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MARINE SILICA CYCLE

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Introduction

Silicate, or silicic acid (H_4SiO_4), is a very important nutrient in the ocean. Unlike the other major nutrients such as phosphate, nitrate, or ammonium, which are needed by almost all marine plankton, silicate is an essential chemical requirement only for certain biota such as diatoms, radiolaria, silico-flagellates, and siliceous sponges. The dissolved silicate in the ocean is converted by these various plants and animals into particulate silica (SiO_2), which serves primarily as structural material (i.e., the biota's hard parts). The reason silicate cycling has received significant scientific attention is that some researchers believe that diatoms (one of the silica-secreting biota) are one of the dominant phytoplankton responsible for export production from the surface ocean (Dugdale *et al.*, 1995). Export production (sometimes called new production) is the transport of particulate material from the euphotic zone (where photosynthesis occurs)

down into the deep ocean. The relevance of this process can be appreciated because it takes dissolved inorganic carbon from surface ocean waters, where it is exchanging with carbon dioxide in the atmosphere, turns it into particulate organic matter, and then transports it to depth, where most of it is regenerated back into the dissolved form. This process, known as the 'biological pump', along with deep-ocean circulation is responsible for the transfer of inorganic carbon into the deep ocean, where it is unable to exchange with the atmosphere for hundreds or even thousands of years. Consequently, silicate and silica play an important role in the global carbon cycle, which affects the world's climate through greenhouse feedback mechanisms. In addition, the accumulation of biogenic silica on the ocean floor can tell us where in the ocean export production has occurred on timescales ranging from hundreds to millions of years, which in turn reveals important information concerning ocean circulation and nutrient distributions.

Basic Concepts

In understanding the cycling of silicate in the oceans, the concept of mean oceanic residence time

is commonly used. Mean oceanic residence time is defined as in eqn. [1].

Mean oceanic residence time =

$$\frac{\text{(amount of dissolved material in a reservoir)}}{\text{(steady-state flux into or out of the reservoir)}} \quad [1]$$

For silicate there are approximately 7×10^{16} moles of dissolved silicon in ocean water. (One mole is equal to 6×10^{23} molecules of a substance, which in the case of silicic acid has a mass of approximately 96 g.) As described later, the various sources of silicate to the ocean supply approximately 7×10^{12} moly⁻¹, which is approximately equal to our best estimates of the removal rate. Most scientists believe that there has been a reasonably good balance between supply and removal of silicate from the oceans on thousand-year timescales because there is little evidence in the oceanic sedimentary record of massive abiological precipitation of silica (indicating enhanced silicate concentrations relative to today), nor is there any evidence in the fossil record over the past several hundred million years that siliceous biota have been absent for any extended period (indicating extremely low silicate levels). Dividing the amount of dissolved silicate in the ocean by the supply/removal rate yields a mean oceanic residence time of approximately 10 000 years. Basically, what this means is that an atom of dissolved silicon supplied to the ocean will remain on average in the water column or surface seabed (being transformed between dissolved and particulate material as part of the silicate cycle) for approximately 10 000 years before it is permanently removed from the oceanic system via long-term burial in the seabed.

Distribution of Silicate in the Marine Environment

Because of biological activity, surface waters throughout most of the marine realm are depleted in dissolved silicate, reaching values as low as a few micromoles per liter ($\mu\text{mol l}^{-1}$). When the siliceous biota die, their skeletons settle through the water column, where more than 90% of the silica is regenerated via inorganic dissolution. This process enriches the deep water in silicate, causing oceanic bottom waters to have as much as 10–100 times more silicate than surface waters in tropical and temperate regions. The magnitude of the deep-ocean silicate concentration depends on the location with-

in the deep thermohaline circulation system. In general, deep water originates in North Atlantic and Antarctic surface waters. The deep water forming in the North Atlantic moves southward, where it joins with Antarctic water, on its way to feeding the deep Indian Ocean basin and then flowing from south to north in the Pacific basin. All along this 'conveyor belt' of deep-ocean water, siliceous biota are continually settling out from surface waters and dissolving at depth, which further increases the silicate concentration of the deep water downstream. Consequently, deep-ocean water in the Atlantic (fairly near the surface ocean source) is not very enriched in silicate (only $60 \mu\text{mol l}^{-1}$), whereas the Indian Ocean deep water exhibits moderate enrichment ($\sim 100 \mu\text{mol l}^{-1}$), and the north Pacific deep water is the most enriched ($\sim 180 \mu\text{mol l}^{-1}$). This trend of increasing concentration is observed as well in the other nutrients such as nitrate and phosphate. Generalized vertical profiles of silicate are shown for the Atlantic and Pacific basins in **Figure 1**. The depth of the silicate maximum in these basins (typically 2000–3000 m depth) is deeper than the nutrient maxima for phosphate or nitrate, primarily because organic matter (the source of the phosphate and nitrate) is generally regenerated at shallower depths in the ocean than is silica. The nutrient concentrations in oceanic deep waters can affect the chemical composition of particles settling through the water column because the vertical transport of nutrients from depth via upwelling and turbulence drives

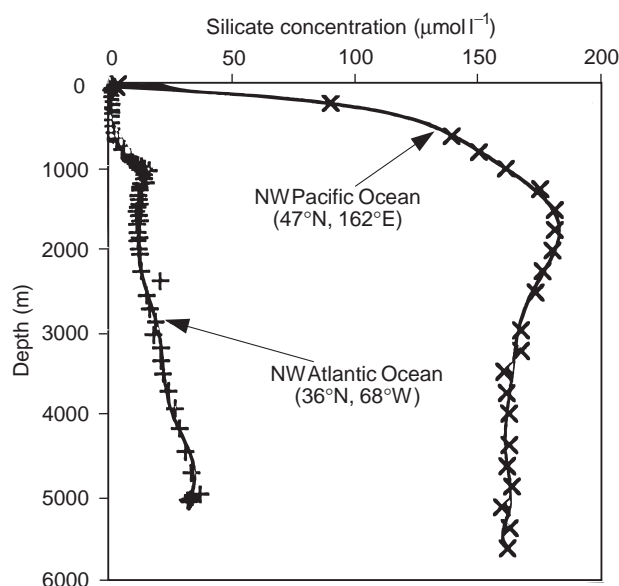


Figure 1 Vertical distribution of dissolved silicate in the Atlantic Ocean and the Pacific Ocean. The Atlantic data come from Spencer (1972), whereas the Pacific data are from Nozaki *et al.* (1997).

the biological production in surface waters. For example, the ratio of biogenic silica to organic carbon in particles settling between 1000 and 4000 m depth in the North Pacific Ocean (typically about 2–3) is substantially higher than that observed in the Arabian Sea (~ 0.7) and much higher than typical values in the Atlantic Ocean (< 0.3). This chemical trend in particle flux, which is caused in part by changes in planktonic species assemblage, is consistent with the systematic increase in silicate and other nutrients along the thermohaline-driven conveyor belt of deep-ocean circulation. The change in the biogenic silica to organic carbon ratio throughout the ocean basins of the world turns out to be one of the most important parameters controlling the nature of biogenic sedimentation in the world (see the global ocean sediment model of Heinze and colleagues, listed in Further Reading).

Silicate concentrations also can be used to distinguish different water masses. The most obvious example is at the Southern Ocean Polar Front (see Figure 2), which separates Antarctic Surface Water from the Subantarctic system. The silicate and nitrate concentration gradients across these Southern Ocean waters occur in different locations (in a manner similar to the distinct maxima in their vertical profiles). The high concentrations of silicate ($50\text{--}100\ \mu\text{mol l}^{-1}$) south of the Polar Front result from wind-induced upwelling bringing silicate to the surface faster than the local biota can turn it into particulate silica. Turnover times between surface waters and deep waters in the Southern Ocean are on the order of 100 years as compared to values of 500–1000 years in the Atlantic, Indian, and Pacific Oceans.

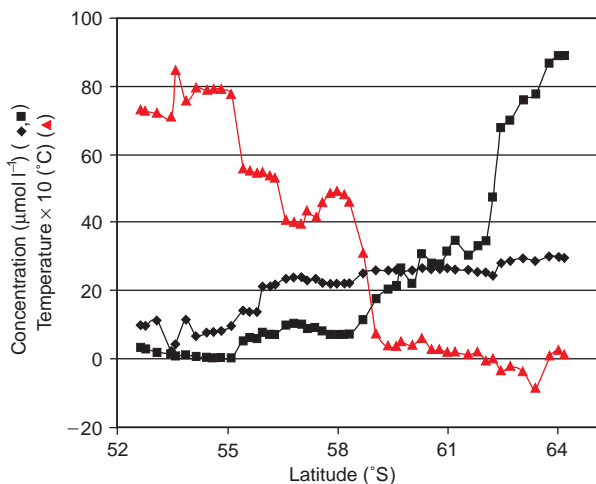


Figure 2 Distribution of silicate (■), nitrate (◆), and temperature (▲) across the Drake Passage illustrating different water masses and frontal features during November, 1999.

In terms of chemical equilibrium, biogenic silica is undersaturated by a factor of 10–1000-fold in surface waters and by at least a factor of 5 in deep waters. Therefore, siliceous biota must expend a good deal of energy concentrating silicate in their cells and bodies before precipitation can take place. This is quite different from the case of calcium carbonate (a material used by another type of plankton to form hard parts), which is supersaturated severalfold in most tropical and temperate surface waters. Deep waters everywhere are undersaturated with respect to biogenic silica (although to different extents). Therefore, inorganic dissolution of silica takes place in the water column as soon as the plankton's protective organic matter is removed from the biota (typically by microbial or grazing activities). It is not until the siliceous skeletal material is buried in the seabed that the water surrounding the silica even approaches saturation levels (see later discussion on sedimentary recycling), which diminishes the rate of dissolution and enhances preservation and burial.

The Marine Silica Cycle

Sources of Dissolved Silicate to the Ocean

Figure 3 shows the main features of the marine silica cycle as portrayed in a STELLA™ model. The main source of silicate to the oceans as a whole is rivers, which commonly contain $\sim 150\ \mu\text{mol l}^{-1}$ silicate but depending on location, climate, and local rock type, can range from 30 to $250\ \mu\text{mol l}^{-1}$. The silicate in rivers results directly from chemical weathering of rocks on land, which is most intense in areas that are warm and wet and exhibit major changes in relief (i.e., elevation). The best estimate of the riverine flux of dissolved silicate to the oceans is $\sim 6 \times 10^{12}\ \text{mol Si y}^{-1}$. Other sources include hydrothermal fluxes ($\sim 0.3 \times 10^{12}\ \text{mol Si y}^{-1}$), dissolution of eolian particles ($0.5 \times 10^{12}\ \text{mol Si y}^{-1}$), submarine volcanic activity (negligible), and submarine weathering of volcanic rocks ($\sim 0.4 \times 10^{12}\ \text{mol Si y}^{-1}$). Ground waters may contribute additional silicate to the marine realm, but the magnitude of this flux is difficult to quantify and it is believed to be small relative to the riverine flux. A more detailed discussion of the various sources of silicate to the marine environment can be found in the works by Treguer *et al.* and DeMaster (listed in Further Reading).

All of these sources of silicate to the oceanic water column are considered to be external. As shown in Figure 3, there are internal sources supplying silicate to oceanic surface waters and they are

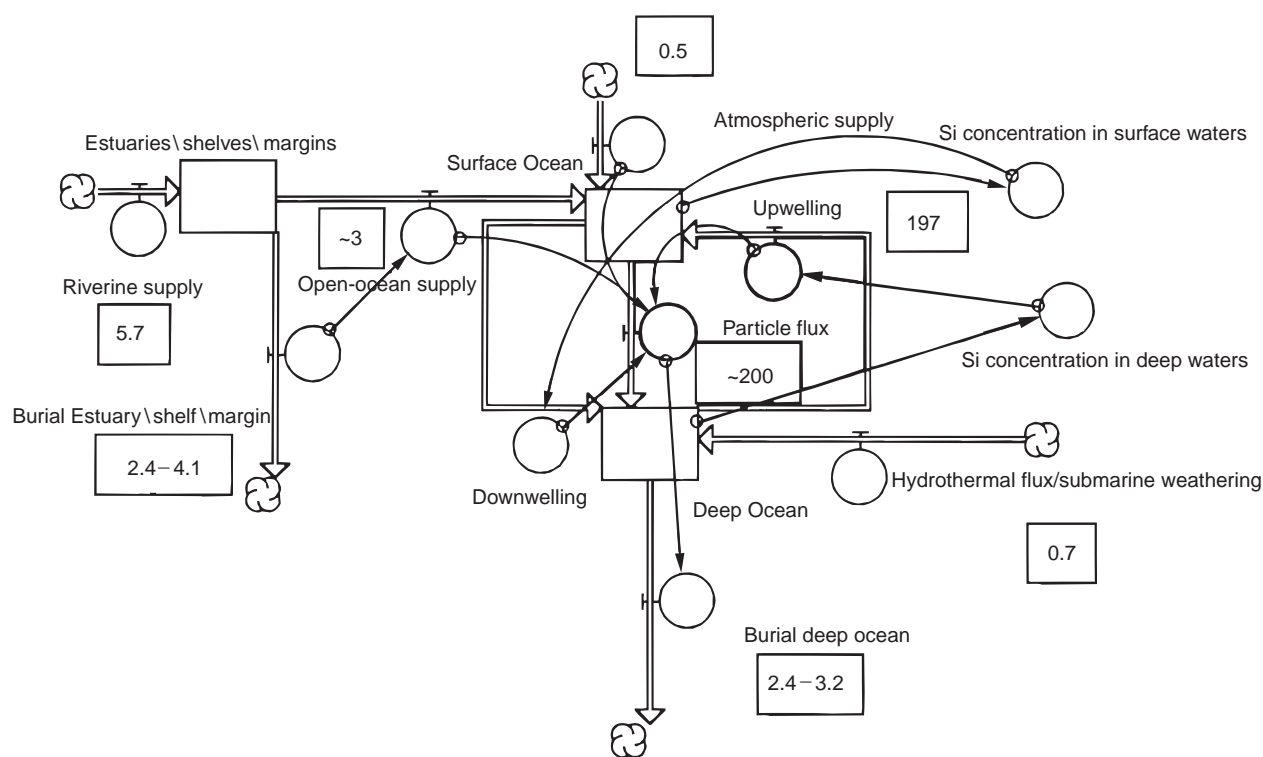


Figure 3 STELLA™ model of the global marine silica cycle showing internal and external sources of silicate to the system, internal recycling, and burial of biogenic silica in the seabed. The various reservoirs are shown as rectangles, whereas the fluxes in and out of the reservoirs are shown as arrows with regulating valves (indicating relationships and functional equations). The flux values (indicated by numbers inside the boxes) have units of $10^{12} \text{ mol y}^{-1}$.

oceanic upwelling and turbulence. Because of the strong gradient in silicate with depth, upwelling of subsurface water (100–200 m depth) by wind-induced processes and turbulence can bring substantial amounts of this nutrient (and others) to surface waters that typically would be depleted in these valuable chemical resources as a result of biological activity. This upwelling flux ($\sim 100 - 300 \times 10^{12} \text{ mol Si y}^{-1}$), in fact, is 20–50 times greater than the riverine flux. The extraction of silicate from surface waters by siliceous biota is so efficient that nearly 100% of the nutrient reaching the surface is converted into biogenic silica. Therefore, the production of biogenic silica in oceanic surface waters is comparable to the flux from upwelling and turbulent transport. Riverine sources may be the dominant external source of silicate to the oceans, but they sustain only a negligible amount (only a few percent) of the overall marine silica production. Internal recycling, upwelling, and turbulence provide nearly all of the silicate necessary to sustain the gross silica production in marine surface waters. Therefore, changes in oceanic stratification and wind intensity may significantly affect the flux of nutrients to the surface and the overall efficiency of

the biological pump. Silicate dynamics in the water column have been simulated using a general circulation model. The results of this study by Gnanadesikan suggest that the model distributions of silicate in the ocean are very sensitive to the parametrization of the turbulent flux. In addition, according to the model, the Southern Ocean and the North Pacific were the two major open-ocean sites where net silica production occurred, accounting for nearly 80% of the biogenic silica leaving the photic zone.

If the entire ocean (surface waters, deep waters, and near-surface sediments) is considered as a single box, the external fluxes of silicate to the ocean (mentioned above) must be balanced by removal terms in order to maintain the silicate levels in the ocean at more or less a constant value over geological time. From this point of view the flux of silicate from oceanic upwelling and turbulence can be treated as part of an internal cycle. The dominant mechanism removing silicate from this system is burial of biogenic silica. There is some controversy about where some of this burial takes place, but most scientists believe that burial of biogenic silica (or some chemically altered by-product thereof) is the primary way that silicate is removed from the ocean.

Removal of Silica from the Ocean

The sediments with the highest rate of silica accumulation (on an areal basis) occur beneath the coastal upwelling zones, where strong winds bring extensive amounts of nutrients to the surface. Examples of these upwelling areas include the west coast of Peru, the Gulf of California, and Walvis Bay (off the west coast of South Africa). Diatom skeletons are the dominant form of biogenic silica in these deposits. The sediments in these upwelling areas accumulate at rates of 0.1–1.0 cm y⁻¹ and they contain as much as 40% biogenic silica by weight. The burial rate for silica in these areas can be as high as 1.7 mol cm⁻² y⁻¹. In calculating the total contribution of these areas to the overall marine silica budget, the accumulation rates (calculated on an areal basis) must be multiplied by the area covered by the particular sedimentary regime. Because these upwelling regimes are confined to such small areas, the overall contribution of coastal upwelling sites to the marine silica budget is quite small (< 10%, see Table 1), despite the fact that (for a given area) they bury biogenic silica more rapidly than anywhere else in the marine realm.

The sediments containing the highest fraction of biogenic silica in the world occur in a 1000 km-wide

belt surrounding Antarctica. These sediments typically contain ~60% biogenic silica by weight (the majority of which are the skeletons of diatoms). Most of these sediments, however, accumulate at rates of only a few centimeters per thousand years, so their silica burial rate is quite small (< 0.008 mol Si cm⁻² y⁻¹), accounting for 1 × 10¹² moly⁻¹ of silica burial or less than 20% of the total burial in the marine environment. Beneath the Polar Front (corresponding to the northern 200–300 km of the Southern Ocean siliceous belt), however, the sediment accumulation rates increase dramatically to values as high as 50 × 10⁻³ cm y⁻¹. Regional averages can be as high as 19 × 10⁻³ cm y⁻¹, yielding a silica burial rate of 0.08 mol Si cm⁻² y⁻¹. Unfortunately, many of the siliceous deposits beneath the Polar Front occur in areas of very rugged bottom topography (because of the submarine Antarctic Ridge), where sediments are focused into the deeper basins from the flanks of the oceanic ridge crests. This distribution of accumulation rates would not create a bias if all of the sedimentary environments are sampled equally. However, it is more likely to collect sediment cores in the deep basins, where the deposits are thicker and accumulating more rapidly, than it is on the flanks where the sediment coverage is thinner. The effects of this sediment focusing can be assessed by measuring the amount in the seabed of a naturally occurring, particle-reactive radioisotope, thorium-230 (²³⁰Th). If there were no sediment focusing, the amount of excess ²³⁰Th in the sediments would equal the production from its parent, uranium-234, in the overlying water column. In some Polar Front Antarctic cores there is 12 times more excess ²³⁰Th in the sediment column than produced in the waters above, indicating that sediment focusing is active. Initial estimates of the biogenic silica accumulation beneath the Polar Front were as high as 3 × 10¹² mol Si y⁻¹, but tracer-corrected values are on the order of 1 × 10¹² mol Si y⁻¹.

There are other high-latitude areas accumulating substantial amounts of biogenic silica, including the Bering Sea, the Sea of Okhotsk, and much of the North Pacific Ocean; however, the accumulation rates are not as high as in the Southern Ocean (see Table 1). The high rate of silica burial in the high-latitude sediments may be attributed in part to the facts that cold waters occurring at the surface and at depth retard the rate of silica dissolution and that many of the diatom species in high latitudes have more robust skeletons than do their counterparts in lower latitudes. Moderately high silica production rates and elevated silica preservation efficiencies (approximately double the world average) combine

Table 1 The marine silica budget

Source/Sink	Flux (10 ¹² mol Si y ⁻¹)
Sources of silicate to the ocean	
Rivers	5.7
Hydrothermal emanations	0.3
Eolian flux (soluble fraction)	0.5
Submarine weathering	0.4
Total supply of silicate	~ 7 × 10 ¹²
Sites of biogenic silica burial	
Deep-Sea Sediments	2.4–3.2
Antarctic	
Polar Front	0.7–0.9
Non Polar Front	0.7–1.1
Bering Sea	0.5
North Pacific	0.3
Sea of Okhotsk	0.2
Equatorial Pacific	0.02
Poorly siliceous sediments	< 0.2
Continental margin sediments	2.4–4.1
Estuaries	< 0.6
Coastal upwelling areas (e.g., Peru, Walvis Bay, Gulf of California)	0.4–0.5
Antarctic margin	0.2
Other continental margins	1.8–2.8
Total burial of biogenic silica	5–7 × 10 ¹²

to yield high-latitude siliceous deposits accounting for approximately one-third of the world's biogenic silica burial.

If the focusing-corrected biogenic silica accumulation rates are correct for the Polar Front, then a large sink for biogenic silica ($\sim 1\text{--}2 \times 10^{12}$ mol Si y^{-1}) needs to be identified in order to maintain agreement between the sources and sinks in the marine silica budget. Continental margin sediments are a likely regime because these environments have fairly high surface productivity (much of which is diatomaceous), a relatively shallow water column (resulting in reduced water column regeneration as compared to the deep sea), rapid sediment accumulation rates ($10\text{--}100 \times 10^{-3}$ cm y^{-1}) and abundant aluminosilicate minerals (see Biogenic Silica Preservation below). The amount of marine organic matter buried in shelf and upper slope deposits is on the order of 3×10^{12} mol C y^{-1} . When this flux is multiplied by the silica/organic carbon mole ratio ($\text{Si}/\text{C}_{\text{org}}$) of sediments in productive continental margin settings ($\text{Si}/\text{C}_{\text{org}} = 0.6$), the result suggests that these nearshore depositional environments can account for sufficient biogenic silica burial ($1.8\text{--}2.8 \times 10^{12}$ mol Si y^{-1}) to bring the silica budget into near balance (i.e., within the errors of calculation).

Biogenic Silica Preservation

As mentioned earlier, all ocean waters are undersaturated with respect to biogenic silica. Surface waters may be more than two orders of magnitude undersaturated, whereas bottom waters are 5–15-fold undersaturated. The solubility of biogenic silica is greater in warm surface waters than in colder deep waters, which, coupled with the increasing silicate concentration with depth in most ocean basins, diminishes the silicate/silica disequilibrium (or corrosiveness of the water) as particles sink into the deep sea. This disequilibrium drives silica regeneration in oceanic waters along with other factors and processes such as particle residence time in the water column, organic and inorganic surface coatings, particle chemistry, particle aggregation, fecal pellet formation, as well as particle surface area. Recycling of biogenic silica occurs via inorganic dissolution; however, the organic coating that siliceous biota use to cover their skeletons (inhibiting dissolution) must be removed by microbial or zooplankton grazing prior to dissolution. This association is highlighted by the fact that bacterial assemblages can accelerate the dissolution of biogenic silica in the water column.

An important aspect of biogenic silica dissolution pertains to surface chemistry and clay-mineral formation on the surface of siliceous tests. Incorporation of aluminum in the initial skeleton as well as aluminosilicate formation on skeletal surfaces during settling and burial greatly decrease the solubility of biogenic silica, in some cases by as much as a factor of 5–10. It appears that some of this 'armoring' of siliceous skeletons occurs up in the water column (possibly in aggregates or fecal pellets), although some aluminosilicate formation may occur in flocs just above the seabed as well as deeper in the sediment column. The occurrence of clay minerals on skeletal surfaces has been documented using a variety of instruments (e.g., the scanning electron microscope). The nature of the settling particles also affects dissolution rates in the water column. If siliceous skeletons settle individually, they settle so slowly (a timescale of years to decades) that most particles dissolve before reaching the seabed. However, if the siliceous skeletons aggregate or are packaged into a fecal pellet by zooplankton, sinking velocities can be enhanced by several orders of magnitude, favoring preservation during passage through the water column. Siliceous tests that have high surface areas (lots of protruding spines and ornate surface structures) also are prone to high dissolution rates and low preservation in the water column relative to species that have more robust skeletons and more compact structures.

Very few studies have documented silica production rates in surface waters, established the vertical fluxes of silica in the water column, and then also examined regeneration and burial rates in the seabed. One place that all of these measurements have been made is in the Ross Sea, Antarctica. In this high-latitude environment, approximately one-third of the biogenic silica produced in surface waters is exported from the euphotic zone, with most of this material (27% of production) making it to the seabed some 500–900 m below. Seabed preservation efficiencies (silica burial rate divided by silica rain rate to the seafloor) vary from 1% to 86%, depending primarily on sediment accumulation rate, but average 22% for the shelf as a whole. Consequently, the overall preservation rate (water column and seabed) is estimated to be $\sim 6\%$ in the Ross Sea. On a global basis, approximately 3% of the biogenic silica produced in surface waters is buried in the seabed. The total preservation efficiencies for different ocean basins vary, with the Atlantic and Indian Oceans having values on the order of 0.4–0.8% and the Pacific and Southern Oceans having values of approximately 5–10%.

Sediment accumulation rate can make a large difference in seabed preservation efficiency. In the Ross Sea, for example, increasing the sediment accumulation rate from 1–2 to $16 \times 10^{-3} \text{ cm y}^{-1}$, increases the seabed preservation efficiency from 1–5% up to 50–60%. In most slowly accumulating deep-sea sediments (rates of $2 \times 10^{-3} \text{ cm y}^{-1}$ or less), nearly all of the biogenic silica deposited on the seafloor dissolves prior to long-term burial. Increasing the sedimentation rate decreases the time that siliceous particles are exposed to the corrosive oceanic bottom waters, by burying them in the seabed where silicate, aluminum, and cation concentrations are high, favoring aluminosilicate formation and preservation. Consequently, continental margin sediments with accumulation rates of $10\text{--}100 \times 10^{-3} \text{ cm y}^{-1}$ are deposits expected to have high preservation efficiencies for biogenic silica and are believed to be an important burial site for this biogenic phase.

Estuaries extend across the river–ocean boundary and are generally regions of high nutrient flux and rapid sediment burial ($0.1\text{--}10 \text{ cm y}^{-1}$). They commonly exhibit extensive diatom production in surface waters, but may not account for substantial biogenic silica burial because of extensive dissolution in the water column. For example, on the Amazon shelf approximately 20% of the world's river water mixes with ocean water and silicate dynamics have been studied in detail. Although nutrient concentrations are highest in the low-salinity regions of the Amazon mixing zone, biological nutrient uptake is limited because light cannot penetrate more than a few centimeters into the water column as a result of the high turbidity in the river (primarily from natural weathering of the Andes Mountains). After the terrigenous particles have flocculated in the river–ocean mixing zone, light is able to penetrate the warm surface waters, leading to some of the highest biogenic silica production rates in the world. However, resuspension on the shelf, zooplankton grazing, and high water temperatures lead to fairly efficient recycling in the water column and nearly all of the dissolved silicate coming down the river makes it out to the open ocean. The Amazon shelf seabed does appear to exhibit clay-mineral formation (primarily through replacement of dissolving diatoms), but the burial fluxes are expected to be small relative to the offshore transport of silicate and biogenic silica.

Biogenic Silica in Marine Sediments

As mentioned above, the primary biota that construct siliceous skeletons are diatoms, radiolaria,

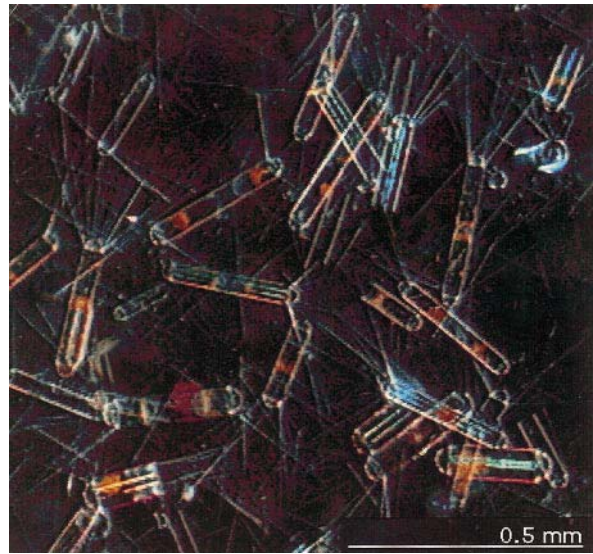


Figure 4 Micrograph of diatoms (genus *Corethron*) collected from an Antarctic plankton tow near Palmer Station.

silicoflagellates, and siliceous sponges. Diatoms are marine algae. These phytoplankton account for 20–40% of the primary production in the ocean and an even greater percentage of the export production from the photic zone. Diatom skeletons are the primary form of biogenic silica in deposits associated with coastal upwelling areas, high-latitude oceans (predominantly in the Pacific and the Southern Oceans), and the continental margins (Figure 4). In equatorial upwelling areas radiolarian skeletons commonly occur in marine sediments along with the diatom frustules. Radiolaria are zooplankton that live in the upper few hundred meters of the water column. Their skeletons are larger and more robust than many diatoms; consequently their preservation in marine sediments is greater than that of most diatoms. Silicoflagellates account for a very small fraction of the biogenic silica in marine sediments because most of them dissolve up in the water column or in surface sediments. They have been used in some continental margin sediments as a paleo-indicator of upwelling intensity. Siliceous sponge spicules can make up a significant fraction of the near-interface sediments in areas in which the sediment accumulation rate is low ($< 5 \times 10^{-3} \text{ cm y}^{-1}$). For example, on the Ross Sea continental shelf, fine sediments accumulate in the basins, whereas the topographic highs ($< 400 \text{ m}$ water depth) have minimal fine-grained material (because of strong currents and turbulence). As a result, mats of siliceous sponge spicules occur in high abundance on some of these banks.

To measure the biogenic silica content of marine sediments, hot (85°C) alkaline solutions are used to

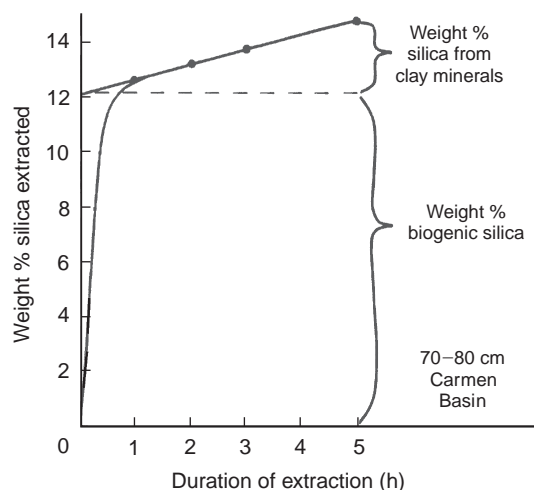


Figure 5 Graphical approach to resolving silicate originating via biogenic silica dissolution from that generated via clay-mineral dissolution during the alkaline leach technique used to quantify biogenic silica abundance. This sample was from the Gulf of California, Carmen Basin.

dissolve biogenic silica over a period of 5–6 hours. The silicate concentration in the leaching solution is measured colorimetrically on a spectrophotometer and related to the dry weight of the original sedimentary material. In many sediments, coexisting clay minerals also may yield silicate during this leaching process; however, this contribution to the leaching solution can be assessed by measuring the silicate concentration in the leaching solution hourly over the course of the dissolution. Most biogenic silica dissolves within 2 hours, whereas clay minerals release silicate at a fairly constant rate over the entire leaching period. Consequently, the contributions of biogenic silica and clay-mineral silica can be resolved using a graphical approach (see Figure 5).

Measuring Rates of Processes in the Marine Silica Cycle

There are several useful chemical tracers for assessing rates of silicate uptake, silica dissolution in the water column, and particle transport in the seabed. Most of these techniques are based on various isotopes of silicon, some of which are stable and some of which are radioactive. Most of the stable silicon occurring naturally in the ocean and crust is ^{28}Si (92.2%) with minor amounts of ^{29}Si (4.7%) and ^{30}Si (3.1%). By adding known quantities of dissolved ^{29}Si or ^{30}Si to surface ocean waters, the natural abundance ratios of Si can be altered, allowing resolution of existing biogenic silica from silica

produced after spiking in incubation studies. Similarly, if the silicate content of ocean water is spiked with either dissolved ^{29}Si or ^{30}Si , then, as biogenic silica dissolves, the ratio of the silicon isotopes will change in proportion to the amount of silica dissolved (enabling characterization of dissolution rates). In addition, the measurement of natural silicon isotopes in sea water and in siliceous sediments has been suggested as a means of assessing the extent of silicate utilization in surface waters on timescales ranging from years to millennia. Addition of radioactive ^{32}Si (half-life 160 y) to incubation solutions recently has been used to simplify the measurement of silica production rates in surface ocean waters. In the past, ^{32}Si has been difficult to obtain, but recent advances in production and isolation protocols have made it possible to produce this radioisotope for oceanographic studies. Distributions of naturally occurring ^{32}Si in the water column and seabed can be used to determine deep-ocean upwelling rates as well as the intensity of eddy diffusion (or turbulence) in the deep ocean. This same radioactive isotope can be used to evaluate rates of bioturbation (biological particle mixing) in the seabed on timescales of hundreds of years.

See also

Carbon Cycle. Current Systems in the Atlantic Ocean. Current Systems in the Southern Ocean. Pelagic Fishes.

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MARINE SNOW

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Introduction

Marine snow is loosely defined as inanimate particles with a diameter greater than 0.5 mm. These particles sink at high rates and are thought to be the principal vehicles by which material sinks in the oceans. In addition to this high sinking rate they have characteristic properties in terms of the microenvironments within them, their chemical composition, the rates of bacterial activity and the fauna associated with them. These properties make such particles important elements in influencing the structure of marine food webs and biogeochemical cycles throughout the world's oceans.

Such an apparently simple definition, however, belies the varied and complex processes which exist in order to produce and destroy these particles (Figure 1). Similarly it gives no clue as to the wide variety of particulate material which, when aggregated together, falls into this category and to the significance of the material in the biogeochemistry of the oceans.

Marine snow particles are found throughout the world's oceans from the surface to the great depths although with a wide range in concentration reaching the highest levels in the sunlit euphotic zone where production is fastest. The principal features which render this particular class of material so important are:

1. high sinking rates such that they are probably the principal vehicles by which material is transported to depth;
2. a microenvironment which differs markedly from the surrounding water such that they provide a specialized niche for a wide variety of faunal groups and a chemical environment which is different from the surrounding water;
3. Elevated biogeochemical rates within the particles over that in the surrounding water;
4. Provision of a food source for organisms swimming freely outside the snow particles.

Historical Developments

The debate about how material is transported to the deep seafloor has been going on for over a century but at the beginning of the last century some surprisingly modern calculations by Hans Lohmann came to the conclusion that large particles must be capable of transporting material from the sunlit surface zone to the abyssal depths. This was based on his observations that near bottom water above the abyssal seabed sometimes contained a surprising range of thin-shelled phytoplankton species, some still in chains and with their fine spines well preserved. He thought that the fecal pellets from some larger members of the plankton (doliolids, salps, and pteropods) were the likely vehicles and in many cases he was entirely correct. The process of aggregation is now thought to involve a variety of different mechanisms of which fecal production is only one (*see Particle Aggregation Dynamics*).

In 1951 Rachael Carson described the sediments of the oceans as the material from the most stupendous snowfall on earth and this prompted a group of Japanese oceanographers to describe as 'marine snow' the large particles they could see from the submersible observation chamber *Kuroshio* (Figure 2). This submersible was a cumbersome device and did not permit anything but the simplest of observations to be made. The scientists did, however, manage to collect some of the material and reported