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ORIGINAL PAPER

# The Global Biogeochemical Silicon Cycle

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**Abstract** Silicon is one of the most important elements in the current age of the anthropocene. It has numerous industrial applications, and supports a high-tech multi-billion Euro industry. Silicon has a fascinating biological and geological cycle, interacting with other globally important biogeochemical cycles. In this review, we bring together both biological and geological aspects of the silicon cycle to provide a general, comprehensive review of the cycling of silicon in the environment. We hope this review will provide inspiration for researchers to study this fascinating element, as well as providing a background environmental context to those interested in silicon.

**Keywords** Silicon biogeochemistry · Geology · Biology · Carbon · Nitrogen · Phosphorus

## 1 An Important Biogeochemical Cycle

The Earth's crust consists primarily of silicates (Si oxides, 90% of all minerals); consequently silicon (hereafter referred to as Si) is the second-most abundant element in the earth's crust (28.8%) after oxygen [1]. During silicate weathering dissolved soil $CO_2$ is used in a reaction where ortho-silicic acid ($H_4SiO_4$) is dissolved and released from the crystalline structure of silicate minerals. In the environment dissolved silicate (DSi), i.e. ortho-silicic acid ($H_4SiO_4$), is transported through soil and exported to rivers and eventually the ocean [2] (Fig. 1). The silicate weathering process consumes $CO_2$. For example, in the weathering of anorthite (over kaolinite) to gibbsite, DSi is produced and $CO_2$ is consumed [3]:

$$CaAl_2Si_2O_8+2.CO_2+8.H_2O\rightarrow Ca^{2+}+2.Al(OH)_3+2.H_4SiO_4+2.HCO_3^-$$
$$Ca^{2+}+2HCO_3^-\rightarrow CaCO_3+H_2CO_3$$

The weathering of silicates is thus an important sink for atmospheric $CO_2$ on geological timescales (thousands to millions of years) and exerts a large influence on the global climate [4]. Currently, global $CO_2$ consumption by chemical weathering is estimated to be ca. 0.26 Gt $C.yr^{-1}$ [5]. Ultimately, $CO_2$ is recycled back to the atmosphere by tectonic processes (metamorphic decarbonation and volcanic outgassing). The concentration of $CO_2$ influences the rate of silicate weathering; the weathering rates of silicates have changed significantly during the development of the biosphere [6].

DSi plays an important role in the production of phytoplankton and the burial of carbon in the coastal zone and in deep-sea sediments [7]. Terrestrial ecosystems buffer the weathering flux of silicon through the terrestrial biogeochemical cycle through uptake, storage and recycling [8]. The biological control on DSi exports from watersheds has only recently started to achieve scientific attention [9, 10].

## 2 Silicon Cycling in the Ocean and Coastal Ecosystems

### 2.1 The Biological Si-pump

Silicon is an essential nutrient for the growth of diatoms (*Bacillariophyceae*). Diatoms take up DSi and use it to build

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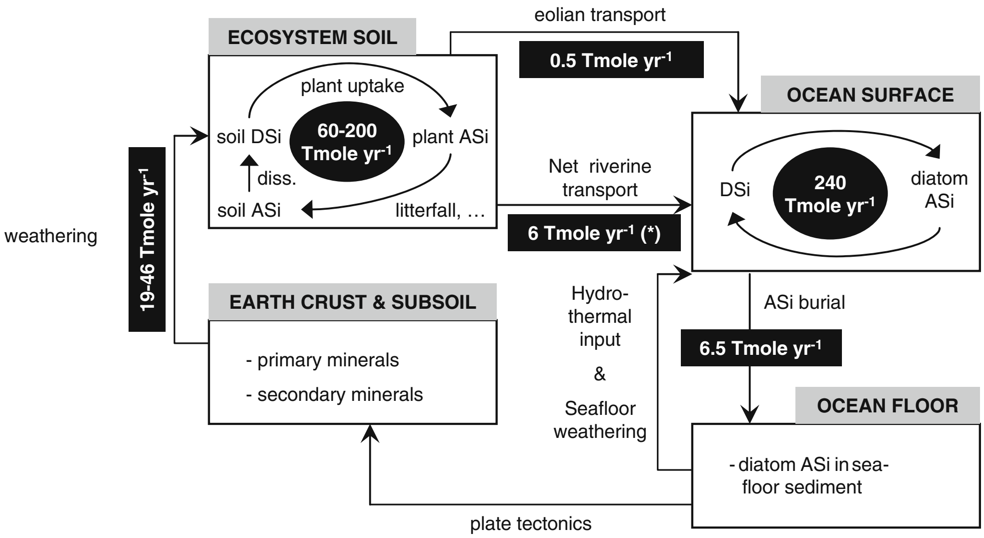

**Fig. 1** The global biogeochemical cycle of Si. The *two left boxes* represent the main continental Si pools, the *two right boxes* the oceanic Si pools. *Rectangular black boxes* represent Si fluxes between the primary Si pools. *Circular black boxes* represent Si fluxes within the primary Si pools. ("diss." stands for the dissolution) (*) The 6 Tmole.yr$^{-1}$ flux is partitioned between the net riverine transport (excluding retained ASi in estuaries) and the flux resulting from hydrothermal activity and seafloor weathering

their siliceous cell wall or "frustule". Consequently, transport of continental DSi to the oceans is an important component in oceanic primary production, a large part of which consists of diatoms [11]. Forty percent of all oceanic C sequestration (~1.5–2.8 Gton C yr$^{-1}$) can be attributed to the growth and sedimentation of diatoms [12, 13]. Although primary production through different groups of marine phytoplankton also results in a net $CO_2$ flux towards the sea bottom (the "biological carbon pump") [14], a crucial difference exists between diatoms and coccolithophores, an important subgroup of non-siliceous phytoplankton. Coccolithophores are characterized by calcite shells (=coccoliths); $CO_2$ is produced when calcium reacts with hydrogen carbonate during calcite formation (the "carbonate counter pump") [15]. Therefore, an increased dominance of coccolithophores decreases the net sequestration of $CO_2$ and consequently the flux of $CO_2$ from the atmosphere towards the ocean floor [11]. The biological carbon pump in the ocean is often referred to as the "biological Si pump" [7].

Changes in Si inputs to marine ecosystems, especially in the coastal ocean, can significantly influence the species composition of oceanic primary producers, especially the balance of production between diatoms and non-siliceous phytoplankton [16]. It has been hypothesized that a higher contribution of diatoms to total oceanic phytoplankton biomass occurred during the Last Glacial Maximum (79% vs. 54% today) as the result of increased eolian inputs of Si [11]. This demonstrates that a link exists between Si transport from terrestrial to oceanic systems, atmospheric $CO_2$ concentrations and variations in global climate.

### 2.2 Silicon and Eutrophication of Coastal and Lake Ecosystems

Silicon plays an important role in the current eutrophication problems of numerous lacustrine, estuarine and coastal ecosystems [17, 18]. In most major rivers worldwide, concentrations of N and P have at least doubled as the result of anthropogenic inputs [19]. Whereas total algal growth is primarily regulated by the availability of N and P, the relative availability of Si and the availability of Si relative to N and P, e.g. the Si:N and Si:P ratios, can influence the composition of the phytoplankton community [18]. The lack of Si can change aquatic ecosystems from those dominated by diatoms to non-diatom based aquatic ecosystems usually dominated by flagellates [20]. Based on an evaluation of long-term algal blooms and nutrient conditions in different regions, it can be concluded that decreased Si:N and Si:P ratios can give rise to Si limitation of diatoms and the reduction of diatoms in the phytoplankton community. In addition, subsequent non-diatom blooms can contain harmful algal species such as *Phaeocystis* sp., *Gonyaulax* sp., *Chrysochromulina* sp. [21].

Diatoms are the primary energetic source for estuarine and coastal food chains [22]. Transfer of energy to higher trophic levels is enhanced by diatoms through their higher nutritional value [23] and the limited amount of trophic steps between diatoms and higher trophic levels [24]. Non-diatom species are known to be less available to higher trophic levels [21, 25] and some non-diatom based food webs are economically undesirable [20]. Therefore, the proportion of diatoms in the phytoplankton community is of primary importance for many fisheries globally [20]. Furthermore, DSi limitation of diatoms and resultant blooms dominated by non-diatom species can result in anoxic conditions, increased water turbidity and excessive production of toxic components [26].

Increases in diatom biomass as a result of higher N and P inputs results in increased diatom sinking rates and increased diatom burial in bottom sediments [27]. Consequently, in anthropogenically eutrophied systems that have experienced increases in N and P loading from human activities with sufficiently long hydrodynamic residence times, the aquatic DSi stock decreases and eutrophication problems are worsened [18]. A similar effect has been described for dams, e.g. the artificial lake effect [28]. Dams increase the residence time of water in river ecosystems, which stimulates phytoplankton productivity [29]. This results in the increased trapping of biogenic Si in lake sediments, and decreased transport of DSi downstream. This effect has been described for major dams worldwide, and is an important component of changed N:P:Si ratio's in coastal ecosystems.

## 3 The Uptake of Silicon into the Terrestrial Biogeochemical Si Cycle

Terrestrial ecosystems can be considered as reactors in which Si, released by silicate weathering, undergoes processes of vertical and horizontal translocation and temporary and permanent immobilization (Fig. 2). Ecosystem Si pools can be subdivided in mineralogical and biogenic pools. As a result of differences in chemical-mineralogical composition and reactive contact surface, Si shows a range in reactivity and water solubility in each of these pools [30]. The flux of Si from terrestrial to aquatic systems is determined by a combination of (1) the relative contribution of the different pools of Si and (2) the characteristics of the driving water flow. DSi in soil solutions can be re-deposited as secondary silicate minerals (allophanes or imogolites) or precipitate into non-biological ASi on mineral surfaces. Chemical absorption of DSi on organic compounds, carbonates, Al-hydroxides and Fe-oxides has been observed, although these physico-chemical controls on DSi in soil water are poorly quantified [30–32].

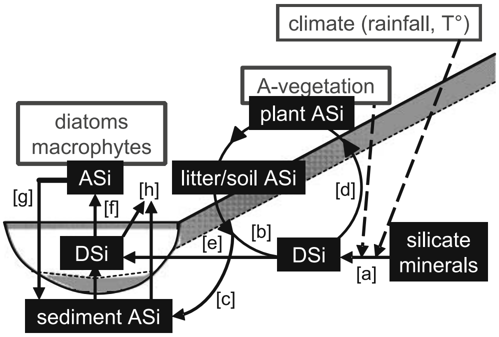

**Fig. 2** Hypothetical representation of the terrestrial biogeochemical cycle of Si in a general ecosystem. *Black boxes* represent the major Si pools. *White boxes* represent factors which influence terrestrial Si cycling. *Solid arrows* indicate Si fluxes; **a** weathering of primary and secondary silicates, **b** dissolution of litter/soil ASi to DSi, **c** ASi transport to rivers through topsoil erosion, **d** plant uptake of DSi, **e** DSi flux towards rivers through the flux of groundwater, **f** uptake of DSi by diatoms and macrophytes in the riverine environment, **g** burial of death diatom and macrophytes biomass, **h** export of DSi and ASi with the downstream river flux. *Dashed arrows* indicate influences on the weathering of silicates exerted by climate and vegetation. T°: temperature

### 3.1 The Mineralogical Soil Pool of Ecosystem Silicon

The mineralogical pool of Si can be subdivided into primary minerals, secondary crystalline minerals (mainly clay minerals) and secondary poorly to non-crystalline (amorphous) phases [33, 34]. The first group can be indicated as parent material, the other two groups find their origin during processes of ecosystem soil formation. Aluminium hydroxides, iron oxides and carbonates play a major role in the interaction between the solid and dissolved Si pools in the soil [35–37]. Silicon is chemically adsorbed at the surfaces of these secondary minerals [38]. When Fe oxides are present, Si dynamics have been hypothesized to be influenced by redox processes. Re-aeration of soils after periods of water-logging was observed to enhance DSi release from silicate minerals [39].

### 3.2 Dissolved Silica in the Soils

In soil solutions, Si occurs primarily as monomeric orthosilicic acid [34]. DSi concentrations in soil solutions are high compared to surface waters and vary between 100 and 500 μM [30]. The influence of pH on the dissolution of silicates can be neglected in the range of pH 2.5 to 8.5 [40]. However, in strong alkaline conditions (pH>9), part of the Si monomers transforms to polymers [41], and DSi concentrations in soil solution increase almost exponentially with pH as a result of growing speciation to $H_3SiO_4^-$ and $H_2SiO_4^{2-}$ [42]. Calcareous soils have higher DSi concentrations compared with non-calcareous soils due their higher pH. Furthermore, DSi concentrations in soil solution are linked to soil temperature and pore water residence time in the soil [33]. A doubling of the equilibrium Si concentration occurs when temperature increases from 5°C to 25°C [42].

### 3.3 The Biological Silicon Pool

Phytogenic, microbial and protozoic forms of Si constitute a third terrestrial Si pool. Numerous studies have shown the capability of plants to take up DSi, passively with the mass flow of water, or through active uptake mechanisms [43, 44]. Si-accumulators, species such as horsetails and wetland *Gramineae* as reed (*Phragmites*), show a DSi uptake which is higher than that expected from the water uptake. Non-accumulators (e.g. dryland grasses and sugarcane) and Si-excluders (e.g. most dicotyledonous species) are characterized by a DSi uptake which is respectively similar to and less than expected from the water uptake. The accumulation of DSi at places of water transpiration in the plant (e.g. stomata) results in its precipitation as hydrated, amorphous silica structures ($SiO_2.nH_2O$), called opal phytoliths [45, 46]. Amorphous silica (ASi) is found in plant leaves, stems, reproductive structures and roots; highest concentrations are deposited in areas from which the greatest quantities of water are lost [36]. Global average plant concentrations of Si per unit dry weight varies between 1 and 3% [8]. However, numerous species contain higher ASi concentrations up to 10% or greater (e.g. bamboo *Arundinaria gigantea*; >20%) [9].

Silicon constitutes a structural component of cell walls [47] and supports plant growth. In the case of Si deficit, phytolith structures are absent and plants are structurally weaker, show abnormal (seedling) growth, development, viability and reproduction with plants more susceptible to biotic (e.g. diseases) and abiotic (e.g. metal toxicity, salinity, drought, temperature extremes) stress [48]. Benefits of Si have been shown both for agricultural crops and natural plants.

Phytolith structures differ significantly in shape and are related to taxonomic units [46]. Dimensions of the Si precipitates vary from 100 nm [49] to 200 mm [46]. The smallest part of plant ASi (<5 μm), which is characterized by the absence of a clear shape, shows a much higher reactivity and ability for vertical and horizontal transport compared with classical phytoliths and is believed to play a central role for the export of Si from terrestrial to aquatic ecosystems [30].

Through litterfall and after plant death, phytoliths contribute to the ASi pool in the upper soil layers and constitute an important component of soil systems. Whereas its content in most upper soil layers ranges from 0.1 to 3% of soil dry weight, numerous soils contain values higher than 5% [50]. The concentration of phytoliths generally decreases with depth in the soil profile, although erosion, vertical translocation and bioturbation can lead to distinct deviations from this pattern [51]. Phytolith storage in soils differs between different terrestrial ecosystems. In general, the concentrations of ASi in soils can be larger than found in living biomass [8, 52].

Phytoliths show higher equilibrium DSi saturation concentrations (~1800 μM) compared with primary minerals (200–600 μM) and secondary minerals (e.g. kaolinite-gibbsite: 30 μM). Lower pH values are known to decrease the dissolution rate of phytoliths [53]. Once released into the saline marine environment, phytoliths rapidly dissolve [54]. From the perspective of oceanic ecosystems, phytoliths can therefore be seen as a bio-available form of Si. The high reactivity of phytolith ASi results in the efficient recycling to DSi in continental ecosystems. In tropical forests, only a small fraction (~8%) of phytoliths' annual deposition in the litter layer remains undissolved at depth [55]. In tidal wetlands, over 90% of ASi associated with *Phragmites australis* growth was estimated to be recycled within one year after plant death [56].

In addition to phytoliths, sponges and diatoms can constitute important ASi pools in wetlands [9, 50], environments at the interface of the terrestrial and aquatic continuum. Testate amoebae have also been identified as potentially important terrestrial bio-reactors of Si [57].

## 4 The Ocean-terrestrial Link in the Global Silicon Cycle

Diatoms deplete oceanic and coastal DSi concentrations to a concentration near limitation for the production of new diatoms (<5 μM DSi) [58]. Most of the DSi sequestered by diatoms, e.g. 97% of the settling ASi, is recycled back to DSi before it is buried in ocean floor sediments. However, without continuous replenishment of the remaining 3% from terrestrial ecosystems, diatom production in the ocean would gradually decline on the long term, with important repercussions on carbon burial and oceanic production [59] (Fig. 1).

On geological time scales, the ultimate source of the continental Si flux to the oceans is the weathering of Si containing minerals. Weathering rates result from the complex interaction between precipitation, runoff, lithology, temperature, topography and vegetation [60]. Land plants and soil microbiota influence the weathering process of silicate minerals in different ways: through production of organic chelating ligands, through alteration of pH, through production of organic acids and $CO_2$, and through alteration of physical properties of the soil (e.g. physical weathering of rocks, increases in the surface area, longer residence time of water) [61, 62].

The link between the continental Si flux and characteristics of terrestrial ecosystems is receiving increased attention. In 2002, Conley [8] published the first estimate of the size of the annual uptake of DSi by vegetation and its importance in terrestrial ecosystems. The global annual phytolith production was estimated to be 60–200 Tmole Si $yr^{-1}$ (Fig. 1). In comparison with the oceanic biogeochemical cycle, the global annual terrestrial ASi production is of the same order of magnitude as the global oceanic ASi production by diatoms (~240 Tmole $yr^{-1}$). By comparison, the annual release of Si by weathering of silicates has been estimated to be ~19–46 Tmole $yr^{-1}$ [63] and the terrestrial production is one order of magnitude larger than the global annual riverine input of DSi to the oceans (5 Tmole Si $yr^{-1}$) [12]. The amount of ASi buried in soils is several orders of magnitude larger than the annual terrestrial production [8]. In addition, amorphous silica transport from the continents by rivers constitutes a substantial part of Si fluxes into the ocean [64].

The largest part of DSi released to Hawaiian stream water has passed through plants at least once [65]. Authors in [66] observed an increase of 82% in Si release from weathering due to the presence of vegetation. The contribution of DSi release by phytoliths to the total DSi efflux from terrestrial ecosystems is observed to vary from about 10% to 30% in pine forests and forest tundra [67, 68] to almost 90% in forested Hawaiian stream basins [10, 65].

Important differences in Si cycling exist between different terrestrial ecosystem types and the highest amount of phytoliths are found in "soils" of coastal and inland swamps, flood plains, grasslands and forests [50]. Plant species composition also influences soil Si content [69].

### 4.1 Forests

An intense biogeochemical cycling of Si is observed in forest ecosystems [55, 70, 71]. Biotic fluxes through forests have been shown to be comparable to macronutrients such as Ca [66]. DSi concentrations in soil solutions of forested podzols are almost entirely biologically controlled [72]. During summer, DSi released by weathering of minerals and dissolution of phytoliths is largely taken up and stored as ASi by forest vegetation. In winter and early spring, dissolution of phytoliths in the litter layer controls the DSi flux out of the forest system as mineral weathering is highly temperature dependent. Silicon uptake by forests was estimated to result in a 30% lower annual DSi flux out of a partly (60%) forested (oak and eastern white pine) watershed [73]. The biogeochemical Si cycle was modelled in a temperate fir forest soil and an estimated average of 60% of the biogeochemical cycle of Si was controlled by biological processes [32].

### 4.2 Grasslands

As most graminoid species are known as strong Si accumulators, grassland ecosystems store large quantities of ASi. Dissolution of DSi from phytoliths in different grassland ecosystems was shown to be several times larger than net weathering release by minerals and high ASi amounts in soil result in a significant buffering capacity of grasslands during periods of low stream DSi concentrations [52]. Grass phytoliths are 10 to 15 times less soluble than forest phytoliths as a result of the latter's greater surface area [74].

### 4.3 Other Graminoid Dominated Ecosystems

Among other graminoid dominated vegetation types, bamboo forests [75], papyrus dominated wetlands [76], alpine and sub-alpine grasslands [77] and temperate tidal marshes [9] are shown to accumulate large quantities of ASi. Freshwater and saltwater marshes in estuaries are important reservoirs of Si through burial of ASi and play an important buffering role for estuarine Si cycling [78]. During summer, freshwater tidal marshes (Scheldt estuary, Belgium) were observed to contribute up to 50% or more of total DSi discharge. Inland wetlands have also been shown to be important regulators of riverine DSi transport. DSi concentrations were observed to be higher in stream basins with high wetland coverage in boreal watersheds [9, 79, 80].

Although relatively few ecosystem studies have been made, all published studies point to an intense terrestrial biogeochemical cycling of Si. Therefore, terrestrial ecosystems cannot be neglected as active part of the biogeochemical cycle of Si and can be expected to play a major regulating role for the transport of Si through river basins. As such, the range of possible human perturbations of this cycle becomes much larger than expected through deforestation and cultivation [81, 82].

## 5 Conclusions

The global silicon cycle is a complex interaction of biological, chemical and geological processes, acting on a wide variety of spatial and temporal scales. The transport of Si along the land-ocean continuum through terrestrial ecosystems and river catchments to the estuarine and coastal zone is controlled by a complex set of terrestrial and aquatic processes, acting at different timescales and differing in reactivity and spatial distribution. The silicon elemental cycle is receiving increasing attention, because of its global environmental impact. For example, the mineral weathering of silicates is an important sink for atmospheric $CO_2$. The import of Si into coastal zones from the terrestrial environment is essential to sustain diatom growth. Diatoms play a key role in the oceanic C-sink and eutrophication of coastal zones. Silicon is also an important element in terrestrial ecosystems, in processes of soil formation and in regulating species composition of vegetation.

The integration between biology, chemistry and geology regarding the silicon biogeochemical cycle is currently not receiving sufficient scientific attention. Focus in the future should be on unravelling the intricacies of the biological Si cycle and the interactions with geological cycling. We need to develop new mechanistic models for the transport of Si at both local and global scales from the continents to the ocean. Effects of land use changes, and changes in hydrology, temperature and biodiversity are just beginning to be addressed. Although individual studies quantifying biological or geological aspects of the Si cycle are valuable in their own respect, the largest advances will be made by taking interdisciplinary approaches to develop the concepts behind the cycling of this fascinating element.

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