General Conclusions and Perspectives

Implications of the study on the silicon isotopic geochemistry

After detailed studies of separate processes (Chapter 7 to 12), this part aims to summarize geochemical behaviors of Si in the soil-plant system, and discusses their implications on the global Si biogeochemical cycle. All the Si isotopic compositions will be discussed as δ^{30}Si vs NBS28. Data measured as δ^{29}Si only were converted to δ^{30}Si using the 1.93 multiplying factor, assuming a mass-dependent fractionation process (Young et al., 2002) following the equilibrium fractionation law, as supported by equilibrium fractionation processes observed in natural rivers (Georg et al., 2006a 2007c).

Silicon isotopes and Ge/Si ratio in the soil-plant system

Silicon isotopic fractionations in the soil-plant system are due to water-rock interactions and biogenic processes (see section 1.5.1). Water-rock interactions include dissolution of solid phases (primary minerals, secondary minerals, biogenic particles), neoformation of secondary minerals, and Si adsorption onto secondary oxides, while biogenic processes involve Si uptake by plants and Si transport within the plant (Figure 1.2). The Si isotopic fractionations induced by these processes are summarized in Figure 1.

Uptake of Si by banana plant depleted the soil solution in light Si isotopes leaving a solution enriched in heavy Si isotopes. Transport of Si from root to shoot induced an intra-plant fractionation. Following uptake and transport processes, Ge accumulated in roots. Consequently, Ge/Si ratio was larger in bulk roots than in shoots, which would explain low Ge/Si ratio in phytoliths (Blecker et al., 2007). In soils, aqueous Si ($H_4SiO_4^0$) is provided from mineral dissolution. Neoformation of secondary clay minerals and $H_4SiO_4^0$ adsorption onto iron oxides retrieve preferentially light Si isotopes from soil solution. Desorption was also shown to impact the Si isotopic composition of the solution in contact with these soils (Chapter 11) and we tried a quantification of its impact (Appendix F). The accumulation of Ge into secondary weathering products (clay minerals and iron oxides) induces a higher Ge/Si ratio in soil clay fractions as compared to parental material. Biogenic phytoliths restituted to the soil affect the Si isotopic composition of amorphous Si fraction in soil surface horizons.

Soil weathering stage modifies soil mineralogy and thus impacts the Si isotope balance. In the selected soil sequences from Cameroon, volcanic ash and glass content decreased with increasing weathering

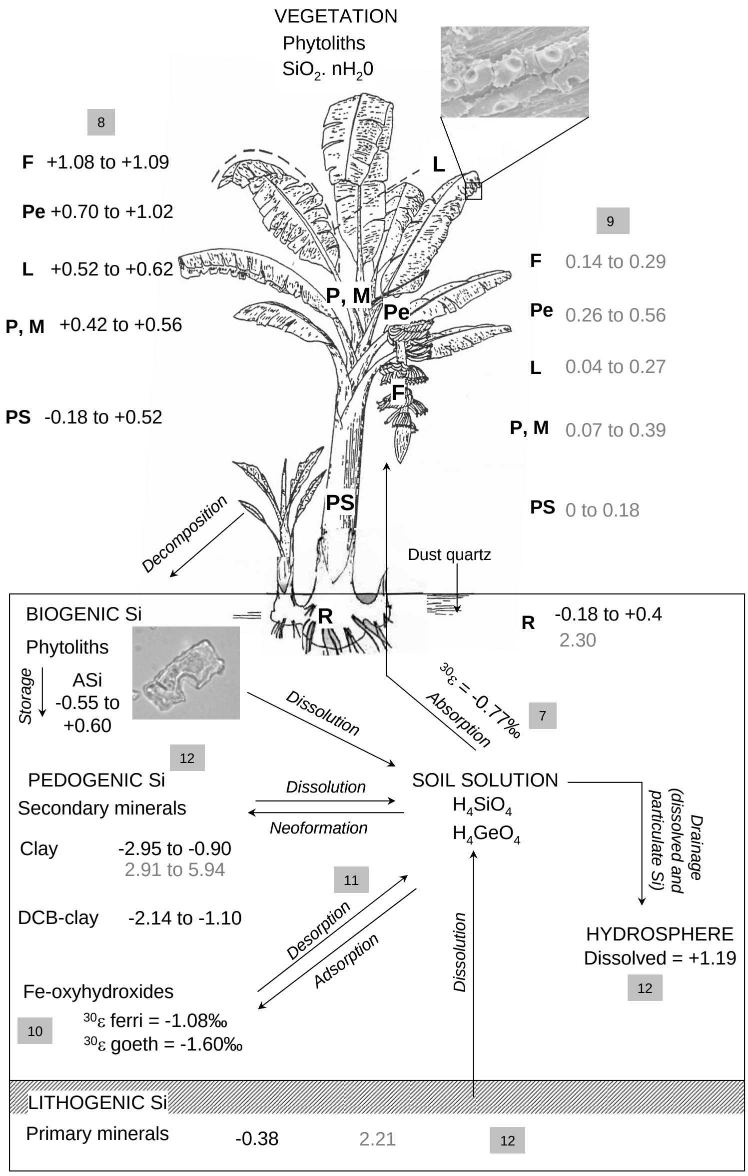

Figure 1: Summary of the Si isotopic compositions (δ^{30}Si in ‰, black) and fractionation factor induced, and Ge/Si ratio (μmol/mol, grey) measured in the soil-plant system in the present thesis. Numbers highlighted in grey refer to chapters of the thesis. ASi = amorphous Si fraction extracted by heavy liquid; R = roots; PS = pseudostem; P, M= petiole and midrib; L = lamina; Pe = peduncle; F = fruit. Banana plant adapted from Champion (1963).

stage whereas clay and free Fe-oxide contents increased, corresponding to the mineralogical sequence ash-allophane-halloysite-kaolinite (Delvaux et al., 1989). As light Si isotopes are preferentially incorporated into secondary clay minerals and adsorbed onto Fe-oxides, strongly weathered volcanic soils display lighter Si isotopic signatures, which was shown to impact the bulk plant Si isotopic composition (Figure 2).

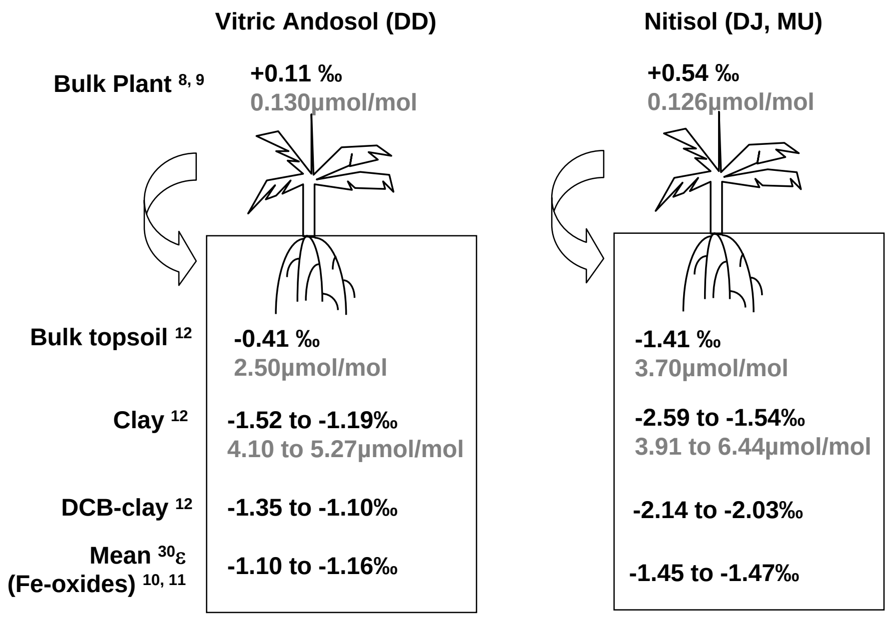

Figure 2: Impact of soil weathering stage on Si isotopic compositions of plants and soil fractions: δ^{30}Si values (black) and Ge/Si ratio (grey). The two end-members of the weathering sequences are presented: (a) Vitric Andosol (DD) - (b) Nitisol (DJ, MU). Andosol (MO, SR, MB) and Cambisol (EK) are considered as intermediary between these two end-members. Superscript numbers refer to chapters of the thesis.

Comparison with Si isotopic variations and Ge/Si ratios in terrestrial samples

Si isotopic variations and Ge/Si ratio in soil and plant samples were presented in the Overview (Figures 1.5 and 1.6). The Si isotopic compositions and Ge/Si ratios measured in the soil-banana system from Cameroon studied here are compared with available data in Figure 3 and Figure 4, respectively. Measurements on basaltic parental material, clay fractions, water samples and phytoliths are in very good agreement with published data. Moreover, this thesis provided the first Si isotopic measurements on deferrated clay fractions (DCB treated, Chapter 12), and the first quantification of a Si isotopic fractionation induced by Si adsorption (Chapter 10).

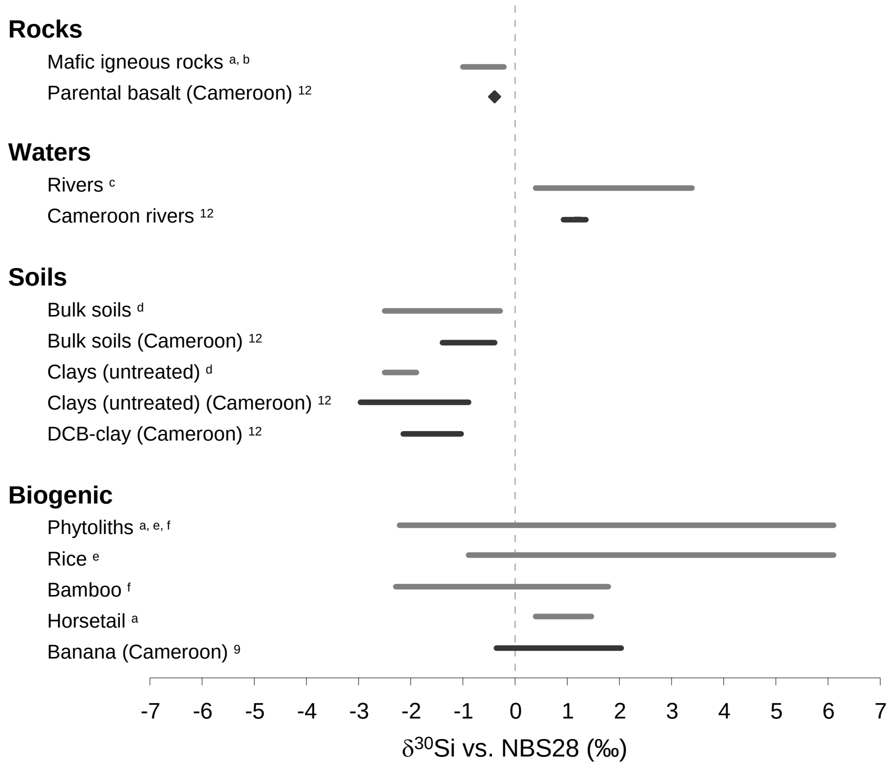

Figure 3: Comparison of the Si isotopic compositions measured in the soil-banana system (black, superscript numbers: chapters of the thesis) with the data available in the literature (grey, (a) Douthitt (1982); (b) Ding et al. (1996); (c) De La Rocha et al. (2000); Ding et al. (2004); Georg et al. (2006a 2007c); (d) Ziegler et al. (2005ab); (e) Ding et al. (2005b); (f) Ding et al. (2008)).

Phytoliths display a very large range of Si isotopic variations. This wide variation did not significantly differ between plant species (Figure 3). However, a larger range of variations occurs in rice and bamboo, relative to banana (very sparse data available for horsetail). This larger range can be attributed to (i) a higher degree of Si accumulation in rice and bamboo relative to banana (Hodson et al., 2005), and (ii) more heterogeneous soil conditions of samples (Ding et al., 2005b 2008) relative to the homogeneous parental material in Cameroon. Moreover, phytoliths display very different isotopic signature depending on their location in the plant as heavier signatures are displayed in upper shoots (Chapter 8). Consequently, Si isotopic compositions of phytoliths are very useful but should be used very carefully in well constrained conditions of plant species, degree of Si accumulation, location in the plant, soil parental material. Hydroponic studies are very useful to constrain the Si isotopic fractionation induced (Ziegler et al. (2005a); Chapter 7; Sun et al. (2008)). Phytolith Ge/Si ratios are less useful within the shoots but can be much easier discriminated from other Si pools in soils (Figure 4).

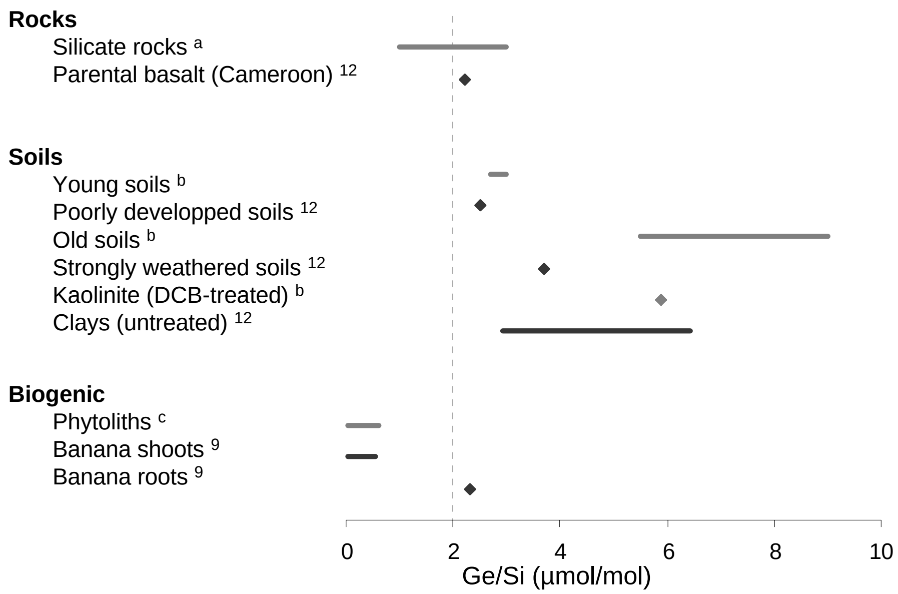

Figure 4: Comparison of the Ge/Si ratio measured in the soil-banana system (black, superscript numbers: chapters of the thesis) with the data available in the literature (grey, (a) Bernstein (1985); De Argollo and Schilling (1978); (b) Kurtz et al. (2002); (c) Derry et al. (2005); Kurtz and Derry (2004)). Bulk soils can display values up to 36μmol/mol (outside of the graph; Kurtz et al. (2002); Murnane and Stallard (1990); Scribner et al. (2006)).

Impact on rivers and ocean silicon cycle

Silica fluxes from the pedosphere to the hydrosphere have long been considered to be exclusively controlled by weathering of aluminosilicate minerals in soils (Drever, 1988). Yet, plants were shown to significantly impact weathering (Alexandre et al., 1997; Lucas, 2001). Riverine dissolved Si displays large range of Si isotopic signatures from 0.4 to 3.4‰ (Alleman et al., 2005; De La Rocha et al., 2000; Ding et al., 2004; Georg et al., 2006a 2007c). These variations were attributed to the range of secondary clay formation in sparsely vegetated area (Georg et al., 2007c), or weathering flux only in high mountainous catchments (Georg et al., 2006a), but also to biomineralization by diatoms (Alleman et al., 2005; De La Rocha et al., 2000), and uptake by plants (Ding et al., 2004; Georg et al., 2006a). As rivers supply 80% of the silicon input to the ocean (Tréguer et al., 1995), the plant impact can not be neglected. Moreover, from this thesis we can infer that an additional process should be taken into account to constrain riverine dissolved Si signature: Si adsorption on soil Fe-oxides and riverine particulate suspended matter.

The biological Si recycling rate through vegetation would impact weathering rate (if at least part of phytoliths are preserved in soil), but not the Si fluxes exported (except if erosion/denudation and phytolith dissolution occured) (Figure 5). By comparing three different cases of phytoliths dissolution/preservation, we can infer that δ^{30}Si and Ge/Si provide very useful tool to evaluate the impact of Si recycling through vegetation on Si exported (Figure 5).

Estuarine silicon dynamics is affected both by biotic (uptake by diatoms, radiolarians and sponges) and abiotic processes (aluminosilicate minerals from weathering) (Chou and Wollast, 2006). Moreover, freshwater marshes and Si uptake by plants were shown to play a key role in estuarine Si cycling (Struyf, 2005). In order to evaluate the dissolved Si fluxes delivered to ocean, it is essential to identify and quantify the various processes responsible for Si removal, retention and regeneration in estuary. Using Si isotopes in these environments would provide better insights to identify the contribution of biogenic processes relative to weathering processes. However, discrimination between plant and diatoms uptake would be difficult as fractionation factors were shown to be very close ($^{30}\varepsilon$ diatoms = -1.1±0.41‰, De La Rocha et al. (1997); $^{30}\varepsilon$ banana plant = -0.77±0.21‰, Opfergelt et al. (2006b)) (further discussed). Dissolved Si delivered by rivers to ocean regulates Si available for oceanic diatoms, and hence controls the ocean carbon cycle (Smetacek, 1999). The dissolved Si signature of seawater is strongly determined by diatoms activity (Cardinal et al., 2005 2007).

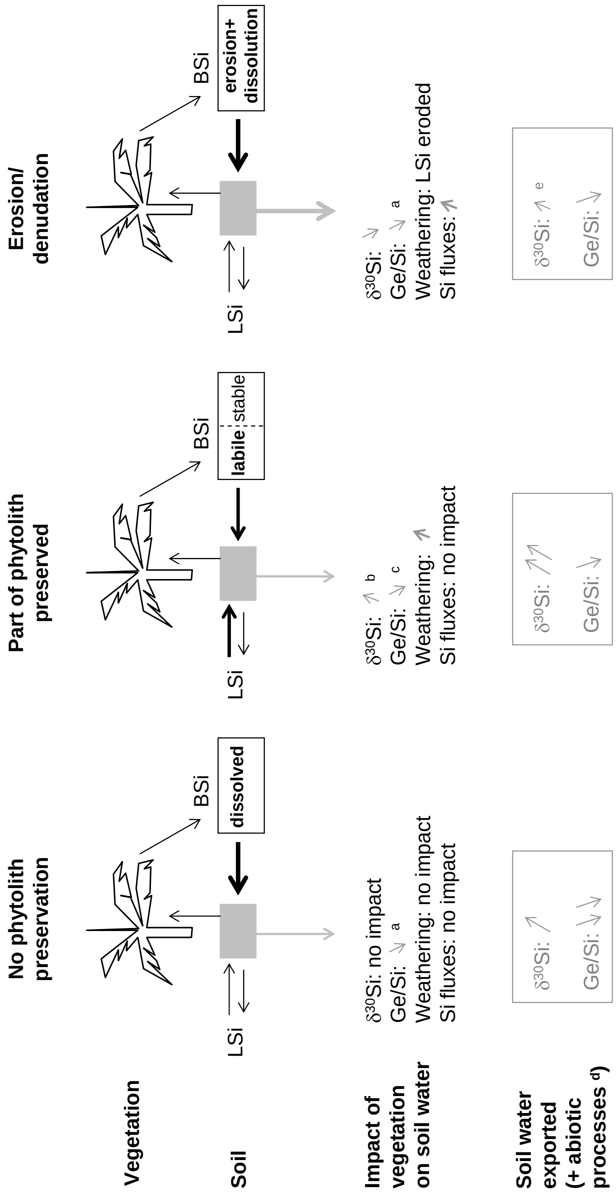

Figure 5: Evaluation of the impact of vegetation on soil water exported in three different cases of phytoliths dissolution/preservation. LSi = lithogenic Si, BSi = biogenic Si. [a] Ge/Si decreases if roots are not decomposed (Ge trapped). [b] δ^{30}Si increases as lighter isotopes are trapped in phytoliths preserved. [c] Ge/Si decreases in a smaller extent as part of the phytoliths are preserved. [d] Abiotic processes included light Si isotopes sequestration by clay minerals and adsoption onto Fe-oxides. [e] δ^{30}Si increases in a smaller extent due to phytolith dissolution (tracer of the erosion process).

Geological impact of the study

This thesis focused on current processes has two major geological implications, i.e. regarding (i) past plant impact onto weathering and hydrosphere, and (ii) impact of Si and Ge adsorption onto iron oxides in early Precambrian Banded Iron Formation (BIFs).

Weathering of silicate and carbonate minerals has controlled atmospheric CO_2 concentration for million of years (Berner, 1995). The advent of vascular plants during the mid-Paleozoic has enhanced rock weathering through nutrient uptake (Hinsinger, 1998; Hinsinger et al., 2001), which enhanced the removal of CO_2 from the atmosphere (Berner, 1992 1997). From this thesis, we can infer that the spread of plants on continents would have significantly modified the Si continental isotopic budget at this period, both by increasing weathering and by biogenic Si recycling. Si isotopic signatures preserved in marine sediments would be a very useful tracer of past oceanic signature, and hence, past plant impact. Temporal variation in weathering intensity on continents would also affect Ge/Si ratio in opal marine sediments as inorganic Ge is incorporated into biogenic opal as Si. Combining Si isotopic measurements with Ge/Si ratio would be very helpful to trace back the impact of vegetation on the weathering of mafic continental rocks.

Banded Iron Formations (BIFs) are prominent sedimentary deposits of the Precambrian, characterized by alternance of Si-rich level (cherts) and Fe-rich level (enriched into iron oxides), inducing characteristic layered rocks. Evidence from Ge/Si ratios implies that the sources of Si and Fe were decoupled during banded iron formation deposition, silica being dominantly derived from continental weathering and iron having a hydrothermal origin (Hamade et al., 2003). However, Si and Ge can be significantly adsorbed onto iron oxides (McKeague and Cline, 1963b; Pokrovsky et al., 2006), which would significantly affect Fe-rich levels. From this thesis, we can infer that Si isotopic composition of Fe-rich level should be enriched in light Si isotopes due to Si isotopic fractionation induced by Si adsorption onto iron oxides. It would be interesting to investigate the Si isotopic variations in these Fe-rich levels in addition to those in Si-rich levels (André et al., 2006). Using the fractionation factors (Chapter 10) would provide information about the Si isotopic composition of the Si source and past oceanic Si signature. Ge/Si ratios in these Fe-rich levels should be used carefully as Ge was shown to be concentrated in secondary weathering products partly due to adsorption onto Fe-oxides (Scribner et al., 2006).

Comparison with other plant-induced isotopic fractionations

Plant-induced isotopic fractionation for different stable isotopes (Fe, Zn, B, Ca, Mg, N, C, O) were briefly reported in the Overview (see section 1.5.1). Most of these elements are isotopically fractionated (i)

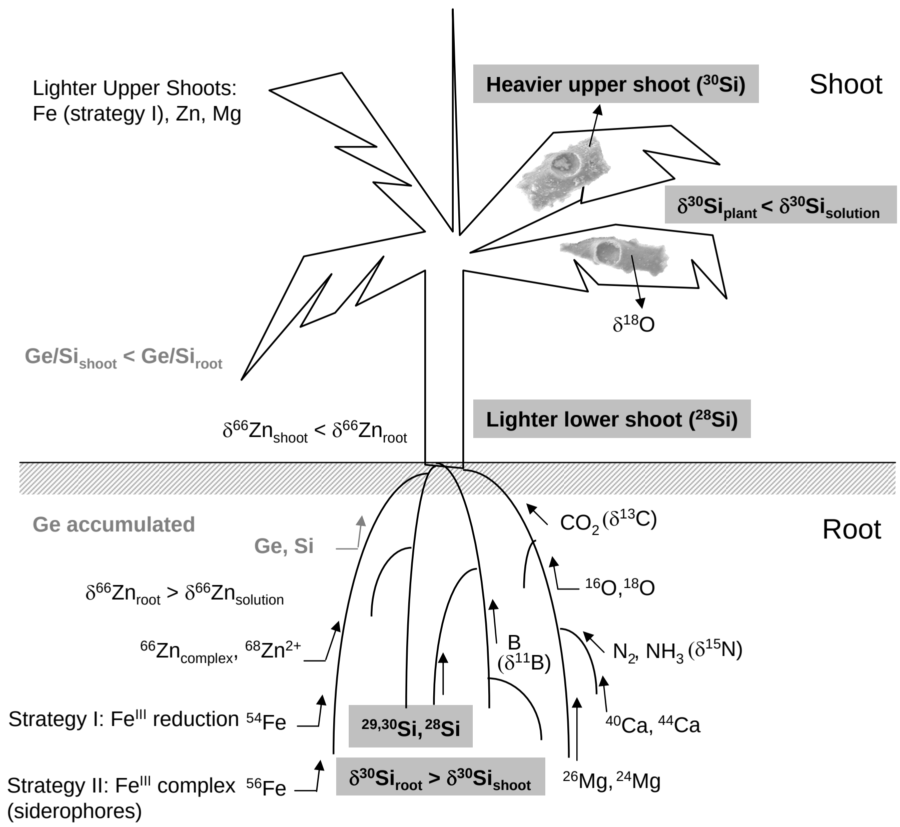

Figure 6: Comparison of the Si isotopic fractionation (bold highlighted in grey, Chapter 7, 8) and Ge/Si fractionation (grey, Chapter 9) induced by the plant with other plant-induced isotopic fractionation (other stable isotopes). Banana plant is used as an example. References for the different elements represented: (O) Shahack-Gross et al. (1996); Webb and Longstaffe (2000); (N) Okito et al. (2004); Yoneyama et al. (2001 1991); (C) Viktor and Cramer (2003); (Fe) Guelke and Von Blanckenburg (2007); (Zn) Viers et al. (2007); Weiss et al. (2005); (Mg) Bi et al. (2007); (B) Wieser et al. (2001); (Ca) Wiegand et al. (2005).

between species in solution (e.g. Zn for which Zn^{2+} is preferred by plants compared to complexed Zn; Fe acquired by Fe^{III} reduction (strategy I) or Fe^{III} complexation by siderophores (strategy II)), or (ii) by plant metabolism (e.g. O, C, N) (Figure 6). Isotopic fractionation by plants was shown to favor heavier isotopes of Zn (Viers et al., 2007; Weiss et al., 2005), Fe (strategy II plants, Guelke and Von Blanckenburg (2007)), and Mg (Bi et al., 2007), whereas light isotopes are preferred for Ca (Wiegand et al., 2005) and Fe (strategy I plants, Guelke and Von Blanckenburg (2007)). The intra-plant fractionation induced upper shoots enriched in light isotopes for Zn (Viers et al., 2007; Weiss et al., 2005), Mg (Bi et al., 2007) and Fe (strategy I plants, Guelke and Von Blanckenburg (2007)).

The plant-induced Si isotopic fractionation and Ge/Si fractionation are compared with those stable isotopic systems in Figure 6. Aqueous monosilicic acid in the only Si species in solution (no fractionation between species) and is taken up by mass flow (Raven, 1983) or active transport (Ma et al., 2006 2007). The intra-plant Si isotopic fractionation induces the accumulation of heavier Si isotopes in upper shoots (Chapter 7 and 8). Ge uptake follows Si uptake, and Ge accumulation in roots induces lower Ge/Si ratio in shoots than in roots (Chapter 9).

Interest of silicon isotopes and limits of the Si tracer

Despite the suspected strong biological imprint on the terrestrial Si cycle (Alexandre et al., 1997; Lucas, 2001), the contribution of plants to the Si continental reservoir compared to non biogenic processes was rarely quantified so far (Alexandre et al., 1997; Conley, 2002; Derry et al., 2005).

In the present thesis, we tested the relevance of using Si stable isotopes to follow the Si cycle in a soil-plant system, and hence identify the plant contribution relative to abiotic processes on the continental Si cycle. From a system with a control on plant (monoculture) and a control on the Si source (homogeneous parental material), we can deduce that Si stable isotopes constitute a promising tracer with respect to three major continental processes: (i) biological fractionation during plant Si uptake and phytolith formation (Chapter 7, 8, 9), (ii) sequestration of Si in soil clay-sized minerals (Chapter 12), and (iii) adsorption of Si by pedogenic iron oxyhydroxides (Chapter 10, 11). This study provides the first quantification of the plant-induced Si isotopic fractionation (Chapter 7) and confirms the trend of intra-plant fractionation measured in rice (Ding et al., 2005b) and bamboo (Ding et al., 2008). This thesis further confirms the sequestration of light Si isotopes in soil clay-sized minerals (Chapter 12), as shown by Ziegler et al. (2005a) and Ziegler et al. (2005b), and quantified for the first time the Si isotopic fractionation induced by adsorption of Si onto pedogenic iron oxyhydroxides (Chapter 10, 11). Ge/Si ratio also constitutes a very useful tracer of plant uptake (Chapter 9) and weathering processes (Chapter 12). Intra-plant Ge/Si fractionation measured (Chapter 9) would explain low phytolith Ge/Si ratio (Blecker et al., 2007). This study further confirms the Ge accumulation in secondary weathering products (Chapter 12), as shown by Mortlock and Froelich (1987) and Scribner et al. (2006), involving both clay formation and Ge adsorption onto Fe-oxides (Chapter 12). Both tracers (Si isotopes and Ge/Si ratio) can be useful to trace plant contribution relative to abiotic processes to Si exported.

Detailed Si isotopic study within the plant (bulk plant parts) was shown to provide new insights in the area of plant physiology, locating Si isotopic discrimination area in the plant following plant transpiration stream (Chapter 7), which was further discussed in a two-components model within bamboo, a Si accumulated pool and Si residing in plant fluid (Ding et al., 2008). Detailed Si isotopic study on soil fractions was shown to provide method to quantify parameters unavailable by direct measurements, e.g. dust-derived quartz, BSi content, and main contributions to bulk soil Si isotopic signatures (Chapter 12).

The present thesis provides a quantification of the fractionation factor induced by banana plant ($^{30}\varepsilon$ banana plant = -0.77±0.21‰, Chapter 7) and by Si adsorption onto iron oxides ($^{30}\varepsilon$ goethite = -1.60±0.05‰, $^{30}\varepsilon$ ferrihydrite = -1.08±0.02‰, Chapter 10). This is in the same range than fractionation generated by Si uptake by rice plant ($^{30}\varepsilon$ rice plant = -1.02±0.33‰, Ding et al. (2005b)), bamboo ($^{30}\varepsilon$ bamboo plant = -1.1‰, Ding et al. (2008)), wheat and corn ($^{30}\varepsilon$ wheat/corn = -1.00±0.31‰, Ziegler et al. (2005a)), and diatoms ($^{30}\varepsilon$ diatoms = -1.1±0.41‰, De La Rocha et al. (1997)). This means that both biological processes (Si uptake by plant and diatoms) and abiotic processes (Si adsorption onto Fe-oxides) deplete the solution in light Si isotopes and generate similar isotopic fractionations (Figure 7). On another hand, isotopic fractionation induced by weathering (clay mineral neoformation) are larger for secondary kaolinite ($^{30}\varepsilon$ secondary kaolinite = -2‰; Ziegler et al. (2005ab)) or smaller for allophane ($^{30}\varepsilon$ allophane = -0.34‰; Ziegler et al. (2005a)) (Figure 7).

Consequently, natural environments impacted simultaneously by all these processes will display a bulk Si isotopic signature resulting from the above processes. The interpretation of that signature will be very complex as resulting from a bulk depletion of light Si isotopes. In that case, the approach should 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 (in addition to irrigation in cultural environment), modifying Si available for Si adsorption 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, to isolate one process considering some processes negligible based on the mineralogy, and hence, interpret the bulk Si isotopic signature. For example, the effect of Si adsorption onto Fe-oxides could be discriminated from biological uptake in a system where goethite only is identified (Figure 7).

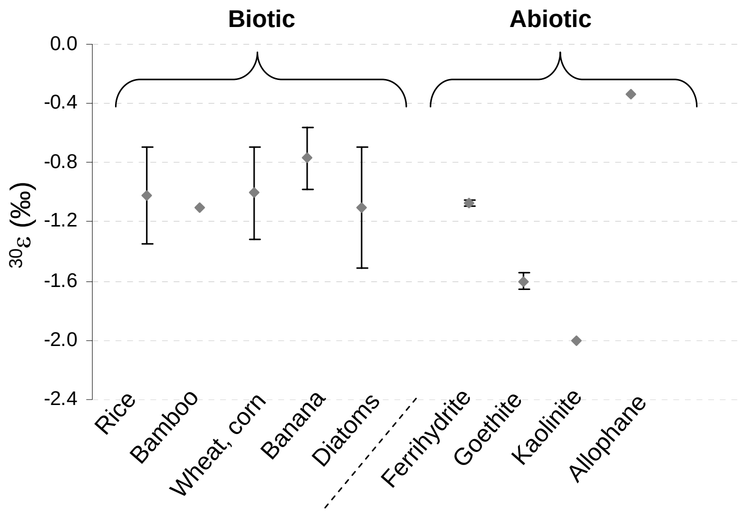

Figure 7: Comparison of fractionation factors ($^{30}\varepsilon$) induced both by biotic and abiotic processes (see references in the text).

In the case of estuarine environment, weathering input could be discriminated from biological input as secondary clay minerals should display lighter isotopic signatures. Yet, discrimination between plant and diatoms uptake would be very difficult as fractionation factors were shown to be very close (Figure 7).

A multi-proxy approach should provide new tool to isolate and quantify the processes, e.g. combining with Ge/Si ratio as Ge accumulates in plant roots but is taken up like Si by diatoms. The evolution of δ^{30}Si and Ge/Si in soil solutions exported was briefly evaluated in Figure 5. From this Figure, we can conclude that δ^{30}Si constitutes a good tracer of the Si recycling through vegetation and of the contribution of BSi vs. LSi in soil water exported if fractionation factors of both processes $^{30}\varepsilon$ can be dissociated. Ge/Si ratio would be very useful to trace Si recycling through vegetation, and much more discriminant than δ^{30}Si to dissociate the dissolution of BSi vs. clay minerals to soil water exported, as phytoliths display low Ge/Si ratio compared to high Ge/Si ratio of clay minerals. However, the sequestration of Ge by clay minerals and Ge depletion induced also need to be taken into account in mass balance calculation. δ^{30}Si and Ge/Si ratio were not used to quantify Si fluxes (net input) exported by vegetation.

Si isotopes are thus a very useful tracer to follow Si cycle and identify major processes impacting soil solutions exported to rivers, but should include a good characterization of the processes involved and take into account the limitations mentioned here above.

General conclusions

The initial objectives of the present thesis were to identify the plant impact in the terrestrial Si cycle relative to abiotic processes by tracing Si pathway in the soil-plant system with Si stable isotopes. In this respect, we quantified the Si isotopic fractionation induced by plants and weathering processes in controlled conditions (*in vitro*) and used these indicators in natural conditions (*in situ*).

In order to measure Si isotopes in a large range of matrix from the soil-plant system, analytical development were conducted in collaboration with the scientific group of the Royal Museum of Central Africa (Tervuren, Belgium). These developments aimed at (i) develop a method to produce confident Si isotopic compositions on rocks and clays (Abraham et al. (2008); see Chapter 5), (ii) develop an adapted method allowing to measure ^{30}Si and express the results as δ^{30}Si (Abraham et al. (2008); see Chapter 5), and (iii) prove accuracy of the measurements on Si isotope standard materials by an interlaboratory comparison (Reynolds et al. (2007); see Chapter 6).

Using this tool in a soil-banana system, the following main conclusions were drawn:

1. **Si isotopic fractionation by plants**
Plants were shown to induce a Si isotopic fractionation at the root-solution interface, and within shoots (Chapter 7), and a Ge/Si fractionation between roots and shoots (Chapter 9). Light Si isotopes are preferentially taken up by the plants ($^{30}\varepsilon$ = -0.77±0.21‰). A similar intra-plant fractionation with heavier isotopic composition in upper shoots has been highlighted in mature banana plants (Chapter 8). The bulk plant Si isotopic composition would reflect soil weathering stage (Chapter 8), whereas bulk plant Ge/Si ratio would not (Chapter 9).

2. **Si isotopic fractionation with weathering**
Weathering induces isotopically lighter and Ge enriched secondary weathering products relative to their parental material (Chapter 12). This is due to a preferential incorporation of light Si isotopes and Ge in clay minerals (Chapter 12) and a combined process of preferential adsorption of light Si isotopes onto secondary clay-sized iron oxides (Chapter 10, 11).

3. **Plant impact on the global Si continental cycle**

The Si isotopic signatures in surface clay fractions in poorly developped volcanic ash soils revealed an additional Si input which could be of biogenic origin. Amorphous Si fractions in all soils were enriched in phytoliths in surface and displayed heavier signature in strongly weathered volcanic soils. This strongly suggests a lower residence time of phytoliths in poorly developped volcanic soils where both weatherable minerals and phytoliths might be used as a Si source for clay mineral formation.

The implications of these various aspects have been considered and should be taken into account in further studies.

Perspectives

The geochemistry of silicon in a soil-plant system and the relevance of Si stable isotopes as a tracer of the continental Si cycling have been explored in the present thesis. However, different questions remain unresolved and could be investigated more deeply. Further perspectives concerns mainly five aspects: (1) plant, (2) adsorption, (3) clay minerals, (4) field studies, and (5) tracing.

In the **plant** research area, it would be interesting to:

(i) Identify whether Si isotopic fractionation by plant is an equilibrium or a kinetic mass-dependent isotope fractionation (see section 1.5.1). This could be approached by comparing banana species with a rapid growth (*Musa balbisiana Tani*) and slow growth (*Musa acuminata ssp. Banksii*), and modify temperature and relative humidity known to impact plant growth (Turner, 1995) directly impacting the transpiration stream, and hence Si uptake.

(ii) Identify Si uptake mechanism of transport in banana plant. An active Si uptake has been identified at low Si concentration provided, in addition to a passive uptake (Henriet et al., 2006). Discrimination of Si isotopes occur at the root-solution interface, for xylem loading and within shoots (Chapter 7), and roots are Ge enriched (Chapter 9). Like Si-tranporters identified in rice plants (Ma et al., 2006 2007), it would be interesting to identify and locate these transporters in banana plant to better understand the Si mobility and fractionation within the plant.

(iii) Explore the variation of the Si isotopic signature and Ge/Si of the xylem sap along Si pathway through plant by sampling xylem sap at different levels and relate this with the bulk plant signatures compared to the Si precipitates in phytoliths (Blecker et al., 2007; Ding et al., 2008).

(iv) Explore the variation of Si isotopic variations through banana leaves as Si accumulation was shown to be related with ageing leaves (Motomura et al., 2004) (see Appendix D).

(v) Compare this Si-accumulating plant system with a non-accumulating plant system, e.g. hevea (available in Cameroon on Nitisol developed on the same parental material) and follow the Si isotopic signature of the different Si pools of the system (see preliminary values in Appendix H).

(vi) Experimentally grow plants in contact with isotopically characterized clays or mixture of clays and biogenic Si (phytoliths) to test the ability of plant to acquire Si from litho/pedogenic pool versus biogenic Si pool.

(vii) Test the role of arbuscular mycorrhiza in the acquisition of Si by plants by symbiosis, and the effect on Si isotopic fractionation, as these organisms favor elements acquisition by plants and should favor weathering exportation to hydrosystem.

In the area of **adsorption**, it would be interesting to characterize the Si isotopic fractionation induced by Si adsorption on a larger range of oxyhydroxides, including Fe and Al-oxides, and whether they are pH-dependent. The specific adsorption of Ge onto Fe-oxides and its impact onto Ge/Si fractionation should also be studied in detail.

In the area of **clay minerals**, it would be interesting to:

(i) Quantify in much detail the Si isotopic fractionation induced by clay mineral formation for different type of clay minerals in controlled conditions.

(ii) Studying in controlled conditions (reconstituted soil column in simulated tropical climatic conditions with rainy season) the impact of biogenic Si input in soil surface on Si source provided for clay mineral neoformation relative to primary minerals present in the soil.

To explore the Si isotopic fractionation in a larger range of natural conditions, it would be interesting to develop some **field studies** to:

(i) Extract soil solutions and quantify dissolved Si sources (biogenic, lithogenic or pedogenic).

(ii) Extend this study to another tropical ecosystem (e.g. Guadeloupe) where very interesting relations between Si content in plants and weatherable mineral reserve were highlighted (Henriet, 2008).

(iii) Extend this study to a temperate forested ecosystem where plant Si mobilisation and litterfall would strongly impact the Si dissolved in soil solutions (Cornélis et al., 2007).

(iv) As felsic igneous rocks and granitoids were shown to display contrasted Si isotopic signature compare to mafic igneous rocks (see section 1.5.1), it would be interesting to compare this study (basaltic parental material) to a system characterized by another parental material (e.g. granitic) to evaluate the impact of the Si source on the processes (see preliminary values in Appendix D).

(v) Test the seasonal variability by comparing rainy season and dry season sampling.

(vi) Identify whether Si isotopic fractionation in soils is an equilibrium or a kinetic mass-dependent isotope fractionation (see section 1.5.1).

To trace continental impact of plant and weathering on the hydrosphere, it would be interesting to combine Si isotopes with **other tracers** (e.g. Ge/Si ratio, Ge, Mg, Li isotopes). This would contribute to the understanding of the rate and type of continental weathering, which are an important part of the biogeochemical budget for all elements released, and play a crucial role in the long-term C cycle.

However, our ability to quantify past weathering rates using geochemical proxies is relatively poor. Yet, some isotopic systems are sensitive to variations in weathering processes, providing a riverine isotopic signal to the oceans, hence potential archives of changes in weathering in response to climate change preserved in marine sedimentary (Burton et al., 2007). Studying current weathering fluxes would be helpful for paleoclimatic studies. During weathering, Si, Mg and Li are partially retained in secondary clay minerals (Borchardt, 1989). Since these elements are isotopically fractionated through clay formation (Georg et al., 2006a; Pistiner and Henderson, 2003; Tipper et al., 2006; Ziegler et al., 2005ab) and by adsorption onto secondary oxides (Pistiner and Henderson (2003); Chapter 10), stable Si, Mg and Li isotopes constitute very interesting proxies of weathering processes. As those three isotopic systems would not be affected with the same intensity by weathering processes, and because one isotopic system is not self-sufficient to distinguish two processes inducing similar isotopic fractionation, a multi-proxy approach would be very helpful to better constrain and quantify weathering fluxes. Considering a negligible effect of vegetation, the formation of secondary clay minerals will favor light Li and Si, and heavy Mg isotopes. Light Li and Si will also be involved in adsorption on secondary oxides. Yet, Li is fluid-mobile and will be mostly evacuated with soil solution. The relative impact of weathering and soil processes on these three elements will be reflected by their isotopic ratio.

Moreover, combining Si and Mg isotopes in a soil-plant system should help to decipher the relative contribution of plants in the clay-soil Si budget. In plants, Mg^{2+} is an essential nutrient with important regulatory signal, both activating and mediating many biochemical reactions (key role in vital functions like e.g. chlorophyll synthesis or cell walls strenghtening). Mg isotopic fractionation induced by plants (Bi et al., 2007) is thus probably related to metabolic activities, and coupling Si-Mg isotopes in plants should help to understand the physiological mechanisms leading to phytolith precipitation. Plant uptake should induce different Mg isotopic signature in residual soil solution compared to the accumulated litter. In soils, Mg is a remarkable tracer of the weathering of secondary clay minerals in unfertilized forest soils (Brahy et al., 2000). So, coupling Si and Mg isotopes on clays is very promising to constrain both clay-forming processes and Si-Mg soil-plant cycling.