



## Silica biogeochemical cycle in temperate ecosystems of the Pampean Plain, Argentina



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### ABSTRACT

Silicophytoliths were produced in the plant communities of the Pampean Plain during the Quaternary. The biogeochemistry of silicon is scarcely known in continental environments of Argentina. The aim of this work is to present a synthesis of: the plant production and the presence of silicophytoliths in soils with grasses, and its relationship with silica content in soil solution, soil matrix and groundwaters in temperate ecosystems of the Pampean Plain, Argentina. We quantified the content of silicophytoliths in representative grasses and soils of the area. Mineralochemical determinations of the soils' matrix were made. The concentration of silica was determined in soil solution and groundwaters. The silicophytoliths assemblages in plants let to differentiate subfamilies within Poaceae. In soils, silicophytoliths represent 40–5% of the total components, conforming a stock of  $59\text{--}72 \times 10^3$  kg/ha in A horizons. The concentration of  $\text{SiO}_2$  in soil solution increases with depth (453–1243  $\mu\text{mol/L}$ ) in relation with plant communities, their nutritional requirements and root development. The average concentration of silica in groundwaters is 840  $\mu\text{mol/L}$ . In the studied soils, inorganic minerals and volcanic shards show no features of weathering. About 10–40% of silicophytoliths were taxonomically unidentified because of their weathering degrees. The matrix of the aggregates is made up by microaggregates composed of carbon and silicon. The weathering of silicophytoliths is a process that contributes to the formation of amorphous silica-rich matrix of the aggregates. So, silicophytoliths could play an important role in the silica cycle being a sink and source of Si in soils and enriching soil solutions and groundwaters.

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## 1. Introduction

The biogeochemical cycles describe the fluxes of the diverse forms of the elements between the biosphere, lithosphere, hydrosphere and atmosphere. In general, biogeochemical cycles refer to natural processes that enable the recycling of nutrients through a continuous exchange between organisms and the environment in which they develop (Exley, 1998).

The importance of silicon (second most abundant element in the earth's crust) is due to occurs in most of the minerals forming rocks and parent materials of soils (Sommer et al., 2006); and for its quality as an important nutrient that controls the functioning of

terrestrial, marine, coastal and inland water ecosystems (Ragueneau et al., 2002; Conley, 2002; Farmer et al., 2005; Borrelli et al., 2012). Although there are several studies focused on the marine silica cycle, the interest in the terrestrial silica cycle has recently begun to increase, since it is involved in the global carbon cycle and much of the reactive Si reaching the oceans has undergone prior biological cycling on the continents through the biomimetic process (Conley, 2002).

The biomimetic processes are a widespread phenomenon in nature. Biomimeticizations are mineral or amorphous structures, with varied chemical composition, of biogenic nature generated starting from the metabolic activity of different organisms (Coe et al., 2014). Since biomimeticizing organisms are distributed over the globe, the process of biomimeticization may be a terrestrial process which acts as a global source and sink of soluble ions (Jahren, 1996). Many living higher plants extract monosilicic acid from the soil by the roots, transport it via the transpiration stream

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and precipitate it as amorphous silica biominerizations (silicophytoliths,  $\text{SiO}_2\text{.nH}_2\text{O}$ ) along cell walls or filling the cell lumen and intercellular spaces (Piperno, 1988); where water evaporates and Si concentrations may exceed solubility limit (Sommer et al., 2006). 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 monosilicic acid is released. The monosilicic acid could be reabsorbed by the plants, remain in the system, form secondary minerals (clays, allophanes and amorphous silica) and organomineral complexes; conform the soil aggregates matrix and/or to flow to the underground water (Martinez and Osterrieth, 1999; Borrelli et al., 2010).

Although silica is an element of almost all parent materials, and it is one of the basic components in most soils (Sommer et al., 2006), the importance of the biogenic cycle of this element in terrestrial environments has been recognized in the latter decades (Alexandre et al., 1997; Conley, 2002; Osterrieth, 2006; Borrelli et al., 2010). Understanding of elemental fluxes at global scale is one of the principal goals of current research in terrestrial and aquatic biogeochemical cycling. In Argentine, in the southeastern Pampas region, the pristine vegetation across the Quaternary has been mainly composed of Poaceae (Ghera and Leon, 2001), one of the major silicophytolith producer along with Cyperaceae and Arecaceae (Piperno, 1988). Although the relevant contribution of these biominerizations from the pristine vegetation in the Pampas region along the Quaternary (Fernández Honaine et al., 2006; Borrelli et al., 2008), there are no studies evaluating the role of silicophytoliths in the different compartments of the silica cycle. Besides, in general, there is little research about the importance of silicophytoliths in the conformation of the soil matrix. So, the aim of this work is to present a synthesis of the quantifications obtained from: the plant production in the predominant communities of the pristine vegetation (grasses) and the presence of amorphous silica biominerizations in soils, and their relationship with silica content in soil solution, soil matrix and groundwaters to contribute the understanding of the silica biogeochemical cycle in temperate ecosystems of the Pampean Plain, Argentina.

## 2. Materials and methods

### 2.1. Study site

The site under study is located in the Partido of General Pueyrredón and in the Partido of Tandil, specially restricted to the low hills (less than 200 m.a.s.l.) from the Tandilia Range ( $37^{\circ}19'S$ – $59^{\circ}15'W$  and  $37^{\circ}50'S$ – $58^{\circ}30'W$ ), both located in the southeastern of the Buenos Aires province (Fig. 1).

The climate is mesothermic and sub-humid, with little or no water deficiency, including an annual precipitation of 809 mm. The annual average temperature is  $13.7^{\circ}\text{C}$ , with minimum mean values ( $8.1^{\circ}\text{C}$ ) in June and maximum ones ( $19.8^{\circ}\text{C}$ ) in January (Mar del Plata National Meteorological Service, according to the 1920–1980 record). In agreement with the standards set by Soil Survey Staff (1996), the soil temperature is of the mesic type, and the humidity regime is udic.

The southeastern Pampas represents one of the most conspicuous region of the Humid Pampean Plain, where holds much of temperate ecosystems of Argentina. Mollisols are the representative soils of this area, where Argiudolls and Hapludolls are predominant. They originated from eolian loessian sediments linked to the latest arid cycle of the late Pleistocene–Holocene. They are, especially Argiudolls, very important from an economic point of view, due to their high productivity and the intense agricultural and horticultural activity which is usually developed in the study area.

This fact has also generated a noticeable decrease in the content of organic matter and clay fraction in the Ap horizon (plowed horizon), of the A horizon and the corresponding loss of structural stability and fertility (Osterrieth and Maggi, 1996).

The typical Argiudolls have an A horizon (mollic epipedon) over 30 cm thick and a B horizon (argillic endopedion) of approximately 50 cm. The A horizons are black (10YR 2/1), with medium-sized, strong, granular structure. The B horizons are very dark brown (10YR 2/2) to dark yellowish brown (10YR 4/4) with medium-sized, strong, blocky structure. The parent material (loess) is dark yellowish brown (10YR 4/4) and shows a massive structure. The organic matter content is high, approximately 9.39% in the A horizon, 3% in the B horizon, and 1.5% in the parent material. The pH values are slightly acid (6–6.3) in the A horizon, and close to neutrality (6.8–7) in the parent material. In the eucalyptus forested areas, pH values are more acidic (4.2) in the A horizon. The soil texture is silt loam, with the silt (55–70%) and clay (20–30%) fractions being the most representative. Soil mineralogy is predominantly composed by light minerals: Ca–Na feldspars (25–30%), vitroclastics (25–30%), quartz (20%), volcanic ashes (10%), and K feldspars (5%). Heavy minerals represent only 0.9–4% (Osterrieth, 2004; Borrelli et al., 2008, 2009).

The “Pampeano” Aquifer at the southeast of the province of Buenos Aires is characterized by high dissolved silica concentrations (50–70 ppm). The sand fraction of the sediments is mainly formed by plagioclases, potassium feldspars and quartz. The smectites are the main components of the clay fraction. Their chemical composition is similar to a dacitic volcanic rock. The groundwater is oversaturated in all the silicate minerals, but it is in equilibrium with amorphous silica (Martinez and Osterrieth, 1999, 2013).

Although the native vegetal communities are mainly represented by Poaceae, their actual distribution in the southern Pampas is largely restricted to the foothills of the Tandilia System, where the poorly developed soil has prevented its replacement by crops (Herrera, 2007). The natural grasslands developed in those areas are mainly characterized by *Stipa*, *Piptochaetium* and *Briza* species, and tussock grasses such as *Paspalum quadrifarium*, among others (Herrera, 2007).

### 2.2. Methodology

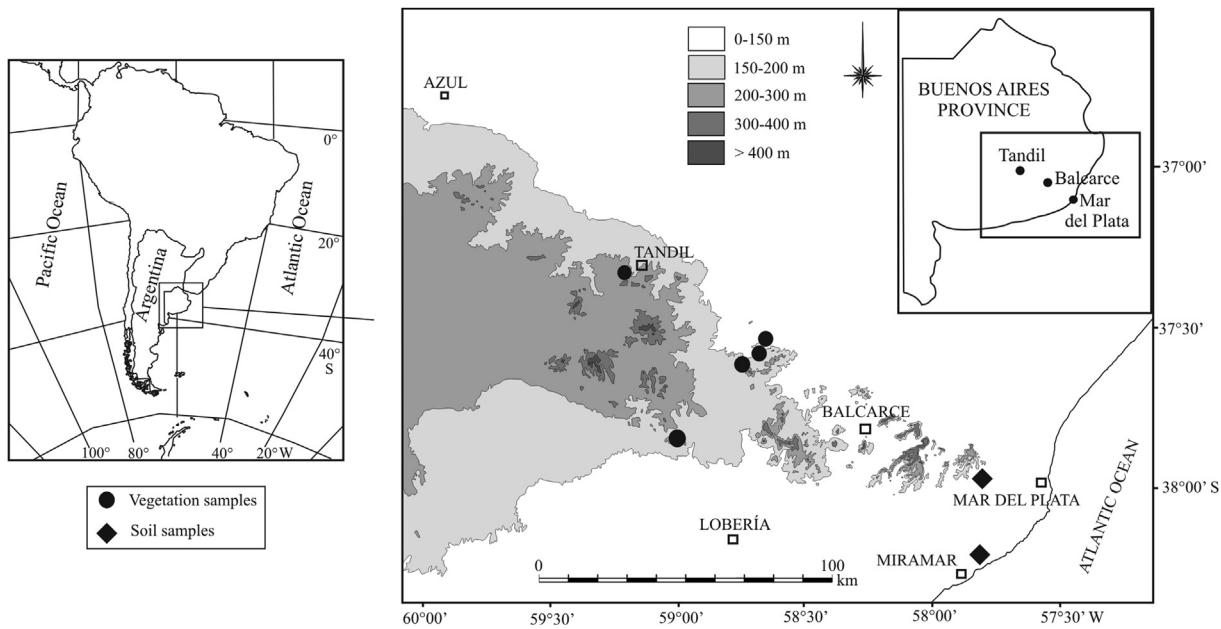
#### 2.2.1. Silicophytoliths in plants

Specimens of 18 species belonging to four subfamilies of Poaceae (Pooideae, n: 7; Panicoideae, n: 7; Stipoideae, n: 3; Arundinoideae, n: 1) at flowering or seedling stage were collected. For each species, the silicophytoliths from leaves were extracted following a calcination technique (Labouriau, 1983). The samples were dried at  $56^{\circ}\text{C}$  for 24 h, and charred at  $200^{\circ}\text{C}$  for 2 h. Later, they were boiled in a 5 N HCl solution for carbonates elimination. Finally, the samples were ignited at  $760^{\circ}\text{C}$  for 3 h. Silica content was calculated as a percentage dry mass. The ashes were mounted with immersion oil and the silicophytolith morphotypes were described with a Leitz Wetzel D35780 microscope at  $400 \times$  magnification. Photographs were taken with a digital camera Kodak Easy Share CX7530. Between 350 and 400 silicophytoliths were counted in each slide and the morphotypes were described according to the ICPN descriptors and previous classifications (Twiss, 1992; Fredlund and Tieszen, 1994; Madella et al., 2005).

The list of species, the number of individuals used and the silicophytolith assemblages of each species are described in detail in Fernández Honaine et al. (2006).

#### 2.2.2. Silicophytoliths in soils

The percentage of silicophytoliths against the total



**Fig. 1.** Map of the study area.

mineralogical components was calculated in the A, B and C horizons of 13 soil profiles. Of each horizon, the analysis was done from 5 g of soil sample, prior organic matter oxidation and clay removal. The clean sample was mounted on immersion oil and 500 grains were counted under optical microscope (OM) Leitz Wetzlar D35780 ( $\times 450$  magnification) (Alvarez et al., 2008).

The amorphous silica concentration was done by heavy liquid separation with sodium polytungstate ( $\delta = 2.3 \text{ g/cm}^3$ ) (Alvarez et al., 2008). The silicophytolith and volcanic ash percentage was determined by observation and counting of 500 grains under OM Leitz Wetzlar D35780 ( $\times 450$  magnification).

In order to calculate the total stock of silicophytoliths in the A horizons (kg/ha), soil silicophytolith content (g/100 g soil) was multiplied by bulk density and the thickness of the level.

Mean and standard deviation of the percentage of silicophytoliths against the total mineralogical components, the percentage of taxonomically unidentified silicophytoliths and percentage of weathered silicophytoliths were calculated in the different soil horizons analyzed. Differences between medians were tested by a Kruskal–Wallis test and a nonparametric multiple comparison test (Steel–Dwass test), since normality and homoscedasticity assumptions were not achieved (Zar, 1984).

#### 2.2.3. Silica in soil solution and groundwaters

Silica concentration was determined in the soil saturated paste extract. Groundwater samples were obtained from domiciliary wells, mills and irrigation wells. Soil saturated paste extract and groundwater samples were filtered through  $0.45 \mu\text{m}$  pore size membrane filters of cellulose nitrate and silica concentration was determined by means of silicomolybdate method (APHA, 1998).

#### 2.2.4. Soil matrix

Undisturbed samples were taken ( $5 \times 3 \times 12 \text{ cm}$ ) with vertical orientation in each soil profile. The samples were then impregnated with a polyester resin and the micromorphological descriptions were performed using petrographic microscope (Bullock et al., 1985).

The study of the submicroscopic characteristics of the matrix of aggregates was made from semi disturbed samples. Three

morphologies of aggregates were studied: elongated, quadrangular and spherical (Alvarez et al., 2006). These were analyzed with a Jeol JSM-6460LV scanning electron microscope (SEM) equipped with an energy dispersive X-ray spectrometer (EDS).

### 3. Results and discussion

#### 3.1. Silicophytoliths in plants

Silicophytolith content of the four subfamilies studied ranged between 3.9 and 14% dry weight. Pooideae species presented the highest values (6.5–14%;  $9.2 \pm 2\%$  dry weight) and Panicoideae the lowest (4–8.3%;  $5.4 \pm 2.5\%$  dry weight). The media of the content in Stipoideae and Arundinoideae species were  $7.4 \pm 2\%$  and 6.1% respectively. Significant differences in the content of silicophytoliths as a percentage of dry weight in leaves were observed between the Pooideae and Panicoideae subfamilies (Fernández Honaine et al., 2008).

Silicophytolith morphologies of the species match general descriptions made by other authors (e.g. Twiss, 1992; Fredlund and Tieszen, 1994) and the Poaceae subfamilies could be distinguished based on their silicophytolith assemblages (Table 1).

Pooideae species were mainly characterized by rondels, trapeziform crenate phytoliths and trichomes (Fig. 2: 1, 2, 8–10); Panicoideae and Arundinoideae were distinguished by panicoid bilobates with concave and/or straight ends, crosses and bulliform phytoliths (Fig. 2: 5–7). Lastly, Stipoideae species were characterized by *Stipa*-type and simple lobates, rondels and trichomes (Fig. 2: 2–4, 8–10).

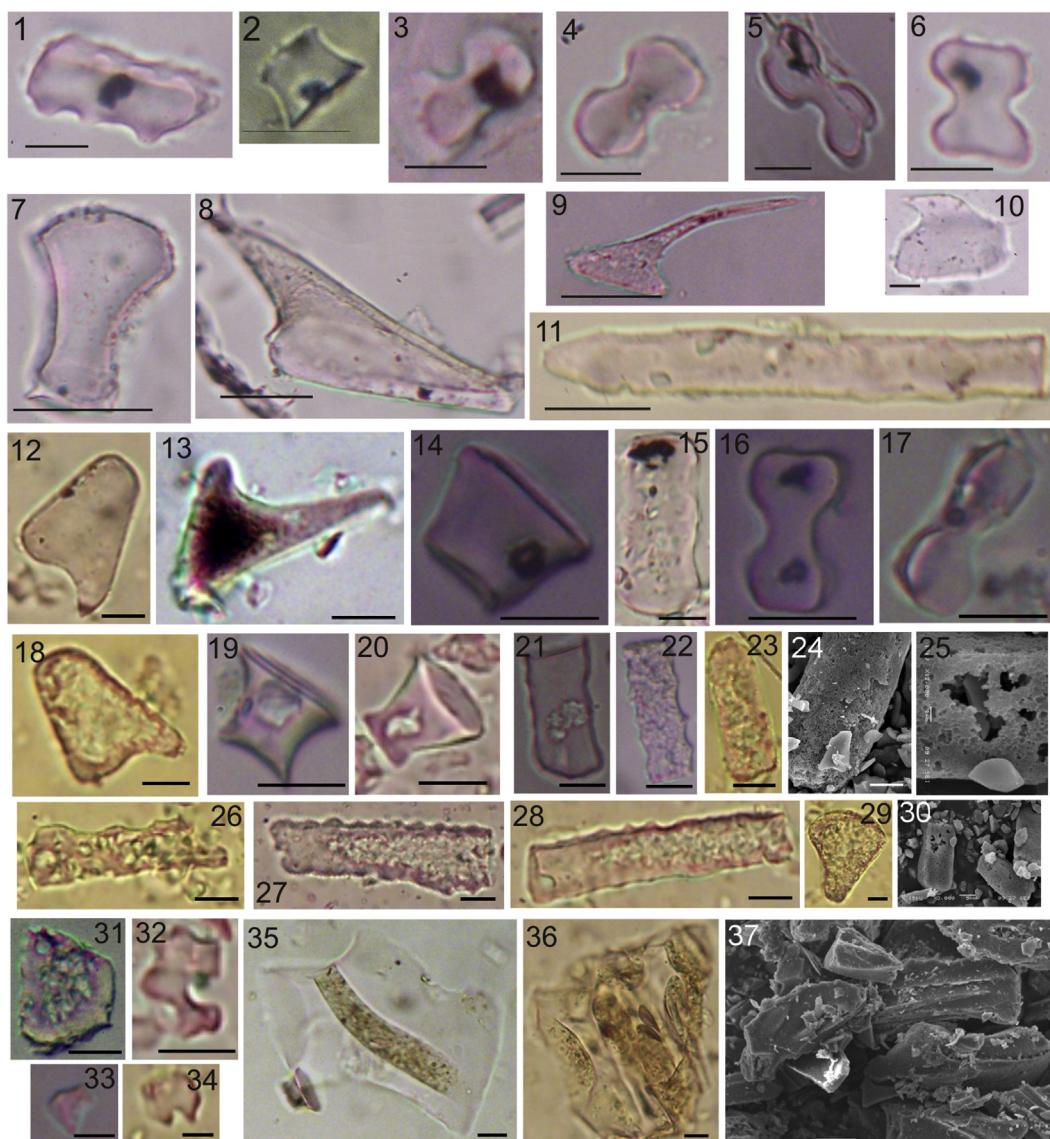
#### 3.2. Silicophytoliths in soils

Silicophytoliths dominated the silt and very fine sand fractions of soils. Their content with respect to the total mineralogical components of the soil significantly decreased with depth (Table 2, H: 29.5,  $p < 0.001$ ), being significative the differences between all the soil horizons analyzed (Table 2). In the epipedons (Hz. A), the stock of silicophytolith is about  $59–72 \times 10^3 \text{ kg/ha}$ , and the stock of Si from silicophytolith is  $25–30 \times 10^3 \text{ kg/ha}$ .

**Table 1**

Mean  $\pm$  standard deviation of relative frequencies of silicophytolith morphotypes produced in different Poaceae subfamilies from the Pampean Region.

Phytolith morphotypes	Poaceae subfamilies			
	Arundinoideae	Panicoideae	Pooideae	Stipoideae
Mean relative frequencies (%)				
Articulated long cells	2.2 $\pm$ 1.6	3.6 $\pm$ 1.8	11.4 $\pm$ 4.8	8 $\pm$ 4.6
Articulated short cells	41.8 $\pm$ 5.7	36.8 $\pm$ 11.2	21.2 $\pm$ 8.9	43.7 $\pm$ 6
Stomata complexes	0.04 $\pm$ 0.09	0.9 $\pm$ 0.6	0.9 $\pm$ 0.7	0.6 $\pm$ 0.3
Trapeziform crenates	0	0	21 $\pm$ 15.6	0.01 $\pm$ 0.02
Crosses	0.3 $\pm$ 0.2	6.3 $\pm$ 7	0	0.2 $\pm$ 0.2
Simple lobates	11.2 $\pm$ 3.4	9 $\pm$ 10.1	0.8 $\pm$ 2	5.2 $\pm$ 3.9
<i>Stipa</i> -type bilobates	4.3 $\pm$ 4.2	0	0.2 $\pm$ 0.6	12.8 $\pm$ 4.1
Panicoid bilobates	25.2 $\pm$ 7.6	19.5 $\pm$ 12.3	0.04 $\pm$ 0.1	0.3 $\pm$ 0.3
Polilobates	1.3 $\pm$ 1.7	1.1 $\pm$ 0.9	0.7 $\pm$ 2	3 $\pm$ 3
Elongates	7.7 $\pm$ 3.2	11.1 $\pm$ 6.5	18.2 $\pm$ 20.3	8.7 $\pm$ 3.1
Bulliforms	0.4 $\pm$ 0.2	2.3 $\pm$ 0.7	0.6 $\pm$ 0.4	2.2 $\pm$ 3
Trichomes	0.5 $\pm$ 0.4	1.2 $\pm$ 1	16.4 $\pm$ 14.1	3.5 $\pm$ 3.3
Rondels	4.5 $\pm$ 4	0.5 $\pm$ 0.6	13 $\pm$ 10.5	6.5 $\pm$ 8.8



**Fig. 2.** Silicophytoliths in plants (1–11) and soils (12–37). 1–11: Characteristics morphologies in grasses. 1. Trapeziform crenate phytolith, 2. Rondel, 3. *Stipa*-type bilobate, 4. Simple lobate, 5–6. Panicoid bilobates, 7. Bulliform phytolith, 8–10. Trichomes, 11. Elongate phytolith. Scale bar: 10  $\mu\text{m}$  (1–6, 8); 25  $\mu\text{m}$  (7, 9–11). 12–37: Most representative silicophytoliths in soils. 12–17: Silicophytoliths in a good preservation state. 12–13. Trichomes, 14. Rondel, 15. Trapeziform crenate, 16–17. Bilobates. 18–30: Silicophytoliths with different weathering states. 18. Trichome, 19–20. Rondels, 21, 30. Trapeziform crenate, 22–25. Rectangular, 26–28. Elongates, 29: Bulliform. 31–32: Taxonomically unidentified silicophytoliths. 33–34: Unidentified amorphous silica particles ( $<7.5 \mu\text{m}$ ). 35–37: Volcanic ashes in soils. Scale bar: 10  $\mu\text{m}$ .

**Table 2**

Mean  $\pm$  standard deviation of relative frequencies of silicophytoliths with respect to the total mineralogical components and their weathering degrees in typical Argiudolls from the Pampean Region. Within each column, different letters indicate a significant difference among the silicophytoliths content in soils ( $p < 0.01$  (\*<sup>1</sup>)), and among the percentage of weathered silicophytoliths ( $p < 0.05$  (\*<sup>2</sup>)) according to Steel–Dwass test.

Soil horizons	Silicophytoliths with respect to the total mineralogical components of the soil (* <sup>1</sup> )	Taxonically unidentified silicophytoliths	Weathered identified silicophytoliths (* <sup>2</sup> )
A	40.2 $\pm$ 16.6 a	8.6 $\pm$ 4.6	28.3 $\pm$ 9 a
B	10.8 $\pm$ 4.8 b	11.1 $\pm$ 3.8	54.9 $\pm$ 9.2 b
C	4.7 $\pm$ 2.8 c	11.6 $\pm$ 5.3	68.4 $\pm$ 11.6 c

The silicophytolith predominant morphologies are rectangulars (28–46%) and rondels (17–43%). Less common are smooth elongates (1–7%), trichomes (0.5–2%) and bilobates (0.5–2%), among others (Fig. 2: 12–25). All these morphotypes are assigned to Poaceae in concordance with the present and past vegetal communities in the study sites. Generally, Pooideae was the most representative, while Panicoideae and Chloridoideae were in much lesser proportion, usually associated with episodic fluctuations of morphoclimatic conditions (Osterrieth, 2008).

A high number of taxonomically unidentified silicophytoliths can be observed in all the samples (Fig. 2: 31–32). Although their content increased with depth, being major in the endopedions Bt and in the parent materials, there is no significant differences between horizons (Table 2, H: 3.53,  $p > 0.05$ ).

The weathering percentages in the identified silicophytoliths significantly increased with depth (Table 2, H: 19.1,  $p < 0.001$ ), with significative differences between all the horizons analyzed (Table 2). In general, they correspond to morphologies elongated, bulliforms and rondels with several degrees of weathering, usually with more than 50% of their surface weathered, reaching about 60% of the surface corroded to the base of the horizons (Fig. 2: 18–30).

Another component evaluated in relation with weathering processes was the content of unidentified amorphous silica particles (<7.5  $\mu\text{m}$ ), which represent tiny loose pieces originated from the fracture and/or the dissolution of silicophytoliths and/or volcanic ashes (Fig. 2: 33–34). These particles decreased toward the bottom of the profiles: 58.1% (Hz. A), 33.6% (Hz. B); 33.8% (Hz. C).

Within the amorphous silica fraction, volcanic ashes were evaluated too. Their content increased with depth: 1.5% (Hz. A), 15% (Hz. B); 18% (Hz. C). This distribution along the profile is in direct relation with the parent material composition, since volcanic ashes are an important component of the loessic sediments in the area (Frenguelli, 1930; Osterrieth et al., 2009). Generally, this fraction showed a hyaline surface with no features of weathering, and in some portions, there were evidences of coatings that could prevent their dissolution (Fig. 2: 35–37).

### 3.3. Silica in soil solution and groundwater

The geomorphology of the southeast of the Pampean Plain, as well as the dense grass vegetal cover during all the Quaternary period in the natural field, more the high permeability of the loessic sediments makes it possible for part of the precipitation to filter through (Osterrieth and Maggi, 1996). This has contributed to generate the high amorphous silica content in the soils and aquifers of the area. So, the concentration of  $\text{SiO}_2$  in soil solution and its distribution along the profile relates to the present and past plant communities, the root development and the nutritional requirements of the species. This is in relation with the preservation state of the soil mineralogy, which present low weathering degrees and could not explain the high silica content in soil and groundwater solutions (Borrelli et al., 2009).

In typical Argiudolls of the Pampean Plain, silica content

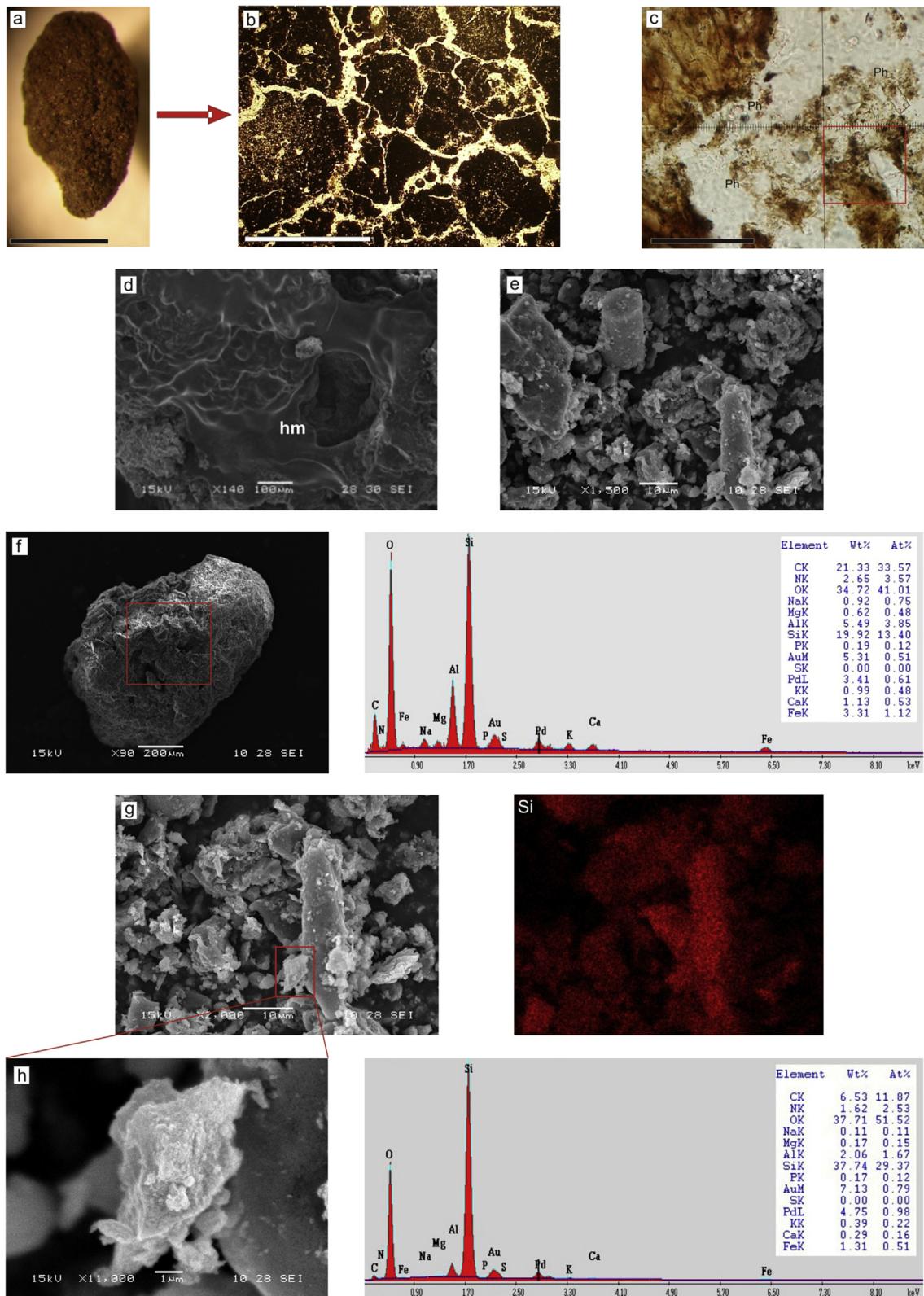
increased with depth: 453  $\mu\text{mol/L}$  (Hz. A), 742  $\mu\text{mol/L}$  (Hz. B), 1243  $\mu\text{mol/L}$  (Hz. C). Grasses are silica accumulators so they have high mean relative Si concentration in their body (Hodson et al., 2005). So their high uptake capacity and their surface root design generate a higher uptake of silica in the soil surface levels, and a lesser silica content in the soil solution. The components of amorphous silica could be contributing to the high Si content with depth: volcanic ashes, silicophytoliths and unidentified small particles. Volcanic ashes increased with depth, but without traces of weathering; instead, silicophytoliths showed a significative increased in their weathering degree with depth. Besides, the small particles of amorphous silica decreased from the top to the base of the soil profile, so, the major sources of silica in depth could be the silicophytoliths and the small particles of amorphous silica, in relation with the good preservation state of the soil minerals and volcanic ashes (Borrelli et al., 2009, 2010). In concordance, Alexandre et al. (1997) and Farmer et al. (2005), concluded that in tropical and acidic forest soils, silicophytoliths represent the principal sink and source of silica to the soil solutions and streams.

According to Sommer et al. (2006), Si concentrations of soil solutions range from 0.4 to 2000  $\mu\text{mol/L}$ , but most values lie between 100 and 500  $\mu\text{mol/L}$ . Our data about Si concentrations in soil saturation paste are, in most cases, higher than these mean values, showing an important contribution of silica to the system.

Silica concentrations in groundwater are in the range of 150–180  $\mu\text{mol/L}$  (Sommer et al., 2006), while our determinations show that in the southeastern area of the Pampean Plain, Si concentrations are much higher ( $840 \pm 232 \mu\text{mol/L}$ ) than these mean values. These results are in agreement with previous works in the study area, where Martínez and Osterrieth (1999, 2013) and Miretzky et al. (2001) found values around 746–870  $\mu\text{mol/L}$ . According to Martínez and Osterrieth (1999, 2013), the samples of groundwaters from the Pampean Aquifer are oversaturated with regard to all silicate minerals, but they are in equilibrium with amorphous silica. Although the origin of the dissolved silica must be the silicates weathering and clay neoformation, the equilibrium with amorphous silica (especially silicophytoliths) is the element that controls silica contents in the aquifer (Martínez and Osterrieth, 1999, 2013; Miretzky et al., 2001).

### 3.4. Soil matrix

The microstructure of soil was complex with a degree of pedality strongly developed. The aggregates were presented as well-defined units each of which is entirely surrounded by a void (Fig. 3a, b, c). Some areas of the matrix of aggregates presented an appearance hyaline, enriched in amorphous silica directly linked to the presence of biomineralizations of Poaceae (silicophytoliths) (Fig. 3d, e), vegetal cover present in the study area since the beginning of the genesis of these typical Argiudolls (Osterrieth et al., 2009; Borrelli et al., 2010). In addition, microaggregates presented silicophytoliths within their matrix enriched of silica. This was corroborated by analyzing EDAXs and mapping, showing a predominance of oxygen, silicon and carbon, accompanied by

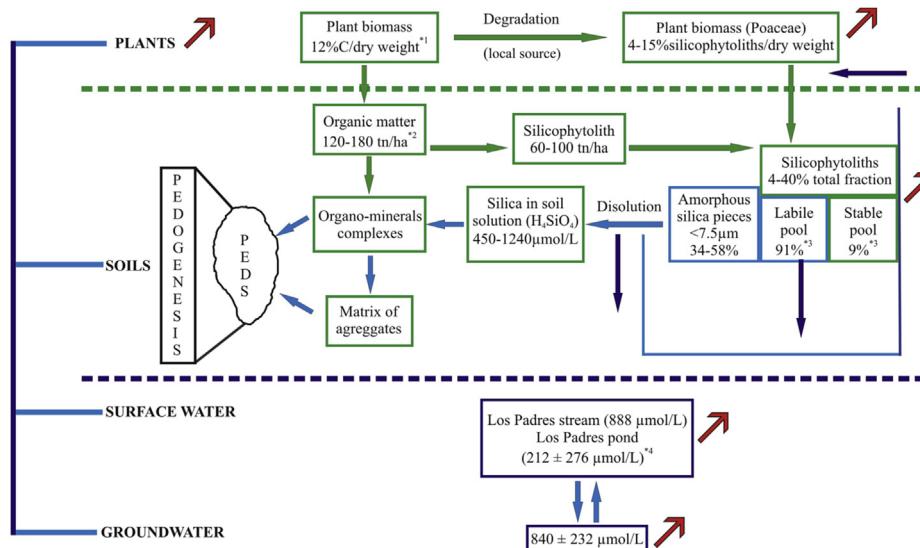


**Fig. 3.** a) Soil aggregate. b) Microstructure of soil aggregate (scale: 5000 µm). c) Matrix detail of aggregates of soil in petrographic microscope (scale: 100 µm). d–e) Matrix detail of aggregates of soil in MEB. f–h) Matrix detail of aggregates of soil and EDS-mapping in the point. Ph: silicophytolith. Mh: hyaline matrix. Si: silica.

nitrogen, aluminum, iron, calcium and potassium, in a lower proportion (Fig. 3f–g).

The structural stability showed a close relation to the skeletal

fraction and the constituents of the matrix (mostly organic matter, humic acids, fulvic acids, humins, clays, oxides, and iron, aluminum and silica hydroxides) (Tisdall and Oades, 1982; Osterrieth and



**Fig. 4.** Silica biogeochemical cycle in typical Argiudolls of the southeast of the Pampean Plain. Green arrows represent the fluxes in relation with the organic fraction. Blue arrows represent the fluxes between different inorganic compartments in the cycle. Red arrows represent the silica losses and/or no availability. <sup>\*1</sup>: Alvarez, 2006. <sup>\*2</sup>: Busquiao et al., 2001. <sup>\*3</sup>: Borrelli et al., 2010. <sup>\*4</sup>: Borrelli et al., 2012. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Maggi, 1996; Galantini et al., 2007). So, the presence of silicon in the matrices of these aggregates could be positively contributing to the stability by the formation of organo–mineral complexes.

#### 4. Conclusions

The contribution of silicophytoliths by grass plant communities has been ongoing during all the Quaternary and it has increased by agricultural and livestock exploitation during the last 150 years in the Mollisols of the Pampean Plain (Osterrieth, 2008).

According to the evidence of silicophytolith dissolution, the good preservation state of the other silicate minerals of the soils and volcanic shards; the balances show that silicophytoliths could play an important role in the silica cycle and could have a prevalent role in the pedogenetic processes of the Mollisols, and especially in Argiudolls of the southeast of the Pampean Plain (Fig. 4). Also show that much of the silicon/biogenic amorphous silica: 1) re-circulates in the unsaturated zone, where it contributes to conform the matrix of soil aggregates enriched in amorphous silica, increasing and maintaining the structural stability of soils; 2) transfers to the surface waters; and 3) transfers to the saturated zone, enriching substantially the content of silicon/amorphous silica in the pampean aquifer (Fig. 4).

Finally, the silicophytoliths are very representative in the system plant-soil-water- environment, so they could be into account in the biogeochemical studies since they could contribute with silica content in the soil solution, affecting the terrestrial silica biogeochemical cycle (Fig. 4).

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