protists with silicic tests that are totally unrelated to diatoms) are not uncommon, and radiolarian shells are abundant in the sediments of Southern Ocean. Silica is also precipitated by various sponges and other protists. As a functional group, the silicate precipitators are identified by their geochemical signatures in the sediments and in the silica chemistry of the oceans.

8.05.10.2 Calcium Carbonate Precipitation

Like silica precipitation, calcium carbonate is not confined to a specific phylogenetically distinct group of organisms, but evolved (apparently independently) several times in marine organisms. Carbonate sediments blanket much of the Atlantic basin, and are formed from the shells of both coccolithophorids and foraminifera (Milliman, 1993). (In the Pacific, the carbon compensation depth is generally higher than the bottom, and hence, in that basin carbonates tend to dissolve rather than become buried.) As the crystal structure of the carbonates in both groups is calcite (as opposed to the more diagenetically susceptible aragonite), the preservation of these minerals and their co-precipitating trace elements provides an invaluable record of ocean history. Although on geological timescales huge amounts of carbon are removed from the atmosphere and ocean and stored in the lithosphere as carbonates, on ecological timescales, carbonate formation leads to the formation of CO$_2$. This reaction can be summarized by the following:

$$2\text{HCO}_3^- + \text{Ca}^{2+} \rightarrow \text{CaCO}_3 + \text{CO}_2 + \text{H}_2\text{O}$$

(11)

Unlike silicate precipitation, calcium carbonate precipitation leads to strong optical signatures that can be detected both in situ and remotely (Balch et al., 1991; Holligan and Balch, 1991). The basic principle of detection is the large, broadband (i.e., “white”) scattering cross-sections of calcite. The high scattering cross-sections are detected by satellites observing the upper ocean as relatively highly reflective properties (i.e., a “bright” ocean).
Using this detection scheme, one can reconstruct global maps of planktonic calcium carbonate precipitating organisms in the upper ocean. *In situ* analysis can be accompanied by optical rotation properties (polarization) to discriminate calcite from other scattering particles. *In situ* profiles of calcite can be used to construct the vertical distribution of calcium carbonate-precipitating planktonic organisms that would otherwise not be detected by satellite remote sensing because they are too deep in the water column.

Over geological time, the relative abundances of key functional groups change. For example, relative coccolithophorid abundances generally increased through the Mesozoic, and underwent a culling at the Cretaceous Tertiary (K/T) boundary, followed by a general waning throughout the Cenozoic. The changes in the coccolithophorid abundances appear to follow eustatic sea-level variations, suggesting that transgressions lead to higher calcium carbonate deposition. In contrast, diatom sedimentation increases with regressions and, since the K/T impact, diatoms have generally replaced coccolithophorids as ecologically important eukaryotic phytoplankton. On much finer timescales during the Pleistocene, it would appear that interglacial periods favor coccolithophorid abundance, while glacial periods favor diatoms. The factors that lead to glacial–interglacial variations between these two functional groups are relevant to elucidating their distributions in the contemporary ecological setting of the ocean (Tozzi, 2001).

### 8.05.10.3 Vacuoles

In addition to a silicic acid requirement, diatoms, in contrast to dinoflagellates and coccolithophores, have evolved a nutrient storage vacuole (Raven, 1987). The vacuole, which occupies ~35% of the volume of the cell, can retain high concentrations of nitrate and phosphate. Importantly, ammonium cannot be (or is not) stored in a vacuole. The vacuole allows diatoms to access and hoard pulses of inorganic nutrients, thereby depriving potentially competing groups of these essential resources. Consequently, diatoms thrive best under eutrophic conditions and in turbulent regions where nutrients are supplied with high pulse frequencies.

The competition between diatoms and coccolithophorids can be easily modeled by a resource acquisition model based on nutrient uptake (Equation (9)). In such a model, diatoms dominate under highly turbulent conditions, when their nutrient storage capacity is maximally advantageous, while coccolithophorids dominate under relatively quiescent conditions (Tozzi et al., 2003).

The geological record during the Pleistocene reveals a periodicity of opal/calcite deposition corresponding to glacial/interglacial periods. Such alterations in mineral deposition are probably related to upper ocean turbulence; i.e., the sedimentary record is a “fax” machine of mixing (Falkowski, 2002). Glacial periods appear to be characterized by higher wind speeds and a stronger thermal contrast between the equator and the poles. These two factors would, in accordance with the simple nutrient uptake model, favor diatoms over coccolithophores. During interglacials, more intense ocean stratification, weaker winds, and a smaller thermal contrast between the equator and the poles would tend to reduce upper-ocean mixing and favor coccolithophores (Iglesias-Rodriguez et al., 2002). While other factors such as silica availability undoubtedly also influenced the relative success of diatoms and coccolithophores on these timescales, we suggest that the climatically forced cycle, played out on timescales of 40 kyr and 100 kyr (over the past 1.9 Myr), can be understood as a long-term competition that never reaches an exclusion equilibrium condition (Falkowski et al., 1998).

Can the turbulence argument be extended to even longer timescales to account for the switch in the dominance from coccolithophorids to diatoms in the Cenozoic? The fossil record of diatoms in the Mesozoic is obscured by problems of preservation; however several species are preserved in the late Jurassic (Harwood and Nikolaev, 1995), suggesting that the origins were in the early Jurassic or perhaps as early as the Triassic. It is clear, however, that this group did not contribute nearly as much to export production during Mesozoic times. We suggest that the ongoing successional displacement of coccolithophores by diatoms in the Cenozoic is, to first order, driven by tectonics (i.e., the Wilson cycle). The Mesozoic period was relatively warm and was characterized by a two-cell Hadley circulation, with obliquity greater than 37°, resulting in a thoroughly mixed atmosphere with nearly uniform temperatures over the surface of the Earth. The atmospheric meridional heat transport decreased the latitudinal thermogradients; global winds and ocean circulation were both sluggish (Huber et al., 1995). This relatively quiescent period of Earth’s history was ideal for coccolithophores. Following the K/T impact, and more critically, the onset of polar ice caps about 32 Ma, the Hadley circulation changed dramatically. Presently, there are six Hadley cells, and the atmosphere has become drier. The net result is more intense thermohaline circulation, greater wind mixing and decreased stability (Barron et al., 1995; Chandler et al., 1992). Associated with this decreased stability is the rise of the diatoms.
Over the past 50 Myr, both carbon and oxygen isotopic records in fossil foraminifera suggest that there has been a long-term depletion of CO$_2$ in the ocean–atmosphere system and a decrease in temperature in the ocean interior. The result has been increased stratification of the ocean, which has, in turn, led to an increased importance for wind-driven upwelling and mesoscale eddy turbulence in providing nutrients to the euphotic zone. The ecological dominance of diatoms under sporadic mixing conditions suggests that their long-term success in the Cenozoic reflects an increase in event-scale turbulent energy dissipation in the upper ocean. But, was the Wilson cycle the only driver?

Although weathering of siliceous minerals by CO$_2$ (the so-called “Urey reactions”; but see Berner and Maasch, 1996) contributed to the long-term flux of silica to the oceans (Berner, 1990), and potentially fostered the radiation of diatoms in the Cenozoic, by itself, orogeny cannot explain the relatively sharp increase in diatoms at the Eocene/Oligocene boundary. Indeed, the seawater strontium isotope record does not correspond with these radiations in diatoms (Raymo and Ruddiman, 1992). We must look for other contributing processes.

Shortly after, or perhaps coincident with Paleocene thermal maximum (55 Ma), was a rise in true grasses (Retallack, 2001). This group, which rapidly radiated in the Eocene, rose to prominence in Oligocene, a period coincident with a global climatic drying. During this period, however, there was a rapid co-evolution of grazing ungulates that displaced browsers (Janis and Damuth, 1990). Grasses contain up to 10% dry weight of silica, which forms micromineral deposits in the cell walls; phytoliths (Conley, 2002). Indeed, the selection of hypsodont (high crown) dentition in ungulates from the brachydont (leaf eating) early-appearing browsing mammals, coincides with the widespread distribution of phytoliths and grit in grassland forage. It is tempting to suggest that the rise of grazing ungulates, which spurred the radiation of grasses, was, in effect, a biologically catalyzed silicate weathering process. The deep-root structure of Eocene grasses certainly facilitated silicate mobilization into rivers and groundwaters (Conley, 2002). Additionally, upon their annual death and decay, the phytoliths of many temperate grasses are potentially transported to the oceans via wind.

The feedback between the co-evolution of mammals and grasses and the supply of silicates to the ocean potentially explains the rapid radiation of diatoms, and their continued dominance in the Cenozoic. There is another potential feedback at play, however, which “locked in” the diatom preeminence. It is likely that the increase in diatom dominance, and the associated increase in the efficiency of carbon burial, played a key role in decreasing atmospheric CO$_2$ over the past 32 Myr. That biological selection may influence climate is clearly controversial; however, the trends in succession between taxa on timescales of tens of millions of years, and cycles in dominance on shorter geological timescales beg for explanation.

8.05.11 HIGH-NUTRIENT, LOW-CHLOROPHYLL REGIONS—IRON LIMITATION

On ecological timescales, the biologically mediated net exchange of CO$_2$ between the ocean and atmosphere is limited by nutrient supply and the efficiency of nutrient utilization in the euphotic zone. There are three major areas of the world ocean where inorganic nitrogen and phosphate are in excess throughout the year, yet the mixed-layer depth appears to be shallower than the critical depth; these are the eastern equatorial Pacific, the subarctic Pacific, and Southern (i.e., Antarctic) Oceans. In the subarctic North Pacific, it has been suggested that there is a tight coupling between phytoplankton production and consumption by zooplankton (Miller et al., 1991). This grazer-limited hypothesis has been used to explain why the phytoplankton in the North Pacific do not form massive blooms in the spring and summer like their counterparts in the North Atlantic (Banse, 1992). In the mid-1980s, however, it became increasingly clear that the concentration of trace metals, especially iron, was extremely low in all three of these regions (Martin, 1991). Indeed, in the eastern equatorial Pacific, for example, the concentration of soluble iron in the euphotic zone is only 100–200 pM. Although iron is the most abundant transition metal in the Earth’s crust, in its most commonly occurring form, Fe$^{3+}$, it is virtually insoluble in seawater. The major source of iron to the euphotic zone is Aeolian dust, originating from continental deserts. In the three major areas of the world oceans with high inorganic nitrogen in the surface waters and low chlorophyll concentrations, the flux of Aeolian iron is extremely low (Duce and Tindale, 1991). In experiments in which iron was artificially added on a relatively large scale to the waters in the equatorial Pacific, Southern Ocean, and subarctic Pacific, there were rapid and dramatic increases in photosynthetic energy conversion efficiency and phytoplankton chlorophyll (Abraham et al., 2000; Behrenfeld et al., 1996; Kolber et al., 1994; Tsuda et al., 2003). Beyond doubt, NPP and export production in all three regions are limited by the availability of a single micronutrient—iron.
8.05.12 GLACIAL–INTERGLACIAL CHANGES IN THE BIOLOGICAL CO₂ PUMP

In the modern (i.e., interglacial) ocean, two major factors affect iron fluxes. First, changes in land-use patterns and climate over the past several thousand years have had, and continue to have, marked effects on the areal distribution and extent of deserts. At the height of the Roman Empire some 2,000 years ago, vast areas of North Africa were forested, whereas today these same areas are desert. These changes were climatologically induced. Similarly, the Gobi Desert in North Central Asia has increased markedly in modern times. The flux of Aeolian iron from the Sahara Desert fuels photosynthesis for most of the North Atlantic Ocean; that from the Gobi is deposited over much of the North Pacific (Duce and Tindale, 1991). The primary source of iron for the Southern Ocean is Australia, but the prevailing wind vectors constrain the delivery of the terrestrial dust to the Indian Ocean. Consequently, the Southern Ocean is iron limited in the modern epoch (Martin, 1990).

The second factor in this climatological feedback is that the major wind vectors are driven by atmosphere–ocean heat gradients. Changes in thermal gradients between the equator and poles lead to changes in wind speed and direction. Wind vectors prior to glaciations appear to have supported high fluxes of iron to the Southern Ocean, thereby presumably stimulating phytoplankton production, the export of carbon to depth, and the drawdown of atmospheric CO₂. The flux of Aeolian iron from the Sahara Desert appears to have accompanied glaciations in the recent geological past (Berger, 1988).

8.05.13 IRON STIMULATION OF NUTRIENT UTILIZATION

The enhancement of net export production (i.e., “true” new production) requires the addition of a limiting nutrient to the ocean, an increase in the efficiency of utilization of preformed nutrients in the upper ocean, and/or a change in the elemental stoichiometry of primary producers (Falkowski et al., 1998; Sarmiento and Bender, 1994). Indeed, an analysis of ice cores from Antarctica, reconstruction of Aeolian iron depositions and concurrent atmospheric CO₂ concentrations over the past 4.2 × 10⁵ yr (spanning four glacial–interglacial cycles) suggests that, when iron fluxes were high, CO₂ levels were low and vice versa (Martin, 1990; Petit et al., 1999). Variations in iron fluxes were presumably a consequence of the areal extent of terrestrial deserts and wind vectors. It is hypothesized that increased fluxes of iron to the high-nutrient, low chlorophyll Southern Ocean stimulated phytoplankton photosynthesis and led to a drawdown of atmospheric CO₂. Model calculations suggest that the magnitude of this drawdown could have been cumulatively significant, and accounted for the observed variations in atmospheric CO₂ recorded in gases trapped in the ice cores. However, the sedimentary records reveal large glacial fluxes of organic carbon in low- and mid-latitude regions; areas that are presumably nutrient impoverished. Was there another factor besides iron addition to high-nutrient, low-chlorophyll regions that contributed to a net export of carbon during glacial times?

Given that N:P ratios in the ocean interior are lower than for the sinking flux, an increase in the net delivery of fixed inorganic nitrogen to the ocean would also potentially contribute to a net drawdown of CO₂. The Antarctic ice core records suggest that atmospheric CO₂ declined from ~290 μmol mol⁻¹ to ~190 μmol mol⁻¹ over a period of ~8 × 10⁷ yr between the interglacial and glacial maxima (Sigman and Boyle, 2000). Assuming a C:N ratio of about 6.5 by atoms for the synthesis of new organic matter in the euphotic zone, a simple equilibrium, three-box model calculation suggests that 600 Pg of inorganic carbon should have been fixed by marine photoautotrophs to account for the change in atmospheric CO₂. This amount of carbon is approximately threefold greater than that released to the atmosphere from the cumulative combustion of fossil fuels since the beginning of the Industrial Revolution. The calculated change in atmospheric CO₂ would have required an addition of ~1.5 Tg fixed nitrogen per annum; this is ~2% of the global mean value in the contemporary ocean.

8.05.14 LINKING IRON TO N₂ FIXATION

Iron also appears to exert a strong constraint on N₂ fixation in the modern ocean. Nitrogen-fixing cyanobacteria, like most cyanobacteria, require relatively high concentrations of iron (Berman-Frank et al., 2001). The high-iron requirements come about because these organisms generally have high requirements for this element in their photosynthetic apparatus (Fujita et al., 1990), as well as for nitrogen fixation and electron carriers that are critical for providing the reductants for CO₂ and N₂ fixation in vivo. Increased Aeolian flux of iron to the oceans during glacial periods may have therefore not only stimulated the utilization of nutrients in high-nutrient, low-chlorophyll regions, but also stimulated nitrogen fixation by cyanobacteria, and hence indirectly provided a significant source of new nitrogen. Both effects would have led to increased photosynthetic carbon
fixation, and a net drawdown of atmospheric CO₂ (Falkowski, 1997; Falkowski et al., 1998).

8.05.15 OTHER TRACE-ELEMENT CONTROLS ON NPP

Is iron the only limiting trace element in the sea? Prior to the evolution of oxygenic photosynthesis, the oceans contained high concentrations (~1 mM) of dissolved iron in the form of Fe²⁺ and manganese (>1 mM) in the form of Mn²⁺, but essentially no copper or molybdenum; these and other elements would have been precipitated as sulfides. Thus, both iron and manganese were readily available to the early phototrophs. The availability of these two elements permitted the evolution of the photosynthetic apparatus and the oxygen-evolving system that ultimately became the genetic template for all oxygenic phototrophs (Blankenship, 1992). Indeed, the availability of these transition metals, which is largely determined by the oxidation state of the environment, appears to account for their use in photosynthetic reactions. However, over geological time, oxygenic phototrophs themselves altered the redox state of the ocean, and hence the availability of the elements in the soluble phase (Anbar and Knoll, 2002).

As photosynthetic oxygen evolution proceeded in the Proterozoic oceans, singlet oxygen (O₁₂), peroxide (H₂O₂), superoxide anion radicals (O₂⁻), and hydroxide radicals (OH⁻) were all formed as by-products (Kasting, 1990; Kasting et al., 1988). These oxygen derivatives can oxidize proteins and photosynthetic pigments as well as cause damage to reaction centers (Asada, 1994). A range of molecules evolved to scavenge or quench the potentially harmful oxygen by-products; these include superoxide dismutase (which converts O₂⁻ to O₂ and H₂O₂), peroxidase (which reduces H₂O₂ to H₂O by oxidizing an organic cosubstrate for the enzyme), and catalase (which converts 2H₂O₂ to H₂O and O₂). The oldest superoxide dismutases contained iron and/or manganese, while the peroxidases and catalases contained iron (Asada et al., 1980). These transition metals facilitate the electron transfer reactions that are at the core of the respective enzyme activity, and their incorporation into the proteins undoubtedly occurred because the metals were readily available (Williams and Frausto da Silva, 1996). As O₂ production proceeded, the oxidation of Fe²⁺, Mn²⁺, and S²⁻ eventually led to the virtual depletion of these forms of the elements in the euphotic zone of the oceans. The depletion of these elements had profound consequences on the subsequent evolution of life. In the first instance, a number of enzymes were selected that incorporated alternative transition metals that were available in the oxidized ocean. For example, a superoxide dismutase evolved in the green algae, and hence higher plants (and many non-photosynthetic eukaryotes) that utilized copper and zinc (Falkowski, 1997). Similar metal substitutions occurred in the photosynthetic apparatus and in mitochondrial electron transport chains.

The overall consequence of the co-evolution of oxygenic photosynthesis and the redox state of the ocean is a relatively well-defined trace-element composition of the bulk phytoplankton. Analogous to Redfield’s relationship between the macronutrients, trace-element analyses of phytoplankton reveals a relation for trace elements normalized to cell phosphorus of (C₁₂₅N₁₆P₁S₁₃K₁.₇Mg₀.₅₆Ca₀.₄)₁₀₀₀Sr₁₃Fe₇.₅Mn₃.₈Zn₀.₃₈Cu₀.₂₅Cd₀.₂₁M₀₀.₃₈. The relative composition of transition trace elements in phytoplankton is reflected in that of black shales (Figure 7). Thus, while there is a strong correlation between N:P ratios in phytoplankton and seawater (Anderson and Sarmiento, 1994; Lenton and Watson, 2000), there is no parallel correlation for trace elements (Whitfield, 2001; Morel and Hudson, 1985) (Figure 7 inset). There are two underlying explanations for the lack of a strong relationship. First, low abundance cations that have a valance state of two or higher are often assimilated with particles, whether or not they are metabolically required. Hence, while zinc, manganese, and cobalt are depleted in surface waters and are used in metabolic cycles, mercury, lanthanum, and other rare-earth elements are also depleted and have no known biological function. The profiles of these elements are dictated, to first order, by particle fluxes and their ligands. Second, the absolute abundance of transition metals is critically dependent on the solubility of the source minerals, which is, in turn, regulated by redox chemistry. Most key metabolic pathways evolved prior to the oxidation of Earth’s atmosphere and ocean, and hence many of the transition metals selected for catalyzing biological redox reactions reflect their relative abundance under anoxic or suboxic conditions. For example, although the contemporary ocean is oxidized, no known metal can substitute for manganese in the water splitting complex in the photosynthetic apparatus. Similarly, the photosynthetic machinery has maintained a strict requirement for iron for over 2.8 Ga, and all nitrogenases require at least 16 iron atoms per enzyme complex. Some key biological processes do not have the flexibility to substitute trace elements based simply on their availability (Williams and Frausto da Silva, 1996). Hence, while oxygenic phototrophs indirectly determine the distribution of the major trace elements in the ocean interior, the distribution of these elements in the soluble phase does not reflect with the composition of the organisms.
On long timescales, seawater concentrations of trace elements reflect the balance between their sources and sinks. For trace elements, the sink term is tightly coupled with the extent of redox conditions throughout the ocean, where periods of extended reducing conditions result in greater partitioning of organic carbon into the deep ocean and sediments. This, in turn, leads to enhanced sequestering of redox-sensitive trace elements into sediments, thereby decreasing their seawater concentrations. These sedimentary rocks have a high content of marine fractions (i.e., organic matter, apatite, biogenic silica and carbonates), and so are enriched by 1–2 orders of magnitude in several trace elements: zinc, copper, nickel, molybdenum, chromium, and vanadium (Piper, 1994). The positive correlation between trace-element ratios in phytoplankton and sediments is consistent with the notion that phytoplankton have imprinted their activities on the lithosphere.

8.05.16 CONCLUDING REMARKS

The evolution of primary producers in the oceans profoundly changed the chemistry of the atmosphere, ocean, and lithosphere of Earth. The photosynthesis processes catalyzed by ensemble of these organisms not only influences the six major light elements, but directly and indirectly affect every major soluble redox-sensitive trace element and transition metal on Earth’s surface. These processes continue to provide, primarily through the utilization of solar radiation, a disequilibrium in geochemical processes, such that Earth maintains an oxidized atmosphere and ocean. This disequilibrium prevents atmospheric oxygen from being depleted, maintains a lowered atmospheric CO₂ concentration, and simultaneously imprints on the ocean interior and lithospheric elemental composition that reflect those of the bulk biological material from which it is derived.

While primary producers in the ocean comprise only ~1% of Earth’s biomass, their metabolic rate and biogeochemical impact rivals the much larger terrestrial ecosystem. On geological timescales, these organisms are the little engines that are essential to maintaining life as we know it on this planet.

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REFERENCES


Redfield A. C. (1958) The biological control of chemical factors in the environment. Am. Sci. 46, 205–221.

References