The Silica Balance in the World Ocean: A Reestimate

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The net inputs of silicic acid (dissolved silica) to the world ocean have been revised to 6.1 ± 2.0 teramoles of silicon per year (1 teramole = 10^{12} moles). The major contribution (about 80 percent) comes from rivers, whose world average silicic acid concentration is 150 micromolar. These inputs are reasonably balanced by the net ouputs of biogenic silica of 7.1 ± 1.8 teramoles of silicon per year in modern marine sediments. The gross production of biogenic silica (the transformation of dissolved silicate to particulate skeletal material) in surface waters was estimated to be 240 ± 40 teramoles of silicon per year, and the preservation ratio (opal accumulation in sediment/gross production in surface waters) averages 3 percent. In the world ocean the residence time of silicon, relative to total biological uptake in surface waters, is about 400 years.

Silicon, which represents 27% of the lithosphere, is an important component of the marine biogenic matter that accumulates in coastal and abyssal sediments. In this article we focus on the marine biogeochemical cycle of Si (Fig. 1), covering time scales from 1 to 10,000 years. Dissolved Si in seawater occurs mostly (~95%) as the undissociated monomeric silicic acid $Si(OH)_4$. On a time scale of 10,000 years or less, the mean concentration of silicic acid in the world ocean is assumed to be constant. The total content of silicic acid in the oceans is close to 10^{17} mol of Si, and the concentration of silicic acid in the world ocean averages about 70 μM. As for its distribution in the world ocean, there are marked regional differences. In surface waters of the central gyres the concentrations are usually <2 μM, but in the Antarctic, concentrations are as high as 80 to 100 μM in surface waters during winter. Deep and bottom waters are usually silicic acid–rich, with concentrations varying from 10 to 40 μM in the North Atlantic to 100 to 160 μM in the Antarctic, and 140 to 180 μM in the North Pacific.

In the modern ocean the distribution of silicic acid in the different water masses is governed by complex interactions among physical, chemical, geological, and biological processes. The silicic acid content is determined by the balance between geological and biological cycles of Si. The surface reservoir (Fig. 1) receives silicic acid inputs from the lithosphere both directly, via chemical weathering of the continental crust, and indirectly, through eolian transport. Through both high- and low-temperature weathering of the oceanic crust and of deposits of siliceous minerals, the ocean's deep reservoir also receives silicic acid inputs from the lithosphere. Except in the Atlantic Ocean, this deep reservoir is oversaturated with respect to lithogenic silica (at low temperature the equilibrium solubility in ocean water ranges from about 100 μM for quartz to 220 μM for montmorillonite), but it is undersaturated with respect to biogenic (or amorphous) silica (at deep-sea temperatures the equilibrium solubility is about 1000 μM).

The transfer of silicic acid from the marine hydrosphere to the biosphere initiates the biological cycle of Si; it is also a way to link the cycle of this element to that of carbon. Marine organisms such as diatoms, silicoflagellates, and radiolarians build up their skeletons by taking up silicic acid from seawater. After these organisms die the biogenic silica accumulated in them dissolves. The portion of biogenic silica that escapes dissolution, either in the surface or in the deep reservoir (Fig. 1), settles downward, ultimately reaching the sediment. The transformation of opal (amorphous biogenic silica) deposits in sediments through diagenetic processes is a way for silica to re-enter the geological cycle. Within sediments silica is a labile component: Some of the silicic acid produced from seabed dissolution diffuses up into the overlying water and another portion is mobilized and involved in the formation of aluminosilicate mineral phases. The biogenic silica that is preserved ultimately crystallizes primarily as chert.

The different processes involved in the biogeochemical cycle of Si occur over a wide range of time scales. The building-up of diatom frustules takes a few hours to a few days. A few days to a few months are necessary for the settling of diatom skeletons to the sea floor of continental margins or abysses. At the sediment-water interface opal remains from a few months to a few hundred years. At any of these steps biogenic silica continues to dissolve, and the recycled silicic acid is transported toward the surface layer. Deeper within the sediments, on the time scale of 10^6 to 10^9 years, the dissolution of silica debris and diagenetic processes continue.

On time scales of $<10^4$ years, the biogeochemical cycle of Si and its budget are affected by inputs of silicic acid from rivers [$F_{R(gross)}$], atmospheric deposition (F_A), sea floor weathering (F_W), and hydrothermal activity (F_H). Silicon is lost through the accumulation of biogenic silica in abyssal (F_B) and coastal sediments (F_{est}). Biogenic silica production [$F_{P(gross)}$] occurs within the surface reservoir. Some Si (F_E) is exported to the deep reservoir where a fraction (F_S) ultimately reaches the sediment-water interface, and an even smaller fraction accumulates in the seabed (F_B) because of seabed dissolution (F_D). At steady state the input fluxes balance the output fluxes. In this article we use updated estimates of inputs, outputs, and biogenic fluxes to revise earlier estimates *(1–4)* and to derive a budget of Si in the world ocean.

Inputs of Silicic Acid to the World Ocean

The net delivery of silicic acid to the world ocean involves three pathways (Fig. 1). The first is chemical weathering of sedimentary and crystalline rocks and, more generally, of silicate and aluminosilicate minerals (for example, feldspar) by CO_2-charged waters. The production of silicic acid is affected by river runoff, a process that is very climate-dependent. Silicic acid enters streams either directly via surface runoff or indirectly via ground water flow; it is then transferred to the ocean. Rivers also transport suspended matter composed of clay minerals and debris from weathered rocks. On a global scale the riverine flux of suspended matter is much greater than that of silicic acid; however, further dissolution of this particulate material is slow, and its contribution to the silicic acid flux from rivers is negligible.

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Eolian erosion of the land surface, especially in deserts, is the second potentially important pathway for long distance transport of siliceous material to the ocean. It results in advection of small lithogenic particles into the atmosphere; some of this airborne material enters the surface ocean where a small fraction dissolves. The third major geological pathway of net transfer of dissolved silica from the lithosphere to the hydrosphere is weathering of submarine basalt, which results from hydrothermal high-temperature reactions at mid-ocean ridges and low-temperature alteration of the basalts of the oceanic crust.

Our best estimate of the discharge-weighted average silicic acid concentration in rivers is 150 μM [about 13% lower than the value calculated in the 1980s (*5*)]. Our estimate takes into account updated values for the Amazon (*6*) and for Siberian rivers (*7*) and new data for Chinese and other rivers. Our value is based on 57% of the world river discharge to the world ocean and on 58% of the area with external drainage. Extrapolating the present data sets to the world river discharge (37,400 km^3 $year^{-1}$) gives a total flux $F_{R(gross)}$ of silicic acid of 5.6 ± 0.6 Tmol of Si per year. Approximately 74% of the riverine Si input is from tropical regions and 20% is from temperate regions. The ±0.6 Tmol Si $year^{-1}$ uncertainty on the one hand reflects our poor knowledge of the seasonal cycle of silica in many rivers, and on the second hand it takes into account the variability in silicic acid concentrations reported during the last several decades. Increasing inputs of nitrate and phosphate into eutrophicated rivers and lakes support enhanced production of diatoms, resulting in decreasing concentrations of dissolved Si (*8*, *9*); the construction of storage lakes in rivers enhances this effect, even in less eutrophicated rivers (*10*). Most of the eutrophicated rivers are in temperate regions, and a maximum estimate of the anthropogenic effect [assuming a 50% decrease in the silicic acid concentration (*11*) in temperate rivers] is about 0.6 Tmol Si $year^{-1}$, which falls within the uncertainty range of ±0.6 Tmol Si $year^{-1}$. Assuming that the use of fertilizers will continue to spread into the tropical areas and that the construction of storage lakes will increase, this could lead in the long run to a larger decrease in riverine Si input to the ocean. Seepage of fresh ground water into the sea, which presumably has a high silicic acid concentration, is another unknown factor in calculating the riverine Si input.

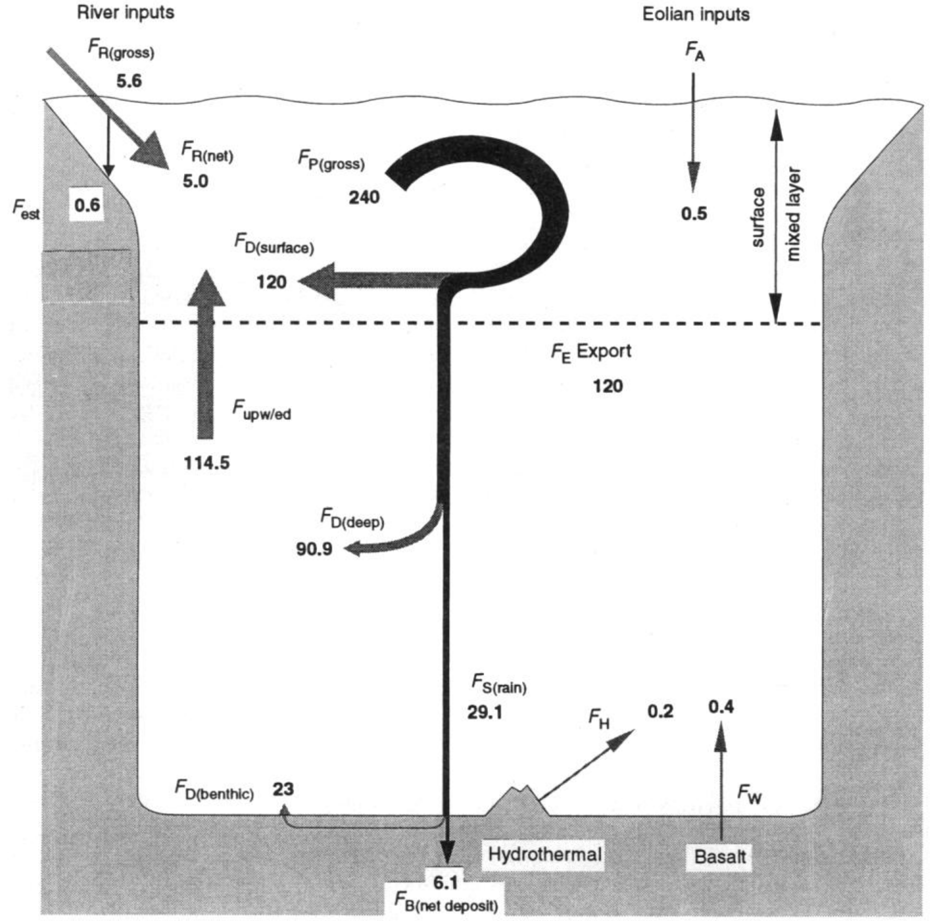

Fig. 1. Biogeochemical cycle of Si in the world ocean at steady state: A possible balance that is in reasonable agreement with the individual range of each flux (*F*) (see text). Gray arrows, fluxes of silicic acid (dissolved silica); black arrows, fluxes of particulate biogenic silica. All fluxes are in teramoles of Si per year. Abbreviations are as follows: River fluxes: gross inputs, $F_{R(gross)}$, and net inputs, $F_{R(net)}$; eolian inputs, F_A; seafloor weathering inputs, F_W; hydrothermal inputs, F_H; net deposit of biogenic silica in estuaries, F_{est}; net deposit of biogenic silica in coastal and abyssal sediments, F_B; biogenic silica gross production, $F_{P(gross)}$; flux of silicic acid recycled in the surface reservoir, $F_{D(surface)}$; flux of biogenic silica exported toward the deep reservoir, F_E; flux of silicic acid recycled in the deep reservoir, $F_{D(deep)}$; and at the sediment-water interface, $F_{D(benthic)}$; flux of biogenic silica that reaches the sediment-water interface, $F_{S(rain)}$; and flux of silicic acid transferred from the deep reservoir to the surface mixed layer, $F_{upw/ed}$.

Because of biological uptake, a significant part of the riverine load of silicic acid does not directly reach the ocean (*12*) but is removed in estuaries (Fig. 1). The major part of this particulate Si is remobilized by the dissolution of biogenic matter in the water column and seabed. The net removal of Si [$F_{(est)}$] in estuaries results from the net excess of the biological removal over benthic resupply. For tropical rivers, the net removal ranges from 4% of $F_{R(gross)}$ for the Amazon (*13*) to 15% of $F_{R(gross)}$ for the Zaïre river (*14*). For temperate rivers, Si removal as high as 50% has been calculated for the Rhine and Meuse rivers (*15*). To constrain these values to a narrower range, more data on benthic supply are needed. As tentative values we took a net removal of 10 ± 6% of $F_{R(gross)}$ for tropical rivers and a net removal of 25 ± 25% for temperate rivers; the calculated net removal (F_{est}) is about 0.6 ± 0.5 Tmol Si $year^{-1}$. Thus, the total net riverine flux of silicic acid [$F_{R(net)}$] to the ocean is 5.0 ± 1.1 Tmol Si $year^{-1}$.

Fluxes of particulate lithogenic Si on the order of 10 Tmol Si $year^{-1}$ (*16*) reach the surface layer of the world ocean by eolian transport. The dissolution of this eolian material depends on a number of factors, including its chemical composition and origin, but 5 to 10% is now thought to dissolve in seawater (*17*). Thus, with an ocean surface area of 360 × 10^{12} m^2 we can expect a flux on the order of 1.4 to 2.8 mmol of Si per square meter of water per year as typical of the silicic acid eolian flux in the ocean. Only a few data sets are available to support these values.

The first data set (*18*) is from analyses of lithogenic silica concentrations in rainwater at Capo Carvallo (Corsica, north Mediterranean Sea) from 1985 to 1987. These concentrations ranged between 0.9 and 220.0 μmol of Si per liter. From the annual amount of rainwater, which varies from 245 to 305 liters per square meter per year, we calculated the flux of lithogenic silica entering the sea surface to be between 0.2 and 67.1 mmol Si m^{-2} year^{-1}; thus, the silicic acid eolian input to seawater ranges between 0.0 and 6.7 mmol Si m^{-2} year^{-1}. Because of the proximity of Capo Carvallo to the Sahara, a major dust source, it is not surprising that the calculated maximum value is significantly higher than that mentioned above as typical of the world ocean.

A second data set was obtained during 1991–1992 at the Bermuda Atlantic Time-Series (BATS) station (*19*). A lithogenic silica flux of 8.8 ± 4.9 mmol Si m^{-2} year^{-1} was measured at a depth of 150 m. This implies that silicic acid inputs range between 0.2 and 1.4 mmol Si m^{-2} year^{-1}. Referring to the distribution of global fluxes of mineral aerosol to the oceans (*16*), the BATS site is more representative of an open-ocean situation than Capo Carvallo. We can constrain the global silicic acid eolian inputs to be between 0.0 (the minimum value reported for the Mediterranean site) and 2.8 mmol Si m^{-2} year^{-1} (twice the maximum value typical from oceanic situations). This range corresponds to a global input of 0 to 1.0 Tmol Si year^{-1}, that is, $F_A = 0.5 \pm 0.5$ Tmol Si year^{-1}.

Submarine weathering of basalt, primarily at sea floor hydrothermal areas, provides additional silicic acid in the deep reservoir. Although values as high as 19 mM (*20*) have been reported for hot (>300°C) hydrothermal waters, the positive anomalies in cold (about 2°C), deep waters at mid-ocean ridges are limited to a few micromolar (*21*). This rapid decrease of the silicic acid concentration in a hydrothermal environment is due not only to intense dilution of hydrothermal efflux in the deep water current but also to amorphous silica precipitation in the immediate vicinity of the vents. In principle, the silicic acid hydrothermal flux, F_H, can be directly determined after measuring the silicic acid concentration and the seawater efflux at the hydrothermal vent, but the efflux parameter is not easy to measure. Fortunately, different geochemical tracers, whose concentration ratios to Si are known, provide an indirect means for estimating F_H. A global hydrothermal input as high as about 3 Tmol Si year^{-1} has been calculated, on the basis of a global heat flux and ^{3}He model (*22*) and on steady-state ^{87}Sr/^{86}Sr balances (*23*). To resolve the various inputs of dissolved Si to the oceans, it is useful to examine germanium, an element located directly under Si in the periodic table. Sea floor hot spring effluents carry a Ge/Si molar ratio of about $(11 \pm 3) \times 10^{-6}$, which is much higher than that for rivers $(0.54 \pm 0.14) \times 10^{-6}$ and for biogenic silica deposits $(0.66 \pm 0.12) \times 10^{-6}$ (*21*). Assuming that biogenic silica from diatoms is the only major sink for Ge in the ocean, Mortlock *et al.* (*21*) constructed a mass balance for riverine and hydrothermal inputs of Ge and Si into the ocean versus biogenic deposits. Given our estimate for riverine Si inputs, this leads to $F_H = 0.15 \pm 0.11$ Tmol Si year^{-1}, which is less than 10% of that predicted from the global ^{3}He model and from the Sr isotope balances.

Net silicic acid flux from the sea floor can also derive from (i) the low-temperature leaching of the basaltic crust at deep and intermediate depths, and (ii) the dissolution of terrigeneous clay minerals and other siliceous materials in the near-surface deposits of the continental margins and abysses. As mentioned above, the solubility of silicate minerals in seawater at low temperature is less than the silicic acid concentration of bottom waters, except for the Atlantic Ocean. Therefore, the contribution of these fluxes to the total net input is expected to be low.

Wollast and Mackenzie (*3*) suggested an average flux of 0.4 ± 0.3 Tmol Si year^{-1} for the contribution of low-temperature alteration of basalt. On a global scale the silicic acid flux due to the dissolution of clay minerals in sediments has been neglected in previous studies (*2, 3*). In the Atlantic this process could significantly contribute to F_W, but presently we have no quantitative basis on which to give an estimate. If the above considerations are correct, it is difficult to explain benthic effluxes from opal-poor deposits as high as 10 to 20 mmol Si m^{-2} year^{-1} (*14*) reported for the abysses of southern Angola Basin (Atlantic Ocean) as well as those averaging 17.2 ± 5.1 mmol Si m^{-2} year^{-1} (*24*) for the Sargasso Sea (Atlantic Ocean). Indeed, if we assume such values to be typical of sediments nearly devoid of opal (which represent about one-third of the world ocean surface area), the estimated flux F_w could be as large as 1.9 ± 0.7 Tmol Si year^{-1}. Sea floor silicic acid effluxes actually measured can reflect not only leaching of lithogenic material but also biogenic silica dissolution at the sediment-water interface.

Although each of these processes has been indivually quantified in laboratory experiments, they are not easy to distinguish in the field, especially for regions with silica-poor sediments. In regions with significant opal in sediments, dissolution of lithogenic silicate phases is estimated to be negligible because pore-water silicic acid concentrations generally exceed saturation for many of the existing mineral phases. The dissolution of biogenic material is obviously an internal recycling system, and its contribution is already included in biologically originated fluxes (see below). Thus, we only took into account the low-temperature leaching of basalt, keeping to the 1980s value (*3*), and took $F_w = 0.4 \pm 0.3$ Tmol Si year^{-1}. The total estimated net input of silicic acid in the world ocean is thus $F_{R(net)} + F_A + F_H + F_W = 6.1 \pm 2.0$ Tmol Si year^{-1}.

Production of Biogenic Silica

Planktonic organisms for which silica is an important structural component include diatoms, radiolarians, and silicoflagellates. The building up of silica skeletons in these organisms requires the transfer of silicic acid from the hydrosphere to the biosphere. At present, diatoms are of great importance among the siliceous planktonic algae, whereas silicoflagellates, which were widespread during the Tertiary period, are less important in modern biogenic silica production. Like diatoms and silicoflagellates, most of the radiolarians live in the top few hundred meters of the water column, but a few inhabit the deep waters of the ocean. A significant amount of Si is immediately remobilized in the upper layers of the ocean by dissolution of the silica cell walls, a process that is dependent on temperature, surface area, and trace metals such as aluminium.

It is clear that the total production of biogenic silica is the sum of the specific contributions from diatoms, silicoflagellates, and radiolarians. In field measurements it is difficult to distinguish between specific contributions. For practical purposes we herein refer to the production by diatoms as production, because diatoms are the dominant source of biogenic silica in the surface layers of the ocean (*25*). On the basis of data on ^{14}C primary productivity for different regions, estimates of the relative contribution of diatoms, and Si/C ratios, the annual gross production of biogenic silica of the world ocean was previously estimated to range between 402 and 417 Tmol Si year^{-1} (*2, 26*), although one study (*1*) suggested that production could range anywhere between 167 and 540 Tmol Si year^{-1}. Any global estimate of biogenic silica production derived in this manner is strongly dependent on (i) regional extrapolations of the ^{14}C productivity determined locally, (ii) the relative contribution of diatoms to the total primary productivity, and (iii) the assumed chemical composition of the diatoms. Consequently, all such estimates are subject to large uncertainties

It is difficult to evaluate a priori whether the previous estimates are too high or too low. On the one hand, it is clear now that the primary production, based on the ^{14}C technique in large regions such as the oligotrophic central gyres, has been underestimated in the past (*27, 28*). As a result, estimates of the global primary production of the world ocean have increased from 20 to 25 Gton of C per year in the early 1970s (*29, 30*) to recent values of 50 to 60 Gton C year^{-1} (*31, 32*). On the other hand, two recent studies on biogenic silica production in the Antarctic Ocean suggest regional estimates of 47.5 Tmol Si year^{-1} (*33*) and 12 to 32 Tmol Si year^{-1} (*34*), which cannot be reconciled with a previous higher estimate (1) of 120 Tmol Si year^{-1} for that region. This higher estimate (1) was based on an assumed ^{14}C primary productivity of 3.3 Gton C year^{-1} for the Southern Ocean, and the estimate attributed 100% of that productivity to diatoms. Recent estimates of the primary productivity of the Southern Ocean, based on large ^{14}C data sets and satellite information on pigment and ice distributions in summer, are 1.0 to 1.3 Gton C year^{-1} (35, 36). This correction alone lowers the antarctic estimate by a factor of 3. Moreover, estimating the correct Si/C ratio of naturally occurring diatoms is difficult: diatoms growing in nutrient-replete conditions show a reasonably constant Si/C ratio of 0.13 ± 0.05 mol mol^{-1} (37), but nutrient-poor conditions can result in large variations of the Si/C ratio of the biogenic particulate matter in phytoplankton, in both oceanic (34, 38, 39) and coastal (40) areas. The Si/C ratios are calculated after the determination of particulate organic carbon (POC) concentration and of particulate biogenic silica (BSi). In natural particle assemblages, POC represents the total organic carbon of both autotrophic and heterotrophic organisms and of organic detritus, and BSi corresponds to the silica content of living diatoms, dead cells, and siliceous fragments. Therefore, the use of the measured Si/C ratios of natural particle assemblages to convert ^{14}C productivity data into estimates of biogenic silica production is subject to a great uncertainty.

We used a different approach to obtain a maximum estimate of the gross production from diatoms in the world ocean. The total primary productivity of the oceans may be as high as 60 Gton C year^{-1} (31, 32). Small, nonsiliceous pico- and nanoplankton are of great importance to the total productivity, especially in oligotrophic regions. The ^{30}Si, ^{32}Si, and ^{14}C uptake data from the Sargasso Sea, the Southern Ocean, and several coastal systems show (41) that the relative contribution of diatoms to the total primary productivity does not exceed 35% in the oligotrophic oceans and 75% in coastal areas and the Antarctic. Estimating that the oligotrophic oceans are the site of 80% of the global primary productivity of the oceans, with coastal systems and the Antarctic accounting for the remaining 20%, the primary productivity attributable to diatoms is 25.8 Gton C year^{-1} or 2150 Tmol C year^{-1} (41). Using the mean Si/C ratio (37) measured for pure diatom cultures under nutrient-replete conditions (0.13 mol mol^{-1}) as a maximum estimate for the Si/C ratio of living diatoms in the ocean, we estimated that the upper limit of the global rate of biogenic silica production is 2150 Tmol C year^{-1} × 0.13 mol Si per mole of C = 280 Tmol Si year^{-1}

The minimum export of biogenic silica from the surface layer is the difference between the inputs and the outputs of silicic acid (1, 42). Refined box models have been developed to simulate the exchanges between the different water masses and compartments of the world ocean. Those models were tested with isotopes and tracers. On the basis of an 11-box model (41, 43), estimates of the minimum flux of biogenic silica to the deep ocean are between 99 and 102 Tmol Si year^{-1}. That estimate of about 100 Tmol year^{-1} was evaluated at depths of 400 to 600 m, making it a minimum estimate of silica from the upper 100 to 200 m. Approximately 60% of the silica produced by diatoms in the photic zone dissolves in the upper 100 m (41). Thus, if we take 50% dissolution as the minimum for the upper 200-m layer, the biogenic silica flux indicated by the 11-box model implies that the minimum gross production in the upper ocean is about 200 Tmol Si year^{-1}. Thus, we estimate that the production of biogenic silica in the surface waters of the ocean is 200 to 280 Tmol Si year^{-1}. Because approximately 50% of the silica dissolves in the upper 100 to 200 m (41), our best estimates for F_P and F_E are 240 ± 40 and 120 ± 20 Tmol Si year^{-1}, respectively, significantly lower than earlier estimates (2, 26).

Sediments and Deep Waters: Outputs of Biogenic Silica and Recycling

The fraction of biogenic material that escapes dissolution in the surface layer settles down through the water column, finally reaching the sea floor where dissolution continues. The net accumulation of opal constitutes the net output of Si from the biogeochemical cycle. In our silica budget, the time scale appropriate for establishing silica accumulation rates is equal to the residence time of Si in the ocean, which is approximately 15,000 years (see later discussion). Unlike the Si inputs, which were quantified reasonably well long ago (44), the Si outputs of the world ocean have been determined only during the last 15 years (45). Major modern biogenic silica deposit sites are the Southern Ocean, the North Pacific, the equatorial divergence, and coastal margins (46). Most of these deposits are composed of diatom frustules, with the exception of the equatorial Pacific abysses where radolarian skeletons dominate. The previous best estimate for the total biogenic silica accumulation rate was F_B = 6.9 Tmol Si year^{-1} (4), which was obtained by determining sediment accumulation rates, dry bulk density, and the percentage of biogenic silica in sediments. Recent studies (47–50) have refined regional components of F_B (Table 1). Excluding the deposits in estuaries, F_B is now 7.1 ± 1.8 Tmol Si year^{-1}. Deposits in the abysses and in the continental margins account for 83 and 17% of the total, respectively. The major contributor of biogenic silica in marine deposits (70% of the total) is the Antarctic Ocean, where 0.2 and 4.75 Tmol Si year^{-1} accumulate in the continental margins and in the abysses, respectively.

Table 1. Budget of silicon in the world ocean (fluxes in teramoles of Si per year).

Flux source	Tmol Si year^{-1}
Inputs	
River influx [$F_{R(net)}$]	5.0 ± 1.1
Eolian (F_A)	0.5 ± 0.5
Seafloor weathering (F_W)	0.4 ± 0.3
Hydrothermal (F_H)	0.2 ± 0.1
Total inputs	6.1 ± 2.0
Outputs (F_B)	
Coastal	1.2 ± 0.7
Abysses	5.9 ± 1.1
Total outputs	7.1 ± 1.8
Biological cycle	
Production [$F_{P(gross)}$]	240 ± 40
Ratio	
Internal cycling/inputs [$F_{P(gross)}/F_B$]	23 to 53

The flux of biogenic silica that reaches the sea floor (the silica rain, F_S) is actually significantly higher than the net removal rate of 7.1 Tmol Si year^{-1}. This flux is deduced after the benthic diffusion of silicic acid across the sediment-water interface is estimated. The increase of silicic acid in pore waters that results from dissolution of opal is a well-known general trend. This positive concentration gradient at the sediment-water interface supports the benthic diffusion flux that is responsible for the transfer of silicic acid to the overlying bottom water and therefore to the deep reservoir. To estimate the benthic diffusion of silicic acid, we calculated the diffusive flux in different regions of the world ocean: It ranges from 10 to 1000 mmol Si m^{-2} year^{-1} (Table 2) and $F_{D(benthic)}$ averages 23 ± 15 Tmol Si year^{-1}. The biogenic silica rain to the sea floor, F_S, is (23 ± 15) + (7.1 ± 1.8) = 30 ± 17 Tmol Si year^{-1}. About 20% of the silica reaching the seabed accumulates in the sediment with the remainder returning to the water column as a result of dissolution. Silica dissolution is unequally distributed: The large oligotrophic areas have the lowest diffusive fluxes per surface area but contribute 57% of the total because they are widespread. Any error in the estimation of the average for these areas could lead to significant differences in the total diffusive flux.

According to the above estimate the dis-

Table 2. Diffusion of silicic acid across the sediment-water interface. Ref., reference number; PFZ, polar front zone.

Regions	Area (10^{12} m^2)	Annual flux (10^{-2} mol Si m^{-2})	Annual flux (Tmol Si)	Ref.
Continental margins				
Antarctic	0.9	42 ± 6	0.4 ± 0.1	(*45*)
Others	18	22 ± 11	4.0 ± 2.0	(*51*)
Subtotal	18.9		4.4 ± 2.1	
Abysses				
Antarctic-PFZ	3	55 ± 45	1.6 ± 1.4	(*47*)
Antarctic-abysses	19	21.5 ± 8.5	4.1 ± 1.6	(*47*)
Subtotal	22		5.7 ± 3.0	
Oligotrophic areas	322	4 ± 3	13 ± 10	(*52, 53*)
Subtotal abysses	341		18.7 ± 13.0	
Total	360		23 ± 15	

solution of biogenic silica in deep waters is $F_{D(deep)} = (120 \pm 20) - (30 \pm 17) = 90 \pm 37$ Tmol Si year^{-1}. Of the siliceous material that escapes the surface water and transits through the deep waters, about 25% reaches the sea floor. Relative to the total production of silica in surface waters, 90% of the dissolution occurs in the water column, whereas only 10% occurs in the seabed.

Our estimate of the global average preservation ratio of biogenic silica (burial/gross production) is about 3% (7.1/240). Actually this average reflects contrasted situations, with virtually no preservation in subtropical areas and preservation as high as 24% in the Southern Ocean (*41*). Even if the biogenic silica production in the Southern Ocean has been underestimated, the Antarctic and sub-Antarctic have a dominant status, in comparison with the rest of the world ocean, and with respect to silica preservation in the water column.

The Oceanic Silicon Budget

Our estimates of the net global inputs of silicic acid and of the net global outputs of biogenic silica are approximately in balance (6.0 ± 1.8 and 7.1 ± 1.8 Tmol Si year^{-1}, respectively). If the small (1 Tmol Si year^{-1}) difference between the central estimates of supply and removal has any significance, it may reflect the fact that we have taken somewhat conservative estimates for the input terms of hydrothermal and sea floor weathering. It may also result, at least in part, from anthropogenic perturbations of the river source term.

The biological processes that produce silica in the surface layers and control its dissolution clearly dominate the geochemical processes quantitatively (Table 2 and Fig. 1). We estimate that the mean concentration of silicic acid in the world ocean is 70.6 μM [derived from the PANDORA model (*41*)] and the total content of silicic acid in the ocean is 0.97×10^5 Tmol Si. The overall steady-state residence time for Si in the ocean is equal to the amount of dissolved Si in the oceans divided by the input (or the ouput) flux, which yields a value of approximately 15,000 years. On this time scale it is clear that recent anthropogenic perturbations of the Si budget have not yet significantly affected the global marine silicic acid distributions. The residence time relative to biological uptake from surface waters averages only [$(0.97 \times 10^5)/240 = 404$)] about 400 years. This difference implies that Si delivered to the ocean passes through the biological uptake and dissolution cycle an average of (240/6.1) about 39 times before being removed to the seabed.

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