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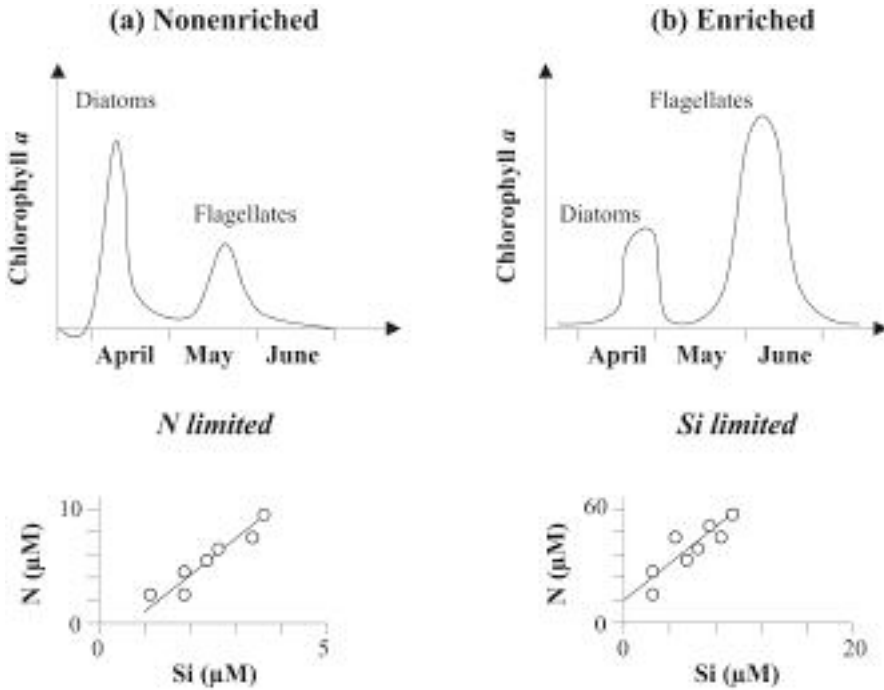
# 11

## Role of Diatoms in Silica Cycling and Coastal Marine Food Webs

Olivier Ragueneau, Daniel J. Conley, Aude Leynaert, SORCHA NI LONGPHUIRT, and Caroline P. Slomp

The importance of studying the marine biogeochemical cycle of Si arises from both an ecological and a biogeochemical perspective and is related to the importance of diatoms in the global C cycle. Diatoms form the basis of some of the most productive food chains and play a fundamental role in the export of C to higher trophic levels (Cushing 1989) and to the deep sea (Goldman 1993, Buesseler 1998). They need dissolved silica (DSi) for growth. When DSi becomes limiting (Figure 11.1), it can cause shifts from diatoms to nonsiliceous algae (Officer and Ryther 1980), which increases the likelihood of harmful algal blooms (HABs) in coastal waters (review in Smayda 1990) and decreases export to the open sea (Dugdale et al. 1995).

This chapter concentrates on the Si cycle and the ecology of diatoms in coastal waters. The role of diatoms in the biogeochemical cycle of C in the open ocean has been reviewed recently by Smetacek (1999). The continental margins are of great importance for the global Si and C cycles for two major reasons. First, continental margins may be the site of the proposed missing sink of biogenic silica (DeMaster 2002). This idea has arisen with the downward revision of the importance of the Southern Ocean in the global accumulation of biogenic silica (BSi), and a new sink is needed to balance the global Si budget. The missing sink may take the form not only of BSi but also of lithogenic silica (LSi) after the conversion of diatoms into new silicate mineral phases through reverse weathering reactions (Michalopoulos and Aller 1995; Michalopoulos et al. 2000). Second, continental margins filter DSi inputs from the land to the ocean. This is essential because DSi has been recognized as a limiting nutrient in several biogeochemical provinces of the ocean (Dugdale and Wilkerson 1998; Pondaven et al. 1998; Wong and Matear 1999), with important consequences for the efficiency of the biological pump, be it in today's ocean or during the last glacial maximum (Smetacek 1999; Ragueneau et al. 2000; Archer et al. 2000).



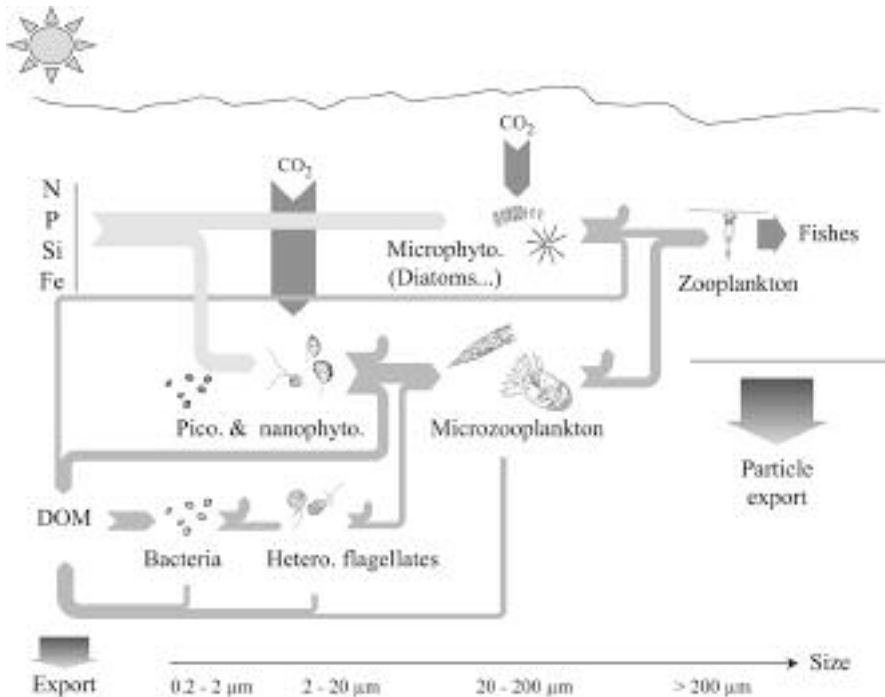
**Figure 11.1.** Classic sequence of phytoplankton dynamics in temperate waters of (a) unperturbed and (b) perturbed, nutrient-enriched coastal areas. Inspired by Billen et al. (1991). Note the switch from N to Si limitation under conditions of excessive N inputs (b).

In this review we examine several paradigms and evaluate their status relative to field and laboratory and mesocosm evidence, including the following: Diatoms are the best food for grazers (Jonasdottir et al. 1998; Irigoien et al. 2002); DSi limitation controls the shift from diatoms to nonsiliceous species (Officer and Ryther 1980); and diatoms always dominate when DSi concentrations are more than 2  $\mu\text{M}$  (Egge and Aksnes 1992). What have we learned in the past two decades that can confirm or invalidate these paradigms? First, we concentrate on the importance of diatoms in the functioning of coastal ecosystems. We start by examining the importance of diatoms in the diet of pelagic and benthic grazers, mostly copepods and bivalves. We continue by discussing the role of diatoms during HABs. We then review our knowledge of the mechanisms that control the Si cycle in coastal waters, focusing on the relative importance of the external (rivers, atmosphere, groundwater, and oceanic inputs) and internal (recycling in the water column and at the sediment–water interface) supply of DSi in sustaining the diatom demand.

## Importance of Diatoms in Coastal Ecosystem Functioning

It is widely believed that diatoms form the basis of the shortest, most economically desirable food webs, leading to fish via copepods or to shellfish without intermediate trophic levels (Ryther 1969; Cushing 1989; Figure 11.2).

This paradigm is based on numerous field observations, with two important aspects that are difficult to contest: Diatoms form the basis of the food web that characterizes the most productive regions and sustains the most important fisheries on the planet, and most of the ecological problems related to eutrophication have been encountered with nondiatom species of phytoplankton. Have we learned anything in the last two decades that could modulate this paradigm?



**Figure 11.2.** Schematic view of a pelagic food chain, inspired by the BIOGEN model (Lancelot et al. 2000), illustrating the direct, short link between diatoms and the higher trophic level, compared with the microbial network. DOM = dissolved organic matter, hetero. = heterotrophic, microphyto. = microphytoplankton, nanophyto. = nanophytoplankton, pico. = picoplankton.

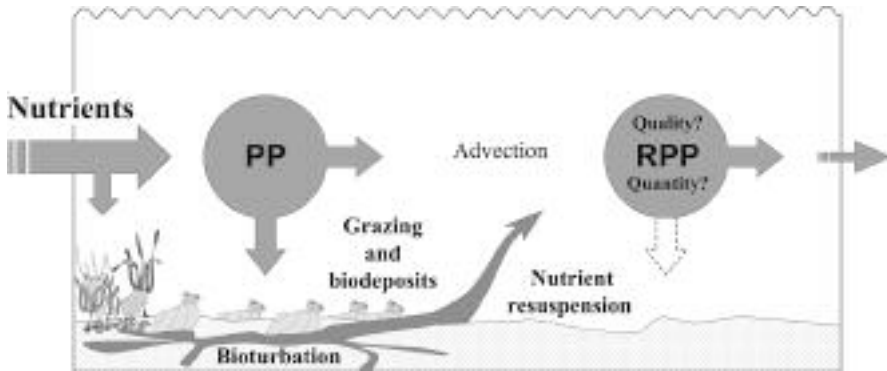
### *Diatoms and Pelagic Food Webs*

Diatoms clearly exhibit the appropriate size range for direct grazing by microzooplankton (Frost 1972). The herbivorous copepods feed directly on cells larger than 5  $\mu\text{m}$ , and the food chain from bacteria to protozoa, ciliates, and copepods is affected by energetic losses at each step (Cushing 1989; Figure 11.2). The quantity of food necessary for copepods to grow has been explored, and ecological models can now be parameterized with appropriate ingestion curves for several zooplankton taxa (Hansen et al. 1997). However, the quality of the food is as important as the quantity and remains to be investigated (Touratier et al. 1999). In this respect, there is little evidence that diatoms represent a better diet than other species of similar size. In fact, dinoflagellates have a higher volume-specific organic content than diatoms under the same growth conditions (Hitchcock 1982) and are increasingly recognized as being important in the diet of *Calanus* (review in Kleppel 1993). In addition, the ability to switch from ambush feeding and motile prey to suspension feeding when food becomes abundant relates to the prey-switching theory described by Kjørboe et al. (1996). It shows that although diatoms are good, they are not the only good food: Diversity in the diet must help copepods survive in the absence of diatom blooms or between blooms. Other groups of zooplankton are also considered nonselective. Salps can ingest 100 percent of primary production per day without performing any selection (Dubischar and Bathmann 1997). Krill shows a nonselective feeding behavior, too.

### *Diatoms and Benthic Food Webs*

In temperate and boreal coastal waters, the most prominent event in the annual flux of organic material to the benthos usually is the spring diatom bloom (Smetacek 1984; Wassmann 1991; Graf 1992; Olesen and Lundsgaard 1995). This bloom may reach the sea floor intact without being ingested by zooplankton (see Smetacek 1985 for review; Alldredge and Gotschalk 1989). Seasonally sedimented phytoplankton blooms are a major source of nutrients that are processed rapidly through the benthic system in open coastal areas (Graf et al. 1982; Gili and Coma 1998). Benthic suspension feeders are among the main contributors to the biomass of benthic communities of coastal and estuarine ecosystems worldwide (Grall and Chauvaud 2002); they benefit directly from pelagic primary production in the overlying water column (Graf et al. 1982; Christiansen and Kannevorf 1986) and are responsible for a large share of the energy flow from the pelagic to the benthic system (Figure 11.3), in addition to secondary production in benthic environments (Petersen and Black 1987; Gili and Coma 1998). What is the importance of diatoms in the diet of benthic suspension feeders?

To our knowledge, there is very little information on preference for diatoms over other phytoplankton for suspension feeders. Food uptake depends on water flow, on the size, shape, and load of the particles, and on their organic composition. The mechanisms involved have been studied in detail, and excellent reviews have been published by Jør-



**Figure 11.3.** Schematic representation of nutrient fluxes and pelagic primary production dynamics in a suspension feeder–dominated ecosystem. PP = primary production, RPP = regenerated primary production. From Grall and Chauvaud (2002).

gensen (1990), Dame (1996), and Wildish and Kristmanson (1997). These mechanisms are complex because selection can occur at different stages of particle processing (Shumway et al. 1985): retention of particles on gills, preingestive selection on gills or labial palps, and differential absorption in the gut (i.e. postingestive selection). Aside from particle sorting by phytoplankton classes, there are controversies over the importance of size, shape, or site of selection (Cognie et al. 2003 and references therein). What seems well established is that suspension feeders are able to ingest a wide spectrum of particle sizes and to sort inorganic and organic particles, preferentially rejecting inorganic particles as pseudofeces (Newell et al. 1989).

As noted by Bougrier et al. (1997), studies on feeding behavior using flow cytometry to determine different populations of particles in mixed samples are scarce (Chrétiennot-Dinet et al. 1991; Cucci et al. 1985). Results do not demonstrate any preference for diatoms compared with other phytoplankters. Even more interestingly, especially compared with zooplankton diet, several studies have shown preferential consumption of a dinoflagellate relative to a diatom of similar size and preferential rejection of these diatoms in pseudofeces (Shumway et al. 1985; Bougrier et al. 1997). Bougrier et al. (1997) hypothesized that diatoms may appear as a mineral particle because of their frustule and be rejected when particles are being sorted at the labial palps level.

Care must be taken in generalizing such results. Indeed, grazing pressure on different species of algae depends on many parameters, linked not only to the characteristics of the prey, as discussed before, but also to the age of the animal studied, the time of day, and the composition of the mixture (Chrétiennot-Dinet et al. 1991). Even among diatoms of the same genus, some species have been shown to be preferentially retained and others rejected simply because of their relative biochemical composition (Robert et al. 1989).

### *Diatoms and Harmful Algal Blooms*

Many coastal eutrophication problems are related to the development of nondiatom species, appearing in the same size range as diatoms but producing HABs. Although only about 20 of more than 1,000 species of dinoflagellates are toxic, their economic impact can be extensive (Steidinger and Baden 1984). Planktonic toxic dinoflagellates, their benthic resting stages, and their toxins can accumulate in filter-feeding animals such as clams and oysters and cause neurotoxic, paralytic, and diarrhetic shellfish poisoning; this can lead to illness or death of consumers such as birds, marine mammals, and humans. There are other ways in which blooms can be considered harmful. For example, some species, such as the prymnesiophyte *Phaeocystis pouchetii*, forms large foam banks on North Sea beaches (Lancelot et al. 1987); it also has deleterious effects on the marine food web, making a poor diet for copepods, causing low egg production and high mortality of nauplii (Tang et al. 2001).

There is abundant literature on HABs. Smayda (1990) revealed a global epidemic and related the increasing frequency and magnitude of these blooms to long-term decreasing Si:N and Si:P nutrient ratios. In a recent review, Anderson et al. (2002) detailed the various mechanisms leading to HABs, showing that nutrient balance is only one of the many factors controlling the appearance of such blooms. This important aspect is discussed further in Chapter 12. We concentrate on diatoms here and examine what we have learned recently that could modulate the previous view of diatoms as not being harmful.

Diatoms can also cause problems for grazers. The diatom *Pseudo-nitzschia australis* produces a neurotoxin, domoic acid, that killed planktivorous fish and sea lions along the central California coast (Scholln et al. 2000). Interestingly, the production of domoic acid has been linked to nutrient depletion, especially DSi (Pan et al. 1996a), P, and possibly Fe (Pan et al. 1996b). Some antiproliferative compounds have also been found in some diatoms (*Thalassiosira rotula*, *Skeletonema costatum*, and *Pseudo-nitzschia delicatissima*), leading to reduced egg hatching rates in copepods and inhibited cleavage of sea urchin embryos (Ban et al. 1997; Miralto et al. 1999). Such results are still debated in the literature (Irigoien et al. 2000). Another means by which diatoms may not be readily available for grazers is in the formation of aggregates. Under conditions that are not completely clear (Passow et al. 2001; Thornton 2002), diatoms may form large aggregates that sink rapidly to the bottom, allowing them to escape grazing by copepods, which may represent a life strategy to avoid being grazed (Smetacek 1985). However, this process may also cause problems for benthic suspension feeders. In the Bay of Brest, it has been shown that massive sedimentation of diatom blooms can cause growth anomalies in *Pecten maximus*, either through gill clogging or oxygen depletion caused by the degradation of the organic matter (Chauvaud et al. 2001; Lorrain et al. 2000).

### *Importance of Diatoms in Pelagic and Benthic Food Chains*

From this brief survey of the literature it appears that for a grazer, a diatom is important because it represents a pool of energy with the appropriate size, but only very lit-

tle preference for diatoms has been shown. If it is not the only good food, why are diatoms so important?

Although this might appear tautological, diatoms are essential simply because they are often there. They tend to dominate whenever conditions become optimal for phytoplankton growth (Guillard and Kilham 1978). These conditions are met in spring blooms (Hulburt 1990), coastal upwelling plumes (Rojas de Mendiola 1981), equatorial divergences (Dugdale and Wilkerson 1998), river plumes (Nelson and Dortch 1996; Ragueneau et al. 2002b), macrotidal coastal ecosystems (Ragueneau et al. 1994, 1996), ice edge blooms (Wilson et al. 1986; Tréguer et al. 1991), and transient open ocean blooms triggered by wind-mixing events (Marra et al. 1990), decay of ocean eddies (Nelson et al. 1989; Brzezinski et al. 1998), and atmospheric dust inputs (Young et al. 1991). Most of these situations constitute hydrodynamic singularities that tend to favor large cells (Margalef 1978; Legendre and Le Fèvre 1989). Large phytoplankton cells (e.g., diatoms and dinoflagellates) generally have a low surface to volume ratio, which leads to a need for a nutrient-rich habitat, in contrast to smaller picophytoplankton (e.g., prochlorophytes and cyanobacteria), whose higher surface to volume ratio allows more efficient exploitation of low nutrient concentrations (Chisholm 1992). Therefore, diatoms dominate in a number of regimes that offer high-nutrient and turbulent conditions. That diatoms often outcompete other algae of similar size could be related to the existence of their frustule, acting as a protection against grazers (Hamm et al. 2003), or their higher division rates under similar environmental conditions (Smetacek 1999).

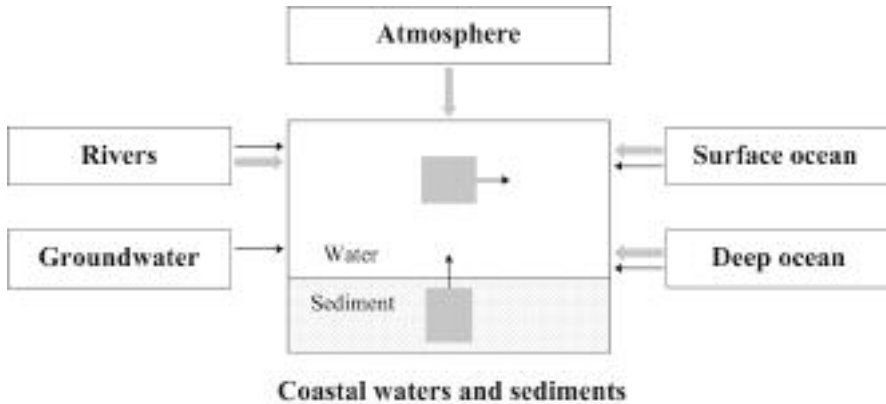
Thus, the combination of the success of diatoms at marine ergoclines (Legendre et al. 1986) and the very efficient export of C to higher trophic levels when the food chain is based on large cells probably explains why diatoms form the basis of the most productive ecosystems on the planet. In addition, there seem to be only few instances of exclusion of diatoms in a grazer diet.

## Silica Cycle in Coastal Waters

Numerous factors control the contribution of diatoms to total primary production in coastal waters. These include hydrodynamics, nutrient concentrations, and grazing by pelagic and benthic animals. In this section we concentrate on nutrients only, particularly on DSi. Physical and direct biological controls and the importance of nutrient balance are discussed in the Chapter 12. The primary question asked here is, “Where do diatoms get their DSi from?”

Coastal diatoms often are seen as being influenced only by river inputs. This is a gross oversimplification of the way diatoms satisfy their demand for DSi. The geographic position of coastal waters at the interface between land and ocean implies that diatoms can use Si coming from land, via rivers, groundwater, or the atmosphere, and from the open ocean, through advection of surface waters and upwelling. These will be called external inputs of DSi (Figure 11.4). Diatoms can also use DSi from recycling in the





**Figure 11.4.** Schematic depiction of the potential sources of Si for coastal diatoms. Coastal diatoms use external sources of Si from rivers, groundwater, the atmosphere, and the ocean; these inputs take place either directly in the form of DSi (*black arrows*) or in particulate form, as BSi or LSi (*gray arrows*), which then dissolve in coastal waters. Diatoms also use DSi coming from the recycling of BSi produced at that site, defined as internal recycling and including water column dissolution and recycling at the sediment–water interface.

water column, at the sediment–water interface and deeper in the sediments. These will be called internal inputs.

## *External Inputs*

### River Fluxes

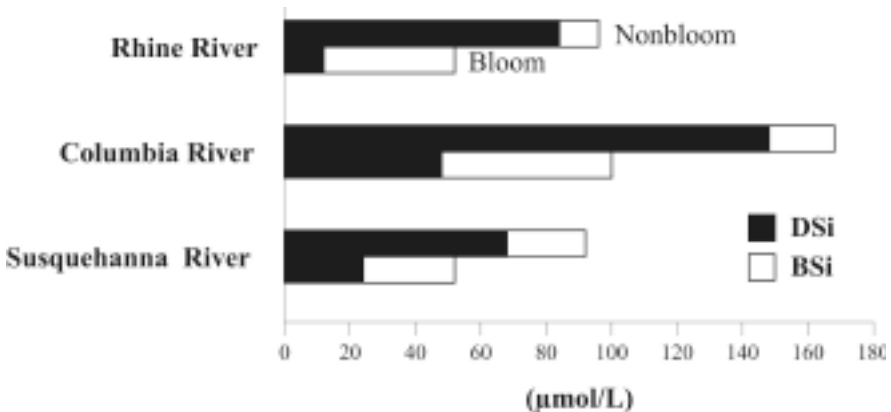
Rivers are responsible for almost 80 percent of the Si entering the global ocean (Tréguer et al. 1995). River inputs have long been seen as transporting only DSi, a product of continental rock weathering (Meybeck 1982). This view has been challenged recently because it has been shown that rivers also carry Si in various forms of particulate matter that can play a significant role as a source of Si for coastal diatoms (Conley 1997).

LSi, consisting of quartz particles, aluminosilicates, and other minerals, has long been thought to react and dissolve slowly and linearly (McKyes et al. 1974). However, many studies have demonstrated that silicate mineral dissolution proceeds in two steps, with an initial dissolution rate, higher and nonlinear, at the beginning of the process (Huertás et al. 1999). LSi concentration in coastal waters can be substantial (Ragueneau and Tréguer 1994). However, it seems reasonable to assume that aged silicate minerals being delivered by rivers will have lost this reactive phase, so the impact of their dissolution on coastal diatoms can be ignored on the time scale of biological processes. The

question of the influence of recently physically weathered silicate minerals as a potential source of DSi for coastal diatoms remains open.

BSi, being amorphous, dissolves five orders of magnitude faster than silicate minerals (Hurd 1983), so its dissolution can constitute an important, albeit poorly known source of Si for coastal diatoms. What is the importance of BSi in Si river inputs? Technical progress has been made in the last 25 years, allowing chemical methods to distinguish between LSi and BSi in suspended matter of rivers and coastal waters (DeMaster 1981; Ragueneau and Tréguer 1994; Ragueneau et al. 2005b and references therein). This allowed Conley (1997) to estimate that 16 percent of the gross riverine Si load is delivered to the world ocean as BSi (Figure 11.5). This estimate hides enormous spatial and temporal variability because the partitioning between DSi and BSi depends on many factors, especially those controlling bloom formation along the river (e.g., turbidity, water residence time).

During blooms, BSi may constitute one third of the gross delivery of Si, as in the Danube (Ragueneau et al. 2002b); it may even exceed DSi inputs, as in the Rhine (Admiraal et al. 1990; Figure 11.5). Most of this BSi was thought to be in the form of freshwater diatoms because it was easily digestible, a characteristic of diatoms. This is not surprising because diatoms have been observed in the suspended matter of many rivers (Anderson 1986; Admiraal et al. 1990; Ragueneau et al. 2002b). More recently, Conley (2002) suggested that phytoliths may well constitute an important fraction of the BSi found in sediments behind dams and may also constitute an important fraction of the BSi carried by rivers (see Chapter 3, this volume).



**Figure 11.5.** Concentrations of DSi and BSi for the Rhine (Admiraal et al. 1990), Columbia, and Susquehanna rivers during nonbloom periods and during periods when diatom blooms are present. The sum of DSi and BSi also decreases during blooms, suggesting sedimentation losses of BSi (Admiraal et al. 1990). Redrawn from Conley (1997).

Phytoliths and freshwater diatoms may constitute an important source of Si for coastal diatoms, provided they dissolve when diluted with coastal waters. What do we know about the fate of this material upon mixing with marine waters? Some fraction of Si (as the sum of DSi and BSi) is lost during transport in rivers (Admiraal et al. 1990), suggesting that sedimentation may be a sink for Si. In fact, freshwater diatoms and phytoliths can be buried in estuarine and marine sediments and constitute a source for reverse weathering reactions (Michalopoulos and Aller 1995). The fraction that is not sedimented can then either dissolve or be exported to the adjacent coastal, shelf, or ocean waters. Export of BSi to the open ocean has rarely been quantified (see DeMaster and Aller 2001 for an exception). Measurements of BSi dissolution in coastal waters have been reported (Brzezinski et al. 2003; Beucher et al. 2004), but none exist for freshwater diatoms and phytoliths. Such measurements are urgently needed to evaluate the importance of freshwater diatoms and phytoliths as a source of DSi for coastal diatoms.

### Groundwater

Submarine groundwater discharge (SGD) is a potentially important but poorly quantified source of nutrients to the coastal ocean. The nutrient flux to coastal waters through SGD is generally determined as the product of the water flux and the nutrient concentrations in the groundwater. Both are often highly variable, both spatially and temporally, which makes them difficult to quantify (Burnett et al. 2001, 2003; Slomp and Van Cappellen 2004).

Most current estimates of the global flux of groundwater entering the ocean through SGD range from 0.01 percent to 10 percent of surface water runoff (Taniguchi et al. 2002). On a regional scale, however, SGD may account for a much larger proportion of the water flux. This is particularly the case in regions where coastal aquifers consist of permeable sand or limestone (Slomp and Van Cappellen 2004 and references therein).

Concentrations of N and P in SGD are controlled mostly by anthropogenic inputs, the water residence time, and the redox conditions in coastal aquifers and sediments; they can be orders of magnitude higher than in river water. This particularly holds true for N, which is generally removed from groundwater less efficiently than P (Slomp and Van Cappellen 2004). Sources of Si are largely natural and involve weathering of feldspars, micas, sedimentary BSi, and phytoliths (Conley 2002). The behavior of Si in groundwater is largely redox independent. Concentrations of Si in groundwater are generally on the same order of magnitude as those of river water (Table 11.1).

As a consequence of the high input of N relative to Si and limited removal relative to P, N:P and N:Si ratios in SGD are generally expected to exceed those in river water and be higher than the Redfield ratio. SGD of nutrients thus could contribute to a higher occurrence of HABs over diatom blooms and hence to a deterioration of water quality in the coastal ocean in the coming decades.

**Table 11.1.** DSi concentrations in coastal groundwater at 4 locations in the United States and in average river water.

Aquifer Type and Location	Si ( $\mu\text{M}$ )	Reference
Volcanic alluvium and calcareous rock (Hawaii)	175–621	Garrison et al. (2003)
Carbonate rock (Florida)	100	Corbett et al. (2002)
Granite, sandstone, and shale (California)	350–430	Oberdorfer et al. (1990)
Sand (Long Island, New York)	50–300	Montlucon and Sanudo-Wilhelmy (2001)
Average river water	150	Tréguer et al. (1995)

### Atmospheric Inputs

Atmospheric deposition of macronutrients may modify the nutrient balance and play a major role in aquatic production by relieving nutrient limitation. There exists some literature on the role of atmospheric deposition of P, especially in lakes, where P is often limiting (Jassby et al. 1995), or during oligotrophic periods in coastal waters (Migon and Sandroni 1999). There are a number of studies regarding the importance of N deposition in coastal waters because of its possible role in eutrophication, hypoxia, and development of HABs (Paerl and Whittall 1999 for review). Literature concerning Si atmospheric deposition is far less abundant. It is discussed in detail by Tegen and Kohfeld (Chapter 7, this volume), mostly from an open ocean perspective. Such studies are of particular interest after the hypothesis of Harisson (2000), who suggested that glacial and interglacial changes in dust deposition may provide changes in DSi availability and induce switches from coccoliths to diatoms, with important implications for atmospheric  $\text{CO}_2$  concentrations.

Closer to the coast, the importance of atmospheric deposition as a source of DSi for coastal diatoms must decrease because the diatom demand is larger and the other DSi inputs to sustain this demand overwhelm that of atmospheric deposition. Let us take an example from a site (Capo Carvallo, Corsica, north Mediterranean Sea) subject to Saharan dust deposition events (Losno 1989). There, the maximum flux of LSi to the surface waters has been estimated at  $67.1 \text{ mmol Si/m}^2/\text{yr}$ . The solubility of LSi is believed to range between 1 and 10 percent (Maring and Duce 1987). Even with a 20 percent solubility, the maximum daily flux of DSi from the atmosphere will be  $0.04 \text{ mmol Si/m}^2/\text{d}$ . This value, clearly representing a maximum for a site directly under the influence of the Sahara and an exaggerated solubility, is one fifth the minimum values of BSi production encountered in oligotrophic regions (Nelson et al. 1995).

Thus, from the limited information available on Si atmospheric deposition in coastal waters, it seems that such a source can be neglected in coastal budgets. More data

will be welcome to challenge this view, especially data on the composition of dust particles and their dissolution kinetics. Dust particles may indeed contain recently eroded LSi particles, which may still contain a reactive surface layer; they may also be constituted of phytoliths (Folger et al. 1967; Romero et al. 2003), transported with burning of tropical vegetation and wind erosion of soils (Abrantes 2003).

### Oceanic Inputs

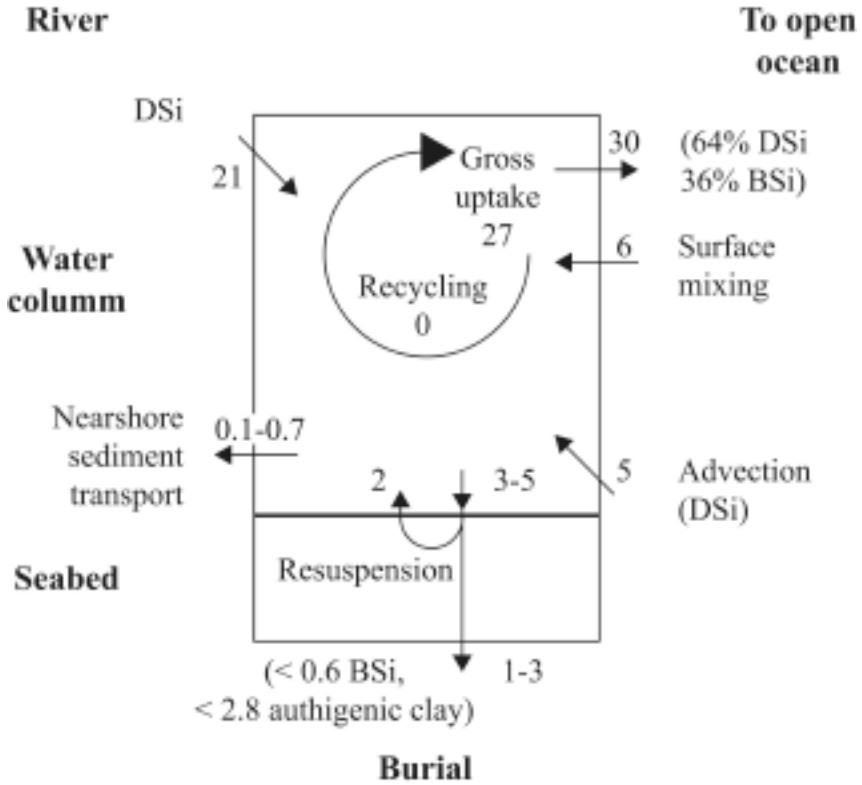
The high productivity of continental margins results from large inputs of nutrients, not only from the continents via rivers but also from the transfer of nutrient-rich deep water across the shelf break (Wollast 2002 and references therein). Obviously, its importance depends on the relative contribution of river and upwelling fluxes, both varying seasonally for a given system. Embayments with limited exchange with the ocean will be less affected than open shelves; eastern ocean boundaries will also be more affected than western ocean boundaries, where upwelling is hindered by stratification.

Ragueneau et al. (1994) estimated that no more than 5 percent of spring diatom production was sustained by oceanic inputs of DSi in a semienclosed ecosystem of northwestern Europe. However, the oceanic influence can be much larger, as reported from other ecosystems. Calvert (1966) estimated that the oceanic DSi input to the Gulf of California was two orders of magnitude higher than the riverine DSi input, and the most recent Si budget for the Amazon shelf (DeMaster and Aller 2001) suggested that advection and upwelling of offshore surface and subsurface waters represented about one third of the main external sources of DSi, and the other two thirds came from the Amazon (Figure 11.6). These examples are given simply to highlight the heterogeneity of coastal zones, especially with respect to the relative influence of external sources of nutrients.

Distinguishing land-derived from upwelling-derived DSi is essential in understanding whether higher productivity on continental margins during the late glacial maximum resulted from increased upwelling or increased supply of riverborne nutrients (Abrantes 2000; Peterson et al. 2000). Unfortunately, in the 200 nutrient budgets of the Land–Ocean Interactions in the Coastal Zone (LOICZ) project ([data.ecology.su.se/MNODE/](http://data.ecology.su.se/MNODE/)), Si is rarely included, and clearly this should be changed (Ragueneau 2004).

### *Internal Recycling*

Productivity does not depend on external inputs of nutrients only. Recycling, both in the water column and at the sediment–water interface, may play a crucial role in sustaining production, and the relative rates of Si, N, and P remineralization may affect phytoplankton dynamics to a large extent, especially the shift from diatom to nondiatom species (Officer and Ryther 1980), as we shall see in Chapter 12. In this section, we briefly discuss the factors that control Si recycling, both in the water column and at the sediment–water interface.



**Figure 11.6.** Biogeochemical Si fluxes on the Amazon shelf (modified after DeMaster and Aller 2001). Si fluxes are given in  $10^8$  mol Si/d. Illustration of the importance of oceanic inputs in total external DSi inputs, using one of the rare Si budgets in coastal waters published to date.

### Dissolution of Biogenic Silica in Surface Waters

As often occurs with recycling, the direct measurement of BSi dissolution under in situ simulated conditions is very difficult; it involves the use of stable  $^{29}\text{Si}$  and  $^{30}\text{Si}$  isotopes (Nelson and Goering 1977a, 1977b; Corvaisier et al. 2005) and the measurement of their relative abundance compared to the most abundant  $^{28}\text{Si}$  isotope, using mass spectrometry. To date, about 430 profiles of BSi production have been obtained (190 in coastal waters), particularly since to the development of the radioactive  $^{32}\text{Si}$  tracer (Tréguer et al. 1991); only 74 profiles have been obtained for dissolution, with only half of them concerning coastal waters (Beucher 2003). The dissolution to production (D:P) ratio in surface waters is very variable in coastal areas, with values as low as 0.02 in Monterey Bay (Brzezinski et al. 2003) and as high as 5.8 in the upwelling off north-

west Africa (Nelson and Goering 1977a). As observed for open ocean waters by Nelson et al. (1995), such variability cannot be explained simply in terms of latitude, temperature, or rate of production.

In fact, numerous factors affect the dissolution of biogenic silica in surface waters (reviews in Nelson et al. 1995; Ragueneau et al. 2000). These include physicochemical controls such as temperature (Lawson et al. 1978; Kamatani 1982), incorporation of trace elements such as Al (Van Bennekom et al. 1989), departure from equilibrium (Hurd 1972), or specific surface area (Hurd and Birdwhistell 1983). The influence of these factors has been reviewed recently by Van Cappellen et al. (2002). But biology also is essential for both dissolution and preservation mechanisms.

It is well known that dissolution is prevented until the organic matter coating opal surfaces has been removed (Kamatani 1982). The first evidence of a biological influence on BSi dissolution was provided by Patrick and Holding (1985) in lake studies. They demonstrated a clear increase in the solubilization of diatom frustules by natural bacterial populations, which produce hydrolytic enzymes that help to degrade the organic matter coating surrounding the frustule. Later, Bidle and Azam (1999) performed similar experiments and demonstrated bacteria-mediated increases in dissolution rates in marine waters.

More recently, it has been shown that dissolution rates of BSi can be reduced by a factor of two to three when diatoms are embedded in zooplankton fecal pellets (Schultes et al. in revision) and in aggregates (Moriceau et al. in press). These studies point to the importance of the way diatom blooms terminate. When diatoms are embedded in zooplankton fecal pellets or form aggregates, they sink very rapidly, with rates that can exceed that of single cells by two orders of magnitude (Fowler and Smaal 1972; Alldredge and Gotschalk 1989). Such fast sinking associated with reduced dissolution rates and very shallow coastal waters implies that diatoms probably spend very little time in the undersaturated surface waters of coastal areas. Thus, it is believed that most BSi dissolution in coastal areas takes place at the sediment–water interface and within the sediment column.

### Dissolution of Biogenic Silica at the Sediment–Water Interface

Coastal waters, from estuaries to the shelf break, are shallow. This unique property induces strong interactions between pelagic and benthic compartments. The ecology and biogeochemistry of the sediment–water interface and upper sediment column depend strongly on pelagic production; in turn, pelagic production can be strongly affected by processes occurring on the seabed. The latter occurs directly, via filtering activities, and indirectly, via the recycling of nutrients caused by shallow depths and tidal mixing. Several excellent reviews demonstrate the importance of this interaction (Suess 1980; Heip et al. 1995; Jørgensen 1996; Marcus and Boero 1998; Soetaert et al. 2000; Cloern 2001; Grall and Chauvaud 2002; Middleburg and Soetaert 2003). In the next section we highlight the importance of the sediment–water interface as an essential

source of DSi for pelagic diatoms. We then describe the processes that affect Si cycling at the sediment–water interface, with a major emphasis on three aspects as they modulate benthic fluxes on various time scales: reverse weathering reactions, BSi production by benthic diatoms, and biodeposition by invasive species.

### *Importance of DSi Benthic Fluxes*

A number of methods are available to quantify Si recycling at the sediment–water interface, including direct measurements of DSi benthic fluxes by means of benthic chambers (Callender and Hammond 1982; D’Elia et al. 1983; Berelson et al. 1987) or core incubation (Ragueneau et al. 1994, 2002a). Fluxes can also be estimated indirectly, using the gradient of porewater DSi concentrations near the sediment–water interface. This approach has often been used in the deep sea (see McManus et al. 1995; Rickert 2000 for details of the calculations) and compared with direct measurements (e.g., Ragueneau et al. 2001). Such a comparison is very interesting because consistent estimates validate the technique used (Berelson et al. 1987), and differences between measured and calculated fluxes have been interpreted as increased dissolution of BSi at the sediment–water interface (Conley et al. 1988). In coastal waters, DSi fluxes are affected by processes such as bottom water currents and irrigation (Berner 1980; Boudreau 1996; Aller and Aller 1998). Therefore, the direct approaches are generally preferred, and the numbers given here have all been derived using these direct measurements.

Examples of DSi benthic fluxes encountered in various coastal environments are shown in Table 11.2. These fluxes typically range from negative values, when the flux is directed toward the sediment, to a few tens of mmol Si/m<sup>2</sup>/d. This is typically the order of magnitude of BSi production in coastal waters (synthesis in Beucher 2003), except for coastal upwelling, where production rates can be much higher (e.g., Brzezinski and Philipps 1996).

The importance of DSi benthic fluxes as a source of coastal diatoms depends on the site, the degree of coupling between the pelagic and benthic ecosystems, and the season (DeMaster and Aller 2001; D’Elia et al. 1983). Clearly, benthic recycling plays a very important role for coastal diatoms, and this source cannot be overlooked in studies of the response of coastal ecosystems to any kind of perturbation (Chapter 12, this volume). We will now examine the mechanisms affecting DSi fluxes from the seabed.

### *Mechanisms Controlling DSi Benthic Fluxes*

Several recent reviews have addressed the processes that control the thermodynamics and kinetics of BSi dissolution in sediments (see Ragueneau et al. 2000; Van Cappellen et al. 2002; Sarmiento and Gruber 2006). Here we discuss physical, chemical, and biological influences on the Si cycling in sediments that are peculiar to the coastal zone: the importance of sediment permeability, because permeable sediments represent some 70



**Table 11.2.** DSi benthic fluxes in various coastal ecosystems.

Site	DSi Flux (mmol Si/m <sup>2</sup> /d)		Period	Reference
Lake Michigan	2.2–10.1	April–Aug (1983–1985)		Conley et al. (1988)
Bay of Brest	0.8–2.6	April–June (1992)		Ragueneau et al. (1994)
Bay of Brest	0.11–6.25	May–November (2000)		Ragueneau et al. (2002a)
San Nicolas Basin	0.9–1.3	August 1983–April 1985		Berelson et al. (1987)
San Pedro Basin	0.48–0.90	August 1983–April 1985		Berelson et al. (1987)
Potomac estuary	1–25	August 1979		Callender and Hammond (1982)
Chesapeake Bay	3.6–43.2	July 1980 and May 1981		D’Elia et al. (1983)
Skagerrak	0.55–3.97	March–September (1991–1994)		Hall et al. (1996)
Northwestern Black Sea	0.2–6.7	May 1997 and August 1995		Friedrich et al. (2002)
Long Island Sound	0.8–1.1	Winter		Aller and Benninger (1981)
Bering Sea, outer shelf	0.3–0.8	1979–1982		Banahan and Goering (1986)
Amazon shelf	0.13–1.25	August 1989– November 1991		DeMaster and Pope (1996)
Oosterschelde	7.2–112.8			Prins and Smaal (1994)
Pontevedra Ria	0.5–5.0	February–October 1998		Dale and Prego (2002)

percent of shelf sediments (Emery 1968); the importance of reverse weathering reactions, because of the importance of Al and detrital inputs to coastal sediments; the importance of benthic diatoms, because light often reaches the sediment–water interface; and the importance of biodeposition, because of the crucial role played by benthic suspension feeders in many ecosystems.

### Sediment Permeability

Sandy sediments are abundant on continental shelves (de Haas et al. 2002). Sands are permeable, and because of bedform topography, high current velocities, and wave activities, exchange of water between sediments and the water column is greatly enhanced (Precht and Huettel 2003 and references therein). This favors the transfer of particles from the benthic boundary layer to sediments and increases influxes of oxidants (Middelburg and Soetaert 2003). This in turn induces high mineralization rates in such permeable sediments, as seen from nutrient profiles and fluxes in various shelf regions (Marinelli et al. 1998; Jahnke et al. 2000; Nedwell et al. 1993). Shum and Sundby (1996) suggest that increased organic matter turnover rates in permeable sediments may be linked to enhanced BSi dissolution in such sediments. Ehrenhauss and Huettel

(2004) confirmed recently that BSi and organic matter are rapidly degraded in permeable coastal sands. Several mechanisms may be involved. The rapid advective solute exchange reduces the accumulation of regenerated nutrients in porewater (Ehrenhauss et al. 2004), which may favor BSi dissolution from a thermodynamic point of view. The macrofaunal activity may help in flushing DSi from sediments (Ehrenhauss et al. 2004), although uptake of DSi by benthic diatoms may modulate DSi efflux from the sediment (Marinelli et al. 1998). Also, desorptive fluxes may be stimulated by the large and rapid variations in porewater concentrations in such permeable sediments, leading to enhanced DSi fluxes (Gehlen and van Raaphorst 2002).

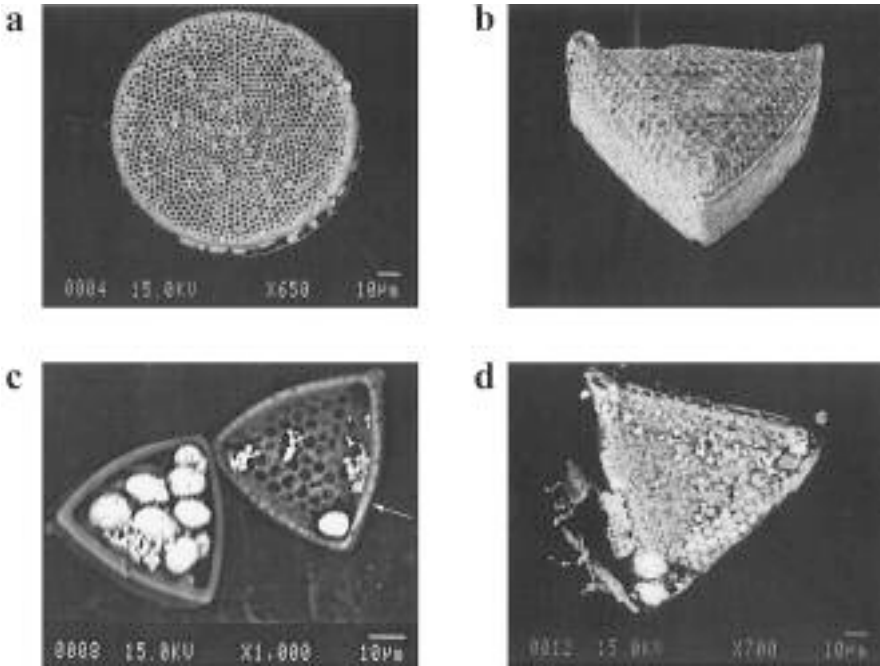
### Reverse Weathering Reactions

Geochemical reactions occurring in the sediment can also modulate the intensity of DSi benthic fluxes because some of the DSi released from diatom frustules does not diffuse out of the sediment but rather enters reverse weathering reactions. Recently, the transformation of diatom BSi to authigenic clay minerals in continental margin sediments was demonstrated (cf. Michalopoulos and Aller 1995, 2004; Michalopoulos et al. 2000) based on porewater stoichiometry, scanning electron microscope studies (Figure 11.7), and acid–base selective leaches in order to resolve whether clay minerals originate from BSi or terrestrial sources.

The BSi content of continental margin sediments is very low (about 1 wt%) and is attributed mostly to diatoms, with minor contributions from silicoflagellate skeletal material (mostly dissolved before burial), radiolarians (rare), and siliceous sponge spicules (limited to low accumulation rates). The contribution of phytoliths as a source of DSi for reverse weathering reactions is unknown. Scanning electron microscope studies confirm the transformation of diatom BSi to authigenic clays but not the extent. Clay mineral formation on the Amazon shelf (0.17 Tmol Si/yr or less) corresponds to 20 percent of the riverine Si discharge, but similar estimates must be obtained for other continental margins and on a global scale.

### Biodeposition

Biodeposition in beds of suspension-feeding bivalves results from active filter feeding by a bivalve, which leads to nondigested material being excreted to the sediment surface as feces and pseudofeces (Norkko et al. 2001). Therefore, bivalves strongly affect physical, chemical, and biological properties near the sediment–water interface (review in Graf and Rosenberg 1997). In particular, these processes typically result in local deposition rates that exceed that of passive physical sedimentation (Dame 1993; Dobson and Mackie 1998) and create an enrichment of sediments in C and N (Kautsky and Evans 1987). Beyond their effect on sediment properties, bivalve mollusks strongly influence the cycling of several biogenic elements such as carbon (Doering et al. 1987), nitrogen (Dame et al. 1991), phosphorus (Asmus et al. 1995), sulfur (Hansen et al. 1996), and inorganic carbon (Chauvaud et al. 2003). Because of the intensity of benthic–pelagic

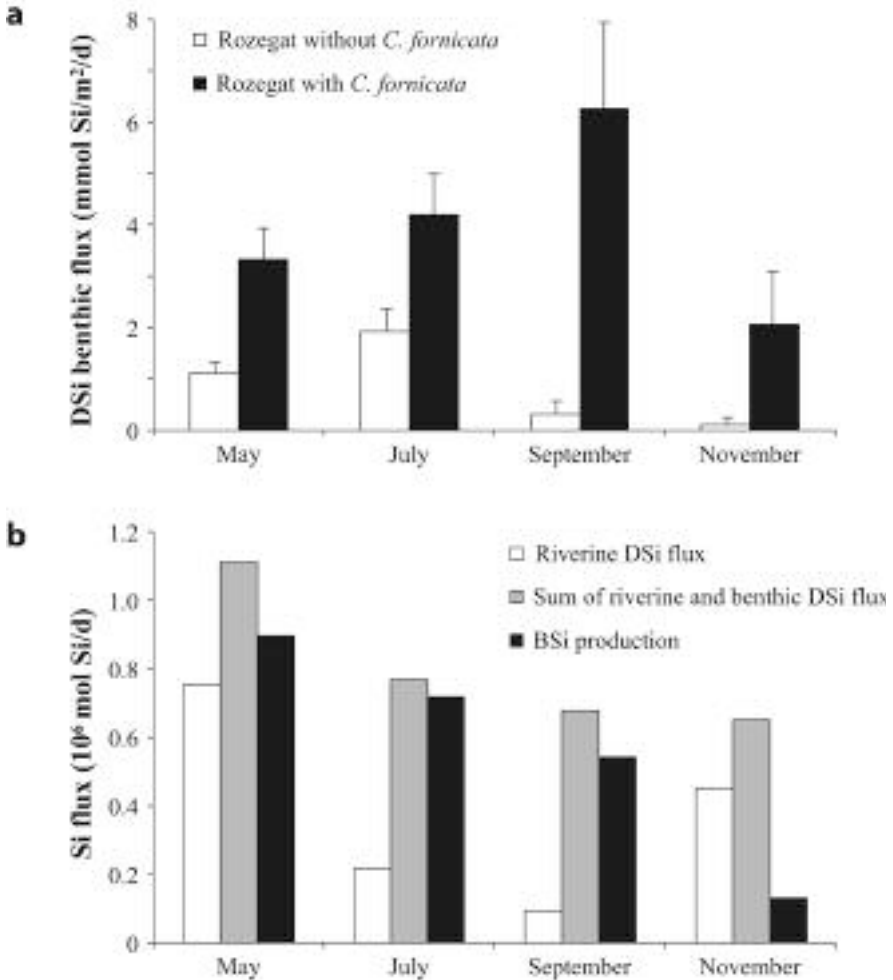


**Figure 11.7.** Representative scanning electron microscope images illustrating the range of preservation modes of distinct diatom cells (from Michalopoulos and Aller 2004). (a) Discoid diatom cell from station OST-2 (393–403 cm). Parts of the frustule aureoles are covered by aluminosilicate coatings. (b) Triagonal diatom, *Triceratium favus*, with nearly continuous authigenic aluminosilicate and metal-rich coating. (c) Valves of triagonal diatom opened to reveal internal framboidal pyrite fill. Parts of the frustule exhibit enrichments in K, Al, and Fe (arrow), whereas the remainder is unaltered. (d) Diatom in advanced stages of alteration and initial fragmentation. The microarchitecture is recognizable but extensively altered. Aureoles are filled with aluminosilicate precipitate, and the cell lumen is occupied by framboidal pyrite (from OST-2, 425–435 cm).

coupling in coastal waters, they play an essential role in the functioning of coastal ecosystems in general (Alpine and Cloern 1992; Dame 1996; Wildish and Kristman-son 1997).

Diatoms are taken up by benthic suspension feeders in the process of feeding, with regeneration of DSi from the biodeposits in the sediments (Asmus et al. 1990). Very few investigations of bivalves and bivalve beds as sources and sinks of silicon exist in the literature (Asmus 1986; Doering et al. 1987; Dame et al. 1991; Prins and Smaal 1994). Recently, Chauvaud et al. (2000) proposed that benthic suspension feeders also affect the Si cycle, with potentially important ecological and biogeochemical implications.

Ragueneau et al. (2002b) explored the ecological implications of the proliferation of a benthic suspension feeder, *Crepidula fornicata*, in the Bay of Brest ecosystem. *C. fornicata* exerts primary control on DSi benthic fluxes (Figure 11.8a), with important implications for summer phytoplankton dynamics in this ecosystem (see also Ragueneau et



**Figure 11.8.** (a) Synthesis of DSi benthic fluxes measured at 2 contrasting sites during the productive period in the Bay of Brest. *Black bars*: site Rozegat with high densities of *Crepidula fornicata* (1,243 individuals/m<sup>2</sup>, Thouzeau et al. 2000); *white bars*: site Rozegat without *C. fornicata* (<30 individuals/m<sup>2</sup>, Thouzeau et al. 2000). (b) Seasonal budgets of DSi fluxes in the Bay of Brest (Ragueneau et al. 2002a). This figure highlights the importance of benthic fluxes in sustaining the diatom demand for DSi in summer in such ecosystems.

al. 2004). Biogeochemical implications are explored by Ragueneau et al. (2005a) and described in Chapter 12 as one example of anthropogenic perturbation (proliferation of invasive species) affecting the Si cycle in coastal waters.

### Role of Microphytobenthos

Distinct benthic microalgal assemblages, consisting primarily of diatoms (McIntyre et al. 1996; Wulff et al. 1997; Facca et al. 2002), develop in most coastal areas where light reaches the sea floor (McIntyre et al. 1996) and in intertidal flats. They have been shown to act as a major control on nutrient fluxes at the sediment–water interface in myriad ways (Sundbäck and Granéli 1988; Sundbäck 1991; Epping 1996; Granéli and Sundbäck 1986; Rizzo 1990).

The combination of the concentrated microphytobenthos (MPBs) present at the sediment surface and the extra polymeric substances (Staats et al. 1999; Smith and Underwood 2000) they produce results in the formation of a biofilm, and the direct uptake of DSi by the MPBs either from the interstitial waters of the sediment or from the overlying pelagic zone can influence the release of nutrients from the underlying sediment (Srithongouthai et al. 2003; Sigmon and Cahoon 1997).

Diel variations of nutrient fluxes at the sediment–water interface in subtidal areas where MPBs are present illustrate that during periods of illumination significantly lower fluxes of DSi have emanated from the sediment than in darkened sediments (Sundbäck 1991; Sigmon et Cahoon 1997; Epping 1996). Explanations have been proposed in terms of DSi uptake being higher during the day (Syrett 1981), although DSi uptake has been recently shown to be coupled more to the cell cycle than to the day–night cycle (Martin-Jézéquel et al. 2000; Claquin et al. 2002) or, in terms of MPB active migration, shown to depend on the day–night cycle on intertidal mudflats (Blanchard et al. 1998; Serodio et al. 1997).

Benthic diatoms are highly silicified (Conley et al. 1994; Sigmon and Cahoon 1997), presumably because they live in a DSi-rich environment and most often in a low-light regime. The rate of primary production by benthic diatoms can exceed that of the pelagic production (Guarini et al. 2002). Because of this importance of benthic primary production and because benthic diatoms take up nutrients at a ratio that probably leaves less DSi behind, relative to dissolved inorganic nitrogen and phosphorus, benthic primary production has the potential to modify drastically the nutrient balance of the overlying waters. This impact must be evaluated at the scale of ecosystems, an exercise that has not been done so far for the Si cycle.

## Conclusion

The importance of diatoms in coastal food webs, both pelagic and benthic, was discussed. Diatoms often are seen as the best food for grazers. From the evidence we have gathered, diatoms are very important in carbon transfer to higher trophic levels because

of their relative size and because they are successful under conditions of high turbulence and high nutrients, not because they constitute a better diet for grazers. Given the importance of diatoms, it is essential to better understand the relative importance of the sources from which they get their nutrients.

There is a clear lack of DSi budgets in coastal waters with which to evaluate the relative importance of external and internal sources of DSi for diatom production, which varies seasonally and spatially. The limitation comes from the fact that too few laboratories measure the rate of DSi uptake directly by means of Si stable and radioactive isotopes, and even fewer measure water column recycling directly. In budgets built using the LOICZ approach (Gordon et al. 1996), Si has received much less attention than N and P, and this should be changed. Nevertheless, we have seen that rivers clearly play an important role, bringing Si in the form of dissolved but also particulate matter, both lithogenic and biogenic (freshwater diatoms, phytoliths). Among other external sources of DSi, atmospheric inputs seem to play a minor role, but data are scarce. A similar conclusion can be drawn for groundwater inputs, especially at global scale. The importance of groundwater at specific locations must be better assessed because it may modify the nutrient balance on a local scale. It is suggested that oceanic inputs may well constitute the most important source of DSi to sustain diatom productivity, especially in continental shelves subject to coastal upwelling.

When external sources decrease, internal recycling becomes very important in sustaining diatom production. More data are needed on recycling in the water column to better quantify the importance of this flux. More data exist concerning recycling at the sediment–water interface. These data show that it can sustain a very significant part of diatom production. Mechanisms that control the fate of BSi at the sediment–water interface have been described, with a particular emphasis on those specific to coastal sediments, such as their permeability, the importance of biodeposition, reverse weathering reactions, and benthic production. These mechanisms are complex, and much work is still needed before Si fluxes can be properly incorporated in models describing benthic–pelagic coupling (Soetaert et al. 2000), which plays an essential role in coastal ecosystem functioning.

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