Introduction

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The name biogeochemistry implies that it is a discipline integrating data, knowledge, concepts and theory from biology, geosciences and chemistry. Biogeochemists extensively use approaches from a wide range of disciplines, including physical, chemical and biological oceanography, limnology, atmospheric sciences, ecology and microbiology, civil and environmental engineering, soil science and geochemistry. This diversity in scientific backgrounds stimulates cross-fertilization and research creativity, which are needed to elucidate the reciprocal relationships between living organisms and their environment at multiple scales during times of global change. Biogeochemistry aims to provide a holistic picture of natural ecosystem functioning. The challenge is to identify the right level of detail needed to understand the dynamics of elemental cycles and the functioning of biological communities. This implies that single-cell organism level studies and molecular orbital calculations of chemical reactions require upscaling to the appropriate temporal and spatial scale (often involving first-principle physics based models) to understand how natural ecosystems deal with perturbations and how life has shaped our planet.

Although biogeochemistry developed as a full discipline in the mid-1980s with the launch of the international geosphere-biosphere program (IGBP, 1987) and the journals Biogeochemistry (1984) and Global Biogeochemical Cycles (1987), its roots can be traced back to early scientists documenting how living organisms transformed chemical substances, such as oxygen production during photosynthesis (Priestly, 1733–1804), phosphorus in organisms' tissues (Lavoisier, 1743–1789) and nitrogen fixation by bacteria (Beijerinck, 1851–1931). Naturalist and avant-la-lettre multidisciplinary scientists, such as Alexander von Humboldt (1769–1859). Charles Darwin (1808–1882) and Alfred Lotka (1880–1949), pioneered what we would recognize as biogeosciences in the 21st century. Darwins' studies of atmospheric deposition, bioturbation and formation and sustenance of coral reefs are still key areas in modern biogeochemistry. The tight relationship between living organisms and their environment figured prominently in Lotka's book "Elements of Physical Biology" (1925): "*It is not so much the organism or the species that*

evolves, but the entire system, species and environment. The two are inseparable."
This concept that organisms shape the environment and govern elemental cycles on
Earth underlies the biosphere concept of Vladimir Vernadsky (1863–1945), a
geochemist and mineralogist, often considered the founder of biogeochemistry.
G. Evelyn Hutchinson (1903–1991) was instrumental in establishing biogeo-
chemical, whole-system approaches to study lakes. Alfred Redfield (1890–1983)
discovered that nitrogen to phosphorus ratios of phytoplankton in seawater are
constant and similar to dissolved ratios, implying co-evolution of the environment
and organisms living in it. His seminal 1958 article started as follows "*It is a
recognized principle of ecology that the interaction of organisms and environment
are reciprocal. The environment not only determines the conditions under which
life exists, but the organisms influence the conditions prevailing in their environ-
ment*" (Redfield 1958). The latter was articulated in the Gaia hypothesis of Love-
lock (1972): The Earth became and is maintained habitable because of multiple
feedback mechanisms involving organisms. For instance, biologically mediated
weathering of rocks removes carbon dioxide from the atmosphere and generates
bicarbonate and cations that eventually arrive in the ocean, where calcifiers produce
the minerals calcite and aragonite and release carbon dioxide back to the
atmosphere.

   The above one-paragraph summary of the history of biogeochemistry does not
mean that it was a linear or smooth process. While the early pioneers (before the
second world war) were not hindered much by disciplinary boundaries between
physics, biology, chemistry and earth sciences, the exponential growth of scientific
knowledge and the consequent specialization and success of reductionism to
advance science, had led to an under appreciation of holistic approaches crossing
disciplinary boundaries during the period 1945–1990. Addressing holistic research
questions may require development of new concepts and methods, but often
involves application and combination of well-established theory or methods from
multiple disciplines. The latter implies finding the optimal balance between biology,
chemistry and physics to advance our understanding of biogeochemical processes.
For instance, all biogeochemical models have to trade-off spatial resolution in the
physical domain with the number of chemical elements/compounds and the
diversity of organisms to be included. Ignoring spatial dimensions and hetero-
geneity through the use of box models may seem highly simplistic to a physical
oceanographer, but may be sufficient to obtain first-order understanding of ele-
mental cycling. Similarly, organic carbon flows can be investigated via study of the
organisms involved, the composition of the organic matter or by quantifying the
rates of transformation, without considering the identity of the organisms involved.
Each disciplinary approach has its strengths and weaknesses, and they are unfor-
tunately not always internally consistent. However, this confrontation of different
disciplinary concepts has advanced our understanding (Middelburg 2018). In the
next section, we will discuss why many geochemists embraced biogeochemistry.

1.1   From Geochemistry and Microbial Ecology to Biogeochemistry

Geochemistry is a branch of earth sciences that applies chemical tools and theory to study earth materials (minerals, rocks, sediments and water) to advance understanding of the Earth and its components. While early studies focused on the distribution of elements and minerals using tools from analytical chemistry, the next step involved the use of chemical thermodynamics to explain and predict the occurrence and assemblages of minerals in sediments and rocks. The thermodynamic approach was and is very powerful in high-temperature systems (igneous rocks, volcanism, metamorphism, hydrothermal vents), but it was less successful in predicting geochemical processes at the earth surface. Geochemists studying earth surface processes soon realized that predictions based on thermodynamics, i.e. the Gibbs free energy change of a reaction, provided a necessary condition whether a certain reaction could take place, but not a sufficient constraint whether it would take place because of kinetics and biology.

Realizing the limitations of the thermodynamic approach, the field of geochemical kinetics developed from the 1980s onwards (Lasaga 1998). Much progress was made studying mineral precipitation and dissolution kinetics as a function of solution composition (e.g. pH) and environmental conditions (e.g., temperature). These laboratory studies were done under well constrained conditions and in the absence of living organisms. However, application of these experimentally determined kinetic parameters to natural systems revealed that chemical kinetics often could not explain the differences between predictions based on chemical thermodynamics and kinetics, and observations in natural systems. These unfortunate discrepancies were attributed to the black box 'biology' or 'bugs'.

Before the molecular biology revolution, microbial ecology was severely method limited. Samples from the field were investigated using microscopy and total counts of bacteria were reported. Microbiologists were isolating a biased subset of microbes from their environment and studying their metabolic capabilities in the laboratory. To investigate whether these microbial processes occur in nature, microbial ecologists developed isotope and micro-sensor techniques to quantify rates of metabolism in natural environments (e.g., oxygen production or consumption, carbon fixation, sulfate reduction). These microbial transformation rates were of interest to geochemists because they represented the actual reaction rates, rather than the ones predicted from geochemical kinetics. Microbial ecologists and geochemists started to collaborate systematically and a new discipline emerged in which cross-fertilization of concepts, approaches and methods stimulated not only research questions at the interface but also in the respective disciplines. Stable isotope and organic geochemical biomarker techniques and detailed knowledge on mineral phases have enriched geomicrobiology, while knowledge on microbes and their capabilities and activities has advanced the understanding of elemental cycling. This integration of microbial ecology and geochemistry has evolved well regarding tools (e.g., the use of compound-specific isotope analysis and nanoSIMS

in microbial ecology for identity-activity measurements), but less so in terms of concepts and theoretical development. Moreover, there is more to biology than microbiology. Animals and plants have a major impact on biogeochemical cycles, not only via their metabolic activities (primary production, nutrient uptake, respiration), but also via their direct impact on microbes (grazing, predation) and their indirect impact via the environment (ecosystem engineering: e.g., bioturbation, soil formation). This additional macrobiological component of biogeochemistry is increasingly being recognized (Middelburg 2018).

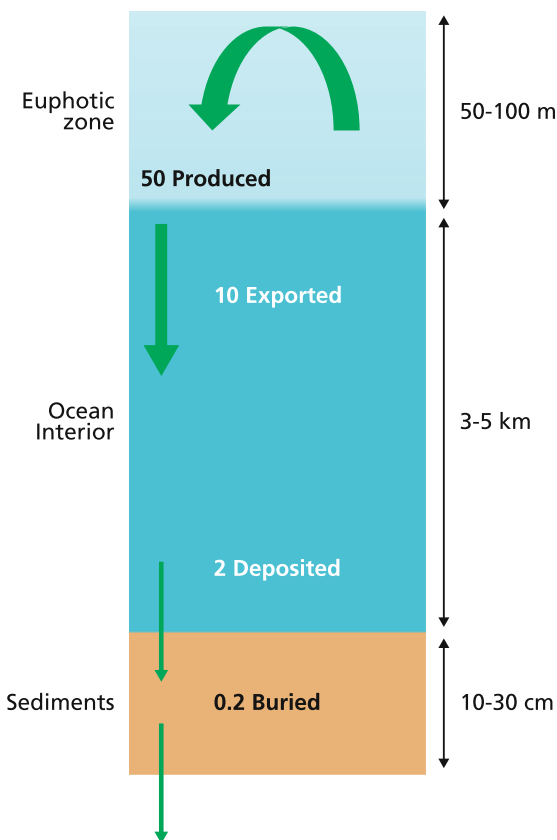## 1.2 Focus on Carbon Processing in the Sea

This book focuses on biogeochemical processes relevant to carbon and aims to provide the reader (graduate students and researchers) with insight into the functioning of marine ecosystems. A carbon centric approach has been adopted, but other elements are included where relevant or needed; the biogeochemical cycles of nitrogen, phosphorus, iron and sulfur are not discussed in detail. Furthermore, the organisms involved in carbon cycling are not discussed in detail for two reasons. First, this book focuses on concepts and the exact identity of the organisms involved or the systems (open ocean, coastal, lake) is then less relevant. Secondly, our knowledge of the link between organism identity and activity in natural environments is limited. For instance, primary production rates are often quantified and phytoplankton community composition is characterized as well, but their relationship is poorly known. The extent of particle mixing by animals in sediments can be quantified and the benthic community composition can be described, but the contribution of individual species to particle mixing cannot be estimated in a simple manner.

The following chapters will respectively deal with production (Chap. 2) and consumption (Chap. 3) of organic carbon in the water column, the processing of organic carbon at the seafloor (Chap. 4), the impact of biogeochemical processes on inorganic carbon dynamics (Chap. 5), and the composition of organic matter (Chap. 6). The carbon cycle is covered using concepts, approaches and theories from different subdisciplines within ecology (phycologists, microbial ecologists and benthic ecologists) and geochemistry (inorganic and organics) and crosses the divides between pelagic and benthic systems, and coastal and open ocean. The book aims to provide the reader with enhanced insight via the use of very simple, generic mathematical models, such as the one presented in Box 1.1. Because of our focus on concepts, in particular the biological processes involved, there will be little attention to biogeochemical budgets and the role of large-scale physical processes in the ocean (Sarmiento and Gruber 2006; Williams and Follows 2011). Accurate carbon budgets are essential for a first-order understanding of biogeochemical cycles, but it is important to understand the mechanisms involved before adequate projections can be made for the functioning of System Earth and its ecosystems in times of change. To set the stage for a detailed presentation of biogeochemical processes, we first introduce a simple organic carbon budget for the ocean.

1.3   A 101 Budget for Organic Carbon in the Ocean

Establishing carbon budgets in the ocean, in particular during the Anthropocene, is a far from trivial task, involving assimilation of synoptic remote sensing and sparse and scarce field observations with deep insight and numerical modelling of the transport and reaction processes in the ocean. The important processes and thus flows of carbon in the ocean are related to primary production, export of organic carbon from the surface layer to ocean interior, deposition of organic carbon at the seafloor and organic carbon burial in sediments. Accepting 25% uncertainty, these numbers are well constrained at 50 Pg C y^{-1} (1 Pg or 1 Gt is 10^{15} gr) for net primary production, 10 Pg C y^{-1} for export production, 2 Pg C y^{-1} for carbon deposition at the seafloor and 0.2 Pg C y^{-1} for organic carbon burial (Fig. 1.1). Although no detailed, closed complete carbon budgets will be presented, estimates for individual processes, including gross primary production, chemoautotrophy and coastal processes, are presented in the following chapters. However, the 50-10-2-0.2 rule for carbon produced, transferred to the ocean interior, deposited at

Fig. 1.1 Simplified budget of carbon flows in the ocean. Each year net phytoplankton production is about 50 Pg C (1 Pg = 1 Gt = 10^{15} g), 10 Pg is exported to the ocean interior, the other 40 Pg is respired in the euphotic zone. Organic carbon degradation continues while particles settle through the ocean interior and only 2 Pg eventually arrives at the seafloor, the other 8 Pg is respired in the dark ocean. In sediments, the time scale available for degradation increases order of magnitude with the result that 90% of the organic carbon delivered is degraded and only 0.2 Pg C yr^{-1} is eventually buried and transferred from the biosphere to the geosphere

Euphotic zone

50 Produced

10 Exported

Ocean Interior

2 Deposited

Sediments   0.2 Buried

50-100 m

3-5 km

10-30 cm

the seafloor and preserved in sediments, respectively, can easily be remembered and should be kept in mind when reading the details of carbon processing in the remaining of this book.

Box 1.1: A simple mathematical model for reaction and transport

In multiple chapters, we will make use of a very simple mathematical model in which the change in C (concentration, biomass) is due to the balance between diffusion (eddy Kz, molecular D), advection (sediment accretion particle/phytoplankton settling, w) and net effects of reactions (production and consumption). The basic equation is:

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - w \frac{\partial C}{\partial x} - kC + R_0$$

where $\frac{\partial C}{\partial t}$ is the change in concentration (mol m^{-3}) with time (t, s), $D \frac{\partial^2 C}{\partial x^2}$ is the spatial change in transport due to diffusion with diffusion coefficient D (m^2 s^{-1}), $w \frac{\partial C}{\partial x}$ is the spatial change in transport due to water flow or particle settling with velocity w (m s^{-1}), positive downwards, $-kC$ is the consumption of substance C via a first order reaction with reactivity constant k (s^{-1}) and R_0 is a zero-order production term (that is, the substance C has no impact on the magnitude of this rate).

This equation is based on spatially uniform mixing and settling rates and reactivity (i.e. D, w and k are constant). Moreover, we consider only steady-state conditions, i.e. there is no dependence on time. This simplifies the math: the partial differential equation $\left(\frac{\partial C}{\partial x}\right)$ becomes an ordinary differential equation $\left(\frac{dC}{dx}\right)$:

$$D \frac{d^2 C}{dx^2} - w \frac{dC}{dx} - kC + R_0 = 0$$

If we first consider the situation without zero-order production or consumption (i.e. $R_o = 0$), the general solution is:

$$C = Ae^{\alpha x} + Be^{\beta x}$$

$$\text{where } \alpha = \frac{w - \sqrt{w^2 + 4kD}}{2D} \text{ and } \beta = \frac{w + \sqrt{w^2 + 4kD}}{2D}$$

and A and B are integration constant depending on the boundary conditions. The number of integration constants sets the number of boundary conditions required. We will use models for the semi-infinite domain: i.e., if $x \to \infty$ then the gradient in C disappears ($\frac{dC}{dx} = 0$). Since all terms in β are positive, the

second term becomes infinite and the integration constant B must thus be zero for this boundary condition.

For the upper boundary condition, we will explore two types: a fixed concentration and a fixed flux condition. If we know $C = C_0$ at depth $x = 0$, then A is C_0 and the solution is:

$$C = C_0 e^{\alpha x}.$$

Sometimes we know the external flux (F) of C, then we have to balance the flux at the interface at $x = 0$, e.g.:

$$F = -D \frac{dC}{dx} \bigg|_{x=0} + wC|_{x=0}$$

Next, we take the derivative of the remaining first-term of the general solution $(Ae^{\alpha x})$, to arrive at:

$$F = -D\alpha A e^{\alpha 0} + wAe^{\alpha 0}$$

Since $e^0 = 1$, $A = \frac{F}{-D\alpha + w}$ and the solution is:

$$C = \frac{F}{-D\alpha + w} e^{\alpha x}.$$

In some systems, transport is dominated by diffusion (e.g. molecular diffusion of oxygen in pore water, eddy diffusion of solutes and particles in water) and the advection term (w) can be ignored. The basic solutions given above remain but now $\alpha = -\sqrt{\frac{k}{D}}$ and the pre-exponential term for the constant flux upper boundary becomes $-\frac{F}{D\alpha}$. In other systems transport is dominated by the advection term (e.g. settling particles in the water column) and then $\alpha = -\frac{k}{w}$ and the flux upper boundary condition becomes $\frac{F}{w}$.

The above solutions are valid in the case that only first-order reaction occurs. The presence of zero-order reactions results in different solutions and these will be presented in the text where relevant. Similarly, the solutions presented are only valid if D, w and k are uniform with depth. In Chap. 3 we present an advection-first order degradation model in which we vary w and k with depth. Although user-friendly packages and accessible textbooks are available for numerical solving these and more complex equations (Boudreau 1997; Soetaert and Herman 2009), we restrict ourselves to analytical solutions because the relations among D, w and k in the various applications reveal important insights in the various process and governing factors, and the reader can implement the analytical solutions for further study.

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