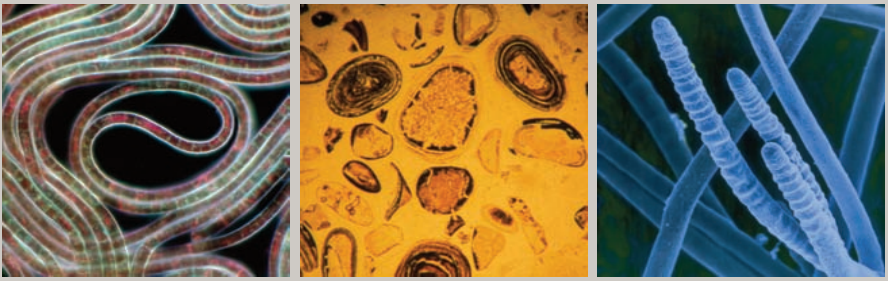

The Role of Marine Biota in the Functioning of the Biosphere

Carlos M. Duarte (Ed.)

Fundación BBVA

CSIC
Consejo Superior de Investigaciones Científicas

The Role of Marine Biota in the Functioning of the Biosphere

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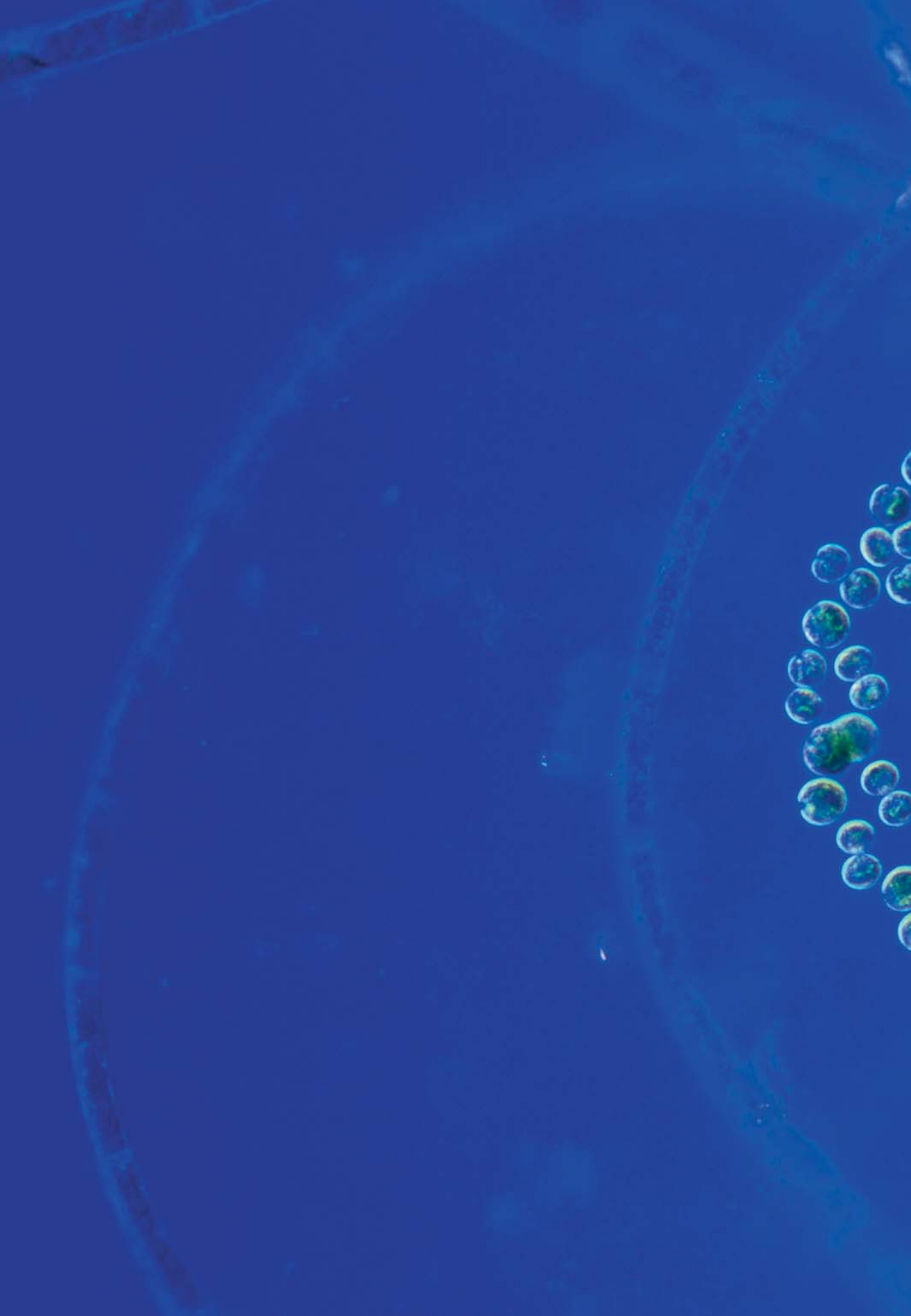

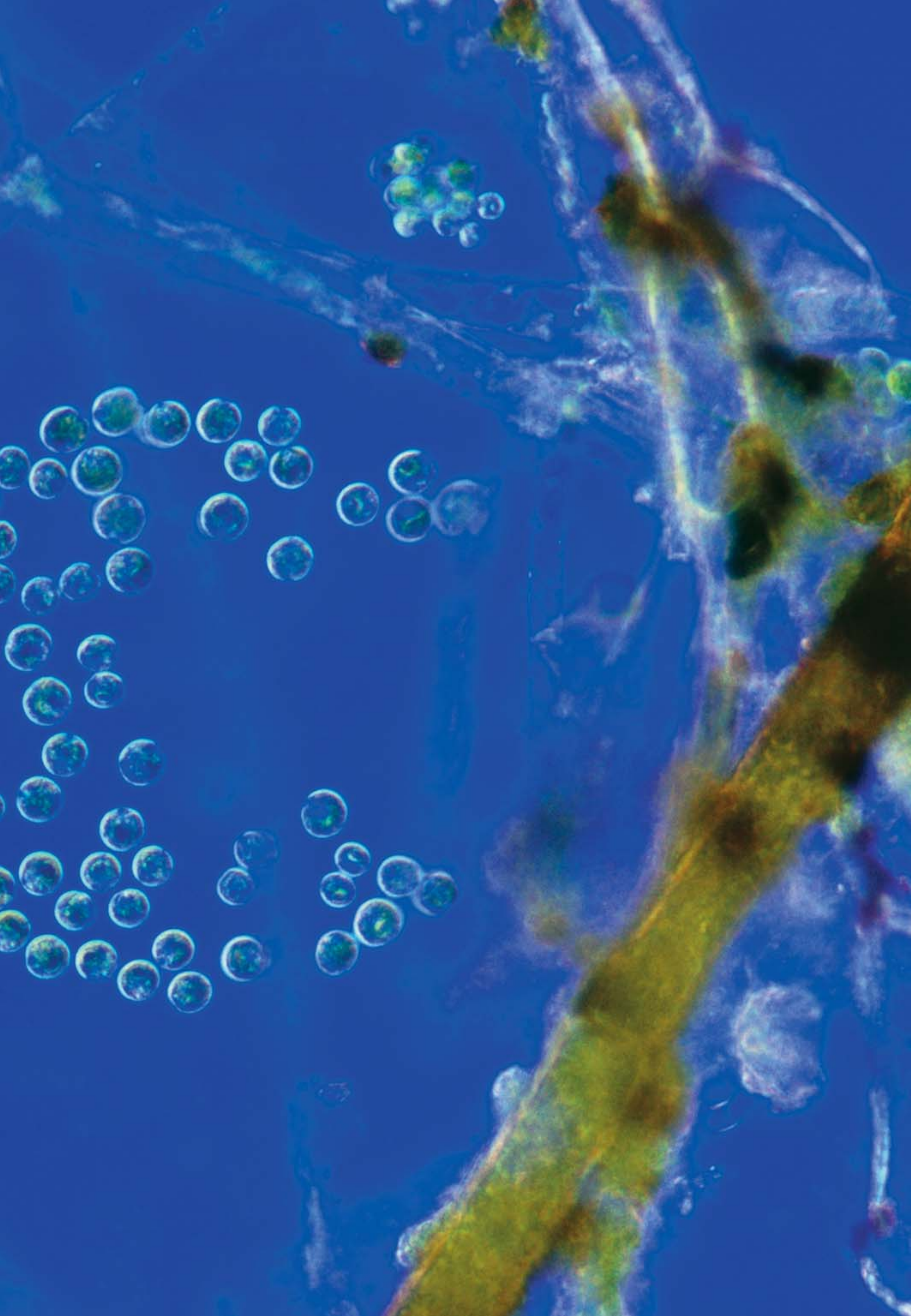

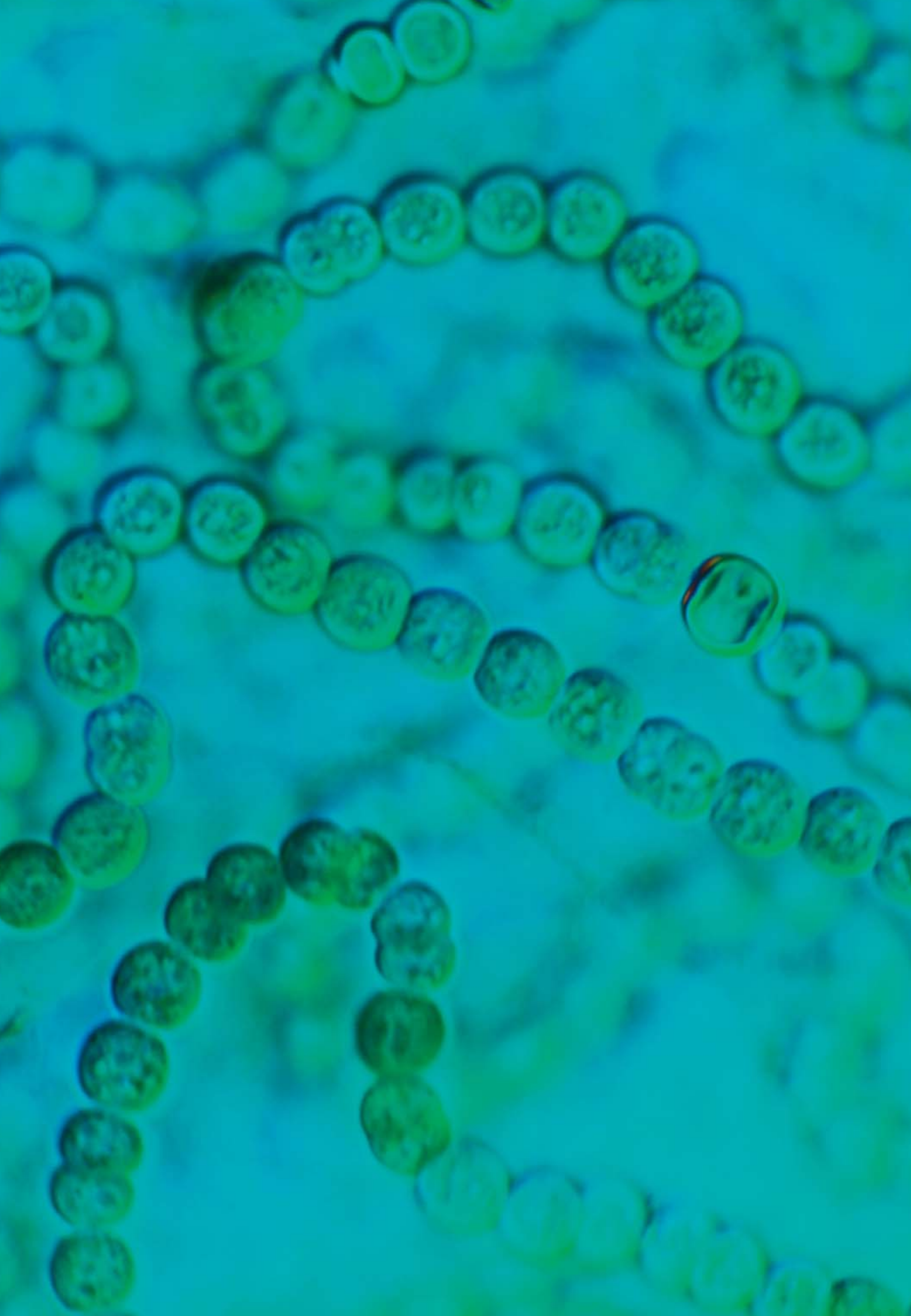

INTRODUCTION

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While society values highly the role of forests, that of plankton communities while performing similar functions in the ocean, remains relatively unknown. This is despite the fact that the oceans encompass 72% of the surface of planet Earth, and play a key role in the functioning of the Biosphere. Yet, Ocean plankton has played a fundamental role in the evolution of the Biosphere in the past, and continues to play a crucial role in regulating the functioning of the Biosphere today. Ocean plankton has been the leading player in the evolution of the chemical properties of the biosphere, particularly in shaping the gaseous composition of the atmosphere.

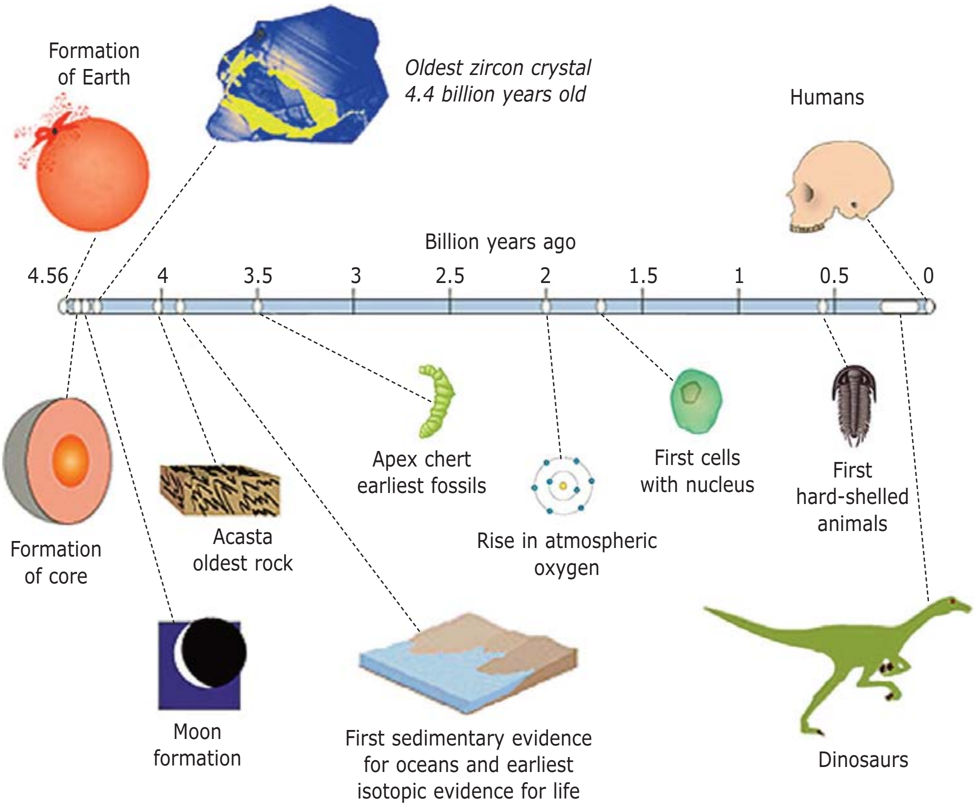
The Earth is unique in the known universe, due to the huge amounts of water it contains in the form of the oceans, which comprise two thirds of the surface of our planet. The oceans are in direct contact with the atmosphere, exchanging matter, energy and momentum. These exchanges ensure that feedback occurs between changes in the composition of the ocean and those in the atmosphere, which is a key characteristic of the functioning of the Earth System.

◂ **Photo 1: *Nostoc algae.* Light micrograph of *Nostoc* sp., a blue-green algae or cyanobacteria**

When the Earth was formed some 4,600 million years ago, the primitive atmosphere had a composition consisting essentially of non-condensed remnants of the original primitive solar nebula (Berkner and Marshall 1965). Since then, this early atmosphere has changed as a consequence of volcanic emissions and processes known as "degassing", which contributed new materials, such as water vapour, carbon dioxide, sulfur dioxide and nitrogen to the atmosphere. The atmosphere has been further enriched by gases derived from comets and other extraterrestrial sources (Dauphas 2003). Some of the materials emitted by volcanoes, such as sulfur oxides and other aerosols have contributed to the cooling of the Earth (Berkner and Marshall 1965). This cooling of the Earth resulted in the condensation of most of the water vapour emitted during volcanic eruptions which, together with water from extraterrestrial origin, contributed the liquid water that formed the ancient oceans (Dauphas 2003). Weathering reactions released the mineral salt and carbonates that dissolved into the new oceans (Berkner and Marshall 1965, Kasting 1993, Dauphas 2003).

The advent of life on Earth introduced a new agent capable of affecting the composition of the atmosphere and the oceans. Primitive photosynthetic organisms appeared about 3,500 million years ago in the form of marine organisms, as indicated by the first fossil recorded on Earth. These organisms were primitive cyanobacteria that began to produce oxygen, which accumulated in the atmosphere so as to reach the stratosphere. When exposed to the high levels of ultraviolet radiation received in the high atmosphere, molecular oxygen (O_2) dissociates into oxygen atoms (O) that react with oxygen molecules to form ozone (O_3), a gas that readily absorbs ultraviolet radiation (Chapman 1930). This process was the origin of the ozone layer, which has since acted as a filter for ultraviolet B radiation, allowing the development of a great diversity of life forms on the Earth's surface and in the oceans. An ozone layer sufficiently dense to be able to offset the damaging consequences of ultraviolet radiation was most probably formed about 2,000 million years ago (Holland 1994). At that time, the atmosphere is believed to have been rich in oxygen with concentrations similar to contemporary ones. By filtering out damaging ultraviolet radiation, the ozone layer permitted the development of life in coastal areas and the evolution of terrestrial organisms. Life was present exclusively in the oceans for more than 3,000 million years, during the Precambrian Era. These life forms were comprised predominantly of marine planktonic microorganisms, whose metabolic activity greatly affected

Figure 1: Epochs in which distinct forms of life appeared. For more than 3,000 years, corresponding to the Precambrian era, life only existed in the ocean, in the form of microorganisms.



the composition of the atmosphere and the oceans (figure 1). The emergence of oxygenic photosynthesis, carried out by cyanobacteria and their descendants, led to a massive presence of oxygen (O_2) to levels comparable to, or higher than, present levels. Indeed, almost all the oxygen that is currently free in the air derives from photosynthesis. This major shift in the composition of the atmosphere led to the emergence of new life forms, including aerobic organisms, which benefited from the new composition of the atmosphere. A third step in the evolution of the atmosphere then occurred, in which increased oxygen consumption and decreased net consumption of CO_2 led to a new gaseous equilibrium in the atmosphere. Since then the balance between gases emitted and absorbed by biota has controlled the composition of the atmosphere, as is evident today in the seasonal fluctuation of atmospheric CO_2 associated with the growing seasons of plants and oceanic plankton.

Marine organisms are also responsible for the formation of carbonate and siliceous rocks and deposits, and play a fundamental role in the regulation of the carbon cycle over both short and long time scales, thereby regulating the long term climate patterns of the Earth (photo 2). Marine organisms are involved in the regulation of cloud formation and hence, the radiative balance of the planet over short time scales, however they also contributed to climate changes during the transition from glacial to interglacial phases. Our contact with ocean plankton is so intimate that it plays a role in our personal hygiene, as every day we ingest several thousand marine diatom cells present in most commercial toothpastes as an abrasive agent (photo 3). In fact, the role and functions of ocean plankton are so prevalent that they can be considered the motor of planet Earth.

During the celebration of the International Year of Planet Earth in 2008, the 4th BBVA Foundation – Cap Salines Lighthouse Coastal Research Station Colloquium on Ecology and Ocean Conservation designed to inform about the role of marine biota in the functioning of the biosphere. To this end, a number of prestigious scientists provided different perspectives on the role marine biota plays in regulating the functioning of the biosphere, from brief scales of a few days to vast geological time scales, and even raised the possibility of using ocean biota to mitigate climate change.

Photo 2: Submarine view showing Stromatolites formed by cyanobacteria and sedimentary grains, in Shark Bay (Australia), close relatives of the Stromatolites that populated the Earth during the Precambrian era. Stromatolites are rare today but are abundant in the fossil record of the Precambrian time.

This volume contains a chapter in which Sañudo addresses how the creation of an oxidative environment by the production of oxygen through photosynthesis by primitive oceanic biota greatly influenced the subsequent evolution of life. In his chapter, Berelson describes the fundamental role of marine biota in the cycles of elements such as silica and carbon and the consequent influence on the sedimentary record of the oceans. Simó addresses the major importance of marine biota in the global sulfur cycle, producing sulfur products which are important for the formation of clouds and influence the weather. Duarte describes the crucial role played by the metabolism of marine biota in determining the function of the oceans as a source or sink of atmospheric CO_2. The capacity of marine biota to absorb atmospheric CO_2 has been the subject of proposals for geoengineering, through plans to stimulate plankton to help remove the excess CO_2 produced by anthropogenic emissions. In his chapter, Sarmiento also discusses the effectiveness and consequences of these geoengineering solutions.

This volume stems from the presentations delivered at the 4th BBVA Foundation – Cap Salines Lighthouse Coastal Research Station Colloquium on Ecology and Ocean Conservation, held in Madrid on October 6, 2008. This Colloquium was the fourth in a series of colloquia addressing issues of marine ecology and biodiversity. Previous editions have addressed the scientific and technological challenges in the exploration of marine biodiversity, the impact of climate warming on polar ecosystems, and the causes and consequences of the global loss of coastal habitats.

The talks delivered at the Colloquium can be viewed in full on the following web page:

http://www.fbbva.es/TLFU/tlfu/ing/agenda/eventos/fichaconfe/index.jsp?codigo=746

This site provides a useful complement, particularly for teaching, to the chapters contained in this book. The reviews provided in the following chapters demonstrate the important role that marine planktonic microorganisms have had and still have in the functioning of planet Earth. The chapter by Sañudo describes how the variety of metabolic processes carried out by marine microbial organisms has modified the chemical composition of the ocean and the atmosphere since the formation of Earth, and that these changes have permitted the colonization of the continents and the relatively recent evolution of *Homo sapiens*. One single process, nitrogen fixation, is pre-

Photo 3: Diverse species of live Antarctic diatoms, a type of microalgae that are important components of planktonic communities in present oceans. Diatoms cells are encased within a unique cell wall made of silica that results in a wide diversity of forms.

sented by Sañudo as a paradigm, demonstrating how the environmental changes caused by Precambriam life greatly influenced the way life has evolved on Earth, including the appearance of *Homo sapiens.*

By the term "ocean metabolism", we understand the different biological processes that both produce and destroy organic matter. Duarte et al. outline how ocean metabolism determines the cycles of carbon, oxygen and important biogenic elements, and constrains the gaseous composition of the atmosphere and the role of the ocean as a sink for CO_2. They offer an overview of the processes that regulate the formation and destruction of matter in the ocean and their importance in the global carbon cycle. The "biological pump" refers to the metabolic capacity of marine organisms to remove CO_2 from the ocean surface, exporting the carbon to great depths, where it remains for a period of time ranging from decades to millennia, before returning to the surface. Changes in the efficiency of this biological CO_2 pump play a decisive role in explaining how atmospheric CO_2 fell from the pre-industrial level of 280 ppm to about 180 ppm during glacial periods or ice ages. Sarmiento explores whether, by analogy, artificially stimulating this process could help to efficiently remove excess CO_2 derived from anthropogenic emissions into the atmosphere.

The global cycles of silica, carbon and carbonate are also affected by the deposition of particles formed by marine organisms. The marine sedimentary record integrates the processes that have taken place on the surface of the oceans for extended periods of time. Burial of carbon as a process that precedes the formation of oil, both in terms of processes that increase the deposition and those that are responsible for the preservation of carbon is discussed in the chapter by Berelson, providing an overview of the history of planet Earth, as organisms that are currently present do not correspond with those that have prevailed throughout its history.

However, ocean life, and particularly microscopic plankton, also influences Earth processes in the short term. This exchange of trace gases between the oceans and the atmosphere produced by microscopic plankton affects the chemical and optical properties of the atmosphere, and Simó shows that, through this exchange, the ocean influences the retention of heat from the atmosphere, regulates the oxidative capacity of the atmosphere by the emission of radical precursors, and, influences the optical balance of the atmosphere (and hence the planet) through the emission of aerosols, and, aerosol precursor gases, influencing cloud formation and the global climate. International efforts towards global data integration together with information derived from orbiting satellites have provided evidence that, to our surprise, marine microbial life not only influences the behaviour of the ocean, but leaves its imprint on the sky above.

In closing, we would like to thank the BBVA Foundation for their support for the Colloquium from which this book stems as well as the careful and professional editing of the book. Thanks are also extended to Cathrin Scupin, the Foundation's publications director, and to the Rubes Editorial production team.

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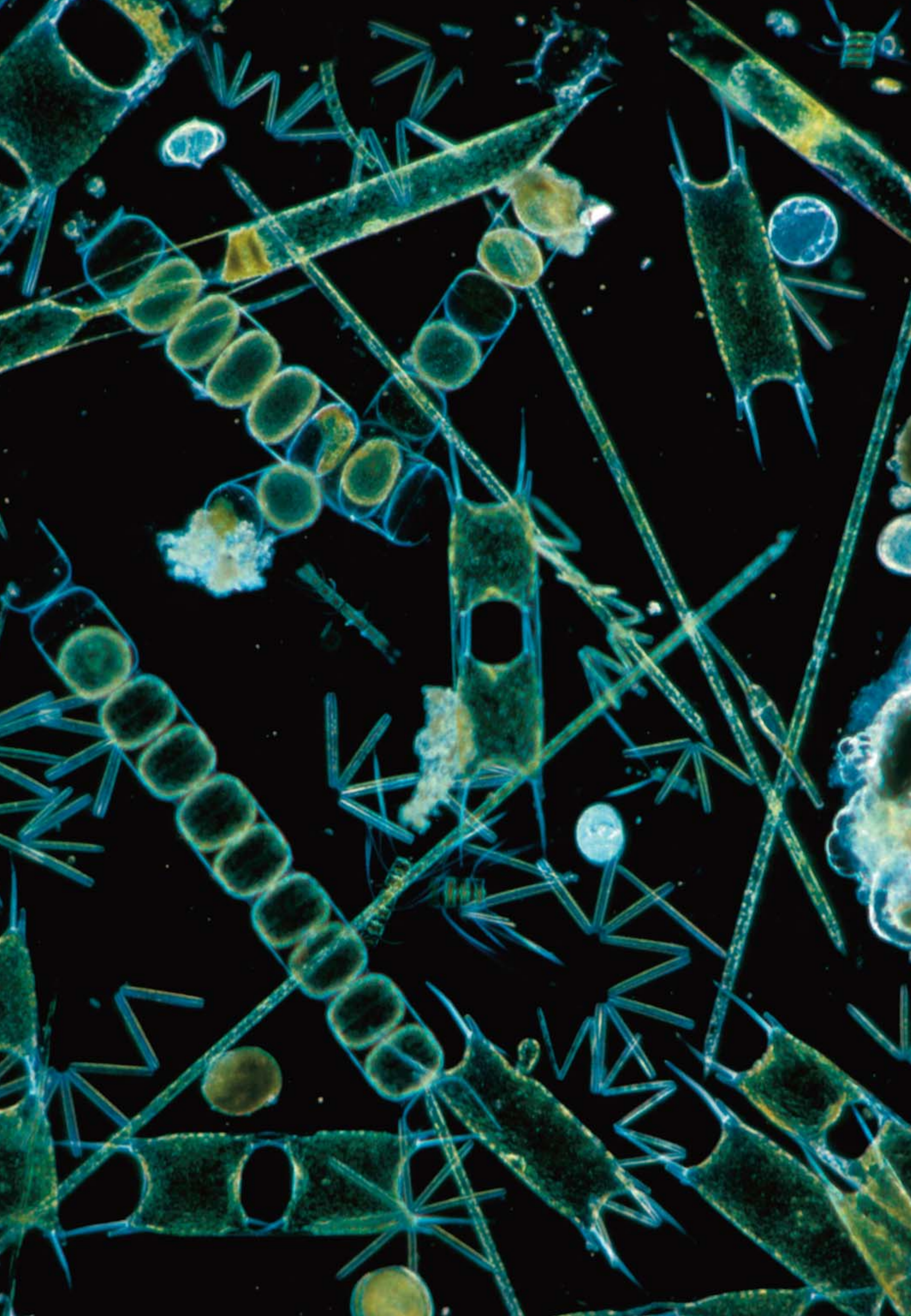

CHAPTER 1

THE ROLE OF MARINE BIOTA IN THE BIOGEOCHEMICAL AND GEOLOGICAL CYCLES OF CARBON

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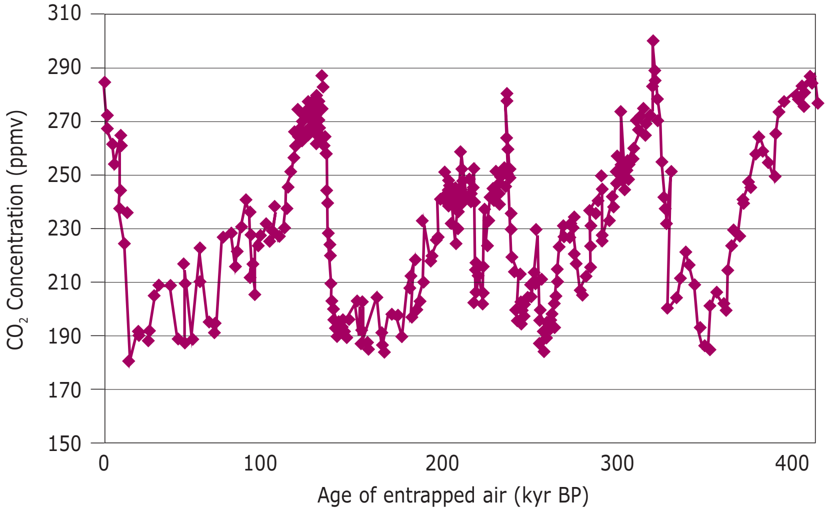
AN EXQUISITE BALANCE EXISTS ON THIS PLANET in which inorganic C is consumed, oxygen is produced and the Earth's temperature and suitability for breathing organisms is thereby regulated. This regulation involves components of biological, physical, chemical and geological systems. A most significant coupling of biological and geological systems is the sedimentation and ultimate burial of photosynthetically produced organic matter (C_{org}) resulting in the net oxygenation of the planet. In early Earth history, photosynthesis by cyanobacteria hosted on sedimentary structures known as stromatolites established an oxygen source and a C_{org} sink in very close proximity. Organic matter that forms on, in or in close proximity to sediments is likely to be buried and escape re-oxidation. Yet soon after the advent of benthic photosynthesizers, the upper ocean's pelagic realm became populated by cyanobacteria. Here the production of oxygen is readily exchanged with atmospheric gases, but the residual organic carbon must settle through the ocean and become buried by the slow accumulation of pelagic sediments before this C_{org} production yields net oxygenation.

◂ **Photo 1.1: Phytoplankton diatoms**

Figure 1.1: Record of atmospheric CO_2 for the last 400,000 years based on ice-core from Antarctica



Source: Jean-Marc Barnola et al.

Intimately coupled to the production of oxygen and the oxygenation of the planet is the biogeochemical cycle of CO_2. As the inorganic substrate of organic matter, total CO_2 (or TCO_2) sources and sinks in the ocean are critical in regulating net production. Moreover, the isotopic fractionation of ^{13}C and ^{12}C between inorganic CO_2 and organic C during carbon fixation provides firm evidence that life on this planet developed the photosynthetic pathway very early on in Earth history. The isotopic record of C through geologic time becomes a strip chart recorder of processes that bury ^{12}C and ^{13}C.

Although buried bits of C_{org} are the likely remains of phytoplankton from ancient oceans, the process of sediment burial, heating and lithification can obliterate the fidelity of their isotopic values. Fortunately, the history of sedimentation on this planet is also recorded by rocks that are predominantly $CaCO_3$. Because the carbonate ion-utilizing reaction with calcium samples the oceans TCO_2 pool and results in the mineral calcite, carbonate-rich rocks become a valuable repository of information about the overall C cycle.

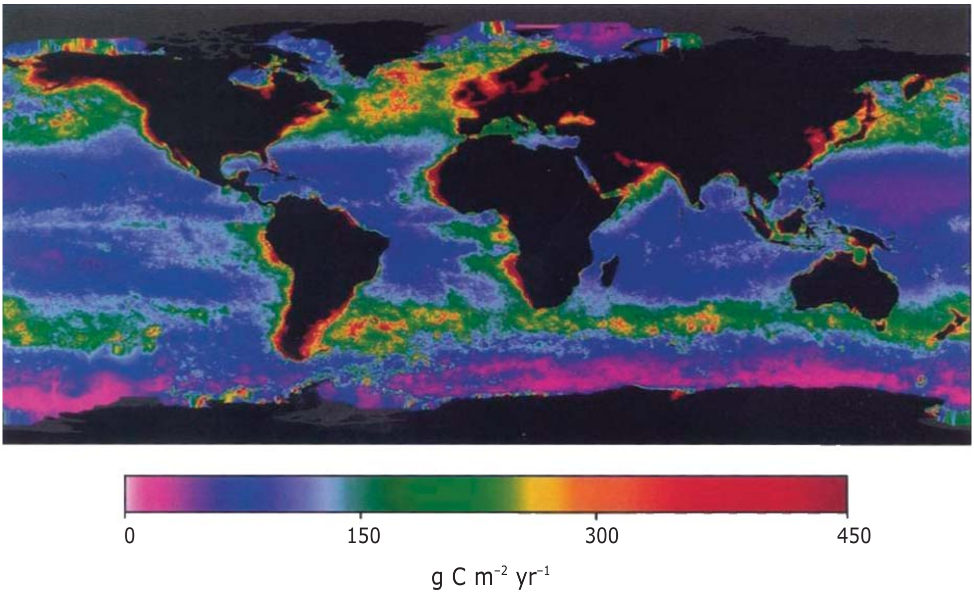
Perhaps the most dramatic example of the importance of the carbon cycle in recent Earth history is the record of CO_2 contained within ice that forms and accumulates at very high latitudes. The Vostock ice core (figure 1.1) contains an excellent example of the rhythmic pacing of planetary CO_2 cycles that correspond with planetary temperature fluctuations known to have occurred over hundreds of thousands of years.

In the following sections of this paper I will discuss patterns of C_{org} and $CaCO_3$ production in the modern open ocean, and give examples of transformations that occur as particles sink through great ocean depths. This chapter will also include a short discussion of major events in Earth history and the relative response of C_{org} and $CaCO_3$ burial through these time periods. I will discuss the advent of the modern pelagic ecosystem (diatoms and coccolithophores) and how the global C cycle responded to this reorganization and finally relate the oceanographic C cycle to the geologic C cycle.

1.1. THE BIOLOGICAL PUMP AND PATTERN OF C_{ORG} AND $CaCO_3$ PRODUCTION

Plant growth in the ocean is partitioned, primarily, between three types of oceanographic regimes, a) the fronts that occur between 40-60° N and S, b) the equatorial upwelling zones and c) within coastal upwelling zones. This distribution (map 1.1) reflects the confluence of environmental parameters (light,

Map 1.1: Surface ocean productivity based on satellite color images



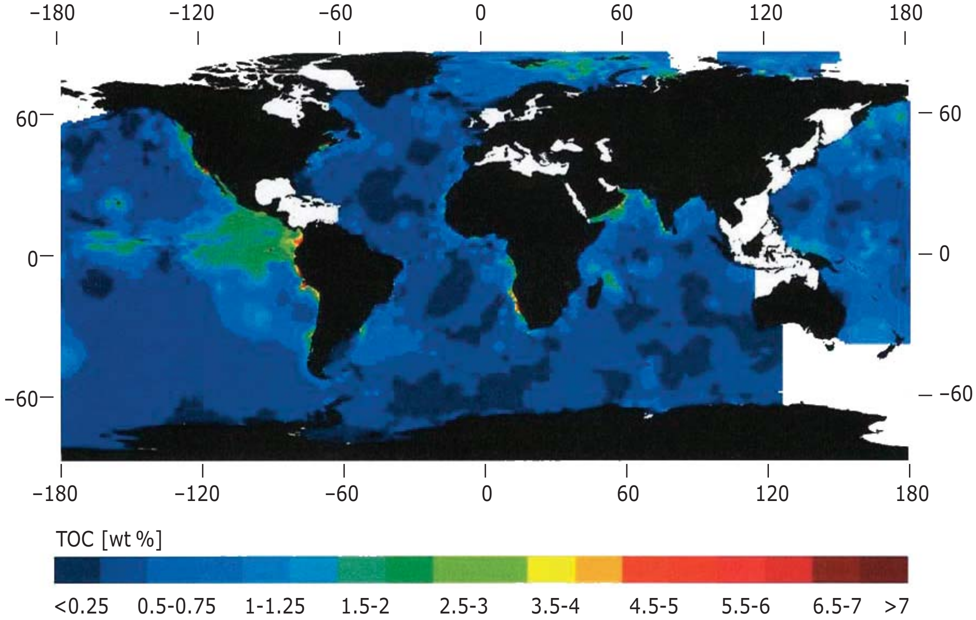
Source: Behrenfeld and Falkowski 1997.

turbulence, temperature) and nutrient availability. In many oceanographic regions the limiting nutrient is iron, as has been demonstrated in numerous iron fertilization experiments (Boyd et al. 2007). Other regions of the surface ocean are limited by the lack of sufficient bio-available phosphorous or nitrate.

The range in primary production of C_{org} (10's to > 500 g C m^{-2} yr^{-1}) is large and seasonal, and there are also large annual fluctuations in production. Yet the general pattern in primary production is striking in its latitudinal zonation (map 1.2).

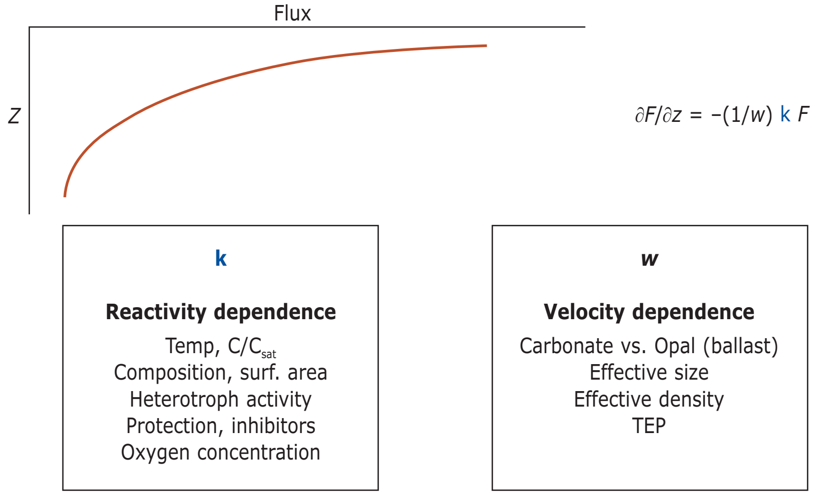
If there were a general translation between primary production and the export of C_{org} from the surface ocean, as may be expected, the latitudinal pattern in phytoplankton growth should be reflected in sedimentary C_{org} content, however, it is not (map 1.2). Although the common sedimentary measurement of wt. % C_{org} is not the best metric for C_{org} flux to the sea floor, the pattern of sediment wt. % C_{org} in no way reflects the pattern of surface water productivity. This result can be explained in three ways, 1) primary productivity and organic carbon export are very poorly correlated (Michaels and Knap 1996; Buesseler 1998), 2) settling through the water column attenuates

Map 1.2: Distribution of weight % C_{org} in superficial sediments



Source: Seiter et al. 2004.

Figure 1.2: The pattern of C_{org} flux vs. depth in ocean. The equation describes the dependence of various factors on the pattern of flux.



C_{org} arriving on the sea floor (Francois et al. 2002) and 3) only a very small fraction of the C_{org} that arrives on the sea floor makes it into the sediment column (Hedges and Keil 1995).

The loss of C_{org} to remineralization as particles leave the upper ocean and sink to the sea floor has been parameterized using a simple power law function first described by Martin et al. (1987). While this function has been used extensively in various models and has been shown to reasonably reflect the C_{org} remineralization of sinking particles, it is important to understand this process from a mechanistic perspective. The following equation sets up the mechanics behind the Martin function:

$$dF/dz = (1/w)\ \mathrm{k}\ F$$

where F is flux of C_{org} with depth (z), w is the particle sinking velocity, k is the rate constant for C_{org} remineralization (1/time) and F is the flux of C_{org} at any given depth (figure 1.2). Various ecologic and environmental factors can affect both w and k. Sinking velocity is poorly constrained and is generally thought to occur at rates on the order of 50-200 m/day. Often overlooked are other factors that influence w, mineral ballast is certainly important (Armstrong et al. 2002), as are effective particle size and effective density and these in turn are related to the TEP (transparent extra polymeric substances) content of sinking particles

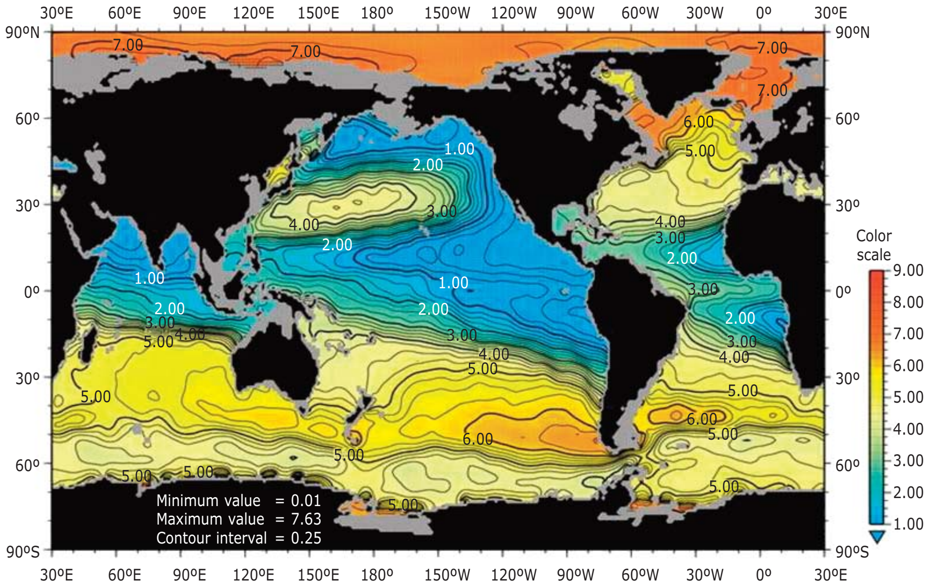
(Alldredge and Gotschalk 1988; Passow and De La Rocha 2006). Both physical factors, such as the erosion of fine-grained sedimentary materials in continents and their delivery to the ocean and ocean ecosystem structure will play a role in organic carbon export to the deep sea. The more we can learn about the factors that influence w and k, the better we will understand the global C cycle.

1.2. TRANSFORMATIONS THAT OCCUR AS PARTICLES SINK

The ocean's biological pump is important to the export of C_{org} from the upper ocean to the ocean's interior. Some portion of the produced organic matter will be exported as long as complete remineralization does not occur in the mixed layer of the ocean. Just how effective this pump will be depends on factors that affect both sinking rate *(w)* and remineralization rate (k) (figure 1.2). One example of how ocean physics and ecological structure conspire to alter the chemistry of particles that fall through the ocean is the 'filtering' effect that takes place within the oxygen minimum zone. As particles containing C_{org} fall through the water column and remineralization takes place, oxygen is consumed. This simple reaction produces TCO_2 and depletes the mid-water column of oxygen in a stoichiometry that is roughly 1:1. Hence the production of oxygen near the surface ocean is neutralized by its consumption at depth. Certainly physics plays an important role in the maintenance of the oxygen minimum zone; water masses that have little mixing and that have been isolated from contact with the atmosphere for long periods are waters that have the most depleted oxygen concentrations (map 1.3). Low oxygen zones in today's oceans are most extensive in the Pacific Ocean, especially along the Eastern boundaries and at low latitudes of this ocean basin. Although most intense to the East, the low oxygen zone in the Pacific extends across the entire basin and is also well expressed in the North Indian Ocean and on the Eastern margins of the Atlantic Ocean basin.

The low oxygen zone (LOZ) acts as a filter to the sedimentation that occurs below it. Particles that pass through the LOZ pass through a water mass with low pH and reduced oxidizing capability. It has been shown that some LOZ's contain substantial concentrations of ammonia (Cline and Richards 1972; Dalsgaard et al. 2005), methane (Sansone et al. 2004) and even sulfide (Diaz and Rosenberg 2008). Biogenic particles passing through this water mass are altered in ways that bias the sedimentary record with respect to the upper water column ecological community structure. Two examples are offered below.

Map 1.3: World ocean atlas, oxygen concentration at 500 m (2005)



Annual oxygen [mL/L] at 500 m depth

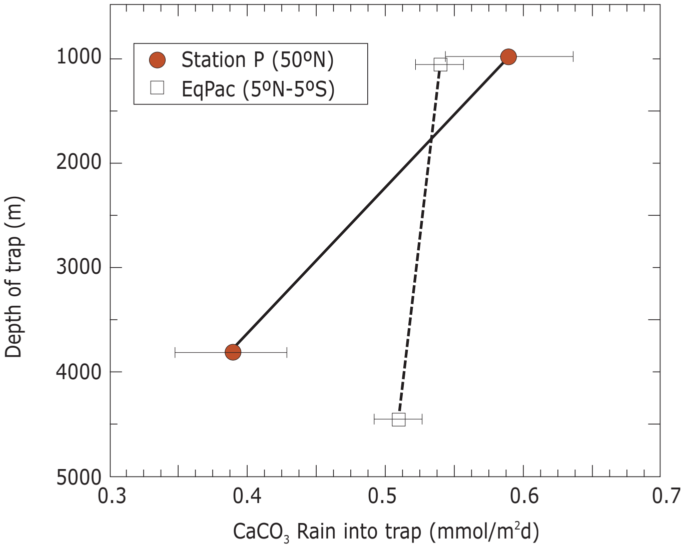
Minimum value = 0.01
Maximum value = 7.63
Contour interval = 0.25

Source: http://www.nodc.noaa.gov/cgi-bin/OC5M/WOA05F/woa05f.pl

Through experiments with sediment traps and laboratory remineralization chambers, Devol and Hartnett (2001) and Van Mooy et al. (2002) have shown that the loss of C_{org} as particles fall through the low oxygen waters off the Northern Tropical Eastern Pacific is attenuated relative to the loss of C_{org} as particles fall through more oxygenated waters. This is reflected in the pattern of flux vs. depth or the Martin 'b' value. Less C_{org} is remineralized as it falls through low oxygen waters than when it falls through oxygenated waters. This, in part, explains the high C_{org} burial efficiencies within sediments underlying LOZ's (Henrichs and Reeburgh 1987). The reason this occurs is not well understood, although Van Mooy et al. (2002) ascribe the transformation of organic C from labile to refractory to its passage through the LOZ.

These systems also have an impact on the signature of upper ocean carbonate ecosystems on the rock record. $CaCO_3$ is supersaturated in the surface ocean and becomes undersaturated within the oxygen minimum zones (Feely et al. 2004, 2008). Sinking carbonate material will dissolve, due to a variety of processes, but more extensive dissolution will occur in highly undersaturated waters. Both aragonite and calcite are susceptible to dissolution, aragonite

Figure 1.3: Sediment trap flux of $CaCO_3$ at two locations, NE Pacific and Equatorial Pacific illustrates the loss of carbonate that settles through the water column.



Source: Berelson et al. 2007.

more so than calcite, yet there is evidence that calcitic material dissolves as it falls through the water column (Berelson et al. 2007). The extent of dissolution that occurs as particles sink can be assessed from long-term sediment trap records of flux to different depths. A comparison of long-term trap results from Station P in the NE Pacific where the oxygen minimum zone is extensive, and from the central Equatorial Pacific (Berelson et al. 2007) where the oxygen minimum zone is less extensive, show (figure 1.3) that although a similar quantity of carbonate is falling through 1000 m, there is a loss of carbonate in the 4000 m traps at Sta. P that is not evident in the traps at EqPac. This greater loss of sinking particulate carbonate may be attributed to the more acidic waters through which particles travel in the NE Pacific. This is evidence of the water column 'filter' in action.

1.3. MAJOR EVENTS IN EARTH HISTORY AND THE RECORD OF C_{ORG} AND $CaCO_3$ BURIAL

The mass balance of C isotopes (^{12}C and ^{13}C) results in one of the most elegant and reliable tools for understanding how ocean ecosystems change through geologic time. As the name 'mass balance' implies, the ratio of ^{12}C and ^{13}C molecules that enter the ocean must be conserved by the ratio of these molecules in the various forms by which they are removed from the ocean. The input ratio (reported in isotope geochemistry δ convention) is set by the gaseous CO_2 and CO emitted from volcanoes with a value, $\delta^{13}C = -6$ per mil. If the input ratio has remained constant throughout geologic time, which most assume to be true; this input value sets the net output of ^{12}C and ^{13}C, which takes two primary forms. Most C is removed with sedimenting $CaCO_3$ and the remaining fraction of C is removed as organic C. Because these two forms of solid C tend to show a distinctive offset in their $\delta^{13}C$ values, a very useful mass balance can be constructed (figure 1.4a).

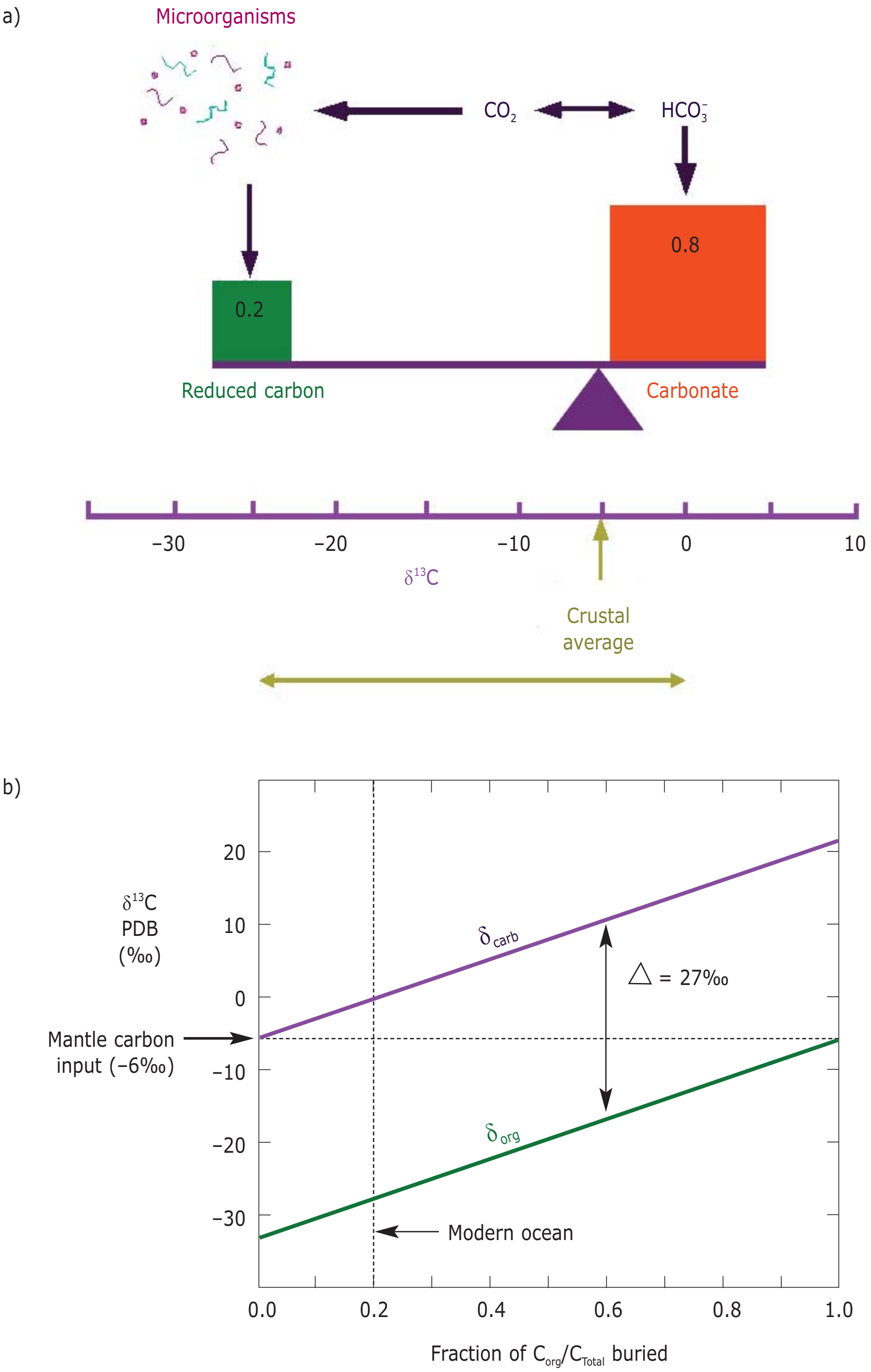
The balance 'fulcrum' is the average input value of $\delta^{13}C$ to the global ocean. The removal terms are adjusted in size given the offset between the $\delta^{13}C$ value of C_{org} and $CaCO_3$. This offset (through much of geologic time and at present) is about 27 per mil (figure 1.4b) and is set by the carbon fixation pathway (for example, the Calvin cycle) by which inorganic C is converted to organic C.

A single measurement of *either* $\delta^{13}C$ of C_{org} or $\delta^{13}C$ of $CaCO_3$ will specify the size of the removal term of one box relative to another. As shown in figure 1.4b, a measured value of $\delta^{13}C$ of $CaCO_3$ will set the $\delta^{13}C$ value of C_{org} and will also define the fraction of C_{org} buried relative to total C buried.

David Des Marais (2001, 1997) and John Hayes (1999) were among the first scientists who showed how remarkably similar the offset between $\delta^{13}C$ of C_{org} and $\delta^{13}C$ of $CaCO_3$ has remained throughout billions of years of earth history. This implies, to the first order, that the ratio of C_{org} burial to the total C buried has been constant at about 20% for eons. Conversely, this means that the net removal of C as $CaCO_3$ has remained constant at 80% of the total C removed. Throughout millions and millions of years of earth history, and as the oceans evolve and ecosystems change, the net removal of C from the oceans as C_{org} (primarily as dead plants and biomass) and as $CaCO_3$ (either abiotic or biotic) has held generally constant at a ratio of 0.2 to 0.8.

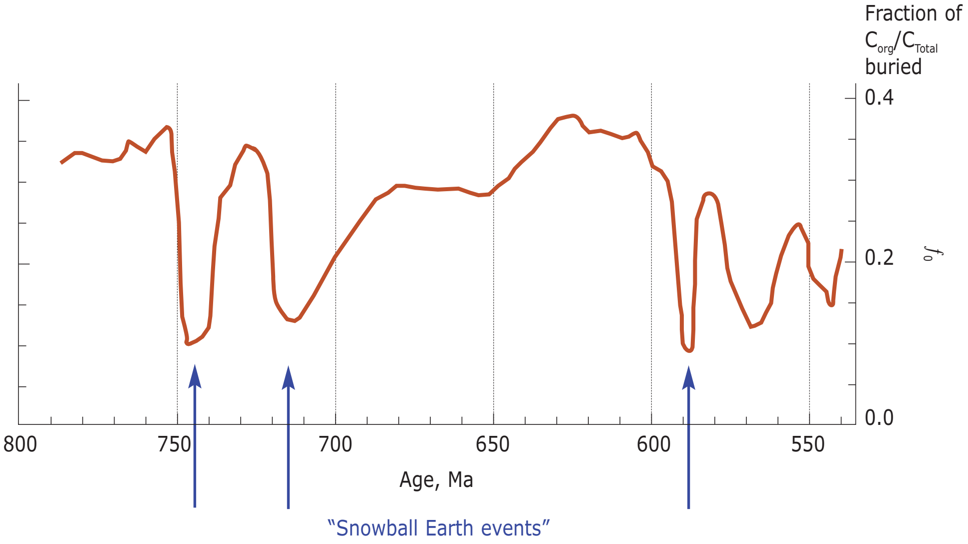
Both the long term mean and deviations from this mean are fascinating. For example, between 800 and 540 million years ago, just as multi-cellular organisms were developing on Earth, there were at least three major 'snowball' events that covered the planet with snow, ice and slush (Kirschvink, 1992). Each of these events was marked by a recovery in which a low fraction of C_{org}

Figure 1.4: Isotope mass balance for ^{13}C



Source: Des Marais 2002.

Figure 1.5: Pattern of the fraction of C_{org} relative to total C, buried between 500 and 800 million years ago. Large excursions, known as "snowball events" are marked.



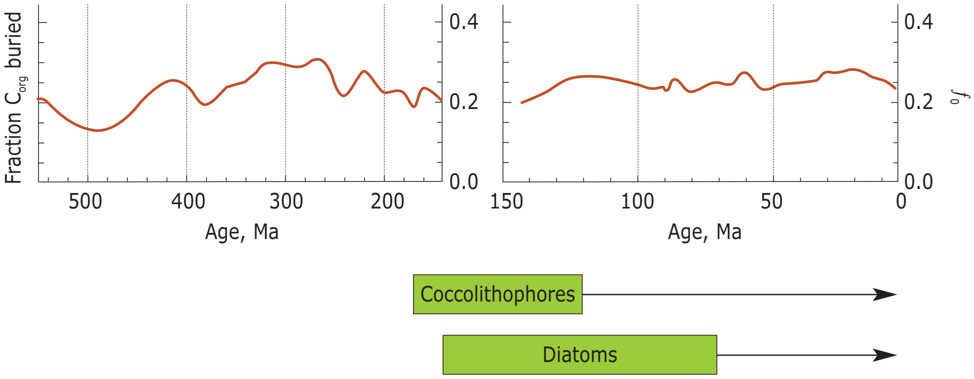
Source: Hayes et al. 1999.

was buried relative to $CaCO_3$ (figure 1.5). Whatever sort of checks and balances normally at work to maintain the ocean C sink and its proportionality between C_{org} and $CaCO_3$ fell apart during these snowball recovery periods.

1.4. MODERN OCEAN ECOLOGY AND THE MODULATION OF THE C_{ORG} AND $CaCO_3$ FRACTION BURIED

A final example of how ocean ecology is reflected in long-term records of Earth history is the 'recent' invention of coccolithophores and diatoms. These two pelagic photosynthetic micro-organisms stand at the base of today's oceanic food chain and represent its most significant biogenic particles. Diatoms construct shells or tests made of SiO_2 and represent the single most important component in the oceans' Si cycle (Ragueneau et al. 2000). They also make up a large fraction of oceanic C fixation, as much as 50% (Treguer et al. 1995). Moreover, export of diatoms via sinking is known to carry C_{org} to the ocean interior (Buesseler et al. 2007). Coccolithophores are the single most important component of the pelagic ocean carbonate producers and their production of C_{org} and sinking drives a major part of the oceanic alkalinity and C_{org} cycles.

Figure 1.6: Pattern of C_{org} buried between 500 million years ago and the present. The green bars show the timing of the onset of coccolithophore and diatom production.



Source: Hayes et al. 1999.

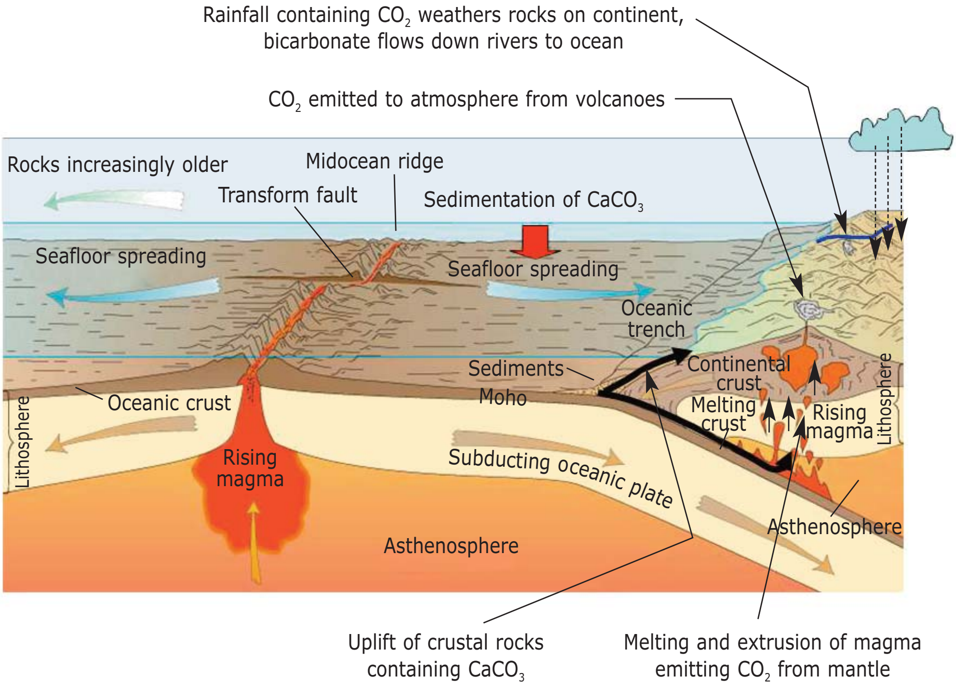
As shown in figure 1.6, the 'invention' of these two types of phytoplankton, between 200 and 150 million years ago, had little impact on the global balance with regard to how much C_{org} and how much $CaCO_3$ was buried. In the same way as the global average prior to 200 million years ago, where ~20% of ocean C was buried as C_{org} and 80% as $CaCO_3$. Yet, upon closer inspection of these plots (figure 1.6), it is apparent that the fluctuations in % C buried as C_{org} were greatly attenuated following the evolution of coccolithophores and diatoms. It may be that prior to the production of oceanic phytoplankton that precipitate $CaCO_3$, much of the $CaCO_3$ burial occurred on continental and island margins and shallow platforms. The abundance of the area for this accumulation would be sensitive to the overall distribution of continents through geologic time, i.e. plate tectonic movements. Once the deep sea became a repository for $CaCO_3$, following the evolution of coccolithophores, the carbonate burial budget would have become less sensitive to these tectonic factors, giving rise to the attenuated variability in f_o in figure 1.6 that has occurred in the last 200 million years. Certainly, there are direct linkages and feedbacks between ocean ecology and geologic history.

1.5. THE GEOLOGIC C CYCLE

It is not clear how long this planet has had the tectonic cycle that is active today. One of the greater uncertainties is when large continental plates developed. Yet some form of the geologic C cycle had been active since early earth history because, with the exception of a few global 'snowball' events, the earth has had vast oceans for about 3.5 billion years and has buried the same relative fraction of C_{org} and $CaCO_3$ for this duration. There is no way for this planet to maintain a moderate mean temperature without the feedbacks imposed by the grand geologic C cycle (figure 1.7).

The geologic C cycle involves inputs and removal terms on geologic time scales as well as on the oceanographic time scales mentioned earlier. The key components of the geologic C cycle include weathering, carbonate precipitation within the ocean and tectonic uplift and volcanism. Weathering is the process that 'scrubs' the CO_2 out of the atmosphere by combining carbonic acid in rain water with mineral surfaces (rocks) to erode rocks and generate solutes in streams and rivers. The dissolved HCO_3^- load of a stream is a measure of chemical weathering within the watershed. Once bicarbonate is delivered to the ocean, its fate is partly in the control of the biological pump and surface ocean ecosystem. Coccolithophorid primary productivity is responsible for the removal of much of the alkalinity from the

Figure 1.7: Geologic C cycle



ocean today (photo 1.2). The biomineralization process combines carbonate with calcium to yield mineral calcite. This mineral eventually falls through the water column and some fraction is retained in the sediment column. The tectonic forces that move plates apart at spreading centers must also yield convergence and subduction, where one plate re-enters the asthenosphere within the mantle.

Photo 1.2: Specimen of *Gephyrocapsa oceanica* originating from Mie (Japan). Digitally processed from an image obtained from an electronic microscope.

Melting of what the plate has been carrying occurs as does melting of the asthenosphere, and the result is rising magma (molten rock), volcanoes and the emission of CO_2. This greenhouse gas helps to keep this planet warm enough to sustain life. Too much CO_2 and global warming occurs, too little CO_2 and 'ice house' conditions ensue. Hence, the importance of precipitation and weathering and the continuance of the cycle. The geologic C cycle, and the important role played by carbonate secreting ocean plants and heterotrophs, is key to planetary homeostasis and survival.

ACKNOWLEDGEMENTS

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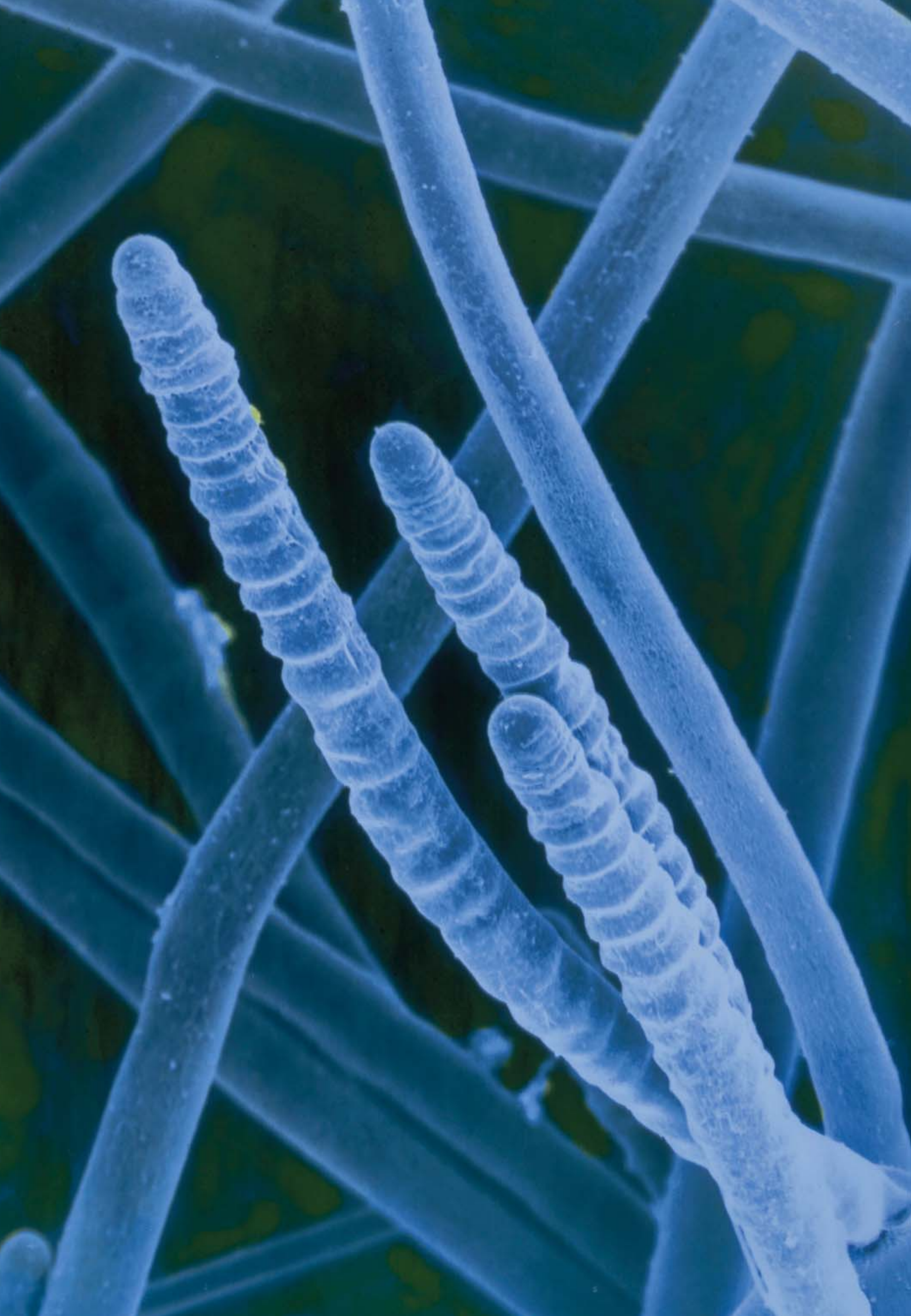

CHAPTER 2

THE ROLE OF MARINE BIOTA IN THE METABOLISM OF THE BIOSPHERE

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THE TERM METABOLISM REFERS to the transformations of materials, involving the use or release of energy, necessary to maintain organisms alive. At the ecosystem level, metabolism refers to the transformations of elements from inorganic to organic form and vice versa, through the aggregated metabolic processes of the individual components of the ecosystem. More specifically, ecosystem metabolism refers to the production and destruction of organic matter and the associated fluxes of materials and energy.

Occupying most of the Earth's surface, the oceans are an active component of the Biosphere, with marine biota supporting a significant fraction of the production and destruction of organic matter. Marine biota has therefore served an important role in the metabolism of the Biosphere, although this has not been sufficiently recognised.

Here we examine the role of marine biota in supporting the metabolism of the Biosphere. We first discuss the major processes involved in ocean metabolism, photosynthesis and respiration, and introduce the concept of net

◂ **Photo 2.1: Cianobacterium *Scytonema.*** Colorized scanning electron micrograph of growing filament tips.

ecosystem production. We then examine the balance between photosynthesis and respiration and the causes and consequences for the functioning of the biosphere of imbalances in these two key properties.

2.1. ECOSYSTEM METABOLISM: DEFINITION AND SIGNIFICANCE

Howard T. Odum, arguably the father of ecosystem science, advanced that the metabolism of ecosystems can be defined and studied, not through the sum of the metabolic rates of their individual components, but as a higher-order property (Odum 1958). He proposed that the metabolism of ecosystems can be represented by the production and destruction of organic matter, and the associated fluxes of nutrients, through the gross photosynthetic and respiratory activity of ecosystems (Odum 1958). Photosynthesis is the main pathway for the production of organic matter in the ecosystem proceeding according to the simplified equation:

$$CO_2 + H_2O + \text{light} \longrightarrow CH_2O + O_2 \qquad (2.1)$$

The organisms able to conduct photosynthesis all have Chlorophyll a, and other accessory pigments, and are known as primary producers. Microorganisms can also use chemical energy to produce organic matter, through a process called chemosynthesis, but although it is significant in some ecosystems such as deep ocean hydrothermal vents, chemosynthesis plays a minor role in the formation of organic matter at the biosphere scale. Photosynthesis is the process responsible for supplying the organic matter required for the ecosystem to function, as all organisms in the food web are consumers of organic matter, which they transform and destroy, to extract energy to support their life processes.

Respiration is the process responsible for the destruction of organic matter to extract energy, in the form of adenosyl triphosphate (ATP), which supports all organismal processes. Respiration can be defined by the simplified equation,

$$CH_2O + O_2 \longrightarrow CO_2 + H_2O + \text{energy} \qquad (2.2)$$

Respiration is the dominant mode of destruction of organic matter, although organic matter can also be destroyed by photochemical oxidation in the presence of strong solar irradiance and high UV levels, but again, this process

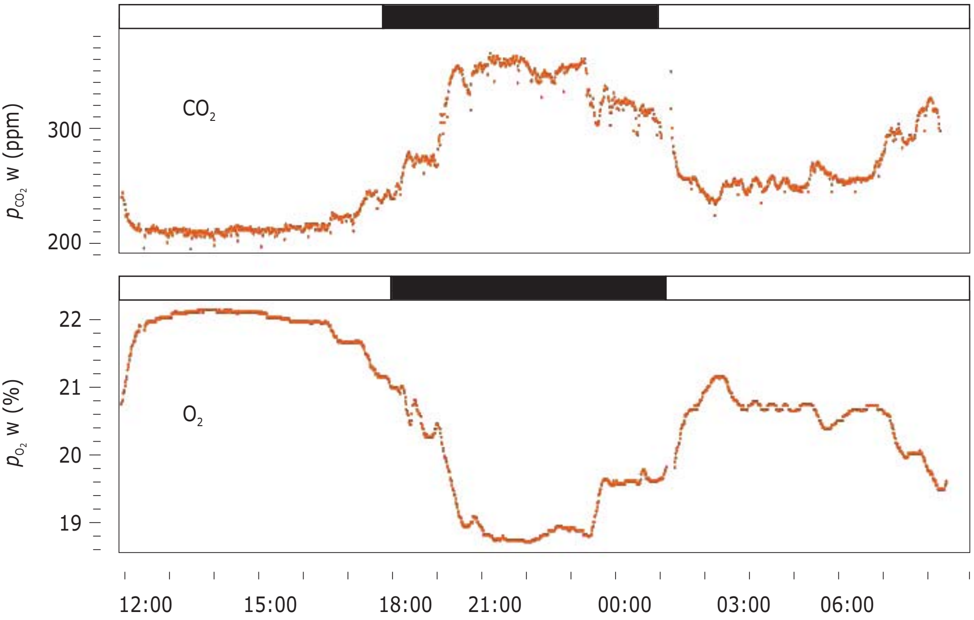
Photo 2.2: Giant moon jellyfish *(Aurita aurita),* from Jellyfish Lake in Pelau Island (Micronesia)

although locally important, contributes a negligible fraction of the organic matter destroyed or remineralised every year in the biosphere (photo 2.2).

Inspection of equations 2.1 and 2.2 readily shows that respiration is the opposite process to photosynthesis. Whereas photosynthesis consumes CO_2 and releases O_2 (equation 2.1), respiration consumes O_2 and releases CO_2 (equation 2.2). These processes link the O_2 and CO_2 fluxes in the biosphere on a stoichiometric ratio of approximately 1 mol O_2: 1 by mol CO_2. Along with the fluxes of O_2 and CO_2, photosynthesis and respiration also support opposite fluxes of nutrients, such as nitrogen phosphorus and iron, among others, which are required to support biological processes, as they are incorporated into organic matter after this is formed through photosynthesis and they are remineralised into inorganic forms, such as ammonia and phosphate, when organic matter is destroyed by respiration. Hence, photosynthetic organisms consume inorganic nutrients and all organisms remineralise nutrients into inorganic forms, thereby linking the fluxes of O_2 and CO_2 in the ecosystem to those of nutrient elements.

Photosynthesis and respiration are not only opposite, but also complementary. A much higher rate of photosynthesis over respiration would lead to a depletion of CO_2 and inorganic nutrients that will eventually compromise, and reduce photosynthetic activity. Likewise, a much higher respiration than photosynthetic rate

Figure 2.1: Diel variation in the partial pressure of O_2 and CO_2 in surface waters of the Weddell Sea, recorded during the ICEPOS cruise on board *R/V Hespérides.* Open and closed bars over the graph denote the daytime and nighttime periods, respectively.



would, if sustained over time, deplete O_2 and organic matter, thereby reducing and compromising further respiratory activity. Hence, ecosystems typically show a close balance between photosynthesis and respiration, particularly when examined over large spatial and temporal scales. For instance, figure 2.1 shows diel changes in O_2 and CO_2 in the surface waters of the Weddell Sea, Antarctica, recorded during the ICEPOS cruise on board *R/V Hespérides*. This is characteristic of the mirror image of changes in O_2 and CO_2 in seawater derived from plankton metabolism, with a decline in p_{O_2} and an increase in p_{CO_2} during the night with the opposite changes occurring during daylight (figure 2.1). Although production and respiration are complementary processes, there has been a historical emphasis in measuring production compared to respiration. Indeed, the numbers of estimates of photosynthetic rates in the open ocean exceed 1 million, compared to a few thousand estimates of respiration rates of plankton communities, resulting in about 20,000 estimates of oceanic production for each estimate of respiration rate (Williams and del Giorgio 2005).

The balance between photosynthesis and respiration is characterised by the net ecosystem production, *NEP (NEP = GPP – R)* as well as the *P/R* ratio

(P/R ratio = *GPP/R)*. Ecosystems with *NEP* > 0 and *P/R* > 1 are termed autotrophic and act as sinks for CO_2 and inorganic nutrients and sources O_2 and organic matter, which they accumulate or export. In contrast, ecosystems *NEP* < 0 and *P/R* < 1 are termed heterotrophic, and act as sinks for O_2 and organic matter, and sources of CO_2 inorganic nutrients. Heterotrophic ecosystems import organic matter from other ecosystems or loss of organic matter. Small miss-matches in ecosystem metabolism at the global scale, where *NEP* and *P/R* ratios deviate significantly from 0 and 1 respectively, are also possible and when sustained over time are responsible, for instance, for the depletion of CO_2 in the atmosphere down to 180 ppm during interglacial periods (Sigman and Boyle 2000). The formation of many coal, oil and gas deposits is a consequence of the Biosphere sustaining autotrophic status (*NEP* > 0, *P/R* > 1) over very extended geological periods. Likewise the current increase in atmospheric CO_2 can be interpreted as a result of greatly increased respiration, due to the proliferation of animal biomass, including humans, brought about by population growth and life stock production (Prairie and Duarte 2007) and the development of technology for the exosomatic combustion of excedentary organic carbon stored through geological time as coal, gas and oil, to derive energy. The burning of fossil fuels to derive energy can be equated to an exosomatic respiration process, as it consumes organic matter, excedentary from past periods of an autotrophic Biosphere, and oxygen to free energy and release CO_2, conducive to a net heterotrophic Biosphere as we will see below.

2.2. ECOSYSTEM METABOLISM AND C AND O_2 MASS BALANCES

H.T. Odum, on recognising the importance of ecosystem metabolism and the connection of carbon and oxygen fluxes through photosynthesis and respiration at the ecosystem level, proposed that ecosystem metabolism in aquatic ecosystems can be derived from changes in O_2 by solving the mass balance equation (Odum 1958):

$$\frac{\partial O_2}{t} = P - R + f_{air\text{-}sea} + A_{input} \tag{2.3}$$

where $\frac{\partial O_2}{t}$

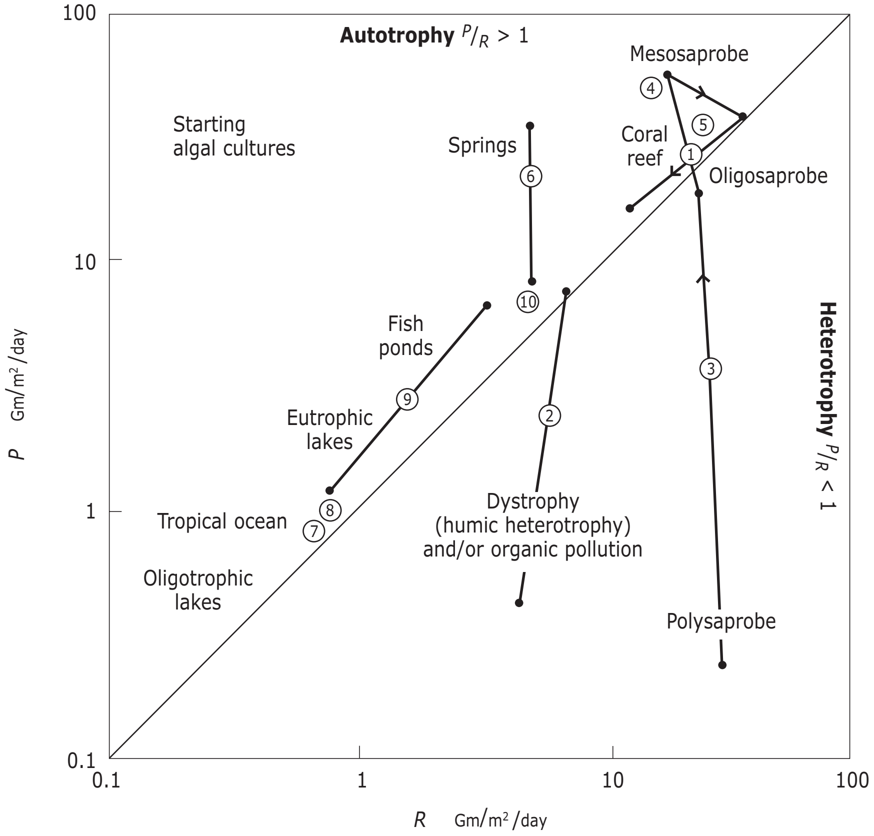
indicates the rate of change in O_2 concentration over time, P indicates gross primary production, R indicates community respiration, $f_{air\text{-}sea}$ indicates the exchange of O_2 between the water and the atmosphere and A_{input} represents the lateral exchanges of O_2 with adjacent ecosystems; all with units µmol O_2 L^{-1} h^{-1}. The same equation can be formulated for CO_2, but changes in oxygen are faster and can be better resolved than those in CO_2. Changes in O_2 along diel cycles in ecosystems can be derived from continuously recording instruments (figure 2.1), and the air-sea exchange of O_2 can be derived from the differential in partial pressures between the air and the ocean surface and an exchange coefficient typically parametrised as a cubic function of wind velocity (Wanninkhof and McGillis 1999). R can be derived from the rates of decline in O_2 (or increase in CO_2) during the night and the rate of increase during the day provides the solution for $P-R$ (figure 2.1). The term A_{input} can then be calculated as the residual in solving the equation, since this term is difficult to calculate directly.

The terms of equation 2.3, when formulated on the basis of CO_2, encompass the subjects of most of the processes that are of interest to global biogeochemistry: the net rate of change in CO_2, essential to determine the role of ecosystems as sinks (positive rates of change) or sources (negative rate of change) of CO_2. The exchange with the atmosphere is the process responsible for the role of the ocean as a sink of CO_2. The inputs from adjacent ecosystems, including the inputs of materials delivered by rivers to the ocean demonstrates the connectivity between ecosystems. Whereas $f_{air\text{-}sea}$ and A_{input} were presented by Odum (1958) as terms necessary to extract P and R, interest has shifted and attention is now focussed on how ecosystem metabolism, the balance between P and R, affects the exchange of CO_2 between the water and the atmosphere ($f_{air\text{-}sea}$).

2.3. PATTERNS IN THE ECOSYSTEM METABOLISM IN MARINE COMMUNITIES

On his first assessment, Odum (1956) characterised marine ecosystems as generally autotrophic, with coral reefs and the tropical ocean being slightly autotrophic, close to metabolic balance (figure 2.2). Indeed, the larger data set available half a century later supports the existence of a broad relationship between production and respiration in marine plankton communities (figure 2.3, Duarte and Agustí 1998; Robinson and Williams 2005).

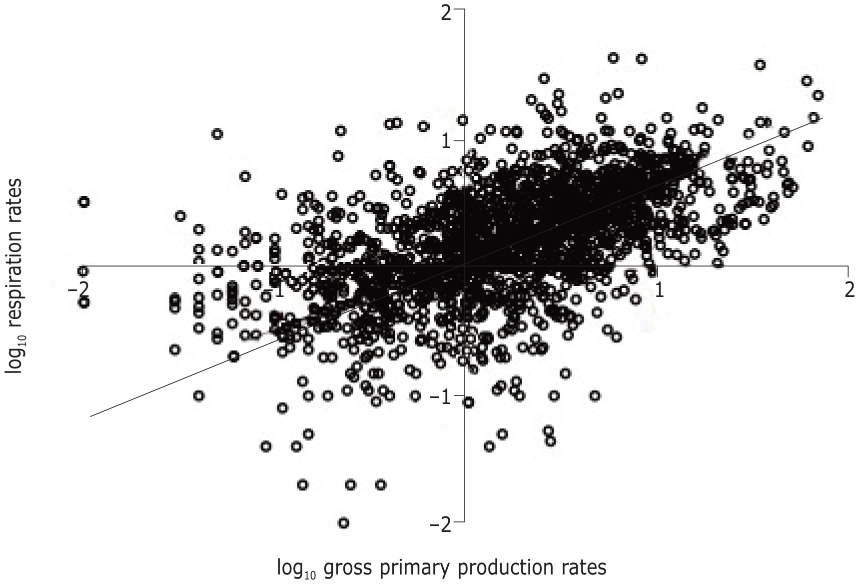
Figure 2.2: The relationship between community production and respiration in a range of ecosystems



Source: Odum 1956.

This relationship indicates that the respiration rates of plankton communities are not proportional to their gross primary production (Duarte and Agustí 1998), but that *GPP* ~ $R^{0.62}$ (Robinson and Williams 2005) indicates that community respiration is highest for any given gross primary production in unproductive waters and that the *P*/*R* ratio increases with increasing production (Duarte and Agustí 1998; Robinson and Williams 2005). Indeed, the relationship between production and respiration implies that *GPP* = *R* at an average *GPP* of 1.06 mmol O_2 m^{-3} d^{-1} and marine plankton communities with a lower *GPP* are, therefore, likely to be heterotrophic (Duarte and Regaudie-de-Gioux 2009). Examination of CO_2 fluxes in the ocean indicates that the equatorial areas and the unproductive tropical gyres in the center of oceanic basins tend to be net sources of CO_2

Figure 2.3: The relationship between the respiration and gross primary production of plankton communities in the ocean (units mmol O_2 m^{-3} d^{-1}). The solid line shows the fitted, model II, regression equation.

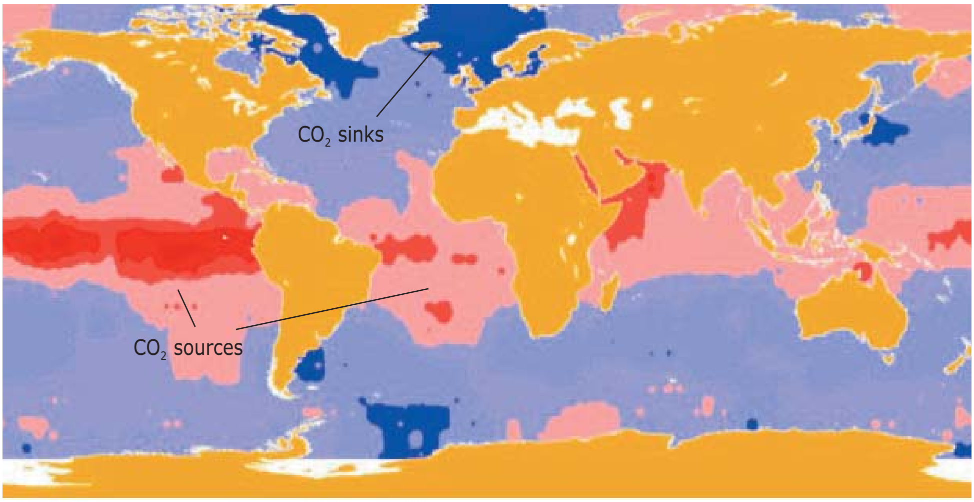


Source: Modified from Robinson and Williams 2005.

to the atmosphere (map 2.1), consistent with the net heterotrophy expected for communities in these ultraoligotrophic ecosystems (Prairie and Duarte 2005).

Heterotrophy was, in Odum's (1956) conceptualisation, a characteristic of a dysfunctional ecosystem, such as those affected by organic inputs (figure 2.2). Indeed, the oceanographic community has long assumed marine ecosystems to be autotrophic, with the implicit rationale that heterotrophic ecosystems cannot sustain harvests, such as fisheries sustained over centuries, nor can they export organic matter as plankton ecosystems in the ocean mixed layer, as was recorded by sediment traps collecting materials below the mixed layer (Duarte and Regaudie-de-Gioux 2009). Indeed, some graphical representations of the ocean carbon budget echo this belief, as no organic inputs to the open ocean, other than the riverine inputs to the coastal ocean, are included, such that the only material the open ocean exchanges with the atmosphere is CO_2 (figure 2.4). These representations of the carbon cycle of the open ocean imply that it must be an autotrophic ecosystem, as heterotrophy can only be sustained if the stocks of organic carbon in the ocean

Map 2.1: Air-sea fluxes of CO_2 in the ocean. Intense blue colored indicates strong sinks whereas strong red colored indicates strong emissions of CO_2 to the atmosphere.



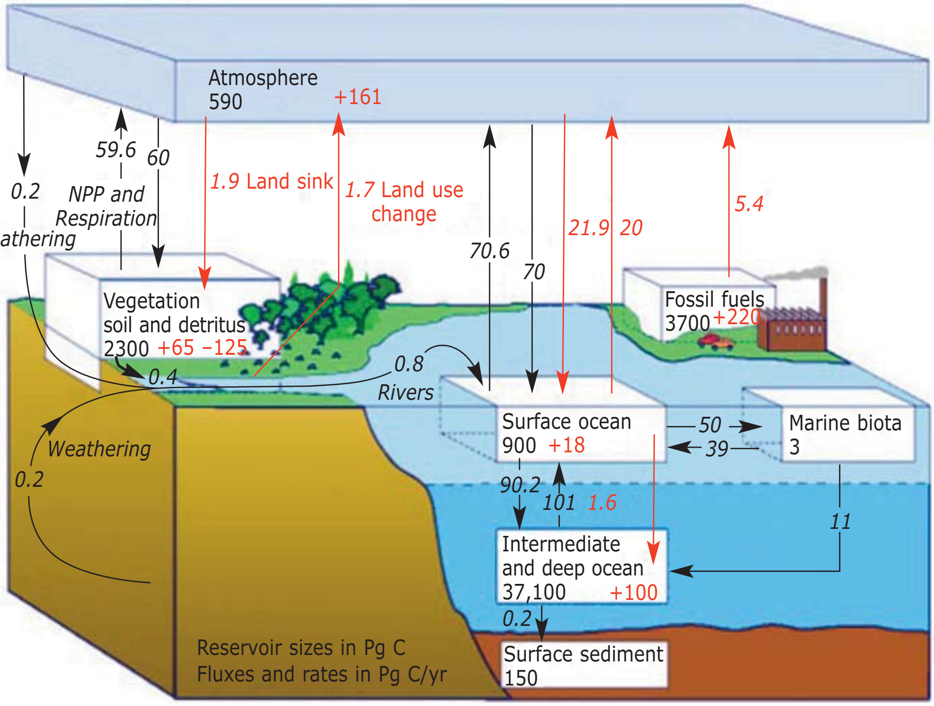
Source: Produced from the data base in Takahashi et al. 2002.

are not declining and if inputs of organic matter from other biosphere domains are significant, a possibility that is not included in these representations (figure 2.4).

Yet, the open ocean is believed to have been a weak source of CO_2 to the atmosphere during the Holocene, because sediment accumulation was lower than the riverine input of organic carbon (Siegenthaler and Sarmiento 1993) and is thought to have become a sink as a consequence of the human perturbation of the carbon budget (Siegenthaler and Sarmiento 1993; Sarmiento and Gruber 2002). Holocene CO_2 emission must have been supported by external inputs of organic matter, which can be delivered by the rivers and from atmospheric deposition. Whereas decades ago, riverine inputs of organic carbon were estimated at 0.8 Pg C yr^{-1} (1 Pg = 10^{15} g, Siegenthaler and Sarmiento 1993), there was until five years ago, not a single estimate of the atmospheric input of organic carbon to the ocean. Yet atmospheric organic carbon inputs to the ocean must be significant (del Giorgio and Duarte 2002), as rainfall contains organic carbon, aerosol—dust—depositing on the ocean contains organic carbon (Duarte et al. 2005), and many organic compounds exist in the atmosphere in a semivolatile form that can be transferred, through diffusive fluxes to the ocean (Dachs et al. 2005). Dachs et al. (2005) and Duarte et al. (2006) reported organic carbon inputs with dry aerosol dep-

Figure 2.4: Global carbon budget showing preindustrial fluxes and those resulting from human perturbation. Arrows show fluxes, in Pg C yr^{-1}, and boxes contain pool sizes, as Pg C. Numbers and arrows in black show pre-industrial fluxes and those in red show the human perturbation. Black: preindustrial; red: human perturbation.

Global carbon cycle



Source: Reproduced from Sarmiento and Gruber 2002.

osition to average 1 mmol C m^{-2} d^{-1}, and these have been calculated to deliver 0.24 Pg C annually to the ocean (Jurado et al. 2008). Dachs et al. (2005) reported a large air-sea exchange of volatile organic carbon, which could sustain an input of about 25 to 31 mmol C m^{-2} d^{-1} to the NE Subtropical Atlantic Ocean. This high atmospheric organic carbon input is likely to be representative of upper values for the ocean, as the NE Subtropical Atlantic is an area supporting particularly high atmospheric inputs (Jickells et al. 2005), but even input rates six fold lower than those reported for the Subtropical NE Atlantic will suffice to support an excess respiration over production in less productive regions of the ocean. The inventory of rates of organic carbon deposition to the ocean is as yet insufficient to attempt the calculation of a global flux. Efforts to assess air-sea exchanges of organic carbon are essential to resolve present inconsistencies in the metabolic and carbon budgets of the ocean.

Whereas the metabolic balance of oceanic planktonic communities remains unresolved, there is evidence that some coastal communities are strongly autotrophic. These are the vegetated coastal habitats formed by macrophytes, including seagrass meadows, salt-marshes and mangrove forests. These ecosystems rank amongst the most productive in the Biosphere and produce organic matter in excess of their respiration rates (Duarte and Cebrián 1998; Gattuso et al. 1998). Indeed, the excess production by these communities is so high that vegetated coastal habitats are important sinks for CO_2, accumulating organic carbon in their sediments (Duarte et al. 2005).

2.4. RESPONSES OF PLANKTON METABOLISM TO CLIMATE CHANGE

The ocean has acted as a strong sink for CO_2 since human perturbations of the C cycle were initiated, removing atmospheric CO_2 at a rate of about 2 Gt C yr^{-1} (Siegenthaler and Sarmiento 1993; Sarmiento and Gruber 2002). However, planktonic metabolism may shift in response to climate change. Warming of the oceans is expected to stimulate respiration rates over photosynthetic rates (Harris et al. 2006; López-Urrutia et al. 2006). A warming by 4 °C, as anticipated for the 21st Century, is expected to directly lead to a 16% decrease in *P/R* ratios (Harris et al. 2006), which may expand the area of the ocean occupied by heterotrophic communities acting as CO_2 sources to the atmosphere. Indeed, there is some evidence that the capacity of the ocean to act as a sink for CO_2 is weakening at present (Doney et al. 2009). In addition, there is evidence that ocean warming leads to a steep decline in seagrass meadows (Marbá and Duarte 2010), adding to the steady decline in this (Waycott et al. 2008) and other communities acting as strong carbon sinks (Duarte 2008). Moreover, a decline in the primary production of the ocean (Gregg et al. 2003) and an expansion of the unproductive gyres (Polovina et al. 2008) has been reported, although the causes for these trends remain unresolved.

Enhancing respiration and decreasing primary production can lead to large metabolic imbalances. Because gross ocean primary production and respiration involve large fluxes, a small, 10% imbalance suffices to generate a perturbation to the global carbon budget much larger than the anthropogenic perturbation that may, partially, be responsible for such changes, thereby accelerating the trend towards a CO_2-rich and warmer Biosphere.

Photo 2.3: Austral ice

Whereas the complementarity between production and respiration sets bounds to this imbalance, the stocks of organic carbon, mostly in dissolved form and ocean sediments, are large enough to support an excess respiration over production for some decades. Hence, the metabolism of the ocean may represent a yet unrecognised tipping element in the Earth System. *Tipping elements* is a term used by Lenton et al. (2008) to describe subsystems of the Earth system that can be switched into a qualitatively different state by small perturbations, with the tipping point defined as the critical point at which the future state of the system is qualitatively altered. Hence, ocean metabolism may represent a tipping element that may be perturbed by climate change, where a relatively small perturbation may offset the close and delicate balance between production and respiration. Once ocean metabolism tips towards increased heterotrophy, the associated net emissions of CO_2 to the atmosphere will strengthen global warming, in turn strengthening respiration on a feed back loop that may accelerate climate change and its negative consequences for society (photo 2.3). It is fundamental to assess, through a combination of empirical cross-system comparisons and experimental analyses designed to test model predictions, what degree of global warming, if any, may tip the ocean ecosystem toward a net heterotrophic state.

ACKNOWLEDGEMENTS

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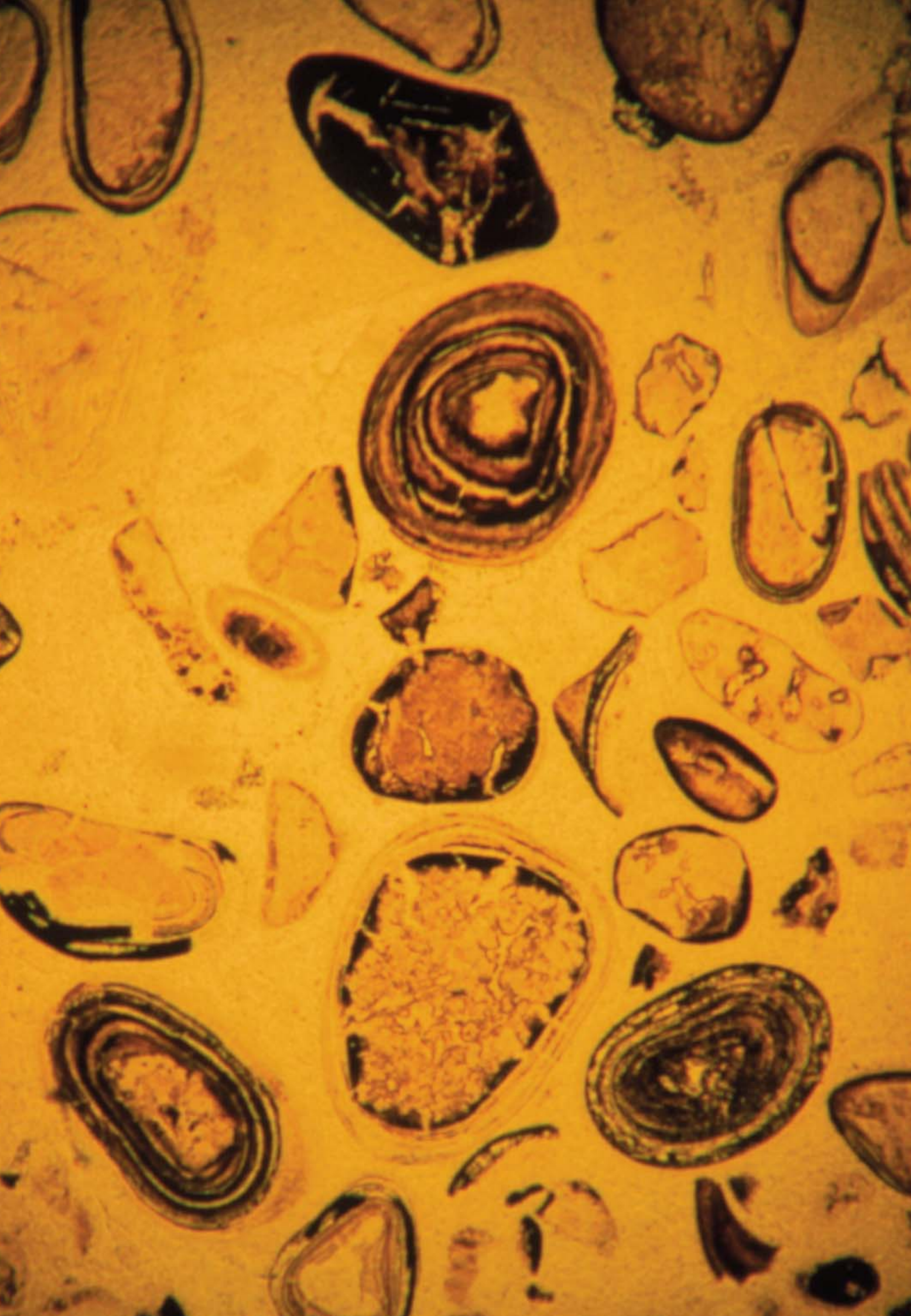

CHAPTER 3

HOW CYANOBACTERIA MADE PLANET EARTH HABITABLE (FOR HUMANS)

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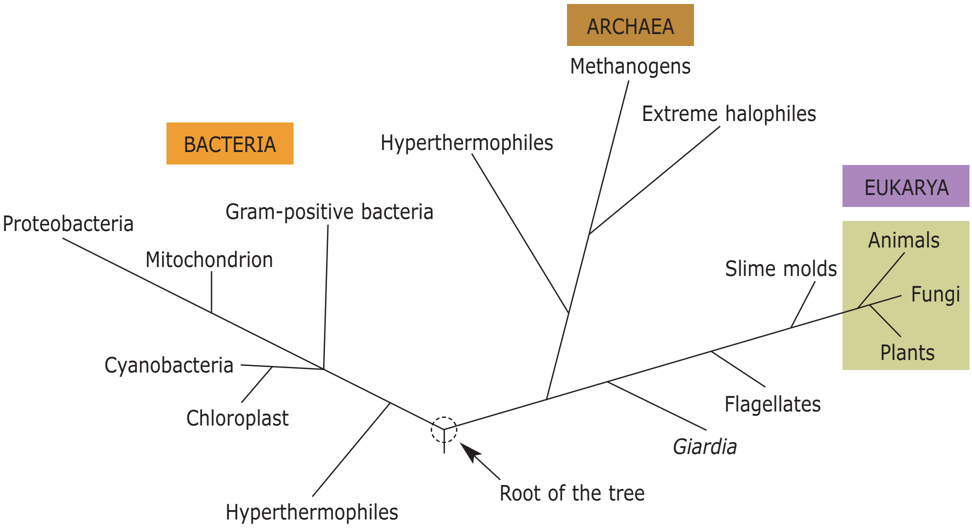
AT THIS VERY INSTANT, the light (as electromagnetic radiation in the 300-700 nm range) reflected from this written page is being absorbed by your eye, converted into electrical signals and transmitted down the optic nerve to the brain resulting in what we call vision. The sequence of biochemical reactions that generates this visual signal starts when light first strikes your retina, producing the photo-isomerization of the visual pigment protein, rhodopsin. This protein activates an enzymatic cascade that regulates the concentrations of other proteins controlling the photoreceptor potential in the rod cells of the retina. This entire sequence of events happens incredibly fast (in a pico-second or 10^{-12} second) and your brain should be able to receive the visual signal and use it, in both muscle actions and in generating thoughts. While the brains of most vertebrates send visual signals to various muscles to generate actions needed for survival, we would like to believe that we are the only species with the mental capacity for complex thought and understanding. For example, we understand

◂ **Photo 3.1: Thin rock section of Gunflint cherts (Ontario, Canada), showing fossil remains of the earliest life forms yet found.** The primitive plants of these colonies of algae derived energy through photosynthesis, releasing free oxygen as a by product. This had far reaching consequences for the subsequent history of the environment.

Figure 3.1: Phylogenetic tree of life based on comparative rRNA gene sequence data. Cyanobacteria comprise a large group of phototrophic bacteria.



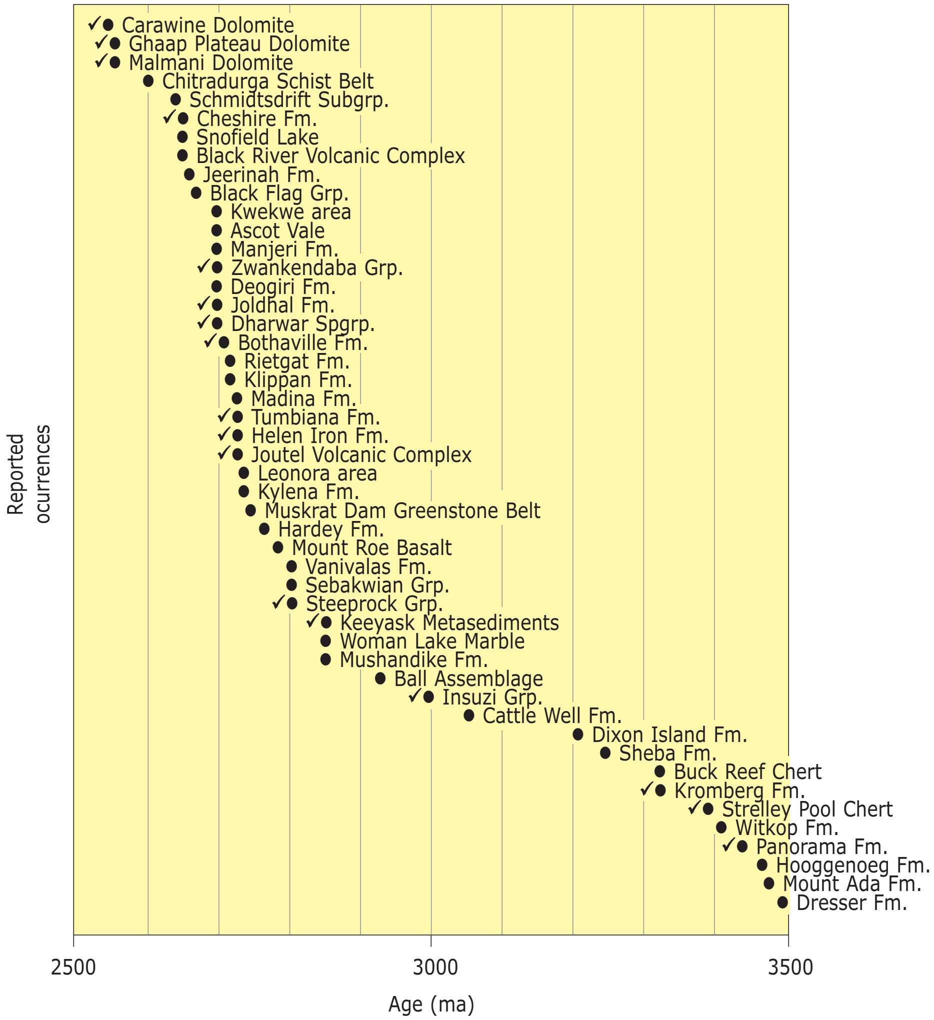
Source: Madigan et al. 2009.

that visual signals are the absorption and transduction of light into electrical signals transmitted through retinal nerve cells to the brain. As you can imagine (maybe another unique ability of the human brain), our brain is a very sophisticated organ and we are just starting to understand how our brain cells process information and generate thoughts, dreams, beliefs, consciousness, and pose questions such as how cyanobacteria made this planet habitable for humans. The main goal of this chapter is to illustrate how the metabolic activity of this group of bacteria permits our existence on this planet by producing the O_2 required for respiration in general, and enables us to maintain an energetically expensive large brain such as ours, in particular. In addition, this group of bacteria is largely responsible for producing bioavailable nitrogen required for the billions of proteins synthesized in our bodies every second to keep us alive, proteins such as the one that allowed you to read these sentences just now.

3.1. WHAT ARE CYANOBACTERIA?

Cyanobacteria comprise one of the major phyla of bacteria (figure 3.1), consisting of a large, morphologically and ecologically heterogeneous group of phototropic bacteria (Whitton and Potts 2000). Cyanobacteria are photosynthetic prokaryotes and as described below, they have transformed the chemical composition of the atmosphere and fundamentally changed the climate of planet Earth. These changes allowed the evolution of multicellular life. Geochemical, geological and paleontological evidence suggests that cyanobacteria are one of the oldest groups of bacteria on Earth. This is indicated by the abundance and widespread distribution of fossilized Proterozoic cyanobacterial communities known as stromatolites (figure 3.2). In fact, the Proterozoic Era

Figure 3.2: Archean geological units that contain fossil stromatolites. Check marks denote conical stramolites indicative of the presence of photosynthetic and phototactic microbes.



Source: Schopf 2006.

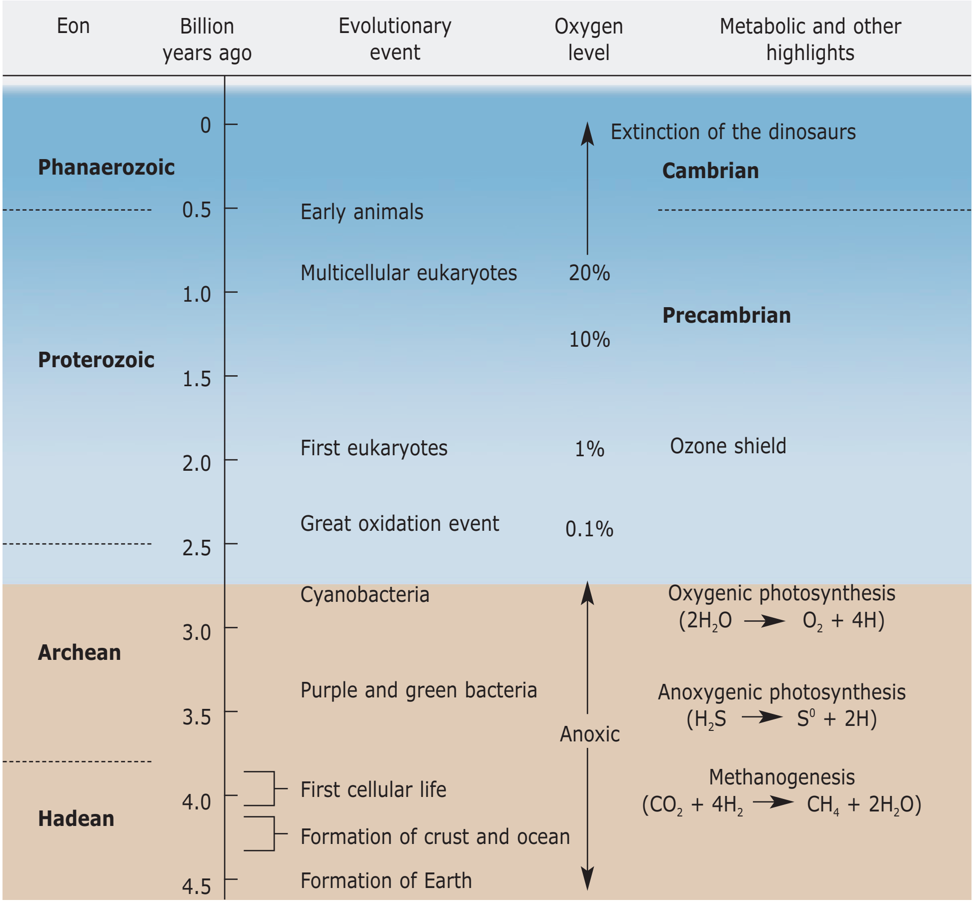
(2500-570 Ma) has been defined as the “Age of Cyanobacteria” because of their high abundance in the fossil record (Schopf and Walter 1982). The documented fossil record also shows the continuous presence of cyanobacteria back to at least 3500 Ma ago (figure 3.2). Therefore, part of the great success of cyanobacteria is their long evolutionary history, which allows them to thrive under different environmental conditions. Their high diversity and abundance is also facilitated by their small size, which favors more rapid exchange with the surrounding environment, accelerated metabolism, rapid growth rate and cellular reproduction (Whitton and Potts 2000). All of these factors have direct consequences for the adaptability and potentially high rate of evolution among the cyanobacteria. They are widely distributed in all types of habitat and in general they are more tolerant of extreme environments than are algae (Whitton and Potts 2000). Falkowski and Raven (1997) calculated that at any given time there are about 10^{25} cyanobacteria cells in the ocean. Therefore, the vast majority of photosynthetic carbon and nitrogen fixation in the contemporary ocean is carried out by this one group of living organisms.

During photosynthetic carbon fixation, cyanobacteria produce O_2 as a waste product. In fact, cyanobacteria are the only phototrophic prokaryotes capable of carrying out oxygen-producing, plant-like photosynthesis. Without that waste product, the evolution of complex multicellular organisms, including us, would not have been possible.

3.2. THE IMPORTANCE OF ATMOSPHERIC OXYGEN ON EARTH

Take a breath. If you are at this moment close to sea level, the chemical composition of the air that you are breathing is mostly N_2 (78%) and O_2 (21%). However, it was not always like that. During the first 3 billion years after the Earth’s formation, the atmosphere was devoid of O_2. The great number of organisms that currently live in oxygen-free environments attests to the fact that the availability of O_2 is not a requirement for “life”, but our (human) existence requires molecular oxygen. In fact, lots of oxygen. We have the largest brain of all the apes, and the energetic cost of that large brain is very high. For instance, in a human body at rest, adenosine triphosphate (ATP) molecules are formed and reformed at a rate of about 9×10^{20} molecules per second, equivalent to a turnover rate of 65 kg per day, with much higher rates during periods of strenuous activity (Rich 2003). The human brain makes up about 2% of a person’s weight, but it consumes 20% of the body’s energy at rest. The

Figure 3.3: Temporal sequence showing the landmarks in biological evolution, Earth's changing geochemistry and microbial metabolic diversification



Source: Madigan et al. 2009.

only element than can produce that much energy is oxygen (the typical adult male requires about 380 liters of O_2 per day, or 7600 liters of air per day).

From the time of Earth's formation, the early ocean and atmosphere were anoxic (without oxygen). Therefore, it is believed that life originated in an oxygen free-environment, and remained strictly anaerobic (generating energy without using oxygen) for more than a billion years. Then cyanobacteria evolved the ability to split water using the energy of sunlight, causing free oxygen to appear in the atmosphere for the first time (figure 3.3). In fact, all of the atmospheric oxygen found on this planet is of biological origin and started with the evolution of oxygenic photosynthesis by cyanobacteria about

2 billion years ago. The production of O_2 during photosynthesis, shown in the following overall and light reactions, seems remarkably simple. However, because water is a very stable compound, its oxidation to molecular oxygen in the light reaction is considered to be one of the major landmarks in biological evolution, transforming the life, the chemical composition and the climate of this planet forever (figure 3.3).

Overall reaction: $CO_2 + H_2O \xrightarrow{\textit{Light}} (CH_2O)\,n + O_2$

Light reaction: $2\,H_2O \xrightarrow{\textit{Light energy}} O_2 + 4\,H^+ + 4\,e^-$

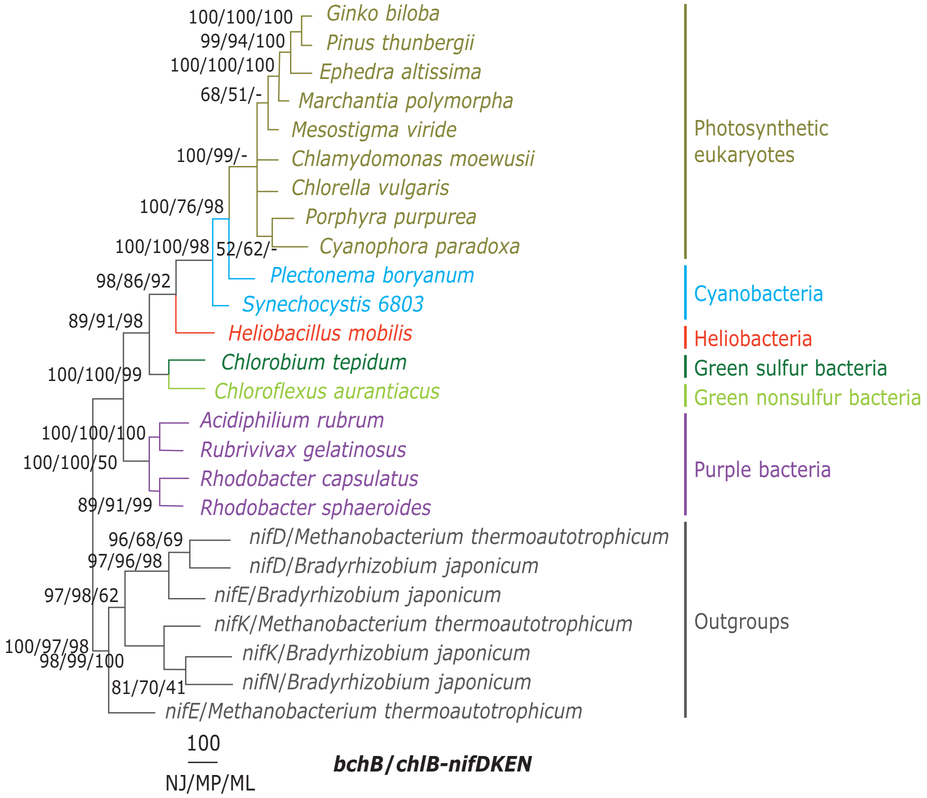
“Dark” reaction: $CO_2 + 4\,H^+ + 4\,e^- \longrightarrow (CH_2O)\,n + H_2O$

3.3. ORIGIN OF PHOTOSYNTHESIS

Because the splitting of water requires a powerful oxidizing agent, major evolutionary developments were required before the oxidation of water could take place. As with any other metabolic pathway that evolved billions of years ago, it is difficult to establish who the first photosynthetic organisms were. However, relatively recent molecular evidence has identified purple bacteria as the earliest photosynthetic bacterial lineage, which later diverged into green nonsulfur bacteria, green sulfur bacteria, heliobacteria, cyanobacteria and finally to photosynthetic eukaryotes (figure 3.4; Xiong et al. 2000). However, other studies have identified heliobacteria or green nonsulfur bacteria as the earliest-evolving phototrophs (Gupta et al. 1999). Although it is still unclear in which bacterial lineage photosynthesis evolved, it is well established that oxygenic photosynthesis was a cyanobacterial invention (Xiong et al. 2000).

Photosynthesis is the biological process by which light energy is transformed into chemical energy in the form of sugar and other organic molecules. Bacterial photosynthesis carried out by purple, green nonsulfur, green sulfur and heliobacteria does not generate O_2 as a by-product. The reason is that these anoxygenic photosynthetic bacteria contain only one type of photosynthetic reaction center (Photosystem I or II), whereas cyanobacteria contain both systems and carry out both photochemical reactions in parallel (figure 3.5). Both systems are needed to use water as an electron source, as PSI or PSII alone don’t have the oxidizing power to cleave water. The oxidation of water

Figure 3.4: Photosynthesis phylogeny based on the *bch*B/*chl*B gene

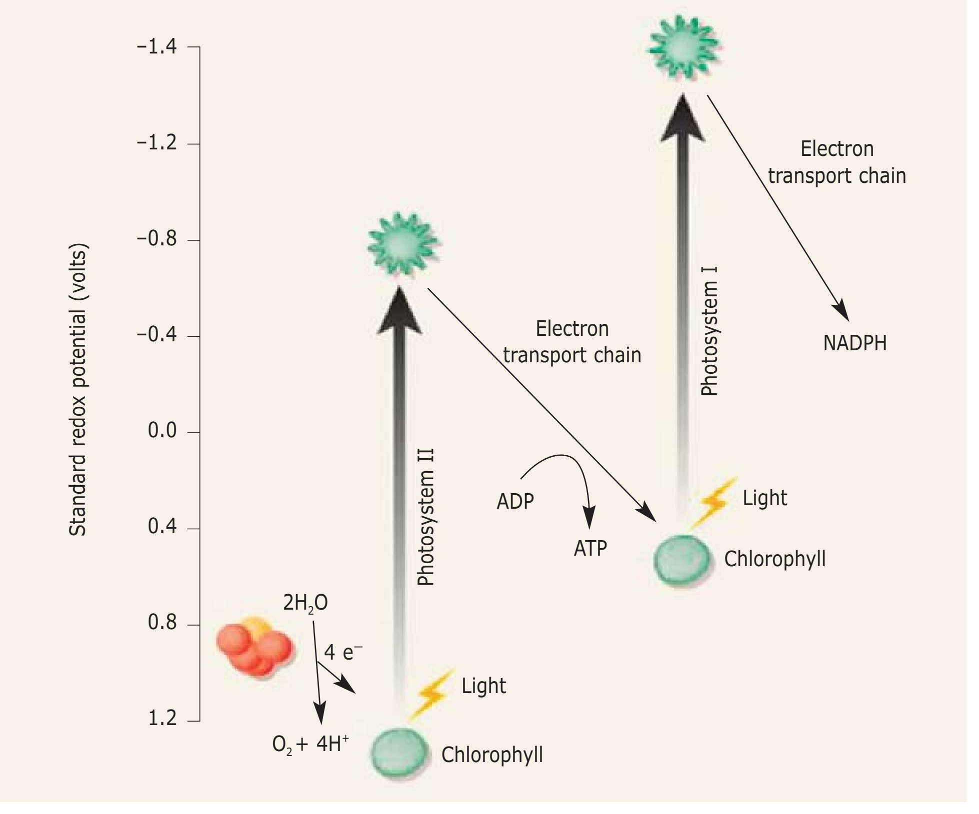


Source: Xiong et al. 2000.

was only possible after cyanobacteria evolved a reaction center pigment with a greater oxidizing potential, chlorophyll a. Anoxygenic photosynthetic bacteria contain bacteriochlorophylls as reaction center pigments. Because bacterichlorophylls absorb longer wavelength and therefore lower energy light, these reaction centers don't have the reducing power to oxidize water.

While the appearance of anoxygenic photosynthesis on Earth would have made some areas with abundant abiotic chemical sources of reducing power (e.g., S, Fe^{2+}, Mn^{2+}, H_2 and CH_4) from rock weathering and shallow hydrothermal systems more productive, the geographical distribution of organisms was still very limited due to the very localized sources of those electron donors. Because liquid water is abundant on the surface of the planet, the ability to oxidize water gave phototrophic organisms a nearly infinite source of electrons, and the ability to colonize every single environment

Figure 3.5: The two photosystems needed to split water during oxygenic photosynthesis

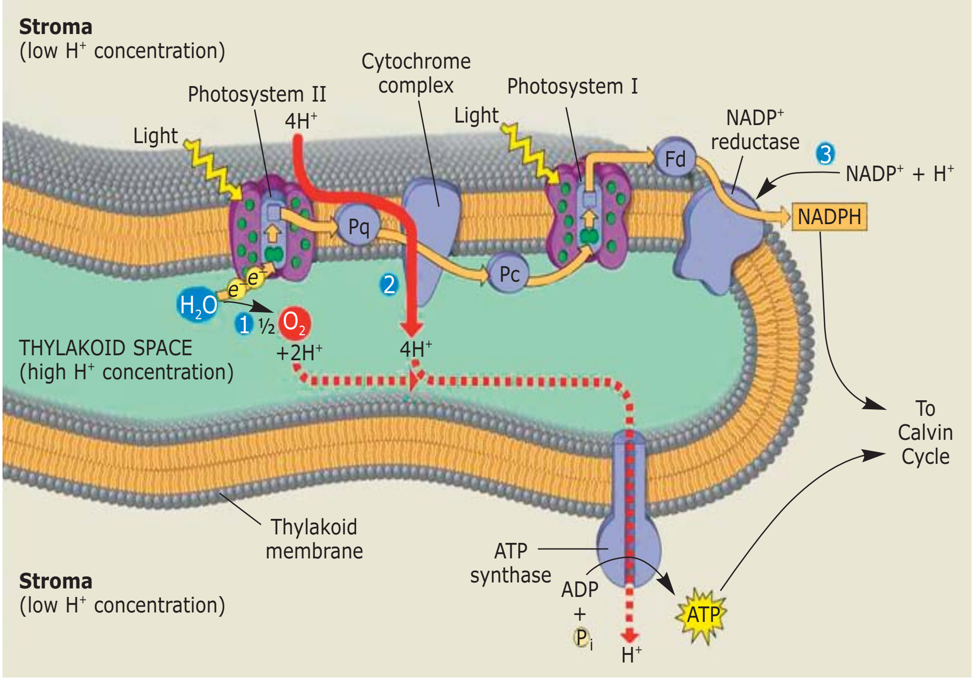


Source: Allen and Martin 2007.

on Earth. In fact, oxygenic photosynthesis underpins the existence of all life forms on the Earth's surface today.

In contrast to anoxygenic bacterial photosynthesis, oxygenic photosynthesis is a relatively recent evolutionary invention (figure 3.3). Oxygenic photosynthesis is probably the most complex energy-transducing process of life on Earth (figures 3.5 and 3.6). In order to use water as an electron-donor in oxygenic photosynthesis, organisms need a very complicated photosynthetic machinery that requires hundreds of genes, and the synthesis of a similar number of proteins clustered in two different photosystems (PSI and PSII), light-harvesting antennae, and cytochromes (Shi et al. 2005; Shi and Falkowski 2008). Furthermore, in order for the photosynthetic apparatus to work, enzymes are required for CO_2 fixation, chlorophyll synthesis and electron transport, as well as various cofactors such as pigments, hemes, Fe-S clusters and the Mn_4Ca water-splitting reaction center (figures 3.5 and 3.6). This breakthrough in bacterial metabolism transformed the chemical composition of the Precambrian period (end of the Proterozoic era) on Earth. Oxygenic photosynthesis facilitated the "great oxidation" of the atmosphere about 2.2 billion years ago, but the final oxidation of the atmosphere (to about current levels of ~20%) did not occur for another 2 billion years (figure 3.3), until tectonically driven changes caused the appearance of shelf seas where reduced organic carbon could be buried. The increased burial efficiency of organic matter on continental margins then produced an excess of global photosynthesis over global respiration, causing the rise of atmospheric O_2. This set the stage for the evolution of eukaryotic organisms (composed of cells with a nucleus and organelles) about 1.5 billion years ago. These much larger eukaryotic cells incorporated mitochondria (formerly free-living bacterial cells) as cellular organelles in which glucose is oxidized to CO_2 and water, thereby completing the energy cycle that started with oxygenic photosynthesis.

Figure 3.6: General depiction of the light reactions and chemiosmosis in the thylakoid membrane

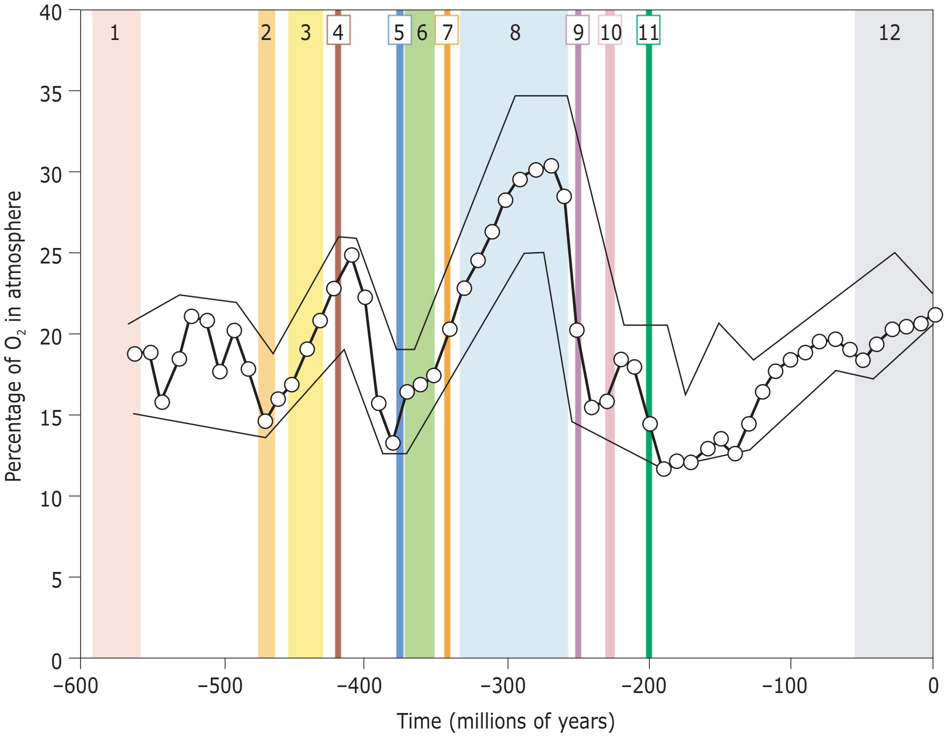


Source: Campbell and Reece 2005.

3.4. THE IMPACT OF OXYGEN ON THE DIVERSIFICATION OF LIFE

The production of O_2 during the early days of oxygenic photosynthesis caused a major ecological disaster, leading to the disappearance of most of the early anaerobic microbial life on Earth. However, as previously stated, the innovation of water oxidation opened an enormous range of new environments in which photosynthesis could occur. For the first time, life was not limited by the availability of electron donors, but only by the availability of light and nutrients. Furthermore, oxygen, the by-product of photosynthesis by cyanobacteria and their descendants (all eukaryotic photoautotrophs found in the modern world) made possible the development of more complex organisms that use more energy-efficient aerobic metabolism (Falkowski et al. 2005; Raymond and Segre 2006). For example, the evolution of metazoan (multicellular) organisms about ~0.5 billion years ago was dependent on the evo-

Figure 3.7: Potential connection between changes in atmospheric oxygen composition and major evolutionary transitions and extinction events



Source: Berner et al. 2007.

lution of oxidative phosphorylation, a very highly efficient energy recovery mechanism that requires O_2. Compared to glycolysis, this cellular respiratory process produces 18 times as much as ATP per mole of glucose, enough energy for the development of all complex multicellular organisms, including humans.

Atmospheric O_2 fluctuations seem to have played a major role as an evolutionary force on this planet, including the diversification of metazoan life forms throughout the Phanerozoic (figure 3.7). In fact, several major evolutionary transitions such as the conquest of land by animals (intervals 4 and 7 in figure 3.7), gigantism through the Carboniferous and Permian (interval 8) and the increase in mammalian body size in the Tertiary (interval 12) have all occurred under high O_2 concentrations (Berner et al. 2007). Low atmospheric O_2 concentrations seem also to have drastic consequences, as three of the major extinctions (Late Devonian (interval 5), Permian-Triassic (interval 9) and Triassic-Jurassic (interval 11: figure 3.7), all followed periods of low O_2 concentrations. One consequence of major extinctions is the rapid evolution of new metabolic pathways, including a more efficient respiratory system that requires less oxygen.

3.5. CYANOBACTERIA AND NITROGEN FIXATION

The extensive anaerobic microbial world attests to the fact that oxygen is not a required element for *all* forms of life. In contrast, all organisms (anaerobic or aerobic) require nitrogen to synthesize the proteins that make life possible. In fact, although genes get a lot of attention, it's the proteins that perform most life functions and make up the majority of cellular structures. Although there is a large nitrogen pool in the atmosphere of this planet (in fact, it is the major component in the Earth's atmosphere; about four-fifths of the air we breathe is N_2), this nitrogen is biologically unavailable because of the triple bond between nitrogen atoms (one of the strongest chemical bonds known) that makes N_2 extremely unreactive. Therefore, before N_2 can be incorporated into different bio-molecules, it has to be chemically reduced to a biologically available form of nitrogen (also called fixed nitrogen), namely, ammonia (NH_3). The critical task of fixing nitrogen for all living things is performed by a group of microorganisms, called diazotrophic prokaryotes that possess the multimeric enzyme complex, nitrogenase. In fact, all known nitrogen-fixing organisms are prokaryotes. During nitrogen fixation, nitrogenase catalyzes the reduction of molecular nitrogen to ammonia according to the following equation:

$$N_2 + 8\ H^+ + 8\ e^- + 16\ ATP \longrightarrow 2\ NH_3 + 16\ ADP + 16\ P_i + H_2$$

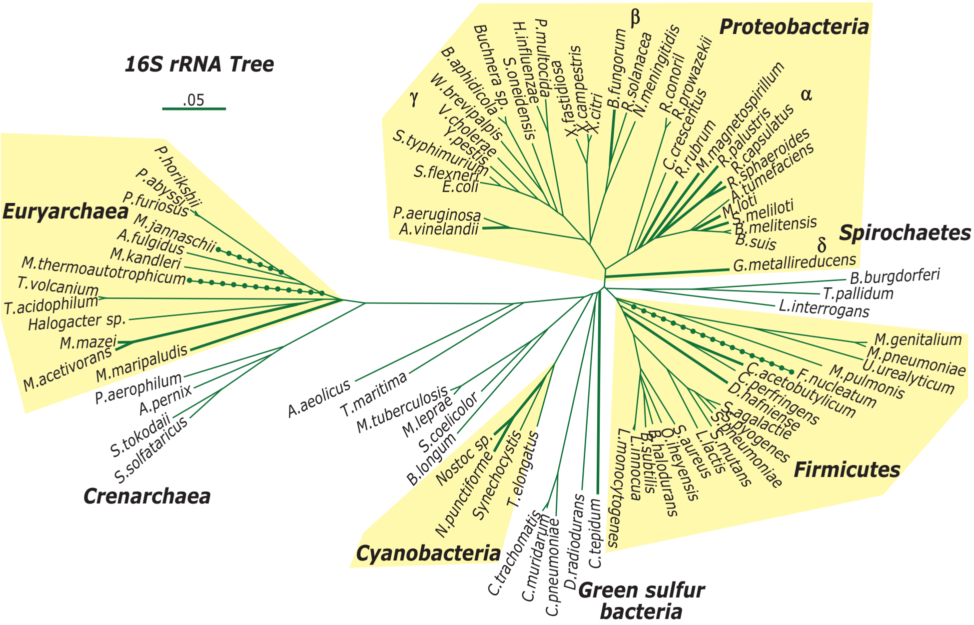
where ATP, ADP and P_i represent adenosine triphosphate, adenosine diphosphate and inorganic phosphorus respectively.

Because the triple-bond in the molecular N_2 is very stable (bond energy of 942 kJ/mol), nitrogen fixation requires an extremely high activation energy. With 16 ATPs needed to hydrolyze every mol N_2 fixed, the nitrogenase enzyme system carries out one of the most metabolically expensive processes in biology (Simpson and Burris 1984). While biological nitrogen fixation occurs at about 0.8 atm of nitrogen, the industrial synthesis of ammonia for fertilizers by the Haber-Bosch process is carried out at temperatures of 400 to 500 °C, and atmospheric pressures of N_2 and H_2 of several hundred, to obtain the necessary activation energy (Lehninger et al. 1993).

In contrast to oxygenic photosynthesis, it is difficult to establish when nitrogen fixation evolved. However, because nitrogen is necessary for the origin of life, nitrogen fixation may be a very ancient metabolic pathway. It is likely that before the evolution of biological nitrogen fixation, the only source of biologically available nitrogen was abiotic reactions produced by lightning discharges (Navarro-González et al. 2001). However, it has been hypothesized that abiotic sources of fixed nitrogen in the early Earth were limited (Raven and Yin 1998; Kasting and Sieferet 2001; Navarro-González et al. 2001), and that at some point in time (probably during the early Archaean), a reduction in the rate of abiotic nitrogen fixation (Navarro-González et al. 2001) could not support the nitrogen requirements of an expanding microbial biomass. This nitrogen crisis probably produced the evolutionary pressure behind the evolution of biological nitrogen fixation (Towe 2002). This scenario suggests that biological nitrogen fixation occurred early in the evolution of life on this planet, as diazotrophic organisms are found exclusively among prokaryotes, although they occur in both Bacteria and Archaea domains, which are not closely related (figure 3.8).

The evolutionary history of nitrogenases also suggests that biological nitrogen fixation is an ancient process. In an anoxic atmosphere containing N_2 and CH_4, photochemical reactions could have produced large amounts of triple-

Figure 3.8: Prokaryotic phylogenetic tree. Diazotrophs are indicated with bold green lines.



Source: Raymond et al. 2004.

bonded compounds such as C_2H_2 (acetylene) and HCN (hydrogen cyanide) (Kasting and Siefert 2001). Therefore, it is possible that this ancestral enzyme acted as a detoxifying agent, used by organisms for protection against acetylene, cyanide, azide, or any other N_2 analog formed in early anoxic atmosphere (Silver and Postgate 1973).

Because fixed nitrogen was necessary for synthesis of the biomolecules that sustain life on this planet, it is not surprising that the ability to fix nitrogen is found in both aerobic and anaerobic environments, and throughout the prokaryotic world, including in the cyanobacteria (figure 3.8), the same bacterial group that "invented" oxygenic photosynthesis. However, although nitrogen fixation genes have only been found in three of the six classified orders of cyanobacteria (Raymond et al. 2004), diazotrophic cyanobacteria contribute substantial amounts of fixed nitrogen in marine environments. This is relevant because most of the world's oceans are depleted in inorganic nitrogen at the surface, and therefore, in those expansive open ocean environments, the net biological activity depends on the amount of fixed nitrogen available. Current estimates of global N_2 fixation are ~240 Tg N yr^{-1} with a marine contribution of

100-190 Tg N y^{-1} that is between 40 to 80% of the global N_2 fixation (Berman-Frank et al. 2003). The critical role played by cyanobacteria in the marine nitrogen cycle is demonstrated by the fact that all marine nitrogen fixation is carried out by these organisms. Therefore, without the N_2 fixation carried out by the small cyanobacteria, most of the world's oceans would be devoid of life.

In summary, in a time when climate change, environmental degradation, overpopulation, conspicuous consumption and another long list of maladies jeopardizes the long-term survival of human societies, I have tried to provide in this chapter a sense of how tiny cyanobacteria have transformed the chemical environment of this planet and eventually allowed the evolution of humans. Because the splitting of water during oxygenic photosynthesis and the destruction of the nitrogen triple-bond during nitrogen fixation are not thermodynamically favored, our life on the surface of this planet, based on solar energy, may be an exception rather than the rule. I hope this chapter will help the reader to appreciate our planet in a different way and to see that luck has been on our side. How long this luck will last is up to us.

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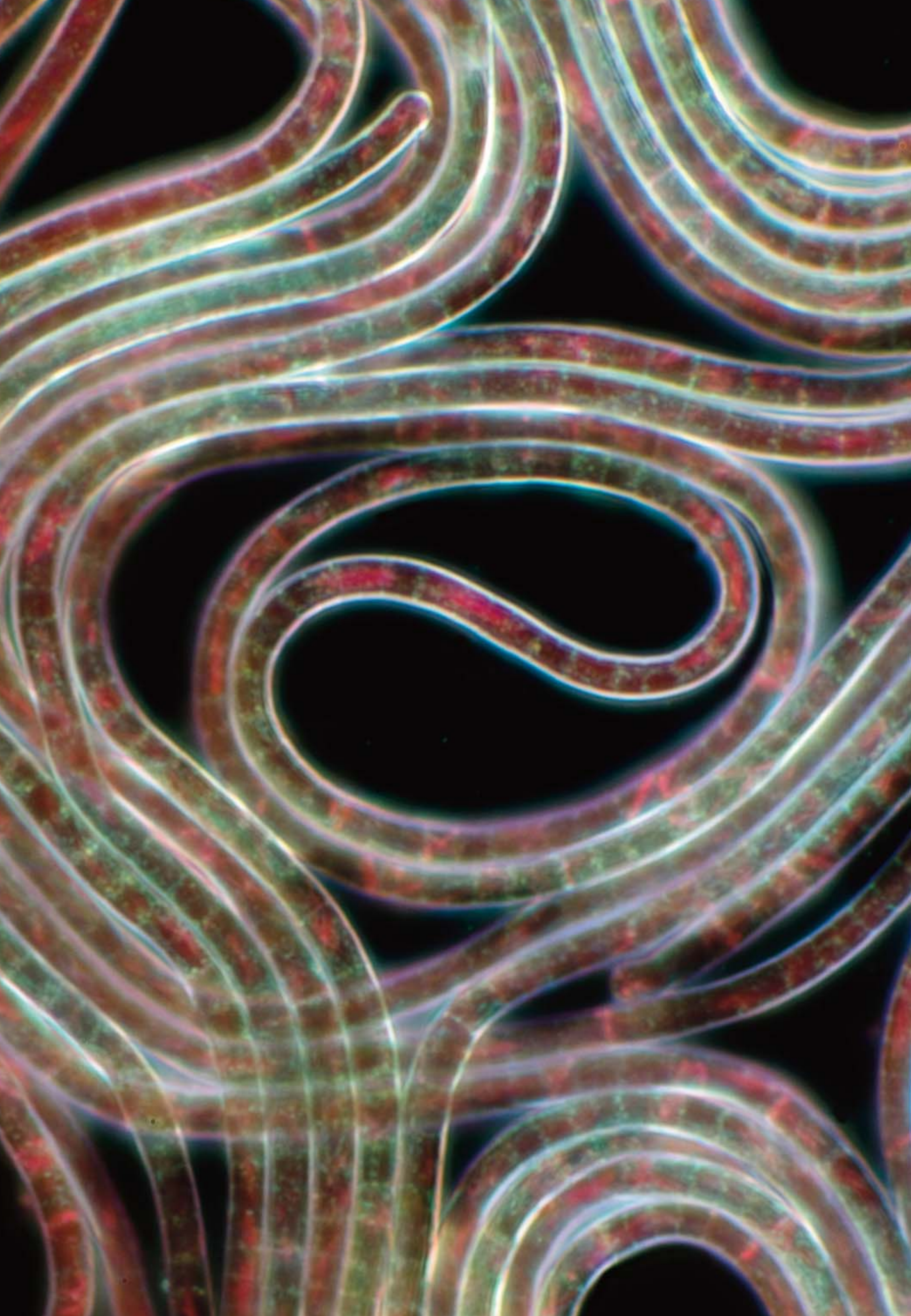

CHAPTER 4

THE ROLE OF MARINE BIOTA IN THE CO_2 BALANCE OF THE OCEAN-ATMOSPHERE SYSTEM

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THE OCEAN CARBON SYSTEM IS SUFFICIENTLY close to linear in its behavior that it is possible to consider it as consisting of two almost independent components due to: 1) the anthropogenic perturbation resulting from CO_2 injection into the atmosphere by human land use changes, the burning of fossil fuels, and a minor input resulting from cement production; and 2) the "natural" carbon cycle that was in place prior to the "Anthropocene" (cf. Crutzen and Stoermer 2000, for a definition), and which is generally assumed to have remained unchanged since then (although see, for example, Le Quéré et al. 2007, for evidence of recent relatively modest changes). This paper provides an overview of the natural carbon cycle and how it influences the air-sea balance of CO_2, with a review of recent ideas on how the natural carbon cycle might be modified to enhance CO_2 removal from the atmosphere as a form of carbon mitigation.

The paper is divided into four sections. The first provides a brief overview of the natural carbon cycle based largely on Sarmiento and Gruber (2006), which the reader is encouraged to consult for a more detailed discussion. The

◂ **Photo 4.1: *Oscillatoria animalis* cyanobacteria, dark field light micrograph.** The genus name for this cyanobacterium comes from the movement it makes as it orientates itself to the brightest light source available, from which it derives energy by photosynthesis.

major focus of this overview is on how biogeochemical processes in the ocean affect the air-sea balance of CO_2; the existence of anomalous regions of very high surface nutrient concentrations and surprisingly low biological activity in areas where the conditions would seem to be ideal for biology to flourish and nutrients to be completely consumed; and how these regions of anomalously high nutrient concentrations affect the air-sea balance of CO_2. The second section discusses the important role of iron limitation in helping to explain these anomalous high nutrient/low biological activity regions. The third and fourth sections turn to a discussion of model simulations of how relief of iron limitation in these regions would affect the air-sea CO_2 balance and the implications of this for carbon mitigation, respectively.

4.1. THE BIOLOGICAL PUMP AND AIR-SEA CO_2 BALANCE

When CO_2 dissolves in the ocean, a series of hydrolysis reactions ensue that added together have the following net effect on ocean carbon chemistry

$$CO_2 + H_2O + CO_3^{2-} \rightleftharpoons 2HCO_3^-$$

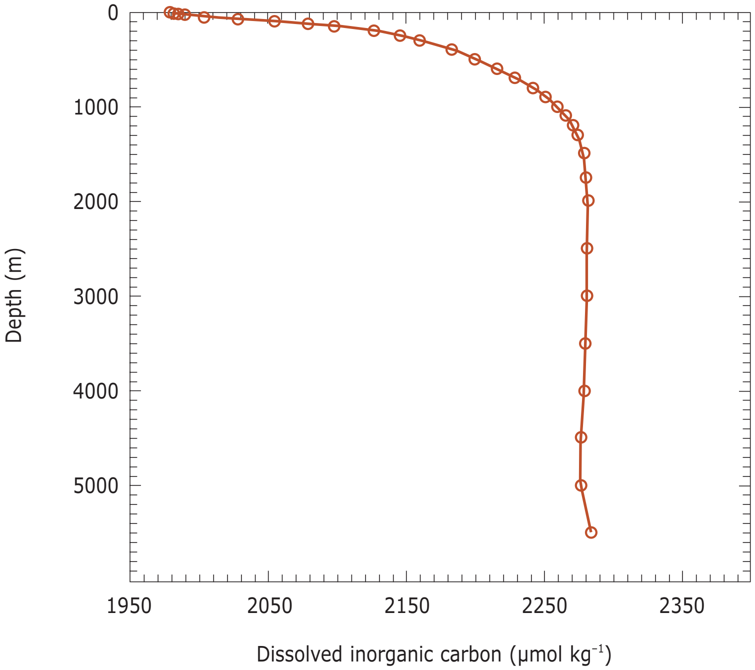
Given that inorganic carbon exists interchangeably as carbon dioxide, carbonate ion, or bicarbonate ion, we generally characterize the inorganic carbon content of the ocean as consisting of the sum of the three of these

$$DIC = CO_2 + HCO_3^- + CO_3^{2-}$$

where *DIC* is the *dissolved inorganic carbon*. On average, only about 0.5% of the *DIC* exists in the surface ocean as carbon dioxide, with 88.6% as bicarbonate ion and 10.9% as carbonate ion. This ability of the ocean carbon system to convert interchangeably between these three species, and the fact that the ocean chemistry is such as to permit the vast majority of *DIC* to exist in the carbonate and bicarbonate forms, is the principal reason why atmospheric CO_2 comprised only 1.5% of the combined atmosphere-ocean inventory of carbon prior to the beginning of the industrial revolution. For most other gases, such as oxygen, the proportions are roughly reversed due to the low solubility of most gases in seawater and the absence of a buffer effect such as that of the carbon system.

The global mean *DIC* concentration is 2,255 $\mu mol\ kg^{-1}$. However, figure 4.1 shows that *DIC* is not uniformly distributed, with *DIC* being about 300 $\mu mol\ kg^{-1}$

Figure 4.1: Vertical profile of horizontally averaged dissolved inorganic carbon in the ocean

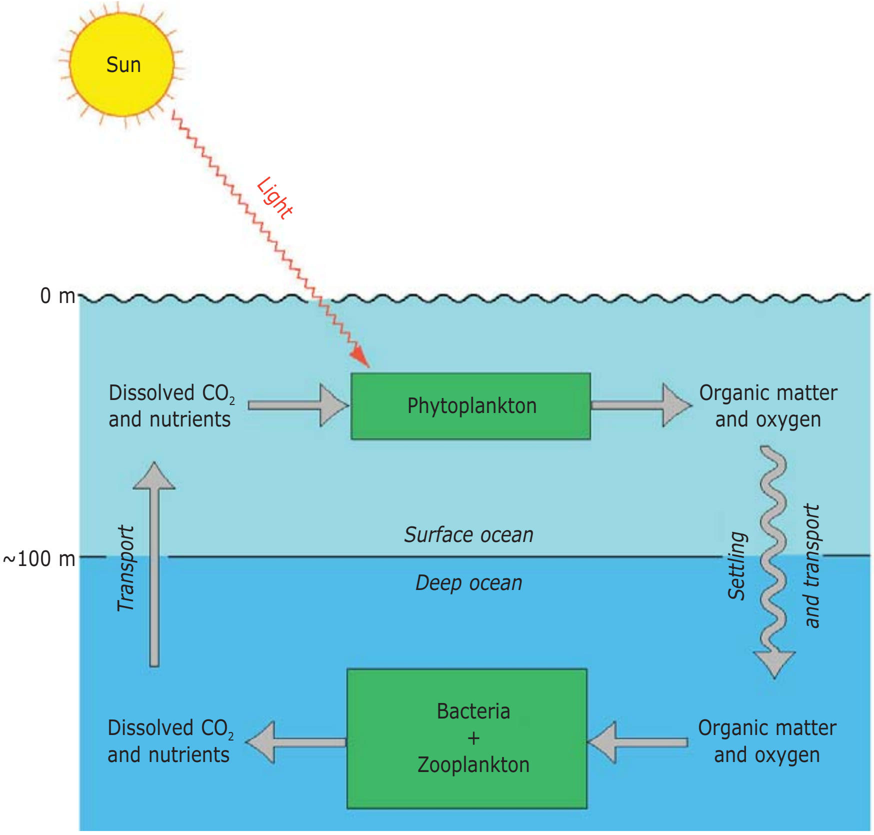


Source: Based on the GLODAP data set of Key et al. 2004.

higher at depth than at the surface. A little less than one-third of this surface to deep difference can be accounted for by the capacity of cold waters to hold more *DIC* than warm waters when brought into equilibrium with the atmosphere. The abyssal ocean is filled entirely with cold waters, whereas the surface waters are warmer on average due especially to the low latitudes. The vertical gradient in *DIC* that results from this solubility difference is referred to as the *solubility pump.*

The remaining two-thirds of the vertical *DIC* gradient is due to the *biological pump* illustrated in figure 4.2. This consists of four components: 1) the formation of organic matter and $CaCO_3$ from dissolved inorganic carbon and nutrients by photosynthesis in the surface ocean, 2) the export into the deep ocean of some of this $CaCO_3$ in particulate form, and some of the organic matter in both particulate and dissolved forms (about 80% of the organic matter is recycled within the surface ocean), 3) the conversion of the organic matter and $CaCO_3$ back into the dissolved inorganic form in the deep ocean by dissolution of $CaCO_3$, and by bacterial and zooplankton pro-

Figure 4.2: The great biogeochemical loop. An illustration of the biological pump described in the text.



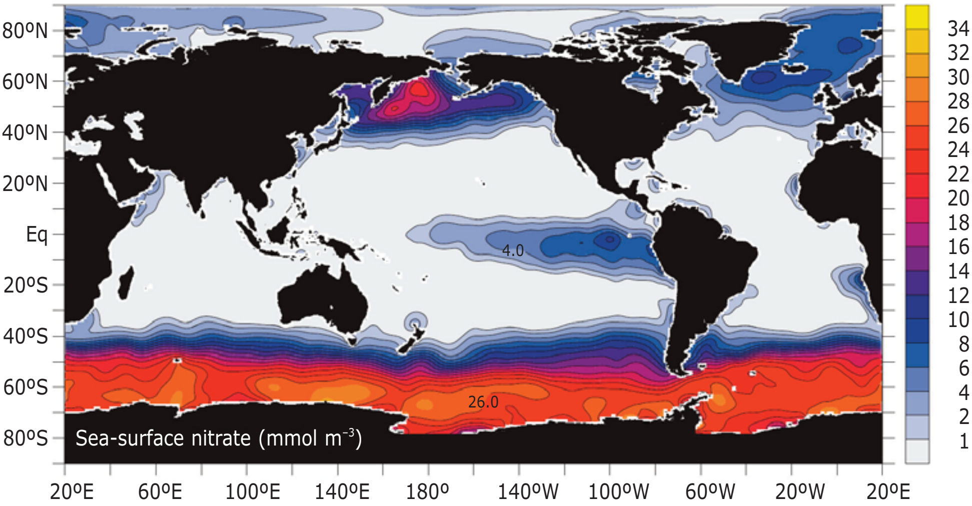
Source: Modified by Gruber (personal communication) from Sarmiento and Gruber 2006.

cessing of organic matter, a process referred to as *remineralization*, and 4) the closing of the loop by the upward transport of inorganic carbon and nutrients by the ocean circulation and mixing. The recycling of carbon and nutrients by this "great biogeochemical loop" is almost 100% efficient, with only a tiny leakage of carbon into the sediments and to the atmosphere by gas exchange, balanced by a river input resulting from weathering reactions and organic matter formation on land (e.g., Sarmiento and Sundquist 1992). While the loop is indeed almost closed in the ocean, the enhancement of the deep ocean *DIC* concentration by the biological pump (as well as the solubility pump) lowers the CO_2 content of the atmosphere relative to a world with the same total inventory of carbon and no biological pump. Simplified model studies show that shutting down the biological pump would release an amount of CO_2 to the atmosphere sufficient to increase its concentration from its pre-industrial value of 280 ppm to something in excess of 450 ppm. Marine biota thus play an important role in establishing the concentration of atmospheric carbon dioxide and therefore in the climate of the planet.

The impact of the marine biota may vary both temporally and spatially. In the modern ocean the biological pump is not working at full efficiency, as measured here by the effectiveness of phytoplankton in depleting nitrate from the surface of the ocean. Nitrate is the limiting nutrient for biological production over much of the ocean, and thus tends to be very close to depleted (map 4.1). However, there are three principal regions of the ocean, in the North Pacific, Equatorial Pacific, and Southern Ocean, where nitrate is never depleted, even in the summer when there is plenty of light. These regions are anomalous not only in having high nutrients, but also in having a low ratio of chlorophyll to nutrients, and are often referred to as High Nutrient/Low Chlorophyll or HNLC regions.

The North Atlantic also has high nitrate concentrations in the annual average, but here the nitrate is depleted in the summer time so it does not fit the definition of a classic HNLC region. In the following section we discuss how iron limitation can explain why nitrate is not depleted in the HNLC regions.

Map 4.1: Annual mean nitrate concentration at the surface of the ocean



Source: Sarmiento and Gruber 2006, based on the *World Ocean Atlas 2001* (Conkright et al. 2002).

Table 4.1: Results of regional nutrient depletion simulations in several models: in the KVHISOUTH ocean circulation and biogeochemistry model described by Gnanadesikan et al. (2002), in the new ocean biogeochemistry (Dunne et al. in prep; and Appendix by Dunne et al. in Sarmiento et al. 2009) and general circulation model described by Sarmiento et al. (2010).

a: KVHISOUTH, diagnostic biology with interactive atmosphere

Region of nutrient depletion	**Atmospheric CO_2 uptake (Pg C)**		
	50 years	**100 years**	**2000 years**
North Pacific (30°N to 67°N)	6.2	7.3	6.7
North Atlantic (30°N to 80°N)	7.2	10.8	32.0
Tropics (18°S to 18°N)	8.3	9.7	7.7
Southern Ocean (90°S to 30°S)	67.6	83.1	146.1
Global	91.2	110.6	178.4

b: New model (prognostic biology) with interactive atmosphere

Region of iron fertilization	**Net atmospheric CO_2 uptake (Pg C)**	
	50 years	**100 years**
North Pacific (30°N to 67°N)	5.0	6.7
North Atlantic (30°N to 80°N)	(0.8)	(1.1)
Tropics (18°S to 18°N)	(13.2)	(20.2)
Southern Ocean (90°S to 30°S)	58.9	74.9
Global	71.6	89.6

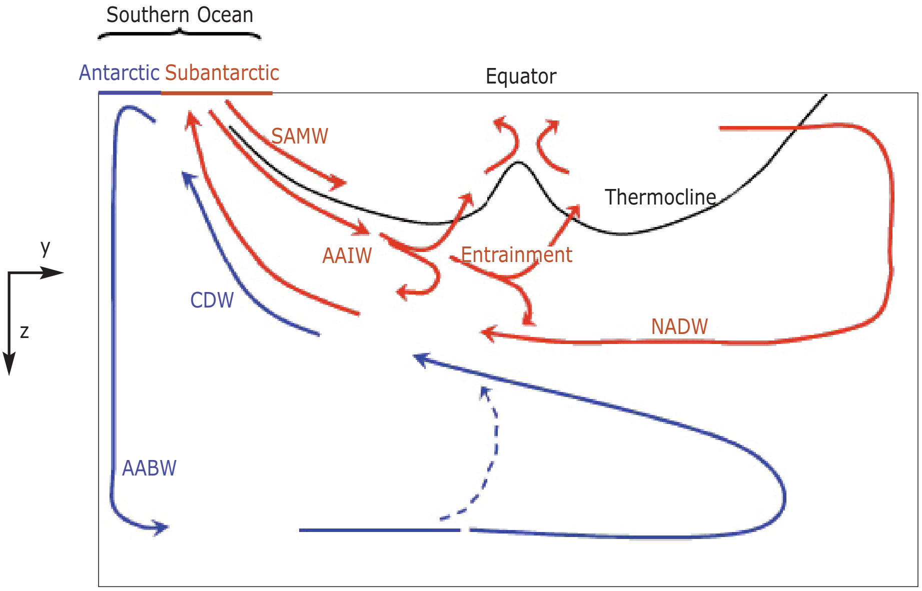
c: New model (prognostic biology) with fixed atmosphere

Region of iron fertilization	**Atmospheric CO_2 uptake (Pg C)**	
	50 years	**100 years**
North Pacific (30°N to 67°N)	8.5	13.7
North Atlantic (30°N to 80°N)	(1.4)	(2.3)
Tropics (18°S to 18°N)	(21.9)	(40.1)
Southern Ocean (90°S to 30°S)	103.8	159.2
Global	127.6	191.6

See text for discussion of these results and for the difference between simulations done with an interactive atmosphere versus those done with a fixed atmosphere. The results in parentheses in tables 4.1b and 4.1c are suspect, as discussed in the text.

Model perturbation studies can be used to isolate the impacts of the HNLC regions on the global carbon balance. Table 4.1a shows an ocean general circulation model study of what would happen in a model with diagnostic biology, that is, one in which surface biological processes are simulated by forcing model predicted surface nutrients towards the observed nutrient distribution, with carbon linked to the nutrients by a stoichiometric ratio, if a way could be found to overcome the barriers to nutrient depletion in these regions such that the nutrient concentrations were drawn down to 0 throughout the year. Consistent with earlier work discussed, for example, in Sarmiento and Gruber (2006), we find that neither the North Pacific nor the tropical region (we depleted nutrients over the entire tropical ocean, not just the Pacific HNLC region), nor the North Atlantic is able to remove a significant amount of CO_2 from the atmosphere. By contrast, nutrient depletion in the Southern Ocean is able to remove 39 ppm of CO_2 over 100 years, which is more than one-third of the increase in CO_2 of almost 110 ppm that has occurred since the beginning of the industrial revolution. Note that this is without the additional uptake due to the ocean alkalinity feedback effect that occurs on millennial time scales (cf. Archer et al. 2000), and which is beyond the scope of this paper.

Figure 4.3: A schematic of the global ocean conveyor belt circulation, consisting of an upper (red) loop and a lower (blue) loop as described in the text.



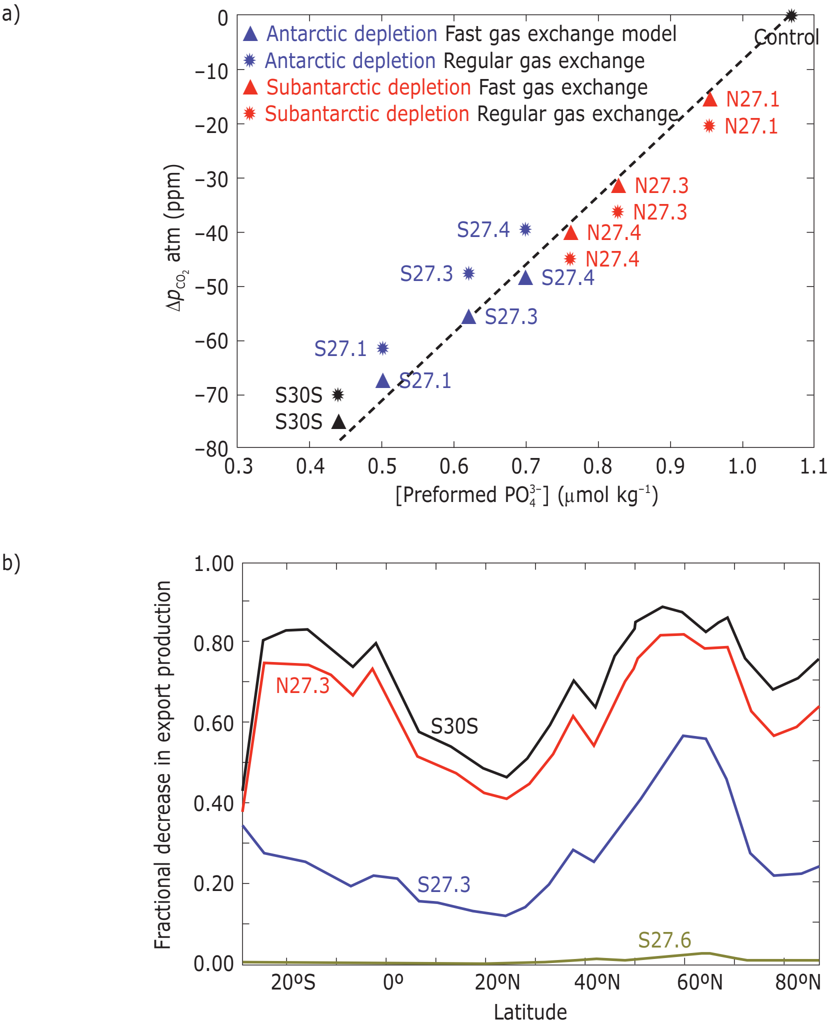
A particularly interesting aspect of the Southern Ocean carbon cycle (discovered by Marinov et al. 2006) is that there is a biogeochemical divide, north of which nutrient depletion has only a minimal effect on atmospheric CO_2, much like the North Pacific and tropics, with most of the atmospheric CO_2 drawdown capacity occurring south of this divide nearer to the Antarctic continent (figure 4.4a and table 4.2). This divide is associated with the surface manifestation of the upper and lower meridional overturning cells illustrated schematically in figure 4.3. As can be seen from the distribution of radiocarbon (cf. Gnanadesikan et al. 2007), the Southern Ocean is the location where the ocean's deepest waters are brought to the ocean surface. Some of these waters move northward into regions where the Subantarctic Mode and Antarctic Intermediate Waters form, sink down to the base of the main thermocline and flow even further northward. Eventually, these waters feed the sinking of deep waters in the North Atlantic Ocean. This upper meridional overturning loop is the main conduit for the return flow of biological pump nutrients from the

Table 4.2: Impacts of seasonality on Southern Ocean nutrient depletion simulations performed with the so-called LL model. The nutrient depletion is performed in different regions of the Southern Ocean as indicated in the top line. The seasons are defined as June, July, August for winter, and December, January and February for the summer. Three results are shown for each season, the first being the change in atmospheric p_{CO_2}, $\Delta p_{CO_{2atm}}$ in ppm; then the physical chemical efficiency defined in equation 4.4 (p. 83) but here calculated with respect to changed production only in the region of fertilization rather than in the world as a whole, $e_{phys\text{-}chem,S30°S} = \Delta p_{CO_{2atm}} / \Delta Prod_{S30°S}$ in units of ppm (Pg C yr^{-1})$^{-1}$; and finally the change in production north of 30°S relative to the removal of CO_2 from the atmosphere, $\Delta Prod_{N30°S} / \Delta p_{CO_{2atm}}$ in (Pg C yr^{-1}) ppm^{-1}.

Region of nutrient depletion		South of 30°S	South of σ_θ 27.1	South of σ_θ 27.6	North of σ_θ 27.1
Winter depletion	$\Delta p_{CO_{2atm}}$	48	42	18	7.9
	$e_{phys\text{-}chem,S30°S}$	-13	-38	-48	-2.6
	$\Delta Prod_{N30°S} / \Delta p_{CO_{2atm}}$	0.068	0.048	0.0012	0.17
Summer depletion	$\Delta p_{CO_{2atm}}$	45	39	17	6.9
	$e_{phys\text{-}chem,S30°S}$	-16	-52	-80	-3.4
	$\Delta Prod_{N30°S} / \Delta p_{CO_{2atm}}$	0.078	0.054	0.0019	0.22
Annual depletion	$\Delta p_{CO_{2atm}}$	73	66	32	16.8
	$e_{phys\text{-}chem,S30°S}$	-13	-26	-45	-3.28
	$\Delta Prod_{N30°S} / \Delta p_{CO_{2atm}}$	0.068	0.054	0.0017	0.19

Source: Results are from Marinov 2005.

Figure 4.4: Oceanic mechanisms for modifying atmospheric p_{co_2} and global production in the Princeton GCM. Results of experiments where surface nutrients are depleted south of 30ºS (experiment S30S), and south and north of the outcrops of σ_θ = 27.1 (experiments S27.1, N27.1), σ_θ = 27.3 (S27.3, S27.3), σ_θ = 27.4 (S27.4, N27.4), respectively. Experiments S27.4, S27.3, S27.1 (in blue) roughly represent depletion in the Antarctic; experiments N27.4, N27.3, N27.1 (in red) roughly represent nutrient depletion in the Subantarctic (see figure 4.3). **a)** Surface nutrient depletion results in a decrease in globally averaged preformed PO_4 (*x*-axis in the figure) and consequently a drawdown in atmospheric pCO_2 (*y*-axis in the figure) relative to the undepleted "Control" simulation (top right corner, black star). For all simulations, CO_2 drawdown is similar in our regular gas exchange (stars) and fast gas exchange (triangles) models. The important observation is that Antarctic nutrient depletion (blue triangles and stars) result in a larger decrease in preformed nutrients and stronger atmospheric CO_2 drawdown than Subantarctic depletion (red triangles and stars). **b)** Fractional decrease in export production (*y*-axis) versus latitude, following nutrient depletion experiments. Depleting nutrients in the Subantarctic (experiment N27.3) has much more impact on global export production north of 20ºS than depleting them in the Antarctic (experiment S27.3).



Source: Marinov et al. 2006.

deep ocean to the upper ocean, single-handedly accounting for about three-quarters of the biological production north of 30°S as shown by Sarmiento et al. (2004) and in figure 4.4b.

As shown in table 4.2, the change in production north of 30°S relative to the removal of CO_2 from the atmosphere, $\Delta \mathrm{Prod}_{N30°S}/\Delta p_{CO_{2atm}}$, is 3.5 to 4 times higher for nutrient depletion south of 30°S and north of the surface outcrop of $\sigma_\theta = 27.1$, than it is for regions to the south of this outcrop, with an even larger contrast for fertilization south of the surface outcrop of $\sigma_\theta = 27.6$. An important reason why nutrient depletion in the surface outcrops of the upper loop (i.e., the Subantarctic region in figure 4.3) does not have much of an impact on atmospheric CO_2 is because most of these nutrients and the associated biological pump carbon are eventually removed from the surface by the efficient biological pump in lower latitudes. Removing the nutrients in the Southern Ocean portion of this loop only accelerates a process that eventually occurs anyway and thus does not have much of an impact on the air-sea balance of carbon. By contrast, the upwelling waters that move southward in the Southern Ocean (i.e., the Antarctic region in figure 4.3) find themselves in an environment where nutrients are not utilized efficiently. This allows a decoupling of carbon from nutrients, with carbon dioxide escaping to the atmosphere while nutrients are reinjected into the abyssal ocean. Depletion of nutrients in the region south of the biogeochemical divide is what accounts for most of the response of the atmospheric CO_2 to Southern Ocean nutrient depletion (figure 4.4a and table 4.2). Thus, by far the greatest remaining capacity for additional removal of CO_2 from the atmosphere in the present ocean south of the biogeochemical divide is in the high latitudes of the Southern Ocean where Antarctic Bottom Water and lower Circumpolar Deep Water are formed. The processes that prevent nutrient removal from occurring in this region are the subject of the next section of this paper.

The large scale macronutrient manipulation simulations demonstrate that the air-sea CO_2 balance is best understood by analyzing the fraction of total nutrients in the ocean that is remineralized, and thus associated with carbon, versus the fraction that is "preformed," i.e. injected into the deep ocean without being associated with carbon (Ito and Follows 2005; Marinov et al. 2008a, 2008b). The key insight is that the remineralized nutrient pool can be thought of as the difference between the total nutrient pool and the preformed pool. The total accumulation of dissolved inorganic carbon in the ocean due to the remineralization process (defined below as the soft-tissue

Ocean Carbon Storage or OCS_{soft}) is stoichiometrically related to the remineralized nutrient pool:

$$OCS_{soft} = r_{C:P} \cdot \overline{PO_{4remin}} \cdot V_{oc} = r_{C:P} \cdot \left(\overline{PO_4} - \overline{PO_{4pref}}\right) \cdot V_{oc} \qquad (4.1)$$

where V_{oc} is the ocean volume, PO_4, PO_{4remin}, PO_{4pref} are the total, remineralized and preformed ocean phosphate and an overbar denotes global mean. Changes in biological cycling or circulation that reduce the preformed pool will thus increase the remineralized pool and draw down atmospheric carbon dioxide. Assuming surface ocean CO_2 equilibrates instantaneously with the atmosphere and disregarding the solubility pump, Marinov et al. (2008a) showed that atmospheric p_{CO_2} decreases exponentially with the remineralized pool:

$$p_{CO_{2a}} = c \cdot e^{-\frac{OCS_{soft}}{a_1}} + c^2 \cdot \frac{a_2}{a_1} e^{-\frac{2\,OCS_{soft}}{a_1}} + c^3 \cdot \frac{3 \cdot a_2^2}{2 \cdot a_1^2} e^{-\frac{3\,OCS_{soft}}{a_1}} + \dots \qquad (4.2)$$

where a_1 and a_2 are coefficients related to buffer chemistry and c is a constant of integration.

Thus, because the region to the south of the biogeochemical divide is the dominant source of preformed nutrients to the deep ocean, increasing biological activity in this region will have a disproportionate impact on the oceanic preformed nutrient inventory and the biggest effect on atmospheric carbon dioxide. However, changes in circulation can also change the preformed nutrient pool. For example, reducing the contribution of high-preformed nutrient Southern Ocean deep water relative to lower preformed nutrient North Atlantic Deep Water will also alter the total preformed nutrient content of the ocean and thus change the atmospheric carbon dioxide. It is this ability to capture the impacts of changing both circulation and biological activity that motivates analysis of the biological pump in terms of preformed nutrients.

Marinov et al. (2008b) examined the biological pump in a suite of models with different circulation patterns, but in which the HNLC regions were constrained to have their modern nutrient concentrations. They found that a circulation scheme in which vertical mixing is strong can result in both higher biological productivity and higher atmospheric carbon dioxide compared to a lower-mixing control. This apparent paradox is resolved by the finding that the higher mixing model injects relatively more deep water via the Southern Ocean and therefore has higher preformed nutrients in the deep than the control model. Higher preformed nutrients imply less remineralized nutrient in the ocean and, according to Equation 4.2, higher atmospheric p_{CO_2}. Thus, contrary to conventional wisdom, atmospheric p_{CO_2} can decrease, while surface nutrients show minimal change and export production decreases.

4.2. THE ROLE OF IRON IN LIMITING THE BIOLOGICAL PUMP

The principal hypothesis for what prevents nutrients from being drawn down in the HNLC regions is that these regions are iron limited, an idea for which observational support first began to appear in a series of papers published by John Martin in the late 1980's and early 1990's (e.g., Martin and Fitzwater 1988; Martin et al. 1990a; Martin 1992). Iron is an important component of electron transport proteins involved in photosynthesis and respiration, as well as in enzymes required to fix nitrogen and utilize nitrate and nitrite. The evidence in support of the iron limitation hypothesis has grown over time based principally on a wide range of mesoscale iron manipulation experiments such as those described by Martin et al. (1994), Coale et al. (1996), Boyd et al. (2000), Gervais et al. (2002), Tsuda et al. (2003), Boyd et al. (2004), Coale et al. (2004), and Hoffmann et al. (2006); reviews by de Baar et al. (2005) and Boyd (2007), and based on studies of natural iron fertilization at the Kerguelen plateau and Crozet Island in the Southern Ocean by Blain et al. (2007) and Pollard et al. (2009), respectively. This brief review of the principal findings of these studies closely follows the recent paper of Sarmiento et al. (2009).

These experimental manipulations and observational studies clearly demonstrate that iron fertilization results in a drawdown of nitrate (cf. summary table given in Sarmiento and Gruber 2006), but what is their impact on carbon? As in Sarmiento et al. (2009), we find it useful in analyzing the impact of the iron manipulation experiments on the carbon distribution to define the overall efficiency of iron fertilization in removing CO_2 from the atmosphere as the cumulative perturbation atmospheric CO_2 uptake $\Delta\Phi^{CO_2}_{air\text{-}sea}$ divided by the cumulative iron addition $\Delta\Phi^{Fe}_{fertilization}$, i.e.,

$$R^{\mathrm{C:Fe}}_{overall} = \frac{\Delta\Phi^{\mathrm{CO_2}}_{air\text{-}sea}}{\Delta\Phi^{\mathrm{Fe}}_{fertilization}} \tag{4.3}$$

where we define Φ (units of mol) as the cumulative area and time integral of a flux (f) of tracers such as Fe, organic matter, $CaCO_3$ or CO_2 across a depth level or the air-sea interface:

$$\Phi = \int_0^{\tau}\!\!\iint f\,\mathrm{d}x\mathrm{d}y$$

The delta symbols refer to the difference between the patch iron fertilization scenario and the control scenario with no fertilization.

We further separate the overall response function into a *physical-chemical efficiency*, $e_{phys\text{-}chem}$, defined as the ratio of the uptake of CO_2 from the atmosphere, $\Delta\Phi^{\mathrm{CO_2}}_{air\text{-}sea}$, to the cumulative perturbation export of carbon from the surface ocean, $\Delta\Phi^{\mathrm{Org\ C\ \&\ CaCO_3}}_{export}$, that results from iron fertilization; and a *biogeochemical response function* $R^{\mathrm{C:Fe}}_{iron\ utilizatión}$ defined as the ratio of $\Delta\Phi^{\mathrm{Org\ C\ \&\ CaCO_3}}_{export}$ to $\Delta\Phi^{\mathrm{Fe}}_{fertilization}$. In equation form, we have that:

$$\begin{aligned} R^{\mathrm{C:Fe}}_{overall} &= e_{phys\text{-}chem} \cdot R^{\mathrm{C:Fe}}_{iron\ utilizatión}, \text{ where} \\ e_{phys\text{-}chem} &= \frac{\Delta\Phi^{\mathrm{CO_2}}_{air\text{-}sea}}{\Delta\Phi^{\mathrm{Org\ C\ \&\ CaCO_3}}_{export}}, \text{ and} \\ R^{\mathrm{C:Fe}}_{iron\ utilizatión} &= \frac{\Delta\Phi^{\mathrm{Org\ C\ \&\ CaCO_3}}_{export}}{\Delta\Phi^{\mathrm{Fe}}_{fertilization}} \end{aligned} \tag{4.4}$$

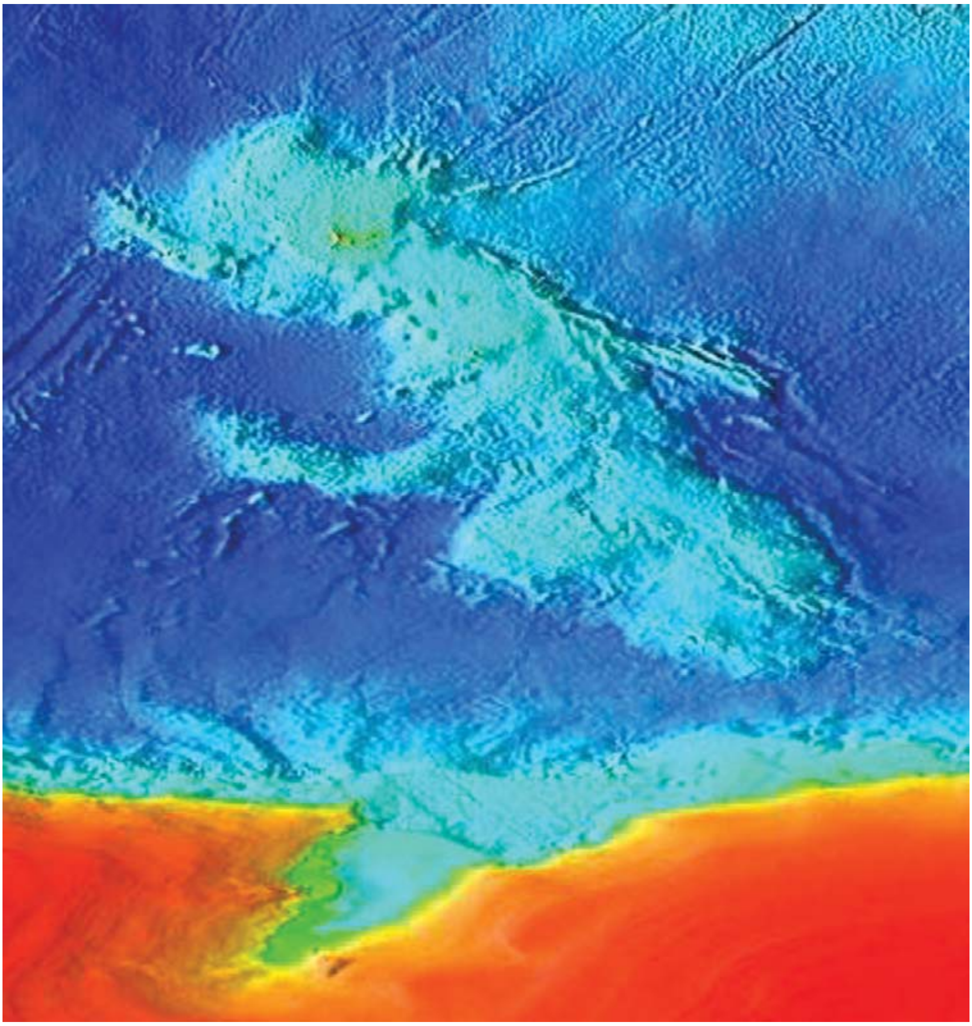
(cf. Jin et al. 2008).

As noted in the summary by Sarmiento et al. (2009), from which the following review paragraphs are taken, the mesoscale iron enrichment experiments referred to above have shown that the drawdown in surface dissolved inorganic carbon (*DIC*) that results from a given iron addition occurs at an average ratio of $R^{\mathrm{C:Fe}}_{iron\ utilizatión} = 5{,}600$ mol C to mol Fe added (de Baar et al. 2005). This is considerably smaller than the intracellular C:Fe ratios of ~20,000 to 500,000 typically observed in laboratory experiments with oceanic phytoplankton as summarized by Fung et al. (2000) and Sunda (2001), or than the mean C:Fe ratio of 200,000 proposed by Johnson et al. (1997). This suggests that most of the iron that is being added to the ocean is not being utilized by phytoplankton, at least on the time-scale of the observations. In addition to this problem, there has been only partial success in demonstrating that *DIC* uptake by iron fertilization actually results in carbon export from the surface ocean. The limited observational period of most experiments seems a likely reason for the failure to observe a significant export flux in many cases (Buesseler et al. 2004; de Baar et al. 2005). For example, in one of the few successful observations of particle fluxes, Bishop et al. (2004) used autonomous floats with optical measurements of the "carbon flux index" to show a large flux of particulate organic carbon at the SOFeX northern patch site beginning only 25 to 45 days after iron addition was initiated. Based on their measurements, Bishop et al. (2004) estimated a C export to Fe added ratio of $R^{\mathrm{C:Fe}}_{iron\ utilizatión}$ = 10,000 to 100,000, which is more consistent with what might be expected from the laboratory experiments.

The problems inherent in short term manipulation experiments have motivated a new series of observational studies at locations within HNLC regions where islands provide a local long-term source of iron. Such studies of natural iron fertilization at the Kerguelen plateau (map 4.2) and Crozet Island in the Southern Ocean have detected a large excess particulate organic carbon export in iron fertilized regions relative to that in adjacent non-fertilized regions using the ^{234}Th deficit method. The ratio of the excess C export to Fe supply is estimated to be $R^{\mathrm{C:Fe}}_{iron\ utilizatión}$ = 70,000 ± 46,000 at Kerguelen at the time of observations by Blain et al. (2007). At Crozet, Pollard et al. (2009) found that the mean daily rates of carbon export were similar in the iron fertilized region and in the HNLC region after the chlorophyll peak. However, they calculated different bloom durations for each region by using ^{234}Th/opal ratios to close the silicate budget. The seasonal ratio of excess C export to Fe supply at Crozet was estimated to be 17,200 (5,400-60,400) at 100 m and 8,600 at 200 m. Estimates based on the seasonal *DIC* and Fe budgets at Kerguelen give a much higher seasonal mol C to mol Fe ratio of $R^{\mathrm{C:Fe}}_{iron\ utilizatión}$ = 668,000. The reason for the large difference between the Kerguelen and Crozet seasonal estimates of $R^{\mathrm{C:Fe}}_{iron\ utilizatión}$ is not understood (e.g., Pollard et al. 2009).

Despite the large uncertainties, the natural iron fertilization studies and some of the iron manipulation studies have clearly demonstrated that iron fertilization of HNLC regions should eventually give rise to an increased particle export flux. What can be said about the physical-chemical efficiency $e_{phys\text{-}chem}$, i.e., the extent to which the resulting reduction in surface *DIC* will actually remove CO_2 from the atmosphere? The short time span of the iron manipulation experiments is problematic for verification of the impact of iron fertilization on the air-sea balance of CO_2. A typical air-sea e-folding equilibration time for a 40 m mixed layer is of the order of six months (cf., Sarmiento and Gruber 2006), as contrasted with the time scale of a few weeks of the experiments. Thus, the air-sea CO_2 flux estimated from the *DIC* deficit during the

Map 4.2: Topographical map of the Kerguelen plateau, a large underwater volcanic igneous province in the Southern Indian Ocean. The red patch below the plateau is the continent of Antarctica.



fertilization period is only a miniscule part of the carbon budget, an average of 8% of the *DIC* drawdown per de Baar et al. (2005).

The time scale of the natural iron fertilization studies is more suitable, though still not ideal. Estimates of air-sea CO_2 gas flux over a 75-day period during the Crozet Island experiment by Bakker et al. (2007) gave an average uptake of 700 ± 600 mmol m^{-2} inside the fertilized patch versus 240 ± 120 mmol m^{-2} outside the patch, for a net uptake of 460 ± 580 mmol m^{-2} due to the added iron. Pollard et al. (2009) give a particulate organic carbon (POC) export of 960 mmol m^{-2} in the patch versus 290 mmol m^{-2} outside for a net of 670 mmol m^{-2}, with no uncertainty reported. The air-sea CO_2 uptake in the Crozet iron fertilized region thus gives a physical-chemical efficiency of $e_{phys\text{-}chem} \sim 69\%$, but with quite a large uncertainty. Using the 90 day seasonal carbon flux estimates of Jouandet et al. (2008) of 5,400 ± 1,900 mmol m^{-2} inside the patch versus 1,700 ± 400 mmol m^{-2} outside the patch, and air-sea flux of 28 ± 24 mmol m^{-2} d^{-1} inside the patch and –2.7 ± 2.3 mmol m^{-2} d^{-1} outside the patch, 90 days/2 to account for the whole season, Sarmiento et al. (2009) calculate $e_{phys\text{-}chem} = 37\%$, again with a very large uncertainty. However, even the 75 and 90 day time periods over which the air-sea flux was estimated in the natural fertilization studies is insufficient to fully capture the equilibration of the surface *DIC* perturbation. More importantly, although such studies very likely capture a substantial fraction of the immediate response to iron fertilization, there are other longer term processes that modify the overall chemical-physical efficiency of the iron fertilization, such as the global backflux of CO_2 that results from reduction of atmospheric CO_2 (cf., Gnanadesikan et al. 2003; Oschlies, 2009; Sarmiento et al. 2009).

In conclusion, while the uncertainties are very large and the extent and solidity of the evidence varies from location to location, the experimental work does clearly show that adding iron to HNLC regions results in a rapid uptake of dissolved inorganic nutrients and carbon that is greater than in the surrounding unfertilized waters. It would be expected that such an enhancement of the uptake would result in an enhanced export of organic matter, but this has only been observed in those few cases where there was longer term monitoring. Finally, it is only in the natural iron fertilization studies where the time scale of the experiments has been long enough for meaningful observations of the impact of iron fertilization on the air-sea flux of CO_2 to be obtained (photo 4.2).

Photo 4.2: Phytoplankton bloom in the South Atlantic Ocean, off the coast of Argentina. Iron is a trace element necessary for photosynthesis, however it is highly insoluble in sea water and is often the limiting nutrient for phytoplankton growth. Large phytoplankton blooms can be created by supplying iron to iron-deficient ocean waters.

4.3. ENHANCEMENT OF OCEANIC CO_2 SEQUESTRATION BY IRON FERTILIZATION

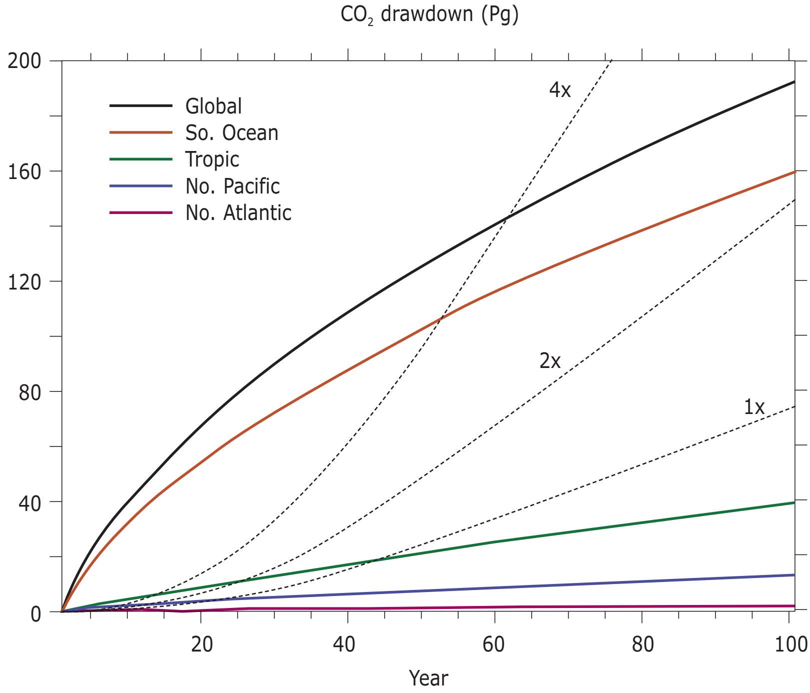
The previous two sections demonstrated that the biological pump can exert a significant control over the air-sea balance of carbon dioxide and that the flux of iron to the ocean can change the biological pump. This section examines the link between these results. Such a connection was first made by Martin (1990) who noted that during the last ice age the delivery of iron-bearing dust to the oceans was much higher than at present and atmospheric carbon dioxide was much lower than at present. Discovered in ice core records (Barnola et al. 1983), lower atmospheric p_{CO_2} during glacial periods is challenging to explain because it is widely accepted that terrestrial vegetation held less carbon, and the ocean, though colder than at present, is unlikely to have been able to absorb all the additional carbon dioxide. Previous work by Knox and McElroy (1984), Sarmiento and Toggweiler (1984), and Siegenthaler and Wenk (1984) using box models had earlier noted that either an increase in high latitude production or a decrease in high latitude vertical exchange (either of which would result in a reduction in preformed nutrients) could easily explain such a drop; but the reason for increased production or decreased exchange had not been identified. An additional major impetus for study of the connection between iron and the ocean carbon inventory has been the carbon mitigation proposal first articulated by Martin et al. (1990a) and Martin et al. (1990b) to artificially fertilize the ocean with iron as a way of removing CO_2 from the atmosphere. In this section, we use a series of models to examine how large an impact on air-sea carbon partitioning could be associated with changes in iron supply.

As already noted, simulations in which nutrients are drawn down at the surface in a diagnostic biology model (table 4.1a, page 76) show that a global drawdown of nutrients could remove 91 Pg C from the atmosphere (~43 ppm) over 50 years or 178 Pg C (83 ppm) over 2000 years. These simulations include the CO_2 lost from the ocean due to the declining concentration of CO_2 in the atmosphere. However, they do not include the effect on the ocean buffer capacity of increasing atmospheric CO_2 due to the anthropogenic sources. The atmospheric p_{CO_2} increase due to the anthropogenic sources reduces the buffer capacity of the ocean, $\partial DIC/\partial CO_2$, thereby resulting in increased oceanic CO_2 uptake following iron fertilization (cf., Cao and Caldeira 2010) relative to our simulations. The long term response of global iron fertilization is a potentially significant fraction of the 100 ppm change needed to explain the glacial/interglacial atmosphere difference and would be even larger if the long term $CaCO_3$ feedback were included (e.g., Archer et al. 1998). What can we say about the short term response to surface nutrient drawdown? And given that iron fertilization has been proposed as a carbon mitigation strategy for these shorter time scales, what can we say about how much nutrient drawdown would result from iron addition?

We take as a metric for the iron fertilization impact the wedges concept introduced by Pacala and Socolow (2004). They proposed that humanity could act to stabilize atmospheric CO_2 at about 500 ± 50 ppm by avoiding an amount of projected future CO_2 emissions equivalent to 7 wedges, each of which consists of a total avoided emission of 25 Pg C increasing linearly from 0 Pg C yr^{-1} or avoided emissions in 2005 and ending at 1 Pg C yr^{-1} fifty years later. Each wedge represents a massive societal effort, for example the replacement of coal and gas power plants by tripling global installed nuclear capacity. The impact of such strategies is illustrated in figure 4.5, where the dashed black lines show the cumulative emissions reduction from implementing one, two and four wedges and the colored lines show fertilization in different regions from the fixed atmosphere model used to generate the results shown in table 4.1c (page 76). Over the first 50 years, ocean fertilization results in apparently significant emissions reductions, particularly if the Southern Ocean is fertilized. But because the impact of fertilization saturates, emissions avoidance strategies eventually win out. Note that this analysis assumes that iron fertilization is carried into the future indefinitely; if it is not, the sequestered carbon would start to leak back to the atmosphere. Ocean iron fertilization thus represents at best a strategy for delaying the necessary implementation of changes in energy use rather than providing permanent reductions.

We consider next how a more realistic representation of the impacts of higher iron delivery to the oceans affects the atmospheric CO_2 drawdown. One potential issue with the nutrient drawdown results reported in table 4.1a (page 76) is that biological cycling can only draw down carbon during the summer months, while deep water formation that injects carbon into the deep ocean occurs during the winter months. Marinov (2005) addressed this issue by performing nutrient depletion in different regions of the Southern Ocean during the Southern Hemisphere winter (June, July, August), the Southern Hemisphere summer (December, January, February), as well as during the entire year (table 4.2, page 78). Somewhat surprisingly, depleting

Figure 4.5: Response of atmospheric carbon inventory (Pg C) to suppression of emissions by 1, 2, and 4 wedges (dashed lines) versus nutrient depletion. The fixed atmosphere simulations are summarized in table 4.1c and indicated in the figure by the colored solid lines.



nutrients during the three summers accounted for 60% of the carbon uptake resulting from the equivalent yearlong depletions and had a similar impact as the (unrealistic) wintertime nutrient depletion experiments. In this model, summertime waters depleted in nutrients still provide a significant fraction of the waters ventilating the deep ocean. Depleting nutrients in the summer results in a smaller increase in Southern Ocean production and a smaller decrease in production north of 30°S compared to winter depletions. Thus, when measured relative to local changes in biological productivity, summer depletion is more effective in reducing atmospheric p_{CO_2} than winter depletion, i.e., it has a higher physical-chemical efficiency ($e_{phys\text{-}chem}$ of Equation (4.4), but defined relative to increased productivity south of 30°S rather than over the whole world table 4.2).

While nutrient depletion simulations provide an upper limit for how much carbon can be drawn out of the atmosphere by the biological pump, they do not directly simulate the impact of iron fertilization *per se*. Ocean biogeochemistry models with an explicit iron cycle as well as an ecosystem component that can simulate a wide range of processes such as light limitation have been in existence for several years now (e.g., Moore et al. 2002b; Aumont et al. 2003; Dutkiewicz et al. 2005; Tagliabue and Arrigo 2006). The representation of iron limitation and impact of its removal on carbon cycling varies substantially amongst these models.

The simplest representation is that of Zahariev et al. (2008) in whose model plankton growth is the *minimum* of light limited growth, nitrogen limitation, and a temporally constant iron limitation factor (iron cycling is not prognostically handled in this model) that is very low in the Southern Ocean, high in the subtropical gyres and at intermediate levels in the Equatorial Pacific and North Pacific. Iron limitation thus acts only when there is sufficient light and macronutrient; otherwise it has no impact on phytoplankton growth. Iron "fertilization" then consists of removing this limitation term but leaving the light limitation unchanged. Zahariev et al. (2008) find a maximum uptake of 1 Pg Cyr^{-1} from this perturbation, with 26 Pg C taken up over 100 yr, approximately one-fourth that of the nutrient depletion results in table 4.1a. Over thousands of years, they do find an uptake of 77 Pg C, a value significantly smaller than that needed to explain glacial-interglacial CO_2 variations. As noted by Marinov et al. (2008b) and Gnanadesikan and Marinov (2008), the increased biological storage of carbon is not necessarily associated with increased biological productivity. Zahariev et al. (2008) see a ~30% decrease in global primary productivity and export under global iron fertilization as more productivity is concentrated in the Southern Ocean.

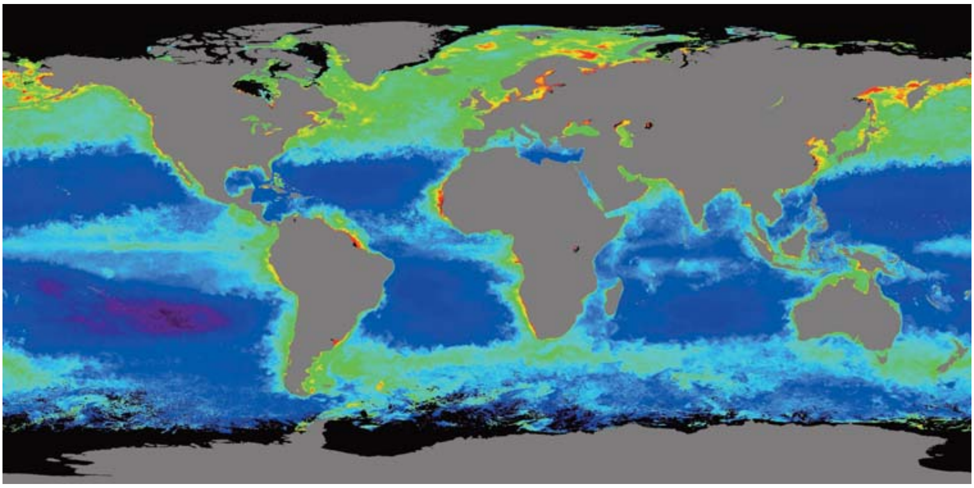
Other relatively simple, yet prognostic, treatments of iron fertilization are those of Parekh et al. (2006) and Dutkiewicz et al. (2006) who simulate an iron cycle in the ocean but have a very simple treatment of how it affects nutrient uptake. In this model, the rate at which nutrients are taken up is the *product* of three limitation terms, one due to iron, a second due to the macronutrient phosphate and a third due to light. In this model, adding iron to the ocean removes carbon primarily in the tropics where light is high. The Southern Ocean is relatively insensitive to the addition of iron and an approximately fivefold higher dust delivery rate typical of the Last Glacial Maximum produces an atmospheric carbon dioxide drawdown of only ~8 ppmv. Making the ocean more iron limited does have a big impact on atmospheric carbon dioxide, however, as iron limitation can then shut down tropical production. Thus a fivefold decrease in iron delivery in this model results in an increase in atmospheric carbon of 181 ppm (map 4.3).

There are also a number of more comprehensive ocean biogeochemical models in which the iron cycle as well as its impact on phytoplankton physiology are directly represented (e.g., Moore et al. 2002b; Aumont et al. 2003; Dutkiewicz et al. 2005; Tagliabue and Arrigo 2006; Dunne et al. in prep.). In all of these codes, iron is allowed to affect the growth rates of individual groups of phytoplankton which then affect the cycles of phosphorus, nitrogen, oxygen and iron as the organic matter they produce is grazed and exported to depth. The representation of how iron limitation affects phytoplankton growth differs significantly across the models.

In Moore et al.'s (2002a) NCAR model and Aumont et al.'s (2003) PISCES model, iron limitation reduces the inherent growth rates of plankton through a Leibig-like "law of the minimum" in which iron only limits growth when it is the most limiting nutrient. Thus in regions where either phosphate or nitrate is limiting but iron is abundant, adding more iron will have little effect, though in the HNLC regions it will be important. Aumont and Bopp (2006) showed that their PISCES model was able to credibly simulate the increase in chlorophyll, diatom biomass and drawdown in surface p_{CO_2} found at a number of field studies. When large-scale iron fertilization was applied in this model, an atmospheric drawdown of 33 ppmv (70 Gt C) was found over a period of 100 years. In comparison to the model of Dutkiewicz et al. (2006), PISCES is much more sensitive to changes in iron supply in the Southern Ocean even though a large-scale fertilization does not deplete Southern Ocean nutrients completely.

In Dunne et al.'s TOPAZ model (in prep. and in appendix in Sarmiento et al. 2009), iron limitation also affects the growth rate of phytoplankton, but additionally reduces the ability of plankton to synthesize chlorophyll. This means that even in regions where iron is not the most limiting nutrient, adding iron can increase phytoplankton growth rates as it relieves light limitation. Thus while in the PISCES model adding iron makes plankton more light-limited, in the TOPAZ model increasing chlorophyll synthesis compensates this effect. Sarmiento et al. (2009) demonstrate that the TOPAZ model is also able to simulate the changes in chlorophyll found in a number of field experiments. Iron fertilization was simulated in this model by removing the effects of iron limitation from phytoplankton growth terms. The resulting drawdown from large-scale fertilization (shown in table 4.1b, page 76) is about 80% of the nu-

Map 4.3: Chlorophyll levels. Observation of global chlorophyll patterns shows where ocean surface plants phytoplankton are growing, and gives an indication of where marine ecosystems are thriving. Maps like this give an idea of how much carbon the plants are soaking up, which is important in understanding the global carbon budget.



trient depletion runs after 50 and 100 years, somewhat larger than Aumont and Bopp (2006), consistent with iron having a somewhat larger impact in high-latitude regions. Most of this difference is attributable to the Southern Ocean. As compared with the nutrient depletion simulations, the tropics show a higher impact from fertilization than do the nutrient depletion simulations, while the North Atlantic shows an order of magnitude lower impact.

In understanding the TOPAZ model results, a number of subtleties need to be taken into account. The first is that the response of the carbon cycle to changes in iron fertilization will depend on the initial state of the ocean biogeochemistry and carbon cycle model. The nutrient depletion results in table 4.1a have as a control a model in which surface nutrients are forced towards their observed concentrations. By contrast, the TOPAZ model used for the simulations shown in tables 4.1b and 4.1c predicts overly high nutrients in the tropics and overly low nutrients in the North Atlantic. As such, the predicted responses to nutrient removal in these two regions shown in tables 4.1b and 4.1c (page 76) are correspondingly distorted. Tables 4.1a and 4.1b would be very close to each other if the control simulations in the prognostic model were more realistic, but in fact the North Atlantic CO_2 response in table 4.1b is $1/10^{th}$ that in table 4.1a, and the tropical result is about twice as large. Since this is due to a poor baseline simulation in the TOPAZ model we discount these particular results.

The second subtlety is the impact of source and sink changes on the atmospheric CO_2 reservoir. Suppose that we remove a wedge of carbon from the atmosphere, i.e., 25 Pg C over a 50-year period. One might think that this would result in 25 Pg C less CO_2 in the atmosphere than otherwise would have been there at the end of the 50 year period (which, divided by the 2.13 Pg C per ppm conversion factor, is equivalent to 11.8 ppm). However, this assumption would be incorrect because the reduced growth rate of atmospheric CO_2 resulting from the CO_2 removed from the atmosphere would lead to less CO_2 uptake by the ocean (the land may do the same but is much more complicated and beyond the scope of this paper). As a result, the actual reduction in atmospheric CO_2 resulting from the removal of CO_2 into the ocean would be less than 25 Pg C (cf. Gnanadesikan et al. 2003; Oschlies 2009; Sarmiento et al. 2009).

The importance of the back flux of carbon to the atmosphere is illustrated in table 4.1. Tables 4.1a and 4.1b show how much CO_2 is removed from the atmosphere in an iron fertilization simulation with an interactive atmosphere, where a removal of CO_2 from the atmosphere leads to a reduction of atmospheric CO_2 and thus a degassing of CO_2 from the ocean. By contrast, table 4.1c shows what happens when this effect is ignored by keeping the atmospheric CO_2 fixed (which, by the way, does not conserve carbon). Comparison of tables 4.1b and 4.1c, which are runs done with the same ocean model, shows that after 50 years the simulation with an interactive atmosphere has only 55% to 60% of the CO_2 removal than the fixed atmosphere simulation does. Which number should we use to analyze the impact of iron fertilization? If we want to compare the iron fertilization with the wedges, which refer to a change in the source of CO_2 to the atmosphere, not to a change in atmospheric CO_2 content, we should use the fixed atmosphere results in table 4.1c; and if we want to know the reduction in the atmospheric CO_2 growth rate that would result from a given fertilization scenario, we should use the results in tables 4.1a and 4.1b.

Finally, we note the important role of oceanic circulation and mixing in determining how much carbon dioxide is removed from the atmosphere in a large scale fertilization simulation. In Marinov et al. (2008b) we proposed that modelers measure the sensitivity of atmospheric carbon dioxide to iron fertilization (or, more broadly, to any change in the biological pump) relative to the total remineralized carbon inventory of the ocean. Equations (4.1) and (4.2) imply that this sensitivity will decrease with the remineralized carbon inventory (OCS_{soft}) and PO_{4remin}, and it will increase with the preformed nutrient inventory:

$$Sensitivity = -\frac{\Delta p_{\mathrm{CO}_{2a}}}{\Delta OCS_{soft}} \approx \frac{c}{a_1} \cdot e^{-\frac{OCS_{soft}}{a_1}} + \cdots \approx \frac{c}{a_1} \cdot e^{-\frac{r_{\mathrm{C:P}} \cdot \left(\overline{PO_4} - \overline{PO_{4pref}}\right) V_{oc}}{a_1}} + \cdot \qquad (4.5)$$

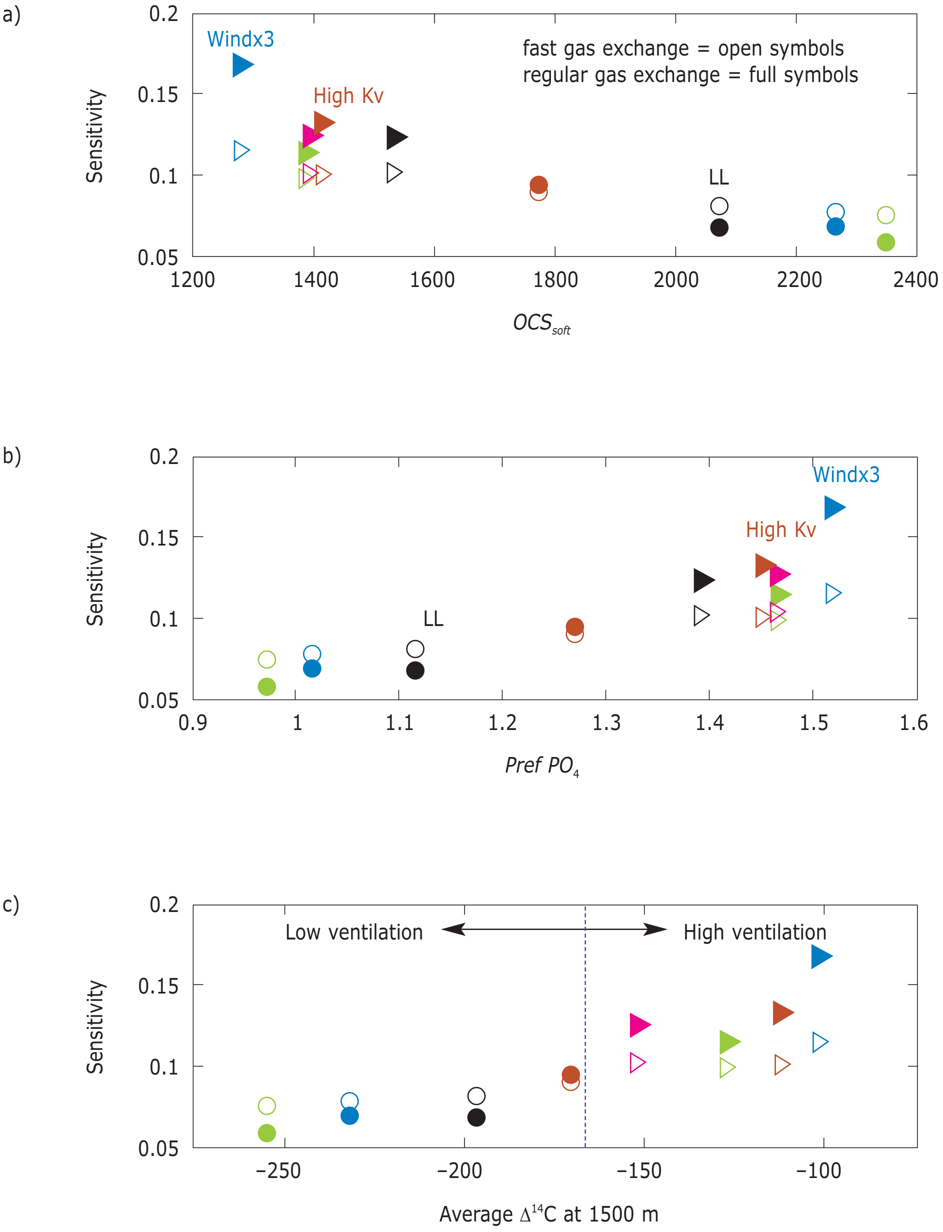
where Δ stands for the respective changes with fertilization. The sensitivity to prolonged (century to thousand year time scale) large scale nutrient depletion in a suite of ocean only General Circulation Models (GCMs) with different oceanic circulations is shown in figure 4.6. Models with high vertical diffusivity or high Southern Ocean winds have higher deep ocean ventilation as indicated by their Δ^{14}C, resulting in more nutrients in the preformed form (see Section 4.1) and a lower remineralized carbon storage OCS_{soft}. Models with initially weak total carbon storage such as the high ventilation models have more room to increase their carbon storage and therefore respond more to decreases in surface nutrients. In fact, high ventilation models will be more sensitive to any kind of changes in the biological pump than lower ventilation models. Slow CO$_2$ exchange at the air-sea interface significantly enhances the sensitivity difference between low ventilation and high ventilation models (figure 4.6) and makes the high ventilation models significantly more efficient at drawing down atmospheric carbon. This theoretical analysis has implications for the future climate. If Southern Ocean circulation were to intensify with climate change following an increase or poleward shift in Southern Ocean westerlies, atmospheric p_{CO_2} might become ever more sensitive to changes in Southern Ocean surface nutrients such as those induced by iron fertilization.

4.4. IMPLICATIONS FOR CARBON MITIGATION

Studies of the issue of iron fertilization for carbon mitigation have centered primarily on determining: 1) the *efficiency* of the fertilization; 2) the *verifiability* of CO$_2$ removal from the atmosphere; and 3) the long term *environmental consequences* of the fertilization (cf. Chisholm et al. 2001; and Buesseler et al. 2008). This paper has focused thus far on the underlying scientific issues regarding the connection of iron, the marine biosphere and the air-sea balance of carbon dioxide. In this section we present a brief discussion of the issues of verifiability and environmental consequences.

Verifiability of carbon uptake is a particularly difficult challenge for fertilization efforts. As has repeatedly been emphasized in this paper, marine biota modulates the air-sea balance of carbon by associating carbon with nutrients. But determining changes in the preformed and remineralized nutrient pools in the

Figure 4.6: Sensitivity of atmospheric p_{CO_2} to Southern Ocean nutrient depletion plotted against: a) Ocean carbon storage $OCS_{soft} = r_{C:P} \cdot (\overline{PO_4} - \overline{PO_{4pref}})$ before depletion (i.e., in the control simulation). **b)** Globally averaged preformed PO_4 before depletion. **c)** Globally averaged $\Delta^{14}C$ at 1500 m depth. Sensitivity defined as $-\Delta p_{CO_{2atm}}/\Delta OCS_{soft}$. Fast gas exchange (open symbols) and regular gas exchange (filled symbols) simulations shown for eight different ocean only GCMs. High ventilation models (triangles) have higher sensitivity than lower ventilation models (circles). Regular gas exchange enhances this effect. The vertical line in panel (c) shows the observed $\Delta^{14}C$ at 1500 m from GLODAP.



Source: Marinov et al. 2008b.

ocean is not straightforward, particularly in the presence of changing circulation and global-warming dependent changes in oxygen. As seen by Marinov et al. (2008b), Zahariev et al. (2008), and Gnanadesikan and Marinov (2008), simply measuring the export of carbon to the abyss is insufficient-more storage of carbon dioxide in the ocean may be associated with less export. The problem becomes even more fraught for large scale patch fertilizations proposed by commercial ventures. As noted by Gnanadesikan et al. (2003), the changes in air-sea carbon flux associated with such activities have spatial scales of thousands of km and temporal scales of months. The fluxes associated with the net uptake represent a small fraction of the background carbon cycle. Additionally, both Gnanadesikan et al. (2003) and Sarmiento et al. (2009) show that the net uptake of carbon by the ocean from a transient iron fertilization depends sensitively on the cycling of iron and carbon within the water column. If iron is rapidly lost, the carbon initially taken up by iron fertilization outgases over long times and large spatial scales. Finally, as noted above, oxygen changes associated with fertilization can lead to denitrification- reducing remineralized nutrients leading to a carbon flux back to the atmosphere.

The potential environmental consequences of extensive iron fertilization alone are sufficient to give pause to anyone seriously considering this as an option for CO_2 removal, as discussed by Chisholm et al. (2001), Jin and Gruber (2003), Schiermeier (2003), Shepherd (2009), and Strong et al. (2009) among others. Potential side effects of ocean iron fertilization include: 1) changes in global patterns of nutrients and ocean productivity, 2) oxygen depletion and changes in the extent and frequency of hypoxia, 3) increased emissions of nitrous oxide and methane, both potent greenhouse gases, 4) alteration of ocean ecology and resulting changes in DMS. Below we briefly discuss each of these.

1) Iron fertilization will reduce the supply of nutrients to surface waters downstream of the fertilized region. Reduction in the macronutrients returning to the ocean surface decreases primary production on the multi-decadal to century timescale, as indicated by model projections of large-scale fertilization in Gnanadesikan et al. (2003), Aumont and Bopp (2006), and Zahariev et al. (2008). A particular striking result follows long-term iron fertilization of the Southern Ocean and is summarized in figure 4.4 from Marinov et al. (2006). Up to two thirds of the low latitude production is fueled by preformed nutrients from the Southern Ocean surface, carried here by the Mode and Intermediate Waters (Sarmiento et al. 2004). Southern Ocean fertilization north of

the biogeochemical divide (i.e., in the Subantarctic region) consumes these preformed nutrients locally and therefore decreases nutrient availability and export production in low latitudes. By contrast, nutrient fertilization performed south of the biogeochemical divide (i.e., in the Antarctic region close to the Antarctic continent) will have minimal impacts on productivity in the rest of the ocean. Because of its large impact on atmospheric CO_2 and relatively small impact on global biological productivity, the area south of the biogeochemical divide emerges as the best candidate for potential Fe fertilization experiments.

2) Iron fertilization will not only increase export production locally at the ocean surface but also increase remineralization and thus oxygen consumption in the ocean interior. Models predict that prolonged fertilization will result in reduced deep ocean oxygen concentrations (e.g., Sarmiento and Orr 1991).

3) Nitrification (the oxidation of ammonium to nitrate with N_2O as an intermediate product) is the main source of nitrous oxide (N_2O) in the open ocean. At low oxygen concentrations, the ecology shifts toward microbes that produce methane and nitrous oxide (N_2O) through nitrification. Most of this newly produced N_2O eventually reaches the surface and is vented to the atmosphere, where it is a much more powerful greenhouse gas than CO_2. Mesoscale iron addition experiments have shown negligible to minor increases in N_2O production, whereas models of long-term ocean iron fertilization suggest significant N_2O production (Law 2008). The degree to which the resulting N_2O emissions might offset the radiative benefit from the CO_2 reduction depends on the location and duration and areal extent of fertilization (Jin et al. 2008) as well as the rate of vertical particle export.

   Rapid sinking of particles would limit N_2O production in the upper water column and maximize the time period before it is vented to the atmosphere (Law 2008). Because of this, Jin and Gruber (2003) find the largest N_2O fluxes to the atmosphere when fertilization, particularly of limited duration and size, is undertaken in the tropics. Smaller but significant offsets are found with Southern Ocean fertilization.

4) Iron fertilization alters the species composition of phytoplankton. An initial increase in small phytoplankton abundance is followed by a shift to increased diatom biomass (Marchetti et al. 2006), with consequences for

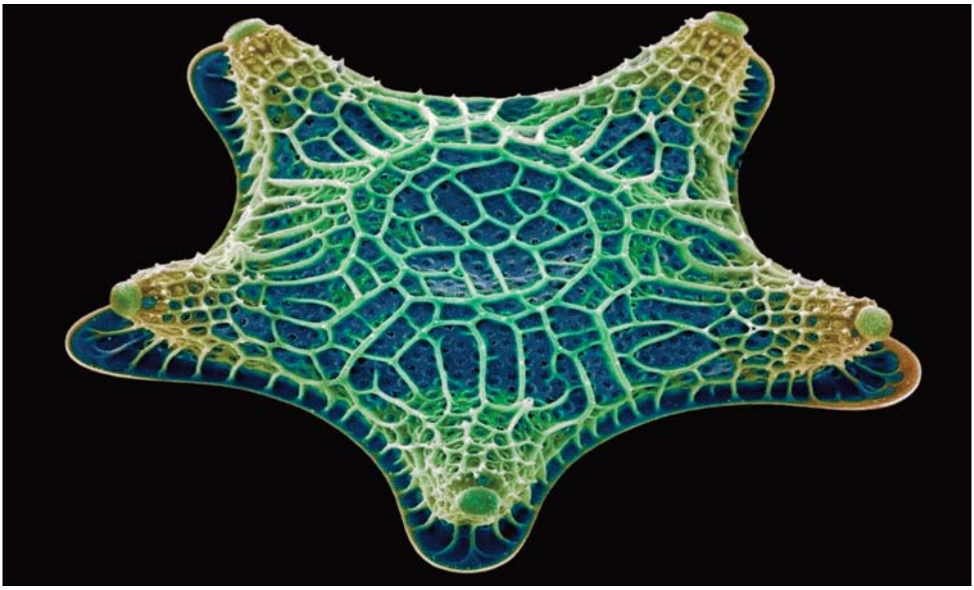


Photo 4.3: Diatom, a planktonic marine unicellular alga. Colored scanning electron micrograph (SEM) of a *Triceratium* sp. diatom.

zooplankton distribution and greater drawdown of silicic acid relative to nitrate (Boyd et al. 2004) (photo 4.3). Iron fertilization experiments can also stimulate small phytoplankton producing dimethylsulfide (DMS), the largest natural source to the atmospheric sulfur budget and a stimulus for the formation of cloud condensation nuclei. Increased input of sulfur to the atmosphere could potentially increase the earth's albedo, enhancing the climate-mitigation effects of iron fertilization. However, mesoscale experiments suggest a complex story, with the resulting DMS signal dependent on the location of the fertilized area (Law 2008). In mesoscale experiments, iron depleted Southern Ocean waters represented a significant DMS source to the atmosphere (Boyd 2007) while iron depleted Subarctic Pacific waters were either a sink or showed no significant change in DMS (Levasseur et al. 2006).

4.5. CONCLUSIONS

We have seen that the marine biosphere exerts an important control on the air-sea balance of carbon dioxide via the biological carbon pump. This balance is particularly sensitive to both physical and biological changes in the regions that ventilate the ocean's deepest waters, particularly the Southern Ocean south of the polar front. These regions are particularly important because nutrients are not used up in surface waters, thus allowing carbon taken up with nutrients elsewhere in the ocean to escape to the atmosphere and injecting preformed nutrients into the deep ocean.

On glacial-interglacial time scales, changes in the ocean biological carbon pump remain a possibility for explaining changes in atmospheric carbon dioxide. The extent to which such changes are driven by changes in upwelling, changes in iron fertilization, or both remains unclear. As we have shown here, some realistic models of ocean biogeochemistry, including the carbon cycle, show that relieving iron limitation in the Southern Ocean is capable of removing significant amounts of carbon dioxide from the surface ocean over centennial time scales, while others do not. This uncertainty highlights the importance of better characterizing the ocean iron cycle as well as understanding how iron affects plankton in realistic environments.

As we have discussed, however, iron is not the only means by which the biological carbon pump may change. A recent paper by Anderson et al. (2009) notes that increases in atmospheric carbon dioxide during the last deglaciation coincide with increases in opal burial in the deep ocean. This correlation is used to argue that a change in the ventilation of the deep ocean drives the repartitioning of carbon dioxide, rather than changes in iron supply. It should be noted that changes in circulation and iron fertilization should not be considered in isolation. Parekh et al. (2005) found that a reduction in the upwelling of deep, iron poor water in the Southern Ocean could enhance the sensitivity of the ocean to iron fertilization by making it easier to draw down surface nutrients. Their work highlights the importance of understanding nutrient and carbon cycling in the regions that ventilate the deep ocean as well as how the fluxes of such source waters may have changed over time.

Finally, we have examined potential impacts of attempts to manipulate marine biota so as to mitigate emissions of greenhouse gases by accelerating the uptake of carbon by the ocean. While our studies indicate that significant amounts of carbon could be sequestered through such methods, this can only be done by fertilizing vast regions of the Southern Ocean. We note that such large-scale sequestration would involve massive changes in oceanic ecosystems, particularly in the Southern Ocean, that verifying the resulting uptake of carbon would be difficult, and that there are significant possibilities for negative consequences.

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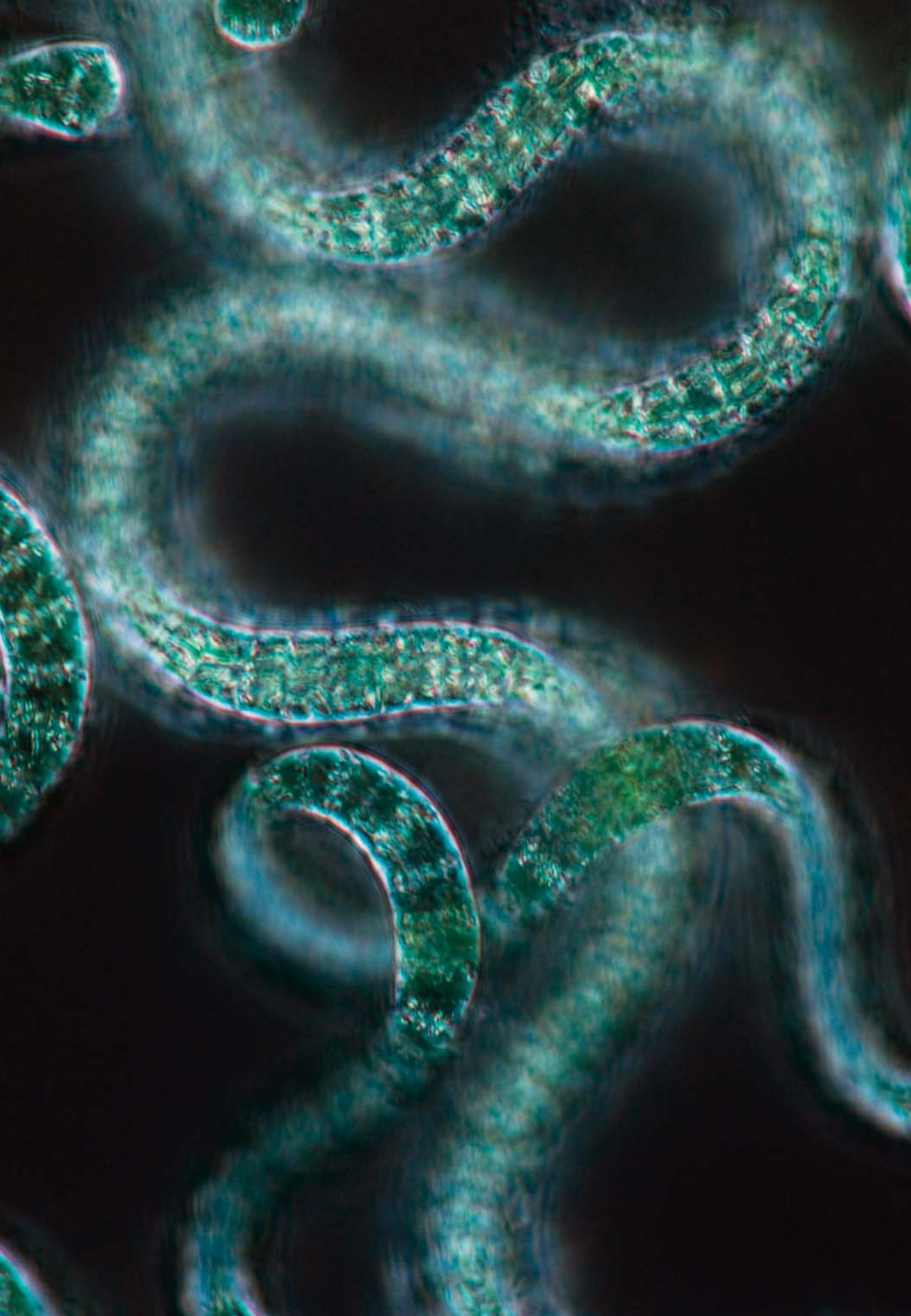

CHAPTER 5

THE ROLE OF MARINE MICROBIOTA IN SHORT-TERM CLIMATE REGULATION

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MARINE LIFE, AND PARTICULARLY MICROSCOPIC PLANKTON, influence climate over long and short time scales. In the long term they do this by shaping the biogeochemical cycles of elements (such as C, O, N, P, Si, S, Fe) essential for Earth-system functioning. In the short term they do it by exchanging climate-active gases with the atmosphere. Here we focuse on the short term effects. Oceans influence heat retention in the atmosphere by the exchange of greenhouse gases, regulate atmospheric photochemistry through the emission of oxidant scavengers and radical precursors, and influence the energy budget of the atmosphere (and, by extension, of the planet) through the emission of primary aerosols and secondary aerosol and cloud precursors. For example, the oceans represent the largest natural source of tropospheric sulfur, with associated significant consequences for planetary albedo, and they compete with continents as emittors of primary aerosols in the form of sea-salt crystals, organic polymers, and microorganisms. Ongoing international initiatives for global data integration, together with the invaluable information registered by remote sensing from satellites, are revealing that marine microbiota do not

◂ **Photo 5.1: Spirulina cyanobacteria. Each filament is a colony of bacterial cells.** Light micrograph of *Spirulina platensis,* photosynthesising bacteria that are found in most habitats where water is present.

Photo 5.2: The *Blue Marble.* Photograph of the Earth as seen from the *Apollo 17* on December 7th, 1972. This is the original image, with Antarctica at the top. It was rotated 180º before it was distributed.

Source: NASA.

only influence the properties and behavior of their host oceans but also leave their footprint in the ocean's sky. A further evidence of the complex and fascinating architecture of our living planet.

5.1. EARTH ALBEDO AND CLIMATE

5.1.1. On the way towards a walk on the Moon

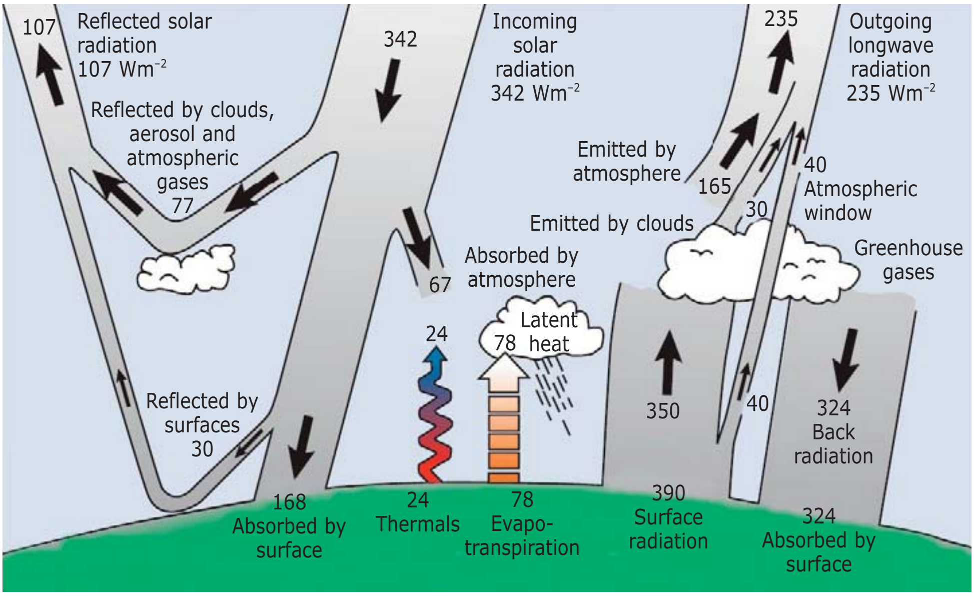
December 7th, 1972, 10:39 UTC. The *Apollo 17* had just left orbit around the Earth to begin its trajectory to the Moon, in what would be the last manned lunar mission. The crew looked at the Earth 29,000 km below and shot the *Blue Marble*, one of the most famous and widely distributed photographs of the past century (photo 5.2). The Earth appeared fully illuminated because the Sun was right behind them and the winter solstice was approaching. It looked like it was made of a bluish glass, dotted with the white and brownish textures of the clouds and the continents. To the last astronauts to walk on the Moon, their home planet was a tiny marble in the middle of the Universe.

5.1.2. Earth textures and albedo

The issue of the textures of the Earth is highly relevant to climate science. The color, brightness and microstructure of the Earth surface, just like those of any body's surface, determine its albedo (i.e., the fraction of short-wave solar irradiance that is reflected back to space) and play a prominent role in the global energy balance. And it is this energy balance that ultimately drives the average climate of the planet (figure 5.1). Of the mean 342 W m^{-2} of incoming solar radiation, as much as 107 W m^{-2} is reflected back, with the remaining 235 W m^{-2} being absorbed by the atmosphere and the surface (including the biosphere) and eventually dissipated as heat and radiated out to space in the form of longwave radiation. Tiny imbalances in this tight budget (e.g., by changes in the atmospheric chemical composition) produce global warming or cooling.

Should the *Blue Marble* have been of a glassy uniform dark blue, like that of an ocean flooded planet, the energy budget would have been very different from that sketched in figure 5.1 simply because of its color. Everyone knows that wearing dark clothes or driving dark cars in hot summers are bad choices be-

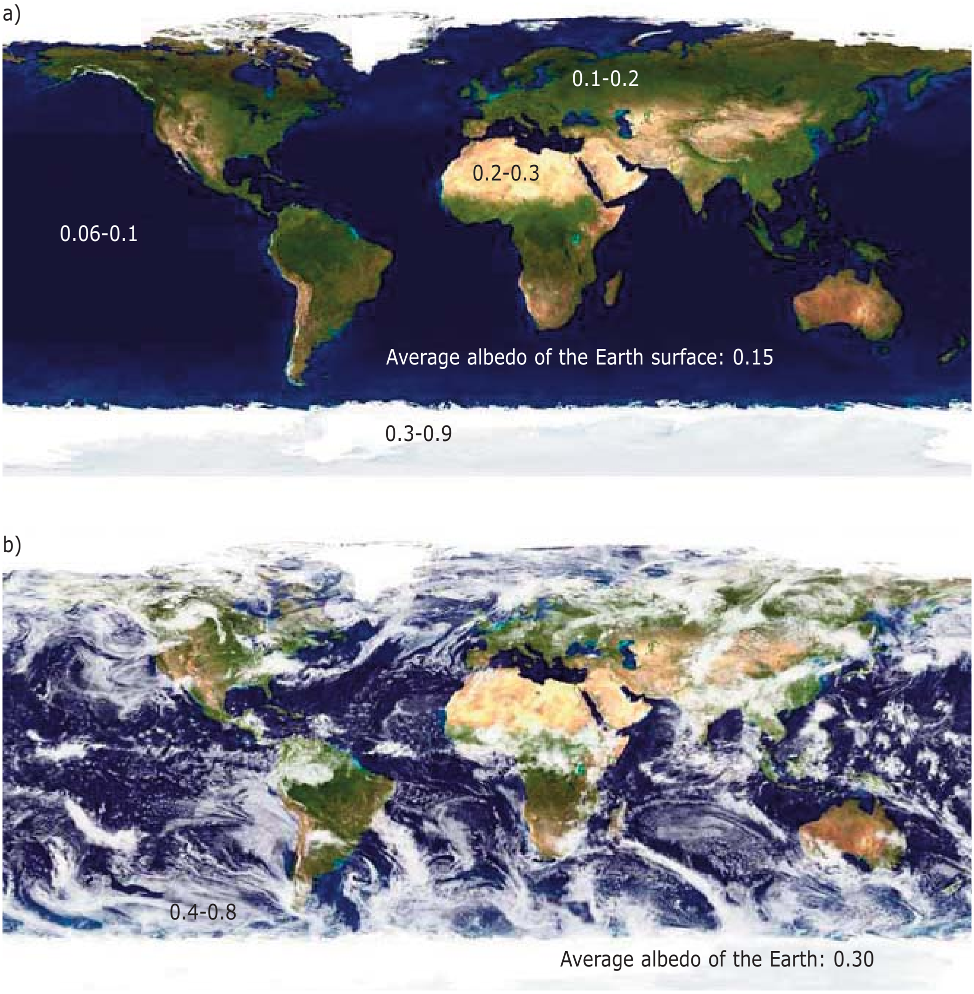
Figure 5.1: The energy balance of the Earth. Incoming solar radiation that is not reflected back to space by the atmosphere and the Earth surface cycles through the components of the Earth system and eventually radiates out to space in the form of longwave (thermal) radiation.



Source: Adapted from Le Treut et al. (2007).

cause they absorb a lot of solar radiation and dissipate it as further warmth; clear colors reflect more, absorb less, and are highly recommended to stay comfortably cool. Likewise, the dark ocean has an albedo of 0.06 to 0.1, it therefore absorbs more than 90% of the solar energy hitting its surface. An ocean planet with a transparent atmosphere would absorb a lot more energy, and who knows how it would be dissipated. But our Earth has continents with sandy and rocky surfaces, generous vegetation covers and seasonal or per-

Map 5.1: Earth albedo. Composite of visible images taken by MODIS from NASA's satellite *Terra.* **a)** The image has been manipulated to remove clouds. Numbers are the albedo values of oceans, sea and continental ice, vegetated land, deserts, and the average of the Earth's surface. **b)** True image of the cloudy Earth, with the albedo of clouds and the resulting planetary albedo, notably higher than that of the surface.



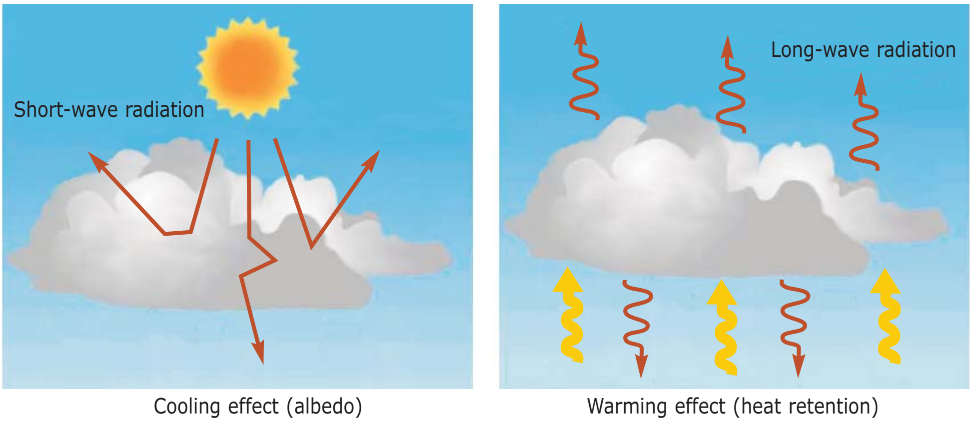
manent snow fields and ice caps (map 5.1a). Vegetated lands, including forests and crops, have albedos of 0.1-0.2, i.e., only slightly higher than that of the oceans. Exposed dry soils and sand deserts have albedos of 0.2-0.3. Only ice and snow covers have really high albedos (0.3-0.9) and reflect more sunlight than they absorb. On average, the albedo of the Earth surface is 0.15; in other words, it absorbs 85% of the solar radiation that traverses the atmosphere.

But the *Apollo 17* crew did not see the Earth as it is shown in map 5.1a. The real *Blue Marble* is a cloudy planet (photo 5.2), and its flat projection shows that ca. 60% of its surface is hidden under white clouds. Since clouds have albedos of 0.4-0.8, the actual average albedo of the Earth is 0.30, i.e., twice that of its surface (map 5.1b).

5.1.3. Clouds and solar radiation

Without clouds the Earth surface would receive far more energy from the Sun because clouds act as parasols. This sounds quite obvious, but, who has not heard weather forecasters say that cloudy nights are warmer nights? And clear winter skies bring freezing nights because heat is quickly lost upwards. So, do we regard clouds as actors playing contradictory roles: parasol clouds or greenhouse clouds? It is true that they play both roles. In general, clouds act as parasols during the day and as a greenhouse roof during the night (figure 5.2).

Figure 5.2: Role of clouds in the energy balance. *Left:* Clouds reflect part of the incoming shortwave solar radiation back to space. *Right:* Clouds retain part of the longwave (thermal) radiation coming from below, and radiate it up (out to space) and down (back to the surface).



Cooling effect (albedo)

Warming effect (heat retention)

Their net effect depends on the type of cloud (figure 5.3). High altitude cirrus clouds, mostly formed by ice crystals, are more efficient at retaining heat from below than at reflecting sunlight from above. They are ‘warming clouds’. Low altitude clouds, stratus and stratocumulus, are better at reflecting short-wave irradiance than at retaining long-wave radiation; hence, they are ‘cooling clouds’. Convective clouds like storm cumulus and cumulonimbus have a virtually neutral net effect. Altogether, clouds have a global radiative effect of net cooling, estimated at ca. -20 W m^{-2}.

The clouds that cover the largest surface of the Earth, and particularly the largest surface of dark ocean, are the low clouds, the marine stratus. Therefore, any factor having an influence on the formation and albedo of marine stratus plays a prominent role in the energy balance of the planet and, consequently, in global climate.

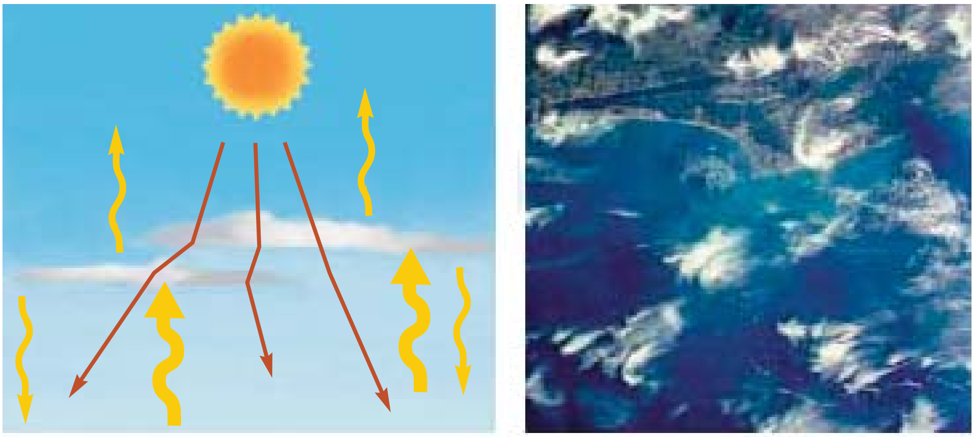
5.2. CLOUD FORMATION

For a cloud to form there must be water vapor in cooling air. This alone, however, would not be enough. Water droplets form only if there are microsurfaces for water molecules to collect and condense upon.

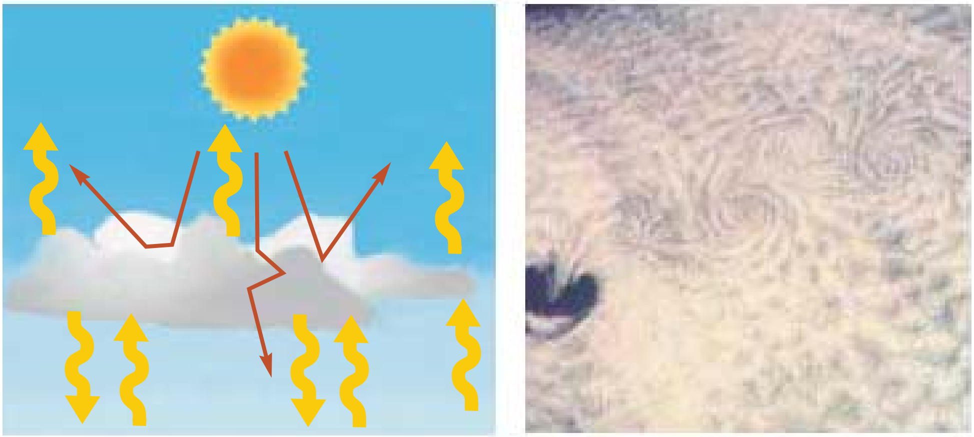
5.2.1. *Une nouvelle propriété de l’air*

In 1875, P.J. Coulier, a professor in a Paris hospital, conducted the first known laboratory experiments aimed at finding the ingredients for cloud formation (Spurny 2000). He poured a little warm water into a glass flask with an inlet and an outlet tube (figure 5.4). A rubber ball was connected to the outlet tube so that pressure changes could be applied inside the flask by hand, upon shutting off the inlet. On removing air, the pressure drop made the air remaining in the flask expand and cool rapidly. Because the air was saturated with vapor, water droplets condensed as the air cooled. These findings showed nothing really exciting simply that upon cooling, water vapor condensation formed a cloud. Nonetheless, Coulier observed that no cloud was formed if the air in the flask was too clean, e.g., if it was filtered to remove particles. Only *regular* air from the lab allowed for mist formation, and mist became dense fog if dirtier air was blown in. Coulier published an article in the *Journal de Pharmacie et de Chimie* entitled *Note sur une nouvelle propriété de l’air*. In it he stated: ‘Fine solid particles suspended in the air are necessary for the production of fogs’ (Coulier 1875).

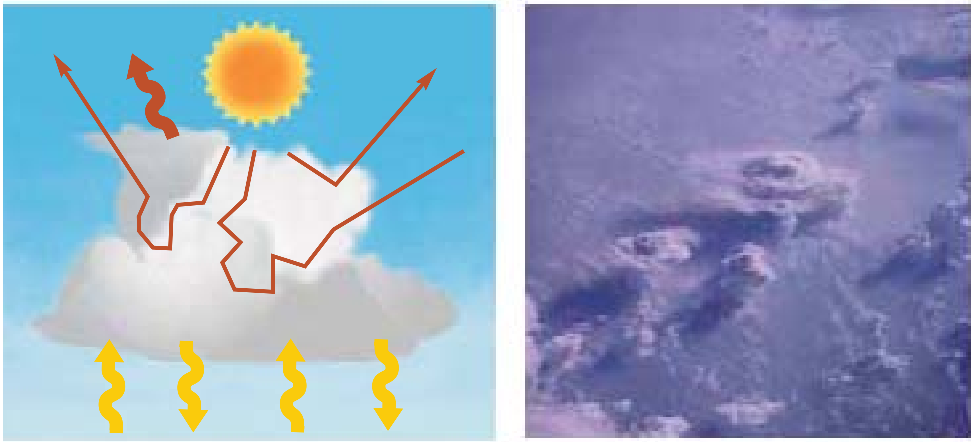
Figure 5.5: Radiative behavior of the different cloud types



High clouds (net heat retention)

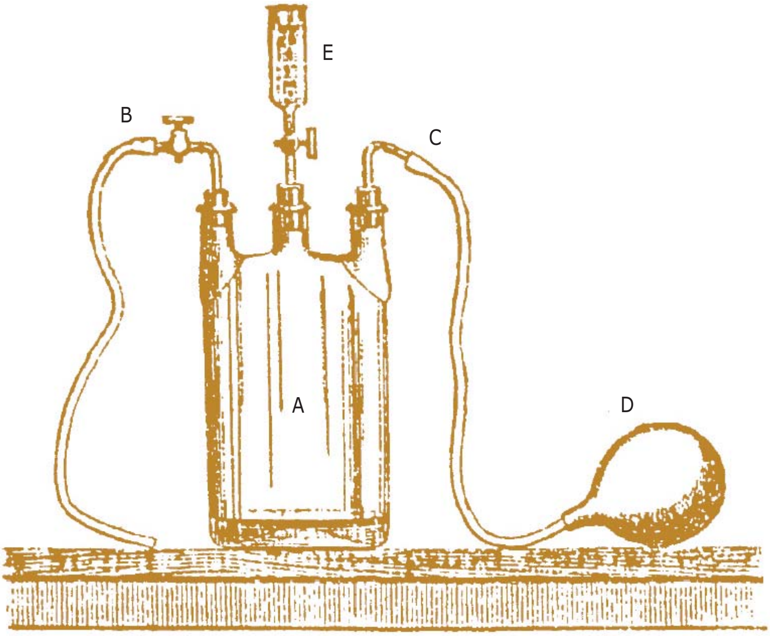


Low clouds (net cooling)



Convective clouds (neutral)

Figure 5.4: Original drawing of the apparatus used by P.J. Coulier to investigate the role of aerosol particles in water vapor condensation and cloud formation



A: glass flask; B: air inlet; C: outlet tube; D: rubber ball for lowering pressure; E: liquid water dispensor.

Source: Coulier 1875.

Unfortunately, Coulier's work was not met with much excitement in the meteorological community, who probably were not subscribers to the journal in which the article was published. Five years later the Scottish meteorologist J. Aitken performed a very similar, indeed practically identical, experiment. Aitken, who was not aware of Coulier's findings, published an article in *Nature* in 1880 where he reported the same conclusions as his ignored French colleague: 'Water vapor condenses in the atmosphere on some solid nuclei; dust particles in the air form these nuclei; if there were no dust, there would be no fogs, no clouds, no mists, and probably no rain.' (Aitken 1880). When Aitken chanced upon and read Coulier's papers on the subject, he recognized publicly that 'Monsieur Coulier was the first to show the important part played by dust in the cloudy condensation of the vapour in air' (Spurny 2000). Nevertheless, and because of his later research, Aitken is considered the discoverer of so-called *cloud condensation nuclei* (CCN) and the father of subsequent investigations into the relationship between aerosols and clouds.

5.3. AEROSOLS AND CLIMATE

5.3.1. Dust in the wind

What Coulier and Aitken called *dust* in the late XIXth century, today we call *aerosols*, which is the general term used to designate any tiny particle suspended in the air. Aerosols can be of a broad size range and have very different composition and optical properties depending on their origin, formation and transformation processes. Aerosols have occurred throughout the Earth's history, as many natural sources exist (Andreae 2007). Irrespective of their source, but in reference to their formation process, aerosols can be categorized into:

> *Primary aerosols*: Those born as particles in their very origin. These include soil dust raised by the wind, soot and ashes from wild fires, vegetal debris, or sea salt and microorganisms ejected by breaking waves.
>
> *Secondary aerosols*: Those born from the transformation of gases into particles through nucleation and coalescence. These include sulfate aerosols produced by oxidation of sulfur gases from volcanoes and living beings, or organic aerosols produced by oxidation of biogenic volatile organic compounds.

Needless to say, human activities represent a major aerosol source, particularly so after the Industrial Revolution. Deforestation, land mobilization, and changes in land use are resulting in the exposure of an increasing surface of soil to wind friction, with the subsequent increase in dust loads. But above all, it is through the use of combustion energy that humankind contributes the most to aerosol levels in the atmosphere. Incomplete combustion produces, along with CO_2 and water vapor, large quantities of pyrogenic black carbon (soot –primary aerosol), and sulfur dioxide plus carbon- and nitrogen-containing volatile organics (all precursors of secondary aerosol).

5.3.2. Aerosols and solar radiation

Aerosols are an important component of the air and, as such, contribute to the configuration of the functioning of the atmosphere as a chemical reactor, substance transporter, and major actor in setting the Earth's energy balance. Depending on their size and characteristics, aerosols are involved in processes as important as cloud formation, sulight absorption and the scattering, transport and deposition of essential elements, pollutants, allergens and disease vectors. Here I provide an overview of their main effects on climate (Penner et al. 2001; Forster et al. 2007).

Direct effect: That derived from the direct interactions between aerosols and solar or thermal radiation. Aerosols that have a low microalbedo absorb solar radiation and dissipate it as thermal radiation (heat), so that they contribute to tropospheric warming. This is the case of black carbon soot. Aerosols with a high microalbedo reflect and scatter solar radiation and contribute to cool the troposphere below. This is the case, for instance, with secondary aerosols produced from biogenic and anthropogenic sulfur emissions.

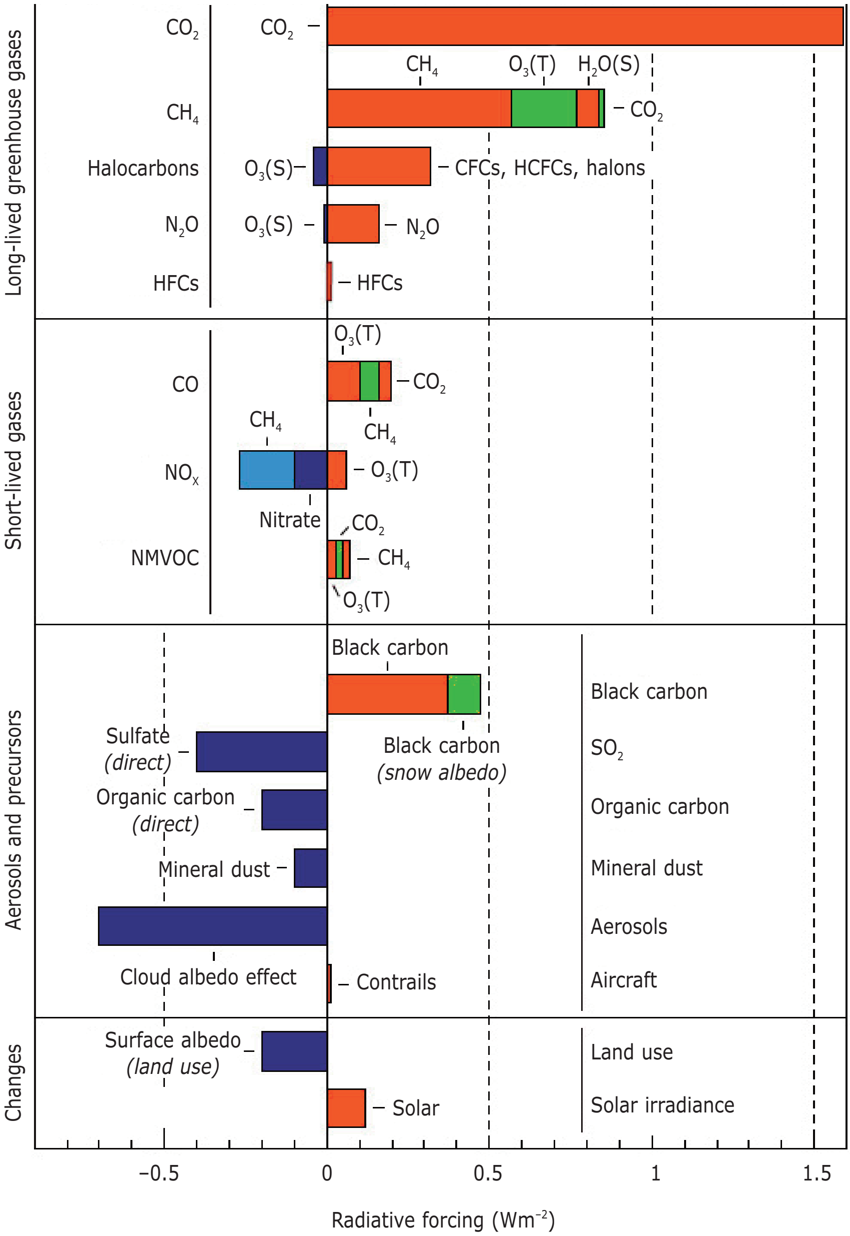
Overall, the direct radiative effect of aerosols is a net cooling estimated as –5.4 (±0.9) Wm^{-2}, and its radiative forcing since the industrial era is –0.5 (±0.4) Wm^{-2} (figure 5.5).

Indirect effects: Those derived from the influence of aerosols on the microphysical (and hence the radiative) properties, amount and lifetime of clouds.

First indirect / Cloud albedo / Twomey effect: As outlined above, aerosols play a key role in cloud formation. Aerosols in the proper size range (0.05-1 µm) and of hygroscopic nature are the most favorable for water vapor condensation into droplets. But the role of aerosols does not end with being a necessary ingredient. A cloud that condenses on few particles will be a cloud with few droplets; for a given liquid water content, fewer droplets means larger droplets. On the contrary, in the presence of high aerosol concentrations, a cloud will form with many droplets of smaller size. A cloud with more (smaller) droplets has a higher albedo than a cloud with fewer (larger) droplets (Twomey 1977). In other words, clouds 'polluted' by either anthropogenic or biogenic aerosols have higher albedos, i.e., act as better parasols.

Second indirect / Cloud lifetime / Albrecht effect: A cloud formed in the presence of high aerosol concentrations will be a longer-lived cloud because small droplets will take longer to reach their precipitable size. In other words, aerosols suppress drizzle and lengthen cloud's life as a parasol (Albrecht 2000).

Figure 5.5: Main components of the radiative forcing of climate change. The columns refer to the radiative forcing (in energy units, W m^{-2}) observed or estimated since the start of the indurstrial era (about 1750) until 2005. The forcings result from the changes caused by human activies during this period. Positive forcings lead to warming of climate and negative forcings lead to a cooling. The only increase in natural forcing of any significance occurred in solar irradiance (bottom column). Note the large cooling effects of aerosols and precursors. (S) and (T) next to gas species represent stratospheric and tropospheric changes, respectively. For uncertainties associated with the estimated values, see the original source (Forster et al. 2007).



Semi-indirect effect: The presence of shortwave radiation absorbing aerosols warms the air around them, which reduces the relative humidity and stability and burns off cloud formation. In other words, soot aerosols reduce cloudiness (Ackerman et al. 2000).

Taken altogether, the indirect radiative effects of aerosols are large but very difficult to quantify. Since the industrial era, the best estimate of their radiative forcing is ca. –0.7 W m^{-2}, with an estimated range from very low to –1.1 W m^{-2} (figure 5.5). As a matter of fact, the indirect aerosol effects are one of the largest sources of uncertainty in the observation and prediction of global warming.

5.4. OCEANIC BIOSPHERE, AEROSOLS AND CLIMATE

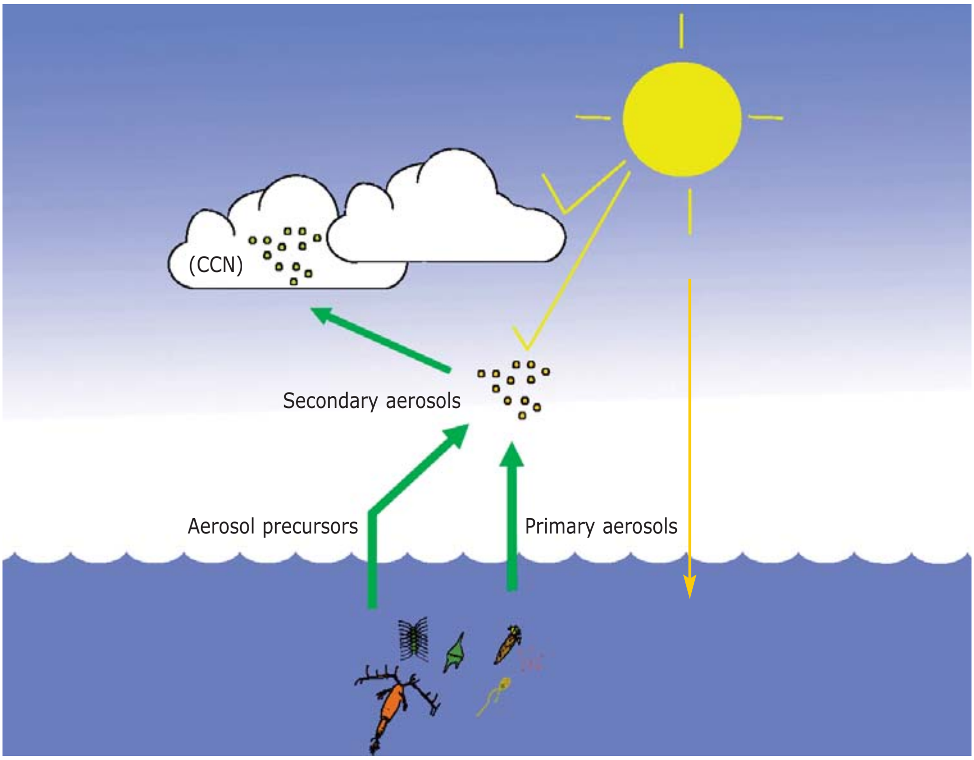
5.4.1. Marine aerosol sources

The oceans are a major aerosol source. Per unit area they are far weaker producers than the continents, where soils, vegetation and human activities represent a constant supply of airborne particles. But the oceans occupy about two thirds of the Earth surface and present little impediment to wind exposure. Marine aerosols can be either primary or secondary, and have either a biotic or an abiotic origin (figure 5.6).

Primary aerosols are produced by wind friction, bubble bursting and breaking waves releasing small seawater droplets into the air, known as sea spray (Andreae and Rosenfeld 2008). As droplets evaporate, the solid particles can coalesce and aggregate with others, absorb vapors, participate in gas-particle reactions, or serve as condensation nuclei. The main mass contributor to marine primary aerosol is sea salt. It occurs mostly in the supermicron aerosol fraction but it also makes a significant contribution to submicron particles and cloud condensation nuclei (Clarke et al. 2006). Other primary aerosols ejected by the oceans are formed by biogenic organic polymers (Leck and Bigg 2005) and microorganisms such as bacteria and viruses (Sun and Ariya 2005; Christner et al. 2008). This primary organic aerosol is very poorly characterized and its source function and mass fluxes are virtually unknown.

Secondary aerosols are generated by the oxidation and nucleation of precursor gases released by the oceans (Andreae and Rosenfeld 2008). The

Figure 5.6: The breath of the sea. The oceans, in addition to their exchange of CO_2, O_2 and water with the troposphere, emit a myriad of trace gases and particles (many of which are biogenic) that influence the chemical and optical properties of the atmosphere and act as cloud precursors.



principal known gases are dimethylsulfide (DMS, which upon oxidation gives rise to secondary sulfate aerosols, which are very efficient as cloud condensation nuclei, CCN, see below), iodomethanes, mainly produced in coastal waters (which give rise to iodine-condensable vapors and aerosols; O'Dowd et al. 2002), ammonia (which neutralizes sulfuric acid during aerosol formation and growth; Quinn et al. 1988), and a number of volatile organic compounds such as isoprene and monoterpenes (which oxidize to form organic aerosol, a main constituent of the total aerosol mass over productive waters; O'Dowd et al. 2004). The oxidation products of all these gases either nucleate to form new particles in the fine size fraction (the ones efficient as CCN) or condense on pre-existing particles and contribute to their growth and, if hygroscopic, to their activation as CCN. Actually, most remote marine aerosols examined by electron microscopy and chemical analyses are made up of mixtures of, at least, organic structures and ammonium sulfate (O'Dowd et al. 2004, Leck and Bigg 2005). As for primary organic aerosols, the source functions for most marine secondary aerosols are not well constrained. This is because, with the exception of DMS, little is known about the concentration patterns and seasonal dynamics of most organic, iodine and nitrogen gases in the surface ocean.

5.4.2. The breath of the sea

As outlined above, the oceans exchange many more gases with the atmosphere than just CO_2, O_2 and water vapor. Volatiles of all kinds are produced in seawater by biological processes and photochemical reactions. Many of them often occur at supersaturation concentrations in surface waters and, therefore, tend to escape to the atmosphere. Some, like those mentioned in the previous section, act as aerosol and cloud precursors. Some others get involved in atmospheric chemistry and contribute to regulating the oxidative capacity of the troposphere. Some others are transported to and deposited on the continents, thus serving to compensate for the continental losses of essential elements (such as sulfur and iodine) over geological time scales. And a few survive tropospheric chemistry and reach the stratosphere, where they form aerosols or participate in ozone destruction. Altogether, marine trace gases are important actors in global biogeochemistry as they play multiple and fundamental roles in Earth system functioning. Table 5.1 shows a compilation of marine trace gases, their role in the Earth system, an estimate of the oceanic emission flux and its contribution to emissions from all sources, an enumeration of the main non-marine sources, and some selected references for further reading (see p. 122-123).

5.4.3. The smell of the sea

Dimethylsulfide (DMS) is, by far, the best studied of all the trace gases of the ocean. Several reasons lie behind the remarkable interest it has aroused in the biogeochemical and oceanographic community:

a) It is the most abundant volatile sulfur compound in the surface ocean, to the extent that it alone accounts for > 90% of the oceanic emission of sulfur; in the case of other elements, the mass fluxes are spread among a number of relative compounds.

b) It occurs at nanomolar concentrations, while other trace gases occur at picomolar levels or even less.

c) A fascinating, holistic hypothesis has been constructed on the basis of this tiny molecule. The CLAW hypothesis (so-called after the initial of its authors) postulates that, if the release of DMS by oceanic plankton and it subsequent emission to the atmosphere affects the concentration of CCN, and these affect cloud albedo over the oceans, the resulting changes in solar irradiance at the surface ocean could feed back on plankton DMS production. This feedback, postulated to be negative, would contribute to stabilize global temperatures (Charlson et al. 1987). In other words, microscopic plankton would help regulate climate through their sulfur-mediated influence on cloud albedo (figure 5.7).

The CLAW hypothesis has stimulated an enormous research effort into the oceanic and atmospheric sulfur cycle over the last two decades. However, ultimate proof has eluded researchers. Facts (observations) tell us that DMS is a by-product of the tight cycling of an abundant, and physiologically and ecologically important organic sulfur compound, dimethylsulfoniopropionate, DMSP (Simó 2001). Facts also tell us that the oceanic DMS emission represents the main natural source of atmospheric sulfur, four times larger than volcanic emissions, but just 40% of the huge sulfur emissions made by mankind during the industrial era (table 5.2). With such a large emission, DMS makes up one of the components of the smell of the sea and seafood. This would not be relevant if we had not discovered that some marine birds can detect the smell of DMS and use it as a foraging cue (Nevitt et al. 2002). Nevertheless, the observations that DMS is produced abundantly by plankton in the surface ocean, that it is a major source of atmospheric sulfate, and that sulfate is a main component of the cloud condensation nuclei of stratus, is not sufficient to accept or rebut the CLAW hypothesis.

At the Institute of Marines Sciences, Barcelona (ICM-CSIC), and in collaboration with international colleagues, for the last 10 years we have been investigating the DMS cycle at local to global scales, its significance for the ecology of microbial plankton and for sulfur fluxes in the pelagic marine ecosystem, and its participation in atmospheric processes. By the use of molecular biology analyses, community-level experiments, ecosystem observations at sea, and analyses of satellite data and oceanographic climatologies, we have been

Table 5.1: The breath of the sea. Volatile compounds (other than CO_2 and O_2) produced in the surface ocean by biological and photochemical reactions, which are emitted into the atmosphere and affect its chemical properties and dynamics.

Compound	Main environmental role[a]	Oceanic emission		Other sources[c]	Token references
		Magnitude	contribution to total emision[b]		
CH_4	Greenhouse	0.6-15 Tg/yr	0.1-2%	Wetlands, livestock, rice fields, landfills, natural gas	Bates et al. 1996; Denman et al. 2007; Rhee et al. 2009
N_2O	Greenhouse	0.9-7 TgN/yr	4-20%	Soils, fertilizers, combustion	Nevison et al. 1995; Bange 2006; Rhee et al. 2009
Sulfur volatiles: Dimethylsulfide (DMS)	Global sulfur budget Aerosol precursor: atmospheric acidity and cloud nucleation	20-35 TgS/yr	90%	Soils, plants	Kettle and Andreae 2000; Simó and Dachs 2002
COS	Precursor of stratospheric aerosol	0.60 TgS/yr	20%	Soils, combustion	Kettle et al. 2002; Uher 2006; Sutharalingam et al. 2008
CS_2	COS precursor	0.15 TgS/yr	?	Soils, wetlands	Xie and Moore 1999; Kettle et al. 2002
Selenium volatiles (methyl selenides)	Global selenium budget	£35 GgSe/yr	50-75%	Soils, plants, wetlands	Amoroux et al. 2001
Halogenated volatiles: CH_3I, CH_2I_2	Global iodine budget, tropospheric photochemistry, coastal aerosol precursor, cloud nucleation	1 TgI/yr	>50%	Rice fields, combustion	Moore and Groszko 1999; O'Dowd et al. 2002

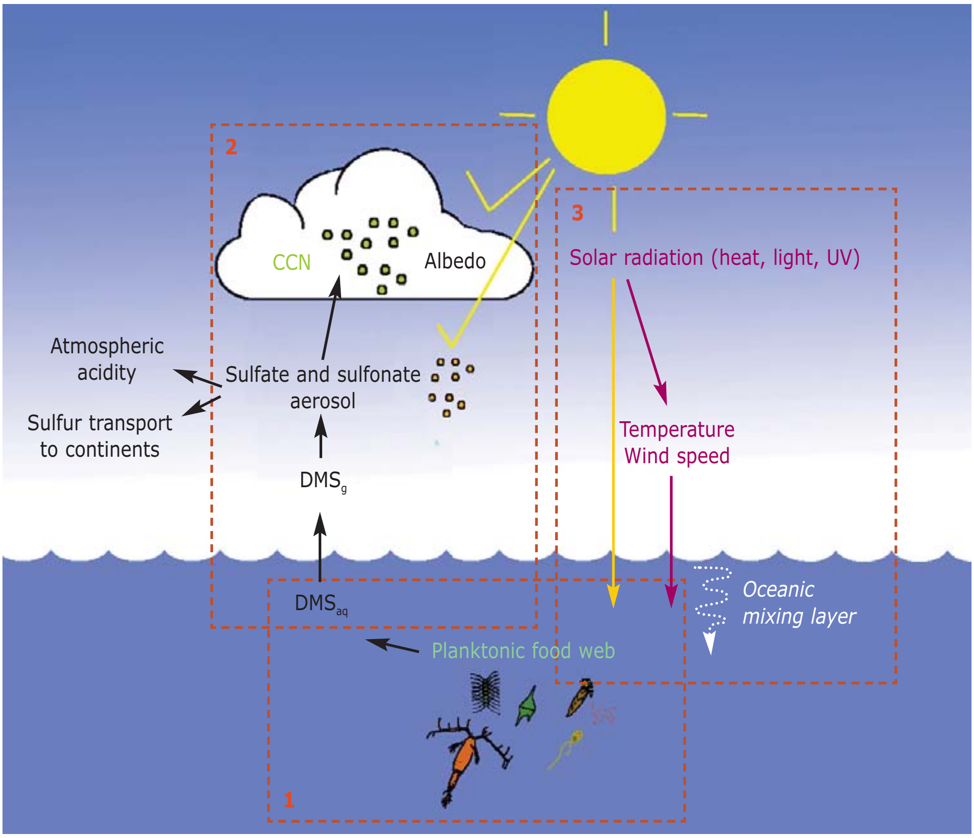
Table 5.1 *(cont.)*: The breath of the sea. Volatile compounds (other than CO_2 and O_2) produced in the surface ocean by biological and photochemical reactions, which are emitted into the atmosphere and affect its chemical properties and dynamics.

Compound	Main environmental role[a]	Oceanic emission		Other sources[c]	Token references
		Magnitude	contribution to total emision[b]		
CH_3Br	Stratospheric ozone destruction	20-46 GgBr/yr	10-40%	Agriculture, combustion, salt marshes	Lobert et al. 1995; Pilinis et al. 1996; Butler 2000; Yvon-Lewis et al. 2009
HCH_3Cl	Tropospheric photochemistry, acidity, stratospheric ozone destruction	0.1-0.3 TgCl/yr	10%	Combustion, industrial	Moore et al. 1996; Khalil and Rasmussen 1999; Butler 2000
Other halomethanes and haloethanes	Tropospheric photochemistry, acidity, stratospheric ozone destruction	?	?	Combustion	Moore et al. 1995; Butler 2000
NH_3 and methylamines (mono-, di-, tri-)	Aerosol acidity-alcalinity	?	?	Soils, wetlands, plants?	Quinn et al. 1988; Gibb et al. 1999; Jickells et al. 2003; Facchini et al. 2008
Alkyl nitrates	Tropospheric photochemistry	?	?	Combustion, poto-reactions	Chuck et al. 2002; Moore and Blough 2002
Volatile hydrocarbons (e.g., C2-C4, isoprene, monoterpenes)	Tropospheric photochemistry, aerosol precursors	2.1 TgC/yr	minor	Plants, combustion	Plass-Dülmer et al. 1995; Broadgate et al. 1997; Yassaa et al. 2008; Arnold et al. 2009; Gantt et al. 2009

In most cases a 'positive' net annual flux has been observed, but this does not mean that the surface ocean is always supersaturated in these traces everywhere. In some cases, such as COS or CH_3Br, throughout the year the oceans change their role as a source or a sink depending on the accumulation rates in the troposphere caused by variability in all sources. The list is intended to be comprehensive but not complete.

[a] Impact of the oceanic emission on the Earth System, mainly through atmospheric chemistry
[b] Estimated contribution of the oceans to the global emission from all sources (natural + anthropogenic)
[c] Main sources to the atmosphere, other than the ocean.

Figure 5.7: The ocean/atmosphere biogeochemical cycle of dimethylsulfide (DMS) and the plankton-climate feedback hypothesis. Plankton produce DMS that escapes tight cycling and vents to the atmosphere, where it is oxidized to sulfate aerosols that can serve as cloud condensation nuclei (CCN). Associated changes in cloud albedo and below-cloud irradiance would feed back to plankton activity, in what could constitute a mechanism by which plankton help regulate climate (Charlson et al. 1987). Numbers 1, 2, 3 (in red) refer to the three major steps in this hypothetical feedback gear, to which research contributions have recently been made at the ICM-CSIC (see text).



able to make contributions that have produced a significant advance towards deciphering the feasibility of the CLAW hypothesis. Here I will briefly outline these contributions, providing a few example references for each. The numbers refer to the boxes in the diagram in figure 5.7.

1) DMS is produced by interactions among microbial plankton components, and among plankton and solar radiation. Phytoplankton acclimation to higher doses of visible and UV radiation, plus the deleterious effects of UV on bacterial DMS consumers, seem to be behind the higher

DMS concentrations generally observed in summer (Simó and Pedrós-Alió 1999; Vallina et al. 2008; Vila-Costa et al. 2008).

2) DMS emission, and not sea salt emission, correlates with the numer of CCN in the atmosphere over most of the global remote oceans. Even though the largest mass fraction of CCN is probably contributed by sea salt, monthly variability seems to be driven by DMS emission and oxidation fluxes (Vallina et al. 2007a).

3) Over most of the global oceans and on the seasonal scale, surface DMS concentrations are proportional to the daily dose of solar radiation received by plankton in the surface mixing layer (Vallina and Simó 2007). This proportionality, when projected to predicted changes in solar radiation doses with global warming, estimates a very low global increase in DMS concentrations by mid 21st century (Vallina et al. 2007b).

Our results seem to support the negative feedback of the CLAW hypothesis (more solar radiation causes more DMS, which leads to increased CCN numbers and increased cloud albedo). The outcome of our studies, however, points to the need for a significant revision of the hypothesis as it was postulated. There is no evidence yet that the strength of the feedback is of enough magnitude to buffer cloudiness and cloud albedo in the short term over a particular oceanic region; and there is no evidence yet that long term (decades to

Table 5.2: Contribution of natural and anthropogenic sources to the global emission and the atmospheric burden of sulfur

Source	**Global S emission ($TgS\ yr^{-1}$)**		**Contribution to emission %**	**Contribution to S burden[a] %**	
	Mean	**Range**			
Humans	70	60-100	67	37	
Volcanos	7	4-16	7	18	
Biota[b]	27	17-34	26	42[c]	<4% Northern mid-latitude continents <20-30% extratropical oceans NH >33% Tropics and SH

[a] Contribution to the total amount of SO_4^{-2} in the atmosphere.

[b] Includes all terrestrial and oceanic biogenic emissions, of which >90% is oceanic DMS.

[c] The biogenic (mostly DMS) contribution to sulfate burden averages 42% but varies greatly among large regions, as detailed in the right column.

NH: Northern hemisphere; SH: Southern hemisphere.

Source: Adapted from Simó 2001.

hundreds of throusands years) changes in DMS emissions could help counteract large climate shifts. There is only evidence for a seasonal negative feedback in solar irradiance: summer plankton produce more DMS that reduces irradiance, and the opposite occurs in winter. Further work should include quantitative calculations of the radiative effect of this *seasonal CLAW*, and combine this with rapidly mounting observations and models of the dynamics of other secondary aerosol precursors.

Irrespective of whether we will ever be able to prove or refute the CLAW hypothesis, it will have left the invaluable legacy of the never-quite-enough joint efforts of physiologists, ecologists, biogeochemists, atmospheric chemists and physicists, experimentalists and modelers to provide an answer to a common question, and highlighted the need to continue this line of investigation, if we are to address the complex and fascinating architecture of our living planet.

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