

THE FUNCTIONAL ROLE OF SILICON IN PLANT BIOLOGY

Soil processes drive the biological silicon feedback loop

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Summary

1. Soil is the primary source of plant silicon (Si) and therefore a key reservoir of the Si biological cycling. Soil processes control the stock of Si-bearing minerals and the release of dissolved Si (DSi), hence the Si fluxes at the Earth's surface. Here, we review the interdependent relationship between soil processes and the return of plant Si in soils, and their controls on the biological Si feedback loop.

2. Dissolution and precipitation of soil silicate minerals govern the bioavailability of Si. Plants affect Si biocycling through mineral weathering, root uptake, phytolith formation, return and dissolution in soil. Thus, soil processes and Si biocycling readily interact in soil–plant systems.

3. Rock mineral weathering and soil formation are driven by the five soil-forming factors: parent rock, climate, topography, age and biota. These factors govern Si fluxes in soil–plant systems since they impact both the mineral weathering rate and fate of DSi. The variability of soil-forming factors at a global scale explains both the soil diversity and high variability of the rates of Si cycling in terrestrial ecosystems.

4. Plants play a crucial role in soil evolution by promoting weathering and forming phytoliths (plant silica bodies). They thus act as Si sinks and sources. With increasing depletion of lithogenic (LSi) and pedogenic (PSi) silicates, the biological Si feedback loop progressively takes over the Si plant uptake from weatherable LSi and PSi minerals. With rising weathering, the soil becomes increasingly concentrated in phytoliths, phytogenic amorphous silicates (PhSi), which are constantly formed in plant and dissolved in soil. Paradoxically, the Si biocycling is thus more intense in soils depleted in primary LSi source. By converting soil LSi and PSi into PhSi, plants increase the mobility of Si in soil and alleviate desilication in the topsoil. Non-essential plant Si is therefore an essential link between mineral and living worlds.

5. The dynamics of Si in terrestrial ecosystems is thus largely governed by pedogenesis and its relationship with plant community and diversity. Consequently, the appraisal of soil constituents and processes is central to further understand their interaction with the biological Si feedback loop.

Key-words: pedogenesis, phytolith, silicon cycling, soil physicochemical processes, soil–plant systems

Soil–plant Si cycle: facts and gaps

Silicon (Si) occurs in a huge number of minerals. The total soil Si content depends on soil mineralogy and ranges from

5 to 470 g kg⁻¹ (McKeague & Cline 1963), whereas the content of bioavailable Si varies from 3×10^{-3} to 4.5×10^{-1} g Si kg⁻¹ (Liang *et al.* 2015). The mean shoot Si concentration in plants ranges between 1 and 100 g Si kg⁻¹ and may exceed that of major nutrients (Hodson *et al.* 2005) despite the non-essentiality of Si (Epstein 1999). Studying the Si biogeochemical cycle is thus crucial to understand Earth systems dynamics and the beneficial

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effects of Si in terrestrial and marine ecosystems, because of its presence in a large variety of minerals, high cycling rates between soil and vegetation, and connection to the cycling of other elements (Exley 1998). Si biogeochemistry affects the global cycle of carbon (C) through the nutrition of marine and terrestrial biota (Conley & Schelske 1993; Smetacek 1999; Tréguer & Pondaven 2000; Carey & Fulweiler 2012; Tréguer & De La Rocha 2013; Cermeno *et al.* 2015; Conley & Carey 2015; Fulweiler *et al.* 2015). The Si biological cycle regulates atmospheric CO₂ through plant-induced silicate weathering and the resulting precipitation of secondary minerals, involved in the formation of soil organomineral associations (Rai & Kittrick 1989; Berner 1995, 1997; Torn *et al.* 1997; Song *et al.* 2012). Si biocycling also impacts the C budget through cycles of dissolution and precipitation of biogenic Si (phytoliths), which partly govern C stabilized in soils as organic C (OC) occluded in phytoliths (Parr & Sullivan 2005; Parr *et al.* 2010; Li *et al.* 2013). The effect of this process on the C budget is unknown as a part of OC occluded in phytoliths has a non-photosynthetic origin (Santos *et al.* 2012; Alexandre *et al.* 2015; Reyerson *et al.* 2016).

Si cycling rates vary widely in terrestrial ecosystems (Conley 2002) wherein Si uptake by vegetation ranges from 2 to 90 kg ha⁻¹ year⁻¹ (Alexandre, Bouvet & Abbadie 2011; Cornelis *et al.* 2011a), and exceptionally up to 640 kg ha⁻¹ year⁻¹ (Meunier, Colin & Alarcon 1999). The Si cycling rates in terrestrial ecosystems depend on environmental factors that govern soil-forming processes: climate,

topography, soil parent material, age and biotic factors such as vegetation, micro-organisms and land use management (Jenny 1941; Alexandre *et al.* 1997; Sommer *et al.* 2006; Street-Perrott & Barker 2008; Alexandre, Bouvet & Abbadie 2011; Cornelis *et al.* 2011a; White *et al.* 2012). The continuous change in soil over time is predominantly controlled by bioclimatic factors such as the water percolation, biomass production and solar energy (Chadwick & Chorover 2001). The interactive balance between these processes is at the root of soil diversity, characterized by contrasting soil mineralogy, linked to the content and stability of soil Si-bearing minerals. The pedogenic transformations are strongly influenced by the pool of silicate minerals, through the activity of monosilicic acid (H₄SiO₄⁰) in the soil solution. Processes involving Si biogeochemistry in soils are therefore central in the evolution of soil constituents and properties and, as such, the functioning of the biosphere. Pedodiversity matters for food production, water quality, loss of biodiversity, climate change, human health and plant diversity (Janzen *et al.* 2011; Laliberté *et al.* 2013; McBratney, Field & Koch 2013), but also for the codependent relationship between the global biogeochemical cycles of elements and the terrestrial Si biogeochemistry (Ragueneau 2000).

Soils are dynamic, multicomponent biogeochemical systems that undergo transformations leading to a sequence of soil horizons (Sposito 2008), which link the pedosphere to the lithosphere, biosphere, atmosphere and hydrosphere. The Si soil-plant cycling (Fig. 1) implies interdependent effects of environmental factors on the fate of Si

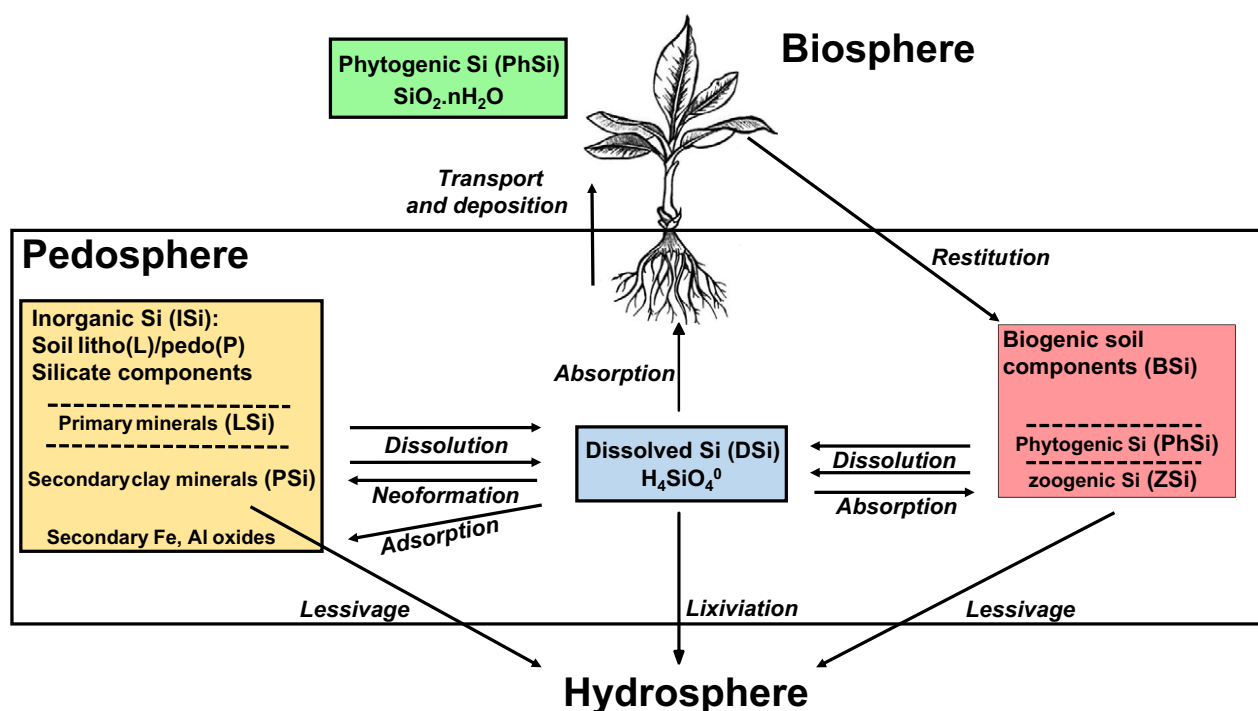
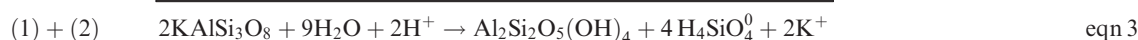
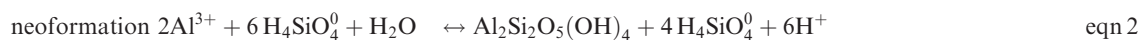
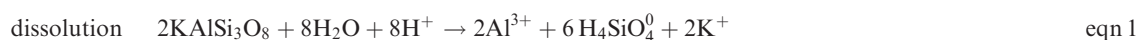


Fig. 1. Conceptual scheme of Si pools and fluxes in the soil-plant system. The original source of DSi is the pool of primary weatherable lithogenic silicates (LSi). DSi may be (1) absorbed by plants (PhSi) or soil heterotrophs (ZSi), (2) leached out to groundwater and rivers, (3) involved in the synthesis of secondary clay minerals (PSi), or (4) adsorbed on oxide surfaces. PSi as well as PhSi soil minerals may in turn dissolve and contribute to the DSi pool, depending on the activity of H₄SiO₄⁰ in the soil solution.

(see, e.g., Alexandre *et al.* 1997; Basile-Doelsch, Meunier & Parron 2005; Derry *et al.* 2005; Blecker *et al.* 2006; Sommer *et al.* 2006; Gérard *et al.* 2008; Opfergelt *et al.* 2010; Alexandre, Bouvet & Abbadie 2011; Cornelis *et al.* 2011a; Li, Lerman & Mackenzie 2011; Carey & Fulweiler 2012; Struyf & Conley 2012; White *et al.* 2012; Sommer 2013; Conley & Carey 2015). The role of soil-forming processes on the respective contribution of inorganic (ISi) and biogenic (BSi) sources to the pool of dissolved Si (DSi) (Fig. 1), and their effect on the biological Si feedback loop are poorly known and quantified. Here, we review the impact of soil, climatic and biotic (plant trait) conditions on Si biocycling in terrestrial ecosystems. We document how plants and soil processes affect the cycling rates, notably the relative contribution of the biological Si feedback loop along a soil weathering gradient. This highlights the role pedogenesis and soil diversity play in the global Si

Inorganic LSi and PSi and biogenic PhSi and ZSi minerals (Fig. 1) all dissolve in water. Yet the pathways and rates of dissolution vary widely between different types of minerals (Sposito 2008; Churchman & Lowe 2012). Consequently, weathering leads to a gradation of products in both space and time, resulting in soil profiles with variations in depth (Churchman & Lowe 2012), notably a decrease in the content of weatherable LSi minerals from deep to surface soil horizons. This gradient is mirrored by the increase in PSi silicates and PhSi minerals supplied through litterfall at the soil surface (Fig. 1). Variations occur in both vertical and horizontal dimensions.

The acid hydrolytic dissolution of a LSi primary aluminosilicate (here K-feldspar KAlSi_3O_8) forms an acid (H_4SiO_4^0) and a base (PSi secondary aluminosilicate: here kaolinite $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$), as illustrated here below:



cycle, which can be overlooked in ecological studies and hence should provide a useful foundation to explore variations in plant Si accumulation and use.

Mineral weathering controls the primary source of bioavailable Si

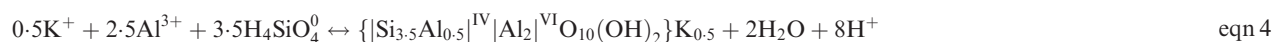
The primary source of Si in the soil–plant system is the reserve of weatherable Si-bearing primary minerals, that is the pool of lithogenic silicates LSi (Fig. 1). This pool is linked to the mineralogy of the soil parent material and weathering stage, which governs the activity of aqueous monosilicic acid, defined as H_4SiO_4^0 or DSi. The activity of DSi in the soil solution, is an important contributor to the Si accumulation in a given plant (Henriet *et al.* 2008a,b). Weathering of LSi primary minerals releases solutes, which can recombine to synthesize neoformed, pedogenic clay-sized silicates (PSi). These clay-sized minerals can in turn dissolve and contribute to resupply the DSi pool with aqueous H_4SiO_4^0 .

Mineral weathering currently occurs in well-drained soils with precipitation exceeding evapotranspiration. The combination of this climatic feature with the development of vegetation results in an irreversible proton flux because of H^+ consumption by mineral weathering and neoformation. Proton sources are numerous in soils, especially the dissociation of carbonic acid and organic acids, mineralization of organic N, S and P, nitrification, plant uptake of cations, complexation of metal ions and oxidation of H_2S , SO_2 , Fe^{2+} and FeS (van Breemen, Mulder & Driscoll 1983).

These equations illustrate the dissolution of LSi in hydrated acidic environments, and the consumption of H^+ ions through the neoformation of PSi, leading to an irreversible flux of protons. They reveal the driving factors in mineral weathering: the content and solubility of primary aluminosilicates LSi (here K-feldspar), water availability and proton input as well as the precipitation of neoformed PSi (here kaolinite) and production of solutes that will be either taken up by plants or leached out of the soil and transferred to the hydrosphere (Fig. 1). These factors are directly linked to parent rock, biota, climate and time. Temperature impacts the rate of mineral dissolution through the Arrhenius law (Rai & Kittrick 1989), whereas neoformation controls solute distribution in the soil profile (Chadwick & Chorover 2001). The topography can also influence chemical equilibria between solid and liquid phases through the leaching and lateral transfer of solutes (H_4SiO_4^0 , K^+) along a slope, and their accumulation downslope. Finally, time is a major factor because it governs the soil weathering stage in given environmental conditions.

As an example of how a soil with a specific DSI might develop, let us consider soils developed from parent rock rich in weatherable minerals in tropical humid environments. The endpoint of soil-forming processes would be a desilicated soil material enriched in Fe and Al oxides with a pH around neutrality as induced by isoelectric weathering (Uehara & Gillman 1981). This occurs in specific perhydrated environments where H_4SiO_4^0 is massively leached out. Depending on the activity of H_4SiO_4^0 (eqn 2), the neoformed mineral could be smectite (eqn 4), kaolinite (eqn 2)

or gibbsite (eqn 5), which can be neofomed from a variety of primary minerals (Rai & Kittrick 1989):



In soil conditions, eqns 1 and 3 are irreversible, whereas eqns 2, 4 and 5 are reversible depending on the activities (...) of solutes in the aqueous phase: (K^+), (H^+), (Al^{3+}) and (H_4SiO_4^0). During soil formation, these parameters control both the nature of the neofomed secondary clay-sized minerals and their dissolution. Desilication leads to the pedogenic weathering sequence [LSi (K-feldspar) → PSi (smectite → kaolinite) → gibbsite], which can be illustrated through the quantity–intensity (Q–I) relationship (Lindsay 1979). The Q–I concept was developed to predict the dynamics of plant nutrients in soils, and widely used for soil fertility appraisal. Here, Q–I links the stock of Si in weatherable Si-bearing minerals (Q) to the activity of H_4SiO_4^0 in soil solution (I) (Fig. 2). The intensity factor is the activity of H_4SiO_4^0 , which depends on the quantity (or capacity) factor, that is the amount of Si-bearing mineral that can potentially be dissolved. Different minerals are each able to maintain different levels of DSi (see Fig. 2). Increasing weathering leads to the successive dominance of different secondary minerals with decreasing Si content, which are each

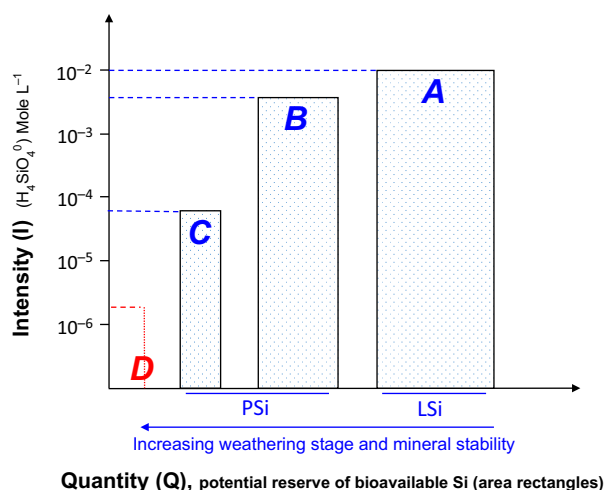


Fig. 2. Schematic view of the Si quantity–intensity (Q–I) relationship in the weathering sequence of minerals A → D reflecting the soil desilication process. At early stage of weathering, the dissolution of A (K-feldspar, eqn 1) controls (H_4SiO_4^0) at highest levels ($10^{-2} \text{ mol L}^{-1}$), causing supersaturation with respect to B (smectite), which slowly precipitates enhancing A dissolution (eqns 1 and 4). Once A stock is exhausted, (H_4SiO_4^0) drops to lower level causing B (smectite) to dissolve (reverse reaction eqn 4) and C (kaolinite) to precipitate eqn 2. Eventually, smectite (B) disappears, (H_4SiO_4^0) decreases to $\sim 10^{-4} \text{ mol L}^{-1}$, kaolinite (C) dissolves (reverse reaction eqn 2) and gibbsite (Si free D) forms (eqn 5) in strongly desilicated environments ($(\text{H}_4\text{SiO}_4^0) \sim 10^{-5} - 10^{-6} \text{ mol L}^{-1}$).

controlled by decreasing DSi levels: this is the natural soil desilication process characterizing well-drained soils.

The water flux and temperature promote the overall process of desilication, causing seasonal cycles of dissolution/precipitation of clay-sized minerals (Zabowski & Ugo lini 1992; White *et al.* 2012). Climate and plant uptake of aqueous substances thus control soil-forming processes through their impact on soil solution chemistry, hence the bio-availability of Si in soils (Blecker *et al.* 2006; Henri et *al.* 2008a), and the Si budget in terrestrial environments (Chadwick & Chorover 2001).

Climate and plant traits impact the biological Si feedback loop

The pool of primary minerals (LSi) is the original source of DSi, while secondary PSi minerals impact the DSi concentration through dissolution (Si source) and precipitation/adsorption (Si sink) (Fig. 1). Some DSi is taken up by plants: active plant uptake affects the concentration of DSi, while a passive uptake, all other conditions being equal, does not. The precipitation of DSi in plants, as amorphous opal-A, forms PhSi minerals. In contrast, terrestrial zoogenic silica (ZSi, Fig. 1) is produced by heterotrophs, such as testate amoebae (Aoki, Hoshino & Matsubara 2007), which have played a key role in the terrestrial Si cycle over geological time-scales, $\sim 370 \text{ Mya}$ (Lahr *et al.* 2015), as plants did at their early evolutionary history in the Palaeozoic Era, over 400 Mya (Trem bath-Reichert *et al.* 2015). Since the Cenozoic era 65 million years ago, and still today grasses and diatoms dominate over the biological Si cycle (Cermen o *et al.* 2015). The annual PhSi production by plants ranges between 60 and $200 \text{ Tmol year}^{-1}$ (Conley 2002) and rivals that produced by diatoms in oceans ($240 \text{ Tmol year}^{-1}$) (Tréguer *et al.* 1995). PhSi and ZSi differ in turnover rates (Sommer 2013) and can substantially contribute to resupply DSi. The relative contribution of ISi and BSi pools to the DSi pool is strongly dependent on environmental conditions (Cornelis *et al.* 2011a). DSi constitutes the intensity (I) factor (Fig. 2) linked to the pool of bioavailable Si (Fig. 1) for plant uptake, transport and deposition in the form of phyto-genic opal $\text{SiO}_2 \cdot n\text{H}_2\text{O}$ (Epstein 1994).

Since plants reconstitute PhSi to soils, they alleviate desilication (Lucas *et al.* 1993), and even retard it (Meunier, Colin & Alarcon 1999), depending on the accessibility of plant roots to bioavailable Si. Amorphous PhSi minerals are more soluble than crystalline LSi and PSi minerals (Fig. 2) (Köhler, Bosbach & Oelkers 2005; Fraysse *et al.*

2006, 2009). Plants may therefore have a dual role in Si cycling in soil–plant systems (Alexandre *et al.* 1997). On the one hand, they enhance mineral dissolution through net acidification and nutrient uptake (Hinsinger 1998). On the other hand, they build up the pool of PhSi minerals in soils (Meunier, Colin & Alarcon 1999), hence promoting the precipitation of PSi minerals (Lucas *et al.* 1993; Lucas 2001; White *et al.* 2012), and their stabilization (Barré, Berger & Velde 2009) through their control of $(\text{H}_4\text{SiO}_4^0)$ (eqns 2 and 4; Fig. 2). The solubility of phytoliths varies depending on plant species, which controls phytolith morphology and elemental composition (Wilding & Drees 1974; Alexandre *et al.* 1997; Blecker *et al.* 2006; Li, Song & Cornelis 2014). The origin of phytoliths returned to soil can therefore influence the contribution of PhSi to the DSi pool. The presence or absence of influx transporters (Deshmukh & Bélanger 2015) and the location of Si precipitates, in leaves or trunk or branches, impact the Si cycling rates in ecosystems and therefore their role in the biological Si feedback loop.

Plant diversity, as well as the interactions between plant and soil, may therefore strongly influence the fate of Si in soil–plant systems. One of the most relevant soil–plant interactions probably lies in the plant nutrient-acquisition strategies changing with soil age (Lambers *et al.* 2008). There is evidence of co-evolution of soil, plants and rhizosphere micro-organisms (Lambers *et al.* 2009, 2010), which may affect the ZSi pool and its contribution to Si fluxes in the soil–plant system (Sommer 2013). Plant species exhibit different abilities to extract nutrients and dissolve minerals (Hinsinger 1998). Specific properties of plant roots, especially active transport, H^+ extrusion, impact the mobility of Si at the soil–root interface and likely explain why plants widely differ in their capacity to take up Si (Hodson *et al.* 2005; Deshmukh & Bélanger 2015). In identical soil and climate conditions, plant species may considerably impact the accumulation of PhSi in the soil–plant system as illustrated in Fig. 3. Here, the uptake of Si varies from 2.3 to 43.5 $\text{kg ha}^{-1} \text{year}^{-1}$ depending on forest tree species (Cornelis *et al.* 2010a).

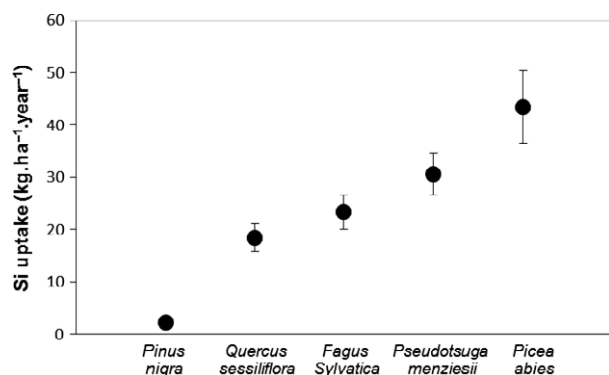


Fig. 3. Effect of tree species on the annual Si uptake in a biosequence of forest stands established on a Dystric Cambisol formed from granite in temperate humid conditions (Cornelis *et al.* 2010a).

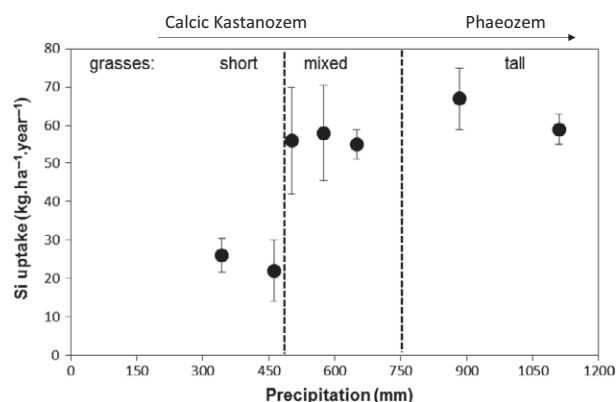


Fig. 4. Annual Si uptake by grasses in a bioclimate sequence as a function of mean annual precipitation (MAP) in the Great Plains (USA). The Si uptake ($\text{kg ha}^{-1} \text{year}^{-1}$) amounts to 22–26 in short, 55–58 in mixed and 59–67 in tall grasses, with respective MAP values of 340–460, 500–650 and 880–1110 mm. The studied prairie soils derived from sedimentary rocks and loess. Their clay content increases while the carbonate content decreases with increasing MAP (Blecker *et al.* 2006).

Another relevant soil–plant interaction concerns the effective rooting depth. In a bioclimate sequence (Fig. 4), plant uptake of Si is related to mean annual precipitation (MAP) and MAP, above-ground net productivity (ANPP), root biomass, soil C stock, depth of humus-rich topsoil and effective rooting depth are all positively and strongly correlated (Kononova 1966; Fenton 1983). In this bioclimate sequence, the uptake of Si by grasses is related to MAP. Precipitation increases weathering intensity and ANPP: from short to mixed and tall grasses, root biomass and effective soil rooting depth increase in parallel. By taking up DSi from both surface and deep horizons beneath, plants may thus alleviate topsoil desilication. Evergreen forest trees generate an upwards transfer of Si from deep, less weathered horizons because of their deep rooting (Canadell *et al.* 1996). This upwards transfer alleviates topsoil desilication (Lucas *et al.* 1993) so that the topsoil becomes richer in neoformed kaolinite than the oxic horizon beneath, rich in Al and Fe oxides. Thus, the thermodynamics predicting increasing desilication from deep to surface horizons (eqns 1–5, Fig. 2; Rai & Kittrick 1989) are challenged by plant-induced resiliation involving deep rooting as well as fast biomass turnover. The architecture of root systems is too often overlooked, yet it is crucial in the Si cycling. Deep rooted forest trees in the humid tropics take up Si from LSi/PSi in deep horizons. They thus sustain the biological Si feedback loop as they minimize DSi export and accumulate a substantial amount of Si though they grow on highly weathered soils depleted in weatherable LSi/PSi minerals (Alexandre *et al.* 1997). Unlike evergreen forest trees, the monocot banana plant has a shallow rooting system mostly confined to the top 30 cms (Delvaux 1995). The accumulation of Si in banana plant is therefore directly related to the reserve of weatherable LSi minerals of the surface horizons and inversely correlated to the soil weathering stage (Fig. 5).

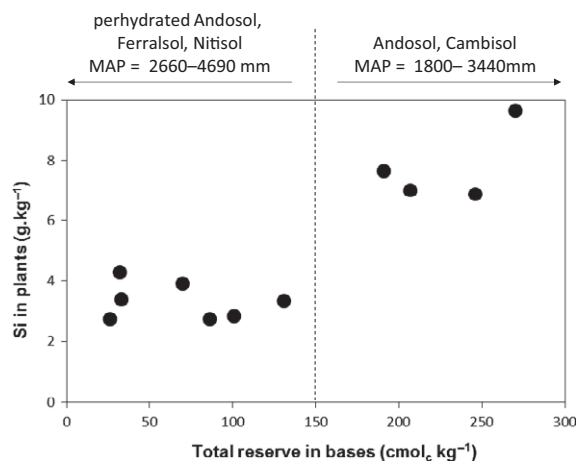


Fig. 5. Si content of banana plants in a soil weathering sequence in humid tropical conditions (MAP = 1800–4700 mm), as a function of the Total Reserve in Bases (TRB). The soils derived from andesitic volcanic ash in Guadeloupe. TRB sums up the total content of major alkaline (Na^+ , K^+) and alkaline-earth (Mg^{2+} , Ca^{2+}) cations, which is directly linked to the content of soil weatherable minerals (Herbillon 1986). The soils characterized by a more advanced weathering stage (perhydrated Andosol, Ferralsol and Nitisol: $\text{TRB} = 26\text{--}131 \text{ cmol}_c \text{ kg}^{-1}$), and thus advanced desilication, support banana vegetation, which accumulates much less Si ($2\text{--}4 \text{ g kg}^{-1}$) than the one cropped on much less weathered soils (Andosol, Cambisol: $\text{TRB} = 190\text{--}270 \text{ cmol}_c \text{ kg}^{-1}$) exhibiting a plant accumulation of Si of $6\text{--}10 \text{ g kg}^{-1}$ (Henriet *et al.* 2008b).

Geoclimatic factors impact the biological Si feedback loop

The lithological nature of soil parent material impacts the quantity factor Q (Fig. 2). Q is the amount of Si-bearing minerals that can potentially be dissolved contributing to the DSi pool that can be taken up by plants (Henriet *et al.* 2008b). The lithological control is impacted by both the age of the substrate (weathering duration) and climate (weathering rate as ruled by temperature and rainfall). Both factors drive soil mineral weathering and impact plant Si uptake, as illustrated in Fig. 5 (Henriet *et al.* 2008a,b). Here, in intensive banana cropping systems in the humid tropics (MAP = 1800–4700 mm), the soils derive from the same parent material, but they differ in weathering stage, depending on both the age of parent rock and MAP, and they support bananas that accumulate different amounts of Si. The plant accumulation of Si and the building-up of soil PhSi reveal the weathering stage of these soils (Henriet *et al.* 2008a,b). Thus, both LSi and PhSi minerals contribute to the Q factor in which the PhSi contribution relatively increases with increasing weathering stage.

Previous data of Blecker *et al.* (2006) lead us to a similar conclusion in Kastanozems and Phaeozems (Fig. 4). In these drier environments (MAP 300–1100 mm), however, the accumulation of Si by grasses increases with increasing MAP and above-ground plant biomass. The least weathered soils (limestone-rich kastanozems) occur in the driest

environments with short grasses. The arid soil moisture regime maintains the stability of the reserve of weatherable minerals. Indeed, soil CaCO_3 is the major H^+ consumer so that net acidification does not result in an increase in H^+ activity in soil solution: the buffering effect of CaCO_3 protects the ISi pool (LSi and PSi minerals) from dissolution. The resulting limited dissolution of ISi minerals, also favoured by limited water availability (eqn 1), readily reduces the Q factor, thus the stock of DSi and hence the availability of Si for plant uptake.

Blecker *et al.* (2006) note these prairie soils contain roughly 10 000 times more PhSi than the above-ground biomass in the whole grassland system and PhSi comprises only 1–3% of the total Si pool. However, the high dissolution rates of PhSi vs. PSi mean the former has a faster turnover and, in conjunction with the annual cycling of Si by grasses, contribute to increase the DSi stock and positively impact the annual Si biocycling. This corroborates that the largest reservoir of PhSi in natural or semi-natural terrestrial ecosystems resides in soils (Meunier, Colin & Alarcon 1999; Struyf 2010; Sommer 2013). The content of PhSi in soils is inversely proportional to MAP, while Si uptake rates and PhSi return through dead biomass increase with precipitation (Fig. 4). Therefore, climatic conditions largely affect Si biocycling, the increase in precipitation accelerates the Si biocycling through higher dissolution rates of PhSi minerals, and vegetation alleviates soil desilication by impacting the turnover rate of Si in the soil–plant system (Lucas *et al.* 1993; Meunier, Colin & Alarcon 1999). This will further depend, however, on (i) the lixiviation of DSi through drainage (Alexandre *et al.* 1997; Cornelis *et al.* 2014a), (ii) the alteration in the processes of formation and return of PhSi into the topsoil through land use changes (Conley *et al.* 2008; Saccone *et al.* 2008; Struyf 2010; Clymans *et al.* 2011; Vandevenne *et al.* 2012) and (iii) the exportation of PhSi through crop harvest (Guntzer *et al.* 2012; Vandevenne *et al.* 2012).

Soil processes drive the progressive dominance of the biological Si feedback loop in the soil–plant cycle

Plants act as a filter of Si between the primary release of DSi by mineral weathering and its transfer to the hydrosystem (Struyf & Conley 2012). Hence, the soil–plant Si cycle strongly impacts since biogeochemical processes in continents govern more than 80% of the DSi input into oceans (Tréguer & De La Rocha 2013). In marine ecosystems, BSi is produced at a rate of $240 \text{ Tmol year}^{-1}$ by diatoms (Tréguer *et al.* 1995). The latter micro-organisms account for 43% of marine net primary production (Tréguer *et al.* 1995), whereas Si-accumulating plants control 55% of terrestrial net primary production (Carey & Fulweiler 2012).

Plants readily impact soil formation and pedodiversity at global scale. Yet, there is increasing evidence that long-term pedogenesis drives plant diversity: some ecosystems

with ancient, strongly weathered soils support an incredibly high number of plant species, whereas younger, more fertile ecosystems are often dominated by considerably fewer species (Laliberté *et al.* 2013). Pedodiversity involves variations in the soil cover depending on the intensity of soil-forming factors and processes. The latter can be traced through the changes in clay mineralogy (PSi) observed during soil profile development. After Sposito (2008), soil changes are known collectively as the Jackson–Sherman weathering stages, and they can be classified as ‘early stage’, ‘intermediate stage’ or ‘advanced stage’ (Jackson & Sherman 1953; Jackson 1965). Early-stage clay mineralogy exhibits salts including carbonates, and primary silicates, other than quartz and muscovite. These minerals are stable in soils lacking throughputs of water, air and thermal energy that usually characterize open systems in nature: the soils are for instance too dry or too cold or too wet. Early-stage weathering limits the bio-availability of Si because carbonates are the privileged H^+ consumers in the system or because LSi minerals dissolve too slowly. Intermediate-stage clay mineralogy features unalterable quartz and muscovite, and an assemblage of primary LSi and secondary PSi aluminosilicates depending on weathering stage. The PSi minerals are stable under conditions that do not deplete DSi and the macro-elements. Intermediate-stage weathering is associated with an increased mobility of Si and thus a Si bio-availability mostly depending on vegetation, climate and the pool of LSi minerals, as illustrated in the previous sections, but also on the stock of weatherable PSi minerals. Advanced-stage weathering is associated with intensive leaching and strongly oxidizing conditions, so that only hydrous oxides of Al, Fe^{III} and Ti persist ultimately. Kaolinite will be an important clay mineral if the level of DSi warrants its stability (Fig. 2) whatever its source: uncomplete DSi removal, DSi lateral transfer, PhSi return into the topsoil. Strong desilication characterizes the advanced-stage weathered soils wherein vegetation plays a major role in modulating Si depletion by concentrating bioavailable Si in the topsoil (Lucas *et al.* 1993). In the same way, Jobbágy & Jackson (2001) show that most limiting nutrients strongly recycled by plants such as P and K are increasingly concentrated in the topsoil along a gradient of weathering-leaching intensity, from arid to continental prairie soils and highly weathered soils in the humid tropics.

By compiling experimental values of the annual Si uptake rate measured in various ecosystems, four scenarios can be identified that link plant/ecosystem Si uptake, pedogenesis and the Si Q-I relationship (Table 1). In weakly developed soils (Table 1, section 1), weathering is limited, restricting the range of annual Si uptake rate to 7–26 $kg\ ha^{-1}\ year^{-1}$. The Si Q-I relationship chiefly depends on both the reserve of weatherable LSi/PSi minerals and plant species (Fulweiler & Nixon 2005; Blecker *et al.* 2006). The major impact of the LSi source on the Q-I relationship likely explains the small Si uptake rate irrespective of forest biodiversity (Meunier *et al.* 2010) and the

dominance of Si-accumulating plants (Blecker *et al.* 2006) in different ecosystems.

In a biosequence of forest stands on a Cambisol, with intermediate weathering (Table 1, section 2), the annual Si uptake rate ranges from 2 to 43 $kg\ ha^{-1}\ year^{-1}$ (Cornelis *et al.* 2010a). Here, the Q-I relationship is affected by forest tree species exhibiting different element-acquisition strategies and rooting depths. In other soils at intermediate stage of weathering, the Si uptake rate in forests varies between 23 and 44 $kg\ ha^{-1}\ year^{-1}$ (Bartoli 1983; Gérard *et al.* 2008; Sommer 2013). These experimental values are within the range of the ones measured by Cornelis *et al.* (2010a).

Also at intermediate stage, but in grasslands (Table 1, section 3), bioclimatic factors and soil age impact the Si uptake rate [55–67 (Blecker *et al.* 2006) and 12–48 $kg\ ha^{-1}\ year^{-1}$ (White *et al.* 2012)]. Grasses pump DSi in quantities increasing in conjunction with MAP and biomass (Blecker *et al.* 2006) as the pool of LSi minerals progressively acts as the privileged H^+ consumer in soil. A similar relationship between phytolith accumulation, MAP and grass productivity was observed in dry savanna ecosystems in the tropics (Issaharou-Matchi *et al.* 2016). Lastly, in a chronosequence of Chernozems under a Mediterranean climate, the annual Si uptake rate of grasses decreases from 46–48 to 12–18 $kg\ ha^{-1}\ year^{-1}$ with increasing soil age (White *et al.* 2012). This illustrates that the Q-I relationship clearly depends on soil age, hence soil weathering stage, in line with the schematic in Fig. 2.

In highly weathered soils of the humid tropics, weatherable LSi/PSi mineral reserves are exhausted (Table 1, section 4: advanced stage) and the biological Si feedback loop becomes increasingly dominant in the Si soil–plant cycle (Fig. 6): the annual Si uptake rate ranges between 41 and 90 $kg\ ha^{-1}\ year^{-1}$ (Lucas *et al.* 1993; Alexandre *et al.* 1997; Alexandre, Bouvet & Abbadie 2011). The DSi uptake and PhSi return to soil are substantially larger than in temperate forests developing on soils with less advanced weathering (Alexandre *et al.* 1997; Street-Perrott & Barker 2008; Meunier *et al.* 2010; Cornelis *et al.* 2011a). Thus in highly weathered soils, the key processes of Si biocycling are the formation, return and dissolution of PhSi. The Si biocycling is largest, as measured by highest Si uptake rates, in these soil–plant systems because of large turnover of C and nutrient cycling (Greenland & Nye 1959), the concentration of limiting nutrients in topsoil (Jobbágy & Jackson 2001), as well as a rapid dissolution of phytoliths with respect to that of clay minerals. The dissolution rates of phytoliths ($1 \times 10^{-12}\ mol\ m^{-2}\ s^{-1}$; pH 2–4 at 25 °C) are 2.5–5 times higher than smectite-type minerals ($2–4 \times 10^{-13}\ mol\ m^{-2}\ s^{-1}$; pH 3 at 25 °C) and 30 times higher than kaolinite ($3 \times 10^{-14}\ mol\ m^{-2}\ s^{-1}$; pH 2 at 25 °C) (Köhler, Bosbach & Oelkers 2005; Fraysse *et al.* 2009). Soil pH is important as topsoil acidity can affect the fate of Si released through PhSi dissolution. At pH < 5, hydroxyaluminosilicates (HAS) can precipitate. Such an event decreases the availability of Si (White *et al.* 2012; Haynes 2014).

Table 1. Experimental values of the Si uptake rate in various forest and grassland ecosystems as measured in the above-ground plant parts. Si uptake is limited in little weathered soils (1), increases in intermediate weathered soils, but with differences in uptake due to plant functional types (2) and environmental factors (3), and further increases in a system dominated by biocycling on highly weathered soils (4)

Ecosystem	Climate* (MAP in mm)	Geology	Soil type	Location	Si uptake (kg ha ⁻¹ year ⁻¹)	References
(1) Early weathering stage – weakly developed soils						
Rain forest	Tropical humid (4200)	Young basaltic flow	Leptosol	Reunion Island	7	Meunier <i>et al.</i> (2010)
Mixed oak and pine	Temperate continental (1200)	Granite	Cambisol– Regosol	USA (Rhode Island)	15	Fulweiler & Nixon (2005)
Grasses	Semi-arid (334)	Sediments and loess	Kastanozem	USA (Colorado)	22	Blecker <i>et al.</i> (2006)
Grasses	Semi-arid (462)	Sediments and loess	Kastanozem	USA (Colorado)	26	Blecker <i>et al.</i> (2006)
(2) Intermediate weathering stage – biosequence of forest stand						
Black pine	Temperate oceanic (1200)	Granite	Cambisol	France (Morvan)	2	Cornelis <i>et al.</i> (2010a,b)
Oak	Temperate oceanic (1200)	Granite	Cambisol	France (Morvan)	18	Cornelis <i>et al.</i> (2010a,b)
European beech	Temperate oceanic (1200)	Granite	Cambisol	France (Morvan)	23	Cornelis <i>et al.</i> (2010a,b)
Douglas fir	Temperate oceanic (1200)	Granite	Cambisol	France (Morvan)	31	Cornelis <i>et al.</i> (2010a,b)
Norway spruce	Temperate oceanic (1200)	Granite	Cambisol	France (Morvan)	43	Cornelis <i>et al.</i> (2010a,b)
Deciduous forest	Temperate oceanic (1100)	Sandstone	Cambisol	France (Vosges)	23	Bartoli (1983)
Beech–pine	Temperate continental (600)	Pleistocene moraine	Arenosol	Germany (Brandenburg)	35	Sommer (2013)
Douglas fir	Temperate oceanic (1000)	Volcanic tuff	Cambisol	France (Beaujolais)	44	Gérard <i>et al.</i> (2008)
(3) Intermediate weathering stage – soil bioclimosequence and chronosequence						
Grasses	Warm continental (502)	Sediments and loess	Kastanozem	USA (Missouri)	56	Blecker <i>et al.</i> (2006)
Grasses	Warm continental (575)	Sediments and loess	Kastanozem	USA (Missouri)	58	Blecker <i>et al.</i> (2006)
Grasses	Warm continental (650)	Sediments and loess	Phaeozem	USA (Missouri)	55	Blecker <i>et al.</i> (2006)
Grasses	Warm continental (884)	Sediments and loess	Phaeozem	USA (Missouri)	67	Blecker <i>et al.</i> (2006)
Grasses	Warm oceanic (1110)	Sediments and loess	Phaeozem	USA (Missouri)	59	Blecker <i>et al.</i> (2006)
Grasses	Mediterranean (720)	Granitic sediment	Chernozem – 65 kyrs	USA (California)	46	White <i>et al.</i> (2012)
Grasses	Mediterranean (720)	Granitic sediment	Chernozem – 90 kyrs	USA (California)	48	White <i>et al.</i> (2012)
Grasses	Mediterranean (720)	Granitic sediment	Chernozem – 137 kyrs	USA (California)	23	White <i>et al.</i> (2012)
Grasses	Mediterranean (720)	Granitic sediment	Chernozem – 194 kyrs	USA (California)	12	White <i>et al.</i> (2012)
Grasses	Mediterranean (720)	Granitic sediment	Chernozem – 226 kyrs	USA (California)	18	White <i>et al.</i> (2012)
(4) Advanced weathering stage – highly weathered soils						
Rain forest	Tropical humid (2100)	Sandy clay sediment	Ferralsol	Brazil (Manaus)	41	Lucas <i>et al.</i> (1993)
Rain forest	Tropical humid (1500)	Schist & quartzite	Ferralsol	Congo (Mayombé)	58	Alexandre <i>et al.</i> (1997)
Rain forest	Tropical humid (1500)	Schist & quartzite	Ferralsol	Congo (Mayombe)	76	Alexandre <i>et al.</i> (1997)
Tall grass savanna	Tropical humid (1200)	Granitic bedrock	Lixisol	Ivory Coast (Lamto)	90	Alexandre, Bouvet & Abbadie (2011)
Bamboo forest	Tropical humid (1600)	Trachytic ashes	Podzol	Island of Reunion	640	Meunier, Colin & Alarcon (1999)

*Köppen Classification.

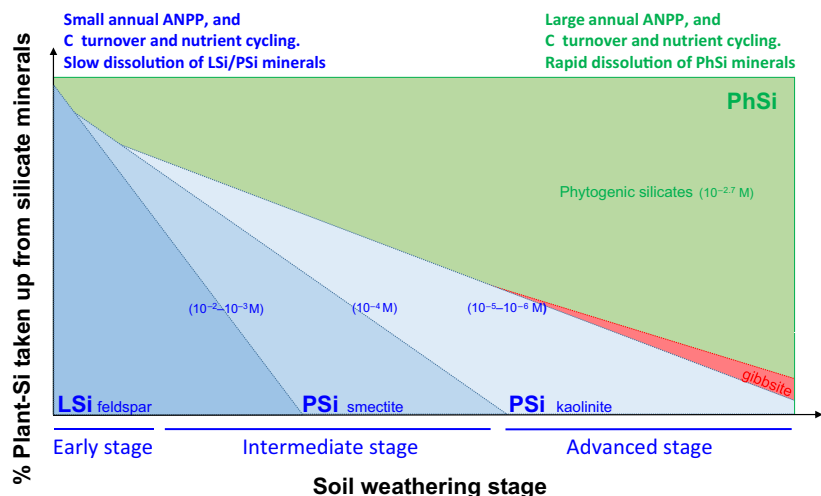


Fig. 6. Schematic evolution of the relative distribution of the soil mineral sources of plant Si taken up from lithogenic (LSi), pedogenic (PSi) and phytogenic (PhSi) minerals in soils as a function of soil weathering stage (eqns 1–5, Fig. 2) (into brackets: activity in mol L⁻¹ of H₄SiO₄ controlled by the LSi, PSi and PhSi minerals).

In line with the above global interpretation, an exceptional Si uptake rate of 640 kg ha⁻¹ year⁻¹ was measured in a humid tropical environment (Table 1, section 4). In this case, a '15-cm-thick phytolith-rich horizon developed at the expense of highly weathered trachytic ashes' (Meunier, Colin & Alarcon 1999). The mineral soil beneath is a 'specific podzol' marked by a profound depletion of weatherable LSi/PSi minerals, and the relative accumulation of Fe oxide and, to a much lesser extent, gibbsite. Thus here, such a phytoaccumulation of PhSi results from a unique combination of processes favouring the exclusive dominance of the biological Si feedback loop in the Si biocycling: (i) a strong advanced weathering in a humid tropical environment, (ii) the complete dissolution of LSi/PSi minerals in a very aggressive podzolizing soil environment, (iii) the relative accumulation of Fe oxide, perfectly comparable to gibbsite along the overall desilication process illustrated in Fig. 6, (iv) the occurrence of weatherable LSi (feldspar) and PSi allophane–imogolite at depth, beneath the surface podzol, and (v) the presence of a well-known Si-accumulator plant (bamboo). The final component emphasizes that plant functional type in an important factor in characterizing Si biocycling rates (as also shown in comparison between sections 2 and 3, Table 1) in addition to soil weathering status.

Thus, in the course of soil evolution from early- to advanced-stage of weathering, different processes impact soil Si status. In early weathering, the Si soil–plant cycle is first controlled by soil processes involving LSi/PSi mineral dissolution (eqns 1–5). At early and intermediate stages (Table 1, sections 1–3), soil age and weathering stage, plant functional type and climate (Figs 3–5) are important sources of the plant Si uptake rate. Here, the Q-I relationship is chiefly controlled by the LSi/PSi pool. The progressive depletion of this pool (Figs 2 and 6) leads to the progressive predominance of the biological Si feedback loop in the Si soil-to-plant cycle. At advanced stage, the Q-I relationship is largely controlled by PhSi. Thus, the Si soil–plant cycle is nearly entirely controlled by the biological Si feedback loop. The remarkable effectiveness of

which is linked to the progressive concentration of bioavailable Si in the topsoil along a gradient of weathering-leaching intensity, from early to advanced weathering stage. The non-essentiality of Si could be significant here since Si depletion may not affect plant biomass production as essential nutrient depletion may do. Thus, a decrease in ISi Q and I factors (Fig. 2) will not perturb the efficiency of Si biological pumping. This statement further supports that the PhSi contribution to Q proportionally increases with increasing soil weathering stage. Collectively, this (Figs 2 and 6, Table 1) suggests that soil–plant systems have likely co-evolved over hundred millions of years through their influence on Si fluxes. The evolution of higher plants, particularly high Si-accumulating monocots, has impacted both the continental weathering of silicates and DSi exportation to the hydrosystem (Cermeno *et al.* 2015; Conley & Carey 2015).

Challenges in understanding the interactive feedbacks between soil and plant processes

Further understanding of the continental Si cycle requires an integrated knowledge of soil processes, including quantification of pools and fluxes, particularly the variations in soil DSi.

The stability of silicate minerals in soils varies according to seasonal climatic conditions which impact temperature, water availability and plant growth, hence evapotranspiration and thus water balance at ecosystem level. Zabowski & Ugolini (1992) have shown in a Podzol that clay minerals dissolve in spring, while they are stable or neoformed in summer. They also showed that capillary soil solutions were more sensitive to seasonal changes than the gravity solutions drained to ground waters because of the much higher residence time of the former. As shown in podzolic soils, LSi and PSi minerals are more subject to dissolution in the eluvial than in the illuvial horizon (Cornelis *et al.* 2014b). Minerals are alternately dissolving and precipitating in soils depending on water availability; hence, seasonal changes occur in the activity of DSi. Soil DSi in

general is currently poorly understood, and we need further research to develop our understanding.

Soil solution studies have been widely used to diagnose current processes in soils (Zabowski & Ugolini 1992; Giesler, Lundström & Grip 1996; Cornu *et al.* 1998; Brahy *et al.* 2000; Markewitz *et al.* 2001; Gérard, François & Ranger 2002; Gérard *et al.* 2003), and there are a range of methods available to explore DSi dynamics. The analysis of gravity waters collected with zero tension lysimeters is appropriate to calculate the balance between Si inputs and outputs in an ecosystem. In addition, the analysis of capillary solutions collected with ceramic suction cups allows to study the chemical reactions and equilibria between solid and liquid phases (dissolution/precipitation/adsorption processes and Si uptake by plants) (Marques *et al.* 1996). The crystallinity of Si minerals impacts their solubility and ability to provide DSi. Continuous alkaline dissolution allows to separate reactive silicates (amorphous and short-range order) from the crystalline ones (DeMaster 1981; Koning, Epping & van Raaphorst 2002; Sauer *et al.* 2006; Sommer *et al.* 2006; Saccone *et al.* 2007; Cornelis *et al.* 2011b). This technique was used to study the impact of a land use change on the PhSi stock in soils (Struyf 2010; Barão *et al.* 2014; Vandevenne *et al.* 2015). Diversity in these factors, in addition to their interactions, explains the large variability of the Si uptake rate. We must better understand soil DSi dynamics to evaluate impacts of changes in land use on Si biocycling and the biological Si feedback loop, which could be substantial and have downstream implications (Vandevenne *et al.* 2015). There is also promising potential to use Si isotopes to better understand the soil processes controlling the Si soil–plant cycle. Isotopic analysis is a tool to trace the origin of DSi and identify the LSi, PSi and PhSi minerals controlling the activity of DSi in soil solution (Ziegler *et al.* 2005; Opfergelt *et al.* 2009; Cornelis *et al.* 2010b; White *et al.* 2012).

Further global understanding of the Si soil–plant cycle relies on our knowledge of soil diversity, particularly on our understanding of soil processes since they control pedodiversity. Future challenges are to investigate (i) the effects of geologic, biological and climatic variables on the reciprocal interaction between the Si biocycling rates and the evolution of soil and (ii) how this interaction impacts the transfer of Si from land to ocean. In this respect, it is promising to combine process-oriented soil research with advanced geochemical and isotopic tools recently applied in soil and plant sciences. Such advances will contribute to a better understanding of the origin of Si in soil–plant systems and through this its use by plants and ultimate fate.

Conclusion

The driving forces leading to soil formation are the five pedogenetic factors: parent rock, climate, relief, biota and age, which in turn drive the soil–plant cycle of Si according to the weathering stage of soils. The mobility of Si in the soil–plant system is lowest at early stages of weathering

because of limited alteration. It increases at intermediate stage because LSi minerals dissolve and supply soil solution in DSi, which controls the precipitation and stability of PSi clay minerals as well as the transfer of Si to plant. At advanced stage of weathering, the stock of weatherable LSi/PSi minerals is exhausted so that the biological Si feedback loop controls the mobility of Si in the soil–plant system. The plant-mediated PhSi formation and further dissolution in soil alleviate mineral desilication and take over the soil processes involving the five pedogenetic factors, resulting in the concentration of bioavailable Si in the topsoil. Plant diversity and functional type, in rain forest and humid tropical savannas, enhance the efficiency of the biological Si feedback loop in environments conducive to biomass production. Thus, the pedo-evolution from early to advanced weathering stage parallels a progressive and large shift of the Si source for DSi from rock to plant, demonstrating the critical role of plants as the link between Si in the mineral and living worlds in terrestrial ecosystems. This process taking place in the soil–plant system is crucial for the transfer of Si from land to ocean through the continuum of soil solution–groundwater–river–ocean. Combining research on soil–plant processes with geochemical and isotopic tools is thus extremely promising to progress in our knowledge on Si fluxes at the Earth's surface, including for ecological research.

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Data accessibility

All data used in this manuscript have already been published or archived elsewhere.

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