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Interrelations of vegetal cover, silicophytolith content and pedogenesis of Typical Argiudolls of the Pampean Plain, Argentina

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ABSTRACT

Knowledge of the origin, evolution and weathering of Pampean soils is still limited. There are few prior studies of silicophytoliths, even though they could be important pedogenetic indicators that provide information about the role of amorphous silica in the reestablishment of soil structure. The aim of this work is to determine the silicophytolith content in Typical Argiudolls of the Pampean Plain, Argentina, its relation with vegetal cover and its effect on pedogenesis. We worked in three plots with different vegetal cover: grasses and shelter-belt plantations of *Acacia melanoxylon* – *Celtis tala* and *Eucalyptus globulus* – *Celtis tala*. In the study area, morphological characterization and particle size distribution analysis of soils were completed, and pH and organic matter content were determined. The heavy liquid separation was realized with sodium polytungstate (δ=2.3 g/cm^3) and an average of around 500 mineral grains were counted under optical microscope for the quali-quantitative analysis. There were no differences between profiles with respect to their morphological properties, organic matter content and particle size distribution, except for the higher organic horizon development of the forest plots as compared with the grass plot. The silicophytolith content was higher in the forest plots than in the grass one; within each profile, this fraction content decreased from the surface (63–40%) to the subsurface levels (23–5%) of soils. This decrease parallels the pieces of amorphous silica (<7.5 μm) distribution in all plots analyzed. Afforestation over the past 50 years does not affect either the morphological or the physico-chemical properties of soils. These forest species, through the organic horizons, preserve soil conditions, which insures a higher representativity of silicophytoliths in comparison with the grass plot.

1. Introduction

The southeastern Pampas region represents one of the most conspicuous sites of the Humid Pampean Plain. Typical Argiudolls are the representative soils. Composed of silts, fine sands, and clays, they originated from eolian sediments linked to the last arid cycle of the late Pleistocene–Holocene (Osterrieth and Cionchi, 1985). These soils have supported the agricultural, horticultural and livestock raising activity of the study area. In Typical Argiudolls, light minerals predominate. Minerals composed of amorphous silica, both of inorganic (volcanic ashes and vitroclastics) and organic origin (silicobioliths: deposited silica minerals in living organisms (Wüst and Bustin, 2003) as phytoliths, diatoms, sponges, silicified cuticle casts, pollen, spores, plant detritus and charcoal (Golyeva, 2001)), are always present with values over 20% of the total amount of mineralogical components of the soil (Teruggi, 1955; Osterrieth, 2000; Borrelli and Osterrieth, 2001). Silicophytoliths are particles of hydrated amorphous silica ($SiO_2.nH_2O$) formed in the cells of living plants, who deposit solid silica in an intracellular or extracellular location after absorbing silica in a soluble state from groundwater (Piperno, 1988). Upon death and decay of the plants, silicophytoliths become part of the clastic materials, thus being exposed to the same weathering processes that affect the soil minerals. These processes generate surfaces with pores or cavities, through which are released unsaturated monosilic acid, ready to be reabsorbed by the plants, to remain in the system, to be involved in the neoformation of clay minerals and to flow to the underground water (Alexandre et al., 1997; Kelly et al., 1998; Martínez and Osterrieth, 1999).

The representatives of the Poaceae family, a pristine vegetation predominant in the study area across the Quaternary (Cabrera, 1976), have been described as one of the major producers of silicophytoliths, together with Cyperaceae and Arecaeae (Piperno, 1988). Approximately 50 years ago, a process of artificial forestation was started in the study area, with the aim of creating recreation areas. This process generated the replacement of the natural grass vegetation by forest species in numerous wide zones. Included in the artificial vegetation were specimens of *Eucalyptus* sp., *Pinus* sp., *Cupressus* sp., *Acacia* sp., among others.

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From an economic point of view, Typical Argiudolls are very important due to their high productivity and intense agricultural and horticultural activity developed in the study area. This agricultural activity caused a noticeable decrease in the organic matter and clay fraction content of the A horizon's arable layer, with the subsequent loss of structural stability and fertility (Osterrieth and Maggi, 1996; Osterrieth et al., 1998 and 2001). Knowledge of the genesis, evolution, and degradation of Pampean soils still remains limited, in spite of interdisciplinary investigations that have approached their study from geomorphological, sedimentological, pedological and palaeontological points of view, among others. Since phytolith analysis can provide information on conditions of soil development and landscape evolution, and silicophytoliths can indicate modern and past conditions of pedogenesis, they are considered pedogenetic indicators (Golyeva, 2001). Even though their importance was pointed out by Frenguelli (1930), Bertoldi de Pomar (1970), Rovner (1971), Golyeva (2001) and Borba-Roschel et al. (2006), among others; mineralogical studies, especially those referring to silicophytoliths as pedogenetic indicators, are scarce. So, the aim of this work is to determine the silicophytolith content in Typical Argiudolls of the Pampean Plain, Argentina, its relation with vegetal cover and its effect on pedogenesis.

2. Materials and methods

2.1. Area description

The site under study is located in the Partido de General Pueyrredón, around Los Padres Pond, Province of Buenos Aires (38° S–58° W) (Fig. 1A).

The climate is mesothermic and subhumid, with little or no water deficiency (Burgos and Vidal, 1951). The annual precipitation is 809 mm. The annual average temperature is 13.7 °C; the average minimum temperature is 8.1 °C in June, while the average maximum temperature reaches 19.8 °C in January (Servicio Meteorológico Nacional de Mar del Plata, according to the 1920–1980 record). Following the standards set by the Soil Survey Staff (1996), the soil temperature is mesic, and the regime of humidity is udic.

The Los Padres Pond site belongs in the geomorphological unit known as "Perinange eolian hills", which comprises a relief of morphologically complex hills, with relative heights of up to 30 m and concave–convex profiles with intermediate straight patches and slopes between 6 and 8% (Osterrieth et al., 1998). It originated from processes of primary eolian accumulation, modified later by superficial wash (Osterrieth and Martínez, 1993) (Fig. 1A).

The terrain morphology, as well as the dense vegetal cover in the natural field, makes sheet runoff a predominant feature. The high permeability of the loessian sediments makes it possible for part of the precipitation to filter through (Osterrieth and Maggi, 1996).

2.2. Sample units

The research was done on three plots located in the same landscape unit and topographic position, but with different vegetal cover (Fig. 1B). The three plots under analysis are part of the Los Padres Pond Natural Reserve, and their soils have never been tilled.

Plot 1 (*P1*): It is a natural plot characterized by grasses (Poaceae): *Holcus lanatus*, *Poa lanigera*, *Bromus unioloides*, *Paspalum quadrifarium*,

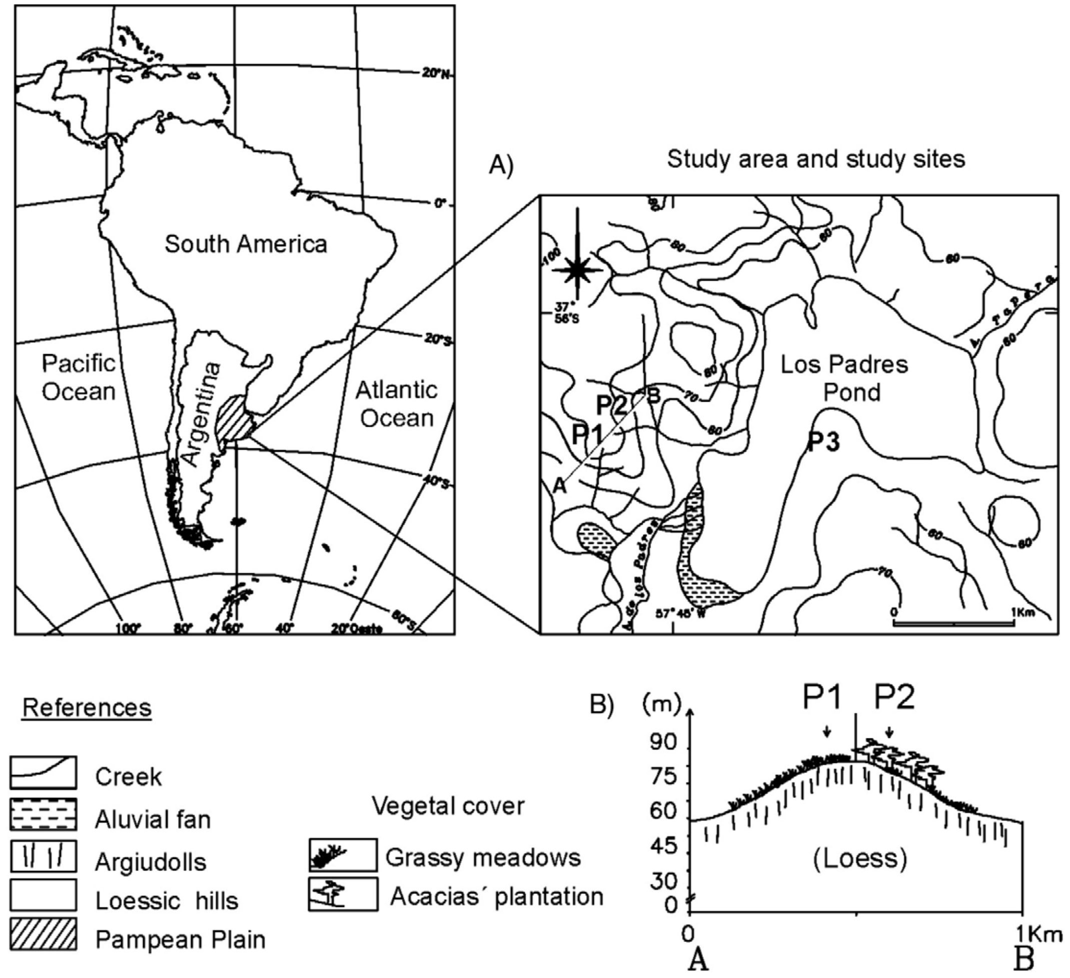

Fig. 1. A) Location of the study area and study sites. P1: Grasses, P2: Acacias' plantation, P3: Eucalyptus' plantation. B) Topographic profile of one of the study sites (Line A–B in A).

Dactylis glomerata, and *Brassica* sp. It is surrounded by an association of *Colletia paradoxa* (Ramnaceae), a native species widely disseminated in virgin zones, and *Rubus ulmifolius* (Rosaceae: Rosoidea), an invasive species with wide dissemination during the last decades. Both are thick, impenetrable bushes over 3 m high.

Plot 2 (*P2*): The predominant vegetation is a shelter-belt plantation of *Acacia melanoxylon* (Fabaceae-Mimosoidea) of about 50 years-old, a species associated with *Rubus ulmifolius* (Rosaceae: Rosoidea) and young individuals of *Celtis tala* (Celtidaceae), a native species.

Plot 3 (*P3*): The vegetation is a shelter-belt plantation of *Eucalyptus globulus* (Myrtaceae) associated with young individuals of *Celtis tala* (Celtidaceae).

2.3. Methodology

2.3.1. Morphological and physico-chemical properties

Morphological profile descriptions were made according to the standards established by the Soil Survey Staff (1996). Color was determined according to the Munsell Soil Color Chart. The study focused on organic horizons, mollic epipedons, argilic endopedions, and parental material. In the eucalyptus plot (P3), we took only samples of the mollic epipedon because of their great development, since it is greater than 50 cm. As the parental material (loess) is the same in all of the profiles that were analyzed, we took only samples in the grass plot (P1). The samples were air-dried prior to any analysis. For each sample we

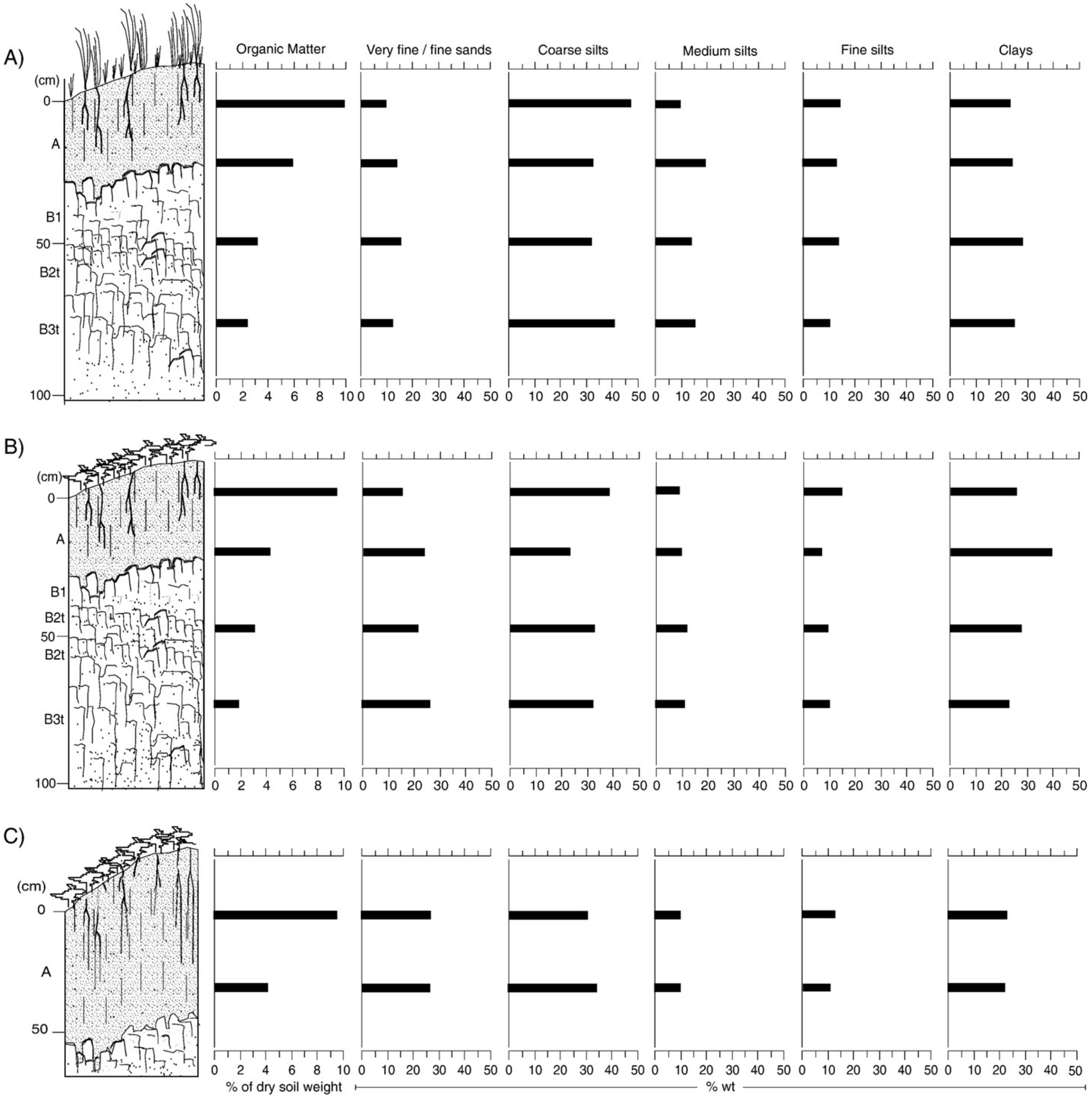

Fig. 2. Physico-chemical properties of three plots analyzed: A): Grasses, B): Acacias' plantation, C): Eucalyptus' plantation. Organic matter content (% of dry soil weight) and particle size distribution (% wt of sands, silts and clays) are indicated. ▨ Granular structure ▨ Blocky structure ▨ Massive structure.

determined the pH in 1:1 paste and in 1:2.5 solution with a digital Orion Research 501 pHmeter; the organic matter content (Walkley and Black, 1965); and the particle size distribution, with sieve and pipette analysis (Ingram, 1971; Galehouse, 1971).

2.3.2. Amorphous silica and silicophytolith fraction

For the determination of the percentage of amorphous silica fraction, both organic and inorganic, against the total sum of mineralogical components, 5 g soil samples were taken from each level. Organic matter was oxidized with 30% hydrogen peroxide at 70 °C. The clay minerals were extracted by repeated centrifugation at 1000 rpm for 3 min. Once the sample was clean, it was mounted on Balsam Canada; 500 grains were counted under optical microscope (OM) Leitz Wetzlar D35780 (450× magnification). The heavy liquid separation of the amorphous silica components was done with sodium polytungstate (δ=2.3 g/cm^3) through repeated centrifugation at 1500 rpm for 3 min. Cleansing of the sample was then done with distilled water and alcohol. The silicophytolith and volcanic ash percentage was determined by observation and counting of 500 grains under optical microscope (OM) Leitz Wetzlar D35780 (450× magnification). The qualitative analysis of the silicophytolith morphologies was made according to Mulholland and Rapp (1992) and Twiss (1992) specifications. The estimated number of silicophytoliths per soil gram was determined according to Albert and Weiner (2001), by means of these calculations:

Number of silicophytoliths on slide=(number of silicophytoliths counted)×(number of total fields of slide/number of fields counted)

Number of silicophytoliths on amorphous silica fraction=(number of silicophytoliths on slide)×(weight of amorphous silica fraction (g)/weight of sample on slide (g))

Number of silicophytoliths per soil gram=number of silicophytoliths on amorphous silica fraction/weight of total soil sample (g).

2.3.3. Cluster analysis

To analyze the similarity between the horizons of the different plots in terms of their morphological and physico-chemical properties and

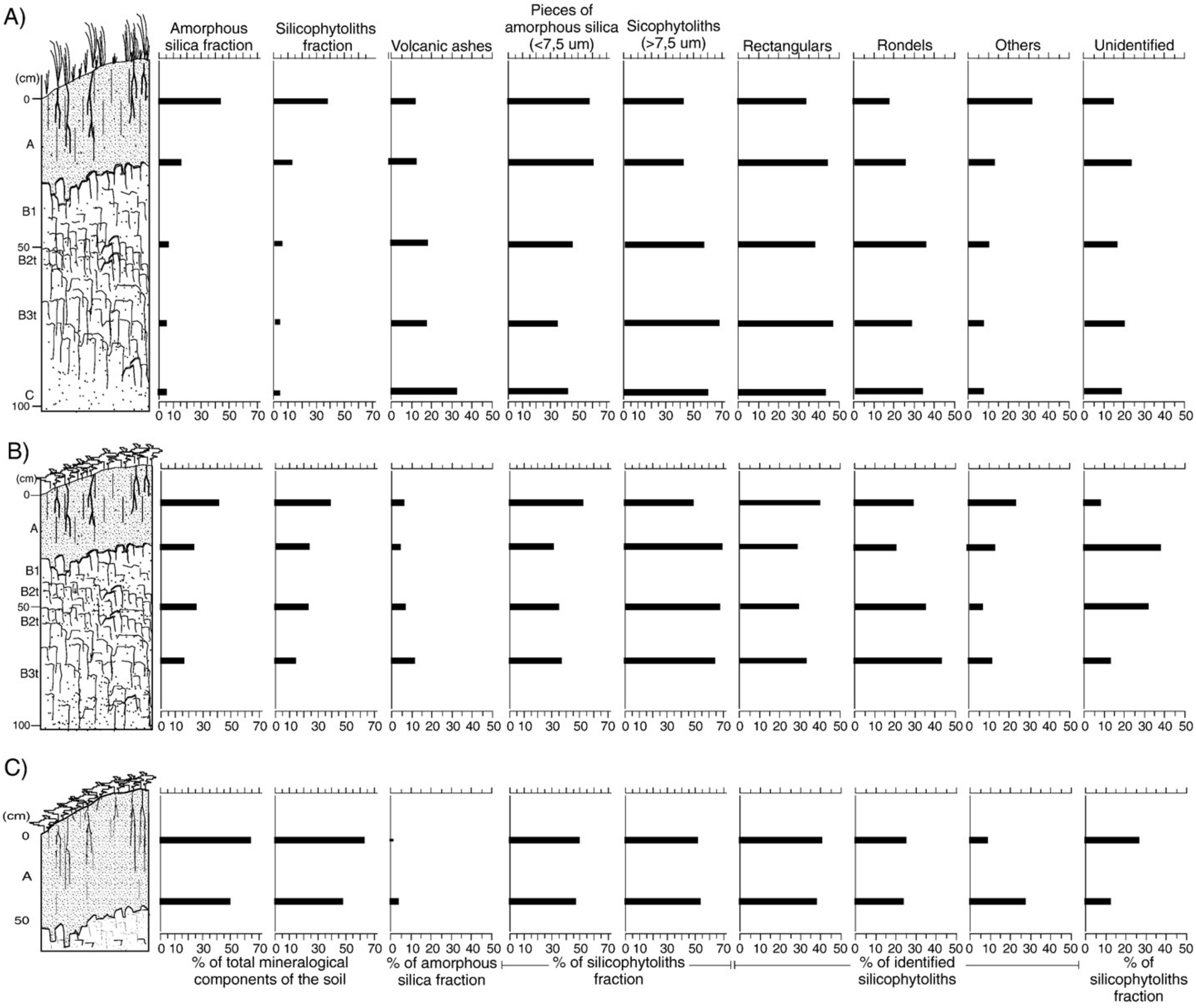

Fig. 3. Amorphous silica analysis of the three plots studied: A): Grasses, B): Acacias' plantation, C): Eucalyptus' plantation. Amorphous silica and silicophytoliths contents (% of total mineralogical components of the soil), volcanic ashes content (% of amorphous silica fraction), content of pieces of amorphous silica (% of silicophytolith fraction), silicophytoliths content (% of silicophytolith fraction), silicophytoliths predominant morphologies (% of identified silicophytolith) and unidentified silicophytoliths content (% of silicophytolith fraction) are indicated. ▨ Granular structure ▧ Blocky structure ▩ Massive structure.

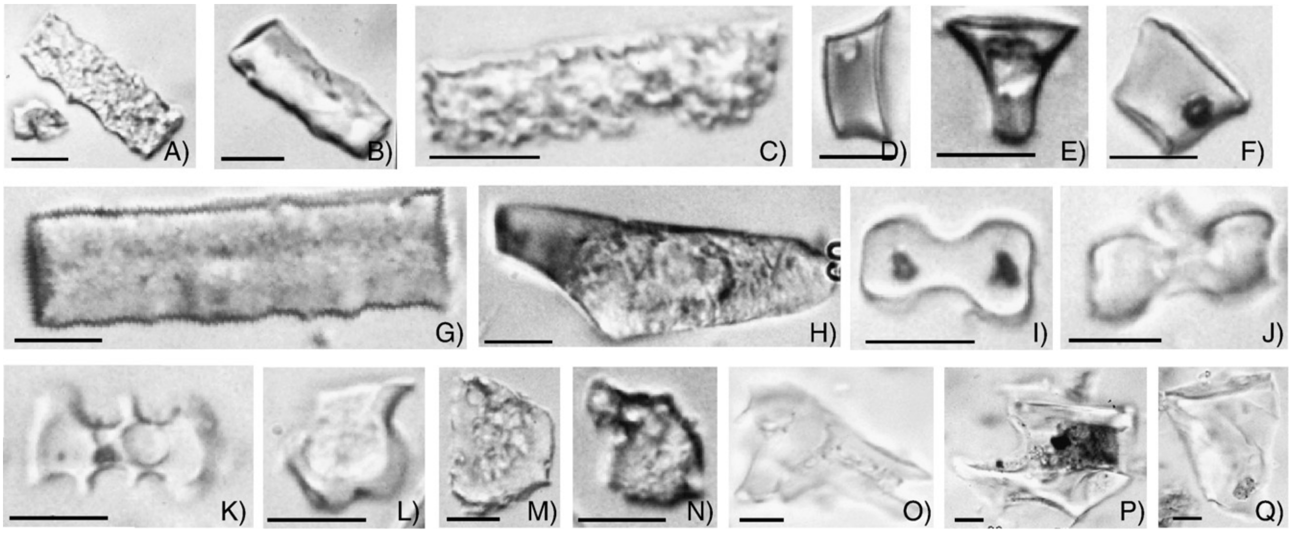

Fig. 4. OMs of predominant morphologies of silicophytoliths and volcanic ashes. A–C: rectangular silicophytoliths (A, C are weathered); D–F: rondels; G: smooth elongate silicophytolith; H: point-shaped silicophytolith; I–J: dumbbells; L–N: unidentified silicophytoliths; O–Q: volcanic ashes. Bars: 10 μm.

their silicophytolith content, a cluster analysis was carried out using the unweighted pair-group method and the arithmetical average linkage (UPGMA), and applying the distance coefficient (Euclidean distance).

3. Results

3.1. Morphological analysis

Typical Argiudolls have a mollic epipedon over 30 cm thick and an argillic endopedion of 50 cm approx. (Fig. 2A, B, and C). The morphological properties of the soils in the three plots under different vegetal cover are very similar, except for the greater development of mollic epipedon in the plots under acacias' (P2) (45 cm) and eucalyptus' (P3) plantations (60 cm approximately) in comparison with the plot under grass cover (P1) (35 cm) (Fig. 2A, B, and C). Mollic epipedons are black (10YR 2/1) and exhibit a medium, strong, granular structure. Argillic endopedions are very dark brown (10YR 2/2) to dark yellowish brown (10YR 4/4) and have a medium, strong, blocky structure. Parent material (loess) is dark yellowish brown (10YR 4/4) and shows a massive structure. As regards the development of the organic horizons (O), some differences were noticed among the three plots under analysis. In plot 1, the development is incipient (3 cm), whereas in the arboreal plots (P2 and P3), it is higher (8 to 11 cm). The higher organic horizon development causes an increase in humidity retention, which in turn favors fungus development (Osterrieth et al., 1998 and Oyarbide et al., 2001).

Table 1
Estimated number of silicophytoliths per soil gram

Vegetal cover	Horizon	Depth (cm)	Estimated number of silicophytoliths/soil gram
Eucalyptus' plantation	A	10–20	14.338.019
		40–50	6.060.442
Acacia's plantation	A	7	6.980.109
		30	1.666.664
	B2t	52	1.764.076
	B3t	73	2.351.898
Grass	A	7	8.222.313
		30	3.260.917
	B2t	52	1.903.818
	B3t	73	969.128
	C	100	952.298

3.2. Organic matter content and pH

The content of organic matter decreases from top to bottom in the profile (Fig. 2). In forested soils (P2 and P3), the content of organic matter is slightly lower in comparison with the profile under grass cover (P1) in all the levels that were analyzed (Fig. 2). Although the pH values are quite homogeneous, they match the organic matter content. The surface and subsurface levels present slightly acid values (6–6.3) in the grass (P1) and acacia plots (P2), and acid to slightly acid values (4.2–6) in the eucalyptus plot (P3); while the deeper levels present values close to neutrality (6.8–7).

3.3. Particle size distribution

In every analyzed level, under different vegetal cover, the silt textural size (62 to 2 μm; φ 4.5–9) is predominant (Fig. 2); within this fraction, the coarse silts size (φ 4.5–5) prevails. The results of textural analysis reveal distributions of a preponderantly bi-modal type, the coarse silt fractions (φ 4.5) and clay fractions (φ 11) being the most representative (Fig. 2). In the forested soil samples (P2 and P3), there is a noticeable increase in the fine sand fraction (φ 3–4) in comparison with the levels found in plot 1 (Fig. 2).

3.4. Quantitative evaluation of organic and inorganic amorphous silica in relation to the total amount of mineralogical components of the soil

We focused on the silt fraction because it is the most representative and the richest in silicophytolith content, whose median size is about 30 μm.

The amorphous silica fraction is composed of volcanic ashes, vitroclastics, and silicophytoliths. These elements have a 2.3 g/cm^3 density, but they differ from each other in their optical properties. The volcanic ashes are completely transparent or brown, the vitroclastics range from brown to reddish, whereas the silicophytoliths show a characteristic and defining pink hue; in addition, they have more relief and contrast (Teruggi, 1955).

The content of this fraction and, more specifically, of silicophytoliths in relation to the total amount of mineralogical components of the soil is higher on the top and it decreases to the bottom of the profiles in all the plots analyzed (Fig. 3). The arboreal plots (P2 and P3) show a higher content of amorphous silica; within them, plot 3 is the densest (49–63%). Although in the surface level of the grass (P1) and acacia (P2) plots the content of amorphous silica is similar (43% and

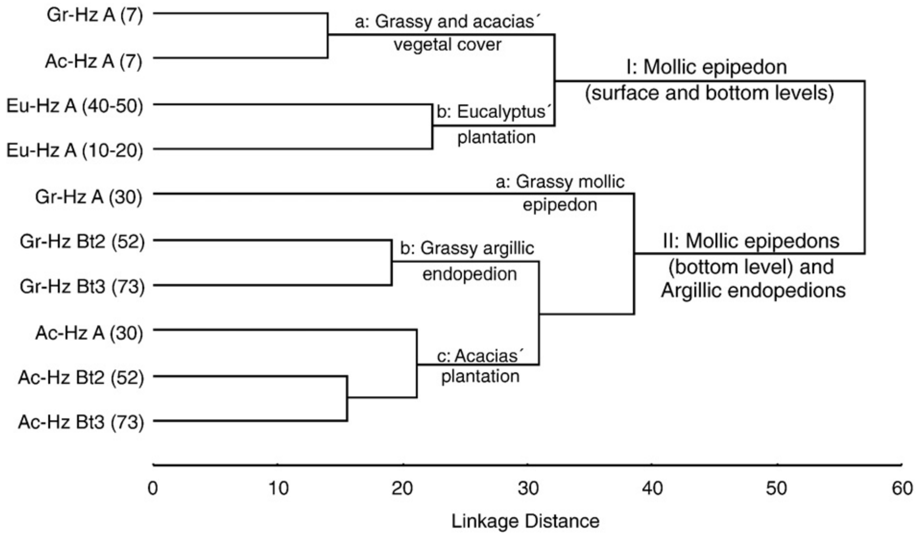

Fig. 5. Dendogram showing the relation among vegetal cover, morphological and physico-chemical properties, and silicophytolith content of soil profiles. Gr: Grasses, Ac: Acacias' plantation, Eu: Eucalyptus' plantation.

40% respectively), below 20 cm, amorphous silica content in the acacia plot (25–15%) is two to three times bigger than in the grass plot (15–5%) (Fig. 3).

3.5. Quantitative evaluation of the organic and inorganic amorphous silica fraction of the soil

When the amorphous silica fraction was analyzed, silicophytoliths (>7.5 µm) and pieces of amorphous silica (<7.5 µm) were discriminated, and morphologies of silicophytoliths were determined. The silicophytoliths and pieces of amorphous silica contents present a similar distribution in the grass (P1) and the acacia (P2) plots. The silicophytoliths increase and the pieces of amorphous silica decrease toward the bottom of the profiles (Fig. 3).

The silicophytolith predominant morphologies are rectangulars (28–46%) and rondels (17–43%) (Figs. 3 and 4). Less common are smooth elongates (1–7%), point-shaped (0.5–2%) and dumbbells (0.5–2%), among others. The latter morphologies were included in the "others" category (Figs. 3 and 4) because of their minor representativity. A high number of unidentified silicophytoliths can be observed in all the samples. In general, they correspond to morphologies with several degrees of weathering whose number rises in the subsurface levels of the soil. At the same time, the weathering process of silicophytoliths is also evident by the great representativity of amorphous silica particles of a size lesser than 7.5 µm (Fig. 3), which, for the most part, represent tiny loose pieces originated from the fracture and/or the dissolution of silicophytoliths and/or volcanic ashes. At the bottom of the profile, not only the number of silicophytoliths noticeably decrease, but also the "others" category does (Figs. 3 and 4), which implies a diminution in morphology diversity.

In all the plots, the volcanic ash content increases at the bottom of the profiles (Figs. 3 and 4).

3.6. Estimated number of silicophytoliths per gram of soil

Upon analyzing the amorphous silica fraction, the percentage of this fraction in the total amount of mineralogical components was calculated, and an estimate of the number of silicophytoliths (>7.5 µm) per gram of soil in all the levels analyzed was also calculated (Table 1). These data confirm the results of the count of amorphous silica fraction under optical microscope, where plot 3 had the highest content of siliceous biominerals. In addition, these date show the important representativity of silicophytoliths in the soils.

3.7. Cluster analysis

From the cluster analysis, two sizable groups were discriminated (Fig. 5). Group I covers the surface levels of mollic epipedons from the three plots analyzed, and the bottom of the same soil horizon from the eucalyptus plot; group II comprises the bottom levels (7–30 cm) of mollic epipedons and the argillic endopedions of the acacia and grass plots. Within the first group, two subgroups are clearly defined: a) the surface levels of the grass and acacia plots, and b) the eucalyptus plot. Within the second group were discriminated: a, b) grass plot, and c) acacia plot (Fig. 5).

4. Discussion

The analyzed soils occupy the same geomorphological unit and equal topographical position, and they have an identical pedogenesis. Only the vegetal cover makes them different. The analysis of the data makes it evident that the vegetation has an influence over: a) the organic horizon development, b) the mollic epipedon development and c) the contribution of silicophytoliths.

The organic horizon development stands in close relation with the degree of humidity of the environment, the abundance of the organic vegetal resource, and fungus colonization (Osterrieth et al., 1998 and Oyarbide et al., 2001). Arboreal species cause a greater development of organic horizons, which favors better humidity retention of the environment and a higher rate of fungus development. This implies a higher organic matter weathering and incorporation to the mineral horizons, which could explain the greater development of the mollic epipedon in these plots (P2 and P3) in contrast to grass plot (P1). This could be also linked to the different rooting depths of the vegetation, since, according to Duchaufour (1984), a deep rooting, typical of forest vegetation, favors leaching processes and, in consequence, facilitates the wash of colloidal elements while making the formation of a thicker mollic epipedon possible. Instead, when the rooting is superficial, typical of grass vegetation, water absorption by the roots stops the dragging phenomenon and, therefore, the wash is less accentuated and the mollic epipedon is less thick. Cluster analysis shows differences inside the mollic epipedon of the grass (P1) and the acacia (P2) plots. The bottom of this horizon separates from the surface level (group I) and is in close relation to the underlying horizon B (group II). This could imply a redefinition of the horizons as they were determined through the morphological properties of the field, since "the bottom of the mollic epipedon" could be part of the illuvial horizon or a transition horizon.

The results from the determination of the silicophytolith content in relation to the total amount of mineralogical components of the soil and the estimation of the number of silicophytoliths per gram of soil, reflect the important representativity of these amorphous silica biominerals, especially in the mollic epipedon of the Pampean Plain's Typical Argiudolls. There are no prior studies of the absolute number of silicophytoliths in this region, and there are only few prior studies in other regions of the world. Albert et al. (2006) found a lesser representativity of silicophytoliths in piroclastic, volcanic, saline and sandy-clay soils than in the Typical Argiudolls, but the data they produced are not comparable with ours, since the analyzed soils belong to different orders because of their different pedogenesis.

Regardless of the vegetal cover, silicophytolith content is always greater in the surface horizons than in the subsurface ones. According to Hard and Humphreys (2003), this silicophytoliths distribution along the profile corresponds to Type-1(ii) depth function, since silicophytoliths decrease with depth and penetrate into argillic endopedions. In addition, in the subsurface horizons of the arboreal plots (P2 and P3), silicophytolith content is greater than in the grass plot (P1). This could also be explained through the root design, since the rooting depth of the forest species could favor silicophytolith transference from the surface horizons to subsurface ones. This is in agreement with Alexandre et al. (1997) and Hard and Humphreys (2003), who explain the translocation of silicophytoliths throughout the soil profile mainly due to bioturbation, among other mechanisms. The silicophytolith content found in this work is surprising since, according to Wallis (2003), the Fabaceae family (P2) produces just a small number of siliceous biominerals, and the Myrtaceae family (P3) does not produce silicophytoliths, or it does only in trace amounts. This shows that whatever generates these differences in silicophytolith content, it is not the current vegetation. The differences could be due to several causes: a) a portion of silicophytolith content in the Typical Argiudolls could be inherited from the grass vegetation previous to forestation (Osterrieth, 2006), 2) a portion could be inherited from loessic parental material (Teruggi, 1957) and 3) the organic horizons have a protective effect on the mineral horizons of the soil with respect to eolian and/or hydric weathering during the evolution of these soils.

Alexandre et al. (1997) and Hard and Humphreys (2003), claim that silicophytoliths distribution along the profile involves, besides translocation, the biominerals dissolution. So, the decrease in silicophytolith content from the top to the bottom of the analyzed profiles could be linked to the weathering or dissolution of the siliceous biominerals because there is a recurrent relation between porosity, specific surface, and silicophytolith weathering processes, depending on the environment and its interactive components. In general, the specific surface of silicophytoliths is high; values ranging from 15 $m^2\ g^{-1}$ in oat silicophytoliths (Jones and Milne, 1963) to 122 $m^2\ g^{-1}$ in *Stipa* sp. silicophytoliths (Peineman et al., 1970), and intermediate values in forest species silicophytoliths (Alexandre et al., 1997; Vallejo Gómez et al., 2000) have been found. Dissolution may remove small, fragile silicophytoliths, leaving the more robust morphologies (Hard and Humphreys, 2003). So, the decrease of the pieces of amorphous silica at the bottom of the soil profile could indicate the total dissolution of this fraction of amorphous silica in direct relation with the pedological evolution of the Typical Argiudolls. In turn, the weathering processes of silicophytoliths are also evident in the significant content of unidentified morphologies that exhibit a great abundance of dissolution pits, so their classification is impossible because their real shape is doubtful. Though the distribution along the soil profile is different from that founded by Borba-Roschel et al. (2006), the contents in the surface levels are similar.

Traditionally, silica fluxes to soil solutions and stream waters are thought to be controlled by the weathering and subsequent dissolution of silicate minerals (Derry et al., 2005). However, non-crystalline forms of silica are much more soluble than crystalline forms (Oehler, 1979, in Clarke, 2003), e.g. amorphous silica is more soluble than quartz by a factor of 10 or more (Wilding and Dress, 1974). Therefore, according to Farmer et al. (2005), phytoliths could be the only soil component likely to account for the equilibrium concentrations of Si, so separate soil-plant silica cycle can be significant in comparison with weathering input and hydrologic output (Derry et al., 2005). In this sense, our work shows the important role of silicophytoliths could have in the silica cycle, since this fraction is too weathered against the other silica soil minerals which show no features of weathering (Borrelli et al., in press). Research on forested ecosystems demonstrates a prominent biologic role in silica storage and export from terrestrial environments (Blecker et al., 2006). In temperate deciduous forests, 80% of soluble silica is derived from biogenic silica, and in coniferous forest systems only 20% (Blecker et al., 2006). In tropical forests, the contribution of biogenic silica to soil solution, soil mineral formation and stream export can exceed the contribution from weathering of primary minerals (Alexandre et al., 1997; Derry et al., 2005). In these environments, the rapid biomass turnover results in rapid chemical and biocycling of plant organic matter and their associated phytoliths, creating a potentially large pool of reactive biogenic silica relative to low availability of mineral-derived Si (Wüst and Bustin, 2003, Derry et al., 2005). According to this, Alexandre et al. (1997) reported that in ferrallitic soils of the tropical Congo, 92% of the biogenic silica in the soil is recycled by plants and only the remaining 8% accumulates in the soil, and that, Si release from phytolith dissolution is twice that of Si release due to silicate weathering. In a Hawaiian tropical volcanic system, silica cycle has a strong biological imprint, since most of the silica released to Hawaiian stream water has passed through the biogenic silica pool (Derry et al., 2005). Farmer et al. (2005) showed that, in Scandinavian forest podzols, phytoliths must be the principal sink and source of Si in soils, and their solubility limits the concentration of Si in soil drainage water and streams.

In agreement with Derry et al. (2005) who expect that grasslands, that are rich in biogenic silica and have high turnover rates, also have a strong biological control on Si cycling and export; and with Blecker et al. (2006) who claimed that in grasslands, this more soluble pool of biogenic Si (comprising 1–3% of the total Si pool) has a direct impact on Si flux to both soil solution and streams; we show the importance of weathering and dissolution processes of silicophytoliths in Typical Argiudolls of the Pampean Plain. Therefore, these weathering processes of the silicophytoliths could explain the high concentration of silica (60–70 ppm) found in the Pampean Aquifer (Martínez and Osterrieth, 1999; Miretzky et al., 2001). According to Martínez and Osterrieth (1999), the samples of groundwaters from the Pampean Aquifer are oversaturated in all the silicate minerals, but they are in equilibrium with amorphous silica. Therefore, though the origin of the dissolved silica must be the silicates weathering and clay neoformation, the equilibrium with respect to the amorphous silica (especially silicophytoliths) is the element that controls silica contents in the aquifer. Especially considering that the grasslands and paleograsslands evolution have been recurrent during the Quaternary and, that in previous studies (Osterrieth et al., 1998 and Oyarbide et al., 2001), within the amorphous silica fraction, silicophytoliths show different degrees of weathering, while volcanic ashes (other potential source of amorphous silica) show no or some very incipient features of weathering (Osterrieth and Martínez, 1993; González and Osterrieth, 1996; Osterrieth, 2000). Therefore, most of the geochemical control over the silica concentrations in the area groundwater could be exerted by these amorphous silica biominerals.

There is some evidence about the role of silicophytoliths in soil pedogenesis. In this sense, Wüst and Bustin (2003) found that in acid peat accumulating environments, most of silica neoformed minerals may originate from biogenic silica and especially phytoliths. And, Lucas et al. (1993) showed that the input of silica released by plants in the topsoils is responsible for the neoformation of kaolinite in

Brazilian latosols. According to the evidence of silicophytoliths dissolution and their role in silica minerals neoformation, and because of the good preservation state of the others silicate minerals of the soils (Borrelli et al., in press); silicophytoliths play an important role in the silica cycle and could have a prevalent role in typical Argiudolls pedogenesis through soil mineral neoformation and soil matrix conformation.

5. Conclusions

The greater development of the organic horizons in the arboreal plots and the tap-root system, typical of these vegetal species, contribute to the greater development of the mollic epipedons in these plots as compared to the grass plot. Silicophytolith content is higher in the arboreal plots but this does not correspond to the current vegetation, so it could be the result of the protective effect of the organic horizons on soil weathering, which preserves the previous vegetal history. Owing to the important representativity of silicophytoliths, mostly in the mollic epipedon of the Typical Argiudolls, the weathering processes that affect them could indicate not only the pedological evolution of these soils, but also the inclusion of silica in the system, available for the formation of new silicophytoliths and of organo-mineral complexes, and capable of being transferred to groundwater.

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References

Albert, R.M., Weiner, S., 2001. Study of phytoliths in prehistoric ash layers from Kebara and Tabun caves using a quantitative approach. In: Meunier, J.-D., Colin, F. (Eds.), Phytoliths: Applications in Earth Sciences and Human History. A. A. Balkema Publishers, pp. 251–266.

Albert, R.M., Bamford, M.K., Cabanes, D., 2006. Taphonomy of phytoliths and macroplants in different soils from Olduvai Gorge (Tanzania) and the application to Plio-Pleistocene palaeoanthropological samples. Quaternary International 148, 78–94.

Alexandre, A., Meunier, J., Colin, F., Kova, J., 1997. Les phytolithes, indicateurs du cycle biogéochimique du silicium eu foret équatoriales. C.R. Acad. Sci. Paris 319 (II), 453–458.

Bertoldi de Pomar, H., 1970. Fitolitos y Zoolitos. Su significado geológico en sedimentos continentales. Boletín de la Asociación Geológica de Córdoba I (I), 21–31.

Blecker, S.W., McCulley, R.L., Chadwick, O.A., Kelly, E.F., 2006. Biologic cycling of silica across a grassland bioclimosequence. Global Biogeochemical Cycles 20, GB3023.

Borba-Roschel, M., Alexandre, A., Fortes Drummond Chicarino Varajao, A., Meunier, J., Chicrino Varajao, C., Colin, F., 2006. Phytoliths as indicators of pedogenesis and paleoenvironmental changes in the Brazilian *cerrado*. Journal of Geochemical Exploration 88, 172–176.

Borrelli, N., Osterrieth, M., 2001. Sílice amorfo de origen orgánico e inorgánico en suelos de agroecosistemas y campos naturales de Laguna de Los Padres, Buenos Aires. Evaluación preliminar. Natura Neotropicalis 32 (1), 27–32.

Borrelli, N., Osterrieth, M., Oyarbide, F., Marcovecchio, J., in press. Calcium biominerals in typical Argiudolls from the Pampean Plain, Argentina: an approach to the understanding of their role within the calcium biogeochemical cycle. Quaternary Internationa. doi:10.1016/j.quatint.2007.11.002.

Burgos, J.J., Vidal, A., 1951. Los climas de la República Argentina según la nueva clasificación de Thornthwaite. Meteoros 1 (1), 3–32.

Cabrera, A.L., 1976. Regiones fitogeográficas argentinas. Enciclopedia Argentina de Agricultura y Jardinería, I, p. 85.

Clarke, J., 2003. The occurrence and significance of biogenic opal in the regolith. Earth-Science Reviews 60, 175–194.

Derry, L., Kurtz, A., Ziegler, K., Chadwick, O., 2005. Biological control of terrestrial silica cycling and export fluxes to watersheds. Nature 433, 728–731.

Duchaufour, P., 1984. Manual de Edafología. Masson S.A., Barcelona, p. 501.

Farmer, V.C., Delbos, E., Miller, J.D., 2005. The role of phytolith formation and dissolution in controlling concentrations of silica in soil solutions and streams. Geoderma 127, 71–79.

Frenguelli, J., 1930. Partículas de sílice organizada en el loess y en los limos pampeanos. Células silíceas de Gramíneas. Anales de la Sociedad Científica de Santa Fe 2, 64–109.

Galehouse, J.S., 1971. Sedimentation analysis. In: Carver (Ed.), Procedures in Sedimentary Petrology. Wiley Interscience, Wisconsin, USA, pp. 69–94.

Golyeva, A., 2001. Biomorphic analysis as a part of soil morphological investigations. Catena 43, 217–230.

González, G., Osterrieth, M., 1996. Silicobiolitos en Suelos Paleosuelos y sus materiales parentales, Buenos Aires, Argentina. In: Pinilla, Tresserras, Machado (Eds.), The state -of-the-art-phytoliths in soils and plants. C.S.I.C., España, pp. 83–92.

Hard, D., Humphreys, G., 2003. Phytolith depth functions in surface regolith materials. In: Roach, I.C. (Ed.), Advances in Regolith. CRC LEME, pp. 159–163.

Ingram, R.L., 1971. Sieve analysis. In: Carver (Ed.), Procedures in Sedimentary Petrology. Wiley Interscience, Wisconsin, USA, pp. 41–68.

Jones, L., Milne, A., 1963. Plant and Soil 18, 207–220.

Kelly, E., Chadwick, O., Hilinski, T., 1998. The effect of plants on mineral weathering. Biogeochemistry 42, 21–53.

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

Martínez, D.E., Osterrieth, M., 1999. Geoquímica de la sílice disuelta en el Acuífero Pampeano en la Vertiente Sudoriental de Tandilia. Hidrología Subterránea 13, 241–250.

Miretzky, P., Conzonno, V., Fernández Cirelli, A., 2001. Geochemical proceses controlling silica concentrations in groundwaters of the Salado River drainage basin, Argentina. Journal of Geochemical Exploration 73, 155–166.

Mulholland, S.C., Rapp, G., 1992. A morphological classification of grass silica-bodies. In: Rapp, Mulholland (Eds.), Phytolith systematics. Plenum Press, New York, pp. 65–89.

Oehler, J.H., 1979. Deposition and diagenesis of biogenic silica. In: Trudinger, P.A., Swain, D.J. (Eds.), The Biogeochemical Cycling of Mineral-Forming Elements. Elsevier, Amsterdan, pp. 467–479.

Osterrieth, M., 2000. Silicofitolitos una herramienta para la comprensión de procesos pedológicos del Cuaternario. Actas XVII Congreso Argentino de la Ciencia del Suelo. CD.

Osterrieth, M., 2006. Silicofitolitos en suelos, paleosuelos y sedimentos. Actas III Congreso Argentino de Cuaternario y Geomorfología, I, pp. 351–366.

Osterrieth, M., Cionchi, J.L., 1985. Estratigrafía del Cuaternario de Laguna de Los Padres, provincia de Buenos Aires. Actas I Jornadas Geológicas Bonaerenses, p. 41.

Osterrieth, M.L., Martínez, G., 1993. Paleosols on Late Cainozoic Sequences in the Northeastern side of Tandilia Range, Buenos Aires, Argentina. Quaternary International XVII, 57–65.

Osterrieth, M., Maggi, J., 1996. Variaciones cuali-cuantitativas de la fracción arcilla en Argiudoles afectados por prácticas agrícolas en Laguna de Los Padres, Buenos Aires. Actas VI Reunión Argentina de Sedimentología, pp. 337–342.

Osterrieth, M., Fernández, C., Bilat, Y., Martínez, P., Martínez, G., Trassens, M., 1998. Geoecología de Argiudoles típicos afectados por prácticas hortícolas en la Llanura Pampeana, Buenos Aires, Argentina. Actas XVI Congreso Mundial de la Ciencia del Suelo, pp. 1–8.

Osterrieth, M., Borrelli, N., Martínez, P., García Calderón, N., Scampini, E., Trassens, M., Bernava, L.V., Miglioranza, K., 2001. Geoecología y degradación de Argiudoles típicos afectados por prácticas hortícolas, Buenos Aires, Argentina. Actas III Reunión Nacional de Geología Ambiental y Ordenación del Territorio. I Reunión de Geología Ambiental y Ordenación del Territorio del área del Mercosur, p. 49.

Oyarbide, F., Osterrieth, M.L., Cabello, M., 2001. Trichoderma koningii as a biomineraliziting fungous agent of calcium oxalate crystals in typical Argiudolls of the Los Padres Lake natural reserve (Buenos Aires, Argentina). Microbiology Research 156, 1–7.

Peineman, N., Tchapek, M., Grassi, R., 1970. Properties of phytoliths II. Pflanzernahr Bodeukunde 127, 126–133.

Piperno, D., 1988. Phytolith Analysis: An Archaeological and Geological Perspective. Academic Press, New York. 280 pp.

Rovner, I., 1971. Potential of opal phytoliths for the use of palaoecological reconstruction. Quaternary Research 1, 343–359.

Soil Survey Staff, 1996. Keys to Soil Taxonomy, Seventh edition. United States Department of agriculture, Washington D.C.

Teruggi, M., 1955. Algunas observaciones microscópicas sobre vidrio volcánico y ópalo organógeno en sedimentos pampianos. Revista Museo de La Plata XVIII (66), 17–26.

Teruggi, M., 1957. Nature and origin of Argentine loess. Journal of Sedimentary Petrology 27 (3), 322–332.

Twiss, P.C., 1992. Predicted world distribution of C3 and C4 grass phytoliths. In: Rapp, Mulholland (Eds.), Phytolith systematics. Plenum Press, New York, pp. 113–128.

Vallejo Gómez, E., Sedov, S., Oleschko, C., Shoba, S., , 2000. Phytoliths in surface and burried Andosols of Central Mexico. Morphological variety, rates of accumulation and weathering. Actas III IMPR. Man and the (paleo) environment. The phytolith evidence: 17.

Walkley, Black, 1965. In: Black, C. (Ed.), Methods of Soil Analysis. American Society of Agronomy, pp. 1372–1375.

Wallis, L., 2003. An overview of leaf phytolith production patterns in selected northwest Australian flora. Review of Palaeobotany and Palynology 125, 201–248.

Wilding, L.P., Dress, L.R., 1974. Contributions of forest opal and associated crystalline phases to fine silt and clay fractions of soils. Clays and Clay Minerals 22, 295–306.

Wüst, R., Bustin, R., 2003. Opaline and Al–Si phytoliths from a tropical mire system of West Malaysia: abundance, habit, elemental composition, preservation and significance. Chemical Geology 200, 267–292.