



BIOGEOCHEMICAL CYCLES

Paul G. Falkowski
Rutgers University

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GLOSSARY

- anion** Negatively charged atom or molecule.
cation Positively charged atom or molecule.
chemoautotroph Capable of growing on inorganic substrates without light energy.
eolian Wind blown.
felsic rock Continental crustal rocks relatively rich in silicon and aluminum.
fixation To make nonvolatile (forming organic molecules from inorganic gases).
heterotroph Growth dependent on the oxidation of organic matter.
mafic rock Oceanic crustal rocks relatively rich in magnesium and iron.
orogenesis Formation of mountains.
photoautotroph Growth dependent on the conversion of light to chemical energy (photosynthetic).
spallation Thermally induced neutron and proton ejection following high-energy proton collision.
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VIRTUALLY ALL NATURALLY OCCURRING ELEMENTS are found in living organisms. The biological assimilation, biochemical transformation, physical transport, and geological sequestration and mobilization of many elements are self-perpetuating and self-regenerating, leading to a “cycling” of the elements. Although the biochemical cycle for each element is unique, general reaction pathways can be discerned depending on the chemistry of the element, its role in metabolism, and its distribution on Earth.

I. INTRODUCTION

Like life itself, biogeochemical cycles are far from thermodynamic equilibrium, have evolved over hundreds of millions of years, and are interdependent, forming biogeochemical systems replete with feedback controls (Schlesinger, 1997). Biogeochemical cycles depend on, and co-evolved with, specific metabolic pathways. Hence, biogeochemical cycles depend on and are a selective force in metabolic (i.e., biological) diversity. Over geological time, biogeochemical cycles are responsible for altering the chemistry of the ocean, atmosphere, and terrestrial ecosystems such that rate-limiting reactions within key cycles modify the tempo and mode of evolution. Here, we examine some of the key biogeochemical cycles in the context of their evolution and biological diversity.

II. THE DISTRIBUTION OF ELEMENTS ON EARTH

A. The Origin of the Elements

The relative abundance of the crustal elements reveals a distribution of much more abundant light elements to lesser abundant heavier elements (Fig. 1). Although the two lightest elements, H and He, were formed approximately 16 billion years ago in the "big bang," all the heavier elements result from fusion of ^2He nuclei or fusion/spallation (proton or neutron loss) reactions in stars (Degens, 1989). The fusion reactions involving ^2He with itself, H, O, C, or N tend to form even-numbered atomic nuclei, whereas spallation and proton capture leads to odd-numbered nuclei. Additionally, because the nuclei of elements with paired protons are slightly more stable than those with an odd number, there is generally a larger relative abundance of even-numbered elements.

In the origin of our solar system approximately 4.6 billion years ago, elemental composition and planetary accretion were strongly influenced by the gravitational forces of the sun. Planet bodies closer to the sun contain

relatively higher proportions of heavy elements than bodies further away. The four innermost planets are approximately three times denser than the outer planets and have solid-rock surfaces that contain a relatively high proportion of metals, especially iron and aluminum. In the accretion process, a further gravitational distillation occurred within the planets. On Earth, the abundant heavier elements, such as nickel and iron, tended to migrate toward the center of the internal gravitational field, whereas lighter elements tended to float above the metal core and, upon cooling, accumulated as a solid surface and crust. The lightest elements formed a gaseous phase. Almost all of the two lightest gases, H_2 and He, escaped the gravitational field and diffused into interplanetary space during this initial period of Earth's history.

The composition of the gases in Earth's atmosphere following accretion is not completely resolved but almost certainly contained high concentrations of CO_2 , N_2 , and H_2O , HCl, and H_2SO_4 . This gas composition is similar to that currently on Venus. Precipitation of minerals and formation of felsic rocks led to the condensation and upward migration of liquid, precipitable water that overlies vast regions of denser, mafic rocks.

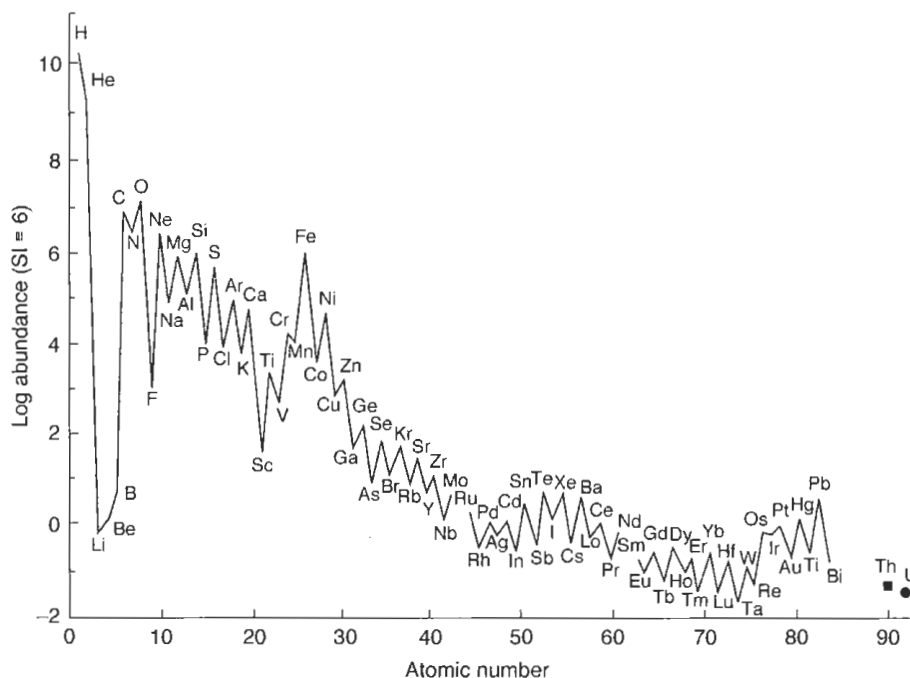


FIGURE 1 Relative abundances of the elements in the universe (based on log abundance of Si = 6). ●, even atomic numbers; ○, odd atomic numbers (reproduced with permission from Williams and Frausto da Silva, 1996, p. 290, *The Natural Selection of the Chemical Elements*, Clarendon Press, Oxford).

Additional water may have been provided by meteoritic bombardment. Based on thermodynamic equilibrium calculations with crustal elements, the acidic gases or hydrated equivalents (e.g., HCl and H₂SO₄) would have solubilized mineral cations in the primordial ocean leading to a seawater dominated by Na⁺, K⁺, Mg²⁺, and Ca²⁺. The anion balance would have been supplied by vulcanism and outgassing from deep crustal sources. The dominant anions were Cl⁻ and, to a lesser extent, SO₄²⁻ and HCO₃⁻. PO₄³⁻ was probably present but to a lesser extent, and fixed inorganic N (as NH₃ or NO₃) was almost certainly very scarce. The pH of the early oceans was probably close to neutral or slightly acidic (6.8–7.0). Additionally, radiogenically produced heat, the high concentrations of greenhouse gases, and geothermal activity would have provided a source of heat to maintain elevated temperatures in Earth's early ocean history.

From these conditions, life arose and evolved. Over the course of Earth's history, there has been a continuous trajectory from the mildly reducing conditions that prevailed at the time of origin of the planet to the highly oxidizing conditions that prevail in the contemporary geological epoch. This oxidation trajectory is driven by biological processes but has also led to the increased diversity of life forms.

B. Phase State Transitions and Elemental Partitioning

The distribution of elements between the atmosphere, lithosphere, and hydrosphere depends, to first order, on the phase state of the element, its chemical reactivity, and its partitioning coefficients between water, the atmosphere, and the lithosphere (Table I). Gases such as N₂ and O₂ partition between the atmosphere and liquid phase according to the solubility coefficient. CO₂, H₂S, and NO₂ undergo hydration to form carbonic, sulfuric, and nitric acids. These acids deprotonate, according to the pH of the aqueous environment, forming anions. Consequently, the total solubility of these species in the aqueous phase exceeds that predicted from the vapor pressure alone, assuming the gases are chemically inert and obey idealized gas laws. Similarly, the distribution of elements between the aqueous phase and the lithosphere is dictated, to first order, by the solubility coefficient of the element, its reactivity or ionic form, and the saturation level. For example, all the alkali and alkali earth metals (i.e., Li, Na, K, Cs, Ca, and Mg) are highly reactive with water and are highly soluble. Precipitation reactions of alkali earth metal cations with carbonate, sulfate, or phosphate anions result in min-

eral deposits in the solid phase. The movement of elements between the lithosphere, atmosphere, and hydrosphere is mediated by both purely physical/chemical processes and biological processes.

C. Physical/Chemical Transport Processes: Weathering

The flux of elements from continental rock sources to the atmosphere and oceans is promoted by weathering, which is the physical and chemical degradation of rocks to smaller physical pieces and soluble chemical constituents. The physical processes that promote weathering include erosion by water and wind, cracking through freeze-thaw cycles, and active abrasion by the movement of ice (e.g., glaciers), other rock formations (e.g., earthquakes and tectonic uplifting), or rocks (e.g., tidal abrasion). Ultimately, these processes lead to the formation of sediments that are transported by rivers to the ocean. In addition to physical weathering, chemical weathering is promoted by weak acids (e.g., carbonic and sulfuric) in precipitation as well as microbial and plant growth. Over geological time, the weak acids in precipitation remove alkaline cations, such as Mg and Ca, from carbonates and silicates, leading to the mobilization of these elements. Moreover, the production of weak organic acids by lichens, terrestrial plant roots, and the microbial degradation of decaying organic matter greatly promote chemical weathering. Thus, the invasion of land by terrestrial plants led to increased mobility of numerous elements and enhanced the fluxes of materials to the oceans. This results in a feedback between biogeochemical processes on land and in the ocean.

D. The Hydrological Cycle

Weathering is strongly dependent on the hydrological cycle, which is one of the earliest and most critical cycles on Earth. Water is both a solvent and a vehicle for the transport of elements. It is also critically necessary for life. Hence, the distribution of biota is critically related to the availability of water. By far, the oceans are the largest reservoir of water on Earth (Fig. 2). Flux of water into and from the oceans is driven by evaporation and precipitation, processes that are in turn driven by the heat budget of the planet. Over the oceans, evaporation exceeds precipitation; the net difference leads to precipitation over land. Because precipitation exceeds evaporation over land, there is a flux of water from land to the oceans in rivers. The atmospheric

TABLE I
Major Chemical Constituents of the Earth's Crust, Sediments, Ocean Water, and Atmosphere^a

Element	Crystal ionic charge and radius	r (Å)	Continental crust		Oceanic crust		Average sediments		Ocean water		Atmosphere	
			(wt%)	(Vol.%)	(wt%)	(Vol.%)	(wt%)	(Vol.%)	(wt%)	(Vol.%)	(wt%)	(mol%)
O	-2	1.32	46.40	93.04	43.80	92.57	47.61	91.32	86.0	99.0 as H ₂ O	23.15	20.95 (O ₂)
Si	+4	0.42	28.15	1.04	24.00	0.93	24.40	0.86				
Al	+3	0.51	8.23	0.56	8.76	0.63	6.03	0.40				
Fe	+3	0.64	5.63	0.46	8.56	0.74	3.79	0.30				
	+2	0.74										
Ca	+2	0.99	4.15	1.40	6.72	2.39	7.86	2.54	0.04	0.025		
Na	+1	0.97	2.36	1.31	1.94	1.13	1.36	0.72	1.08	0.11		
Mg	+2	0.66	2.33	0.38	4.5	0.78	2.44	0.39	0.13	0.04		
K	+1	1.33	2.09	1.75	0.83	0.73	2.00	1.61	0.04	0.062		
Ti	+4	0.68	0.54	0.05	0.90	0.09						
Mn			0.095		0.15							
H			0.14		0.2				10.7	See O		
P	+5	0.35	0.105		0.14		0.16	0.003				
S	+6	0.30	0.026		0.025		0.62	0.007	0.09	0.0002		
C	+4	0.16					2.91	0.013	0.28	0.002	0.046	0.03 (CO ₂)
Cl	-1	1.81					0.83	1.85	1.94	0.833		
N											75.53	78.09 (N ₂)
Ar											1.28	0.93 (Ar)

^a Adapted from A. Lerman (1979). *Geochemical Processes Water and Sediment Environments*. John Wiley & Sons. New York.

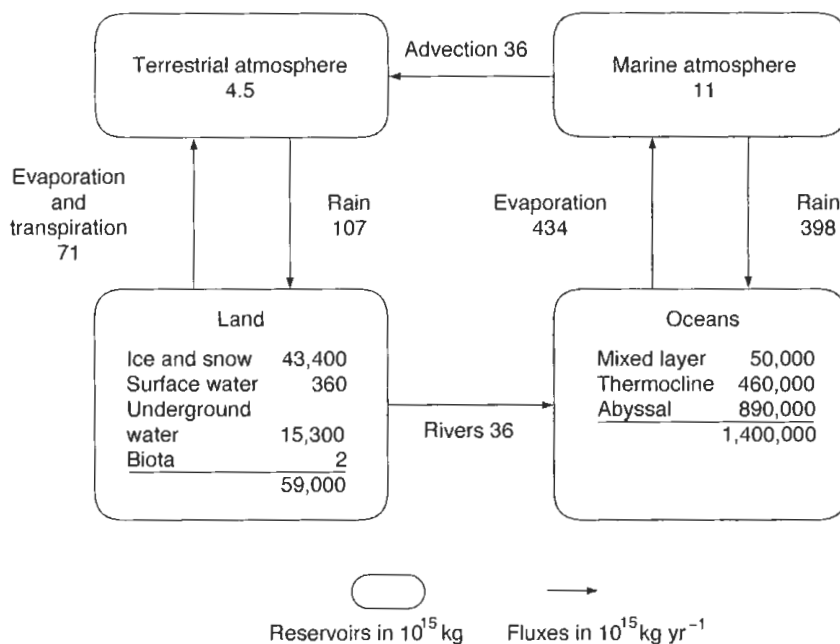


FIGURE 2 Estimates of the global water cycle and its reserves. The accuracy of several of its components is poor, resulting in a closure error for the whole cycle of about a factor of 2. The obvious interactive nature of the cycle makes it impossible to reduce current closure errors without studying the whole cycle. (Reprinted by permission from *Nature*, Chahine, Moustafa T., The hydrological cycle and its influence on climate. Vol. 359, p. 373, copyright 1992, Macmillan Magazines Ltd.)

lifetime of water is extremely short—on the order of ca. 10 days. This lifetime compares with the average for the oceans of ca. 3000 years, whereas deep groundwater can have lifetimes exceeding 10,000 years. These differences in lifetimes are critical determinants of fluxes of elements and climate feedbacks.

E. Vulcanism and Orogenesis

The riverine and eolian (wind-blown) transport of sediments from land to the oceans would, over geological time, erode the continents to the peneplane—the lowest level achievable. Vulcanism and other orogenic processes counterbalance erosion and supply new crustal rock and atmospheric sources of minerals. In the subduction regions of converging tectonic plates, sedimentary rocks are injected back into the deeper crust, where they are reprocessed by heat and pressure, emerging again in uplifting regions and through volcanic eruptions. In addition to the formation of igneous rock, vulcanism provides significant sources of iron, sulfate, and CO_2 to the atmosphere. These elements and materials are transported through the atmosphere and deposited over both the oceans and on land.

F. Biological Transport

Biological processes influence the distribution of elements primarily through phase state transitions. The chemical reduction of inorganic carbon to organic matter is a conversion of a gas to solid phase; the latter is often dissolved in an aqueous phase of the cell cytoplasm. For oxygenic photoautotrophs, the evolution of molecular oxygen leads to the formation of a gas from the liquid phase of water. Biological mediation of phase state transitions is critical for the movement of elements between the atmosphere, lithosphere, and hydrosphere. For example, CaCO_3 is by far the largest reservoir of carbon on Earth (Table II). The formation of CaCO_3 is the consequence of the biological precipitation by marine organisms and, over geological time, represents an important sink for atmospheric CO_2 . The oxidation of organic matter leads to the formation of CO_2 , which equilibrates with the atmosphere. Similarly, the biologically catalyzed oxidation of H_2S to S or SO_4 is a phase state transition that influences the partitioning of sulfur between aquatic ecosystems and the atmosphere. It should be noted that the biologically catalyzed phase state transitions need not be direct but can result from

TABLE II
Carbon Pools in the Major Reservoirs on Earth^a

Pools	Quantity ($\times 10^{15}$ g)
Atmosphere	720
Oceans	38,400
Total inorganic	37,400
Surface layer	670
Deep layer	36,730
Total organic	1,000
Lithosphere	
Sedimentary carbonates	>60,000,000
Kerogens	15,000,000
Terrestrial biosphere (total)	2,000
Living biomass	600–1,000
Dead biomass	1,200
Aquatic biosphere	1–2
Fossil fuels	4,130
Coal	3,510
Oil	230
Gas	140
Other (peat)	250

^a From Falkowski and Raven (1997, p. 130).

the indirect modification of the redox state of the environment. For example, the oxidation of H_2S occurs spontaneously in the presence of O_2 ; however, the O_2 is formed from oxygenic photoautotrophs.

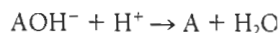
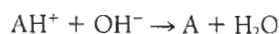
G. Biological Assimilation

To accomplish phase state transitions, biological processes catalyze chemical and/or physical reactions. Reaction sequences require an assimilation of the elements. The elemental composition of organisms is dictated, to first order, by the biochemical machinery required for maintenance, growth, mobility, reproduction, and defenses against predation. The four fundamental biochemical constituents that comprise all organisms, namely, proteins, nucleic acids, lipids, and carbohydrates, are primarily synthesized from six light elements: H, C, N, O, P, and S. Of these, N, C, and O are generally reduced, P is oxidized, and S can be both reduced and oxidized. These six elements comprise approximately 98% of all living biomass. The remainder consists of approximately 20 ion-forming elements, including Na, Mg, Si, Cl, Ca, V, C, Mn, Fe, Co, Ni, Cu, Zn, Se, Mo, Sn, and I. The transition metals are frequently used in the mediation of electron transfer (redox) reactions.

III. KEY BIOGEOCHEMICAL REACTIONS AND CYCLES

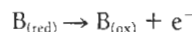
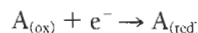
A. Hydrolysis and Oxidation-Reduction Reactions

Two biologically mediated chemical reactions are key to understanding biogeochemical cycles, namely, hydrolysis and oxidation-reduction processes. Hydrolytic reactions chemically remove from or add water to specific elements or molecules; the reactions are almost always accompanied by the transfer of protons and thus are pH-dependent processes. Hydrolytic reactions can be described in a general form by

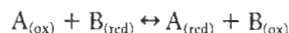


Hydration/dehydration reactions can thermodynamically store or discharge energy and determine the reactivity and solubility of elements in the first series (H, Li, Na, etc.) and of phosphorous, (inorganic) carbon, and silica in the environment.

Redox reactions are characterized by the addition or loss of electrons, hydrogen atoms (but not simply a proton), or molecular oxygen. Redox reactions are the primary engines of life, and the consequences of redox chemistry strongly impact the distributions of oxygen, carbon, nitrogen, sulfur, and transition metals in the environment. Redox reactions are always paired; there must be an oxidant and a reductant. The reaction process can be generalized by half-cells:



where the overall reaction is



For each half-cell, the tendency for a substrate to be oxidized or reduced is described by the Nernst equation:

$$E = (E_0 + 2.3 RT)/(nF \log_{10}[A_{ox}]/[A_{red}])$$

where E is the redox potential (in volts), E_0 is an arbitrarily accepted standard redox potential, F is the Faraday's constant ($= 96,487 \text{ C} = 1 \text{ mol electrons}$), n is the number of moles of electrons (Faraday's) transferred in the half-cell reaction, R is the Boltzmann gas constant,

T is temperature in Kelvin, and A_{ox} and A_{red} are the activities (or more commonly the concentrations) of the oxidized and reduced forms of the molecules, respectively. The Nernst equation describes the equilibrium condition for both electronic and ionic processes.

To maintain perpetual redox reactions, reductants consumed in one reaction must be regenerated in another (Table III). Hence, by the very fact that redox reactions are paired, a cycle is potentiated. However, to sustain a cycle of redox chemistry requires an input of energy (e.g., solar or thermal) that can be used to drive the initial condition far from thermodynamic equilibrium. Biological reduction of inorganic carbon is one such process.

B. Fundamental Biogeochemical Processes Related to Carbon

The biogeochemistry of carbon is regulated by both hydrolytic and redox reactions. On geological time-scales (>1 million years), the concentration of CO_2 in the atmosphere is a balance between crustal outgassing primarily through vulcanism which provides a source of CO_2 to the atmosphere, and chemical weathering of silica-rich rocks on the earth's surface. These reactions can be simplified as

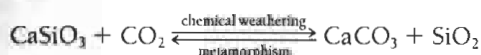


TABLE III

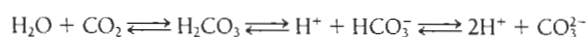
Thermodynamic Sequence for Reduction of Inorganic Substances by Hydrogen at pH 7.0 and 25°C^a

Reaction	E_h (V)	ΔG^b
Reduction of O_2 $O_2 + 4H^+ + 4e^- \leftrightarrow 2H_2O$	0.812	-29.9
Reduction of NO_3^- $2NO_3^- + 6H^+ + 6e^- \leftrightarrow N_2 + 3H_2O$	0.747	-28.4
Reduction of Mn^{4+} to Mn^{2+} $MnO_2 + 4H^+ + 2e^- \leftrightarrow Mn^{2+} + 2H_2O$	0.526	-23.3
Reduction of Fe^{3+} to Fe^{2+} $Fe(OH)_3 + 3H^+ + e^- \leftrightarrow Fe^{2+} + 3H_2O$	-0.047	-10.1
Reduction of SO_4^{2-} to H_2S $SO_4^{2-} + 10H^+ + 8e^- \leftrightarrow H_2S + 4H_2O$	-0.221	-5.9
Reduction of CO_2 to CH_4 $CO_2 + 8H^+ + 8e^- \leftrightarrow CH_4 + 2H_2O$	-0.244	-5.6

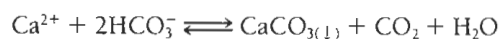
^a From Schlesinger (1997, p. 234), calculated from Stumm and Morgan (1981, p. 459).

^b Kcal mole⁻¹ per e⁻, assuming coupling to the oxidation reaction $1/4 CH_2O + 1/4 H_2O \rightarrow 1/4 CO_2 + H^+ + e^-$ and $\Delta G = -RT \ln(K)$.

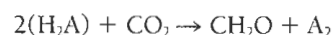
The weathering process is stimulated by the hydration of CO_2 in the atmosphere in rain, forming carbonic acid. This is a self-limiting cycle; as CO_2 rises, weathering accelerates leading to a depletion of the atmospheric inventory, which reduces weathering. In the oceans there is an excess of Ca^{2+} , and an equilibrium in the inorganic carbon system is reached. This reaction series can be specified as



and



Note that the precipitation of $CaCO_3$ leads to the formation of CO_2 . In the absence of any biological activity, the geochemical processes would lead to a cycle of inorganic carbon between the three major reservoirs, namely, the atmosphere, oceans, and continents; however, biological processes interact in two critical ways to affect carbon chemistry. First, biological pathways lead to the reduction and oxidation of carbon. Photochemical and chemoautotrophic organisms oxidize alternative substrates to reduce carbon to the equivalent of carbohydrate. These reactions can be broadly classified in the reaction sequence



where A can be sulfur, oxygen, or organic compounds. This is an example of redox reactions applied to the formation of organic material.

Under mildly reducing conditions, photosynthetic carbon fixation is catalyzed by bacteria that couple the oxidation of H_2S or organic compounds to the reduction of CO_2 to form organic compounds. The thermodynamic energy gradient in such systems is relatively low, requiring inputs of ~0.4 eV of photon energy. Such energy demands are satisfied in the infrared spectrum.

C. Biomineralization and its Biogeochemical Inferences

Many organisms precipitate carbonates, phosphates, or silicates to produce minerals. In the marine environment, the precipitation of $CaCO_3$ by phytoplankton, corals, and several genera of marine invertebrates leads to the formation of aragonite and calcite, two forms of carbonate that are relatively resistant to degradation. Virtually all the carbonate precipitated on Earth is the

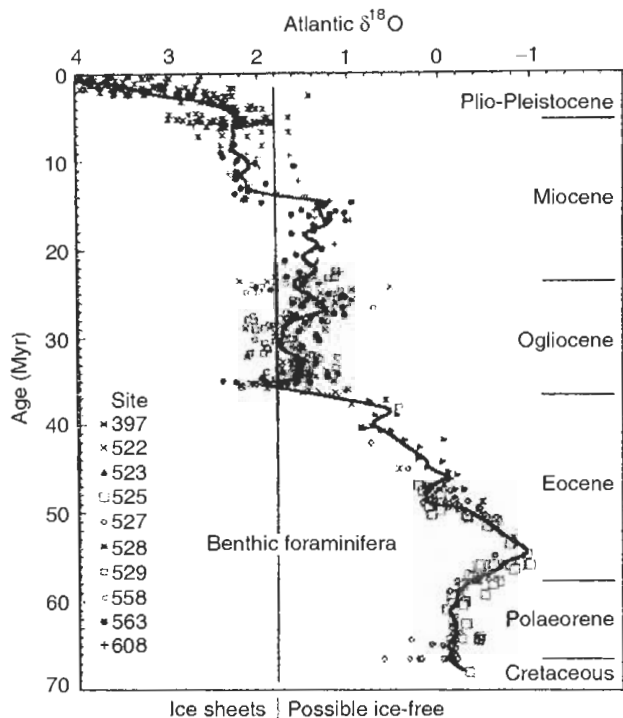


FIGURE 3 Compilation of benthic $\delta^{18}\text{O}$ measurements from Deep Sea Drilling Program sites, spanning the past 70 Ma. The long-term increase in $\delta^{18}\text{O}$ values reflects cooling of the deep ocean and growth of ice sheets at high latitudes. $\delta^{18}\text{O} = [^{18}\text{O}/^{16}\text{O}]_{\text{standard}} - 1$, where standard is PDB. (Reprinted by permission from *Nature*, Raymo, M. E., and Ruddiman, W. F. Tectonic forcing of late Cenozoic climate. Vol. 359: 117–122, copyright 1992, Macmillan Magazines Ltd.)

consequence of biological mineralization in the ocean. Over geological time, the production of carbonates produced vast beds of chalk, limestones, and marbles. The deposition of carbonates accounts for the largest reservoir of carbon on Earth. The isotopic fractionation of the stable isotopes of oxygen (^{18}O and ^{16}O) in carbonate sediments is strongly influenced by the temperature of the ocean when and where the carbonates are formed. The isotopic fractionation of the stable isotopes of carbon (^{13}C and ^{12}C) is related to the atmospheric/oceanic inventory of CO_2 . Hence, isotopic analyses of carbonates provide clues about both oceanic temperatures and carbon dioxide concentrations over geological time (Fig. 3).

Some groups of marine planktonic organisms, including diatoms and radiolaria, as well as several genera of higher plant grasses, precipitate silica to form hydrated opal. Silica is supplied to the oceans from the weathering of continental rocks and the subsequent

flux of soluble silicic acid via rivers. Like carbonates, the precipitation of silicates over geological time leads to sedimentary deposits. In terrestrial ecosystems, several groups of higher plants incorporate silica from soils into stems and shoots.

Under basic conditions, calcium and phosphate ions will spontaneously precipitate to form apatites, which are often mined as a source of phosphate for fertilizers and chemical feedstock. Vertebrates biologically control the precipitation of calcium phosphate to form bones and teeth. Approximately 85% of the phosphate and 95% of the calcium assimilated by vertebrates is incorporated in bones. The fossil record of these biomineral components provides a significant signature of vertebrate evolution but is not a significant component of crustal minerals.

D. The Oxygen Cycle

One of the most important characteristics of Earth's atmosphere is the relatively high concentration of free molecular oxygen (O_2). The mere presence of high concentrations of free molecular oxygen suggests that the chemistry of the planet is far from thermodynamic equilibrium. For all practical purposes, all the oxygen in the atmosphere originated from the photosynthetically mediated oxidation of water by oxygenic photoautotrophs. The oxidation of water to form free oxygen requires an oxidant with a potential of at least 0.83 V at pH 7. The bacterial photosynthetic apparatus could not achieve such a high oxidation potential without evolutionary modification. These modifications included the incorporation of Mn as the transient electron acceptor in the photosynthetic reaction center, the alteration of proteins that permitted the oxidation of water, and the raising of the potential of the primary electron donor by ~ 0.4 V. The latter was achieved by altering the pigment involved in the photosynthetic reaction from the relatively low energy levels that characterize bacteriochlorophylls to the higher energy levels found in chlorophyll *a*, a pigment that distinguishes cyanobacteria (i.e., blue-green algae) from all other photosynthetic bacteria.

The cyanobacteria are the oldest extant oxygenic photoautotrophs. The exact timing of the origin of cyanobacteria is uncertain, but micropaleological evidence suggests that organisms with features remarkably similar to those of modern cyanobacteria existed in the Archean ocean at least 3.5 billion years before present. Based on geochemical evidence (primarily the oxidation of iron by molecular oxygen), it appears that oxidation of Earth's atmosphere occurred over a relatively short

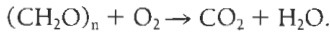
interval of ~100 million years, beginning ~2.2 billion years before present (Fig. 4).

Prior to the photosynthetic production of oxygen, all heterotrophic organisms oxidized organic carbon under anaerobic conditions. The biochemical oxidation of carbon under such conditions is thermodynamically inefficient, often leading to fermentation. For example, in the absence of oxygen, molecules such as acetate are potentially oxidized to methane and CO₂:



where the methane is liberated to the environment.

The generation of oxygen led to thermodynamically favorable conditions for the oxidation of organic matter via aerobic respiration. The basic redox sequence for aerobic respiration is



This thermodynamic coupling between the photosynthetic reduction of organic carbon and the oxidation of water is reversed in mitochondria, in which oxygen is

used as a sink for electrons and the oxidation of organic carbon is coupled to biochemical energy. Initially, the oxygen could be utilized by single-celled organisms via diffusion; subsequently, however, proteins and structures evolved that facilitated the diffusion and transport of O₂ and led to the evolution of metazoans.

E. Sequestration and Burial

From a biogeochemical perspective, the net evolution (i.e., accumulation) of molecular oxygen in the atmosphere means that oxidation of water and the (bio)geochemical reduction of free oxygen are not balanced, i.e., photosynthetic oxygen evolution must have exceeded oxygen consumption. Given the vast quantities of water on the surface of the planet, oxygenic photosynthesis could produce enormous quantities of oxygen without running out of substrate. When can such conditions occur and what are the oxygen-consuming reactions?

Prior to the net accumulation of oxygen in the atmosphere, oxygen produced by oxygenic photoautotrophs in the oceans would have been exposed to several potential reductants, two of which are especially biogeochemically important, namely, sulfur and iron. After Cl⁻,

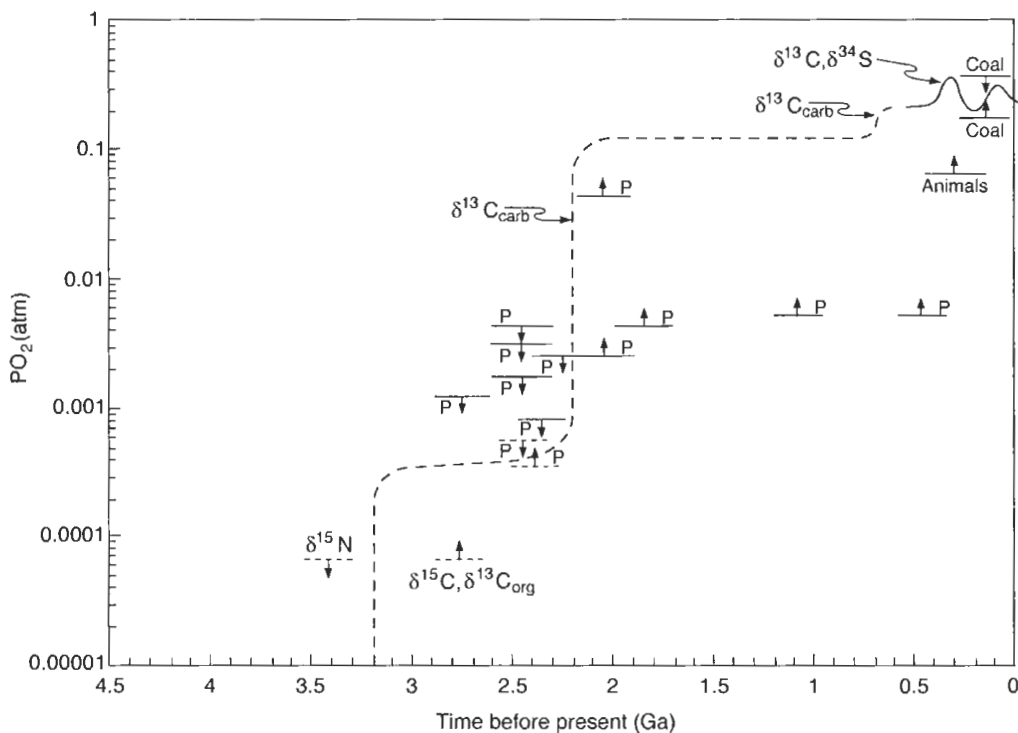


FIGURE 4 The evolution of oxygen on Earth (reproduced with permission from *American Journal of Science*, Rye, R. and H. Holland (1998). *Paleosols and the evolution of atmospheric oxygen: a critical review*. Vol. 298).

SO_4^{2-} is the most abundant anion in the ocean. Under the mildly reducing conditions of the Archean ocean, dissolved aqueous sulfur in the ocean would have been in equilibrium between a reduced form, probably sulfide (H_2S), and the hydrated, oxidized form H_2SO_4 . The latter (sulfuric acid) would equilibrate with the alkaline or earth alkaline elements of the first and second series, resulting in the formation of ionized sulfate salts. The precipitation of sulfate minerals (e.g., gypsum) could occur in shallow seas when evaporation leads to supersaturation and during periods when the influx of Ca from continental sources is high. The latter occurred during periods of rapid invasion of land by terrestrial plants (e.g., during the Triassic Period), where plant growth promoted weathering. Thus, photosynthetic evolution of oxygen led to the formation of vast quantities of sulfate via the oxidation of reduced sulfur anions; sulfur oxidation acted as a sink for molecular oxygen.

Under reducing conditions, iron, as Fe(II), is relatively soluble in seawater, whereas its oxidized counterpart, Fe(III), is virtually insoluble. The photosynthetic oxidation of the Archean ocean not only resulted in the oxidation of sulfur but also led to the oxidation and subsequent precipitation of iron oxides (rust) in ocean

sediments. Thus, the biologically catalyzed oxidation of iron served as a second electron sink for molecular oxygen—a sink that ultimately came to represent the largest reservoir for the transition metal on Earth. The deposition of iron oxides would proceed until virtually no soluble iron remained in the ocean. The deposition of iron in Archean sediments is recorded in several deposits, the dating of which provides a record of the oxidation of the atmosphere (Fig. 5).

When the electron sinks in reduced iron and sulfur were consumed, oxygen could be consumed in respiratory reactions involving (photosynthetically) reduced carbon. If, however, there was a net evasion of photosynthetically derived oxygen to the environment (i.e., the oceans and atmosphere), then a stoichiometric amount of organic carbon must have avoided oxidation, i.e., organic carbon must have accumulated. The primary sink for organic carbon is marine sediment in which, in the absence of oxygen, carbon adsorbs to inorganic sedimentary particles and becomes buried in the sedimentation process. The sequestration and burial process occurred over hundreds of millions, if not billions, of years, and it resulted in the accumulation of massive amounts of organic carbon associated with sedimentary and lightly metamorphosed rocks (e.g., shales

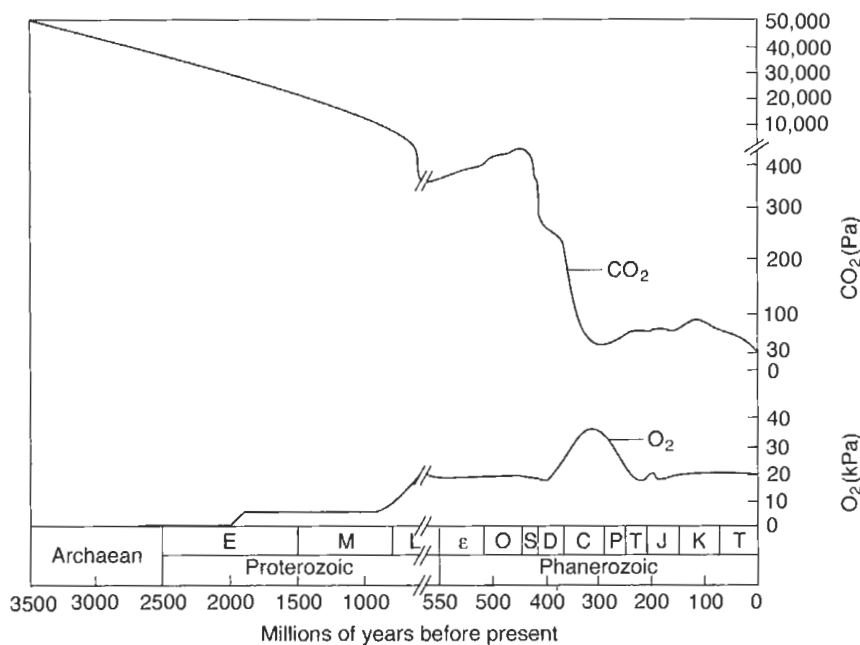


FIGURE 5 A reconstruction of variations in the partial pressures of CO_2 and O_2 in the atmosphere through geological time using data from Berner (1990, 1993) and Berner and Canfield (1989) for the post-Cambrian epochs (i.e., the Phanerozoic). The absolute values and timing for the evolution of oxygen are not constrained in the Proterozoic Epoch. (From Falkowski and Raven, 1997.)

TABLE IV
Annual and Seasonal NPP of the Major Units of the Biosphere, from CASA-VGPM^a

	Ocean NPP		Land NPP
Seasonal			
April to June	10.9		15.7
July to September	13.0		18.0
October to December	12.3		11.5
January to March	11.3		11.2
Biogeographic			
Oligotrophic	11.0	Tropical rain forests	17.8
Mesotrophic	27.4	Broadleaf deciduous forests	1.5
Eutrophic	9.1	Broadleaf and needleleaf forests	3.1
Macrophytes	1.0	Needleleaf evergreen forests	3.1
		Needleleaf deciduous forest	1.4
		Savannas	16.8
		Perennial grasslands	2.4
		Broadleaf shrubs with bare soil	1.0
		Tundra	0.8
		Desert	0.5
		Cultivation	8.0
Total	48.5		56.4

^a Ocean data are averages from 1978 to 1983. The land vegetation index is from 1982 to 1990. All values are in petagrams of carbon (1 pg = 10¹⁵ g). Oligotrophic < 0.1 μg Chl/L; mesotrophic 0.1–1.0 μg Chl/L; eutrophic > 1.0 μg Chl/L. The macrophyte contribution to ocean production is not included in the seasonal totals. (Reprinted with permission from Field *et al.* (1998). "Primary production of the biosphere: integrating terrestrial and oceanic components." *Science* 281, 237–240).

and cherts). A very small fraction of the buried organic carbon underwent alterations due to heat and pressure (i.e., diagenesis) to become fossilized carbon that literally fuels the industrialized world in the current geological epoch (Table II).

F. Primary Production in the Contemporary World

The carbon remaining in photosynthetic organisms following their own respiratory costs is potentially available for consumption by other organisms. This remaining carbon, or net primary production (NPP), provides the energy requirements of all ecosystems. The distribution of NPP between the terrestrial and marine ecosystems is given in Table IV. These data suggest that terrestrial ecosystems, containing approximately 99% of the plant biomass, account for approximately 55% of the global NPP, whereas marine ecosystems, containing approximately 1% of the plant biomass, account for 45% of the productivity. The huge discrepancy between

NPP per unit biomass between these two ecosystems suggests that, on average, the lifetime of marine primary producers is less than 1 week, whereas the lifetime of terrestrial primary producers is on the order of a decade or more. On land, NPP is primarily limited by the availability of water, whereas in the oceans NPP is primarily limited by the availability of essential nutrients, especially fixed forms of nitrogen.

During the past several hundred thousand years, global NPP has remained relatively constant, whereas the distribution of NPP between terrestrial and marine ecosystems has waxed and waned with climatic shifts. Briefly, every 100,000 years or so, changes in Earth's orbital relation to the sun lead to a small reduction in surface temperature, which is amplified (through unknown processes) to produce glacial periods. The advance of ice sheets in the Northern Hemisphere, combined with a reduction in liquid precipitation at low latitudes, leads to the loss of terrestrial NPP by approximately 30%. Simultaneously, however, enhanced upwelling fluxes of nutrients in the oceans combined with a strengthened eolian flux of iron stimulate oceanic

NPP, such that the change between the terrestrial loss and oceanic gain is approximately balanced. During interglacial periods, the situation reverses, with a retreat of the ice sheets and the relaxation of nutrient enrichment of the upper ocean to lead to the situation shown in Table IV for the contemporary world.

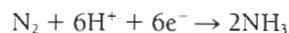
G. Oceanic Solubility and Biological "Pumps"

The oceans contain approximately 50-fold more organic carbon than the atmosphere, and on timescales of centuries the former reservoir controls the concentration of CO₂ in the latter. The vertical gradient of inorganic carbon in the oceans is "inverted"—that is, there is a higher concentration of inorganic carbon in the ocean interior than at the surface (Fig. 6). Because the ocean surface tends to equilibrate with the atmosphere, the vertical gradient is maintained by processes other than simple equilibrium diffusion. There are two major processes responsible for the observed gradient. First, cooling of waters at high latitudes increases the solubility of CO₂ while simultaneously increasing the density of the waters. The cold, CO₂-rich waters sink into the ocean interior, where they are transported by density

discontinuities and the motion of the earth throughout the world oceans. The round-trip takes approximately 1000 years before the waters are again in contact with the atmosphere in the high latitude from whence they originated the journey. This "solubility" pump is responsible for approximately 50% of the inorganic carbon gradient. The other 50% is a consequence of biological activity. In the upper, lighted portion of the ocean, photosynthetic fixation of inorganic carbon by phytoplankton leads to the formation of organic matter, largely in the form of particulate materials. Gravity, acting on the particles, leads to a persistent "rain" of organic matter into the ocean interior. The organic matter is oxidized by heterotrophic bacteria and other organisms, leading to the production of inorganic carbon. Thus, this vertical flux of organic carbon and its subsequent oxidation effectively pumps up the ocean interior with inorganic carbon. The biological pump is maintained by the upward flux of inorganic nutrients from the ocean interior, especially fixed nitrogen and phosphate. Such nutrients are essential to supporting the photosynthetic activity of phytoplankton in the upper ocean.

H. The Nitrogen Cycle

All organisms contain nitrogen that is reduced to the equivalent of NH₃ (ammonia). The most abundant form of nitrogen in the environment is N₂, which at the temperature and pressure on Earth's surface is a gas and forms 78% by volume of the planet's atmosphere. Conversion of N₂ to NH₃ requires the addition of three protons and three electrons per atom of N; the balanced equation is



This reaction is kinetically limited at low pressure and the physiological temperatures, and without some catalytic enhancement there would be no ammonia in the environment. A small subset of bacteria evolved with the capability to "fix" N₂. Nitrogen fixation, or diazotrophy ("eating nitrogen"), is catalyzed by a protein complex (nitrogenase) which is irreversibly inactivated by oxygen. The enzyme complex normally contains an Fe subunit and a Mo, Fe subunit; however, V and Fe can substitute for Mo as mediators of electron transfer in some organisms. Gene sequence analysis suggests that nitrogenase evolved from a single common ancestor, and the enzyme is primarily found in eubacteria, although some Archea, such as methanogens, can also fix nitrogen. *In vivo* nitrogen fixation consumes approx-

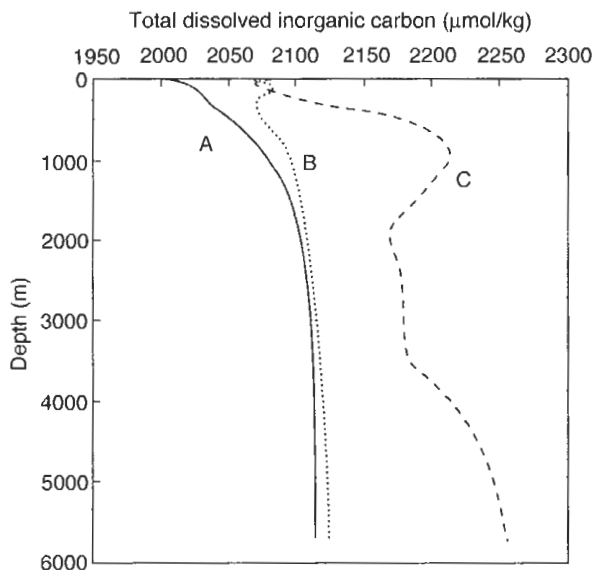
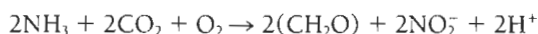


FIGURE 6 Total dissolved inorganic carbon (DIC) concentration in the ocean. (A) Modeled values prior to 1765; (B) modeled values from 1990; (C) observed totals in 1990. The difference between curves C and B represents the contribution of the biological pump to the sequestration of DIC in the ocean interior.

imately 16 ATP molecules per mole of N_2 fixed; this high-energy demand requires significant energy supply. In eubacteria, the supply of energy is either light (for N_2 fixing cyanobacteria), or reduced carbon substrates (for heterotrophic bacteria). For methanogens it is H_2 . Whatever the energy source, N_2 fixation is a metabolically expensive process, and hence, in the presence of high concentrations of fixed nitrogen, it usually is repressed. Many nitrogen-fixing bacteria live symbiotically with a host organism. One classical symbiosis is found in the Legumacea, which are higher plants such as peas and clover in which nitrogen-fixing bacteria are found in nodules attached to the plant root. In a second symbiosis, some insects, such as termites, contain nitrogen-fixing bacteria within their guts to supply essential amino acids to the host.

In most oxidized environments, fixed inorganic nitrogen is found in the form of nitrate (NO_3^-) or, to a lesser extent, nitrite (NO_2^-). These two oxidized forms of nitrogen are formed from ammonium via the action of nitrifying bacteria. Nitrification is a metabolic process in which the oxidation of ammonium can be coupled to the reduction of inorganic carbon to form organic molecules without light energy. This type of metabolic process is called chemoautotrophy. For example,



The pathway for ammonium oxidation is broken down between organisms that can oxidize the substrate to nitrite and those that further oxidize nitrite to nitrate. Nitrification is a metabolically inefficient process; one mole of NH_3 is oxidized to produce each mole of organic carbon. Hence, the growth rate of nitrifying bacteria is generally low, whereas in the presence of O_2 the rate of ammonium oxidation is generally rapid. Nitrification is confined to a small number of eubacteria; the gene sequence analysis of these organisms suggests the pathways evolved from single ancestral genes and are relatively conserved. Nitrate (NO_3^-) is a thermodynamically stable molecule under the oxidizing conditions of the contemporary world, and as such it is the most prevalent form of fixed nitrogen in the world oceans.

The cycle of nitrogen is completed when oxidized species of nitrogen, especially NO_3^- , are subsequently reduced to form N_2O and N_2 . This anaerobic process, called denitrification, is mediated by a wide range of diverse bacteria and Archaea. Denitrification is a respiratory pathway in which the terminal electron acceptor is NO_3^- or NO_2^- . Organisms generally reduce these two substrates "opportunisticly," that is, when they are deprived of oxygen. The reduction of nitrate to nitrous

oxide and N_2 represents a large loss of fixed nitrogen in the environment and largely occurs in anaerobic sediments of marine and lacustrine environments and in areas of soil rich in organic carbon that are periodically flooded (e.g., rice paddies and river deltas).

Although approximately half of all the nitrogen fixed on Earth is due to natural biological activity in the environment, half is due to deliberate fixation by human activities (Fig. 7). Developed in the latter part of the nineteenth century by a German chemist, the Haber reaction permits the formation of ammonium from N_2 by a high-temperature, high-pressure reduction in the presence of H_2 . This reaction is the primary source of fertilizer nitrogen for commercial crops, without which agricultural production would be much smaller than it is currently. However, approximately 25% of the applied nitrogen to agricultural crops is lost through denitrification, leading to an increase in N_2O in the atmosphere. A significant fraction of the applied nitrogen in terrestrial ecosystems is further solubilized in waters, flowing either into groundwater or through surface waters to the sea. Most of this fixed nitrogen seldom makes its way to the open oceans; rather, due to the high rates of denitrification on continental margins (especially in sediments on the margins), the fixed nitrogen tends to be lost to the atmosphere through denitrification.

I. Profiles of Elements in the Sea

In the oceans there are three basic profiles to describe the distribution of elements. If an element is conservative, and is either extraordinarily abundant or does not interact with particulate matter (i.e., biological material), it will be homogeneously distributed. The soluble salts in seawater represent a vast quantity of alkaline metals, halides, and sulfates. These elements are so abundant relative to biological demands and biomass that they behave as conservative tracers; that is, their distributions are effectively uniform through the oceans. If an element is biologically reactive and can be absorbed in surface waters and subsequently transported by sinking to the ocean interior, the interior ocean can be enriched in the element relative to the surface. Such elements are said to have "nutrient-like" behavior. Examples of such elements include C, P, fixed N, Si, Fe, Cu, Ni, Cd, Hg, and the rare earth elements (REE's). It is important to note that simply because an element has a nutrient-like behavior it is not necessarily a true nutrient and vice versa. A REE, such as La^{3+} , is highly reactive with sulfhydryl ($-SH$) groups found in most proteins and hence can be "scavenged" from the surface ocean by particles. In contrast, sulfate is so

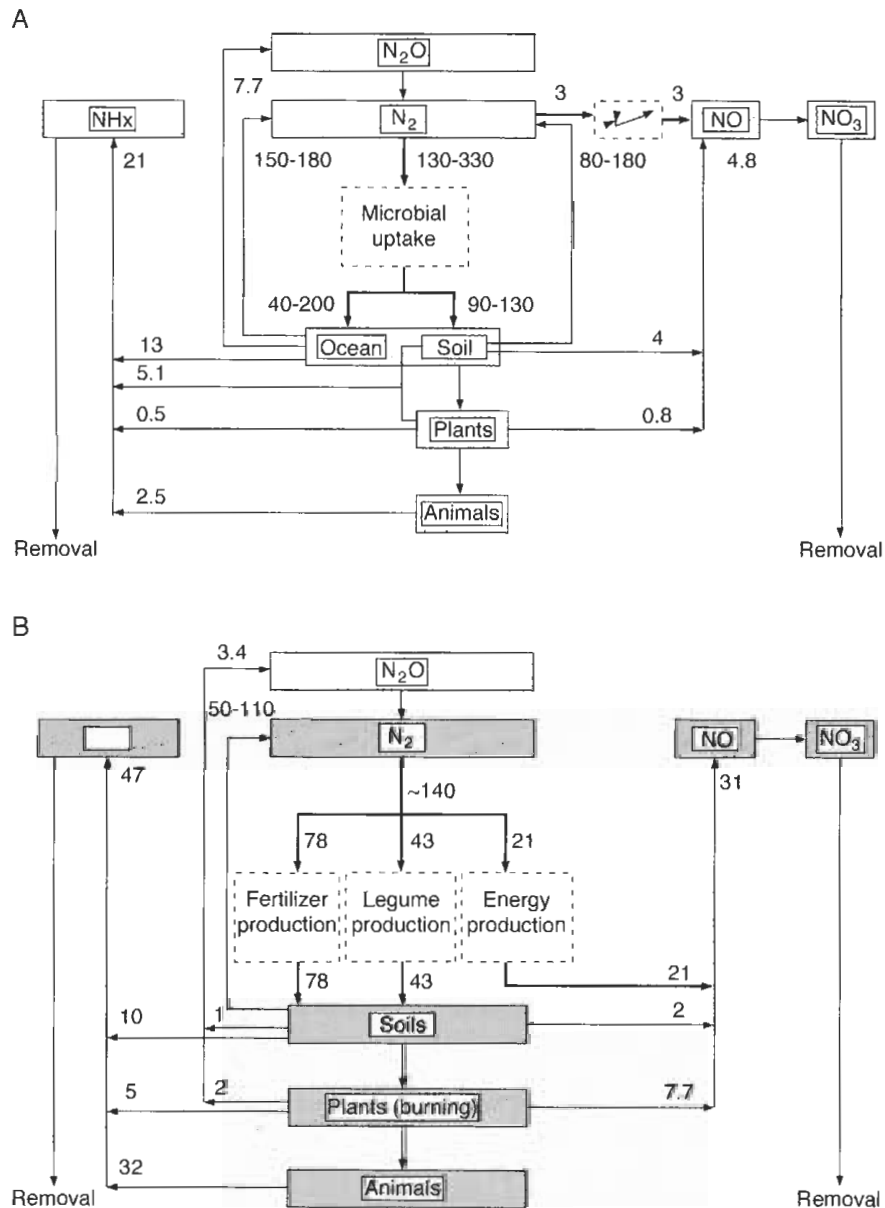


FIGURE 7 Global N-fixation rates and emission to the atmosphere (Tg N year⁻¹) from (A) preindustrial and (B) anthropogenic sources. The boxes with dashed lines represent processes that convert unreactive N to reactive N (reproduced with permission from Galloway *et al.* (1995) N-fixation, anthropogenic influence. *Global Biogeochem. Cycles* 9, 235–252).

abundant in the ocean that even though it is used as a nutrient in formation of proteins, the level of utilization is so small in comparison with its concentration that it behaves more like a conservative tracer than a nutrient. The third category of elemental distributions leads to an elevation in surface water and is primarily associated with an upper ocean source. One example is the vertical profile of O₂, which is generated by photosyn-

thetic activity in the upper ocean and consumed in the sea interior by respiration.

J. Sulfur

Sulfur is an integral element in two amino acids, methionine and cysteine, and hence is an essential element for

protein synthesis in all organisms. The biogeochemical cycle of sulfur is primarily dependent on microbial metabolism. Under anaerobic conditions, sulfate is used as an electron sink for a wide variety of anaerobic heterotrophic microbes, leading to the formation of H_2S . This same gaseous product can be photochemically oxidized by anaerobic photosynthetic bacteria to produce reductants for inorganic carbon. Thus, a simple cycle of sulfur can be generated under totally anaerobic conditions, as long as an external energy source (e.g., light) is available to keep the system far from thermodynamic equilibrium. H_2S is also produced from geochemical reduction of sulfur in the earth's mantle and is emitted to the atmosphere and oceans through vulcanism and geothermal springs (e.g., hyperthermal deep-sea vents). The reduced sulfur flux at deep-sea vents provides a reductant for carbon fixation in symbiotic non-photosynthetic (i.e., chemoautotrophic) bacteria found in the guts of a variety of invertebrates that colonize vent regions. This metabolic pathway is also sustained by photosynthesis, albeit indirectly. The thermodynamic gradient that allows chemoautotrophic sulfur-oxidizing bacteria to extract reducing power from H_2S depends on the oxidation of the ocean by oxygenic photoautotrophs. Under aerobic conditions, sulfur is primarily found in an oxidized form, usually as a sulfate salt, that is assimilated and reduced by photoautotrophs and microbes to a sulfhydryl (-SH). Hence, sulfur is both a source and a sink for metabolic electrons.

In the oceans, sulfate is the second most abundant anion following chloride. The biological assimilation and reduction of sulfur by marine microbes and plankton leads to the formation of volatile sulfur gases, notably dimethylsulfide and, in anaerobic aquatic systems, H_2S . Upon exposure to oxygen in the atmosphere, these reduced forms of sulfur are oxidized and hydrolyzed to form sulfate salts that are transported as aerosol particles. Additional sources of aerosol sulfate include volcanic eruptions and the combustion by-products of fossil fuels, especially coal. Aerosol sulfate plays two important roles in climate feedbacks. First, the particles are hygroscopic, and upon absorption of water vapor they enhance the scattering of shortwave solar radiation (i.e., the planetary albedo). This light-scattering process tends to reduce the heating of the earth by the sun (the so-called "white house effect"). Second, as hygroscopic particles, aerosol sulfate particles provide a nucleation site for water precipitation in clouds, i.e., the particles act as cloud condensation nuclei. The atmospheric lifetime of sulfate particles is short, on the order of weeks. As water vapor builds in clouds, or the clouds are advected aloft and cool, precipitation of liquid water (i.e., rain) washes sulfate from the atmosphere. When aerosol

sulfate loading is excessive (e.g., when fossil fuel combustion is high), a small fraction of hydrated sulfate in rain is not buffered by cations, and the sulfate reacts with water to form a dilute solution of sulfuric acid (H_2SO_4), producing acidic rain. Note that the transport of sulfur from continental and aquatic sources to and from the atmosphere is a consequence of phase state transitions, redox reactions, and hydrolysis.

K. Phosphorus Cycle

Phosphorus is an essential component of all cells; the element forms the backbone of nucleic acids, without which cells cannot reproduce. Phosphorus is also incorporated in nucleotides, sugars, proteins, and lipids. In vertebrates, almost all the phosphorus is combined with calcium to form hydroxylapatite, which is the central molecule to build bones.

In the environment, phosphorus is found almost invariably in the oxidized form as hydrated phosphate. Mineral phosphate salts erode and weather from continental sources and are carried to aquatic ecosystems as soluble ions. There is no eolian phosphorus source and no significant transfer of phosphate from aquatic or terrestrial environments to the atmosphere. Unlike carbon, nitrogen, phosphate, or oxygen, phosphorus does not undergo significant biologically mediated redox reactions; the chemistry of phosphorus is solely based on hydrolysis.

L. Trace Metals

Transition metals play a key role in biological electron transfer (redox) reactions and biological processes in turn affect the availability of metals in the environment. The metals are incorporated into protein "scaffolds" in specific orientations and associated with specific ligands such that the electron transfer reactions are highly specified and optimized. The transfer of electrons to given substrates is often keyed to specific metals. For example, electron transfers involving O_2 frequently are mediated by Mn, whereas electron transfers involving N frequently are mediated by Mo. The availability of transition metals, in turn, is dictated by solubility and redox conditions. Under anaerobic conditions, Mn and Mo are often sequestered as sulfide precipitates, but they become more available under oxidizing conditions. In contrast, Fe, which is a required electron transition metal in all organisms, is abundant under reducing conditions but scarce under oxidizing conditions.

As previously noted, electron transfers through iron are essential to both anaerobic and oxygenic photosynthesis, heterotrophic respiration, and nitrogen fixation.

In some cases, anaerobic bacteria can oxidize Fe(II) to Fe(III), thereby precipitating iron as a ferric hydroxide in the sediment. Although iron is the most abundant transition metal in the earth's crust, its concentration in the open ocean is extremely low, averaging no more than ~ 1 nM. To satisfy iron fluxes, eolian sources of iron are critical. Wind-blown dust from major desert areas supplies much of the iron to the open oceans. Consequently, open ocean areas, far removed from continental dust regions, have extremely low iron concentrations that result in a direct limitation of photosynthetic electron transport. Three such areas are the Southern Ocean, the eastern Equatorial Pacific, and the sub-Arctic Pacific. Ice core records suggest that during glacial periods eolian iron fluxes were much greater. The variations in dust supply appear to correspond with changes in the hydrological cycle; warm, wet climate regimes tend to reduce the eolian supply and hence may limit the biological sequestration of carbon in the oceans, whereas cold, dry periods may stimulate oceanic primary production.

Mn is essential for oxygen evolution and, like iron, its concentration is extremely low in the oceans. The Mn requirements for biological activity are lower than those for Fe; consequently, there is no evidence of Mn limitation in either the oceans or the terrestrial ecosystems. Interestingly, Mn and Fe can exchange electrons spontaneously and, in the presence of a redox gradient established in sediments, can cycle between oxidized and reduced states. Mn has two main oxidation states, namely, Mn(II) and Mn(IV). Organic carbon and NH_4 can be oxidized by Mn(IV), forming CO_2 and N_2 , respectively, whereas reduced Mn can be oxidized by O_2 and possibly by NO_3 .

Many other transition metals have been co-opted for various biologically mediated electron transfers. Mo is often utilized biologically in electron transfer reactions involving nitrogen. Most nitrogenases contain Mo, as do all nitrate reductases. Copper is frequently found in hydrophyllic proteins that either catalyze single electron transfer reactions (e.g., plastocyanin) or coordinate oxygen binding (in the case of hemocyanin). The availability of these metals is inverse to those of Mn and Fe, namely, under oxidizing conditions, Mo and Cu are more abundant than under reducing conditions (Williams and Frausto da Silva, 1996).

IV. EVOLUTION OF BIOGEOCHEMICAL CYCLES

By definition, biogeochemical cycles are mediated in part by living organisms. The origins of biogeochemical

cycles are presumably entwined with the origins of life. Although there is no consensus on the definition of life, to sustain life all living organisms must grow and reproduce. Growth is dependent on the availability of substrates and energy. C, N, P, H, O, and S are required substrates; often these substrates are combined (e.g., all organisms require phosphorus in the form of the phosphate anion, H_2PO_4^-). All life forms either oxidize or reduce carbon; hence, carbon is either an electron sink or a source, depending on the thermodynamic basis of the organism's metabolism. Given an external energy source, the redox reactions can run "uphill," where an environmental redox gradient is used to thermodynamically provide the free energy for the subsequent carbon reduction. This metabolic strategy characterizes chemoautotrophs. In photoautotrophs, the energy is externally provided by light. All carbon-oxidizing organisms require an alternative electron sink, such as O_2 , NO_3 , and SO_4 .

All the basic biogeochemical cycles evolved more than 2 billion years ago in unicellular organisms. The evolution of the cycles is interdependent; that is, the requirement by all organisms to obtain reduced carbon for energy and growth created a selection pressure. Under moderately reducing conditions of the early earth, processes that led to N_2 fixation and methane production were more favorable than under oxidizing conditions; hence, these biogeochemical processes are among the earliest. Phylogenetic trees, constructed from 16S RNA sequence homology, suggest that the earliest organisms were nonphotosynthetic, thermophilic chemoautotrophs that are placed at the root branch between the Archea and Eubacterial kingdoms. These early organisms could have used inorganic substrates, such as H_2 , H_2S , and Fe^{2+} , to reduce CO_2 to carbohydrate. Indeed, such organisms persist and thrive in deep-sea vents, in volcanic hot springs deep in Earth's crust, and in other "extreme" environments in which liquid water and suitable oxidizable inorganic substrates are available. Chemoautotrophs are almost certainly the precursors of photosynthetic cells. The evolution of a photosynthetic process in a chemoautotroph forces consideration of both the selective forces responsible and the mechanism of evolution.

Reductants for chemoautotrophs are generally deep in the earth's crust. Vent fluids are produced in magma chambers connected to the athenosphere. Therefore, the supply of vent fluids is virtually unlimited. In the contemporary ocean, the chemical disequilibria between vent fluids and bulk seawater (which is highly oxidized) provides a sufficient thermodynamic gradient to continuously support chemoautotrophic metabolism. However, the redox gradient in early Earth's

oceans did not exist prior to oxygenic photosynthesis. Moreover, magma chambers, vulcanism, and vent fluid fluxes are tied to tectonic subduction regions, which are transient features of Earth's crust and hence only temporary habitats for chemoautotrophs. To colonize new vent regions, the chemoautotrophs would need to have been dispersed throughout the oceans by physical mixing. This same dispersion process would have helped ancestral chemoautotrophs exploit solar energy near the ocean surface. The evolution of photosynthetic organisms led to a highly redundant process; that is, many organisms are capable of reducing inorganic carbon to form organic materials utilizing solar energy. The ecological (i.e., "functional") redundancy ensures a continuity of photosynthetic carbon fixation in all environments in which light and liquid water are available. Currently, there are approximately 20,000 species of aquatic oxygenic photosynthetic organisms belonging to 10 divisions; there are approximately 250,000 species of terrestrial (vascular) plants belonging to 3 divisions (Falkowski and Raven, 1997).

The evolution of oxygenic photosynthesis provided a niche for the co-evolution of ammonium and sulfide-oxidizing bacteria. The action of these organisms led to the chemoautotrophic production of NO_3^- and SO_4^{2-} , which are the most common forms of N and S found in the oceans and most terrestrial ecosystems today. The cycles of these elements are completed under anaerobic conditions, in which the oxidized forms of the elements are used as electron sinks in respiratory pathways. Under many conditions, fixed nitrogen limits primary production in both terrestrial and aquatic ecosystems. In contrast to photosynthesis, N_2 fixation is constrained to a relatively small number of bacteria, and hence the process is "functionally singular." The lack of diversity among N_2 fixers and the subsequent low supply of fixed N to many ecosystems represents a bottleneck in biogeochemical cycles. In the oceans,

N_2 fixers appear to be limited by the availability of Fe and P.

See Also the Following Articles

ATMOSPHERIC GASES • CARBON CYCLE • DIVERSITY, ORGANISM LEVEL • GEOLOGIC TIME, HISTORY OF BIODIVERSITY IN • GREENHOUSE EFFECT • NITROGEN AND NITROGEN CYCLE • THERMOPHILES, ORIGIN OF • VENTS

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