Biogenic silica storage in soils

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ABSTRACT

The role of plants in soil development has became of crucial interest in quantifying global weathering processes. On the volcanic Reunion Island (Indian Ocean), a 15-cm-thick phytolith-rich horizon (biogenic opal-A) developed at the expense of trachytic ashes between 3820 ± 85 and 335 ± 90 yr B.P. Then, 97–138 t/km²/yr of SiO_2 were biogeochemically recycled from the weathering of parent rocks through a past forest of bamboos (*Nastus borbonicus*). This rate is in the same range as the present chemical weathering rates of silica in the area, considered to be among the highest in the world. These results demonstrate that the storage of biogenic silica in soils may be significant and may retard the output of silica to rivers and ocean.

INTRODUCTION

Weathering, including soil development, has became of global concern during the past decade because it may partly control the global CO_2 budget and consequently may influence global climatic changes (Nahon, 1991; Berner, 1997; Torn et al., 1997; Moulton and Berner, 1998). The model of in situ transformation of parent rocks into supergene products by percolating waters has been extensively used for explaining structures and textures as well as the mineralogy of soils (Birkeland, 1984; Schlesinger, 1991; Tardy, 1993). Other inputs, however, may significantly affect the weathered surficial part of the lithosphere, such as translocation processes of continental fine particles (Colin et al., 1997) at soil surfaces, importation of eolian particles into surficial soil horizons (Brimhall et al., 1988; Simonson, 1995), and plant turnover, which reinjects silica and other elements into topsoils (Lucas et al., 1993). A recent study of the biogeochemical cycle of silica in the Congo rain forest (Alexandre et al., 1997) shows that biogenic silica, reincorporated into soils as hydrated opal-A particles (phytoliths), controls the dynamics of silica in soil solution. This result casts doubt on the generally accepted idea that dissolved silica in surficial waters is mainly controlled by the dissolution of quartz (Rimstidt, 1997; White et al., 1998). Determining the role of biogenic silica as a sink or a pool in soils is therefore essential for a better understanding of the mechanisms and rates of weathering. Phytolith-rich tropical soils, formed on the volcanic island of Reunion (Indian Ocean) (Lacroix, 1936; Riquier, 1960), offer an ideal opportunity to evaluate the potential storage of biogenic silica.

MATERIAL AND METHODS

The island of Reunion (Fig. 1) is located 700 km west of Madagascar (55°32′E; 21°07′S). The phytolith-rich formations mainly developed on the west side of the Piton des Neiges volcano (Raunet, 1991), between 1600 and 1800 m in elevation. The last basaltic lava flows (mugearite) took place between 230 and 70 ka and were covered by a 2-m-thick trachytic ash layer during successive eruptions that ended 15 ka. The temperatures and the annual rainfall prevailing in the area average 12 °C and 1600 mm. The vegetation has been highly disturbed by human activities since the settlement of the island in the mid-seventeenth century. The trachitic ash-derived soils support a forest with dominant tamarinds (*Acacia heterophylla*) and Philippia sites (mainly *Philippia montana*) associated with an understory of ferns (*Histiapteris incisa*) and a few bamboo (*Nastus borbonicus*) sites. We sampled the plants and the soil horizons (Fig. 1) in order to determine the origin of the phytolith M horizon (also called mascareignite) and to evaluate its impact on the weathering rates.

The mineralogical composition was determined using X-ray diffraction (XRD; Philips P 1729), an optical microscope (Leica DMRXP), a scanning electron microscope (SEM; Philips 500 coupled with an energy dispersive spectrometer), and a Fourier transformed infrared spectrometer (Perkin Elmer). Bulk density (ρw) measurements were made on rock samples after drying and weighing and coating them with molten paraffin wax, followed by immersion in water to measure their displaced volume. Bulk density was estimated by mass per unit volume with errors of about 10%. Grain density (ρg) was measured by air picnometer with errors of about 10%. Porosity (ϕ) equals (ρg – rw)/ρw. Radiocarbon dating was done by accelerator mass spectrometry (AMS; University of Arizona) on charcoal pieces. Organic carbon was determined using a C-H-N analyzer (random standard deviation, RSD, of about 5%). SiO_2, Al_2O_3, and Fe_2O_3 were measured by inductively coupled plasma/atomic emission spectrometry (ICP/AES) after fusion of the ground and dried samples in Li methaborate at 1000 °C (RSD of about 10%). The silica and phytoliths from the plants were analyzed and compared to the soil. The phytoliths were extracted using the dry method (Kelly, 1990), which consists of putting plant pieces (leaves, stems, and roots), after washing in 1N HCl, in an oven at 450 °C for 6 h; the organic matter was destroyed by combustion and the phytoliths were concentrated in the ash. Phytoliths were recognized and counted (about 500 particles per slide) under optical microscope and SEM.

RESULTS AND DISCUSSION

The composition of a typical representative soil column from top to base is given in Table 1. Ao and M horizons exhibit XRD patterns with a diffuse band centered at 4.1 A and infrared spectra with main bands at 470, 800, and 1100 cm^{-1}, which indicate the presence of amorphous silica or opal, in the form of phytolith particles. The Bh horizon is mainly composed of organic carbon, magnetite, hematite, and a minor amount of opal and ferrihydrite. The content of organic carbon in the Bh horizon is believed to result from organic matter leaching from the surface litter downward into the M horizon. The trachytic ash horizon (Bt1) is composed of feldspar and

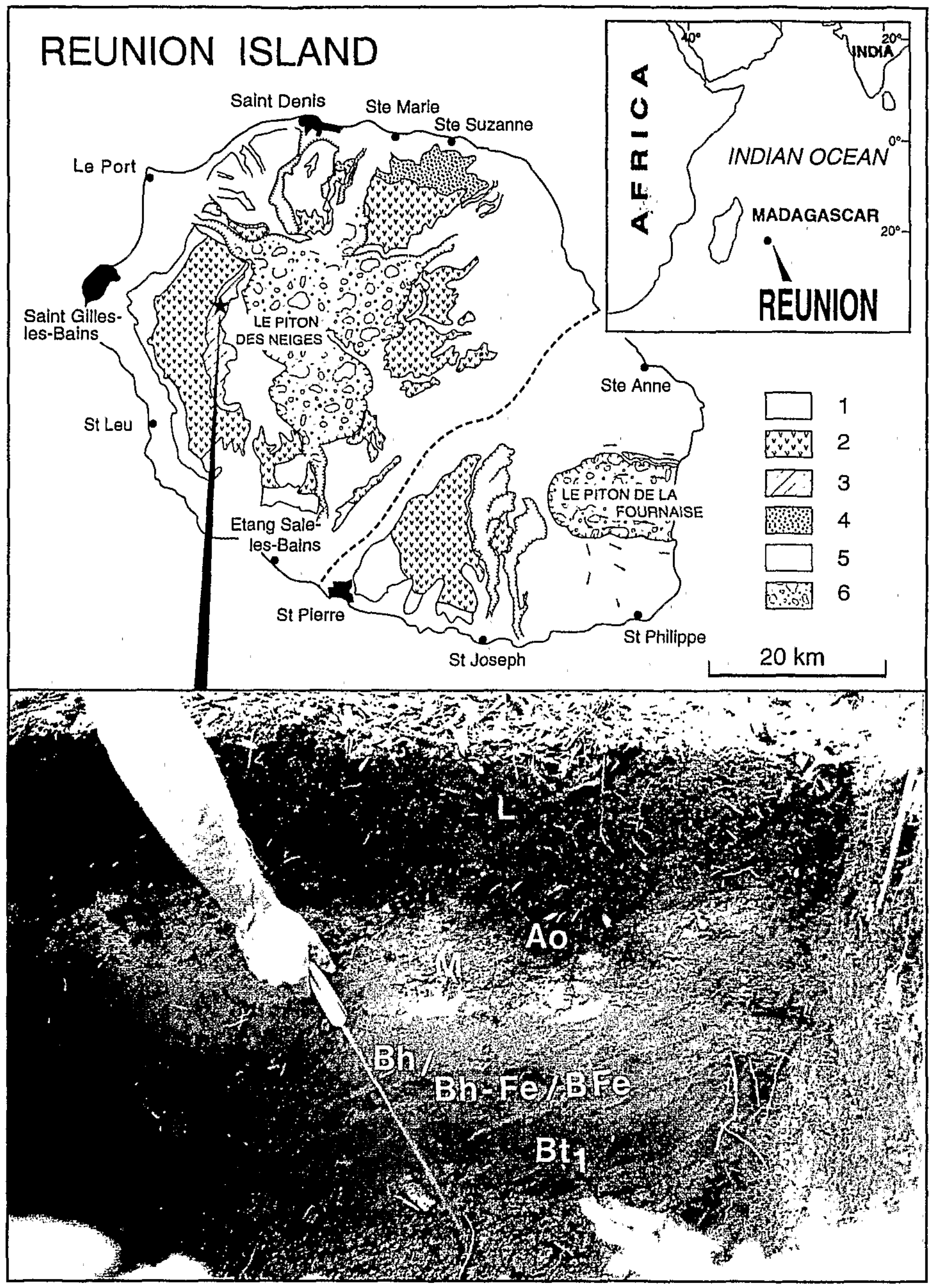

Figure 1. Location and description of studied profile. Map illustrates main soil types in Réunion Island, featuring Piton de la Fournaise and Piton des Neiges volcanoes: (1) brown soils; (2) andosols; (3) M horizon andosols; (4) ferralitic soils; (5) lithosols, alluvial soils; (6) volcanic crater. Photograph illustrates typical profile composed as follows from top to bottom. (1) 2–4-cm-thick litter (L). (2) 2–10-cm-thick black horizon with limonitic texture and millimeter-size pores, containing many root fragments and charcoal (Ao). (3) Phytolith horizon (M) from 10 to 27 cm depth; it is pink (5YR 6/2) and friable when it is saturated with water and gray-white (10 YR 6/1) and pulverulent when dried; texture is silty with fine porosity. It contains many fine roots and few charcoal fragments. Boundary with Ao is tongued. This M horizon is locally called mascareignite (in relation to name Mascareignes given to isles of area). (4) Black, organic-rich horizon from 27 to 34 cm depth; texture is silty and contains few red millimeter-size nodules. Boundary with M is sharp but forms gradual transition with horizon from below (Bh). (5) Brown to black horizon from 34 to 37 cm depth with abundant centimeter-size to millimeter-size red nodules. Boundary with horizon below is sharp (Bh-Fe). (6) Red, nodular indurated horizon from 37 to 39 cm depth (Bfe). (7) Between 39 and 60 cm depth, ash layer is composed of light brown silty matrix with 10% (volume) of brown to yellow centimeter-size to decimeter-size indurated pieces of angular volcanic rocks. It contains few charcoal fragments (Bt_1).

magnetite as residual primary minerals, an allophane-imogolite matrix, and minor gibbsite as secondary supergene phases.

The chemical composition of the M horizon is largely dominated by SiO_2. C and other trace elements are present. The M horizon particle sizes range from 2 to 60 µm in maximum length. In addition, the occurrence of a few diatoms, chrysostomaceas, and sponge spicules may indicate an allochthonous origin. An alternative hypothesis is that the M horizon results from the in situ turnover of silicon by local vegetation. In order to determine if the phytoliths of the M horizon originate from the plant growing in the area, we compared the phytolith morphotypes and the silica content of the plants growing in the area. The M horizon (Fig. 2) is mainly composed of 22% square and round, 11% fan shaped, and 10% elongated particles, which constitute typical phytoliths from poaceae (Piperno, 1988; Twiss, 1992). The other particles are diatoms, chrysostomaceas, and sponge spicules (<1%) and silicified vessels (<1%) that originated from dicotyledon plants (Piperno, 1988). About 56% of the phytolith morphotypes are unclassified, including 34% of round, flat (<5 µm diameter) particles.

Observations of the phytoliths extracted from the plants growing in the area show that: (1) tamarinds and ferns contain only a small amount

TABLE 1. PHYSICAL AND CHEMICAL COMPOSITIONS OF HORIZONS IN FIGURE 1

Sample	Depth (cm)	Density (g/cm^3)	Porosity (%)	Charcoal ^{14}C ages (yr B.P.)	C (%)	SiO_2 (%)	Al_2O_3 (%)	Fe_2O_3 (%)
Ao	5			335 ± 90	19.25	54.83	0.59	1.18
M	20	1.8; 0.6	69	745 ± 105	1.70	89.11	0.14	0.22
Bh	32				12.84	33.31	4.08	20.16
Bh-Fe	36			3820 ± 85		8.14	6.45	44.03
Bt_1	49	2.5; 0.6	76	12 925 ± 135	4.41	27.47	27.19	10.19

Note: The first value of density is grain density (ρg); the second value is bulk density (ρw).

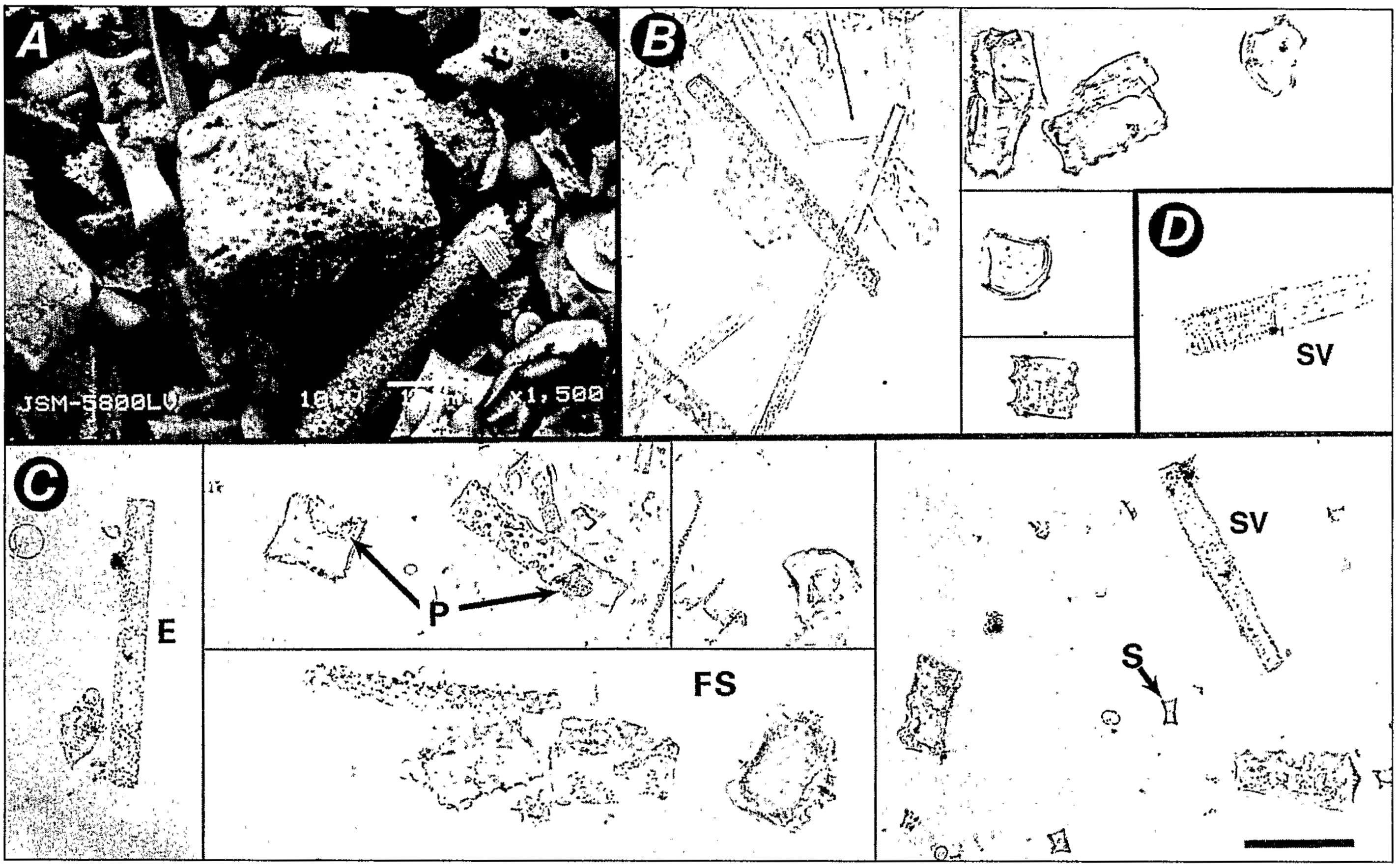

Figure 2. Phytoliths extracted from M horizon and plants. A (scanning electron microscope) and B (optical microscope; bar = 2 cm = 30 μm) illustrate typical morphotypes (E, elongated; FS, fan shaped; S, square; SV, silicified vessel) with dissolution pits (P) in M horizon. *Nastus borbonicus* (C) exhibits similar morphotypes but surface is smooth. *Philippia montana* (D) shows few elongated phytoliths that are similar to morphotypes found in M horizon. We did not observed dissolution pits in plant phytoliths.

of phytoliths of poorly defined morphotypes; (2) *Philippia montana* have a few silicified vessels but mostly poorly defined morphotypes in the leaves; and (3) only leaves and stems of *Nastus borbonicus*, a poaceae, exhibit phytolith morphotypes that resemble the M horizon morphotypes, including square and round (44%), elongated (27%), fan-shaped (12%) types, and 17% unclassified. The morphological study suggests that the M horizon originates from accumulation of bamboo phytoliths from stems and leaves. However, the proportion of the morphotypes as well as the morphology of the phytoliths differ slightly from those of the bamboo phytoliths. The surface of the M horizon morphotypes is highly pitted, whereas the surface of bamboo phytoliths is smooth (Fig. 2). Pits are due to dissolution in the soil (Alexandre et al., 1997). The morphotypes in the M horizon may be explained by the preferential dissolution of square and round and elongated particles. The silica particles of the Ao′ horizon are mostly phytoliths (>99%) composed of the following morphotypes: square and round, 20%; fan shaped, 16%; elongated, 10%; round and flat, 14%; vessels <1%; and undetermined, 39%, similar to the composition of the phytoliths in the M horizon. The Si analyses (Table 2) corroborate these results by demonstrating that the bamboos are the most silica-rich plant of the area. In addition, within Ao and the upper part of the M horizon, charcoal dated as 335 and 745 yr B.P., respectively, was identified as *Nastus borbonicus* (Ouar, 1998).

As a consequence, we interpret the surficial Ao and M horizons as resulting from in situ biopedogenic processes where an episode of mostly bamboo-inherited phytolith accumulation was followed by an episode of organic matter leaching as described here. This is typical of podzolitic dynamics. The M horizon is a specific podzol containing opal phytoliths instead of usual residual quartz grains. Therefore, the M horizon occurrence demonstrates that phytolith accumulation may be a significant sink of silica in soil.

Because *Nastus borbonicus* occurs sporadically among the present-day vegetation on the west side of the Piton des Neiges volcano, the M horizon provides a record of a past environment which, according to charcoal dating, ended two or three centuries ago. The disappearance of bamboos may be due either to climatic changes or to anthropogenic activity. This period corresponds to the flourishing development of the human activity in the island. Because the bamboos were intensely used at that time for domestic purposes and house building, fires and the action of humans are believed to have caused the nearly complete disappearance of *Nastus borbonicus* forest.

We estimated the time necessary to form a 15-cm-thick layer of phytoliths by taking into account the range of SiO_2 contents in *Nastus borbonicus* (from 12.57 wt% [from stems] to 8.8 wt% [from the leaves]), the density (1.8 g/cm^3) of phytoliths, the weight percent SiO_2 in the M horizon (89%), and the productivity of bamboos, estimated as 11 t/ha/yr from *Oxytenanthera* species data (Cannell, 1982).

Assuming a soil-plant steady state where silica injected in soils from the dead biomass (plant productivity) equals the uptake of silica into plants

TABLE 2. SILICA CONTENT OF THE PLANTS GROWING IN THE STUDIED AREA

Sample	Si (mg/g)
Nastus borbonicus	leaves 41.13 stems 58.73 rhizome 3.01
Acacia heterophylla	leaves 0.29 roots 0.19
Philippia montana	leaves and stems 0.75 roots 0.2
Histiapteris incisa	leaves and stems 18.36

from soil solution, calculation of the rate of the SiO_2 injected in soil by *Nastus borbonicus* gives values of 0.97–1.38 t/ha/yr, or 97–138 t/km²/yr. The development of the M horizon thus required 1738–2482 yr. Because the phytoliths are weathered and did not entirely originate from *Nastus borbonicus,* this time is a minimum value. This time is consistent with independent estimates of the M horizon age using charcoal ages from the overlying and underlying horizons between 3660 and 3310 yr. If we assume that the role of other silica particles from other origins in the rate of M horizon accumulation is minor because of their low amount (vessels from dicots) and their small size (the round flat of unknown origin), the difference between the duration of *Nastus borbonicus* phytoliths accumulation at steady state (no dissolution) and the ages given by charcoals allows us to estimate that 25%–53% of the mass of phytoliths has been lost by dissolution. Comparing the silica content recycled by plants to the silica content of the rivers studied by Louvat and Allègre (1997) leads to a better understanding of the weathering processes of the island. By knowing the basin drainage surfaces (114 km^2), the runoff (1250 mm/yr), and the sum of the dissolved species in rivers of the drainage basin (28 mg/l; cirque de Mafate, which includes our study area), the rate of silica dissolution from the basalt equals 35 t/km²/yr. This is 40% of the chemical erosion. This rate is slightly lower than the productivity and uptake of SiO_2 by *Nastus borbonicus*. Our estimates of 25%–53% of dissolved phytoliths give a minimum rate of biogenic silica release of 24 t/km²/yr, which is in the same range as the rate of silica release due to parent-rock dissolution. Moreover, 45–104 t/km²/yr of SiO_2 from undissolved phytoliths would have been stored. Our results support the proposition that soil dynamics and erosion rates were strongly influenced by the biogenic silica turnover. The exceptional enrichment in phytoliths in the topsoil was favored by the efficiency of the bamboos in extracting silica from poorly crystallized supergene phases, which resulted from the intense weathering of trachytic Si-rich ashes in the tropical climate.

CONCLUSIONS

Our results demonstrate that the net storage of silica by the dead biomass could be highly significant and cast doubt on the use of silica as a reference for determining the balance of relative solute weathering. A significant part of the SiO_2 dissolved from the parent rocks has been retained in the soil and not injected into the rivers. The phytoliths stored in soil are equivalent to the net storage in the soil organic matter sink given in the mass-balance model of Likens and Bormann (1995) for evaluating cationic denudation. More analyses of the phytolith content of soils are required to evaluate the importance of silica storage by biomass and the consequences for global weathering models.

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REFERENCES CITED

Alexandre, A., Meunier, J. D., Colin, F., and Koud, J. M., 1997, Plant impact on the biogeochemical cycle of silicon and related weathering processes: Geochimica et Cosmochimica Acta, v. 61, p. 677–682.

Berner, R. A., 1997, The rise of plants and their effect on weathering and atmospheric CO_2: Science, v. 276, p. 544–545.

Birkeland, P. W., 1984, Soils and geomorphology: New York, Oxford University Press, 372 p.

Brimhall, G. H., Lewis, C. J., Ague, J. J., Dietrich, W. E., Hampel, J., Teague, R., and Rix, P., 1988, Metal enrichment in bauxites by deposition of chemically mature aeolian dust: Nature, v. 333, p. 819–824.

Cannell, M. G. R., ed., 1982, World forest biomass and primary production data: London, Academic Press, 391 p.

Colin, F., Sanfo, Z., Brown, E., Bourlès, D., and Edou Minko, A., 1997, Gold: A tracer of the dynamics of tropical laterites: Geology, v. 25, p. 81–84.

Kelly, E. F., 1990, Methods for extracting opal phytoliths from soil and plant material: Fort Collins, Colorado State University Department of Agronomy, Internal Document, 10 p.

Lacroix, A., 1936, Le volcan actif de La Réunion et ses produits: Paris, Gauthier-Villard, 297 p.

Likens, G. E., and Borman, F. H., 1995, Biogeochemistry of a forested ecosystem: New York, Springer-Verlag, 159 p.

Louvat, P., and Allègre, C. J., 1997, Present denudation rates on the island of Réunion determined by river geochemistry: Basalt weathering and mass budget between chemical and mechanical erosions: Geochimica et Cosmochimica Acta, v. 61, p. 3645–3669.

Lucas, Y., Luizao, F. J., Chauvel, A., Rouiller, J., and Nahon, D., 1993, The relation between biological activity of the rain forest and mineral composition of soils: Science, v. 260, p. 521–523.

Moulton, K. L., and Berner, R. A., 1998, Quantification of the effects of plants on weathering: Studies in Iceland: Geology, v. 26, p. 895–898.

Nahon, D., 1991, Introduction to the petrology of soils and chemical weathering: New York, John Wiley and Sons, 313 p.

Ouar, S., 1998, Caractérisation spacio-temporelle du couvert végétal des zones à Mascaréignite des hauts de l'Ile de la Réunion [thesis]: Aix en Provence, France, University de Aix-Marseille III, 156 p.

Piperno, D. R., 1988, Phytolith analysis. An archaeological and geological perspective: London, Academic Press, 280 p.

Raunet, M., 1991, Le milieu physique et les sols de l'Ile de la Réunion: Montpellier, France, Centre International de Recherche Agronomique pour le Développement, 438 p.

Rimstidt, J. D., 1997, Quartz solubility at low temperatures: Geochimica et Cosmochimica Acta, v. 61, p. 2553–2558.

Riquier, J., 1960, Les phytolithes de certains sols tropicaux et des podzols (International Congress of Soil Science, 7th, Madison, Wisconsin): International Society of Soil Science, v. 60, p. 425–431.

Schlesinger, W. H., 1991, Biogeochemistry: An analysis of global change: San Diego, California, Academic Press, 443 p.

Simonson, R. W., 1995, Airborne dust and its significance to soils: Geoderma, v. 65, p. 1–43.

Tardy, Y., 1993, Pétrologie des latérites et des sols tropicaux: Paris, Masson, 461 p.

Torn, M. S., Trumbore, S. E., Chadwick, O. A., Vitousek, P. M., and Hendricks, D. M., 1997, Mineral control of soil organic carbon storage and turnover: Nature, v. 389, p. 170–173.

Twiss, P. C., 1992, Predicted word distribution of C3 and C4 grass phytoliths, *in* Rapp G., Jr., and Mulholland, S. C., eds., Phytolith systematics. Emerging issues: New York, Plenum Press. p. 113–128.

White, A. W., Blum, A. E., Schulz, S., Vivit, D. V., Stonestrom, D. A., Larsen, M., Murphy, S. F., and Eberl, D., 1998, Chemical weathering in a tropical watershed, Luquillo Mountains, Puerto Rico: I. Long-term versus short-term weathering fluxes: Geochimica et Cosmochimica Acta, v. 62, p. 209–226.

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