

Biom mineralization and Global Biogeochemical Cycles

Philippe Van Cappellen

Faculty of Geosciences, Utrecht University

P.O. Box 80021

3508 TA Utrecht, The Netherlands

INTRODUCTION

Biological activity is a dominant force shaping the chemical structure and evolution of the earth surface environment. The presence of an oxygenated atmosphere-hydrosphere surrounding an otherwise highly reducing solid earth is the most striking consequence of the rise of life on earth. Biological evolution and the functioning of ecosystems, in turn, are to a large degree conditioned by geophysical and geological processes. Understanding the interactions between organisms and their abiotic environment, and the resulting coupled evolution of the biosphere and geosphere is a central theme of research in biogeology. Biogeochemists contribute to this understanding by studying the transformations and transport of chemical substrates and products of biological activity in the environment.

Biogeochemical cycles provide a general framework in which geochemists organize their knowledge and interpret their data. The cycle of a given element or substance maps out the rates of transformation in, and transport fluxes between, adjoining environmental reservoirs. The temporal and spatial scales of interest dictate the selection of reservoirs and processes included in the cycle. Typically, the need for a detailed representation of biological process rates and ecosystem structure decreases as the spatial and temporal time scales considered increase.

Much progress has been made in the development of global-scale models of biogeochemical cycles. Although these models are based on fairly simple representations of the biosphere and hydrosphere, they account for the large-scale changes in the composition, redox state and biological productivity of the earth surface environment that have occurred over geological time. Since the Cambrian explosion, mineralized body parts have been secreted in large quantities by biota. Because calcium carbonate, silica and calcium phosphate are the main mineral phases constituting these hard parts, biomineralization plays an important role in the global biogeochemical cycles of carbon, calcium, silicon and phosphorus.

The chapter starts with introducing the basic concepts of global biogeochemical cycles. An overview of the main forcing mechanisms is presented, followed by a discussion of box models used to simulate global elemental cycles. Emphasis is on the variety of spatial and temporal scales over which biogeochemical cycles operate, and the resulting need to identify and describe processes and system variables that are relevant at the different spatio-temporal scales. The first part concludes with a short discussion of the carbon cycle, because of the central role of this element in biogeochemistry.

Next, the impact of biomineralization on the cycles of C, Ca, Si and P is reviewed. A comparison is made between elemental fluxes associated with soft and hard tissues in the oceans. An important conclusion is that calcareous and biosiliceous skeletal remains are the dominant forms under which C, Ca and Si are removed from the oceans. Burial of biogenic calcium phosphate is a relatively unimportant sink for P in the modern ocean,

but this may have been different in the past during periods of ocean anoxia. The intense cycling of silicon in terrestrial ecosystems is briefly discussed. A geochemist's perspective on the implications of the "hard body part revolution" marking the end of the Precambrian is then given. While calcifying organisms essentially took advantage of the existing (abiotic) equilibria of the calcium carbonate-seawater system, silicifying organisms completely changed how the marine silicon cycle functions.

The last part of the chapter deals with the marine silicon cycle. A simple steady state analysis highlights the importance of geological and geochemical controls on the production of biogenic silica in the oceans. Then the upscaling of silicate dissolution rates to the global weathering flux of dissolved silicic acid is briefly discussed. The final section summarizes some recent work on biogenic silica preservation in marine sediments. In particular, the results point to aluminum as an important long-term regulator of marine biosiliceous production.

BIOGEOCHEMICAL CYCLES

Forcing mechanisms and time scales

Biogeochemical cycles operate on many different spatial and temporal scales (Fig. 1). At the level of individual ecosystems, biogeochemical fluxes are controlled by interactions between organisms and by external forcings that typically fluctuate on diurnal to decadal time scales. Interactions include competition for food and habitat, parasitism and predation, while examples of forcings are air temperature, rainfall, tidal inundation, wind stress and flooding events. At this level, biogeochemistry is closely linked to ecology, and the emphasis is on relating fluxes of chemical elements to the

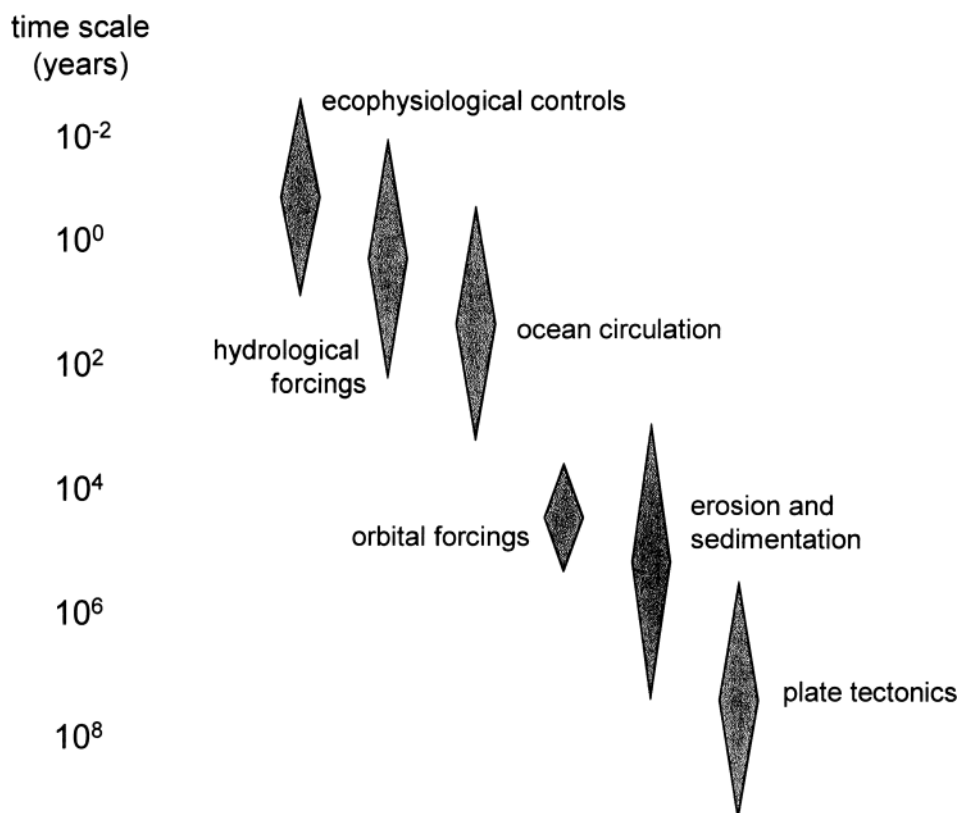


Figure 1. Examples of forcings of biogeochemical cycles and their characteristic time scales.

structure and functioning of the ecosystem. The monographs of De Angelis (1992) and Valiela (1995) illustrate this close integration of ecology and biogeochemistry.

At the other end of the spectrum, the biogeochemical dynamics of the global earth system respond to geophysical forcings on time scales of millions of years and longer. Plate tectonics continuously rearrange the physical setting in which the biosphere functions and evolves, by shaping the morphology of ocean basins and modifying the position and elevation of the continents. Equally important, plate tectonics control the intensity of chemical exchanges between the earth's surface environment and the underlying lithosphere (e.g., Berner 1990).

The major bioessential elements, including carbon and the nutrient elements N, P, S, Si, K and Ca, are efficiently recycled within terrestrial and marine ecosystems (Schlesinger 1997). As a consequence, on a yearly basis, only very small fractions of these elements escape through removal to the lithosphere. Therefore, on relatively short time scales, say, less than 1000 years, the lithosphere is a minor sink in most biogeochemical cycles. At these time scales, modeling efforts tend to focus on the redistribution of chemical constituents among the atmosphere, hydrosphere and biosphere. A good example is provided by global carbon cycle models used in predicting the future fate of anthropogenic CO₂ emissions to the atmosphere. How much of this CO₂ remains in the atmosphere is, in the short term, mainly determined by transfer of CO₂ from the atmosphere to the ocean, and to vegetation plus soils on land (e.g., Sarmiento and Gruber 2002).

With the passing of time, however, the cumulative loss of bioessential elements to the lithosphere becomes significant. For most major nutrient elements, the principal escape route is incorporation in marine sedimentary deposits. Unless somehow compensated, burial in ocean sediments would ultimately deplete the surface reservoirs of nutrients, resulting in the collapse of biological activity on earth. Marine turnover times (Equation 3) of limiting nutrients, relative to removal by sediment burial, provide rough estimates of the time scale over which such a collapse would take place. These turnover times are on the order of 10⁴ to 10⁵ years.

Fortunately, the loss of bioessential elements to the lithosphere is countered by their release by volcanic outgassing and chemical weathering of rocks. Hence, the latter processes are essential for the continued survival of life on geological time scales. From the point of view of the global cycles of bioessential elements, we can therefore distinguish between long and short time scales, depending on whether the lithosphere is a significant sink and source, or not. The distinction between short and long times is not a sharp one and varies from one element to the other. It is safe to state, however, that for time spans $\geq 10^4$ years chemical exchanges with the lithosphere become a key factor controlling biogeochemical cycles.

With the exception of N, the lithosphere is the largest reservoir of the major nutrient elements. Sediments and rocks contain orders of magnitude more C, P, S, Fe, Si, Ca, and K than the atmosphere, hydrosphere, pedosphere and biosphere combined (e.g., Garrels and Mackenzie 1971; Drever et al. 1988; Chameides and Perdue 1997; Reeburgh 1997; Mackenzie 1998). The transit times of these elements through the lithosphere are similarly orders of magnitude longer than their turnover times at the earth surface. On average, it takes several hundreds of millions of years for non-volatile materials buried in marine sediments to be exposed on land by plate tectonic processes. Once incorporated in the lithosphere, bioessential elements may follow a variety of different pathways, however (Fig. 2). As a result, transit times through the lithosphere exhibit a broad range of values.

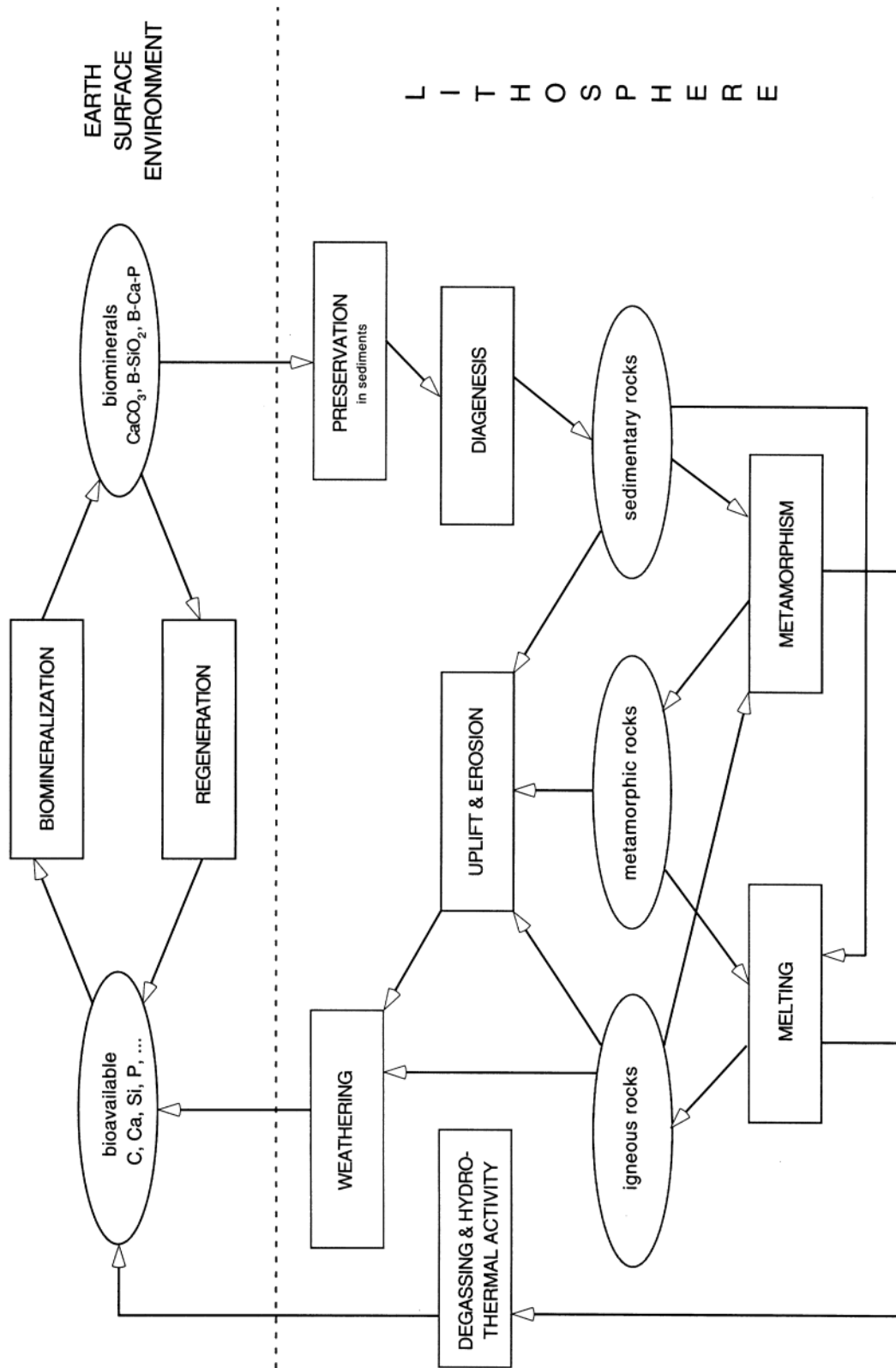


Figure 2. Biomineralization and the rock cycle. On geological time scales, the rock cycle regulates the supply of biomineralizing elements from the lithosphere, as well as their removal from the earth surface environment.

Pathways through the lithosphere not only determine how long a given element is removed from the earth surface environment, but also its chemical state and reactivity when it reappears. Marine sediments may be entrained deep into the mantle at subduction zones, and their chemical constituents return to the earth surface as part of igneous and metamorphic rocks, or they make their way back with volcanic emanations and hydrothermal discharge. Alternatively, sediments accumulating in sedimentary basins may never experience temperatures and pressures sufficient to cause melting and metamorphism. Instead, they resurface as sedimentary rocks, after having undergone variable degrees of diagenesis.

Biogenic constituents of sediments are particularly sensitive to diagenetic alteration. With advancing diagenesis, organic debris mature into kerogen, while calcareous and siliceous shell fragments are subject to recrystallization and cementation processes (e.g., Pettijohn 1957; Tegelaar et al. 1989). As diagenetic transformations generally increase the resistance of rocks to chemical weathering, carbon and nutrient elements tend to be more efficiently remobilized from younger sedimentary rocks that resurface after a relatively brief cycle of burial and uplift. For instance, sedimentary rocks younger than 250 Ma are estimated to release about three times as much dissolved silicic acid to the world's rivers as do older sedimentary rocks, although twice as much Si is locked up in the older rock reservoir (Garrels and Mackenzie 1972). In a similar vein, Berner (1987) proposes that more realistic simulations of the biogeochemical cycles of C and S over Phanerozoic time are obtained when splitting the sedimentary rock reservoir into young and old sub-reservoirs. Model results indicate that first-order rate constants for weathering of C and S are 10-100 times higher for rocks younger than 100 Ma, compared to older rocks (Berner and Canfield 1989).

On million-year time scales, earth surface reservoirs respond near-instantaneously to changes in the supply rates of bioessential elements from the lithosphere. The fast transit times through the earth surface environment, relative to those through the lithosphere, mean that the global sources and sinks of carbon and nutrient elements track each other closely, when integrated over 1 Ma or more. Hence, on these long time scales, biogeochemical cycles at the earth surface can be thought of as evolving from one quasi-steady state to another, under the influence of tectonically-driven variations in the intensity of exchanges with the lithosphere. Major transitions in the biogeochemical state and functioning of the earth surface system can therefore often be traced back to large-scale geological events, such as the opening or closing of ocean basins, massive lava eruptions (plateau basalts), and mountain building episodes.

There are additional forcings acting on global biogeochemical cycles, however. In particular, the evolution of the sun and the evolution of life itself impose their constraints on the biogeochemical dynamics of the earth surface environment (e.g., Caldeira and Kasting 1992; Van Andel 1994). Some of the most dramatic biogeochemical changes that have taken place on earth are related to the build-up in the atmosphere and oceans of O₂ produced by photosynthetic organisms. This build-up is a billion year-long story of complex interactions between changing solar luminosity, microbial evolution, weathering, ecosystem development, climate, sediment burial and volcanic activity (for a lively and up-to-date account, see Lane 2002). In the more recent geological past, the widespread appearance of mineralized body parts, and the colonization of continents by plants have markedly modified biogeochemical cycles at the earth's surface (e.g., Siever 1992; Berner 1992).

Besides being the principal energy source for biological activity, incoming solar radiation also drives the hydrological cycle, as well as atmospheric and oceanic circulation. On temporal scales of months to millennia, groundwater flow, river runoff,

atmospheric transport and ocean circulation redistribute bioessential elements at the earth's surface. On time scales of thousands of years and more, rainfall, air temperature and thermohaline circulation play major roles in regulating rock weathering (e.g., Berner and Berner 1997), ocean fertility (e.g., Van Cappellen and Ingall 1994) and sealevel (Turekian 1996). As the time span of interest increases, the solar-driven forcings of biogeochemical cycles (and climate) increasingly overlap with plate tectonic forcings. Because of the multiple forcings acting over a wide range of time scales, as well as the numerous feedbacks and couplings within and among elemental cycles, the interpretation of the earth's biogeochemical workings in terms of simple cause and effect is often no longer possible. At this point, it is best to turn to models.

Models

Environmental conditions and the persistence of a biosphere at the earth's surface are dependent on the continuous flow of matter between different parts of the earth system. This flow is ultimately sustained by the supply of energy from the sun and by the release of heat deep within the earth. As matter is moved around it is also continuously transformed from one chemical form into another. The biogeochemical cycle of an element describes the combined transformation and transport pathways of that element in the earth system. A numerical biogeochemical model is an attempt to translate the conceptual understanding of an element's cycle into mathematical expressions that account for its transport and transformation.

An important aspect in the development of numerical biogeochemical models is discretization. One approach uses a continuous representation of space and time. This approach yields partial derivatives with respect to the spatial coordinates as well as time. The set of partial differential equations that describe mass conservation of the basis species considered are usually referred to as a reactive transport model. Reactive transport models are used when the detailed chemical structure of the system, and its evolution over time, are desired model outcomes. For example, reactive transport modeling may help predict the spreading of pollutants through a groundwater system. Various applications of reactive transport modeling in the earth and environmental sciences can be found in Steefel and Van Cappellen (1998). It is worth noting that reactive transport models have also been used to describe biomineralization processes at the cellular level (e.g., Wolf-Gladrow and Riebesell 1997).

Reactive transport models are mathematically and numerically demanding. When dealing with multicomponent systems, finite difference or finite element methods are needed to solve the equations (see, for example, Steefel and MacQuarry 1996). Therefore, a simpler approach to modeling biogeochemical cycles is frequently used. This so-called box model approach is based on reactor modeling concepts borrowed from chemical engineering. The biogeochemical system is subdivided in a finite number of *reservoirs*. In each reservoir, the relevant chemical, physical and biological properties are assumed to be (reasonably) uniform. *Fluxes* transfer matter from one reservoir to another. A flux into a reservoir is sometimes referred to as a *source*, a flux out of the reservoir as a *sink*. In box models of biogeochemical cycles, matter leaving a given reservoir may ultimately return to that reservoir, often via a number of alternative pathways.

In chemical engineering applications, the reservoir is a physically well-defined reacting system, i.e. the reactor. No attempt is made at describing the mixing processes inside the reactor; rather the extent of reaction is derived from the *residence time distribution* in the reactor. For a perfectly mixed reactor, the concentration of a reactant or product in the outflow is equal to the uniform concentration inside the reactor, C_{res} . The mass balance equation for a reacting species in a perfectly mixed, constant volume

reactor with a single inlet and a single outlet, is

$$\frac{dC_{res}}{dt} = \frac{1}{\bar{t}_f} (C_{in} - C_{res}) + R \quad (1)$$

where C_{in} is the concentration of the species in the inflow, R is the rate, per unit volume, at which the species is produced in the reactor (note: when the species is being consumed R is negative), and \bar{t}_f is the mean residence time (or transit time) of the carrier fluid in the reactor:

$$\bar{t}_f = \frac{V}{Q} \quad (2)$$

where V is the volume of the reactor and Q the volumetric flow in and out of the reactor. The residence time thus emerges naturally as a fundamental property in the governing mass balance equation. For reactors, the inflow and outflow are purely advective transport fluxes. As can be seen from Equation (1), governing equations for reactor models, and by extension those of biogeochemical box models, are ordinary differential equations with time as the only independent variable.

Although mathematically similar, box models of biogeochemical cycles differ from simple reactor models in at least two major ways. First, the reservoirs do not have to occupy a continuous physical space, nor do they necessarily correspond to a reacting system. Instead they refer to a collection of matter of a certain chemical type, within given physical and/or biological boundaries. For example, a key reservoir in the carbon cycle is living biomass of marine biota. Included in this reservoir are all organic carbon atoms of living marine organisms. The oceans, as a well-defined physical space, contain many more biogeochemical reservoirs, including other types of organic carbon, e.g., dissolved organic molecules and dead particulate organic matter. Similarly, marine biota encompass other biogeochemically relevant reservoirs, for example, calcium carbonate and nutrient elements such as N, P and Si.

Second, fluxes between reservoirs are not restricted to purely advective flows of matter. Most often, a flux in a biogeochemical box model combines physical transport and biogeochemical transformation processes. For example, the supply of silicic acid to the oceans by weathering of rocks on land may be represented by a flux linking the terrestrial rock reservoir to the marine dissolved silica reservoir. Clearly, this flux encompasses a variety of processes acting in concert, including, uplift and erosion of rocks on land, mineral dissolution and soil formation, continental drainage, and retention of silica by terrestrial and estuarine ecosystems. A large number of geological and environmental variables therefore affects the net flux of dissolved silicic acid to the oceans. Different variables may dominate at different time-scales. Hence, on relatively short time scales, say $\leq 10^3$ years, storage of reactive silica in vegetation and estuaries may be an important regulator of the supply of silicic acid to the oceans. On longer time scales, however, variations in the rate of uplift, rock lithology and climate become the major sources of variability in the supply flux.

The two main tasks facing the developer of a biogeochemical box model is the definition of the reservoirs and the parameterization of the fluxes. There are no magic guidelines, other than to clearly define the goals of the modeling effort and to start as simple as possible. Obviously, a model only provides direct information on reservoirs, fluxes and parameters that are explicitly represented. The reader is referred to the excellent textbook on biogeochemical box modeling by Chameides and Perdue (1997), for a step-by-step introduction to model building and scenario testing. A shorter overview can be found in Rodhe (1992).

It may sometimes be possible to simplify a model by lumping together adjoining reservoirs. The *turnover time* of the reservoirs can help decide whether this is reasonable or not. The turnover time is defined as

$$t_R = \frac{M}{F_{out}} \quad (3)$$

where M is the mass of the reservoir (say, the total number of moles of organic carbon in marine biota) and F_{out} is the total flux out of the reservoir (i.e., the sink). If t_R is much smaller than the time step of the simulations, then joining the reservoir to a larger one does not significantly modify the biogeochemical dynamics of the overall system. For example, the turnover time of reactive phosphorus in the surface ocean is about 2.6 years, while it is on the order of 50,000 years for the ocean as a whole (Reeburgh 1997). For simulations at a million year-time scale, surface ocean phosphorus can therefore be integrated into a single total oceanic phosphorus reservoir. Table 1 compares turnover times at the earth's surface and in the lithosphere of the major elements involved in biomineralization. Note that, at steady state, turnover times of these elements coincide with their (mean) residence times.

Once all the reservoirs are chosen and the fluxes between them identified, mathematical expressions must be derived to describe the fluxes. When dealing with the cycle of a single element, say carbon, a convenient starting point is to adopt a linear box model where the fluxes are assumed to be linearly proportional to the masses in the reservoirs from which they originate:

$$F_{ij} = k_{ij} M_i \quad (4)$$

where F_{ij} and k_{ij} are the flux and linear transfer constant from reservoir i to reservoir j , respectively, while M_i is the mass in reservoir i . If the masses M_i and the fluxes F_{ij} are known at some point in time, then the transfer constants can be derived from Equation (4). The parameterization of the transfer constants for a given element may, for example, be carried out using estimated reservoir sizes and fluxes during the recent geological past, prior to significant human interference.

The great advantage of linear box models is that there exists a general solution, $M_i(t)$, based on the eigenvector-eigenvalue method of matrix calculus (Lasaga 1981). Linear models are not always appropriate for representing biogeochemical systems, however (Lasaga 1981; Rodhe 1992). It has been shown, for instance, that the flux of CO_2 from

Table 1. Turnover times of biomineralizing elements at the earth surface and in the lithosphere. The earth surface environment comprises the atmosphere, hydrosphere and biosphere, plus soils and surficial sediments. The turnover times for the lithosphere are calculated using estimates of the elemental reservoir sizes of the continental and oceanic crust (i.e., the lower part of the lithosphere is excluded). Data used to derive the turnover times are from a variety of sources.

<i>Element</i>	<i>Earth Surface (years)</i>	<i>Lithosphere (years)</i>
C	1.2×10^5	2×10^8
O	3×10^6	—
Si	$1.5\text{--}2.8 \times 10^4$	$5\text{--}50 \times 10^8$
P	6×10^4	$>2 \times 10^8$
Ca	$\geq 10^6$	7×10^8

the oceans to the atmosphere depends in a highly non-linear fashion on the mass of total dissolved inorganic carbon (DIC) in the ocean surface layer (Rodhe 1992). This non-linearity derives from the fact that the actual species being transferred, CO₂, is only a minor form of DIC in seawater.

Furthermore, over long time spans, it may not be realistic to assume strictly constant proportionalities between fluxes and reservoir masses. For example, fluxes of carbon and nutrients from the lithosphere to the earth surface environment vary through time because of changes in plate tectonic regime, climate, and terrestrial vegetation. One way to deal with these multiple variables is to introduce dimensionless parameters that express relative effects on the fluxes as a function of time. The linear equations (4) are then modified to

$$F_{ij} = \{f_A(t)f_B(t)\dots f_K(t)\} \bullet k_{ij}M_i \quad (5)$$

where $f_M(t)$ expresses the effect of variable N , normalized to the value at some point in time. Parameterization now requires one not only to derive values for the transfer constants, k_{ij} , but also to reconstruct the dimensionless functions $f_M(t)$ over the time span of interest (for further details, see, Berner 1990, 1994; Berner and Kothavala 2001).

The derivation of meaningful functions $f_M(t)$ over geological time scales is possible only through integration of data and knowledge from a wide range of scientific fields, from (geo)biology to geophysics and climatology. An example of a dimensionless function $f_M(t)$ in the long-term geochemical carbon cycle introduced by R. A. Berner is the so-called weathering feed-back function. This function expresses the dependence of weathering of silicate rocks on atmospheric CO₂ levels. In a nutshell, the idea is that an increase in atmospheric CO₂ increases global temperature (greenhouse effect), continental river runoff, and land plant productivity (CO₂ fertilization). All three factors accelerate silicate mineral weathering, which is a net sink for atmospheric CO₂. On geological time scales, this negative feedback helps guarding the atmospheric CO₂ concentration against unreasonably large fluctuations.

A feature that is not captured by linear box models is coupling between the cycles of different elements. A typical example is the coupling of photosynthetic production of organic carbon to the availability and regeneration of the limiting nutrient elements N and P. Mathematically, this means that some of the fluxes in the carbon cycle depend on reservoir sizes and fluxes of other elements. In that case, the mass balance equations of the different coupled cycles must be solved together, which requires numerical integration techniques. A good example is provided by Mackenzie et al. (2002), who use a coupled box model to simulate the effects of human activity on the carbon and nutrient cycles on century time scales.

Coupling of elemental cycles may also lead to feedbacks. Van Cappellen and Ingall (1994, 1996) have explored positive and negative feedbacks in the coupled cycles of phosphorus, carbon and oxygen, using a box modeling approach. Feedback mechanisms are a common feature of biogeochemical cycles, although many of the exact mechanisms are still poorly known. An important role of model simulations is to help uncover the existence of feedbacks and constrain their potential effectiveness. Nowadays, access to user-friendly software packages for dynamic modeling greatly facilitates experimentation with box models, even when dealing with coupled, non-linear biogeochemical cycles.

Carbon cycle

Table 2 presents an overview of reservoir sizes in the short and long term carbon cycles. The short term cycle is receiving a lot of attention, because of the potential climatic effects of the fast release of CO₂ to the atmosphere by humans, primarily as a result of fossil fuel burning and deforestation (e.g., Harvey 2000). The global carbon

Table 2. Reservoirs in the carbon cycle.

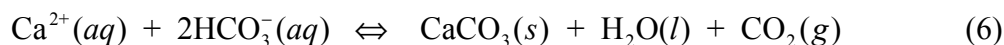
reservoir	carbon (g)
atmosphere	6×10^{17}
terrestrial biota	8×10^{17}
soils & detritus	1.5×10^{18}
marine biota	3×10^{15}
ocean surface water	10^{18}
deep ocean water	3.8×10^{19}
surface sediments	1.5×10^{17}
sediments & sedimentary rocks	5.5×10^{22}
basaltic oceanic crust	7×10^{20}
granitic continental crust	9×10^{21}

Sources: Garrels and Mackenzie (1971), Reeburgh (1997), Chameides and Perdue (1997).

balance on short time scales (≤ 1000 years) is dominated by the relatively small reservoirs of the earth surface environment, including the atmosphere, the oceans, terrestrial and marine biota, soils and nearshore sediments. For a good introduction to the issues related to the short term redistribution of anthropogenic CO_2 among these reservoirs, the reader is referred to Sarmiento and Gruber (2002).

On short time scales, anthropogenic CO_2 may be sequestered by the oceans via the so-called *biological pump*, that is, the export to the deep ocean of organic matter synthesized in the surface ocean. Marine organisms, in particular calcifying algae, coccolithophores and foraminifera, also secrete calcium carbonate (CaCO_3). Part of the calcium carbonate precipitated in the surface ocean sinks to the deep ocean, together with the organic carbon. This so-called *carbonate pump* is an important component of the oceanic carbon cycle. Together, the export fluxes of particulate organic carbon (POC) and particulate inorganic carbon (PIC) to the deep ocean represent about 10 Gt of carbon annually ($1 \text{ Gt} = 10^{15} \text{ g}$), of which 20–40% is under the form of CaCO_3 .

The role of CaCO_3 production and dissolution in the marine carbon cycle is rather complex, however (e.g., Archer and Maier-Reimer 1994). Although it is a net sink for dissolved inorganic carbon (DIC), calcification actually generates CO_2 while consuming alkalinity:



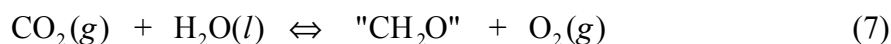
Thus, uptake of atmospheric CO_2 by surface ocean waters depends on the proportion of biomass production carried out by calcifying organisms (mainly coccolithophorids), versus that by non-calcifying organisms (mainly diatoms).

Calcium carbonate dissolution (i.e., reaction (6) in reverse direction) below the photic zone is a net sink for CO_2 . Dissolution is usually assumed to take place at great depths, typically below 3–4 km, where seawater is undersaturated with respect to calcite and aragonite (Broecker and Peng 1982). This deep ocean sink should therefore affect atmospheric CO_2 levels on time scales dictated by the rate of deep water renewal, that is, on the order of 1000 years. Recent studies, however, suggest that substantial CaCO_3 dissolution may take place in the upper 1000 m of the water column, probably coupled to organic matter respiration (e.g. Wollast and Chou 1998; Milliman et al. 1999). If confirmed, shallow CaCO_3 dissolution may represent an important marine sink for

anthropogenic CO₂ on time scales of tens of years.

Long term fluctuations in the level of atmospheric CO₂ are dominated by exchanges with the lithosphere (e.g., Berner 1990). The CO₂ sinks in the long-term carbon cycle are burial of organic carbon and CaCO₃ in marine sediments, and CO₂ consumption during weathering of silicate rocks. The sources are CO₂ produced by the thermal degradation of buried organic matter and carbonate minerals, plus the oxidative weathering of sedimentary organic matter after uplift.

The carbon sinks and sources are often represented by overall chemical reactions, such as



where "CH₂O" is a simplified representation for organic matter. The forward reaction in Equation (7) corresponds to net global photosynthesis, that is, photosynthesis minus respiration. Because the earth surface environment is at (quasi-)steady state, net global photosynthesis is equal to the burial rate of organic matter in sediments. The backward reaction represents total oxidative degradation of organic matter, either through weathering of sedimentary organic matter or the oxidation in the atmosphere of reduced carbon gases derived from the degradation of organic matter during late diagenesis, metamorphism or magmatic activity (Fig. 2). The backward reaction can thus be thought of as the global respiration of the geosphere.

Weathering of carbonate rocks on land does not affect the long term, average concentration of CO₂ in the atmosphere. This is because, on a million-year time scale, the carbonate weathering flux is balanced by an equal amount of carbonate precipitation and burial in the oceans. The latter returns the CO₂ consumed during carbonate weathering back to the atmosphere. The situation is different when marine carbonate minerals are formed with calcium (and magnesium) ions produced by weathering of silicate minerals. In that case, there is a net consumption of atmospheric CO₂, as shown schematically by the overall reaction (e.g., Berner 1990):



where CaSiO₃(s) represents calcium containing silicate minerals. The forward reaction corresponds to silicate mineral weathering coupled to carbonate mineral burial in ocean sediments, and the reverse reaction to the thermal decomposition of the carbonates deep within the lithosphere. Because of the long time span that separates deposition of carbonate minerals at the seafloor and the return of carbon to the earth's surface as volcanic CO₂, reaction (8) can be out of balance, resulting in a net source or sink of atmospheric CO₂.

In box models for the long term carbon cycle, the forward and backward rates of overall reactions such as those represented by Equations (7) and (8) correspond to fluxes linking carbon reservoirs at the earth surface and in the lithosphere. These fluxes obviously combine many different processes and are subject to a variety of controls. For example, the burial flux of organic carbon in sediments (i.e., the forward flux in reaction 7) depends not only on how much organic matter is produced globally, but also on the fraction of organic matter that survives degradation and is ultimately incorporated in the sedimentary column (e.g., Canfield 1989). In other words, the derivation of a mathematical expression for the burial flux of organic carbon must be based on a careful evaluation of the factors controlling both production and preservation of organic matter. The same is true for the burial fluxes of other biogenic materials, in particular the products of biomineralization.

BIOMINERALIZATION IN A GLOBAL CONTEXT

Biom mineralization and biogeochemical cycles

The biogeochemical cycle of carbon is coupled to the cycles of nutrient elements, particularly N, P, through the production and degradation of organic matter. The Redfield ratios of marine phytoplankton biomass exemplify this coupling (Redfield et al. 1963). The ratios express the relative proportions in which N, P and other nutrient elements are used, relative to C, during primary production in the oceans. The concept of limiting nutrient(s) is a direct consequence of the stoichiometric constraints on nutrient uptake fluxes during synthesis of new biomass. The Redfield ratios also provide base line values against which the relative release fluxes of nutrients can be compared during degradation of organic matter. Preferential release or preservation of nutrient elements exerts a major control on the biological productivity of the oceans (e.g., Van Cappellen and Ingall 1994).

The production of skeletal hard parts creates additional coupling among elemental cycles. This is particularly true in the oceans, where vast amounts of calcium carbonate and biogenic opal (B-SiO₂) are secreted by organisms living in the surface waters (i.e. depths <200 m). Table 3 compares the rates of production of soft and mineralized tissues in the surface ocean. Photosynthetic fixation of carbon in organic molecules is estimated to be about 20 times higher than the gross production of calcium carbonate or biogenic opal (on a molar basis). Nearly 90% of the organic matter, however, is rapidly degraded and the carbon and nutrients are returned to the surface waters. In contrast, only about 50% of the biogenic silica dissolves in the upper 200 m of the water column (Tréguer et al. 1995). For calcium carbonate, this fraction is even smaller, because the surface ocean is supersaturated with respect to calcite and aragonite. As a result, net export of organic carbon from the surface ocean is only 2–5 times larger than the corresponding fluxes of B-SiO₂ and CaCO₃. The biogenic materials are removed from the surface waters, either by sinking into deeper waters or deposition in shallow water sediments.

Degradation of organic matter continues in the water column and after deposition at the seafloor. Ultimately, less than 1% of the organic matter originally synthesized in the surface waters is preserved in sediments. A significantly larger fraction of the biogenic CaCO₃ survives dissolution, however (Table 3). The end result is that about twice as much carbon is removed from the earth surface environment as biogenic CaCO₃ than as organic carbon. Because of highly undersaturated ocean waters, relatively more B-SiO₂ dissolves than CaCO₃. About 3% of the total amount of B-SiO₂ secreted by diatoms, silicoflagellates and radiolarians is buried in marine sediments. In terms of absolute magnitudes, the burial fluxes of organic carbon and biogenic silica are fairly similar (Table 3).

Table 3. Fluxes of organic matter and biogenic minerals in the oceans. C_{org} and P_{org} correspond to carbon and phosphorus in particulate organic matter. B-SiO₂ and B-CaP refer to biogenic silica and biogenic calcium phosphate. The latter is mainly associated with fish bones and scales; B-CaP does not include calcium phosphate minerals forming authigenically in sediments. All fluxes are in Tmol phosphorus per year (Tmol = 10¹² mol)¹.

	<i>C_{org}</i>	<i>P_{org}</i>	<i>CaCO₃</i>	<i>B-SiO₂</i>	<i>B-CaP²</i>
Production in surface ocean	4200	39.6	≥ 223	240	0.4
Export to deep ocean	497	4.7	213	120	0.34
Deposition at seafloor	74	0.32	74	30	?
Burial in sediments	8–11	0.02	17–24	6.7	< 10 ⁻³

¹**Sources:** Tréguer et al. (1995); Berner and Berner (1996); Sarmiento and Gruber (2002); Klaas and Archer (2002); Slomp et al. (2003).

Most CaCO_3 and B- SiO_2 is produced by organisms from relatively low trophic levels, including the major marine primary producers, coccolithophorids and diatoms. Therefore, the fluxes of CaCO_3 and B- SiO_2 are large and intimately coupled to those of organic matter. As mentioned earlier, the relative proportion of siliceous versus calcareous production is of global climatic significance, because it regulates the uptake of CO_2 by marine surface waters. When silica-secreting organisms dominate, more CO_2 can be extracted from the atmosphere, because there is no release of CO_2 by reaction (6). In addition, it has been proposed that diatoms are responsible for much of the export of organic matter from the surface waters (e.g., Smetacek 1999). This is because large diatom blooms are usually followed by aggregation and rapid sinking of biomass out of the surface mixed layer. Diatom blooms could thus enhance the efficiency of the biological (organic) carbon pump in the oceans (for an opposing view, see, Klaas and Archer 2002).

Much oceanographic research is currently directed at understanding how circulation patterns, sea surface temperature, nutrient limitation, atmospheric dust input, and ecological factors affect the ratio of silica-secreting organisms to calcium carbonate-secreting organisms in the surface ocean. One particular area of focus is the Southern Ocean, where a significant fraction of available P and N in the surface waters is not being utilized for photosynthesis (e.g., Martin et al. 1990). It is now widely believed that diatoms in the Southern Ocean are limited by the availability of iron and, in some cases, silica. A related hypothesis is that, during glacial times, wind-blown dust alleviates iron limitation of diatom production and, hence, causes a drawdown of atmospheric CO_2 .

Biogenic calcium phosphate (B-CaP) is mainly secreted by marine vertebrates, that is, organisms higher up the food chain. We may therefore expect the fluxes of B-CaP to be of lesser importance in global ocean biogeochemistry, compared to those of CaCO_3 and B- SiO_2 . The estimated gross production of B-CaP in the surface ocean is indeed two orders of magnitude smaller than phosphorus fixation by photosynthesis (Table 3). However, the export fluxes of organic phosphorus and phosphorus associated with B-CaP only differ by one order of magnitude. This reflects the fast remineralization of organic matter in the surface ocean, but also relatively minor B-CaP dissolution in the upper water column. B-CaP consists primarily of hydroxapatite, a rather insoluble mineral phase. Furthermore, a large fraction of B-CaP is probably exported with relatively large, fast sinking fish debris.

As it settles through the water column, and after deposition at the seafloor, most B-CaP dissolves. The soluble phosphate is either recycled back to the surface ocean or it precipitates in sediments as fine-grained (authigenic) carbonate fluorapatite (Ruttenberg and Berner 1993). Globally, the contribution of B-CaP to total burial of reactive P in marine sediments is estimated at less than 1% (Berner and Berner 1996). Burial of B-CaP appears to be mainly associated with coastal upwelling areas that exhibit low bottom water oxygen concentrations. In sediments of the Arabian Sea located within the so-called Oxygen Minimum Zone (OMZ), 25-40% of the total burial flux of P is attributed to biogenic calcium phosphate (Schenau and de Lange 2001). In sediments of the OMZ along the Peru margin, the burial flux of B-CaP may exceed that of organic P (Suess 1981).

The observed enhanced B-CaP preservation under oxygen-depleted bottom waters is puzzling, and the responsible mechanisms are not yet understood. However, it could imply that burial of B-CaP may have been a more significant sink for oceanic phosphorus during so-called Ocean Anoxic Events (OAEs). These are periods during the geological past, for example during the mid-Cretaceous, when anoxic bottom waters were widespread in the oceans. These periods are characterized by the abundant accumulation of laminated, organic-rich shale deposits (e.g., Arthur et al. 1984; Wignall 1994). In many cases, these sediments have, upon deep burial, acted as petroleum source rocks.

Model simulations suggest that oxygen-dependent burial of phosphorus plays a major role in the development of ocean anoxia (Van Cappellen and Ingall 1994).

The biogeochemical cycles of P and Si in the oceans are completely dominated by biological uptake during organic matter synthesis and skeletal secretion in the surface waters, and regeneration in deeper waters and surface sediments (e.g., Broecker and Peng 1982). These elements are extremely efficiently recycled in the oceans and are often limiting nutrients for marine ecosystems (e.g., Ragueneau et al. 1996; Falkowski et al. 1998). Nearly all dissolved phosphate and silicate that enter the photic zone are used for the production of new soft tissue and skeletal hard parts. In contrast, C and Ca rarely limit primary production. Their reservoir sizes and oceanic turnover times are substantially larger than for P and Si. For comparison, the estimated turnover times of Si, P, C and Ca are 1.5×10^4 , 5×10^4 , 1.3×10^5 and 10^6 years, respectively. In essence, C and Ca are less biogenic than P and Si. Abiotic processes play a relatively larger role in their biogeochemical cycles, for example, air-sea gas exchange for C and seawater-basalt reaction for Ca.

So far, the focus has been on biomineralization processes in the oceans. On the continents, calcifying and silicifying organisms may play significant roles, albeit at a more local scale, in the biogeochemistry of aquatic environments, e.g., lakes, wetlands and large river systems. In terrestrial ecosystems, a recent assessment by Conley (2002) emphasizes the very intense biological cycling of silicon by land plants. He estimates that the gross uptake of dissolved silicate by terrestrial vegetation ($60\text{--}200 \text{ Tmol Si yr}^{-1}$) is of the same order of magnitude as biosiliceous production in the oceans ($240 \text{ Tmol Si yr}^{-1}$, Table 3). The plants deposit the silica as structural support elements, or phytoliths, in their tissues. Phytoliths accumulate together with other biogenic detritus in soils, which may therefore constitute a significant but, as yet, poorly quantified terrestrial pool of reactive silica.

While both the continents and oceans are sites of continuous cycling of biogenic elements, a major difference is the generally smaller storage capacity of the terrestrial biosphere plus soils, compared to the oceanic reservoir (for carbon this is illustrated in Table 2). This means that turnover times of these elements on land tend to be shorter than in the oceans. For example, the turnover time of reactive Si in forest ecosystems appears to be on the order of a few thousands of years (Conley 2002), compared to a marine turnover time on the order of $1\text{--}2 \times 10^4$ years. The available estimates, however, are based on a very limited data set. In particular, there is a lack of (steady state) mass balances of reactive Si for grasslands, which are known to produce large amounts of phytoliths. At present, the global terrestrial phytolith reservoir size is a major unknown in the global biogeochemical cycle of Si.

To summarize the discussion so far, the following, admittedly simplified, outline of the biogeochemical cycles of the major elements involved in biomineralization can be drawn. The continents are the main site of mobilization of C, Si, P and Ca from the lithosphere. The elements typically remain on land for a few thousands of years, during which they participate in the biogeochemical cycles of terrestrial and aquatic ecosystems. They are then delivered to the oceans, where they reside for periods ranging from 10^4 to 10^6 years. After extensive recycling within the ocean-atmosphere system, they are ultimately removed by burial in sediments. Tectonic processes close the cycles by returning the elements to the earth surface, on time scales of tens to hundreds of millions of years.

Biomineralization through time

Secretion of mineralized body parts is a relatively recent phenomenon in geological history, with little evidence suggesting it originated much earlier than 600 Ma ago (Van Andel 1994). The Cambrian explosion truly marks the start of the radiation of organisms

with hard parts, first in the oceans and, from about 400 Ma on, also on land. Given the large impact of biomineralization on biogeochemical cycles in today's world, one wonders how the adoption of mineralized body parts has altered the biogeochemical dynamics of the earth surface environment. Unfortunately, there is no easy answer to this question. The available geological records are not only incomplete, they also provide ample evidence that many of the dominant features of the earth surface environment in the past may not have modern analogues.

During the early days of the Cambrian (570–510 Ma B.P.), life probably experimented with a variety of different biominerals. Yet, calcium carbonate rapidly emerged as the dominant building material for shells and skeletons among invertebrates. The geological history of CaCO_3 biomineralization since the end of the Precambrian is fascinating, with periods of massive reef building, e.g., during the Ordovician, and the radiative expansion of calcareous plankton during the Mesozoic (Martin 1995). However, whether in shallow-water environments or in the open ocean, invertebrates have been producing large quantities of CaCO_3 throughout the entire Phanerozoic, with the possible exception of episodes of marine extinction (Martin 1998).

Today, precipitation and dissolution of biogenic CaCO_3 maintain the oceans close to thermodynamic equilibrium with calcite (e.g., Turekian 1976). The widespread availability of CaCO_3 buffers the pH of seawater to mildly alkaline values around 8. Even fairly large variations in the partial pressure of CO_2 therefore only induce relatively small shifts in the pH of ocean waters. It is likely that this buffering mechanism has been operational at least since the early Cambrian, and has effectively kept seawater pH within a relatively narrow range. Buffering of seawater pH by biogenic CaCO_3 may have helped create stable environmental conditions in which complex marine life forms could evolve during the Phanerozoic.

The biological control on seawater carbonate chemistry probably extends much further in time, however. Some of the oldest life forms in the geological record, cyanobacteria, are associated with calcareous formations called stromatolites. These have been around since the Archean, but are particularly abundant in sedimentary rocks from the Proterozoic (Van Andel 1994). The CaCO_3 of stromatolites is a by-product of the photosynthetic activity of the cyanobacteria, not an intracellular biomineralization process under direct genetic control. From the viewpoint of the carbonate chemistry of seawater, however, it makes little difference how CaCO_3 is produced. In fact, given enough time, supersaturated (undersaturated) seawater will precipitate (dissolve) CaCO_3 , even in the absence of any biological involvement. Thus, to a first approximation, cyanobacteria and, later, calcifying invertebrates simply turned the existing chemical equilibria of the CaCO_3 –seawater system to their advantage.

The story is different for silica-secreting organisms. During the Precambrian, prior to biological silicification, the marine silica cycle was probably dominated by sorption reactions of dissolved silicic acid to clay minerals, zeolites and organic matter (Siever 1992). There is no compelling evidence for large-scale accumulation of primary silica deposits. Compared to today, the oceans at the start of the Phanerozoic were highly enriched in dissolved silicic acid, with concentrations on the order of 1 mM (Siever 1992). Silica-secreting biota, in particular radiolarians and siliceous sponges, took advantage of this high abundance of silicic acid.

During the first half of the Phanerozoic, radiolarians were the dominant predators in the plankton food chain. The availability of dissolved silica, however, started to decline dramatically after the appearance of diatoms (Racki and Cordey 2000). It is believed that many of the evolutionary trends in biosiliceous biota are related to increased competition

for a dwindling oceanic reservoir of silicic acid (e.g., Conley et al. 1994). Diatoms clearly won the competition and have been the predominant group of marine siliceous organisms for the last 60 Ma. They currently account for about half of total marine primary production (Nelson et al. 1995).

Today, the concentration of dissolved silicic acid in the deep ocean rarely exceeds 250 μM . In surface waters, the concentrations are typically below 30 μM . The oceanic silica cycle has thus fundamentally changed since the Precambrian. While at first silica was an abundant resource, the oceans are now silica-starved. In order to maintain high siliceous productivity, biogenic silica must be continuously recycled to silicic acid. Efficient recycling is only possible because diatoms keep seawater highly undersaturated with respect to biogenic silica. Silicon in the oceans has thus evolved from a non-biogenic to a highly biogenic element. In contrast, calcium and (inorganic) carbon have retained part of their non-biogenic character.

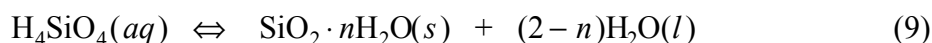
There have been suggestions that during the early Cambrian secretion of phosphatic shells may have been more common than that of calcareous ones (Van Andel 1994). Certainly some brachiopods opted for calcium phosphate mineralization. Nonetheless, the vast majority of phosphatic hard parts in the geological record have been produced by crustaceans and marine vertebrates. The reason why calcium phosphate was never used on a large scale by protists and most invertebrate groups may reflect the scarcity of phosphorus in the environment. Phosphorus is absolutely essential for the synthesis of soft tissue and, hence, indispensable to all organisms. Thus, even at the start of the Phanerozoic, phosphorus was probably in short supply, compared to Ca, C and Si. This would have put organisms building phosphatic hard parts in a competitive disadvantage, compared to those opting for silica or calcium carbonate. The disadvantage would have been most severe for organisms at the lowest trophic levels, which dominate the production of biomass.

In the end, only higher organisms, starting with fishes in the Silurian, have been producing phosphatic body parts to any considerable extent. The production and preservation of B-CaP was probably never a decisive factor in the oceanic phosphorus cycle, except during periods of prolonged ocean anoxia. Recent modeling results indicate that under conditions of reduced circulation and, hence, decreased ocean ventilation, B-CaP may become a significant phosphorus sink (Slomp et al. 2003). Enhanced burial of B-CaP under anoxia fits with the observation that black shales are often enriched in well-preserved fish debris, compared to bioturbated shales (Wignall 1994).

MARINE BIOGEOCHEMICAL CYCLE OF SILICON

Controls on biosiliceous production

With the exception of the earth's core, the geosphere consists primarily of silicon and oxygen atoms, with some cations thrown in between. Silicate compounds, under the form of minerals, rocks and melts, are therefore dominant players in the geological rock cycle. Yet, silicon is also a major biogenic element. The availability of dissolved silicate can dramatically affect the structure, health and productivity of marine, freshwater and terrestrial ecosystems (Brzezinski et al. 1990; Epstein 1994). Some organisms have an absolute requirement for silicon. These organisms use dissolved silicate to build structural elements of hydrated, amorphous silica, or biogenic opal. The overall reaction describing this biomineralization process is



The productivity of the main group of primary producers in the oceans, diatoms, is directly dependent on the supply of dissolved silicic acid. For normal growth, diatoms need

about as much silicon as nitrogen (on a molar basis). When nutrients are plenty, diatoms can displace other primary producers, because of their relatively high photosynthetic capacity and low maintenance energy requirements. Therefore, diatoms often dominate the early stages of open ocean blooms. They are also abundantly present in coastal seas and upwelling areas, where nutrient supplies are high. Accumulation rates of biogenic silica and the composition of diatom assemblages in sediments have been used as indicators of paleo-productivity and paleo-upwelling intensity (e.g., Koning et al. 1997, 2001).

Short-term fluctuations of biogenic silica production by diatoms in a particular oceanic area are controlled by factors such as light intensity, hydrographic conditions and nutrient status of upwelling waters. However, for periods of time on the order of, or longer than, the oceanic turnover time of H_4SiO_4 ($1-2 \times 10^4$ years), global biosiliceous production is regulated by the oceanic sources and sinks of silica. Because the turnover time of H_4SiO_4 is significantly longer than the characteristic time scale of mixing of the oceans, which is on the order of a few thousands of years, a simple box model can be constructed to represent the long-term marine silica cycle (Fig. 3).

The oceans are assumed to consist of two, internally homogeneous, reservoirs: dissolved (bioavailable) H_4SiO_4 and biogenic silica. Input of new H_4SiO_4 to the oceans is due to river inflow and hydrothermal venting. During seawater-basalt interactions at mid-oceanic ridges, H_4SiO_4 is released and transported to the water column by hydrothermal circulation. River inflow is by far the dominant supply route of new H_4SiO_4 to the oceans, however (Bernier and Bernier 1996). Biosiliceous production (i.e., the forward reaction in Eqn. 9) is sustained by the input of new H_4SiO_4 , but also by H_4SiO_4 regenerated during the dissolution of biogenic silica (i.e., the backward reaction in Eqn. 9). Some of the biogenic silica produced by diatoms, but also radiolarians and silicoflagellates, escapes dissolution and is buried in sediments, below the zone of early diagenesis.

At the time scales considered ($\geq 10^4$ years), the oceanic silica cycle remains close to steady state. Hence, the following relationships exist between the fluxes shown in Figure 3:

$$\text{IN} = \text{BUR} \quad (10)$$

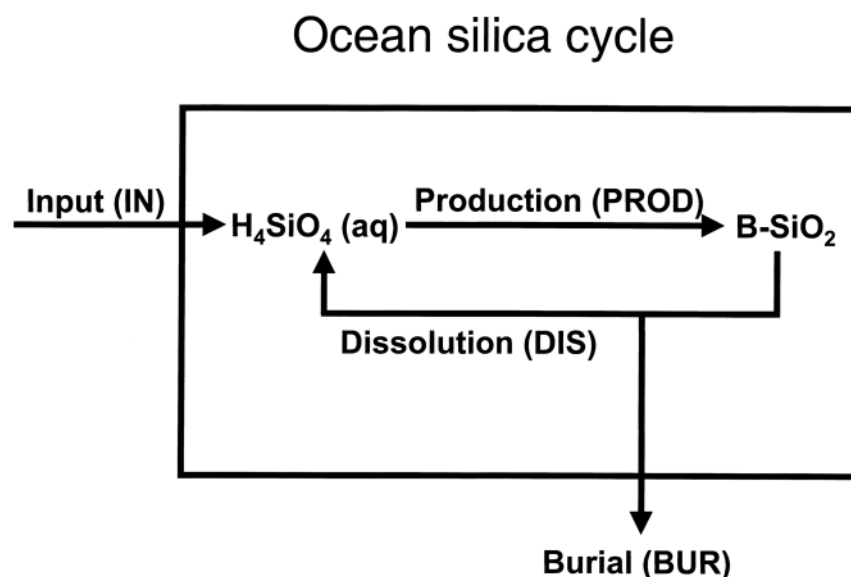


Figure 3. Box model representing the long-term ($\geq 10^4$ years) marine silica cycle. See text for discussion.

and

$$\text{PROD} = \text{IN} + \text{DIS} \quad (11)$$

Furthermore, we can define the dissolution (or recycling) efficiency

$$\alpha = \frac{\text{DIS}}{\text{PROD}} \quad (12)$$

where $0 \leq \alpha \leq 1$. In the modern ocean, α is on the order of 0.97, reflecting very efficient silica recycling. Combining Equations (11) and (12), we obtain

$$\text{PROD} = \frac{\text{IN}}{(1-\alpha)} \quad (13)$$

The denominator in Equation (13), $(1-\alpha)$, can also be viewed as the ocean-wide biogenic silica preservation efficiency.

According to Equation (13), for marine production of biogenic silica to increase either the external supply of H_4SiO_4 must increase or the preservation efficiency must decrease, or both. The numerator and denominator of the right-hand side of Equation (13) are related to processes such as silicate weathering, volcanic-seawater interaction, dissolution plus ageing of biosiliceous shells, and sediment burial. In other words, Equation (13) links the global rate of silica biomineralization in the oceans to geological and geochemical processes that regulate the oceanic sources and sinks of silica.

Weathering

The main source of new silica for the oceans is delivery by rivers of H_4SiO_4 produced by weathering of silicate rocks on the continents. Broadly speaking, silicate minerals consist of SiO_4^{4-} tetrahedra that are linked together by strong (covalent) $\equiv\text{Si}-\text{O}-\text{Si}\equiv$ (siloxane) bonds. The exception is olivine where the SiO_4^{4-} units are not linked, but instead separated from one another by cations, mainly Fe^{2+} and Mg^{2+} . Because its mineral structure is held together by much weaker electrostatic forces, olivine dissolves much faster than other silicates. Olivine is a major constituent of the basaltic oceanic crust, it is relatively rare in continental rocks. Therefore, the rate-controlling steps in the dissolution of silicate minerals commonly exposed on land are rather similar and involve the breaking, or hydrolysis, of $\equiv\text{Si}-\text{O}-\text{Si}\equiv$ and, in aluminosilicates, also $\equiv\text{Si}-\text{O}-\text{Al}\equiv$ bonds.

With the exception of olivine, dissolution rates of silicate minerals measured in the laboratory fall in a fairly narrow range. At room temperature and under near-neutral conditions the rates are typically on the order of 10^{-12} to 10^{-11} mol Si m² s⁻¹ (e.g., Brady and Walther 1989). A long-standing problem in geochemistry is to relate these experimental dissolution rates to regional or global scale weathering rates (e.g., Velbel 1993). To illustrate the magnitude of the problem, a theoretical weathering flux of dissolved silicic acid is calculated by extrapolating the experimental dissolution rates. The calculation also illustrates the type of rough approximations that are often involved in making global flux estimates.

The main difficulty is to estimate the amount of silicate mineral surface area exposed on the continents. Let us start by assuming that limestones, which cover about 15% of the continental surface area (Garrels and Mackenzie 1971), do not contribute significantly to silicate weathering. Let us further assume that a 10 cm deep weathering layer covers 50% of the remaining continental area. The volume of the active weathering layer is then approximately 6.5×10^{12} m³. This is likely a minimum estimate, as nearly 60% of the continental surface are assumed not to be subjected to chemical weathering. Using (low)

estimates of the density (1 g cm^{-3}) and specific surface area ($0.1 \text{ m}^2 \text{ g}^{-1}$) of silicate minerals in the weathering layer, the total exposed silicate mineral surface area is then $6.5 \times 10^{17} \text{ m}^2$. Combining this value with the dissolution rates given above (10^{-12} to $10^{-11} \text{ mol Si m}^2 \text{ s}^{-1}$), the total flux of dissolved H_4SiO_4 produced by weathering should be comprised between 29 and 290 Tmol per year.

This extrapolation is fraught with uncertainties, yet it conveys a simple message. Even with low estimates of the exposed silicate mineral surface area, the laboratory dissolution rates predict weathering rates that are much higher than the total flux of H_4SiO_4 delivered by rivers to the oceans. The latter is on the order of 6 Tmol per year (Tréguer et al. 1995). There are a number of reasons for this discrepancy (Velbel 1993; Berner and Berner 1996). In contrast to experiments conducted in reactors, much of the available mineral surface area in soils may only be intermittently in contact with soil solution. This is particularly true in dry climates and in highly aggregated soils. Thus, the mineral surface area that is actually dissolving is only a fraction of the total available surface area. Soil formation also reduces the net production of silicic acid through the precipitation of secondary silicate minerals. The total river flux of H_4SiO_4 is further reduced because of hydraulic short-circuiting in watersheds, internal continental drainage, as well as biogenic silica retention in aquatic and terrestrial ecosystems.

Upscaling from laboratory dissolution rates to global weathering fluxes thus requires a combination of approaches (Fig. 4). In the same way that biogeochemical cycles respond to different forcings depending on the spatio-temporal scale of interest, the different approaches yield information on processes and variables acting at variable scales. Typically the interpretation of data and observations at a given scale relies on process-based knowledge from the underlying scales. For example, climate may affect continental weathering rates through the direct effect of temperature on mineral dissolution rates, or via its effects on vegetation, rainfall and mechanical erosion. A

scale	approaches/methods	processes/variables
micro	reactor experiments	temperature solution composition
macro	column experiments	mineralogy soil hydraulics
meso	mesocosms	vegetation mechanical weathering dual porosity
subregional	catchment studies	catchment hydraulics lithology soil formation
regional	regional mass balances	climate ice cover lakes
global	global budgets	continental drainage & elevation

Figure 4. Approaches for studying weathering rates: different approaches yield information on controls acting at different scales, from the molecular to global scale. Typically, mechanistic understanding at one scale helps rationalize observations made at higher scales.

mechanistic understanding of the individual effects is therefore needed in order to derive meaningful mathematical representations of the net effect of climate on the global H_4SiO_4 weathering flux. This understanding can be obtained through laboratory experimentation and observations at the catchment level.

Preservation of biogenic silica

The high productivity of diatoms in the oceans requires a very efficient dissolution of diatom frustules after the organisms die, in order to regenerate H_4SiO_4 . The high dissolution efficiency, in turn, is due to the high degrees of undersaturation of seawater with respect to biogenic silica. This is illustrated in Figure 5, which shows silica solubilities measured experimentally on fresh phytoplankton, cultured diatoms and sinking particulate matter collected at different depths of the ocean with so-called sediment traps. The general increasing tendency with depth reflects a moderate effect of pressure on the solubility of amorphous silica (Dixit et al. 2001). The measured

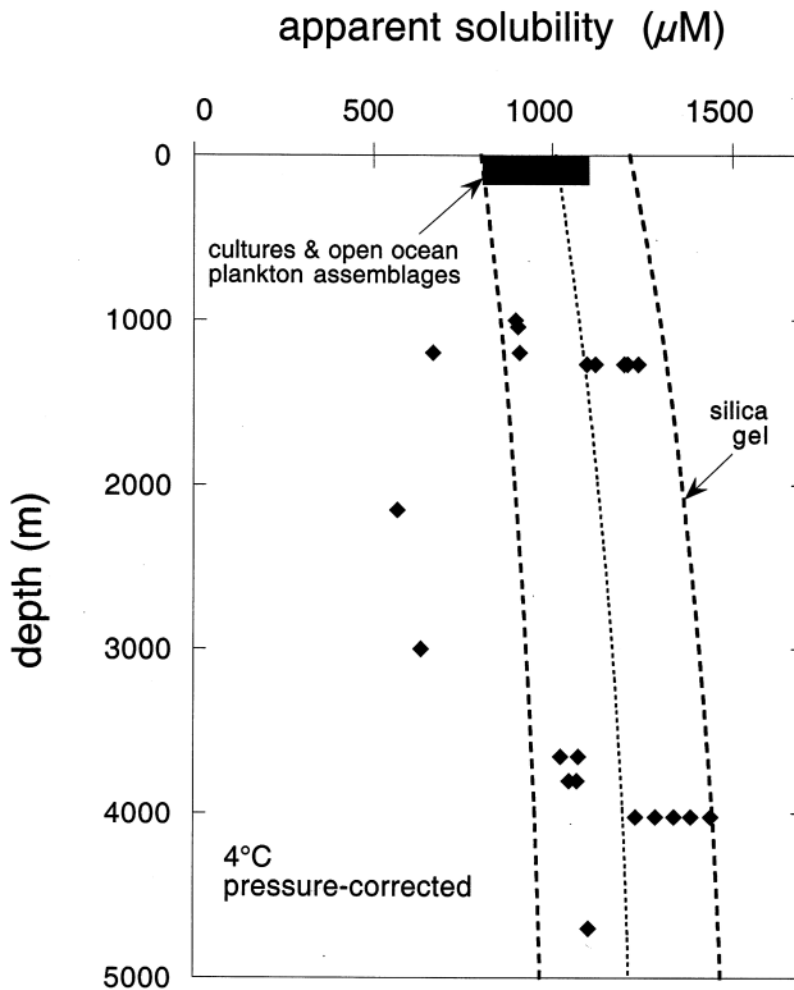


Figure 5. Silica solubilities in seawater, at 4°C. The data points are experimental solubilities measured in flow-through reactors on sediment trap samples (Gallinari 2002). The pressure correction proposed by Dixit et al. (2001) was used to account for differences in water depth. Also shown at zero depth is the range of silica solubilities reported for diatom cultures and open ocean siliceous plankton (Dixit et al. 2001). The thick broken lines are the pressure-corrected solubility of synthetic silica gel and the lower limit for plankton and diatom cultures. The thin broken line is the average biogenic silica solubility as a function of depth. The available data show that solubilities of siliceous materials sinking through the water column are consistent with solubilities measured on fresh diatoms and phytoplankton.

solubilities are all much higher than the concentrations of silicic acid observed in the oceans. In the water column, dissolved silicate concentrations rarely exceed 250 μM .

According to the results in Figure 5, all biogenic silica should dissolve in the oceans. Dissolution is prevented in living organisms by the presence of protective organic membranes. After death of the organisms, however, bacteria rapidly break down the organic membranes and dissolution starts immediately (Biddle and Azam 1999). Despite the high degree of thermodynamic disequilibrium of the oceans, some biogenic shell material nonetheless survives dissolution and accumulates at the seafloor. In its most spectacular form, this accumulation results in diatomaceous oozes that contain more than 85% SiO_2 by weight. The preservation of a fraction of the biogenic silica produced in the surface waters provides paleoceanographers with a precious record for the reconstruction of past patterns in ocean productivity, upwelling intensity and nutrient utilization (e.g., Berger and Herguera 1992; Koning et al. 2001; Brzezinski et al. 2002).

Preservation and burial of biogenic silica is explained in part by the build-up of silicic acid in the pore waters of marine sediments. Siliceous remains that manage to escape dissolution during their transit through the water column continue to dissolve after deposition. Because the solid matrix of the sediment limits turbulent solute transport, H_4SiO_4 released by opal dissolution can accumulate in the pore waters and the H_4SiO_4 concentration increases with depth. Typically, the pore water concentration stabilizes at a near constant value 5–10 cm below the sediment surface; this value is referred to as the asymptotic (or saturation) concentration, C_{sat} . It has been traditionally assumed that this concentration corresponds to the equilibrium solubility of the deposited biogenic opal. Any biogenic silica that reaches the depth of the asymptotic concentration is therefore preserved, because thermodynamic equilibrium has been reached.

A problem with this interpretation is that C_{sat} varies widely from sediment to sediment (Fig. 6). This is in sharp contrast to the fairly narrow range of silica solubilities observed in the water column (Fig. 5). In biosiliceous oozes of the Southern Ocean, C_{sat} approaches silica solubilities measured on water column samples, but in most other sediments C_{sat} is much lower than expected for equilibrium with biogenic silica (compare Figs. 5 and 6). Dixit et al. (2001) showed that the large variations in C_{sat} are related to interactions between deposited biogenic silica remains and lithogenic minerals. The lithogenic (or detrital) fraction of marine sediments consists mostly of oxides and aluminosilicate phases. Soluble aluminum produced by the slow dissolution of the lithogenic minerals interacts with biosiliceous remains, and thereby profoundly modifies their thermodynamic and kinetic properties.

Incorporation of aluminum into the surface layers of biosiliceous fragments decreases their solubility. This effect is seen even when relatively small amounts of detrital minerals are present. In batch reactor experiments where biogenic silica was mixed with model detrital phases (basalt or kaolinite), a measurable drop in apparent silica solubility was observed at mass ratios of detrital matter to biogenic silica (= %detrital:%opal) as low as 0.1 (Dixit et al. 2001). Incorporation of Al also affects the reactivity of biogenic silica. In experiments with cultured diatoms, the rate constant of dissolution decreased by nearly one order of magnitude when the molar Al/Si ratio in the frustules increased from 0.3–0.6 $\times 10^{-3}$ to 2–3 $\times 10^{-3}$ (Van Cappellen et al. 2002).

For open ocean environments, most aluminum uptake by biogenic silica occurs after deposition at the seafloor. In coastal waters, diatoms may also incorporate significant amounts of Al in their frustules during biomineralization, because of the much higher availability of aluminum in the ambient seawater (Van Beusekom 1991). In sediments with high %detrital:%opal ratios, the relatively high supply of soluble aluminum may

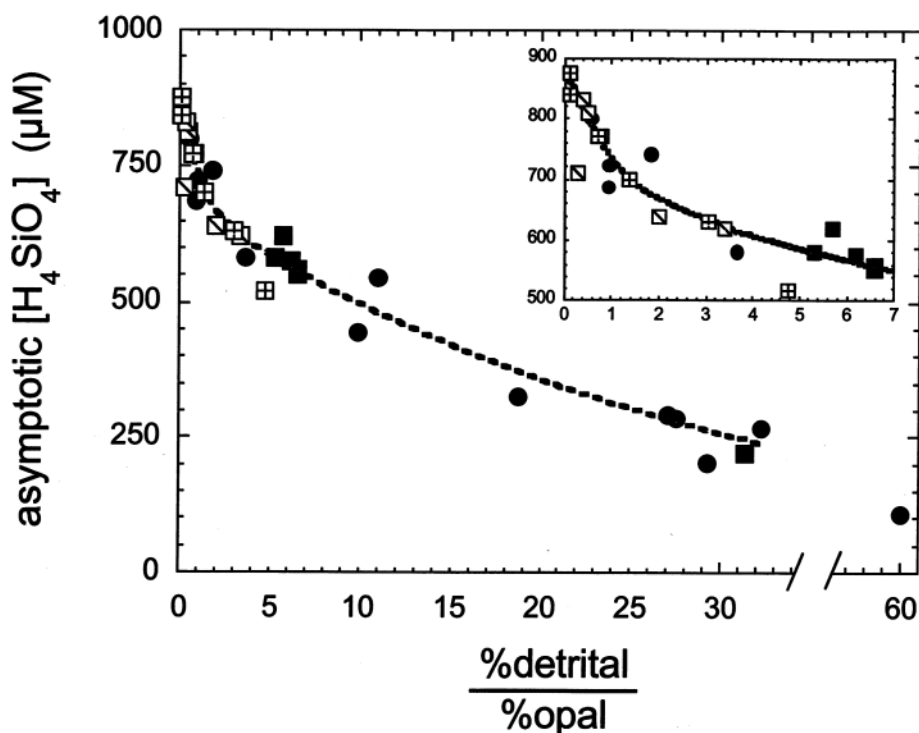


Figure 6. Asymptotic pore water concentration of silicic acid versus the detrital to opal ratio of the sediment. The different symbols correspond to a variety of ocean basins (for detailed site description and original references, see Dixit and Van Cappellen 2003). The observed inverse relationship is the result of early diagenetic interactions between biogenic silica remains and aluminum solubilized from detrital aluminosilicates.

ultimately result in the precipitation of new (authigenic) silicate minerals (Michalopoulos and Aller 1995). Formation of authigenic silicates, a process also known as “reverse weathering,” is a largely overlooked sink for reactive silica in the oceans. Whether through Al incorporation into biogenic opal or via reverse weathering reactions, increased aluminum availability in the oceans decreases the silica recycling efficiency.

The early diagenetic interactions between Al and biogenic silica explain the observed inverse relationship between the asymptotic pore water concentration of silicic acid and the %detrital:%opal ratio of marine sediments (Fig. 6). This relationship provides a striking illustration of the strong coupling between the benthic cycles of silica and aluminum. This coupling has potentially far-reaching consequences for our understanding of regional patterns and global variability of biosiliceous production in the oceans. In particular, the supply of detrital aluminosilicates mobilized by soil erosion and mechanical rock weathering on land may modulate the preservation efficiency of biogenic silica in the oceans and, therefore, by virtue of Equation (13), the biosiliceous productivity of the oceans. It is important to note in this respect that the responses of mechanical erosion and chemical weathering to changes in tectonic regime, climate or vegetation may be very different. For instance, continental glaciation is likely to increase mechanical erosion, but decrease chemical weathering.

In addition to the role of Al, biogenic silica surfaces age with time (Van Cappellen 1996). This aging further protects the biosiliceous fragments from dissolution and, hence, enhances their preservation in the sedimentary record. Preliminary acid-base titrations of freshly cultured diatom shells and older sedimentary biosiliceous oozes suggest that aging

corresponds to a loss in the surface density of ionizable silanol groups (Dixit and Van Cappellen 2002). Clearly much work remains to be done to unravel the changes in the chemical structure of biogenic silica surfaces, from the moment they are first exposed to seawater until their ultimate burial in sediments. These molecular changes, however, are ultimately responsible for the preservation of biogenic silica in marine sediments and, therefore, influence how much silica biomineralization can be sustained in the oceans.

CONCLUSIONS

In this chapter, biomineralization is analyzed within the context of global biogeochemical cycles. Of particular importance are the magnitudes of elemental fluxes associated with the secretion of mineralized tissues, but also the efficiency with which nutrients are regenerated by dissolution of biominerals. Biomineralization and subsequent regeneration are major processes in the marine cycling of C, Ca, P and Si. Biogenic silica production by land plants may rival that by marine diatoms, however. On time scales $\geq 10^4$ years, geological and geochemical processes exert a major control on global biomineralization rates. This is illustrated for the marine silica cycle. The global average rate of biogenic silica production in the oceans is regulated by the intensity of chemical weathering on the continents and by early diagenetic interactions in marine sediments.

ACKNOWLEDGMENTS

The last section is based in large measure on the PhD thesis research of Suvasis Dixit. Caroline Slomp is thanked for providing estimates of B-CaP fluxes prior to publication. The author is grateful to the volume Editors for their patience and help. Financial support from the Netherlands Organisation of Scientific Research is acknowledged (NWO Pionier Grant).

REFERENCES

- Archer DE, Maier-Reimer E (1994) Effect of deep-sea sedimentary calcite preservation on atmospheric CO₂ concentration. *Nature* 367:260-264
- Arthur MA, Dean WE, Stow DAV (1984) Models for the deposition of Mesozoic-Cenozoic fine grained organic-carbon-rich sediment in the deep-sea. *Geol Soc London Special Pub* 26:527-562
- Berger WH, Herguera JC (1992) Reading the sedimentary record of ocean's productivity. *In: Primary Production and Biogeochemical Cycles in the Sea*. Falkowski PG, Woodhead AD (eds) Plenum Press, p 455-486
- Berner RA (1987) Models for carbon and sulfur cycles and atmospheric oxygen: Application to Paleozoic history. *Am J Sci* 287:77-196
- Berner RA (1990) Atmospheric carbon dioxide levels over Phanerozoic time. *Science* 249:1382-1386
- Berner RA (1992) Weathering, plants and the long term carbon cycle. *Geochim Cosmochim Acta* 56:3225-3231
- Berner RA (1994) GEOCARB II: A revised model of atmospheric CO₂ over Phanerozoic time. *Am J Sci* 291:56-91
- Berner RA, Berner EK (1996) *Global Environment: Water, Air, and Geochemical Cycles*. Prentice Hall
- Berner RA, Berner EK (1997) Silicate weathering and climate. *In: Tectonic Uplift and Climate Change*. (Ruddiman WF) Plenum Press, p 353-365
- Berner RA, Canfield DE (1989) A new model for atmospheric oxygen over Phanerozoic time. *Am J Sci* 289:333-361
- Berner RA, Kothavala Z (2001) GEOCARB II: A revised model of atmospheric CO₂ over Phanerozoic time. *Am J Sci* 301:182-204
- Biddle K, Azam F (1999) Accelerated dissolution of diatom silica by marine bacterial assemblages. *Nature* 397:508-512
- Brady PV, Walther JV (1989) Controls on silicate dissolution rates in neutral and basic pH solutions at 25°C. *Geochim Cosmochim Acta* 53:2823-2830
- Broeker WS, Peng TH (1982) *Tracers in the Sea*. Eldigio Press

- Brzezinski MA, Olson RJ, Chisholm SW (1990) Silicon availability and cell-cycle progression in marine diatoms. *Mar Ecology Progress Series* 67:83-96
- Brzezinski MA, Pride CJ, Franck VM, Sigman DM, Sarmiento JL, Matsumoto K, Gruber N, Rau GH, Coale KH (2002) A switch from $\text{Si}(\text{OH})_4$ to NO_3^- depletion in the glacial Southern Ocean. *Geophys Res Letters* 29:doi:10.1029/2001GL014349
- Caldeira K, Kasting JF (1992) The life span of the biosphere revisited. *Nature* 360:721-723
- Canfield DE (1989) Sulfate reduction and oxic respiration in marine sediments: Implications for organic carbon preservation in euxinic environments. *Deep-Sea Res* 36:121-138
- Chameides WL, Perdue EM (1997) *Biogeochemical Cycles: A Computer-Interactive Study of Earth System Science*. Oxford University Press, New York
- Conley DJ (2002) Terrestrial ecosystems and the global biogeochemical silica cycle. *Global Biogeochem Cycles* 16: doi:10.1029/2002GB001894
- Conley DJ, Zimba PV, Theriot E (1994) Silica content of freshwater and marine diatoms. *In: Proceedings of the 11th International Diatom Symposium*. Kocielek JP (ed) California Academy Sci Memoir 17:95-101
- De Angelis DL (1992) *Dynamics of Nutrient Cycling and Food Webs*. Chapman and Hall
- Dixit S, Van Cappellen P (2002) Surface chemistry and reactivity of biogenic silica. *Geochim Cosmochim Acta* 66:2559-2568
- Dixit S, Van Cappellen P (2003) Predicting benthic fluxes of silicic acid from deep-sea sediments. *J Geophys Res – Oceans* (in press)
- Dixit S, Van Cappellen P, van Bennekom AJ (2001) Processes controlling solubility of biogenic silica and pore water build-up of silicic acid in marine sediments. *Mar Chem* 73:333-352
- Drever JI, Li Y-H, Maynard JB (1988) Geochemical cycles: the continental crust and the oceans. *In: Chemical Cycles in the Evolution of the Earth*. Gregor CB, Garrels RM, Mackenzie FT, Maynard JB (eds) Wiley, p 17-53
- Epstein E (1994) The anomaly of silicon in plant biology. *Proceedings of the National Academy of Sciences USA* 91:11-17
- Falkowski PG, Barber RT, Smetacek V (1998) Biogeochemical controls and feedbacks on ocean primary production. *Science* 281:200-206
- Gallinari M (2002) *Dissolution et Préservation de la Silice Biogénique dans les Sédiments Marins*. PhD Thesis, Université de Bretagne Occidentale
- Garrels RM, Mackenzie FT (1971) *Evolution of Sedimentary Rocks*. Norton
- Garrels RM, Mackenzie FT (1972) A quantitative model for the sedimentary rock cycle. *Mar Chem* 1:27-41
- Harvey LDD (2000) *Global Warming: The Hard Science*. Prentice Hall
- Klaas C, Archer DE (2002) Association of sinking organic matter with various types of mineral ballast in the deep sea: Implications for the rain ratio. *Global Biogeochem Cycles* 16:doi:10.1029/2001GB001765
- Koning E, Brummer G-J, van Raaphorst W, van Bennekom AJ, Helder W, Iperen J (1997) Settling, dissolution and burial of biogenic silica in the sediments off Somalia (northwestern Indian Ocean). *Deep-Sea Research* 44:1341-1360
- Koning E, van Iperen JM, van Raaphorst W, Helder W, Brummer G-JA, Weering TCE (2001) Selective preservation of upwelling-indicating diatoms in sediments off Somalia, NW Indian Ocean. *Deep-Sea Research* 48:2473-2495
- Lane N (2002) *Oxygen: The Molecule that Made the World*. Oxford University Press, New York
- Lasaga AC (1981) Dynamic treatment of geochemical cycles: Global kinetics. *Rev Mineral* 8:69-109
- Mackenzie FT (1998) *Our Changing Planet: An Introduction to Earth System Science and Global Environmental Change*. Prentice-Hall
- Mackenzie FT, Ver LM, Lerman A (2002) Century-scale nitrogen and phosphorus controls of the carbon cycle. *Chem Geol* 190:13-32
- Martin RE (1995) Cyclic and secular variation in microfossil biomineralization: Clues to the biogeochemical evolution of Phanerozoic oceans. *Global Planetary Change* 11:1-23
- Martin RE (1998) Catastrophic fluctuations in nutrient levels as an agent of mass extinction: Upward scaling of ecological processes? *In: Biodiversity Dynamics: Turnover of Populations, Taxa, and Communities*. McKinney ML, Drake JA (eds) Columbia University Press, p 405-429
- Martin JH, Fitzwater SR, Gordon RM (1990) Iron deficiency limits phytoplankton growth in Antarctic waters. *Global Biogeochem Cycles* 4:5-12
- Michalopoulos P, Aller RC (1995) Rapid clay mineral formation in Amazon delta sediments: Reverse weathering and oceanic elemental cycles. *Science* 270:614-617
- Milliman JD, Troy PJ, Balch WM, Adams AK, Li Y-H, Mackenzie FT (1999) Biologically mediated dissolution of calcium carbonate above the chemical lysocline? *Deep-Sea Res* 46:1653-1669

- Nelson DM, Tréguer P, Brzezinski MA, Leynaert A, Quéguiner B (1995) Production and dissolution of biogenic silica in the ocean: Revised global estimates, comparison with regional data and relationship to biogenic silica sedimentation. *Global Biogeochem Cycles* 9:359-372
- Pettijohn FJ (1957) *Sedimentary Rocks*. Harper and Row
- Racki G, Cordey F (2000) Radiolarian paleoecology and radiolarites: Is the present the key to the past. *Earth-Sci Reviews* 52:83-120
- Ragueneau O, Leynaerts A, Treguer P, DeMaster DJ, Anderson R (1996) Opal studied as a marker of paleoproductivity. *EOS* 77:491-493
- Redfield AC, Ketchum BH, Richards FA (1963) The influence of organisms on the composition of seawater. *In: The Sea*. Hill MN (ed) John Wiley, p 12-37
- Reeburgh WS (1997) Figures summarizing the global cycles of biogeochemically important elements. *Bull Ecological Soc Am* 78:260-267
- Rodhe H (1992) Modeling biogeochemical cycles. *In: Global Biogeochemical Cycles*. Butcher SS, Charlson RJ, Orians GH, Wolfe GV (eds). Academic Press
- Ruttenberg KC, Berner RA (1993) Authigenic apatite formation and burial in sediments from non-upwelling, continental margin environments. *Geochim Cosmochim Acta* 57:991-1007
- Sarmiento JL, Gruber N (2002) Sinks for anthropogenic carbon. *Physics Today* 55:30-36
- Schenuau SJ, De Lange GJ (2001) Phosphorus regeneration versus burial in sediments of the Arabian Sea. *Mar Chem* 75:201-207
- Schlesinger WH (1997) *Biogeochemistry: An Analysis of Global Change*. Academic Press
- Siever R (1992) The silica cycle in the Precambrian. *Geochim Cosmochim Acta* 56:3265-3272
- Slomp CP, Meile C, Van Cappellen P (2003) The global phosphorus cycle: Response to ocean anoxia (submitted)
- Smetacek V (1999) Diatoms and the ocean carbon cycle. *Protist* 150:25-32
- Steeffel CI, MacQuarry KT (1996) Approaches to modeling reactive transport in porous media. *Rev Mineral* 34:83-129
- Steeffel CI, Van Cappellen P (eds) (1998) *Reactive transport modeling of natural systems*. *J Hydrology* 209:1-388
- Suess E (1981) Phosphate regeneration from sediments of the Peru continental margin by dissolution of fish debris. *Geochim Cosmochim Acta* 45:577-588
- Tegelaar EW, de Leeuw JW, Derenne S, Largeau C (1989) A reappraisal of kerogen formation. *Geochim Cosmochim Acta* 53:3103-3106
- Tréguer P, Nelson DM, Van Bennekom AJ, Demaster DJ, Leynaerts A, Quéguiner B (1995) The silica balance in the world ocean: A re-estimate. *Science* 268:375-379
- Turekian KK (1976) *Oceans*. Prentice Hall
- Turekian KK (1996) *Global Environmental Change*. Prentice Hall
- Valiela I (1995) *Marine Ecological Processes*. Springer-Verlag, Berlin
- Van Andel TH (1994) *New Views on an Old Planet*. Cambridge University Press, Cambridge
- Van Beusekom JEE (1991) *Weschelwirkungen zwischen Gelöstem Aluminium und Phytoplankton in Marinen Gewässern*. PhD Thesis, University of Hamburg
- Van Cappellen P (1996) Reactive surface area control of the dissolution kinetics of biogenic silica in deep-sea sediments. *Chem Geol* 132:125-130
- Van Cappellen P, Ingall ED (1994) Benthic phosphorus regeneration, net primary production, and ocean anoxia: A model of the coupled marine biogeochemical cycles of carbon and phosphorus. *Paleoceanography* 9:677-692
- Van Cappellen P, Ingall ED (1996) Redox stabilization of the atmosphere and oceans by phosphorus-limited marine productivity. *Science* 271:493-496
- Van Cappellen P, Dixit S, van Beusekom J (2002) Biogenic silica dissolution in the oceans: Reconciling experimental and field-based dissolution rates. *Global Biogeochem Cycles* 16:1075:doi:10.1029/2001GB001431
- Velbel MA (1993) Constancy of silicate-mineral weathering-rate ratios between natural and experimental weathering: Implications for hydrologic control of differences in absolute rates. *Chem Geol* 105:89-99
- Wignall PB (1994) *Black Shales*. Clarendon Press
- Wolf-Gladrow DA, Riebesell U (1997) Diffusion and reactions in the vicinity of microalgae: A refined model. *Mar Chem* 59:17-34
- Wollast R, Chou L (1998) Distribution and fluxes of calcium carbonate along the continental margin in the Gulf of Biscay. *Aquatic Geochem* 4:369-393