

# Cation exchange capacity and mineralogy of loess soils with different amounts of volcanic ashes



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## ABSTRACT

The cation exchange capacity of soils (CEC) is largely affected by the mineralogy of their parent material. Soils of the Argentinean Pampas develop on illitic loess, mixed, in variable proportions, with volcanic ashes. It is whether a question of how pedogenesis can modify this mineralogy, affecting CEC differentially. In order to answer this question, we analyzed four soils, two of them placed in semiarid conditions and developing on parent materials with high volcanic ash contents, and two placed in the humid Pampas, developing on ash-free parent materials. Results indicated that pedogenesis transformed coarse lithogenic illites into smaller illites in ash free soils, accumulating them not only in clays but also in silts. In ash enriched soils, illites were not altered by pedogenesis but they were the volcanic glasses, which were transformed into less crystallized smectites. These smectites accumulated mainly not only in clays but also in fine silts. The mineral fraction of ash free soils had higher CEC ( $15.07 \text{ cmol}_c \text{ kg}^{-1}$ ) than ash enriched soils ( $9.50 \text{ cmol}_c \text{ kg}^{-1}$ ), being the contribution of the  $<50 \mu\text{m}$  sized fractions to the total CEC similar in all the studied soils (on average, 54%). As a consequence of this, clays and silts of ash free soils made a relatively low contribution to the total CEC, while poorly crystallized smectites of ash enriched soils made a relatively high contribution. This was explained on the basis of the kind of minerals present (smectitic minerals with high CEC) rather than on the proportion of the mineral fraction itself in ash enriched soils, and on the relatively high content of the mineral fractions rather than on their mineralogy (illites with low CEC) in ash free soils. The contribution of silts to CEC was similar and relatively high in all the studied soils: 17.5% of the total CEC and 32% of the mineral fraction CEC. These results confirm that the electrochemical properties of the studied soils are defined not only by clays but also by silts, mainly those with sizes between 2 and  $20 \mu\text{m}$ .

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## 1. Introduction

The cation exchange capacity of soils (CEC) is one of the most important parameters defining soil fertility (Martel et al., 1978; Thompson et al., 1989). Besides organic matter- and clay contents, the clay mineralogy defines CEC. For example, it is largely known that 1:1 minerals have lower CEC than 2:1 minerals and that, within 2:1 minerals, illites contribute less to CEC than smectites (Martín-García et al., 1999; Peinemann et al., 2000).

Less attention has been paid to the contribution of fractions coarser than clays to CEC. This is a sound question for soils of the Argentinean Pampas, as their silt fractions show some cation sorption capacity. As a matter of fact, Morrás (1995) found that silts of soils of the Chaco region of Argentina have CEC varying from 8 to  $23 \text{ cmol}_c \text{ kg}^{-1}$ , while Peinemann et al. (2000), for Entic Haplustolls and Typic Hapludolls of

the semiarid Pampas, found that silts have CEC varying from 6.5 to  $7.1 \text{ cmol}_c \text{ kg}^{-1}$ . Thompson et al. (1989) found similar results for Mollisols and Alfisols of the USA, in which silt fractions had CEC between 2 and  $29 \text{ cmol}_c \text{ kg}^{-1}$ .

The origin of the electrostatic properties of silts of the Pampas soils seems to be related to their mineralogy. Though the pleistocenic and holocenic loess sediments on which the soils develop are mineralogically homogeneous, illites being the predominant minerals (Buschiazco, 1988; Zárate, 2003), the variable amounts of volcanic ashes, mixed with the loess, can modify this homogeneity.

The volcanic ashes were accumulated by frequent eruptions of Andes volcanoes during the Pleistocene and Holocene (Teruggi, 1957). One of the most recent events occurred in 1932, when the Quizapu volcano sedimented a 10 cm thick, 1000 km long and 30 to 50 km broad W–E oriented ash layer in the semiarid Pampas (Larsson, 1936). The highest amounts of volcanic glasses are currently found in soils of the dryer Pampas (Hepper et al., 2006).

The presence or absence of volcanic ashes seems to define the mineralogy of the clay fraction of Pampas soils: ash free soils contain illites

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with traces of kaolinite, while ash enriched soils contain poorly crystallized smectites with traces of kaolinite (González Bonorino, 1965, 1966; Nabel et al., 1999). Zárate and Blasi (1991) and Camilión (1993) told about a possible transformation of these volcanic ashes in new mineral species without defining which one.

The different behavior of ash enriched- and ash free soils of the Pampas was detected by Buschiazzo et al. (1998) and Urioste et al. (2006) through their different P-sorption capacities: ash enriched soils showed much higher P-sorption than ash free soils. Authors attributed these differences to the presence of minerals with high P sorption capacity in the ash enriched soils of the semiarid Pampas produced, apparently, by the transformation of volcanic ashes.

It is whether a question of how far lithogenic illites or volcanic glasses, originally accumulated in size fractions coarser than silts, transformed into new mineralogical species and how these transformations affected CEC of clays and silts in each soil group. It is known that under moist conditions illites can decrease their size, accumulating in the finer fractions changing little their crystallographic structure. In dry environments, on the other hand, illites mostly remain unaltered (Dahlgren et al., 2004; Hepper et al., 2006).

Volcanic glasses are known to transform rapidly in new clay species like amorphous oxides, allophane or even smectites, depending on the environmental conditions (Dubroeuq et al., 1998; Georgoulas and Moustakas, 2010; Shoji et al., 1993).

If the transformation of illites and volcanic glasses mentioned above occurred in the Pampas soils, the relative contribution of silts to CEC should be higher in ash free- than in ash enriched soils, due to the large presence of illites in silts. The opposite is expected in ash enriched soils, in which the newly formed minerals should be mostly accumulated in the clay fraction.

In view of the former queries, the aims of this study were to determine the mineralogy of different size fractions of soils containing different amounts of volcanic ashes, and to assess how this mineralogical composition affects CEC of different size fractions.

## 2. Materials & methods

### 2.1. Studied area and soils

Soil samples from the topsoil (0–20 cm) were randomly taken by triplicate from a 10 m<sup>2</sup> surface in four sites of the Pampean region of Argentina (Fig. 1). All the studied soils develop on the same parent material, the so-called Pampas loess (Buschiazzo, 1988; Teruggi, 1957; Zárate, 2003). The mineralogy of the loess is qualitatively- but not quantitatively homogeneous. This is because the sedimentation of the aeolian materials by winds of different speeds, and therefore different transport energies, sedimented variable amounts of minerals with different densities at different depths (Buschiazzo and Taylor, 1993). This makes the mineralogy of C-horizons of current soils to be not strictly related with the mineralogy of A horizons (Buschiazzo, 1988). Because of that, only the A- and not the C-horizon was analyzed in this study.

The studied soils were two ash enriched soils: an Entic Haplustoll (EH) and a Typic Hapludoll (TH-I), and two volcanic ash free soils: a Typic Hapludoll (TH-II) and a Typic Argiudoll (TA) (Table 1). Management conditions were similar in all the studied soils and representative of management systems of the whole Pampean region: a wheat (*Triticum aestivum*)–soybean (*Glycine max*) crop sequence, carried out under no-till conditions since more than 20 years.

### 2.2. Laboratory procedures

Soil samples were air dried and sieved through 2 mm. The pH was determined potentiometrically using a combined glass-calomel electrode, in both water (pH<sub>H2O</sub>) and KCl 1 mol dm<sup>-3</sup> (pH<sub>KCl</sub>) (1:2.5 soil:liquid); the equation  $\text{pH} = \text{pH}_{\text{KCl}} - \text{pH}_{\text{H}_2\text{O}}$  was used to determine charge characterization (Mekaru and Uehara, 1972). The organic

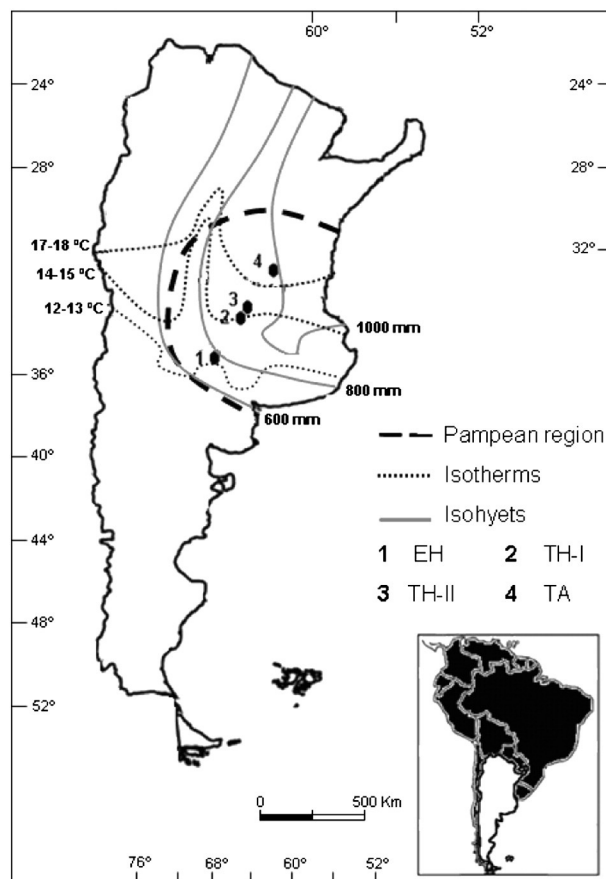


Fig. 1. Location of the studied soils. EH = Entic Haplustoll; TH-I = Typic Hapludoll I; TH-II = Typic Hapludoll II; TA = Typic Argiudoll.

matter content (OM) was determined by wet digestion (Walkley and Black, 1934) and the CEC by saturation with an ammonia acetate dissolution 1 mol dm<sup>-3</sup> at pH 7 (Rhoades, 1982). Amorphous Al- and Fe oxides were extracted in the darkness with oxalic acid, and crystalline Al- and Fe oxides (Alos and Feos, respectively) with boiled oxalic acid (Schlichting et al., 1995). All procedures mentioned above were performed on triplicate samples.

Over a composed soil sample of each soil, the grain size distribution was determined by the combined pipette and sieving method (Gee and Bauder, 1986). Clays (C, soil particles with a diameter ( $\phi$ ) < 2  $\mu\text{m}$ ), fine silt (FSi, 2  $\mu\text{m}$  <  $\phi$  < 10  $\mu\text{m}$ ) and medium silt (MSi, 10  $\mu\text{m}$  <  $\phi$  < 20  $\mu\text{m}$ ) fractions, were separated and concentrated by centrifugation and siphoning, on organic matter-free and dispersed soil samples. The settling times were selected with the centrifugation methodology provided by Tanner and Jackson (1947). After this procedure, the sand fraction (S) was separated by wet sieving. Coarse silt (CSi, 20 <  $\phi$  < 50  $\mu\text{m}$ ) was obtained as a remnant of the sand separation procedure and its content was calculated with Eq. (1):

$$\text{CSi} = \text{Soil} - (\text{C} + \text{FSi} + \text{MSi} + \text{S}) \quad (1)$$

where CSi, MSi, FSi, C and S are, respectively, the masses of coarse, medium and fine silts, clay and sand, and Soil is the mass of the soil sample. All the parameters of the equation are expressed in grams (g). In addition, on other < 2 mm fraction of a composed soil sample of each soil, fine clay fraction (FC;  $\phi$  < 0.2  $\mu\text{m}$ ) was separated following the same procedure described for C, FSi and MSi.

Mineralogical analysis of the FC, C, FSi, MSi and CSi fractions was determined by X-ray diffraction on MgCl<sub>2</sub> saturated samples. For this determination a diffractometer with a Cu anticatode ( $\lambda = 1.54 \text{ \AA}$ ), operating at 45 kV and 40 mA was used. The angular interval was

**Table 1**  
Main properties of studied soils.

Site	Soil classification <sup>a</sup>	Particle size distribution			pH			OM (%)	CEC <sub>T</sub> (cmol <sub>c</sub> kg <sup>-1</sup> )	Alo (mg kg <sup>-1</sup> )	Feo (mg kg <sup>-1</sup> )	Alos	Feos
		Clay (%)	Silt	Sand	pH <sub>H2O</sub>	pH <sub>KCl</sub>	ΔpH						
<i>Ash enriched soils</i>													
EH	Entic Haplustoll	12.3	23.4	64.2	6.51	5.14	-1.37	2.52	19.35	1282	1269	4881	13,160
TH-I	Typic Hapludoll I	12.5	22.8	64.7	6.50	5.16	-1.34	2.75	17.33	174	1260	2112	13,089
<i>Ash free soils</i>													
TH-II	Typic Hapludoll II	17.0	34.2	48.8	6.17	4.96	-1.21	2.16	23.96	1042	976	5806	18,281
TA	Typic Argiudoll	28.5	63.7	7.8	6.03	4.90	-1.13	3.32	24.51	1817	1853	7598	12,683

OM = organic matter; CEC = cation exchange capacity; Alo = amorphous aluminum oxides; Feo = amorphous iron oxides; Alos = crystalline aluminum oxides; Feos = crystalline iron oxides.

<sup>a</sup> Soil Survey Staff (1999).

scanned between 3° and 17° 2θ at 0.02° 1.5 s<sup>-1</sup>. The semiquantitative determination was performed by comparison of the spectra obtained from a) magnesium-saturated samples, b) solvated with ethylene glycol and c) heated at 550 °C for 2 h (Brown and Brindley, 1984). Degree of crystallization was estimated using the XRD spectra.

The single grain mineralogy of the coarse silt fraction was determined with a petrographic microscope Nikon Eclipse E400POL using the methodology provided by Carver (1971). This procedure allowed determining the nature, morphology and weathering stage of minerals.

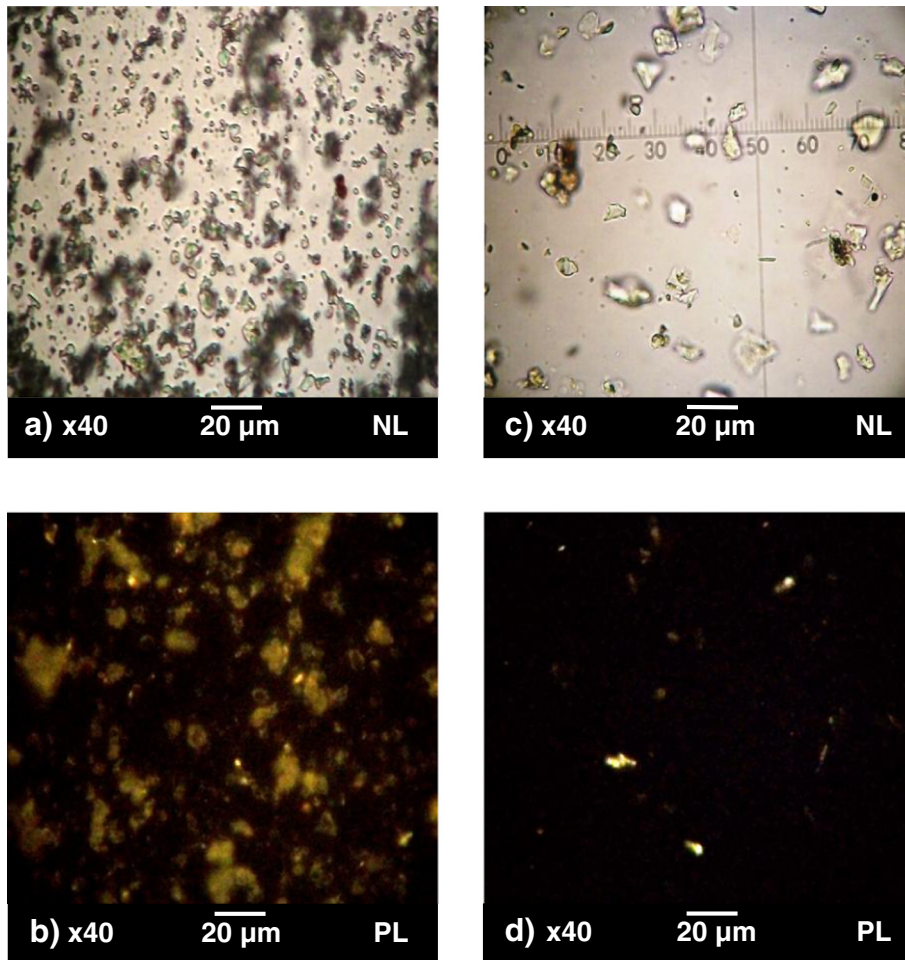
The CEC of C, FSi, MSi and CSi was determined using the methodology provided by Rhoades (1982). The relative cation exchange capacity

of each soil-size fraction (CEC<sub>R</sub>), i.e. the CEC of each mineral fraction in relation to the CEC of the complete soil sample, was calculated without considering the possible contribution of sand to CEC, using Eq. (2):

$$CEC_R = (X \times CEC_A) \div 100 \tag{2}$$

CEC<sub>A</sub> being the absolute cation exchange capacity of each soil-size fraction. Both, CEC<sub>R</sub>, and CEC<sub>A</sub> are expressed in cmol<sub>c</sub> kg<sup>-1</sup> soil; X is the percentage of each fraction in the whole soil sample.

The comparison of chemical properties between both ash free- and ash enriched soils was performed by means of the Student's t-test for independent samples (similar variance for α = 0.05).



**Fig. 2.** Overview of the mineral composition of the coarse soil fraction (20 ≤ φ ≤ 50 μm) of an ash free soil with a) quartz grains with normal (NL) light, and b) quartz grains with polarized light (PL) and of an ash enriched soil with c) quartz and volcanic glasses at NL and d) PL.

### 3. Results & discussion

#### 3.1. Soil mineralogy

Fig. 2 shows that the coarse silt fraction of ash enriched soils contains quartz and volcanic glasses while ash free soils contain only quartz. The coarse silt fraction theoretically contains the lithogenic minerals, i.e. those inherited from the parent material. Volcanic ashes are only

present in soils of the semiarid Pampas and are lacking in soils of the humid Pampas. It is a question if volcanic glasses were originally also present in soils of the humid Pampas and are currently absent because of their weathering under the moister conditions of that region. Nevertheless, it has been widely reported that volcanic glasses are lacking or their contents are very low in the parent materials of soils of the humid Pampas (Hepper et al., 2006; Imbellone and Camilión, 1993; Teruggi, 1957; Zárate and Blasi, 1993).

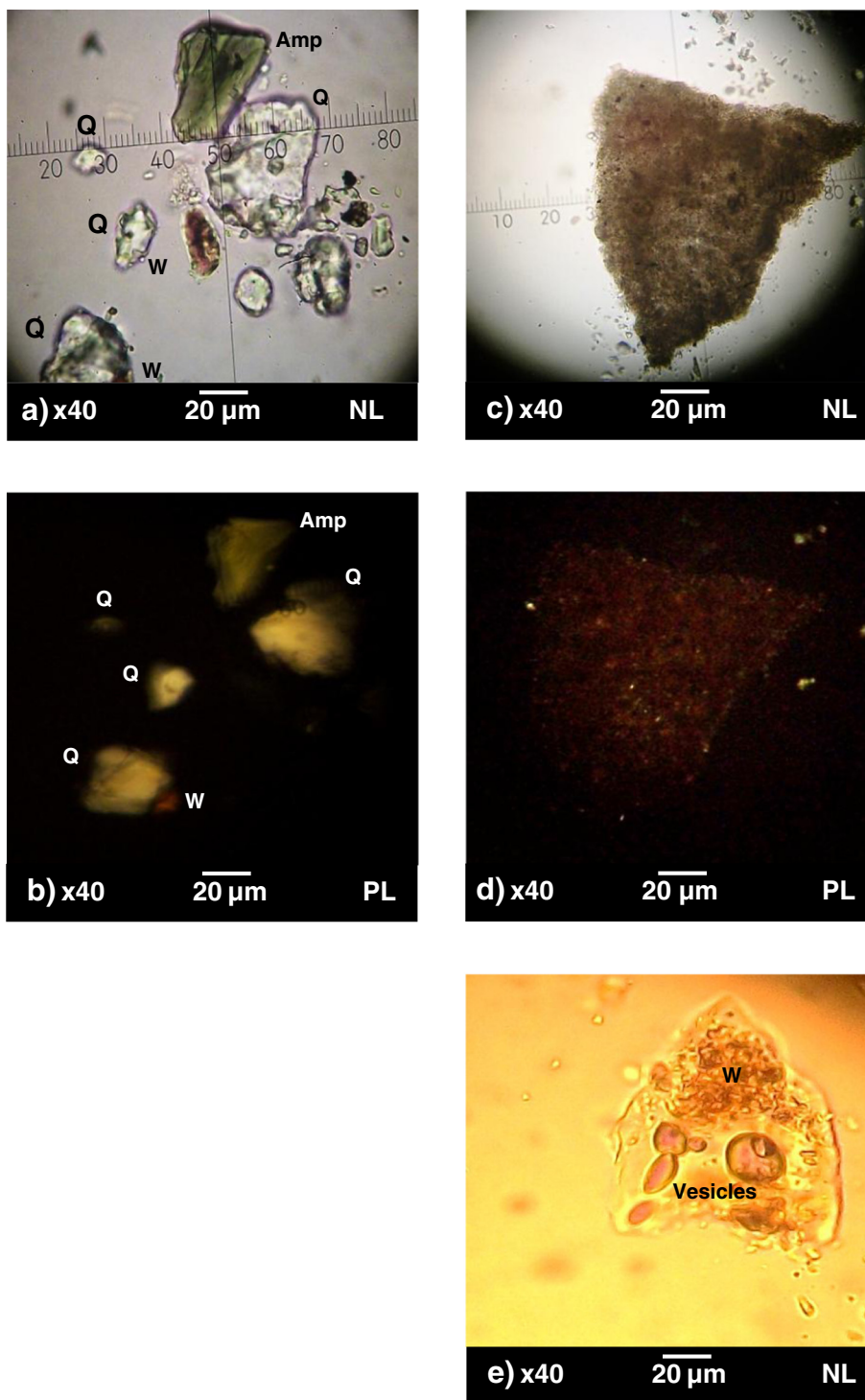


Fig. 3. Detailed view of the mineralogical composition of the coarse silt fraction ( $20 \leq \phi \leq 50 \mu\text{m}$ ) of an ash free soil: a) non-weathered quartz grains with normal light (NL) and b) non-weathered quartz grains with polarized light (PL); same size fraction of an ash enriched soil: c) a highly weathered glass with NL, d) a highly weathered glass with PL, and e) a less weathered vesicular volcanic glass with weathered minerals in its upper internal part (NL). Q = quartz, W = weathered particle, Amp = amphibole.

Volcanic glasses (Fig. 3) are mostly highly weathered, showing vesicular structures, numerous vesicles of different sizes and different degree of weathering of their edges.

The quartz grains of both ash enriched- and ash free soils do not show weathering signs (Fig. 3). Quartz grains are bonded with each other, possibly by physical mechanisms, acting the spaces between grains as sites for the deposition of colloidal materials. Such effect can be seen in the weathered particle bonded to a quartz grain in the lower part of Fig. 3a.

As is largely known, illites are not detectable by means of petrographic microscope observations. Nevertheless, X-ray analysis detected crystallized illites in all silt fractions (FSi, MSi and CSi) of all the studied soils, indicating that they were already present in their parent materials (Table 2).

Contents of illites in the silt fraction were higher in ash free- (between 75 and 95%) than in ash enriched soils (between 60 and 80%). The lower amount of illites of silts of ash enriched soils can be probably linked with the higher proportion of glasses of these soils.

The clay fraction of all soils contains illites and less crystallized smectites (Table 2). The proportion of smectites was higher in ash enriched- (10% on average in both soils) than in ash free soils (7.5% on average in both soils) and the opposite occurred with illites (40% and 62.5%, respectively). Illites of the clay fraction of ash free soils were also almost unaltered.

The higher proportion of smectites in ash enriched soils may have been produced by the weathering of volcanic ashes. Volcanic ashes transform into amorphous oxides or allophane in many soils (Georgoulas and Moustakas, 2010; Prudêncio et al., 2002; Vidales et al., 1985). This seems not to happen in this case, as the quotients  $Al_0/Al_{0s}$  and  $Fe_0/Fe_{0s}$ , indexes of the relative amounts of amorphous Al and Fe oxides in relation to crystalline oxides, were not different from those of ash free soils ( $p > 0.05$ , Table 2). These results agree with those of Hepper et al. (2006), who found that ash enriched soils of the semiarid Pampas did not contain allophanes. Results are also in agreement with those of Parfitt and Kimble (1989) who found that non-crystalline components are rarely present in soils with ustic, xeric or aridic soil moisture regimes due to the restricted leaching of silica. Singer et al. (2004) found that the lack of allophane and amorphous oxides in volcanic soils of semiarid regions must be attributed to the existence of long dry periods, which are not suitable for a new formation of such minerals.

The high negative  $\Delta pH$  values (Table 1) indicated that both ash enriched- and ash free soils have only negative surface charges

(Mekaru and Uehara, 1972) and that positive charges are not present. This also means that substances like amorphous oxides or allophane, which are positively charged, are also not present in the analyzed samples.  $\Delta pH$  values lower in ash enriched than in ash free soils ( $p < 0.05$ ) were probably due to the presence of free lime in topsoil samples of the semiarid Pampas (Buschiazzo, 1988).

The smectites of the clay fraction of all the studied soils were poorly crystallized, whereas illites of the same fraction of ash free soils tended to be better crystallized. The transformation of lithogenic illites into finer ones by pedogenesis in soils of the humid Pampas mentioned by several authors (Camilión, 1993; González Bonorino, 1965, 1966; Zárate and Blasi, 1991) should produce the accumulation of illites in finer fractions. Fig. 4 shows that the fine clay fraction ( $< 0.2 \mu m$ ) of ash free soils is dominated by illites, while ash enriched soils do not show reflections for any mineral. Possibly, the incipient pedogenesis did not accumulate smectites in the fine clay fraction of ash enriched soils.

### 3.2. Cation exchange capacity

CEC was significantly higher in ash free- ( $24 \text{ cmol}_c \text{ kg}^{-1}$  on average) than in ash enriched soils ( $18 \text{ cmol}_c \text{ kg}^{-1}$  on average) (Table 1). This is in agreement with the finer textures of ash free soils, and not with their OM contents, which are rather similar between ash free and ash enriched soils.

Fig. 5 shows that CEC of the mineral fractions (excluding the effect of organic matter contents) was lower in ash enriched- ( $9.50 \text{ cmol}_c \text{ kg}^{-1}$  on average in both soils) than in ash free soils ( $15.07 \text{ cmol}_c \text{ kg}^{-1}$  on average in both soils). This difference agrees with the larger amounts of clays of the ash free soils, mainly TA (Table 1). The relative contribution of the whole mineral fraction (C, FSi, MSi and CSi) to the total CEC was nevertheless similar in all soils, averaging 54% of the total CEC.

CEC of the silt fractions (FSi, MSi and CSi) was rather similar between ash enriched- (18% of the total CEC and 32% of the mineral CEC, on average in both soils) and ash free soils (17% of total CEC and 31% of the mineral CEC, on average in both soils).

FSi contributed between 3 and 14% to CEC of the whole soil and between 6 and 23% to mineral CEC. This contribution ordered in the sequence TH-I ( $CEC_R = 2.37 \text{ cmol}_c \text{ kg}^{-1}$ ) > TA ( $2.24 \text{ cmol}_c \text{ kg}^{-1}$ ) > TH-II ( $1.47 \text{ cmol}_c \text{ kg}^{-1}$ ) > EH ( $0.57 \text{ cmol}_c \text{ kg}^{-1}$ ), the mean values being 1.47 and  $1.86 \text{ cmol}_c \text{ kg}^{-1}$  for ash enriched- and ash free soils, respectively. Such values were, nevertheless, not different between them ( $p > 0.05$ ).

The relatively high contribution of silts to CEC in TH-I can be attributed to its mineralogical composition, based on illite but mainly smectite and intergrades. TA showed lower CEC than expected for its high FSi contents, probably due to the illitic nature of this fraction. In TH-II and EH, the relatively low contribution of FSi to CEC seems to be a result of the low proportion of the size fraction (7 and 8%, respectively) and, in the TH-II, of its illitic mineralogy.

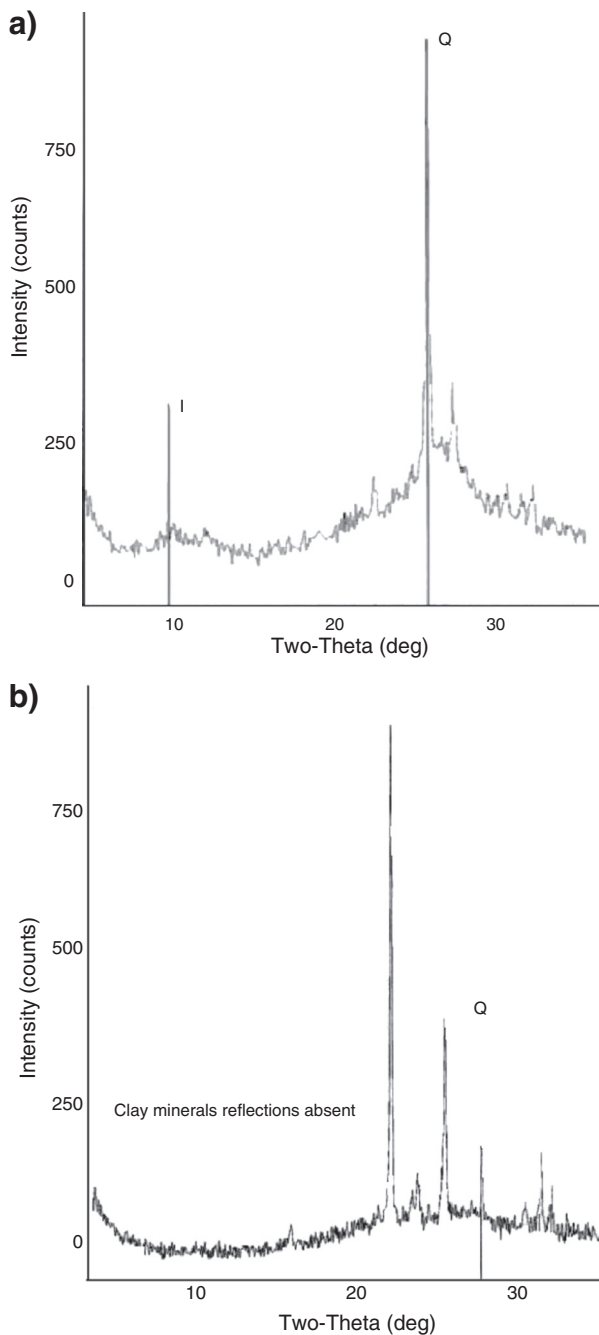
The contribution of MSi and CSi to CEC of the whole soil was similar and relatively low in all soils: between 5–7% and 2–5%, respectively. Besides, the contribution of MSi and CSi to mineral CEC was respectively, 11–12% and 3–11%.

The contribution of clays to the total CEC was rather similar in ash enriched- and ash free soils (36 and 38%, respectively). Clays also made similar contributions to the mineral CEC of both soil types (68 and 69%, respectively).

Despite the similar contributions to CEC of the mineral fraction in all the studied soils, the origin of CEC seems to be different in both soil groups. In ash enriched soils CEC seems to be more related to the presence of both illitic and smectitic minerals (Table 2). Even when the amount of smectites is relatively low in these soils (5–10%), they make large contributions to CEC due to their relatively high CEC values (Borchardt, 1985). In ash free soils, CEC seems to be related more with the high proportion of fine fractions within the mineral components,

**Table 2**  
Relative contents and crystallinity (c) of clay minerals accumulated in different soil-size fractions of the studied soils.

Fraction	Illites		Smectites		Intergrades		
	%	c	%	c	%	c	
<i>Ash enriched soils</i>							
EH	C	40	M	10	M	50	P
	FSi	60	M	10	M	25	P
	MSi	70	H	5	M	20	P
	CSi	65	H	T	–	15	P
TH-I	C	40	M	10	M	50	P
	FSi	80	H	T	–	20	P
	MSi	70	H	T	–	20	P
	CSi	70	H	T	–	20	P
<i>Ash free soils</i>							
TH-II	C	60	M	10	M	15	P
	FSi	75	H	T	–	15	P
	MSi	80	H	T	–	5	P
	CSi	85	H	T	–	5	P
TA	C	65	H	5	M	25	P
	FSi	85	H	T	–	5	P
	MSi	95	H	T	–	5	P
	CSi	95	H	T	–	5	P

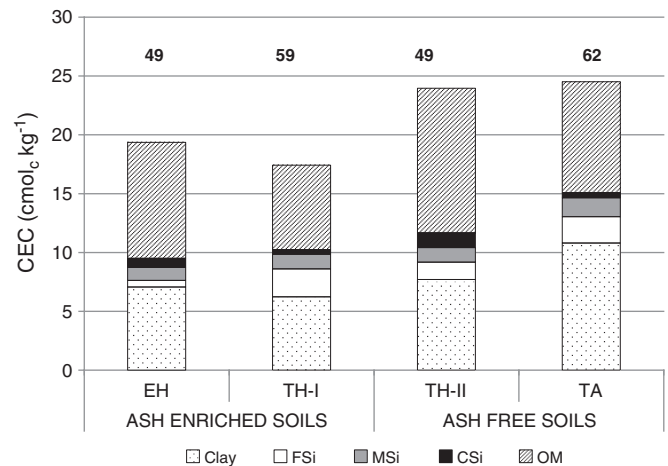


**Fig. 4.** XRD analysis of the fine clay fraction (FC,  $\phi < 0.2 \mu\text{m}$ ) of a) an ash free (TH-II) and b) an ash enriched (EH) soil. I = illite; Q = quartz. Non-identified peaks correspond to substances used during the pre-treatment of samples.

mainly clays and silts (Table 1) rather than to a high contribution of less negative charged illites (Borchardt, 1985).

Total silts contributed, on average in all the studied soils, 17% to the total CEC. CEC values found here were somehow lower than those found by Morrás (1995), Asadu et al. (1997), and Soares et al. (2005) but quite similar to those of Peinemann et al. (2000). Differences may be related with soil type and soil-size fractions analyzed in each case: Morrás (1995), Asadu et al. (1997), and Soares et al. (2005) analyzed the silt fraction between 2 and 20  $\mu\text{m}$ , while Peinemann et al. (2000) and in our study the whole silt fraction (2 to 50  $\mu\text{m}$ ) was analyzed.

FSi contributed around 43% to CEC of the whole silt fraction in both, ash enriched- and ash free soils. The summation of FSi and MSi (silt fractions between 2 and 20  $\mu\text{m}$ ) contributed 79%. These results indicate



**Fig. 5.** CEC of the studied soils and contribution of the inorganic- and organic fractions. Numbers above the bars are the ratios between CEC of inorganic and organic fractions. C = clay; FSi = fine silt; MSi = medium silt; CSi = coarse silt; EH = Entic Hapludoll; TH-I = Typic Hapludoll I; TH-II = Typic Hapludoll II; TA = Typic Argiudoll.

that both silt fractions largely contribute to CEC. Therefore, studies related with soil chemistry of Pampas soils do not need to analyze separately silt fractions between these sizes.

It can be concluded that the presence or absence of volcanic ashes, did not affect their relative contribution to CEC, but the origin of this contribution: in ash free soils it was more related with the amount of the fine size fractions while in ash enriched soils it was with the high amount of negatively charged minerals.

#### 4. Conclusions

- Coarse silt fractions of ash free soils of the humid Pampas were dominated by well preserved quartz grains and good crystallized illites. In volcanic ash enriched soils of the dryer Pampas, weathered volcanic glasses were also present.
- Pedogenesis transformed coarse lithogenic illites into smaller illites in ash free soils of humid sites, accumulating them not only in clays but also in silts. In ash enriched soils of dryer site, illites were not altered by pedogenesis but they did the volcanic glasses, which were transformed into less crystallized smectites.
- Illites of clays and silts of ash free soils made a relatively low contribution to the total CEC, while poorly crystallized smectites of ash enriched soils made relatively high contributions.
- The relative contribution of silts to CEC was relatively high in all soils: 17.5% to the total CEC and 32% to the mineral fraction CEC. Therefore, the electrochemical properties of the mineral fraction of the studied soils are defined not only by clays but also by silts, mainly those with sizes between 2 and 20  $\mu\text{m}$ .

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