

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

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Received: 12 July 2010 – Published in Biogeosciences Discuss.: 11 August 2010

Revised: 20 December 2010 – Accepted: 6 January 2011 – Published: 18 January 2011

**Abstract.** Silicon (Si) released as  $H_4SiO_4$  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  $H_4SiO_4$  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. We recommend the use of biogeochemical tracers in combination with Si mass-balances and detailed physico-chemical characterization of soil-plant systems to allow better insight in the sources and fate of Si in these biogeochemical systems.

### 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 ( $H_4SiO_4^0$ ). DSi contributes to soil formation through biogeochemical reactions on continents – such as (1) neoformation of secondary minerals (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; Hartmann et al., 2009). Indeed, the interaction between the Si cycle and C cycle regulates the atmospheric  $CO_2$  through silicate mineral weathering (Berner, 1997), soil organic carbon sequestration in stable organo-mineral complexes (Torn et al., 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).



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In the terrestrial Si cycle, higher plants should largely contribute to the global Si cycle since their annual BSi production ranges from  $1.7$  to  $5.6 \times 10^{12}$  kg Si yr<sup>-1</sup> (Conley, 2002), which rivals BSi production of diatoms in the oceans ( $6.7 \times 10^{12}$  kg Si yr<sup>-1</sup>) (Tréguer et al., 1995). More recently, BSi biologically fixed was shown to be at  $2.5 \times 10^{12}$  kg Si yr<sup>-1</sup> (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., 2010c), 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<sub>4</sub>SiO<sub>4</sub><sup>0</sup> 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 neof ormation of authigenic Si-constituents, (iii) Si adsorption/desorption

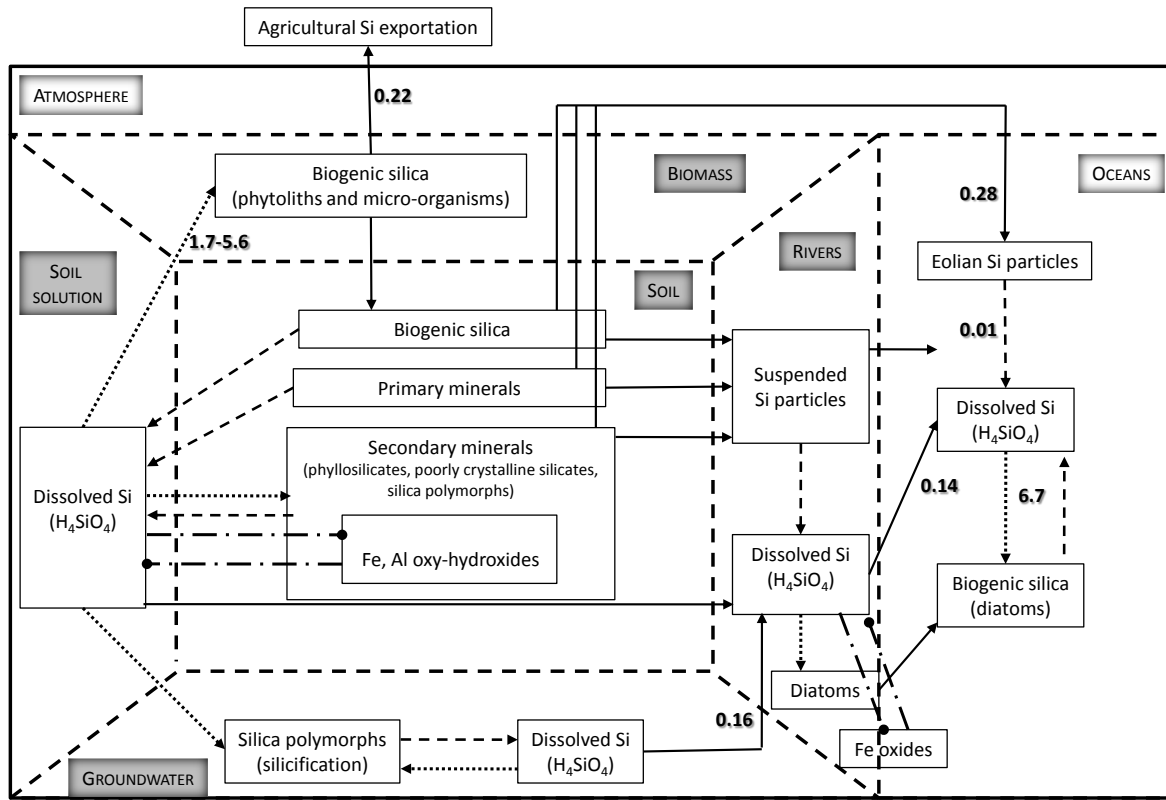
on various solid phases, (iv) Si absorption by vegetation and micro-organisms, (v) preservation of stable Si forms in the profile and (vi) external atmospheric inputs. The continental Si cycle can be represented by five components (Fig. 1): soil solution, groundwater, rivers, biomass and soils, which are linked to the global Si cycle by two other major reservoirs (oceans and atmosphere).

### 2.1 Solubility of Si-minerals

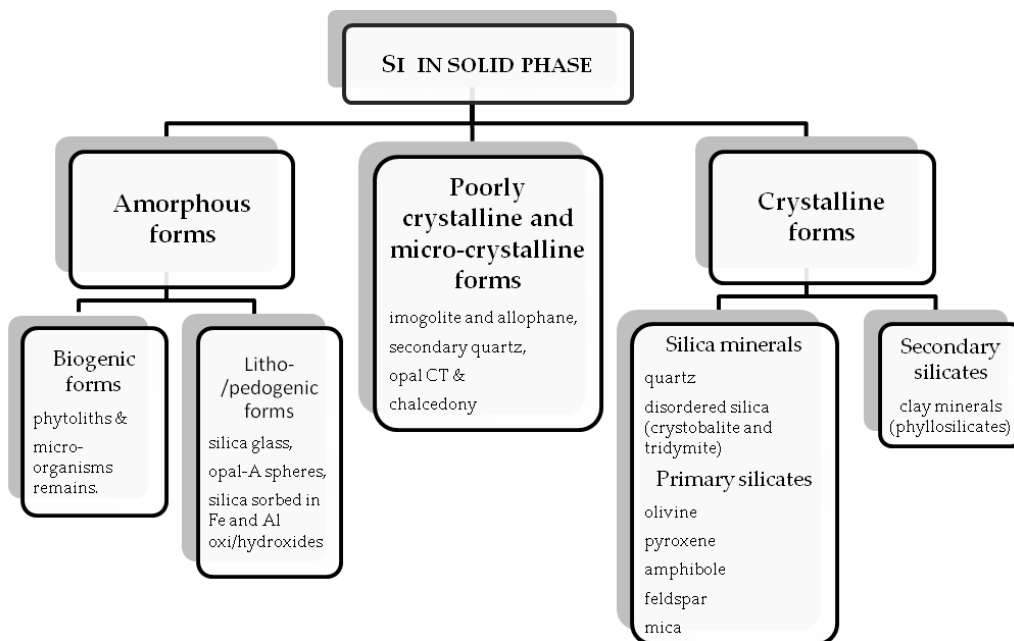
In rocks, Si ranges from more than 46.5% (e.g. ortho-quartzite) to 23% in basic rocks (e.g. basalt) to trace amounts in carbonaceous rocks (e.g. limestones and carbonatites) (Monger and Kelly, 2002). In derived soils, Si ranges from 46.0% in silcretes to 7.9% in petrocalcic horizons, and even lower in some highly weathered Oxisols such 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).

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.

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), volcanic glasses and opal coatings on secondary minerals (McKeague and Cline, 1963b; Chadwick et al., 1987). 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 comprises phytoliths (opal-A polymerized in leaves) and remnants 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).



**Fig. 1.** Biogeochemical Si cycle on continents (compartments modified from Basile-Doelsch et al., 2005). Solid line: transport; dashed line: dissolution; small dotted line: neof ormation/precipitation; pointed-dotted line: adsorption/desorption. Numbers on arrows show inter-pool Si transfers in  $10^{12} \text{ kg Si yr}^{-1}$  (Tréguer et al., 1995; Matichenkov and Bocharnikova, 2001).



**Fig. 2.** Classification of solid Si compounds in the soil (modified from Sauer et al., 2006).

### 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 undergoes hydrolysis at  $\text{pH} < 9$  by the overall reaction:



The solubility of biogenic silica is equivalent to that of vitreous silica (1.8 mM Si) and is 17 times higher than quartz (Frayssé 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 (Frayssé et al., 2010). The plants need to find a balance between cellulose, lignin and Si incorporation to be rigid but still flexible. Thus, it could be assumed that aquatic macrophyte Si metabolism is closely linked with cellulose and lignin metabolism (Schoelynck 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; Frayssé 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 ( $\text{Fe}^{3+}$ ,  $\text{Zn}^{2+}$  and  $\text{Cu}^{2+}$ ) 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 (Bartoli, 1985).

Dissolution rates of amorphous silica should simply increase linear 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  $\text{H}_4\text{SiO}_4$  dissociates appreciably such that the first reaction is written (Dove, 1995):



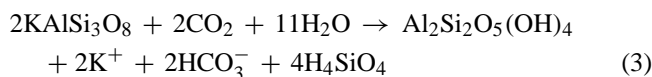
This reaction is an important buffer for some natural systems and, as a result, only environments with unusually low-silica status, like carbonatites and serpentinites, can reach a pH above the first pK of silicic acid ( $\text{pK}_{a1} = 9.82$  at 25 °C).

The Si-polymeric species become stable at  $\text{pH} \sim 9$  (Knight and Kinrade, 2001; Dietzel, 2000, 2002).

### 2.1.2 Silicate minerals

The weathering rates of silicate minerals are important for soil development, soil buffering capacities related to acidic deposition, control of carbon cycle and cycling of many inorganic elements which are critical for 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  $\text{K}^+$ ,  $\text{Na}^+$  and  $\text{Ca}^{2+}$  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:



The mineral weathering rate depends on mainly chemical equilibrium, where any processes consuming free silicic acid, e.g. secondary precipitates, adsorption and uptake by vegetation (Eq. 3), can considerably accelerate mineral dissolution (Exley, 1998; Dove, 1995; Street-Perrott and Barker, 2008). 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., 2010a).

### 2.2 Neoformation and precipitation of Si-minerals

The Si concentration in soil solutions strongly depends on equilibrium to secondary phases, and is thus strongly related to the stage of soil development as influenced by age, 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  $\text{H}_4\text{SiO}_4$  ( $\sim 1.6$  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

**Table 1.** Mineral weathering sequence (Goldich, 1938) 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).

Relative degree of soil development	Stability	Minerals*	Formula
	STABLE		
13	↑	Anatase	TiO <sub>2</sub>
		RUTILE	TiO <sub>2</sub>
		CORUNDUM	Al <sub>2</sub> O <sub>3</sub>
12		Hematite	α-Fe <sub>2</sub> O <sub>3</sub>
		Goethite	α-FeOOH
11		Gibbsite	Al(OH) <sub>3</sub>
		Allophane	(Al <sub>2</sub> O <sub>3</sub> )(SiO <sub>2</sub> ) <sub>1,3</sub> .2.5(H <sub>2</sub> O)
10		Kaolinite	Si <sub>2</sub> Al <sub>2</sub> O <sub>5</sub> (OH) <sub>4</sub>
		Halloysite	
9		Smectites	M <sub>x</sub> Si <sub>4</sub> (Al <sub>2-x</sub> Mg <sub>x</sub> )O <sub>10</sub> (OH) <sub>2</sub>
8		2:1 layer silicates	(Mg,Fe) <sub>3</sub> (Al <sub>x</sub> Si <sub>4-x</sub> )O <sub>10</sub> (OH) <sub>2</sub> 4H <sub>2</sub> O Mg <sub>x</sub>
		Vermiculite	
7		MUSCOVITE	KAl <sub>2</sub> (Si <sub>3</sub> Al)O <sub>10</sub> (OH) <sub>2</sub>
	Illite	K <sub>x</sub> Al <sub>2</sub> (Si <sub>4-x</sub> Al <sub>x</sub> )O <sub>10</sub> (OH) <sub>2</sub>	
6	QUARTZ	SiO <sub>2</sub>	
5	FELDSPARS	KAlSi <sub>3</sub> O <sub>8</sub> , NaAlSi <sub>3</sub> O <sub>8</sub> -CaAl <sub>2</sub> Si <sub>2</sub> O <sub>8</sub>	
4	BIOTITE	K(Mg,Fe) <sub>3</sub> (Si <sub>3</sub> Al)O <sub>10</sub> (OH) <sub>2</sub>	
3	OLIVINE	(Mg,Fe) <sub>2</sub> SiO <sub>4</sub>	
	HORNBLLENDE	Ca <sub>2</sub> Na(Mg,Fe) <sub>4</sub> (Al,Si) <sub>8</sub> O <sub>22</sub> (OH,F) <sub>2</sub>	
	PYROXENE	Ca(Mg,Fe,Al)(Si,Al) <sub>2</sub> O <sub>6</sub>	
2	CALCITE	CaCO <sub>3</sub>	
	DOLOMITE	Ca,Mg(CO <sub>3</sub> ) <sub>2</sub>	
	APATITE	Ca <sub>5</sub> (F,Cl,OH)(PO <sub>4</sub> ) <sub>3</sub>	
1	GYPSUM	CaSO <sub>4</sub> 2H <sub>2</sub> O	
	HALITE	NaCl	
	UNSTABLE		

\* Primary minerals are capitalized.

horizons with pH(H<sub>2</sub>O) values >5.0 (Wada, 1989). Moreover the precipitation of H<sub>4</sub>SiO<sub>4</sub> with Al hydroxides forms hydroxialuminosilicates (HAS), which might be considered as amorphous precursors to imogolite (Exley, 1998; Doucet et al., 2001). In environments with very active humus, characterized by high decomposition rates, the formation 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<sub>4</sub>SiO<sub>4</sub> concentration 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 formation of opal-A, opal-CT and microquartz (Chadwick et al., 1987). 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; 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<sub>2</sub> (Conrad et al., 2007). The partial dissolution of the biogenic opal-A in topsoil also provides DSi for sequestration in secondary minerals (clay neof ormation and Si adsorption) in upper soil horizons (Lucas et al., 1993; Lucas, 2001; Michalopoulos and Aller, 2004; Barré et al., 2009; Opfergelt et al., 2010).

It must be emphasized that the pedogenic formation of secondary Si-containing minerals (phyllosilicates, silica and short-range ordered aluminosilicates) is strongly influenced by Si activity in soil solution which depends on (i) parent material as the ultimate and readily source of  $\text{H}_4\text{SiO}_4$ , and (ii) climate providing water for weathering and preventing intensive leaching of  $\text{H}_4\text{SiO}_4$  (Jackson et al., 1948; Dove, 1995; White, 1995; Berner, 1995; Gérard et al., 2002; Monger and Kelly, 2002). Climate (mainly moisture 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 precipitation intensity and seasonality, humidity, evapotranspiration, 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 neof ormation 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). A convergence from both climate and time leads to highly weathered tropical soils whatever the parent material, except likely for detrital 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, 1996).

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).  $\text{H}_4\text{SiO}_4$  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). 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 recycling by vegetation

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). Silicon 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 simple mass flow, while passive Si uptake is directly proportional to mass flow. Rejective uptake is characterized by low Si uptake by plants implying  $H_4SiO_4$  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; Henriot et al., 2006; Cornelis et al., 2010b).

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 > polypodiophyta (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 Equisitaceae (Epstein, 1999). Silicon is not considered as an essential element for higher plants (Epstein, 1994; Epstein, 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; Korndörfer 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; Hodson and Sangster, 1999; Liang et al., 2001, 2007). Currently, there is no evidence of Si involved in plant metabolism (Ma et al., 2001) since no Si bearing organic compound has been identified in higher plants 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).

## 2.5 Biogenic Si preservation

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 kg Si ha<sup>-1</sup> yr<sup>-1</sup>) 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<sup>-1</sup> yr<sup>-1</sup>, respectively (Bartoli, 1983). The storage of BSi in grasslands ecosystem ranges from 4 to 16 kg Si ha<sup>-1</sup> yr<sup>-1</sup> (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.

The amount of ASi in soils commonly ranges from <1 to 30 mg g<sup>-1</sup> on a total soil basis (Drees et al., 1989). The highly soluble BSi pool returns to topsoil through litterfall, contributing Si to 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 readily soluble Si, whether from biogenic or pedogenic origin, in the soil can be obtained by alkaline dissolution (Sauer et al., 2006; Saccone et al., 2007; Cornelis et al., 2011).

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

**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.

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

\* , – , ± and +: Si non-, intermediate- and high-accumulator.



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 ( $0.28 \times 10^{12}$  kg Si yr<sup>-1</sup>) where a small fraction dissolves ( $0.01 \times 10^{12}$  kg Si yr<sup>-1</sup>) (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<sup>-1</sup> year<sup>-1</sup>. 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  $3 \pm 2$  kg Si ha<sup>-1</sup> yr<sup>-1</sup> (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 kg Si ha<sup>-1</sup> yr<sup>-1</sup> (Cornu et al., 1998). Finally, in humid climates, most values of annual Si inputs through rainfall are <1.4 kg Si ha<sup>-1</sup> yr<sup>-1</sup> (Sommer et al., 2006). More generally, atmospheric inputs were estimated at <1, 1.5 and 2 kg Si ha<sup>-1</sup> yr<sup>-1</sup> (Alexandre et al., 1997; Bartoli, 1983; Blecker et al., 2006, respectively). In a forested Japanese catchment, increasing atmospheric Si deposition from dust storm events does not noticeably impact short-term stream water fluxes (Hartmann et al., 2008). 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

### 3.1 Si in soil-plant systems

Terrestrial plants and their associated microbiota directly affect silicate mineral weathering in several ways: (i) affecting the temperature of the soil, (ii) protecting soil against erosion, (iii) generating of chelating ligands, (iv) modifying pH through production of CO<sub>2</sub> 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 (Draver, 1994; Moulton et al., 2000).

Silicon accumulation process by vegetation can be important. For instance, a Si-accumulator forest (1.1% Si in leaves) with a biomass production of 16 tons dry weight yr<sup>-1</sup> would extract about 200 kg Si ha<sup>-1</sup> yr<sup>-1</sup> (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., 2010c).

It is well known that aquatic macrophytes and wetland species can contain significant amounts of Si (Struyf and Conley, 2009; Struyf et al., 2009). In a reed-dominated small freshwater tidal marsh and given the high solubility of biogenic silica, more than 40% of DSi export can be attributed to reed decomposition (Struyf et al., 2007). Moreover, the transport of Si through boreal watersheds could be impacted by silica storage originating from diatoms accumulation in peat layers (Kokfelt et al., 2009, 2010).

In temperate forest ecosystem, the Si uptake depends on tree species and soil type, ranging from 2 to 44 kg Si ha<sup>-1</sup> yr<sup>-1</sup> (Bartoli, 1983; Markewitz and Richter, 1998; Fulweiler and Nixon, 2005; Gérard et al., 2008; Cornelis et al., 2010c). In humid tropical conditions, the Si recycling by forest trees is evaluated to up to 67 kg ha<sup>-1</sup> yr<sup>-1</sup> (Congo rainforest; Alexandre et al., 1997), an extremely high value (970–1380 kg ha<sup>-1</sup> yr<sup>-1</sup>) 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<sup>-1</sup> yr<sup>-1</sup> (Blecker et al., 2006). The active uptake by vegetation decreases H<sub>4</sub>SiO<sub>4</sub> concentration in soil solution, and thus accelerates the mineral weathering rate (see Eq. 3) (Exley, 1998). Indeed, Si-accumulating plants are able to accelerate the dissolution of basalt (Hinsinger et al., 2001).

The Si recycling by vegetation (forest, grassland and wetlands) strongly controls the amount of Si restituted on

**Table 3.** Si fluxes (uptake, restitution and drainage) in forest and grassland ecosystems.

	Si (kg ha <sup>-1</sup> yr <sup>-1</sup> )			
	Vegetation uptake	Restitution by litterfall	Export by drainage	Reference
Equatorial forest (Ferralsols)		41	11	1
Equatorial forest (Ferralsols)	58–76	58–76	16	2
Temperate deciduous forest (Cambisols)	23	22	3	3
Temperate deciduous forest (Cambisols)	18–23	18–19	6–7	4
Temperate coniferous forest (Cambisols)	30–43	29–42	0.7–1	4
Temperate coniferous forest (Cambisols)	44	36	5	6
Temperate pine forest (Cambisols)	2.3	2.1	9.4	4
Temperate pine forest (Podzols)	6	5	28	3
Temperate pine forest	16	14	17	5
Dry grasslands (Aridisols)	–	26	0.2	7
Humid grasslands (Mollisols)		59	11	7

1. Lucas et al. (1993); 2. Alexandre et al. (1997); 3. Bartoli (1983); 4. Cornelis et al. (2010c); 5. Markewitz and Richter (1998); 6. Gérard et al. (2008); 7. Blecker et al. (2006)

topsoil, litterfall being the most important Si flux from vegetation to soil (Sommer et al., 2006; Blecker et al., 2006; Struyf and Conley, 2009; Cornelis et al., 2010c; Struyf et al., 2010). Silicon recycling by vegetation seems to be of the same order of magnitude as DSi outputs from soils (Table 3). 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., 2010c). In 2005, the total forest area worldwide was estimated to be 3952 million hectares, 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<sup>-1</sup> yr<sup>-1</sup> (Table 3), the annual forest BSi production would be  $0.15 \times 10^{12}$  kg Si yr<sup>-1</sup>, which represents 6.3% of the amount of the total terrestrial Si biologically fixed as BSi ( $2.5 \times 10^{12}$  kg Si yr<sup>-1</sup>) (Laruelle et al., 2009). In addition, considering a mean Si output from forested land of 10 kg Si ha<sup>-1</sup> yr<sup>-1</sup> (Table 3), the global DSi leached out from forest ecosystem would be  $0.04 \times 10^{12}$  kg Si yr<sup>-1</sup>, which represents 27% of the net DSi inputs from continents to oceans.

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., 2010c). 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  $0.22 \times 10^{12}$  kg Si yr<sup>-1</sup> (Matichenkov and

Bocharnikova, 2001), which is of the order of magnitude as the total dissolved Si transferred from continents to oceans by rivers ( $0.14 \times 10^{12}$  kg Si yr<sup>-1</sup>) (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).

The large Si biocycling by terrestrial vegetation highlights the necessity to incorporate the part of H<sub>4</sub>SiO<sub>4</sub> polymerized in higher plants and in phytoplankton as BSi (Bormann et al., 1998; Meunier, 2003; Street-Perrott and Barker, 2008) in studies using DSi concentrations in rivers to understand chemical weathering rates and solute generation processes (Gaillardet et al., 1997, 1999a, b; Oliva et al., 1999; Vuai and Tokuyama, 2007). 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

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

	DSi ( $\mu\text{mol l}^{-1}$ )
Australia	65
Europe	126
North America	151
Asia	196
South America	200
Africa	389
Global average*	150

\* Estimation of discharge-weighted average silicic acid concentration in rivers (Tréguer et al., 1995).

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.

### 3.2 Dissolved Si transfer

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., 2006b).

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 ( $0.12 \times$

**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).

	DSi flux ( $\text{kg Si ha}^{-1} \text{ yr}^{-1}$ )	DSi load ( $10^9 \text{ kg Si yr}^{-1}$ )
<b>Tropical rivers</b>		
Africa	11.3	8.9
South America	21.9	24.3
Asia	23.6	11.5
Oceania	95.1	1.4
<b>Non-tropical rivers</b>		
Oceania	0.2	0.2
Africa	0.6	0.3
North America	7.5	5.4
Asia	7.9	12.9
Europe	7.9	1.6
South America	32.0	6.6
<b>Total Load</b>		<b>74.5*</b>

\* 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 ( $37\,400 \text{ km}^3 \text{ yr}^{-1}$ ) (Tréguer et al., 1995).

$10^{12} \text{ kg Si yr}^{-1}$ ) and 20% from temperate regions ( $0.03 \times 10^{12} \text{ kg Si yr}^{-1}$ ). 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  $\text{CO}_2$  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). The DSi yield in the Japanese Archipelago, a hyperactive region, is 6.6 times higher than the world average (Hartmann et al., 2010). These volcanic “hot spots” 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; Hartmann 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). Slope constitutes another important controlling factor on DSi fluxes besides lithology and runoff (Hartmann et al., 2010).

*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  $\sim 10\%$  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., 2006b) 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., 2006b). Furthermore, a recent study shows that land use is the most important controlling factor of total biologically reactive silica fluxes in a temperate European river basin (Struyf et al., 2010).

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 geomorphology, (3) the hydrologi-

cal conditions (discharge), (4) the soil development in the catchment, and (5) the biological processes (Sommer et al., 2006; Beusen et al., 2009; Hartmann et al., 2010). Although the drivers of DSi fluxes from land to oceans are identified, the relative contribution of the two different solid Si pools (litho/pedogenic and biogenic) to the release of DSi in aqueous phase is still poorly constrained.

#### 4 Tracing biogeochemical Si cycle in the soil-plant system

Since Si is a ubiquitous element in the biogeosphere, 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., 2010c) 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, 2009a; Bern et al., 2010; Cardinal et al., 2010; Cornelis et al., 2010a; 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 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, neof ormation of secondary clay minerals, opaline spheres precipitation and Si adsorption onto Fe and Al (hydr)oxides. Thus, we recommend that Si mass balances should be determined and a detailed physico-chemical characterization of the soil-plant system should be performed when using geochemical tracers (Ge/Si ratios and  $\delta^{30}\text{Si}$ ) to obtain insight in the sources and fate of Si in these biogeochemical 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., 2010a) 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., 2010a; 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., 2009b; Cornelis et al., 2010a). The Si isotope composition of a sample is expressed as  $\delta^{30}\text{Si}$  defined as follows:

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

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., 2010a), the plant Si uptake producing biogenic opal (Douthitt, 1982; Ziegler et al., 2005a; Ding et al., 2005; Opfergelt et al., 2006a, b; Ding et al., 2008; Opfergelt et al., 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 display a bulk Si isotopic signature of DSi. Understanding the contribution of those three processes on DSi output can hardly be done with  $\delta^{30}\text{Si}$  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., 2010a) may provide a better understanding of the origin of DSi exported from various soil-plant systems towards rivers.

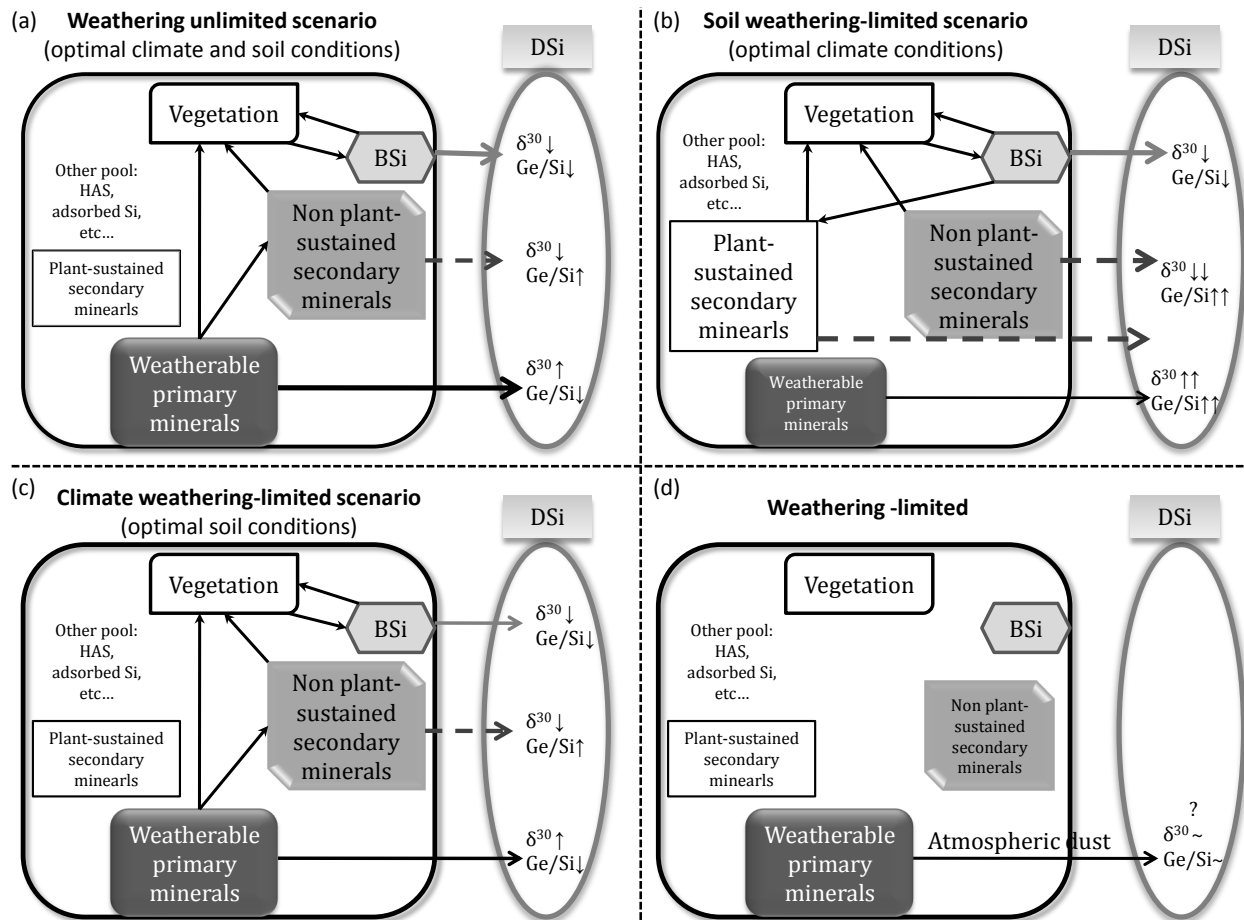
The interpretation of Ge/Si ratios and  $\delta^{30}\text{Si}$  signatures in waters exported from the soil-plant system should thus combine a detailed characterization of (i) the processes involved, (ii) the seasonal variation of these processes, and (iii) the mineralogy of secondary weathering products. 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  $\delta^{30}\text{Si}$  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  $\delta^{30}\text{Si}$ ) 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  $\delta^{30}\text{Si}$  values and Ge/Si ratios.

In addition to the impact of vegetation, the geochemical signature of 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  $\delta^{30}\text{Si}$  values and higher Ge/Si ratios (Cardinal et al., 2010; Cornelis et al., 2010a). 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 dissolved Si output 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*; Fig. 3d) where the environmental conditions do not favour silicate weathering, and where no Si soil-plant cycling takes place. The variations of biogeochemical Si signatures (Ge/Si ratios and  $\delta^{30}\text{Si}$ ) in those contrasted environments are discussed.



**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)** weathering-limited scenario. The arrows represent the dissolution of the various Si pools and its impact on the DSi geochemical ( $\delta^{30}\text{Si}$ , Ge/Si) signatures relative to parental material. The black arrow from the weatherable mineral pool means a DSi signature resulting from weathering of primary minerals assuming secondary precipitate formation and stability. The sizes of the arrows represent relative DSi fluxes.

These four scenarios are like “end members” described to understand the processes. Natural conditions are not as simplified as in these scenarios, since the environmental conditions can oscillate between these scenarios; e.g., a soil chronosequence is characterized by a decrease of weatherable mineral content with the age of soils in identical climatic conditions; a soil climosequence is characterized by identical weatherable mineral content in different climatic conditions (temperature and runoff). Thus, the DSi signature of a local soil-plant ecosystem can be influenced by a mix of two scenarios (1 and 2 or 1 and 3, for a chronosequence and a climosequence respectively). The biogeochemical tracers are therefore very useful to understand the transfer of elements in environments that are well-defined and characterized.

### 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, the relative contribution of weathering and BSi cycling in weathering-unlimited systems is still poorly quantified.

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  $\delta^{30}\text{Si}$  values of soil solution (Ziegler et al., 2005b). However, the  $\delta^{30}\text{Si}$

signature ( $-1.5\text{‰}$ ) of the pore-water in the top 0.3 m of soil is lighter suggesting the recycling and dissolution of BSi enriched in  $^{28}\text{Si}$ . Lugolobi et al. (2010) study the Ge/Si fractionation in the same site and also conclude that biological cycling 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 and rivers varying between  $+1.3$  and  $-0.2\text{‰}$  (Georg et al., 2009a). The lighter Si isotope composition of groundwater might be 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., 2009b).

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 is directly governed by the soil weatherable mineral reserves (Henriet et al., 2008a, b). Depending on the type of soil solution (organic layer leachates or mineral soil solutions), the DSi exported from the soil-plant systems could have a biogenic signature in organic soil surface or pedo/lithogenic signature in organo-mineral and mineral soil (Fig. 3a). Assuming BSi dissolution and secondary precipitate stability, Si signatures can evolve towards lower Ge/Si ratio and  $\delta^{30}\text{Si}$  values relatively to the initial Si signature. When dissolution of secondary minerals occurs, the release of light Si isotopes and Ge can induce lower  $\delta^{30}\text{Si}$  values and higher Ge/Si ratios. On the other hand, assuming weathering of primary silicate minerals and formation of secondary precipitates, soil solutions tend to have higher  $\delta^{30}\text{Si}$  values and lower Ge/Si ratios relatively to the initial Si signature. Related to secondary neoformation and considering identical climatic, geomorphologic and land-use conditions, the lithology of the parental material can also influence the DSi signature exported from soil-plant systems through distinct clay mineralogy (Ziegler et al., 2005b; Cornelis et al., 2010a).

## 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 biogeo-

chemical cycling within the plant/surface-soil component of the ecosystem (Markewitz et al., 2001). In a tropical rain-forest 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 ( $\text{Ge/Si} \sim 0.25 \times 10^{-6}$ ) derived from dissolution of BSi in upper soil horizons, and (ii) a Si-poor component with a relatively high Ge/Si ratio ( $\text{Ge/Si} \sim 2.6 \times 10^{-6}$ ), 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 (Frayssse 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 al., 2010).

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 the other hand, the signature of DSi release (higher  $\delta^{30}\text{Si}$  values and lower Ge/Si ratios) in those environments can also be influenced by neoformation of secondary clay minerals (relatively higher incorporation of light Si isotopes and Ge in clay minerals) (Fig. 3b). Indeed, in intense weathering environment characterized by low weathering rates such as Congo basin (transport-limited regime),  $\delta^{30}\text{Si}$  in the river was correlated with weathering intensity rather than Si fluxes (Cardinal et al., 2010). Silicon 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  $\delta^{30}\text{Si}$  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; Cornelis et al., 2010c).

In a French forest site, Bartoli (1983) has estimated that 80% of DSi exported from the soil profile has been recycled through the BSi pool in deciduous woods, compared to only 20% in coniferous counterparts. This led Bartoli (1983) to conclude that biocycling of Si has a substantial impact on DSi sources. Moreover, in central Siberia, besides basaltic bedrocks and soil minerals, the main sources of DSi under permafrost conditions can be the litter-fall ( $3.4 \text{ kg Si ha}^{-1} \text{ yr}^{-1}$ ) and subsequent dissolution of phytoliths (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 and increase in silicate weathering by BSi dissolution (Veselý 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). All these studies, performed in climate weathering-limited environments, support the likely impact of the biological Si cycle on the DSi land-to-river transfer.

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 the other hand, some of the lowest seasonal  $\delta^{30}\text{Si}$  values of the dissolved Si in some Swiss rivers in high mountain area (Georg et al., 2006) appear to be clearly correlated with high silicate weathering rates. During snowmelt and high river discharge events, elevated Al concentrations and high base-cation fluxes support a weathering controlled Si isotope fractionation. A similar isotope systematic, although not as pronounced as in the Swiss study, has been found in rivers all across Iceland (Georg et al., 2007). In Icelandic rivers, dissolved Si is derived from weathering of basalt and biological effects are absent. The lowest  $\delta^{30}\text{Si}$

values coincide with high physical and chemical weathering rates and confirm the observation from the study of Swiss rivers (Georg et al., 2006) that instantaneous silicate weathering rates are inversely correlated with  $\delta^{30}\text{Si}$  values. The effect of biogenic recycling superimposed weathering induced fractionation is still to be investigated. In one Swiss river it seems that Si biocycling might actually mitigate weathering induced fractionation to smooth out seasonal isotope trends (Georg et al., 2006). In contrast to Engström et al. (2010) biological recycling has been used to explain unusually high fractionated Si isotope compositions found in the Asian Yangtze River (up to +3‰, 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  $\delta^{30}\text{Si}$  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 biochemical activity (Ding et al., 2008). However, in these systems, the role of secondary clay-sized mineral formation/dissolution/adsorption on the DSi isotope compositions is not clearly determined, while they play a major role in the DSi signature. 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 mineral neoformation. In the Navajo Sandstone aquifer (Arizona, USA), the negative  $\delta^{30}\text{Si}$  values (−1.42‰) could also be due to dissolution of both secondary clay minerals and low-temperature silcretes (Georg et al., 2009b). In addition, DSi fluxes in Boreal and Arctic rivers seem to be influenced by vegetation only through promoting silicate weathering (Humborg et al., 2006b). Similarly, in a temperate granitic forest system, the  $\delta^{30}\text{Si}$  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‰; Cornelis et al., 2010a). 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  $^{28}\text{Si}$  and Ge-enriched secondary clays minerals incorporated by bioturbation in organic-rich horizons, preferentially releasing light Si isotopes and Ge (Cornelis et al., 2010a). 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 a mix of biogenic and pedo/lithogenic signature. Nevertheless, in some environmental conditions (lithology, geomorphology and land use) and soil horizons, DSi could have specific biogenic or litho/pedogenic signature, hence the interest to combine two geochemical tracers,



hydrological parameters and water chemistry to understand the origin of pedogenetic processes.

In the specific podzolic case, the signature of DSi in soil solution of the eluvial horizon will not be 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  $\delta^{30}\text{Si}$  values in DSi) and dissolution (high Ge/Si ratios and low  $\delta^{30}\text{Si}$  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.

At a local scale (pedon, ecosystem), Si isotope values and Ge/Si ratios are very helpful to decipher between biological and pedological process impact on the DSi dynamics in the soil-plant system. However, the interpretation of the DSi signature at a regional scale should be performed with caution when the intensity of driving bio/pedo/litho-genic variables is not clearly defined.

#### 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  $\delta^{30}\text{Si}$ ) in order to assess their impact on the DSi fluxes following dissolution, which remains poorly investigated (Fig. 3d).

## 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 the other 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 in a number of experimental sites to better understand the global export of DSi from continents to oceans, and the impact on the global  $\text{CO}_2$  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 (*Scenario 2*).

Promising and well-recognized geochemical tracers (Ge/Si ratios and  $\delta^{30}\text{Si}$ ) were shown to represent useful tools for tracing dissolved Si through the critical zone including the biosphere. However, these tracers unfold their full potential only in conjunction with other geochemical and biochemical data, and 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 mountain 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 predicted to be most pronounced in high latitudes such as the Arctic environments in North America, Russia and Greenland. It is conceivable that large-scale global change will affect the global Si cycle as a result of temperature and precipitation perturbations. The enrichment of “greenhouse” gases in the atmosphere has led to an increase in the average global surface temperature of  $0.6^\circ\text{C}$  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  $\text{CO}_2$  (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. DSi fluxes are also influenced by eutrophication and dams providing sedimental burial sites for diatom bloom and trapping of BSi (Humborg et al., 2006a). The geochemical tracers (Ge/Si ratios and  $\delta^{30}\text{Si}$ ) will help us quantifying anthropogenic and natural variations that should be incorporated into predictive models (Garnier et al., 2006; Bernard et al., 2010) for 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” (FRRIA) 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. We would like to thank all referees for their constructive comments.

Edited by: C. P. Slomp

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