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Plant silicon isotopic signature might reflect soil weathering degree

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Abstract Plants fractionate Si isotopes which provides a useful Si tracer in the Si soil-plant cycle. This study reports plant Si content and Si-isotopic signatures in mature banana plants grown on soils with different weathering degree, but all developed from basaltic pyroclasts in the Mungo area, Cameroon. The δ^{30}Si compositions were determined in various plant parts and soil surface horizons by MC-ICP-MS in dry plasma mode with external Mg doping to a precision of $\pm$ 0.15‰ ($\pm 2\sigma_{SD}$). The Si-isotopic compositions in banana plants grown on weathered clayey soils (+0.54 ± 0.15‰) are heavier than on weakly developed soils rich in fresh ash and pumice (+0.02 ± 0.15‰). The corresponding bulk soils display lower δ^{30}Si value in weathered soil (−1.41‰) than in poorly developed soil (−0.41‰). We suggest that the dissolved Si source for the plant, governed firstly by dissolution of easily weatherable minerals, was isotopically enriched in heavy isotopes through clay formation over long periods. At seasonal to annual time scale, this source is influenced by a combination of following processes: Si adsorption of light isotopes onto Fe oxides, plant Si uptake and recycling in surface horizons. This would provide an isotopically heavier Si source in the more weathered soil since the Fe oxides content increases with weathering. Plant Si-isotopic signature might thus reflect the soil weathering degree. This study further suggests that in addition to weathering processes, rivers isotopic signatures likely depend on the fate of phytoliths in the soil-plant-river system.

Keywords Isotopic fractionation · *Musa* · Si cycle · Cameroon · Soil · Weathering sequence

Introduction

Silicon plays a crucial role in global biogeochemical processes such as carbon dioxide regulation (Volk 1987; Berner 1997), the buffering of proton fluxes through silicate dissolution (Rai and Kittrick 1989), and both marine and terrestrial biota nutrition (Smetacek 1999). Since mineral dissolution rates can be enhanced by plant effects on silicate weathering (Moulton et al. 2000), plants can leave a considerable imprint on the Si continental cycle, and thereby on Si release in water streams (Alexandre et al. 1997; Conley 2002; Derry et al. 2005). However, only few studies have been carried out so far to quantify their contribution to the continental cycle of Si, and more specifically within the soil-plant system. The

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quantification of silicon isotopic fractionation by biotic and abiotic processes can readily contribute to the understanding of the continental cycle of silicon. These processes involve Si uptake by biota (Douthitt 1982; De La Rocha et al. 1997; De La Rocha 2003; Ding et al. 2005, 2008; Ziegler et al. 2005a; Opfergelt et al. 2006a), silicate weathering (Ziegler et al. 2005a, b; Georg et al. 2006, 2007), clay formation (Ziegler et al. 2005a), and silicon adsorption on oxide surfaces (Delstanche et al. in press). They all imply lighter Si-isotopic compositions in the biota-, clay-and oxide-compartments, thereby involving heavier Si-isotopic signatures in nutrient, equilibrium or drainage solutions (Ziegler et al. 2005a; Opfergelt et al. 2006a; Delstanche et al. in press). The Si-isotopic signature of a given plant species or cultivar could thus be impacted not only by Si uptake, but also by the soil weathering degree, which indeed results in the formation of both clay minerals and iron oxides (Bikerland 1974).

We have recently shown that Si accumulation by young banana plantlets (*Musa acuminata* Colla, cv Grande Naine) in hydroponics is controlled by Si availability in the nutrient solution (Henriet et al. 2006), and involves a Si-isotopic fractionation at the root-solution interface and between plant parts (Opfergelt et al. 2006a). Here, we determine the first Si-isotopic compositions in mature banana plants (*Musa acuminata* Colla, cv Grande Naine) from root to fruit. We use banana plants grown on soils developed from basaltic pyroclasts, but differing in their weathering degree, and thus in their clay and oxide contents (Delvaux et al. 1989). Hence, though derived from similar volcanic ash, these contrasted soils are here viewed as distinct Si sources.

Materials and methods

Study area

The study area lies in the Mungo plain of Cameroon, West Africa (Njombé-Penja-Loum, 4°30′–4°53′N 9°37′–9°50′E, 70 km north of Douala). This area is characterized by a humid tropical climate: the rainy season lasts from March to November with a total average annual rainfall of 2,700 mm per year, and the temperature ranges from 22.4°C (870 m) to 27.5°C (40 m) according to the altitude (Martin and Sieffermann 1966). The Mungo plain is a graben extending over 80 km on a south-west–north-east axis, covered by basaltic lava flows, ash and pumice deposits, dating from the Quaternary (early Quaternary to present times) (Nkouathio et al. 2002). This graben is part of the N30°E Cameroon Hot Line (Déruelle et al. 2007). The soils devoted to intensive banana cropping derive from pyroclastic deposits and are located at 100–250 m above see level. The soils belong to a weathering sequence corresponding to the soil mineralogical sequence ash–allophane–halloysite–kaolinite: as the weathering degree increases, volcanic ash and glass content decreases whereas clay and free Fe oxides contents rise (Delvaux et al. 1989). The soils thus strongly differ in their mineralogical and physico-chemical properties despite their similar parent rock, according to their weathering degree.

The Mungo area has long been used for intensive banana cropping since the 50s of last century (Delvaux 1988). The cropping systems are based on successive cycles of 7–9 months before harvesting. At harvesting time, banana leaves and pseudostems are cut and left on the soil surface. Banana fields are irrigated during the dry season by surrounding river waters; fertilizers (N, P, K, Mg) are applied on a monthly basis whereas lime amendments (Ca) are applied every other year. Four stations were selected from poorly developed to strongly weathered volcanic soils respectively, determining the weathering sequence: Dia-Dia, Sir, Mbomé, Djungo. The former are rich in weatherable minerals and poor in clay (10–35%) containing allophane, halloysite and ferrihydrite. Conversely, the latter are fine clayey soils (70–96% clay), rich in halloysite, kaolinite, gibbsite and goethite (Delvaux et al. 1989, 1990b).

Sampling

Banana plant parts (*Musa acuminata* Colla, cv Grande Naine) were sampled in each station (Dia-Dia, Sir, Mbomé, Djungo) in November 2005, at the end of the rainy season. In each station, five plants were selected at the flowering stage according to the international foliar sampling procedure (Martin-Prével 1984) involving the sampling of petiole (P), midrib (M), internal and external lamina (IL, EL) of leaf III (Fig. 1). Among the five, one plant was sampled from root to fruit: root (R), internal pseudostem (PSi), external pseudostem (PSe), P, M, IL, EL, peduncle (Pe)

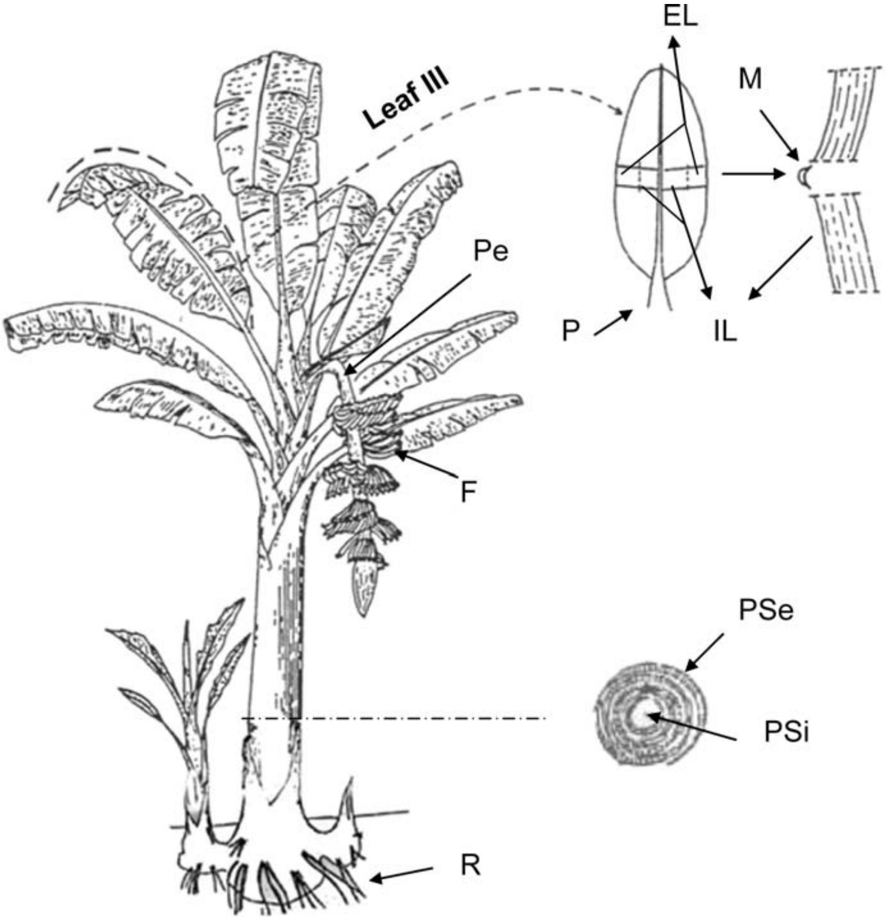

Fig. 1 Schematic banana plant morphology at flowering stage: root (*R*), peduncle (*Pe*), fruit (*F*); cross section indicating internal (*PSi*) and external pseudostem (*PSe*); leaf III with petiole (*P*), midrib (*M*), internal lamina (*IL*), and external lamina (*EL*) (adapted from Champion 1963; Martin-Prével 1984)

and fruit (F) (Fig. 1). The other four plants were used to build up four composite foliar samples (P, M, IL, EL). As the pseudostem is made up of leaf sheaths, with external sheaths corresponding to the oldest leaves, the external green sheaths (PSe) were collected separately from the internal white sheaths (PSi) (Fig. 1), considering a possible Si accumulation in external sheats related to leaf age and transpiration (Motomura et al. 2004). Upon flowering, a flower cluster emerges, supported by a peduncle, and produces individual clusters of fruits (hand) constituted by individual fruits (fingers). As to the fruit (F), we sampled the middle fingers of the second hand.

Topsoils (00–05 cm) were sampled in each station 50 cm around each plant, after cleaning up the soil surface from banana litter residues. The topsoils were then mixed to build up a topsoil composite sample. Fresh pumice particles were collected from the flanks of the most recent volcanic cone in the Mungo plain (Mont Pelé).

Stream water used for both crop irrigation at Dia-Dia and Djungo station was sampled. The water sample was immediately filtered through 0.4 µm polycarbonate membrane, acidified with suprapur HNO_3 and stored at ~4°C in the dark, in acid-cleaned polypropylene bottle.

Bulk elemental, chemical and physical analyses

The dry weight of plant materials from the four stations (Dia-Dia, Sir, Mbomé, Djungo) was determined after drying all plant parts at 60°C for 1 week. Elemental analysis was carried out after borate fusion at 1,000°C and dissolution of fusion beads in 10% HNO_3 (Chao and Sanzolone 1992). The concentrations of Si, Al, Ca, Mg and K were determined by inductively coupled plasma atomic emission spectrometry (ICP-AES); the detection threshold for Si in solution was set at 0.7 µM Si.

The soil samples were air dried at room temperature during 24 h, and sieved at 2 mm. Elemental analysis was carried out after calcination and Li-metaborate and Li-tetraborate fusion (Chao and Sanzolone 1992). To put it briefly, a crushed sample of 100 mg was melted at 1,000°C for 5 min in a graphite crucible in the presence of 0.4 g Li-tetraborate and 1.6 g Li-metaborate. The cooled melt was then dissolved in 200 ml of 2 M HNO_3 under magnetic agitation at 90–100°C. The contents of Si, Al, Fe, Ca, Mg, K were determined by ICP-AES. The total contents of alkaline and alkaline-earth cations were summed up as the total reserve in bases (TRB), which estimates the content of weatherable minerals in mineral soil horizons (Herbillon 1986). The content of free iron oxides was determined after selective dissolution of Fe oxides in the Na-dithionite-citrate-bicarbonate (DCB) extract (Mehra and Jackson 1960). The ratio of DCB-extractable Fe over total Fe content (Fe_d/Fe_t) is an index of the soil weathering degree, just as TRB and clay content (Delvaux et al. 1989). The particle size distribution was determined by quantitative recovery of clay, silt and sand fractions after sonication and dispersion with Na^+-saturated resins (Rouiller et al. 1972; Bartoli et al. 1991). Purity of clay fractions (i.e. secondary phases) was checked by X-ray diffraction.

Silicon isotopes analyses

The Si-isotopic composition was measured: (1) both in the soil samples (<2 mm) and clay fractions (<2 µm) from the four stations (Dia-Dia, Sir, Mbomé, Djungo), (2) in the fresh pumice material (3) in the irrigation water and (4) in plant materials from two selected stations (Dia-Dia, Djungo), in order to compare two contrasted Si sources: the weakly developed soil of Dia-Dia versus the strongly weathered soil of Djungo.

In the soil and clay samples, silicon was recovered from each aliquot by alkaline fusion at 1,000°C of 5 mg of silicate powder mixed with 30 mg of $LiBO_2$ flux in a covered Pt crucible and dissolution in double distilled 5% HNO_3 (Abraham et al. 2008).

Silicon was recovered from each plant aliquot after (1) mineralization at 450°C during 24 h in Pt crucibles, (2) opal dissolution by 0.2 M NaOH leaching at 100°C during 2 h (adapted from Ragueneau et al. 2005).

Dissolved Si from soil, plant and water samples was purified by triethylamine molybdate (TEA-moly) co-precipitation and combustion in covered Pt crucibles at 1,000°C (De La Rocha et al. 1996), and dissolved in a dilute suprapur HF-HCl mixture (Cardinal et al. 2003).

The Si-isotopic compositions in soil, clay, pumice and plant samples were measured using a Nu Plasma multicollector plasma source mass spectrometer (MC-ICP-MS) operating in dry plasma mode, with an external Mg doping to correct mass bias (Cardinal et al. 2003). To avoid matrix effects, purity of the samples (absence of major elements and Mo) was controlled by ICP-AES prior to MC-ICP-MS analyses. Data were obtained by the sample-standard bracketing technique relative to the NBS28 silica sand standard (National Institute of Standard and Technology RM #8546) for silicon isotopes. The analytical method was supported by an inter-laboratory comparison exercise and proved to be accurate on secondary reference materials (Reynolds et al. 2007). Quality control of the chemical procedure and analytical measurements was given by a secondary reference material (diatomite) and rock standard (BHVO) processed with the sample series (Reynolds et al. 2007; Abraham et al. 2008). A new method solving the isobaric interference of $^{14}N^{16}O$ on ^{30}Si was developed (Abraham et al. 2008). Previously, only ^{29}Si:^{28}Si ratios were accurately measured (Cardinal et al. 2003). In this study, our results are expressed as $\delta^{30}Si$ (‰) with an average precision and accuracy of ± 0.15‰ (± $2\sigma_{SD}$) following:

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

Part of the data measured only as $\delta^{29}Si$ before the development of the new method were converted to $\delta^{30}Si$ values by using the multiplying factor 1.93 assuming a mass-dependent fractionation process (Young et al. 2002) following the equilibrium fractionation law. This is supported by equilibrium fractionation processes observed in natural rivers (Georg et al. 2006, 2007).

Results

Soil properties

Table 1 shows the soil data. These data are highly consistent with the increase of soil weathering degree

Table 1 Characteristics of the topsoils (0–5 cm)

Station	TRB cmol$_c$ kg^{-1}	Fe$_d$/Fe$_t$	Clay content (%)
Dia-Dia	703	0.22	25
Sir	469	0.36	42
Mbomé	323	0.40	58
Djungo	183	0.60	72

TRB total reserve in bases, DCB-extractable Fe content over total Fe content (Fe$_d$/Fe$_t$), and clay content

from Dia-Dia to Djungo, as previously reported for this weathering sequence (Delvaux et al. 1989). Indeed, TRB decreases with increasing values of both clay content and Fe$_d$/Fe$_t$ ratio, indicating that the dissolution of primary weatherable minerals resulted in the synthesis of clays and iron oxides. In this respect, Dia-Dia and Djungo strongly differ in soil weathering degree, as they exhibit contrasting TRB values (703 vs. 183 cmol$_c$ kg^{-1}) and clay contents (25 vs. 72%). In Dia-Dia, 22% of Fe accounts for free oxides (vs. 78% for Fe-silicate) against 60% of Fe as free oxides in Djungo.

Si-isotopic data are presented in Table 2. The δ^{30}Si value determined in the fresh pumice material can be considered as the Si-source value (−0.38‰). With respect to this value, δ^{30}Si was similar in the poorly developed soil (Dia-Dia = −0.41‰), but much lower in the strongly weathered soil (Djungo = −1.41‰). As expected (Ziegler et al. 2005b), the δ^{30}Si values decrease in the respective clay fractions of Dia-Dia (−1.19‰) and Djungo (−2.37‰) together with the increase of soil weathering degree, Djungo being much more weathered than Dia-Dia. The lighter Si-isotopic signatures in more weathered soil and clay fractions are related to preferential incorporation of light Si isotopes for clay neoformation (Ziegler et al. 2005a, b), and preferential adsorption of light Si isotopes on clay sized Fe-oxides (Delstanche et al. in press). Considering the SiO$_2$ content in the bulk soil and in the clay fraction (Table 2), the proportion of SiO$_2$ from the clay fraction in the bulk soil can be calculated with clay content (proportion = 10% and 62% for Dia-Dia and Djungo, respectively). Using the bulk soil Si-isotopic signature, the remaining fraction should display δ^{30}Si values computed by mass balance of −0.32 and +0.16‰ at Dia-Dia and Djungo, respectively. This remaining fraction of the bulk soil includes unweathered pumice material (−0.38‰) and biogenic input from plant litter return to the soil at harvesting time. Stream water used for crop irrigation displays a positive isotopic signature (+1.35‰) which lies in the usual range of river isotopic compositions (De La Rocha et al. 2000; Ding et al. 2004; Alleman et al. 2005).

Mineral content in plants

Table 3 presents the contents of Ca, Mg, K, Al in the internal lamina (IL) of leaf III, and Al content of roots, as determined in the samples collected in the four stations Dia-Dia, Sir, Mbomé, Djungo. All along the sequence from Dia-Dia to Djungo, the foliar IL Ca content decreases compared with K content. This supports the idea that the nutritional status of banana plants is strongly governed by soil weathering degree in this area since poorly developed soils are rich in Ca-bearing primary minerals, and strongly weathered soils selectively sorb K$^+$ ions on their clay surfaces, thereby contributing positively to the storage and bioavailability of potassium (Delvaux et al. 1989, 1990a). Al content in roots is substantial compared with Al content in IL (Table 3). The contribution of Al^{3+} adsorbed onto root surfaces is likely to be

Table 2 SiO$_2$ content (%) and δ^{30}Si (‰) values of the topsoil (< 2 mm; n = 2) and clay (<2 μm; n = 1) samples, as compared with δ^{30}Si value of fresh pumice material (n = 2). Si content (μM) and δ^{30}Si value of the stream water used for crop irrigation (n = 1)

Station	Soil[a]			Clay			Pumice[a]			Water[a]	
	SiO$_2$	δ^{30}Si	2σ_{SD}	SiO$_2$	δ^{30}Si	2σ_{SEM}	SiO$_2$	δ^{30}Si	2σ_{SD}	Si	δ^{30}Si
Mont Pelé	–	–	–	–	–	–	48.1	−0.38	0.07	–	–
Dia-Dia	38.5	−0.41	0.30	15.8	−1.19	0.12	–	–	–	–	–
Djungo	34.9	−1.41	0.18	30.1	−2.37	0.12	–	–	–	–	–
Irrigation water	–	–	–	–	–	–	–	–	–	306	+1.35

[a] δ^{30}Si value calculated from δ^{29}Si measured using factor 1.93

Table 3 Ca, Mg, K and Al content (%) and K/Ca ratio ($\text{cmol}_c\ \text{kg}^{-1}$) within internal lamina (*IL*) and Al, Si content (%) in root all along the weathering sequence

Internal lamina	Ca	Mg	K	K/Ca	Al
Dia-Dia	0.81	0.29	3.82	2.41	0.006
Sir	0.61	0.21	4.73	3.97	<DL
Mbomé	0.61	0.25	4.33	3.66	<DL
Djungo	0.45	0.28	4.01	4.52	<DL

Root	Al	Si uncorr.	Si corr.	Si clay[a]	Si plant[b]
Dia-Dia	0.15	0.53	0.38	29	71
Sir	0.09	0.31	0.22	–	–
Mbomé	0.07	0.27	0.21	–	–
Djungo	0.05	0.37	0.32	14	86

Si content in root has been corrected by substracting clay minerals contribution (see text for detailed calculation). *DL* detection limit, *uncorr.* uncorrected, *corr.* corrected

[a] proportion of Si attributed to clay minerals (%)

[b] proportion of Si attributed to the plant (%)

negligible at a soil pH above 7, as measured in these soils, despite the fact that proton extrusion by banana roots may decrease pH in the surrounding environment and mobilize Al from mineral dissolution (Rufyikiri et al. 2004). Here, we consider that root-Al (Table 3) is in fact a signature of clay minerals adhering to root surfaces and that these clay minerals are dominantly phyllosilicates exhibiting a 1:1 Si:Al atomic ratio (Delvaux et al. 1990b). We thus correct the Si content of banana roots accordingly (Table 3).

Figure 2 illustrates the bulk Si contents in the various plant parts collected at the four stations. Si content in roots ranges between 0.2 and 0.4% after Si:Al correction. Si content in banana shoots ranges between 0.1 and 0.9%. The largest Si content was recorded in the external green sheaths of the pseudostem (PSe). In banana leaves, the concentration of Si follows a gradient from the petiole (P) to the external lamina (EL) from 0.1 to 0.7%Si. The Si concentration ranges from 0.3 to 0.5% in the peduncle (Pe), and from 0.1 to 0.2% in the fruit.

Si-isotopic compositions in banana plants

Table 4 and Fig. 3 provide the isotopic compositions in the plant parts from the two contrasted stations Dia-Dia and Djungo. The Si-isotopic compositions measured in banana roots (uncorrected values, Table 4) have been corrected for clay contribution, assuming (1) a clay isotopic composition δ^{30}Si of −1.19 and −2.37‰ as measured in Dia-Dia and Djungo clay samples, respectively (Table 2), and (2) a proportion of Si attributed to clay minerals and to the plant calculated on the basis of Si content (Table 3). The corrected root Si-isotopic signatures are slightly heavier than those determined in the internal pseudostem, as measured in hydroponics (Opfergelt et al. 2006a), which validates our correction (Fig. 3).

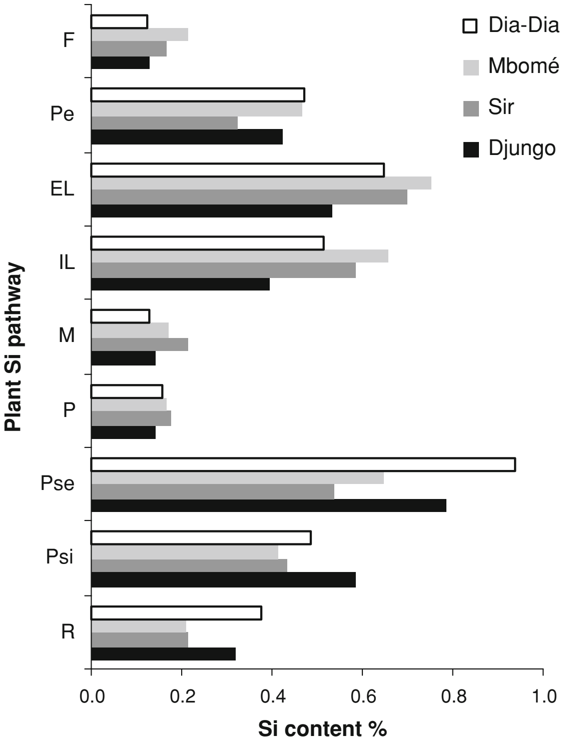

Fig. 2 Si content (% dry weight) in banana plant parts collected in the four stations Dia-Dia, Sir, Mbomé, Djungo. *R* roots, *PSi*, *PSe* internal and external pseudostem, *P* petiole, *M* midrib, *IL*, *EL* internal and external lamina, *Pe* peduncle; *F* fruit

Silicon isotopic compositions in various plant parts (δ^{30}Si values at Dia-Dia and Djungo) range between −0.18 and +1.09‰ showing a clear trend from lighter to heavier Si-isotopic composition from pseudostem to fruit (Fig. 3). This trend is similar in both stations, at Dia-Dia and Djungo.

The bulk plant isotopic composition is a weighted average as for rice in Ding et al. (2005) (Table 5). Si proportion of each plant part is calculated using the Si content measured in this study and the biomasses measured by Martin-Prével and Montagut (1966) in

Table 4 Si-isotopic compositions (‰) in banana plant parts

Plant part	δ^{29}Si	$2\sigma_{SEM}$	δ^{30}Si[a]
Dia-Dia			
R uncorr.	−0.24	0.07	−0.46
R corr.	−0.08	–	−0.16
PSi	−0.09	0.07	−0.18
PSe	−0.11[b]	0.18[c]	−0.22
P	+0.27[b]	0.03[c]	+0.53
M	+0.15	0.06	+0.30
IL	−0.01[b]	0.12[c]	−0.02
EL	+0.51	0.07	+0.98
Pe	+0.36	0.07	+0.70
F	+0.56	0.06	+1.09
Djungo			
R uncorr.	+0.01	0.08	+0.02
R corr.	+0.22	–	+0.42
PSi	+0.05	0.08	+0.10
PSe	+0.27	0.08	+0.52
P	+0.37	0.08	+0.70
M	+0.21	0.08	+0.41
IL	+0.17	0.09	+0.32
EL	+0.47	0.08	+0.91
Pe	+0.53	0.06	+1.02
F	+0.56	0.08	+1.08

R roots (before and after the correction for clay minerals, see text for details), *PSi*, *PSe* internal and external pseudostem, *P* petiole, *M* midrib, *IL*, *EL* internal and external lamina, *Pe* peduncle, *F* fruit, *uncorr.* uncorrected, *corr.* corrected

[a] calculated from δ^{29}Si using factor 1.93

[b] mean between two measurements

[c] standard deviation ($2\sigma_{SD}$)

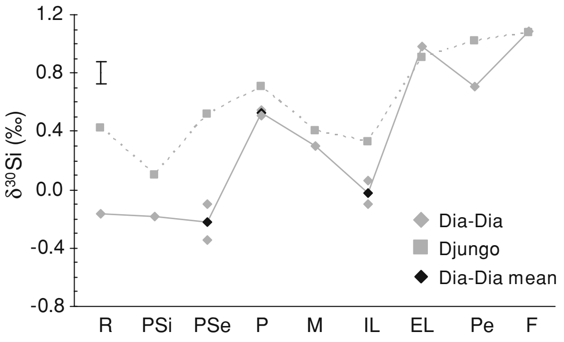

Fig. 3 Si-isotopic compositions of various plant parts at Dia-Dia and Djungo. Bracket refers to the standard error (± $2\sigma_{SEM}$). *R* roots, *PSi*, *PSe* internal and external pseudostem, *P* petiole, *M* midrib, *IL*, *EL* internal and external lamina, *Pe* peduncle, *F* fruit

each respective plant part of banana (roots were excluded from this calculation as no biomass data were acquired). The computed bulk plant isotopic composition is clearly heavier at Djungo (δ^{30}Si = +0.54 ± 0.15‰) than at Dia-Dia (+0.02 ± 0.15‰) (Table 5).

Discussion

Si content in banana

Si contents in mature banana plants are similar to the ones measured in young banana plantlets grown in hydroponics (0.05 and 1.3%Si), in which they varied depending on the Si concentration in the nutrient solution ranging between 0.08 and 1.66 mMSi (Henriet et al. 2006). This concentration falls within the range of Si concentrations in soil solution, varying between 0.01 and 1.99 mMSi (Karathanasis 2002), and most commonly between 0.1 and 0.6 mMSi (Faure 1991). The highest Si content recorded in the pseudostem confirms the results of Jauhari et al. (1974). The difference in Si contents between PSi and PSe can be related to the ageing of leaf tissues (Motomura et al. 2004), leading to a larger Si accumulation in older sheaths. The gradient of Si concentration in leaves from petiole to external lamina is similar to the one observed in juvenile banana plantlets from the same cultivar (Henriet et al. 2006) as well as in mature plants representing 61 species and varieties of *Musa* spp. from the World *Musa* Collection of the Centre Africain de Recherches sur Bananiers et Plantains (CARBAP), Nyombé, Cameroon (Henriet 2008). This gradient is governed by the transport and accumulation of Si in major plant transpiration termini (Raven 1983). The rather low content of Si in banana fruit (0.02%) confirms the previous data reported by Powell et al. (2005).

Intra-plant Si-isotopic fractionation

Mature banana plants present heavier Si-isotopic compositions in the upper shoots than in the pseudostem, corroborating the previously reported trend for the same variety in hydroponics (Opfergelt et al. 2006a). This experimental convergence validates our plant-source fractionation factor determined experimentally in hydroponics. It also highlights the fact

Table 5 Detailed calculation of the bulk plant Si-isotopic composition (weighted average)

Plant Part	Mass fraction[a] % total mass	Si content % dw	Si[b] % mass fraction	Si[c] % total	δ^{30}Si[d] ‰
Dia-Dia					
PSi	7.4	0.48	3.6	0.06	−0.18
PSe	39.4	0.94	36.9	0.64	−0.22
P, M	8.4	0.14	1.2	0.02	+0.41
IL, EL	20.2	0.58	11.7	0.20	+0.48
Pe	2.6	0.47	1.2	0.02	+0.70
F	22.0	0.12	2.7	0.05	+1.09
				Bulk plant	+0.02[e]
Djungo					
PSi	7.4	0.58	4.3	0.09	+0.10
PSe	39.4	0.79	30.9	0.62	+0.52
P, M	8.4	0.14	1.2	0.02	+0.56
IL, EL	20.2	0.46	9.4	0.19	+0.62
Pe	2.6	0.43	1.1	0.02	+1.02
F	22.0	0.13	2.8	0.06	+1.08
				Bulk plant	+0.54[e]

PSi, *PSe* internal and external pseudostem, *P*, *M* petiole and midrib, *IL*, *EL* internal and external lamina, *Pe* peduncle, *F* fruit

[a] calculated from Martin-Prével and Montagut (1966)

[b] Si (% mass fraction) = Mass fraction × Si content

[c] Si (% total) = Si (% mass fraction)/$\sum$ Si (%mass fraction)

[d] calculated from δ^{29}Si measured using factor 1.93

[e] weighted average = $\sum$ (Si (% total) × δ^{30}Si)

that juvenile banana plantlets in hydroponics and mature banana plants in field conditions behave according to similar dynamics of Si-isotopic mass fractionation. Moreover, the observed intra-plant gradient proves to be similar in mature banana plants grown on two contrasted soils (Dia-Dia and Djungo), as illustrated in Fig. 3. The first Si-isotopic signatures of banana peduncle and fruit are provided in the present study. These two ultimate Si pools were isotopically heavier than the other parts of the shoots, which is in very good agreement with the general intra-plant trend.

Si-isotopic data in plants are scarce. Here, we compare our Si-isotopic data on banana (*Musa acuminata* Colla, cv Grande Naine; Opfergelt et al. 2006b; this study) with published data obtained for three other plant species: rice (*Oryza* sp.; Ding et al. 2005), bamboo (*Bambusa* sp.; Ding et al. 2008; Douthitt 1982) and horsetail (*Equisetum* sp.; Douthitt 1982) (Fig. 4).

The available δ^{30}Si values of phytoliths in various plant species range between −2.2 and +6.1‰ (Fig. 4). There is a general trend revealing lighter to heavier isotopic composition from stem to leaf, indicating a homogeneous intra-plant Si-isotopic fractionation process within three plant species: banana (the present study), rice (Ding et al. 2005) and bamboo (Ding et al. 2008). This suggests that the Si-isotopic composition of phytoliths depends on their precipitation locus. However, the Si-isotopic range in banana is narrower than the one observed in rice and bamboo (Fig. 4) and there is a difference between Dia-Dia and Djungo (Fig. 3). As discussed below, this might be attributed to (1) a difference in Si accumulation among plant species, (2) a different physiological stage, (3) a difference between Si sources from soils.

1. Rice and bamboo accumulate much more Si on a dry weight basis (up to 5.7% in rice: Ding et al.

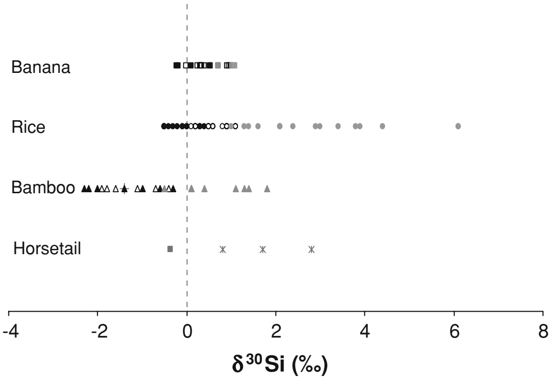

Fig. 4 Si-isotopic compositions in various plant species: (1) banana (*Musa acuminata* Colla, cv Grande Naine; Opfergelt et al. 2006b; this study); (2) rice (*Oryza* sp.; Ding et al. 2005); (3) bamboo (*Bambusa* sp.; triangle, Ding et al. 2008; cross, Douthitt 1982); (4) horsetail (*Equisetum* sp.; star, Douthitt 1982; square, unpublished data, S. Opfergelt). Detailed isotopic compositions of plant parts are indicated by *black*, *open and grey dots*, respectively, when available: banana (pseudostem, leaf, peduncle-fruit, respectively), rice (stem-leaf, husk, grains, respectively), bamboo (stem, branch, leaf, respectively)

2005; up to 4.7% in bamboo: Ding et al. 2008) than banana plants analysed in this study (up to 0.9%). Passive and active Si uptake coexist in the banana plant (Henriet et al. 2006). Proteinaceous Si transporters were identified in rice roots (Ma et al. 2006, 2007), and their possible impact on δ^{30}Si in rice were discussed in hydroponic culture (Sun et al. 2008). The density of Si transporters should differ between plant species and may thus impact plant Si accumulation (Ma and Yamaji 2006). These transporters might be responsible for Si-isotopic fractionation between plant parts in banana (Opfergelt et al. 2006a). We therefore suggest that the extent of the isotopic fractionation factor might differ between vegetal species in relation to the density of Si transporters in plants.

2. Here, banana plants were collected at flowering stage whereas rice plants were sampled at harvesting stage (Ding et al. 2005). A higher Si accumulation at this stage would probably have induced a larger isotopic fractionation in rice.
3. Si source from soil solution would definitely impact the bulk plant isotopic compositions. No information has yet been published about the Si-isotopic composition of the source for rice and bamboo considered in Fig. 4. In the present study, the Si source could have impacted the isotopic fractionation of Si in banana plants sampled at Dia-Dia and Djungo, since the plant physiological stage and Si content do not differ between the sites. We examine this hypothesis hereafter.

Plant δ^{30}Si might reflect the weathering degree of soils

Confirming previous studies (Delvaux 1988; Delvaux et al. 1989), our bulk analytical data show that Dia-Dia and Djungo stations clearly correspond to, respectively, weakly developed soils rich in volcanic glass, and weathered clayey soils rich in secondary phyllosilicates, Fe and Al oxides. These soils display decreasing Si-isotopic signatures with weathering (Table 2). By contrast, banana plants are isotopically heavier on the most weathered soil considered here ($\delta^{30}\text{Si} = +0.54‰$ at Djungo against $+0.02‰$ at Dia-Dia). The heavier Si-isotopic signature in banana plants cropped at Djungo might result from an isotopically heavier Si source in the soil solution, which might in turn be due to a combination of different processes.

To assess the Si-isotopic signature of the dissolved Si source for the plant, we could apply the plant-source fractionation factor measured experimentally ($^{30}\varepsilon = -0.77‰$; Opfergelt et al. 2006a) to the bulk plant isotopic compositions reported in the present study:

$$\delta^{30}\text{Si}_{\text{source}} = \delta^{30}\text{Si}_{\text{bulk plant}} - {}^{30}\varepsilon.$$

This equation would provide a computed δ^{30}Si value of $+0.79 \pm 0.15‰$ for the Si source at Dia-Dia, and of $+1.32 \pm 0.15‰$ at Djungo. This would indicate that the Si source available for plants at Djungo is relatively strongly depleted in light Si isotopes.

Both the Dia-Dia and Djungo cropping areas are supplied during the dry season (from December to February) by a single source of irrigation water ($\delta^{30}\text{Si} = +1.35‰$; Table 2). Consequently, an isotopically heavier soil solution at Djungo could not be accounted for by any difference in the isotopic composition of the waters supplied at Dia-Dia and Djungo. Moreover, plants were sampled in November at the end of the rainy season, and thus mainly grown on a soil drained by rain water rather than irrigation water. So, the observed contrast in the plant Si-isotopic compositions is likely to reflect some soil-related mineralogical control.

In a Hawaiian soil sequence, soil solutions Si-isotopic compositions were shown to be determined by the combined effects of rock dissolution, clay neoformation and Si biocycling (Ziegler et al. 2005a). Iceland river waters in poorly vegetated area were also shown to be controlled by clay neoformation (Georg et al. 2007). Relatively lighter isotopic signatures were measured in waters oversaturated in cations from basalt weathering. On the other hand, river waters undersaturated in these cations were isotopically heavier as a result of clay neoformation. In Cameroon weathered soils, two abiotic processes would deplete the soil solution in lighter Si isotopes: (1) synthesis of clay minerals, forming isotopically lighter clay minerals in the weathered soil compared with the weakly developed soil (Ziegler et al. 2005b; Table 2), and (2) Si adsorption onto iron oxides (Delstanche et al. in press), which are far more abundant in clayey weathered soils (Table 1). However, the time scale of the processes needs to be considered to evaluate their potential impact on the dissolved Si source for the plant. Clay formation spanned a very long time scale ranging from less than a year to a geological time scale compared with Si adsorption or biological uptake ranging from a day to a season.

In the Hawaiian basaltic sequence, soil solutions Si-isotopic compositions in deep horizons were shown to be lighter with the increasing weathering degree of the soil, following the soil Si-isotopic composition (Ziegler et al. 2005a). But in surface horizons, biological uptake and atmospheric dust input modified the soil solution isotopic signature. In Cameroon topsoils, successive rainy seasons would have drained soil solutions impacted by clay neoformation. Seasonal dissolved Si source available for plants would mainly be influenced by short time scale processes: Si adsorption onto Fe-oxides and biological uptake. These two processes may produce additional effects to control the Si-isotopic composition of the soil solution and thereby the plant Si-isotopic signature. Secondary mineral dissolution would account for a smaller contribution in these fertilized surface horizons under banana culture as relatively high pH ($\mathrm{pH}_{\mathrm{water}}$ measured with solid:liquid ratio of 1 g:5 ml = 7.14 at Dia-Dia and 7.55 at Djungo) favours mineral stability.

The initial dissolved Si source available for the plant in Dia-Dia would essentially be controlled by weatherable minerals massively present in the parent ash and pumice particles ($\delta^{30}\mathrm{Si} = -0.38‰$; Table 2), since the reserve of easily weatherable lithogenic silicates directly controls the Si soil-to-plant transfer (Henriet et al. 2008). This solution would be enriched in heavy Si isotopes by preferential adsorption of light Si isotopes onto Fe-oxides (fractionation factor $^{30}\varepsilon = -1.3 \pm 0.5‰$; Delstanche et al. in press). This adsorption process would affect weathered soils in a higher proportion, as these are enriched in Fe-oxides (60% of free iron oxides in Djungo against 22% in Dia-Dia; Table 1). This would explain a heavier bulk plant Si-isotopic signature in Djungo compared with Dia-Dia.

In addition to this process, biological recycling should have produced an additional control on the dissolved Si source. These soils have been devoted to banana culture since the 50s, and banana plants return to the soil at harvesting time. If at least part of the phytoliths in the soil dissolved, the Si source for the plant would be progressively impacted by biogenic Si. This biogenic Si source will be relatively isotopically heavier in Djungo than in Dia-Dia and will thus contribute to build a heavier dissolved Si source for the plant in the more weathered soil. In bamboo, more positive $\delta^{30}\mathrm{Si}$ values were measured in plants grown in soils rich in organic matter compared with soils that are poor in organic matter (Ding et al. 2008). This would indicate some sort of relation with biological recycling. As no information about the weathering degree of the soil was available in that study, no relation can be established with the plant Si-isotopic composition.

The heavier bulk plant Si-isotopic composition at Djungo might thus be due to an isotopically heavier soil solution resulting mainly from Si adsorption onto Fe oxides, combined with a biological Si recycling through vegetation. As Fe oxides content and type are strongly related with weathering, we thus believe that plant Si-isotopic signature might reflect the weathering degree of soils.

Implications

Our data confirm that the banana plant fractionates Si isotopes and concentrates heavier isotopes in the upper part of the plant. Banana phytoliths return to the soil through plant litter decay. Depending on the extent of their preservation and/or dissolution, this will likely impact the continental isotopic Si budget of soils and rivers differently. If phytoliths are dissolved within the soil, plants will have a minor impact on the isotopic budget at the continental scale, i.e. in soils and rivers. If part of phytoliths enriched in light isotopes are preserved and accumulated in soil horizons, surface bulk soil isotopic signatures will be progressively modified and heavier soil solutions will be exported from the soil-plant system.

By contrast with banana, many other cultures involve plant biomass removal at harvesting time (e.g. rice, wheat, corn, …) inducing Si export from the soil-plant system. In those cases, the bulk soil would be progressively depleted in light Si isotopes, leaving soil solutions and rivers with heavier Si-isotopic compositions.

Consequently, biological Si recycling through vegetation could impact the Si-isotopic signature of water exported if at least part of the phytoliths are preserved. Quantification of such impact remains to be established by further studies on phytoliths dissolution rates in soils along with silicon fluxes analyses and isotopic compositions in soil solutions.

Conclusion

Mature banana plants readily fractionate Si stable isotopes, as do young banana plantlets grown in hydroponics (Opfergelt et al. 2006a). The intra-plant trend in banana is similar to the one observed in rice and bamboo.

This study highlights that the Si-isotopic plant signature differs between soils depending on the weathering degree. The relatively light and heavy plant isotopic signatures, as measured, respectively, in the weakly developed and the weathered soil, might result from increasing Si adsorption onto Fe oxides, combined with biological Si uptake by vegetation and recycling in surface horizons. Since iron oxides content increases with weathering, we conclude that plant Si-isotopic signature might reflect the soil weathering degree.

In addition to mineral weathering and clay formation, the preferential uptake of light Si isotopes and the accumulation of phytoliths by terrestrial plants may thus have an impact on the Si-isotopic budget at the continental scale. The magnitude of that impact would depend on the fate of phytoliths. Indeed, rivers Si-isotopic compositions would be poorly impacted by plant recycling if phytoliths are dissolved in soils, and would be enriched in heavy isotopes if phytoliths accumulate in soils.

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