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Biogenic silica: a neglected component of the coupled global continental biogeochemical cycles of carbon and silicon

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Abstract

On geological time-scales (≥10^6 years), the global geochemical cycles of carbon and silicon are coupled by the drawdown of atmospheric CO_2 through chemical weathering of Ca- and Mg-silicate minerals in continental rocks. Rivers transport the soluble products of weathering (cations, alkalinity and silicic acid) to the oceans, where they are utilized by marine ecosystems. On decadal to glacial–interglacial time-scales, however, large biotic fluxes and storages of Si within terrestrial and freshwater ecosystems need to be taken into account. Recent studies have emphasized the importance of Si-accumulating plants, which deposit significant amounts of amorphous hydrated silica in their tissues as opal phytoliths. These include grasses, sedges, palms, some temperate deciduous trees and conifers, and many tropical hardwoods. Landscapes dominated by accumulator plants, such as tropical rainforests, grasslands, herbaceous wetlands and bamboo forests, act as 'silica factories'. Important 'silica bioengineers' in freshwater ecosystems comprise diatoms, sponges and chrysophytes. This paper reviews the biological role of Si in higher plants, the impact of vegetation on rates of chemical weathering, the fluxes of Si through catchment ecosystems, lakes and rivers, and the potential contribution of new geochemical and isotopic tracers to Si biogeochemistry. Multiproxy investigations of lake sediments will provide novel insights into past variations in Si biocycling from terrestrial to aquatic realms on 10–10^6 year time-scales.

Keywords: Si biogeochemistry; carbon cycle; biogenic silica; terrestrial ecosystems; aquatic ecosystems; phytoliths; diatoms; Late Quaternary; lake sediments

Introduction

'The ability of some plants to accumulate certain major elements, such as Si, Al, Ca, Mn, and Fe has geologic implications. Many kinds of vegetation, especially in the tropics, contain several percent silica dry weight. Some 10 to 20 tons dry weight of new growth per acre is added each year above ground in tropical jungles, and the roots add several tons more. A forest of silica-accumulator plants averaging 2.5% silica and 16 tons dry weight new growth per year would extract about 2000 tons of silica per acre in 5000 years – equivalent to the silica in 1 acre-ft. of basalt. Comparison of lateritic soils with parent rock indicates that a silica-accumulator jungle could convert basalt into lateritic soil rapidly – geologically speaking. The silica in ground water increases with depth and time in contact with the rock, but vadose water seems inadequate to yield the silica required by such a jungle of silica-accumulator plants; biochemical factors must therefore cause much more rapid solution of silica. Under favorable conditions, much soluble organically derived silica may be recycled or added to ground water, but nevertheless, in tropical regions with high rainfall and appreciable runoff, large amounts of siliceous organic debris must be swept off the forest floor into the drainage system. On the other hand, if insoluble silicic phytoliths result from the disintegration of the vegetal litter, the upper soil horizons may become enriched in silica from disintegrating silica-accumulator plants, where erosion does not equal the rate of accumulation, as in many prairie and savannah soils' (Lovering, 1959).

This ground-breaking paper on the 'Significance of Accumulator Plants in Rock Weathering', by the former Chief of Geochemical Exploration at the United States Geological Survey, Thomas Seward Lovering (Morris, 1996) must surely rank as one of the most unjustly neglected contributions to geomorphology since World War II, or indeed of all time. Lovering argued that biogeochemical cycling has a crucial impact on processes of soil formation and denudation involving silicate weathering.

Unfortunately for Lovering, geochemists interested in the coupling between the terrestrial carbon and silicon cycles bypassed his work in favour of a focus on time-scales longer than the time taken for rivers to replenish the amount of inorganic carbon stored in the oceans (5×10^5 years: Kump *et al.*, 2004). Viewed from a long-term, steady-state perspective, the most important processes are weathering of rock minerals, oxidation of organic matter contained in ancient sediments, burial of carbonates and silica in ocean sediments, and recycling of CO_2 to the atmosphere by plate tectonics (Sundquist, 1985; Berner, 1995; Berner and Berner, 1996). Drawdown of atmospheric CO_2 through weathering of Ca and Mg silicates is followed by flushing of the products of weathering into rivers and groundwater, carbonate precipitation in the oceans and ocean–atmosphere exchange of CO_2. These processes are exemplified by the idealized reactions (Berner, 1995; Kump *et al.*, 2004):

$$CaSiO_3 + 2H_2CO_3 \rightarrow Ca^{++} + 2HCO_3^{-} + SiO_2 + H_2O \tag{1}$$

$$Ca^{++} + 2HCO_3^{-} \rightarrow CaCO_3 + H_2CO_3 \tag{2}$$

$$H_2CO_3 \rightarrow CO_2 + H_2O \tag{3}$$

The net result of Equations 1–3 is:

$$CaSiO_3 + CO_2 \rightarrow CaCO_3 + SiO_2 \tag{4}$$

The contribution of organic acids to weathering is implicitly included in Equation 1 because their anions oxidize to bicarbonate in stream water (Berner and Berner, 1996). In practice, dissolution of silicate minerals is normally incongruent, resulting in formation of secondary clays, oxides and hydroxides in addition to the production of solutes. Hence the actual stoichiometry of the weathering reactions is significantly more complex. For example, the transformation of Ca-plagioclase feldspar (anorthite) to kaolinite can be represented by:

$$CaAlSi_2O_8 + 2H_2CO_3 + H_2O \rightarrow Al_2Si_2O_5(OH)_4 + 2HCO_3^{-} + Ca^{++} \tag{5}$$

(Stumm and Morgan, 1970). Further weathering results in leaching of SiO_2 from the kaolinite lattice, leaving gibbsite:

$$Al_2Si_2O_5(OH)_4 + H_2O \rightarrow 2Al(OH)_3 + 2SiO_2 \tag{6}$$

(Loughnan, 1969).

In contrast, weathering of carbonate rocks, followed by the precipitation of an equivalent amount of carbonate minerals by marine organisms, does not result in net consumption of atmospheric CO_2 (Berner, 1995; Kump *et al.*, 2004):

$$CaCO_3 + H_2CO_3 \rightarrow Ca^{++} + 2HCO_3^{-} \tag{7}$$

$$Ca^{++} + 2HCO_3^{-} \rightarrow CaCO_3 + H_2CO_3 \tag{8}$$

Weathering of Na and K silicates is neglected in steady-state geochemical models because the resulting drawdown of atmospheric CO_2 is deemed to be balanced by equivalent CO_2-liberating processes involving seawater–basalt reactions and reverse weathering of marine sediments (Berner *et al.*, 1983; Berner and Berner, 1996).

To complete the long-term carbonate–silicate cycle, CO_2 is returned to the atmosphere on plate-tectonic time-scales by metamorphic decarbonation and volcanic outgassing (Berner *et al.*, 1983). In turn, variations in atmospheric CO_2 concentration influence continental weathering rates. This crucial negative feedback helps to prevent the development of a runaway greenhouse or icehouse (Walker *et al.*, 1981; Brady and Carroll, 1994; Berner, 1995). The terrestrial biosphere also plays an important feedback role. According to Knoll and James (1987), Berner (1992) and Mora *et al.* (1996), the spread of rooted vascular plants during the Devonian permanently reduced CO_2 levels by accelerating rock weathering. However, Si cycling by terrestrial biota (Figure 1) has not yet been explicitly incorporated into global

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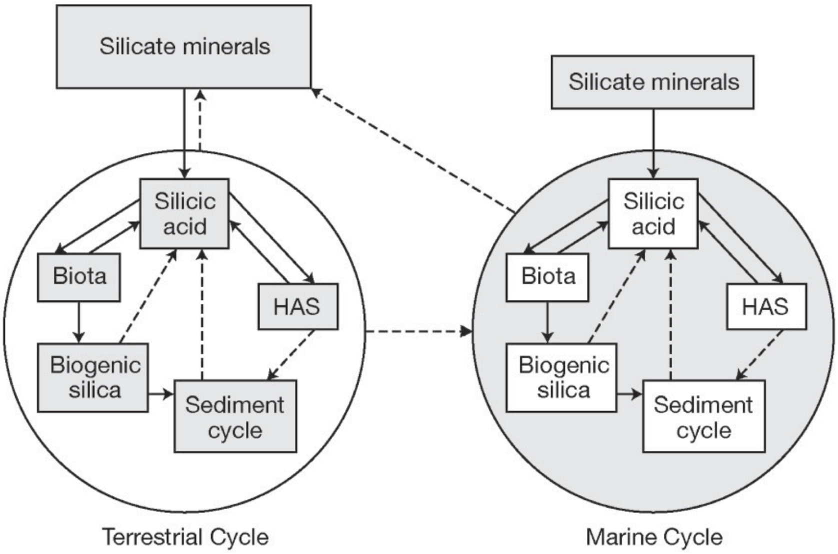

Figure 1. The coupled terrestrial and marine biogeochemical cycles of silicon (from Exley, 1998): HAS, hydroxyaluminosilicates such as allophane.

geochemical models. This is surprising because recent evolutionary syntheses have concluded that the expansion of C_4 grasslands during the Miocene greatly accelerated the 'biologically catalyzed silicate weathering process' (Falkowski *et al.*, 2004), leading to rapid diversification and increased accumulation rates of both marine and freshwater diatoms (Falkowski *et al.*, 2004; Kidder and Gierlowski-Kordesch, 2005). These relatively large, siliceous microalgae dominate the carbon export to the deep ocean (Smetacek, 1999; Yool and Tyrrell, 2003).

Most syntheses of the global carbon cycle on short ($<10^3$ years) time-scales omit its connections with silicate weathering and terrestrial Si biocycling entirely, presumably because these processes are assumed to operate on too long a time-scale to be relevant (Falkowski *et al.*, 2000; Wigley and Schimel, 2000). A notable exception is Exley (1998), who argued that biological uptake of dissolved silica drives Equation 1 to the right, thereby enhancing mineral weathering and CO_2 drawdown. Stallard (1998) examined the possible contribution of anthropogenic increases in continental sediment storage to the 'missing sink' problem, concluding that burial of organic carbon in colluvial, alluvial and reservoir sediments may result in significant removal of anthropogenic CO_2 from the atmosphere. However, he did not consider other key nutrients such as Si that might be retained by the cascade of biomass, soil and sediment storages that are found along river systems, a process termed 'fluvial filtering' by Meybeck and Vörösmarty (2005).

Sitting somewhat awkwardly between these two temporal extremes is a small group of papers that examines the potential contribution of changing weathering rates to glacial–interglacial variations in atmospheric CO_2. On this time-scale, complications arise because the total inventory of dissolved inorganic carbon in the oceans is not constant (Archer *et al.*, 2000; Sigman and Boyle, 2000); hence, the global carbonate–silicate system is far from steady state and the weathering of carbonate rocks cannot be ignored (Sundquist, 1985). Investigations of glacial–interglacial variations in rock weathering have relied on measurements of geochemical or isotopic tracers in ocean sediments (Froelich *et al.*, 1992; Henderson *et al.*, 1994; Oxburgh, 1998; Foster and Vance, 2006), or on modelling the changes in silicate and carbonate weathering that would be expected to result from variations in temperature, runoff, exposed continental land area and in some cases, ice-sheet extent (Gibbs and Kump, 1994; Kump and Alley, 1994; Munhoven and François, 1996; Ludwig *et al.*, 1999; Jones *et al.*, 2002; Munhoven, 2002; Tranter *et al.*, 2002). None of these studies has so far considered the crucial contribution of the terrestrial biosphere to silicate weathering. Indeed, any reference to 'plants' and 'vegetation' is conspicuously lacking.

Despite this astonishing neglect, considerable progress has been made in understanding the biological role of Si in terrestrial organisms (Jones and Handreck, 1967; Raven, 1983; Sangster and Hodson, 1986; Takahashi *et al.*, 1990; Epstein, 1994, 1999; Sangster *et al.*, 2001). Catchment-ecosystem-scale studies of Si cycling have demonstrated the power of vascular plants to pump Si from rocks and recycle it between plant tissues, soils and sediments, from which stored silica is released to drainage waters, or as aeolian dust, on annual or longer time-scales (Simonson, 1995;

Clarke, 2003; Meunier, 2003). A particularly strong tradition of field-based Si biogeochemistry has developed in France (Bartoli, 1983; Lucas *et al.*, 1993; Alexandre *et al.*, 1997; Meunier *et al.*, 2001). Experiments have demonstrated that certain crops benefit significantly from Si supplementation (Takahashi *et al.*, 1990). In lakes, biogenic silica (BSi) accumulation has been shown to vary with trophic status (Schelske *et al.*, 1983; Conley *et al.*, 1993; Conley and Schelske, 2001), while the ability of diatoms and other Si-secreting organisms to strip dissolved silica (DSi) from river, lake and reservoir waters is increasingly being blamed for blooms of harmful, non-siliceous algae (Conley *et al.*, 1993; Humborg *et al.*, 2000).

Notwithstanding these significant advances at the organism-to-ecosystem scale, the full global significance of the coupling between the continental biogeochemical C and Si cycles on Quaternary time-scales is still largely unrecognised. In this paper, we join Exley (1998), Conley (2002), Markewitz and Richter (1998) and Struyf and Conley (in press) in calling for the 'bio' in Si biogeochemistry to be taken more seriously by earth-system scientists. First, we summarize the modern global pattern of net CO_2 drawdown by silicate weathering estimated from geochemical analyses of river-transport data, which provides the backdrop for studies of the impact of the continental biota on the Si cycle. We then review the physiological and ecological literature dealing with BSi in terrestrial and freshwater ecosystems, and point to the existence of novel geochemical and isotopic techniques that are revolutionizing our ability to trace the pathways followed by Si from rocks and soils through plants and surface waters to sediments. Finally, we illustrate the ways in which Late Quaternary variations in Si biocycling can be reconstructed through analyses of lake sediments.

The Global Pattern of CO_2 Drawdown by Silicate Weathering

The global pattern of CO_2 drawdown by silicate weathering has been estimated from the dissolved load of large rivers, corrected for atmospheric inputs (Stallard, 1995; Kump *et al.*, 2000). At pH values <9, DSi is predominantly transported in the form of undissociated monosilicic acid (H_4SiO_4), often written as $Si(OH)_4$ (Knight and Kinrade, 2001). The river basins with the largest *total* CO_2 consumption fluxes are all located in the humid tropics: the Irrawady, the Ganges, the Amazon, the Paraná and the Congo (Gaillardet *et al.*, 1999b) (Figure 2). About 30–35 per cent of global CO_2 consumption is attributable to chemical weathering of basalt (Dessert *et al.*, 2003; Dupré *et al.*, 2003). Despite its restricted spatial distribution, basalt contains a high proportion of ferromagnesian minerals and is very susceptible to chemical weathering by higher plants (Cochran and Berner, 1996). The remainder of the estimated CO_2 flux is derived from granitoid and to a lesser extent, sedimentary rocks. In general, rapid rates of physical weathering and erosion in areas of high relief enhance chemical weathering and CO_2 consumption by continually exposing fresh

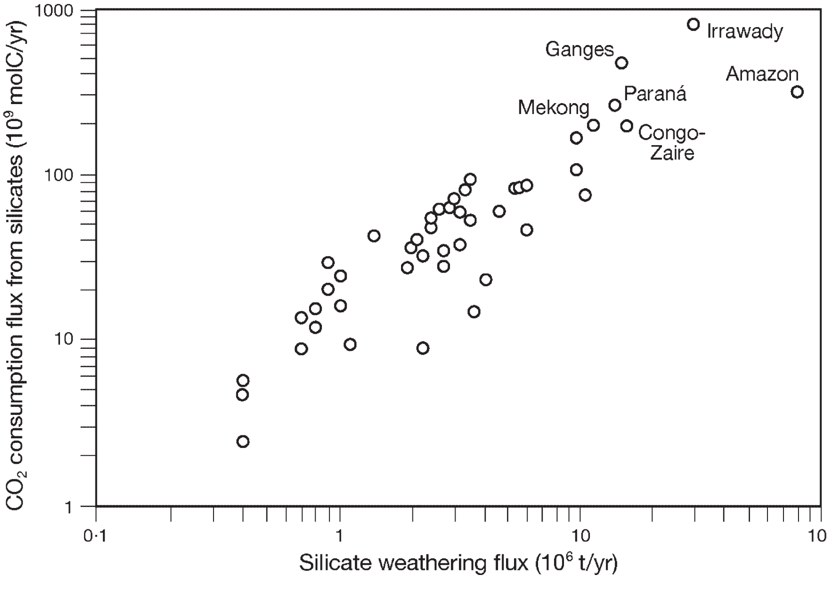

Figure 2. The drawdown of atmospheric CO_2 by silicate weathering, based on the dissolved load of large rivers, corrected for atmospheric inputs (from Gaillardet *et al.*, 1999b).

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mineral surfaces (Summerfield and Hulton, 1994; Gaillardet *et al.*, 1999a,b). Hence, two end-member states can be distinguished with respect to chemical denudation (Stallard, 1995). Weathering-limited regimes occur in steep terrain, where physical transport is capable of moving all loose debris and rates of denudation, silicate weathering and CO_2 drawdown are high, but the intensity of chemical weathering is low. In contrast, transport-limited regimes are characterized by deep lateritic weathering profiles dominated by secondary minerals, minimal surface erosion and large quantities of very dilute runoff, but low rates of CO_2 consumption *per unit area*. The Andes and the Amazonian lowlands exemplify these two extremes, respectively (Gaillardet *et al.*, 1997; Mortatti and Probst, 2003) (Figure 3).

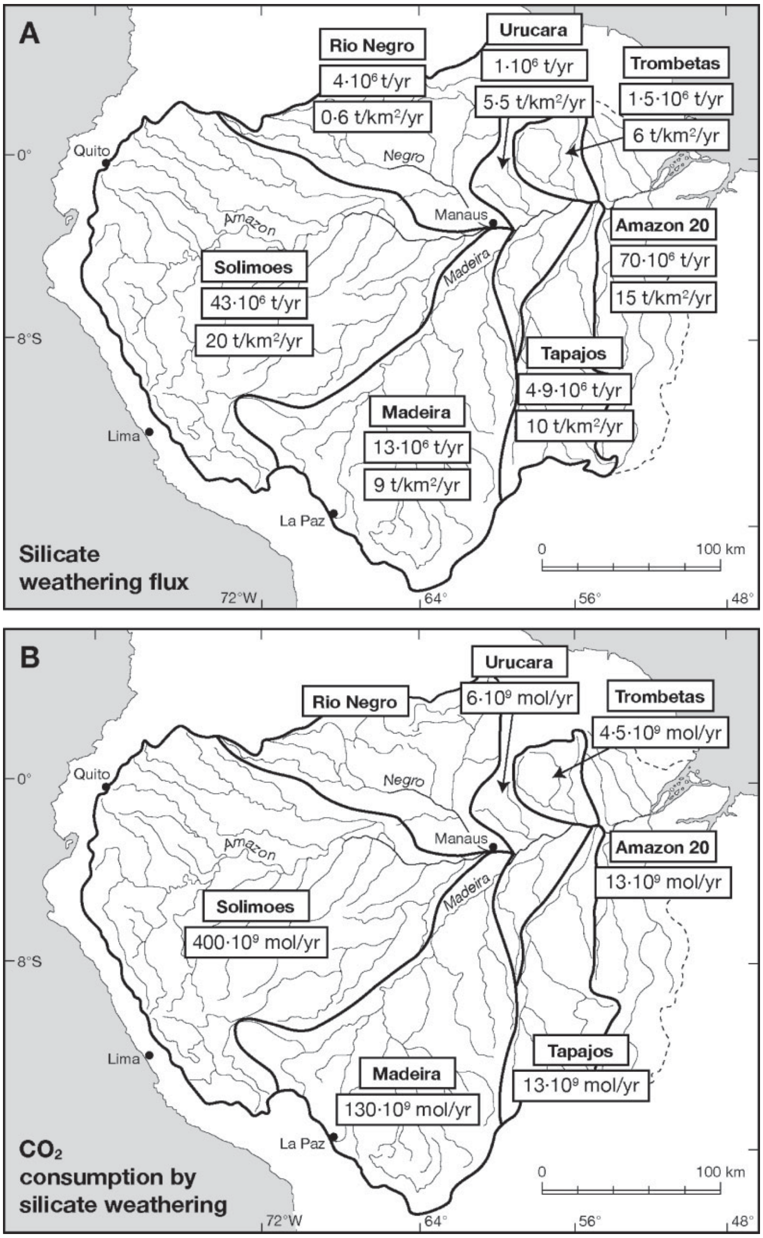

Figure 3. Spatial distribution of the silicate weathering flux (A) and CO_2 consumption by silicate weathering (B) in northern South America, based on river-transport data corrected for atmospheric inputs, emphasizing the contrast between the weathering-limited regime of the Andes and the transport-limited regime of the Amazon lowlands (from Gaillardet *et al.*, 1997).

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Biogenic Silica in Terrestrial Ecosystems

Among the land biota, only horsetails (Equisitaceae) were traditionally accepted as having an absolute requirement for Si (Epstein, 1999). Although 19th century plant physiologists recognized that many families of land plants contained Si in amounts comparable to macronutrients such as P, S, Ca and Mg, or even in some cases K and N, Si was considered to be a benign but non-essential plant constituent. This reflects both the technical difficulty of purging Si from experimental cultures and a flawed definition of essentiality (Epstein, 1994, 1999). Notwithstanding this lack of general interest, a select band of independent-minded plant scientists has made considerable progress in unravelling the complexities of Si biochemistry.

As befits the status of Si as the second most abundant element in the Earth's crust, DSi is present in significant concentrations in soil moisture, apart from highly desilicated tropical weathering profiles rich in Al and Fe oxides (Jones and Handreck, 1967; Epstein, 1994). Terrestrial higher plants take up $Si(OH)_4$ from the soil solution through their roots. It is then carried in the transpiration stream and irreversibly deposited as amorphous hydrated silica in roots, stems, leaves, inflorescences and fruits. Biogenic silica is assigned the general formula $[SiO_n{\cdot}OH_{(4-2n)}]_m$, where n is <2 and m is very large, implying a range of compositions between the end members $mSiO_2$ and $mSi(OH)_4$ (Sangster *et al.*, 2001). Discrete silica bodies that form in plant tissues are commonly known as opal phytoliths (Sangster and Hodson, 1986; Piperno, 1988). Reported leaf SiO_2 contents range from <0·5 per cent to ~19 per cent dry weight (Lewin and Reimann, 1969; Marschner, 1995; Euliss *et al.*, 2005; Struyf and Conley, in press); however, wide variations are normally observed between different parts of the same plant (Jones and Handreck, 1967; Sangster and Hodson, 1986; Epstein, 1999; Sangster *et al.*, 2001). As a rule of thumb, BSi is deposited in highest concentrations in the organs from which water is lost in greatest quantities (Jones and Handreck, 1967).

Silica contents also show marked phylogenetic variability (Jones and Handreck, 1967; Piperno, 1988; Takahashi *et al.*, 1990). Hodson *et al.* (2005) found that shoot Si concentrations declined in the order: liverworts > horsetails > clubmosses > mosses > angiosperms > gymnosperms > ferns. Among the angiosperms, they reported particularly high concentrations in monocots, including grasses (notably bamboo and wetland taxa such as rice and *Phragmites*), sedges, palms and bananas, as well as in a few dicots, including several temperate-forest trees (beech, elm, sugar maple, oak), stinging nettles, cannabis and some composites (e.g. sunflower). A few conifers (gymnosperms) such as spruce and larch are noteworthy Si accumulators (Hodson and Sangster, 1999). Silica has also been reported in the wood of several hundred rainforest hardwood trees (Sangster and Hodson, 1986).

Higher plants can be categorized as high, intermediate and non-Si accumulators (Ma *et al.*, 2001). High accumulators typically exhibit SiO_2 concentrations >1 per cent dry weight and take up DSi faster than water; this suggests that an active-uptake mechanism is involved. Recently, Ma and co-workers identified a Si-transporter gene in rice (Ma *et al.*, 2004). Plants in the intermediate group, containing ~1 per cent SiO_2, absorb DSi passively with water, whereas non-accumulators, which display much lower BSi contents, effectively exclude it (Raven, 1983; Takahashi *et al.*, 1990; Richmond and Sussman, 2003). Within any individual group, the amounts of BSi accumulated vary as a function of soil type, pH, DSi concentration, plant maturation, presence of ectomycorrhizal fungi on plant roots, transpiration rate and availability of nutrients such as N and P (Jones and Handreck, 1967; Sangster *et al.*, 2001; van Hees *et al.*, 2004; Euliss *et al.*, 2005).

Various beneficial effects of Si have been identified in higher plants (Jones and Handreck, 1967; McNaughton and Tarrants, 1983; Raven, 1983; Epstein, 1999; Ma *et al.*, 2001; Richmond and Sussman, 2003). They can be categorized as structural, physiological and protective (Sangster *et al.*, 2001). Biogenic silica acts as an energetically cheap stiffening material, promoting root oxygen supply, upright stature, resistance to lodging (flattening by wind or rain) and favourable exposure of leaves to light. It enhances growth and yield, especially in accumulator species. It reduces vulnerability to pathogens such as mildew and confers resistance to grazing insects, molluscs and mammals. Silica uptake improves the supply of P and N, as well as ameliorating heavy metal toxicity by immobilizing Al, Fe, Mn and Zn. In acidic environments such as conifer forests, tropical rainforests and swamp forests, significant amounts of Al may co-precipitate with BSi (Hodson and Sangster, 1999; Wüst and Bustin, 2003). Silicification helps to protect against temperature extremes. It also reduces transpiration, thereby diminishing the impact of drought and salinity stress.

Although primitive plants and fungi are very effective weathering agents, higher plants are more important on a global scale because their substantially greater primary production necessitates a much larger uptake of water and nutrients via deeply penetrating root systems (Cochran and Berner, 1996; Hinsinger *et al.*, 2001). They accelerate the weathering of silicate minerals by increasing the moisture and organic-matter status of soils, by introducing sources of H^+ ions (CO_2, detritus and organic acids) into close proximity with mineral surfaces, and by exuding potent chelating agents such as citric acid, malic acid and non-proteinogenic amino acids (phytosiderophores) into the root micro-environment (the rhizosphere) (Richards, 1974; Bormann *et al.*, 1998; Kelly *et al.*, 1998; Hinsinger *et al.*, 2001; Lucas, 2001). Together with low-molecular-weight organic acids produced by microorganisms living on root exudates, these

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ligands form soluble complexes with Fe and numerous other metals, increasing the dissolution rates of soil minerals. Active uptake of essential nutrients by higher plants also helps to destabilize silicate minerals.

The efficacy of higher plants at pumping Si (as opposed to P and metallic cations) from both primary and secondary minerals was overlooked for many years, despite early experimental work by Lovering and Engel (1967). A recent resurgence of interest has been led by forest ecologists and agronomists, particularly since the discovery that Si supplementation is highly beneficial to commercial crops of rice and sugar cane (Takahashi *et al.*, 1990; Datnoff *et al.*, 2001). Convincing evidence has been gathered not only from culture experiments using known Si-accumulator plants, but also at the catchment-ecosystem scale, by means of Si budgets drawn up for various temperate and tropical ecosystems (Table I). For example, Hinsinger *et al.* (2001) carried out leaching experiments on finely ground basalt in the presence or absence of four different crop plants: lupin, rape, maize and banana. All four accelerated the dissolution of basalt. The amount of Si released was approximately doubled by the recognized Si-accumulators maize and banana, which stored a significant proportion in their tissues.

At the ecosystem scale, geochemists have attempted to evaluate the impact of higher plants on silicate weathering by comparing the dissolved loads of streams draining paired rocky and vegetated catchments. Cawley *et al.* (1969), Drever and Zobrist (1992) and Moulton *et al.* (2000) found that the weathering flux of Si was enhanced two- to eightfold by vegetation. On Icelandic basalts, drawdown of atmospheric CO_2 by chemical weathering is significantly correlated with net primary productivity, net ecosystem exchange and percentage wetland cover (Kardjilov *et al.*, 2006). However, none of these studies quantified the biocycling of Si through living biomass and soils. In contrast, Bartoli (1983) and Alexandre *et al.* (1997) pioneered the construction of detailed mass balances for Si that included biotic fluxes (Table I). Following Bormann *et al.* (1998) and Moulton *et al.* (2000), the biogeochemical mass balance of Si for a terrestrial soil can be written:

$$F_{\text{atmospheric}} + F_{\text{weathering}} + F_{\text{litterfall}} = F_{\text{vegetation uptake}} + F_{\text{soil storage}} + F_{\text{drainage}} \tag{9}$$

where F is the flux of Si in kg ha^{-1} year^{-1}; note that $F_{\text{weathering}}$ is the net result of weathering and neoformation of secondary silicates (Alexandre *et al.*, 1997; Lucas, 2001), $F_{\text{litterfall}}$ includes DSi leached from the canopy by throughfall, $F_{\text{soil storage}}$ refers to BSi in soil, and F_{drainage} comprises DSi export to groundwater and runoff. Furthermore,

$$F_{\text{vegetation storage}} = F_{\text{vegetation uptake}} - F_{\text{litterfall}} \tag{10}$$

Hence, from Equations 9 and 10,

$$F_{\text{weathering}} = F_{\text{vegetation storage}} + F_{\text{soil storage}} + F_{\text{drainage}} - F_{\text{atmospheric}} \tag{11}$$

Table I summarizes the Si budgets of various forest and grassland ecosystems. The biotic fluxes through forests are surprisingly large for a supposedly non-essential element, being comparable to macronutrients such as Ca (Markewitz and Richter, 1998). Biocycling of Si is particularly important in the humid tropics. In Congo rainforest, Alexandre *et al.* (1997) found that $F_{\text{vegetation uptake}}$ was about three to four times greater than $F_{\text{weathering}}$. They showed that *c.* 92 per cent of the BSi produced by the vegetation was rapidly recycled by dissolution of the more labile silica particles in leaf litter. The remaining *c.* 8 per cent (mainly wood phytoliths) formed a resistant pool that accumulated in the upper soil horizons for thousands of years.

Graminoid vegetation types such as grasslands (Blecker *et al.*, 2006), savannas and herbaceous wetlands also contain a high proportion of Si-accumulator plants. These prolific opal-producing landscapes have been christened 'silica factories' by Clarke (2003). A partial Si mass balance for bamboo forest on the basaltic island of Réunion, Indian Ocean, reveals extraordinarily high rates of Si pumping (Meunier *et al.*, 1999; Table 1). Bamboo, a giant C_3 grass, acts as a Si 'hyperaccumulator' (Meunier, 2003). On Réunion, it combines high tissue concentrations (*c.* 12 per cent dry weight SiO_2 in stems) with high primary productivity and susceptibility to natural fires, helping to explain the rapid desilication of the underlying volcanics and the accumulation of a thick layer of burned phytoliths in the topsoil (Meunier *et al.*, 2001; Meunier, 2003). Another plant with comparable rates of Si deposition (*c.* 700 kg Si ha^{-1} year^{-1}) is papyrus, a giant C_4 sedge that dominates the emergent-macrophyte communities of many African wetlands such as the Okavango Delta, where phytoliths constitute *c.* 32 per cent of the inorganic fraction of the underlying peat (McCarthy *et al.*, 1989). Other largely herbaceous plant communities with high BSi contents in biomass include tropical palm swamps (Oliva *et al.*, 1999; Braun *et al.*, 2005), temperate tidal marshes (Norris and Hackney, 1999; Struyf *et al.*, 2007), and alpine and subalpine grasslands. Estimates of $F_{\text{litterfall}}$ for the latter attain 48 kg Si ha^{-1} year^{-1} (Carnelli *et al.*, 2001). It is important to note, however, that the silica source for emergent macrophytes in both freshwater and tidal wetlands is normally DSi exported from upslope/upstream ecosystems rather than *in situ* weathering.

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Table I. Measured Si fluxes in forest and grassland ecosystems (kg Si ha^{-1} year^{-1}). Values in parentheses are calculated from balance

Vegetation type	Atmospheric input ($F_{\text{atmospheric}}$)	Net weathering release ($F_{\text{weathering}}$)	Vegetation uptake ($F_{\text{vegetation uptake}}$)	Vegetation storage ($F_{\text{vegetation storage}}$)	Litterfall and throughfall ($F_{\text{litterfall}}$)	Soil storage ($F_{\text{soil storage}}$)	Phytolith dissolution ($F_{\text{litterfall}} - F_{\text{soil storage}}$)	Loss to drainage waters (F_{drainage})	Reference
Coniferous forest	1·5	29·5	8	3	5	1	4	26	1
Coniferous forest	0·04	(31·53)	15·8	2·32	13·9	11·95		17·3	2
Mixed hardwood–conifer forest	Negligible	15·8–17·4	10·8–32·3	Steady state	10·8–32·3	0·8–2·4	(10·0–29·9)	15·0	3
Temperate deciduous forest	1·5	2·5	26	4	22	0	22	0	1
Amazon rainforest (ferralsol)					41			11	4
Amazon rainforest (podzol)					21			4·5	4
Congo rainforest (ferralsol)	<1	20–22	58–76	Steady state	58–76	4–6	54–70	16	5
Bamboo forest					453–645	210–496	112	164	6
Tall grassland (two sites)	2	14·3–25·0	(59–67)	Steady state	59–67	10–16	43–57	6·3–11	7
Mixed grassland (three sites)	2	3·7–11·5	(55–58)	Steady state	55–58	4–13	43–51	0·3–1·7	7
Short grassland (two sites)	2	4·5–7·2	(22–26)	Steady state	22–26	6–9	16–17	0·2–0·5	7

1, Bartoli (1983); 2, Markewitz and Richter (1998); 3, Garvin (2006); 4, Lucas *et al.* (1993); 5, Alexandre *et al.* (1997); 6, Meunier *et al.* (1999); 7, Blecker *et al.* (2006).

The studies summarized in Table I imply that changes in Si pumping by terrestrial vegetation play a role in the carbon cycle on time-scales as short as 10^2–10^3 years. Equation 11 also demonstrates that the DSi load of rivers is significantly reduced when significant amounts of BSi accumulate in vegetation (in the case of aggrading ecosystems) and/or plant litter (Markewitz and Richter, 1998). Soils underlying tropical rainforests and temperate grasslands typically store large quantities (*c*. 10–30 t Si ha^{-1}) of opal phytoliths (Alexandre *et al.*, 1997; Blecker *et al.*, 2006). F_{drainage} may underestimate $F_{\mathrm{weathering}}$ by ≤45 per cent in forests and ≤97 per cent in grasslands (Table I). In other words, the uptake of Si by terrestrial ecosystems significantly increases the chemical weathering rate without necessarily increasing the measured denudation rate. This conclusion applies with particular force to transport-limited landscapes (Alexandre *et al.*, 1997).

Given the lack of adequate data for many biomes, it is difficult to quantify the total BSi production by terrestrial ecosystems. Conley (2002) used the total net primary production and average BSi content of land vegetation to derive an estimate of 60–200 Tmol year^{-1} (*c*. 2–6 Gt SiO_2 year^{-1}) for the annual fixation of phytolith silica, rivalling the total marine BSi production of 240 Tmol year^{-1} (6·7 Gt SiO_2 year^{-1}). Most of this enormous quantity is added as litterfall to the surface of soils. There is still some uncertainty about the factors controlling the relative solubility of different phytolith types (Wilding and Drees, 1974; Alexandre *et al.*, 1997; Kelly *et al.*, 1998; Meunier, 2003; Fraysse *et al.*, 2005). Fraysse *et al.* (2006) found that the solubility product of bamboo phytoliths was 17 times greater than quartz. Their experiments support recent studies suggesting that the unexpected stability of kaolinite in the upper horizons of Amazonian ferralsols (Lucas *et al.*, 1993; Lucas, 2001), as well as the concentrations of DSi in drainage waters from humid tropical, temperate and high-latitude catchments, are controlled by phytolith production and recycling rather than by dissolution of quartz or other crystalline mineral phases (Oliva *et al.*, 1999; Miretsky *et al.*, 2001; Farmer *et al.*, 2004; Pokrovsky *et al.*, 2005). The estimated contribution of phytolith dissolution in soils to DSi export from terrestrial ecosystems ranged from *c*. 12 per cent in a French pine plantation (Bartoli, 1983), *c*. 30 per cent in Siberian larch forest–tundra (Pokrovsky *et al.*, 2005) and *c*. 75 per cent in Congo rainforest (Alexandre *et al.*, 1997), to ≤90 per cent in some Hawaiian catchments (Derry *et al.*, 2005) (Figure 4).

The concentration of phytoliths in vegetation, litter and upper soil horizons renders them vulnerable to entrainment by fluvial and aeolian processes. Higher plants also convert DSi in soil and swamp waters to silt- and sand-sized BSi particles, which are easily removed by surface runoff (Lovering, 1959; Cary *et al.*, 2005). Fluvial transport of silica in the form of BSi is another, potentially serious, source of bias in Si budgets for tropical ecosystems. For example, Cary *et al.* (2005) found that 1·3–4 wt per cent of the suspended load of rivers in Cameroon consisted of BSi, of which phytoliths made up 89–99 per cent.

Fragments of burnt grass epidermis from East African and Amazonian lake sediments commonly contain embedded phytoliths (Wooller *et al.*, 2000; Metcalfe, 2004), implying that savanna fires are a significant source of atmospheric and riverine particulate SiO_2. Charred particles from brush fires form an important component of the suspended load of the Congo, especially at the start of the wet season (Giresse *et al.*, 1990). The Si cycle in Lake Malawi, the deepest lake in the East African Rift system (*c*. 700 m), has been a major focus of the International Decade for the East

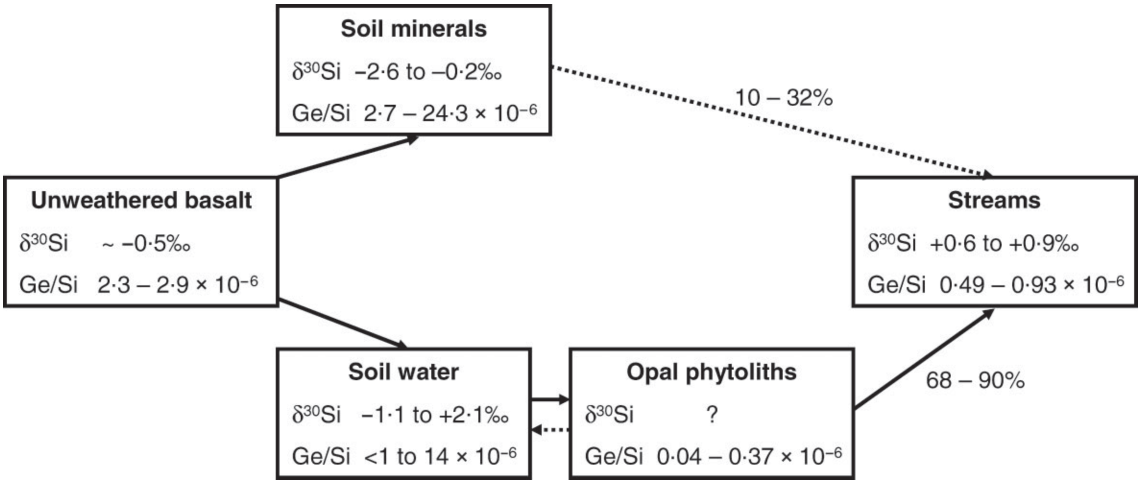

Figure 4. The biogeochemical Si cycle in a transport-limited tropical environment, rainforest on deep-weathered basalt, Hawaii, showing measured δ^{30}Si and Ge/Si values. From data in Kurtz *et al.* (2002), Derry *et al.* (2005) and Ziegler *et al.* (2005).

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African Lakes (IDEAL) (Johnson *et al.*, 2001, 2002; Bootsma *et al.*, 2003). Bootsma *et al.* (2003) estimated that BSi accounted for 60 per cent of its riverine Si input. Charred phytoliths from maize and natural vegetation predominated. Dust storms provide another mechanism by which phytoliths are exported from drylands to more humid areas or to the oceans (Baker, 1959; Twiss *et al.*, 1969; Melia, 1984; Bowdery, 1999). Transported BSi is believed to play an important role in the cementation of regolith to form weathering-resistant hardpans and silcretes (Clarke, 2003).

Biogenic Silica in Aquatic Ecosystems

Freshwater organisms actively cycle DSi leaking from terrestrial ecosystems. Although few submerged or floating vascular plants have been shown to contain significant amounts of BSi (Lovering, 1959; Sangster and Hodson, 1986), the number is increasing (Hodson *et al.*, 2005). *Trapa natans* (water chestnut) and *Ruppia maritima*, which colonizes salt lakes, are notable examples (Lovering, 1959; Hodson *et al.*, 2005).

On the other hand, Si is an essential nutrient for a small number of highly significant aquatic 'silica bioengineers' including diatoms, sponges and chrysophytes (flagellates) (Simpson and Volcani, 1981). Diatoms and chrysophytes also use dissolved inorganic C for photosynthesis. Diatoms are generally assumed to represent the most important Si sink in lakes and rivers, in view of their proliferation across a wide spectrum of depth habitats, water chemistries and flow conditions (Battarbee *et al.*, 2001). They synthesize DSi into nanospheres in the presence of proteins known as silaffins (Kröger *et al.*, 1999). These spheres then become the building blocks for frustule formation. An organic membrane protects the frustule from dissolution; thick polysaccharide gels associated with certain species add to this coating. The membrane aids the adsorption of dissolution-retarding cations such as Fe and Al (Lewin, 1961; van Bennekom, 1981), as well as providing a physical barrier. It decomposes rapidly on death, partly as a result of bacterial activity, which hastens the dissolution process, hinting at a bacterial loop in the Si cycle (Bidle *et al.*, 2003).

Siliceous sponges have a worldwide distribution in marine and fresh waters. They flourish in deep lakes with hydrothermal Si inputs such as Baikal, Tanganyika and Taupo (de Ronde *et al.*, 2002; Belikov *et al.*, 2005), but are also common in many shallower waterbodies, contributing *c.* 40 per cent of the BSi in the surface sediments of Florida lakes (Conley and Schelske, 1993). Biosilicification by sponges is similar to diatoms. They secrete needle-like spicules, which provide structural support and act as a defence against predation. The spicules enclose an axial organic filament containing the protein silicatein, which promotes condensation of amorphous silica. Maldonado *et al.* (2005) argued that the role of sponges in the global biogeochemical Si cycle has been underestimated, especially as sponge spicules are an order of magnitude larger and have a lower specific surface area than diatom frustules. A higher Al content may also make them significantly more resistant to dissolution (Conley and Schelske, 1993; Maldonado *et al.*, 2005).

Chrysophyte microalgae are efficient competitors for nutrients, but are more restricted in distribution than diatoms or sponges. They are common in the cold, oligotrophic waters of Arctic and Antarctic lakes (Sandgren, 1988; Zeeb and Smol, 2001) as well as in some tropical swamps (Ruppert *et al.*, 1993). Unlike diatoms, chrysophytes are relatively rare in alkaline, eutrophic waters, although exceptions exist. They adopt various life forms and are especially common in the plankton of lakes of low trophic status, where they use their flagella to stay in the pelagic zone and compete for nutrients. Their siliceous components, including scales and cysts, are synthesized in a similar way to those of sponges and diatoms.

Lakes are efficient silica traps. In Lake Malawi, diatoms dominate the phytoplankton during the dry season when upwelling brings nutrients to the surface from the anoxic hypolimnion. Only c. 1 per cent of the external Si input to the lake (*c.* 600–1100 mmol Si m^{-2} $year^{-1}$) is lost through the outflow. In contrast, diatom production cycles *c.* 9000 mmol Si m^{-2} $year^{-1}$, of which 7–11 per cent is buried in the sediments (Bootsma *et al.*, 2003). This study indicates that the sediments of deep lakes in unglaciated areas represent permanent sinks in the biogeochemical Si cycle on all but plate-tectonic time-scales, although different lakes leak varying amounts of DSi; for example 35 per cent of the inputs pass through Lake Superior (Johnson and Eisenreich, 1979) and 20 per cent through Lake Michigan (Schelske, 1985), both of which have larger outflows than Lake Malawi. Shallower lakes are less acquisitive and may release silica if they desiccate. Vast expanses of early Holocene diatomite in the Sahara are now being deflated and transported to the equatorial Atlantic and Amazonia as aeolian dust (Melia, 1984; Koren *et al.*, 2006). Under the drier, windier climate of the Last Glacial Maximum (LGM), the aeolian flux of BSi was greatly strengthened (Pokras and Mix, 1985). These examples suggest that lakes store significant amounts of BSi on time-scales varying from 1–10 years in hydrologically open systems to 10^6 years in the case of deep closed basins.

Tropical rivers dominate the fluvial transport of DSi to the oceans (Figure 2). Not surprisingly, siliceous organisms sequester large amounts of DSi (Saunders and Lewis Jr III, 1989), although Si recycling may be more rapid and storage of BSi in river channels and floodplains less permanent than in lakes. For example, sponges living on trees in the seasonally flooded forests along the Río Negro (a highly transport-limited tributary of the Amazon: Figure 3)

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convert large amounts of DSi to spicules that accumulate in alluvial deposits (Chauvel *et al.*, 1996). Extensive diatom growth on submerged wood leads to progressive silicification by silica gel, forming an additional Si storage (Konhauser *et al.*, 1992). The bed of the main Amazon near Manaus is also carpeted with sponges, despite the high turbidity of the water.

On a global basis, riverine ecosystems convert *c.* 16 per cent of the gross fluvial DSi load to suspended BSi (mainly diatoms), thereby decreasing the net export of DSi to the oceans (Conley, 1997). Human impacts such as eutrophication, modification of river channels and manipulation of macrophyte communities also affect silica transport (Conley *et al.*, 1993; Humborg *et al.*, 2000; Struyf and Conley, in press); the construction of reservoirs being an extreme example of how human agency increases fluvial filtering of Si on the continents. Declining river flow and DSi availability are exerting a negative influence on many lakes and coastal waters such as the Black and Baltic Seas by favouring toxic blooms of N-fixing cyanobacteria or flagellates (Humborg *et al.*, 2000; Schindler, 2006).

New Analytical Techniques for the Study of Si Biogeochemistry

Growing interest in the Si cycle has spawned a variety of geochemical techniques for the measurement of BSi concentrations in soils and sediments (Conley and Schelske, 2001). The one in most common use is wet chemical digestion in hot alkali (Na_2CO_3 or NaOH) (Conley, 1998; Saccone *et al.*, 2006). This is relatively straightforward and reproducible, provided that allowance is made for variations in dissolution rate between different forms of BSi such as diatoms and sponge spicules (Conley and Schelske, 1993). However, the application of BSi analysis to continental sediments, especially those of small lakes, seems likely be most insightful when combined with an assessment of the relative importance of the different terrestrial and aquatic microfossil types present (Smol *et al.*, 2001), even if this is based on smear slides rather than on full palaeoecological analyses.

Various isotopic techniques are currently being applied to reconstruct the environmental conditions prevailing when biogenic opal was formed. The oxygen-isotope record in diatoms has been hailed as a particularly useful tool for palaeoclimate reconstruction in carbonate-free systems (Leng and Barker, 2006). In freshwater lakes, the $^{18}O/^{16}O$ signal mainly reflects past changes in the isotope values of precipitation, which are strongly correlated with air temperature in mid- to high latitudes and with precipitation amount in the tropics (Rozanski *et al.*, 1993; Barker *et al.*, 2001; Shemesh *et al.*, 2001). Interpretation of oxygen-isotope measurements on opal phytoliths is more complex in view of the progressive enrichment in the heavier isotope between plant roots and aerial parts, where transpiration takes place in response to evaporative demand (Shahack-Gross *et al.*, 1996; Webb and Longstaffe, 2000, 2003, 2006). It is also possible to measure the stable carbon-isotope composition of organic inclusions in BSi: this provides a direct link to the carbon cycle at the time of plant or diatom growth (Kelly *et al.*, 1991; Singer and Shemesh, 1995).

Silicon isotopes hold great potential as tracers of the terrestrial Si cycle and its influence on the marine Si cycle (Douthitt, 1982; Lucas *et al.*, 1993; Ding *et al.*, 1996; De La Rocha, 2002, 2006; Basile-Doelsch *et al.*, 2005; Basile-Doelsch, 2006; Georg *et al.*, 2006). The cosmogenic radionuclide ^{32}Si (half-life *c.* 140–178 years) is being actively researched as a dating tool for waters and sediments of late Holocene age (Morgenstern *et al.*, 1996; Nijampurkar *et al.*, 1998). Silicon also possesses three stable isotopes, ^{28}Si, ^{29}Si and ^{30}Si, which are fractionated by chemical and biological processes. The most commonly used isotope parameter is $\delta^{30}Si$, defined as follows:

$$\delta^{30}\mathrm{Si} = [(R_{\mathrm{sample}}/R_{\mathrm{standard}}) - 1] \times 10^3 \tag{12}$$

where $R = {}^{30}Si/{}^{28}Si$ (Ding *et al.*, 1996). Measured $\delta^{30}Si$ values are expressed in per mille (‰) with respect to the NBS-28 standard. $\delta^{29}Si$ is sometimes measured (Georg *et al.*, 2006; Opfergelt *et al.*, 2006), but exhibits roughly half the signal amplitude.

When Si precipitates from aqueous solution to form secondary minerals or is sequestered by organisms, the light isotope ^{28}Si is preferentially partitioned into the precipitate, which acquires depleted (lower) values of $\delta^{29}Si$ and $\delta^{30}Si$ compared with the residual fluid, in which the heavier isotopes ^{29}Si and ^{30}Si accumulate. Hence, secondary clays and bulk soils display more negative isotope values than primary rock minerals, whereas those of ambient waters tend to be more positive (Ding *et al.*, 1996; Basile-Doelsch, 2006) (Figure 4). In transport-limited environments such as deeply weathered Hawaiian basalts, the $\delta^{30}Si$ values of bulk soil become progressively more negative with age, although the interpretation of Si isotope profiles is complicated by surface inputs of phytoliths and aeolian dust, which have higher $\delta^{30}Si$ values (Ziegler *et al.*, 2005). The isotopically most depleted continental Si pool (with $\delta^{30}Si$ values as low as −7·5‰) is found in groundwater silcretes formed by multistage dissolution and recrystallization of quartz (Basile-Doelsch *et al.*, 2005). In contrast, measured $\delta^{30}Si$ values for DSi in soil moisture and surface waters range from −1·1 to +3·4‰ (De La Rocha *et al.*, 2000; Ding *et al.*, 2004; Ziegler *et al.*, 2005; Basile-Doelsch, 2006).

In plants, which represent a closed system for Si, cumulative isotopic enrichment of DSi, and hence BSi, occurs as silica is precipitated along the water-flow paths from roots through stems to leaves or inflorescences and seeds (Ding *et al.*, 2005; Opfergelt *et al.*, 2006; Hodson *et al.*, 2008). This process, known as 'Rayleigh distillation' (De La Rocha, 2002) is beautifully illustrated by paddy rice, which exhibits δ^{30}Si values in BSi ranging from –0·8‰ in roots and −0·5 to +0·4‰ in stems and leaves, to +6.1‰ in rice grains (Ding *et al.*, 2005). Unfortunately, only accumulator plants such as horsetail, bamboo, banana, rice and wheat have been investigated to date (Douthitt, 1982; Ding *et al.*, 2005, 2008; Opfergelt *et al.*, 2006; Hodson *et al.*, 2008). It is not clear whether their Si-isotope values are representative of terrestrial biomass as a whole, or indeed whether systematic differences should be anticipated between different taxonomic groups, life forms and metabolic pathways.

Aquatic organisms also fractionate Si isotopes. Marine diatoms generally display near-zero to positive values (–0·3 to +2·6‰), resulting from progressive isotopic enrichment of surface waters as DSi is depleted during blooms (De La Rocha, 2002; Varela *et al.*, 2004). Although few measurements have been made in lakes, a comparable shift towards higher isotope values in both DSi and BSi is believed to occur in the epilimnion during diatom production (Alleman *et al.*, 2005). In contrast, marine sponges, which occupy benthic habitats and have a lower affinity for silica than diatoms, exhibit the lowest δ^{30}Si values so far measured in biological systems (–3·7 to −1·2‰) (Douthitt, 1982; De La Rocha, 2003); unfortunately no data are available for freshwater species. Once their isotope systematics have been investigated in sufficient detail, however, the degree of isotopic enrichment of DSi in surface waters (rivers and lakes) should provide a means of quantifying Si retention (fluvial filtering) by aquatic ecosystems. For example, Ding *et al.* (2004) attributed the strong downstream increase in the δ^{30}Si values of DSi in the Yangtse River, from +0·7 to +3·4‰, to trapping of silica by wetlands, rice paddies and lakes. These enhanced isotope values contrast markedly with those measured by Georg *et al.* (2006) in DSi from a typical rocky, weathering-limited Alpine catchment (+0·5 to +1·1‰). On a glacial–interglacial time-scale, variations in the riverine output of DSi or its mean δ^{30}Si may influence the average δ^{30}Si value of the world ocean (De La Rocha, 2006).

Ge/Si ratios also show great promise as a tracer for the biogeochemical Si cycle, with the potential to resolve ambiguities in the terrestrial Si-isotope record. Germanium, a trace element in the same group of the periodic table, behaves like a 'pseudoisotope' of silicon (Kurtz *et al.*, 2002), substituting for Si in the lattices of aluminosilicate minerals, notably hornblende, biotite mica and clays such as kaolinite (Ge/Si *c.* $2–7 \times 10^{-6}$). In contrast, quartz (pure SiO_2) typically has a low Ge content (Ge/Si *c.* $0·5 \times 10^{-6}$) (Filippelli *et al.*, 2000; Kurtz *et al.*, 2002; Derry *et al.*, 2006). Germanium exists in aqueous solution as $Ge(OH)_4$. The average molar Ge/Si ratio of unpolluted stream waters, *c.* $0·6 \times 10^{-6} \pm 10$ per cent, is significantly lower than typical bedrock ratios of *c.* $1–3 \times 10^{-6}$ (Froelich *et al.*, 1992; Kurtz *et al.*, 2002). Murnane and Stallard (1990) found that the Ge/Si ratios of Orinoco tributaries increased with chemical-weathering intensity, defined as the fraction of total Si dissolved from bedrock during weathering. The lowest DSi concentrations and highest Ge/Si ratios occurred in transport-limited catchments, regardless of lithology. According to the two-component Murnane–Stallard–Froelich (MSF) model of chemical weathering (Froelich *et al.*, 1992), this pattern arises from preferential retention of Ge in secondary aluminosilicates such as allophane (an amorphous hydroxyaluminosilicate: Figure 1) and kaolinite. The Ge/Si ratio of river waters then depends on the relative importance of a low-Ge end member derived from incongruent dissolution of fresh rock minerals, which dominates in weathering-limited environments (cf. Equation 5) and a high-Ge end member produced by congruent dissolution of pedogenic minerals, which dominates in transport-limited systems (cf. Equation 6) (Kurtz *et al.*, 2002).

The MSF model has recently been challenged by an elegant biogeochemical study of the runoff from tropical rainforest overlying deeply weathered Hawaiian basalt. Derry *et al.* (2005) established that the Ge/Si ratios of streamwaters were controlled by mixing between a Si-rich, Ge-poor component (Ge/Si ~$0·25 \times 10^{-6}$) derived from dissolution of opal phytoliths in upper soil horizons, and a Si-poor component with a relatively high Ge/Si ratio (Ge/Si ~$2·6 \times 10^{-6}$), originating through dissolution of secondary pedogenic minerals. On a discharge-weighted basis, BSi contributed 68–90 per cent of the DSi transported by Hawaiian stream water (Figure 4). Their analysis supports the catchment-ecosystem studies summarized in Table I. The general implication is that three possible sources of DSi must be considered in most geomorphological systems: weathering of primary rock minerals, weathering of pedogenic silicates and dissolution of BSi; hence the potential benefit of applying Si-isotope and Ge/Si tracers in combination to understand the dynamics of specific systems.

The Derry *et al.* (2005) study has important implications for our understanding of global patterns of silicate weathering and CO_2 drawdown on a Quaternary time-scale. Palaeoceanographers have attempted to reconstruct glacial–interglacial variations in continental weathering using the Ge/Si ratios of diatoms from deep-sea sediments, assuming that no significant fractionation of Ge and Si takes place during silicification (Froelich *et al.*, 1992; Bareille *et al.*, 1998) (Figure 5). Cores from the Southern Ocean show a consistent pattern of variation in Ge/Si over the past five glacial–interglacial cycles. The average ratio of Holocene core tops ($0·69 \pm 0·03 \times 10^{-6}$) is not significantly different from modern seawater, whereas the corresponding value for the LGM was $0·55 \pm 0·03 \times 10^{-6}$ (Bareille *et al.*,

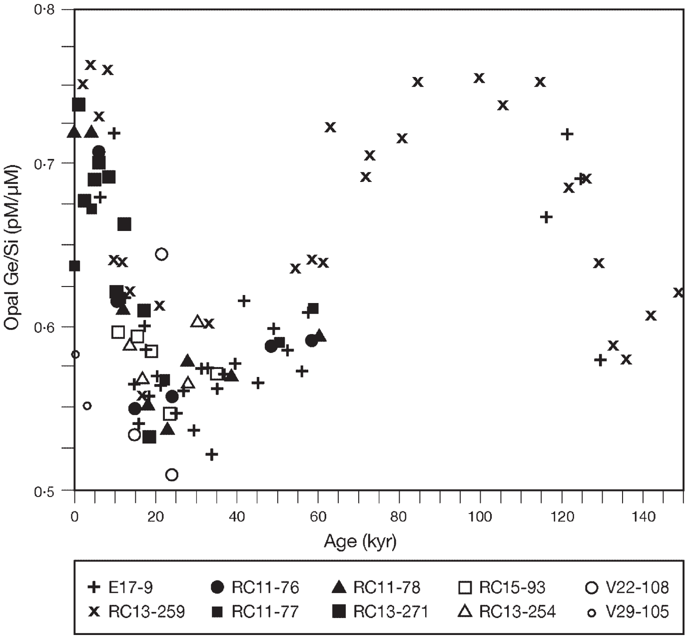

Figure 5. Glacial–interglacial variations in the Ge/Si ratios of diatoms from Southern Ocean sediment cores (from Froelich *et al.*, 1992).

1998). Based on the implied *c*. 20 per cent reduction in the average Ge/Si ratio of river water, Froelich *et al.* (1992) argued that weathering of primary rock minerals was of greater relative importance during glacial times than today, resulting in a doubling of the riverine DSi flux. This conclusion made some geochemists uncomfortable, leading to attempts to explain the observed glacial–interglacial signal as the result of temporal variations in opal diagenesis (Hammond *et al.*, 2000; King *et al.*, 2000). Jones *et al.* (2002) failed to reproduce the observed Ge/Si decrease in a global geochemical model of the LGM. All these studies, however, neglected the possibility that significant reserves of opal phytoliths with low Ge/Si ratios ($\sim 0{\cdot}25 \times 10^{-6}$) (Derry *et al.*, 2005) were mobilized from continental ecosystems by enhanced erosion and vegetation degradation during glacial times. This process could theoretically decouple variations in Ge/Si ratios in marine sediments from those of other lithogenic tracers such as Sr, Os and Pb isotopes (Henderson *et al.*, 1994; Oxburgh, 1998; Foster and Vance, 2006).

Case Studies of Late Quaternary Lake Sediments

Reconstructions of Quaternary changes in continental silicate weathering and CO_2 drawdown are currently dominated by geochemical analyses of marine cores and global geochemical models, which treat the land surface as devoid of life. This situation is unbalanced and unrealistic. Lake sediments provide a record of past environmental changes based on a wide array of terrestrial and aquatic indicators (Smol *et al.*, 2001). The following examples illustrate the scope for reconstructing past changes in the continental Si cycle, using multiproxy palaeolimnological data to shed light on biocycling by terrestrial and freshwater ecosystems.

In Lake Malawi, the mass accumulation rate (MAR) of BSi, consisting mainly of diatoms, approximately doubled between the LGM and the Holocene (Johnson *et al.*, 2002) (Figure 6). Assuming that the sediment depocentre did not shift significantly, a large increase in silica burial on a multimillennial time-scale could be sustained only by a corresponding increase in the riverine input of DSi (Bootsma *et al.*, 2003). The low BSi MAR during glacial times therefore can be attributed to a drop in the net output of DSi from the catchment under a cooler, drier climate, which also resulted in an increased proportion of periphytic diatoms (Johnson *et al.*, 2002). Further investigation using Si isotopes and/or Ge/Si ratios might determine whether this reduction in DSi output was associated with a decrease in silicate weathering or an increase in fluvial filtering of Si within the drainage basin.

A pioneering application of Ge/Si ratios to lake sediments was reported by Filippelli *et al.* (2000), who analysed two, carefully cleaned samples of Holocene diatoms from Dry Lake, a small moraine-dammed basin located at 2763 m

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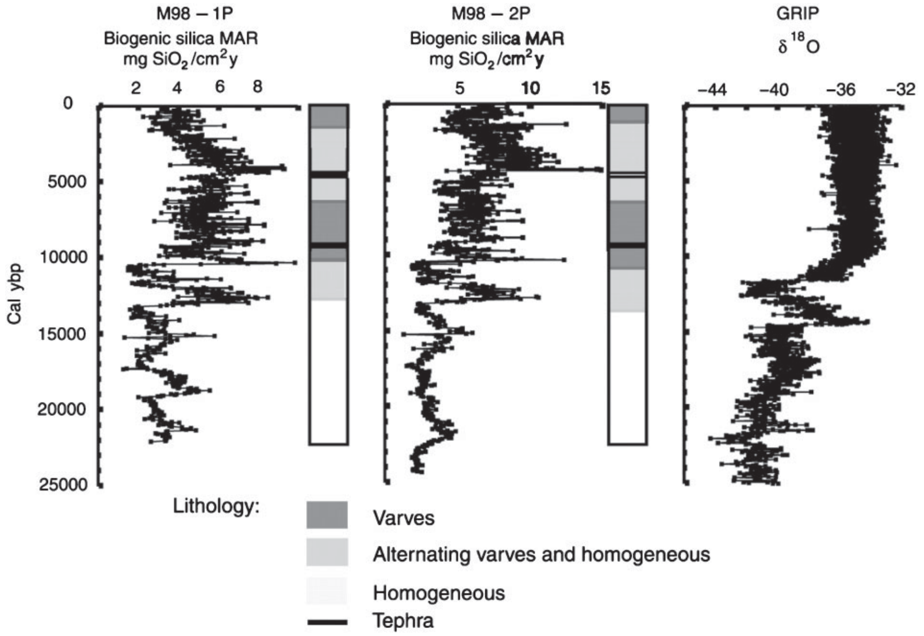

Figure 6. The glacial–interglacial increase in BSi accumulation (mainly diatoms) in Lake Malawi, southeastern Africa. The $\delta^{18}O$ record in the GRIP ice core, Greenland is shown for comparison. (From Johnson TC, Brown ET, McManus J, Barry S, Barker PA, Gasse F. 2002. A high-resolution paleoclimate record spanning the past 25 000 years in southern East Africa. *Science* **296**: 113–132. Reprinted with permission from A.A.A.S.).

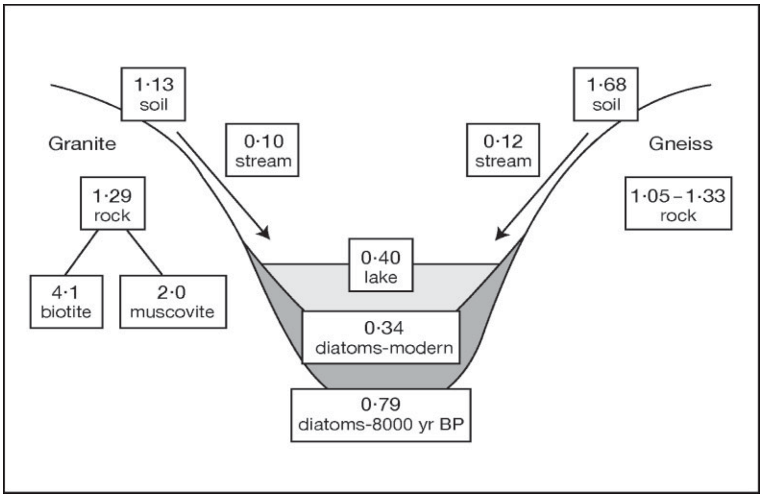

Figure 7. The Holocene decrease in the Ge/Si ratios of diatoms ($\times 10^{-6}$) in a core from Dry Lake, California, compared with modern data for rocks, soils and waters (from Filippelli *et al.*, 2000).

a.s.l. in the San Bernadino Mountains, California (Figure 7). The surrounding slopes consist of biotite–muscovite gneiss and granite, overlain by weakly developed alpine soils under open pine forest. Diatoms from the basal lake sediments (*c.* 8000 years BP) displayed a Ge/Si ratio of $0{\cdot}79 \times 10^{-6}$, more than twice as high as in sediments deposited during the past 100 years ($0{\cdot}33$–$0{\cdot}35 \times 10^{-6}$). Since diatoms do not fractionate Ge and Si with respect to their source water, Filippelli *et al.* (2000) attributed the observed temporal decrease in Ge/Si to preferential early Holocene weathering of micas with high Ge/Si ratios (Figure 7). An alternative view based on the Derry *et al.* (2005) model would be that post-glacial vegetation succession resulted in increasingly tight biocycling of Si, leading to the creation of a labile

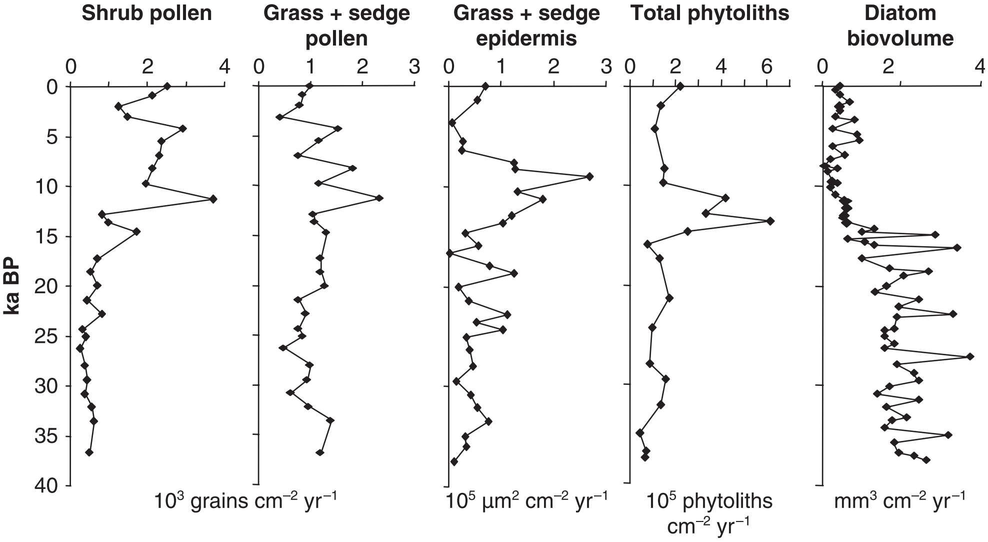

Figure 8. Palaeoecological evidence for glacial–interglacial changes in Si biocycling by the catchment–lake ecosystem of Lake Rutundu, Mount Kenya, based on lacustrine-sediment fluxes (from Street-Perrott *et al.*, 2008).

pool of stored BSi with low Ge/Si values in soils (and presumably a corresponding reduction in DSi output to streams). Clearly, a carefully chosen package of geochemical, isotopic and palaeoecological analyses would help to clarify the causes of long-term changes in the Si cycle within this weathering-limited geomorphological system.

Lake Rutundu is a small, closed maar lake situated at 3078 m a.s.l. in tall subalpine shrubland on Mount Kenya, East Africa. A core extending back to *c*. 38 300 years BP has been analysed for bulk and molecular carbon isotopes (Street-Perrott *et al.*, 2004), δ^{18}O and δ^{30}Si in diatom silica, and a wide range of sedimentological and palaeoecological indicators including magnetic susceptibility, pollen, grass epidermis, diatoms and opal phytoliths (Street-Perrott *et al.*, 2007; Street-Perrott *et al.*, 2008) (Figure 8). High δ^{18}O values in diatoms show that the climate prevailing during the LGM (38 300–14 300 years BP) was relatively dry (Street-Perrott *et al.*, 2008). The lake was surrounded by a sparse, C_4-dominated grassland dotted with fire-tolerant shrubs (Street-Perrott *et al.*, 2007). An increased input of soil nutrients, coupled with enhanced leakage of DSi from the catchment, led to a much higher accumulation rate of diatoms than today (Street-Perrott *et al.*, 2008). At *c*. 14 300 years BP, the transition to a warmer and wetter, but markedly seasonal, climate resulted in the establishment of a lush, mixed C_3–C_4 montane grassland subject to frequent grass fires, revealed by maxima in the fluxes of graminoid pollen, charred grass epidermis and grass phytoliths. A corresponding peak of spherical rugose phytoliths (Scurfield *et al.*, 1974) may represent wood from burned rainforest trees or subalpine shrubs. Meanwhile, the output of DSi and eroded soil from the catchment decreased, mainly as a result of increased graminoid biomass, leading to a collapse of diatom production in the lake. Since *c*. 9500 years BP, a decline in seasonal contrast and fire frequency has permitted colonization by tall subalpine shrubs with a C_3 grass understorey. Effective retention of Si by the catchment ecosystem is implied by low Holocene burial rates of both opal phytoliths and diatoms. This study suggests that glacial–interglacial variations in the relative extent and biomass of woody and herbaceous vegetation across intertropical Africa (Barker *et al.*, 2004) would have had a significant impact on fluvial outputs of DSi and BSi. It also shows that large quantities of phytoliths were lofted by grassland fires and transported in fragments of charred grass epidermis.

Conclusions

Geochemists have recognized since the late 19th century that the global carbon and silicon cycles are coupled on geological time-scales by chemical weathering of silicate minerals. Biologists discovered even earlier that accumulator plants and some freshwater organisms take up large quantities of Si from rocks, soils, lakes and rivers. Yet these separate bodies of knowledge were never integrated to arrive at an overall understanding of the biogeochemical cycle of Si and its significance for geomorphology and earth-system science. Almost every molecule of dissolved silica that

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finds its way into drainage waters (with the possible exception of some glacial melt streams) has first passed through an ecosystem, even if only a bacterial community living in the weathering rinds of boulders.

Higher plants accelerate silicate weathering by a factor of at least two to eight compared with bare rock surfaces. They are particularly effective in basaltic terrain. Measured biotic fluxes of Si through grassland and broad-leaved forest ecosystems are about two to ten times times larger than the net release of Si by mineral weathering (Table I), while in lakes, cycling of Si by diatoms may also exceed the annual input of DSi by an order of magnitude. In many parts of the world, the solubility of opal phytoliths controls the concentrations of DSi in runoff. At the present day, *c*. 5–50 per cent of the measured annual BSi production by terrestrial and freshwater ecosystems goes into storage, most notably in grasslands and young forests (Table I). At regional to global scales, fluvial filtering by biomass, soil and sediment storages may introduce substantial negative bias into estimates of denudation based on the dissolved load of rivers, particularly in transport-limited environments. In the case of Si, potential sources of error include sequestration of BSi as opal phytoliths in soils and aggrading ecosystems, accumulation of siliceous microfossils in alluvial, lacustrine and swamp sediments, and silicification of dead wood in tropical swamp forests. Biogenic silica forms *c*. 1–18 per cent of the suspended load of major rivers (Conley, 1997). It is also transported long distances by wind in dust and charred grass fragments. Hence, global models of the coupling between the C and Si cycles on decadal to glacial–interglacial time-scales must take into account the response of continental ecosystems to climatic and anthropogenic perturbations, including temporal variations in the effectiveness of fluvial filtering and aeolian transport.

Despite the recent advances summarized in this paper, there are still serious gaps in present understanding of the terrestrial Si cycle – few data exist for tropical savannas, wetlands, shrublands and tropical dry forests, for example. New geochemical and isotopic tracers hold considerable promise for quantifying both past and present biocycling of Si. They include the cosmogenic (^{32}Si) and stable isotopes of Si, other stable isotopes in BSi, and Ge/Si ratios. Measurement of BSi contents of sediments by alkali digestion should ideally be supplemented by microscopic analysis in order to evaluate the proportions derived from different sources; it is not valid to assume that all BSi particles present in soils are phytoliths and all those in waterlain sediments are diatoms. Multiproxy palaeolimnological studies of Quaternary lake sediments represent an underexploited but potentially valuable source of data on past changes in Si biocycling by both terrestrial and aquatic ecosystems, and will play a key role in validating future generations of global biogeochemical models.

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References

Alexandre A, Meunier J-D, Colin F, Koud J-M. 1997. Plant impact on the biogeochemical cycle of silicon and related weathering processes. *Geochimica et Cosmochimica Acta* **61**(3): 677–682.

Alleman LY, Cardinal D, Cocquyt C *et al.* 2005. Silicon isotopic fractionation in Lake Tanganyika and its main tributaries. *Journal of Great Lakes Research* **31**: 509–519.

Archer DE, Winguth A, Lea D, Mahowald N. 2000. What caused the glacial/interglacial pCO$_2$ cycles? *Reviews of Geophysics* **38**: 159–189.

Baker G. 1959. Opal phytoliths in some Victorian soils and 'red rain' residues. *Australian Journal of Botany* **7**: 64–87.

Bareille G, Labracherie M, Mortlock RA, Maier-Reimer E, Froelich PN. 1998. A test of $(Ge/Si)_{opal}$ as a paleorecorder of $(Ge/Si)_{seawater}$. *Geology* **26**(2): 179–182.

Barker PA, Street-Perrott FA, Leng MJ *et al.* 2001. A 14 ka oxygen isotope record from diatom silica in two alpine tarns on Mt. Kenya. *Science* **292**: 2307–2310.

Barker PA, Talbot MR, Street-Perrott FA, Marret F, Scourse J, Odada EO. 2004. Late Quaternary climatic variability in intertropical Africa. In *Past Climate Variability through Europe and Africa*, Battarbee RW, Gasse F, Stickley CE (eds). Springer: Dordrecht; 117–138.

Bartoli F. 1983. The biogeochemical cycle of silicon in two temperate forest ecosystems. *Ecological Bulletin* **35**: 469–476.

Basile-Doelsch I. 2006. Si stable isotopes in the Earth's surface: a review. *Journal of Geochemical Exploration* **88**(1–3): 252–256. DOI: 10.1016/j.gexplo.2005.08.050

Basile-Doelsch I, Meunier J-D, Parron C. 2005. Another continental pool in the terrestrial silicon cycle. *Nature* **433**: 399–402.

Battarbee RW, Jones VJ, Flower RJ *et al.* 2001. Diatoms. In *Tracking Environmental Change Using Lake Sediments. Volume 3: Terrestrial, Algal and Siliceous Indicators*, Smol JP, Birks HJB, Last WM (eds). Kluwer: Dordrecht; 155–202.

Belikov SI, Kaluzhnaya OV, Schoder HC, Krasko A, Muller IM, Muller WEG. 2005. Expression of silicatein in spicules from the Baikalian sponge *Lubomirskia baicalensis*. *Cell Biology International* **29**(11): 943–951.

Berner EK, Berner RA. 1996. *Global Environment: Water, Air, and Geochemical Cycles*. Prentice Hall: New York.

Berner RA. 1992. Weathering, plants, and the long-term carbon cycle. *Geochimica et Cosmochimica Acta* **56**: 3225–3231.

Berner RA. 1995. Chemical weathering and its effect on atmospheric CO_2 and climate. *Reviews in Mineralogy* **31**: 565–583.

Berner RA, Lasaga AC, Garrels RM. 1983. The carbonate–silicate geochemical cycle and its effect on atmospheric carbon dioxide over the past 100 million years. *American Journal of Science* **283**: 641–683.

Bidle KD, Brzezinski MA, Long RA, Jones JL, Azam F. 2003. Diminished efficiency in the oceanic silica pump caused by bacteria-mediated silica dissolution. *Limnology and Oceanography* **48**: 1855–1868.

Blecker SW, McCulley RL, Chadwick OA, Kelly EF. 2006. Biologic cycling of silica across a grassland bioclimosequence. *Global Biogeochemical Cycles* **20**(GB3023). DOI: 10.1029/2006GB002690

Bootsma HA, Hecky RE, Johnson TC, Kling HJ, Mwita J. 2003. Inputs, outputs, and internal cycling of silica in a large, tropical lake. *Journal of Great Lakes Research* **29**(Supplement 2): 121–138.

Bormann BT, Wang D, Bormann FH, Benoit G, April R, Snyder MC. 1998. Rapid, plant-induced weathering in an aggrading experimental ecosystem. *Biogeochemistry* **43**: 129–155.

Bowdery D. 1999. Taphonomy, phytoliths and the African dust plume. In *Taphonomy: The Analysis of Processes from Phytoliths to Megafauna*, Mountain M-J, Bowdery D (eds). Research Papers in Archaeology and Natural History, ANH Publications, Australian National University: Canberra; 3–8.

Brady PV, Carroll SA. 1994. Direct effects of CO_2 and temperature on silicate weathering: possible implications for climate control. *Geochimica et Cosmochimica Acta* **58**: 1853–1856.

Braun J-J, Ndam Ngoupayou JR, Viers J *et al.* 2005. Present weathering rates in a humid tropical watershed, Nsimi, South Cameroon. *Geochimica et Cosmochimica Acta* **69**(2): 357–387.

Carnelli AL, Madella M, Theurillat J-P. 2001. Biogenic silica production in selected alpine plant species and plant communities. *Annals of Botany* **87**: 425–434. DOI: 10.1006/anbo.2000.1355

Cary L, Alexandre A, Meunier J-D, Boeglin J-L, Braun J-J. 2005. Contribution of phytoliths to the suspended load of biogenic silica in the Nyong Basin rivers (Cameroon). *Biogeochemistry* **74**(1): 101–114. DOI: 10.1007/s10533-004-2945-1

Cawley JL, Burruss RC, Holland HD. 1969. Chemical weathering in central Iceland: an analog of pre-Silurian weathering. *Science* **391**: 391–392.

Chauvel A, Walker I, Lucas Y. 1996. Sedimentation and pedogenesis in a Central Amazonian black water basin. *Biogeochemistry* **33**: 77–95.

Clarke J. 2003. The occurrence and significance of biogenic opal in the regolith. *Earth-Science Reviews* **60**: 175–194.

Cochran MF, Berner RA. 1996. Promotion of chemical weathering by higher plants: field observations on Hawaiian basalts. *Chemical Geology* **132**: 71–77.

Conley DJ. 1997. Riverine contribution of biogenic silica to the oceanic silica budget. *Limnology and Oceanography* **42**: 774–777.

Conley DJ. 1998. An interlaboratory comparison for the measurement of biogenic silica in sediments. *Marine Chemistry* **63**: 39–48.

Conley DJ. 2002. Terrestrial ecosystems and the global biogeochemical silica cycle. *Global Biogeochemical Cycles* **16**(4): 68-61–68-69. DOI: 10.1029/2002GB001894

Conley DJ, Schelske CL. 1993. Potential role of sponge spicules in influencing the silicon biogeochemistry of Florida lakes. *Canadian Journal of Fisheries and Aquatic Science* **50**: 296–302.

Conley DJ, Schelske CL. 2001. Biogenic silica. In *Tracking Environmental Change Using Lake Sediments. Volume 3: Terrestrial, Algal and Siliceous Indicators*, Smol JP, Birks HJB, Last WM (eds). Kluwer: Dordrecht; 281–293.

Conley DJ, Schelske CL, Stoermer EF. 1993. Modification of the biogeochemical cycle of silica with eutrophication. *Marine Ecology Progress Series* **101**: 179–192.

Datnoff LE, Korndörfer GH, Snyder GH. 2001. *Silicon in Agriculture*. Elsevier Science: New York.

De La Rocha CL. 2002. Tracing the silica cycle with silicon isotopes. *Océanis* **28**(3–4): 369–389.

De La Rocha CL. 2003. Silicon isotope fractionation by marine sponges and the reconstruction of the silicon isotope composition of ancient deep water. *Geology* **31**: 423–426.

De La Rocha CL. 2006. Opal-based isotopic proxies of paleoenvironmental conditions. *Global Biogeochemical Cycles* **20**: GB4S09. DOI: 10.1029/2005GB002664

De La Rocha CL, Brzezinski MA, DeNiro MJ. 2000. A first look at the distribution of the stable isotopes of silicon in natural waters. *Geochimica et Cosmochimica Acta* **64**(14): 2467–2477.

De Ronde CEJ, Stoffers P, Garbe-Schonberg D *et al.* 2002. Discovery of active hydrothermal venting in Lake Taupo, New Zealand. *Journal of Volcanology and Geothermal Research* **115**(3–4): 257–275.

Derry LA, Kurtz AC, Ziegler K, Chadwick OA. 2005. Biological control of terrestrial silica cycling and export fluxes to watersheds. *Nature* **433**: 728–731. DOI: 10.1038/nature03299

Derry LA, Pett-Ridge JC, Kurtz AC, Troester JW. 2006. Ge/Si and $^{87}Sr/^{86}Sr$ tracers of weathering reactions and hydrologic pathways in a tropical granitoid system. *Journal of Geochemical Exploration* **88**(1–3): 271–271. DOI: 10.1016/j.gexplo.2005.08.054

Dessert C, Dupré B, Gaillardet J, François L, Allègre CJ. 2003. Basalt weathering laws and the impact of basalt weathering on the global carbon cycle. *Chemical Geology* **202**: 257–273.

Ding TP, Jiang SY, Wan DF, Li YH, Li JC, Song HB, Liu ZJ, Yao XM. 1996. *Silicon Isotope Geochemistry* (Ding TP, Tang LJ, Trans.). Geological Publishing House: Beijing.

Ding TP, Wan DF, Wang C, Zhang F. 2004. Silicon isotope compositions of dissolved silicon and suspended matter in the Yangtse River, China. *Geochimica et Cosmochimica Acta* **68**(2): 205–216. DOI: 10.1016/S0016-7037(03)00264-3

Ding TP, Ma GR, Shui MX, Wan DF, Li RH. 2005. Silicon isotope study on rice plants from the Zhejiang Province, China. *Chemical Geology* **218**: 41–50. DOI: 10.1016/j.chemgeo.2005.01.018

Ding TP, Zhou JX, Wan DF, Chen ZY, Wang CY, Zhang F. 2008. Silicon isotope fractionation in bamboo and its significance to the biogeochemical cycle of silicon. *Geochimica et Cosmochimica Acta* **72**(5): 1381–1395. DOI: 10.1016/j.gca.2008.01.008

Douthitt CB. 1982. The geochemistry of the stable isotopes of silicon. *Geochimica et Cosmochimica Acta* **46**: 1449–1458.

Drever JI, Zobrist J. 1992. Chemical weathering of silicate rocks as a function of elevation in the southern Swiss Alps. *Geochimica et Cosmochimica Acta* **56**: 3209–3216.

Dupré B, Dessert C, Oliva P, Goddéris Y, Viers J, François LM, Millot R, Gaillardet J. 2003. Rivers, chemical weathering and Earth's climate. *Comptes Rendus Geoscience* **335**: 1141–1160.

Epstein E. 1994. The anomaly of silicon in plant biology. *Proceedings of the National Academy of Sciences of the USA* **91**: 11–17.

Epstein E. 1999. Silicon. *Annual Review of Plant Physiology and Plant Molecular Biology* **50**: 641–664.

Euliss KW, Dorsey BL, Benke KC, Banks MK, Schwab AP. 2005. The use of plant tissue silica content for estimating transpiration. *Ecological Engineering* **25**: 343–348. DOI: 10.1016/j.ecoleng.2005.06.003

Exley C. 1998. Silicon in life: A bioinorganic solution to bioorganic essentiality. *Journal of Inorganic Biochemistry* **69**: 139–144.

Falkowski P, Scholes RJ, Boyle EA *et al.* 2000. The global carbon cycle: a test of our knowledge of Earth as a system. *Science* **290**: 291–296.

Falkowski PG, Katz ME, Knoll AH *et al.* 2004. The evolution of modern eukaryotic plankton. *Science* **305**: 354–360.

Farmer VI, Delbos E, Miller JD. 2004. The role of phytolith formation and dissolution in controlling concentrations of silica in soil solutions and streams. *Geoderma*.

Filipelli GM, Carnahan JW, Derry LA, Kurtz AC. 2000. Terrestrial records of Ge/Si cycling derived from lake diatoms. *Chemical Geology* **168**: 9–26.

Foster GL, Vance D. 2006. Negligible glacial–interglacial variation in continental chemical weathering rates. *Nature* **444**: 918–921. DOI: 10.1038/nature05365

Fraysse F, Cantais F, Pokrovsky OS, Schott J, Meunier J-D. 2005. Aqueous reactivity of phytoliths and plant litter: physico-chemical constraints on terrestrial biogeochemical cycle of silicon. *Journal of Geochemical Exploration* **88**(1–3): 202–205. DOI: 10.1016/j.gexplo.2005.08.039

Fraysse F, Pokrovsky OS, Schott J, Meunier J-D. 2006. Surface properties, solubility and dissolution kinetics of bamboo phytoliths. *Geochimica et Cosmochimica Acta* **70**: 1939–1951. DOI: 10.1016/j.gca.2005.12.025

Froelich PN, Blanc V, Mortlock RA *et al.* 1992. River fluxes of dissolved silicate to the ocean were higher during glacials: Ge/Si in diatoms, rivers and oceans. *Paleoceanography* **7**: 739–767.

Gaillardet J, Dupré B, Allègre CJ, Négrel P. 1997. Chemical and physical denudation in the Amazon River Basin. *Chemical Geology* **142**: 141–173.

Gaillardet J, Dupré B, Allègre CJ. 1999a. Geochemistry of large river suspended sediments: silicate weathering or recycling tracer? *Geochimica et Cosmochimica Acta* **63**: 4037–4051.

Gaillardet J, Dupré B, Louvat P, Allègre CJ. 1999b. Global silicate weathering and CO_2 consumption rates deduced from the chemistry of large rivers. *Chemical Geology* **159**: 3–30.

Garvin CJ. 2006. *An exploratory study of the terrestrial biogeochemical silicon cycle at a forested watershed in northern Vermont.* Unpublished MSc, Cornell University, http://hdl.handle.net/1813/2934.

Georg RB, Reynolds BC, Frank M, Halliday AN. 2006. Mechanisms controlling the silicon isotopic compositions of river waters. *Earth and Planetary Science Letters* **249**(3–4): 290–306.

Gibbs M, Kump LR. 1994. Global chemical erosion during the Last Glacial Maximum and the present: Sensitivity to changes in lithology and hydrology. *Paleoceanography* **9**: 529–543.

Giresse P, Ouetiningue R, Barusseau JP. 1990. Minéralogie et micro-granulométrie des suspensions et des alluvions du Congo et de l'Oubangui. *Sciences Géologiques, Bulletin* **43**(2–4): 151–173.

Hammond DE, McManus J, Berelson WM, Meredith C, Klinkhammer GP, Coale HK. 2000. Diagenetic fractionation of Ge and Si in reducing sediments: The missing Ge sink and a possible mechanism to cause glacial/interglacial variations in oceanic Ge/Si. *Geochimica et Cosmochimica Acta* **64**(14): 2453–4565.

Henderson GM, Martel DJ, O'Nions RK, Shackleton NJ. 1994. Evolution of seawater ^{87}Sr/^{86}Sr over the last 400 ka: The absence of glacial/interglacial cycles. *Earth and Planetary Science Letters* **128**: 643–651.

Hinsinger P, Fernandes Barros ON, Benedetti MF, Noack Y, Callot G. 2001. Plant-induced weathering of a basaltic rock: Experimental evidence. *Geochimica et Cosmochimica Acta* **65**(1): 137–152.

Hodson MJ, Parker AJ, Leng MJ, Sloane HJ. 2008. Silicone, oxygen and carbon isotope composition of wheat (*Triticum aestivum* L.) phytoliths implications for palaeoecology and archaeology. *Journal of Quartenary Science* **23**: 331–339.

Hodson MJ, Sangster AG. 1999. Aluminium/silicon interactions in conifers. *Journal of Inorganic Biochemistry* **76**(2): 89–98. DOI: 10.1016/S0162-0134(99)00119-1

Hodson MJ, White PJ, Mead A, Broadley MR. 2005. Phylogenetic variation in the silicon composition of plants. *Annals of Botany* **96**: 1027–1046. DOI: 10.1093/aob/mci255

Humborg C, Conley D, Rahm L, Wulff F, Cociasu A, Ittekkot V. 2000. Silicon retention in river basins: Far-reaching effects on biogeochemistry and aquatic food webs in coastal marine environments. *Ambio* **29**(1): 45–50.

Johnson TC, Eisenreich SJ. 1979. Silica in Lake Superior: mass balance considerations and a model for dynamic response to eutrophication. *Geochimica et Cosmochimica Acta* **43**: 77–91.

Johnson TC, Barry SL, Chan Y, Wilkinson P. 2001. Decadal record of climate variability spanning the past 700 yr in the Southern Tropics of East Africa. *Geology* **29**(1): 83–86.

Johnson TC, Brown ET, McManus J, Barry S, Barker PA, Gasse F. 2002. A high-resolution paleoclimate record spanning the past 25 000 years in southern East Africa. *Science* **296**: 113–132.

Jones IW, Munhoven G, Tranter M, Huybrechts P, Sharp MJ. 2002. Modelled glacial and non-glacial HCO_3^-, Si and Ge fluxes since the LGM: little potential for impact on atmospheric CO_2 concentrations and a potential proxy of continental chemical erosion, the marine Ge/Si ratio. *Global and Planetary Change* **33**: 139–153.

Jones LHP, Handreck KA. 1967. Silica in soils, plants and animals. *Advances in Agronomy* **19**: 107–149.

Kardjilov MI, Gíslason SR, Gísladóttir G. 2006. The effect of gross primary production, net primary production and net ecosystem exchange on the carbon fixation by chemical weathering of basalt in northeastern Iceland *Journal of Geochemical Exploration* **88**: 292–295. DOI: 10.1016/j.gexplo.2005.08.059

Kelly EF, Amundson RG, Marino BD, DeNiro MJ. 1991. Stable isotope ratios of carbon in phytoliths as a quantitative method of monitoring vegetation and climate change. *Quaternary Research* **35**(2): 222–233.

Kelly EF, Chadwick OA, Hilinski TE. 1998. The effect of plants on mineral weathering. *Biogeochemistry* **42**: 21–53.

Kidder DL, Gierlowski-Kordesch EH. 2005. Impact of grassland radiation on the nonmarine silica cycle and Miocene diatomite. *Palaios* **20**: 198–206.

King SL, Froelich PN, Jahnke RA. 2000. Early diagenesis of germanium in sediments of the Antarctic South Atlantic: In search of the missing Ge sink *Geochimica et Cosmochimica Acta* **64**(8): 1375–1390.

Knight CTG, Kinrade SD. 2001. A primer on the aqueous chemistry of silicon. In *Silicon in Agriculture*, Datnoff LE, Snyder GH, Korndörfer GH (eds). Studies in Plant Science, Elsevier: Amsterdam; 57–84.

Knoll MA, James WC. 1987. Effect of the advent and diversification of vascular land plants on mineral weathering through geologic time. *Geology* **15**: 1099–1102.

Konhauser KO, Mann H, Fyfe WS. 1992. Prolific organic SiO_2 precipitation in a solute-deficient river: Rio Negro, Brazil. *Geology* **20**: 227–230.

Koren I, Kaufman YJ, Washington R *et al.* 2006. The Bodélé depression: a single spot in the Sahara that provides most of the mineral dust to the Amazon forest. *Environmental Research Letters* **1**: 014005. DOI: 10.1088/1748-9326/1/1/014005

Kröger N, Deutzmann R, Sumper M. 1999. Polycationic peptides from diatom biosilica that direct silica nanosphere formation. *Science* **286**(5442): 1129–1132. DOI: 10.1126/science.286.5442.1129

Kump LR, Alley RB. 1994. Global chemical weathering on glacial time scales. In *Material Fluxes on the Surface of the Earth***,** Usselman TM, Hay WW (eds). National Academy Press: Washington, DC; 46–60.

Kump LR, Brantley SL, Arthur MA. 2000. Chemical weathering, atmospheric CO_2 and climate. *Annual Review of Earth and Planetary Sciences* **28**: 611–667.

Kump LR, Kasting JF, Crane RG. 2004. *The Earth System: an Introduction to Earth Systems Science*, 2nd edn. Pearson Prentice Hall: Upper Saddle River, New Jersey.

Kurtz AC, Derry LA, Chadwick OA. 2002. Germanium–silicon fractionation in the weathering environment. *Geochimica et Cosmochimica Acta* **66**: 1525–1537.

Leng MJ, Barker PA. 2006. A review of the oxygen isotope composition of lacustrine diatom silica for palaeoclimate reconstruction. *Earth-Science Reviews* **75**: 5–27. DOI: 10.1016/j.earscirev.2005.10.01

Lewin J. 1961. The dissolution of silica from diatom walls. *Geochimica et Cosmochimica Acta* **21**: 182–198.

Lewin J, Reimann BEF. 1969. Silicon and plant growth. *Annual Review of Plant Physiology* **20**: 289–304.

Loughnan FC. 1969. *Chemical Weathering of the Silicate Minerals*. American Elsevier: New York.

Lovering TS. 1959. Significance of accumulator plants in rock weathering. *Bulletin of the Geological Society of America* **70**: 781–800.

Lovering TS, Engel C. 1967. Translocation of silica and other elements from rock into *Equisetum* and three grasses. *United States Geological Survey Professional Paper* **594-B**: B1–B16.

Lucas Y. 2001. The role of plants in controlling rates and products of weathering: importance of biological pumping. *Annual Review of Earth and Planetary Sciences* **29**: 135–163.

Lucas Y, Luizao FJ, Chauvel A, Rouiller J, Nahon D. 1993. The relation between biological activity of the rain forest and mineral composition of soils. *Science* **260**: 521–523.

Ludwig W, Amiotte-Suchet P, Probst J-L. 1999. Enhanced chemical weathering of rocks during the last glacial maximum: a sink for atmospheric CO_2? *Chemical Geology* **159**: 147–161.

Ma JF, Miyake Y, Takahashi E. 2001. Silicon as a beneficial element for crop plants. In *Silicon in Agriculture*, Datnoff LE, Snyder GH, Korndörfer GH (eds). Studies in Plant Science, Elsevier: Amsterdam; 17–39.

Ma JF, Mitani N, Nagao S *et al.* 2004. Characterization of the silicon uptake system and molecular mapping of the silicon transporter gene in rice. *Plant Physiology* **136**(2): 3284–3289.

Maldonado M, Carmona C, Velasquez Z, Puig A, Cruzado A, Lopez A, Young CM. 2005. Siliceous sponges as a silicon sink: An overlooked aspect of benthopelagic coupling in the marine silicon cycle. *Limnology and Oceanography* **50**(3): 799–809.

Markewitz D, Richter DD. 1998. The *bio* in aluminium and silicon biogeochemistry. *Biogeochemistry* **42**: 235–252.

Marschner H. 1995. *Mineral Nutrition of Higher Plants* (2nd ed). Academic Press: London.

McCarthy TS, McIver JR, Cairncross B, Ellery WN, Ellery K. 1989. The inorganic geochemistry of peat from the Maunachira channel-swamp system, Okavango Delta, Botswana. *Geochimica et Cosmochimica Acta* **53**: 1077–1089.

McNaughton SJ, Tarrants JL. 1983. Grass leaf silicification: Natural selection for an inducible defense against herbivores. *Proceedings of the National Academy of Sciences of the USA* **80**: 790–791.

Melia MB. 1984. The distribution and relationship between palynomorphs in aerosols and deep-sea sediments off the coast of Northwest Africa. *Marine Geology* **58**: 345–371.

Metcalfe PR. 2004. *The Late Quaternary History of the Rainforest–Savanna Boundary of Southwest Amazonia.* Unpublished Ph.D., University of Wales, Swansea.

Meunier J-D. 2003. Le rôle des plantes dans le transfert du silicium à la surface des continents. *Comptes Rendus Geoscience* **335**: 1199–1206.

Meunier J-D, Colin F, Alarcon C. 1999. Biogenic silica storage in soils. *Geology* **27**(9): 835–838.

Meunier J-D, Alexandre A, Colin F, Braun J-J. 2001. Intérêt de l'étude du cycle biogéochimique du silicium pour interpréter la dynamique des sols tropicaux. *Bulletin de la Société géologique de France* **172**(5): 533–538.

Meybeck M, Vörösmarty C. 2005. Fluvial filtering of land-to-ocean fluxes: from natural Holocene variations to Anthropocene. *Comptes Rendus Geoscience* **337**: 107–123. DOI: 10.1016/j.crte.2004.09.016

Miretsky P, Conzonno V, Fernández Cirelli A. 2001. Geochemical processes controlling silica concentrations in groundwaters of the Salado River drainage basin, Argentina. *Journal of Geochemical Exploration* **73**: 155–166.

Mora CI, Driese SG, Colarusso LA. 1996. Middle to Late Paleozoic atmospheric CO_2 levels from soil carbonate and soil organic matter. *Science* **271**: 1105–1107.

Morgenstern U, Taylor CB, Parrat Y, Gäggeler HW, Eichler B. 1996. ^{32}Si in precipitation: evaluation of temporal and spatial variation and as dating tool for glacial ice. *Earth and Planetary Science Letters* **144**(1–2): 289–296. DOI: 10.1016/0012-821X(96)00160-4

Morris HT. 1996. Thomas Seward Lovering. In *Biographical Memoirs, National Academy of Sciences*, **69**. National Academies Press: Washington, DC; 176–187.

Mortatti J, Probst J-L. 2003. Silicate rock weathering and atmospheric/soil CO_2 uptake in the Amazon Basin estimated from river water geochemistry: seasonal and spatial variations. *Chemical Geology* **197**: 177–196.

Moulton KL, West J, Berner RA. 2000. Solute flux and mineral mass balance approaches to the quantification of plant effects on silicate weathering. *American Journal of Science* **300**: 539–570.

Munhoven G. 2002. Glacial–interglacial changes in continental weathering: estimates of the related CO_2 and HCO_3^- flux variations and their uncertainties. *Global and Planetary Change* **33**: 155–176.

Munhoven G, François LM. 1996. Glacial–interglacial variability of atmospheric CO_2 due to changing continental silicate weathering: a model study. *Journal of Geophysical Research* **101**(D16): 21423–421437.

Murnane RJ, Stallard RF. 1990. Germanium and silicon in rivers of the Orinoco drainage basin. *Nature* **344**: 749–752.

Nijampurkar VN, Rao DK, Oldfield F, Renberg I. 1998. The half-life of 32Si: a new estimate based on varved lake sediments. *Earth and Planetary Science Letters* **163**(1–4): 191–196.

Norris AR, Hackney CT. 1999. Silica content of a mesohaline tidal marsh in North Carolina. *Estuarine, Coastal and Shelf Science* **49**: 597–605.

Oliva P, Viers J, Dupré B *et al.* 1999. The effect of organic matter on chemical weathering: Study of a small tropical watershed: Nsimi-Zoétélé, Cameroon. *Geochimica et Cosmochimica Acta* **63**(23/24): 4013–4035.

Opfergelt S, Cardinal D, Henriet C, André L, Delvaux B. 2006. Silicon isotope fractionation between plant parts in banana: In situ vs. in vitro. *Journal of Geochemical Exploration* **88**(1–3): 224–227. DOI: 10.1016/j.gexplo.2005.08.044

Oxburgh R. 1998. Variations in the osmium isotope composition of sea water over the past 200 000 years. *Earth and Planetary Science Letters* **159**: 183–191.

Piperno DR. 1988. *Phytolith Analysis: An Archaeological and Geological Perspective*. Academic Press: San Diego.

Pokras EM, Mix AC. 1985. Eolian evidence for spatial variations of Late Quaternary climates in tropical Africa. *Quaternary Research* **24**(2): 137–149.

Pokrovsky OS, Schott J, Kudryavtzev DI, Dupré B. 2005. Basalt weathering in Central Siberia under permafrost conditions. *Geochimica et Cosmochimica Acta* **69**(24): 5659–5680.

Raven JA. 1983. The transport and function of silicon in plants. *Biological Reviews* **58**: 179–207.

Richards BN. 1974. *Introduction to the Soil Ecosystem*. Longman: Harlow.

Richmond KE, Sussman M. 2003. Got silicon? The non-essential beneficial plant nutrient. *Current Opinion in Plant Biology* **6**: 268–272.

Rozanski K, Araguás-Araguás L, Gonfiantini R. 1993. Isotopic patterns in modern global precipitation. In *Climate Change in Continental Isotopic Records*, Geophysical Monograph, **78**. American Geophysical Union: Washington; 1–36.

Ruppert LF, Neuzil SG, Cecil CB, Kane JS. 1993. Inorganic constituents from samples of a domed and a lacustrine peat, Sumatra, Indonesia. In *Ancient Coal-Forming Environments*, Geological Society of America Special Paper, Cobb JC, Cecil CB (eds). Geological Society of America: Boulder, Colorado; 83–96.

Saccone L, Conley DJ, Sauer D. 2006. Methodologies for amorphous silica analysis. *Journal of Geochemical Exploration* **88**(1–3): 235–238. DOI: 10.1016/j.gexplo.2005.08.045

Sandgren CD. 1988. The ecology of chrysophyte flagellates: their growth and perennation strategies as freshwater phytoplankton. In *Growth and Reproductive Strategies of Freshwater Phytoplankton*, Sandgren CD (ed.). CUP: Cambridge; 9–104.

Sangster AG, Hodson MJ. 1986. Silica in higher plants. In *Silicon Biochemistry*, Evered D, O'Connor M (eds). Ciba Foundation Symposium, John Wiley: Chichester; 90–107.

Sangster AG, Hodson MJ, Tubb HJ. 2001. Silicon deposition in higher plants. In *Silicon in Agriculture*, Datnoff LE, Snyder GH, Korndörfer GH (eds). Studies in Plant Science, Elsevier: Amsterdam; 85–113.

Saunders JF, Lewis Jr. III WM. 1989. Transport of major solutes and the relationship between solute concentrations and discharge in the Apure River, Venezuela. *Biogeochemistry* **8**(101–113).

Schelske CL. 1985. Biogeochemical silica mass balance in Lake Michigan and Lake Superior. *Biogeochemistry* **1**: 197–218.

Schelske CL, Stoermer EF, Conley D, Robbins JA, Glover R. 1983. Early eutrophication in the lower Great Lakes: New evidence from biogenic silica in sediments. *Science* **222**: 320–322.

Schindler DW. 2006. Recent advances in the understanding and management of eutrophication. *Limnology and Oceanography* **51**: 356–363.

Scurfield G, Anderson CA, Segnit ER. 1974. Silica in woody stems. *Australian Journal of Botany* **22**: 211–229.

Shahack-Gross R, Shemesh A, Yakir D, Weiner S. 1996. Oxygen isotopic composition of opaline phytoliths: Potential for terrestrial climatic reconstruction. *Geochimica et Cosmochimica Acta* **60**(20): 3949–3953.

Shemesh A, Rosqvist G, Rietti-Shati M *et al.* 2001. Holocene climatic change in Swedish Lapland inferred from an oxygen-isotope record of lacustrine biogenic silica. *The Holocene* **11**: 447–454.

Sigman DM, Boyle EA. 2000. Glacial/interglacial variations in atmospheric carbon dioxide. *Nature* **407**: 859–869.

Simonson RW. 1995. Airborne dust and its significance to soils. *Geoderma* **65**: 1–43.

Simpson TL, Volcani BE. 1981. *Silicon and Siliceous Structures in Biological Systems*. Springer-Verlag: New York.

Singer AJ, Shemesh A. 1995. Climatically linked carbon isotope variation during the past 430 000 years in Southern Ocean sediments. *Paleoceanography* **10**(2): 171–178. DOI: 10.1029/94PA03319

Smetacek V. 1999. Diatoms and the ocean carbon cycle. *Protist* **150**: 25–32.

Smol JP, Birks HJB, Last WM (eds). 2001. *Tracking Environmental Change Using Lake Sediments. Volume 3: Terrestrial, Algal and Siliceous Indicators*. Dordrecht: Kluwer.

Stallard RF. 1995. Tectonic, environmental and human aspects of weathering and erosion: a global review using a steady-state perspective. *Annual Review of Earth and Planetary Sciences* **23**: 11–39.

Stallard RF. 1998. Terrestrial sedimentation and the carbon cycle: coupling weathering and erosion to carbon burial. *Global Biogeochemical Cycles* **12**: 231–257.

Street-Perrott FA, Ficken KJ, Huang Y, Eglinton G. 2004. Late Quaternary changes in carbon cycling on Mt. Kenya, East Africa: an overview of the d^{13}C record in lacustrine organic matter. *Quaternary Science Reviews* **23**: 861–879.

Street-Perrott FA, Barker PA, Swain DL, Ficken KJ, Wooller MJ, Olago DO, Huang Y. 2007. Late Quaternary changes in ecosystems and carbon cycling on Mt. Kenya, East Africa: a landscape-ecological perspective based on lake-sediment fluxes. *Quaternary Science Reviews* **26**(13–14): 1838–1860. DOI: 10.1016/j.quascirev.2007.02.014

Street-Perrott FA, Barker PA, Leng MJ, Sloane HJ, Wooller MJ, Ficken KJ, Swain DL. 2008. Towards an understanding of Late Quaternary variations in the continental biogeochemical cycle of silicon: multi-isotope and sediment-flux data for Lake Rutundu, Mt. Kenya, East Africa, since 38 ka BP. *Journal of Quaternary Science* **23**: 375–387.

Struyf E, Conley DJ. In press. Silica: an essential nutrient in wetland biogeochemistry. *Frontiers in Ecology and the Environment*. DOI: 10.1089/070126

Struyf E, Van Damme S, Gribsholt B *et al.* 2007. *Phragmites australis* and silica cycling in tidal wetlands. *Aquatic Botany* **87**: 134–140.

Stumm W, Morgan JJ. 1970. *Aquatic Chemistry: An Introduction Emphasizing Chemical Equilibria in Natural Waters*. Wiley-Interscience: New York.

Summerfield MA, Hulton NJ. 1994. Natural controls of fluvial denudation rates in major world drainage basins. *Journal of Geophysical Research* **99**(B7): 13871–813883.

Sundquist ET. 1985. Geological perspectives on carbon dioxide and the carbon cycle. In *The Carbon Cycle and Atmospheric CO_2: Natural Variations Archaean to Present*, Sundquist E, Broecker W (eds). American Geophysical Union: Washington, DC; 5–59.

Takahashi E, Ma JF, Miyake Y. 1990. The possibility of silicon as an essential element for higher plants. *Comments on Agricultural and Food Chemistry* **2**(2): 99–122.

Tranter M, Huybrechts P, Munhoven G *et al.* 2002. Direct effects of ice sheets on terrestrial bicarbonate, sulphate and base cation fluxes during the last glacial cycle: minimal impact on atmospheric CO_2 concentrations. *Chemical Geology* **190**: 33–44.

Twiss PC, Suess E, Smith RM. 1969. Morphological classification of grass phytoliths. *Soil Science Society of America Proceedings* **33**: 109–115.

Van Bennekom AJ. 1981. On the role of aluminium in the dissolution kinetics of diatom frustules. In *Proceedings of the 6th International Symposium on Recent and Fossil Diatoms*, Ross R (ed.). Koeltz: Koenigstein; 455–456.

Van Hees PAW, Jones DL, Jentschke G, Godbold DL. 2004. Mobilization of aluminium, iron and silicon by *Picea abies* and ectomycorrhizas in a forest soil. *European Journal of Soil Science* **55**: 101–111. DOI: 10.1046/j.1365-2389.2003.00581.x

Varela DE, Pride CJ, Brzezinski MA. 2004. Biological fractionations of silicon isotopes in southern ocean surface waters. *Global Biogeochemical Cycles* **18**: GB1047. DOI: 10.1029/2003GB002140

Walker JCG, Hays PB, Kasting JF. 1981. A negative feedback mechanism for the long-term stabilization of Earth's surface temperature. *Journal of Geophysical Research* **86**: 9776–9782.

Webb EA, Longstaffe FJ. 2000. The oxygen isotopic compositions of silica phytoliths and plant water in grasses: Implications for the study of palaeoclimate. *Geochimica et Cosmochimica Acta* **64**(5): 767–780.

Webb EA, Longstaffe FJ. 2003. The relationship between phytolith- and plant-water $\delta^{18}O$ values in grasses. *Geochimica et Cosmochimica Acta* **67**(8): 1437–1449. DOI: 10.1016/S0016-7037(02)01300-5

Webb EA, Longstaffe FJ. 2006. Identifying the δ^{18}O signature of precipitation in grass cellulose and phytoliths: Refining the paleoclimate model. *Geochimica et Cosmochimica Acta* **70**: 2417–2426.

Wigley TML, Schimel DS. 2000. *The Carbon Cycle*. Cambridge University Press: Cambridge.

Wilding LP, Drees LR. 1974. Contributions of forest opal and associated crystalline phases to fine silt and clay fractions of soils. *Clays and Clay Minerals* **22**: 295–306.

Wooller MJ, Street-Perrott FA, Agnew ADQ. 2000. Late Quaternary fires and grassland palaeoecology of Mt. Kenya, East Africa: evidence from charred grass cuticles in lake sediments. *Palaeogeography, Palaeoclimatology, Palaeoecology* **164**: 207–230.

Wüst RAJ, Bustin RM. 2003. Opaline and Al–Si phytoliths from a tropical mire system of West Malaysia: abundance, habit, elemental composition, preservation and significance. *Chemical Geology* **200**: 267–292. DOI: 10.1016/S0009-2541(03)00196-7

Yool A, Tyrrell T. 2003. Role of diatoms in regulating the ocean's silicon cycle. *Global Biogeochemical Cycles* **17**(4): 1103. DOI: 10.1029/2002GB002018

Zeeb BA, Smol JP. 2001. Chrysophyte scales and cysts. In *Tracking Environmental Change Using Lake Sediments. Volume 3: Terrestrial, Algal and Siliceous Indicators*, Smol JP, Birks HJB, Last WM (eds). Kluwer: Dordrecht; 203–223.

Ziegler K, Chadwick OA, Brzezinski MA, Kelly EF. 2005. Natural variations of δ30Si ratios during progressive basalt weathering, Hawaiian Islands. *Geochimica et Cosmochimica Acta* **69**(19): 4597–4610.