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Silicon cycle in the soil-plant system: biogeochemical tracing using Si isotopes

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*Le temps présent est semblable à la boule d'argile, le temps passé
à la poussière de la terre, et le temps futur à la cruche.*

Nagarjuna
Extrait de *Le Traité de la Grande Vertu de Sagesse*

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Contents

Remerciements	iii
Summary	xiii
Résumé	xiv
Introduction and Objectives	3
General introduction	3
General objectives	4
Thesis outline	4
Part I General Overview	7
1 The biogeochemical silicon cycle	9
1.1 The superficial silicon cycle	9
1.2 The continental silicon cycle: focus on the soil-plant system	11
1.3 Silicon in plants	13
1.3.1 Silicon uptake, transport and deposition in plants .	13
1.3.2 Silicon accumulation by plants	15
1.3.3 Beneficial effects of silicon for plants	16
1.4 Silicon in soils	17
1.4.1 Lithogenic silicon	18
1.4.2 Pedogenic silicon	18
1.4.3 Biogenic silicon	19
1.4.4 Adsorbed silicon	19
1.4.5 Silicon in soil solutions and drainage	20
1.5 Tracers of silicon cycle	20
1.5.1 Silicon stable isotopes	21
1.5.2 Germanium/silicon ratio	28
2 Banana (<i>Musa</i> spp.) as silicon accumulating plant	31
2.1 Origin and varieties	31

2.2	Banana morphology	32
2.3	Crop requirements	32
2.4	Silicon in banana	33
3	Study sites in Cameroon: environmental settings	37
3.1	Geography	37
3.2	Climate	38
3.3	Geological context	41
3.4	Weathering sequences of volcanic ash soils	44
Part II	Silicon isotopes: Analytical development	49
4	Measurement of silicon isotopes	51
4.1	Analytical methods for silicon isotope determinations . . .	51
4.2	Sample preparation	52
4.3	Principles of MC-ICP-MS	56
4.4	Silicon isotopic analysis following Cardinal et al 2003 . . .	60
5	Isotopic determination of rock reference materials	67
5.1	Introduction	68
5.2	Instrumental	69
5.2.1	New configuration of the Nu Plasma mass spec-	
	trimeter	69
5.2.2	Analytical conditions	71
5.3	Experimental	72
5.3.1	Standard preparation	72
5.4	Results	74
5.5	Discussion	78
5.6	Conclusions	80
6	Inter-laboratory comparison of reference materials	81
6.1	Introduction	82
6.2	Samples and methods	84
6.3	Advances in mass spectrometry	86
6.3.1	IRMS	86
6.3.2	MC-ICP-MS	87
6.4	Results	88
6.5	Discussion	93
6.6	Conclusions	95

Part III Plant-induced silicon isotopic fractionation 97**7 Silicon isotopic fractionation by plants in hydroponics 99**

7.1	Introduction	100
7.2	Materials and methods	101
7.2.1	Hydroponics	101
7.2.2	Sampling	102
7.2.3	SiO ₂ content analyses	102
7.2.4	SEM observations and EDX analyses of phytoliths	103
7.2.5	Silicon isotopes analyses	104
7.2.6	Fractionation factors	105
7.3	Results	105
7.3.1	SiO ₂ content	105
7.3.2	Observations of silica deposits (SEM)	106
7.3.3	Silicon isotopic compositions	107
7.4	Discussion	109
7.4.1	The bulk fractionation factor	109
7.4.2	Intra-plant fractionation	111
7.4.3	Banana plant fractionation model	113
7.5	Conclusions	115

8 Plant silicon isotopic signature might reflect soil weathering stage 117

8.1	Introduction	118
8.2	Materials and methods	119
8.2.1	Study area	119
8.2.2	Sampling	119
8.2.3	Bulk elemental, chemical and physical analyses . .	121
8.2.4	Silicon isotopes analyses	122
8.3	Results	123
8.3.1	Soil properties	123
8.3.2	Mineral content in plants	124
8.3.3	Silicon isotopic compositions in plants	125
8.4	Discussion	126
8.4.1	Silicon content in banana	126
8.4.2	Intra-plant silicon isotopic fractionation	128
8.4.3	Plant silicon isotopic signature might reflect soil weathering stage	130
8.5	Conclusion	132

9	Silicon and germanium uptake by plants	133
9.1	Introduction	134
9.2	Materials and methods	136
9.2.1	Hydroponic experiment on banana in a closed system	136
9.2.2	Plant collecting <i>in situ</i>	137
9.2.3	Germanium and silicon content analyses	138
9.2.4	Silicon isotopes analyses	139
9.3	Results	140
9.3.1	Germanium and silicon contents	140
9.3.2	Silicon isotopic variations	146
9.4	Discussion	146
9.4.1	Germanium-silicon fractionation by plants	146
9.4.2	Proposed mechanism for Ge accumulation in roots	148
9.4.3	Intra-plant germanium-silicon fractionation	148
9.4.4	Impact of the soil	150
9.4.5	Implications	151
9.5	Conclusion	153
Part IV	Silicon isotopic variations in soils	155
10	Silicon isotopic fractionation during adsorption onto synthetic iron oxides	157
10.1	Introduction	158
10.2	Materials and methods	159
10.2.1	Synthesis and characterization of ferrihydrite and goethite	160
10.2.2	Adsorption experiments	162
10.2.3	Isotopic composition of solutions at given contact times	163
10.3	Results and discussion	164
10.3.1	Monomeric silicon adsorption by ferrihydrite and goethite	164
10.3.2	Quantitative silicon adsorption by ferrihydrite and goethite	165
10.3.3	Adsorption kinetics	167
10.3.4	Silicon isotopic fractionation during adsorption of monosilic acid	168
10.4	Implications	171
10.4.1	Mechanisms of isotopic fractionation	171
10.4.2	Environmental significance	173

10.5 Conclusion	174
11 Silicon isotopic fractionation during adsorption onto iron oxides in basaltic ash soils differing in weathering stage	175
11.1 Introduction	176
11.2 Materials and methods	177
11.2.1 Environmental framework and major soil mineral components	177
11.2.2 Soil and clay materials	178
11.2.3 Characterization of soil and clay properties	179
11.2.4 Adsorption experiments	179
11.2.5 Silicon isotopes analyses	180
11.3 Results	181
11.3.1 Properties of soil and clay materials	181
11.3.2 Silicon adsorption in soils	182
11.3.3 Silicon isotopic fractionation during adsorption of monosilic acid	185
11.4 Discussion	188
11.4.1 Quantitative silicon adsorption and soil components	188
11.4.2 Isotopic fractionation during silicon adsorption as influenced by soil weathering stage	190
11.4.3 Isotopic impact on soil solution and rivers	192
11.5 Conclusions	193
12 Soil-plant cycle of silicon in basaltic ash soils under intensive banana cropping	195
12.1 Introduction	196
12.2 Materials and methods	197
12.2.1 Environmental setting	197
12.2.2 Sampling	199
12.2.3 Characterization of the samples	199
12.2.4 Tracers of silicon	201
12.3 Results	203
12.3.1 Properties of soil and clay materials	203
12.3.2 Silicon distribution in the soil	203
12.3.3 Silicon isotopic signatures of soil fractions	205
12.3.4 Germanium/silicon ratios in soils	206
12.3.5 Silicon in river waters	208
12.4 Discussion	209
12.4.1 Si tracers and soil weathering stage	209
12.4.2 Silicon isotopic balance in the soil	211
12.4.3 Plant impact on silicon cycle in soil	217

12.4.4 Implications on the biogeochemical Si cycle	219
12.5 Conclusions	220
General Conclusions and Perspectives	223
Implications of the study on the silicon isotopic geochemistry .	223
General conclusions	236
Perspectives	237
Appendix	243
A Soil profiles description	243
B GPS coordinates of the sampling sites	247
C Preliminary results on intra-plant silicon isotopic frac- tionation <i>in situ</i> vs. <i>in vitro</i>*	249
D Explore the silicon isotopic variations through banana leaves (Cameroon)	255
E Complementary silicon isotopic compositions in banana	259
F Evaluation of the silicon source for adsorption and desorption	261
G Supplementary material of Chapter 12	267
H Explore the impact of hevea as a non Si-accumulating plant	275
References	308
Related Publications	309

Summary

Despite the suspected biological imprint on the terrestrial silicon (Si) cycle, plant contribution to the Si continental reservoir is poorly quantified. Within the soil-plant system, aqueous silicon (H_4SiO_4^0) can be retrieved from soil solution by plant uptake, clay formation and adsorption onto secondary oxides, or leached out and transferred to stream waters. Two approaches are very promising to trace Si within the soil-plant cycle: the Si stable isotopes and Ge/Si ratio. This thesis aims at quantifying the Si isotopic fractionation induced by plants and soil processes in both controlled (*in vitro*) and natural conditions (*in situ*). The model used is a tropical soil-plant system involving a Si-accumulating plant (banana, *Musa acuminata* Colla, cv Grande Naine) cropped on soils derived from basaltic ash but differing in weathering stage (Cameroon, West Africa). Si isotopic compositions in the different compartments of the soil-plant system were measured by MC-ICP-MS in dry plasma mode with external Mg doping. The analytical method required specific developments, and was validated by an inter-laboratory comparison of reference materials. Plant root uptake of Si, and Si transport within the plant induce an isotopic fractionation quantified *in vitro* and measured *in situ*. The plant Si isotopic signature is influenced by soil weathering stage, precisely by soil contents of clay and iron oxide. Soil clay-sized fractions sequester light Si isotopes following abiotic fractionating processes of mineral weathering and clay formation, leaving a residual solution enriched in heavy Si isotopes. Biogenic Si, enriched in light Si isotopes, constitutes a Si source for clay formation. Clay-sized Fe-oxides concentrate with increasing weathering and soil development. They selectively adsorb light Si isotopes by surface complexation of monomeric H_4SiO_4^0 . Silicon transport within the plant produces a Ge/Si fractionation involving Ge sequestration in roots whereas weathering and clay formation induce a selective Ge sequestration in clay minerals, producing an increased Ge/Si ratio with increasing weathering, in excellent agreement with Si isotopic data. In the soil-plant system studied, Si stable isotopes thus trace three major continental processes: plant uptake and phytolith formation, sequestration of Si in clay minerals, and adsorption of Si by Fe-oxides. These biotic and abiotic processes all lead to a progressive enrichment of pore waters in heavy Si isotopes.

Résumé

Les plantes ont un impact majeur sur le cycle terrestre du silicium (Si), mais leur contribution reste peu quantifiée. Dans le système sol-plante, le silicium dissous (H_4SiO_4^0) dans la solution du sol peut être prélevé par les plantes, utilisé dans la néoformation de minéraux argileux, adsorbé par les oxydes secondaires, ou lessivé et transféré vers l'hydrosphère. Deux approches sont très prometteuses pour tracer le Si au sein du cycle sol-plante: les isotopes stables du Si et le rapport Ge/Si. Cette étude vise à quantifier le fractionnement isotopique de Si induit par les plantes et les processus d'altération en conditions contrôlées (*in vitro*) et naturelles (*in situ*). Le modèle utilisé est un système sol-plante tropical composé d'une plante accumulatrice de Si (le bananier, *Musa acuminata* Colla, cv Grande Naine) cultivée sur des sols dérivés de cendres basaltiques de degrés d'altération divers (Cameroun, Afrique de l'Ouest). Les compositions isotopiques de Si sont mesurées dans les différents compartiments du système sol-plante par MC-ICP-MS en plasma sec avec un dopage externe en Mg. La méthode d'analyse a nécessité des développements analytiques et a été validée par une comparaison inter-laboratoire sur des matériaux de référence. Le prélèvement de Si par la plante et son transport au sein de celle-ci induisent un fractionnement isotopique quantifié *in vitro* et mesuré *in situ*. La signature isotopique de la plante est influencée par le degré d'altération du sol, et plus particulièrement par la teneur en argile, et en oxydes de fer. La fraction argileuse de ces sols concentre les isotopes légers de Si suite aux fractionnements induits par les processus abiotiques d'altération et de néoformation d'argiles, induisant une solution enrichie en isotopes lourds de Si. L'apport de silice biogénique enrichie en isotopes légers constitue une source de Si pour la néoformation des minéraux argileux. Les oxydes de Fe qui s'accumulent dans la fraction argileuse au cours de l'altération et de la pédogenèse, adsorbent sélectivement les isotopes légers de Si par complexation de surface de H_4SiO_4^0 monomérique. Le transport de Si au sein de la plante induit un fractionnement Ge/Si avec accumulation de Ge dans les racines, alors que l'altération et l'argilogenèse concentrent le Ge dans les minéraux argileux, induisant un rapport Ge/Si croissant avec le degré d'altération en bon accord avec les données isotopiques. Les isotopes stables de Si constituent donc, pour le système sol-plante étudié, un outil de traçage biogéochimique à l'égard de trois processus majeurs de l'altération : le prélèvement biologique et la formation de phytolithes, la formation de minéraux argileux, et l'adsorption de Si par les oxydes de Fe. Ces processus biotiques et abiotiques induisent un enrichissement en isotopes lourds de Si dans la solution du sol.

Introduction and Objectives

General introduction

Silicon (Si) is a major element on Earth, the second most abundant after oxygen in the Earth's crust (Epstein, 1999). The global Si cycle is closely linked to the C cycle through the combined processes of CO₂ consumption by silicate weathering (Raven and Edwards, 2001) and by diatoms growth (Smetacek, 1999), and is thus of great concern in global change studies.

Silica fluxes from the pedosphere to the hydrosphere have long been considered to be exclusively controlled by weathering of aluminosilicate minerals in soils (Drever, 1988). However, solute fluxes exported from vegetated areas were shown to be about four times larger than those measured in bare areas (Moulton et al., 2000), and recent data provide evidence that Si released to water stream has passed through a biogenic silica pool, whereas direct mineral-water interactions would account for a smaller fraction of the stream silica flux (Derry et al., 2005). This supports the idea of a major impact of the terrestrial biogenic Si pool on river Si fluxes (Alexandre et al., 1997; Lucas, 2001).

Silicon is taken up by plants as monosilic acid (H₄SiO₄⁰) and precipitates in vegetal tissues as biogenic opal called phytoliths (Jones and Handreck, 1965; Raven, 1983). These phytoliths are restituted to the soil by the decomposition of organic matter (Smithson, 1956), and can be preserved or dissolved; their dissolution can imply Si recycling in the soil-plant system. In soil solutions, H₄SiO₄⁰ is a major solute mainly provided by silicate weathering (White, 1995). Aqueous monosilicic acid can be (1) used for the neoformation of secondary clay minerals (White, 1995), (2) adsorbed onto iron and aluminium oxyhydroxides (McKeague and Cline, 1963c), or (3) taken up by plants (Jones and Handreck, 1965). The residual solution is exported to rivers. Although occurring at very different timescales (from the rainy event to soil formation), these processes would significantly impact the Si signal to ocean, as continental runoff water contributes to more than 80% of the input to the marine Si budget (Tréguer et al., 1995).

However, the contributions of these respective processes are still poorly quantified (e.g. plants: Alexandre et al. (1997); Conley (2002); Derry et al. (2005)). In this respect, two new approaches are available: the stable Si isotopes and the determination of Ge/Si ratios.

Si isotopes are likely to offer an ideal tracer to identify sources involved in Si delivery to the watershed. Compared to crustal rocks (Douthitt, 1982), river and sea waters are enriched in heavy Si isotopes (Alleman et al., 2005; Cardinal et al., 2005; De La Rocha et al., 2000; Ding et al., 2004). This results from a combination of processes depleting

water reservoir of light isotopes: (1) neoformation of secondary clay minerals (Ziegler et al., 2005ab), (2) formation of silcretes (Basile-Doelsch et al., 2005), and (3) biomineralization by diatoms (De La Rocha et al., 1997), sponges (De La Rocha, 2003), and plants (Ding et al., 2005b 2008). In the continental context, Ge/Si ratios have been used to trace weathering (Kurtz et al., 2002; Scribner et al., 2006) and plant impact (Blecker et al., 2007; Derry et al., 2005).

In the soil-plant system, quantifying the fractionation factor induced by each process would be helpful to identify their respective contribution to Si exported to water streams. In this respect, the tropical environment constitutes an ideal natural laboratory as the Si biogenic turnover is very high (58 to 76 kg.ha⁻¹.yr⁻¹; Alexandre et al. (1997)). Among the monocotyledons cultivated in the tropics, banana (*Musa* spp.) is particularly relevant. Banana is a Si-accumulating plant (Henriet et al., 2006; Jauhari et al., 1974; Lahav, 1995), a very high demanding crop, especially for potassium (Delvaux, 1995), characterized by a strong rhizosphere weathering potential (Delvaux and Rufyikiri, 2003). Indeed, banana roots can mobilize various elements from alumino-silicates (Hinsinger et al., 2001; Rufyikiri et al., 2004). Moreover, the presence of phytoliths was reported in banana (Mbida et al., 2001; Prychid et al., 2004; Tomlinson, 1969). The present thesis focuses on the Si cycle in the soil-banana system in Cameroon.

General objectives

Plants display a strong biological imprint on the terrestrial Si cycle, but their contribution to the Si continental reservoir compared to non biogenic processes was poorly quantified.

The present thesis uses the Si stable isotopes to trace Si pathway in the soil-plant system. The approach consists of quantifying the Si isotopic fractionation induced by plants and weathering processes in controlled conditions (*in vitro*) and of using the Si isotopic tracer in natural conditions (*in situ*).

Thesis outline

Figure A gives an overview of the thesis outline. The main results (Chapter 5 to Chapter 12) are presented as a succession of articles either published or prepared for submission to peer review journals. This presentation has the advantage that each chapter can be easily read and understood independently. Nevertheless, I would like to apologize for

the discomfort that the redundancies among chapters may provide to people who would afford a complete and continuous reading.

The thesis is structured in four parts.

Part I gives a general overview of the current knowledge on the continental silicon cycle, including silicon in plants and soils and the tracers of Si cycle (*Chapter 1*), provides the major characteristics of banana plant chosen as Si-accumulating plant (*Chapter 2*), and describes the environmental settings of the studied area in Cameroon and the selected weathering sequences (*Chapter 3*).

Part II focuses on Si isotopes measurements, giving the principles of MC-ICP-MS and the method to measure ^{28}Si and ^{29}Si isotopes (*Chapter 4*), explaining the analytical development realized to measure ^{30}Si (*Chapter 5*), and detailing an inter-laboratory comparison of Si isotope reference materials (*Chapter 6*).

Part III is centered on the plant induced Si isotopic fractionation. *Chapter 7* reports a study *in vitro* in hydroponics which provides evidence and quantification of a Si isotopic fractionation by plant uptake and between plant parts. These fractionations are discussed in relation with Si-transporters recently identified in rice plant. *Chapter 8* confirms intra-plant fractionation measured *in vitro* (*Chapter 7*) on mature banana from Cameroon. Moreover, variations of the bulk plant Si isotopic compositions are related to the weathering stage of the soil. *Chapter 9* explores the Ge/Si fractionation by plant *in vitro* and *in situ* and compares this tracer with Si isotopes. This contributes to understand the Ge and Si uptake by plant and the low Ge/Si ratio found in phytoliths.

Part IV develops the soil processes and the Si isotopic fractionation induced by them. *Chapter 10* aims to identify and quantify the Si isotopic fractionation induced by adsorption onto synthetic iron oxides. The impacts of Si adsorption mechanisms on Si isotopic fractionation are discussed, and emphasis is given to the environmental significance of this process unconsidered until now. *Chapter 11* reports on the Si isotopic fractionation induced by adsorption onto Fe-oxides in soils with various Fe-oxide content and type. It further links Si adsorption and isotopic fractionation with soil weathering stage, and discusses the impact of Si adsorption upon Si isotopic signature of pore waters. *Chapter 12* is devoted to the detailed Si isotopic measurements of the various soil

fractions (sand, silt, clay, amorphous Si) and presents a Si isotopic balance of the soil to identify the main processes impacting the bulk soil signature. Combination of $\delta^{30}\text{Si}$ data with Ge/Si ratios through weathering sequences contributes to the understanding of weathering processes.

Implications of this study, general conclusions and perspectives are given at the end of the thesis.

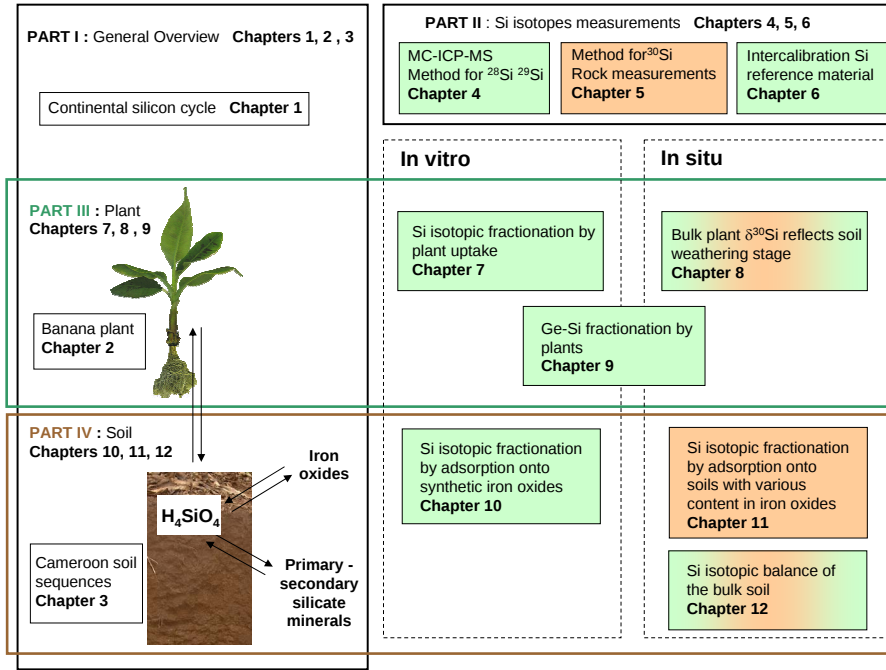


Figure A: Schematic presentation of the thesis outline. Studies presenting $\delta^{29}\text{Si}$ data only are indicated in green (method of Cardinal et al. (2003); Chapter 4), while studies presenting $\delta^{30}\text{Si}$ data as well are indicated in orange (method of Abraham et al. (2008); Chapter 5). When both methods were used, both colors are mentioned. For comparison, $\delta^{29}\text{Si}$ data can be converted to $\delta^{30}\text{Si}$ values by multiplying the former by 1.93 (Young et al., 2002).

Part I

General Overview

Chapter 1

The biogeochemical silicon cycle

1.1 The superficial silicon cycle

Silicon is the eighth most abundant element in the Universe (Ding et al., 1996). In the Earth's crust, silicon (28%) is the second most abundant element after oxygen (49%) (Epstein, 1999). In the global biosphere, however, Si average concentration (0.03%) ranges below H, O, C, N, S, Ca and K (Exley, 1998). Silicon is present in a diversity of matrixes in the Universe (extra-terrestrial rocks) and on Earth (rocks, clay minerals, waters, and biogenic samples such as diatoms, radiolarians, sponges, phytoliths). During weathering of silicate and carbonate minerals, atmospheric CO₂ is taken up and converted to dissolved HCO₃⁻ in natural waters, inducing a net loss of atmospheric CO₂ (Berner, 1995). This process has controlled atmospheric CO₂ concentration for million of years (Berner, 1995). Knowledge of the global biogeochemical Si cycle is thus of great concern in global change studies, because of its impact on global CO₂ concentrations through the combined processes of CO₂ consumption by silicate weathering (Raven and Edwards, 2001) and by diatoms growth (Smetacek, 1999), which are very sensitive to silica limitation (Hamm et al., 2003; Yool and Tyrrell, 2003). As Si fluxes to fresh and marine waters decrease significantly (Humborg et al., 2002 2000; Ittekkot et al., 2000), severe environmental consequences have to be feared, since fresh stream silicon constitutes 85% of the supply to the oceans (Tréguer et al., 1995). This nutrient is essential for marine diatoms which contribute to 45 % of total marine primary production. Silicon deficiency would thus affect coastal marine ecosystems. This should unbalance the marine food web (Mann, 1999) and perturbing

the capacity of the ocean to store CO₂ (Ittekkot et al., 2006). The flux of silica from terrestrial ecosystems towards the aquatic continuum is also of utmost importance in the context of eutrophication triggered by excess input of the nutrients N and P into the aquatic ecosystem, leading to excessive blooms of non-diatom phytoplankton species (Struyf et al., 2006 2005).

Silica fluxes from the pedosphere to the hydrosphere have long been considered to be exclusively controlled by weathering of aluminosilicate minerals in soils (Drever, 1988). Yet, the advent of vascular plants has enhanced rock weathering through nutrient uptake (Hinsinger, 1998), which enhanced the removal of CO₂ from the atmosphere (Berner, 1992 1997). Indeed, plants may significantly contribute to mineral weathering through nutrient uptake and acid excretion in the rhizosphere (Hinsinger et al., 2001). The biogenic feedbacks in the carbonate-silicate geochemical cycle played a key role in the major glacial- interglacial cycles of Pleistocene (van der Sluijs et al., 1996). Recent data provide evidence of the major impact of the terrestrial biogenic Si pool on river Si fluxes (Derry et al., 2005). In this study on Hawaiian watersheds, it has been suggested that most (80%) of the silica cycling released to stream water has passed through a biogenic silica pool, whereas direct mineral-water interactions would account for a smaller fraction of the stream silica flux (Derry et al., 2005). Solute fluxes exported from vegetated areas were shown to be about four times larger than those measured in bare areas, which supports the idea of a biological control of silica fluxes from soils to stream waters (Moulton et al., 2000).

Plants may influence silica fluxes to stream water through their transpiration regime. Besides, recent studies show that worldwide fresh water run off from the continent to the ocean increased through the 20th century, because plant transpiration decreased with the elevated atmospheric CO₂ (Gedney et al., 2006; Matthews, 2006). One process responsible for this increase is the reduction of plant transpiration due to elevated atmospheric CO₂ and subsequent leaf stomata closure (Gedney et al., 2006). As developed below, a decrease of plant transpiration may thus decrease the plant uptake of silica, thereby possibly decrease the release of Si to stream water.

Taken up as monosilicic acid (H₄SiO₄) in the soil solution, silicon precipitates in plant transpiration termini as amorphous opal-A (SiO₂.*n*H₂O) particles, named phytoliths. Organic debris restored to soil from dead plant biomass release phytolithic silica (Smithson, 1956). The solubility of phytolith particles may be 10 to 100 times higher than that of other silicate minerals in soils (Lucas, 2001). Thus, the dissolution of

phytoliths can largely contribute to Si release in soil solution (Farmer et al., 2005) and Si exports to water streams. Locally, the concentrations of dissolved Si in rivers reflect seasonal variations linked with vegetation uptake (Fulweiler and Nixon, 2005). These processes could impact the hydrological output of Si to oceans, as continental runoff contributes to more than 80% of the input to the marine Si budget (Tréguer et al., 1995) (Figure 1.1).

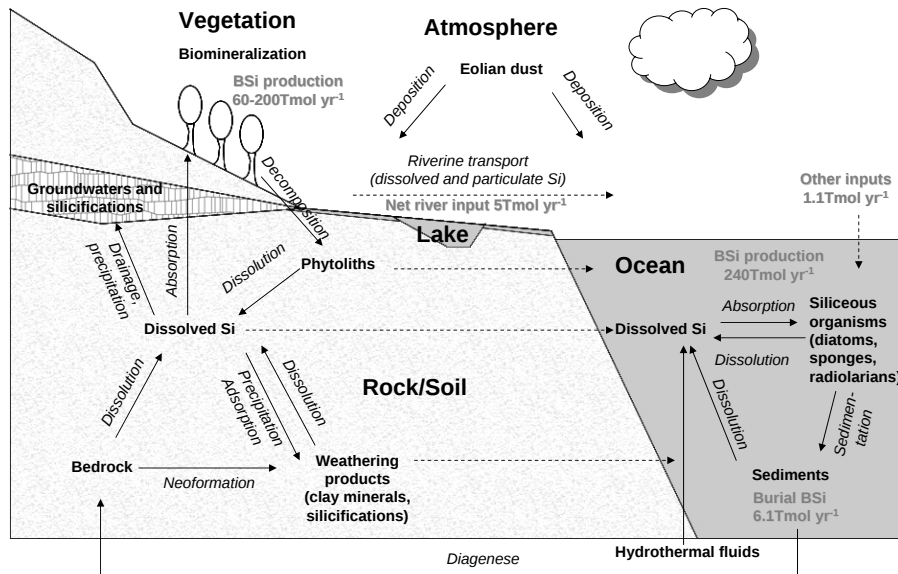


Figure 1.1: Global biogeochemical Si cycle on Earth (reservoirs modified from Basile-Doelsch (2006)). Si balance (1teramole (Tmol) = 10^{12} moles) for rivers and oceans from Tréguer et al. (1995). Biogenic Si (BSi) production by vegetation from Conley (2002).

1.2 The continental silicon cycle: focus on the soil-plant system

Plants significantly impact silicate weathering (Cochran and Berner, 1996; Lucas, 2001; Moulton and Berner, 1998; Moulton et al., 2000). By taking up huge quantities of silica, plants induce a strong biological imprint on the terrestrial Si cycle (Alexandre et al., 1997; Conley, 2002; Derry et al., 2005). Indeed, biogenic silica (BSi) production by vegetation (phytolith) was estimated at $60-200 \text{ Tmol yr}^{-1}$ (1teramole

(Tmol) = 10^{12} moles) (Conley, 2002). This is in the same order of magnitude than the BSi production by diatoms in ocean (240Tmol yr^{-1} ; Tréguer et al. (1995)) (Figure 1.1). The role of plants on the biogeochemical cycle of silicon is therefore major, but only few studies have been carried out to quantify the contribution of plants to the silicon continental reservoir (Alexandre et al., 1997; Derry et al., 2005). As Si is a ubiquitous element, it is necessary to find a tracer of Si biogenic recycling through vegetation, providing a tool to dissociate the contribution of plants vs. Si from mineral dissolution to Si exported to rivers. The present thesis will be focused on Si in the soil-plant system and uses the isotopic approach to follow the Si pathway.

The biogeochemical cycle of silicon in the soil-plant system can be summarized as illustrated in Figure 1.2. Dissolved Si provided by silicate weathering can be (1) incorporated into secondary clay minerals, (2) adsorbed onto iron and/or aluminium oxides, (3) taken up by plants, or (4) exported to the hydrosphere. Restitution of biogenic Si produced by plants (opaline phytoliths; 0.5-15% dry weight; Conley (2002)) to the soil will build a biogenic Si pool in soils (0.1-15% dry weight; e.g. Runge (1999)), which will be dissolved, preserved and/or exported to rivers (suspended load 1-4% dry weight; Cary et al. (2005)). The different Si pools in the soil-plant system will be described in more details in sections 1.3 and 1.4.

In terrestrial ecosystems, Si dynamics has been approached under tropical and temperate ecosystems (Table 1.1). In a temperate forest ecosystem (Bartoli, 1981), acid soils contain less phytoliths compared to

Table 1.1: Comparison of Si biocycling between forest and grassland ecosystems on an annual basis. Equatorial forest: Congo (Alexandre et al., 1997), Amazon (Lucas et al., 1993) - Temperate forest (Bartoli, 1981) - Grassland (Blecker et al., 2006).

	Si (kg.ha.yr^{-1})				
	Uptake ^a	Restitution ^b	Labile ^c	Stable ^d	Export ^e
Equatorial forest - Congo	67	67	62	5	16
Equatorial forest - Amazon	-	41	-	-	11
Temperate forest - deciduous	23	22	22	0	3
Temperate forest - coniferous	6	5	4	1	28
Dry grassland	26	26	17	9	0.2
Humid grassland	59	59	43	16	11

^a Si uptake by plants

^b Si restituted by decomposition of plant tissues

^c Labile pool of phytoliths dissolved

^d Stable pool of phytoliths preserved in the soil

^e Si exported by drainage

grassland (Blecker et al., 2006), due to higher Si accumulation in grass (section 1.3.2) and lower acidity of grassland soil compared to forest soil. In equatorial forest, the biological Si turnover was shown to be very high ($58\text{--}76 \text{ kg ha}^{-1} \text{ yr}^{-1}$; Alexandre et al. (1997)), with a rapid dissolution of phytoliths in litter (Alexandre et al., 1994). These authors estimated a very short residence time of phytoliths, between 1 month and 1.5 year, which promotes a high Si recycling rate. The present thesis focuses on a tropical ecosystem, involving a Si-accumulating plant as a model, i.e. banana plant (Chapter 2), and a weathering sequence of soils in Cameroon (Chapter 3). The monospecific plant stand was preferred in order to stabilize plant constraints, hence limiting combined effects of various plant species.

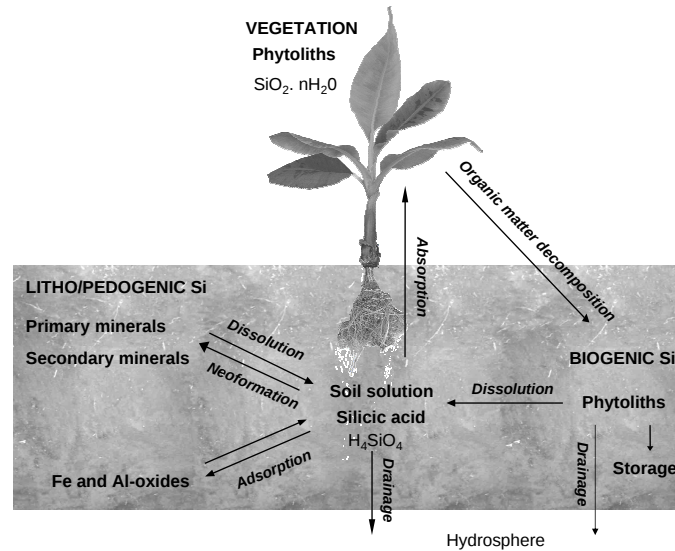


Figure 1.2: Continental silicon cycle in the soil-plant system.

1.3 Silicon in plants

1.3.1 Silicon uptake, transport and deposition in plants

Silicon is absorbed by plants as uncharged monosilicic acid H_4SiO_4^0 through mass flow (water transpiration flux) (Raven, 1983), transported into the xylem as dissolved H_4SiO_4 (Mitani et al., 2005), and precipitates in aerial parts of the plant as hydrated amorphous silica $\text{SiO}_2 \cdot n\text{H}_2\text{O}$ (biogenic opaline phytolith) (Jones and Handreck, 1965). Phytolith

literally means “plant stone”. Although non-silicic phytoliths do exist in plants (e.g. calcium oxalate; Skinner and Jahren (2004)), the term “phytolith” is more usually restricted to opaline plant inclusions or “silica bodies”. These phytoliths are restored to soil by decomposition of organic debris from plant material.

It was commonly accepted that silica deposits in plants resulted from a passive uptake of silicic acid by the roots, concentration due to water loss (transpiration), and Si polymerization (Jones and Handreck, 1967), resulting in SiO_2 precipitation near transpiration termini (Raven, 1983). Studies on grasses confirmed the presence of Si deposits in cell walls (an important silicon pathway), which supports the hypothesis that silicon is transported passively by transpiration (Sangster and Hodson, 1986). Since then, however, evidence of a genetic control of phytolith formation in dicotyledons has been provided (Piperno et al., 2002). Moreover, an active Si-uptake mechanism has been highlighted in rice (Ma et al., 2006). Transporters involved in Si-transport across the biological membrane occur in diatoms (Hildebrand et al., 1997). In plants, endocytotic process was proposed to explain Si-accumulation inside the cytoplasm and vacuoles without a membrane passage (Neumann and De Figueiredo, 2002). Protein transporters were highlighted in rice roots (Tamai and Ma, 2003), for the radial Si-transport to the cortical cells and xylem loading (Ma et al., 2004; Mitani et al., 2005). The gene for active Si transport belongs to the aquaporin family (Ma et al., 2006 2007). With an influx transporter on the one side (Ma et al., 2006) and an efflux transporter on the other side (Ma et al., 2007) of the cell, an effective transcellular transport of Si can be insured in the plant.

Silica deposits in higher plants are reported (1) inside living cells, (2) in cell walls and membranes, and (3) in intercellular spaces (Lewin and Reimann, 1969; Sangster and Parry, 1981; Waterkeyn et al., 1982). Commonly, the epidermis is the principal deposition site in shoots, in contrast with roots where silica settles in the endodermis and the vascular system (Lux et al., 2003ab; Sangster and Hodson, 1986). In *Musaceae* (banana plant), phytoliths are reported (Mbida et al., 2001; Tomlinson, 1969) mainly in or near the bundle sheath sclerenchyma rather than in the epidermis (in the sheath cells of vascular bundles, Prychid et al. (2004)). To be absorbed by the roots, water, and nutrients and monosilicic acid can flow through (1) an intercellular pathway (apoplast) along cell walls and intercellular spaces without crossing any membrane, or (2) a cellular pathway: (i) transmembrane, or (ii) by symplast, through the cytoplasm of adjacent cells interconnected by junctions (plasmodesmata). Silica deposits were reported in cell walls of roots and leaves in forest trees (Watteau and Villemain, 2001),

and phytoliths were reported in wood (Vrydaghs et al., 1995) and pine needles (Hodson and Sangster, 1998).

Phytoliths present a broad range of morphologies depending on plant species (Figure 1.3) and location of Si deposits. A systematic approach has been established for monocotyledons (Prychid et al., 2004). An International Code for Phytolith Nomenclature (ICPN) has been proposed, based on their shape, their texture or ornamentation, and their anatomical origin (Madella et al. (2005); e.g. Figure 1.3). Phytoliths restituted to the soil by plant decay are used by paleobotanists, paleontologists and archaeologists for environmental and paleoenvironmental reconstitutions (Kelly et al., 1998; Pearsall and Piperno, 1993; Piperno, 1988; Rovner, 1971). Fossil phytolith assemblages in paleosoils are compared with modern soil phytolith assemblages for paleovegetation reconstruction (Alexandre et al., 1999; Bremond et al., 2005 2008; Strömberg, 2004).

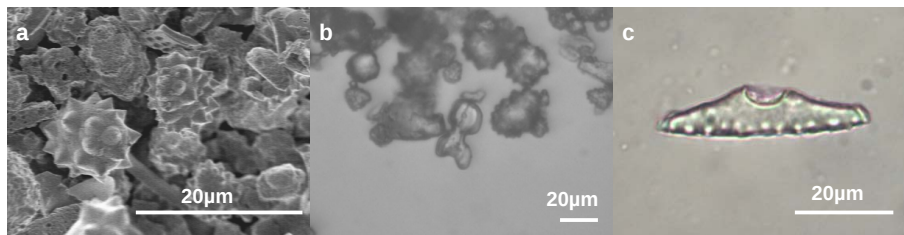


Figure 1.3: Various morphologies of phytoliths in different plant species: (a) spherical crenate from Palmae (SEM) - (b) bilobate short cell from grass (optical) - (c) rectangle cavate tuberculate from *Musa* (optical).

1.3.2 Silicon accumulation by plants

Silicon content in plants ranges between 0.1 and 10 % Si dry weight. (Hodson et al., 2005; Ma and Takahashi, 2002), which is significantly above the average Si content estimated for the global biosphere (0.03%). Silica biomineralization seems to be restricted to some plant families (Epstein, 1999; Hodson et al., 2005). Several monocotyledons (*Poaceae*, *Cyperaceae*) are Si-accumulating plants, in contrast with dicotyledons, mostly non Si-accumulating (Ma et al., 2001; Ma and Takahashi, 2002). Primitive land plants like horsetails (*Equisetum* sp.) are high Si-accumulating plants (mean shoot 3.9 %Si; Hodson et al. (2005)). This raises the question of the impact of these plants on the Si continental

cycle during the land colonization by plants during the Carboniferous period.

According to their Si-uptake modes, plants species are classified into three categories (Epstein, 1999; Sangster and Hodson, 1986; Takahashi et al., 1990):

- (1) Si-accumulating plants with an active uptake: Si is taken up in larger quantity than that predicted by mass flow,
- (2) non Si-accumulating plants with a rejective uptake inducing a Si-accumulation in the soil solution,
- (3) intermediate plants with passive diffusion by mass flow: Si is taken up in equal quantity as that predicted by mass flow.

Bananas (*Musa* sp., mean shoot 0.9 %Si; Hodson et al. (2005)) are Si-accumulating plants (Henriet et al., 2006). They actively take up Si from nutrient solution. However, the active transport is masked within the mass flow at large Si concentration in the solution (Henriet et al., 2006). A similar behavior was reported for other plant species (Liang et al., 2006). Some important Si-accumulating plants can be reported according to their mean shoot content of Si (Hodson et al., 2005):

- bamboo (*Bambusa* sp., up to 7% Si; Li et al. (2006)),
- sugar cane (*Saccharum* sp., 1.5 %Si),
- soybean (*Glycine* sp., 1.4 %Si),
- cereals: corn (*Zea* sp., 0.8 %Si), rice (*Oryza* sp., 4.2 %Si), wheat (*Triticum* sp., 2.4 %Si), barley (*Hordeum* sp., 1.8 %Si), sorghum (*Sorghum* sp., 1.5 %Si), mil (*Pennisetum* sp., 0.9 %Si), and oat (*Avena* sp., 1.5 %Si).

The difference in Si-accumulation between plant species is attributed to a higher density of transporters for Si uptake in high Si accumulating plants (Mitani et al., 2005).

1.3.3 Beneficial effects of silicon for plants

The essentiality of silicon as a plant nutrient has been debated, since Si nutrition has positive effects on crop yield (Epstein, 1999; Richmond and Sussman, 2003; Takahashi et al., 1990). Henriet et al. (2006) have shown that silicon accumulation in bananas did not have any effect on plant growth and biomass. There is a general consensus that plant silicon increases plant tolerance to biotic and abiotic stresses. It ensures structural, physiological and protective functions (Marschner, 1995; Sangster and Hodson, 1986): (1) structural by keeping leaf blades erected, thus improving light interception, (2) physiological by

reducing transpiration, thus improving drought resistance and tolerance to salts, (3) protective against mineral toxicity, fungal and insects attacks (Bélanger et al., 2003; Jones and Handreck, 1967). The positive effects of Si nutrition are so large that Si-containing fertilizers are routinely supplied to several crops to increase crop yield and quality, e.g. rice (Ma et al., 2001) and sugar cane (Savant et al., 1999).

1.4 Silicon in soils

Silicon is very abundant in soils and distributed between solid, liquid and adsorbed phase (McKeague and Cline, 1963c; Sommer et al., 2006) (Figure 1.4). In the solid phase, Si occurs in crystalline, poorly crystalline or microcrystalline, or amorphous forms (Drees et al., 1989). Soil Si constituents can be from litho- or pedo-genic origin corresponding to primary minerals inherited from parental material and to secondary minerals developed during soil formation, respectively. Biogenic Si

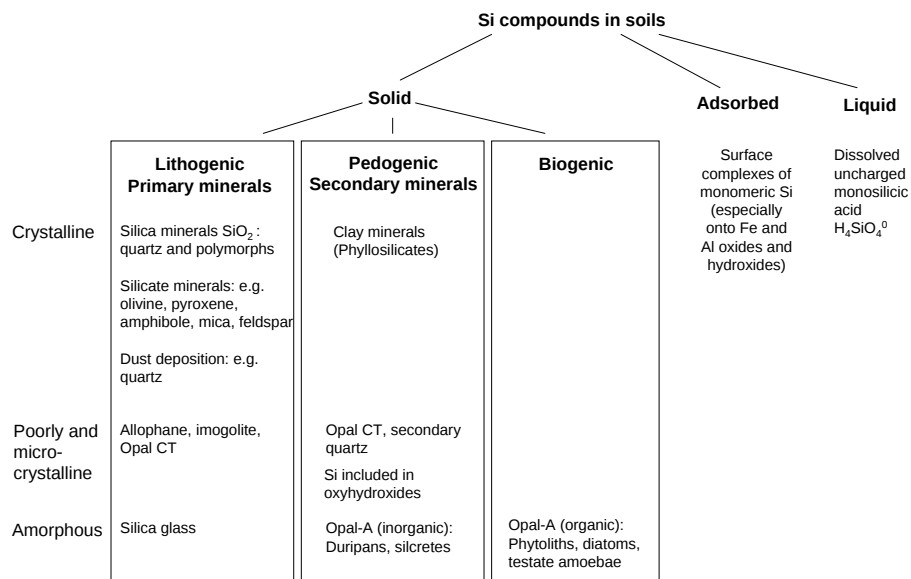


Figure 1.4: Silicon compounds in soils distributed between solid, adsorbed and liquid phase. Solid phase categories are based on the litho-, pedo- or bio-genic origin of the particles, taking into account crystalline, poorly crystalline and amorphous fractions (modified from Matichenkov and Bocharnikova (2001); Sauer et al. (2006)).

particles are also ubiquitous in soils and need to be taken into account in soil Si cycling. Adapted physical (grain size distribution, densimetric separation) or chemical (selective extractions) methods are required to separate the various Si fractions in soils to quantify and characterize them. In this thesis, attempts will be made to separate Si soil particles based on their litho-, pedo- or bio-genic origin, in order to tentatively quantify the biogenic Si recycling compared to weathering processes and neoformation of secondary minerals.

1.4.1 Lithogenic silicon

Depending on the nature of the parental material, primary minerals in soils will be distributed in variable proportion between crystalline, poorly crystalline or microcrystalline, and amorphous Si compounds. Crystalline forms of Si include silica SiO_2 (quartz and polymorphs: cristobalite and tridymite) (Monger and Kelly, 2002) and silicate minerals. The most common primary minerals from igneous rocks are olivine, pyroxene, amphibole, mica and feldspar (Schulze, 2002). Mineralogy of primary minerals in soils will strongly depend on the mafic (e.g. basalt) or felsic (e.g. granite) nature of the parental material. These primary minerals will be concentrated in the sand ($>50\mu\text{m}$) and silt ($2\text{--}50\mu\text{m}$) fractions, and can be extracted by particle size separation.

1.4.2 Pedogenic silicon

Secondary minerals are mainly constituted by clay-sized phyllosilicates and Al- and Fe-oxides. These minerals are formed from weathering solutions enriched by the products of the hydrolysis of primary minerals. The nature of clay minerals depends on silica activity in weathering solution, which strongly depends on soil mineralogy, soil weathering stage, and drainage governed by the rainfall pattern (White, 1995). Aqueous Si can be adsorbed onto Al- and Fe-oxides and integrated into their crystalline structure (Carlson and Schwertmann, 1981) contributing to the solid fraction of secondary Si. Secondary precipitates of opal-A and opal-CT rather than microcrystalline quartz were reported in duric soils (Chadwick et al., 1987b). Secondary clay minerals concentrate in the clay fraction ($<2\mu\text{m}$) extracted, and are mixed with clay-sized primary minerals and Al- and Fe-oxides. Clay-sized opaline particles precipitated following Si oversaturation were reported in soils (Henmi and Parfitt, 1980; Shoji and Masui, 1971; Tokashiki and Wada, 1975). To our knowledge, no method is available to separate this opal from the silicate clay minerals.

1.4.3 Biogenic silicon

Plant opal is ubiquitous in soils (Smithson, 1956) and usually ranges between 1 and 30 g kg⁻¹ (Drees et al., 1989). Within the biogenic Si (BSi) pool in soils, in addition to phytogenic Si from plants, microbial (bacterial, fungi) and protozoic Si were reported in soils (Sommer et al., 2006). Testate amoebae in soils also contribute as Si consumers and suppliers (Aoki et al., 2007).

Mineralogically, phytoliths are opal-A particles (Bartoli and Wilding, 1980) exhibiting an XRD spectrum characterized by a large broad range at 0.4nm (Drees et al., 1989). Their density varies between 1.5 and 2.3 g.cm⁻³, depending on particle porosity, H₂O content, and occluded organic matter (Drees et al., 1989). The solubility of amorphous Si in water to form monomeric H₄SiO₄ strongly depends on pH and increases from pH above 8 (Alexander et al., 1953). In neutral or slightly alkaline natural waters, H₄SiO₄ is the only species in equilibrium with amorphous Si, while at more alkaline pH, polymeric species are formed and solubility of amorphous Si increases (Stumm and Morgan, 1996). The solubility product of soil phytoliths ($pK_{sp}^0 = 2.74$ at 25°C) is equal to that of vitreous silica and is 17 times higher than that of quartz (Frayssé et al., 2006). However, phytoliths solubility strongly depends on their physical and chemical properties: specific surface area, Al content, hydration state, age, rate of decomposition of organic residues (Bartoli and Wilding, 1980). Phytolith solubility can also be affected by the chemical composition and the surface properties of biogenic opal particles. For instance, chemisorbed Al makes phytolith particles less soluble (Bartoli, 1985).

Through the soil profile, phytoliths can be preserved and thus constitute a stable BSi pool, or they can be dissolved (labile pool). Phytoliths can migrate through soil profile by drainage or bioturbation, and be accumulated at depth, inducing a variable depth-distribution of phytoliths in the soil profile (Clarke, 2003; Hart and Humphreys, 2004). In addition to paleoenvironmental reconstructions (section 1.3.1), phytoliths can be used to solve soil genesis and evolution questions (Gol'eva and Aleksandrovskii, 1999).

1.4.4 Adsorbed silicon

Among Si compounds in soils, Si adsorbed onto soils compounds need to be taken into account (McKeague and Cline, 1963c). Iron and aluminium oxides are the main components of soils with a significant capacity of adsorption (Beckwith and Reeve, 1963; McKeague and Cline,

1963b), although little adsorption has been reported onto clay minerals (Siever and Woodford, 1973). Aluminium oxides have a greater effect on Si sorption compared to iron oxides (Jones and Handreck, 1963). The Si species adsorbed is monosilicic acid (H_4SiO_4^0). Silicon adsorption is strongly pH-dependent and increases from pH 4 to pH 9 (McKeague and Cline, 1963b). Silicon adsorption on oxide surface is highly specific since it involves surface complexation through a ligand exchange reaction between OH^- ions (A type) from oxide surface and monosilicic acid (Parfitt, 1978). Surface Si polymerization readily occurs on oxide surface (Swedlund and Webster, 1999), and Si can be further integrated into the mineral structure (Vempati and Loeppert, 1989). Selective dissolutions of amorphous iron oxides (Blakemore et al., 1981) and free iron oxides (Mehra and Jackson, 1960) also extract Si adsorbed and included into mineral structure.

1.4.5 Silicon in soil solutions and drainage

The aqueous chemistry of Si is regulated by a number of coupled processes such as dissolution/precipitation, biogenic uptake and adsorption (Iler, 1979; Sjöberg, 1996). Si concentrations in soil solution usually range between 0.01 and 1.99 mM Si (below saturation limit of amorphous silica at 25°C; Karathanasis (2002)), and most commonly between 0.1 and 0.6 mM Si (Faure, 1991). This concentration strongly depends on parental material, soil weathering stage, temperature, rainfall pattern and residence time of pore water, and is controlled by the dissolution of given unstable minerals at given pH values, as predicted from a stability diagram (Karathanasis, 2002). Dissolved Si in soils is mainly uncharged monomeric H_4SiO_4^0 (McKeague and Cline, 1963a), stable in common soil pH values. Aqueous polymeric forms of Si occur at pH above 9 (Stumm and Morgan, 1996). Monosilicic acid is a very weak acid (dissociation constant at 25°C: $\text{pK}_1 = 9.51$; $\text{pK}_2 = 11.77$). Si has a very low affinity for organic compounds in natural waters (Pokrovski and Schott, 1998), and no organosilicon compounds have been identified so far under natural physiological conditions (Knight and Kinrade, 2001). Dissolved Si in soil solutions is exported by drainage and can be accumulated in silicified soil horizons (Chadwick et al., 1987a) or evacuated to the hydrosphere.

1.5 Tracers of silicon cycle

As silicon is a very abundant element on Earth, tracers are needed to study Si pathways in the continental context (Conley, 2002; Meunier, 2003). Isotopic (stable Si isotopes ^{28}Si , ^{29}Si , ^{30}Si) or geochemical

(germanium to silicon ratio) tools have been shown to be very useful tracers of weathering and biogeochemical processes. These tracers are affected by biological, chemical and/or physical processes under natural conditions.

1.5.1 Silicon stable isotopes

Stable isotopes

Isotopes of one element are atoms with similar number of protons (z) and electrons but differing by their number of neutrons (n). Therefore, isotopes have different atomic mass (m) given by the total protons and neutrons ($z + n$). Most of the elements have more than one isotope (except e.g. Be, Na, Al, Mn, F). Stable isotopes are not concerned by radioactive decay. Every isotope is characterized by its own vibration energy and capacity of movement depending on its mass: light isotopes react faster than heavy isotopes in a chemical reaction. Reactions thus induce an isotope fractionation, and would occur following chemical, physical or biological processes.

Two main types of mass-dependent isotope fractionation are reported for stable isotopes: kinetic and equilibrium (Young et al., 2002). Kinetic fractionation results from motions described using effective masses, while equilibrium exchange is a quantum phenomenon only depending on atomic masses. Kinetic fractionation is due to the higher mobility of light molecules and produces a phase enriched in light isotopes in fast chemical reactions such as diffusion and evaporation (e.g. liquid to vapor). Isotopic exchange occurs at thermodynamic equilibrium between species, and is governed by mass law. Heavy isotopes will be concentrated in the phase with the lower energy state (e.g. liquid phase in the condensation process).

The isotopic composition of a sample can be expressed as a δ variation (in parts per thousand ‰) relative to a standard: (1) the ratio R between the heavy isotope (rare) and the light isotope (abundant) in the sample, relative to (2) the same ratio R in a reference standard:

$$\delta = [(R_{\text{sample}}/R_{\text{standard}}) - 1] \times 1000$$

A positive delta value ($\delta > 0\text{‰}$) corresponds to an enrichment in the heavy isotope compared to the reference standard (heavier signature), while a negative delta value ($\delta < 0\text{‰}$) is depleted in heavy isotope compared to the reference material (lighter signature).

The degree of isotope fractionation between two materials is expressed in two ways, as α or ε . The fractionation factor α is the ratio R of the two materials A and B, with B considered as the source:

$$\alpha_{A-B} = R_A/R_B$$

When $\alpha = 1$, there is no isotopic fractionation. The fractionation between two materials A and B can also be expressed in ε notation. For small isotopic fractionations, the difference between the two δ of the materials A and B (Δ_{A-B}) offers a good approximation for ε if an isotopic equilibrium has been reached between the two phases:

$$\varepsilon \sim \Delta_{A-B} = \delta_A - \delta_B$$

First stable isotope studies were focused on very abundant elements with large isotopic variations (H, C, N, O, S). Isotopic variations (range of δ) decrease with increasing atomic masses due to smaller relative mass differences ($\Delta m/m$): e.g. ^{13}C is 8.3% heavier than ^{12}C while ^{97}Mo is 2.1% heavier than ^{95}Mo . Development of MC-ICP-MS (Chapter 4) provided a better precision to detect very small fractionations allowing the development of studies on “non-traditional” isotopic systems so far (e.g. B, Li, Mg, Si, K, Ca, Cr, Fe, Cu, Zn, Se, Mo). These elements are characterized by similar mass difference ($\Delta m/m$) but smaller natural isotopic variations (range of δ) compared to traditional stable isotopes (H, C, N, O, S). This has opened up a very promising and wide range of new studies in (bio)geosciences (Johnson et al., 2004).

To illustrate stable isotope fractionation in the context of the present thesis, plant-induced isotopic fractionation on different elements (Fe, Zn, B, Ca, Mg, N, C, O) are briefly reported.

For traditional isotopes (N, C, O):

$\delta^{18}\text{O}$ measured in plant phytoliths can be related to plant water and, and hence to soil water and climatic conditions (precipitations, temperature) during plant growth (Shahack-Gross et al., 1996; Webb and Longstaffe, 2000). Nitrogen isotopes were shown to be fractionated during the uptake and assimilation of ammonium ion (Yoneyama et al., 2001 1991) and N_2 fixation by plants (Okito et al., 2004). CO_2 concentration in root-zone impacts both C and N isotopic fractionation, hence modifying plant uptake and accumulation (Viktor and Cramer, 2003).

For non traditional isotopes (Fe, Zn, Mg, B, Ca):

Iron isotopic fractionation induced by plants is related to the strategies developed by plants to acquire Fe: strategy I plants acquiring Fe by

Fe^{III} reduction preferentially incorporate light Fe isotopes, while strategy II plants acquiring Fe through Fe^{III} complexation by siderophores preferentially take up heavy Fe isotopes (Guelke and Von Blanckenburg, 2007). Zn isotopic composition of plants depends on Zn speciation in solution (Zn²⁺ is preferred compared to complexed Zn). Plant uptake of Zn was shown to induce two fractionation steps: from solution, roots preferentially take up heavy isotopes whereas from roots, light isotopes are preferentially transferred to shoots (Viers et al., 2007; Weiss et al., 2005). Preliminary results on Mg suggest the preferential uptake of heavy Mg by plants (Bi et al., 2007). Boron, an essential micronutrient for plants, displays variations of $\delta^{11}\text{B}$ in plants influenced by soil type, water content and fertilizer use (Wieser et al., 2001). Calcium uptake by plants was shown to favor light ⁴⁰Ca relative to ⁴⁴Ca, which produces a significant increase in ⁴⁴Ca content in soil exchangeable pools (Wiegand et al., 2005). The plant-induced Si isotopic fractionation will be developed in details in this thesis.

Fractionation of silicon stable isotopes

Silicon ($z = 14$, atomic mass = 28.0855) is a metalloid of valence +4 covalently bonded to O as a tetrahedron in the stable silicate anion (SiO_4^{4-}). Silicon has three stable isotopes of atomic mass units (amu) ²⁸Si (27.976927), ²⁹Si (28.976495), and ³⁰Si (29.973770) with respective abundance 92.23%, 4.67%, 3.10% (Faure and Mensing, 2005). The relative mass differences ($\Delta m/m$) are 7.8% between ³⁰Si and ²⁸Si compared to 3.5% between ²⁹Si and ²⁸Si. It has to be mentioned that Si has also a fourth naturally occurring but radioactive isotope (³²Si) of cosmogenic origin ($T_{1/2} = 140 \pm 6$ years).

So far there exists no trustable certified standard for Si isotopic composition (Reynolds et al., 2006b). The Si isotopic composition of a sample is therefore expressed as a δ variation relative to the NBS28 silica sand standard (National Institute of Standard and Technology RM #8546) for silicon isotopes (Carignan et al., 2004). Although not certified for its Si isotopic composition, the NBS28 is certified for its oxygen isotopic composition, and has long been used as the $\delta^{18}\text{O}$ standard for silicated samples, and has been found to be isotopically very homogeneous. The Si isotopic compositions are commonly expressed as $\delta^{30}\text{Si}$ and can also be measured and expressed as $\delta^{29}\text{Si}$ (‰) as following:

$$\delta^{30}\text{Si} = \left[\frac{\left(\frac{{}^{30}\text{Si}}{{}^{28}\text{Si}} \right)_{\text{sample}}}{\left(\frac{{}^{30}\text{Si}}{{}^{28}\text{Si}} \right)_{\text{NBS28}}} - 1 \right] \times 1000 \quad \text{or} \quad \delta^{29}\text{Si} = \left[\frac{\left(\frac{{}^{29}\text{Si}}{{}^{28}\text{Si}} \right)_{\text{sample}}}{\left(\frac{{}^{29}\text{Si}}{{}^{28}\text{Si}} \right)_{\text{NBS28}}} - 1 \right] \times 1000$$

The first isotopic compositions measured in earth samples were reported to the CalTech Rose Quartz Standard (RQS) (Douthitt, 1982). Although long been considered as fractionated compared to NBS28 (De La Rocha et al., 1998; Molini-Velsko et al., 1986; Robert and Chaussidon, 2006), the Rose Quartz Standard has been recently shown to be isotopically similar to NBS28 ($\delta^{30}\text{Si}$ vs. NBS28 = -0.02‰; Georg et al. (2007b)) which allows direct comparison between data reported to RQS and NBS28.

Stable isotope variations are commonly described as mass-dependent fractionations (section 1.5.1). For Si, this corresponds to a three-isotope space as $\delta^{29}\text{Si}$ vs. $\delta^{30}\text{Si}$ plot. With a mass-dependent fractionation, measurements should fit onto a straight line within the three-isotope space, and any deviation from this trend could be attributed to mass-independent fractionations (Clayton et al., 1973). Extraterrestrial SiC grains in meteorites do not fit to the mass-dependent fractionation line (Stone et al., 1991), which reveals anomalies of mass-independent ^{30}Si enrichment during presolar nucleosynthesis (Zinner et al., 1989). No mass-independent fractionations have been reported so far in terrestrial materials, so measurements in terrestrial samples should fit to a straight line within a $\delta^{29}\text{Si}$ vs. $\delta^{30}\text{Si}$ plot. The slope depends on the fractionation process, e.g. equilibrium or kinetic (section 1.5.1) and can be calculated with the exact atomic masses of Si isotopes (Young et al., 2002):

$$\text{Equilibrium fractionation} \quad \beta = \frac{(1/m_1 - 1/m_2)}{(1/m_1 - 1/m_3)}$$

$$\text{Kinetic fractionation} \quad \beta = \frac{\ln(m_1/m_2)}{\ln(m_1/m_3)}$$

With $m_1 = ^{28}\text{Si}$ (27.976927), $m_2 = ^{29}\text{Si}$ (28.976495), and $m_3 = ^{30}\text{Si}$ (29.973770). The corresponding slopes are 0.5178 for equilibrium and 0.5092 for kinetic fractionation. These two slopes are very close and the current precision and/or number on the measurements is not sufficient in most cases to resolve differences between kinetic or equilibrium fractionation. Using the above equations, data measured as $\delta^{29}\text{Si}$ only can be converted into $\delta^{30}\text{Si}$ data with $\delta^{30}\text{Si} = \delta^{29}\text{Si} \times 1.93$ following an equilibrium mass-dependent fractionation, or $\delta^{30}\text{Si} = \delta^{29}\text{Si} \times 1.96$ following a kinetic mass-dependent fractionation. In the present thesis, data measured as $\delta^{29}\text{Si}$ only can be converted as $\delta^{30}\text{Si}$ using the

multiplying factor 1.93 assuming a mass-dependent fractionation process following the equilibrium fractionation law, as supported by equilibrium fractionation processes observed in natural rivers (Georg et al., 2006a 2007c).

Silicon isotopic variations on Earth

Only Si-O components are found on Earth (no gaseous phase) and Si stands with one valence +4 in natural conditions. For these reasons, the range of terrestrial Si isotopic variations is small ($\delta^{30}\text{Si} = -5.7$ to $+6.1\text{‰}$; Basile-Doelsch et al. (2005); Ding et al. (2005b)) compared to other light stable isotopic systems (C, H, O, N and S) (Ding et al., 1996).

The bulk silicate Earth (BSE) signature estimated from meteoritic (chondritic) composition is at -0.55‰ (Molini-Velsko et al., 1986). The differentiation produced three main reservoirs with distinct signatures. The Earth's crust (felsic igneous rocks including granitoids, gneiss, granulites, migmatites) is significantly heavier than the BSE (0‰ ; Ding et al. (1996)). The Earth's mantle (mafic igneous rocks (terrestrial and lunar basalts), mantle peridotite, lherzolite) displays intermediate signature (-0.3‰ ; Georg et al. (2007b)). From these data, it was suggested that Si was incorporated preferentially as a light isotope in the Earth's core before the Moon formed, following partition between metal and silicate (Georg et al., 2007b) inducing a lighter core signature relative to the BSE.

Silicon isotopic variations at the Earth's surface

The range of isotopic variations at the Earth surface is 11.8‰ large from -5.7‰ in silcretes (Basile-Doelsch et al., 2005) to $+6.1\text{‰}$ in rice grains (Ding et al., 2005b). This range can be attributed to three distinct processes of isotopic fractionation: (1) rock-forming processes, (2) water-rock interactions, and (3) biogenic processes.

Rock-forming processes are based on exchange reactions (i) solid-liquid (silicate crystal and silicate melt) or (ii) solid-solid (crystal-crystal). Exchange between silicate minerals (Quartz-Feldspar, Feldspar-Hornblende, Feldspar-Pyroxene) induces small fractionations of 0.2 - 0.5‰ (Ding et al., 1996). Theoretical calculations attest for equilibrium fractionation of Si isotopes between kaolinite and quartz (Méheut et al., 2007) and support that the ^{30}Si content increases with the degree of silicate polymerization due to vibrational properties of silicates (Ding et al., 1996).

Water-rock interactions concern liquid-solid exchanges between monosilicic acid and (i) inorganic silica, (ii) adsorption onto oxides, or (iii) clay minerals. This includes low temperature processes like weathering but also high temperature processes like hydrothermalism, diagenetic and metamorphic reactions. Samples are slightly fractionated by these water-rock interactions (0.5-3‰) but as these processes can be repeated, a large final fractionation can be produced (Figure 1.5).

Biogenic processes concern liquid- biota transfer of monosilicic acid leading to the formation of biogenic opal, e.g. in plants, diatoms and sponges, and can induce large isotopic fractionations (Figure 1.5).

Apart from recent published data, most available Si isotopic data were compiled into some reviews (Basile-Doelsch, 2006; Ding et al., 1996; Douthitt, 1982). The different reservoirs in continental and marine environments are presented in Figure 1.5.

Endogeneous rocks present signatures ranging from -1.1‰ to +0.5‰: crustal rocks (felsic igneous rocks, gneiss, granulites and migmatites: mean of 0‰) are heavier than mantle rocks (mafic igneous rocks, peridotite: mean of -0.3‰) (Ding et al., 1996; Douthitt, 1982). Sedimentary rocks (schist, slate, quartzite, sandstone) and river suspended matter display signatures in the same range than endogeneous rocks (Ding et al., 1996). Seawater-rocks interactions are involved in modern continental and seafloor siliceous deposits (Ding et al., 1996), but also in Precambrian Banded Iron Formations (BIFs), cherts and silicified basalts induced by past interactions of seafloor basalts with oceanic hydrothermal fluids (Abraham et al., 2007; André et al., 2006; Robert and Chaussidon, 2006; van den Boorn et al., 2007).

Dissolved Si in fresh waters (rivers and lakes) and seawater is ^{30}Si -enriched. Signatures of fresh waters range between +0.4 and +3.4‰ (Alleman et al., 2005; De La Rocha et al., 2000; Ding et al., 2004; Georg et al., 2006a 2007c) and that of groundwaters between -1.43 and +0.43‰ (Georg et al., 2007a 2005). Seawater and sea ice display signatures between +0.4 and +3.1‰ (Cardinal et al., 2005; De La Rocha et al., 2000; Fripiat et al., 2007; Reynolds et al., 2006a; Varela et al., 2004).

Compared to the water ^{30}Si -enriched pool, a continental ^{30}Si -depleted reservoir has been constituted by different processes discriminating against heavy Si isotopes. (i) Clay minerals signatures range between -2.5 and -1.9‰ and are generally lighter than the parental igneous rocks (Douthitt, 1982; Ziegler et al., 2005ab). This means that Si isotopic signatures in soils can be used as an indicator of lithogenic or pedogenic mineral origin (see sections 1.4.1 and 1.4.2). (ii) Formation

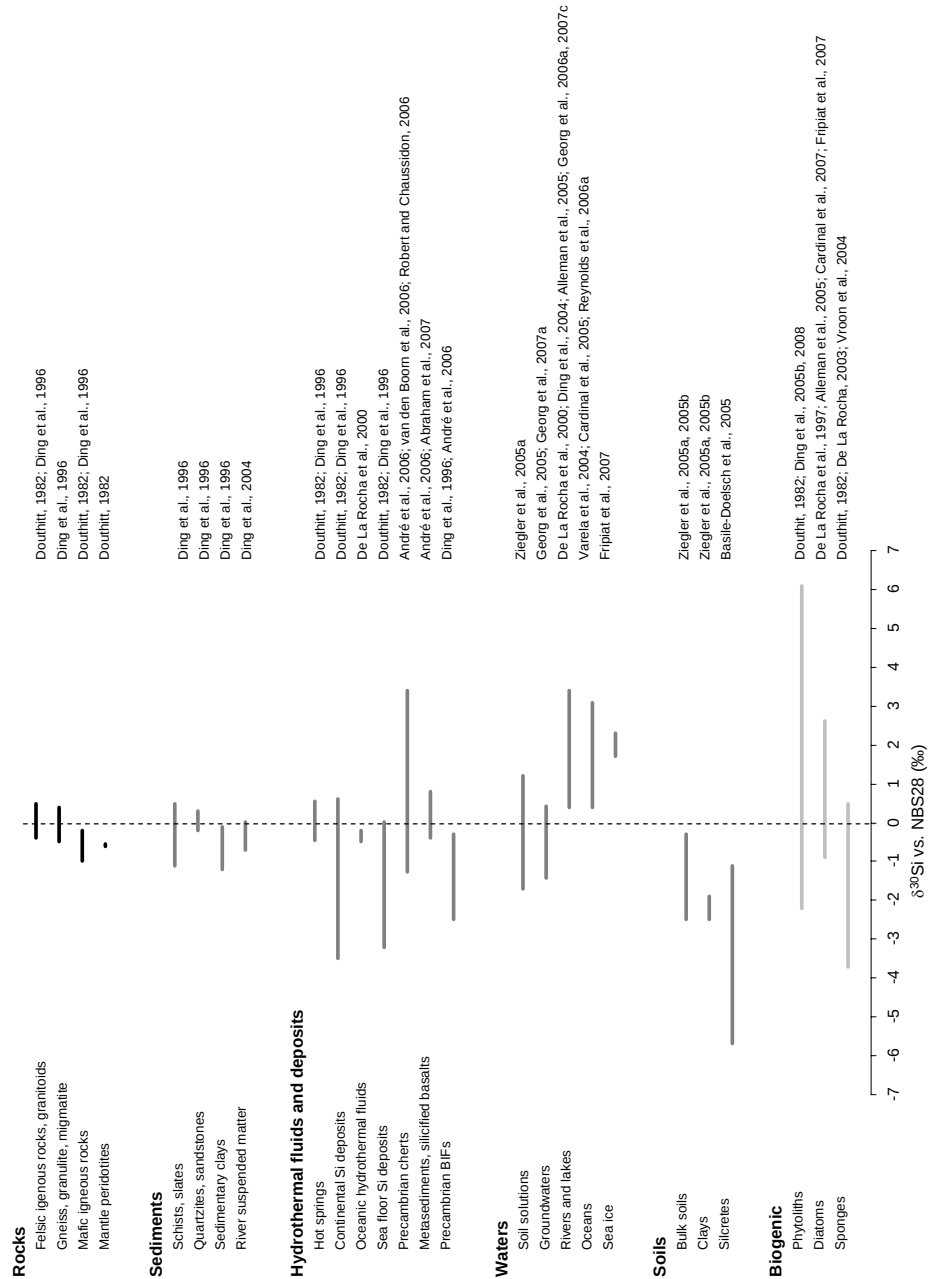


Figure 1.5: Si isotopic variations on Earth: small fractionation by rock-forming processes (black), larger fractionation with water-rock interactions (dark grey), and large fractionation by biogenic processes (light grey). The vertical dotted line represents the crustal isotopic composition.

of silcretes is the currently lightest Si isotopic reservoir on Earth (mean = -3.8‰ ; Basile-Doelsch et al. (2005)). (iii) Biomineralization induces a range of isotopic variations of 9.8‰ corresponding to 83% of the whole terrestrial isotopic range (11.8‰) which gives to this pool a large impact on the continental Si isotopic budget, through Si uptake by diatoms (Alleman et al., 2005; Cardinal et al., 2007; De La Rocha et al., 1997; Fripiat et al., 2007), sponges (De La Rocha, 2003; Douthitt, 1982; Vroon et al., 2004), and plants (Ding et al., 2005b 2008; Douthitt, 1982; Engström et al., 2007; Ziegler et al., 2005a).

Si stable isotopes are still considered as a new tracer as few data in terrestrial samples are available, and fractionation factors are poorly quantified. The present thesis uses the Si stable isotopes to contribute to identify processes responsible for isotopic fractionation in the soil-plant system and quantify their fractionation factors, and hence trace the Si continental recycling.

1.5.2 Germanium/silicon ratio

Germanium ($z = 32$, atomic mass = 72.64) is a metalloid from group IV elements like Si, exhibiting the coordination numbers 4 and 6 in its oxygen compounds, but mainly occurring in tetrahedral coordination based on structural analogies with silicates ($\text{Ge-O} = 1.75 \text{ \AA}$; $\text{Si-O} = 1.64 \text{ \AA}$). This allows isomorphic substitution of Ge for Si in tetrahedral sites of silicate lattice by the principle of “camouflage” (Goldschmidt, 1958). Ge is a trace element in the Earth’s crust (mean of 1.7 ppm Ge ranging from 0.08 to 6 ppm Ge; Bernstein (1985); Wittmann and Hörmann (1972)) and presents very low concentration in rivers and ocean (0.06 ppb Ge; Burton et al. (1959)). Ge is considered as a chemical analog to Si which allows using Ge/Si ratio as a tracer of terrestrial Si cycling in weathering and hydrological processes. Range of Ge/Si variations on Earth are presented by reservoirs in Figure 1.6.

In aquatic environments, Ge and Si follow similar inorganic geochemical pathways (Froelich et al., 1985; Mortlock and Froelich, 1987; Murnane and Stallard, 1990). Inorganic Ge (H_4GeO_4 , germanic acid, $\text{pK}_1 = 8.5\text{--}8.8$, $\text{pK}_2 = 12.7$) is removed from solution and incorporated into biogenic opal from diatoms and sponges just like Si (H_4SiO_4) (Ellwood et al., 2006; Froelich et al., 1992 1989). The registered Ge/Si ratio in buried biogenic opal can be used to trace past Si contributions from weathering and hydrothermal circulation to lakes and oceans (Ellwood et al., 2006; Filippelli et al., 2000; Froelich et al., 1992 1985). However, the Ge/Si tracer must be used with caution as (i) Ge can also be removed from oceans in iron-rich reducing sediments (Hammond

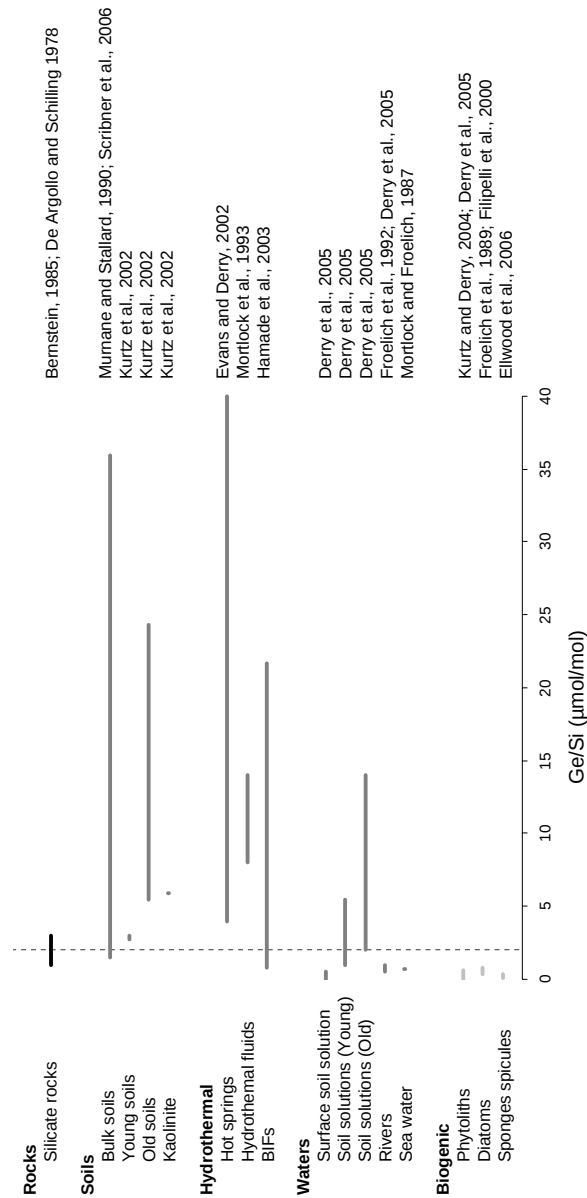


Figure 1.6: Variations of the Ge/Si ratios in terrestrial samples. The vertical dotted line represent the mean crustal Ge/Si ratio: on the left side of this line, there is a relative Ge depletion, while on the right side there is a relative Ge enrichment. Hot springs are ranging beyond this graph (4 to 1000 $\mu\text{mol/mol}$; [Evans and Derry \(2002\)](#)).

et al., 2000; King et al., 2000; McManus et al., 2003), and (ii) in organic-rich surface waters, Ge forms stable organic complexes while Si-organic complexation is significantly weaker or does not occur (Pokrovski and Schott, 1998), which would differently affect the biogeochemical cycles of Ge and Si (Pokrovski et al., 2000; Pokrovski and Schott, 1998). An important Ge/Si fractionation occurs in hot springs, hydrothermal fluids and Precambrian Banded Iron Formations (BIFs) (Evans and Derry, 2002; Hamade et al., 2003; Mortlock et al., 1993).

Under a continental context, the Ge/Si ratio has been used to trace weathering (Kurtz et al., 2002; Scribner et al., 2006). Secondary silicate minerals, iron oxyhydroxides and organic matter are potential reservoirs of Ge in soils. Ge sequestration in secondary clay minerals is the main factor responsible for Ge/Si fractionation, but Ge retention onto oxyhydroxides also contributes to this fractionation (Scribner et al., 2006). However, Ge/Si fractionation is not related to the precipitation of Fe-oxyhydroxides (Scribner et al., 2006). Compared to crustal rocks ($\text{Ge/Si} = 1\text{--}3\mu\text{mol/mol}$; De Argollo and Schilling (1978)), Ge is concentrated in secondary clay minerals ($\text{Ge/Si} = 5.9\mu\text{mol/mol}$ in kaolinite; Kurtz et al. (2002)) as shown by comparison between bedrock and bulk soils (Kurtz et al., 2002; Mortlock and Froelich, 1987; Murnane and Stallard, 1990).

Just as for diatoms, Ge is taken by plants. However, high Ge concentration could be toxic for plants partly due to Ge specific competitive inhibition of Si metabolism (Sankhla and Sankhla, 1967; Takahashi et al., 1976). Very low Ge/Si ratio were reported in phytoliths ($0.05\text{--}0.6\mu\text{mol/mol}$; Derry et al. (2005); Kurtz and Derry (2004)). Phytoliths Ge/Si ratios were shown to be smaller than their feeding source (e.g. for wheat in hydroponics: phytoliths = $0.05\mu\text{mol/mol}$, source = $0.4\mu\text{mol/mol}$) (Blecker et al., 2007; Kurtz and Derry, 2004). However, plant uptake of Ge and the very low Ge/Si ratio of phytoliths are still poorly understood. Besides, very low Ge/Si ratio in phytoliths were shown to impact significantly the Ge/Si ratio of soil solution in surface horizons (Derry et al., 2005).

In the present thesis, the tracer provided by Ge/Si ratio is compared with Si isotopes measurements (i) in plants to contribute to the understanding of Ge and Si uptake by plant and the low Ge/Si ratio found in phytoliths, and (ii) in soils to evaluate the biogenic Si input relative to weathering processes.

Chapter 2

Banana (*Musa* spp.) as silicon accumulating plant

2.1 Origin and varieties

Banana is a plant from the Genus *Musa*, Family *Musaceae*, Order Zingiberales. This genus includes bananas and plantains, which are one of the world most important crops developed almost exclusively in developing countries in the tropics. There are over 50 species of *Musa*. The main group of edible bananas derived from *Musa acuminata* and *Musa balbisiana*. *Musa* species are grouped according to “ploidy”, the number of chromosome sets they contain, and the relative proportion of *Musa acuminata* (A) and *Musa balbisiana* (B) in their genome. Most familiar cultivated varieties (cultivars) of banana are triploid hybrids (AAA, AAB, ABB). The Cavendish or Dwarf Cavendish (AAA group) is the most commonly banana cultivar in the world banana trade. Cultivated *Musa* species are sterile or have extremely low fertility. They produce fruit pulp without pollination and fruits lacking seed ([Champion, 1963](#)).

Musa species are native from the Indo-Malesian, Asian, and Australian tropics ([Price, 1995b](#)). The earliest known occurrence of banana cultivation (*Musa*) in central Africa is dated from 2500 before present, and was evidenced by archaeologists who observed phytoliths (biogenic opal) in soils from central Cameroon ([Mbida et al., 2001](#)). These phytoliths were compared with phytoliths from fresh vegetal tissues of Genus *Musa* and Genus *Ensete* (wild banana), and were clearly identified as *Musa* phytoliths ([Mbida et al., 2001](#)).

In this thesis, experiments in hydroponics and sampling in Cameroun were focused on *Musa acuminata* Colla cv Grande Naine (from the AAA

Cavendish group).

2.2 Banana morphology

Banana is a giant perennial monocotyledonous herb 2-9m height arising from large subterranean rhizomes (corm) (see Figure 8.1). From the mother rhizome emerges a sucker (new plant). Roots are formed from the corm and spread laterally (4-5m) and vertically (75cm), but they mostly develop in the top 15cm (Price, 1995a). Leaves emerge from the central part of the plant, and leaf sheaths constitute the “pseudostem”, with external sheaths corresponding to oldest leaves. The leaf sheath becomes thinner in upper parts, and constitutes the petiole then the midrib in the middle of the limb. Leaves emerge following a left-handed spiral at the top of the pseudostem, first as a cigar tightly rolled, and further unfold. There is constantly around 10-15 functioning leaves with a new leaf produced every 7-10 days (Karamura and Karamura, 1995). Upon flowering, a flower cluster emerges from the center of the bunch of leaves. The flower cluster is supported by a peduncle. A flower cluster produces about 9-12 flowers (hand, female) and ends by a bract (male). Flowers evolve as individual clusters of fruits (referred to as “hands”) with individual fruits (referred to as “fingers”). The flowering parts and fruit are referred to as the bunch (Karamura and Karamura, 1995). The flowering stage where hand female flowers are uncovered is known as a reference stage for leaf sampling in mineral nutrition studies (see Figure 8.1). The international foliar sampling procedure recommend to sample the third leaf before the flower cluster, referred to as leaf III (Martin-Prével (1984); see Figure 8.1).

2.3 Crop requirements

Optimum conditions for banana culture are: latitude between 30°N-30°S, altitude between 0-1800m, temperature tolerated between 17-28°C but optimum around 25-28°C, precipitations from 1500 to 2500mm, pH from 4.5 to 8.5 but optimum at 6-7 (Westphal, 1985). Changes in climate, water supply or light would induce a response of banana plant to changes in the environment (Turner, 1995).

To produce a crop yield of 50t ha⁻¹ year⁻¹ of fruits, bananas require high amounts of nutrients, which are only supplied in part by soil (Lahav, 1995). The large mineral requirement of banana induces a high rhizosphere weathering potential (Delvaux and Rufyikiri, 2003). Indeed, banana roots mobilize nutrients from alumino-silicates (Hinsinger et al.,

2001; Rufyikiri et al., 2004). Organic mulching and mineral fertilizers are applied in available forms to ensure macroelemental (N, P, K, Ca, Mg) and microelemental nutrition (S, B, Fe, Mn, Zn, Cu, Mo, Na, Cl) (Lahav, 1995). However, to optimize the mineral nutrition, fertilization has to be adapted depending on the soil retention capacity for the elements (Delvaux, 1995). Weathering stage of the soil will directly impact mineral reserve, cationic exchange capacity (CEC) and pH. Soil management practices have to be developed consequently, as irrigation and drainage, splitting fertilization, or tillage (Delvaux, 1995).

In tropical areas, banana is cultivated as permanent plantations (Central and South America) or small farms replanted after 3-8 years (French Antilles, Africa) (Stover, 1987). Cameroon plantations are typically large plantations, where banana plots are usually replanted after around 5-8 years because of declining yields. Banana fields are commonly irrigated during the dry season; in Cameroon, fertilizers (N, P, K, Mg) are applied on a monthly basis whereas lime amendments (Ca) are applied on a two-years basis. Rotations with other cultures (e.g. pineapple) are sometimes used.

The planting density (depending on the species) is defined as a good ratio between space and canopy overlap to avoid reducing light interception (Robinson, 1995): e.g. an arrangement of 1666 plants/ha consists of twins rows (2 m) every 6m which allow access in large rows but optimize irrigation and fertilization by plant. In Cameroon, plantations are arranged as single rows spaced every 3 meters, with mulching at the center of the rows. Senescent hanging leaves are removed and left on the ground along the plant cycle and functioning leaves may be sacrificed to improve fruit quality (Robinson, 1995). The cropping systems are based on successive cycles of 7-9 months before harvesting. At harvesting time, the bunch is exported, while banana leaves and pseudostem of the flowered plant are cut and left on soil surface. The sucker 6-8 months old standing close to the mother plant starts a new cycle of 7-9 months. Sucker management consists in selecting the following sucker but also destroying unwanted suckers (Robinson, 1995). These cultural practices ensure that the only vegetal output from the soil-banana system is the bunch, as all leaves and stems are left on the ground and used for mulching.

2.4 Silicon in banana

Phytoliths in banana were reported as silica cells common in all parts except roots (Tomlinson, 1969). They were drawn as typical cone shaped

(Tomlinson, 1969) truncated saddle-like, with a basal part rectangular to squarish with protuberances on surface, corresponding to the typical *Musa* phytolith (Mbida et al. (2001); Figure 2.1a), forming long chain in vegetal tissue (Figure 2.1b). These silica bodies were localized as one per cell over foliar vascular bundle sheath fibers (Prychid et al., 2004).

Silicon concentration was found to increase with growth in banana shoots but not in roots, with up to 3.8%Si in pseudostem (Jauhari et al., 1974). Even with 2% of Si in plant, Si was not considered as an essential element for banana (Lahav, 1995). Banana plant takes up silicon through both massflow and active transport (Henriet et al., 2006). Consequently, banana can be considered as a Si-accumulating plant (Hodson et al., 2005; Ma and Takahashi, 2002).

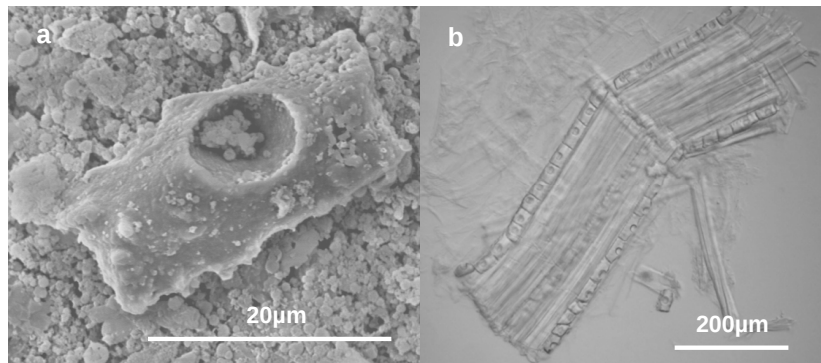


Figure 2.1: Banana (*Musa* spp.) phytoliths: (a) single morphotype (SEM, hydroponics) - (b) long chain of phytoliths in vegetal tissue (optical, Cameroon).

A gradient of Si concentration from root to pseudostem to leaf was identified in hydroponic culture (Henriet et al., 2006) and within leaf (from petiole to external limb) in mature banana plants, following transpiration rate of these organs (Henriet, 2008). The Si status of the plant was shown to be strongly correlated to Si supply (Henriet et al., 2006) and to mineral reserve in soils (Henriet, 2008). Moreover, Si biomineralization by the plant and restitution of phytoliths to soil by decomposition of vegetal tissues was shown to induce a stock of biogenic Si in soils strongly related to the mineral reserve of soils (Henriet, 2008).

With a Si gradient within the plant (Henriet et al., 2006) related to the presence of phytoliths (Prychid et al., 2004; Tomlinson, 1969), and a potential root-induced mineral dissolution of silicates (Delvaux and Rufyikiri (2003); Hinsinger et al. (2001); Rufyikiri et al. (2004);

see section 2.3), banana plant constitute a valuable model to study the impact of plants on the Si continental cycle, and hence the plant-induced Si isotope fractionation.

Chapter 3

Study sites in Cameroon: environmental settings

3.1 Geography

The studied areas are located in Cameroon (3-12° N; 9-16° E; 475 400 km²), West Africa, a country surrounded by Nigeria, Tchad, Central African Republic, Congo, Gabon, Equatorial Guinea, and the Gulf of Guinea (Figure 3.1). Cameroon can be subdivided in three main zones of altitude (Figure 3.2) with (i) lowlands (Manfé, Bénoué, North plain), (ii) plateaux (South-Cameroon), and (iii) the Cameroon volcanic line oriented SSW-NNE including Mounts Cameroon (alt. 4095m), Koupé (alt. 2050m), Manengouba (alt. 2396m), Bamboutos, N’Kogam, M’Bam, Bamenda, Atlantika, and Mandara. Yaoundé is the capital of Cameroon but Douala (harbor) is the central economical city of Cameroon. In the surrounding provinces of Douala, volcanic soils were allocated to intensive banana culture (Delvaux, 1988).

Banana plantations in Cameroon are essentially concentrated in the Mount Cameroon area (South West province) and in the Mungo area (Littoral Province) (Figure 3.1, Figure 3.3): in the Mount Cameroon area, banana plantations are located (i) on low East slopes of Mount Cameroon (alt. 300 to 600m) between 4°09’-4°13’N and 9°16’-9°21’E and (ii) in the Tiko plain (alt. 50-60m) between 4°05’-4°06’N and 9°21’-9°22’E; in the Mungo area, plantations are spread from 4°30’-4°53’N and 9°37’-9°50’E between 45 and 520m altitude between volcanic cones and lava slopes (40-600m altitude) (Delvaux, 1988). The two studied areas are affected to intensive banana cropping since the fifties and will be referred to as Mungo and Mt Cameroon respectively. The first site is located in the Mungo plain between 100 and 250m asl, axis Njombé-

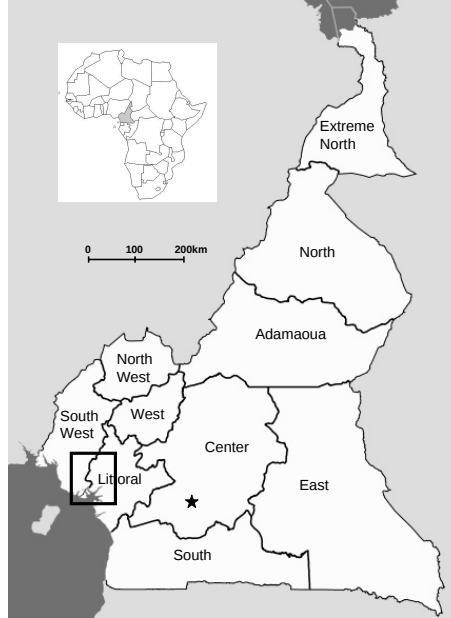


Figure 3.1: Cameroon map (West Africa) and provinces of Cameroon (Yaoundé = star). The black square indicates the zone of interest.

Penja-Loum ($4^{\circ}30'-4^{\circ}53'N$ $9^{\circ}37'-9^{\circ}50'E$) at 70km north of Douala, in the PHP plantations (Plantations du Haut Penja). The second site is located on the low East slopes of Mt Cameroon volcano between 500 and 700m asl around Molyko-Ekona-Mussaka ($4^{\circ}09'-4^{\circ}13'N$ $9^{\circ}16'-9^{\circ}21'E$) close to the city of Buea, in the CDC plantations (Cameroon Development Corporation).

3.2 Climate

Cameroon is located in the inter-tropical zone. The climate is influenced by both the winter Saharan anticyclone (NE winds -harmattan-), and the summer austral Saint-Helena anticyclone (SW rain-bearing winds) (Génieux, 1959). This results in a large range of climatic regimes from North to South: from a tropical climate in the North (two seasons) to an equatorial climate with four seasons in the Center and the South: two rainy seasons (March-June and September-November) and two dry seasons (December-March and July-August) (Sieffermann, 1973). Locally, in the South West Cameroon, the climate is modified by the relief, as continental air masses are blocked between Mount

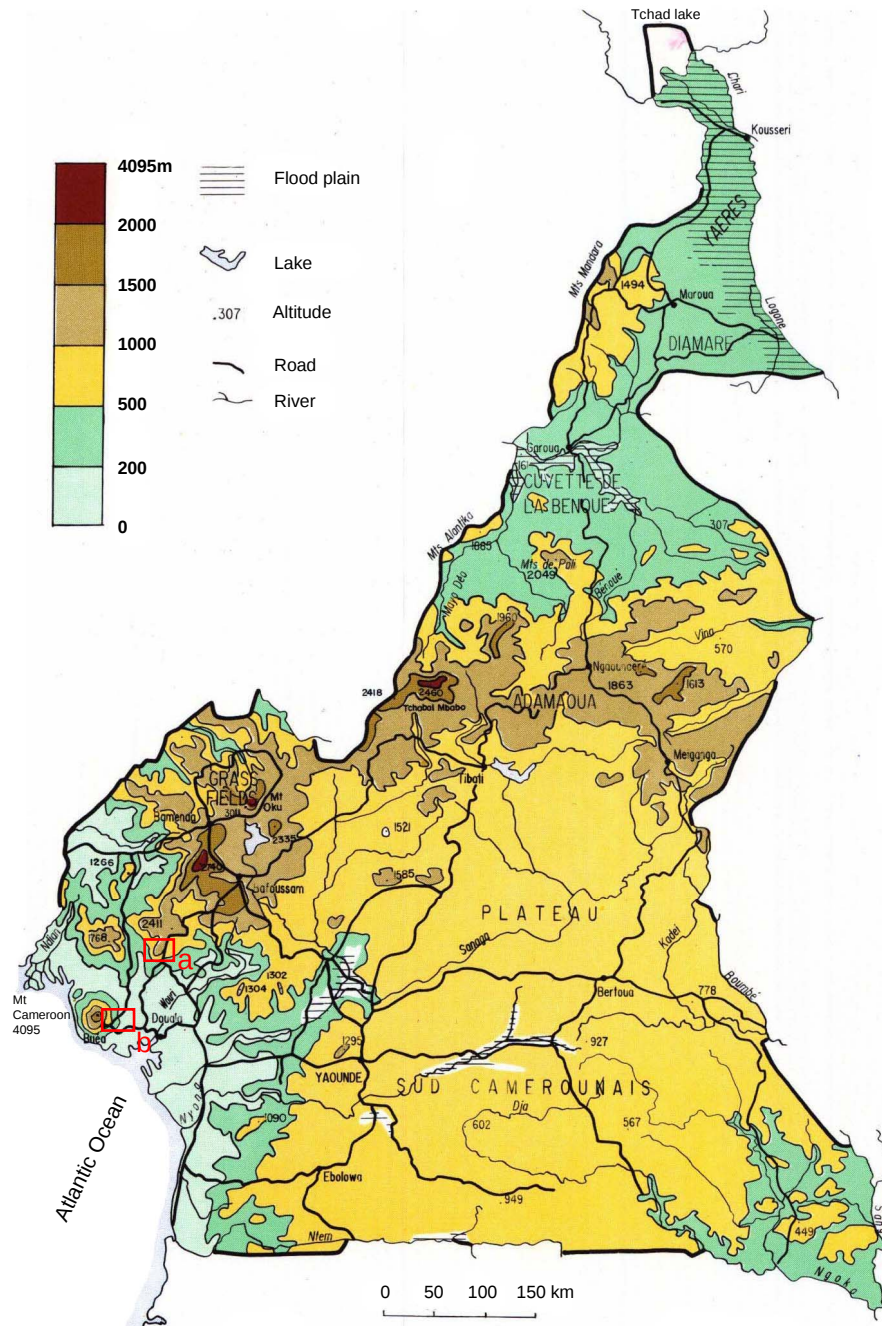


Figure 3.2: Orohydrography of Cameroon (modified from [Laclavère \(1979\)](#)) with the main South Cameroon plateau and the Cameroon volcanic line: (a) Mungo area - (b) Mount Cameroon area.

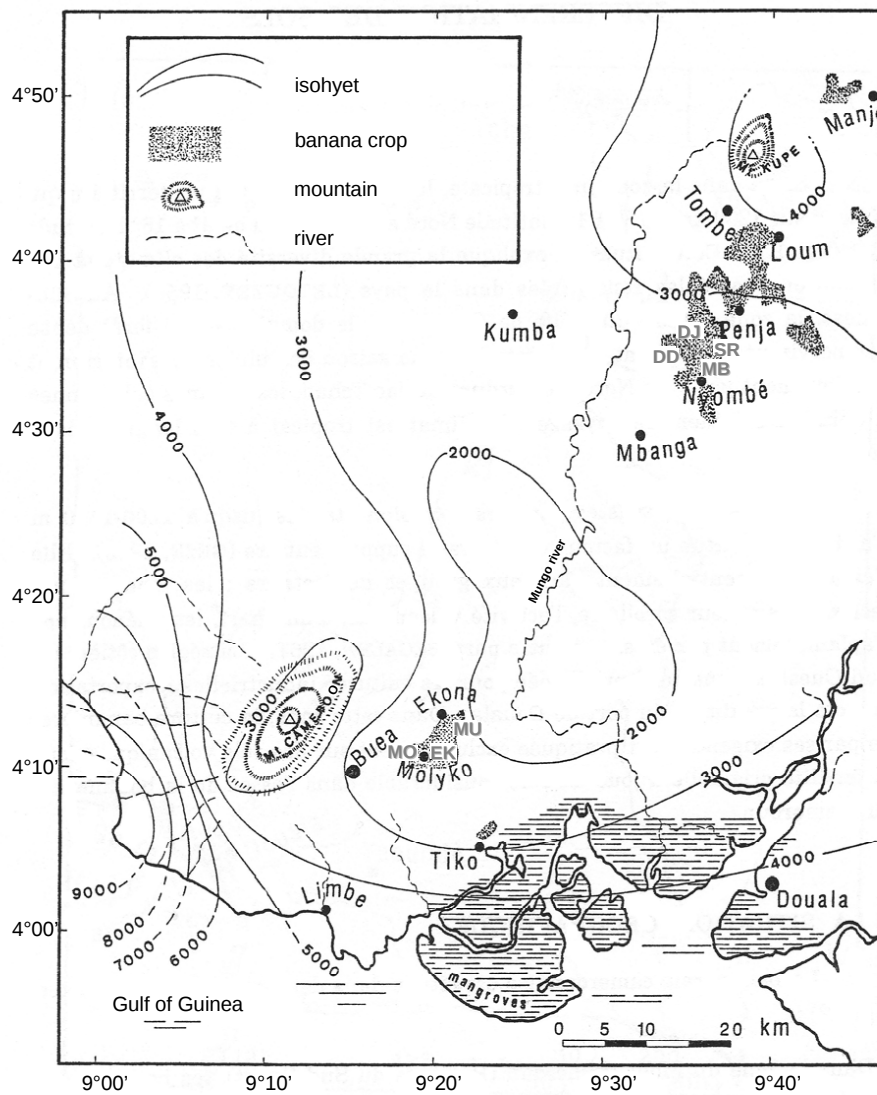


Figure 3.3: Localisation of banana plantations and isohyet curves. The soil profiles sampled in the Mungo (DD, SR, MB, DJ) and in the Mt Cameroon area (MO, EK, MU) are localised in grey. Adapted from Delvaux (1988).

Cameroon (alt. 4095m) and Mounts of NNE Cameroon line (alt. 2000-3000m) (Sieffermann, 1973). Mountains generate rain shadow effects and promote high rainfall patterns in July-August (Figure 3.3). In the South West Province and the western part of Littoral Province, the climate is humid equatorial with a long rainy season extending from March to November and a dry season from December to February.

In the Mungo, the mean annual rainfall increases from North (2650mm, Penja) to South (2900mm, Njombé), while in the Mt Cameroon area, the mean annual rainfall varies between 2200mm (alt. 300m) and 2500 mm (alt. 600m): Mussaka 2207 mm (alt. 405 m, 4°11'N, 9°20'E), Ekona 2288 mm (alt. 410m, 4°13'N, 9°20'E), Molyko 2234 mm (alt. 560m, 4°13'N, 9°20'E) (FAO-IRA, 1980). Temperature varies with altitude between 22.4°C (870m) and 27.5°C (40m) (Martin and Sieffermann, 1966). The relative humidity is very high throughout the whole year (76-91%) even during the dry season (60-80%) (FAO-IRA, 1980). Sunshine is only 1-2hours per day during the rainy season, and 3-6hours per day during the dry season (Sieffermann, 1973). The mean annual sunshine amounts to 1364 hours (FAO-IRA, 1980).

3.3 Geological context

The geology of Cameroon is presented in Figure 3.4. The Precambrian is largely represented in Cameroon (Gazel et al., 1956). The base complex forming the substratum (mainly in the center) is formed by schists, migmatites and syntectonic granites, and is attributed to the lower Precambrian. Middle Precambrian (Poli, Lom, Ayos, M'Balmayo-Bengbis series) and Upper Precambrian (Dja Serie) are mainly metamorphic rocks (quartzites and schists). No formations were reported for the primary era. Cretaceous is represented by two sedimentary basins, in the North and in the Gulf of Guinea. Post Cretaceous is represented by Cenozoic sedimentary deposits and Quaternary alluvial deposits. Granitic intrusions (syn-tectonic and post-tectonic) are very abundant in Precambrian formations. The Cameroon volcanic line oriented SSW-NNE is related to the recent (Cretaceous and Quaternary) volcanic activity. Three main eruptive phases can be distinguish: the Lower black Serie (basalt and andesite from Cretaceous to Eocene), the Middle white Serie (trachytes, phonolites, rhyolites from Neogene), and the Upper black Serie (exclusively basalt from Quaternary era). The Upper black Serie include e.g. lavas flows on the slopes of Mount Cameroon, and ash and pumice deposits from volcanic cones located between Mount Koupe and Mbanga in the Mungo area

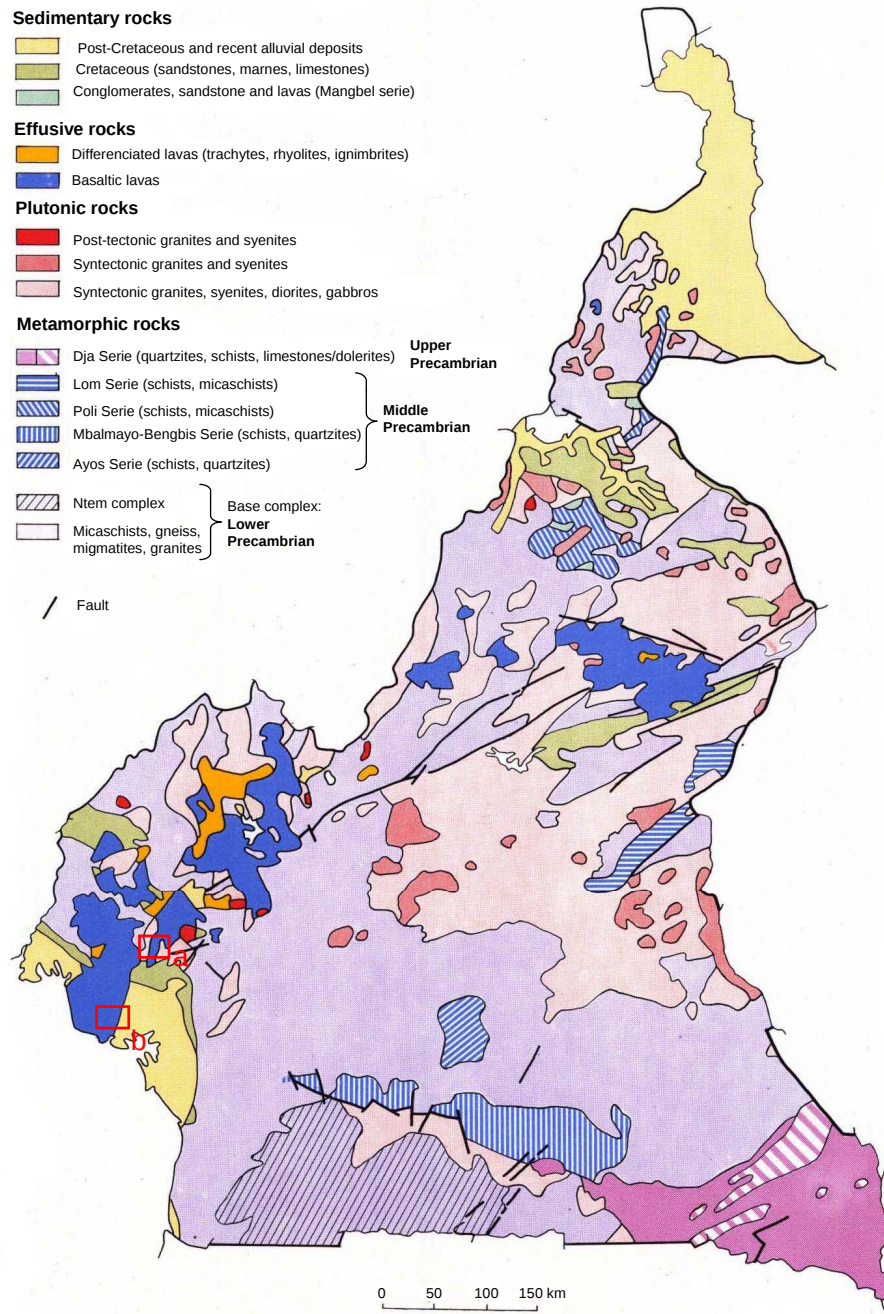


Figure 3.4: Geological map of Cameroon (modified from Laclavère (1979)); correspondence with geological timescale from Sieffermann (1973): (a) Mungo area - (b) Mount Cameroon area.

(around 80 cones on 70km long and 30km large) (Dumort, 1968; Segalen, 1967). Our study sites are located in this Upper black Serie.

The *Mungo plain* is a graben located between the stratovolcanoes of Mt Cameroon and Mt Manengouba (Nkouathio et al., 2002), part of the N30°E Cameroon Hot Line (Déruelle et al., 2007). In the Mungo area, a range of well preserved volcanic cones (Figure 3.5) provides gently sloping lava flows (alt. 40-600m) covered by ash and pumice deposits. From these, soils have developed to produce fertile arable lands devoted to intensive banana cropping. These deposits can be up to 20-30m deep locally (Martin and Sieffermann, 1966).



Figure 3.5: The typical volcanic cones preserved in the Mungo area with banana plantations.

The *Mount Cameroon* is a Hawaiian volcano with a dome shape summit without crater (Figure 3.6). Lavas are erupted from lateral cracks. The last eruptions occurred in 1922, 1929, 1959, 1982, 1999 and 2000. Pyroclastic ash deposits cover the summit of the volcano. With rainfall, these non coherent deposits were transported by mudflows and accumulated on low eastern slopes of the volcano, near Molyko and Buea. In the Mount Cameroun area, the soils used for intensive banana cropping derive from these mudflows deposits.

The primary minerals occurring in these basalts from the Upper black Serie are mainly plagioclase (large dominance of anorthite over albite), ferromagnesian minerals (pyroxenes: augite; olivine and



Figure 3.6: The Mount Cameroon (alt. 4095m), Hawaiian volcano. View on the road from Tiko-Mutengene in the direction of Muea-Ekona.

iddingsite) (Dumort, 1968). These materials also contain vitreous elements (volcanic glass) (Dumort, 1968; Sieffermann, 1973).

3.4 Weathering sequences of volcanic ash soils

The volcanic ash soils affected to banana culture are developed on a homogeneous basaltic parental material (Upper black Serie, Quaternary) from pyroclastic deposits (i) Aeolian in the Mungo, or (ii) transported by mudflows in the Mount Cameroon.

With increasing time (age of the deposits), ash pyroclasts are converted into allophane - halloysite - kaolinite inducing a typical sequence in humid tropical conditions: andosol - brown soil - ferrallitic soil (Sieffermann, 1973). In addition to the chronological factor, soil development depends also on other factors (Delvaux, 1988): (1) type of deposits: Aeolian or mudflow, (2) particle size distribution: distance from the volcanic cone (Mungo), (3) altitude. Climate conditions vary with altitude level (Figure 3.3): temperature decreases and rainfall increases. Allophane and halloysite are well-known secondary products of basalt weathering in soils enriched in glass, plagioclase and ferromagnesian minerals in tropical humid conditions (Wada, 1982). In addition to primary minerals and secondary aluminosilicate minerals (allophane - halloysite - kaolinite), these soils contain Fe- and Al-oxides and hydroxides (gibbsite, goethite, hematite, ferrihydrite, magnetite, maghemite), and Ti-oxides (anatase, rutile) (Delvaux, 1988; Sieffermann, 1973). With increasing weathering stage, volcanic ash and glass content decreases whereas clay and Fe-oxide contents increase (Delvaux et al., 1989). Soils thus strongly differ in their mineralogical and physico-

chemical properties despite their similar parent rock, according to their weathering stage and thus to the age of deposit.

The global distribution of major soil types in both studied areas is presented in Figure 3.9. In the first French soil classification system, soils are mainly eutrophic brown soils and typical ferrallitic soils from basic rocks (Figure 3.9).

In the *Mungo area*, volcanic activity was constant during the Quaternary era with new emission cones occurring. Spatially, old deposits stand close to younger deposits (Figure 3.7) (Delvaux, 1988). Moreover, pyroclastic deposits in this area are Aeolian and the particle size distribution is related to the distance from the cone. More weathered soils are developed on older and finer (more far from the cone) volcanic deposits, which results in a large range of soils corresponding to a toposequence. The sequence Andosol - Brown Soil - Ferrallitic Soil was identified (Delvaux et al., 1989). In the current World Reference Base system (ISSS, 1998), the soils of this sequence would key out as Andosol-Cambisol-Nitisol.

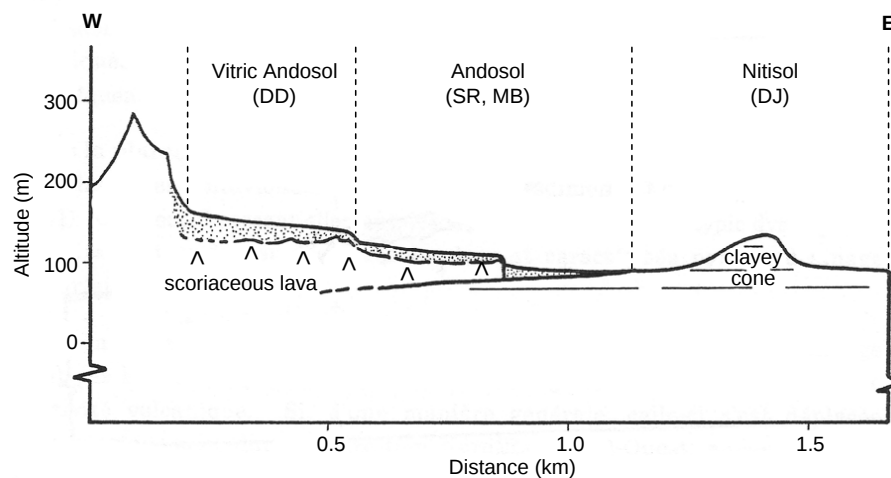


Figure 3.7: Schematic section of the toposequence in the Mungo area (Mt Pelé-Njombé): distribution of soils developed on pyroclastic deposits differing in age. Adapted from Delvaux (1988).

In the *Mount Cameroon area*, the weathering stage increases with decreasing altitude. The spatial distribution of soils corresponds to a chronotoposequence, as older deposits are located at lower altitude and correspond to more weathered soils (Figure 3.8). Andosols developed

from younger deposits (alt. 600m), Cambisols on intermediate age deposits (alt. 500m) and Nitisols on older deposits (alt. 400m). This soil sequence corresponds to the mineralogical sequence ash - allophane - halloysite - kaolinite (Delvaux, 1988).

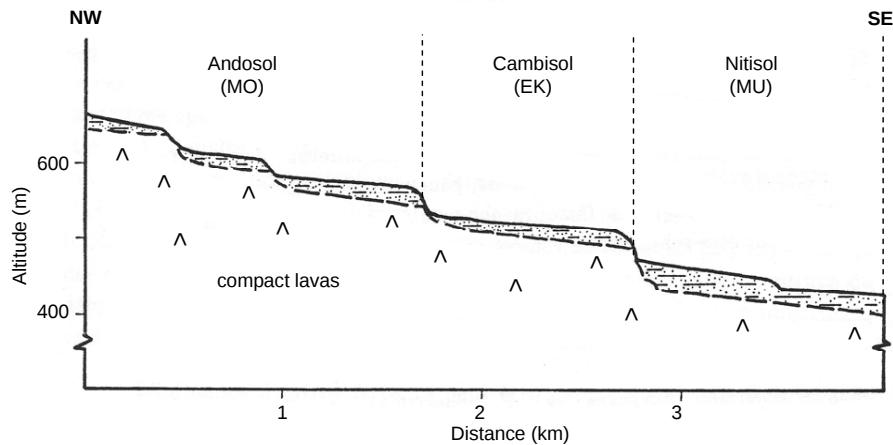


Figure 3.8: Schematic section of the chronotoposequence of the low East slopes of Mt Cameroon: position of the different soil types following a NW-SE direction. Adapted from Delvaux (1988).

Detailed soil studies in the banana plantations area (Delvaux et al., 1989; Delvaux and Lassoudière, 1984; FAO-IRA, 1980) were used to select the soils considered in the present thesis, with a homogeneous parental material (same Si source) but differing by their weathering stage and hence mineralogical composition (decreasing primary minerals and increasing clay content). These mineralogical characteristics could be related with a decreasing Si availability for plants (Henriet, 2008). In the Mungo area, four soil profiles (Dia-Dia, Sir, Mbomé, Djungo) were sampled (Figure A.1) forming a sequence from Andosol (DD, SR and MB) to Nitisol (DJ); in the Mount Cameroon area, three soil profiles (Molyko, Ekona, Mussaka) were sampled (Figure A.2) forming a sequence Andosol (MO) Cambisol (EK) Nitisol (MU). Each soil profile was described according to FAO guidelines (Appendix A) and precisely located by GPS (Appendix B). A brief description of the main characteristics of Andosol, Cambisol, and Nitisol is presented here below.

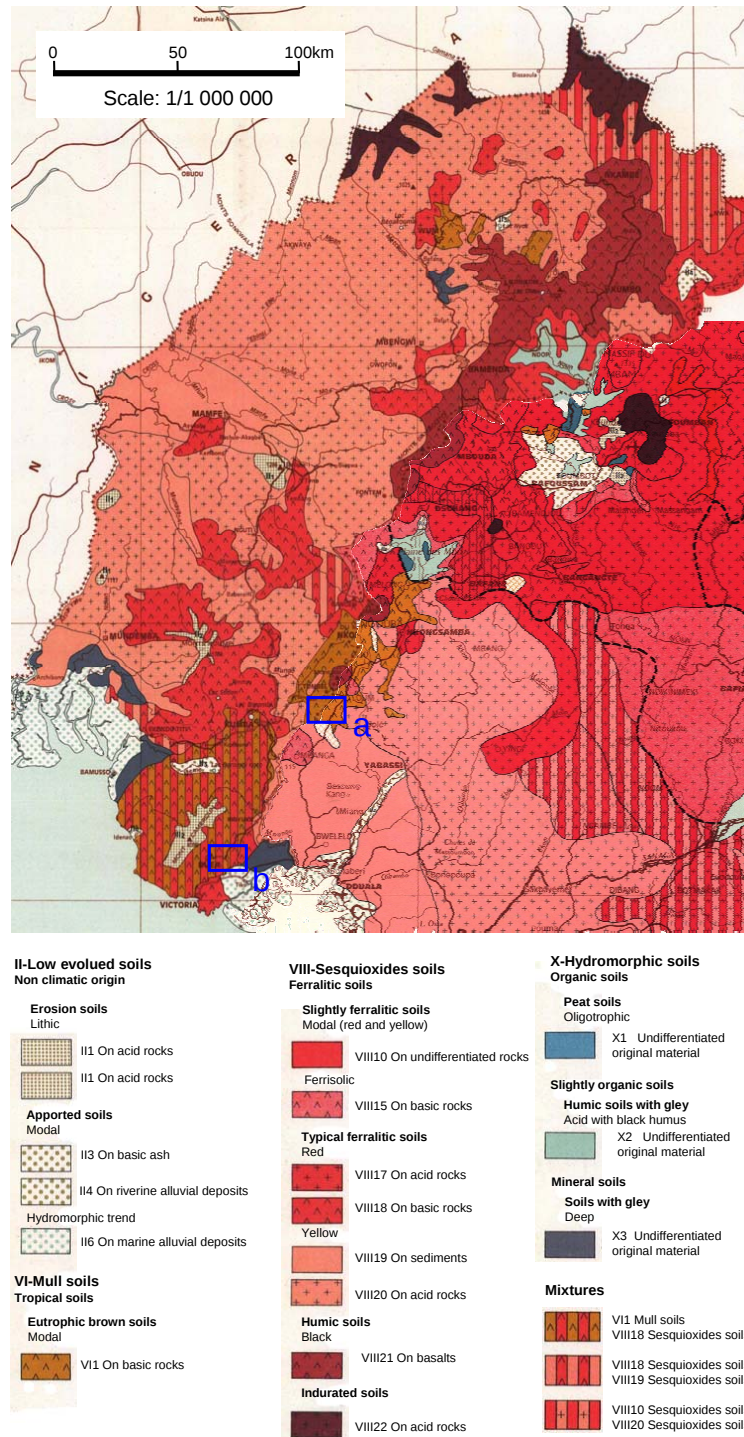


Figure 3.9: Distribution of the soils in South West Cameroon province (Vallerie, 1970) and Littoral province (Segalen and Martin, 1965): (a) Mungo area - (b) Mount Cameroon area.

Andosols (ISSS, 1998): Particle size distribution corresponds to clay-silt or sand silt which provides a water retention capacity. These soils are permeable as not deep and with large quantity of gravels. These soils are characterized by a high content in organic matter (6-12% in surface horizon), high cation exchange capacity (CEC, 40-70 $\text{cmol}_c.\text{kg}^{-1}$) and pH higher than 6. Exchange complex is dominated by Ca and Mg. These soils contain large reserves of weatherable minerals (Martin and Sieffermann, 1966).

Cambisols (ISSS, 1998): Variable texture but mainly silt and fine sand. Good permeability and water retention capacity. Still high organic matter content (4-10%) and high CEC (15-40 $\text{cmol}_c.\text{kg}^{-1}$) which gives a good potential for ion retention (Martin and Sieffermann, 1966).

Nitisols (ISSS, 1998): High clay content (up to 86%) giving a water retention capacity but which could induce a bad drainage in flat area. Variable organic matter content (3-8%), CEC depending on organic matter content, less mineral reserves compared with Cambisols (10-20 $\text{cmol}_c.\text{kg}^{-1}$) (Martin and Sieffermann, 1966).

With such contrasted characteristics, the two soil weathering sequences constitute ideal experimental sites to study the role of plant uptake of Si in the dynamics of continental Si, and hence in silicate weathering. In this environment, the relevance of the Si isotopic tracer as an indicator of the Si cycle in the soil-plant system will be tested.

Part II

Silicon isotopes: Analytical development

Chapter 4

Measurement of silicon isotopes

4.1 Analytical methods for silicon isotope determinations

Before the development of multicollector inductively coupled plasma mass spectrometry (MC-ICP-MS), Si stable isotopes were measured by gas source isotope ratio mass spectrometry (**IRMS**) and secondary ion microprobe mass spectrometry (**SIMS**) (Ding, 2004). The first Si isotopic data reported were measured by IRMS after transformation of the samples into SiF₄ (Reynolds and Verhoogen, 1953). Transformation into SiF₄ was realized by: (1) the BaSiF₆ decomposition method (Reynolds and Verhoogen, 1953), (2) the direct fluorination method using F₂ and HF (Taylor and Epstein, 1962), or (3) the direct fluorination method using BrF₅ (Clayton and Mayeda, 1963). This technique was largely applied to Si isotope determination in meteorites and rocks (Epstein and Taylor, 1970; Molini-Velsko et al., 1986). Douthitt (1982) reported a number of $\delta^{30}\text{Si}$ data on terrestrial samples, followed by Ding et al. (1996). The precision (2σ) on measurements has improved in IRMS from 0.7‰ (Reynolds and Verhoogen, 1953) to 0.6‰ (Epstein and Taylor, 1970), 0.4‰ (Clayton et al., 1974) and lastly 0.1‰ (De La Rocha et al., 1996) (Figure 4.1).

Development of SIMS gave a higher sensitivity and allow to reduce sample size but with a poor precision of 0.2‰ (Basile-Doelsch et al., 2005; Huneke et al., 1983; Zinner et al., 1987). This poor precision can be partially offset by a high number of replications due to the rapidity of measurements.

The recent development of Si measurement by **MC-ICP-MS** in wet Plasma (De La Rocha, 2002) gave a precision of 0.18‰, while the dry plasma method (Cardinal et al., 2003) reaches a precision below 0.1‰ (Figure 4.1). This last method has been used in the present thesis and will be detailed further (see section 4.4).

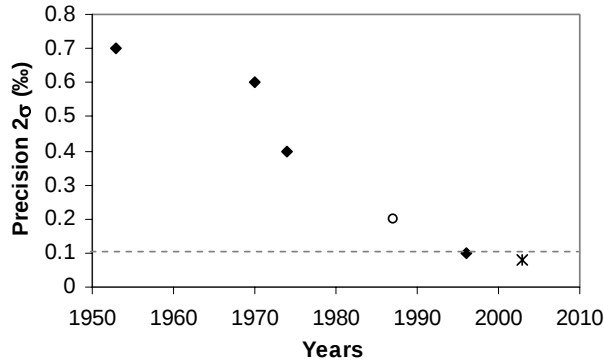


Figure 4.1: Evolution of the precision for Si isotope measurements through time: IRMS (diamond), SIMS (open circle), MC-ICP-MS dry plasma (star).

Today, MC-ICP-MS measurements can be done in several different modes allowing to rapidly measure $\delta^{29}\text{Si}$ and $\delta^{30}\text{Si}$ in low or high resolution, dry or wet plasma, with or without external Mg doping (Table 4.1). MC-ICP-MS has improved the precision and has opened up a new area of research of small fractionations in the range of terrestrial samples.

Recent progress in IRMS involved the conversion of silica to Cs_2SiF_6 by addition of HF and CsCl, followed by decomposition into SiF_4 by addition of sulfuric acid, thus avoiding the use of the direct fluorination method with the dangerous BrF_5 reagent. This method has a 0.1‰ reproducibility, comparable to MC-ICP-MS method (Brzezinski et al., 2006).

4.2 Sample preparation

Before Si isotopic analysis, samples have to be carefully prepared in a clean air environment to avoid Si contamination. The different steps of the preparation are summarized in Table 4.2.

Briefly, digestion of organic matter from *plants* is realized (1) by $\text{HNO}_3/\text{H}_2\text{O}_2$ digestion in teflon vials on hot plate during one week (at the beginning of this thesis) or more quickly (2) by mineralization at

Table 4.1: Details about MC-ICP-MS methods to measure Si isotopes. (*) Recent technique of a UV-femtosecond laser ablation connected to a MC-ICP-MS.

Group	Instrument	External doping	Plasma	Resolution	Si requirement $\mu\text{g Si}$	Precision ($\pm 1\sigma$) Reproducibility
De La Rocha (2002)	Nu Plasma	-	wet	low	$\sim 160 \mu\text{g}$	$\delta^{29}\text{Si} \pm 0.09\%_a$
Cardinal et al. (2003)	Nu Plasma	Mg	dry	low	$2 \mu\text{g}$	$\delta^{29}\text{Si} \pm 0.04\%_a$
Abraham et al. (2008)	Nu Plasma	Mg	dry	medium	$4 \mu\text{g}$	$\delta^{30}\text{Si} \pm 0.07\%_a$
Georg et al. (2006b)	Nu 1700	-	dry	high	$2 \mu\text{g}$	$\delta^{30}\text{Si} \pm 0.07\%_a$
Engström et al. (2006)	Neptune	Mg	wet	high	$20 \mu\text{g}$	$\delta^{30}\text{Si} \pm 0.25\%_a$
van den Boorn et al. (2006)	Neptune	-	dry	medium-high	$4 \mu\text{g}$	$\delta^{30}\text{Si} \pm 0.18\%_a$
Chmieleff et al. (2008)	Neptune	-	dry*	medium	50ng	$\delta^{30}\text{Si} \pm 0.12\%_a$

^a $\delta^{29}\text{Si}$ data instead of $\delta^{30}\text{Si}$

450°C during 16 hours in Pt crucibles preceded by 1h at 100°C and 1h at 250°C, which is the preferred method and was used afterwards. Si from biogenic opal is then recovered by 0.2 M NaOH leaching at 100°C during 1 hour and neutralized by HCl 1M (adapted from [Ragueneau et al. \(2005\)](#)).

Rock, soil and clay samples are digested by alkaline fusion at 1000°C of 5mg of silicate powder (sample) mixed with 30mg of LiBO₂ flux in a covered Pt crucible. The entire crucible is then quickly transferred into double distilled 5% HNO₃ and dissolution of fusion beads is realized under magnetic stirring ([Abraham et al. \(2008\)](#); Chapter 5).

Dissolved Si from soil, plant and water samples is then purified by triethylamine (TEA) molybdate co-precipitation ([De La Rocha et al., 1996](#)). In the presence of dissolved silicic acid, acid molybdate forms a silicomolybdic complex $\text{SiMo}_{12}\text{O}_{40}^{4-}$, which precipitates as a yellow triethylamine silicomolybdate in presence of TEA hydrochloride ([De Freitas et al., 1991](#)). The TEA-molybdate reagent (2 liters) is prepared by dissolution of ammonium molybdate (16g) and triethylammoniumchloride (29.2g) with concentrated hydrochloric acid (48ml) and filled with pure water. This reagent has to be prepared at least one week before use, stored in the dark, and filtered before use through 0.4μm polycarbonate membrane. The amount of sample to be processed is calculated to provide at least 0.1mg Si for the total chemical procedure. The sample is diluted with pure water to reach around 100μMSi (need to be between 10 and 300μMSi to ensure a good coprecipitation), and the volume of TEA added is equivalent to 60% of the diluted sample volume. After 48h coprecipitation in the dark, the yellow precipitate obtained is filtered through 0.4μm polycarbonate membrane, rinsed 3 times with 30ml of 2 parts of TEA for 3 parts of pure water. Then, the filter is carefully transferred into covered Pt crucibles for combustion at 1000°C (Figure 4.2) ([De La Rocha et al., 1996](#)).

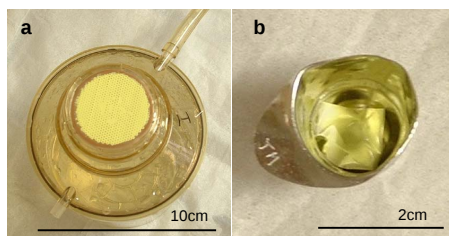


Figure 4.2: Yellow precipitate formed by coprecipitation of silicic acid with TEA-molybdate: (1) filtration through 0.4μm polycarbonate membrane - (2) transfer of the filter into Pt crucible for combustion.

Table 4.2: Summary of the sample preparation used in this thesis before Si isotopic analysis by MC-ICP-MS.

Step	Sample	Principle	Duration	Reference
Digestion	Plant	Organic matter digestion $\text{HNO}_3/\text{H}_2\text{O}_2$ or calcination at 450°C	1 week 16h	- -
		Opal dissolution by hot NaOH leaching	1h	Ragueneau et al. (2005)
	Rock/Soil/Clay	Alkaline fusion with LiBO_2 / HNO_3 dissol.	2 days	Abraham et al. (2008)
	River waters	-	-	-
Recovery		Control of Si concentration by ICP-AES	1 day	-
Purification		TEA-molybdate coprecipitation	min. 48h	De La Rocha et al. (1996)
Filtration		Polycarbonate membrane $0.4\mu\text{m}$	1 day	De La Rocha et al. (1996)
Combustion		1h at 450°C and 5h at 1000°C	1 day	De La Rocha et al. (1996)
Dissolution		Dilute suprapur HF/HCl mixture	1 week	Cardinal et al. (2003)
Matrix control		Major elements and Mo (ICP-AES)	1 day	Cardinal et al. (2003)

The white residue obtained after combustion is constituted of SiO_2 polymorphs cristobalite and tridymite (De La Rocha et al., 1996). This solid residue is carefully transferred in polypropylene vials and dissolved in dilute suprapur HF-HCl mixture (Cardinal et al., 2003). Absence of Mo or major elements is controlled by ICP-AES before Si isotopic analysis, and the final Si concentration is measured to allow precise dilution of samples for MC-ICP-MS analyses.

Analyses by inductively coupled plasma atomic emission spectrometry (ICP-AES) during the sample preparation were realized on an Iris Advantage (Thermo Jarrel Ash Corporation) at the MRAC in Tervuren (radial viewing). Sample is ionized into the plasma where the different species emit energy as electromagnetic radiation with a characteristic wavelength, depending on the electron configuration of the atom of the emitting species. This radiation is converted into electric energy by the photomultiplier. Internal standards Au and Y are used to correct for instrument drift. Calibration of the machine for Si concentration measurements is based on pure artificial Si solution (0.1, 1 and 10ppm Si), multi-elements artificial (all major but Si) solutions (0.1, 1, 10ppm elements), Mo standard (0.1 and 1ppmMo), and highly diluted natural rock reference standards (limestone CCH-1, shale SGR-1, gabbro JGb-1, basalt BHVO-1, granodiorite JG-1a). Blank level is measured in pure water and a blank of alkaline attack. The same HNO_3 and LiBO_2 matrix between standards and sampled is carefully taken into account to ensure precise measurements, especially to calculate recovery of alkaline attack after rocks digestion. Detection limit for Si is around 15ppb Si (MRAC, radial viewing).

4.3 Principles of MC-ICP-MS

The MC-ICP-MS used in the present thesis has been installed in Brussels in 2001 (at Université Libre de Bruxelles, ULB) and is the second of three existing instruments in Belgium. The others are at IRMM, Geel (Nu Plasma) and at UGent (ThermoFinnigan Neptune). Our instrument is a double-focusing MC-ICP-MS Nu PlasmaTM (Nu Instruments, Wrexham, UK) already described in details elsewhere (Belshaw et al., 1998; Young et al., 2002).

Briefly, a MC-ICP-MS is mainly constituted of four parts: (1) a sample introduction system, (2) an ion source, (3) a mass analyzer, and (4) a detector (Figure 4.3; Figure 4.5).

The **sample introduction system** is constituted of a Cetac (Omaha, NE, USA) AridusTM desolvating device equipped with a

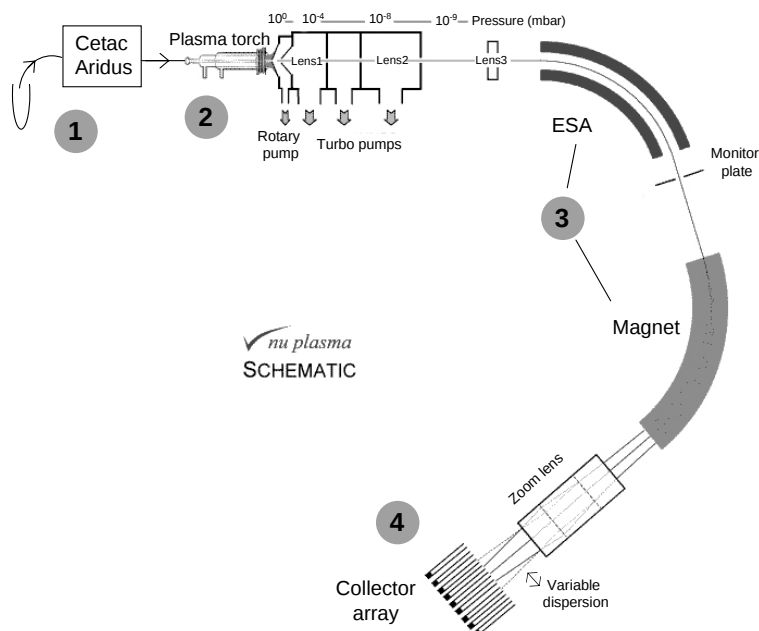


Figure 4.3: Schematic representation of a NuPlasma mass spectrometer, with (1) sample introduction system Cetac Aridus desolvating device, (2) Ar-plasma ion source, (3) mass analyzer consisting of ESA and magnet, and (4) detection unit with 12 fixed Faraday detectors (figure adapted from Nu Instruments).

PFA spray chamber (heated to 105°C) and a PFA microconcentric nebulizer from Elemental Scientific Inc. (Omaha, NE, USA) under free aspiration. Typical running uptake was $100\mu\text{l}\cdot\text{min}^{-1}$. The aerosol coming out of the spray chamber is dried through a semi-permeable Teflon membrane heated at 160°C and conducted to the plasma by an Ar flux (sweep gas). This desolvating device ensures the removal of matrix components that could compete for ionisation energy in the plasma, which greatly enhances the sensitivity as compared with wet plasma conditions (De La Rocha, 2002), and reduces isobaric interferences with solvent molecules (H_2O , CO_2 , O_2 and N_2). The membrane of the Aridus needs to be cleaned on a daily basis to avoid memory effect from the membrane. The dried aerosol is injected through the plasma torch into the plasma to be ionized. An alumina injector (Glass ExpansionTM) was preferred over a platinum injector, even with 1-5% Si potential source of contamination in the alumina material, as lower interferences and similar background for same sensitivity were obtained.

The **ion source** is an inductively coupled argon (Ar) plasma at high

temperature (7500 K). The plasma is formed at the end of the plasma torch, where the Ar stream ($15\text{ l}\cdot\text{min}^{-1}$) meets a high frequency electromagnetic field induced by a high frequency oscillating current within the RF coil. A high voltage ignition spark is applied to the Ar gas and electrons from Ar atoms are ripped off. These electrons are accelerated into the magnetic field and induce a chain of collision with other Ar atoms. This creates the plasma where the dried aerosol will be injected and transformed through desolvation, vaporization, atomization and ionization. These ions are transferred through the sampler and skimmer nickel cones (Figure 4.4) where they get separated from the plasma and accelerated into the mass spectrometer. Through this interface (10^0 mbar), ions are transferred from atmospheric pressure (10^3 mbar) to very low pressure (10^{-9} mbar) into the mass-spectrometer (Figure 4.3). As pressure is reduced, the ion beam expands and needs to be focused by electrostatic lenses with adapted current applied. To avoid too much loss of ions, vacuum pumps ensure a large vacuum in the interface region (Figure 4.3). Ions are accelerated into the mass spectrometer with several potentials and ion beam is focused by several optical lenses (Lens 1, 2 and 3; Figure 4.3).

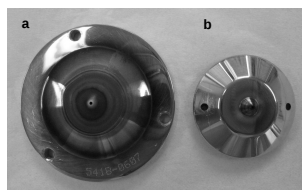


Figure 4.4: Nickel cones used at the interface between plasma and mass analyzer: (a) sampler and (b) skimmer cone B.

The **mass-analyser** splits the ion beam into the mass spectrum of the contained ions with a double focusing unit composed of an electrostatic analyzer (ESA) and a magnet. The ESA deflects the ions as a function of their kinetic energy, so slow ions are more deflected than faster ions. The magnet deflects the ions based on their m/z ratio of their mass (m) and charge (z), which results in deflecting more faster ions than slower ions (opposite to ESA). Ions are thus separated and focused on collectors based on mass and energy. The combination of ESA and magnet ensures a good sample focusing on the same collector of sample with similar m/z ratio entering the mass analyzer with different kinetic energy from the plasma, and provides a good peak shape (wide plateau). The magnet needs to be calibrated for each range of masses of interest.

The **detector** unit of a MC-ICP-MS Nu Plasma is constituted of twelve fixed position ceramic and sapphire Faraday cups equipped with $10^{11}\Omega$ resistors. This collector array is complemented by an electron multiplier ion-counting system. Variable dispersion in front of the collectors is achieved by a zoom lens combination focusing the beam on the collector. In the method of [Cardinal et al. \(2003\)](#), Si isotopes of m/z 28, 29 and 30 are measured respectively on low mass (L4), Axial, and high mass (H5) Faraday cups during the first cycle, and Mg isotopes of m/z 24, 25 and 26 on L5, Axial and H6 collectors during the second cycle. When the ion beam enters the Faraday cup, the positively charged ions are neutralized by inducing a current through the resistor, which can be registered as a change in voltage. The ion-counting system is based on electron multipliers to allow low level measurements. Low analyte concentrations inducing very small currents can not easily be detected by Faraday cups, as their lower sensitivity and intrinsic background noise limits their use (below 0.02mV). Multiple collector arrays allow the detection of multiple ion beams of adjacent isotope masses simultaneously which cancels out beam fluctuations. Measuring simultaneously different isotopes of the same element significantly improves the precision of isotopic ratios.

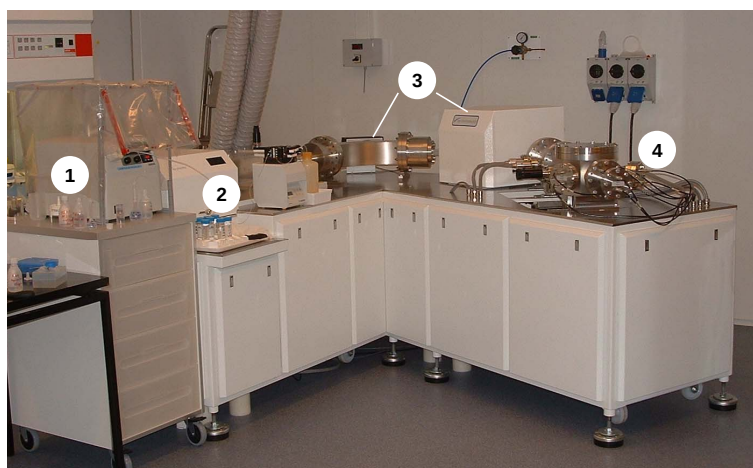


Figure 4.5: NuPlasma mass spectrometer in Brussels (ULB), with (1) sample introduction system Cetac Aridus desolvating device, (2) Ar-plasma ion source, (3) mass analyzer consisting of ESA and magnet, and (4) detection unit (detailed in Figure 4.3).

4.4 Silicon isotopic analysis following Cardinal et al 2003

The method used for Si isotopes measurements ($\delta^{29}\text{Si}$ measurements only) during the main part of this thesis has been developed at the Royal Museum for Central Africa, Tervuren (Cardinal et al., 2003) and is explained in this section. During the thesis, we developed an adapted method allowing to measure ^{30}Si following an upgrade of the instrument and express the results as $\delta^{30}\text{Si}$. This modified method will be explained in Chapter 5 (Abraham et al., 2008).

Analytical conditions are summarized in Table 5.1 (except running concentrations at 1ppm Si and 0.5ppm Mg in the method of Cardinal et al. (2003)). Si isotopic measurements were realized in **dry plasma mode** using a Cetac Aridus desolvating nebulization system (section 4.3). Compared to the wet plasma (160 μg , De La Rocha (2002)), this allows to reduce the quantity of Si needed for one isotopic measurement (2 μg). Samples are prepared following the procedure described above (section 4.2) and analyzed as dilute HF/HCl solution.

The **sensitivity** is around 6V for 1ppm ^{28}Si and 0.5ppm ^{24}Mg . Flat top peaks of Si and Mg are obtained by using the low mass resolution

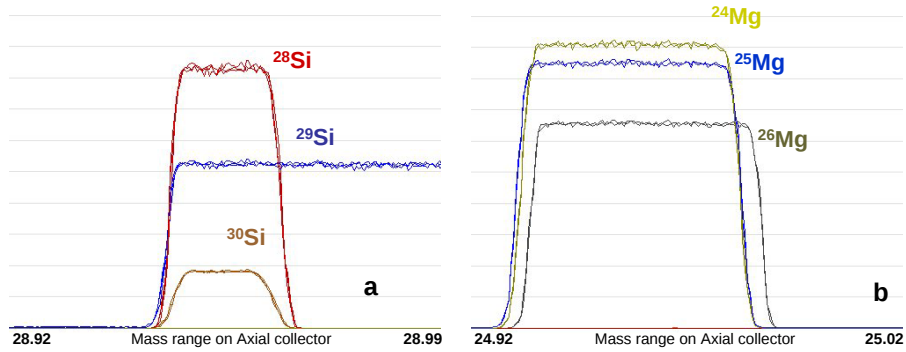
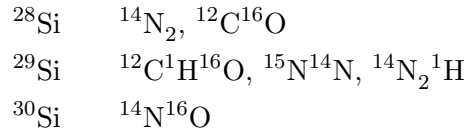


Figure 4.6: Centered peak shape and signal stability (two successive scans) on (a) silicon isotopes and (b) magnesium isotopes in a standard solution 1ppm ^{28}Si NBS28 and 0.5ppm ^{24}Mg SRM980 in dilute HCl-HF (0.7-1.2mM). Abscissa represents the magnet scan mass range on the Axial collector (^{29}Si , ^{25}Mg) and should be adapted ± 1 amu for low (^{28}Si , ^{24}Mg) and high (^{30}Si , ^{26}Mg) masses. Ordinate indicates signal intensity (different scale for each peak): (a) ^{28}Si ($\sim 6\text{V}$), ^{29}Si ($\sim 300\text{mV}$), ^{30}Si ($\sim 200\text{mV}$), and (b) ^{24}Mg ($\sim 6\text{V}$), ^{25}Mg ($\sim 800\text{mV}$), ^{26}Mg ($\sim 100\text{mV}$).

mode of the instrument. The peak shape should be as steep and symmetrical as possible on the edges, and as flat as possible on the plateau with a good stability both in Si and Mg (Figure 4.6). Blank acid solutions HCl-HF (0.7-1.2mM) provides a ^{28}Si signal usually below 50mV (less than 1% on the Si measured intensity) and a ^{24}Mg signal below 5mV (less than 0.1% on the Mg measured intensity) and is monitored between each sample analysis.

The **potential molecular mass interferences** on stable Si isotopes are:



The desolvating device reduces the introduction of H_2O , CO_2 , O_2 and N_2 into the plasma, decreasing the interfering molecular species. The resolution defines the smallest difference of mass that can be distinguished. In this method, measurements are performed in low resolution ($\sim m/\Delta M = 300$). With such a configuration, isobaric $^{14}\text{N}^{16}\text{O}$ interference on ^{30}Si can not be solved. Gas flows have to be optimized to reduce $^{14}\text{N}_2$ and $^{14}\text{N}_2^1\text{H}$ interferences on ^{28}Si and ^{29}Si , respectively. Interferences have to be negligible compared to Si signal, which has been empirically estimated at 2-6 mV relative to $\sim 6\text{V}$ on ^{28}Si , and below 0.5mV relative to $\sim 300\text{mV}$ on ^{29}Si (Figure 4.7). The ^{30}Si can not be

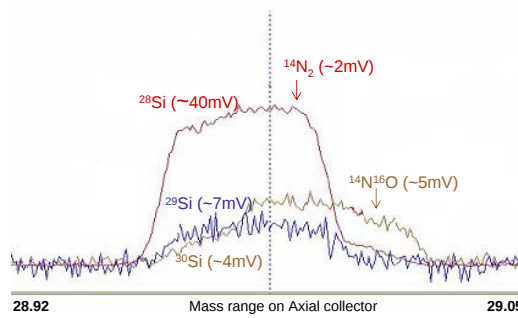


Figure 4.7: Interferences on Si stable isotopes in a blank acid solution HCl-HF (0.7-1.2mM), negligible on ^{28}Si , controlled on ^{29}Si and too high on ^{30}Si . Abscissa represents the magnet scan mass range on the Axial collector (^{29}Si) and should be adapted ± 1 amu for low (^{28}Si) and high (^{30}Si) masses. Ordinate indicates signal intensity (different scale for each peak).

measured accurately as the 5mV interference is not negligible relative to ^{30}Si signal (Figure 4.7). Results are expressed as $\delta^{29}\text{Si}$ vs. NBS28 $\pm 0.08\text{‰}$ ($\pm 2\sigma$). No detectable interferences are present on Mg.

To correct for the large instrumental mass bias occurring in all ICP, which is even larger for light isotopes due to their high fractionation potential, a **sample-standard bracketing technique** is used. This also reduces Si blanks and interferences since both affect the standard and sample almost equally. However, this requires a constant intensity ratio and the same matrix in the sample and the standard. To avoid matrix effects, all the solutions were checked by ICP-AES in order to confirm that no other contaminant (major elements or Mo) was present in a significant amount in purified Si sample solutions. Moreover, the same Si/Mg ratio and acid content is needed. As one sample is surrounded by two standards, this allows computing a delta value by the mean of the sample relative to each standard. The fractionation between standard is monitored along one analytical session.

In addition to the sample-standard bracketing technique, the instrumental bias is corrected by an **external Mg standardization**. Mg doping has been chosen as external standard because the stable Mg isotopes masses (24, 25, 26) are very close to Si stable isotopes masses (28, 29, 30). For this reason, the mass discrimination occurring at the plasma spectrometer interface should affect similarly Si and Mg isotopes. Mg isotopes are measured in dynamic mode by a switch of the mass spectrometer magnet and zoom lenses between the first cycle (Si isotopes measurements) and the second cycle (Mg isotopes measurements). This allows adequate correction of instrumental mass bias, applying the fractionation exponential law and external normalization (see below). Si isotopic measurements are thus corrected in the procedure by the isotopic measurements on Mg isotopes. Sample and standard solutions are spiked with Mg as the reference standard SRM 980. The Mg concentration is adjusted to allow an intensity ratio Si:Mg $\sim 1:1$. Analyses are performed in dynamic mode (2 cycles: alternatively Si then Mg) with 3 blocks of 20 measurements of 5 seconds each, with one peak centering on ^{28}Si at the beginning of the run. This provides satisfactory standard error on the measured isotopic ratios (~ 40 ppm).

The external Mg standardization is based on instantaneous mass discrimination described by the exponential mass bias law:

$$f_{\text{Mg}} = \frac{\ln[(^{25}\text{Mg}/^{24}\text{Mg})_{\text{true}}/(^{25}\text{Mg}/^{24}\text{Mg})_{\text{meas}}]}{\ln[(\text{mass}^{25}\text{Mg})/(\text{mass}^{24}\text{Mg})]}$$

Considering that the ratio between fractionation of Si and fractionation of Mg is constant during one analytical session ($f_{\text{Si}} / f_{\text{Mg}} = \text{constant}$), Si isotopic measurements can be corrected by this equation:

$$(^{29}\text{Si}/^{28}\text{Si})_{\text{true}} = (^{29}\text{Si}/^{28}\text{Si})_{\text{meas}} \times (\text{mass}^{29}\text{Si}/\text{mass}^{28}\text{Si})^f$$

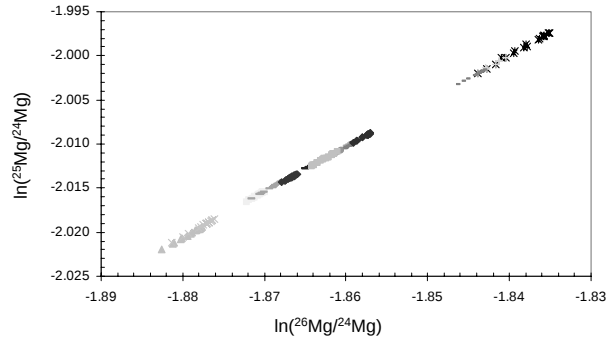


Figure 4.8: Mass bias fractionation line: Mg vs. Mg isotopes (slope = 0.51; Galy et al. (2001)). Different symbols stand for different analytical sessions between July and October 2006.

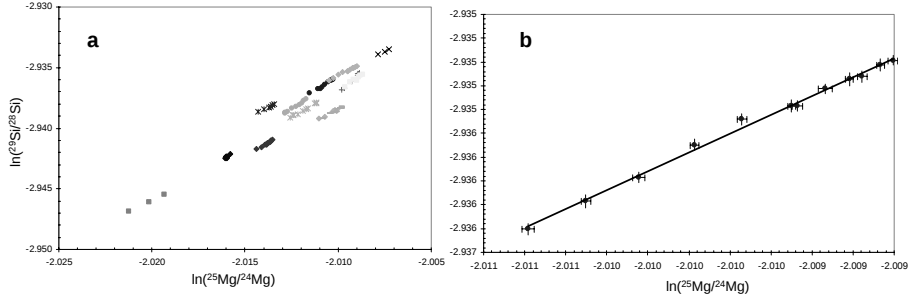


Figure 4.9: Mass bias fractionation line: Mg vs. Si isotopes (theoretical slope = 0.86): (a) variation of the slope from one analytical session to another between July and October 2006 - (b) detailed slope for one analytical session showing the quality control of the standard on the slope.

During one analytical session, the mass bias fractionation line between Mg and Mg isotopes displayed a constant slope around 0.51 (Galy et al. (2001); Figure 4.8). Similarly, the mass bias fractionation line between Mg and Si isotopes has to be monitored for standards during

one analytical session, and should display a constant slope during one day (Figure 4.9a). When $f_{\text{Si}} = f_{\text{Mg}}$, theoretical slope $\ln(^{29}\text{Si}/^{28}\text{Si})_{\text{meas}}$ vs. $\ln(^{25}\text{Mg}/^{24}\text{Mg})_{\text{meas}} = 0.86$. As long as $f_{\text{Si}} / f_{\text{Mg}}$ is constant during one day session, this slope can vary from one day to another for maximum 25% (e.g. 0.81 ± 0.03 to 1.08 ± 0.03 ; Cardinal et al. (2003)). The quality control of the data is monitored on the $\ln(^{29}\text{Si}/^{28}\text{Si})_{\text{meas}}$ vs. $\ln(^{25}\text{Mg}/^{24}\text{Mg})_{\text{meas}}$ slope as the standard must be on the line taking into account their standard errors (Figure 4.9b).

During the thesis, we participated in an inter-laboratory comparison of Si isotope reference materials, and the method of Cardinal et al. (2003) was confirmed to be accurate compared to other techniques for Si isotope measurements. This intercalibration exercise is fully presented in Chapter 6 (Reynolds et al., 2007).

To be able to measure ^{30}Si , the method of Cardinal et al. (2003)

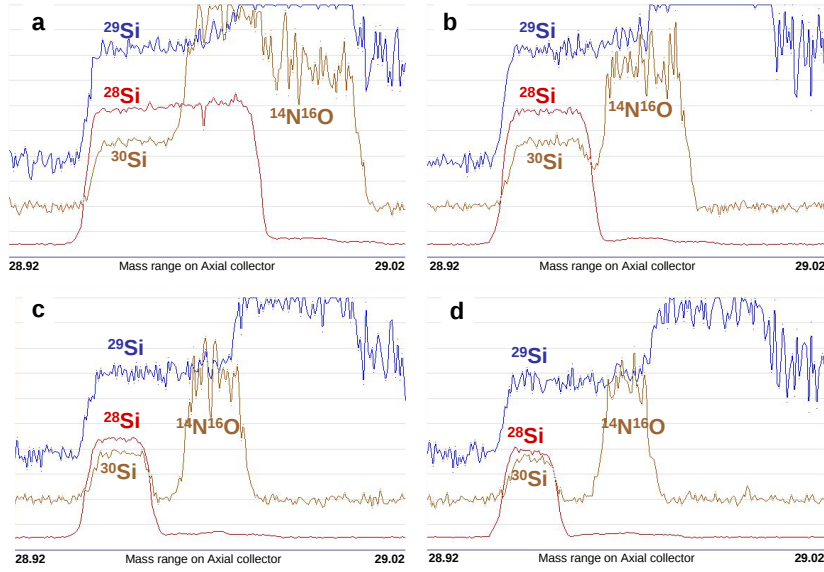


Figure 4.10: Separation of the $^{14}\text{N}^{16}\text{O}$ interference on ^{30}Si by adjusting the collector slit (CS) in a blank acid solution HCl-HF (0.7-1.2mM): (a) interference is not separated (CS=7) - (b) separation starts (CS = 7.84) - (c) interference is well separated (CS = 7.94) - (d) separation is too far and the ^{30}Si plateau is not flat enough to allow accurate measurements (CS = 7.98). Abscissa represents the magnet scan mass range on the Axial collector (^{29}Si) and should be adapted ± 1 amu for low (^{28}Si) and high (^{30}Si) masses. Ordinate indicates signal intensity (different scale for each peak): ^{28}Si ($\sim 40\text{mV}$), ^{29}Si ($\sim 7\text{mV}$), ^{30}Si ($\sim 4\text{mV}$).

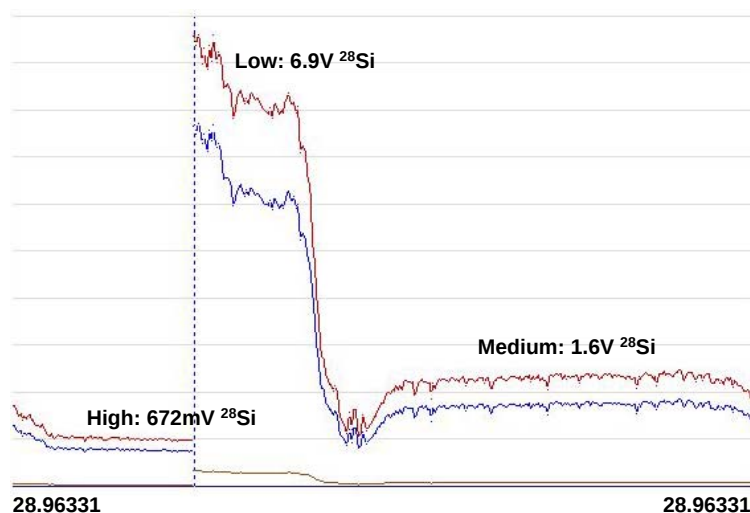


Figure 4.11: Decreasing sensitivity in ^{28}Si (red) from low to medium to high resolution by modifying source definition slit (entrance slit). Abscissa represents the magnet scan mass on the Axial collector (^{29}Si) fixed at one mass to observe the decreasing signal. Ordinate indicates signal intensity.

has been adapted in medium resolution using a new source definition slit/entrance slit (medium resolution) and two collector slits to solve isobaric interference on ^{30}Si and ^{28}Si (Figure 4.10), thanks to an upgrade of a new vacuum pump to balance the loss in sensitivity due to the medium resolution (Figure 4.11). This adapted method (Abraham et al., 2008) has been developed in December 2006 and is fully described in Chapter 5. This new method has been used since January 2007 in a large part of this thesis (see Figure A).

Compared to the method of Cardinal et al. (2003) here are the relevant differences. The method measures in dynamic mode (Si, Mg) with 4 blocks of 15 meas. of 5 second each with a peak centering at the beginning of each block on ^{30}Si . Measurements are performed in high resolution (entrance slit and collector slit: $\sim m/\Delta M = 1200$) with a new vacuum rotary pump (Big 80). Solutions measured are prepared at 1.7 to 2.2ppm Si - 0.9 to 1.1ppm Mg for a sensitivity at 7V/2ppm ^{28}Si with blank acid <50mV. Results are expressed as $\delta^{30}\text{Si}$ vs.NBS28 $\pm 0.07\%$ and $\delta^{29}\text{Si}$ vs.NBS28 $\pm 0.04\%$. Si isotopic measurements require long analytical sessions (minimum 15h) allowing between 7 and 10 sample measurements per session.

