Biogeochemistry (2008) 90:209–223
DOI 10.1007/s10533-008-9245-0

The reserve of weatherable primary silicates impacts the accumulation of biogenic silicon in volcanic ash soils

C. Henriet · N. De Jaeger · M. Dorel ·
S. Opfergelt · B. Delvaux

Received: 29 February 2008 / Accepted: 3 September 2008 / Published online: 26 September 2008

Abstract Banana plantlets (*Musa acuminata* cv Grande Naine) cultivated in hydroponics take up silicon proportionally to the concentration of Si in the nutrient solution (0–1.66 mM Si). Here we study the Si status of banana plantlets grown under controlled greenhouse conditions on five soils developed from andesitic volcanic ash, but differing in weathering stage. The mineralogical composition of soils was inferred from X-ray diffraction, elemental analysis and selective chemical/mineralogical extractions. With increasing weathering, the content of weatherable primary minerals decreased. Conversely, clay content increased and stable secondary minerals were increasingly dominant: gibbsite, Fe oxides, allophane, halloysite and kaolinite. The contents of biogenic Si in plant and soil were governed by the reserve of weatherable primary minerals. The largest concentrations of biogenic Si in plant (6.9–7 g kg^{-1}) and soil (50–58 g kg^{-1}) occurred in the least weathered soils, where total Si content was above 225 g kg^{-1}. The lowest contents of biogenic Si in plant (2.8–4.3 g kg^{-1}) and soil (8–31 g kg^{-1}) occurred in the most weathered desilicated soils enriched with secondary oxides and clay minerals. Our data imply that soil weathering stage directly impacted the soil-to-plant transfer of silicon, and thereby the stock of biogenic Si in a soil–plant system involving a Si-accumulating plant. They further imply that soil type can influence the silicon soil–plant cycle and its hydrological output.

Keywords Silicon · *Musa* · Biogenic Si · Weatherable primary silicates · Volcanic ash soils

Introduction

The global cycle of silicon receives increasing attention because Si has a crucial role in major biogeochemical processes such as the regulation of atmospheric CO_2, nutrition of aquatic biota, and proton buffering through weathering (Sommer et al. 2006). It is being increasingly appreciated that terrestrial plants can exert a strong control on Si fluxes in the biogeosphere (Derry et al. 2005). Numerous plant species take up considerable quantities of H_4SiO_4 from soil solution (Raven 1983), which is carried from roots to transpiration sites through mass flow (Raven 2001) and active transport (Ma et al. 2006, 2007) and precipitates as biogenic

C. Henriet · N. De Jaeger · S. Opfergelt ·
B. Delvaux (✉)
Unité des Sciences du Sol, Université Catholique de
Louvain, Place Croix du Sud 2/10,
1348 Louvain-la-Neuve, Belgium
e-mail: bruno.delvaux@uclouvain.be

M. Dorel
Département des productions fruitières et horticoles,
Centre de coopération internationale en recherche
agronomique pour le développement (CIRAD), Station de
Neufchâteau, Capesterre-Belle-Eau, Guadeloupe

opal ($SiO_2 \cdot nH_2O$) called phytolith (Smithson 1956). Silicon is recycled into the soil from falling litter and decomposition of plant debris. A biogenic Si (BSi) pool is thus built up in both plant and soil compartments of terrestrial ecosystems (Alexandre et al. 1997; Markewitz and Richter 1998; Meunier et al. 1999). The soil BSi pool can be substantial, particularly in the humid tropics (10–40 g kg^{-1}), and can be rapidly recycled (Alexandre et al. 1997; Cary et al. 2005). The soil–plant Si cycle is significant in comparison with weathering input and hydrologic output (Lucas et al. 1993; Alexandre et al. 1997; Markewitz and Richter 1998; Meunier et al. 1999), as most of the Si released to water streams can pass through the BSi pool (Derry et al. 2005). The building-up of that pool would primarily depend on the availability of H_4SiO_4 in the soil solution, which is controlled by silicate dissolution and clay formation in soil (Garrels 1967; Kittrick 1969), which both reflect soil constitution and weathering stage. The relationship between the soil mineral composition and Si soil-to-plant transfer is, however, poorly investigated though plant-BSi has been reported to vary depending on soil type (Fox et al. 1967; Berthelsen et al. 1999; Matichenkov et al. 2000; Schwandes et al. 2001). In humid tropical regions, weathering sequences of soils developed on volcanic ash are remarkably suited to study the impact of soil weathering stage on soil constitution and properties (Parfitt et al. 1983; Delvaux et al. 1989; Chorover et al. 1999; Chadwick et al. 2003), and on plant nutrient status (Delvaux et al. 1989; Chadwick et al. 1999). We have recently shown from a field study that soil weathering stage governs the leaf Si status in mature banana plants cultivated on soils derived from similar parent ash (Henriet et al. 2008). However, plant transpiration may have influenced the Si soil-to-plant transfer since climatic conditions were not homogeneous over the studied weathering sequence.

The objective of this study is twofold. Firstly, we assess the soil-to-plant transfer of Si by young banana plantlets (*Musa acuminata* cv Grande Naine) from soils developed on andesitic ash under controlled homogeneous greenhouse conditions. Secondly, we measure the BSi pool in soils. We further assess the link between the accumulation of BSi in plants and soil with the reserve of weatherable primary silicate minerals. We use banana plants to measure the availability of silicon since they take up Si proportionally to its concentration in the nutrient solution (0–1.66 mM Si: Henriet et al. 2006).

Materials and methods

Environmental and soil conditions

The soils were sampled in cropping areas used for a long time for intensive banana cultivation (Dorel et al. 2000), located on the Western (Ws) and Eastern (Es) slopes of the active volcano La Soufrière (Basse-Terre, Guadeloupe, 16°N, 61°W). The soils developed from andesitic ash deposits of Pliocene to Holocene age (4,000 year BP), dominated by plagioclase, pyroxene and ferromagnesian volcanic glasses (Dagain et al. 1981; Ndayiragije 1996; Ndayiragije and Delvaux 2003). The area is influenced by a strong rain shadow with mean annual rainfall (MAR) decreasing from ~3,200 mm at 450 m asl to ~850 mm at sea level on Ws slopes, and from ~5,000 mm at 450 m asl to ~2,500 mm at sea level on Es slopes (Fig. 1) (Chaperon et al. 1985). The soils are distributed according to climotoposequences, and they strongly differ in weathering stage (Fig. 1) (Colmet-Daage and Lagache 1965; Ndayiragije 1996; Ndayiragije and Delvaux 2003, 2004). Similar soil weathering sequences have been described in other environments (e.g., Chadwick et al. 2003).

Soil materials

Recent data from a topsoil-foliar survey highlighted the positive relationship between the Si leaf concentration of mature banana plants and the soil reserve of weatherable primary minerals (Henriet et al. 2008). From that study and from the detailed 1:20,000 soil map of Guadeloupe (Colmet-Daage 1969), we selected five soil types corresponding to well-known weathering sequences Andosol-Cambisol (Ws-An, Ws-Ca) and Andosol-Nitisol-Ferralsol (Es-An1, Es-Ni, Es-Fe) from Ws and Es sites, respectively (Colmet-Daage and Lagache 1965; Ndayiragije 1996; Ndayiragije and Delvaux 2003, 2004). The Ws and Es soil transects are sketched out in relation to MAR and elevation in Fig. 1. Our previous field study involved 10 cultivated banana plots per soil type and 10 banana plants per plot (Henriet et al. 2008). All cultivated plots had a past and long banana cropping history.

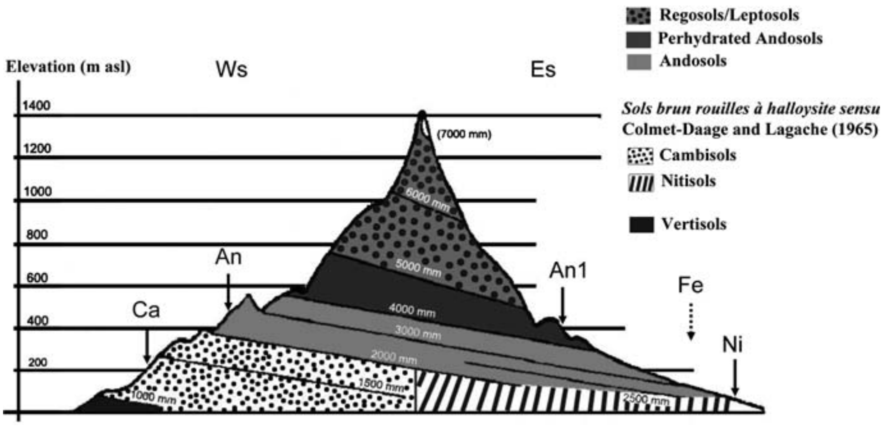


Fig. 1 Sketch transects of Western (Ws) and Eastern (Es) rainfall pattern in relation to elevation (m asl) and major soil type in the island of Basse-Terre (Guadeloupe): Andosol (An), Cambisol (Ca), Nitisol (Ni), Ferralsol (Fe). MAR in mm (adapted from Chaperon et al. 1985; Dorel 2001). Arrows indicate the localization of experimental sites. Ferralsols (Fe) are located at elevations ranging between 150 and 320 m in the Northern part of the island

Based on soil characteristics and Si leaf concentration of mature banana plants (Henriet et al. 2008), we selected a representative banana plot for each soil type. Plot identification, elevation, MAR and soil classification are presented in Table 1. In each plot, soil samples were collected from 00 to 20 cm depth. They were sieved at 5 mm and mixed up to produce a homogeneous bulk sample per plot for further soil–plant pot experiment. For each bulk sample, a separate aliquot was moderately air-dried (12 h) and sieved at 2 mm for further physical, chemical and mineralogical analyses. No replicates were done for these analyses, which were consistent with previous data (Ndayiragije 1996; Henriet et al. 2008).

Soil analyses

pH was measured in 5 g:25 ml soil:water suspensions (Page et al., 1982). Organic carbon content was determined according to the method of Walkley and Black (1934). Cation exchange capacity (CEC) and the content of exchangeable bases were determined according to Jackson (1965). Total elemental contents were measured by inductively coupled plasma/atomic emission spectrometry (ICP–AES) after fusion in Li-metaborate + Li-tetraborate at 1,000°C (Chao and Sanzolone 1992). Within a first set of selective extractions, dark oxalate-extractable (o), dithionite-citrate-bicarbonate (DCB) extractable (d) and pyrophosphate-extractable (p) contents of Si, Al and Fe were determined in the respective extracts by ICP–AES following the methods compiled in Dahlgren (1994). A second set of selective extractions was applied to address the pools of the so-called available Si (Sauer et al. 2006), by using the following extractants: (1) H_2O extraction (adapted from Fox et al. 1967), (2) H_2O extraction adapted here by adding flocculant $SrCl_2$, (3) 0.01 M $CaCl_2$ (adapted

Table 1 Soil type, mean annual rainfall (MAR) and elevation at each reference banana plot for each soil (Ws: Western slopes; Es: Eastern slopes)

Soil	Farm	Plot	Elevation(m asl)	MAR(mm)	Soil type (IUSS Working Group WRB 2006)
Ws-An	Grand Marigot	GM29	470	3,442	Humic Andosol
Ws-Ca	Belle Vue	BV 3	222	1,929	Haplic Cambisol
Es-An1	Moïse	M 1	424	4,767	Molli-silicic Andosol
Es-Ni	Changy	Doyon 1	32	2,550	Haplic Nitisol
Es-Fe	Feneteau	Fen 5	164	3,296	Haplic Ferralsol

from Haysom and Chapman 1975), (4) 0.87 M acetic acid + 0.18 M Na acetate, buffered at pH4 (adapted from Imaizumi and Yoshida 1958), (5) 0.6 M citric acid + 0.4 M Na citrate, buffered at pH4 (adapted from Beckwith and Reeve 1963). The extraction procedure was standardised for all extractants as follows: a 5-g dry soil sample was placed into a 100 ml polyethylene cup with 50 ml extractant (soil:extractant ratio = 1:10) and shaken for 5 h at 20°C. The tubes were then centrifuged at 3,400*g* for 10 min and the supernatant was filtered through Whatman cellulose membrane (20–25 μm pore size). The concentrations of Si, Al, and Fe were determined by ICP–AES.

Soil particle-size analysis was achieved by quantitative recovery of clay (<2 μm), silt (2–50 μm) and sand (>50 μm) fractions after sonication and dispersion with Na^+-saturated resins without any previous H_2O_2 oxidation of organic matter (Rouiller et al. 1972; Bartoli et al. 1991). This procedure is known for its great efficiency to disperse strongly microaggregated soils such as Andosols, Nitisols and Ferralsols (Bartoli et al. 1991; Delvaux et al. 1992; Pochet et al. 2007). Briefly, sand fractions were separated after ultrasonic dispersion of fine earth fraction (<2 mm) and repeated wet sieving. Clay and silt fractions were then collected and submitted to prolonged dispersion with Na^+-resin. Clay was separated from silt by successive cycles of 24 h decanting and pipetting. The mineralogical composition was determined using X-ray diffraction (XRD) (Druker D8 Advance diffractometer). Prior to XRD, the clay and silt fractions were submitted to two successive treatments: H_2O_2 (6%, 40°C), and DCB extraction of residual free iron (Dahlgren 1994).

Soil biogenic Si (BSi) extraction and quantification

The five H_2O_2- and DCB-treated silt fractions (2–50 μm) were further submitted to an additional overnight dispersion (16 h) with Na^+-saturated resins to avoid any clay contamination. Each silt fraction was divided into light (biogenic opal) and heavy components (other minerals), through a series of heavy liquid separations, using an aqueous zinc bromide ($ZnBr_2$) solution with a density of 2.3 g cm^{-3} (adapted from Kelly 1990). Each silt fraction (2–5 g) was mixed with 20 ml of $ZnBr_2$ and centrifuged at 3,400*g* for 10 min. After centrifugation, the supernatant containing the floating phytoliths was carefully and slowly removed with a pipette and collected in a glass vessel through a Teflon (polytetrafluoroethylene—PTFE) filter (2 μm) soaked with methanol. The sample was then remixed with 20 ml of $ZnBr_2$ solution and again submitted to centrifugation at 3,400*g* for 10 min. The operation was repeated until the supernatant was clear. The filter was then abundantly rinsed with 1 M HCl, washed with distilled water, transferred with its opal load to a steel PTFE-lined pressure vessel, with 15 ml of 0.5 M NaOH, and placed overnight in an oven at 150°C. After cooling, the NaOH solution was filtered into a 25 ml polyethylene volumetric flask (Herbauts et al. 1994). Si and Al in solution were determined by ICP–AES and expressed on a soil dry matter basis at 105°C. Considering the selective floating process and the specific NaOH dissolution of opal in sediments (Ragueneau et al. 2005), the Si measured by ICP–AES corresponds to the BSi content in the silt fraction. As no method is currently available to determine BSi in the clay fraction, that Si content represents the minimum value of soil BSi content. Indeed, though this method selectively dissolves BSi, it does not extract it quantitatively (Saccone et al. 2007).

Plant materials

We used young banana plantlets (*Musa acuminata* cv Grande Naine, AAA group, Cavendish, dessert banana) issued from tissue culture, and produced in nutrient medium devoid of silicon. A total of 150 plantlets were weaned in a nursery under controlled conditions also devoid of any Si supply. Seventy homogeneous plantlets with an average height of 9.5 cm were selected: 10 per soil for the pot experiment, and four per soil for biomass correction (see below). Ten plantlets were stored after weaning and dried at 60°C for 1 week for further elemental analysis to assess the Si concentration of initial plant materials.

Experimental conditions

The experimental design involved five soils (Table 1) and 10 replicates per soil, consisting of 50 individual banana plantlets. Each plantlet was planted in a 2 l plastic pot containing a known soil mass depending on soil bulk density (620–1,300 g dry weight). Nitrogen (N), phosphorus (P_2O_5), and potassium (K_2O) were applied at amounts of 0.4, 0.3, and 1 g pot^{-1}, respectively. Nemathorin® (1 g pot^{-1}) was used to prevent nematode attack. The soil was covered by an inert black plastic sheet to avoid weed development and limit direct evaporation. The soil moisture content was adjusted at field capacity: (1) each pot, including soil and plant was weighted to determine the reference pot weight at field capacity; (2) three times a week, each pot was weighted, and distilled water was supplied to reach the reference pot weight; daily plant transpiration was deduced; (3) every 3 weeks, the reference pot weight was corrected by measuring the fresh biomass of one plant per soil. The pot experiment was conducted for 84 days in a greenhouse with a global radiance of 8.25 MJ m^{-2} (day:night ~12 h:12 h), 83.4% mean relative humidity, and 23.8°C mean temperature. Once a week, the numbers of totally and partially unfurled leaves were measured (Carlier et al. 2002), the length (l) and width (w) of the unfurled leaves. The leaf surface area (LA) was computed from the equation LA = 0.7 × l × w (Rufyikiri et al. 2000).

After 84 days, the banana plantlets were harvested separately. Each plant was cut in different parts: roots (R), pseudostem (PS), petiole and midrib of the young leaves (y[P + M]), lamina of the young leaves (yLa) and complete old leaves (petiole, midrib, and lamina) (oLe) (Henriet et al. 2006). The separation between old and young leaves corresponded to a clearcut slope change in the “LA vs. time” curve. The dry weight of all plant parts was measured after drying at 60°C for 1 week. Mineral analysis was done for all plant parts, except roots, and was carried out after calcination at 450°C for 1 day, followed by borate fusion at 1,000°C and dissolution of fusion beads in 10% HNO_3 (Chao and Sanzolone 1992). Elemental concentrations were measured by ICP–AES. The balanced nutrient concentration was calculated for the aerial part (shoot) for each plant as followed:

$$\sum(\text{nutrient concentration} * \text{dry weight})_i / \sum(\text{dry weight})_i,$$

with i referring to each aerial plant part: PS, y[P + M], yLa and oLe. Mineral analysis was carried out on plantlets dried and stored after weaning phase to assess the initial Si concentration.

Results

Plant growth, transpiration and Si concentration

Silicon content (<10^{-3} mg per plantlet) was negligible in the initial plant materials. The respective average values of cumulated LA, shoot dry matter and cumulated transpiration of banana plants were significantly lower in Es-Ni and Ws-An than in the other soils (Table 2).

In all soils, the Si concentration in plant significantly increased from the pseudostem towards the complete old leaves (PS ≤ y[P + M] < yLa < oLe) (Table 3). For each plant part, the Si concentration in plants was significantly larger in Ws-soils than in Es-soils. Within the Es-soils, Es-An1 displayed systematically smaller Si concentration in the various plant parts than Es-Ni and Es-Fe. The same trend was observed for the balanced Si concentration (Table 3), which significantly decreased in the sequence Ws-An = Ws-Ca > Es-Ni > Es-Fe > Es-An1.

Although this experiment has been conducted under controlled homogeneous greenhouse conditions, plant growth parameters differed among the five soils, with lower average values of shoot dry matter and cumulated leaf area in Es-Ni and Ws-An.

Table 2 Averages of growth parameters and cumulated transpiration calculated for each soil at the end of the experiment (n = 10)

Soil	Cumulated leaf area[a] (cm^2)	Shoot dry matter (g)	Cumulated transpiration[b] (g)
Ws-An	690	3.5	1,163
Ws-Ca	973	5.3	1,273
Es-An 1	888	4.7	1,572
Es-Ni	562	2.7	1,008
Es-Fe	808	4.3	1,225
LSD[c]	152	0.7	217

[a] Cumulated leaf area is the sum of area of all leaves produced by the plant during the experiment (84 days)

[b] Cumulated transpiration is the sum of the water amounts lost by plant transpiration and measured daily during the experiment (84 days)

[c] Least significant difference (LSD) is given for each growth parameter and for cumulated transpiration (∝ = 0.05)

Table 3 Si concentration in banana plant parts, balanced Si concentration and quantity of Si exported in banana shoot (aerial parts excluding roots), and quantity of Si exported with respect to the cumulated transpiration (Si:transpiration ratio: mg Si per kg of water transpired) ($n = 10$)

Soil	Si concentration in various organs (g kg^{-1} DM)					Balanced Si conc. in shoot (g kg^{-1} DM)	Quantity of Si in shoot (mg pot^{-1})	Si:transpiration ratio (mg kg^{-1})
	PS[a]	y[M + P]	yLa	oLe	LSD			
Ws-An	2.85	4.13	7.09	13.00	0.79	6.99	24	21
Ws-Ca	3.29	4.47	6.15	11.93	0.89	6.87	36	29
Es-An1	1.66	2.34	2.52	5.01	0.20	2.83	13	9
Es-Ni	1.80	2.43	4.52	7.52	0.42	4.29	12	11
Es-Fe	2.04	2.79	3.38	5.60	0.63	3.40	15	12
LSD[b]	0.31	0.26	0.57	1.06		0.44	4.1	2.5

[a] PS, pseudostem; y[P + M], petiole and midrib of the young leaves; yLa, lamina of the young leaves; oLe, complete old leaves

[b] Least significant difference (LSD) is given for each part of the plant and for each soil ($\propto = 0.05$)

These differences result from physical constraints to root development at the beginning of the experiment leading to delayed plant growth. Lower cumulated leaf area and shoot dry matter thus induced lower cumulated transpiration in Es-Ni and Ws-An, which may have interfered with the Si status of banana plants. We thus expressed the quantity of Si exported in banana shoot relative to cumulated transpiration for further comparison between soils (Table 3). This parameter defines the Si:transpiration ratio, and is expressed in mg Si per kg of water readily transpired by plant.

Physical and chemical properties of soils

The organic carbon content, pH, CEC, and textural analysis of the soil samples are presented in Table 4. The pH ranged between 5.5 and 6.7. Organic carbon content (C_{org}) and CEC were larger in the Andosols Es-An1 and Ws-An (C_{org}: 5.88–9.10%; CEC: 40–55 cmol$_c$ kg^{-1}) than in the other soils (C_{org}: 1.96–2.53%; CEC: 23–29 cmol$_c$ kg^{-1}). The contents of exchangeable Ca and Mg were larger in Ws-Ca and Es-An1 than in other soils. The clay content was much larger in the Es-soils (59–81%) than in Ws-soils (35–41%), and was particularly high (80–81%) in the most weathered Ferralsol (Es-Fe) and Nitisol (Es-Ni).

Total element contents and selective extractions

The total reserve in bases (TRB) is the sum of total Na, K, Ca, and Mg and estimates the content of these elements in weatherable minerals in mineral soils (Herbillon 1986). TRB was invariably smaller in Es-soils (101–32 cmol$_c$ kg^{-1}) than in Ws-soils (246–207 cmol$_c$ kg^{-1}) (Table 5). TRB strongly differed between Ws- and Es-soils because of much larger contents of total Ca, Mg and Na in Ws-soils, in good agreement with the dominance of plagioclase, pyroxene and ferromagnesian glass in the parent ash. In Es-soils, the TRB of the perhydrated Andosol Es-An1 (101 cmol$_c$ kg^{-1}) was largely above that of the most weathered Nitisol Es-Ni and Ferralsol Es-

Table 4 Major soil properties, as measured in the fine earth (<2 mm): pH, organic carbon content (C_{org}), exchangeable cations, cation exchange capacity (CEC), and particle-size distribution

Soil	pH (H_2O)	C_{org} (%)	Exchangeable bases (cmol$_c$ kg^{-1})				CEC (cmol$_c$ kg^{-1})	Particle-size analysis (%)		
			Ca	Mg	Na	K		Sand	Silt	Clay
Ws-An	6.37	5.88	5.0	1.2	0.1	1.2	40	21.9	38.9	41.5
Ws-Ca	6.74	2.41	9.2	4.2	0.1	2.4	23	26.1	38.8	34.9
Es-An1	6.15	9.10	8.8	4.9	0.2	1.5	55	18.5	23.0	59.1
Es-Ni	5.48	1.96	2.3	1.4	0.1	1.6	29	4.4	17.0	80.7
Es-Fe	6.25	2.53	5.2	2.2	0.1	1.9	27	5.9	14.5	81.6

Fe (32–33 cmol$_c$ kg^{-1}) because of larger total Mg content (64.7 cmol$_c$ kg^{-1} in Es-An1 versus 13.0–15.3 cmol$_c$ kg^{-1}). The total Si content in Ws-soils (226–266 g kg^{-1}) was larger than in Es-soils (136–184 g kg^{-1}) (Table 6). Inversely, the total Al and Fe contents were smaller in Ws-soils (~90 and ~65 g kg^{-1}, respectively) than in Es-soils (110–139 g kg^{-1} and 98–114 g kg^{-1}, respectively). Oxalate-extractable Si and Al contents were substantial in the two Andosols Ws-An and Es-An1 (Si: ~10 g kg^{-1}; Al: ~30 g kg^{-1}), and negligible in the other soils (<5 g kg^{-1}).

Table 5 Total elemental contents (t) and total reserve in bases (TRB)

Soil	Ca_t (cmol$_c$kg^{-1})	K_t	Mg_t	Na_t	TRB
Ws-An	73.8	14.1	89.6	29.4	207
Ws-Ca	107.9	15.4	80.5	42.2	246
Es-An1	21.1	11.7	64.7	3.7	101
Es-Ni	5.9	8.1	15.3	2.3	32
Es-Fe	8.7	10.2	13.0	1.2	33

Table 6 Total elemental contents (t) and Si, Al and Fe contents in oxalate (o), dithionite (d) and pyrophosphate (p) extracts

Soil	Al_t (g kg^{-1})	Fe_t	Si_t	Al_o	Si_o	Fe_d	Al_p	Fe_d/Fe_t
Ws-An	94.6	60.8	225.6	32.1	13.2	24.6	6.9	0.41
Ws-Ca	87.3	64.8	265.9	2.6	0.9	21.6	1.9	0.33
Es-An1	110.4	104.8	135.8	29.3	11.5	53.6	15.5	0.51
Es-Ni	136.2	113.7	180.0	4.0	0.4	70.0	3.3	0.62
Es-Fe	139.4	98.3	184.3	3.1	0.3	75.5	2.9	0.77

Soil mineralogy

The relative importance of free iron oxide was assessed through the Fe_d/Fe_t ratio, which was below 0.5 in the Ws-soils and above 0.5 in Es-soils (Table 6), denoting a more advanced tage of weathering in the Es-soils, particularly in Es-Ni and Es-Fe. The XRD analyses led to the identification of primary and secondary crystalline minerals. The presence of plagioclase and pyroxenes was confirmed in the coarse fractions of Ws-An, Ws-Ca, and Es-An1 (not shown). The silt fraction (2–50 μm) in all soils was largely dominated by quartz and crystobalite; tridymite was observed in traces (not shown). Gibbsite was detected in the silt fraction of Es-soils. In the clay fraction (Table 7), crystobalite and halloysite were detected in Ws-soils. In the Cambisol Ws-Ca, halloysite was mixed-layered with smectite. The clay fraction of the perhydrated Andosol Es-An1 was dominated by kaolinite and particularly gibbsite (also present in the sand and silt fractions). Hydroxy-Al-interlayered 2:1 clay minerals (HIS, HIV) were also detected in that soil. Halloysite and kaolinite were the dominant clay minerals in, respectively, the Nitisol Es-Ni and the Ferralsol Es-Fe. The contents of Si_o, Al_o and Al_p were used to compute the allophane contents according to Parfitt and Wilson (1985). The allophane content was 10% in Ws-An, and 6% in Es-An1. The other soils were devoid of allophane.

Soil BSi content

The soil BSi content (g kg^{-1}) was the largest in Ws-soils (50–58) (Table 8); in Es-soils, it was larger in the perhydrated Andosol Es-An1 (31) than in the most weathered Es-Ni (18) and Es-Fe (8). The NaOH-extractable Al content was relatively small

Table 7 Minerals detected by X-ray diffraction in the clay fraction (<2 μm) of soils

Soil	Quartz	Crystobalite	Gibbsite	Kaolinite	Halloysite	HIV/HIS[a]	Halloysite/smectite
Ws-An		+++		+	+		
Ws-Ca		+++		+	+		+
Es-An1	+		++	+		++	
Es-Ni	+	+		++	++		
Es-Fe	+		+	+++		+	

[a] HIV: Hydroxy-Al-interlayered vermiculite; HIS: Hydroxy-Al-interlayered smectite

Table 8 Soil biogenic Si (BSi) content and Al impurities as extracted by NaOH (0.5 M) in the silt fraction (2–50 µm) after densimetric separation

Soil	NaOH-extractable elements (g kg^{-1})		Al/Si atomic ratio	Quantity of soil BSi (g pot^{-1})
	BSi	Al		
Ws-An	50	1.41	0.030	41
Ws-Ca	58	1.32	0.024	76
Es-An1	31	2.78	0.094	19
Es-Ni	18	0.26	0.015	18
Es-Fe	8	0.10	0.014	8

denoting low Al-contamination of the soil BSi pool except in Es-An1.

Si, Al and Fe extracted from soils

H_2O-, ($H_2O + SrCl_2$)-, $CaCl_2$-, acid Na acetate-, and acid Na citrate-extractable contents of Si, Al and Fe are presented in Table 9. The $CaCl_2$- and ($H_2O + SrCl_2$)-extractable contents of Si were larger in Ws-soils (33–48 mg kg^{-1}) than in Es-soils (9–27 mg kg^{-1}). These contents were similar for each soil. H_2O- and $CaCl_2$-extractable contents of Si, Al, and Fe were similar in the Andosols Ws-An and Es-An1, but largely differed in Ws-Ca, Es-Ni and Es-Fe; the relatively large contents of H_2O-extractable Si in these three soils parallels the relatively large H_2O-extractable contents of Al and Fe, denoting the presence of dispersed secondary constituents in the H_2O-supernatant. The acid Na acetate-extractable Si content was larger in Ws-soils (135–176 mg kg^{-1}) than in Es-soils (64–83 mg kg^{-1}). The acid Na citrate-extractable contents of Si, Al and Fe were the largest in the Andosols Ws-An and Es-An1 than in the other soils.

Discussion

Si gradient in the banana plant

The Si gradient follows the sequence of increasing Si concentration from pseudostem to old leaves PS $\leq$ y[P + M] $<$ yLa $<$ oLe, confirming the gradient observed in hydroponics (Henriet et al. 2006), and thus the major impact of transpiration on the Si deposition in banana plant (Raven 1983).

Soil weathering stage and mineralogical properties

Mineral weathering involves the partial loss of Si, the relative concentration of Al and Fe, the formation of secondary clay minerals and the individualization of free iron oxide (Chadwick et al. 2003). Figure 2 illustrates these well-known facts in the Ws and Es weathering sequence: with increasing weathering stage, TRB decreases from 246 to 32 $cmol_c\ kg^{-1}$, below the upper threshold (40 $cmol_c\ kg^{-1}$) proposed by Herbillon (1986) to delineate the strongly weathered ferrallitic soils. In parallel, the clay content, the Al/Si atomic ratio and the proportion of free iron oxide all increase (Fig. 2). Weathering and desilication thus increase in the sequence Ws-Ca $<$ Ws-An $<$ Es-An1 $<$ Es-Ni $=$ Es-Fe. Figure 2 also illustrates that Ws-soils markedly differ from Es-soils, as the former represent a less advanced weathering stage than the latter in the process of soil development from similar andesitic ash. The dominant soil components

Table 9 Average extractable contents of elements (from 2 replicates of each soil) for the various selective extractants

Soil	Extractable soil elements (mg kg^{-1})														
	Na citrate pH4			Na Acetate pH4			H_2O			$H_2O + SrCl_2$			$CaCl_2$ (0.01 M)		
	Al	Fe	Si	Al	Fe	Si	Al	Fe	Si	Al	Fe	Si	Al	Fe	Si
Ws-An	6,427	1,437	1,310	903	16	176	1.1	0.5	30	nd[a]	nd	33	<0.250	<0.010	33
Ws-Ca	836	1,385	361	58	7	135	263.4	106.3	350	nd	nd	46	<0.250	<0.010	48
Es-An1	10,852	6,782	2,856	593	18	65	1.3	0.9	10	nd	nd	9	<0.250	<0.010	9
Es-Ni	1,511	858	152	307	6	64	32.0	11.9	52	nd	nd	24	10.27	<0.010	27
Es-Fe	1,147	574	147	190	2	83	19.8	9.2	33	nd	nd	16	<0.250	<0.010	18

[a] nd: no data

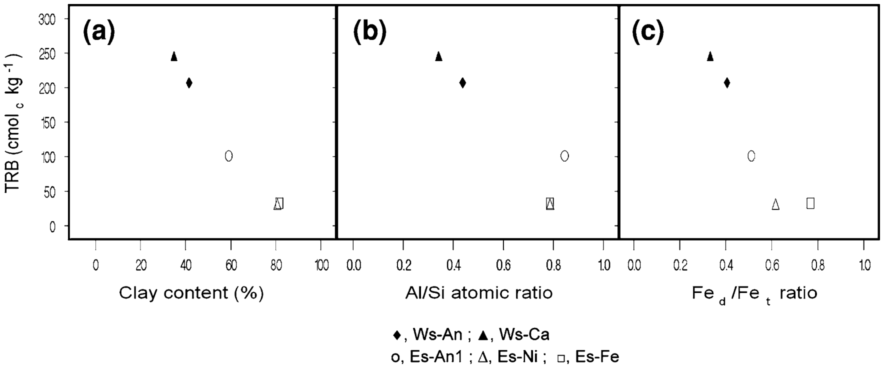


Fig. 2 Relationship between total reserve in bases (TRB) and (**a**) clay content, (**b**) Al/Si atomic ratio, (**c**) Fe_d/Fe_t ratio in soils

in Ws-soils are primarily weatherable minerals (plagioclase, pyroxene, ferromagnesian glass; Dagain et al. 1981), whereas the ones in the more desilicated Es-soils are secondary minerals such as gibbsite and kaolinite in Es-An1, halloysite and Fe oxides in Es-Ni, and kaolinite, gibbsite, and Fe oxides in Es-Fe (Tables 6 and 7). Our data confirm previous studies concerning the soils of Basse-Basse-Terre Terre, Guadeloupe (Colmet-Daage and Lagache 1965; Colmet-Daage and Gautheyrou 1974; Ndayiragije 1996; Ndayiragije and Delvaux 2003, 2004), and corroborate findings from other volcanic areas (Parfitt et al. 1983; Delvaux et al. 1989; Chorover et al. 1999; Chadwick et al. 2003).

Contents of extractable silicon in soils

The extractable Si content decreases in the sequence Na citrate pH4 > Na acetate pH4 > $H_2O \geq CaCl_2 = (H_2O + SrCl_2)$ (Table 9). Only the $CaCl_2$-, $(H_2O + SrCl_2)$- and acid Na acetate-extractable Si contents follow a similar trend in that they clearly differ between Ws- and Es-soils with the largest values in the former. The pH values of the $CaCl_2$, H_2O, and $(H_2O + SrCl_2)$ extracts range between 5.5 and 6. The $CaCl_2$ solution is recognised to extract the aqueous Si fraction (Haysom and Chapman 1975) and to provide a measure of readily available Si (Chapman et al. 1981; Berthelsen et al. 2001). H_2O extraction induces the dispersion of clay minerals in Es-Ni, Es-Fe and Ws-Ca, as suggested by the relatively large values of H_2O-extractable Si, and by the values of the atomic Si/(Al + Fe) ratio ranging between 1 and 1.3, characteristic for clay fractions dominated by 1:1 phyllosilicates. Considering the similar contents of $CaCl_2$- and $(H_2O + SrCl_2)$-extractable Si in soils, we conclude that water-soluble Si is extracted by both extractants, $CaCl_2$ and $SrCl_2$ acting as flocculent. The acid buffered Na acetate extracted 3-5 times more Si than $CaCl_2$ and $(H_2O + SrCl_2)$. This extractant is recognised to mobilise the labile Si from soils (Sauer et al. 2006). As an acid buffer, it partially dissolves weatherable minerals, and extracts substantial amounts of Al, invariably larger than Si in all soils, except in Ws-Ca. The Na citrate-extractable Si contents are the largest, as compared to the Si contents measured in the other extractants (Table 9). They are particularly high in the Andosols, where the acid Na citrate extraction likely promotes mineral dissolution, because of the ability of citrate to complex Al and Fe from amorphous constituents, as suggested by the correlation between oxalate- and Na citrate-extractable contents of Al ($r = 0.91$) and Si ($r = 0.83$) (Tables 6 and 9).

Silicon bioavailability and soil weathering stage

Since the plants were virtually devoid of silicon at the beginning of the experiment, the Si bioavailability in the Ws- and Es-soils can be measured through the determination of the balanced Si concentration in shoot and/or the quantity of Si exported in the banana shoot with respect to the cumulated transpiration (Si:transpiration ratio) (Table 3). Both parameters give a similar trend with larger values in Ws- than in Es-soils. As illustrated in Fig. 3, the Si:transpiration ratio clearly differs between Ws- and Es-soils, and is positively correlated with the soil total Si content ($r = 0.92$), $CaCl_2$- and acid Na acetate-extractable Si contents ($r = 0.90$ and $r = 0.76$, respectively), and with $(H_2O + SrCl_2)$-extractable Si ($r = 0.92$; not illustrated). As already shown in hydroponics (Henriet et al. 2006), our data from pot experiments imply

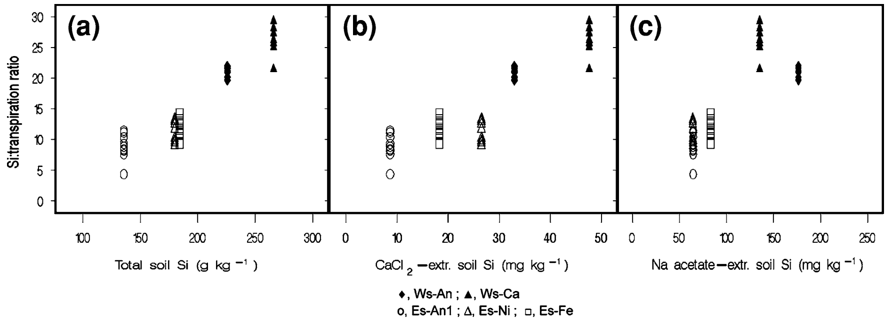


Fig. 3 Relationship between the quantity of Si exported in banana shoot reported to the cumulated transpiration (mg Si per kg of water transpired) and (**a**) total Si content, (**b**) $CaCl_2$-extractable Si content, (**c**) acid Na acetate-extractable Si content in soils

that the concentration of aqueous and acid-soluble Si in soil governs the uptake of silicon by banana plants, and thus impacts the plant shoot content of Si.

Figure 4a supports that the reserve of weatherable minerals (TRB) influences the Si content in the various plant parts, the balanced Si concentration in the shoot, and the Si:transpiration ratio. The largest values of the Si:transpiration ratio occur for the least weathered Ws-soils, whereas the lowest ones correspond to the most weathered desilicated Es-soils. Since the concentration of aqueous Si in soil is controlled by mineral composition (Kittrick 1969; Karathanasis 2002), mineral weathering is a major process in the Si soil-to-plant transfer. Bananas take up exceptional quantities of potassium (Lahav 1995). The excess of cation over anion uptake promotes the excretion of protons by their roots (Rufyikiri et al. 2001), and thereby silicate dissolution (Hinsinger et al. 2001; Rufyikiri et al. 2004). Figure 4b and c support that plagioclase reserve principally governs the Si soil-to-plant transfer in the perhydrated Andosol Es-An1, in which both the occlusion of octahedral Mg in hydroxyl Al-interlayered 2:1 clay minerals and the coating of weathered pyroxene and ferromagnesian particles by iron oxides (Ndayiragije 1996) may protect these Mg-bearing minerals from further weathering (Baert and Van Ranst 1997). Similarly, clay coatings on surfaces of weathered volcanic glass were shown to protect weatherable primary minerals (Certini et al. 2006). The largest values of the Si:transpiration ratio are associated with the largest values of the soil BSi content (Fig. 4d) suggesting that the building-up of the BSi pool in the soil–plant system considered here could depend on the reserve of readily weatherable primary minerals (Fig. 4b).

Soil weathering stage impacts the BSi pool in the soil–plant system

The soil BSi content in the soils used in this experiment (8–58 g kg^{-1}) corresponds to the range

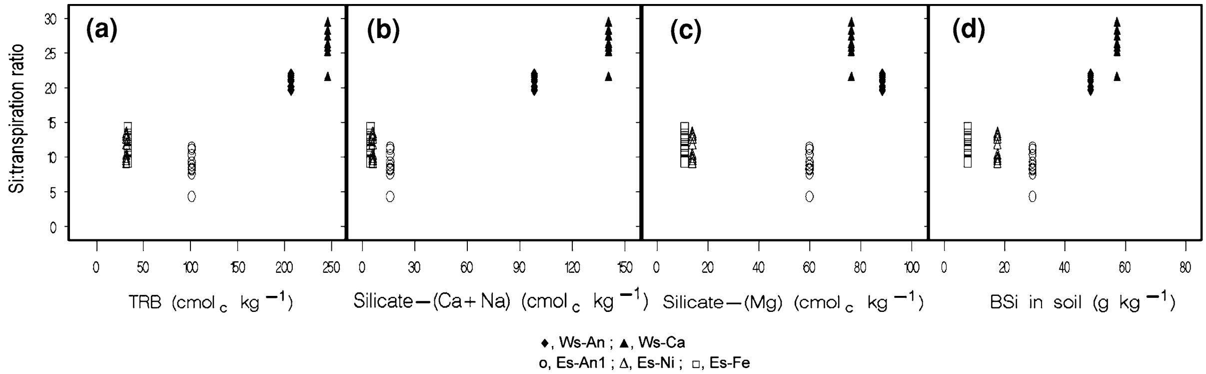


Fig. 4 Relationship between the quantity of Si exported in banana shoot reported to the cumulated transpiration (mg Si per kg of water transpired) and (**a**) TRB, (**b**) silicate-(Ca + Na), (**c**) silicate-(Mg), (**d**) soil biogenic Si (BSi) content. Silicate-(Ca + Na) and silicate-(Mg) contents are the contents of non-exchangeable (Ca + Na) and Mg, respectively: they are computed from the respective subtractions between total contents of (Ca + Na) and Mg, and exchangeable contents of (Ca + Na) and Mg

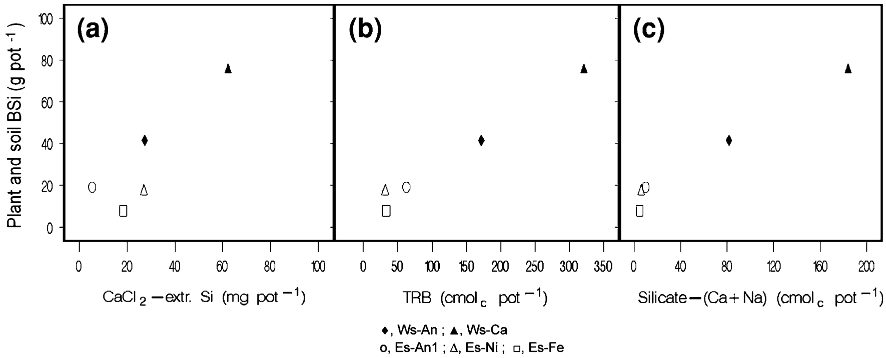
reported so far in tropical environments (9–40 g kg^{-1}) (Alexandre et al. 1997; Cary et al. 2005). These soil BSi contents are 10–20 times larger than in soils under temperate climates (Wilding and Drees 1971). The relatively large soil BSi pool in tropical soils results from warm and wet climatic conditions promoting the rapid recycling of silicon in the soil–plant system (Drees et al. 1989; Conley et al. 2006). The above-ground standing vegetation also plays an important role in the BSi content in soil: the soil BSi production of a rainforest in Congo ranges from 58 to 76 kg ha^{-1} year^{-1} (Alexandre et al. 1997).

The soils considered here were sampled in areas under long-term intensive cultivation of banana (Dorel et al. 2000), which is known to be a Si-accumulator (Henriet et al. 2006). For a 25 tons year^{-1} yield with 2,100 plants ha^{-1}, the total dry matter production of a banana crop is estimated to 14 tons ha^{-1} year^{-1} from which ~10 tons DM of residues are left in the field (Twyford and Walmsley 1973). The mean Si concentration in the mature banana plant can be estimated to 5–10 g kg^{-1} DM (Opfergelt et al. under revision) so that the Si immobilisation of a banana crop would range from 50 to 110 kg ha^{-1} year^{-1}. The BSi contents in litterfall and soil will therefore largely depend on Si concentration of the plant, and thus on soil weathering stage. Indeed, the largest BSi contents occur in the least weathered Ws-soils (50–58 g kg^{-1}) whereas the smallest BSi contents (8–31 g kg^{-1}) occur in the more weathered Es-soils (Table 8). Adding up the quantities of biogenic silicon in both plant (Table 3) and soil (Table 8) per pot allows calculating the BSi quantity in the soil–plant system per pot. Figure 5 shows that the quantity of BSi in the soil–plant system is positively correlated with the available quantity of aqueous Si extracted by $CaCl_2$, the stock of weatherable minerals (TRB), and particularly the stock of plagioclase minerals (Ca + Na reserve). Although the transect Andosol-Nitisol-Ferralsol forms a sequence of increasing weathering and soil development, the soils did not really differ with regard to the build-up of a BSi pool, suggesting that silicate minerals acting as main source for BSi in Ws-soils may be either absent or less active in Es-soils, as coatings can stabilise primary minerals (Ndayiragije 1996; Baert and Van Ranst 1997; Certini et al. 2006). Our data thus imply that the reserve of easily weatherable primary minerals governs the availability of aqueous Si in soil, and thus in turn the soil-to-plant transfer of silicon, and hence, in the long-term, the building-up of the BSi pool in a soil–plant system where the plant component is a silicon-accumulator. Figure 4d indeed shows that the largest soil BSi contents are associated with the largest values of the Si:transpiration ratio, soil BSi clearly differing between Es- and Ws-soils. Yet, soil BSi would poorly contribute to the pool of plant-available Si in Es-An1 (Fig. 4d). This can be due to the higher Al content of biogenic opal (Table 8), which is known to decrease its solubility (Dixit et al. 2001; Rickert et al. 2002), and therefore its availability to plant. Dissolved Al can be structurally incorporated into the biogenic silica, leading to the formation of alumino-silicates coatings (Michalopoulos and Aller 2004), which inhibit the dissolution of BSi. The high Al activity in Es-An1 might be largely driven by the importance of gibbsite and Al-humus components in this soil (Ndayiragije and Delvaux 2003).

Implications

The contribution of plants to the Si continental reservoir can be significant (Alexandre et al. 1997).

Fig. 5 Relationship between the quantity of biogenic silicon (BSi) in plant and soil per pot and the stock per pot of: (**a**) $CaCl_2$-extractable Si, (**b**) total reserve in bases (TRB), (**c**) silicate-(Ca + Na)



The annual BSi production by plants at global scale indeed ranges between 60 and 200 Tmol year^{-1} (Conley 2002) and rivals that produced by diatoms in the oceanic biogeochemical cycle (240 Tmol year^{-1}) (Tréguer et al. 1995). Moreover, plant-BSi is recycled into the soil from falling litter in a separate soil–plant Si cycle that can be significant in comparison with weathering input and hydrologic output (Derry et al. 2005). Consequently, as already stated by Conley (2002), consideration must be given to the influence of the terrestrial BSi pool on variations in the global biogeochemical Si cycle over different times scales. The results presented here and in our previous study (Henriet et al. 2008) show that soil mineralogical composition, and more generally soil weathering stage and soil development, can strongly influence the bioavailability of silicon for plant uptake, and hence the building-up of the terrestrial BSi pool. We thus believe that more consideration should be given to soils as major sink-source actors in the soil–plant Si cycle to further study the mobility of Si at continental scale, better understand Si export to water streams, and thus better assess Si mass balances at watershed scale.

Conclusion

We have studied the soil-to-plant transfer of Si using young banana plants cultivated in controlled greenhouse conditions, on volcanic ash soils differing in mineralogical composition, weathering stage and soil development. The largest concentrations of biogenic Si in plant (6.9–7 g kg^{-1}) and soil (50–58 g kg^{-1}) occur in the least weathered soils, where total soil Si content is above 225 g kg^{-1}. The lowest contents of biogenic Si in plant (2.8–4.3 g kg^{-1}) and soil (8–31 g kg^{-1}) occur in the most weathered desilicated soils enriched with secondary oxides and clay minerals, where total soil Si content is below 185 g kg^{-1}. These experimental data obtained in controlled conditions are strongly consistent with those acquired in the framework of a large scale topsoil-foliar survey carried out in mature banana fields (Henriet et al. 2008). These data indicate that silicon availability is positively influenced by the reserve of easily weatherable primary minerals, and thus more generally by soil weathering stage and soil development. We conclude that soil weathering stage impacts the soil-to-plant transfer of Si, and thereby the stock of biogenic Si in a soil–plant system involving a Si-accumulating plant. Our data further suggest that soil type can influence the silicon soil–plant cycle and its hydrological output. We thus believe that more consideration should be given to soils as key sink-source actors in the Si soil–plant cycle at watershed and continental scales.

Acknowledgments We are grateful to L. Bodarwé, A. Iserentant and C. Givron for their strong analytical and technical support, X. Draye for fruitful discussions (UCL), and T. Drouet de la Thibauderie (ULB, Belgium) for the loan of the PTFE-lined pressure vessels. We thank the reviewers and the Associate Editor for their constructive comments and attractive suggestions. C·H. is supported by the "Fonds pour la formation à la Recherche dans l'Industrie et dans l'Agriculture" (FRIA) of Belgium, and S·O. by the "Fonds National de la Recherche Scientifique" (FNRS) of Belgium. This research was supported by the FNRS research convention N°2.4629.05 and by the "Fonds Spécial de Recherche" (FSR) 2005 of the UCL.

References

Alexandre A, Meunier JD, Colin F, Koud JM (1997) Plant impact on the biogeochemical cycle of silicon and related weathering processes. Geochim Cosmochim Acta 61:677–682. doi:10.1016/S0016-7037(97)00001-X

Baert G, Van Ranst E (1997) Total reserve in bases as an alternative for weatherable mineral content in soil classification: a micromorphological investigation. In: Shoba S, Gerasimova M, Miedema R (eds) Soil micromorphology: studies on soil diversity, diagnostics, dynamics. Proceedings of 10th internal working meeting on soil micromorphology, Moscow-Wageningen

Bartoli F, Burtin G, Herbillon AJ (1991) Disaggregation and clay dispersion of oxisols: Na resin, a recommended methodology. Geoderma 49:301–317. doi:10.1016/0016-7061(91)90082-5

Beckwith RS, Reeve R (1963) Studies on soluble silica in soils I. The sorption of silicic acid by soils and minerals. Aust J Soil Res 1:157–168. doi:10.1071/SR9630157

Berthelsen S, Noble AD, Garside AL (1999) An assessment of soil and plant silicon levels in North Queensland. In: Proc conf Aust soc sugar cane technologists, vol 21, pp 92–100

Berthelsen S, Noble AD, Garside AL (2001) Silicon research down under: past, present, and future. In: Datnoff LE, Snyder GH, Korndörfer GH (eds) Silicon in agriculture. Elsevier, The Netherlands, pp 241–256

Carlier J, De Waele D, Escalant JV (2002) Evaluation globale de la résistance des bananiers à la fusariose, aux maladies foliaires causées par les Mycosphaerella spp. et aux nématodes. In: Vezina A, Picq C, (eds) Guides techniques INIBAP 6. Réseau international pour l'amélioration de la banane et de la banane plantain, Montpellier, France

Cary L, Alexandre A, Meunier JD, Boeglin JL, Braun JJ (2005) Contribution of phytoliths to the suspended load of biogenic silica in the Nyong Basin rivers (Cameroon).

Biogeochemistry 74:101–114. doi:10.1007/s10533-004-2945-1

Certini G, Wilson MJ, Hillier SJ, Fraser AR, Belbos E (2006) Mineral weathering in trachydacitic-derived soils and saprolites involving formation of embryonic halloysite and gibbsite at Mt. Amiata, Central Italy. Geoderma 133:173–190. doi:10.1016/j.geoderma.2005.07.005

Chadwick OA, Derry LA, Vitousek PM, Heubert BJ, Hedin LO (1999) Changing sources of nutrients during four million years of ecosystem development. Nature 397:491–497. doi:10.1038/17276

Chadwick OA, Gavenda RT, Kelly EF, Ziegler K, Olson CG, Elliott WC et al (2003) The impact of climate on the biogeochemical functioning of volcanic soils. Chem Geol 202:195–223. doi:10.1016/j.chemgeo.2002.09.001

Chao TT, Sanzolone RF (1992) Decomposition techniques. J Geochem Explor 44:65–106. doi:10.1016/0375-6742(92)90048-D

Chaperon P, L'Hote Y, Vuillaume G (1985) Les ressources en eau de surface de la Guadeloupe. Editions de l'ORSTOM, Collection Monographies Hydrologiques n°7, France

Chapman LS, Haysom BC, Chardon CW (1981) Checking the fertility of Queensland's sugarland. In: Proc conf Aust soc sugar cane technologists, vol 3, pp 325–332

Chorover J, DiChiaro MJ, Chadwick OA (1999) Structural charge and cesium retention in a chronosequence of tephritic soils. Proc Soil Sci Soc Am 63:169–177

Colmet-Daage F (1969) Carte des sols des Antilles au 1/20 000. Atlas des départements français d'Outre-Mer, IGN, Paris

Colmet-Daage F, Gautheyrou J (1974) Soil association on volcanic material in tropical America with special reference to Martinique and Guadeloupe. Trop Agric Trinidad 51:121–128

Colmet-Daage F, Lagache P (1965) Caractéristiques de quelques sols dérivés de roches aux Antilles Françaises. Cah ORSTOM Ser Pedol 3:91–121

Conley DJ (2002) Terrestrial ecosystems and the global biogeochemical silica cycle. Global Biogeochem Cycles 16:1121–1127. doi:10.1029/2002GB001894

Conley DJ, Sommer M, Meunier JD, Kaczorek D, Saccone L (2006) Silicon in the terrestrial biogeosphere. In: Ittekot V, Humborg C, Garnier J (eds) Land-ocean nutrient fluxes: silica cycle. SCOPE, Island Press, Washington, pp 13–28

Dagain J, Paterne M, Westercamp D (1981) La mise en place du massif volcanique Madeleine-Soufrière, Basse-Terre de Guadeloupe, Antilles. C R Acad Sci Paris 292:921–926

Dahlgren RA (1994) Quantification of allophane and imogolite. In: Amonette JE, Zelazny LW (eds) Quantitative methods in soil mineralogy. Soil Science Society of America, Madison, pp 430–451

Delvaux B, Herbillon AJ, Vielvoye L (1989) Characterization of a weathering sequence of soils derived from volcanic ash in Cameroon—taxonomic, mineralogical and agronomic implications. Geoderma 45:375–388. doi:10.1016/0016-7061(89)90017-7

Delvaux B, Tessier D, Herbillon AJ, Burtin G, Jaunet AM, Vielvoye L (1992) Morphology, texture and microstructure of halloysitic soil clays as related to weathering and exchangeable cation. Clays Clay Miner 40:446–456. doi:10.1346/CCMN.1992.0400409

Derry LA, Kurtz CA, Ziegler K, Chadwick OA (2005) Biological control of terrestrial silica cycling and export fluxes to watersheds. Nature 433:728–730. doi:10.1038/nature03299

Dixit S, Van Cappellen P, Johan van Bennekom A (2001) Processes controlling solubility of biogenic silica and pore water build-up of silicic acid in marine sediments. Mar Chem 73:333–352. doi:10.1016/S0304-4203(00)00118-3

Dorel M (2001) Effet des pratiques culturales sur les propriétés physiques des sols volcaniques de Guadeloupe et influence sur l'enracinement du bananier. PhD Thesis, Université catholique de Louvain, Belgium

Dorel M, Roger-Estrade J, Manichon H, Delvaux B (2000) Porosity and soil water properties of Caribbean volcanic ash soils. Soil Use Manage 16:133–140

Drees LR, Wilding LP, Smeck NE, Senkayi AL (1989) Silica in soils: quartz and disorders polymorphs. In: Dixon JB, Weed SB (eds) Minerals in soil environments. Soil Science Society of America, Madison, pp 914–974

Fox RL, Silva JA, Younge OR, Plucknett DL, Sherman GD (1967) Soil and plant silicon and silicate response by sugarcane. Soil Sci Soc Am Proc 31:775–779

Garrels RM (1967) Genesis of some ground waters from igneous rocks. In: Abelson P (ed) Research in geochemistry. Wiley, NewYork, pp 405–420

Haysom MB, Chapman LS (1975) Some aspects of the calcium silicate trials at Mackay. In: Proc conf Qld soc sugar cane technologists, vol 42, pp 117–122

Henriet C, Draye X, Oppitz I, Swennen R, Delvaux B (2006) Effects, distribution, and uptake of silicon in banana (*Musa* spp.) under controlled conditions. Plant Soil 287:359–374. doi:10.1007/s11104-006-9085-4

Henriet C, Bodarwé L, Dorel M, Draye X, Delvaux B (2008) Silicon leaf content in banana (*Musa* spp.) reveals the weathering stage of volcanic ash soils in Guadeloupe. Plant Soil (in press). doi:10.1007/s11104-008-9680-7

Herbauts J, Dehalu FA, Gruber W (1994) Quantitative-determination of plant opal content in soils, using a combined method of heavy liquid separation and alkali dissolution. Eur J Soil Sci 45:379–385. doi:10.1111/j.1365-2389.1994.tb00522.x

Herbillon AJ (1986) Chemical estimation of weatherable minerals present in the diagnostic horizons of low activity clay soils. In: Beinroth FH, Camargo MN, Eswaran H (eds) Proceedings of the 8th international soil classification workshop: classification, characterization and utilization of oxisols, Part 1 EMBRAPA, Rio de Janeiro, pp 39–48

Hinsinger P, Barros ONF, Benedetti MF, Noack Y, Callot G (2001) Plant-induced weathering of a basaltic rock: experimental evidence. Geochim Cosmochim Acta 65:137–152. doi:10.1016/S0016-7037(00)00524-X

Imaizumi K, Yoshida S (1958) Edaphological studies on silicon supplying power of paddy soils. Bull Natl Inst Agric Sci 8:261–304

IUSS Working Group WRB (2006) World reference base for soil resources 2006, 2nd edn. World Soil Resources Reports No. 103. FAO, Rome

Jackson ML (1965) Soil chemical analysis-advanced course. Dept. of soil science, Madison

Karathanasis AD (2002) Mineral equilibria in environmental soil systems. In: Dixon JB, Weed SB (eds) Soil mineralogy with environmental applications. Soil Science Society of America, Madison, pp 109–151

Kelly EF (1990) Methods for extracting opal phytoliths from soil and plant material. Workshop on biotic indicators of global change, Seattle, Washington

Kittrick JA (1969) Soil minerals in the Al_2O_3–SiO_2–H_2O system and the theory of their formation. Clays Clay Miner 51:1457–1466

Lahav E (1995) Banana nutrition. In: Gowen S (ed) Bananas and plantains. Chapman & Hall, London, pp 258–316

Lucas Y, Luizao FJ, Chauvel A, Rouiller J, Nahon D (1993) The relation between biological-activity of the rainforest and mineral composition of soils. Science 260:521–523. doi:10.1126/science.260.5107.521

Ma JF, Tamai K, Yamaji N, Mitani N, Konishi S, Katsuhara M et al (2006) A silicon transporter in rice. Nature 440:688–691. doi:10.1038/nature04590

Ma JF, Yamaji N, Mitani N, Tamai K, Konishi S, Fujiwara T et al (2007) An efflux transporter of silicon in rice. Nature 448:209–213. doi:10.1038/nature05964

Markewitz D, Richter DD (1998) The bio in aluminum and silicon geochemistry. Biogeochemistry 42:235–252. doi:10.1023/A:1005901417165

Matichenkov VV, Bocharnikova EA, Calvert DV, Snyder GH (2000) Comparison study of soil silicon status in sandy soils of South Florida. Soil Crop Sci Soc Fla Proc 59:132–137

Meunier JD, Colin F, Alarcon C (1999) Biogenic silica storage in soils. Geology 27:835–838. doi:10.1130/0091-7613(1999)027<;0835:BSSIS>;2.3.CO;2

Michalopoulos P, Aller RC (2004) Early diagenesis of biogenic silica in the Amazon delta: alteration, authigenic clay formation, and storage. Geochim Cosmochim Acta 68:1061–1085. doi:10.1016/j.gca.2003.07.018

Ndayiragije S (1996) Caractérisation d'une séquence d'altération de sols dérivés de matériaux pyroclastiques sous climat tropical humide des Antilles (Guadeloupe). PhD Thesis, Université catholique de Louvain

Ndayiragije S, Delvaux B (2003) Coexistence of allophane, gibbsite, kaolinite and hydroxy-Al-interlayered 2: 1 clay minerals in a Perudic Andosol. Geoderma 117:203–214. doi:10.1016/S0016-7061(03)00123-X

Ndayiragije S, Delvaux B (2004) Selective sorption of potassium in a weathering sequence of volcanic ash soils from Guadeloupe, French West Indies. Catena 56:185–198. doi:10.1016/j.catena.2003.10.010

Opfergelt S (2008) Silicon cycle in the soil-plant system: Biogeochemical tracing using Si isotopes. PhD Thesis, Université Catholique de Louvain, n° 127, Louvain-la-Neuve, p 311

Page AL, Miller RH, Keeney DR (1982) Methods of soil analysis: part 2, chemical and microbiological properties, 2nd edn. American Society of Agronomy and Soil Science Society of America, Madison

Parfitt RL, Wilson AD (1985) Estimation of allophane and halloysite in three sequences of volcanic soils, New Zealand. In: Fernandez Caldas E, Yaalon DH (eds) Volcanic soils. Catena Verlag, Cremlingen, pp 914–974

Parfitt RL, Russell M, Orbell GE (1983) Weathering sequence of soil from volcanic ash involving allophane and halloysite, New Zealand. Geoderma 29:41–57. doi:10.1016/0016-7061(83)90029-0

Pochet G, Van der Velde M, Vanclooster M, Delvaux B (2007) Hydric properties of high charge, halloysitic clay soils from the tropical South Pacific region. Geoderma 138:96–109. doi:10.1016/j.geoderma.2006.10.019

Ragueneau O, Savoye N, Del Amo Y, Cotten J, Tardiveau B, Leynaert A (2005) A new method for the measurement of biogenic silica in suspended matter of coastal waters: using Si:Al ratios to correct for the mineral interference. Cont Shelf Res 25:697–710. doi:10.1016/j.csr.2004.09.017

Raven JA (1983) The transport and function of silicon in plants. Biol Rev Camb Philos Soc 58:179–207. doi:10.1111/j.1469-185X.1983.tb00385.x

Raven JA (2001) Silicon transport at the cell and tissue level. In: Datnoff LE, Snyder GH, Korndörfer GH (eds) Silicon in agriculture. Elsevier, The Netherlands, pp 41–55

Rickert D, Schülter M, Wallmann K (2002) Dissolution kinetics of biogenic silica from the water column to the sediments. Geochim Cosmochim Acta 66:439–455. doi:10.1016/S0016-7037(01)00757-8

Rouiller J, Burtin G, Souchier B (1972) La dispersion des sols dans l'analyse granulométrique Méthode utilisant les résines échangeuses d'ions. Bull ENSAIA Nancy 14:193–205

Rufyikiri G, Dufey J, Nootens D, Delvaux B (2000) Effect of aluminium on bananas (*Musa* spp.) cultivated in acid solutions. I. plant growth and chemical composition. Fruits 55:367–379

Rufyikiri G, Nootens D, Dufey J, Delvaux B (2001) Effect of aluminium on bananas (*Musa* spp.) cultivated in acid solutions. II. water and nutrient uptake. Fruits 56:3–14. doi:10.1051/fruits:2001107

Rufyikiri G, Nootens D, Dufey JE, Delvaux B (2004) Mobilization of aluminium and magnesium by roots of banana (*Musa* spp.) from kaolinite and smectite clay minerals. Appl Geochem 19:633–643. doi:10.1016/j.apgeochem.2003.07.001

Saccone L, Conley DJ, Koning E, Sauer D, Sommer M, Kaczorek D et al (2007) Assessing the extraction and quantification of amorphous silica in soils of forest and grassland ecosystems. Eur J Soil Sci 58:1446–1459. doi:10.1111/j.1365-2389.2007.00949.x

Sauer D, Saccone L, Conley DJ, Herrmann L, Sommer M (2006) Review of methodologies for extracting plant-available and amorphous Si from soils and aquatic sediments. Biogeochemistry 80:89–108. doi:10.1007/s10533-005-5879-3

Schwandes LP, Snyder GH, Wilkerson J (2001) Plant-available silicon in selected alfisols and ultisols of Florida. Soil Crop Sci Soc Fla Proc 60:57–59

Smithson F (1956) Plant opal in soil. Nature 178:107. doi:10.1038/178107a0

Sommer M, Kaczorek D, Kuzyakov Y, Breuer J (2006) Silicon pools and fluxes in soils and landscapes—a review. J Plant Nutr Soil Sci 169:310–329. doi:10.1002/jpln.200521981

Tréguer P, Nelson DM, Van Bennekom AJ, De Master DJ, Leynaert A, Quéguiner B (1995) The silica balance in the world ocean: a reestimate. Science 268:375–379. doi:10.1126/science.268.5209.375

Twyford IT, Walmsley D (1973) The mineral composition of the Robusta banana plant I methods and plant growth studies. Plant Soil 39:227–243. doi:10.1007/BF00014790

Walkley A, Black IA (1934) An examination of the Degiareff method for determining SOM and a proposed modification of the chromic acid titration method. Soil Sci 37:29–38. doi:10.1097/00010694-193401000-00003

Wilding LP, Drees LR (1971) Biogenic opal in Ohio soils. Soil Sci Soc Am Proc 35:1004–1010