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To cite this version:

Olivier Ragueneau, Sabine Schultes, Kay Bidle, Pascal Claquin, Brivaëla Moriceau. Si and C interactions in the world ocean: Importance of ecological processes and implications for the role of diatoms in the biological pump. Global Biogeochemical Cycles, 2006, 20 (4), pp.GB4S02. 10.1029/2006GB002688 . hal-00473808

HAL Id: hal-00473808

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Si and C interactions in the world ocean: Importance of ecological processes and implications for the role of diatoms in the biological pump

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Received 12 January 2006; revised 25 October 2006; accepted 6 November 2006; published 21 December 2006.

[1] Diatoms play a major role in carbon export from surface waters, but their role in the transport of carbon to the deep sea has been questioned by global analyses of sediment trap fluxes which suggest that organic carbon fluxes and transfer efficiencies through the mesopelagic are tightly correlated with $CaCO_3$ (Klaas and Archer, 2002; François et al., 2002). Here we explore the role of diatoms in the biological pump through a study of Si and C interactions from the molecular to the global scale. Recent findings on molecular interactions between Si and C are reviewed. The roles of bacteria, grazers and aggregation are explored and combined, to account for the extent of Si and C decoupling between surface waters and 1000 m, observed to be very homogeneous in different biogeochemical provinces of the ocean. It is suggested that the mesopelagic food web plays a crucial role in this homogeneity: Sites of high export are also sites where diatom C is being either remineralized or channeled toward the long-lived carbon pool most efficiently in the mesopelagic zone. The amount of carbon participating in the biological pump but not collected in sediment traps remains to be explored. It is also demonstrated that statistical analyses performed at global scales hide spatial variability in carrying coefficients, indicating a clear need to understand the mechanisms that control spatial and temporal variations in the relative importance of ballast minerals and other export mechanisms such as particle dynamics.

Citation: Ragueneau, O., S. Schultes, K. Bidle, P. Claquin, and B. Moriceau (2006), Si and C interactions in the world ocean: Importance of ecological processes and implications for the role of diatoms in the biological pump, *Global Biogeochem. Cycles*, *20*, GB4S02, doi:10.1029/2006GB002688.

1. Introduction

[2] The silicon (Si) and carbon (C) biogeochemical cycles are coupled owing to intimate interactions which start at the small, molecular scale and extend to the largest possible temporal and spatial scales in the ocean. Diatoms play the crucial role in the active interaction between Si and C cycles during their production in the upper ocean. Diatoms are unique among phytoplankton in that they require Si, in the form of silicic acid ($Si(OH)_4$) for growth and the production of their delicate frustules (made of biogenic silica, $bSiO_2$), which they must protect from rapidly dissolving away in undersaturated seawater. The employment of a unique biochemical strategy, whereby specific glycoproteins surround and also are embedded within the frustule architecture [*Kröger et al.*, 1994, 1997; *Kröger and Sumper*, 1998] not only stabilizes the frustule and lowers dissolution rates [*Lewin*, 1961], but it also results in an intimate interaction between C and Si, relevant to their subsequent cycling and preservation.

[3] The term "decoupling" has appeared in the literature, to describe spatial and temporal variations in the interaction between Si and C cycles which take place at a variety of scales. At the cellular level, the Si:C ratio appears to depend upon environmental conditions. For instance, on continental margins, freshwater diatoms and benthic diatoms have a much higher Si:C ratio than open ocean diatoms [*Conley et al.*, 1989]. In planktonic marine species, limitation by N, P [*Claquin et al.*, 2002] or Fe [*Hutchins and Bruland*, 1998; *Takeda*, 1998] has been shown to increase the Si:C ratio by a factor 2–3. A similar increase occurs when diatoms are exposed to grazers [*Pondaven et al.*, 2006].

[4] At global scale, the decoupling between the Si and C cycles initially derived from observations indicating that 50–75% of Si was lost in the abyssal sediments surrounding Antarctica [*DeMaster*, 1981; *Tréguer et al.*, 1995] while 80% of C was accumulating on continental margins [*Hedges and Keil*, 1995]. At this scale, the term "decou-

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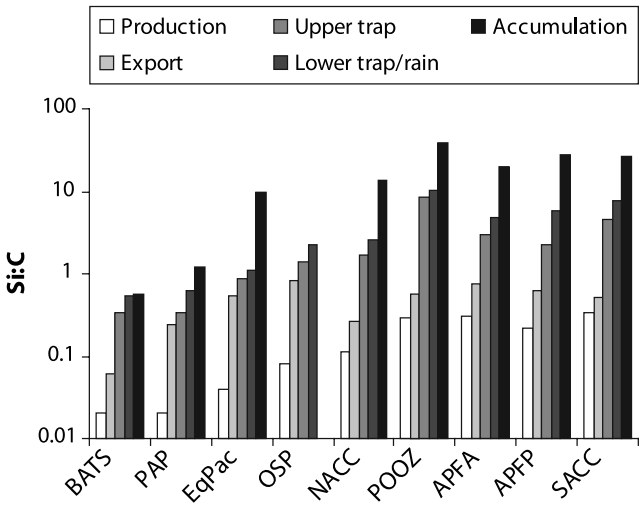

Figure 1. Increase in Si:C molar ratio with depth, from production in surface waters down to accumulation below the bioturbated layer in underlying sediments, in nine biogeochemical provinces of the world ocean [from *Ragueneau et al.*, 2002]. BATS (Bermuda Atlantic Time Series) and PAP (Porcupine Abyssal Plain) are located in the Atlantic Ocean. EqPac (Equatorial Pacific) and OSP (Ocean Station Papa) are located in the Pacific Ocean. The other five sites are located in the Southern Ocean: SACC (Southern ACC, Antarctic Circumpolar Current), NACC (Northern ACC) and APFP (Antarctic Polar Front in the Pacific) are located in the Pacific sector, APFA (Antarctic Polar Front in the Atlantic) is located in the Atlantic sector, and POOZ (Permanently Open Ocean Zone) is located in the Indian Ocean. See *Ragueneau et al.* [2002] for a detailed description of the sites and of the way fluxes have been measured or estimated. Note that for the POOZ site, the Si:C ratio during export was 2.62 in the work by *Ragueneau et al.* [2002]; this was clearly an overestimate as this value was derived from Si and C fluxes measured at 500 m instead of 100–200 m for the eight other provinces. The most recent estimate of these fluxes at 200 m (P. Pondaven, personal communication, 2006) yields a Si:C ratio of 0.58, reported in the present figure.

pling" has also been used to describe the variation of Si:C ratio (by an order of magnitude) during primary production among different oceanic regions [*Ragueneau et al.*, 2002, and references therein]. Likewise, a large body of sediment trap data reveals poor correlations between $bSiO_2$ and C_{org} fluxes [*Klaas and Archer*, 2002]. The transfer efficiency of C_{org} through the mesopelagic seems to be independent from diatom-silica fluxes [*François et al.*, 2002], giving the impression that even if diatoms play an important role in the export of C_{org} from the upper surface layer [*Buesseler*, 1998; *Sarmiento*, 2006], they play only a little role in the transfer of C_{org} to the ocean interior.

[5] Given that decoupling between the Si and C biogeochemical cycles causes major problems in the interpretation of the opal sediment record in terms of paleoproductivity [*Berger and Herguera*, 1992; *Kumar et al.*, 1995], it is important to further explore this phenomenon [*Ragueneau et al.*, 2000]. Following the resolution of the opal paradox in the Southern Ocean [*Pondaven et al.*, 2000; *Hoppema et al.*, 2000; *Nelson et al.*, 2002], *DeMaster* [2002] concluded that $bSiO_2$ accumulation in the opal belt surrounding Antarctica has been greatly overestimated and suggested that the subsequent missing Si sink could be located on continental margins. If confirmed, then the Si and C cycles would be more tightly coupled than previously thought [*DeMaster*, 2002]. Also building on the study of the opal paradox in the Southern Ocean [*Pondaven et al.*, 2000], *Ragueneau et al.* [2002] studied the development with depth of the Si:C ratio in nine biogeochemical provinces where reasonable data sets exist for $bSiO_2$ and C_{org} fluxes during production, export, sinking and accumulation (Figure 1). Two major patterns emerged from this synthesis. First, clear regional differences exist in the Si:C ratio during production but these differences appear to be conveyed down to the sediment-water interface quasi-unchanged; therefore the order of increasing Si:C ratios in sediments from the North Atlantic, the equatorial Pacific and the Southern Ocean clearly find their origins in the water column. Second, a similar increase in the Si:C ratio with depth occurs among the nine provinces allowing the development of the Si:C ratio with depth z to be modeled from a good estimate of $(Si:C)_0$, the Si:C ratio during production using equation (1),

$$(Si:C)_z = (Si:C)_0 . z^{0.41}. \quad (1)$$

[6] Thus there seems to exist some consistency in terms of regional or downward variations in Si:C ratios. What have we learned in the last five years concerning the decoupling between marine Si and C biogeochemical cycles? In the present study, we will first review the most recent findings on Si and C interactions during production in surface waters and when diatoms are being recycled by bacteria, grazed by higher trophic levels, or exported toward the ocean interior. We will then integrate these recent findings in surface water and the mesopelagic, to address the following questions at global scale: What explains the spatial variations in Si:C ratios during production and sinking? Can we quantify the exact role of biological processes (e.g., bacterial activity, grazing, aggregation) in the observed increase in Si:C ratios with depth? Why does the Si:C ratio increase in such a remarkably similar manner in biogeochemical provinces that are characterized by different temperature, productivity and seasonality of primary production? Addressing these questions will lead us toward a discussion on the role of diatoms and other organisms in the biological pump and perspectives for future work.

2. Si and C Interactions During Production and Growth

2.1. Silicon and Carbon Metabolism of the Diatom Cell: Bottom-Up and Top-Down Control of Silicification

2.1.1. Bottom-Up Control of Silicification: Importance of Growth Rate

[7] Recent progress has been made in our understanding of the silicon and carbon metabolism relationship, and how

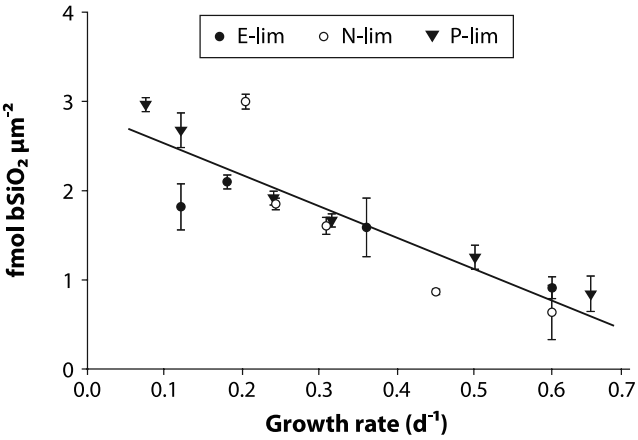

Figure 2. Silica content ($bSiO_2$) per cell surface area (indicative of the silicification degree) as a function of growth rate under light (solid circles), nitrogen (open circles) and phosphorus (solid triangles) limitations [from *Claquin et al.*, 2002].

they are regulated independently of each other. Carbon metabolism depends directly on photosynthesis, whereas the silicon metabolism is related to the cell cycle [*Martin-Jézéquel et al.*, 2000], requiring energy from respiration [*Sullivan*, 1980; *Raven*, 1983]. Consequently, silicic acid uptake takes place in the dark as well as in the light [*Chisholm*, 1981; *Martin-Jézéquel et al.*, 2000]. Silicon uptake and deposition appear to be mainly associated with the formation of new siliceous valves during the G2 and M phase just prior to cell division [*Sullivan*, 1986; *Hildebrand*, 2000; *Claquin and Martin-Jézéquel*, 2005], although some species can assimilate silicon during an earlier phase of the cell cycle and stock it [*Chisholm et al.*, 1978; *Brzezinski and Conley*, 1994]. A part of silicon is incorporated in girdle bands; these bands allow the increase of the cell volume during the cell life and may contain, in some species, a large amount of Si [*Round et al.*, 1990]. Depending on the species, girdle bands can be formed before daughter cells separation or they can be added later during cell growth [*Hildebrand and Wetherbee*, 2003]. The coupling of silicon uptake and girdle bands formation is poorly documented. Many studies showed that diatoms build thicker frustules when limited by temperature [*Durbin*, 1977], light [*Taylor*, 1985] or micronutrients, especially iron [*Takeda*, 1998; *Hutchins and Bruland*, 1998]. It was suggested [*Martin-Jézéquel et al.*, 2000] that a decrease of growth rate entails an increase of silicate uptake. *Claquin et al.* [2002] confirmed this trend in *Thalassiosira pseudonana*. When growth rate is slowed by various limitations cells remain longer in G_2 + M phase, which leads to an increase of the total amount of Si uptake and an increase of frustule thickness (i.e., $bSiO_2$ per cell surface). Variations in silicon content are thereby not so much linked to the type but rather to the intensity of limitation acting on the growth rate (Figure 2). Under silicon limitation however, diatoms grow thinner frustules [*Nelson and Brzezinski*, 1997; *Martin-Jézéquel et al.*, 2000]. Recently, *Claquin and Martin-Jézéquel* [2005] showed in a synchronized culture of *Cylindrotheca fusiformis* how the Si/C ratio is controlled by the cell cycle and the photocycle.

2.1.2. Bottom-Up Control of Silicification: Other Environmental Factors

[8] Factors such as salinity, pH or metals (iron, aluminum, germanium) can also influence the silicon metabolism and frustule morphology without any alteration in growth rate [*Hildebrand*, 2005]. *Conley et al.* [1989] showed that marine diatoms have one order of magnitude less silica per unit cell volume than freshwater species which may be related to the reduced silicate availability in the marine environment, differences in sinking strategies, or salinity effects. Iron limitation, on the other hand, may affect the silicon metabolism by influencing the silicon uptake kinetics [*Leynaert et al.*, 2004]. In *Cylindrotheca fusiformis* iron stress decreases the maximal specific Si uptake rate (V_{max}) and the half-saturation constant for silicic acid (Ks). pCO_2 may also influence silicon metabolism and content [*Milligan et al.*, 2004], with low pCO_2 resulting in an increase of silicon content due to lower silicon efflux and dissolution.

2.1.3. Top-Down Control of Silicification

[9] *Smetacek* [1999] proposed an intriguing ecological mechanism for the build up of highly silicified frustules: protection against grazers. Diatom frustules can be very resistant [*Hamm et al.*, 2003] so that small copepods for instance seem to prefer protozoa over robust diatoms [*Verity and Smetacek*, 1996]. Recent experiments supported this hypothesis. The diatom *Thalassiosira weissflogii* placed in a medium which had previously contained copepods *Calanus helgolandicus* built more heavily silicified frustules than control diatoms grown in medium without grazers, with a difference notably similar to that found from the bottom-up control of the silicification [*Pondaven et al.*, 2006].

2.2. Molecular Control of Biomineralization: Consequences for $bSiO_2$ Dissolution

[10] The slower remineralization of Si compared to C [*Officer and Ryther*, 1980] is the basis for the silicate pump mechanism proposed by *Dugdale et al.* [1995] and for the increase in the Si:C ratio with depth synthesized by *Ragueneau et al.* [2002]. The rates of Si and C remineralization have historically been studied independently, because $bSiO_2$ dissolution was thought to be a purely physico-chemical process whereas C_{org} recycling is biologically mediated by bacteria and grazers.

[11] The physico-chemical controls on silica dissolution have been reviewed by *Nelson et al.* [1995], *Ragueneau et al.* [2000] or *Van Cappellen et al.* [2002] and will not be detailed here. The latter review pointed out the importance of temperature, aluminum content of the frustules, departure from equilibrium and specific surface area, as essential controls on the thermodynamic and kinetic properties of diatom-silica dissolution. Actually, temperature is the only factor accounted for in recent biogeochemical models [*Fuji and Chai*, 2005]. A closer look at the constitution of a diatom frustule, however, suggests that Si and C interactions at both the molecular and cellular levels play critical roles in their subsequent remineralization and ultimately, the relative fate of Si and C in surface waters.

2.2.1. Si and C Biochemical Interactions During Silica Deposition: Influence on Diatom Shape and Surface Area

[12] The large variety of frustule shapes, of setae and other protuberances, induces large fluctuations in diatom dissolution kinetics [*Kamatani*, 1982; *Bidle and Azam*, 1999, 2001]. The species-specific design of the frustule and the processes involved in biomineralization are directly related to the importance of the specific surface area in all dissolution processes [*Van Cappellen et al.*, 2002].

[13] The silicic acid taken up from the environment is concentrated in an intracellular organelle called silica-deposition vesicle (SDV), where silicates are polymerized to $bSiO_2$. Studies suggest that, in the SDV, an organic matrix influences $bSiO_2$ formation and controls $bSiO_2$ nanopatterning [*Hecky et al.*, 1973; *Swift and Wheeler*, 1992]. Kröger and collaborators have isolated novel peptides known as silaffins and long-chain polyamines (LCPA) from diatom cell walls, which can precipitate Si as nanospheres in vitro suggesting that they participate in biomineralization processes within the SDV [*Kröger et al.*, 1999, 2002; *Poulsen et al.*, 2003; *Poulsen and Kröger*, 2004]. At the moment it is unknown if the silaffins are completely or partially embedded in vivo within $bSiO_2$, or just tightly associated with the surface [*Hildebrand and Wetherbee*, 2003]. Spherical structures of $bSiO_2$ that conglomerate on the nanometer scale, so called micro spheres, vary in size among diatom species and been observed by using atomic force microscopy [*Crawford et al.*, 2001]. This type of micromorphogenesis determines the contact surface area at microscale and interactions of Si and C_{org} on the molecular scale are probably largely involved in the dissolution properties of the frustule. Quantifying these effects on dissolution properties will be most challenging, given the difficulty of dissolution measurements with small quantities, and given the difficulties in measuring properly surface areas of $bSiO_2$ in natural samples.

2.2.2. Si and C Biochemical Interactions During Silica Deposition: Influence on Dissolution Properties?

[14] The strong interaction between Si and C at molecular scales might also provide an alternative explanation to the existence of different $bSiO_2$ phases. Working with material collected in sediment traps of the North Atlantic, *Gallinari et al.* [2002] measured $bSiO_2$ solubility values between 500 and 700 μM, i.e., 30–50% lower than the solubility measured at 2°C for fresh diatoms (close to 1100 μM, synthesis in work by *Dixit et al.* [2001]). Such a decrease, commonly observed in sediments and attributed to early diagenetic properties, cannot be explained in traps by a strong influence of the detrital:biogenic silica ratio. Rather, *Gallinari et al.* [2002] suggested that the most reactive fraction had dissolved in the cups prior to collection, so that the flow-through experiments has been carried out on a remaining phase with different dissolution properties. This resembles observations of selective dissolution of delicate frustule structures compared to more robust ones reported earlier [*Kamatani and Riley*, 1979; *Kamatani*, 1982]. Are these "phases" related to dissolution properties of the $bSiO_2$ alone, or related to the existence of variable strength in the biochemical interactions between Si and C described above? It could be that the strength of Si and C interactions at molecular scales not only influence the shape and surface area of the diatoms, but also, the dissolution properties of the surfaces exposed. In their review, *Hildebrand and Wetherbee* [2003] draw a comparison between the diatom frustule and the abalone shell. This shell made mainly from calcium carbonate is 3000 times more fracture-resistant than the crystalline form of calcium carbonate because it also contains a few percent of organic material. Progress on this topic will require some detailed work at nanoscale, and will be most challenging.

2.2.3. Si and C Biochemical Interactions During Silica Deposition: The Origin for an Essential Role Played by Bacteria

[15] Seawater is everywhere undersaturated with respect to $bSiO_2$ causing any surface that is exposed to undergo rapid chemical dissolution. Living diatoms protect their frustules from dissolution with an organic matrix [*Lewin*, 1961], which consists of a variety of organic components, including glycoproteins (e.g., frustulins, silafins, described earlier) and polysaccharides, and probably derives from the SDV. It is often so thin that it is not observable in transmission electronic microscope [*Round et al.*, 1990]. Mucilage secreted by the cell can also surround the wall and can be also involved in movement or adhesion of the cell. This mucilage is largely formed by exopolymeric substances (EPS), rich in polysaccharides, at the origin of the formation of aggregates, discussed later.

[16] $bSiO_2$ from intact diatom detritus is remarkably resistant to dissolution (specific $bSiO_2$ dissolution rates, or V_{dis}, of 0.001 d^{-1}), when incubated in either autoclaved or filter-sterilized (0.02 μm pore size) seawater [*Bidle and Azam*, 1999, 2001], even at temperatures as high as 33°C (*Bidle et al. 2002*). This striking resistance to dissolution under such harsh abiotic conditions demonstrates the effectiveness of the organic matrix as a protective barrier against chemical hydrolysis. Hence high $bSiO_2$ dissolution kinetics requires that $bSiO_2$ frustules be denuded of this protective organic matrix [*Kamatani*, 1982; *Bidle et al.*, 2002], revealing a critical role for biology in both $bSiO_2$ and POC regeneration processes.

3. Si and C Interactions During Transformation and Degradation of Diatoms

3.1. Essential Role of Bacteria in Silica Dissolution

[17] The hydrolysis of the diatom's protective glycoproteins via bacterial ectoproteases has emerged as a major mechanism regulating C and Si biogeochemistry by simultaneously accelerating their regeneration [*Bidle and Azam*, 1999; *Patrick and Holding*, 1985], a direct demonstration of how a biologically driven process adventitiously controls the cycling of a inorganic macronutrient. Extensive C and Si regeneration from diatom detritus is dependent on the rapid and intense colonization of diatom detritus by bacteria [*Biddanda*, 1988; *Biddanda and Pomeroy*, 1988; *Bidle and Azam*, 1999], which serves to dramatically elevate both the local bacterial concentration (to 10^{11} cells mL^{-1} in detritus microenvironment; $\sim 10^5$ times the bulk phase bacterial concentration) and the biochemical pressure

exerted on the organic matrix via ectohydrolases [*Bidle and Azam*, 1999]. Hence colonization intensity and the biochemical activity of colonizers, rather than bulk bacterial abundance, critically control C and Si cycling.

[18] Amazingly, the rates of bacteria-mediated silica dissolution were nearly as fast as those reported for acid-digested frustules at a slightly higher temperature (5.5–18% d^{-1}) [*Kamatani*, 1982], indicating that bacterial activity efficiently denudes the organic matrix, allowing for subsequent chemical dissolution of the naked frustule, and that its regulation is the rate-limiting step. Indeed, C and Si regeneration rates show significant variability (~fourfold) among different bacterial assemblages and isolates [*Bidle and Azam*, 1999, 2001], implicating species composition, colonization dynamics, metabolic state and ectoprotease profiles as important variables. Experiments using bacterial isolates and natural bacterial assemblages directly demonstrated that colonizer protease activity is the dominant ectohydrolase leading to adventitious $bSiO_2$ dissolution [*Bidle and Azam*, 1999, 2001; *Bidle et al.*, 2003]. Only protease activity, rather than glucosidase, lipase and chitinase activities, strongly correlated with silica dissolution rates. Furthermore, direct addition of purified protease (Pronase E) to uniformly ^{14}C-labeled diatom detritus directly verified this role in regenerating POC and $bSiO_2$ [*Bidle and Azam*, 1999].

[19] Subsequent field studies during a natural diatom bloom in the Monterey, California upwelling system, confirmed that proteolytic removal of the protective organic matrix significantly accelerated $bSiO_2$ dissolution rates in situ and contributed to the variability in oceanic $\int D$: $\int P$ ratios [*Bidle et al.*, 2003]. Selective inhibition of bacterial activity with antibiotics and protease inhibitors reduced abundance, production and proteolytic activity of attached bacteria in general, and V_{dis} of diatom detritus in particular by 44% ± 27% s.d. (n = 6) over 24 h. The generally observed increase in V_{dis} with depth is not caused by the presence of more active bacterial assemblages deeper in the euphotic zone. Correlations between proteolytic hydrolysis by attached bacteria and $bSiO_2$ dissolution rates at a given depth were weak and insignificant [*Bidle et al.*, 2003]. Instead, integrated protease activities, accounting for the cumulative effect of proteolytic attack over the depth range sampled, strongly correlated with dissolution rates measured at the depth of the lower bound of the integration [*Bidle et al.*, 2003]. Thus increased V_{dis} with depth in the upper 20–80 m of the ocean is caused by the progressive removal of organic matter from frustules during sinking.

3.2. Temperature Control of Bacteria-Mediated Selective Preservation of Si and C

[20] Temperature exerts perhaps the strongest control of relative Si and C preservation efficiencies since V_{dis} increases ~10-fold with each 15°C temperature increase [*Kamatani*, 1982; *Kamatani and Riley*, 1979]. Bacterial mediation of $bSiO_2$ dissolution suggests that temperature controls not only its chemical depolymerization [*Lewin*, 1961; *Lawson et al.*, 1978] but also the rate of bacterial removal of the protective organic matrix. Since the removal of organic matrix is essential for the initiation of $bSiO_2$ dissolution, temperature control would initially be exerted on the rate of organic matter degradation by colonizing bacteria.

[21] *Bidle et al.* [2002] demonstrated that bacteria isolated from Antarctic waters (−1.8°C) and from temperate waters off Scripps Pier (15–20°C) mediated different degrees of POC decomposition and $bSiO_2$ dissolution at their respective in situ temperature due to differential temperature regulation of their respective ectoprotease activities. Antarctic isolates caused ~sixfold preferential preservation of Si compared to C at −1.8°C, primarily owing to very low $bSiO_2$ dissolution rates (V_{dis} of 0.003–0.006 d^{-1}). In contrast, temperate isolates incubating at 17°C decreased the Si:C preservation ratio to ~2.4 owing to higher mediation of $bSiO_2$ dissolution (V_{dis} = 0.023–0.036 d^{-1}). Likewise, natural bacterial assemblages from California coastal waters showed similar differences in Si:C preservation over wide temperature ranges, like those seen vertically through the water column (5° to >30°C) [*Bidle et al.*, 2002]. Thus warmer temperatures dramatically intensified coupling and reduced the Si:C preservation ratio from ~6 at −1.8°C to ~1 at 33°C by hastening POC hydrolysis and initiating rapid frustule dissolution.

[22] Importantly, decomposition of diatom detritus and/or aggregates by surface-derived bacterial colonizers would appear slow as they sink across the thermocline and sink to depth, with implications for the efficiency of the both biological and silica pumps [*Longhurst and Harrison*, 1989; *Dugdale and Wilkerson*, 1998]. Mesophylic, surface-derived bacterial assemblages incubating at 5°C did not regenerate diatom POC after 3 days, despite large POC enrichment (~60 μM C) [*Bidle et al.*, 2002], largely owing to severe limitation of ectoprotease activity and bacterial growth rates at 5°C [*Bidle et al.*, 2002]. Furthermore, the catalytic activity of ectoproteases from temperate and Antarctic bacterial isolates, and from natural bacterial assemblages, displayed distinct temperature dependence and strong limitation at in situ temperature [*Bidle et al.*, 2002]. It follows that even small temperature perturbations may significantly increase the processing efficiency of organic matter and lead to variations in Si:C preservation [*Bidle et al.*, 2002].

[23] An empirical relationship has now emerged between diatom POC decomposition and $bSiO_2$ dissolution at different temperatures (Figure 3) to interpret the relative preservation dynamics of Si and C in surface waters and possibly during sinking. Importantly, this functional relationship relates $bSiO_2$ dissolution specifically to diatom POC and incorporates temperature effects on chemical dissolution of naked $bSiO_2$ frustules [*Kamatani and Riley*, 1979; *Lewin*, 1961]. Thus it should retain its general shape regardless of diatom identity, although the actual values of C and Si decoupling will depend on diatom biochemical makeup and morphology. A key feature of the relationship is that substantial POC utilization is required for the initiation of rapid $bSiO_2$ dissolution, even at high temperatures (Figure 3a). More extensive carbon removal is required for $bSiO_2$ dissolution at low temperatures resulting in a progressive increase in the relative preservation of Si to C (~1 at 33°C to ~6 at −1.8°C) (Figure 3b). Slow (but detectable) POC hydrolysis and negligible V_{dis} at <0°C

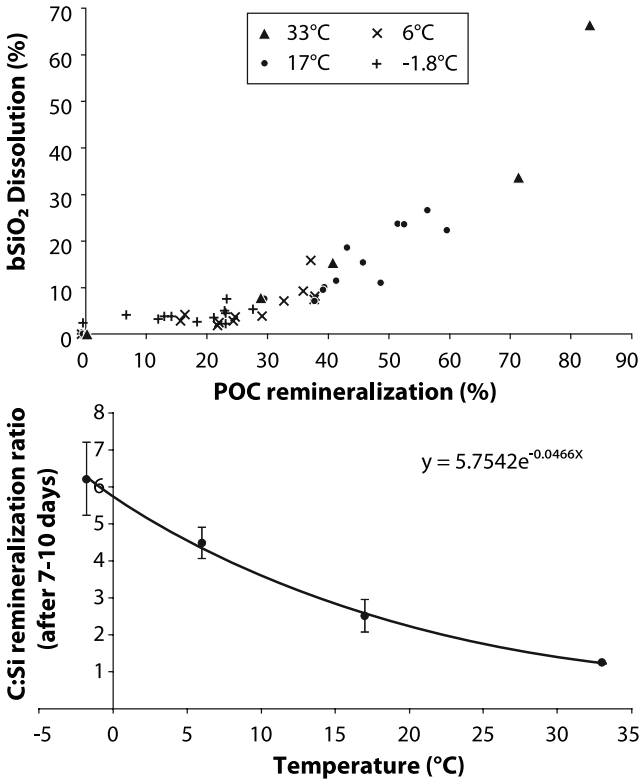

Figure 3. (top) Dependence of biogenic silica ($bSiO_2$) dissolution on the remineralization of particulate organic carbon (POC) at different temperatures. Shown is a composite for *T. weissflogii* detritus incubating with different species of bacteria and natural bacterial assemblages during a 7-day time period in order to illustrate the general trend in Si:C remineralization with temperature. Note the significant increase in slope with elevated temperatures, indicating little $bSiO_2$ dissolution at modest POC removal at low temperatures, while, at higher temperatures, the elevated POC remineralization leads to significant $bSiO_2$ dissolution and a lowering of Si:C enrichment. The general shape of the relationship is noteworthy because it incorporates biological removal of carbon (first step) and physico-chemical dissolution of $bSiO_2$ (second step). (bottom) The influence of temperature on the relative C and Si preservation. Each point represents an average (+standard deviation) of the C:Si remineralization ratio after 7 days for at least three experiments at each temperature. Data were fitted to exponential regression.

leads to a larger cumulative POC removal relative to $bSiO_2$. Small increases in temperature will stimulate POC hydrolysis and expose a larger surface area of $bSiO_2$ frustules to chemical dissolution.

[24] We need to further explore the role of bacterial biochemistry, especially concerning the molecular diversity, identity and activity of bacterial proteases. It is increasingly clear that bacterial proteases specifically regulate the marine C and Si cycles from diatoms [*Bidle and Azam*, 1999, 2001; *Bidle et al.*, 2002, 2003], but our knowledge of their diversity is still surprisingly vague. How many different ectoproteases do individual marine bacteria employ? What is the effective proteolytic biodiversity at play during a diatom bloom? We are presently poised to successfully address these questions with innovative technical approaches to marine biochemistry. The fundamental role of bacterial biochemistry in mediating $bSiO_2$ dissolution also needs to be incorporated in models, as suggested by experimentalists [*Bidle et al.*, 2003] and modelers [*Fuji and Chai*, 2005], but not done yet.

3.3. Role of Grazers

[25] Most of the increase in Si:C ratio with depth occurs first in surface waters and in the mesopelagic layer, then at the sediment-water interface, with very little changes occurring throughout the deep ocean (Figure 1). This suggests that trophic interactions in pelagic and benthic food webs must play an important role in the relative preservation of Si and C [*Ragueneau et al.*, 2002]. Zooplankton grazing on diatoms has been shown to digest the majority of ingested organic material leading to preferential preservation of $bSiO_2$ within faecal pellets [*Cowie and Hedges*, 1996; *Tande and Slagstad*, 1985]. Biochemical analysis of digested diatoms show that zooplankton preferentially digest intracellular materials with concomitant preservation of cell-wall polymers, leading to egested material with altered Si:C composition relative to diet [*Cowie and Hedges*, 1996].

[26] Carbon assimilation efficiency in pelagic grazers varies between 50 and 90% [*Daly*, 1997]. Assuming that 100% of ingested $bSiO_2$ is found in faecal pellets, a theoretical increase in the Si:C ratio of 2–10 can be expected between the food and the material egested in faecal pellets. Such increases have been observed both during in vitro experiments and during in situ surveys. Calanoid copepods feeding on *Thalassiosira* sp. egest material that has been enriched for Si by a factor of 4–5, with >85% of $bSiO_2$ remaining in faecal pellets [*Cowie and Hedges*, 1996; *Tande and Slagstad*, 1985]. Along 170°W in the Pacific sector of the Southern Ocean, a very similar range of increasing factor (IF) in the Si:C ratio between food and faecal pellets has been observed by *Dagg et al.* [2003]. Enrichment by pelagic grazers can thus contribute to measured increase by a mean factor of 6 between production and export (Figure 1), [*Ragueneau et al.*, 2002].

[27] The effect of grazing on $bSiO_2$ recycling remains ambiguous, however. Diatoms that have passed through the gut of a grazer have experienced a series of transformations, of which mechanical destruction, digestion of carbon and packaging into condensed faecal matter are only the most obvious. Grazing activity also increases the number of broken diatom frustules in the water column (e.g., *Roman and Rublee*, 1980], which would prepare them for subsequent colonization by bacteria. Of these phenomena associated with grazing, some may enhance opal dissolution and some slow down or prevent its remineralization. Microzooplankton grazing on diatoms is substantial [*Calbet and Landry*, 2004] and the feeding mode [*Jacobson and Anderson*, 1986] can be expected to have a dissolution enhancing effect similar to bacteria. For copepod grazers, the first signs of dissolution are observed for frustules inside

freshly produced faecal pellets indicating that digestion initiates dissolution [*Jansen*, 2002]. This is possibly due to enzyme activities in the gut [*Jansen*, 2002] which also hastens carbonate dissolution [*Jansen and Wolf-Gladrow*, 2001] or due to the activity of enteric bacteria [*Nagasawa*, 1992]. Subsequent dissolution inside the faecal pellet is reduced however [*Jansen*, 2002] probably owing to processes acting within aggregates (see below). Grazing by copepods and krill also reduces the V_{dis} of Antarctic diatom communities by a factor of 4 to 26 [*Schultes*, 2004, S. Schultes et al., Influence of mesozooplankton grazing on the dissolution rate of Antarctic diatom silica, submitted to *Marine Ecology Progress Series*, 2006], the large variability being correlated to the amount of ingested $bSiO_2$ and the solidity of the faeces. Faecal pellets therefore preserve $bSiO_2$ as had been proposed earlier [*Schrader*, 1972; *Honjo and Roman*, 1978]. Feeding and destruction of faecal pellets, i.e., coprophagy, coprorhexy and coprochaly [*Noji et al.*, 1991] possibly hastens the rate of $bSiO_2$ dissolution by exposing crushed frustule material to undersaturated seawater and bacterial activity. The trophic position of grazers will hence strongly influence the role of grazing with respect to Si and C cycling [*Schultes*, 2004].

[28] If the direct effect of copepod grazing on Si and C decoupling has been reasonably well demonstrated, there is virtually no information on the effects of other grazers and especially on large microphages feeding on the sinking flux of faecal pellets and aggregates. Importantly, such effects can be studied in the laboratory; the application of experimental results to the field however, is complicated by numerous, often unknown, processes that take place in the twilight zone including, among others, vertical migrations of organisms, be they nycthemeral or onthogenic.

3.4. Role of Aggregation

[29] An important characteristic of diatom cells is their excretion of dissolved polysaccharides that abiotically form transparent exopolymer particles (TEP) [*Passow*, 2000]. TEP increase the stickiness of cells which then aggregate [*Alldredge et al.*, 1993; *Passow et al.*, 1994; *Passow and Alldredge*, 1995]. Very few studies have explored Si cycling inside aggregates [*Brzezinski et al.*, 1997; *Passow et al.*, 2003; *Moriceau et al.*, 2006] and results appear to be contradictory. *Brzezinski et al.* [1997] demonstrated enhanced internal $bSiO_2$ solubilization for diatom-containing marine snow aggregates because aggregates harbored high bacterial concentrations expressing intense ectohydrolase activities [*Smith et al.*, 1992]. Two other studies conducted in aggregated versus nonaggregated diatoms showed a decreased apparent $bSiO_2$ dissolution rate from aggregates [*Passow et al.*, 2003; *Moriceau et al.*, 2006].

[30] When dissolution is examined by following the exchange and accumulation of silicic acid in the medium surrounding aggregated cells, the decreased dissolution rate is termed "apparent" to take into account the retention of regenerated silicic acid within the aggregate [*Brzezinski et al.*, 1997; B. Moriceau et al., Modeling biogenic silica dissolution in an aggregate, submitted to *Marine Ecology Progress Series*, 2006) (hereinafter referred to as Moriceau et al., submitted manuscript, 2006a). Modeling of the experimental results of *Moriceau et al.* [2006] demonstrated that both high retention inside aggregates and a lower net dissolution rate of the $bSiO_2$ within aggregates must be invoked to explain the observed difference in bulk silicic acid accumulation in the medium between aggregated and unaggregated cells (Moriceau et al., submitted manuscript, 2006a). The lower dissolution rate within aggregates can in part be attributed to the enhanced viability of entrapped cells, as *Nelson et al.* [1976] measured near-zero dissolution rates in living diatoms. Indeed, *Brzezinski et al.* [1997] measured elevated $bSiO_2$ production rates due to elevated silicic acid availability to viable cells. In addition, the higher silicic acid concentration inside the aggregates can have a strong, nonlinear, impact on $bSiO_2$ dissolution kinetics [*Van Cappellen and Qiu*, 1997]. The diffusion of silicic acid from inside to outside the aggregate is reduced by two orders of magnitude possibly owing to an adsorption of silicic acid on the aggregate matrix (Moriceau et al. submitted manuscript, 2006a), but this phenomenon clearly warrants further work.

[31] The important role that bacteria play in the dissolution of single cells and Si and C decoupling is probably attenuated in aggregates. First, bacteria mostly act on detrital diatoms whereas diatoms stay alive longer in aggregates [*Moriceau et al.*, 2006]. Second, the net impact of aggregation is a clear lowering of Si remineralization and exchange to bulk water phase because silicic acid is retained inside aggregates. Interestingly, certain bacterial species can stimulate aggregation, through the production of exopolysaccharides upon colonization [*Alldredge et al.*, 1993; *Bidle and Azam*, 2001] and in these cases, very little recycling of $bSiO_2$ was observed even under expression of extremely high cell-specific ectoprotease activity [*Bidle and Azam*, 2001]. Here active colonization would prevent release of C and Si into the bulk water and serve to essentially fix the Si:C ratio in particles during the transit through the water column.

[32] Thus laboratory experiments have demonstrated a clear influence of bacteria and grazers on Si and C decoupling, and suggest that aggregation may exert a contrary influence by stimulating $bSiO_2$ production, and, ultimately, preventing the release of Si and C into the surrounding water. In principle, the Si:C ratio of the aggregates leaving the surface layer will depend upon the physiological status of the cells by the time the aggregates are being formed. It may be low if aggregate formation occurs from physical factors (turbulence and differential settling rates of healthy cells); it may be higher if aggregation occurs after nutrient limitation, among senescent cells which are more susceptible to bacterial attack.

4. Global Patterns

[33] This increased understanding of the mechanisms that decouple Si and C cycles in surface waters and in the mesopelagic, may help to address three major questions relevant to global-scale phenomena: (1) What explains the increase of Si:C ratio with depth by a factor close to 17 between surface and 1000 m? (2) What explains the homogeneity of this downward increase in the various provinces of the ocean? (3) What are the implications, concerning the role of diatoms in the biological pump?

4.1. What Causes the Strong Decoupling Between Surface and 1000 m?

[34] The relative fate of Si and C will be fundamentally different, whether cells remain in surface waters or sink. Given the relative timescales of $bSiO_2$ dissolution (0.005–0.2 d^{-1} [*Ragueneau et al.*, 2000, and references therein]) and sinking (large faecal pellets and aggregates can sink at rates up to several hundred meters per day), the extent of $bSiO_2$ dissolution in surface waters is mostly dependent upon particle dynamics (B. Moriceau et al., Quantitative and qualitative reconstruction of water column biogenic silica fluxes from dissolution experiments, submitted to *Global Biogeochemical Cycles*, 2006) (hereinafter referred to as Moriceau et al., submitted manuscript, 2006b). Note that this characteristic could provide an explanation for the importance of diatom blooms in controlling the spatial and temporal variations observed in the dissolution to production ratio at global scale [*Brzezinski et al.*, 2003]. Indeed, under bloom conditions, the probability for diatoms to be grazed upon or to incorporate an aggregate increases, diminishing the potential for dissolution in surface waters (Moriceau et al., submitted manuscript, 2006b).

[35] The fraction of diatom productivity that escapes aggregation and grazing [*Bidle and Falkowski*, 2004; *Brussaard et al.*, 1995; *Vanboekel et al.*, 1992], instead undergo cell lysis in response to physiological stress [*Berges and Falkowski*, 1998; *Brussaard et al.*, 1997] and viral infection [*Nagasaki et al.*, 2004, 2005]. Ultimately, death and lysis becomes a conduit to microbial processing [*Azam*, 1998; *Bidle and Falkowski*, 2004; *Kirchman*, 1999] and recycling. As a consequence, $bSiO_2$ dissolution (and the contribution of resident bacterial colonizers) likely varies as a bloom develops and finally enters senescence, when it is more susceptible to bacterial attack. Under such conditions, the relative fate of Si and C in surface waters will be strongly dependent upon temperature as illustrated in Figure 3. For example, in the permanently cold waters of the Southern Ocean, the relative preservation of Si to C will have a tendency to increase by a factor of 6, upon microbial processing. There it is quite common to observe diatoms with a Si:C ratio close to 1 [*Quéguiner et al.*, 1997]. Conversely, in the warm temperatures of the tropical gyres, bacterial activity applied to nonsinking diatoms will tend to "recouple" the Si and C cycles.

[36] What are the relative fates of Si and C in sinking particles? Equation (1) predicts that the Si:C increases by a factor 17 between surface waters and 1000 m [*Ragueneau et al.*, 2002]. We have seen that the production of faecal pellets decouples Si and C by a factor of ~5, but that the formation of aggregates does not decouple Si and C, or at least, will retard the decoupling. Given that aggregates constitute a large fraction of the sinking flux [*Thornton*, 2002; *Turner*, 2002; Moriceau et al., submitted manuscript, 2006b], how can we account for such a high decoupling between Si and C?

[37] The high bacterial concentrations inside aggregates [*Smith et al.*, 1992] and the fact that they can survive gut passage of copepod grazers and account for up to 84% of protease activity on the pellets [*Lawrence et al.*, 1993] suggest that bacteria will continue to increase Si:C ratios inside the large particles. The net effect of bacterial activity on Si and C release however, will be retarded owing to the retention of diatom viability in aggregates [*Brzezinski et al.*, 1997; *Moriceau et al.*, 2006] and owing to the retarded diffusion of silicic acid from the aggregate or the pellet to the surrounding medium [*Schultes*, 2004; Moriceau et al., submitted manuscript, 2006a]. In addition, because bacterial activity is strongly temperature-dependent and assemblages can be physiologically limited at low temperatures [*Bidle et al.*, 2002] and high pressure [*Tamburini et al.*, 2006], subsequent decomposition of diatom detritus and/or aggregates by surface-derived colonizers would be retarded as they sink across the thermocline and at cold depths. Altogether, bacteria would seem to play a comparatively minimal role for changes Si:C ratios between export and the base of the mesopelagic, compared to surface waters, but this remains to be explored.

[38] It is well known that the biogenic material that is sinking through the water column is being utilized by the organisms inhabiting the mesopelagic, leading to profound modifications of the composition of the sinking flux [*Jackson and Burd*, 2002] and of its settling rate [*Berelson*, 2002, and references therein]. Processes such as coprophagy probably contribute to increase the Si:C ratio of sinking particles, but because detrital C is of lower nutritional value and its assimilation efficiency only around 50%, we can assume that the increase in Si:C ratio of sinking faecal pellets due to coprophagy is not as strong as that observed experimentally for copepods grazing on diatoms (see above). In addition, coprophagy will also tend to break the pellets, increasing subsequent dissolution by exposing crushed frustule material to undersaturated seawater and bacterial activity [*Schultes*, 2004].

[39] Perhaps, a better way to explain the strong decoupling observed at 1000 m between Si and C is to consider that aggregates are profoundly transformed during their descent. First, aggregates incorporate all kinds of particles, including detrital material and faecal pellets [*Passow*, 2004], already enriched in Si relative to C. Second, even if $bSiO_2$ dissolution is slowed down in aggregates [*Moriceau et al.*, 2006], POC is being utilized by bacteria inside the aggregates [*Smith et al.*, 1992]; the distributions of Si and C among the dissolved and particulate phase are modified, with a progressive removal of C and simultaneous enrichment in Si in the particulate phase. Finally, aggregation is a mechanism to bring particles into the food size range of fish and other organisms [*Lampitt et al.*, 1993; *Green and Dagg*, 1997]; compared to faecal pellets, aggregates represent a much better source of energy for heterotrophic bacteria, protozoans and metazoans inhabiting the surface waters and the mesopelagic [*Silver et al.*, 1978; *Thornton*, 2002, and references therein]. Through their feeding activity, animals disrupt marine snow [*Dilling and Alldredge*, 2000], which may reduce the flux of material sinking through the water column but which will further enhance the decoupling between Si and C. *Jackson* [1993] and *Jackson and Burd* [2002] describe the feeding mode of flux feeders, which sit in the water and feed preferentially on large, rapidly settling particles with a rate proportional to the flux rather than to the concentration. Thus ingestion and digestion of aggregates by mesopelagic flux feeders poten-

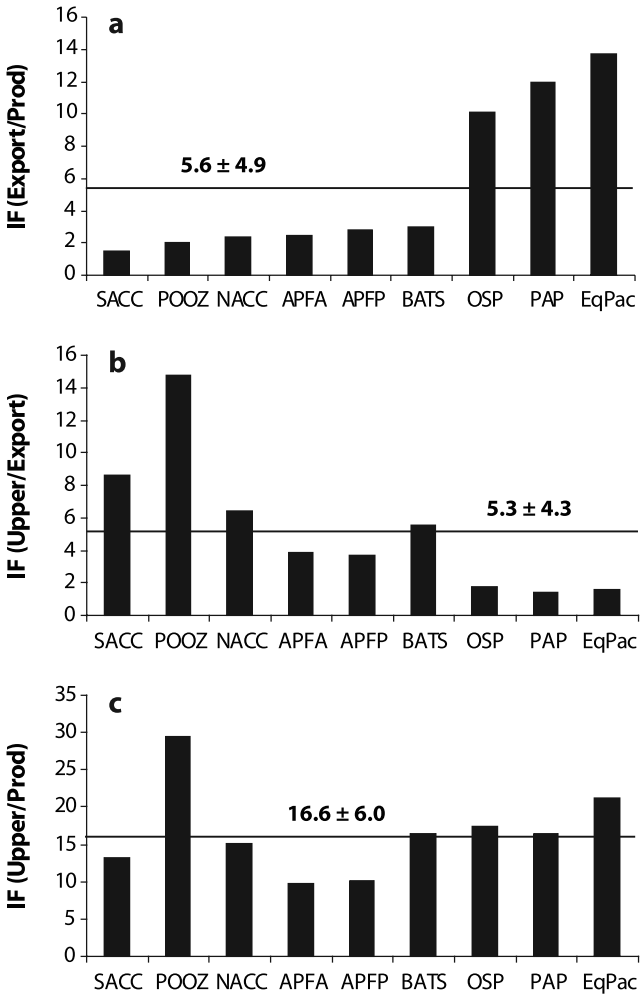

Figure 4. Increasing Factor (IF) of the Si:C ratio in nine biogeochemical provinces, (a) between production and export, (b) between export and the base of the mesopelagic zone (noted "upper" for "upper sediment trap" located in the range 980–1500 m [see *Ragueneau et al.*, 2002]), and (c) between production and the base of the mesopelagic zone. See Figure 1 and *Ragueneau et al.* [2002] for exact values and abbreviations.

tially plays a prominent role in Si and C decoupling throughout the mesopelagic zone.

4.2. Why Is the Decoupling Between Surface and 1000 m So Homogeneous Among Different Biogeochemical Provinces?

[40] The mean increasing factor of the Si:C ratio (IF) between surface and ~1000 m for these nine sites is 16.6, consistent with equation (1), and Figure 4c shows that this mean value displays a reasonably low standard deviation of 36% (range: 9.8–29.5). Note that the POOZ site looks as an outlier; without this point, the mean would be 15 ± 4, with a standard deviation even lower. It is particularly interesting to further explore the underlying reasons of such homogeneity between provinces that are so different in terms of oceanic basin, type of primary production, seasonality etc.

[41] To do so, we have dissected the depth horizons at which the decoupling seems to occur at these nine sites (Figures 4a and 4b). Interestingly, the homogeneity observed at 1000 m disappears when the decoupling is studied between production and export (Figure 4a: IF = 5.6 ± 4.9) and between export and the base of the mesopelagic (Figure 4b: IF = 5.3 ± 4.3), with ranges encompassing almost one order of magnitude and standard deviations between 80 and 90%. All the sites located in the Southern Ocean exhibit a low decoupling between surface and export whereas the sites located outside the Southern Ocean display a much higher decoupling in surface waters. The BATS site looks as an exception to this pattern. Until we understand the reasons for this and gather more data for additional sites, it is premature to argue that the Southern Ocean behaves differently from the rest of the ocean. What seems very clear though, from the comparison of Figure 4a and 4b, is that when the decoupling does not take place in surface waters, it takes place in the mesopelagic. Also, it is the combination of these two figures that helps explaining the homogeneity observed at 1000 m.

[42] At this stage, let us recall a sentence from *Vinogradov* [1968]: "The cycling of chemicals in the ocean, the migration of chemicals through the water and the processes of

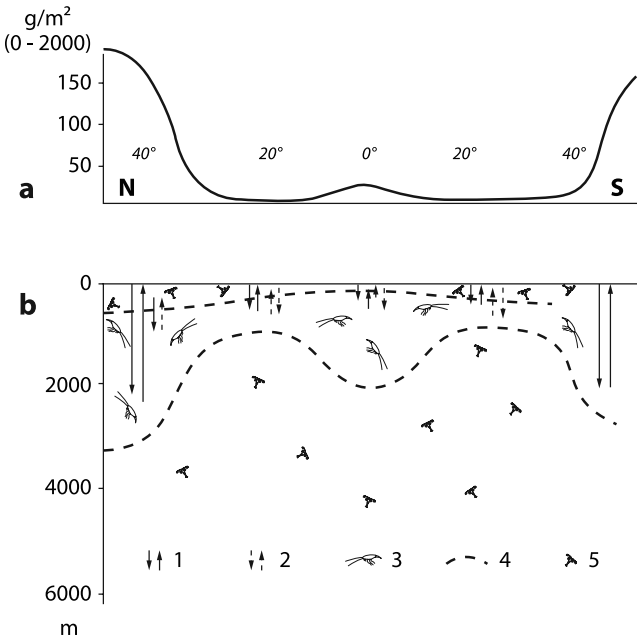

Figure 5. Scheme of the distribution of mesoplankton and macroplankton in a longitudinal section in the Pacific Ocean [from *Vinogradov*, 1968]. (top) Total amount of net plankton (g m^{-2}) in the 0–2000 m layer. (bottom) Vertical distribution of plankton: 1, amplitude of the diurnal or seasonal migration of interzonal mesoplankton; 2, amplitude of the diurnal migration of macroplankton; 3, zone of macroplanktonic concentration; 4, borders of the zone of macroplanktonic concentration; 5, zone dominated by mesoplankton.

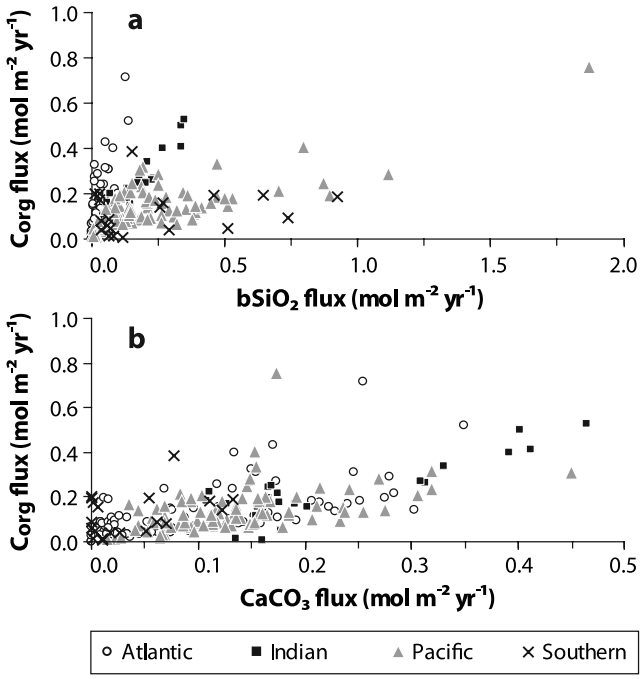

Figure 6. C_{org} fluxes versus (a) $bSiO_2$ fluxes and (b) $CaCO_3$ fluxes as measured by means of sediment traps for 101 sites of the world ocean. All measurements performed during at least one year (almost one year in few cases), and for a depth > 980 m. Data are available at http://www.pangaea.de. Note in Figure 6a the decrease in slope of $bSiO_2$ versus C_{org} fluxes, as we move from the Atlantic to the Indian, then the Pacific and Southern oceans [*Ragueneau et al.*, 2000].

sedimentation are also largely determined by biogenous factors and depend upon the vertical distribution of plankton." Figure 5 shows a scheme of the distribution of meso- and macro-plankton along a longitudinal section through eutrophic subpolar regions and oligotrophic tropical parts of the ocean [*Vinogradov*, 1968]. The total amount of net plankton in the 0–2000 m layer displays latitudinal variations that resemble latitudinal variations in diatom dominance and export production, with high values at midlatitudes and a slight peak near the equator [*Buesseler*, 1998]. This resemblance is not surprising; since these organisms have to collect their food from above, their concentration can be taken as an indirect measure of export production. Interestingly enough, below these regions of diatom dominance and elevated export production, meso- and macro-zooplankton are distributed over a large depth range, suggesting that the mesopelagic ecosystem has developed to maximally exploit this sinking food supply from the surface waters. On the contrary, in the tropical regions of low export, zooplankton are concentrated in surface waters and in a layer immediately adjacent to the productive layer [*Vinogradov*, 1968].

[43] In other words, the stronger the export (low Si:C decoupling in surface waters), the higher the probability that the sinking material will be used by the mesopelagic food web (strong Si:C decoupling between 100 and 1000 m), leading to the observed strong, but homogeneous, decoupling between surface and 1000 m.

4.3. What are the Implications for the Role of Diatoms in the Biological Pump?

[44] Diatoms have long been considered as playing an essential role in the biological pump because they contribute such an important fraction of carbon export from surface waters [*Goldman*, 1993; *Buesseler*, 1998; *Sarmiento*, 2006]. Since an important fraction of the diatom C exported from the surface layer is being used efficiently by the mesopelagic food web, this "diatom-only" view needs to be updated. In fact, recent studies suggested that calcifiers, rather than diatoms, play perhaps a more important role in transferring carbon to depth [*François et al.*, 2002; *Klaas and Archer*, 2002] with potential important implications concerning the rain ratio hypothesis and the controls on late quaternary atmospheric CO_2 concentrations [*Ridgwell*, 2003]. As we shall see, this "carbonate-only" view will also need to be updated.

[45] *Klaas and Archer* [2002], building on the ballast hypothesis proposed by *Armstrong et al.* [2002], used a global database of sediment trap fluxes to demonstrate that the flux of organic carbon to the deep is carried essentially by calcium carbonate. The organic carbon flux to the deep is given by [*Klaas and Archer*, 2002]

$$F(z) = f_o.F_o(z) + f_{ca}.F_{ca}(z) + f_l.F_l(z), \quad (2)$$

where $F_o(z)$, $F_{ca}(z)$ and $F_l(z)$ are the mass fluxes of opal, calcium carbonate and the lithogenic fraction and f are the corresponding carrying coefficients which can be determined by multiple linear regressions (passing through the origin). When applied to the global data set of sediment trap fluxes (>1000 m, annual estimates), the carrying coefficients vary according to the density of the ballast minerals: CaCO3 > Lithogenic > Opal, which led *Klaas and Archer* [2002] to suggest that 83% of the global POC fluxes to the deep sea are associated with calcium carbonate. We have used the same approach, but applying it to a global database of sediment trap fluxes (data at http://pangaea.de) in which these fluxes have been sorted by oceanic basin. The rationale for this distinction is found in Figure 6 where clearly, the Si:C ratio measured in sediment traps >1000 m differs from one ocean basin to another, increasing from the Atlantic to the Indian and Pacific oceans [*Ragueneau et al.*, 2000]. Results are shown in Table 1. Although the database is not exactly similar to the one used by *Klaas and Archer* [2002], the carrying coefficients determined globally are similar. However, it is also apparent that these carrying coefficients differ from one basin to another. Therefore searching for a unique correlation between POC fluxes and either opal, carbonate or lithogenic fractions is probably useless. Rather, we should reformulate the question, not in terms of "which ballast best explain POC fluxes?" but rather "what controls the spatial and temporal variations in the relative importance of a specific ballast in controlling POC fluxes to the deep?"

Table 1. Carrying Coefficients for Multiple Correlation Analysis of POC Fluxes Versus $CaCO_3$, $bSiO_2$, and Lithogenic Fluxes[a]

Ocean Basin	$CaCO_3$	$bSiO_2$	Lithogenic	r^2	p	N
Global	0.081 ± 0.004 (<0.001)	0.031 ± 0.004 (<0.001)	0.035 ± 0.003 (<0.001)	0.8917	<0.001	189
Atlantic	0.077 ± 0.012 (<0.01)	0.171 ± 0.062 (<0.001)	0.031 ± 0.004 (<0.001)	0.8697	<0.001	84
Indian	0.026 ± 0.016 (<1)	0.201 ± 0.039 (<0.001)	0.015 ± 0.017 (<1)	0.9593	<0.001	16
Pacific	0.063 ± 0.004 (<0.001)	0.041 ± 0.003 (<0.001)	0.024 ± 0.003 (<0.001)	0.9545	<0.001	89

[a]The analysis is presented for the global ocean, and for each ocean basin separately (see Figure 6). Sediment trap data (data are available at http://www.pangaea.de) are annual estimates, measured at z > 1000 m. Lithogenic fluxes estimated as in the work of *Klaas and Archer* [2002], i.e., total mass less $CaCO_3$, $bSiO_2$ and 2.199 × POC. Carrying coefficients are given with their standard deviation. Numbers in parentheses represent the probability that the slope is different from zero. The r^2 is also given, as well as the overall significance of the analysis (p) and the number of observations (N).

[46] *François et al.* [2002] reached a conclusion similar to that of *Klaas and Archer* [2002], although derived from a different perspective. Also using a global database of sediment trap fluxes, they related the transfer efficiency of POC between export and the base of the mesopelagic zone to essentially $CaCO_3$. The explanation proposed by *François et al.* [2002] is that the carbon associated with diatoms, while it is efficiently exported from surface waters, is more labile and rapidly recycled during sinking throughout the mesopelagic, ultimately yielding low transfer efficiency. In a way, this view agrees with previous observations in the Southern Ocean [*Ragueneau et al.*, 2002] and with our previous discussion about Figure 4: the excess carbon exported by diatoms, possibly at the most seasonal sites [*Berger and Wefer*, 1990; *Buesseler*, 1998], is utilized in the mesopelagic, leading to the observations that the transfer efficiency throughout the mesopelagic is lower at these sites [*François et al.*, 2002], and that IF is so homogeneous between surface and 1000 m (Figure 4c). However, putting aside issues of data extrapolation to global scales (Table 1 and Figure 6), there are two important reasons suggesting that the "carbonate-only" view [see *François et al.*, 2002, Figure 5] is too extreme. First, the high transfer efficiencies are measured at sites of low POC export, but they are relative values. The efficient transfer of a low POC flux will not necessarily result in a higher flux at 1000 m, compared to less efficient transfer of a much higher POC flux exported from diatoms. In fact, the fraction of PP that reaches the deep ocean is quite homogeneous throughout the world ocean (1–2% [*Lampitt and Antia*, 1997; *Poulton et al.*, 2006]). Second, recycling diatom-C or channeling it toward higher trophic level in the mesopelagic zone does not necessarily imply that this will result in little transfer of POC to the deep ocean. A fraction of the diatom-C lost above 1000 m can be remineralized below the depth of the wind mixed layer or be partly exported toward higher trophic levels, mobilizing it from a short-lived carbon pool ($<10^{-2}$ year) to a long-lived carbon pool (10^{-2}–10^{2} year [*Legendre and Le Fèvre*, 1992]). Depending upon a competition between upward migration and sinking of faecal material and cadavers, part of this long-lived carbon pool eventually ends up in the pool of biogenic carbon, that will be sequestered on timescales relevant to climate change [*Legendre and Le Fèvre*, 1992], thereby participating actively in the biological pump. Thus there is a clear need to quantify the fraction of the biological pump that is fuelled by upper ocean diatom production and export, and that may not be accounted for in sediment traps.

5. Conclusions and Perspectives

[47] Perhaps the most significant conclusion of this study is to recognize that despite early warnings sent by ecologists [*Banse*, 1990; *Wassmann*, 1998], our community of biogeochemists has tried to understand the functioning of the biological pump from a too extreme "flux oriented" perspective and most importantly, probably looking at the wrong temporal and spatial scales.

[48] Working at the global scale with unique relationships can lead to dramatic misinterpretations with important implications for the reconstruction of POC fluxes to the deep and paleoceanographic interpretations. Looking at the functioning of the biological pump from a "diatom only" view, simply on the basis of their importance in export mechanisms without taking into account mesopelagic transformations is probably too simplistic. Similarly, we demonstrate that a "carbonate only" perspective cannot be correct either. What controls the spatial variability of Si:C ratios or carrying coefficients among oceanic basins or different biogeochemical provinces and under what conditions a certain ballast type dominates, are probably more challenging questions to be answered, than a useless search for a unique descriptor of POC fluxes to the deep. Interestingly, there exist also other hypotheses that confer to aggregates, rather than mineral ballasts, a major role in the transport of carbon to the deep [*Passow*, 2004; *Passow and De La Rocha*, 2006]. Possibly, we should also avoid asking whether aggregates or ballasts play the prominent role in transporting POC to the deep, but rather wonder how their interaction may account for spatial and temporal variations in the efficiency of the biological pump [*Gehlen et al.*, 2006; Moriceau et al., submitted manuscript, 2006b].

[49] A second result illustrating misinterpretations by using global relationships is given by our exploration of the mechanisms behind the global relationship describing the fate of Si:C ratio with depth (equation (1) [*Ragueneau et al.*, 2002]). Amazingly, this relationship holds in provinces that are extremely diverse, from many ecological and

biogeochemical aspects. Sorting the flux data by depth horizon (Figure 4c versus Figures 4a and 4b) demonstrated that the homogeneity of IF between surface waters and the base of the mesopelagic hides important variability: At sites of low export, recycling takes place in surface waters and most of the decoupling between Si and C has been achieved above the depth of export. At sites of high export, typically mid- and high-latitude regions where diatoms form blooms, more carbon is being exported and Si and C decoupling is achieved in the mesopelagic. Therefore looking at fluxes measured at 1000 m and below yields homogeneity in terms of fraction of PP that reaches these depths and in terms of Si and C decoupling (Figure 4c) which may be misleading. Integration of equation (1) into OGCMs, just as the classical algorithms describing the fate of PP with depth [*Suess*, 1980; *Martin et al.*, 1987], would hence be of very little prognostic value since this relationship hides mechanisms that take place at various depth horizons, with implications for C recycling that would not be accounted for in the model.

[50] A very elegant way of explaining the homogenization of the biogeochemical patterns is to invoke the ecology of pelagic food webs in surface waters and the mesopelagic zone. This has been proposed for the role of zooplankton dynamics in buffering variability of primary production on the way up the food chain [*Runge*, 1988] and more recently by *Wassmann* [1998] with the existence of a "pelagic mill" grinding suspended and sinking particles in the mesopelagic zone. Below 1000 m (because sediment traps do not work properly in the mesopelagic [*Yu et al.*, 2001]) we are looking at the garbage of the surface and mesopelagic food webs, which altogether are very efficient, leaving us with only 1% of PP.

[51] Perhaps the biggest challenge ahead of us is to improve our understanding of the role of plankton ecology on vertical flux. Interestingly enough, because these food webs have no direct need for the element Si, they leave behind more of this element; hence the study of the changes in Si:C ratio with depth can yield useful information on the efficiency of the pelagic mill or how well the surface and mesopelagic trophic network is adapted to exploit temporal and spatial variability in production and export fluxes. High export has been related to seasonality [*Berger and Wefer*, 1990; *Buesseler*, 1998]. The fate of Si:C ratios in surface waters (Figure 4a) and in the mesopelagic zone (Figure 4b) at the EqPac and BATS sites, both regions of low seasonality, differs dramatically in terms of depth of Si and C decoupling. Perhaps more important than seasonality, stochasticity of export events may play a fundamental role in the biological pump as they may lead to the rapid sinking of particles that will not be fully exploited by a mesopelagic ecosystem "taken by surprise," thereby reducing the efficiency of the pelagic mill. In some cases, these episodic events highlight the importance of ocean physics influencing the biological fate. For example, the passage of Tropical Instability Waves in the equatorial Pacific have been invoked by *Smith et al.* [1996], to explain the rapid sinking of diatoms and the observation of fresh phytodetritus on the seafloor. Likewise, the sudden breaking of the thermocline has been invoked by *Kemp et al.* [2000] to explain what they called the "fall dump", the massive sinking of large, slowly growing diatoms living during summer at the base of the thermocline. Such episodic events, generally associated with inputs of auxiliary energy at marine ergoclines [*Legendre et al.*, 1986], may be recurrent but how adapted the mesopelagic food web is to such events is not known. There is a critical need to elucidate the relationship between surface and mesopelagic processes at a much finer temporal scale and among contrasted biogeochemical provinces, if we are to fully understand the functioning of the biological pump and the role played by surface and mesopelagic organisms.

[52] **Acknowledgments.** The authors wish to thank R. C. Dugdale and A. E. S. Kemp for the organization of the Chapman Conference devoted to diatoms and the global carbon cycle. This conference allowed the authors to meet and launch discussions about the ideas presented in this paper. We appreciated the detailed comments of R. Armstrong and an anonymous reviewer, who both provided very helpful comments to improve a previous version of the manuscript. Thank you very much to F. Jean for his help with statistics, and to Monique Briand for the figures. This work is funded by the European Commission and especially the Marie Curie Programme which supports S. Schultes through the project ZOOPALIS (MEIF-CT-2005-010882) and B. Moriceau through the project CARBALIS (MOIF-CT-2006-022278) and funds the Si-WEBS Research Training Network (HPRN-CT-2002-0218). K. Bidle is supported by the U.S. National Science Foundation (IOB-0414536; OCE-0526365) and the Gordon and Betty Moore Foundation.

References

Alldredge, A. L., U. Passow, and B. E. Logan (1993), The abundance and significance of a class of large, transparent organic particles in the ocean, *Deep Sea Res., Part I*, *40*, 1131–1140.

Armstrong, R. A., C. Lee, J. I. Hedges, S. Honjo, and S. G. Wakeham (2002), A new, mechanistic model for organic carbon fluxes in the ocean based on the quantitative association of POC with ballast minerals, *Deep Sea Res., Part II*, *49*, 219–236.

Azam, F. (1998), Microbial control of oceanic carbon flux: The plot thickens, *Science*, *280*, 694–696.

Banse, K. (1990), New views on the degradation and deposition of organic particles as collected by sediment traps in the open sea, *Deep Sea Res., Part I*, *37*, 1177–1195.

Berelson, W. (2002), Biogenic particle settling rates increase with depth in the ocean, *Deep Sea Res., Part II*, *49*, 237–251.

Berger, W. H., and J.-C Herguera (1992), Reading the sedimentary record of the ocean's productivity, in *Primary Productivity and Biogeochemical Cycles in the Sea*, edited by P. G. Falkowski and A. D. Woodhead, pp. 455–486, Springer, New York.

Berger, W. H., and G. Wefer (1990), Export production: Seasonality and intermittency, and paleoceanographic implications, *Palaeogeogr. Palaeoclimatol. Palaeoecol.*, *89*, 245–254.

Berges, J. A., and P. G. Falkowski (1998), Physiological stress and cell death in marine phytoplankton: Induction of proteases in response to nitrogen or light limitation, *Limnol. Oceanogr.*, *43*, 129–135.

Biddanda, B. A. (1988), Microbial aggregation and degradation of phytoplankton-derived detritus in seawater: II. Microbial metabolism, *Mar. Ecol. Prog. Ser.*, *42*, 89–95.

Biddanda, B. A., and L. R. Pomeroy (1988), Microbial aggregation and degradation of phytoplankton-derived detritus in seawater: I. Microbial succession, *Mar. Ecol. Prog. Ser.*, *42*, 79–88.

Bidle, K. D., and F. Azam (1999), Accelerated dissolution of diatom silica by natural marine bacterial assemblages, *Nature*, *397*, 508–512.

Bidle, K. D., and F. Azam (2001), Bacterial control of silicon regeneration from diatom detritus: Significance of bacterial ectohydrolases and species identity, *Limnol. Oceanogr.*, *46*, 1606–1623.

Bidle, K. D., and P. G. Falkowski (2004), Cell death in planktonic photosynthetic microorganisms, *Nat. Rev. Microbiol.*, *2*, 643–655.

Bidle, K. D., M. Manganelli, and F. Azam (2002), Regulation of oceanic silicon and carbon preservation by temperature control on bacterial activity, *Science*, *298*, 1980–1984.

Bidle, K. D., M. A. Brzezinski, R. A. Long, J. Jones, and F. Azam (2003), Diminished efficiency in the oceanic silica pump caused by bacteria-mediated silica dissolution, *Limnol. Oceanogr.*, *48*, 1855–1868.

Brussaard, C. P. D., et al. (1995), Effects of grazing, sedimentation and phytoplankton cell lysis on the structure of a coastal pelagic food web, *Mar. Ecol. Prog. Ser.*, *123*, 259–271.

Brussaard, C. P. D., A. A. M. Noordeloos, and R. Riegman (1997), Autolysis kinetics of the marine diatom *Ditylum brightwellii* (Bacillariophyceae) under nitrogen and phosphorus limitation and starvation, *J. Phycol.*, *33*, 980–987.

Brzezinski, M. A., and D. J. Conley (1994), Silicon deposition during the cell cycle of *Thalassiosira weisflogii* (Bacillariophycae) determined using rhodamine 123 and propidium iodide staining, *J. Phycol.*, *30*, 45–55.

Brzezinski, M. A., A. L. Alldredge, and L. M. O'Bryan (1997), Silica cycling within marine snow, *Limnol. Oceanogr.*, *42*, 1706–1713.

Brzezinski, M. A., J. Jones, A. L. Alldredge, and F. Azam (2003), The balance between silica production and silica dissolution in the sea, *Limnol. Oceanogr.*, *48*, 1846–1854.

Buesseler, K. O. (1998), The decoupling of production and particulate export in the surface ocean, *Global Biogeochem. Cycles*, *12*, 297–310.

Calbet, A., and M. R. Landry (2004), Phytoplankton growth, microzooplankton grazing, and carbon cycling in marine systems, *Limnol. Oceanogr.*, *49*, 51–57.

Chisholm, S. W. (1981), Temporal patterns of cell division in unicellular algae: Physiological bases of phytoplankton ecology, *Can. Bull. Fish. Aquat. Sci.*, *210*, 150–181.

Chisholm, S. W., F. Azam, and R. W. Eppley (1978), Silicic acid incorporation in marine diatoms on light:dark cycles: Use as an essay for phased cell division, *Limnol. Oceanogr.*, *23*, 518–529.

Claquin, P., and V. Martin-Jézéquel (2005), Regulation of the Si and C uptake and of the soluble free-silicon pool in a synchronized culture of *Cylindrotheca fusiformis* (Bacillariophyceae): effects on the Si/C ratio, *Mar. Biol.*, *146*, 877–886.

Claquin, P., V. Martin-Jézéquel, J. C. Kromkamp, M. J. W. Veldhuis, and G. W. Kraay (2002), Uncoupling of silicon compared to carbon and nitrogen metabolism, and role of the cell cycle, in continuous cultures of *Thalassiosira pseudonana* (Bacillariophyceae) under light, nitrogen and phosphorus control, *J. Phycol.*, *38*, 922–930.

Conley, D. J., S. S. Kilham, and E. Theriot (1989), Differences in silica content between marine and freshwater diatoms, *Limnol. Oceanogr.*, *34*, 205–213.

Cowie, G. L., and J. I. Hedges (1996), Digestion and alteration for the biochemical constituents of a diatom (*Thalassiosira weissflogii*) ingested by an herbivorous copepod (*Calanus pacificus*), *Limnol. Oceanogr.*, *41*, 581–594.

Crawford, S. A., M. J. Higgins, P. Mulvaney, and R. Wetherbee (2001), Nanostructure of the diatom frustule as revealed by atomic force and scanning electron microscopy, *J. Phycol.*, *37*, 543–554.

Dagg, M. J., J. Urban-Rich, and J. O. Peterson (2003), The potential contribution of faecal pellets from large copepods to the flux of biogenic silica and particulate organic carbon in the Antarctic Polar Front region near 170°W, *Deep Sea Res., Part II*, *50*, 675–691.

Daly, K. L. (1997), Flux of particulate matter through copepods in the Northeast Water Polynya, *J. Mar. Syst.*, *10*, 319–342.

DeMaster, D. J. (1981), The supply and accumulation of silica in the marine environment, *Geochim. Cosmochim. Acta*, *45*, 1715–1732.

DeMaster, D. J. (2002), The accumulation and cycling of biogenic silica in the Southern Ocean: Revisiting the marine silica budget, *Deep Sea Res., Part II*, *49*, 3155–3167.

Dilling, L., and A. L. Alldredge (2000), Fragmentation of marine snow by swimming macrozooplankton: A new process impacting carbon cycling in the sea, *Deep Sea Res., Part I*, *47*, 1227–1245.

Dixit, S., P. Van Cappellen, and A. J. Van Bennekom (2001), Processes controlling solubility of biogenic silica and pore water build-up of DSi in marine sediments, *Mar. Chem.*, *73*, 333–352.

Dugdale, R. C., and F. P. Wilkerson (1998), Silicate regulation of new production in the equatorial Pacific upwelling, *Nature*, *391*, 270–273.

Dugdale, R. C., F. P. Wilkerson, and H. J. Minas (1995), The role of a silicate pump in driving new production, *Deep Sea Res., Part I*, *42*, 697–719.

Durbin, E. G. (1977), Studies of the autoecology of the marine diatom *Thalassiosira nordenskioeldii*: II. The influence of cell size on growth rate, and carbon, nitrogen, chlorophyll a and silica content, *J. Phycol.*, *13*, 150–155.

François, R., S. Honjo, R. Krishfield, and S. Manganini (2002), Factors controlling the flux of organic carbon to the bathypelagic zone of the ocean, *Global Biogeochem. Cycles*, *16*(4), 1087, doi:10.1029/2001GB001722.

Fuji, M., and F. Chai (2005), Effects of biogenic silica dissolution on silicon cycling and export production, *Geophys. Res. Lett.*, *32*, L05617, doi:10.1029/2004GL022054.

Gallinari, M., O. Ragueneau, L. Corrin, D. J. DeMaster, and P. Tréguer (2002), The importance of water column processes on the dissolution kinetics of biogenic silica in deep-sea sediments: I. Solubility, *Geochim. Cosmochim. Acta*, *66*, 2701–2717.

Gehlen, M., L. Bopp, N. Emprin, O. Aumont, C. Heinze, and O. Ragueneau (2006), Reconciling surface ocean productivity, export fluxes and sediment composition in a global biogeochemical ocean model, *Biogeosciences*, *3*, 521–537.

Goldman, J. C. (1993), Potential role of large oceanic diatoms in new primary production, *Deep Sea Res.*, *40*, 159–186.

Green, E. P., and M. J. Dagg (1997), Mesozooplankton associations with medium to large marine snow aggregates in the northern Gulf of Mexico, *J. Plankton Res.*, *19*, 435–447.

Hamm, C. E., R. Merkel, O. Springer, P. Jurkojc, C. Maier, K. Prechtel, and V. Smetacek (2003), Architecture and material properties of diatom shells provide effective mechanical protection, *Nature*, *421*, 841–843.

Hecky, R. E., K. Mopper, P. Kilham, and E. T. Degens (1973), The amino acid and sugar composition of diatom cell-walls, *Mar. Biol.*, *19*, 323–331.

Hedges, J. I., and R. G. Keil (1995), Sedimentary organic matter preservation: An assessment and speculative synthesis, *Mar. Chem.*, *49*, 81–115.

Hildebrand, M. (2000), Silicic acid transport and its control during cell wall silicification in diatoms, in *Biomineralization of Nano-and Micro-Structures*, edited by E. Bauerlein, pp. 171–188, John Wiley, Hoboken, N. J.

Hildebrand, M. (2005), Prospects of manipulating diatom silica nanostructure, *J. Nanosci. Nanotechnol.*, *5*, 146–157.

Hildebrand, M., and R. Wetherbee (2003), Components and control of silicification in diatoms, in *Silicon Biomineralization: Biology, Biochemistry, Molecular Biology, Biotechnology*, *Prog. Mol. Subcellular Biol.*, vol. 33, edited by W. E. G. Mueller, pp. 11–57, Springer, New York.

Honjo, S., and M. R. Roman (1978), Marine copepod fecal pellets: Production, preservation and sedimentation, *J. Mar. Res.*, *36*, 45–57.

Hoppema, M., E. Fahrbach, and H. J. W. De Baar (2000), Surface layer balance of the Southern Antarctic Circumpolar Current (prime meridian) used to derive carbon and silicate consumptions and annual air-sea exchange for CO_2 and oxygen, *J. Geophys. Res.*, *105*(C5), 11,359–11,371.

Hutchins, D. A., and K. W. Bruland (1998), Iron limited diatom growth and Si:N uptake ratios in a coastal upwelling regime, *Nature*, *393*, 561–564.

Jackson, G. A. (1993), Flux feeding as a mechanism for zooplankton grazing and its implications for vertical particulate flux, *Limnol. Oceanogr.*, *38*, 1328–1331.

Jackson, G. A., and A. B. Burd (2002), A model for the distribution of particle flux in the mid-water column controlled by subsurface biotic interactions, *Deep Sea Res., Part II*, *49*, 193–217.

Jacobson, D. M., and D. M. Anderson (1986), Thecate heterotrophic dinoflagellates: Feeding behavior and mechanisms, *J. Phycol.*, *22*, 249–258.

Jansen, H., and D. A. Wolf-Gladrow (2001), Carbonate dissolution in copepod guts: A numerical model, *Mar. Ecol. Prog. Ser.*, *221*, 199–207.

Jansen, S. (2002), Silikatlösung von Diatomeen durch Zooplanktonfraß, Diplomarbeit, 82 pp., Univ. zu Köln, Cologne, Germany.

Kamatani, A. (1982), Dissolution rates of silica from diatoms decomposing at various temperatures, *Mar. Biol.*, *68*, 91–98.

Kamatani, A., and J. P. Riley (1979), Rate of dissolution of diatom silica walls in seawater, *Mar. Biol.*, *55*, 29–35.

Kemp, A. E. S., J. Pike, R. B. Pearce, and C. B. Lange (2000), The "Fall dump"—A new perspective on the role of a "shade flora" in the annual cycle of diatom production and export flux, *Deep Sea Res., Part II*, *47*, 2129–2154.

Kirchman, D. L. (1999), Phytoplankton death in the sea, *Nature*, *398*, 293–294.

Klaas, C., and D. E. Archer (2002), Association of sinking organic matter with various types of mineral ballast in the deep sea: Implications for the rain ratio, *Global Biogeochem. Cycles*, *16*(4), 1116, doi:10.1029/2001GB001765.

Kröger, N., and M. Sumper (1998), Diatom cell wall proteins and the cell biology of silica biomineralization, *Protist*, *149*, 213–219.

Kröger, N., C. Bergsdorf, and M. Sumper (1994), A new calcium binding glycoprotein family constitutes a major diatom cell wall component, *EMBO J.*, *13*, 4676–4683.

Kröger, N., G. Lehmann, R. Rachel, and M. Sumper (1997), Characterization of a 200-kDa diatom protein that is specifically associated with a silica-based substructure of the cell wall, *Eur. J. Biochem.*, *250*, 99–105.

Kröger, N., R. Deutzmann, and M. Sumper (1999), Polycationic peptides from diatom biosilica that direct silica nanosphere formation, *Science*, *286*, 1129–1132.

Kröger, N., S. Lorenz, E. Brunner, and M. Sumper (2002), Self-assembly of highly phosphorylated silaffins and their function in biosilica morphogenesis, *Science*, *298*, 584–586.

Kumar, N., R. F. Anderson, R. A. Mortlock, P. N. Froelich, P. Kubik, B. Dittrich-Hannen, and M. Suter (1995), Increased biological productivity and export production in the glacial Southern Ocean, *Nature*, *378*, 675–680.

Lampitt, R. S., and A. N. Antia (1997), Particle flux in deep seas: Regional characteristics and temporal variability, *Deep Sea Res., Part I*, *44*, 1377–1403.

Lampitt, R. S., W. R. Hillier, and P. G. Challenor (1993), Seasonal and diel variation in the open ocean concentration of marine snow aggregates, *Nature*, *362*, 737–739.

Lawrence, S. G., A. Ahmad, and F. Azam (1993), Fate of particle-bound bacteria ingested by *Calanus pacificus*, *Mar. Ecol. Prog. Ser.*, *97*, 299–307.

Lawson, D. S., D. C. Hurd, and H. S. Pankratz (1978), Silica dissolution rates of decomposing assemblages at various temperatures, *Am. J. Sci.*, *278*, 1373–1393.

Legendre, L., and J. Le Fèvre (1992), Interactions between hydrodynamics and pelagic ecosystems: Relevance to resource exploitation and climate change, *S. Afr. J. Mar. Sci.*, *12*, 477–486.

Legendre, L., S. Demers, and D. Lefaivre (1986), Biological production at marine ergoclines, in *Marine Interface Ecohydrodynamics*, edited by J. C. J. Nihoul, pp. 1–29, Elsevier, New York.

Lewin, J. C. (1961), The dissolution of silica from diatom walls, *Geochim. Cosmochim. Acta*, *21*, 182–198.

Leynaert, A., E. Bucciarelli, P. Claquin, R. C. Dugdale, V. Martin-Jézéquel, P. Pondaven, and O. Ragueneau (2004), Effect of iron deficiency on diatom cell size and DSi uptake kinetics, *Limnol. Oceanogr.*, *49*, 1134–1143.

Longhurst, A. R., and W. G. Harrison (1989), The biological pump: Profiles of plankton production and consumption in the upper ocean, *Prog. Oceanogr.*, *22*, 47–123.

Martin, J. H., G. A. Knauer, D. M. Karl, and W. W. Broenkow (1987), VERTEX: Carbon cycling in the northeast Pacific, *Deep Sea Res., Part A*, *34*, 267–285.

Martin-Jézéquel, V., M. Hildebrand, and M. A. Brzezinski (2000), Silicon metabolism in diatoms: Implications for growth, *J. Phycol.*, *36*, 821–840.

Milligan, A. J., D. E. Varela, M. A. Brzezinski, and F. M. M. Morel (2004), Dynamics of silicon metabolism and silicon isotopic discrimination in a marine diatom as a function of pCO_2, *Limnol. Oceanogr.*, *49*, 322–329.

Moriceau, B., O. Ragueneau, M. Garvey, and U. Passow (2006), Lower biogenic silica dissolution rates in diatom aggregates, *Mar. Ecol. Prog. Ser.*, in press.

Nagasaki, K., Y. Tomaru, N. Katanozaka, Y. Shirai, K. Nishida, S. Itakura, and M. Yamaguchi (2004), Isolation and characterization of a novel single-stranded RNA virus infecting the bloom-forming diatom *Rhizosolenia setigera*, *Appl. Environ. Microbiol.*, *70*, 702–711.

Nagasaki, K., Y. Tomaru, Y. Takao, K. Nishida, Y. Shirai, H. Suzuki, and T. Nagumo (2005), Previously unknown virus infects marine diatom, *Appl. Environ. Microbiol.*, *71*, 3528–3535.

Nagasawa, S. (1992), Concurrent observation on gut interiour and fecal pellets of marine crustaceans, *J. Plankton Res.*, *14*, 1625–1630.

Nelson, D. M., and M. A. Brzezinski (1997), Diatom growth and productivity in an oligotrophic mid-ocean gyre: A 3-yr record from the Sargasso Sea near Bermuda, *Limnol. Oceanogr.*, *42*, 473–486.

Nelson, D. M., J. J. Goering, S. S. Kilham, and R. R. L. Guillard (1976), Kinetics of DSi uptake and rates of silica dissolution in the marine diatom *Thalassiosira pseudonana*, *J. Phycol.*, *12*, 246–252.

Nelson, D. M., P. Tréguer, M. A. Brzezinski, A. Leynaert, and B. Quéguiner (1995), Production and dissolution of biogenic silica in the ocean: Revised global estimates, comparison with regional data and relationship to biogenic sedimentation, *Global Biogeochem. Cycles*, *9*, 359–372.

Nelson, D. M., et al. (2002), Estimated vertical budgets for organic carbon and biogenic silica in the Pacific Sector of the Southern Ocean, 1996–1998, *Deep Sea Res., Part II*, *49*, 1645–1674.

Noji, T. T., K. W. Estep, F. Macintyre, and F. Norrbin (1991), Image analysis of faecal material grazed upon by three species of copepods: Evidence for coprorhexy, coprophagy and coprochaly, *J. Mar. Biol. Assoc. U. K.*, *71*, 465–480.

Officer, C. B., and J. H. Ryther (1980), The possible importance of silicon in marine eutrophication, *Mar. Ecol. Prog. Ser.*, *3*, 83–91.

Passow, U. (2000), Formation of Transparent Exopolymer Particles, TEP, from dissolved precursors, *Mar. Ecol. Prog. Ser.*, *192*, 1–11.

Passow, U. (2004), Switching perspectives: Do mineral fluxes determine particulate organic carbon fluxes or vice versa?, *Geochem. Geophys. Geosyst.*, *5*, Q04002, doi:10.1029/2003GC000670.

Passow, U., and A. L. Alldredge (1995), Mass aggregation of a diatom bloom in a mesocosm: The role of TEP, *Deep Sea Res., Part II*, *42*, 99–110.

Passow, U., and C. L. De La Rocha (2006), Accumulation of mineral ballast on organic aggregates, *Global Biogeochem. Cycles*, *20*, GB1013, doi:10.1029/2005GB002579.

Passow, U., A. L. Alldredge, and B. Logan (1994), The role of particulate carbohydrate exudates in the flocculation of diatom blooms, *Deep Sea Res., Part I*, *41*, 335–357.

Passow, U., A. Engel, and H. Ploug (2003), The role of aggregation for the dissolution of diatom frustules, *FEMS Microbiol. Ecol.*, *46*, 247–255.

Patrick, S., and A. J. Holding (1985), The effect of bacteria on the solubilization of silica in diatom frustules, *J. Appl. Bacteriol.*, *59*, 7–16.

Pondaven, P., O. Ragueneau, P. Tréguer, A. Hauvespre, L. Dezileau, and J.-L. Reyss (2000), Resolving the opal paradox in the Southern Ocean, *Nature*, *405*, 168–172.

Pondaven, P., M. Gallinari, S. Chollet, E. Buciarelli, G. Sarthou, S. Schultes, and F. Jean (2006), Grazing-induced changes in cell wall silicification in a marine diatom, *Protist*, in press.

Poulsen, N., and N. Kröger (2004), Silica morphogenesis by alternative processing of silaffins in the diatom Thalassiosira pseudonana, *J. Biol. Chem.*, *279*, 42,993–42,999.

Poulsen, N., M. Sumper, and N. Kröger (2003), Biosilica formation in diatoms: Characterization of native silaffin-2 and its role in silica morphogenesis, *Proc. Natl. Acad. Sci. U. S. A.*, *100*, 12,075–12,080.

Poulton, A. J., R. Sanders, P. M. Holligan, M. C. Stinchcombe, T. R. Adey, L. Brown, and K. Chamberlain (2006), Phytoplankton mineralization in the tropical and subtropical Atlantic Ocean, *Global Biogeochem. Cycles*, *20*, GB4002, doi:10.1029/2006GB002712.

Quéguiner, B., P. Tréguer, I. Peeken, and R. Scharek (1997), Biogeochemical dynamics and the silicon cycle in the Atlantic sector of the Southern Ocean during austral spring 1992, *Deep Sea Res., Part II*, *44*, 69–89.

Ragueneau, O., et al. (2000), 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, *Global Planet. Change*, *26*(4), 315–366.

Ragueneau, O., N. Dittert, L. Corrin, P. Tréguer, and P. Pondaven (2002), Si:C decoupling in the world ocean: Is the Southern Ocean different?, *Deep Sea Res., Part II*, *49*, 3127–3154.

Raven, J. A. (1983), The transport and function of silicon in plants, *Biol. Rev.*, *58*, 178–207.

Ridgwell, A. J. (2003), An end to the "rain ratio" reign?, *Geochem. Geophys. Geosyst.*, *4*(6), 1051, doi:10.1029/2003GC000512.

Roman, M. R., and P. A. Rublee (1980), Containment effects in copepod grazing experiments: A plea to end the black box approach, *Limnol. Oceanogr.*, *25*, 982–990.

Round, F. E., R. M. Crawford, and D. G. Mann (1990), *The Diatoms, Biology and Morphology of the Genera*, Cambridge Univ. Press, New York.

Runge, J. A. (1988), Should we expect a relationship between primary production and fisheries? The role of copepod dynamics as a filter of trophic variability, *Hydrobiologia*, *167/168*, 61–71.

Sarmiento, J. L. (2006), Silicate cycle, in *Ocean Biogeochemical Dynamics*, edited by J. L. Sarmiento and N. Gruber, pp. 270–317, Princeton Univ. Press, Princeton, N. J.

Schrader, H.-J. (1972), Anlösung und Konservation von Diatomeenschalen beim Absinken am Beispiel des Landsort-Tiefs in der Ostsee, *Beih. Nova Hedwigia*, *39*, 191–216.

Schultes, S. (2004), The role of mesozooplankton grazing in the biogeochemical cycle of silicon in the Southern Ocean, dissertation, 167 pp., Univ. Bremen, Bremen, Germany.

Silver, M. W., A. L. Shanks, and J. D. Trent (1978), Marine snow: Microplankton habitat and source of small-scale patchiness in pelagic populations, *Science*, *201*, 371–373.

Smetacek, V. S. (1999), Diatoms and the ocean carbon cycle, *Protist*, *150*, 25–32.

Smith, C. R., D. J. Hoover, S. E. Doan, R. H. Pope, D. J. DeMaster, F. C. Dobbs, and M. A. Altabet (1996), Phytodetritus at the abyssal seafloor across 10° of latitude in the central equatorial Pacific, *Deep Sea Res., Part II*, *43*, 1309–1338.

Smith, D. C., M. Simon, A. L. Alldrege, and F. Azam (1992), Intense hydrolytic enzyme activity on marine aggregates and implications for rapid particle dissolution, *Nature*, *359*, 139–142.

Suess, E. (1980), Particulate organic carbon flux in the oceans—Surface productivity and oxygen utilization, *Nature*, *288*, 260–263.

Sullivan, C. W. (1980), Diatom mineralization of silicic acid: V. Energetic and macromolecular requirements for $Si(OH)_4$ mineralization events during the cell cycle of *Navicula pelliculosa*, *J. Phycol.*, *16*, 321–328.

Sullivan, C. W. (1986), Silicification by diatoms, in *Silicon Biochemistry, CIBA Found. Symp. Ser.*, vol. 121, edited by D. Evered and M. O'Connor, pp. 59–89, Wiley-Intersci., Hoboken, N. J.

Swift, D. M., and A. P. Wheeler (1992), Evidence of an organic matrix from diatom biosilica, *J. Phycol.*, *28*, 202–209.

Takeda, S. (1998), Influence of iron availability on nutrient consumption ratio of diatoms in oceanic waters, *Nature*, *393*, 774–777.

Tamburini, C., J. Garcin, G. Grégori, K. Leblanc, P. Rimmelin, and D. L. Kirchman (2006), Pressure effects on marine prokaryotes responsible for biogenic silica dissolution during a diatom sinking experiment, *Aquat. Microbiol. Ecol.*, *43*, 267–276.

Tande, K. S., and D. Slagstad (1985), Assimilation efficiency in herbivorous aquatic organisms—The potential of the ratio methods using ^{14}C and biogenic silica as markers, *Limnol. Oceanogr.*, *30*, 1093–1099.

Taylor, N. J. (1985), Silica incorporation in the diatom *Coscinodiscus granii* as affected by light intensity, *Brit. Phycol. J.*, *20*, 365–374.

Thornton, D. C. O. (2002), Diatom aggregation in the sea: mechanisms and ecological implications, *Eur. J. Phycol.*, *37*, 149–161.

Tréguer, P., D. M. Nelson, A. J. Van Bennekom, D. J. DeMaster, A. Leynaert, and B. Quéguiner (1995), The silica balance in the world ocean: A reestimate, *Science*, *268*, 375–379.

Turner, J. T. (2002), Zooplankton faecal pellets, marine snow and sinking phytoplankton blooms, *Aquat. Microbiol. Ecol.*, *27*, 57–102.

Vanboekel, W. H. M., F. C. Hansen, R. Riegman, and R. P. M. Bak (1992), Lysis-induced decline of a Phaeocystis spring bloom and coupling with the microbial foodweb, *Mar. Ecol. Prog. Ser.*, *81*, 269–276.

Van Cappellen, P., and L. Qiu (1997), Biogenic silica dissolution in sediments of the Southern Ocean: I. Solubility, *Deep Sea Res., Part II*, *44*, 1109–1128.

Van Cappellen, P., S. Dixit, and J. Van Beusekom (2002), Biogenic silica dissolution in the oceans: Reconciling experimental and field-based dissolution rates, *Global Biogeochem. Cycles*, *16*(4), 1075, doi:10.1029/2001GB001431.

Verity, P., and V. Smetacek (1996), Organism life cycles, predation and the structure of marine pelagic ecosystems, *Mar. Ecol. Prog. Ser.*, *130*, 277–293.

Vinogradov, M. E. (1968), *Vertical Distribution of the Oceanic Zooplankton* (in Russian), 339 pp., Acad. of Sci. of the USSR, St. Petersburg, Russia. (English translation, Inst. of Oceanol., Isr. Program for Sci. Transl,. Jerusalem.)

Wassmann, P. (1998), Retention versus export food chains: Processes controlling sinking loss from marine pelagic systems, *Hydrobiologia*, *363*, 29–57.

Yu, E.-F., R. Francois, M. P. Bacon, S. Honjo, A. P. Fleer, S. J. Manganini, L. M. M. van der Rutgers, and V. Ittekkot (2001), Trapping efficiency of bottom-tethered sediment traps estimated from the intercepted fluxes of 230Th and 231Pa, *Deep Sea Res., Part I*, *48*, 865–889.

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