Tracing the origin of dissolved silicon transferred from various soil-plant systems towards rivers: a review

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Received: 12 July 2010 – Accepted: 24 July 2010 – Published: 11 August 2010

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Published by Copernicus Publications on behalf of the European Geosciences Union.
Abstract

Silicon (Si) released as H$_4$SiO$_4$ by weathering of Si-containing solid phases is partly recycled through vegetation before its land-to-rivers transfer. By accumulating in terrestrial plants to a similar extent as some major macronutrients (0.1–10% Si dry weight), Si becomes largely mobile in the soil-plant system. Litter-fall leads to a substantial reactive biogenic silica pool in soil, which contributes to the release of dissolved Si (DSi) in soil solution. Understanding the biogeochemical cycle of silicon in surface environments and the DSi export from soils into rivers is crucial given that the marine primary bio-productivity depends on the availability of H$_4$SiO$_4$ for phytoplankton that requires Si. Continental fluxes of DSi seem to be deeply influenced by climate (temperature and runoff) as well as soil-vegetation systems. Therefore, continental areas can be characterized by various abilities to transfer DSi from soil-plant systems towards rivers. Here we pay special attention to those processes taking place in soil-plant systems and controlling the Si transfer towards rivers. We aim at identifying relevant geochemical tracers of Si pathways within the soil-plant system to obtain a better understanding of the origin of DSi exported towards rivers. In this review, we compare different soil-plant systems (weathering-unlimited and weathering-limited environments) and the variations of the geochemical tracers (Ge/Si ratios and $\delta^{30}$Si) in DSi outputs.

1 Introduction

Silicon (Si) is the second most abundant element of the Earth’s crust with a mean content of 28.8 wt% (Wedepohl, 1995) and it occurs in a large range of minerals at the earth surface, ranging from <0.5 wt% to $\sim$47 wt% in the pedosphere (McKeague and Cline, 1963a).

As the ultimate source, chemical weathering of silicate minerals liberates dissolved Si (DSi) as monosilicic acid (H$_4$SiO$_4^0$). DSi contributes to soil formation through biogeochemical reactions on continents – such as (1) neoformation of secondary min-
erals (Drees et al., 1989; Wada, 1989; White, 1995), (2) adsorption onto Fe and Al (hydr)oxides (Jones and Handreck, 1963; McKeague and Cline, 1963b), and (3) uptake by plants and return of biogenic silica (BSi) on topsoil (Jones and Handreck, 1965) – and is carried from the lithosphere to the hydrosphere (Drever, 1988; Conley, 2002; Conley et al., 2006; Sommer et al., 2006). Over geological timescales (>10^6 years), weathering of silicate minerals plays an integral role in soil development promoting the decrease in atmospheric CO_2 (Rai and Kittrick, 1989; Chadwick et al., 1994; White and Blum, 1995; Berner, 1997). Indeed, the interaction between the Si cycle and C cycle regulates the atmospheric CO_2 through silicate mineral weathering (Berner, 1997) and the DSi nutrition of phytoplankton CO_2-consumers in oceans (Conley et al., 1993; Smetacek, 1999; Tréguer and Pondaven, 2000). The leaching of DSi from soil to river strongly impacts the oceanic biogeochemical cycle of Si, as the land-ocean flux would contribute to more than 80% of the input of DSi in the oceans (Tréguer et al., 1995).

In the terrestrial Si cycle, higher plants largely contribute to the global Si cycle since their annual BSi production ranges from 1.7 to 5.6×10^{12} kg Si yr^{-1} (Conley, 2002), which rivals BSi production of diatoms in the oceans (6.7×10^{12} kg Si yr^{-1}) (Tréguer et al., 1995). More recently, BSi biologically fixed was shown to be at 2.5×10^{12} kg Si yr^{-1} (Laruelle et al., 2009), which is in the range of Conley (2002).

The global Si cycle is influenced by the type of vegetation (Bartoli, 1983; Alexandre et al., 1997; Blecker et al., 2006; Cornelis et al., 2010a), the stage of soil development (Henriet et al., 2008a,b), the climate characterized by specific moisture and temperature (Raven, 1983; White and Blum, 1995), anthropogenic actions (Conley et al., 1993, 2002), and orogenesis at the geological timescale (Raymo et al., 1988; Exley, 1998).

Despite Si (i) being a quantitatively important pool in soil, (ii) having a vital effect on plant productivity, (iii) and representing a fundamental link with the C-cycle, the role of the type of ecosystem on the biogeochemical Si cycle and its strategic importance in the transfer of Si towards the hydrosphere are poorly studied. Sommer et al. (2006) summarize the existing knowledge on Si pools in soils and fluxes within the
terrestrial biogeosphere. Conley (2002) demonstrates that biological processes in terrestrial ecosystems play an important role in global Si mass balances. However, the impact of different soil-plant systems on the continental DSi flux to the hydrosphere is not reviewed in greater detail. Therefore, the major challenges of this review are (i) to identify the Si-components and processes controlling DSi concentration in weathering environments (see Sect. 2), (ii) to assess processes governing the transfer of DSi from the soil-plant system towards rivers (see Sect. 3), (iii) to identify relevant geochemical tracers of Si pathways within the soil-plant system (see Sect. 4) and (iv) to compare different soil-plant environments and the variations of the tracers in DSi outputs (see Sect. 5).

2 Processes controlling the dissolved Si concentration in weathering environments

Silicon is a main component of soil solutions and occurs mainly in the molecular form of uncharged monomeric silicic acid $H_4SiO_4$ at common soil pH values (Iler, 1979). Silicon concentrations in soil solution can range from 0.01 to 1.99 mM Si (Karathanasis, 2002), but more commonly from 0.1 to 0.6 mM (Faure, 1991; Epstein, 2001).

Silicon hardly forms complexes with dissolved organic matter, but can combine with Al along the whole soil solution range of pH to form colloidal Al-Si polymers (Doucet et al., 2001). The aqueous chemistry of Si is regulated by a number of linked processes (Fig. 1): (i) dissolution of the Si-containing solid phases, (ii) precipitation and neo-formation of authigenic Si-constituents, (iii) Si adsorption/desorption on various solid phases, (iv) Si absorption by vegetation and micro-organisms, (v) preservation of stable Si forms in the profile and (vi) external atmospheric inputs. The continental Si cycle can be represented by five compartments (Fig. 1): soil solution, groundwater, rivers, biomass and soils, which are linked to the global Si cycle by two other major compartments (oceans and atmosphere).
2.1 Solubility of Si-minerals

In rocks, Si ranges from more than 46.5% (e.g., orthoquartzite) to 23% in basic rocks (e.g., basalt) to trace amounts in carbonaceous rocks (e.g., limestones and carbonatites) (Monger and Kelly, 2002). In derived soils, Si ranges from 46.0% in silcretes to 7.9% in petrocalcic horizons, and even lower in some highly weathered Oxisols as bauxites or ferricretes (Monger and Kelly, 2002). Soils mainly contain Si as silica minerals, primary silicates and secondary silicates, especially phyllosilicates (Iler, 1979). More than 100 relatively common crystallized silicates have been listed in soils in addition to an important variety of amorphous forms of inorganic and biogenic silica as well as poorly-crystalline silicates (McKeague and Cline, 1963a) (Fig. 2). The most common inorganic Si bearing phases are primary silicates, secondary aluminosilicates and secondary silica precipitates in various forms.

Primary minerals inherited in soils are concentrated in sand and silt fractions (50–2000 µm and 2–50 µm, respectively). Conversely, secondary minerals are concentrated in the clay fraction (<2 µm) as a result of pedogenic processes (Allen and Hajek, 1989), involving phyllosilicates and Al-Fe (hydr)oxides. As shown in Fig. 2, Si also occurs as poorly crystalline phases such as short-range ordered silicates (allophane and imogolite), and micro-crystalline phases such as authigenic quartz and chalcedony. Poorly ordered Al-Si compounds with a molar Si:Al ratio of 1:2 to 1:1 are likely to occur in acid soils (Farmer et al., 1980; Buurman and Van Reeuwijk, 1984; Wada, 1989). Imogolite is mostly reported from podzols (Dahlgren and Ugolini, 1989; Lundström et al., 2000), whereas allophane occurs mainly in volcanic soils (Wada, 1989).

The amorphous silica (ASi) pool of soil has both a pedogenic and biogenic (BSi) origin. Pedogenic ASi corresponds to the non-crystalline inorganic fraction such as opal-A formed under supersaturated soluble Si levels (Drees et al., 1989), and ASi formed from polysilicic acid adsorbed on Fe and Al oxides/hydroxides (Dietzel, 2002; Sauer et al., 2006). The formation of ASi coatings (silcretes, cements) on other mineral surfaces as a secondary product of weathering is widely recognized in soils and...
sediments (Dove, 1995; Basile-Doelsch et al., 2005). On the other hand, the biogenic Si pool in soil is constituted by phytoliths (opal-A polymerized in leaves) and remains of micro-organisms (microbial and protozoic Si) (Sauer et al., 2006; Sommer et al., 2006; Aoki et al., 2007). Biogenic opal is a ubiquitous and significant component of soils developed under a wide range of environmental conditions, while inorganic pedogenic opal is formed only under specific physico-chemical soil conditions (Drees et al., 1989).

### 2.1.1 Silica

In soils, the solubility of amorphous silica is higher (1.8–2 mM Si) than quartz (0.10–0.25 mM Si) since solubility is a function of the packing density of the silica tetrahedral and long-range crystal order (Iler, 1979; Lindsay, 1979; Drees et al., 1989). Quartz, abundant in both residual and transported parent material, is highly stable and thermodynamically more resistant to weathering, being the last mineral to crystallize from magma (Drees et al., 1989; Monger and Kelly, 2002). The dissolution of silica polymorphs is strongly pH-dependent and undergoes hydrolysis at pH<9 by the overall reaction:

$$\text{SiO}_2(s) + 2\text{H}_2\text{O} = \text{H}_4\text{SiO}_4^0 \quad (1)$$

The solubility of biogenic silica is equivalent to that of vitreous silica (1.8 mM Si) and is 17 times higher than quartz (Fraysse et al., 2006). The rate at which Si is released from plant litter is independent of cellulose hydrolysis, which suggests that most of the litter-Si is contained in the phytoliths as a pure "inorganic" pool, and not complexed with organic matter (Fraysse et al., 2010). Despite the various morphologies and different specific surface area of phytoliths, mass-normalized dissolution rates are similar among all types of plant species (horsetail, larch, elm and fern; Fraysse et al., 2009) and these dissolution rates are an order of magnitude higher than those for typical soil clay minerals. The sorption of Al and other bi- and trivalent metals (Fe$^{3+}$, Zn$^{2+}$ and Cu$^{2+}$) affects the surface properties of the silica polymorphs and decreases their rates of dissolution (Dove, 1995; McKeague and Cline, 1963a). So is the solubility of pine
phytoliths for instance three times lower than the one of beech phytoliths because of a higher Al substitution in pine phytoliths (Bartoli, 1985).

Dissolution rates of amorphous silica should simply increase linearly with undersaturation. However, Dove et al. (2008) observe that the dissolution rates of amorphous silica exhibit an exponential dependence on electrolytes (alkaline or alkaline earth cations) like their crystalline counterpart, quartz.

The solubility of silica polymorphs, both crystalline and amorphous, is essentially constant between the pH limits of 2 and 8.5, but increases rapidly near pH 9 since the weakly acidic $H_4SiO_4$ dissociates appreciably such that the first reaction is written (Dove, 1995):

$$H_4SiO_4 = H_3SiO^- + H^+$$

This reaction is an important buffer for some natural systems and, as a result, only highly unusual low-silica environments like carbonatites and serpentinites can reach a pH above the first pK of silica ($pK_{a1} = 9.82$ at 25°C). The Si-polymeric species become stable at pH~9 (Knight and Kinrade, 2001; Dietzel 2000, 2002).

### 2.1.2 Silicate minerals

The weathering rates of silicate minerals have a major importance in soil development, soil buffering capacities related to acidic deposition, control of carbon cycle and cycling of many inorganic elements which are important in soil fertility (White, 1995). The weathering rate of a mineral in a given environment can be considered as a function of intensity factors (temperature, moisture, pH and Eh) and capacity factors (specific surface area and nature of the mineral) (McKeague and Cline, 1963a). This results in a sequence of increasing stability of soil minerals (Table 1) from the least stable primary minerals to the secondary phyllosilicates (e.g., kaolinite, allophane, Al and Fe (hydr)oxides) (Nagy, 1995).

Since relatively large $K^+$, $Na^+$ and $Ca^{2+}$ ions balance the charge deficit, feldspar weathers more rapidly than quartz (McKeague and Cline, 1963a; White, 1995) to yield
secondary minerals and silicic acid as for example:

$$2\text{KAlSi}_3\text{O}_8 + 2\text{CO}_2 + 11\text{H}_2\text{O} \rightarrow \text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 + 2\text{K}^+ + 2\text{HCO}_3^- + 4\text{H}_4\text{SiO}_4$$  \(3\)

The mineral weathering rate depends on mainly chemical equilibrium, where any processes consuming free silicic acid, e.g. sary precipitates, adsorption and uptake by vegetation (Eq. 3), can considerably accelerate mineral dissolution (Exley, 1998; Dove, 1995; Street-Perrott and Barker, 2008). Finally, acidification of soil solution in Podzols and Luvisols leads to disintegration of secondary clay minerals providing a source of Si (Sommer et al., 2006). The high concentration of low molecular organic acids in the organic horizons is likely to promote primary and secondary minerals weathering through complexation and acid attack (Bennet et al., 1991; Barman et al., 1992; Oliva et al., 1999; Giesler et al., 2000; Gérard et al., 2002; Cornelis et al., 2010b).

2.2 Neoformation and precipitation of Si-minerals

The Si concentrations in soil solutions strongly depend on equilibrium to secondary phases, and are thus strongly related to the stage of soil development as influenced by climate and parent material (Rai and Kittrick, 1989; Karathanasis, 2002). Indeed, at fixed pH, smectite stability in Vertisols is associated with a relatively high concentration of aqueous $\text{H}_4\text{SiO}_4$ (~1.6 mM Si) whereas kaolinite, predominantly occurring in Ferralsols, Acrisols, and Lixisols, is associated with a low $\text{H}_4\text{SiO}_4$ concentration (0.03 mM Si) (Rai and Kittrick, 1989).

Besides the fact that Al coatings suppresses the solubility of silica, the decrease in Al activity in soil solution would enhance the dissolution of secondary Al-containing minerals and, hence, release of $\text{H}_4\text{SiO}_4$ in soil solution (McKeague and Cline, 1963a; Rai and Kittrick, 1989). The formation of short-range ordered Al-Si compounds occurs in horizons with pH($\text{H}_2\text{O}$) values >5.0 (Wada, 1989). Moreover the precipitation of $\text{H}_4\text{SiO}_4$ with Al hydroxides forms hydroxialuminosilicates (HAS), which might be considered as amorphous precursors to imogolite (Exley, 1998; Doucet et al., 2001). In
environment with very active humus characterized by high decomposition rates, the for-
5 mation of Al-organic matter complex inhibits the formation of allophane and imogolite
and favours formation of opaline silica (Huang, 1991).

If the ecological and climatic conditions favour evapotranspiration, the H$_4$SiO$_4$ con-
centration of some soil solutions might exceed the solubility of ASi defined as 2.1 mM
Si at 25°C (Alexander et al., 1953; Monger and Kelly, 2002), and promote the for-
10 mation of opal-A, opal-CT and microquartz (Chadwick et al., 1987). Basile-Doelsch
(2005) suggests that the quartz re-precipitation plays an important role in the biogeo-
chemical cycle of Si. This pedogenic silicification is associated with arid climates, and
its contribution to the Si cycle probably followed climatic variations. In fact, biogenic
opal-A plays an important role in the genesis of the siliceous cements of hardpans
and silcretes (Clarke, 2003). The dissolution of opal-A and reprecipitation to opal-CT,
which in turn is transformed into secondary micro-crystalline quartz, may be mediated
by condensation reactions of silica polymers onto metal hydroxides (Drees et al., 1989;
15 Monger and Kelly, 2002). Moreover, nano-colloidal silica particles (<3 nm, equivalent
to 300 silica monomer units) can be important for the precipitation of SiO$_2$ (Conrad et
al., 2007). The partial dissolution of the biogenic opal-A in topsoil also provides DSi
for sequestration in secondary minerals (clay neoformation and Si adsorption) in upper
soil horizons (Lucas et al., 1993; Lucas, 2001; Michalopoulos and Aller, 2004; Barré et
18 al., 2009; Opfergelt et al., 2010). In addition, the polymerized silicic acid may also indi-
cate a type of precursor material for neoformation of secondary Al-silicates (Wonisch
et al., 2008).

It must be emphasized that the pedogenic formation of secondary Si-containing min-
erals (phyllosilicates, silica and short-range ordered aluminosilicates) is strongly influ-
25 enced by Si activity in soil solution which depends on (i) parent material as the ultimate
and readily source of H$_4$SiO$_4$, and (ii) climate providing water for weathering and pre-
venting intensive leaching of H$_4$SiO$_4$ (Jackson et al., 1948; Dove, 1995; White, 1995;
Berner, 1995; Gérard et al., 2002; Monger and Kelly, 2002). Climate (mainly mois-
ture and temperature) plays thus a major role in the Si distribution in soils: worldwide,
a large range of soil types can derive from the same rock (climosequence). Moisture is influenced by the total amount of precipitation, its intensity and seasonality, humidity, evapo-transpiration, runoff and infiltration. Thermal effects, described by the Arrhenius relationship, include average air temperatures, seasonal temperature variations, and thermal gradients in soils (White, 1995). Generally, we can schematize the world weathering system and the distribution of Si-containing minerals as a function of climate (Pédro, 1968, 1984; Millot, 1979; IUSS WRB, 2006; Legros, 2007).

With regard to Si-bearing minerals and based on a fixed time scale, the rough result of pedogenesis is firstly dependent on the rainfall, which determines both weathering rates and element concentrations in the soil solutions. In dry deserts, the weathering of minerals is zero or very low. In Mediterranean and dry tropical climates, Si leaching is low, soil solutions are Si-concentrated so that authigenic Si-bearing minerals are Si-rich clay from the smectite group (Si/Al ratio around 2) or, over Al-poor rocks, opal and quartz. In tropical humid and equatorial areas, as well in high rainfall temperate areas, Si leaching is high, soil solutions are depleted in dissolved Si so that authigenic Si-bearing minerals are Si-poor clays from the kaolinite group (Si/Al ratio around 1), or none as for bauxite genesis. In cold temperate climate, the rate of weathering is restricted inducing secondary Si-bearing minerals derived from limited transformation of existing minerals in rocks (micas) into new species (vermiculites), when in cold climates primary clays (illites and chlorites) are directly inherited from the parent material (detrital origin) without forming new minerals. As most of secondary Si-bearing minerals are clay minerals, their neoformation also depends on Al disponibility, so that where Al can be sequestered and leached out of the soil as organometallic compounds, no precipitation of secondary minerals occurs and podzol formation begins (Lucas, 2001).

As a consequence of the pedogenesis, the soil type influences the form and the content of Si (McKeague and Cline, 1963a). For example, Podzols (IUSS WRB, 2006), occurring mainly in cold temperate and boreal humid areas or in humid equatorial areas with siliceous rock, are characterized by a siliceous eluvial horizon with quartz as the main form of Si and by a spodic illuvial accumulation of humus complexes and
secondary clay minerals. Cambisols (IUSS WRB, 2006) are recognized by their in-cipient soil formation with a limited degree of weathering derived from a wide range of rocks. Cambisols are particularly well represented in temperate and boreal regions with a young parent material; they cover an estimated 1.5 billion hectares worldwide (IUSS WRB, 2006), and Si is commonly present in a mixture of weatherable primary silicates, quartz, and secondary clay minerals. Ferralsols (IUSS WRB, 2006) represent the most highly weathered soil mainly from basic rock of the humid tropics, in which the low concentrations of dissolved weathering products promote desilication (Si leaching by drainage). These soils display a mineral assemblage dominated by low activity clays (mainly kaolinite) and a high content of sesquioxides. A convergence from both climate and time leads to highly weathered tropical soils whatever the parent material, except likely for detritical parent material deriving into arenosol.

2.3 Si adsorption on solid phases

The monosilicic acid can be withdrawn from soil solution through the adsorption onto a variety of solid phases in soils (McKeague and Cline, 1963b). Although little Si adsorption has been reported onto secondary clay minerals (Siever and Woodford, 1973), Fe and Al oxides are the main soil components with a significant capacity for Si adsorption (Beckwith and Reeve, 1963; McKeague and Cline, 1963b; Cornell and Schwertmann, 1966).

The adsorption of monosilicic acid by oxides depends on (i) pH with an increase from pH 4 to pH 9, and (ii) metal type, e.g. aluminium oxides were found to be more effective in adsorbing monosilicic acid than iron oxides (Jones and Handreck, 1963, 1965, 1967; McKeague and Cline, 1963b). H₄SiO₄ interacts with Fe-oxide surface OH groups through ligand exchange to form silicate bi-dendate innersphere complex (Parfitt, 1978; Pokrovsky et al., 2003; Hiemstra et al., 2007). Silicic acid is specifically adsorbed onto secondary oxides, with a higher amount adsorbed onto synthetic short-range ordered ferrihydrite compared to crystalline goethite (Delstanche et al., 2009). On Fe oxide surfaces, polysilicic acid might be formed by specific interaction with orthosilicic acid.
(Dietzel, 2002), which should significantly influence the amorphous silica content in soils. Since iron oxides are ubiquitous in soils (Schwertmann and Taylor, 1989), they partly control the concentration of $\text{H}_4\text{SiO}_4$ in the aqueous phase (McKeague and Cline, 1963b; Opfergelt et al., 2009).

### 2.4 Si recyling by vegetation

#### 2.4.1 Plant Si uptake

Silicon is taken up by terrestrial plants from soil solution as uncharged monosilicic acid ($\text{H}_4\text{SiO}_4^0$), transported into the xylem (Casey et al., 2003) and mainly deposited in transpiration sites where polymerization of hydrated amorphous silica occurs to form phytoliths ($\text{SiO}_2\cdot n\text{H}_2\text{O}$; BSi) (Jones and Handreck, 1965, 1967; Raven, 1983; Sangster and Hodson, 1986). $\text{SiO}_2$ precipitation occurs mainly in epidermis of shoots but can also occur in the vascular system and endodermis of roots (Raven, 1983; Lux et al., 2003a,b). Beside, phytoliths, diffuse silica precipitation in cell walls and silica deposits associated to polyphenolic compounds in cells were observed (Watteau and Villemin, 2001). Si seems to be unavailable for retranslocation once amorphous silica polymerizes in aerial parts of the plants (Raven, 1983). Phytoliths are released in the topsoil through organic matter decomposition (Smithson, 1956). The biomineralization of amorphous silica seems to be restricted to some plant families (Epstein, 1999; Hodson et al., 2005) and appear in various shapes depending on the location of Si deposits and plant species (Carnelli et al., 2001, 2004). The International Code for Phytolith Nomenclature (ICPN) has been proposed to describe and name phytoliths (Madella et al., 2005), as the preservation of phytoliths in terrestrial and aquatic paleoenvironments can be used for reconstructing past environments and human activity (Piperno, 1988; Pearsall and Piperno, 1993; Piperno and Stothert, 2003). The amount of Si accumulated in plants is species dependent and ranges from 0.1 to 10% of dry weight (Raven, 1983; Marschner, 1995; Epstein, 1999; Hodson et al., 2005; Ma and Yamaji, 2006).
The Si uptake by plants can be active, passive or rejective. An active mechanism corresponds to a Si uptake in larger quantity than predicted by mass flow, while a passive mechanism is the Si uptake proportional to mass flow. Rejective uptake is characterized by low Si uptake by plants implying H$_4$SiO$_4$ accumulation in soil solution. Among the plants with an active Si uptake, a difference in Si accumulation is commonly attributed to the density of Si transporters in roots (coded by the low-silicon genes Lsi1 and Lsi2) and in shoots (Lsi6) (Mitani and Ma, 2005; Ma et al., 2006, 2007; Yamaji et al., 2008). For the mass-flow driven Si uptake (passive), given a same Si concentration in soil solution, the difference in Si accumulation between plant species could be explained by various transpiration rates (Bartoli and Souchier, 1978; Jones and Handreck, 1967; Raven, 1983; Henri et al., 2006; Cornelis et al., 2010c).

Based on active, passive or exclusive mechanisms of Si uptake, plant species are classified as high-, intermediate- or non-accumulator, respectively (Takahashi et al., 1990). A classification of the plant kingdom shows that the majority of Si high-accumulators (1.0–10 wt% shoots) belong to the monocotyledons (e.g., banana, bamboo, sugar cane, soybean, rice, wheat, barley, sorghum and oat), while most dicotyledons absorb Si passively (0.5–1.0 wt% shoots), and some dicots such as legumes have limited Si uptake (<0.5 wt% shoots) (Ma et al., 2001; Ma and Takahashi, 2002; Liang et al., 2007). Hodson et al. (2005) carried out a detailed data analysis of mean relative shoot Si concentration of 735 plant species. These data reveal that a high shoot Si concentration is not a general feature of monocot species and indicate that phytolith production is strongly controlled by the genetic code: the mean relative shoot Si concentration declines in the order: marchantiophyta (liverworts) > equisetophyta (horsetails) > angiosperms > gymnosperms > polypdiophyta (ferns) (Table 2).

The essentiality of Si for terrestrial plants is still extensively debated (Takahashi et al., 1990; Richmond and Sussman, 2003). So far, only two groups of plants are known to have an absolute and quantitatively major requirement for Si: the diatoms and other members of the yellow-brown or golden algae, the Chrysophyceae and the Equisi-
Silicon is not considered as an essential element for higher plants (Epstein, 1994, 1999; Ma and Takahashi, 2002), but its beneficial effects on growth have been reported in a wide variety of crops, including rice, wheat, barley, and cucumber (Ma et al., 2001; Korndorfer and Lepsch, 2001; Ma and Takahashi, 2002; Ma, 2004). There is a general consensus that Si improves the plant resistance to various biotic and abiotic stresses. Silica deposition in leaves is a resistant structural component (Raven, 1983; Rafi et al., 1997), providing a more upright position, which favours light interception, hence promoting photosynthesis (Epstein, 1994; Marschner, 1995). Moreover, biogenic silica in plant tissues creates a hard outer layer that serves as a defense against fungal and insect attacks (Bélanger et al., 2003; Sangster et al., 2001). Finally, it is widely accepted that Si alleviates the toxicity of Al and other metal ions such as Mn in higher plants (Birchall, 1990; Hammond et al., 1995; Hodson and Evans, 1995; Cocker et al., 1998; Perry and Keeling-Tucker, 1998; Liang et al., 2001, 2007). In acidic coniferous forest, the free Al co-deposited with Si reduces the toxicity associated with high Al contents (Hodson and Sangster, 1999). Currently, there is no evidence of Si involved in plant metabolism (Ma et al., 2001) since no silicon bearing organic compound has been identified in higher plant to date (Knight and Kinrade, 2001). The beneficial effects of Si remain reduced under optimum growth conditions, but are more obvious under stress conditions (Epstein, 1994; Bélanger et al., 1995).

The Si accumulators wheat (*Triticum aestivum*) and rice (*Oryza sativa*), the premier crops for the nutrition of mankind, are susceptible to a variety of diseases if the Si supply is low (Epstein, 2001). Therefore, soils that are intensively used for cropping are fertilized on a regular basis with silicate amendments, such as wollastonite (Korndörfer and Lepsch, 2001).

### 2.4.2 Plant Si accumulation

Terrestrial plants and their associated microbiota directly affect silicate mineral weathering in several ways by: (i) affecting the temperature of the soil, (ii) protecting soil against erosion, (iii) generating of chelating ligands, (iv) modifying pH through produc-
tion of CO$_2$ and organic acids (mainly when pH is below 4–5), (v) modifying element concentrations in soil solution by root uptake and return by litter and (vi) altering the physical properties of a soil, particularly the exposed surface areas of minerals and the residence time of water (Drever, 1994; Moulton et al., 2000). The relative importance of each of these processes depends upon plant type, climate and geology (Moulton et al., 2000). Soil temperature strongly influences the chemical weathering rates and may be considered as the dominant factor for seasonal variations in soil solution Si concentration (Gérard et al., 2002).

Silicon accumulation process by vegetation can also be important. For instance, a Si-accumulator forest (1.1% Si in leaves) with a biomass production of 16 tons dry weight yr$^{-1}$ would extract about 200 kg Si ha$^{-1}$ yr$^{-1}$ (Lovering, 1959). Following the conversion of silicates into silicic acid, terrestrial higher plants convert silicic acid into biogenic silica (Raven, 1983, 2001). It is well known that a part of the DSi released by mineral weathering is cycled through vegetation at the surface of the earth (Conley, 2002) before its transfer to oceans (Bartoli, 1983; Lucas et al., 1993; Alexandre et al., 1997; Markewitz and Richter, 1998; Conley, 2002; Derry et al., 2005; Fulweiler and Nixon, 2005; Blecker et al., 2006; Sommer et al., 2006; Gérard et al., 2008; Cornelis et al., 2010a).

In temperate forest ecosystem, the Si uptake depends on tree species and soil type, ranging from 2 to 44 kg Si ha$^{-1}$ yr$^{-1}$ (Bartoli, 1983; Markewitz and Richter, 1998; Fulweiler and Nixon, 2005; Gérard et al., 2008; Cornelis et al., 2010a). In humid tropical conditions, the Si recycling by forest trees is evaluated to up to 67 kg ha$^{-1}$ yr$^{-1}$ (Congo rainforest; Alexandre et al., 1997), an extremely high value (970–1380 kg ha$^{-1}$ yr$^{-1}$) was obtained in the particular case of a bamboo forest (Meunier et al., 1999). Dry and humid temperate grasslands display a Si uptake between 22 and 59 kg ha$^{-1}$ yr$^{-1}$ (Blecker et al., 2006). The active uptake by vegetation decreases H$_4$SiO$_4$ concentration in soil solution, and thus accelerates the mineral weathering rate (see Eq. 3) (Exley, 1998). Indeed, Si-accumulating plants such as maize and banana are able to accelerate the dissolution of basalt (Hinsinger et al., 2001).
The Si recycling by vegetation strongly controls the amount of Si restituted on topsoil, litterfall being the most important Si flux from vegetation to soil, followed by throughfall (dry deposition+crown leaching) (Sommer et al., 2006; Cornelis et al., 2010a); the cycling by roots is still poorly known. Silicon recycling by vegetation seems to be of the same order of magnitude as DSi outputs from soils (Table 3; Sommer et al., 2006; Street-Perrott and Barker, 2008). More specifically, the Si uptake by forest vegetation is negatively correlated with the amount of DSi leached out from the soil profile (Cornelis et al., 2010a). In 2005, the total forest area worldwide was estimated to be 3.952 × 10^6 ha, which corresponds to about 30% of the land area (FAO, 2006). Assuming a mean Si uptake by global forest vegetation of 40 kg Si ha\(^{-1}\) yr\(^{-1}\) (Table 3), the annual forest BSi production would be 0.15 × 10^{12} kg Si yr\(^{-1}\), which represents 6.3% of the amount of the total terrestrial Si biologically fixed as BSi (2.5 × 10^{12} kg Si yr\(^{-1}\)) (Laruelle et al., 2009). In addition, considering a mean Si output from forested land of 10 kg Si ha\(^{-1}\) yr\(^{-1}\) (Table 3), the global DSi leached out from forest ecosystem would be 0.04 × 10^{12} kg Si yr\(^{-1}\), which represents 27% of the net DSi inputs from continents to oceans.

Even with a lower biomass, the Si restitution on topsoil through litterfall by grasses is comparable to forests, since grasslands are characterized by higher Si concentrations and turnover (Blecker et al., 2006).

The DSi load to rivers is significantly reduced when significant amounts of BSi accumulate in vegetation. Indeed, the Si uptake by terrestrial ecosystems thus significantly increases the chemical weathering rate without necessarily increasing the measured denudation rate (Alexandre et al., 1997; Street-Perrott and Barker, 2008; Cornelis et al., 2010a). This observation is confirmed by the significant increase in the transport of DSi by rivers with deforestation (Saccone et al., 2008; Conley et al., 2008). Conley et al. (2008) showed the effect of deforestation in a temperate forest ecosystem where an increase in DSi output to the hydrosphere was caused by dissolution of the amorphous BSi, which was restituted on topsoil.

As shown in Fig. 1, the global agricultural Si export is estimated to be
$0.22 \times 10^{12} \text{ kg Si yr}^{-1}$ (Matichenkov and Bocharnikova, 2001), which is of the order of magnitude as the total dissolved Si transferred from continents to oceans by rivers ($0.14 \times 10^{12} \text{ kg Si yr}^{-1}$) (Tréguer et al., 1995). When Si accumulators such as rice and wheat are cultivated, their biomass exported from the field represents a net loss of Si from the soil-plant system (Meunier et al., 2008). As a consequence, intensive cropping of Si-accumulating plants (rice and sugar cane), is responsible for a significant decrease of Si in soils within a few decades (Meunier, 2003).

### 2.5 Biogenic Si preservation

A large terrestrial BSi cycle exerts a strong biological control on the global Si cycle (Conley, 2002). The BSi accumulation in the soil-plant system is directly governed by the soil weatherable mineral reserves (Henriet et al., 2008a,b) and the kinetic of Si dissolution of solid phases in soils (Sommer et al., 2006), controlling the Si concentrations in the soil aqueous phase.

If the restitution rate of phytoliths on topsoil is higher than their dissolution rate, they may accumulate, as described on the volcanic island of La Réunion under Si-accumulating bamboos (Meunier et al., 1999). The phytolith is an adsorptive surface and is implicated in the removal of metal ions, such as Al, from the soil solution (Epstein, 2001). These adsorptive processes tend to stabilize a part of phytoliths from dissolution (Bartoli and Wilding, 1980) and thereby reduce the amount of silicic acid returning to the biosphere through the BSi preservation in soil profile (Alexandre et al., 1997). In an equatorial rainforest, 8% of the BSi input ($4–6 \text{ kg Si ha}^{-1} \text{ yr}^{-1}$) supplies a stable pool of phytoliths with a lower turnover (Alexandre et al., 1997). In temperate deciduous and coniferous forest, the preservation of phytoliths represents 0 and 1 kg Si ha$^{-1}$ yr$^{-1}$, respectively (Bartoli, 1983). The storage of BSi in grasslands ecosystem ranges from 4 to 16 kg Si ha$^{-1}$ yr$^{-1}$ (Blecker et al., 2006). Wilding and Drees (1974) have shown that forest BSi is about 10–15 times more soluble than grass BSi, owing to its greater specific surface area. In Podzols, Bartoli and Souchier (1978) calculated
a mean residence time of 30 and 300 years for beech and pine phytoliths, respectively. The amount of ASi in soils commonly ranges from <1 to 30 mg g\(^{-1}\) on a total soil basis (Drees et al., 1989). The highly soluble BSi pool returns to topsoil through litterfall contributing Si release in soil solution (Drees et al., 1989; Van Cappellen et al., 2003; Farmer et al., 2005; Saccone et al., 2007; Fraysse et al., 2009). A quantitative assessment of the actual amount of ASi, whether from biogenic or pedogenic origin, in the soil can be obtained by alkaline dissolution (Sauer et al., 2006; Saccone et al., 2007).

If preserved in soil, phytoliths will be stored, dissolved and/or exported to rivers (see Fig. 1). When vegetation is highly productive and top soil erosion is significant, phytoliths may significantly contribute to the suspended load of rivers. In the Nyong basin (Cameroon), phytoliths originating from the soil erosion contribute to more than 90% of the BSi pool in Nyong River suspended load, and account for 4% of the total suspended load (Cary et al., 2005).

### 2.6 Atmospheric Si input

The Si atmospheric dust inputs in the biogeosphere must be taken into account in biogeochemical studies. In highly weathered soils, Chadwick et al. (1999) show that atmospheric inputs alone (marine aerosols and dusts) can sustain the productivity of Hawaiian rainforest.

In addition to the DSi transfer by rivers, the eolian erosion of the land surface is a potentially important transport of Si to the oceans. Airborne particles enter the surface ocean \((0.28 \times 10^{12} \text{ kg Si yr}^{-1})\) where a small fraction dissolves \((0.01 \times 10^{12} \text{ kg Si yr}^{-1})\) (Tréguer et al., 1995) (Fig. 1). Depending on its mineralogy, the impact of dust on soil genesis and on terrestrial biogeochemical cycle of Si varies greatly by region (Simonson, 1995). Street-Perrott and Barker (2008) show that atmospheric Si input in temperate and tropical forests ranges from 0.04 to 2 kg Si ha\(^{-1}\) yr\(^{-1}\). Dry Si deposition is highest near the sources of the African, Arabian, Asian and Australian deserts (Tegen et al., 2002). In East African, savanna fires would be a significant source of atmospheric
phytolith particles (Street-Perrott and Barker, 2008). In most intensely weathered soils, wind-blown dust becomes the dominant source of Si on topsoil: near-surface horizons of Hawaiian soils contain as much as 30% quartz, a mineral absent from local parent material (Kurtz et al., 2001). In soil derived from basaltic ash (Cameroon), the content of quartz from Saharan dust deposition on topsoil ranges from 2–8%, depending on soil localization (Opfergelt et al., 2010). In Northeast Sweden, the Si content in tree leaves originates both from Si plant uptake and from local airborne particulate material, quantifying this exogenous Si contribution between 1 and 70% (Engström et al., 2008).

Wet precipitation can also sustain Si to the soil-plant system, such as in a rice field in Camargue (France) where the annual precipitation flux give a DSi input of $3 \pm 2 \text{ kg Si ha}^{-1} \text{ yr}^{-1}$ (Desplanques et al., 2006). Similarly, in two Amazonian forest sides in Brazil, Si inputs on topsoil from the rain and from dust were small but not negligible: $0.6 \text{ kg Si ha}^{-1} \text{ yr}^{-1}$ (Cornu et al., 1998). Finally, in humid climates, most values of annual Si inputs through rainfall are $<1.4 \text{ kg Si ha}^{-1} \text{ yr}^{-1}$ (Sommer et al., 2006). More generally, atmospheric inputs were estimated at $<1$, $1.5$ and $2 \text{ kg Si ha}^{-1} \text{ yr}^{-1}$ (Alexandre et al., 1997; Bartoli, 1983; Blecker et al., 2006, respectively). The atmospheric Si supply in biogeosphere is thus ubiquitous but very low compared to other Si inputs in the soil-plant system (Street-Perrott and Barker, 2008).

3 Transfer of dissolved Si from soil-plant systems towards rivers

The DSi concentrations in rivers can be useful to quantify chemical weathering rates and CO$_2$ consumption (Gaillardet et al., 1997, 1999a,b; Oliva et al., 1999; Vuai and Tokuyama, 2007). However, values can be misinterpreted if the part of H$_4$SiO$_4$ polymerized in higher plants and in phytoplankton as BSi is neglected (Bormann et al., 1998; Meunier, 2003; Street-Perrott and Barker, 2008). Indeed, the mass-balance of Si at the watershed scale has to be evaluated taking into account the pathways of Si between lithosphere and biosphere (recycling, immobilization, exportation and restitution of Si by vegetation) before its transfer to rivers. Moreover, most watershed studies,
which have estimated soil weathering rates, assume that surface discharge chemistry reflects the soil water chemistry. However significant discrepancies between soil and surface chemistries are apparent in some cases and could be explained by rapid surface runoff (DSi in surface discharge < DSi in soil water) and weathering at a narrow interface between the bedrock and soil zone in saprolite (DSi in surface discharge > DSi in soil water) (White, 1995). Finally, before its transfer to oceans, the dissolved and particulate load can be deposited and DSi can be extracted by grasses and stored in phytoliths (Wüst and Bustin, 2003; Ding et al., 2004), taken up by sponges and stored in spicules (Chauvel et al., 1996) or taken up by phytoplankton and stored in diatom frustules (Ragueneau et al., 2006). Struyf et al. (2009) confirm that wetlands, as a biological Si sink, control the fluxes of both DSi and ASi along the land-ocean continuum boundary.

The average DSi concentration in freshwater at the global scale displays huge variations depending on the geographical region (Table 4; Exley, 1998). The low DSi concentration of Australian freshwater reflects the heavily weathered soils in this region. In boreal and arctic rivers, the concentration of DSi, 30–50% lower than the global average, seems to be mainly controlled by the soil and vegetation through the production of organic acids, as shown by a positive correlation between total organic carbon and DSi in these rivers (Humborg et al., 2006).

However, the DSi concentration alone does not provide clues on the sources and processes affecting riverine fluxes of DSi. In weathering-limited systems, transport processes may remove products of weathering faster than the neoformation and precipitation of secondary phases. In contrast, in transport-limited systems, river load depends on the availability of water as a transporting agent (Drever, 1988; Gaillardet et al., 1995). This will induce variations in DSi transfer towards rivers between geographical regions. Because mineral weathering (temperature and physical denudation) and transport conditions (runoff) exert a major control on processes governing the DSi inputs to rivers (Meybeck, 1979; Anderson et al., 1997; Gaillardet et al., 1999a; Turner et al., 2003; Fulweiler and Nixon, 2005; Jennerjahn et al., 2006; Georg et al., 2006;
Gislason et al., 2009) and differ geographically, DSi fluxes will be discussed separately in tropical and non-tropical rivers following various geographical regions (Jennerjahn et al., 2006; Table 5).

Currently, the average global DSi flux is two to three times higher in tropical than in non-tropical rivers (Tréguer et al., 1995): 74% of the total annual DSi input by rivers into the oceans originates from tropical regions (0.12 × 10^{12} kg Si yr^{-1}) and 20% from temperate regions (0.03 × 10^{12} kg Si yr^{-1}). This distribution could vary as precipitation patterns change with an increase in most of the Northern Hemisphere (0.5–1%/decade) and decrease in sub-tropical land areas (0.3%/decade) (Lal, 2004).

Tropical ecosystems represent 33% of the land mass (Meunier et al., 2001) and contribute the major part of the DSi transfer from continents to the oceans. Indeed, the river basins with the largest fluxes of total CO_{2} consumption are all located in the humid tropics (Gaillardet et al., 1999b). Tropical rivers in Asia and Oceania display high DSi fluxes that match the optimum weathering and transport conditions (Jennerjahn et al., 2006; Beusen et al., 2009). These tropical environments are characterized by a young geology, an active tectonic region of the circum-Pacific ring of fire, a high runoff and a high silicate weathering rate (Milliman and Meade, 1983; Milliman and Syvitski, 1992; Sommer et al., 2006). Basic igneous rocks show the highest DSi yields with respect to a given runoff while the least DSi per runoff is mobilized from acidic plutonic rocks (Jansen et al., 2010). The model predictions of Beusen et al. (2009) give a strong indication that DSi fluxes depend on the precipitation and the occurrence of volcanic rocks. Despite its restricted spatial distribution, basalts are eight times more soluble than granites (Dupré et al., 2003), and contain a high proportion of ferromagnesian minerals susceptible to chemical weathering by higher plants (Cochran and Berner, 1996).

Non-tropical rivers generally display much lower relative silicate weathering rates and DSi fluxes (Jennerjahn et al., 2006). Especially the Siberian and Canadian rivers contribute to ~10% to the total DSi input into oceans (Gordeev et al., 1996). With low temperature and runoff in weathering-limited temperate regions, DSi fluxes should
be driven by soil and vegetation (Humborg et al., 2006) through (i) the high supply of organic protons lowering pH in topsoils (ii) the high Si recycling rates by vegetation compared to DSi fluxes in rivers (Table 3), and (iii) the production of reactive phytoliths on topsoil, the two former phenomena being likely to accelerate the mineral weathering rates. In a granitic forested ecosystem, the river DSi concentrations exhibit a strong seasonal signal that did not vary in a regular way with water discharge or water temperature (Fulweiler and Nixon, 2005). In this study, the spring decline in river DSi concentration could be due to Si uptake by terrestrial vegetation (Fulweiler and Nixon, 2005; Engström et al., 2010). According to the low DSi fluxes and loads in non-tropical rivers, we could conclude that the biological processes are insufficient to counterbalance the lower weathering rates with regard to transferring DSi from continents to oceans.

The soil-vegetation system type may also impact the DSi fluxes in weathering-limited tropical watersheds (Sommer et al., 2006) since the DSi flux in poorly developed soils under subarctic climate (Anderson et al., 1997, 2000) is of the same order of magnitude as that of strongly developed soils of tropical climate (Oliva et al., 1999).

The relatively high DSi flux from non-tropical South America (Beusen et al., 2009) could be explained by the physical denudation in mountainous areas combined with high runoff and temperature which provide ideal conditions for high chemical weathering rates and high DSi transport (Milliman and Syvitski, 1992, Gaillardet et al., 1999a; Georg et al., 2006). Indeed, physical weathering and erosion in areas of high relief enhance weathering by continually exposing fresh mineral surfaces (Summerfield and Hulton, 1994; Street-Perrott and Barker, 2008). However, physical weathering in high-latitude watersheds seems to lead mostly to the formation of clay minerals, but does not immediately lead to higher DSi fluxes as observed for tropical regions with active tectonics (Anderson et al., 2000; Humborg et al., 2006).

In summary, a hierarchy of driving variables that control Si fluxes from the continents to the oceans can be identified. At the global scale, runoff is the main driver of DSi fluxes, followed by temperature. At regional scale, DSi fluxes are a function of (1) the catchment lithology (content of weatherable minerals), (2) the hydrological conditions...
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4 Tracing biogeochemical Si cycle in the soil-plant system

Since Si is a ubiquitous element in the biogeoosphere, tracing the origin of the DSi output from a soil-plant system requires the use of (1) a Si mass-balance (Bartoli, 1983; Lucas et al., 1993; Alexandre et al., 1997; Farmer et al., 2005; Gérard et al., 2008; Cornelis et al., 2010a) and (2) geochemical tracers. Two tracers of the Si cycle in weathering environments have been identified so far: Ge/Si ratios (Derry et al., 2005; Lugolobi et al., 2010) and stable Si isotopes (Ding et al., 2004; Ziegler et al., 2005a; Georg et al., 2006, 2007, 2009b; Bern et al., 2010; Cardinal et al., 2010; Cornelis et al., 2010b; Engström et al., 2010; Opfergelt et al., 2010).

Through the calculation of Si uptake, Si restitution, Si drainage (Table 3), atmospheric Si inputs and phytolith preservation in soils, a Si mass-balance in specific ecosystems allows an estimation of the Si release by primary silicate weathering and by phytolith dissolution, respectively. However, these approximations ignore other important Si sinks in the soil-plant system such as HAS and short-range ordered aluminosilicates formation, neoformation of secondary clay minerals, opaline spheres precipitation and Si adsorption onto Fe and Al (hydr)oxides. Thus, we suggest that Si mass-balance study should be combined with geochemical tracers (Ge/Si ratios and δ30Si) to make better assumptions about the Si origin in the aqueous phase of well-defined soil-plant systems.

Germanium (Ge) is a trace element with very similar geochemical properties when compared to Si because it substitutes for Si in aluminosilicates mineral lattices. Studying Ge/Si fractionation allows for tracing the weathering of Si-containing phases and the
dynamics of DSi produced in soil-plant systems (Kurtz et al., 2002; Derry et al., 2005; Scribner et al., 2006). Secondary clay minerals and biogenic opal display contrasting Ge/Si ratios since clay-sized weathering products are enriched in Ge (Murnane and Stallard, 1990; Kurtz et al., 2002; Kurtz and Derry, 2004; Delvigne et al., 2009; Opfergelt et al., 2010; Lugolobi et al., 2010; Cornelis et al., 2010b) and biogenic silica (BSi) polymerized in plants as phytoliths is depleted in Ge (Derry et al., 2005; Blecker et al., 2007; Delvigne et al., 2009; Cornelis et al., 2010b; Lugolobi et al., 2010). The current interpretation of Ge/Si ratios of soil solutions relies on the relative importance of a low-Ge end member derived from incongruent dissolution of fresh rock minerals and biomineralization and a high-Ge end member produced by congruent dissolution of pedogenic minerals (Kurtz et al., 2002).

The fractionation of stable Si isotopes also holds a great potential to assess the relative contribution of Si released from litho/pedogenic and biogenic Si pools in the soil solution (Ziegler et al., 2005a; Engström et al., 2008; Georg et al., 2009a; Cornelis et al., 2010b). The Si isotope composition of a sample is expressed as $\delta^{30}\text{Si}$ defined as follows:

$$\delta^{30}\text{Si}=\left[\frac{\left(\frac{^{30}\text{Si}}{^{28}\text{Si}}\right)_{\text{sample}}}{\left(\frac{^{30}\text{Si}}{^{28}\text{Si}}\right)_{\text{NBS28}}} - 1\right] \cdot 1000$$

Measured $\delta^{30}\text{Si}$ values are expressed in ‰ with respect to the NBS-28 standard. The neoformation of secondary precipitates such as clay minerals (Ziegler et al., 2005a,b; Opfergelt et al., 2008, 2010; Bern et al., 2010; Cornelis et al., 2010b), the plant Si uptake producing biogenic opal (Douthitt, 1982; Ziegler et al., 2005a; Ding et al., 2005, 2008; Opfergelt et al., 2006a,b, 2008), and the adsorption of Si onto Fe-oxides (Delstanche et al., 2009; Opfergelt et al., 2009) are three processes favouring the incorporation of light Si isotopes, contributing to enrich rivers in heavy Si isotopes (De La Rocha et al., 2000; Ding et al., 2004; Georg et al., 2006, 2007; Cardinal et al., 2010). Natural environments impacted simultaneously by all these processes will dis-
play a bulk Si isotopic signature of DSi. Understanding the contribution of those three processes on DSi output can hardly be done with $\delta^{30}$Si systematics alone. Comparing Ge/Si ratios with Si isotope data (Delvigne et al., 2009; Opfergelt et al., 2010; Lugolobi et al., 2010; Cornelis et al., 2010b) may provide a better understanding of the origin of DSi exported from various soil-plant systems towards rivers.

The interpretation of Ge/Si ratios and $\delta^{30}$Si signatures in waters exported from the soil-plant system should thus combine a detailed characterization of (i) the processes involved, (ii) the seasonal variation of these processes, and (iii) the mineralogy of secondary weathering products. The seasonal variation should help to isolate biological uptake, but also include alternating dry and rainy seasons impacting drainage, modifying Si available for secondary precipitates and Si export from soil solutions to rivers. The timescale of processes also needs to be considered, as biological uptake and Si adsorption occurred at a very short timescale (day to season) compared to clay mineral formation (year to geological timescale). This should help to identify the dominant process depending on seasonal variations, considering that some processes can also be neglected based on the mineralogy.

By comparing different combinations of processes interacting in the soil-plant system, we can infer how $\delta^{30}$Si and Ge/Si ratios can be useful to evaluate the impact of Si recycling through vegetation on DSi exported. Plant Si uptake, polymerization and return in phytoliths to the soil induce a BSi pool enriched in light isotopes (lower $\delta^{30}$Si) and depleted in Ge (lower Ge/Si) relative to the initial Si signature. A stable pool of phytoliths can be preserved in soils, therefore producing soil water relatively enriched in heavy Si isotopes, but depleted in Ge if plant roots are not decomposed since Ge can be organically trapped in roots (Delvigne et al., 2009). Dissolution of the labile pool of phytoliths will impact soil water signature by decreasing $\delta^{30}$Si values and Ge/Si ratios.

In addition to the impact of vegetation, DSi output from the soil-plant system can also be affected by abiotic processes, including light Si isotopes sequestration by clay minerals and adsorption onto Fe-oxides and Ge sequestration into secondary clay minerals.
Assuming no dissolution of these secondary precipitates, DSi in soil solution exported will evolve towards isotopically heavier and Ge depleted relative to the parent material. However in organic rich environments, dissolution of secondary minerals occurs and releases light Si isotopes and Ge inducing lower $\delta^{30}$Si values and higher Ge/Si ratios (Cardinal et al., 2010; Cornelis et al., 2010b). Given the contrasted variation of Ge/Si and Si-isotopic ratios, both tracers are useful to evaluate the origin of DSi in some specific environments. However, those tracers are not designed to calculate net Si fluxes exported from the soil-plant system.

5 The origin of the dissolved Si output from various soil-plant systems

The origin of the output of DSi from various soil-plant systems towards rivers will be assessed through two controlling factors: (i) the weathering ability of the system, and (ii) the impact of vegetation on weathering products (Fig. 3). The sources of DSi fluxes including litho/pedogenic Si components and/or biogenic Si components can thus be classified more systematically. In this classification, it is assumed that some young tropical soils still have significant amounts of weatherable minerals available (Scenario 1; Fig. 3a). For Scenario 2 we assume that many tropical systems have old and highly weathered soils, in which the reservoir of primary minerals is exhausted (Scenario 2; Fig. 3b). In non-tropical regions, the climate is relatively less favorable to silicate weathering while the stock of mineral-derived Si is usually higher than in tropical environments (Scenario 3; Fig. 3c), except for arid climates (Scenario 4) where the environmental conditions do not favour silicate weathering, and where no Si soil-plant cycling takes place. The variations of geochemical Si signatures (Ge/Si ratios and $\delta^{30}$Si) in those contrasted environments will be discussed.
5.1 Scenario 1: weathering-unlimited

In a system with unlimited weathering ability, the release of DSi from land mass to oceans is largely driven by climatic conditions such as temperature and runoff promoting silicate weathering and transport (Gaillardet et al., 1999a; Jennerjahn et al., 2006). However, two recent studies demonstrate the impact of BSi recycling and restitution in topsoil on the mobility of DSi from continents to rivers. The Luquillo stream from a granitic mountain range characterized by the fastest measured rates of granitoid weathering (Puerto Rico) is dominated by Si derived from incongruent mineral weathering at the bedrock-saprolite interface as revealed by the positive $\delta^{30}$Si values of soil solution (Ziegler et al., 2005b). However, the $\delta^{30}$Si signature ($-1.5\%$) of the pore-water in the top 0.3 m of soil is lighter suggesting the recycling and dissolution of BSi enriched in $^{28}$Si. Lugolobi et al. (2010) study the Ge/Si fractionation in the same site and also conclude that biological cycling should influence DSi transfer but does not dominate as in Hawaii (see Scenario 2, Derry et al., 2005). The DSi fluxes into the Bay of Bengal might equal as much as 3.5% of the global DSi flux into the oceans are characterized by Si isotope compositions of groundwater varying between $+1.3$ and $-0.2\%$ (Georg et al., 2009b), reflecting the change from primary to secondary Si sources, mainly clay minerals and silcretes (Basile-Doelsch et al., 2005; Ziegler et al., 2005a; Georg et al., 2009a).

The relative contribution of weathering and BSi cycling in weathering-unlimited systems is still poorly quantified. Under these conditions, besides the high mineral Si stock in soils, a high biomass production and turnover should create a relatively large pool of reactive BSi. Indeed, the BSi accumulation in the soil-plant system was shown to be directly governed by the soil weatherable mineral reserves (Henriet et al., 2008a,b). The DSi exported from the soil-plant systems has biogenic, pedogenic and lithogenic signatures (Fig. 3a) and the dominance of any of these depends on specific environmental conditions. Assuming BSi dissolution and secondary precipitate stability, Si signatures can evolve towards lower Ge/Si ratio and $\delta^{30}$Si values relatively to the initial
Si signature. When dissolution of secondary minerals occurs, the release of light Si isotopes and Ge can induce lower $\delta^{30}$Si values and higher Ge/Si ratios.

5.2 Scenario 2: soil weathering-limited

In a humid tropical environment, the vegetation will increase the chemical weathering rate without increasing the Si removal from the profile towards regional drainage as a result of the transport limited landscape. Alexandre et al. (1997) model that the Si releases from phytolith dissolution is twice that of Si release from silicate weathering. Indeed ecosystems exhibiting strong depletion of mineral-derived Si and high Si uptake rates by biomass should have a strong biological control on Si cycling and export. In highly weathered soils, with optimal climatic conditions, a large fraction of silicic acid is cycling through plants before its transfer to rivers (Lucas et al., 1993). This implies that the Si concentration of stream water is not controlled by the geochemical processes of the lower soil profile, but rather by the biogeochemical cycling within the plant/surface-soil component of the ecosystem (Markewitz et al., 2001). Indeed, in a tropical rainforest overlying deeply weathered Hawaiian basalt, Derry et al. (2005) established that the Ge/Si ratios of stream waters can be controlled by (i) a Si-rich component with a relatively low Ge/Si ratio (Ge/Si~0.25×10$^{-6}$) derived from dissolution of BSi in upper soil horizons, and (ii) a Si-poor component with a relatively high Ge/Si ratio (Ge/Si~2.6×10$^{-6}$), originating from dissolution of secondary pedogenic minerals. Therefore on a discharge-weighted basis, they found that BSi contributes to 68–90% of the DSi transported by Hawaiian stream water.

The fact that the solubility of bamboo phytoliths is 17 times greater than quartz (Fraysse et al., 2006) supports recent studies suggesting that the clay mineral stability or formation in the upper soil horizons (Lucas et al., 1993, 2001; Kleber et al., 2007; Opfergelt et al., 2010) are controlled by phytolith production and recycling rather than by dissolution of quartz or other crystalline mineral phases (Barré et al., 2009). The BSi pool potentially controls the DSi in shallow soils (Lucas et al., 1993; Derry et al., 2005), and DSi available for the neoformation of secondary minerals (Opfergelt et
In an environment with very low availability of mineral-derived Si and with significant Si biocycling, we can consider that the DSi fluxes will be highly influenced by the existing BSi pool. Therefore, DSi fluxes in highly weathered systems without BSi recycling will be insignificant compared to the highly weathered systems biologically active. On another hand, the DSi release in soil surface in those environments can also have a pedogenic signature controlled by secondary clay minerals (Fig. 3b). Indeed, in intense weathering environment characterized by low weathering rates such as Congo basin (transport-limited regime), $\delta^{30}$Si in the river was correlated with weathering intensity rather than Si fluxes (Cardinal et al., 2010). Si isotope signatures in the Congo Basin were controlled by a mixing of both neoformation and dissolution of clay minerals (Cardinal et al., 2010).

The geochemical signatures will therefore be strongly influenced by secondary precipitates: the Ge/Si ratio will increase in soil solution if secondary clay-sized mineral dissolution is larger than the BSi dissolution, and $\delta^{30}$Si in soil solution will decrease with both secondary clay-sized mineral and phytolith dissolution since they are both enriched in light Si isotopes (Fig. 3b).

### 5.3 Scenario 3: climate weathering-limited

It appears that basin lithology and runoff alone are not very reliable indicators of DSi flux in vegetated watersheds where the influence of terrestrial vegetation appears to be important (Fulweiler and Nixon, 2005), promoting silicate weathering and BSi restitution on topsoil. Indeed, the presence of coniferous forest with high productivity and significant concentration of Si in needles can largely contribute to the terrestrial biogeochemical Si cycle even in temperate climate (Gérard et al., 2008).

In a French forest site, Bartoli (1983) has estimated that 80% of DSi exported from the soil profile derives from the BSi pool in deciduous stands against 20% in coniferous ones arguing for a substantial impact of Si biocycling on the DSi-sources. Moreover, in central Siberia, besides bedrocks and soil minerals, the main sources of DSi can be the...
litterfall (3.4 kg Si ha\(^{-1}\) yr\(^{-1}\)) and dissolution of phytoliths, in a basaltic environment under permafrost conditions (Pokrovsky et al., 2005). Similarly, some fraction of the DSi exported from a deforested temperate ecosystem derive from the dissolution of a biologically derived pool of ASi (phytoliths), which supports the impact of Si biocycling in this environment (Conley et al., 2008). In a Bohemian forest, despite lower atmospheric deposition of acids, the higher leaching of DSi in five glacial lakes could be explained by the decline of Al activity increasing silicate weathering but also by BSi dissolution (Vesely et al., 2005). In the wet climate of the Buenos Aires province, ASi from volcanic or biogenic origin is likely responsible for the high concentration of DSi (1 mM) in the shallow groundwater (Miretzky et al., 2001). Moreover, it has been shown that rivers draining areas with carbonate rocks have surprisingly higher DSi fluxes than silicate rocks, which could be attributed to rapid dissolution of disseminated or interbedded BSi of the carbonate rocks (Bluth and Kump, 1994). Finally, Si biocycling is comparable between forests and grasslands on a watershed scale (Table 3). Since grasslands cover about 40% of terrestrial Earth (White et al., 2000) they likely play an important role in terrestrial Si fluxes, constituting an ideal natural laboratory to use geochemical tracers (Blecker et al., 2007).

In boreal forests, DSi outputs in rivers display lighter Si isotope composition when the Si-concentration increases (Engström et al., 2010). This suggests the release of isotopically-light plant derived Si mainly during the spring snowmelt. A large fraction of DSi input to the Baltic Sea was thus assumed to be from biogenic origin (Engström et al., 2010). On another hand, the lower \(\delta^{30}\)Si values of dissolved phase of Swiss rivers in high mountain area (+0.84‰, Georg et al., 2006) and of Iceland rivers in high latitude area (+0.63‰, Georg et al., 2007) support a lower biological Si cycling compared to the Asian Yangtze River (+2.13‰, Ding et al., 2004). In the Yangtze, the preferential uptake of light Si isotopes by rice plant leads to a progressive enrichment of aqueous phase in heavy Si isotopes. Conversely, in the Yellow River in China, the average \(\delta^{30}\)Si value of DSi is +1.7‰ (Gao et al., 2006) and suggests the impact of the colder weather and lower precipitation in this agriculture area on the decreasing bio-
chemical activity (Ding et al., 2008). However, in these systems, the role of secondary clay mineral formation/dissolution on the DSi isotope compositions is not clearly determined. Indeed, the Si isotope data combined with the water chemistry of Iceland Rivers show that an average of 50% of the primary weathered Si is precipitated into secondary weathering products within the watersheds (Georg et al., 2007). In this climate weathering-limited environment, the DSi load to rivers seems mainly governed by the litho/pedogenic processes such as silicate weathering and clay minerals neoformation. Moreover, in a temperate granitic forest system, the $\delta^{30}$Si values of DSi in surface soil solution (relatively rich in phytoliths) are the most negative never found in natural aqueous system ($-1.38$ and $-2.05\%\text{o}$; Cornelis et al., 2010b). Moreover, the surface soil solution is clearly enriched in Ge with higher Ge/Si ratio than the parent material. This finding suggests that forest floor leachate solutions are deeply influenced by the dissolution of $^{28}$Si and Ge-enriched secondary clays minerals incorporated by bioturbation in organic-rich horizons, preferentially releasing light Si isotopes and Ge (Cornelis et al., 2010b). Similarly, in the Navado Sandstone aquifer (Arizona, USA), the negative $\delta^{30}$Si values ($-1.42\%\text{o}$) could also be due to dissolution of both secondary clay minerals and low-temperature silcretes (Georg et al., 2009a). In addition, DSi fluxes in Boreal and Artic rivers seem to be influenced by vegetation only through promoting silicate weathering (Humborg et al., 2006). Indeed, besides the impact of Si recycling and restitution of reactive BSi in topsoil, the Si fluxes exported from vegetated areas should be higher than those measured in bare areas (Moulton et al., 2000). In this scenario (Fig. 3c), the DSi exported from the soil profile could have biogenic, lithogenic and pedogenic signatures as in Scenario 1 even if the weathering rates and Si fluxes are lower.

In an additional podzolic scenario, the signature of DSi in soil solution of the eluvial horizon will not influenced by pedogenic components, while in the illuvial horizon the geochemical signature of DSi can be influenced by the neoformation (low Ge/Si ratios and high $\delta^{30}$Si values in DSi) and dissolution (high Ge/Si ratios and low $\delta^{30}$Si values in DSi) of secondary minerals. Assuming no impact of pedogenic components in some
specific podzols, the Si signature will be strongly influenced by primary minerals and phytoliths (Fig. 3d).

5.4 Scenario 4: weathering-limited

In African, Arabian, Asian and Australian deserts, Si can be transported through the atmosphere associated with airborne particles that should be the only form of Si exports from these arid environments (Tegen et al., 2002, 2006). However, since the transport of soil-derived dust in the atmosphere is an effective means of redistributing Si in the environment, further studies should focus on their signatures (Ge/Si ratios and $\delta^{30}$Si) in order to assess their impact on the DSi fluxes following dissolution.

6 Conclusions

The origin of DSi exported from a soil-plant system is a dynamic balance between the release of DSi from primary and secondary minerals (litho/pedogenic origin) and from phytoliths (biogenic origin). In tropical environments (Scenarios 1 and 2), DSi fluxes towards rivers are higher compared with climate weathering-limited environments (Scenarios 3 and 4). On another hand, the very low DSi concentration in soil solution of a soil weathering-limited system (Scenarios 2 and 4) is responsible for the low DSi output. Thus, the major load of DSi towards rivers is from the weathering-unlimited system (Scenario 1) where the origin of the Si-sources (litho/pedo or biogenic) needs to be elucidated to better understand the global export of DSi from continents to oceans, and the impact on the global CO$_2$ consumption rates through silicate weathering. In the future, more attention should be given to the systems with high ability for weathering and transport, since the recent studies were focused on the biological control on Si cycling and export in highly weathered tropical systems with low availability of mineral-derived Si (Derry et al., 2005).
Promising and well-recognized geochemical tracers (Ge/Si ratios and $\delta^{30}$Si) were shown to be useful to evaluate proportion of Si recycled through the vegetation. However those tracers are not designed to calculate net Si fluxes exported by vegetation. Geochemical tracers as well as Si mass-balance calculations at the watershed scale should be implemented in tropical systems in Asia and Oceania displaying the highest DSi fluxes because of their reactive geology, high runoff and high silicate weathering rates. Further studies in mountains areas of high relief would also improve our knowledge about the global impact of the Si-sources on the DSi fluxes towards rivers.

Finally, identifying mechanisms controlling the release of DSi in soil solution in climate weathering-limited environment is of great concern as global warming is believed to be mainly pronounced at high latitudes. It is conceivable that large-scale global change processes will affect the global Si cycle as a result of temperature and precipitation perturbations. For example, the enrichment of "greenhouse" gases in the atmosphere has led to an increase in the average global surface temperature of 0.6°C since the late 19th century (IPCC, 2001), and recent studies show that worldwide fresh water runoff from the continent to the ocean increases through the 20th century because plant transpiration decreases with the elevated atmospheric CO$_2$ (Gedney et al., 2006; Matthews, 2006). As a consequence, since DSi fluxes from continents to oceans are correlated with runoff, temperature and vegetation, we can assume that a change in a climatic variable could disrupt quite rapidly the biogeochemistry of the hydrosphere. The geochemical tracers (Ge/Si ratios and $\delta^{30}$Si) will help us quantify anthropogenic and natural variations and allow the relevant processes to be incorporated into predictive models for DSi loads in rivers (Garnier et al., 2006; Bernard et al., 2009) to predict DSi loads in rivers.

Acknowledgements. J.-T. Cornelis is supported by the “Fonds pour la formation à la Recherche dans l’Industrie et dans l’Agriculture” (FRIA) of Belgium, and S.O. by the “Fonds National de la Recherche Scientifique” (FNRS) of Belgium. This research was also supported by the “Fonds Spécial de Recherche” (FSR) 2008 of the UCL. The authors acknowledge the financial support
from the GIP-Ecofor for the management of the Breuil field site, part of the French Ministry of Research “Observatoire de Recherche pour l’Environnement” network.

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Table 1. Mineral weathering sequence and type of minerals as indicators of relative degree of soil development (the higher the number, the higher the degree of soil development) (Rai and Kittrick, 1989; Nagy, 1995; Allen and Hajek, 1989).

<table>
<thead>
<tr>
<th>Relative degree of soil development</th>
<th>Stability</th>
<th>Minerals&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>STABLE</td>
<td></td>
<td>Anatase</td>
<td>TiO&lt;sub&gt;2&lt;/sub&gt;</td>
</tr>
<tr>
<td>13</td>
<td></td>
<td>Rutile</td>
<td>TiO&lt;sub&gt;2&lt;/sub&gt;</td>
</tr>
<tr>
<td>12</td>
<td></td>
<td>Corundum</td>
<td>Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
</tr>
<tr>
<td>12</td>
<td></td>
<td>Hematite</td>
<td>α-Fe&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
</tr>
<tr>
<td>11</td>
<td></td>
<td>Goethite</td>
<td>α-FeOOH</td>
</tr>
<tr>
<td>10</td>
<td></td>
<td>Gibbsite</td>
<td>Al(OH)&lt;sub&gt;3&lt;/sub&gt;</td>
</tr>
<tr>
<td>9</td>
<td></td>
<td>Allophane</td>
<td>(Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;)(SiO&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;1.3&lt;/sub&gt;·2.5(H&lt;sub&gt;2&lt;/sub&gt;O)</td>
</tr>
<tr>
<td>8</td>
<td></td>
<td>Kaolinite</td>
<td>Si&lt;sub&gt;2&lt;/sub&gt;Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;5&lt;/sub&gt;(OH)&lt;sub&gt;4&lt;/sub&gt;</td>
</tr>
<tr>
<td>8</td>
<td></td>
<td>Halloysite</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td></td>
<td>Smectites</td>
<td>M&lt;sub&gt;x&lt;/sub&gt;Si&lt;sub&gt;4&lt;/sub&gt;(Al&lt;sub&gt;2-x&lt;/sub&gt;Mg&lt;sub&gt;x&lt;/sub&gt;)O&lt;sub&gt;10&lt;/sub&gt;(OH)&lt;sub&gt;2&lt;/sub&gt;</td>
</tr>
<tr>
<td>6</td>
<td></td>
<td>2:1 layer silicates</td>
<td>(Mg,Fe)&lt;sub&gt;3&lt;/sub&gt;(Al&lt;sub&gt;x&lt;/sub&gt;Si&lt;sub&gt;4-x&lt;/sub&gt;)O&lt;sub&gt;10&lt;/sub&gt;(OH)&lt;sub&gt;2&lt;/sub&gt;·4H&lt;sub&gt;2&lt;/sub&gt;OMg&lt;sub&gt;x&lt;/sub&gt;</td>
</tr>
<tr>
<td>6</td>
<td></td>
<td>Vermiculite</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td></td>
<td>Muscovite</td>
<td>KAl&lt;sub&gt;2&lt;/sub&gt;(Si&lt;sub&gt;3&lt;/sub&gt;Al)O&lt;sub&gt;10&lt;/sub&gt;(OH)&lt;sub&gt;2&lt;/sub&gt;</td>
</tr>
<tr>
<td>6</td>
<td></td>
<td>Illite</td>
<td>K&lt;sub&gt;x&lt;/sub&gt;Al&lt;sub&gt;2&lt;/sub&gt;(Si&lt;sub&gt;4-x&lt;/sub&gt;Al&lt;sub&gt;x&lt;/sub&gt;)O&lt;sub&gt;10&lt;/sub&gt;(OH)&lt;sub&gt;2&lt;/sub&gt;</td>
</tr>
<tr>
<td>5</td>
<td></td>
<td>QUARTZ</td>
<td>SiO&lt;sub&gt;2&lt;/sub&gt;</td>
</tr>
<tr>
<td>5</td>
<td></td>
<td>FELDSPARS</td>
<td>KAlSi&lt;sub&gt;3&lt;/sub&gt;O&lt;sub&gt;8&lt;/sub&gt;, NaAlSi&lt;sub&gt;3&lt;/sub&gt;O&lt;sub&gt;8&lt;/sub&gt;-CaAl&lt;sub&gt;2&lt;/sub&gt;Si&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;8&lt;/sub&gt;</td>
</tr>
<tr>
<td>4</td>
<td></td>
<td>Biotite</td>
<td>K(Mg,Fe)&lt;sub&gt;3&lt;/sub&gt;(Si&lt;sub&gt;3&lt;/sub&gt;Al)O&lt;sub&gt;10&lt;/sub&gt;(OH)&lt;sub&gt;2&lt;/sub&gt;</td>
</tr>
<tr>
<td>3</td>
<td></td>
<td>OLIVINE</td>
<td>(Mg,Fe)&lt;sub&gt;2&lt;/sub&gt;SiO&lt;sub&gt;4&lt;/sub&gt;</td>
</tr>
<tr>
<td>3</td>
<td></td>
<td>HORNBLENDE</td>
<td>Ca&lt;sub&gt;2&lt;/sub&gt;Na(Mg,Fe)&lt;sub&gt;4&lt;/sub&gt;(Al, Si)&lt;sub&gt;8&lt;/sub&gt;O&lt;sub&gt;22&lt;/sub&gt;(OH,F)&lt;sub&gt;2&lt;/sub&gt;</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td>PYROXENE</td>
<td>Ca(Mg,Fe, Al)(Si&lt;sub&gt;3&lt;/sub&gt;Al)&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;6&lt;/sub&gt;</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td>CALCITE</td>
<td>CaCO&lt;sub&gt;3&lt;/sub&gt;</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td>DOLOMITE</td>
<td>Ca,Mg(CO&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;</td>
</tr>
<tr>
<td>1</td>
<td></td>
<td>APATITE</td>
<td>Ca&lt;sub&gt;5&lt;/sub&gt;(F,Cl,OH)(PO&lt;sub&gt;4&lt;/sub&gt;)&lt;sub&gt;3&lt;/sub&gt;</td>
</tr>
<tr>
<td>1</td>
<td></td>
<td>GYPSUM</td>
<td>CaSO&lt;sub&gt;4&lt;/sub&gt;·2H&lt;sub&gt;2&lt;/sub&gt;O</td>
</tr>
<tr>
<td>1</td>
<td></td>
<td>HALITE</td>
<td>NaCl</td>
</tr>
</tbody>
</table>

<sup>a</sup> Primary minerals are capitalized.
Table 2. Degree of Si accumulation in plants estimated from mean relative shoot Si concentration of plant species (non-: <0.5% Si, intermediate-: 0.5–1% Si and high-accumulator: >1% Si) (Ma and Takahashi, 2002), using the data analysis of Hodson et al. (2005) who adjust an average shoot Si concentration for each species across studies.

<table>
<thead>
<tr>
<th>Group</th>
<th>Species</th>
<th>Common name</th>
<th>Si (wt%) in shoots</th>
<th>Degree of Si accumulationa</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>MARCHANTIOPHYTA</strong></td>
<td>Marchantia polymorpha</td>
<td>liverworts</td>
<td>5.45</td>
<td>+</td>
</tr>
<tr>
<td><strong>EQUISETOPHYTA</strong></td>
<td>Equisetum arvense</td>
<td>Common horsetail</td>
<td>3.99</td>
<td>+</td>
</tr>
<tr>
<td></td>
<td>Equisetum hyemale</td>
<td>Rough horsetail</td>
<td>2.92</td>
<td>+</td>
</tr>
<tr>
<td><strong>ANGIOSPERM</strong></td>
<td>Phoenix roebelenii</td>
<td>Date palm</td>
<td>0.20</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>Whashingtonia filifora</td>
<td>palm</td>
<td>1.74</td>
<td>+</td>
</tr>
<tr>
<td><strong>Asteraceae</strong></td>
<td>Lactuca serriola</td>
<td>lettuce</td>
<td>0.79</td>
<td>±</td>
</tr>
<tr>
<td></td>
<td>Helianthus annuus</td>
<td>sunflower</td>
<td>1.88</td>
<td>+</td>
</tr>
<tr>
<td><strong>Cyperaceae</strong></td>
<td>Carex cinica</td>
<td>sedge</td>
<td>2.44</td>
<td>+</td>
</tr>
<tr>
<td><strong>Fabaceae</strong></td>
<td>Glycine max</td>
<td>soybean</td>
<td>1.39</td>
<td>+</td>
</tr>
<tr>
<td></td>
<td>Lupinus nanus</td>
<td>lupine</td>
<td>0.28</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>Phaseolus vulgaris</td>
<td>bean</td>
<td>0.95</td>
<td>±</td>
</tr>
<tr>
<td></td>
<td>Trifolium incarnatum</td>
<td>crimson clover</td>
<td>0.22</td>
<td>–</td>
</tr>
<tr>
<td><strong>Fagaceae</strong></td>
<td>Quercus robur</td>
<td>pedunculate oak</td>
<td>1.54</td>
<td>+</td>
</tr>
<tr>
<td></td>
<td>Fagus sylvatica</td>
<td>European beech</td>
<td>6.08</td>
<td>±</td>
</tr>
<tr>
<td><strong>Lamiaceae</strong></td>
<td>Mentha longifolia</td>
<td>mint</td>
<td>0.73</td>
<td>±</td>
</tr>
<tr>
<td></td>
<td>Mentha piperita</td>
<td>peppermint</td>
<td>1.22</td>
<td>+</td>
</tr>
<tr>
<td><strong>Lilaceae</strong></td>
<td>Allium fistulosum</td>
<td>onion</td>
<td>0.31</td>
<td>–</td>
</tr>
<tr>
<td><strong>Musaceae</strong></td>
<td>Musa basjoo</td>
<td>banana</td>
<td>0.98</td>
<td>±</td>
</tr>
<tr>
<td><strong>Poaceae</strong></td>
<td>Arundinaria gigantea</td>
<td>cane</td>
<td>8.77</td>
<td>+</td>
</tr>
<tr>
<td></td>
<td>Avena sativa</td>
<td>oat</td>
<td>1.51</td>
<td>+</td>
</tr>
<tr>
<td></td>
<td>Hordeum vulgare</td>
<td>barley</td>
<td>1.82</td>
<td>+</td>
</tr>
<tr>
<td></td>
<td>Oryza sativa</td>
<td>rice</td>
<td>4.17</td>
<td>+</td>
</tr>
<tr>
<td></td>
<td>Saccharum officinarum</td>
<td>sugarcane</td>
<td>1.51</td>
<td>+</td>
</tr>
<tr>
<td></td>
<td>Secale cereale</td>
<td>rye</td>
<td>1.26</td>
<td>+</td>
</tr>
<tr>
<td></td>
<td>Sorghum bicolor</td>
<td>sorghum</td>
<td>1.54</td>
<td>+</td>
</tr>
<tr>
<td></td>
<td>Triticum aestivum</td>
<td>wheat</td>
<td>2.45</td>
<td>+</td>
</tr>
<tr>
<td></td>
<td>Zea mays</td>
<td>maize</td>
<td>0.83</td>
<td>±</td>
</tr>
<tr>
<td><strong>Urticaceae</strong></td>
<td>Urtica dioica</td>
<td>nettle</td>
<td>1.34</td>
<td>+</td>
</tr>
<tr>
<td><strong>GYMNOSPERM</strong></td>
<td>Abies alba</td>
<td>European silver fir</td>
<td>0.34</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>Larix decidua</td>
<td>European larch</td>
<td>0.87</td>
<td>±</td>
</tr>
<tr>
<td></td>
<td>Picea abies</td>
<td>Norway spruce</td>
<td>1.36</td>
<td>+</td>
</tr>
<tr>
<td></td>
<td>Picea rubens</td>
<td>Red spruce</td>
<td>0.32</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>Pinus strobus</td>
<td>White pine</td>
<td>0.12</td>
<td>–</td>
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<tr>
<td><strong>POLYPODIOPHYTA</strong></td>
<td>Dryopteris carthusiana</td>
<td>Narrow-buckler fern</td>
<td>0.18</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>Polypodiaceae</td>
<td>Rockcap fern</td>
<td>0.15</td>
<td>–</td>
</tr>
</tbody>
</table>

a –, ± and +: Si non-, intermediate- and high-accumulator.
Table 3. Si fluxes (uptake, restitution and drainage) in forest and grassland ecosystems.

<table>
<thead>
<tr>
<th>Vegetation uptake</th>
<th>Si (kg ha(^{-1}) yr(^{-1}))</th>
<th>Export by drainage</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Vegetation Restitution Export by Reference</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Equatorial forest (Ferralsols)</td>
<td>41</td>
<td>11</td>
<td>1</td>
</tr>
<tr>
<td>Equatorial forest (Ferralsols)</td>
<td>58–76</td>
<td>58–76</td>
<td>16</td>
</tr>
<tr>
<td>Temperate deciduous forest (Cambisols)</td>
<td>23</td>
<td>22</td>
<td>3</td>
</tr>
<tr>
<td>Temperate deciduous forest (Cambisols)</td>
<td>18–23</td>
<td>18–19</td>
<td>6–7</td>
</tr>
<tr>
<td>Temperate coniferous forest (Cambisols)</td>
<td>30–43</td>
<td>29–42</td>
<td>0.7–1</td>
</tr>
<tr>
<td>Temperate coniferous forest (Cambisols)</td>
<td>44</td>
<td>36</td>
<td>5</td>
</tr>
<tr>
<td>Temperate pine forest (Cambisols)</td>
<td>2.3</td>
<td>2.1</td>
<td>9.4</td>
</tr>
<tr>
<td>Temperate pine forest (Podzols)</td>
<td>6</td>
<td>5</td>
<td>28</td>
</tr>
<tr>
<td>Temperate pine forest</td>
<td>16</td>
<td>14</td>
<td>17</td>
</tr>
<tr>
<td>Dry grasslands (Aridisols)</td>
<td>–</td>
<td>26</td>
<td>0.2</td>
</tr>
<tr>
<td>Humid grasslands (Mollisols)</td>
<td>59</td>
<td>11</td>
<td>7</td>
</tr>
</tbody>
</table>

Table 4. The DSi concentration of freshwater at the global scale (modified from Exley, 1998).

<table>
<thead>
<tr>
<th>Location</th>
<th>DSi (µmol l(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Australia</td>
<td>65</td>
</tr>
<tr>
<td>Europe</td>
<td>126</td>
</tr>
<tr>
<td>North America</td>
<td>151</td>
</tr>
<tr>
<td>Asia</td>
<td>196</td>
</tr>
<tr>
<td>South America</td>
<td>200</td>
</tr>
<tr>
<td>Africa</td>
<td>389</td>
</tr>
<tr>
<td>Global average(^a)</td>
<td>150</td>
</tr>
</tbody>
</table>

\(^a\) Estimation of discharge-weighted average silicic acid concentration in rivers (Tréguer et al., 1995).
Table 5. Average DSi flux and load per continent and per latitude (tropical or not) towards large rivers. Data are from Jennerjahn et al. (2006).

<table>
<thead>
<tr>
<th>Continent</th>
<th>DSi flux (kg Si ha(^{-1}) yr(^{-1}))</th>
<th>DSi load (10(^{9}) kg Si yr(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Tropical rivers</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Africa</td>
<td>11.3</td>
<td>8.9</td>
</tr>
<tr>
<td>South America</td>
<td>21.9</td>
<td>24.3</td>
</tr>
<tr>
<td>Asia</td>
<td>23.6</td>
<td>11.5</td>
</tr>
<tr>
<td>Oceania</td>
<td>95.1</td>
<td>1.4</td>
</tr>
<tr>
<td><strong>Non-tropical rivers</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Oceania</td>
<td>0.2</td>
<td>0.2</td>
</tr>
<tr>
<td>Africa</td>
<td>0.6</td>
<td>0.3</td>
</tr>
<tr>
<td>North America</td>
<td>7.5</td>
<td>5.4</td>
</tr>
<tr>
<td>Asia</td>
<td>7.9</td>
<td>12.9</td>
</tr>
<tr>
<td>Europe</td>
<td>7.9</td>
<td>1.6</td>
</tr>
<tr>
<td>South America</td>
<td>32.0</td>
<td>6.6</td>
</tr>
<tr>
<td><strong>Total load</strong></td>
<td></td>
<td>74.5(^{a})</td>
</tr>
</tbody>
</table>

\(^{a}\) This estimation of DSi load from rivers into oceans represents 50% of the total riverine DSi load calculated by Tréguer et al. (1995) (see Fig. 1) since this table only represents half of the world river discharge (37 400 km\(^{3}\) yr\(^{-1}\)) (Tréguer et al., 1995).
Fig. 1. Biogeochemical Si cycle on continents (compartments modified from Basile-Doelsch et al., 2005). Solid line: Transport; dashed line: Dissolution; small dotted line: Neoformation/Precipitation; pointed-dotted line: Adsorption/Desorption. Numbers on arrows show interpool Si transfers in $10^{12}$ kg Si yr$^{-1}$ (Tréguer et al., 1995; Matichenkov and Bocharnikova, 2001).
Fig. 2. Classification of solid Si compounds in the soil (modified from Sauer et al., 2006).
Fig. 3. Schematic representation of the weathering ability of a soil-plant system as a function of the climate (runoff and temperature), soil conditions (presence of weatherable minerals) and recycling by vegetation. The scenarios are described in the text: (a) Weathering unlimited (Scenario 1); (b) Soil weathering-limited (Scenario 2); (c) Climate weathering-limited (Scenario 3); (d) podzolic scenario. The scenario 4 (weathering-limited) is not represented on this figure but described in the text.