The World Ocean Silica Cycle

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Keywords

Abstract

Over the past few decades, we have realized that the silica cycle is strongly in-
tertwined with other major biogeochemical cycles, like those of carbon and
nitrogen, and as such is intimately related to marine primary production,
the efficiency of carbon export to the deep sea, and the inventory of carbon
dioxide in the atmosphere. For nearly 20 years, the marine silica budget com-
piled by Tréguer et al. (1995), with its exploration of reservoirs, processes,
sources, and sinks in the silica cycle, has provided context and information
fundamental to study of the silica cycle. Today, the budget needs revisiting
to incorporate advances that have notably changed estimates of river and
groundwater inputs to the ocean of dissolved silicon and easily dissolvable
amorphous silica, inputs from the dissolution of terrestrial lithogenic silica
in ocean margin sediments, reverse weathering removal fluxes, and outputs
of biogenic silica (especially on ocean margins and in the form of nondi-
atomaceous biogenic silica). The resulting budget recognizes significantly
higher input and output fluxes and notes that the recycling of silicon occurs
mostly at the sediment-water interface and not during the sinking of silica
particles through deep waters.

INTRODUCTION

Silicon, the seventh-most-abundant element in the universe, is a key nutrient element in the ocean, required for the growth of diatoms and some sponges and utilized by radiolarians, silicoflagellates, several species of choanoflagellates, and potentially some picocyanobacteria. Despite long-standing interest in siliceous organisms and silica sediments (Haeckel 1904, plate 71), only since the late twentieth century have processes controlling the marine biogeochemistry of silicon been quantified (e.g., Nelson et al. 1995, Ragueneau et al. 2000) and silica budgets for the world ocean constructed (Wollast 1974, Tréguer et al. 1995, Laruelle et al. 2009), showing, for instance, that the silica cycle is strongly intertwined with the inventory of carbon dioxide in the atmosphere (Pondaven et al. 2000). The resulting estimates for the residence time of silicon in the modern ocean are 15,000 years (Tréguer et al. 1995) to 17,000 years (Laruelle et al. 2009), a timescale over which the silica cycle has been considered to be at steady state (Tréguer et al. 1995, Laruelle et al. 2009). Thus, it has been assumed that human activities have not yet affected the marine silica cycle. However, recent studies suggest that the silica cycle in coastal zones is highly sensitive to anthropogenic pressure, with, for instance, damming resulting in a decrease of the dissolved silicon (DSi) concentrations in rivers and estuaries (Ittekkot et al. 2006, Laruelle et al. 2009, Bernard et al. 2011). The silica cycle is liable to undergo significant further alteration as the climate changes (Bernard et al. 2010), resulting in drastic changes in coastal primary production and to coastal ecosystems.

The global estimates of biogenic silica production and recycling along with the marine silica budgets produced in the 1990s (Nelson et al. 1995, Tréguer et al. 1995) have been invaluable to silica cycle research and to a broad array of efforts to model food webs and other biogeochemical cycles, providing constraints for the modeling and allowing results to be placed in a broader context. Given the wealth of data collected since then, especially concerning the land-ocean interface and [230]Th-normalized opal burial rates in the Southern Ocean, the marine silica budget needs revisiting. Key aspects to update include input fluxes related to mineral weathering and to the dissolution of amorphous silica on ocean margins, off-axis hydrothermal fluxes, biogenic silica production and recycling, biogenic silica burial in coastal regions and the Southern Ocean, and output fluxes related to reverse weathering in estuaries and to sponges.

REVISITING SILICON FLUXES AT THE GLOBAL SCALE

In this article, in accordance with Tréguer et al. (1995), the ocean includes the coastal zone—i.e., in the transition zone from continent to ocean, we enter the ocean as soon as we leave the estuary (**Figure 1**). **Figure 1** is to be used as a guide through this revisiting of the silicon fluxes. We consider first the input fluxes and then the biogeochemical fluxes (internal cycling) from the surface ocean to the deep ocean, and finally propose new estimates for the output fluxes.

THE INPUT FLUXES

Four pathways serve as external sources of silicic acid (also called DSi) to the ocean, all of which ultimately derive from the weathering of Earth's crust (**Figure 1**). DSi from the chemical weathering of continental rocks is discharged into the coastal zone by rivers and groundwater. Rivers also transport significant quantities of particulate amorphous silica that may dissolve, as may dust deposited on the ocean's surface. Lastly, terrigenous silicates in sediments of continental margins may dissolve, and submarine basalts react with high- and low-temperature hydrothermal fluids, releasing DSi.

Continental inputs. The continental inputs to the ocean are composed of the silicic acid flux and the dissolvable biogenic silica transported to estuaries by rivers, hereafter corrected for the
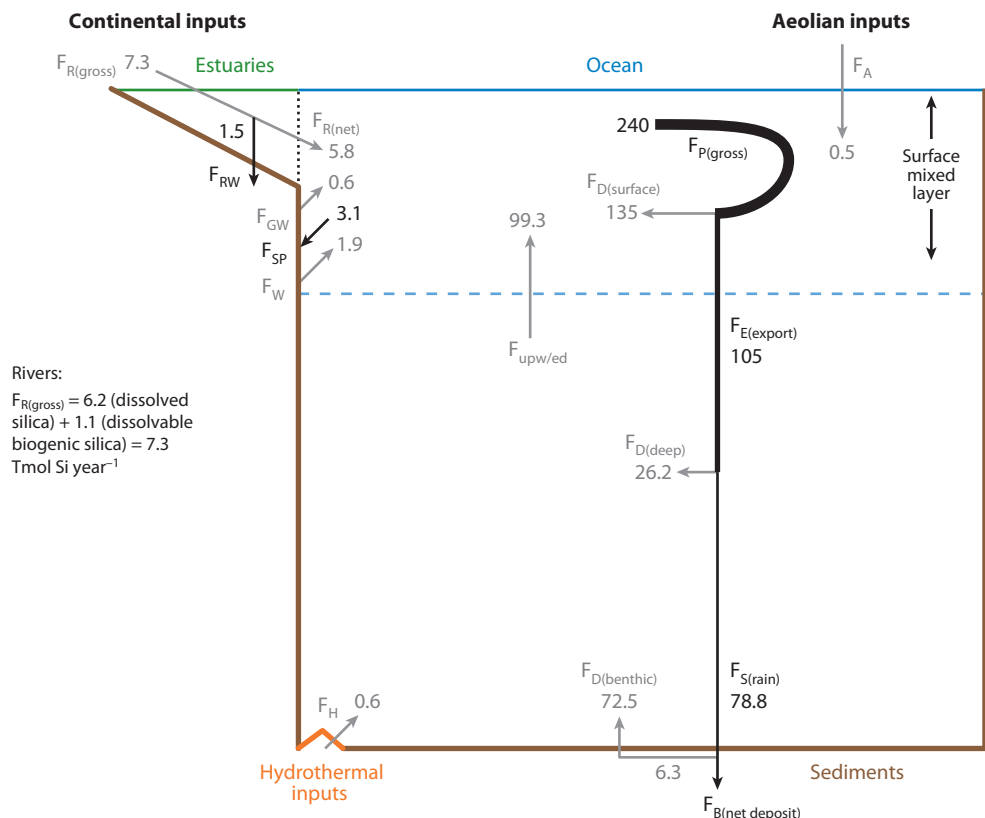
Figure 1

Biogeochemical cycle of silicon in the world ocean at steady state: a possible balance that is in reasonable
agreement with the individual range of each flux (F). The dotted line represents the limit between the
estuaries and the ocean. Gray arrows represent fluxes of silicic acid (dissolved silica) and black arrows
represent fluxes of particulate biogenic silica; all fluxes are in teramoles of silicon per year. Abbreviations:
$F_{R(gross)}$, gross river inputs; $F_{R(net)}$, net river inputs; F_{RW}, deposits of biogenic silica and reverse weathering
in estuaries; F_{GW}, groundwater flux; F_A, aeolian inputs; F_H, hydrothermal inputs; F_W, seafloor weathering
inputs; $F_{P(gross)}$, biogenic silica gross production; $F_{D(surface)}$, flux of silicic acid recycled in the surface
reservoir; $F_{E(export)}$, flux of biogenic silica exported toward the deep reservoir; $F_{D(deep)}$, flux of silicic acid
recycled in deep waters; $F_{D(benthic)}$, flux of silicic acid recycled at the sediment-water interface; $F_{S(rain)}$, flux of
biogenic silica that reaches the sediment-water interface; $F_{upw/ed}$, flux of silicic acid transferred from the
deep reservoir to the surface mixed layer (upwelling, eddy diffusion); $F_{B(netdeposit)}$, net deposit of biogenic
silica in coastal and abyssal sediments; F_{SP}, net sink of biogenic silica in sponges on continental shelves.
Adapted from Tréguer et al. (1995).

trapping of biogenic silica and the reverse weathering in estuaries to yield the net flux to the ocean.
Additional silicon input from the continents occurs through submarine discharge of groundwater.

Dissolved silicon transported to estuaries by rivers. The current best estimate (based on data
representing 60% of the world river discharge to the ocean of 39,080 km^3 year^{-1}) of the discharge-
weighted average DSi concentration of rivers is 158 μM (Dürr et al. 2011), in close agreement
with the older estimate (Tréguer et al. 1995). This yields an updated estimate for the gross input
of DSi to estuaries of $F_{R(grossDSi)}$ = 6.2 ± 1.8 Tmol Si year^{-1}. Although it is noteworthy that
51% of this DSi flux is based on direct measurements of DSi and river discharge—no small

accomplishment—the 30% uncertainty in $F_{R(gross)}$ reflects our poor knowledge of the seasonal silica cycle in many rivers and the errors associated with the extrapolation of discharge data to the global scale.

Dissolvable biogenic silica transported by rivers. The flux of particulate silica (lithogenic and biogenic) to estuaries calculated by Dürr et al. (2011) is 147 ± 44 Tmol Si year^{-1}. How much of this flux actually dissolves remains unknown. Whereas the lithogenic component of this flux is fairly insoluble, the amorphous, largely biogenic component (phytoliths, freshwater diatoms, sponge spicules) is easily dissolvable. Dissolution of a significant fraction of this silica in ocean margins would be a notable input of DSi to the ocean. But if the amorphous silica is transformed into clay minerals in margin sediments, marine DSi would be removed via reverse weathering (see below). Because amorphous silica is a small fraction of the particulate silica transported, we adopt Conley's (1997) amorphous-specific estimate of $F_{R(bSiO_2)} = 1.1 \pm 0.2$ Tmol Si year^{-1}. The total gross input of rivers to estuaries is thus $F_{R(gross)} = 6.2\,(\pm 1.8) + 1.1\,(\pm 0.2) = 7.3 \pm 2.0$ Tmol Si year^{-1} (**Figure 1**).

Reverse weathering and trapping of silicon in estuaries and river plumes. Two processes occurring in estuaries and river plumes have a significant impact on the global silica budget. Riverine silicon may be incorporated into biogenic silica in diatom blooms fueled by the river-borne nutrients and exported to the sediments. Riverine silicon, in particulate or dissolved form, may fuel diagenetic reactions that result in the formation of authigenic silicate minerals and, potentially, the removal of additional DSi from the system (Michalopoulos & Aller 1995). This reverse weathering is particularly active in deltaic environments like those of the Amazon and Mississippi Rivers, the Gulf of Papua, and French Guinea (Michalopoulos & Aller 2004; Presti & Michalopoulos 2008; R.C. Aller, personal communication). In the case of the Amazon, DeMaster et al. (1983) estimated the burial rate of biogenic silica at 0.03 Tmol Si year^{-1}. Adding the authigenic silicates increases this number to 0.17 Tmol Si year^{-1}, which represents a total removal of 22% of the river DSi flux (Michalopoulos & Aller 2004). In the Mississippi delta, the authigenic mineral component may account for 40% of the long-term storage of reactive silicon.

Reverse weathering means that nontropical deltaic systems are significantly more important silica sinks than previously considered (Presti & Michalopoulos 2008). In agreement with R.C. Aller (personal communication), Holland (2005) proposed that this process removes 20%–25% of the total river input of silicon to the ocean. This estimate takes into account pore water solute fluxes of K^+, F^-, and Li^+; stoichiometric models of clay composition; non-steady-state diagenetic modeling based on seasonal sampling; direct measurements of the formation rates and composition of clays in the laboratory; and various leaches of sediment designed to separate biogenic silica and reactive clays (R.C. Aller, personal communication). Thus, the estuarine removal flux should be $F_{RW} = 1.5 \pm 0.5$ Tmol Si year^{-1} (**Figure 1**), compatible with the estimate of Laruelle et al. (2009) but two times greater than that of Tréguer et al. (1995). The net input of rivers to the ocean then becomes $F_{R(net)} = 6.2\,(\pm 1.8) + 1.1\,(\pm 0.2) - 1.5\,(\pm 0.5) = 5.8 \pm 2.5$ Tmol Si year^{-1} (**Figure 1**).

Submarine water discharge. DSi input via submarine groundwater (SGW) influx to the ocean was not considered in the previous budget but may be considerable, and is similar in some places to surface river inputs (e.g., Kim et al. 2005). For instance, DSi input to the Bay of Bengal via SGW of 0.093 Tmol Si year^{-1} (Georg et al. 2009) is equivalent to 66% of the Ganges-Brahmaputra river flux of DSi to the ocean. If global SGW discharge is 2,000 km^3 year^{-1} (Slomp & Van Cappelen 2004) and its average DSi concentration is 340 μM (the midpoint of the reported 62–620-μM

range) (Niencheski 2007, Georg et al. 2009), then our best estimate for the SGW flux of DSi to the ocean is $F_{GW} = 0.6 \pm 0.6$ Tmol Si year^{-1} (**Figure 1**), compatible with the estimate of Laruelle et al. (2009).

Aeolian inputs. Estimation of aeolian inputs of DSi to the ocean (F_A) requires knowledge of dust fluxes and dissolution rates. Dry deposition of particulate lithogenic silica onto the ocean ranges from 2.8 to 4.6 Tmol Si year^{-1} (Tegen & Kohfeld 2006), localized mainly in the North Atlantic (downwind of the Sahara Desert) and the western North Pacific (downwind of the Gobi Desert). How much dissolves is difficult to estimate because of large differences in the solubility of the varieties of lithogenic and biogenic silica that constitute dust (Dürr et al. 2011). Silicon solubility ranges from 0.02% to 1.1% for Saharan dust, which is mainly quartz (Baker et al. 2006). However, 10% of silicon may be soluble from feldspar dust (Harrison 2000), and even more may be soluble from biogenic silica present in dust. Rainwater (wet deposition) also delivers DSi, with reported values ranging from 0.0 to 6.7 mmol Si m^{-2} year^{-1} near Corsica, in the Mediterranean Sea (Tréguer et al. 1995), and from 2.55 to 2.60 mmol Si m^{-2} year^{-1} in the Yellow and East China Seas (Zhang et al. 2005). These authors estimated the total aeolian input of DSi to be 0.15 ± 0.05 Tmol Si year^{-1} for the continental margins and 0.75 ± 0.25 Tmol Si year^{-1} for the open ocean, bringing the total atmospheric input to 0.9 ± 0.3 Tmol Si year^{-1}. Given the uncertainties associated with the deposition and solubility of dust, we retain Tréguer et al.'s (1995) estimate of $F_A = 0.5 \pm 0.5$ Tmol Si year^{-1} (**Figure 1**).

Hydrothermal inputs. Deep-sea hydrothermal inputs consist of high-temperature (350°C $\pm$ 30°C) inputs from midocean ridges (the axial component of the flux) and low-temperature (<75°C) inputs from ridge flanks (the diffuse, off-axis component). They are inherently different because reactions at high temperatures leach silicon from the oceanic crust, resulting in high-DSi hydrothermal fluids, whereas cooling of these fluids before they exit from the seabed removes DSi through precipitation of clays like smectite (Wheat & McManus 2005).

Budgets based on germanium-to-silicon (Ge/Si) ratios have been used to constrain hydrothermal fluxes of DSi (Mortlock et al. 1993, Tréguer et al. 1995) but have overlooked non-opaline germanium sinks in the ocean (Hammond et al. 2000, King et al. 2000), biasing the estimate. DSi inputs estimated from heat-budget-based water fluxes (Elderfield & Schultz 1996, Wheat & McManus 2005) are likewise complicated by uncertainty in the partitioning of the heat flux between high-temperature axial and lower-temperature off-axis flows and by a lack of precise knowledge of the average temperature of the off-axis water flux.

Axis hydrothermal systems. Correcting the previous Ge/Si-based estimate of hydrothermal DSi input (0.2 ± 0.1 Tmol Si year^{-1}) for a non-opaline sink of 6–7 Mmol Ge year^{-1} [estimated by S. Mantoura, C.L. De La Rocha, A. Galy, J. Latimer & A. Shemesh (manuscript in preparation)] yields a revised estimate of 0.5 Tmol Si year^{-1} for overall (axial + ridge flank) hydrothermal inputs of DSi to the ocean. This closely resembles the axial-only estimates of 0.55 ± 0.25 (Elderfield & Schultz 1996) and 0.53 ± 0.11 (Wheat & McManus 2005) Tmol Si year^{-1} based on water fluxes. For the axis hydrothermal system flux, we take an estimate of 0.5 ± 0.3 Tmol Si year^{-1}.

Ridge flank hydrothermal systems. Of the 7–11 TW of convective heat flux at ridges, 2 TW are lost through axial venting (Elderfield & Schultz 1996), leaving 5–9 TW for warm springs and diffuse ridge flank flow (Wheat & McManus 2005). The chemical composition of these altered fluids cannot be measured directly. If the ridge flank flux averages between 10°C and 50°C, then the ridge flank water flux would be between 8.1×10^{14} and 8.8×10^{15} kg year^{-1}. If the difference

in the DSi concentration of bottom water versus that of the ridge flank fluids is between 5 and 150 μM (Wheat & McManus 2005), then the net DSi input would be between 4.1×10^9 and 1.3×10^{12} mol Si year^{-1}, or 0.7 ± 0.6 Tmol Si year^{-1}. However, a coupled Ge/Si and Ge isotope budget suggests that this value is more likely to be at least an order of magnitude lower (S. Mantoura, C.L. De La Rocha, A. Galy, J. Latimer & A. Shemesh, manuscript in preparation), e.g., 0.07 ± 0.07 Tmol Si year^{-1}. We thus update the total hydrothermal flux of DSi to be $F_H = 0.6 \pm 0.4$ Tmol Si year^{-1} (**Figure 1**).

A huge plume with DSi concentrations exceeding 200 μM Si has been discovered on the eastern side of the North Pacific (Talley & Joyce 1992). Centered on the 47th degree of northern latitude, the volume of water affected by this anomaly (approximately 15 μM Si) is delimited by depths of 2,000 and 3,000 m. A flux of 1–2 Tmol Si year^{-1} is required to maintain this anomaly (Johnson et al. 2006). From the Ge/Si ratios (Esther et al. 2010) and silicon isotope composition (δ^{30}Si) (M.A. Brzezinski, personal communication) of deepwater samples, it appears that geothermal/hydrothermal processes can explain no more than 5% of the silicon excess in the Canadian Basin bottom water. In other words, this Northeast Pacific anomaly does not correspond to an external input of DSi to the world ocean but is explainable by internal biogeochemical processes, i.e., by silica recycling. However, this is a preliminary conclusion, as a balanced silicon budget for this anomaly has not been reached (Johnson et al. 2006, Esther et al. 2010). Alternatively, the anomaly might be due to the remobilization of relatively old biogenic silica that accumulated over a long time interval; this is possible to consider as an external input and would correspond to a non-steady-state situation (M.A. Brzezinski, personal communication).

Low-temperature dissolution of terrigenous material in marine sediments and seafloor basalt. The low-temperature dissolution of seafloor basalt and terrigenous silicates deposited in sediments is an additional external source of DSi to the ocean. Previous budgets have included 0.4 ± 0.3 Tmol Si year^{-1} from seafloor basalt (Wollast & Mackenzie 1983, Tréguer et al. 1995) but not dissolution of terrigenous silicates in sediments. Benthic effluxes as high as 10–20 mmol Si m^{-2} year^{-1} have been reported for the biogenic, silica-poor seafloor of the southern Angola Basin (van Bennekom & Berger 1984) and Sargasso Sea (Sayles et al. 1996). Extrapolation to the entire 120-million-km^2 zone of sediments devoid of opal yields $F_W = 1.9 \pm 0.7$ Tmol Si year^{-1} (Tréguer et al. 1995), and recent studies suggest that lithogenic material deposited along ocean margins may release considerable DSi into seawater (Jeandel et al. 2011; C. Jeandel, B. Peucker-Ehrenbrink, Y. Godderis, F. Lacan & M.T. Jones, manuscript in review).

In batch reactor experiments (Oelkers et al. 2011), the dissolution of lithogenic silicates is initially rapid, but saturation of the fluid with respect to numerous silicate minerals quickly removes much of the dissolved mass by the precipitation of secondary minerals. In contrast, neodymium isotope distributions in the ocean imply that 3% of the lithogenic material in continental sediments dissolves into seawater (Lacan & Jeandel 2005). Assuming congruent dissolution yields a silicon flux of 22 ± 11, 7 ± 3, 35 ± 18, and 5 ± 2 mmol Si m^{-2} year^{-1} for margin sediments composed entirely of clay, shale, basalt, and sand, respectively (C. Jeandel, B. Peucker-Ehrenbrink, Y. Godderis, F. Lacan & M.T. Jones, manuscript in review). Although the congruence hypothesis is too simplistic, such fluxes are compatible with the older field measurements, supporting the adoption of a higher estimate of $F_W = 1.9 \pm 0.7$ Tmol Si year^{-1} (**Figure 1**).

Total net input. All of the above yields a total net input of $F_{C(net)} = 6.2 \pm 1.8$ (river DSi) + 1.1 ± 0.2 (river biogenic silica) − 1.5 ± 0.5 (reverse weathering) + 0.6 ± 0.6 (SGW) + 0.5 ± 0.5 (aeolian) + 0.6 ± 0.4 (hydrothermal) + 1.9 ± 0.7 (lithogenic sediment and basalt dissolution) = 9.4 ± 4.7 Tmol Si year^{-1}.

The Biogeochemical Fluxes

Biogenic silica is produced by siliceous organisms in the photic layer. Part of this flux is directly recycled in the surface ocean, and part is exported to the deep ocean. The exported biogenic silica continues to dissolve as it sinks through the deep ocean, regenerating silicic acid. The surviving biogenic opal accumulates at the sediment-water interface, where dissolution continues.

Producers. On the basis of box modeling and stoichiometric conversion of net primary production to silica production, the gross production of biogenic silica in the ocean was previously estimated to be $F_{P(gross)} = 240 \pm 40$ Tmol Si year^{-1}, or 0.67 ± 11 mol Si m^{-2} year^{-1} (Nelson et al. 1995). This production was attributed mainly to diatoms, the contribution of other siliceous protists (like silicoflagellates and radiolarians) being unknown but likely significantly less than that of diatoms.

Radiolarians inhabit all major oceans, and in the upper 1,000 m of the ocean are typically found at densities between 1 and 5,000 individuals m^{-3} (Boltovskoy et al. 2010). Not all radiolarians produce a silica skeleton, and the lack of information about silica per radiolarian and rates of DSi uptake make it currently impossible to estimate the contribution of radiolarians to silica production. However, if 0.6 μg is a representative weight for a radiolarian skeleton (Takahashi 1981), anywhere from 1 μmol to 6 mmol of the 2–26 mmol m^{-2} of biogenic silica standing stocks in the upper 120 m of the ocean (Adjou et al. 2011) could be associated with radiolarians.

Recent work in the eastern equatorial Pacific has intriguingly suggested that silicon-containing picoplankton may be responsible for up to 60% of the standing stocks of biogenic silica in the water column (Baines et al. 2010). If true and widespread, this would revolutionize our understanding of the biogenic silica cycle.

Silica production in different ecosystems (photic zone). Nelson et al. (1995) estimated a total gross production of biogenic silica of 240 ± 40 Tmol Si year^{-1}. This estimate was calculated both from the total primary production of the world ocean and a mean Si/C ratio and from the export production of biogenic silica calculated using a PANDORA model and then transformed into gross production using the mean dissolution-to-production-rate ratio for the surface world ocean. Hereafter, we calculate specific estimates of biogenic silica production for the coastal zone, the open ocean, and the Southern Ocean.

Coastal zone. Diatoms are major contributors of phytoplankton in the coastal zone and support major fisheries. Average silica production has been estimated at 6 Tmol Si year^{-1} in the major upwelling zones of the ocean and at 74 Tmol Si year^{-1} for eastern boundary coastal regions outside of the major upwelling zones (Shipe & Brzezinski 2001). The mean primary production of western boundary coastal waters (approximately 5% of the surface world ocean) being 380 g C m^{-2} year^{-1} (Longhurst et al. 1995), and assuming that diatoms contribute to a maximum of 75% to this total (Nelson et al. 1995), an Si/C ratio of 0.13 mol Si (mol C)$^{-1}$ (Brzezinski 1985) gives a rough estimate of western boundary biogenic silica production of 56 Tmol Si year^{-1}, for a total biogenic silica production in the coastal zone of 136 Tmol Si year^{-1}.

Open ocean. Unlike those in the coastal zone, diatoms in open ocean zones are not major contributors to the silica cycle. Data from the Bermuda Atlantic Time-Series Study (BATS) and Hawaii Ocean Time-Series (HOT) sites yield an estimate of the silica production of the subtropical gyres in the North Atlantic and North Pacific of 13 Tmol Si year^{-1}, reducing the contribution of subtropical gyres to only 5%–7% of global annual marine silica production (Brzezinski et al.

2011). The case is likely different in the North Pacific subarctic gyre, a region of 6.1 million km^2 (Longhurst et al. 1995). Although there do not appear to be published silica production measurements from this region, export fluxes of biogenic silica to 2,000 m as high as 1.1 mol Si m^{-2} year^{-1} are known (Honjo et al. 2008), i.e., higher than anywhere else in the ocean (see below). If the silica cycle in the subarctic Pacific is comparable to that in the Southern Ocean (cf. Nelson et al. 2002), then we can assume that slightly less than two-thirds of the silica produced in surface waters dissolves in the upper 2,000 m, and the average export production of 0.575 mol Si m^{-2} year^{-1} yields an estimate for the gross production of the subarctic gyre of approximately 10 Tmol Si year^{-1}. Interestingly, changes in the DSi inventory at subarctic station P (time series 1970–1980; Wong & Matear 1999) give an underestimate of the gross production of 5.1 mmol Si m^{-2} day^{-1} for 150 days; extrapolating across the entire gyre yields >4.7 Tmol Si year^{-1} for this region, which gives support to the above estimate. Thus, the open ocean total is 23 Tmol Si year^{-1}.

Southern Ocean. Tréguer & van Bennekom (1991) first estimated the gross production of the Southern Ocean to be approximately 50 Tmol Si year^{-1}. Pondaven et al. (2000) revised this production upward to 80 $\pm$ 18 Tmol Si year^{-1}, which is approximately one-third of the total marine production of biogenic silica. This corresponds to a mean daily production of 2.35 $\pm$ 0.5 mol Si m^{-2} year^{-1}, which fits reasonably well with field data from the various zones of the Southern Ocean (Brzezinski et al. 2001, Quéguiner 2001, Leblanc et al. 2002, Nelson et al. 2002, Beucher et al. 2004b, Fripiat et al. 2011b).

Summing up yields a total silica production of approximately 239 Tmol Si year^{-1}, not distinguishable from 240 $\pm$ 40 Tmol Si year^{-1} (Nelson et al. 1995), which we retain. The major contributors to this total are the coastal areas, the North Pacific, and the Southern Ocean, the subtropical gyres being of less importance.

Losses due to silica dissolution in the photic zone. A part of the gross production [$F_{P(gross)}$ or P] is recycled in the surface layer via the dissolution (D) of the biogenic silica. The material that escapes dissolution is exported toward the ocean interior in sinking particles. Multiplying the gross production by D:P, the ratio of annual biogenic silica dissolution to production, yields the export production. The first estimate of D:P was calculated at 0.58 based on 45 vertically integrated sets of data for production and dissolution simultaneously determined using isotopic tracer methods (Nelson et al. 1995). **Table 1** gives an expanded set of data. Noteworthy are the many D:P values >1 in the top half of **Table 1**, reflecting scenarios where the integrated dissolution rate measured in the photic zone exceeds the measured integrated production rate, which is possible only over short timescales or small areas. Studies measuring D:P have generally occurred during the spring or summer, making it unwise to average the data in **Table 1** to produce a typical global annual D:P value.

Also complicating the D:P estimate is that different methods have been used to quantify silica dissolution rates. However, time series (italicized locations in the bottom half of **Table 1**) offer an alternative way to estimate the annual average D:P for a region.

Coastal zone. Annual data on silica production and biogenic silica export flux to 470 m are available from the Santa Barbara Basin time series (bottom half of **Table 1**) (Shipe & Brzezinski 2001) and give an annual average D:P for the 0–470-m layer of 0.67. The average D:P for the photic zone must be significantly less than this. A similar result may be obtained from the SOMLIT (Service d'Observation en Milieu Littoral) time series from the Bay of Brest, France, for which Beucher et al. (2004a; C. Beucher, unpublished results, surface water only, data not shown in

Table 1 Mean ratio of biogenic silica dissolution (D) to silica production (P) in systems for which vertically integrated data are available

Location	Time	n	D:P Low	D:P Mean	D:P High	Reference(s)
Euphotic zone (isotopic methods)						
Coastal ocean (30 stations)						
Northwest Africa upwelling	April–May 1974	7	0.45	1.0	5.8	Nelson & Goering 1977
Peru upwelling	March–April 1976	4		0.1		Nelson et al. 1981
Southern California upwelling	April 1992	2	0.05	0.1	0.16	M.A. Brzezinski, unpublished data
Monterey Bay upwelling	April 2000	8	0.02	0.15	0.67	Brzezinski et al. 2003
Amazon River plume	August 1989	11	0.22	0.65	2.4	DeMaster et al. 1991
Open ocean (25 stations)						
Gulf Stream warm-core rings	April–June 1982	11	<0.19	0.47	0.79	Brzezinski & Nelson 1989
Eastern equatorial Pacific	September 2005	14	−0.53	0.35	1.23	Demarest et al. 2011
Southern Ocean (38 stations)						
Southern Ocean, spring (16 stations)						
Pacific sector	October–November 1978	6	0.18	0.34	0.58	Nelson & Gordon 1982
US Survey Pacific sector I	October–November 1997	3	0.61	0.64	0.69	Brzezinski et al. 2001
US Prod I Pacific sector	December 1997	7	0.01	0.27	0.72	Brzezinski et al. 2001
Southern Ocean, summer (26 stations)						
Ross Sea	January–February 1990	9	0.41	0.61	1.10	Nelson et al. 1991; D.M. Nelson, unpublished data
US Prod II	February–March 1998	6	0.04	0.83	2.71	Brzezinski et al. 2001
Indian sector	February 2003	6	0.00	1.42	3.05	Beucher et al. 2004b
SAZ-Sense Pacific sector	January–February 2007	5	0.02	1.68	2.08	Fripiat et al. 2011b
Surface waters (combination of methods; italics = time series)[a]						
Coastal ocean						
Santa Barbara Basin[b]	January–December 1996	22		0.67		Shipe & Brzezinski 2001
Open ocean						
BATS North Atlantic subtropical gyre[c]	August 1991–December 1994	41		0.82		Nelson & Brzezinski 1997
BATS[c]	April 2007	1	−0.29	8.6	0.47	Krause et al. 2010
Sargasso Sea mesoscale eddy[d]	April 2007	2	−0.41	0.31	+0.81	Krause et al. 2010
HOT North Pacific subtropical gyre[e]	January 2008–December 2009	18		0.46		Brzezinski et al. 2011
North Pacific subtropical gyre[b]	May 2008–December 2009	7	1.94	3.25	5.98	M.A. Brzezinski, personal communication
Eastern equatorial Pacific[d]	December 2004	7	0.37	1.2	2.45	Adjou et al. 2011
Eastern equatorial Pacific	September 2005	14	−0.53	0.35	1.23	Demarest et al. 2011
Southern Ocean						
US JGOFS Pacific sector[f]	December 1997–March 1998	31				Nelson et al. 2002

(Continued)

Table 1 (*Continued*)

Location	Time	*n*	D:P Low	D:P Mean	D:P High	Reference(s)
Northern Antarctic Circumpolar Current (55°–59° S, subantarctic zone)		6		0.16		
Polar front (59°–61.5° S, polar frontal zone)		9		0.26		
Southern Antarctic Circumpolar Current (61.5°–65.5° S, seasonal ice zone)		10		0.53		
Ross Sea gyre (65.5°–71.5° S, seasonal ice zone)		6		0.74		

Abbreviations: BATS, Bermuda Atlantic Time-Series Study; HOT, Hawaii Ocean Time-Series; JGOFS, Joint Global Ocean Flux Study; SAZ, subantarctic zone.

[a]"Surface waters" usually means the euphotic zone but can mean the 0–100-m or 0–150-m layer. Measurement of silica dissolution by isotopic dilution is generally not possible for oligotrophic waters; see footnotes b–f regarding the methods used to determine the dissolution rate and D:P ratio.

[b]Production flux: isotopic; export flux (= net production): sediment traps at 470 m; dissolution flux: difference between these two fluxes.

[c]Production flux: isotopic tracer methods; export flux (= net production): sediment traps; dissolution flux: difference between these two fluxes.

[d]Production flux: isotopic; dissolution flux: variation in silica during bottle incubation.

[e]Production flux: isotopic; export flux (= net production): sediment traps at 150 m; dissolution flux: difference between these two fluxes.

[f]Production flux: isotopic method (31 stations, eight depths per station, 100%–0.1% light); export flux (= net production estimated by [234]Th deficit and ratio of [234]Th particulate to biogenic silica): sediment traps at 100 m (one mooring per zone); dissolution flux: difference between these two fluxes.

Table 1) reported a mean annual D:P of 0.51 (April 2001–March 2003, 69 data points), with seasonal average values decreasing to 0.32 and 0.42 during the spring and summer, respectively (i.e., the bloom periods).

Open ocean. Silica production and export fluxes are available for two time series located in the two large oligotrophic gyres of the Northern Hemisphere (bottom half of **Table 1**). The annual average D:P for the North Atlantic (0.82) is much higher than that for the North Pacific (0.46), indicating that a significantly larger fraction of biogenic silica production is lost to dissolution in the upper waters of the North Atlantic. This might be related to the large size of some of the North Pacific diatoms increasing export efficiency (Brzezinski et al. 2011). Because the surface area of the Pacific Ocean is approximately twice that of the Atlantic, our best estimate for the annual average of D:P for the open ocean central gyres is 0.58. Note that no data are available for the subarctic gyre.

Southern Ocean. Biogenic silica production and [234]Th-normalized silica export fluxes were measured during the US Joint Global Ocean Flux Study (JGOFS) Antarctic Environment and Southern Ocean Process Study (AESOPS) cruises (Nelson et al. 2002) in the subantarctic zone, polar frontal zone, and seasonal ice zone of the Pacific sector from December 1997 to March 2008. D:P averaged 0.16, 0.26, and 0.70 for these three zones, respectively, yielding a production-weighted average for the whole system of 0.46.

Combining these estimates for the coastal zone (10% of the surface ocean), the open ocean (80% of the surface ocean), and the Southern Ocean (10% of the surface ocean) yields an estimate for the mean annual D:P ratio of the world ocean of 0.56, close to the first estimate of Nelson

et al. (1995). Thus, the global export flux from the photic zone (F_E) should be ∼44% of gross production, or 105 ± 17 Tmol Si year^{-1}.

Export flux of opal. According to Honjo et al. (2008), the Th-normalized export flux of biogenic opal into sediment traps at depths greater than 2 km averages 0.114 mol Si m^{-2} year^{-1}. The ocean area at 2 km is 301.3 million km^2 (after Pautot 1983), yielding a total global export of biogenic silica into the bathypelagic zone of 34.4 ± 2.6 Tmol Si year^{-1} (Honjo et al. 2008). The normalized silicon flux at 2-km depths ranges from 0.006 in the North Atlantic drift to 1.229 mol Si m^{-2} year^{-1} in the North Pacific subarctic gyre. Honjo et al. (2008) showed that the average silica flux is generally quite small in the Atlantic (0.039 mol Si m^{-2} year^{-1}) and Pacific warm pool (0.007 mol Si m^{-2} year^{-1}) compared with the equatorial zone (0.165 mol Si m^{-2} year^{-1}), Arabian Sea (0.265 mol Si m^{-2} year^{-1}), Southern Ocean (0.409 mol Si m^{-2} year^{-1}), and North Pacific polar front/Bering Sea (0.578 mol Si m^{-2} year^{-1}). This total export flux is an underestimate of the total export flux because it does not include coastal zones and continental slopes, both of which tend to have high export fluxes (e.g., Collins et al. 2011).

Opal rain rate and recycling at the water-sediment interface. Summing the net accumulation rates of opal [$F_{B(netdeposit)}$] and the pore water recycling flux [$F_{D(benthic)}$] across the sediment-water interface gives the silica rain rate [$F_{S(rain)}$], i.e., the rate of silica deposition on the seafloor (**Figure 1**, **Table 2**). Ragueneau et al. (2009) compared the reconstructed burial rate with the directly measured flux of silica into sediment traps moored just above the nepheloid layer (data not shown in **Table 2**) for typical ecosystems of the world ocean. The two approaches usually gave comparable rain rates.

Accordingly, generally in the open ocean and in the Southern Ocean, more than 90% of the opal rain appears to be recycled at the sediment-water interface. Note that these opal rain rates are uncorrected for sediment focusing (see below) that might introduce significant bias into the estimate, especially for regions with strong bottom water currents (e.g., the Southern Ocean).

The diffusive flux of DSi at the water-sediment interface [$F_{D(benthic)}$] was previously estimated at 23 ± 15 Tmol Si year^{-1} (see Tréguer et al. 1995, table 2), based on a set of measurements.

Table 2 Silicon fluxes at the sediment-water interface in different ecosystems of the world ocean

Ecosystem	Flux (mol Si m^{-2} year^{-1})			
	$F_{S(rain)}$	$F_{B(net deposit)}$	$F_{D(benthic)}$	$F_{D(benthic)}/F_{S(rain)}$
Open ocean				
BATS (North Atlantic)	0.018	0.001	0.017	0.95
Northeast Atlantic	0.020	0.001	0.019[a]	0.95
Porcupine Abyssal Plain (North Pacific)	0.065	0.008	0.057	0.88
Indian Ocean (northwest Somali Basin)	0.280	0.018	0.262	0.94
Equatorial Pacific	0.140	0.009	0.131	0.94
Southern Ocean				
Permanently open ocean zone	2.24	0.210	2.03	0.91
Polar frontal zone	0.805	0.075	0.73	0.91
Outer Ross Sea	0.374	0.007	0.367	0.98
Inner Ross Sea	2.13	1.24	0.89	0.42

Abbreviations: BATS, Bermuda Atlantic Time-Series Study; $F_{S(rain)}$, opal rain rates; $F_{B(net deposit)}$, opal net accumulation rates; $F_{D(benthic)}$, silicon recycled at the sediment-water interface. Table modeled after Ragueneau et al. (2009).
[a]Calculated by the difference between the measured rain rate and opal accumulation rate (Pondaven et al. 2000).

Table 3 Diffusive flux of silicic acid across the sediment-water interface [$F_{D(benthic)}$]

	Area (millions of km^2)	Average annual flux		Region	Reference
		Mol Si m^{-2}	Tmol Si year^{-1}		
Coastal zone (30–200 m)					
Option 1 (minimum)	30	0.47	14.2	Amazon	Berelson et al. 2003
Option 2 (maximum)	30	2.28	68.4	Monterey Bay	Berelson et al. 2003
Continental slope (200–1,000 m)					
Option 1 (minimum)	13.3	0.10	1.3	South Atlantic	Hensen et al. 1998
Option 2 (maximum)	13.3	1.39	18.5	Northwest Atlantic	Jahnke & Jahnke 2000
Open ocean					
Option 1 (minimum)	162.8	0.06	9.9	South Atlantic	Hensen et al. 1998
Option 2 (maximum)	162.8	0.22	35.0	Northwest Atlantic	Jahnke & Jahnke 2000
Southern Ocean					
Option 1 (minimum)					
Coastal continental shelf zone	0.9	0.42	0.38	Inner Ross Sea	Tréguer et al. 1995
Polar frontal zone	3	0.55	1.7	Indian sector	Tréguer et al. 1995
Permanently open ocean zone	14	0.22	3.1	Indian sector	Tréguer et al. 1995
Seasonal ice zone	16	0.16	2.6	Outer Ross Sea	Nelson et al. 2002
Southern Ocean subtotal, option 1	*33.9*		*7.7*		
Option 2 (maximum)					
Coastal continental shelf zone	0.9	0.89	0.8	Inner Ross Sea	Ragueneau et al. 2009
Polar frontal zone	3	0.73	2.2	Indian sector	Ragueneau et al. 2009
Permanently open ocean zone	14	2.03	28.4	Indian sector	Ragueneau et al. 2009
Seasonal ice zone	16	0.37	5.9	Outer Ross Sea	Ragueneau et al. 2009
Southern Ocean subtotal, option 2	*33.9*		*37.3*		
Total, option 1	*240*		*33*		
Total, option 2	*240*		*159*		

World ocean surface: 240 million km^2 = 360 million km^2 −120 million km^2 (sediments devoid of biogenic opal).

However, values determined for diffusive exchanges are methodologically sensitive. Fluxes calculated from pore water gradients can be two to five times smaller than those estimated using benthic chambers (e.g., Berelson et al. 2003, Hammond et al. 2004), reflecting the impact of irrigation by benthic organisms. From pore water gradients at 180 stations located along the continental margins of South America and southwest Africa, and in the mid–South Atlantic (the study area of 32 million km^2), Hensen et al. (1998) quantified $F_{D(benthic)}$ at 0.097 ± 0.055 mol Si m^{-2} year^{-1} and 0.061 ± 0.035 mol Si m^{-2} year^{-1} for the continental margins and the open ocean, respectively. These values are consistent with Tréguer et al.'s (1995) estimates. However, benthic chamber incubations carried out at 13 locations on the North Carolina continental slope in the Northwest Atlantic (Jahnke & Jahnke 2000) suggest much higher fluxes: In this study, values averaged 1.392 ± 0.060 mol Si m^{-2} year^{-1} for the continental margins and 0.215 ± 0.014 mol Si m^{-2} year^{-1} for the two open ocean stations. From Berelson et al. (2003), we calculate that in the coastal zone the average benthic flux of silicon ranges from 0.47 mol m^{-2} year^{-1} (Amazon shelf) to 2.28 mol m^{-2} year^{-1} (Monterey Bay). **Table 3** summarizes the available data [including those gathered by Nelson et al. (2002) for the Southern Ocean] to delimit a range for the total diffusive flux of silicon

from areas of the ocean containing biogenic silica in sediments. $F_{D(benthic)}$ stands between 33 and 159 Tmol Si year^{-1}, although the upper limit, being greater than export production (see above), is unrealistic. More observations are needed to better constrain the benthic flux, particularly for the coastal zone and the open ocean.

Figure 1, which assumes that the marine silica cycle is at steady state (see below), shows tentative values for $F_{S(rain)}$ (78.8 Tmol Si year^{-1}) and $F_{D(benthic)}$ (72.5 Tmol Si year^{-1}) compatible with **Table 3**, and an assumption that $F_{D(benthic)}/F_{S(rain)} = 0.92$, which is according to **Table 2**. It is noteworthy that in this updated view, different from that presented in Tréguer et al. (1995), the recycling of silicon occurs mostly at the sediment-water interface and not during the sinking of silica particles through deep waters, in accordance with observations (e.g., Nelson et al. 2002, Honjo et al. 2008).

The Output Fluxes

The permanent removal of silicon from the water column of the ocean occurs mostly via the burial of biogenic silica in sediments. Abiotic precipitation of amorphous silica can occur in hydrothermal vent plumes, and authigenic aluminosilicate formation may occur in sediments, but these two processes support minor export fluxes compared with biogenic silica burial. Siliceous sponges might also act as a significant silica sink, at least regionally.

Note that, as shown above for the estuarine zones, reverse weathering is also a process that can contribute to significant output fluxes of silicon. So far, rates of reverse weathering in open ocean sediments are not well quantified, and as such, no estimate is included in our revised silica budget.

Long-term burial rate (net accumulation of opal in sediments). Biogenic silica deposited at the sediment-water interface continues to dissolve until a saturating DSi concentration in sediment pore fluids is reached, meaning that long-term burial rates are smaller than rain rates. Strictly speaking, the long-term burial of biogenic silica occurs below the upper 10–20 cm of sediment. The largest long-term burial rates of biogenic silica occur in continental margins, the North Pacific, the equatorial Pacific, and the Southern Ocean (DeMaster 2002).

Determination of burial rates is complicated by postdepositional redistribution (winnowing or focusing) of sediment by bottom currents. Focusing factors often well above unity for sediment core sampling sites (e.g., François et al. 1993) mean that uncorrected sedimentation and burial rates are overestimates. The correction can be made by normalizing silica accumulation to the particle-reactive nuclide ^{230}Th (Bacon 1984, Geibert et al. 2005). The most recent estimate of the silica burial rate for the world ocean (DeMaster 2002), based on such ^{230}Th-normalized accumulation rates, showed that silica burial rates at high southern latitudes (Tréguer et al. 1995) were previously overestimated.

Coastal zone and continental margins. As there are few Th-normalized silica burial rates for the coastal zone and continental margins, DeMaster (2002) suggested estimating silica burial by relating it to organic carbon. Slopes ranging from 0.4 to 1.2 mol Si (mol C)$^{-1}$ are observed, allowing extrapolation from the 3.0 to 4.6 Tmol C year^{-1} of organic carbon burial (Berger et al. 1989, Hedges & Keil 1995, DeMaster 2002) to a silica burial rate of 3.3 ± 2.1 Tmol Si year^{-1}.

Not all of the biogenic silica produced in continental margins, however, may accumulate there. Using an Si/C ratio of 0.6 and Chen's (2010) estimate for downslope transport of particulate organic carbon of 21 Tmol C year^{-1}, Ragueneau et al. (2009) inferred a global downslope transport of biogenic silica from continental margin to deep sea of 12 Tmol Si year^{-1}. The extent to which this silica then dissolves (supporting, for example, the marked DSi anomaly at 4,000 m offshore

of the Congo) (Ragueneau et al. 2009) as opposed to becoming a part of the long-term burial of silica remains unclear.

Open ocean. Most published accumulation rates for deep-sea sediments have not been Th normalized. We must assume that sediment redistribution by bottom currents is negligible in such deep environments. Most biogenic silica burial rates for open ocean sediments (uninfluenced by continental margins) are <0.010 mol Si m^{-2} year^{-1} (DeMaster 1981; Sayles et al. 1996; Berelson et al. 1997; O. Ragueneau, unpublished data). Based on such data and assuming an uncertainty of 30% in DeMaster's (2002) estimate, silica burial rate in the open ocean is $<1.04 \pm 0.34$ Tmol Si year^{-1}.

Southern Ocean. Nelson et al. (1995) considered the preservation of biogenic silica to be much more efficient in Antarctic sediments than in the rest of the world ocean, implying that the high-opal belt underlying the Antarctic polar frontal zone was the result of this uniquely high preservation efficiency. Since then, estimates of silica production in the Southern Ocean have increased while estimates of burial have decreased owing to correction for focusing. According to Pondaven et al. (2000) and DeMaster (2002), the burial efficiency of silica in the Southern Ocean is not significantly different from the global average of 3%. In terms of preservation efficiency, the Southern Ocean is not operating differently from the rest of the world ocean.

Regarding the updated estimate for silica burial in the Southern Ocean, DeMaster (2002) used 31 ^{230}Th-normalized accumulation rates from Frank (1996), François et al. (1997), Frank et al. (1999), and Pondaven et al. (2000) to obtain the estimated burial of 3.1 ± 2.2 Tmol Si year^{-1} in the Southern Ocean's opal belt. Geibert et al. (2005) added a further 103 samples, improving both the numerical and geographic coverage, especially in the Atlantic sector, yielding an estimate of silica burial for the Atlantic sector (70° W–20° E) of 0.42 ± 0.14 Tmol Si year^{-1}. Adding the new data from Pondaven et al. (2000), Dezileau et al. (2003), and Geibert et al. (2005) results in a new estimate for silica burial in the Indian sector (20° E–150° E) of 1.4 ± 0.9 Tmol Si year^{-1}. Together, DeMaster's and Geibert et al.'s data for the Pacific sector (150° E–70° W) (5.9 million km^2) yield a total of 0.14 ± 0.13 Tmol Si year^{-1}. Thus the overall estimate for the Southern Ocean burial rate is 2.0 ± 1.2 Tmol Si year^{-1}, with the majority of the accumulation occurring south of the polar front. Although this updated flux is not significantly different from DeMaster's in terms of range, the mean is approximately one-third lower.

This estimate is conservative for at least three reasons. First, the full extent of the opal belt may extend northward well beyond the limits of Lisitzin's opal belt (Geibert et al. 2005), which would increase the size of the estimates. Second, the contribution of the seasonal ice zone is incomplete (because there are no ^{230}Th-normalized data available from the Indian sector). Third, opal burial in the coastal and continental zone has not been included, as uncorrected ^{230}Th data are available only for the Ross Sea (0.04 Tmol m^{-2} year^{-1}; DeMaster 2002), an exceptional region.

The resulting revised estimate for silica burial in the world ocean (**Table 4**) is $F_B = 6.3 \pm 3.6$ Tmol Si year^{-1} (**Figure 1**). This is nearly identical to DeMaster's (2002) estimate of 6.35 ± 1.05 Tmol Si year^{-1}.

Sponges: the missing sink? One of the notable features of the revised silica budget is that although the estimate of silicon inputs to the oceans has been revised significantly upward to 9.4 Tmol Si year^{-1}, in no small part because of the inclusion of previously unrecognized input fluxes (e.g., groundwater fluxes, amorphous silica in river inputs), the output based on the sedimentary burial rate of biogenic silica produced in the upper ocean has not (mean of total burial rate = 6.3 Tmol Si year^{-1}; **Table 5**). The resulting imbalance can potentially be redressed by considering

Table 4 Net annual accumulation rate of biogenic silica (F_B) in different ecosystems of the world ocean

Ecosystem	F_B (Tmol Si year^{-1})	Reference
Coastal zone and continental margins	3.3 ± 2.1	Modified from DeMaster 2002
Deep open ocean	<1.04 ± 0.34	DeMaster 2002
Southern Ocean[a]	>2.0 ± 1.2	Calculated in this review
Total removal rate	6.3 ± 3.6	

[a]Based on ^{230}Th-normalized sediment silica accumulation rates.

Table 5 Silicon budget in the world ocean

Component	Flux (Tmol Si year^{-1})
Inputs	
Rivers, dissolved silicon [$F_{R(grossDSi)}$]	+6.2 ± 1.8
Rivers, biogenic silica [$F_{R(bSiO_2)}$]	+1.1 ± 0.2
Reverse weathering and trapping (estuaries/plumes) (F_{RW})	−1.5 ± 0.5
Groundwater (F_{GW})	+0.6 ± 0.6
Atmosphere (aeolian) (F_A)	+0.5 ± 0.5
Hydrothermal (high and low temperature) (F_H)	+0.6 ± 0.4
Seafloor weathering (F_W)	+1.9 ± 0.7
Total net inputs	*+9.4 ± 4.7*
Outputs (F_B)	
Burial rate (diatoms)	6.3 ± 3.6
Sponges (continental shelves)	3.6 ± 3.7
Total net outputs	*9.9 ± 7.3*
Total production [$F_{P(gross)}$]	*240 ± 40*

the contribution of sponges. Silica-secreting sponges in relatively shallow, DSi-rich environments like the continental margins of the Southern Ocean (Dayton et al. 1974, Dayton 1979, Gatti 2002) and the North Pacific (Chu et al. 2011) create reefs that might serve as significant and previously overlooked silica sinks. Siliceous sponge reefs have also been described in DSi-poor environments like the Bahamas (Atlantic Ocean), the Western Mediterranean, the Hawaiian Archipelago, and the Belizean continental shelf (Maldonado et al. 2005, 2010). In such areas, standing stocks of living sponge silica may be greater than those of diatom silica (Maldonado et al. 2010), and dissolution rates may be lower (Hurd & Birdwhistell 1983). Experimental DSi uptake rates have been measured for individuals of only three Atlantic-Mediterranean demosponges (Maldonado et al. 2011). Unsurprisingly, compared with those of diatoms, their uptake rates are low at ambient DSi concentrations. When these limited data are used to estimate DSi demand (Maldonado et al. 2011), they suggest that in specific ecosystems, siliceous sponges utilize DSi to an extent comparable to diatoms: 0.01–0.9 mmol Si m^{-2} day^{-1} for sponges in continental shelf reefs (Maldonado et al. 2011) versus the ocean average of 1.6–2.2 mmol Si m^{-2} day^{-1} for diatoms (Nelson et al. 1995), or, in the Ross Sea, 23 mmol Si m^{-2} day^{-1} for sponges (Maldonado et al. 2011) versus 65 mmol Si m^{-2} day^{-1} for diatoms (Ragueneau et al. 2000).

The first tentative estimate of global silicon consumption by sponges has been carried out by Maldonado et al. (2011). Taking the estimated silicon consumption rates for sublittoral sponges

per unit area of seafloor at sites situated in the Mediterranean, Baltic, and Caribbean Seas and extrapolating to the entire 22 million km^2 of continental shelf in the world ocean yields an estimate of 3.7 $\pm$ 3.6 Tmol Si year^{-1} for the DSi demand due to sponges. Chu et al. (2011) set up a regional silicon budget for the Fraser glass sponge reef (British Columbia, Canadian Pacific), which hosts an amount of live sponges (DSi uptake) that is 2.5 times that of dead skeletons (DSi release). Extrapolating this budget to the total continental shelf area in the ocean gives a flux of DSi dissolving from sponges of 0.15 $\pm$ 0.15 Tmol Si year^{-1} (although it is unlikely that this unusual environment paints a typical picture of the ratio of the rate of silicon sequestering from the growth of living sponges to that of DSi dissolving from dead sponges on the seafloor). The net sink of biogenic silica in sponges on continental shelves could then be F_{SP} = 3.6 $\pm$ 3.7 Tmol Si year^{-1} (**Figure 1**).

AN UPDATED SILICA BUDGET FOR THE GLOBAL OCEAN AND THE STEADY-STATE HYPOTHESIS

Residence Time

The overall residence time for silicon in the ocean (τ_G) is equal to the total amount of DSi in the ocean divided by the net input (or output) flux. The updated budget (**Table 5**) suggests a mean residence time of approximately 10,000 years, i.e., shorter than that calculated by Tréguer et al. (1995) and Laruelle et al. (2009) and falling between that of nitrogen (<3,000 years; Sarmiento & Gruber 2006) and phosphorus (30,000–50,000 years; Delaney 1998). The residence time relative to biological uptake of DSi (τ_B) from surface waters is calculated by dividing the total DSi content of the world ocean (97,000 Tmol Si) by gross silica production by diatoms (240 Tmol Si year^{-1}) and sponges (3.7 Tmol Si year^{-1}). τ_B is approximately 400 years. The difference between τ_B and τ_G implies that silicon delivered to the ocean passes through the biological uptake and dissolution cycle an average of 25 times [(240 + 3.7)/9.9] before being removed to the seabed.

Is the Marine Silica Cycle at Steady State?

Because of the large uncertainty in the estimates of input and output fluxes (**Table 5**), it is difficult to say whether the current silica cycle is balanced, although an increase in continental weathering due to agricultural expansion and recent changes seen in rivers and the coastal ocean related to damming and eutrophication (Ittekkot et al. 2000, Laruelle et al. 2009) (see above) imply that the cycle is currently perturbed and has been for centuries. We take a moment to ponder the strength of the coupling between silicon inputs and outputs, assuming that, in the modern ocean, output fluxes are determined largely by rates of silica production.

Yool & Tyrell (2003) have shown that a simple box model at steady state, coupling the phosphorus and silica cycles, reproduces the behavior of both cycles in the modern ocean. In their model, although phosphate is the "ultimate limiting nutrient" [as defined by Tyrell (1999)] controlling primary production, DSi controls the fraction of the total produced by diatoms. Owing to diatoms' ability to decrease, within limits, the silicon content of their frustules over successive generations (Sarthou et al. 2005), diatoms can maintain cell division rates close to their maximum, even when their specific rate of silicon uptake is significantly submaximal. Thus the model-implied silicon limitation of diatom primary production could translate even more severely into silicon limitation of silica production. Indeed, there are numerous examples of DSi limiting the gross production of biogenic silica, at least seasonally, in different regions of the oceans—e.g., in the DSi-poor Mediterranean Sea (Leblanc et al. 2005) and North Atlantic (Leblanc et al. 2005) and

in the DSi-rich equatorial Pacific (Dugdale & Wilkerson 1998, Leynaert et al. 2001, Brzezinski et al. 2008, Dugdale et al. 2011) and Southern Ocean (Nelson & Tréguer 1992, Franck et al. 2000, Nelson et al. 2001, Quéguiner 2001). DSi can thus be seen as limiting the gross production of biogenic silica, supporting the balanced-budget (steady-state) hypothesis.

However, for most of these marine ecosystems, the gross production of biogenic silica is only moderately limited by DSi availability—for example, the measured uptake rates of silicic acid usually stand at over half the value of the maximum uptake rates (e.g., Nelson & Tréguer 1992), and nitrate and silicate are available in a molar ratio close to unity, the ratio in which they are, on average, required by diatoms (e.g., Brzezinski 1985). In addition, for high-nutrient, low-chlorophyll systems it is iron availability more than DSi availability that limits the DSi uptake rate and the gross production of biogenic silica (e.g., De La Rocha et al. 2000, Brzezinski et al. 2001, Leynaert et al. 2004, Mosseri et al. 2008, Marchetti et al. 2010). Such limitation of the gross production of biogenic silica by iron has a drastic impact on the export and burial of biogenic silica (Ragueneau et al. 2006).

If the gross production of biogenic silica is not silicon-limited in a large part of the world ocean, an increase in external DSi input does not need to be followed by an increase in biogenic silica production (and, by extension, output), resulting in an imbalanced budget. Also, in the shorter term, rates of biogenic silica production are entirely decoupled from rates of DSi input to the ocean because the total amount of DSi entering the euphotic zone each year depends more on upwelling out of the very large pool of DSi in the deep. Because of the relatively long residence time of DSi in the deep pool, it would take a change in the rate of silicon inputs to the ocean sustained over hundreds to thousands of years to have an influence on overall rates of biogenic silica production in the surface ocean (De La Rocha & Bickle 2005).

Therefore, assuming that the main control over silica burial rate is biogenic silica production rate, the hypothesis of a non-steady-state silica cycle in the modern ocean cannot be discarded, especially on relatively short timescales.

We know that the average DSi concentration in the ocean has varied considerably over geologic time (Siever 1991, Racki & Cordey 2000), reflecting changes in the relationship between DSi concentrations and the rate of silicon output from the ocean (meaning that silicon output from the ocean is not always silicon-limited). In the Precambrian, when average marine DSi concentrations were at least 20 times higher than they are today, the removal of DSi from the ocean was governed by diagenetic reactions and thus limited by a combination of DSi concentrations and the area of seafloor available for these reactions. During the last 550 million years, silicon output has been mainly as biogenic silica, with sponge and radiolarian silica dominating until the Cretaceous and silica production limited just as easily by DSi concentrations as by supplies of food for these animals. Since at least the early Eocene, biogenic silica production has been predominantly from diatoms. Owing to the great abundance and short generation time of diatoms, their high affinity for DSi, and their trend over time toward less silicified frustules (i.e., lower Si/N ratios), diatoms have all but stripped the ocean of DSi (Siever 1991), bringing concentrations down to the roughly 73-μM average of the deep sea and <10-μM average of surface waters.

Sponges aside, this Cenozoic isolation of silica production to an upper ocean fed largely from the large, deep ocean pool of DSi lengthens the response time of the silica cycle to changes in silicon inputs to the ocean, increasing the potential for the silica cycle to be out of balance. But by fueling silica production predominantly through upwelling, it also allows the silica production rate to vary independently of silicon input rates—for example, by maintaining the DSi supply to the surface even if river inputs are curtailed, or by changing the supply rate of DSi to the surface through changes in the mixing time of the ocean.

ANTHROPOGENIC PERTURBATION OF THE SILICA CYCLE IN THE COASTAL ZONE

Over the past 20 years, research has increasingly revealed anthropogenic disturbance of the silica cycle, especially in rivers, estuaries, and the coastal zone (Ittekkot et al. 2000). Conversion of forests to farmland over the past 5,000 years has altered rock weathering rates and intensity and decreased stocks of amorphous silica (primarily biogenic silica) in soils, greatly altering fluxes of reactive silicon to rivers (Struyf et al. 2010, Clymans et al. 2011, Struyf & Conley 2012), with an initial period of higher fluxes due to the diminution of the soil reservoir of reactive silicon followed by lower fluxes due to diminished weathering rates. Because of the rapid agricultural expansion of the past 400 years and the resulting flux of silicon out of soils as their amorphous silica stocks decrease, it is likely that fluxes of silicon to rivers remain significantly elevated over "pristine" conditions (Clymans et al. 2011).

The postwar profusion of dams (Rosenberg et al. 2000), which currently retain a third of the global sediment discharge (Vörösmarty & Sahagian 2000), changed that. By trapping biogenic and other forms of particulate, easily soluble silica, dams starve downstream areas of DSi (Humborg et al. 1997, 2000; Ittekkot et al. 2000), significantly reducing flux to the ocean. Meanwhile, the doubling of phosphate and nitrate inputs to the coastal ocean from agriculture (Meybeck 1998) has both increased biogenic silica production (further drawing down DSi concentrations, pushing diatoms toward silicon limitation) and diminished the relative importance of diatoms in coastal ecosystems (Turner & Rabalais 1994, Nelson & Dortch, 1996, Humborg et al. 2000). These effects are partly responsible for increases in harmful algal blooms, as silicon-limited diatoms cede the excess nitrate and phosphate to nonsiliceous phytoplankton such as dinoflagellates.

Further changes in the silica cycle related to additional damming and global warming are expected in the near future (Laruelle et al. 2009). More dams should further decrease the DSi concentrations of rivers and estuaries (Laruelle et al. 2009) and should be accompanied by a 10%–30% decrease in standing stocks of biogenic silica in rivers and estuaries and in the accumulation of biogenic silica in estuarine and coastal zone sediments. In the coastal zone, increased dissolution of biogenic silica with warming should also diminish the export of biogenic silica to deeper waters. Altogether, the coastal ocean is likely to continue toward silicon limitation of diatom growth and primary production dominated by nonsiliceous phytoplankton.

In addition, increased stratification in the open (not coastal) ocean due to global warming may diminish the DSi inputs from below, resulting in less biogenic silica (and primary) production in surface waters and less export toward the ocean interior.

CONCLUSIONS AND PERSPECTIVE

Over the past several decades, considerable research effort has significantly increased our understanding of the silica cycle. Beginning in the second half of the twentieth century, the importance of the silicon cycle in marine biogeochemistry began to be appreciated (e.g., Wollast & Mackenzie 1983) and the key role of diatoms in the export of carbon toward the ocean interior was noted (Smetacek 1999). Quantification of the input fluxes of DSi and the output fluxes of biogenic silica suggested that silicon has a longer geochemical residence time in the ocean (Tréguer et al. 1995) than nitrogen. The preservation efficiency of biogenic silica (∼3%) in sediments was recognized at 30 times greater than carbon, making silica of major interest as a proxy for export production (Ragueneau et al. 2000). Early in the twenty-first century, it was shown that continental shelves and margins had been previously underestimated as sinks for biogenic silica (DeMaster 2002). Also, the impacts of anthropogenic activities like dam building and deforestation were shown to

be significantly affecting the silicon cycle and biogeochemistry of the coastal zone as a whole (Laruelle et al. 2009), and the sensitivity of the marine silicon cycle to variations in the river inputs was then examined for timescales ranging from several centuries to millennia (Bernard et al. 2010).

In the new silica budget presented here, the total net inputs of DSi to the world ocean are larger than previously considered, diminishing the current residence time of silicon in the ocean to approximately 10,000 years, a value approximately 35% smaller than previous estimates. Rivers remain the dominant source of DSi inputs in the modern ocean, but it is now recognized that the dissolution of siliceous materials transferred from land to the continental margin contribute significantly to the total inputs. Groundwater is now also recognized as a significant part of the continental input. Updated values for burial rates of diatomaceous silica show that the long-term burial in the sediments of the coastal zone is probably greater than in the Southern Ocean. The total burial flux of biogenic silica due to diatoms in the coastal zone, the open ocean, and the Southern Ocean does not balance against the total input of DSi, lending credence to the hypothesis that the marine silica cycle is not currently at steady state (although it should be noted that uncertainties in the estimates are large). Significant uptake of DSi by siliceous sponges has been demonstrated on local and regional scales, giving some support to the idea that sponges play a significant, if thus far overlooked, role at the global scale. Lastly and significantly, the dissolution of biogenic silica appears to occur predominantly in the upper ocean and at the seabed, with only minor remineralization of biogenic silica occurring during its transit through the deep ocean.

The large uncertainties in many of the estimates in this revised silica budget need to be minimized, especially if we are to determine whether the budget is at steady state. Our first recommendation is to continue the world-scale effort to develop and maintain time series in the coastal zone, the open ocean, the Southern Ocean, and particularly the subarctic Pacific, and to include in these time series studies measurements of input and output fluxes of DSi, standing stocks and production rates of biogenic silica, and silica burial rates and benthic fluxes of DSi. The natural silicon isotopic composition of biogenic silica and dissolved silica represents a powerful but as yet underutilized tool for identifying silicon sources and silica production over large temporal and spatial scales (De La Rocha et al. 1997, 1998; De La Rocha & Bickle 2005; Fripiat et al. 2011a) and is a promising avenue for future work in this regard, especially in light of the current unavailability of the enriched isotopes needed for production estimates based on incubations. Our second recommendation is for further investigation into the possibility of silica-producing picoplankton and their potentially significant role in the silica cycle, particularly in oligotrophic surface waters (Baines et al. 2010). Third, there is a need to better constrain silica production by other ignored or overlooked groups, such as benthic diatoms in the coastal zone (Leynaert et al. 2011), radiolarians and other siliceous plankton, and siliceous sponges. Fourth, field experiments are needed to quantify the benthic input of DSi from the dissolution of terrigenous lithogenic materials in ocean margin sediments (Jeandel et al. 2011). And last but not least, considering the recent intense modifications of cultural practices (conversion of forest to farmland) over large areas of the African and South American continents (much as has previously occurred on other continents), to better quantify the transfer of terrestrial siliceous materials from land to the continental margins is of major importance to understanding future modifications of the marine silica cycle (Ragueneau et al. 2009).

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Contents

Errata

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