

A review of the Si cycle in the modern ocean: recent progress and missing gaps in the application of biogenic opal as a paleoproductivity proxy

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Accepted 10 April 2000

Abstract

Due to the major role played by diatoms in the biological pump of CO₂, and to the presence of silica-rich sediments in areas that play a major role in air–sea CO₂ exchange (e.g. the Southern Ocean and the Equatorial Pacific), opal has a strong potential as a proxy for paleoproductivity reconstructions. However, because of spatial variations in the biogenic silica preservation, and in the degree of coupling between the marine Si and C biogeochemical cycles, paleoreconstructions are not straightforward. A better calibration of this proxy in the modern ocean is required, which needs a good understanding of the mechanisms that control the Si cycle, in close relation to the carbon cycle.

This review of the Si cycle in the modern ocean starts with the mechanisms that control the uptake of silicic acid (Si(OH)₄) by diatoms and the subsequent silicification processes, the regulatory mechanisms of which are uncoupled. This has strong implications for the direct measurement in the field of the kinetics of Si(OH)₄ uptake and diatom growth. It also strongly influences the Si:C ratio within diatoms, clearly linked to environmental conditions. Diatoms tend to dominate new production at marine ergoclines. At depth, they also succeed to form mats, which sedimentation is at the origin of laminated sediments and marine sapropels. The concentration of Si(OH)₄ with respect to other macronutrients exerts a major influence on diatom dominance and on the rain ratio between siliceous and calcareous material, which severely impacts surface waters pCO₂. A compilation of biogenic fluxes collected at about 40 sites by means of sediment traps also shows a remarkable pattern of increasing BSi:C_{org} ratio along the path of the “conveyor belt”, accompanying the relative enrichment of waters in

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Si compared to N and P. This observation suggests an extension of the Si pump model described by Dugdale and Wilkerson (Dugdale, R.C., Wilkerson, F.P., 1998. Understanding the eastern equatorial Pacific as a continuous new production system regulating on silicate. *Nature* 391, 270–273.), giving to Si(OH)_4 a major role in the control of the rain ratio, which is of major importance in the global carbon cycle.

The fate of the BSi produced in surface waters is then described, in relation to C_{org} , in terms of both dissolution and preservation mechanisms. Difficulties in quantifying the dissolution of biogenic silica in the water column as well as the sinking rates and forms of BSi to the deep, provide evidence for a major gap in our understanding of the mechanisms controlling the competition between retention in and export from surface waters. The relative influences of environmental conditions, seasonality, food web structure or aggregation are however explored. Quantitatively, assuming steady state, the measurements of the opal rain rate by means of sediment traps matches reasonably well those obtained by adding the recycling and burial fluxes in the underlying abyssal sediments, for most of the sites where such a comparison is possible. The major exception is the Southern Ocean where sediment focusing precludes the closing of mass balances. Focusing in fact is also an important aspect of the downward revision of the importance of Southern Ocean sediments in the global biogenic silica accumulation. Qualitatively, little is known about the duration of the transfer through the deep and the quality of the material that reaches the seabed, which is suggested to represent a major gap in our understanding of the processes governing the early diagenesis of BSi in sediments. The sediment composition (special emphasis on Al availability), the sedimentation rate or bioturbation are shown to exert an important control on the competition between dissolution and preservation of BSi in sediments. It is suggested that a primary control on the kinetic and thermodynamic properties of BSi dissolution, both in coastal and abyssal sediments, is exerted by water column processes, either occurring in surface waters during the formation of the frustules, or linked to the transfer of the particles through the water column, which duration may influence the quality of the biogenic rain. This highlights the importance of studying the factors controlling the degree of coupling between pelagic and benthic processes in various regions of the world ocean, and its consequences, not only in terms of benthic biology but also for the constitution of the sediment archive.

The last section, first calls for the end of the “NPZD” models, and for the introduction of processes linked to the Si cycle, into models describing the phytoplankton cycles in surface waters and the early diagenesis of BSi in sediments. It also calls for the creation of an integrated 1-D diagnostic model of the Si:C coupling, for a better understanding of the interactions between surface waters, deep waters and the upper sedimentary column. The importance of Si(OH)_4 in the control of the rain ratio and the improved parametrization of the Si cycle in the 1-D diagnostic models should lead to a reasonable incorporation of the Si cycle into 3-D regional circulation models and OGCMs, with important implications for climate change studies and paleoreconstructions at regional and global scale. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Si cycle; biogenic opal; paleoproductivity

1. Introduction

1.1. Prognostic climate models and paleoceanographic proxies

A thorough understanding of the interactions between the biosphere and the global environment is necessary to develop prognostic models for climate change. These models are to be used to (1) help deciphering the marine sediment record of climate change, (2) quantify the influence of the biological pump on atmospheric CO_2 , (3) make the best quantitative forecast of atmospheric CO_2 concentrations for given scenarios of future climate evolution and (4) evaluate the impact of such climate change on

marine ecosystems and biodiversity. To propose *realistic* future scenarios, these models need to be properly parametrized and validated. Process studies of the factors controlling the efficiency of the biological pump in various regions of the world ocean provide a means of both parametrizing the biogeochemical processes included in the models and testing the ability of these models to reproduce today's climate. To further test the reliability of the climate models, attempts at reconstructing past climates can be performed and validation achieved through comparison with the sedimentary record of various paleoceanographic proxies.

Past changes in oceanic productivity, which in part control the partitioning of CO_2 between the

deep sea and the atmosphere, have been inferred from the accumulation of biogenic components (organic carbon, calcium carbonate and biogenic opal; Pedersen, 1983; Lyle et al., 1988; Sarnthein et al., 1988; Brummer and van Eijden, 1992; Mortlock et al., 1991; Charles et al., 1991; Bareille et al., 1991), from the accumulation of certain metals sensitive to organic carbon fluxes (U, e.g. Kumar et al., 1995; Ba, e.g. Dymond et al., 1992), from the ratio of radionuclides scavenged from the water column ($^{231}\text{Pa}/^{230}\text{Th}$, $^{10}\text{Be}/^{230}\text{Th}$; e.g. Rutgers van der Loeff and Berger, 1993; Kumar et al., 1993, 1995), or from transfer functions based on microfossil assemblages (e.g. Mix, 1989). One of these proxies, biogenic silica (opal), holds crucial information with respect to the functioning of the biological pump, present and past.

1.2. *Biogenic opal and the global C cycle*

Diatoms play a major role in the export of organic carbon to the deep sea (Goldman, 1988, 1993; Nelson et al., 1995; Buesseler, 1998). Studying the factors controlling the contribution of diatoms to total production is therefore essential for our understanding of the mechanisms controlling the efficiency of the biological pump of carbon in various regions of today's ocean. Reconstruction of biogenic silica export is therefore also crucial for establishing export fluxes of organic carbon to the deep sea (Nelson et al., 1995; Dugdale and Wilkerson, 1998; Pollock, 1997) and $C_{\text{org}}/C_{\text{carb}}$ of the settling material (Dymond and Lyle, 1985; Archer and Maier-Reimer, 1994), two important factors for controlling TCO_2 and alkalinity of surface waters and therefore atmospheric CO_2 .

The biogenic opal record is of global significance as opal-rich sediments are found at all depths (from the shelf to the abysses), all latitudes (NW Pacific or South African coastal upwellings, Equatorial Pacific, Southern Ocean) and all climate zones of the ocean, especially in HNLC areas that play a major role in Earth climate. The Southern Ocean is the best illustration of this phenomenon since it is a system where very substantial biogenic silica accumulation takes place in today's ocean (DeMaster, 1981; Tréguer et al., 1995). This region is also considered to play a

key role in glacial/interglacial atmospheric pCO_2 variations (e.g. François et al., 1997; Broecker and Henderson, 1998). According to Sarmiento et al. (1998), the Southern Ocean may have a significant effect on a modification of the biological CO_2 pump through a greenhouse gas induced climate change, while other model studies indicate that this effect is of rather marginal importance (Maier-Reimer et al., 1996). For this reason, the opal record allows to study past ecological and climatic changes through regionally varying distributions with crucial implications at global scale. Finally, the global overall preservation efficiency (the ratio of global burial to global production in surface waters) of biogenic opal is close to 3% (Tréguer et al., 1995), which is more than one order of magnitude higher than the preservation efficiency reported by Westbroeck et al. (1993) for organic carbon. Thus, the long-term record left by opal exported from surface waters is significantly greater than that for organic carbon.

1.3. *Difficulties in interpreting the opal sedimentary record*

The role of diatoms in the biological pump, the global significance of the opal sedimentary record and the reasonably good overall preservation efficiency of biogenic opal all contribute to the idea that opal is a potentially important paleoproductivity proxy. However, the use of this proxy has been seriously questioned in the recent literature (Berger and Herguera, 1992; Kumar et al., 1995; Nelson et al., 1995; Boyle, 1998; Anderson et al., 1998). Two major arguments have been put forward: spatial and temporal variations of opal preservation and a strong decoupling of the Si and C biogeochemical cycles.

The tenet of paleoproductivity is the assumption that spatial variations in any biogenic component of marine sediments reflect spatial variations in the production of these components in the overlying surface waters. The robustness of this calibration against present-day primary production in a wide variety of oceanographic and sedimentologic settings implies that the calibration will not change through time, as conditions change (Berger and Herguera, 1992). During the last decade however, the accumulation of data related to the primary production of organic carbon and biogenic silica, resulting both

from in situ measurements and algorithms from remote sensing observations, have brought this basic concept into question. Examples of inconsistencies between surface and sedimentary fluxes are given, at global scale, for organic carbon by Jahnke (1996) and for biogenic opal by Nelson et al. (1995). Clearly, lateral advection of water masses, sediment redistribution and most importantly, spatial variations in the preservation efficiency of the biogenic matter formed in surface waters all affect the relationship potentially existing between surface water processes and the burial in underlying sediments.

The main problem in reading the opal sedimentary record in one given ecosystem in terms of biogenic silica export from overlying surface waters is the spatial and temporal variations in opal preservation. Following the assumption that the Si cycle has been at steady state for the last 15,000 years, a reasonable balance has been presented by Tréguer et al. (1995). The production of biogenic silica in surface waters is mainly sustained by the recycling of Si in the surface mixed layer, in deep waters and at the sediment–water interface. Inputs and outputs of Si (mainly introduced by rivers and removed in sediments of the Southern Ocean, the equatorial and North Pacific and along continental margins) are reasonably balanced. The high preservation efficiency of opal compared to organic constituents hides enormous spatial variations in opal recycling intensity. These variations induce a spatial distribution of silica-rich sediments in the world ocean that does not necessarily correspond to areas where carbon and silica production rates in surface water are high (Nelson et al., 1995). Although the Si budget in the Southern Ocean is actually being revised and the Antarctic Si paradox seriously diminished through higher estimates of silica productivity and lower estimates of opal accumulation (Pondaven et al., 2000b), the Southern Ocean still represents a typical example of such a contrast, since most of the global biogenic silica accumulation occurs in its sediments (DeMaster, 1981; Ledford-Hoffman et al., 1986; Leinen et al., 1986) while this ocean contributes to less than 4% of the total primary productivity of the ocean and only ~ 10% of the biogenic silica production in surface waters (Nelson et al., 1995).

The reading of the opal sedimentary record in terms of C export is further complicated by the

variable degree of coupling between the Si and C biogeochemical cycles. Such a decoupling has been invoked by Berger and Herguera (1992) and Kumar et al. (1995) to explain why the glacial increase in Equatorial Pacific and Southern Ocean productivity, evidenced by the use of other proxies, was not reflected in the siliceous sedimentary record. Several reasons may explain the existence of such a decoupling which, as we shall see, increases with depth in the water column and in the sediment. First of all, the contribution of diatoms to the total production varies from one system to another, depending upon physical (e.g. seasonality, presence of spatial and temporal ergoclines...), chemical (nutrient availability) and biological (e.g. formation of blooms) processes. These processes significantly affect the Si:C ratio of the overall phytoplankton community. In addition, the Si:C ratio of sedimenting diatoms also varies within species, depending upon the numerous factors that may influence the silicification degree of diatoms and the relative recycling of Si and C. A typical Si:C ratio of cultured diatoms grown under nutrient replete conditions is 0.13 (Brzezinski, 1985) but ratios one order of magnitude higher have been encountered in marine diatoms of the Southern Ocean for example (Quéguiner et al., 1997). The most recent studies on the role of iron in the control of nutrient consumption ratios (Hutchins and Bruland, 1998; Takeda, 1998) have been taken as strong arguments against the use of opal as a proxy for past carbon export production (Boyle, 1998).

1.4. Evidence for the need of a better calibration of proxies in the modern ocean

All proxies are subject to biasing processes such as those described for opal. The objective of this paragraph is not to review the advantages and inconvenients in using this or that proxy but simply to show a few examples of biasing processes. These include the existence of a saturation horizon for calcite preservation (Archer, 1991); the dependence of organic matter preservation upon oxygen availability (Emerson et al., 1985); the influence of air–sea exchange on the $\delta^{13}\text{C}$ of DIC (Broecker and Maier-Reimer, 1992) or the influence on the $\delta^{13}\text{C}$ of organic matter from phytoplankton growth rates (Laws et al., 1995), size (Popp et al., submitted), and

inorganic carbon source (Raven and Johnston, 1991); the spatial and temporal variability of N isotopic fractionation during nitrate uptake by phytoplankton, which affects the $\delta^{15}\text{N}$ of sedimented biogenic matter, which is also affected by further modifications at the sediment–water interface; the effect of particle composition (Taguchi et al., 1989; Walter et al., 1999; Dymond et al., 1997) and water circulation (Yu, 1994) on the ratios of trace metals and radionuclides scavenged from the water column or the dependence of trace elements accumulation upon redox conditions (François et al., 1997).

Because of the precious information they contain, paleoceanographers have to find ways of being able to interpret the records of all these proxies accurately, to derive the crucial information that will be used to better understand the relationship between climate and the biosphere and validate climate prognostic models. The first way is to develop, at a given site, a multi-proxy approach. Indeed, because every proxy is subject to different biases, combining them provides a better means of constraining past export productivity while also providing insight into the nature of the individual biasing processes. Changes in the latter (e.g. deep water circulation, oxygen concentration in bottom water, preservation of biogenic matter) can be as important for our understanding of past climatic variability as are changes in productivity. A good example is given by the debate surrounding, which of the high latitude mechanisms, higher productivity or lower vertical mixing, may be a serious candidate for the lowering of the atmospheric CO_2 concentration during glacial periods (François et al., 1997). In one case, the accumulation of authigenic uranium is taken as representative of increased organic matter deposition (Kumar et al., 1995), in the other, it reflects reduced oxygen concentrations in bottom waters as a result of reduced deep water ventilation (François et al., 1997). Resolving these competing views is one of the principle challenges facing paleoceanographers working in the Southern Ocean because each interpretation holds important implications for ocean productivity or for ocean circulation (Anderson et al., 1998).

This example of contradictory evidence from the use of several proxies at the same site calls for the crucial need of a better calibration of each proxy in the modern ocean. The inconsistencies among differ-

ent proxies probably does not result from the infidelity of each proxy, because their records are most often highly consistent at a given site, at least from a qualitative point of view, and because multiple records from a single proxy, at different but related sites, generally produce coherent responses to climate variability. Rather, quantitative interpretation of each record is difficult because of our incomplete understanding of the processes that control the production and the preservation of this proxy and its relation to the carbon cycle (Ragueneau et al., 1996a, 1997).

In this context of a more process-oriented paleoceanography (see Pisias, 1995, for other process), and given the importance of diatoms in the biological pump of CO_2 , the objective of this paper will be to review in a top-to-bottom framework, the processes affecting the production and the preservation of biogenic opal in the modern ocean, as well as those controlling the degree of coupling between the Si and C biogeochemical cycles. The aim is to show the most recent progress achieved in the study of the silica cycle in various ecosystems, to evidence the gaps in our knowledge concerning this cycle and finally to suggest some general recommendations for process and modelling studies that could be performed to enhance our ability to accurately decipher the opal sedimentary record in terms of paleoproductivity.

2. Silicon cycling: processes in the modern ocean

2.1. Cellular Si metabolism

Almost all the biogenic silica produced in the oceans is precipitated by planktonic organisms in the surface layers, and the global production of biogenic silica is dominated by diatoms (Lisitzin, 1972; Nelson et al., 1995). At this stage, it is important to note that in the context of this paper, biogenic opal will refer mostly to diatoms. Truly, although they do not contribute much to the production of biogenic silica, radiolaria can be present in important quantities in underlying sediments, especially in areas of low accumulation rates. Their record has been suggested to represent a proxy for various oceanic processes (Takahashi, 1987). But because their flux is not linked to primary production in surface waters, they

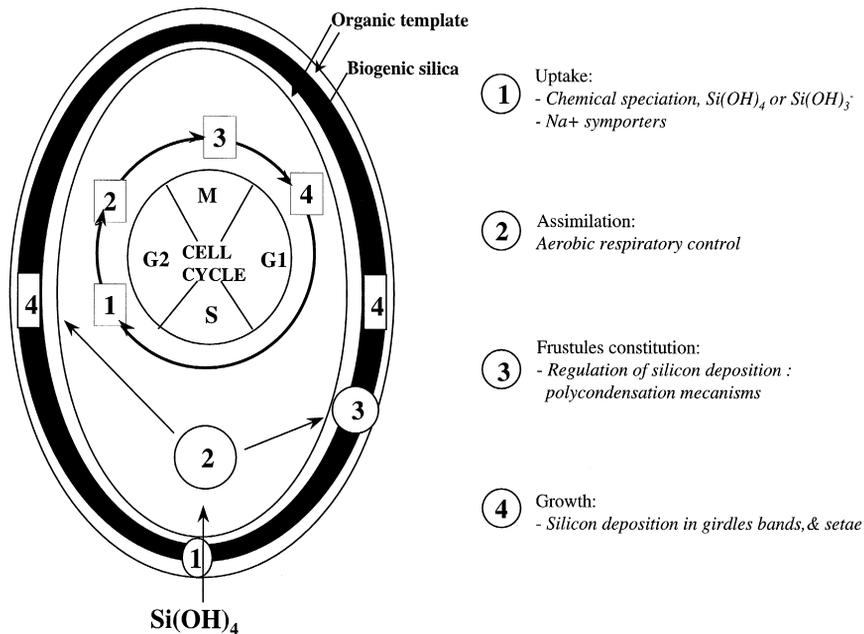


Fig. 1. Schematic view of a diatom cell, and events of the silicification processes in relation with the cell cycle. G1 and G2: gap phases; S: DNA replication; M: mitosis.

will interfere in our attempts to relate biogenic silica accumulation to export fluxes and the biological pump of CO_2 . This aspect will be discussed again in the section devoted to the measurement of biogenic opal in sediments. The focus will therefore be on diatoms, which reproduce their ornate opaline frustules with fidelity from generation to generation under strict genetic control resulting in a unique frustule morphology for each of the > 3000 known species. The details of valve morphogenesis during cell division have been examined extensively since the advent of the electron microscope and were reviewed by Pickett-Heaps et al. (1990). The biochemistry and molecular biology of diatom biomineralization is less well understood. Below the major steps in the silicification process are briefly reviewed (Fig. 1), emphasizing those aspects with significant impact on silica production, cycling and preservation in the sea.

2.1.1. Si uptake

A new class of transporters are involved in the uptake of silicon from the environment into a diatom cell, with different levels of expression during the

cell wall synthesis (Hildebrand et al., 1997; Martin-Jézéquel et al., submitted). A relatively large number of studies have examined the kinetics of Si uptake by both natural diatom assemblages (Fig. 2) and cultured clones (see below). The specific rate of Si

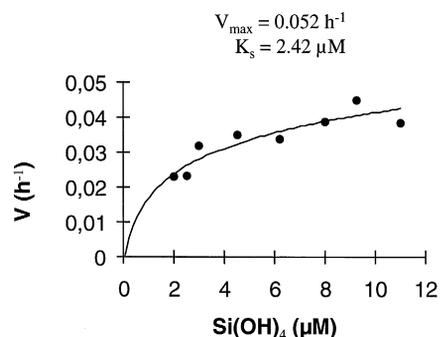


Fig. 2. Concentration dependency of silicic acid uptake rate (V) by natural diatom assemblages. Example taken from the equatorial Pacific at 180°W (Leynaert et al., in revision). Data points show the measured values of V , the curve represents the Michaelis–Menten hyperbola fitted to the data by the non-linear regression method of Wilkinson (1961).

uptake by diatoms (V) and the specific cell-division rate (μ) both increase with increasing extracellular $[\text{Si}(\text{OH})_4]$ in a manner that closely follows the Michaelis–Menten or Monod (1942) saturation functions (Goering et al., 1973; Guillard et al., 1973):

$$V = \frac{V_{\max} [\text{Si}(\text{OH})_4]}{K_s + [\text{Si}(\text{OH})_4]} \quad (1)$$

$$\mu = \frac{\mu_{\max} [\text{Si}(\text{OH})_4]}{K_\mu + [\text{Si}(\text{OH})_4]} \quad (2)$$

where V_{\max} and μ_{\max} represent the maximum rates of uptake and division, respectively, at infinite substrate concentration, K_s represents the $[\text{Si}(\text{OH})_4]$ that limits V to $0.5 V_{\max}$ and K_μ the $[\text{Si}(\text{OH})_4]$ that limits μ to $0.5 \mu_{\max}$ (e.g. Nelson et al., 1976; Harrison et al., 1976; Davis et al., 1978).

The distinction between Eqs. (1) and (2) is related to the differential regulation of uptake and growth. For many diatom species $K_\mu \ll K_s$. For temperate and tropical species K_μ typically ranges from 0.04 to 1.00 μM , and K_s from 0.5 to 5.0 μM (see numerous studies, summarized by Nelson and Dortch, 1996). Thus, many diatoms can maintain division rates very close to μ_{\max} at extracellular $[\text{Si}(\text{OH})_4]$ that clearly limits — and may strongly limit — Si uptake. Diatoms do this by producing thinner frustules thus decreasing their cellular Si content and Si:C ratio (Paasche, 1973; Brzezinski et al., 1990). This effect is clearly observable morphologically; frustules are thinner (Paasche, 1975; Davis, 1976; Harrison et al., 1977; Brzezinski et al., 1990), and siliceous spines in those species that form them are diminished or absent (e.g. Harrison et al., 1976; Brzezinski et al., 1990). Diminished frustules may make such cells more susceptible to destruction by dissolution, decreasing the likelihood of their preservation in the sediments (Lewin, 1961; Lisitzin, 1966). It is interesting to observe that other limitation, such as iron (Hutchins and Bruland, 1998; Takeda, 1998) or nitrogen (Flynn and Martin-Jézéquel, in press), can lead to the reverse effect with the building of frustules that are more heavily silicified. It has been recently hypothesized that the regulation of the silicification and the Si/cell content depends on the growth rate of the diatoms, through the proximal

agency of light and the various limiting nutrients (Martin-Jézéquel et al., submitted).

2.1.2. Silicification processes and silicon pools

The deposition of silica by diatoms is not a continuous process (Fig. 1). Individual components of the frustule are deposited during specific phases of the cell cycle (Pickett-Heaps, 1991; Schmid, 1994). The diatom frustule is basically composed of two valves, separated by a cingulum composed of intercalary bands. New valves are constructed during cell division, followed by sequential deposition of the girdle bands (Round, 1972). All diatoms deposit their valves following mitosis, but the timing of girdle band deposition and of the formation of other siliceous structures such as setae is species specific (Pickett-Heaps et al., 1990).

Diatoms do not take up silicic acid continuously or at a constant rate throughout the cell cycle. Si uptake immediately preceding cell division and valve formation has been observed for several species (Sullivan and Volcani, 1981, and references therein), while the coupling of Si uptake and its deposition during formation of the cingulum is less well known. Si uptake in *Navicula pelliculosa* is largely confined to the latter part of the cell cycle when both the valves and cingulum are being deposited (Sullivan, 1977). The coupling of uptake and division, however, may be weaker for species like *Thalassiosira weissflogii* that construct a significant fraction of their frustules (as girdle bands) at other points in the cell cycle (Brzezinski and Conley, 1994). The lack of knowledge concerning the timing of Si uptake by most diatoms hampers our ability to interpret the results of experiments examining the kinetics of Si use. Kinetic parameters for Si uptake obtained by assuming constant Si uptake by all cells can cause the K_s and V_{\max} of the active cells to be underestimated by as much as an order of magnitude (Brzezinski, 1992).

Unlike the case of nitrogen or phosphorus, internal pools of dissolved silicon are generally not sufficient to support an entire cell division without substantial additional uptake of Si from the external environment even though pools of intracellular Si play a fundamental role in mineralization processes (Azam and Volcani, 1981; Werner, 1966; Sullivan,

1979, 1986; Brzezinski and Conley, 1994). The pool size appears to depend upon the degree of coupling between uptake and mineralization during growth (Martin-Jézéquel et al., submitted, and references therein). For *Chaetoceros gracilis*, uptake and biogenic silica mineralization are tightly phased and the silicon pool is low (Chisholm et al., 1978). In contrast, Brzezinski and Conley (1994) have demonstrated that the free pool in *Thalassiosira weissflogii* can sustain up to 120% of the Si requirement for one division, because uptake and biogenic silica mineralization are uncoupled within the cell cycle for that species. Efflux of internal dissolved pools of Si has been demonstrated in culture (Sullivan, 1976). To the extent that this efflux occurs in nature, measurements of Si uptake using tracers or silica dissolution experiments employing isotope dilution techniques may be compromised.

During biogenic silica mineralization, silicon accumulates inside of a silica deposition vesicle after having been transported through the cell. Little is known regarding intracellular silicon transport in diatoms. Hypotheses range from transport via the combined interaction of small transport vesicles, dictyosomes, endoplasmic reticulum (Lee and Li, 1992) or via a silicon ionophore (Bhattacharyya and Volcani, 1983). In the mature frustule, the presence of proteins associated within the opaline matrix (Swift and Wheeler, 1992) suggests that the intricate architecture of the frustule is mediated by organic molecules. The proteins are consistently enriched with glycine and hydroxyl-containing amino acids (threonine and serine) (Hecky et al., 1973; Swift and Wheeler, 1992) that may have directly interacted with Si during its polymerization according to the polycondensation model of Lobel et al. (1996). The possible importance of glycine and serine in the biomineralization process provides a possible explanation for the relationship between Si uptake and light, as the biosynthesis of those amino acids is linked to photorespiratory metabolism in diatoms (Winkler and Stabenau, 1995) and building of these organic compounds has been shown to be closely timed to cell division in *Thalassiosira weissflogii* (Martin-Jézéquel, 1992). Once completed, the mature valve is extruded to the exterior of the cell and is coated with polysaccharides (Sullivan, 1980, 1986; Coombs and Volcani, 1968; Volcani, 1981; Li et al.,

1989; Pickett-Heaps et al., 1990; Gordon and Drum, 1994) protecting it from dissolution (Lewin, 1961).

2.1.3. Silicon uptake, diatom cell cycle and light

Silicon uptake has been shown to be tightly coupled to cell division (see above), which is not synchronized to photocycles (Prézélin, 1992). Different diatom species phase their cell-division cycles differently to daily light–dark cycles with individual species exhibiting one or more periods of enhanced cell division during the day and/or night (e.g. Azam and Chisholm, 1976; Nelson and Brand, 1979; Chisholm et al., 1978; Chisholm and Costello, 1980). Silicon metabolism and photosynthesis are not directly coupled in diatoms, even though biogenic silica production profiles generally follow carbon primary production in the field. Volcani (1978) reported that the Si uptake period of *Navicula pelliculosa* is coupled to an increase in respiration. Werner (1977) indicated that besides the energy required for transmembrane transport no further energy is needed for the biogenic silica mineralization itself. More recently, Lobel et al. (1996), using a biochemical simulation model, identified a possible low-energy reaction pathway for nucleation and biogenic silica growth during the mineralization process. According to Blank and Sullivan (1979), the differential Si uptake between light and dark should not reflect a light-dependent energy requirement for uptake itself, but rather the synthesis or activation in the light of an unstable component of the transport system.

In the field, attention should be given to this periodicity. Furthermore, uptake and mineralization are two distinct processes and their regulatory mechanisms are generally uncoupled. Uptake is the obligatory step to provide Si for silicification and other metabolism, and mineralization is an obligatory step for cell division and growth.

2.2. Biogenic silica production in surface waters

Many observations in the field are directly related to the intracellular processes described in Section 2.1.3. The rate of biogenic silica production by diatoms has been measured in numerous marine systems by means of isotopic tracers (see Table 1). As discussed above, this rate is closely linked to the rate of Si uptake in any incubation experiment longer

Table 1

Direct measurements of biogenic silica production in the world ocean, by means of the Si-30 and Si-32 isotopes. Updated from Nelson et al. (1995). “ud” means “unpublished data”

Region	# profiles	Production rate (mmol Si m ⁻² day ⁻¹)			Season	References
		Low	Mean	High		
Coastal Upwelling Areas	77	2.3	90.0	1140.0		
Baja California	25	2.3	89.0	307.0	Spring 73	Nelson and Goering, 1978
NW Africa	17	2.4	22.0	99.0	Spring 74	Nelson and Goering, 1978
Peru	25	2.6	27.0	97.0	Spring 74	Nelson et al., 1981
Monterey Bay	10	70.0	222.0	1140.0	Spring 95	Brzezinski and Phillips, 1996
Other Coastal Areas	55	0.2	14.7	131.0		
Amazon river plume	15	3.2	24.0	131.0	All year round	Nelson, ud
NW Black Sea shelf	9	0.2	6.3	16.5	Spring 97/Summer 95	Ragueneau et al., in prep.
(including Danube river plume)	5	4.4	10.6	16.5	Spring 97/Summer 95	Ragueneau et al., in prep.
Bering Sea shelf	31	1.8	17.7	51.0	Spring/Summer 78–80	Banahan and Goering, 1986
Oceanic regions	84	0.2	2.3	11.7		
Gulf Stream warm core ring	14	2.0	6.4	11.7	Spring 82	Brzezinski and Nelson, 1989
North Pacific	20	0.5	1.2	2.9	Summer 95/96	Brzezinski et al., 1998
Equatorial Pacific (Oligo.)	5	0.8	1.0	2.1	Autumn 94	Blain et al., 1997; Leynaert et al., in revision
Equatorial Pacific (HNLC)	5		3.9		Autumn 94	Blain et al., 1997
North Atlantic	3	0.5	0.9	1.3	Summer 97	Ragueneau et al., 1997
Sargasso Sea	37	0.2	0.5	1.6	all year round	Nelson and Brzezinski, 1997
Southern Ocean	74	0.9	15.1	93.0		
CCSZ (Ross Sea)	12	7.1	37.0	93.0	Summer 83 and 90	Nelson and Smith, 1986; Nelson et al., 1991
<i>SIZ</i>	37	2.0	6.8	22.9		
Weddell Sea	9	2.0	2.6	3.2	Late Winter 90	Leynaert, 1993
Weddell/Scotia Confluence	18	2.3	10.9	22.9	Spring/Summer 88/89	Quéguiner et al., 1991; Tréguer et al., 1991
Pacific sector	1	–	6.8	–	Spring 78	Nelson and Gordon, 1982
Indian sector	4	5.7	7.0	8.9	Spring 95/ Summer 94	Caubert, 1998
Atlantic sector	5	3.8	6.9	11.0	Spring 92	Quéguiner and Brzezinski, in prep.
<i>POOZ</i>	12	2.3	3.7	6.9		
Pacific sector	1	–	3.6	–	Spring 78	Nelson and Gordon, 1982
Indian sector	6	2.3	3.1	3.9	Spring 95/Summer 94	Caubert, 1998
Atlantic sector	5	2.5	4.5	6.9	Spring 92	Quéguiner and Brzezinski, in prep.
<i>PFZ</i>	13	0.9	13.0	60.7		
Pacific sector	3	0.9	2.1	3.1	Spring 78	Nelson and Gordon, 1982
Indian sector	2	1.7	2.0	2.2	Spring 95/Summer 94	Caubert, 1998
Atlantic sector	8	12.6	34.8	60.7	Spring 92	Quéguiner and Brzezinski, in prep.

than the relatively short residence time of Si in stored intracellular pools. Thus, the terms “Si up-

take” and “biogenic silica production” are nearly synonymous when discussing field data. The isotopic

tracer methods used, including some significant recent advances, will be described before an overview of the spatial and temporal variability of biogenic silica production is given and the factors controlling this variability are discussed.

2.2.1. Methodological developments

The global data set of directly measured silica production rates in the ocean is very small. The published record consists of < 350 station profiles, obtained in < 40 geographic regions (see Table 1). The main reason for this scarcity of data has been methodological. For many years, the only available methods were based on the uptake of the rare stable isotopes ^{29}Si and ^{30}Si and subsequent determination by mass spectrometry (Nelson and Goering, 1977a). Although improvements to the original methods have been developed (Brzezinski and Nelson, 1989; Nelson and Brzezinski, 1997), stable-isotope methods are still time consuming and tedious.

The use of the radioisotope ^{32}Si for oceanographic studies was introduced by Tréguer et al. (1991) and it has changed the situation dramatically. ^{32}Si is a β -emitter with a half-life of ~ 134 years (Browne et al., 1986). Its activity can be measured either by Cerenkov counting of the daughter isotope ^{32}P , several months after the uptake experiment is performed, when secular equilibrium with ^{32}Si is reached (e.g. Tréguer et al., 1991; Leynaert, 1993) or by direct liquid-scintillation counting of ^{32}Si (e.g. Leynaert et al., 1996; Brzezinski and Phillips, 1997). Both are much less labor-intensive than the stable-isotope methods. Besides its high purchasing price, the successful production of commercial quantities of ^{32}Si with high specific activity (Phillips et al., 1995) makes it possible to measure silica production rates in the ocean with approximately the same spatial and temporal resolution achievable for ^{14}C measurements of primary productivity. Such studies are beginning to be reported (Brzezinski and Phillips, 1996; Nelson et al., 1996; Blain et al., 1997; Brzezinski et al., 1998; Ragueneau et al., in press).

2.2.2. Range of silica production rates measured in the ocean

The global rate of biogenic silica production has been estimated to be between 2.0 and 2.8×10^{14} mol Si year $^{-1}$ (Nelson et al., 1995), equivalent to a mean

production rate of 0.6–0.8 mol Si m $^{-2}$ year $^{-1}$ or 1.5–2.1 mmol Si m $^{-2}$ day $^{-1}$. That estimate was derived independently of direct measurements of silica production rates in surface waters at specific sites. Those data at the local scale are consistent with this global estimate, but they indicate enormous spatial and temporal variability (Table 1). Measured daily production rates span more than four orders of magnitude, with the lowest thus far reported being ~ 0.1 mmol Si m $^{-2}$ day $^{-1}$ in oligotrophic waters of the Atlantic and the Pacific (Nelson and Brzezinski, 1997; Blain et al., 1997; Brzezinski et al., 1998) and the highest ~ 1100 mmol m $^{-2}$ day $^{-1}$ in the Monterey Bay coastal upwelling (Brzezinski and Phillips, 1996). Annual silica production rates for the few locations from which enough measurements have been reported to permit such estimates range from ~ 0.2 mol Si m $^{-2}$ year $^{-1}$ (25–33% of the calculated global mean) in the western Sargasso Sea (Nelson and Brzezinski, 1997) to ~ 8.3 mol Si m $^{-2}$ year $^{-1}$ (10–15 times the global mean) off the coast of Peru (Nelson et al., 1981), an approximately 40-fold difference.

2.2.3. Areas of diatom dominance

Direct observations of diatom abundances reveal that they tend to dominate whenever conditions become optimal for phytoplankton growth (Guillard and Kilham, 1978). These diatom-dominated situations include (at least) 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., in press), macrotidal coastal ecosystems (Ragueneau et al., 1994, 1996b), 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 fall in the scope of the hydrodynamical singularities, which tend to favor large cells, as suggested by Margalef (1978) and extended by 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 requirement for a nutrient-rich habitat, in contrast to smaller picophytoplankton (e.g.

prochlorophytes and cyanobacteria) whose higher surface to volume ratio allows for more efficient exploitation of low nutrient concentrations (Chisholm, 1992). Therefore, diatoms will dominate in a number of regimes that offer the high-nutrient and turbulent conditions.

It is interesting to note that diatoms are also able to grow outside these ergoline-like situations, as defined by Legendre et al. (1986). It seems that during the season of thermal stratification, some species (e.g. *Rhizosolenia* spp., *Thalassiothrix* spp.) are able to generate substantial production at depth (Kemp et al., 2000), owing to their capability to grow under low light conditions (Goldman, 1993) and to regulate their buoyancy (Moore and Villareal, 1996), especially through the formation of vertically migrating mats (Villareal et al., 1996, 1999). The significance of this type of diatom production to new production may have been largely underestimated (Goldman, 1993). The fall dump, which corresponds to the subsequent downward flux of these diatoms following the breakdown of the thermal stratification by early autumn (Kemp et al., 2000), may be responsible for a large fraction of the export production and the formation of sapropels (Kemp et al., 1999).

2.2.4. Coupling with organic carbon

The increase of diatom productivity and silica production with increasing total primary productivity is non-linear. Total daily primary productivity in coastal blooms is seldom as much as 50 times that in the central gyres (typically $5\text{--}10\text{ g C m}^{-2}\text{ day}^{-1}$ vs. $\sim 0.2\text{ g C m}^{-2}\text{ day}^{-1}$; e.g. DeMaster et al., 1996a; Michaels et al., 1994). In contrast, silica production rates vary by four orders of magnitude among these same types of systems.

There exist important spatial variations in the Si:C production ratio. Comparing the silicon and carbon production in the Southern Ocean, the North Pacific and the North Atlantic, Pondaven et al. (1999) found molar ratios of 0.2, 0.1 and 0.02, respectively. This order of magnitude difference is also reflected in the biomass, being even exacerbated when the population ages, as faster C degradation (Officer and Ryther, 1980) leads to a rapid increase in the Si:C biomass ratios. Typically, the Si:C ratio during the bloom in the North Atlantic is 0.05 while it reaches

values up to 1 in the Polar Front Zone of the Southern Ocean (Quéguiner et al., 1997).

Clearly, the relative contribution of diatoms to the total primary production (see before) will strongly impact the values observed in the Si:C production and biomass ratios. Differential Si and C degradation will subsequently affect the Si:C biomass ratio. But the reasons for the observed spatial variability in the Si:C ratios in surface waters are not only linked to a variable contribution of diatoms to the total production. Several factors have been shown to influence the Si:C ratio within species: temperature (Durbin, 1977; Paasche, 1980), light intensity (Davis, 1976; Paasche, 1980; Taylor, 1985), photoperiod (Eppley et al., 1967), macronutrient limitation (Davis, 1976; Harrisson et al., 1977; Flynn and Martin-Jézéquel, in press). Recent laboratory (Takeda, 1998) and field work (Hutchins and Bruland, 1998) have demonstrated that Fe availability may have a similar influence and Martin-Jézéquel et al. (submitted) constructed a hypothesis linking silicification to diatom growth rate, which is influenced by all these factors.

2.2.5. Controlling mechanisms

2.2.5.1. Light. As discussed above, there is no direct light requirement for Si uptake by diatoms, but the cells must be actively growing to take up Si. As a result, Si uptake is generally confined to surface waters but often extends to 1.5–2 times the maximum depths to which photosynthesis is measurable (e.g. Nelson et al., 1981, 1991). Si uptake also continues through the night in many marine surface waters, sometimes at rates that are undiminished from those in daytime (e.g. Nelson et al., 1981; Brzezinski and Nelson, 1989; Nelson and Brzezinski, 1997; Brzezinski et al., 1998).

2.2.5.2. Silicic acid and micronutrient availability. Kinetic studies of Si uptake by natural diatom assemblages (see Fig. 2) have provided direct evidence of substrate limitation of silica production in many coastal waters (e.g. Goering et al., 1973; Nelson and Tréguer, 1992; Nelson and Dortch, 1996) and in the open ocean (e.g. Nelson and Brzezinski, 1990; Brzezinski and Nelson, 1996; Leynaert et al., in revision). In coastal waters, Si limitation induced by eutrophication and river regulation has important

implications for the functioning of the ecosystem and several examples of shifts from siliceous phytoplankton to less desirable planktonic organisms have been documented (Officer and Ryther, 1980; review in Smayda, 1990; Bodeanu, 1992; Conley et al., 1993; Humborg et al., 1997). In the open ocean, Si limitation of diatom growth has been inferred in a number of systems. Tréguer et al. (1979) suggested a possible Si limitation of diatom growth in the Bay of Biscay. Sieracki et al. (1993) related to the Si limitation the shift from diatoms to nanoflagellates at the end of the spring bloom during the JGOFS North Atlantic Bloom Experiment, with important implications in terms of export fluxes. Dugdale and Wilkerson (1998) have recently applied a “silicate pump” model (Dugdale et al., 1995) to the EEP upwelling region, long known to have relatively high surface $[\text{NO}_3^-]$, but low and almost constant chlorophyll concentrations. Several observations point to $[\text{Si}(\text{OH})_4]$ control of new production in the narrow band of upwelling in the EEP. The source water for upwelling occurs in a region of the equatorial undercurrent that has lower $[\text{Si}(\text{OH})_4]$ than $[\text{NO}_3^-]$ and Ku et al. (1995), using ^{228}Ra as a tracer of water mixing concluded that surface productivity was Si limited because of the relatively low input of new $\text{Si}(\text{OH})_4$ compared to new NO_3^- . As in the North Atlantic, important consequences of Si limitation on the downward flux of biogenic matter are expected and the role of silicic acid in controlling the export fluxes to the deep sea will be further explored in the section below devoted to export fluxes from the photic layer.

As discussed in the section on cellular processes, the half-saturation constant for Si-limited growth (K_μ) is significantly lower than that for Si uptake (K_s) in many diatoms. Therefore, evidence that Si uptake rates are limited by $\text{Si}(\text{OH})_4$ availability in a given natural system does not necessarily imply that diatom growth rates are limited by Si in that system. Direct field information on K_μ for individual diatom species under natural conditions would be of great value in quantifying the role of Si limitation in controlling diatom growth in the sea, but no reliable method has yet been devised for obtaining that information. Comparison between the ranges of K_μ and K_s measured in culture studies, and the good agreement between K_s values obtained in cultures and at sea, suggest that in surface waters, where $[\text{Si}(\text{OH})_4]$

is between 1 and 10 μM , most diatoms should be capable of sustaining division rates at or near μ_{max} but Si uptake should be measurably limited by Si availability. As a consequence, one would expect diminished frustule thickness and increased susceptibility to dissolution. The effects of these conditions for the subsequent preservation of opal in the water column and sediment have not been examined adequately, and this is a significant gap in our understanding of the marine Si cycle because $\sim 60\%$ of marine surface waters have $[\text{Si}(\text{OH})_4]$ between 1 and 10 μM (Bainbridge, 1980; Craig et al., 1981).

Micronutrient requirements for Si uptake and silica deposition by diatoms have rarely been examined directly. Rueter and Morel (1981) observed an apparent Zn dependency on silicification rates in culture, possibly linked to the active uptake of bicarbonate (Tortell et al., 1997). Recent work on Fe as a limiting nutrient in HNLC areas have shown a strong link between Fe availability and the importance of diatoms in the phytoplankton assemblage. Almost all Fe enrichment experiments that have shown enhancement of phytoplankton growth rates or final biomass yield have shown that diatoms are stimulated to a greater degree than are other taxa (Martin et al., 1989, 1994; Coale et al., 1996).

At a large spatial scale, in the Southern Ocean, the recent US JGOFS field program in the Pacific sector found direct evidence of Si limitation (often strong enough to imply Si-limited growth) north of the Antarctic Polar Front (Nelson et al. in preparation), Fe limitation to the south, and a temporal transition from Fe limitation to Si limitation in a $\sim 500\text{-km}$ -wide zone immediately south of the Polar Front as silicic acid is depleted during the spring and summer (Franck et al., submitted).

The relationship between Si limitation and Fe limitation may be more complex than a simple spatial/temporal mosaic, however. In the Equatorial Pacific, direct examination of uptake kinetics by natural diatoms populations (Leynaert et al., in revision), provides evidence that the rate of Si uptake is limited by the extracellular $[\text{Si}(\text{OH})_4]$. Nevertheless, such Si limitation is not sufficient in itself to explain the low diatom growth rates observed, and additional limitation is suggested. One hypothesis that is consistent with the results of the Fe limitation studies of Coale et al. (1996) at 140 W and with the Si uptake

kinetics observed at 180 W by Leynaert et al. (in revision) is that when Si and Fe are both depleted to potentially limiting concentrations, diatom Si uptake rates are limited by $[\text{Si}(\text{OH})_4]$, but diatom growth rates, N uptake rates and productivity are limited by Fe (not yet proven by direct experiment). Confirmation of that hypothesis by direct experimental evidence would mean that the “silicate pump” model (Dugdale et al., 1995; Dugdale and Wilkerson, 1998) would have to be modified to account for a more complex set of relationships that involve the interacting effects of Fe limitation and Si limitation.

A modulation of Si limitation by Fe has been suggested recently, which draws upon the observed effect of Fe limitation on the Si:N uptake ratio of diatoms. Fe deficiency can increase this ratio from ~ 1.0 to ~ 3.0 in California coastal waters (Hutchins and Bruland, 1998) and in each of the major HNLC regions of the world ocean including the Southern Ocean (Takeda, 1998). In culture experiments (Takeda, 1998), this shift results from an increase in cellular silica and/or a decrease in the cellular N content. Elevated diatom Si:N ratios would intensify the selective removal of $\text{Si}(\text{OH})_4$, increasing the likelihood of Si limitation as upwelled waters advect away from their source and macronutrients are depleted. It is not clear, however, what the relationship between Fe limitation and cellular Si content would be once $[\text{Si}(\text{OH})_4]$ is depleted to levels that limit the rate of Si uptake. All experiments to date that show increases in cellular Si under Fe limitation have been performed at non-limiting $[\text{Si}(\text{OH})_4]$, and once Si uptake is limited by $[\text{Si}(\text{OH})_4]$, it would be more difficult for diatom cells to produce frustules cells with elevated Si content.

Additional data on those interactions could be of great value, in view of the observation that diatom may also be frequently limited by Fe in the ocean (Martin et al., 1989, 1994; De Baar et al., 1995; Coale et al., 1996).

2.3. Biogenic silica export from surface waters

The fate of the biogenic silica produced in the euphotic layer is governed by the competition between recycling in and export from the upper surface waters. Therefore, following an overview of the

spatial and temporal variability of biogenic silica export fluxes, the factors controlling this competition will be detailed and a major emphasis will be given on the potential role of silicic acid concentrations in controlling the export of biogenic matter from the surface.

2.3.1. Spatial and temporal variability of export fluxes

A preliminary data set of biogenic fluxes measured at about 40 sites by means of sediment traps has been gathered for the purposes of the present review (Table 2). These fluxes include sediment traps corresponding to the criteria described by Lampitt and Antia (1997), i.e. most of the data are given below a depth of 1000 m (with the exception of coastal upwellings and high latitude coastal sites), the bottom trap was located several hundreds meters above the seafloor to avoid resuspension artefacts and reasonable annual estimates are available.

Opal fluxes in the ocean vary regionally by more than a factor of 100 (Table 2; Fig. 3). The highest annual fluxes (between 0.6 and 0.9 mol Si m⁻² year⁻¹) are found in the Southern Ocean, either in coastal environments (Table 2; KG1u, Wefer et al., 1988; Wefer, 1989) or in the abyssal opal belt of the Permanently Open Ocean Zone (Table 2; M2, Pondaven et al., 2000b) and in the Polar Front Zone (Table 2; PF3, Fischer and Wefer, unpublished data). However, large open-ocean areas of the Southern Ocean (Weddell Sea, SIZ) are characterized by a surprisingly low opal rain rate (Table 2; WS1u, Fischer et al., 1988). Annual opal export fluxes generally decrease rapidly towards lower latitudes, when the carbonate flux increases (Fig. 3); upwelling regions are exceptions to this pattern. High opal fluxes are found in upwelling areas within the California Current (NS2, 0.5 mol Si m⁻² year⁻¹) and in the equatorial Pacific (C, 0.33 mol Si m⁻² year⁻¹). Intermediate opal flux values (0.03–0.10 mol Si m⁻² year⁻¹) were found in the equatorial upwelling belt of the Atlantic Ocean (Guinea Basin, GBN and GBS) and in coastal upwelling areas (Walvis Ridge (WR2), Cape Blanc (CB3), 0.03–0.07 mol Si m⁻² year⁻¹; Table 2). However, the latter sites were located at the edge of upwelling cells (mesotrophic sites) and must be viewed as a lower-limit estimate. It is important to note that both the equatorial and

Table 2

Annual sediment trap flux data for the various biogenic components in the world ocean, rain ratios between these components and seasonality index, as defined by Berger and Wefer (1990). Numbers in the 2nd column refer to the following references: (1) Von Bodungen et al. (1995); (2) Fischer and Wefer (1996); (3) Wefer and Fischer (1993); (4) Dymond and Lyle (1994); (5) Honjo and Manganini (1993); (6) Wefer et al. (1988); (7) Fischer et al. (1988); (8) Wefer and Fischer (1991); (9) Dymond and Collier (1988); (10) Dymond and Lyle (1982); (11) Honjo et al. (1995); (12) Roth and Dymond (1989); (13) Wong et al. (1999), mean values for the 3 years 1989, 1990 and 1993; (14) Lampitt et al. (submitted) and Ragueneau et al. (in revision), mean value for 1996–1998; (ud) Unpublished Data. Abbreviations in the same column refer to: C. Upw = Coastal Upwelling, Eq. Upw. = Equatorial Upwelling, OO Upw. = Open-Ocean Upwelling, oligo = oligotrophic, meso = mesotrophic, OO = Open Ocean, Ant. Zone = Antarctic Zone and PFZ = Polar Front Zone. Note that most of these data, on a cup by cup basis, will shortly be available online at: <http://www.pangaea.de>

Region	Type and Ref.	Trap	Depth (m)	Latitude	Longitude	Fluxes (mol m ⁻²)			Flux ratios			SI	Duration
						C _{org}	Si	CaCO ₃	Si:C _{org}	C _{org} :C _{carb}	Si:CaCO ₃		
<i>Norwegian–Greenland Sea</i>													
Norwegian Sea	1	1986	500	70.0	0.0	0.25	0.02	0.13	0.080	1.89	0.15	annual	
			1000			0.15	0.01	0.07	0.071	2.09	0.15		
			3000			0.27	0.03	0.17	0.105	1.63	0.17		
	1	1987	500	70.0	0.0	0.37	0.04	0.13	0.117	2.95	0.34	annual	
			1000			0.14	0.01	0.07	0.062	1.92	0.12		
			3000			0.29	0.05	0.27	0.163	1.08	0.18		
	1	1988	500	70.0	0.0	0.28	0.02	0.11	0.062	2.41	0.15	annual	
			1000			0.26	0.02	0.11	0.079	2.26	0.18		
			3000			0.33	0.02	0.14	0.064	2.24	0.14		
Greenland Sea	1	1986	500	72.5	−8.0	0.32	0.09	0.09	0.269	3.70	0.99	annual	
			1000			0.11	0.04	0.03	0.394	3.28	1.29		
			3000			0.03	0.02		0.613				
	1	1987	500	72.5	−8.0	0.31	0.06	0.09	0.209	3.56	0.74	annual	
			1000			0.12	0.04	0.03	0.341	4.47	1.53		
			3000										
	1	1988	500	72.5	−8.0	0.09	0.02	0.02	0.229	3.99	0.91	annual	
			1000			0.07	0.02	0.02	0.273	4.25	1.16		
			3000			0.03	0.01	0.03	0.445	1.20	0.54		
<i>Atlantic Ocean</i>													
Walvis Ridge	C. Upw. (2)	WR2u	599	−20.1	9.2	0.42	0.07	0.22	0.160	1.91	0.31	4.0	annual
	Meso (3)	WR2l	1648			0.32	0.05	0.24	0.158	1.32	0.21		
East. Atlantic	Meso-Oligo (ud)	EA8o	598	−5.8	9.4	0.18	0.02	0.14	0.100	1.30	0.13	3.6	296 days
		EA8i	1833			0.16	0.03	0.16	0.158	1.02	0.16		296 days
		EA8l	2890			0.10	0.02	0.15	0.200	0.66	0.13		296 days
West. Atlantic	Oligo (ud)	WA3u	671	−7.5	−28.0	0.03	0.01	0.06	0.205	0.54	0.11	3.0	annual
		WA3l	5031			0.03	0.01	0.04	0.227	0.68	0.15		
Hatteras Abyssal Plain	4	HAP-4	2835	32.7	−70.8	0.06	0.03	0.10	0.501	0.60	0.30	annual	
		HAP-13	2835	32.7	−70.8	0.04	0.02	0.07	0.539	0.52	0.28		
Nares Abyssal Plain	Oligo (4)	NAP	1464	23.2	−64.0	0.04	0.01	0.04	0.271	0.97	0.26	annual	
Guinea Basin North	Eq. Upw. (2)	GBNu	853	1.8	−11.1	0.25	0.06	0.15	0.227	1.71	0.39	3.0	annual
	Meso (3)	GBN3l	3920			0.18	0.08	0.20	0.418	0.92	0.39		

Guinea Basin South	Eq. Upw. (2)	GBS5u	597	−2.2	−9.9	0.25	0.03	0.11	0.100	2.27	0.23	3.0	annual
	Meso (3)	GBS5l	3382			0.19	0.10	0.26	0.504	0.73	0.37		
Cape Blanc	C. Upw. (2)	CB3u	730	21.1	−20.7	0.23	0.03	0.21	0.133	1.09	0.14	3.2	annual
ex	Meso (3)	CB3l	3557			0.18	0.03	0.23	0.181	0.75	0.14		
NABE	Oligo (5)	34N	1000	34.3	−21.0	0.08	0.03	0.13	0.328	0.64	0.21		annual
	Meso (5)	48N	1000	48.3	−21.0	0.12	0.06	0.11	0.477	1.12	0.53	3.8	annual
BENGAL	Meso (14)	PAP	1000	48.8	−16.5	0.08	0.03	0.07	0.33	1.11	0.37	3.8	annual
			3000			0.10	0.04	0.10	0.39	1.06	0.41		
			4700			0.10	0.03	0.13	0.34	0.73	0.25		
<i>Southern Ocean</i>													
Bransfield Strait	Coastal (6)	KG1u	494	−62.3	−57.5	0.64	0.91	0.04	1.423	14.92	21.24	5.5	annual
		KG1l	1588			0.27	0.65	0.05	2.431	5.13	12.47		
Weddell Sea	OO (7)	WS1u	863	−62.4	−34.8	0.002	0.005	0.0001	2.930	15.15	44.39		annual
Maud Rise	OO (8)	WS3u	360	−64.9	−2.6	0.19	0.40	0.03	2.088	6.79	14.17	4.8	annual
Indian Sector	POOZ (ud)	M2	1213	−52	62	0.09	0.74	0.06	8.22	1.5	12.33		annual
			4023	−52	62	0.05	0.51	0.07	10.2	1.0	10.20		
Bouvet Island	Ant. Zone (ud)	BO1u	450	−54.3	−3.4	0.23	0.89	0.12	3.970	1.91	7.57	4.5	annual
Polar Front	PFZ (ud)	PF3	614	−50.1	5.9	0.28	0.40	0.11	1.406	2.49	3.49	3.4	annual
<i>Arabian Sea</i>													
	C. Upw. (ud)	AS2u	914	17.4	58.8	0.51	0.24	0.37	0.471	1.37	0.65		
		AS2m	1985			0.53	0.35	0.45	0.670	1.17	0.78	4.3	annual
		AS2l	3150			0.41	0.34	0.40	0.833	1.03	0.86		
		AS3u	873	17.2	59.6	0.55	0.26	0.42	0.474	1.33	0.63		
	(ud)	AS3m	1970			0.50	0.34	0.39	0.683	1.26	0.86	4.0	annual
		AS3l	2931			0.40	0.27	0.38	0.677	1.05	0.71		
	OO Upw. (ud)	AS4u	814	16.0	61.5	0.38	0.14	0.27	0.360	1.41	0.51		
		AS4m	2222			0.34	0.21	0.32	0.613	1.07	0.66	3.2	annual
		AS4l	3484			0.27	0.18	0.30	0.684	0.91	0.62		
	Oligo (ud)	AS5u	800	10.0	65.0	0.17	0.05	0.17	0.286	1.03	0.30		
		AS5m	2363			0.12	0.05	0.15	0.431	0.77	0.33	0.2	annual
		AS5l	3915			0.10	0.04	0.13	0.437	0.79	0.35		
<i>Pacific Ocean</i>													
Equatorial	Oligo (9)	S	1600	11.1	−140.1	0.07	0.07	0.08	0.953	0.86	0.82		annual
	10	M	1565	8.8	−104.0	0.21	0.12	0.10	0.578	2.08	1.20		annual
	10	H	1465	6.6	−92.8	0.32	0.19	0.31	0.603	1.01	0.61		annual
	Eq. Upw. (9)	C	1883	1.0	−138.9	0.21	0.33	0.30	1.581	0.70	1.10		annual
	Oligo (11)	EP9N	2250	9.0	−140.0	0.04	0.03	0.05	0.800	0.85	0.68	1.4	annual
	11	EP5N	1200	5.0	−140.0	0.18	0.10	0.15	0.558	1.20	0.67		
	11	EP5N	2100			0.13	0.11	0.18	0.840	0.70	0.59	2.7	annual
	11	EP5N	3800			0.12	0.10	0.16	0.892	0.74	0.66		

(continued on next page)

Table 2 (continued)

Region	Type and Ref.	Trap	Depth (m)	Latitude	Longitude	Fluxes (mol m ⁻²)			Flux ratios			SI	Duration
						C _{org}	Si	CaCO ₃	Si:C _{org}	C _{org} :C _{carb}	Si:CaCO ₃		
California current	Eq. Upw. (11)	EP2N	2200	2.0	-140.0	0.11	0.10	0.18	0.938	0.60	0.56	2.3	annual
	Eq. Upw. (11)	EQ-1	2284	0.0	-140.0	0.14	0.14	0.23	0.991	0.60	0.59	2.8	annual
	Eq. Upw. (11)	EQ-2	3650	0.0	-140.0	0.14	0.16	0.24	1.113	0.61	0.68		annual
	Eq. Upw. (11)	EP2S	3593	-2.0	-140.0	0.11	0.12	0.18	1.062	0.61	0.65	2.8	annual
	11	EP5S	2209	-5.0	-140.0	0.08	0.08	0.15	0.920	0.57	0.52	3.1	annual
	Oligo (11)	EP12S	3594	-12.0	-135.0	0.03	0.01	0.06	0.533	0.40	0.22	1.5	annual
	C. Upw. (4)	MFZ-4	3785	39.5	-127.7	0.12	0.18	0.06	1.540	1.80	2.77		annual
	C. Upw. (4)	MFZ-11	3785	39.5	-127.7	0.08	0.11	0.05	1.445	1.56	2.25		annual
	Meso (4)	G2	1500	41.6	-132.0	0.09	0.08	0.09	0.889	1.05	0.93	3.8	annual
North	C. Upw. (4)	MW2	1500	42.2	-127.6	0.14	0.21	0.11	1.484	1.24	1.84	2.9	annual
	C. Upw. (4)	NS2	1500	42.1	-125.8	0.33	0.47	0.15	1.404	2.23	3.13	1.6	annual
	12	JDF-1	1700	48.0	-128.1	0.11	0.14	0.13	1.320	0.81	1.07		336 days
	11	PC85-6	3500	48.0	-138.0	0.10	0.18	0.12	1.817	0.81	1.48		
	11	P83-4	3800	50.0	-145.0	0.08	0.11	0.09	1.467	0.84	1.24		
	11	P84-5	3800	50.0	-145.0	0.05	0.17	0.11	3.300	0.46	1.53		
	11	Okhotsk 92	3137	53.0	149.0	0.14	0.42	0.04	2.929	3.37	9.88		
	11	Bering 92	1061	58.0	179.0	0.15	0.51	0.06	3.422	2.54	8.70		
	13	1989-1993	200	50.0	-145.0	0.55	0.12	0.04	0.22	13.75	3.00		annual
	1989-1993	1000	50.0	-145.0	0.16	0.11	0.02	0.69	8.00	5.50		annual	
	1989-1993	3800	50.0	-145.0	0.08	0.08	0.02	1.00	4.00	4.00		annual	

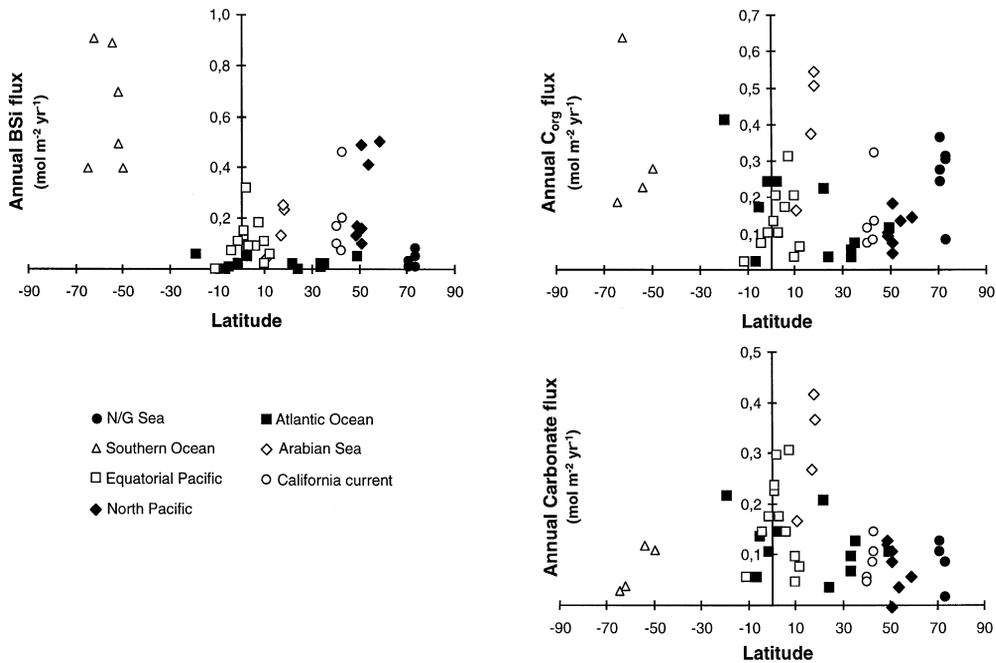


Fig. 3. Latitudinal variations in the biogenic silica (BSi), organic carbon (C_{org}) and carbonate ($CaCO_3$) annual fluxes as measured by means of sediment traps (all data in $\text{mol m}^{-2} \text{ year}^{-1}$). See Table 2 for the detailed description of study sites and positions.

the coastal upwelling areas in the Pacific Ocean provide a higher opal export rate than that in the Atlantic Ocean. The central oligotrophic gyres can be clearly distinguished from mesotrophic and eutrophic areas and are characterized by export values less than $0.03 \text{ mol Si m}^{-2} \text{ year}^{-1}$, as for example in the northern Brazil Basin (Table 2, WA3).

Large interannual variability in opal export fluxes have been reported for the Southern Ocean, both for the Bransfield Strait (Wefer and Fischer, 1991; Table 2) and for the opal belt (Wefer and Fischer, 1991). In the tropical–subtropical Atlantic (coastal and equatorial upwelling sites), year-to-year opal flux variations appear to be less (Table 2, Fischer et al., 1996; Fischer and Wefer, 1996), ranging from a factor 1.4 in the Northern Guinea Basin to a factor 3.4 off Cape Blanc. Almost similar interannual variations were observed in the Norwegian Sea and the Greenland Sea (Von Bodungen et al., 1995). Only one long-term record from an oligotrophic site is presently available, indicating also year-to-year variability in opal fluxes in the deep Sargasso Sea (Deuser, 1986; Deuser et al., 1995). Excluding the unusual sedimentation event in 1982, probably caused by El Niño

conditions, interannual variability appears to be lower in oligotrophic oceans compared to upwelling areas or the Southern Ocean. An El Niño event resulted in more than a two-fold lower opal flux in the equatorial Pacific, from $0.15 \text{ mol Si m}^{-2} \text{ year}^{-1}$ in 1982–1983 to $0.33 \text{ mol Si m}^{-2} \text{ year}^{-1}$ in 1983–1984 (Dymond and Collier, 1988).

2.4. Mechanisms that control the export of biogenic silica from the photic layer

External (physical, chemical and biological) factors combine with intrinsic properties governing the dissolution of the biogenic opal formed in surface waters to control the competition between biogenic silica dissolution in surface waters and its export to the deep waters.

2.4.1. Biogenic silica dissolution

2.4.1.1. Overview of biogenic silica dissolution. A steady-state geochemical box model of the ocean (PANDORA, Peng et al., 1993), applied to the large-scale spatial distribution of $[\text{Si}(\text{OH})_4]$, indicates

a global net opal flux of $\sim 1.0 \times 10^{14}$ mol Si year⁻¹ from surface waters, less than half of the estimated global production rate. Direct comparisons between measured dissolution rates and production rates in several marine habitats have indicated that from 10% to 100% of the silica produced in the euphotic zone dissolves in the upper 50–100 m, with an overall mean of $\sim 60\%$ (review in Nelson et al., 1995). There is no clear latitudinal, nor other spatial trend in the ratio of silica dissolution to silica production in surface waters (Nelson and Brzezinski, 1997; DeMaster et al., 1991; Nelson et al., 1996). There is also no clear trend of increased or decreased recycling with changes in primary productivity or in the relative importance of diatoms (Nelson and Goering, 1977b; Nelson et al., 1981, Brzezinski, unpublished data). Thus, differences in the intensity of biogenic silica recycling in surface waters are at least as important as differences in silica production rates in controlling the spatial pattern of opal efflux from the upper ocean, and the controls of that recycling intensity are poorly understood.

Before discussing the factors controlling the intensity of biogenic silica dissolution, it is important to note that there is a very small data set available on direct estimates of upper ocean biogenic silica dissolution. Only 45 individual station profiles have been reported (Nelson et al., 1995). The problem is again methodological, as ³²Si tracer methods have not yet been successfully applied to dissolution-rate measurements and relatively difficult mass-spectrometric methods using the stable isotopes ²⁹Si and ³⁰Si (e.g. Brzezinski and Nelson, 1989; Nelson et al., 1991; Caubert, 1998) have been the only methods available.

2.4.1.2. Mechanisms controlling biogenic silica dissolution. The specific dissolution rate of opal in seawater (V_{dis}) has been shown to conform to the following rate equation (Hurd and Birdwhistell, 1983):

$$V_{\text{dis}} = k ([\text{Si}(\text{OH})_4]_{\text{sat}} - [\text{Si}(\text{OH})_4]) A_{\text{sp}} \quad (3)$$

where k is the first-order rate constant (cm h⁻¹), $[\text{Si}(\text{OH})_4]_{\text{sat}}$ represents the solubility of opal (mol cm⁻³), $[\text{Si}(\text{OH})_4]$ is the ambient silicic acid concen-

tration (mol cm⁻³) and A_{sp} represents the specific surface area of the opal present (cm² mol⁻¹). V_{dis} is expressed in h⁻¹. According to Eq. (3), V_{dis} increases linearly with k , A_{sp} and $([\text{Si}(\text{OH})_4]_{\text{sat}} - [\text{Si}(\text{OH})_4])$. These relationships permit us to evaluate the conditions most likely to affect V_{dis} in the ocean. Both $[\text{Si}(\text{OH})_4]_{\text{sat}}$ and k for opal in seawater increase sharply with temperature (e.g. Hurd, 1972; Kamatani, 1982). The combined effect, calculated according to Eq. (3), implies an almost 50-fold increase in V_{dis} between 0°C and 25°C (Hurd and Birdwhistell, 1983). The lowest V_{dis} values reported from marine surface waters ($\sim 3 \times 10^{-4}$ h⁻¹) have been in two Antarctic systems (temperatures between -1.5°C and +6°C, Nelson and Gordon, 1982; Tréguer et al., 1989; Nelson et al., 1991) and the highest ($\sim 5\text{--}8 \times 10^{-3}$ h⁻¹) in coastal waters off northwest Africa and a Gulf Stream warm-core ring at temperatures ranging from 14°C to 22°C (Nelson and Goering, 1977b; Brzezinski and Nelson, 1989). The observed 15–25-fold difference between V_{dis} in warm and cold surface waters is highly consistent with the known temperature effect on the dissolution kinetics of opal, and implies that surface-layer temperature plays a primary role in determining V_{dis} .

The direct effect of the ambient silicic acid concentration on biogenic silica dissolution is difficult to assess. Because $[\text{Si}(\text{OH})_4]_{\text{sat}}$ for opal is > 1 mM at ocean temperatures (e.g. Hurd, 1973; Stumm and Morgan, 1981), the predicted decrease in V_{dis} for a given opal particle as $[\text{Si}(\text{OH})_4]$ increases from 0 to 100 μM would be $< 10\%$. However, two factors may alter this assumption. First, the incorporation of trace elements within the opaline matrix can decrease significantly opal solubility and thus reduce the departure from equilibrium in the upper waters. The key role of Al has been reported by various authors (e.g. Lewin, 1961; Van Bennekom et al., 1989, 1991; Van Beusekom et al., 1997). The second important element is the non-linearity between dissolution kinetics of biogenic opal and the degree of undersaturation, evidenced by Van Cappellen and Qiu (1997b) by means of a flow-through experiment. Below a critical level, corresponding to $[\text{Si}(\text{OH})_4]$ observed in deep oceans, the dissolution rate rises exponentially with increasing undersaturation so that surface $[\text{Si}(\text{OH})_4]$ concentrations may influence the dissolution rate.

The specific dissolution rate varies from one species to another, spanning over an order of magnitude even at constant external conditions (Kamatani, 1982; Tréguer et al., 1989). Species-specific differences in dissolution rates reflect variability in specific surface areas (e.g. Lewin, 1961; Lawson et al., 1978; Kamatani and Riley, 1979) or morphology and structure of the frustules (Kamatani et al., 1980), as well as in the growth of organic and inorganic surface coatings (Lewin, 1961; Luce et al., 1972; Lawson et al., 1978; Kamatani et al., 1988). Thus, any process that removes organic matter from the opal surfaces, and hence exposes silica directly to seawater, should increase V_{dis} . Both microbial degradation and grazing could potentially clean the silica surfaces in this way. The potential for bacterial degradation of diatom organic matter to accelerate dissolution rates has recently been demonstrated in the laboratory (Bidle and Azam, 1999) and high concentrations of silicic acid inside particles of marine snow imply that this process occurs in nature (Brzezinski et al., 1997). Grazing by heterotrophic dinoflagellates has been shown to extract virtually all organic matter from diatoms, leaving exposed frustules (Jacobson and Anderson, 1986). Grazing by microcrustaceans would have the added effect of breaking the frustules up into smaller fragments (e.g. Sullivan et al., 1975; Miller et al., 1990). Grazing could also have an opposite effect however, as we shall illustrate below when discussing the role of the food web structure in governing the partitioning of the products of surface primary production into recycling or export.

For a given rate of biogenic silica dissolution, the extent of recycling will depend on the residence time of the particles in the water column, especially in the warmer surface waters. Therefore, external factors that control the efficiency of the export of the biogenic matter out of the euphotic layer will strongly impact the extent of biogenic silica recycling.

2.4.2. External factors controlling the relative roles of recycling vs. export

2.4.2.1. Seasonality. Export production depends greatly upon seasonality and intermittency and Berger and Wefer (1990) defined a seasonality index (six minus the number of months needed to reach half of

the annual primary production; a constant production site has a seasonality index of 0) to quantify this phenomenon, concluding that the export of pulsed production could exceed that of an equal but constant production by a factor of 2. Contrarily to the carbonate flux, which shows no clear trend with increasing seasonality, a general increase of opal fluxes with seasonality is observed (Table 2, Fig. 4 with the exception of the California Current), which may be related to the ability of diatoms to respond rapidly to changes in light and nutrient availability, as driven by changes in physical factors (Legendre et al., 1986).

2.4.2.2. Food web structure. The structure of the food web strongly influences the fate of the biogenic matter produced in surface waters (Goldman, 1988; Peinert et al., 1989; Legendre and Le Fèvre, 1989 and references therein; Newton and Boyd, 1998). Goldman (1988) distinguishes between two production systems that are separated, both spatially and temporally. The first system (the microbial food loop) is based on small phytoplankters; its products are dissipated in long trophic pathways, leaving little residual material for export to the deep sea. The second system is based on larger cells (e.g. diatoms), growing in response to short-lived and localized mixing events, accounting for much of the export production from the photic zone (Michaels and Silver, 1988; Buesseler, 1998). In the latter system, large grazers that produce large and rapidly sinking fecal pellets (e.g. anchovies and sardines in Peruvian coastal waters, euphausiids and salps in the Antarctic) would be very effective in minimizing the recycling of opal in surface waters and delivering it to the deep ocean and seabed.

2.4.2.3. Aggregation. Diatom aggregation is another mechanism that allows a rapid transport of opal through the water column, thereby reducing the time spent by the opal in undersaturated surface waters (Smetacek, 1985; Alldredge and Gotschalk, 1989; Jackson, 1990; Hill, 1992; Alldredge and Jackson, 1995). As noted by Nelson et al. (1995), diatom flocculation may be globally significant in opal preservation, since it has been observed in coastal environments (Alldredge and Gotschalk, 1989; Kiorbe et al., 1994), in the Southern Ocean (Von

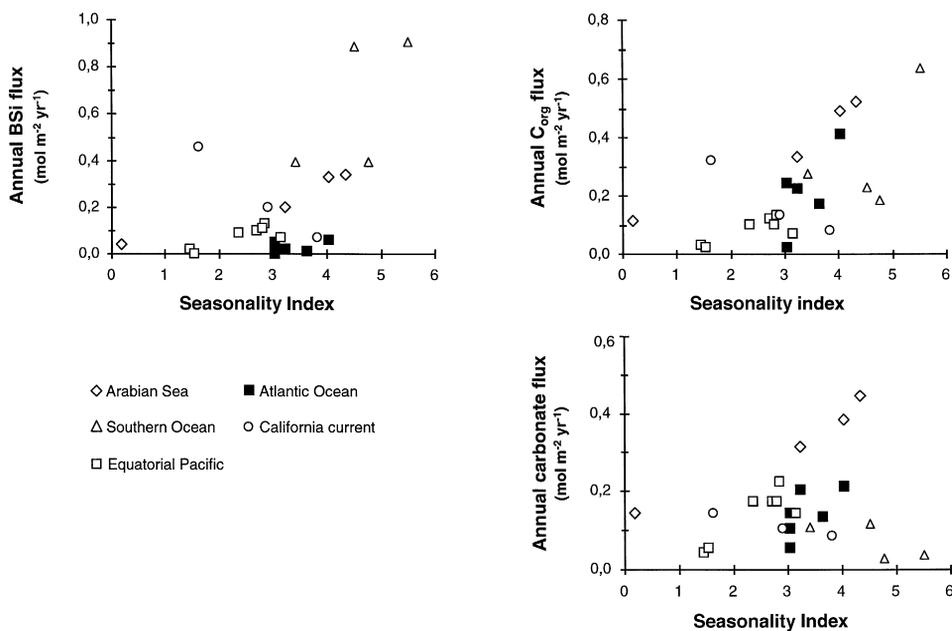


Fig. 4. Annual BSi, C_{org} and CaCO₃ fluxes (all data in mol m⁻² year⁻¹ from Table 2 and references therein), plotted versus the stability index (see text) for various regions of the world ocean.

Bodungen et al., 1986) and has been inferred for blooms in the North Atlantic (Sieracki et al., 1993). While the aggregation and mass settlement of diatoms at the termination of blooms results in significant export of carbon from the surface ocean, the mechanism of blooms aggregation is poorly understood and does not seem to be necessarily related to the physiological state of the cells; the reader is referred to the special issue of Deep-Sea Research II (1995, vol. 42 (1)) for a detailed overview of the possible mechanisms involved. It is however interesting to mention that in addition to flocculation and the formation of aggregates, a sexual phase can also trigger downward transport of empty diatom cell walls. Observed on *Corethron criophilum* in the Southern Ocean by Crawford (1995), this phenomenon appeared significant enough to increase the vertical flux of biogenic silica and create the monospecific layers of this species in Southern Ocean sediments (Jordan et al., 1991).

At present, only a few studies have been conducted to assess the seasonal distribution of large particles such as large fecal pellets and amorphous aggregates (e.g. Lampitt et al., 1993; Ratmeyer and

Wefer, 1996). The larger fragile particles generally disintegrate in the sampling cups of the particle traps; consequently, sediment trap techniques alone will not provide reliable information on the seasonal variability of large particle formation. Because this information could enhance our understanding of opal dissolution in the water column, there is a strong need to develop optical techniques such as high-resolution particle cameras (e.g. Lampitt et al., 1993; Ratmeyer and Wefer, 1996) to obtain data about particle transport in the water column.

2.4.3. Silicic acid availability and export fluxes: a hypothesis

In the last 5 years, the importance of silicic acid availability in controlling the contribution of diatoms to the total production and hence, the export fluxes of biogenic matter out of the photic layer, has emerged both for the modern ocean (e.g. Sieracki et al., 1993; Dugdale and Wilkerson, 1998) and for the glacial ocean (Herguera, 1992; Pollock, 1997). Based on inter-ocean differences in the relationship between opal and organic carbon export fluxes (Fig. 5), we propose to extend the idea of the silicate pump

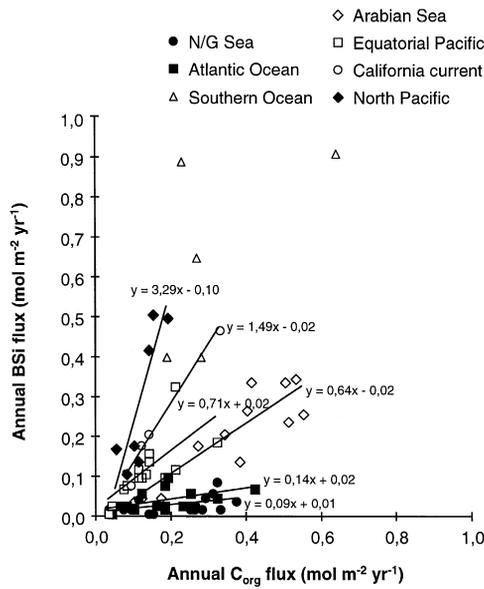


Fig. 5. Annual opal versus organic carbon fluxes in the Pacific/Southern Ocean, the Arabian Sea and the Central and North Atlantic Ocean. Note the basin-wide differences between the Pacific/Southern Ocean (“silicate ocean”) and the Atlantic ocean (“carbonate ocean”) and the track of the conveyor belt as you move counterclockwise with increasing Si:C ratios.

developed by Dugdale et al. (1995) to other oceanic settings. If correct, this hypothesis implies that silicic acid availability could play a major role in controlling the production of biogenic silica and the export of biogenic matter to the deep sea.

2.4.3.1. C_{org} –opal flux relationships and ratios. In areas with high opal flux such as the Southern Ocean, there seems to be a linear relationship between mean daily fluxes of organic carbon and biogenic opal (e.g. in the Bransfield Strait, KG1u station, the molar Si: C_{org} flux ratio was around 1.4, Table 2). This is also the case in some oligotrophic areas (Northern Brazil Basin, WA3u) as well as in some coastal upwelling environments with moderate fluxes (off Namibia, WR2u). However, sediment trap experiments that employ high temporal resolution sample collections, commonly reveal non-linearity between organic carbon and opal fluxes; conditions of high carbon export have very high opal fluxes and high opal to carbon ratios (Dymond, unpublished data). An exponential relationship be-

tween organic carbon and opal fluxes is observed in the highly productive opal belt (BO1u, Antarctic Zone). The unusually high fraction of opal in the sinking particles in this region indicates a decoupling of organic carbon and opal fluxes in the Southern Ocean. In general, the tropical subtropical oceans (GBN3u, Pacific, Arabian Sea) are also characterized by a non-linear relationship between daily organic carbon and opal fluxes. This non-linearity between daily opal and organic carbon fluxes may reflect the ability of diatoms to respond quickly to physical-forced mixing events and other temporally short-lived conditions and to out-compete non-siliceous organisms for new nutrients.

There is a clear tendency for increasing Si: C_{org} flux ratio towards high latitude, the highest values being found in the Southern Ocean and North Pacific (as can be seen from Fig. 3). There exist important exceptions to this general pattern, with low values found in the Weddell Sea and in the Norwegian/Greenland Sea and high values in the Equatorial Pacific. In fact, differences between oceans surpasses the latitudinal changes. A plot of annual C_{org} flux versus opal flux for all sites (Fig. 5), clearly shows the ocean-to-ocean differences in the relationship. There is a remarkable increase in the Si:C flux ratio along the path of the conveyor belt (Broecker and Peng, 1982). Starting from below 0.1 in the Northern North Atlantic, this ratio increases between 0.3 and 0.6 in the Indian Ocean, reaches 0.7 in the Equatorial Pacific before exceeding largely 1 in the California current and the North Pacific.

2.4.3.2. The possible role of silicic acid in controlling inter-basin differences. The inter-basin flux differences shown in Fig. 5 may be a consequence of differences in the nutrient concentrations between the major basins (Figs. 6 and 7). Because opal recycles more slowly than organic matter, as discussed above, silicic acid tends to accumulate along the path of deep water flow through the oceans (Broecker and Peng, 1982). Consequently, on average the nutrient source waters in the Pacific have higher ratios of silicic acid to nitrate and phosphate than in the Atlantic (see Fig. 7). Inter-basin silicon fractionation has been described by Codispoti (1983) through comparisons of nutrient data from the North Pacific and the North Atlantic. Even when upwelling

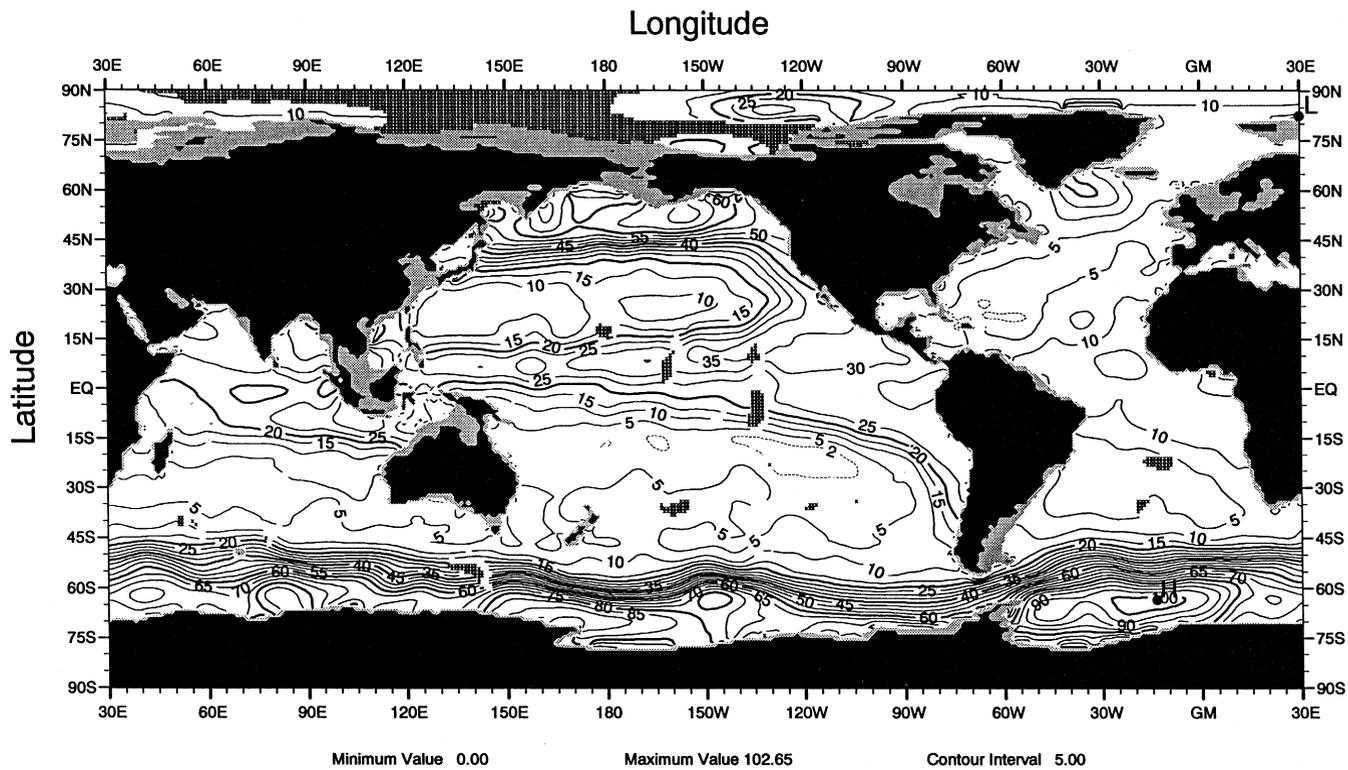


Fig. 6. The global distribution of silicic acid concentrations (annual mean) at 250 m. From the Levitus et al. (1994) atlas.

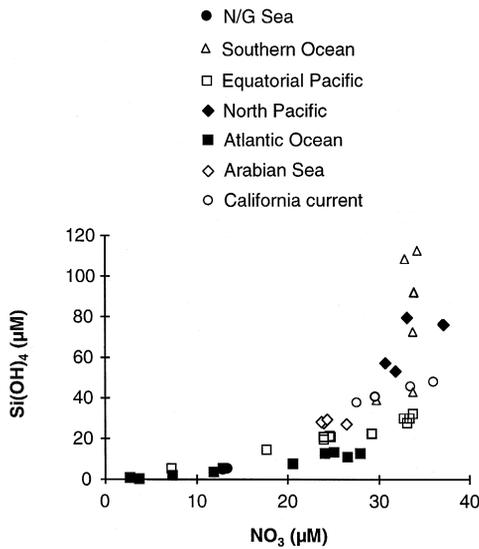


Fig. 7. Silicic acid versus nitrate concentrations (annual mean) at 250 m in various oceanic regions (from the Levitus atlas, at the stations where biogenic fluxes shown in Figs. 3–5 have been measured), showing the enrichment of intermediate waters in silicic acid, with the age of the water masses.

dynamics are physically the same, silicate in the upwelling source waters varies greatly. Thus, a higher ratio of silicic acid to nitrate or phosphate in the Pacific than in the Atlantic (Fig. 7) could favor diatoms in the former ocean, inducing a higher opal/carbonate rain ratio. Fig. 8 indeed supports this hypothesis as the opal/carbonate ratios increases linearly with increasing Si:N ratio in intermediate waters, until this Si:N ratio reaches a value of 2. Above this threshold, the opal/carbonate flux ratio increases exponentially with the highest values being found in the north Pacific and the Southern Ocean. Interestingly, this Si:N ratio of 2 corresponds to the value given by Egge and Aksnes (1992) for diatom dominance over other phytoplanktonic groups.

Figs. 7–10 provide strong support to the “silicate pump” model of Dugdale et al. (1995) and Dugdale and Wilkerson (1998). It needs to be further tested, as Si regeneration dynamics, when combined with the deep water flow of the oceans, may control spatial variations in opal production and in the rain ratio between biogenic components (Fig. 8), with important implications for atmospheric CO₂ concentrations and climate change (e.g. Archer and Maier-Reimer, 1994).

2.4.3.3. A few applications in the modern and past oceans. Such a hypothesis can be invoked to explain why coastal upwelling areas in the Pacific Ocean provide a higher opal export compared to the Atlantic Ocean (Table 2). Indeed, silicic acid concentrations in the coastal upwelling source waters off Peru and California are much higher than the ones off northwest Africa, where values remain below 10 μM (Codispoti, 1983; Dugdale, 1983). It is interesting to observe that the low ambient silicic acid concentrations off northwest Africa can induce the growth of diatoms more susceptible to dissolution, which will further decrease their flux out of the euphotic zone, because of intense recycling. This is consistent with directly measured rates of opal production and dissolution in the northwest Africa and Peru upwelling regions. A very high fraction (approaching 100%) of biogenic silica produced over the northwest Africa shelf has been shown to dissolve in the upper 50–60 m (Nelson and Goering, 1977b), whereas only ~10% of the opal produced over the Peruvian shelf is recycled in that manner (Nelson et al., 1981).

Such a basin-to-basin fractionation between the Atlantic (“carbonate ocean”) having an anti-estuarine

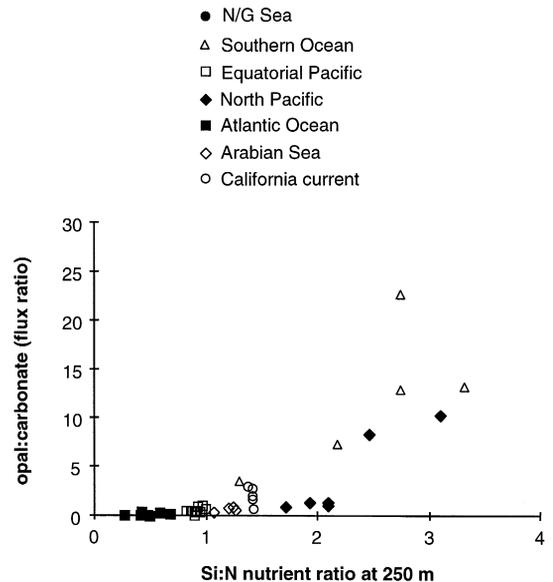


Fig. 8. Evidence for an increase in the opal:carbonate flux ratio (molar ratios, all data from Table 2) with an increase in the nutrient Si:N ratio in intermediate waters (250 m).

circulation and the Pacific (“silicate ocean”) with an estuarine circulation have been described by Berger (1970) on the basis of sediment data. As Berger (1970) pointed out, estuarine basins such as the North Pacific accumulate silica and dissolved CO_2 , a situation, which favors dissolution of CaCO_3 and preservation of opal. He used this interbasin distinction to account for the abundance of CaCO_3 in Atlantic sediments and the relatively higher opal abundance in Pacific sediments. The sediment trap data indicate that in addition to the preservation distinctions between the basins, there are strong differences in opal export and its rain to the seafloor. These production differences can further enhance the poor carbonate preservation that result from the accumulation of CO_2 in the Pacific; the higher opal export may result in relatively high $C_{\text{org}}/\text{CaCO}_3$ in raining particles that produces conditions favorable to metabolic dissolution of CaCO_3 in the sediments. Archer and Maier-Reimer (1994) attributed the glacial decrease of atmospheric pCO_2 to the latter process (induced by an ecological shift from calcareous to siliceous organisms).

Deuser et al. (1995) observed a significant decrease in the opal/carbonate molar ratio from 0.50 in 1978 down to 0.25 in 1991, in sediment traps deployed in the deep Sargasso Sea during a 14-year time series; although such changes in the plankton community structure could reflect a subtle climate change, the exact mechanism is still puzzling and it would be valuable to examine at this site time series of nutrient concentrations and ratios in intermediate waters. A relationship such as the one presented on Fig. 8 would suggest a significant decrease in the Si:N ratio in intermediate waters from 0.7 in 1978 to 0.3 in 1991, which should be detectable if such nutrient time series data indeed are available.

The strong nutrient gradients (i.e. of silicon) between basins in the present-day ocean probably have changed during the geological past (Codispoti, 1983). Such changes may have produced differences in the dissolved silicic acid to nitrate ratio of the upwelling source waters, thereby affecting not only the rain of opal to the seafloor, but also the preservation of CaCO_3 , resulting in a modification of the present-day basinal fractionation of a “silicate-rich” Pacific and a “carbonate-rich” Atlantic Ocean. Indeed, Herguera (1992) invoked such a change in the pattern of ocean

circulation to explain the Equatorial Pacific sedimentary record, which shows a higher total productivity, but lower opal burial during the last glacial.

The potential role of silicic acid in governing the export of biogenic matter to the deep sea has been illustrated by Pollock (1997) who linked the onset of global cooling during glacials to a drawdown of atmospheric CO_2 driven by increased productivity at the equatorial divergences and in coastal upwelling systems. Increased productivity in these regions is hypothesized to derive from the upwelling of silicic acid-enriched deep and intermediate waters, resulting from the accelerated melting of the west Antarctic ice sheet during the later stages of interglacial periods. The proliferation of large, rapidly sinking diatoms, having a high requirement for silicic acid, accelerates the rate of organic carbon production, export and sequestration in shelf and slope sediments and in the deep sea, and the subsequent atmospheric CO_2 drawdown initiates global cooling.

The role of silicic acid in controlling the export of carbon to the deep sea still needs to be fully demonstrated. Mesocosm experiments have already provided some confirmation of this hypothesis (Wassmann et al., 1996), but future field programs devoted to a better understanding of silica fluxes in today’s ocean should emphasize this important aspect of the silicon cycle as well as its implications for the rain ratio and paleoproductivity reconstructions.

2.5. Deep water and benthic processes

2.5.1. Transfer of opal through the deep sea

We do not know much about the transfer of biogenic opal through the deep waters down to the seafloor. Our understanding of opal flux changes with depth is limited by insufficient data concerning the influences of lateral advection, resuspension processes, or by collection biases due to strong currents in the trap vicinity. In the upper few hundred meters, where probably most of the biogenic opal is recycled (see previous sections), there are very few long-term opal flux measurements. Moreover, there are few particle flux measurements that use multiple sediment traps (> 3) distributed over the entire water column. Particle flux data from oligotrophic/pelagic sites that are assumed to be less influenced by advection, resuspension, and high currents are shown

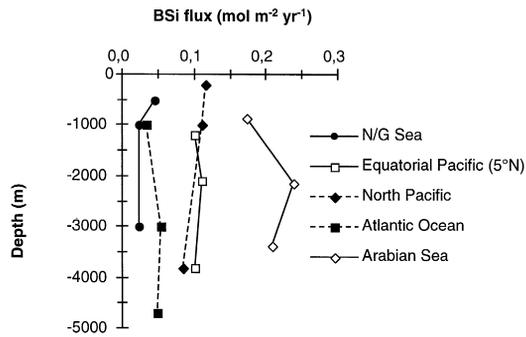


Fig. 9. Annual opal flux changes with depth. Note that except in the equatorial Pacific where only the station at 5°N is shown, other profiles correspond to mean annual values, either for three different years (Norwegian/Greenland Sea 1986–1988, North Pacific, Station P 1989–1990–1993) or for different sites in a given region (Arabian Sea, northeast Atlantic). See Table 2 for the exact position of these sites, dates of sediment trap deployments, and relevant references.

in Fig. 9 (all data in Table 2). In the cold ocean, e.g., the Greenland Sea, a distinct decrease in opal fluxes from 0.09 to 0.02 mol Si m⁻² year⁻¹ can be observed (Von Bodungen et al., 1995); such a decrease seems to be also true for the Southern Ocean where flux data could be partly biased due to strong currents in the Antarctic Circumpolar Current (ACC). All other oligotrophic/pelagic sites located in the warm tropical/subtropical Atlantic, Arabian Sea and the Pacific show almost no change in opal fluxes with depth or a slight increase in the intermediate water column. The most significant increase of opal fluxes in the intermediate water column is obtained at site EA8 in the Atlantic Ocean where opal fluxes are low. This observation can be explained by sinking of deep-living radiolarians or by lateral advection of diatoms (see for example Treppke et al., 1996a, b). Of course, some bias of opal fluxes may also occur in the sub-surface traps, underestimating the true fluxes due to strong currents. Considering all data (Table 2), only a few sites have decreasing opal fluxes, that would be expected because of ubiquitous silica undersaturation in the water column and most the sites show little changes with depth (Fig. 9). Thus, it appears that below the euphotic zone, fluxes remain quite unchanged during the settling through the water column. This is consistent with the idea that the only way to carry significant amounts of biogenic opal down to the seafloor is by rapid trans-

port (aggregates, faecal pellets of large grazers), which does not allow much dissolution to go on.

2.5.2. Decoupling with organic carbon?

If biogenic opal fluxes do not severely decrease with depth (Fig. 9), the Si:C ratio shows clear variations during sedimentation. It is well known that organic matter is recycled more rapidly than biogenic silica (see before), one good reason being that one first needs to get rid of the organic matter coating the frustule surface (rapid biologically mediated process) to trigger silica dissolution by exposing the silica surfaces to the undersaturated waters (slower chemical process). This phenomenon leads to a relative better preservation of biogenic silica compared to organic carbon during sedimentation and a subsequent increase in the Si:C ratio with depth. Fig. 10 illustrates this process for two sites, namely the Southern Ocean and the North Atlantic. For both sites, the Si:C ratio is increasing between 1000 and 3000/4000 m, sometimes by over a factor of 2.

The seasonal variations in the Si:C ratio bring numerous important information concerning this decoupling between silicon and carbon. Firstly, there is a clear tendency towards higher Si:C ratios following bloom periods, obviously due to the increasing contribution of diatoms to the total production during blooms and to their subsequent efficient export. Secondly, the relative increase with depth in the Si:C ratio appears stronger in the North Atlantic compared to the Southern Ocean, especially during the period of blooms. The extent of the Si:C decoupling in the water column depends greatly upon the rapidity of the sedimentation. In the Southern Ocean, a very rapid transfer of biogenic matter during the first days of the sediment trap deployment (Fig. 10, see also Pondaven et al., 2000b, for the flux measurements and Riaux-Gobin et al., 1997 for the observation of fresh phytodetritus on the sediment–water interface) prevented a strong decoupling between Si and C (Fig. 10). Rance (1997) has also shown that the Si:C ratio of mats found in laminated diatom oozes can be very similar to that during initial production.

It is interesting to note that the Si:C is about one order of magnitude higher in the Southern Ocean compared to the North Atlantic, which is in agree-

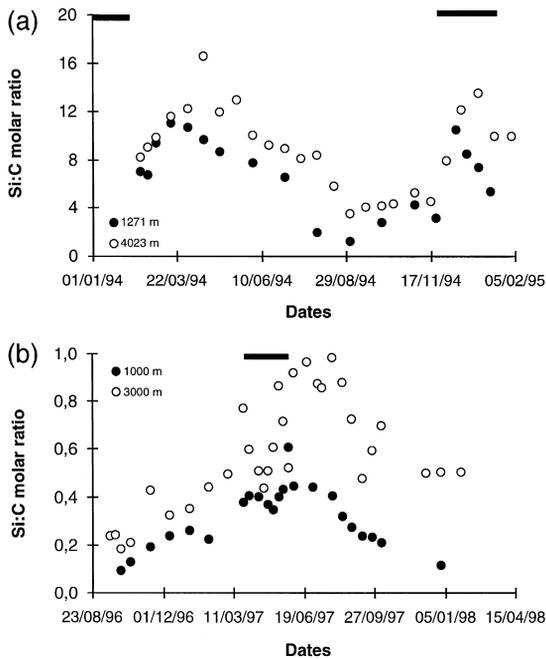


Fig. 10. Seasonal variations in the Si:C molar ratio in the sedimenting particles, as measured in sediment trap material. Upper traps are filled circles and lower traps are open circles. Data from Pondaven et al. (2000b) for the Southern Ocean (a) and from Lampitt et al. (submitted) and Ragueneau et al. (in revision) for the Northeast Atlantic (b). Horizontal black bars indicate the period when the phytoplankton bloom is the most likely to occur in these two ecosystems, according to Pondaven et al. (1999) for the Southern Ocean and to Sieracki et al. (1993) and Lochte et al. (1993) for the north Atlantic.

ment with the basinwide contrast shown in Fig. 5 and may clearly be related to both the relative contri-

bution of diatoms to the total production and the silicification degree of these diatoms, which in turn both depend upon silicic acid availability (Fig. 8, see the discussion on the silicic acid pump, Dugdale and Wilkerson, 1998) and environmental conditions (see, e.g. Takeda, 1998). Thus, similar mechanisms appear to be at play at both sites, which lead to an increase of about one order of magnitude in the Si:C ratio between fresh phytoplankton (growing at a Si:C ratio close to 0.02 in the North Atlantic and 0.2 in the Southern Ocean, Pondaven et al., 1999) and the biogenic matter, which is collected in the upper traps. Such a comparison needs to be extended to other deep sea sites, and downward to the sediment–water interface. Clearly, the Si:C ratio is increasing from surface waters to the upper trap, then from the upper traps to the lower traps (Fig. 10) and again at the sediment–water interface; but, one has a chance to model this so-called decoupling between Si and C if similar mechanisms, or at least non-random mechanisms, are operating in various regions of the world ocean, and this is very important in the perspective of calibrating BSi as a paleoproductivity proxy.

2.5.3. Biogenic silica deposition on the seafloor

There are two common ways to assess silica deposition rates on the ocean floor. Measuring the particle flux with particle traps moored just above the benthic nepheloid layer provides one way (e.g. Fig. 9) and an overview of the spatial variability of these fluxes has already been given above. Summing the biogenic silica burial rate and the porewater

Table 3

Comparison of opal rain rates ($\text{mol Si m}^{-2} \text{ year}^{-1}$) either measured by means of sediment traps or reconstructed from sedimentary fluxes (assuming steady state, see text), for the few sites where such a comparison is possible. Data from Sayles et al. (1996) for the BATS site, from Köning et al. (1997) for the Indian Ocean, from Ragueneau et al. (in revision) for the northeast Atlantic Ocean, from Berelson et al. (1997) for the equatorial Pacific (mean fluxes between 5 S–5 N), from Rabouille et al. (1997) for the Indian sector of the Southern Ocean (POOZ and PFZ) and from DeMaster et al. (1996a,b) for the Ross Sea. Also given for each site: the sedimentation rate. Note that the sedimentation rate (cm ka^{-1}) at the BATS site has been recalculated from the data given by Sayles et al. (1996) and the sedimentation rate at the Indian Ocean site has been kindly provided by E. Köning

Study site	PAP	BATS	Indian	EqPac	Outer Ross Sea	Inner Ross Sea	POOZ	PFZ
Measured RR	0.062	0.019	0.32	0.109	0.400	1.30	0.51	0.40
Reconstructed RR	0.065	0.018	0.28	0.140	0.374	2.13	2.45	1.09
Recycling flux	0.057	0.017	0.26	0.131	0.367	0.89	2.03	0.73
Accumulation flux	0.008	0.001	0.018	0.009	0.007	1.24	0.42	0.36
Rec/Mes* 100	104.8	94.7	87.5	128.4	93.5	163.8	480.4	272.5
Sedimentation rate	7.5	0.74	4	1.7	1.2	16	10	10

regenerative flux is the other way, which assumes steady state conditions. Comparison of these two approaches is very interesting (Table 3) but possible only when both techniques are employed simultaneously. This has occurred only in a few locations including the Equatorial Pacific (JGOFS, Berelson et al., 1997), the Ross Sea (DeMaster et al., 1996b; Nelson et al., 1996), the northwest Indian Ocean (Köning et al., 1997), the Bermuda Time Series Station (Sayles et al., 1996), the Indian sector of the Permanently Open Ocean Zone (POOZ) and the Polar Front Zone (PFZ) of the Southern Ocean (Rabouille et al., 1997) and the northeast Atlantic ocean (Ragueneau et al., in revision). Fig. 11 shows that both approaches yield consistent estimates for all sites except those located in the Southern Ocean. Considering that the regenerative fluxes may integrate dissolution over time periods as long as hundreds of years (Sayles et al., 1996) compared to the trap data covering often 1 to 2 years (Table 2) and at most 20 years (Deuser et al., 1995), the agreement between the trap data and summed sedimentary fluxes is quite good, at most 30%. In fact, burial rates commonly characterize processes on a thousand-year time scale in the deep sea, however, the burial term in the deep sea generally contributes less than 10%

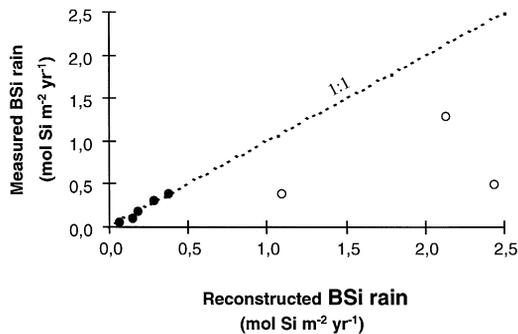


Fig. 11. Comparison of measured (by means of sediment traps) and calculated (by adding the recycling and burial fluxes, assuming steady-state) biogenic opal rain rates, showing a good agreement (the dotted line shows the 1:1 relationship) between both approaches for all sites (filled circles for the BATS site, the northeast Atlantic, the equatorial Pacific, the Indian Ocean and the Outer Ross Sea, in the order of increasing measured BSi rain) but the Southern Ocean (open circles for the PFZ, the POOZ and the inner Ross Sea, same order). See text and Table 3 for values and references.

of the total deposition rate (see Fig. 12), which may explain this good agreement. The poorer agreement in the Southern Ocean is most probably the result of sediment focusing, which is intense in this region (Dezileau, 2000; Dezileau et al., 2000; Pondaven et al., 2000b), and which will be discussed in more details in the following sections.

2.5.4. Recycling of silica at the sediment–water interface

Silicic acid fluxes at the sediment–water interface can be estimated using two major approaches: the deployment of benthic chambers and the calculation using the porewater silicic acid gradients that exist immediately below the sediment–water interface.

A first estimate of the benthic silicic acid efflux at the sediment–water interface can be obtained using Eq. (4) and a linear approximation for the first derivative of the silicic acid gradient at the interface:

$$J_{\text{rec}} = -F_0 D_s [dC/dx]_{x=0}. \quad (4)$$

J is the diffusive flux, expressed in $\text{mmol Si m}^{-2} \text{day}^{-1}$; F_0 is the porosity at the interface, D_s is the whole sediment molecular diffusion coefficient for silicic acid, which is the molecular diffusion coefficient in free solution (D_m) corrected for tortuosity (Berner, 1980). D_s can be expressed as a function of D_m and porosity: $D_s = D_m F^{n-1}$ (Ullman and Aller, 1982) and $D_m = 5.5 \cdot 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ (Wollast and Garrels, 1971). Using a linear approximation, the concentration gradient at the sediment–water interface is a simple two-point calculation between the bottom water DSi concentration and the DSi content of the top 0.5 cm of the sediment column (Hensen et al., 1998). As noted by these authors, the calculation of fluxes from linear gradients might introduce uncertainties since silicic acid concentrations typically display an asymptotic curvature (see Fig. 14) to the sediment surface.

To avoid these problems, a second estimate also makes use of the porewater gradients but follows a non-linear approximation. The DSi profiles are fitted by Eq. (5) (McManus et al., 1995):

$$C_x = C_d - (C_d - C_0) \exp(-\beta x). \quad (5)$$

C_x is the DSi concentration at the depth x , C_d is the asymptotic DSi concentration, C_0 is the bottom water DSi concentration and β is the curvature of the profile, which may have several physical meanings, depending upon the hypothesis used in the models describing the early diagenesis of opal (McManus et al., 1995). The flux is then determined using Eq. (6) (McManus et al., 1995):

$$J_{\text{rec}} = -F_0^n D_m \beta (C_d - C_0). \quad (6)$$

Fluxes can also be measured in situ by means of benthic chambers deployed using the benthic landers (see Tengberg et al., 1995 for a review of their operating systems). The slopes of the DSi increase with time in the chambers are used to calculate the flux of silicic acid coming from the dissolution of biogenic opal, either at the sediment–water interface or within the sediment column.

The comparison of the results obtained by means of benthic chambers or from porewater gradients is always very interesting. Dissolution of biogenic silica occurring right at the sediment–water interface can lead to fluxes, which are higher when measured in situ compared to the diffusional fluxes as estimated from Eq. (6) (Conley, 1987). Infaunal activity creates bioirrigation (Aller, 1982), which also may lead to flux estimates, which are higher when measured in situ compared to those estimated from porewater gradients (Matisoff, 1995, cited in Van Cappellen and Gaillard, 1996).

It is important to note that the good agreement shown in Fig. 11 between the measured and reconstructed opal rain rates provide important confidence on both sediment trap measurements and benthic fluxes, as the latter represent typically over 90% of the reconstructed opal rain for the sites where the measured rain matches the reconstructed rain (i.e. out of the Southern Ocean, Fig. 11).

2.5.5. Burial of silica in marine sediments

2.5.5.1. Measurement. Burial of biogenic opal is calculated by multiplying the weight percent opal, the dry bulk density of the sediments and the sedimentation rate. Opal concentration in sediments has been measured by a variety of techniques (various chemical leaching in different alkaline solutions, XRD...). A recent study (Conley, 1998) has established that the interlaboratory reproducibility can be

rather poor for sediments with a low ratio of biogenic versus lithogenic silica. The XRD technique appears to provide results, which are systematically too high. With alkaline digestions (either single extractions, Mortlock and Froelich, 1989, or sequential extractions, DeMaster, 1981), there is a need to define a new protocol (strength (pH) and duration of the digestion, slope of the mineral correction) when using alkaline digestions for the first time in a given environment. There is also some evidence (Schlüter and Rickert, 1998) that the assumption of linear dissolution of silicate minerals, which is fundamental in the sequential extraction proposed by DeMaster (1981) to correct for the mineral interference, may not be valid at the beginning of the alkaline digestion, as some mineral phases exhibit similar trends as the biogenic silica itself with a faster dissolution during the first hour (Schlüter and Rickert, 1998). Clearly, there is a need to characterize the mineral phases at each site where such a measurement is to be done, and perform alkaline digestions on these minerals, either in the form of pure aluminosilicate standards as did Hurd (1973), which may not be representative of in situ conditions, or using natural samples. The use of the Si:Al ratio (Eggemann et al., 1980) can be a good alternative to perform this mineral correction, as recently proposed by Schlüter and Rickert (1998) and Kamatani and Oku (2000) for the sediments, and by Ragueneau et al. (in press) for the measurement of biogenic silica in the suspended matter of coastal waters. By no means, can the measurement of biogenic silica be considered as a routine one.

In the perspective of relating opal accumulation rates to export fluxes and use them in the field of paleoproductivity, there is an important complicating factor, namely radiolaria. Although phaeodarian radiolaria can be susceptible to dissolution (Erez et al., 1982), polycystine ones are much more resistant (Berger, 1968) and make their way to the sediments where they finally get buried. Because their production is not directly linked to photosynthesis, radiolaria can be seen more as an interference in our attempts to relate BSi accumulation rates to upper ocean processes. Thus, one has to be able to separate diatoms from them when analyzing biogenic opal in the sediments. Unfortunately, most of the data on opal accumulation rates published to date do not

distinguish between diatom-BSi and radiolaria-BSi. A technique has been developed recently (Rance, 1997), which is based on the better resistance to dissolution of radiolaria compared to diatoms. A complete description of this double alkaline extraction can be found in Rance (1997).

Another complication in the estimation of opal burial, as a potential proxy of upper ocean processes, comes from the lateral redistribution of sediments by bottom currents from areas of sediment winnowing to areas of sediment focussing, which can greatly enhance opal burial (and recycling) rates in the latter (see Table 3 and Fig. 10). This is especially important in the Southern Ocean where sediments can be scoured by strong bottom currents associated with the AABW and CPDW (Dezileau et al., 2000). Normalization to ^{230}Th (Kumar et al., 1993, 1995; François et al., 1990, 1993, 1997) have shown that a 5- to 10-fold increase in sediment accumulation rate by lateral transport is not uncommon in this region. Sediment cores are typically collected in areas of sediment ponding, while few successful retrievals of cores were made in areas of sediment winnowing. As a result, extrapolating measured sediment burial rates over an entire area, which includes zones of winnowing leads to overestimating regional burial rates. In theory, Th-230 normalization largely corrects for this effect.

2.5.5.2. Overview. The most recent update of the marine silica budget is provided in Tréguer et al. (1995). The burial terms in this budget are fairly similar to those of DeMaster (1981) with over half of the biogenic silica burial in the oceans occurring in the deep-sea Southern Ocean. However, DeMaster and Ragueneau (1996) have shown that the Polar Front burial rates of biogenic opal in the Southern Ocean may well be overestimated by 20–40% and a more recent calculation (Pondaven et al., 2000b; DeMaster, unpublished data) suggests that this overestimation may even lead to a two-fold decrease in the burial rate of biogenic opal in the Southern Ocean. If correct, this calculation, based on ^{230}Th normalized accumulation rates, leads to opal burial rates in the Southern Ocean to be in the range $0.7\text{--}1.5 \times 10^{14} \text{ g SiO}_2 \text{ year}^{-1}$, i.e. still 17–37 % of the global burial of biogenic silica, which is high but far from the two thirds previously suggested (De-

Master, 1981; Ledford-Hofmann et al., 1986; Tréguer et al., 1995).

One depositional environment that has not been quantified accurately is the continental margin where the missing (following the previous calculation) biogenic silica burial may occur (DeMaster and Ragueneau, 1996). Although biogenic silica contents in these sediments typically are less than 10 weight percent, the sedimentation rates in these deposits are considerably greater than in the deep sea. One approach to quantifying silica burial in continental margins is to normalize the silica flux to organic carbon. DeMaster and Ragueneau (1996) report a biogenic silica/organic carbon weight ratio of 3.1 from several continental margins stations off of the east coast of the United States. This value is typical of the ratio in many continental margin deposits including the California borderland, the Peru margin, the Gulf of California, the Ross Sea, and Walvis Bay. The rate of biogenic silica burial in continental margin deposits can be estimated by multiplying this silica/organic carbon ratio by the burial rate of organic carbon in continental margin deposits ($0.36 \times 10^{14} \text{ g C year}^{-1}$, Hedges and Keil, 1995). The product of these values ($1.1 \times 10^{14} \text{ g SiO}_2 \text{ year}^{-1}$) suggests that continental margin deposits may concentrate 32% to 39% of the total burial of biogenic opal in the marine environment ($4 \times 10^{14} \text{ g C}_{\text{org}} \text{ year}^{-1}$), which provides a reasonable balance to the burial “lost” in the Southern Ocean following the ^{230}Th normalization.

2.5.6. Preservation of biogenic silica in marine sediments: controlling mechanisms

2.5.6.1. Recycling vs. Preservation. A compilation of Si recycling and burial for many deep sea sites shows (Fig. 12) that 95% of the biogenic silica arriving at the sediment–water interface (the opal rain rate) dissolves prior to burial. This proportion decreases to 70% for the sites where the opal rain is the highest, generally located at high latitudes (Bering Sea and Southern Ocean). Because opal rain is calculated as the sum of burial and recycling and because recycling represents by far the largest contribution to the reconstructed opal rain, the correlation between opal recycling and opal rain is obviously excellent. This allows the possibility to derive, in the modern

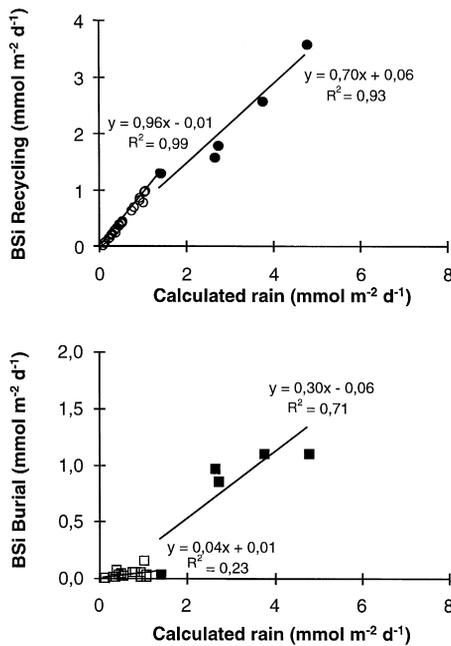


Fig. 12. Opal burial (lower graph) and opal recycling (upper graph) versus the opal rain rate, as reconstructed from the sum of the opal burial and silicic acid fluxes, assuming steady state (all fluxes in $\text{mmol Si m}^{-2} \text{ day}^{-1}$). Filled symbols: conditions of high opal rain rate; open symbols: condition of low opal rain rates. The slope of the lines provides an estimate of the recycling (upper graph) and preservation (lower graph) efficiencies, which are different depending upon the range of opal rain rate. Data from Dymond and Lyle (1994), Rabouille et al. (1997), McManus et al. (1995), Berelson et al. (1997), Van Bennekom et al. (1988), Köning et al. (1997), DeMaster et al. (1992), Sayles et al. (1996), DeMaster et al. (1996a,b), Schneider et al. (1996), Ragueneau et al. (in revision) for the north Atlantic and unpublished data from O. Ragueneau for the Equatorial Pacific. Data for which sediment focusing is suspected (Continental shelves, see also Fig. 11 for deep-sea sites in the Southern Ocean) have been discarded.

ocean, opal rain rates from the benthic silicic acid efflux in a large range of oceanic settings. Because the fraction preserved is much smaller (5% burial for most of the deep sea sites, 30% at higher latitudes), the global correlation between opal burial and opal rain rate is much poorer, making it difficult to derive past changes in the opal rain rate from observed variations in opal burial on the basis of such global relationships. Consequently, it will be essential to develop means of quantifying and understanding opal preservation efficiency at local scale before making any attempt at estimating export fluxes of opal from the sedimentary record.

The seabed preservation efficiency of biogenic opal depends upon several processes, including the sedimentation rate, the bioturbation intensity and the processes influencing the kinetic (dissolution rate) and thermodynamic (solubility) properties of opal dissolution. Porewater silicic acid concentrations rapidly increase below the sediment–water interface, reaching an asymptotic concentration ranging from 50 to almost 900 μM (Fanning and Pilson, 1971; Archer et al., 1993; Rabouille et al., 1997). The traditional paradigm to account for such an increase is that biogenic silica undergoes dissolution during its progressive burial in the sediments, thereby enriching the porewaters in silicic acid. Two important questions still puzzle biogeochemists working on the early diagenesis of biogenic opal: how can opal get preserved in sediments where the porewater silicic acid concentration does not reach saturation with respect to the biogenic silica, as measured in the laboratory (close to 1100 μM at 4°C, Hurd, 1973)? What controls the spatial variations in the porewater asymptotic silicic acid concentration? Several hypotheses have been proposed, described in detail in McManus et al. (1995). Basically, this concentration could be either thermodynamically or kinetically controlled, as illustrated in Fig. 13. In the former case, the asymptotic concentration would reflect true equilibrium between the porewaters and the dissolving biogenic silica (with varying solubility, see Archer et al., 1993). In the latter, this equilibrium may be kinetically inhibited by a number of different mechanisms (Mackin, 1987; Van Cappellen and Qiu (1997a,b), which include the build-up of organic or inorganic coatings, the blocking of reactive surface sites by adsorption of inhibitors, the reduction of the surface density of reactive sites via dissolution and reprecipitation (aging), the preferential dissolution of the most reactive fraction of siliceous particles or the precipitation of authigenic silicate phases.

2.5.6.2. The role of aluminum. With this respect, the dynamic technique developed by Van Cappellen and Qiu (1997a,b) is very promising. This technique allows the direct quantification of biogenic silica solubility and dissolution kinetics and permits the study of the dissolution properties of opal as a function of different parameters such as temperature, pH, ionic strength, departure from equilibrium or

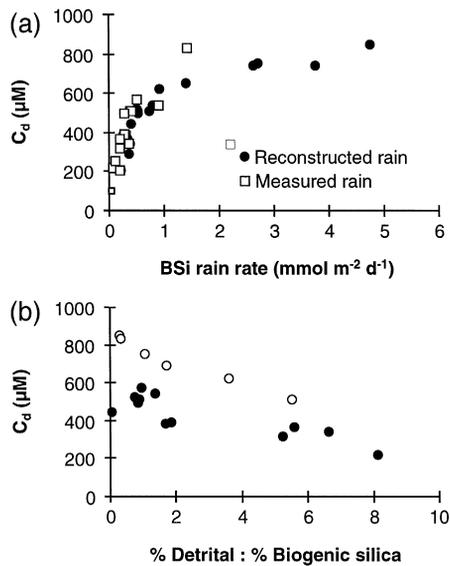


Fig. 13. Asymptotic silicic acid concentration in porewaters (C_d) as a function of the opal rain rate (a), either measured (open squares) or reconstructed (filled circles, see Fig. 11) and as a function of the sediment ratio of detrital to biogenic silica content (b). For (a), data are from the same origin as in Fig. 12. For (b), Southern Ocean data (open circles) are from Van Cappellen and Qiu (1997a) and Rabouille et al. (1997) and Equatorial Pacific + north Atlantic data are from McManus et al. (1995), Honjo et al. (1995), Dymond and Lyle (1994), Ragueneau et al. (in revision) and Ragueneau et al., unpublished data.

trace metal content of the solution. The only study published to date applying flow-through reactors to the problem of biogenic silica early diagenesis is the one of Van Cappellen and Qiu (1997a,b) who have been working in the sediments of the Southern Ocean. They have demonstrated a clear effect of Al on the early diagenesis of opal, which tends to support the kinetic hypothesis.

Upon reaching the seabed, dissolved Al can be taken up by the deposited biogenic silica particles, causing chemical changes that further modify their solubility (Van Cappellen and Qiu, 1997a,b). The extent and speed of this process appears to depend on the amount of Al available from coexisting detrital sediments. When porewater Al builds up to sufficient levels, part of the silicic acid released by the dissolution of the siliceous microfossils may reprecipitate with Al as amorphous Al–Si coatings or as an authigenic clay mineral (Johnson, 1976;

Michalopoulos and Aller, 1995). The combined effects of porewater Al on the solubility of biogenic silica and the reprecipitation of porewater silicic acid with Al result in an inverse relationship between the asymptotic silicic acid concentration (C_d) and the ratio of the detrital and biosiliceous (det:bio) contents of the sediments (Fig. 13b). Such a relationship, described by Van Cappellen and Qiu (1997a) for the Southern Ocean and Ragueneau et al. (1996c) for the Equatorial Pacific is consistent with the idea of a kinetic balance between a slow dissolution of biogenic opal and the precipitation of a less soluble mineral phase as proposed by Mackin (1987). This balance implies a strong decrease of biogenic silica dissolution kinetics downcore, as quantified by Sayles et al. (1996) and by Van Cappellen and Qiu (1997b), due to the growth of surface coatings or to the aging process. Whereas the influence of Al on opal solubility now appears to be well established (see previous sections), the details of the process(es) involved remain obscure which complicates the incorporation of the role of Al in models describing biogenic opal early diagenesis. Adsorption of Al onto the surface of opal may influence the kinetics of opal dissolution, but ultimately does not affect the solubility of opal. Therefore, an Al-induced reduction of opal solubility implies that Al becomes structurally integrated in the tetrahedral structure of the opal itself (Van Cappellen, 1996). Similarly, the occurrence of other impurities, or of defects (e.g., H_2O molecules) within the opal matrix would affect its solubility. For example, the apparent decrease with age of opal solubility might be related to the systematic loss over time of H_2O molecules originally contained within the opal matrix. Therefore, besides the use of flow-through experiments, the molecular structure of opal needs to be deeply explored in order to study the factors affecting the kinetic and thermodynamic properties of opal dissolution (Hurd, 1973).

2.5.6.3. Possible water column influence. A careful examination of Fig. 13b will show that for a similar det:bio ratio, the C_d value is clearly different between the equatorial Pacific and the Southern Ocean sediments. This difference suggests that the diagenetic processes mentioned above affect the deposited biogenic opal, which may already hold variable thermodynamic and kinetic properties from one site to

another, depending upon the intensity of other processes occurring in the water column.

McManus et al. (1995) indeed have shown, using sediment trap material, that if C_d can be lower than the solubility of the biogenic opal present in the overlying sediment traps (because of early diagenetic processes), the solubility they estimated did not exceed 600 μM , which is much lower than the one (at in situ temperature) measured by Van Cappellen and Qiu (1997a) in Southern Ocean sediments (700–900 μM) and than the one measured by Hurd (1983) for fresh phytoplankton (1100 μM). This can be linked to the “equilibrium” hypothesis of Archer et al. (1993) who deny the existence in the field of such a high opal solubility measured on “naked” frustules. These authors indeed argue that the asymptotic concentration represents the solubility of the opal present in situ and its correlation to the rain rate (Fig. 13a) implies a systematic variation of opal solubility with biogenic silica production. In fact, temperature, plankton assemblages or the incorporation of trace elements within the opaline matrix may play a role in affecting the opal solubility.

A recent experiment has been performed (Gallinari et al., submitted), applying the flow-through reactor technique on sediments collected in the north Atlantic and in the equatorial Pacific, enabling an extension of solubility measurements over almost the entire range of observed C_d values. This experiment tends to support the idea that the observed C_d values represent a combination of processes occurring both in the water column and in the sediments (Gallinari et al., submitted). Fig. 14 shows the direct comparison of porewater $\text{Si}(\text{OH})_4$ concentrations with solubilities measured under in-situ simulated conditions ($T = 4^\circ\text{C}$). Clearly, (1) C_d indeed always remains lower than the experimental solubility as observed by Van Cappellen and Qiu (1997a,b) in the Southern Ocean but (2) C_d tends towards the experimental solubility of the opal present in situ, which in fact exhibits strong spatial variations. As an example, in the equatorial Pacific, the relationship between C_d and the det:bio ratio (Fig. 13b) clearly suggests the influence of Al acting probably in a similar way than in Southern Ocean sediments. However, these diagenetic reactions affect a biogenic silica phase which is incorporated in the sediments with a solubility close to 600 μM (Fig. 14), i.e. lower than the solubility

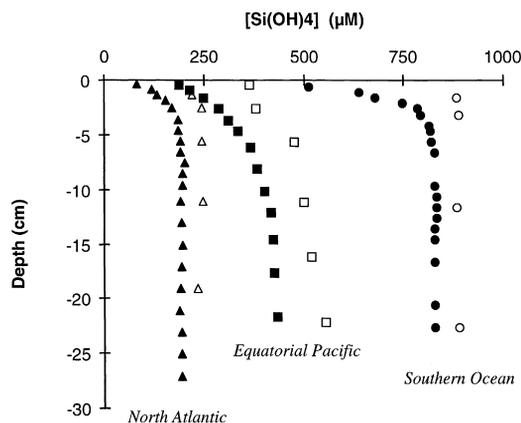


Fig. 14. Direct comparison of porewater $\text{Si}(\text{OH})_4$ concentrations (filled symbols) and experimental solubilities (open symbols), measured under in-situ-simulated conditions ($T = 4^\circ\text{C}$, $\text{pH} = 8$) and corrected for pressure (Van Cappellen, personal communication). Symbols are triangles for the North Atlantic, squares for the equatorial Pacific and circles for the Southern Ocean. Solubility data are from Van Cappellen and Qiu (1997a) for the Southern Ocean and from Gallinari et al. (submitted) for the north Atlantic and the equatorial Pacific. $\text{Si}(\text{OH})_4$ data are from Rabouille et al. (1997) for the Southern Ocean, McManus et al. (1995) for the equatorial Pacific and Ragueneau et al. (in revision) for the north Atlantic.

measured by Van Cappellen and Qiu (1997a) or Hurd (1983), but highly consistent with both the value observed for C_d at low det:bio ratios in the equatorial Pacific (Fig. 13b) and the estimation of opal solubility in sediment trap material made by McManus et al. (1995) using a batch experiment.

What controls the spatial variability of opal solubility is another interesting question. The recent application of flow-through experiments on sediment trap material collected in the north Atlantic clearly shows the presence of various types of opal at 3000 m, with various solubilities (Gallinari et al., submitted). These types of opal may reflect differences in the type of material formed in surface waters: different species, variable incorporation of trace elements (Van Bennekom et al., 1989), variable degree of silicification depending on environmental conditions such as light (Taylor, 1985) or Fe availability (Takeda, 1998; Hutchins and Bruland, 1998). They may also reflect a variable extent of biogenic silica dissolution in surface waters, which has been shown (see previous sections) to depend upon a number of biogeochemical processes. In particular, the duration

of the transfer through the deep waters might contribute to explain the increasing solubility with increasing rain rate (Fig. 13a, as C_d may be taken as a simple proxy for the solubility, see Fig. 14), through the differential removal of the most soluble fractions of the sedimenting opal in regions where this transfer is low and inefficient. In other words, regions where biogenic opal is rapidly conveyed to the seafloor (e.g. the POOZ of the Southern Ocean, Riaux-Gobin et al., 1997) would allow the conservation of the opal quality (high solubility for Archer et al., 1993, high dissolution rate for Rabouille et al., 1997) while others with slow transfer to the seabed would tend to accumulate silica with lower solubility (Ragueneau et al., in revision). The implication of these recent developments is that the quality of the material reaching the sediment–water interface may be different from one site to another, depending upon the history of the particles in the overlying surface and deep waters (Gallinari et al., submitted). This quality will affect the kinetic and thermodynamic properties of opal dissolution in underlying sediments, be it quantitatively (spatial variations in dissolution kinetics or richness in porewater Si(OH)_4 concentrations) or qualitatively (linearity or non-linearity of dissolution kinetics with respect to the departure from equilibrium).

Clearly, there is a crucial need to perform additional dissolution experiments, using batch and flow-through reactors, to study the kinetic and thermodynamic properties of various types of biogenic silica, including structural differences (under the dependence of the diatom life cycle and environmental conditions) or variable degradation degrees (under the dependence of the factors that control the competition between the retention and the export of the biogenic matter, in and out of the euphotic layer, respectively).

As C_d approaches the in situ solubility (Fig. 14), any process that will transport rapidly the biogenic silica particles to the depth where C_d is reached will help at preserving the material (Ragueneau et al., in revision). This thermodynamic preservation clearly will add to the mechanisms affecting the kinetic properties of opal dissolution (see before). Both the sedimentation rate and the bioturbation intensity affect the time spent by the siliceous particles in the upper zone of the sediment column where intense

dissolution can occur, thereby affecting their preservation.

2.5.6.4. Influence of the sedimentation rate. DeMaster et al. (1996b) showed that in rapidly accumulating Ross Sea sediments ($S = 250 \text{ cm ka}^{-1}$), as much as 86% of the silica deposited at the seafloor ultimately was buried. In contrast, for sediments accumulating rates of 1–3 cm/ka, only 1–5% of the silica deposited on the seafloor accumulated in the sediment column. A more general relationship between the opal seabed preservation efficiency and the sedimentation rate is given on Fig. 15, where the slope is very similar to the one found by DeMaster et al. (1996b) for Ross Sea sediments only. Consequently, the siliceous deep-sea sediments beneath the Antarctic Polar Front have a higher than average seabed preservation efficiency because their sedimentation rates (typically 10–30 cm ka^{-1} , but largely controlled by sediment focussing) are higher than most open-ocean deposits (commonly 1–4 cm ka^{-1} or less).

2.5.6.5. Possible role of bioturbation. Bioturbation, and in particular the combination of rapid biodiffusive mixing (Smith et al., 1993) and non-local transport (Pope et al., 1996) allows recently deposited reactive biogenic debris to be rapidly mixed into the seabed. This might affect the dissolution of recently deposited siliceous material which could be trans-

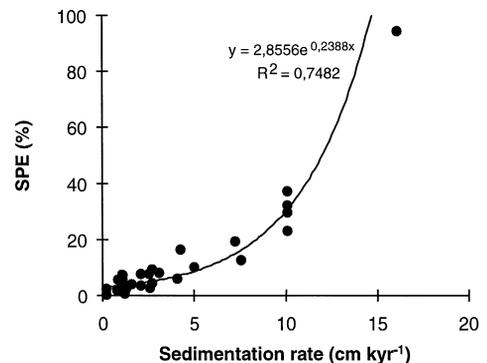


Fig. 15. Seabed preservation efficiency (SPE) versus the sediment accumulation rate for various sites in the ocean, including the Southern Ocean (Rabouille et al., 1997), the Equatorial Pacific (Dymond and Lyle, 1994; Berelson et al., 1997), the North Atlantic (Sayles et al., 1996; Ragueneau et al., submitted) and the Indian Ocean (Köning et al., 1997). See also Table 3.

ported by this process to depth in the sediment column where silicic acid concentrations approach the solubility (Fig. 14; Ragueneau et al., in revision). Note that bioturbation may also affect porewater fluxes by enhancing the irrigation (Aller, 1982) or by redistributing the dissolved substances adsorbed onto biogenic debris (Schink and Guinasso, 1978). The potential role of bioturbation on the preservation of biogenic silica needs to be further addressed. It stresses again the strong influence of the quality of the biogenic matter that reaches the seabed on the preservation of the biogenic silica. Not only the quality of the opal (see before), but also the quality of the organic matter which constitutes the only resource of deep-sea organisms and it has been shown that the benthic macrofauna can be very sensitive to the seasonal variations in the deposition of organic matter at the sediment–water interface (Rice et al., 1986; Smith et al., 1993).

2.5.6.6. The special case of diatom mats. The deposition of diatom mats (Kemp, 1995; Pike and Kemp, 1997; Pearce et al., 1998) provides a striking example, which combines all these factors that may lead to a good preservation of the diatom frustules. The rapid sedimentation through the water column is a first important factor (Rance, 1997). The rapid deposition also induces high sedimentation rates and retards bioturbation, it stabilizes the sediment–water interface, thereby reducing the losses by winnowing, and it finally leads to a rapid saturation of the porewaters, especially if a species prone to dissolution is present within the mats (Rance, 1997).

The suggested dependency of opal dissolution properties (kinetics and thermodynamics) and preservation mechanisms (e.g. bioturbation) upon the quality and quantity of the biogenic matter (BSi and C_{org}) being deposited at the sediment–water interface points to the need to study and model the effect of seasonal variations in the rain rate onto the dissolution and preservation mechanisms of biogenic opal in deep-sea sediments.

3. Modelling the silicon cycle at local and global scales

Modelling studies concerning biogenic silica can be structured into 1-D process models, prognostic

global models of geochemical fluxes (simple box models, biogeochemical OGCMs) and diagnostic inverse models. In this section, the need for a parallel development of these approaches, in close collaboration with experimentalists and involving different spatial and temporal scales, will be demonstrated.

3.1. 1-D diagnostic models

The purpose of 1-D models is to provide a detailed description of processes, which can be tested for individual locations and cases. The overall objective of the modelling effort at this local scale is an integrated description of the fate of the biogenic silica produced in the surface waters, by describing the competition between its dissolution and its preservation as it is exported from surface waters, transported through deep waters and buried in sediments. Once properly parametrized and validated by field data, such integrated models could be used to reconstruct surface processes from the burial of biogenic opal.

3.1.1. Sediment

General introductions to sediment modelling are given in Lerman (1977), Berner (1980), and Boudreau (1997). A summary of 1-D approaches of different complexity to the specific opal recycling issue is given by Boudreau (1990), Archer et al. (1993) and McManus et al. (1995). The basic model, which includes dynamics of opal (i.e. advection and mixing of the solid phase) was published by Schink et al. (1975). Though analytical solutions for this model have been suggested (Wong and Grosch, 1978), generally numerical methods are necessary to solve the model equations due to the increasing complexity of the basic models and the following approaches. Since the publication of this first model, several approaches have been used to describe the reaction term, which is responsible for the biogenic silica dissolution and the build-up of silicic acid concentration in interstitial waters (reviewed in McManus et al., 1995). They all reproduce the exponential increase in the silicic acid concentration, despite being based on fundamentally different assumptions for the control of biogenic silica dissolution. Clearly, independent constraints are needed to choose the most valid model. In particular, surface aging, the

role of Al in the early diagenesis of biogenic silica and the possibility of precipitation of new mineral phases may have to be considered. The dynamic technique of Van Cappellen and Qiu (1997a,b), which quantifies directly the reactivity and the solubility of biogenic opal, provides such constraints and the proliferation of its use should help in the development of a rigorous algorithm for opal dissolution, based on first principles.

Most of these models have been developed in a steady state mode, with the only exception of Rabouille and Gaillard (1990) who studied the effects of the rapid mixing and the deposition of turbidites on biogenic silica early diagenesis. In particular, porewater silicic acid gradients in the top 2–3 cm are greatly affected by these processes, which in turn impacts the silicic acid fluxes at the sediment–water interface. To date however, no model describing the early diagenesis of biogenic opal has incorporated the non-steady state processes linked to seasonal variations in the deposition of biogenic matter. It has been suggested earlier that the latter may have serious implications, not only in terms of silicic acid fluxes at the sediment–water interface, but also for biogenic silica final preservation.

3.1.2. *Surface and deep waters*

Few models have been developed in the water column, that separate diatoms and non-siliceous phytoplankton and that give to silicic acid a role of limiting nutrient (Dugdale et al., 1995; Tusseau et al., 1997; Van Eeckhout and Lancelot, 1997; Dugdale and Wilkerson, 1998; Pondaven et al., 1998, 1999, 2000a). Only one physical/biogeochemical model describes the production and the fate of the biogenic silica (Pondaven et al., 1998, 1999, 2000a). This model has been developed for the Permanently Open Ocean Zone in the Indian Sector of the Southern Ocean (Pondaven et al., 1998, 2000a) and is currently being tested in other oceanic regions (North Pacific, North Atlantic: Pondaven et al., 1999). It relates the export of biogenic silica from the surface layer to the gross production in the euphotic zone. For these models also, there is a crucial need for better parametrization of diatom production, regeneration and export. In particular, better knowledge on the rates of silicic acid recycling or diatom sinking (as single cells, following particle aggregation or

included within grazers fecal pellets) is required before the products of diatom production between export and recycling can be accurately modelled.

3.1.3. *Coupling between surface and sediments*

The present review of the processes that control the production and fate of the biogenic silica in the ocean suggests a tight coupling between surface, water column and sedimentary processes. In the perspective of developing the needed integrated 1-D model coupling surface waters and benthic processes, it is important to note that to our knowledge, no model describing the transfer of biogenic opal in the deep ocean (from the bottom of the surface mixed layer down to the sediment–water interface), has been published. Such a gap probably reflects our lack of understanding of the processes controlling this aspect of the silicon cycle. There is a crucial need to fill this gap, as we have just seen how spatial and temporal variations in the quantity and quality of the material deposited at the sediment–water interface may greatly influence the early diagenetic processes that control the competition between recycling and burial and thereby the spatial variations in the preservation efficiency of biogenic silica. Obviously, such an integrated model would be extremely valuable in the perspective of improving our understanding of the factors that control the fate of the biogenic silica produced in surface waters. It may lead to improvements in the parametrization of global prognostic models as well (see below). To realistically describe the reality of the Si cycle of a given region, such a model needs to be included in a 3-D model describing the regional circulation, which may impact both the production processes and the coupling between surface and sedimentary signals.

3.2. *3-D prognostic models*

The ultimate modelling task at the global scale is to include the Si cycle in a coupled atmosphere/ocean general circulation model. The opal sedimentary record could become an additional tuning parameter that would help differentiate between different scenarios attempting to describe changes in biogeochemical cycling that occurred during past climatic variations. As can be deduced from the previous sections of this review, much remains to be done to achieve this goal.

Simple 3-D box models were developed in order to study the large scale (basin wide) fluxes of silica and associated oceanic tracers for present and past conditions (Broecker and Peng, 1986; Munhoven and François, 1996). While these models can give important insights into possible scenarios, they lack direct quantitative comparison with observations and have reduced prognostic value due to the prescribed kinetics of water flow. Any sediment–water column interaction is, at best, crudely parameterized in this type of model.

Prognostic 3-D ocean general circulation models are in principle able to merge the process oriented 1-D models with the large scale approach of fluxes as used in the kinetic box models. At present, only a few ocean general circulation models are used in conjunction with geochemical tracer studies (Najjar et al., 1992; Loukos et al., 1993; Maier-Reimer, 1993; Drange, 1994). The model of Maier-Reimer (1993) and subsequent versions (Bareille et al., 1998; Heinze et al., 1999) includes the silicon cycle with respect to water column and sediment. Gnanadesikan (1999) uses a simplified Si model for testing the eddy parameterizations in a coarse resolution OGCM. The biogeochemical GCMs are based on velocity fields for the tracer transport, which are the result of a dynamic ocean model. As long as the physical boundary conditions for the ocean are known (i.e., heat and freshwater fluxes as well as wind stress), velocities and resulting tracer concentrations are predicted by the model and self consistent provided gross conservation laws — especially mass conservation — are not violated by the numerical scheme. A sediment module following the approach of Archer et al. (1993) was coupled to the model of Maier-Reimer (1993) and tested for the annually averaged case in order to allow a fast integration of the model to an equilibrium state (Heinze et al., 1999; Heinze and Maier-Reimer, 1999). The opal concentration in the bioturbated mixed layer sediment after 50,000 years of integration are shown in Fig. 16a, using this model, on a carbonate-free basis. The major opal belts as known from the observations are reproduced such as the Southern Ocean, equatorial Pacific and northwest Pacific biogenic silica distributions. Locally, the opal weight percentages still lack quantitative agreement when compared to real observations as derived from an extensive Si data base (Fig. 16b).

This is remarkable in the equatorial Pacific, where opal accumulation rates are strongly overestimated by the model with respect to the observations. This is due to a typical feature of particle-only models where nutrients are trapped in upwelling regions (cf. the discussion on “nutrient trapping” in Najjar et al., 1992) leading to locally too high production rates in the surface ocean. This problem is reduced if a seasonal plankton model including also zooplankton (Six and Maier-Reimer, 1996) is used instead of an annually averaged simple trophic model.

General model deficiencies as those shown on Fig. 16b will be further reduced for the sediment part when the processes governing opal preservation and production are better understood. New developments of 1-D models are a vital pre-requisite for the projected OGCM improvements. The striking advantage of 3-D models with respect to 1-D models is that the water column and sediment are fully interactive, and that single model parameterizations can be tested simultaneously for the global ocean.

3.2.1. Inverse modelling

Inverse modelling approaches offer a quasi-automatic and systematic optimization of model parameters in order to minimize the difference between model results and observations (see for an introduction: Wunsch, 1988). In these models, observed property distributions are the input and the results are the model parameters. In this sense, inverse models are diagnostic with respect to the observations. Since the observations have a limited areal coverage, however, inverse models also help in interpolating existing observations and in deriving global estimates of oceanic processes, such as opal new production rates and dissolution rates from sinking and deposited particles (Usbeck and Schlitzer, 1996; Usbeck, 1999). Some inverse methods, such as the adjoint method (Schlitzer, 1999), can also be extended to time-dependent problems and complete OGCMs including biogeochemistry. A first successful attempt has been made to optimize a dynamical OGCM including a simplified trophic model with respect to sediment $\delta^{13}\text{C}$ data from the last glacial maximum in order to systematically reconstruct the associated velocity and forcing fields (Winguth, 1997). In principle, though a complex task requiring comprehensive code developing and computer

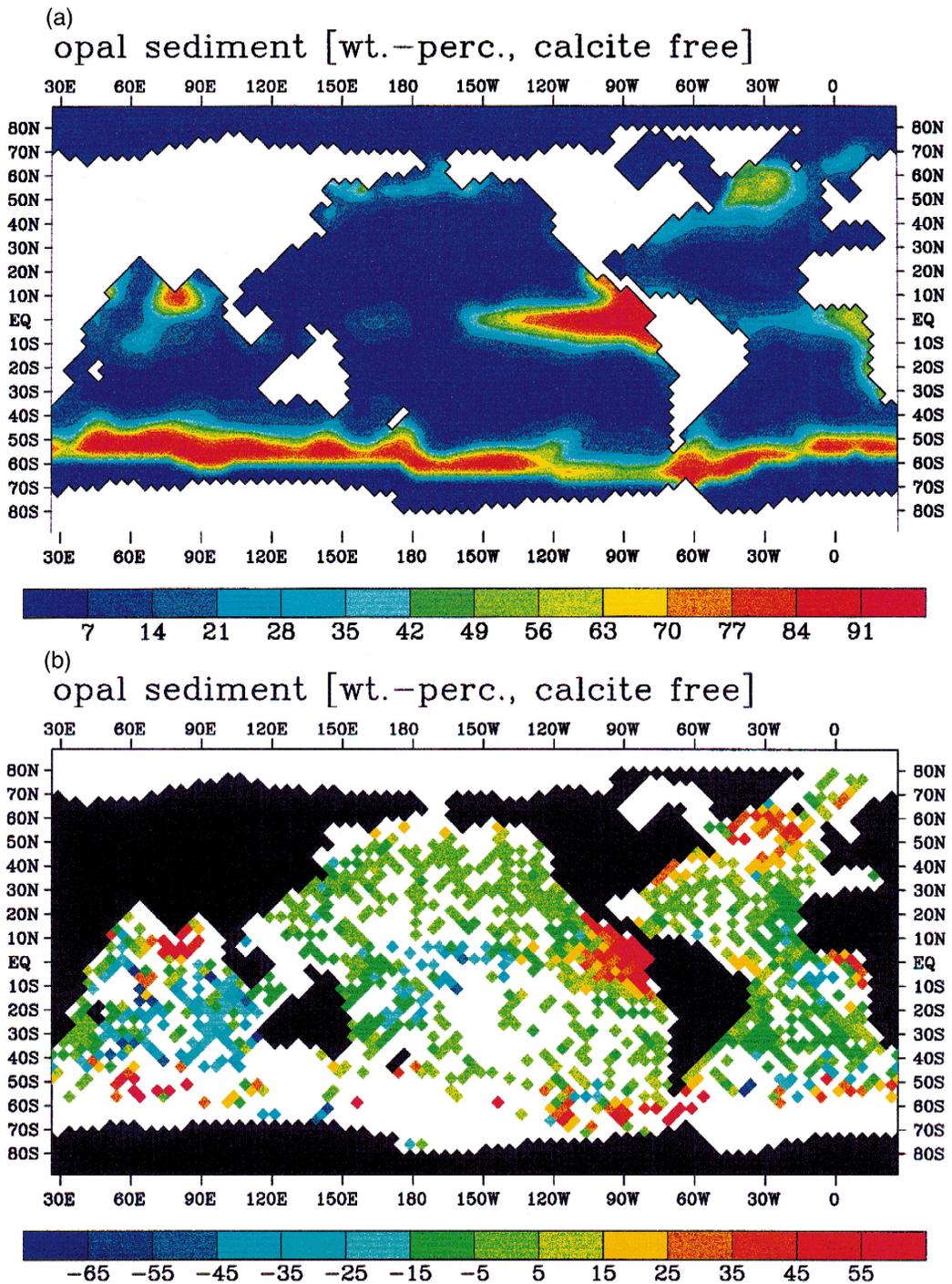


Fig. 16. (a) Opal sediment distribution (in weight % of the total bioturbated sediment mixed layer, on a calcite-free basis) for the late Holocene pre-industrial ocean, as predicted by the annually averaged version of the Hamburg Ocean Carbon Cycle model (from Heinze et al., 1999). (b) Comparison between model outputs and real observations (from Heinze and Maier-Reimer, 1999). For each grid point where data is available, the difference between the model output given in (a) and the corresponding data from the data base (see <http://www.pan-gaea.de>), is calculated and displayed towards the red for overestimates and towards the blue for underestimates.

ressources, this method can be extended to the biogenic silica cycle. Sediment core data for different time periods are available to provide the observational data base for model paleo-reconstructions. Besides the last glacial maximum, the mid-Miocene change in geophysical boundary conditions (open/closed Central American Isthmus) provides a promising test situation (Keller and Barron, 1983; Woodruff and Savin, 1989; Maier-Reimer et al., 1990; Mikolajewicz et al., 1993; Heinze and Crowley, 1997).

4. Perspectives

This review of the way we understand and model the marine biogeochemical cycle of silicon allows us to evidence the major progress, performed in the last decade, and the remaining gaps, which need to be addressed in future studies in order to calibrate properly the biogenic opal as a paleoproductivity proxy.

Major advances have been performed within the last decade in relation to the study of the Si marine biogeochemical cycle. The three most important aspects are: (1) the evidence for an essential role played by the nutrient silicic acid in the control of the export of biogenic matter and the relative proportion of organic and inorganic carbon, (2) the better understanding we have now of the factors that control the spatial variations in the Si:C ratio, in surface waters and in the water column and (3), the interdependency of the surface, water column and sediment reservoirs in the production, dissolution and finally preservation of biogenic silica.

Each of these three important points calls for a continuation of the process studies because major points still need to be addressed. The idea of extending to the world ocean the silicate pump model of Dugdale and Wilkerson (1998) needs to be tested and if silicic acid indeed must play a significant role in the control of the rain ratio, other factors probably also enter the play, such as iron. Ideas on co-limitation begin to emerge (Leynaert et al., in revision) and they need to be further developed in diagnostic models and tested in the field. Nutrient availability has been shown to influence the Si:C ratio, both in surface and deep waters, either by selecting diatoms

over other phytoplankton groups, or by governing the nutrient uptake ratios and the degree of silicification of diatoms. Clearly, the effects of multiple limitation on the Si:C ratio needs to be further addressed and the consequences of the influence of environmental conditions onto diatom growth and silicification need to be explored in terms of the subsequent dissolution of biogenic silica. Dissolution properties of biogenic silica in the sediments have been suggested to be under the dependency of not only diagenetic reactions but also of water column processes such as the extent of surface water dissolution and the degree of freshness of the particles, as they arrive at the sediment–water interface. Testing these hypotheses will clearly depend upon our ability to develop the appropriate tools to directly measure biogenic silica dissolution in surface waters, directly measure the sedimentation rate of the particles and provide direct observations of the mode of transport of opal through the water column.

At this stage, it is important to emphasize that in the perspective of developing a quantitative tracer of paleoproductivity, not only dissolution should be studied but also preservation. Models describing the early diagenesis of biogenic silica put the accent onto dissolution. Interestingly, still discussing about dissolution, this biogeochemical approach based on first principles could be completed by independent approaches that could be used in parallel. The use of the Al/Ti ratio is very promising with this respect, it needs to be further developed to evaluate its ability to reconstruct both the opal rain to the seafloor and the extent of opal dissolution (Dymond, 1996). The micropaleontological approach also has a strong potential. Diatom assemblages have been used for various purposes, which unfortunately cannot be detailed within the scope of the present review article. Beyond their use in the fields of paleoecology, paleogeography and paleoclimatology, diatom assemblages have been used to study spatial and temporal variations in the extent of frustule dissolution (e.g. Pichon et al., 1992). SEM ultrastructure analysis can also be used to develop dissolution indexes (Rance, 1997), in a similar manner as Dittert et al. (1999) did for benthic foraminifera. Beyond these possibilities of improving our ability to estimate the dissolution of biogenic opal, preservation mechanisms are much less well understood. Linked to the sedimentation

rate, the intensity of bioturbation or the build up of surface coatings, these processes need to be further explored and modelled if one is to accurately distinguish between production and preservation in the opal sedimentary records.

4.1. Implications for climate change

Despite these missing gaps, the recent progress performed in the study of the Si marine cycle and the hypotheses that have been formulated to approach these gaps suggest that the use of opal as a paleoproductivity proxy can be looked at in a more optimistic view than recently reported in the literature (e.g. Boyle, 1998), provided progress can be made in three areas. The effort on process studies needs to be continued to answer those major questions which remain uncompletely answered. New parametrizations need to be integrated into biogeochemical models, both 1-D diagnostic models and 3-D (regional and global) prognostic models. The information derived from such a properly calibrated paleoproductivity proxy finally needs to be confronted to other informations derived from the use of a multiproxy approach. Progress in those three directions will make it possible use of the opal sediment record in a much more informed way to understand previous biological conditions in the ocean and the responses of pelagic ecosystems to past climatic changes. Because opal-rich deposits are extensive in both modern and ancient marine sediments, a more accurate interpretation of the information they contain will result in a better mechanistic understanding of the causal linkages connecting Si cycling, ocean productivity, atmospheric CO₂ levels and global climate on time scales ranging from seasonal to glacial/interglacial. Understanding those linkages should lead also to more informed predictions about the likely responses of biological systems in the ocean to any future climatic change, either natural or anthropogenic.

Acknowledgements

This manuscript benefited from the very helpful comments by M. Lyle, G. Filippelli and an anonymous reviewer.

This review was initiated after the first two OPA-LEO workshops, which took place in Brest (June 1996) and Corvallis (February 1997). The first OPA-LEO workshop has been supported by the EC (Sponsorship Grant MAS3 CT96 6332), NATO (Collaborative Research Grant 960269) and by various National and Regional agencies such as the C.N.R.S., the M.E.N.E.S.R., the University of Western Brittany, the Conseil Régional de Bretagne and the Town of Brest. All these organizations are greatly acknowledged for their financial support. The authors wish to thank all the workshop participants, about 50 worldwide, whose contribution made this workshop fascinating and led to this review article, which would have not been written without them all. We are also indebted to the members of the local organizing committee (M. Jouan, M.-T. Joly, A. Masson and R. Corvaisier) who offered their help and support for the logistics.

The global modelling work and the build up of the Si data base (see legends of Table 2 and Fig. 16) are carried out within the EU-funded SINOPS project (MAS3-CT97-0141), many thanks are due to N. Dittert, the Si data curator.

Thanks finally to S. Levitus who provided us with original maps of silicic acid concentrations in the ocean basins (Fig. 6).

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