ORIGINAL ARTICLE

Origin of superparamagnetic particles in Argiudolls developed on loess, Buenos Aires (Argentina)

Carlos Alberto Vasquez · Maria Julia Orgeira · Ana Maria Sinito

Received: 6 September 2007/Accepted: 24 February 2008/Published online: 7 March 2008 © Springer-Verlag 2008

Abstract Records from magnetic signals in Buenos Aires loess-paleosol sequences have been published, but their relationship with environmental changes has been difficult to establish. Studies on the superparamagnetic (SP) population in present soils can help to understand these processes. Samples from present soils (Argiudolls) and a paleosol from the Buenos Aires Province (Argentina) were analyzed using low and room temperature magnetic measurements. They show that it is possible to support the hypothesis of a lognormal distribution of superparamagnetic particles, the median diameter near 15 nm. The presence of detritic pseudosingledomain (PSD) titanomagnetite, with low titanium content ranging between TM 28 and TM40, has been established. The linear correlation of SP content with ferrimagnetic susceptibility and with magnetization suggests that ferrimagnetic minerals drive the SP generation. Finally, it can be concluded that SP magnetic grains, in the Pampean plain, are generated by an inorganic process in adequate environmental pH and Eh of the soils.

C. A. Vasquez (⊠) · M. J. Orgeira
CONICET- Departamento de Geología,
Fac. Cs. Exactas y Naturales, Universidad de Buenos Aires,
Ciudad Universitaria, Pabellón II,
Ciudad Autonoma de Buenos Aires, Argentina
e-mail: vasquez@gl.fcen.uba.ar

C. A. Vasquez

Ciclo Básico Común, Universidad de Buenos Aires, Ciudad Universitaria, Pabellón III, Ciudad Autonoma, de Buenos Aires, Argentina

A. M. Sinito

CONICET- Instituto de Física Arroyo Seco, Universidad Nacional del Centro de la Pcia. de Buenos Aires, Pinto 399. Tandil. Pcia, Buenos Aires, Argentina **Keywords** Superparamagnetism · Susceptibility · Magnetization · Verwey · Low temperatures · Lognormal distribution · Argiudolls

Introduction

The presence and concentration of SP magnetite, maghemite or titanomagnetite particles are related to past climatic changes (Hunt et al. 1995; Maher and Thompson 1999; Banerjee and Hunt 1993; Vasquez et al. 1998; Orgeira et al. 1998; Jordanova and Jornanova 1999).

Studies carried out in soils, paleosols and loess sequences show an enhancement of magnetic susceptibility in the upper pedogenic horizon. During the pedological processes magnetite or maghemite superparamagnetic grains can be generated. The presence of this magnetic fraction was determined using percentage frequency-dependent susceptibility $\chi_{\rm fd}$ % (e.g. Hunt et al. 1995; Petrovsky et al. 2001; Jordanova and Jordanova 1999; Dearing et al. 1996).

In the Pampean plain (Argentina), the magnetic susceptibility signal usually has an opposite trend to that observed in other geographic areas; it is lower in paleosols than in loess horizons. Mean values are 3.5×10^{-7} m³/kg in loess, and 1.5×10^{-7} m³/kg in paleosols. Furthermore, a frequency dependence of the room temperature (RT) susceptibility was not observed in either horizon (Bidegain et al. 2005; Orgeira et al. 1998, 2003; Vasquez et al. 1998). On the other hand, in samples from a location near Veronica (La Plata, 34° 54″ 14′ S and 58° 2′ W) Mössbauer spectroscopy has shown hematite as a dominant iron-bearing magnetic component in loess and paleosols, a remarkable increase in the content of magnetic iron oxides in paleosols (Terminiello et al. 2001).

The aim of this contribution is to characterize the SP pedogenic fraction in the Pampean soil. The SP distribution was studied in samples taken from two present soils (Argiudolls) under different drainage condition, located at Verónica (35° 17.5' S to 57° 38.8' W) and Zarate (34° 10' S to 59° 3' W), Buenos Aires province, Argentina. These soils were analyzed in a previous paper using standard pedological techniques and rock magnetism, showing that the differential soil humidity, pH and oxidation-reduction condition changes could explain the higher concentration of superparamagnetic (SP) particles at Zárate; while at Verónica, the process seems to be controlled by the degree of drainage, causing smaller SP concentration (Orgeira et al. 2007). Paleosol sample TPO73, from Arroyo Tapalque section, located in the central region of the Buenos Aires province and described in a previous paper (Orgeira et al. 2003), was included due to the fact that it matches up with the model.

Theory

According to Neels theory (Neél 1949; Dunlop and Ozdemir 1997), a magnetic particle becomes SP when the energy barriers, E_m , between different magnetization states are lower than the thermal energy, which is near 25 kT for experimental times lasting a few minutes, (where k is the Boltzmann constant and T the temperature in absolute Kelvin). The magnetic energy barriers are related to particle volume V, saturation magnetization M_s , and microcoercivity H_K . According to Dunlop and Ozdemir (1997), the critical or blocking volume V_B below which a magnetic particle becomes a SP grain is determined by:

$$V_{\rm B} = (2kT \ln (2\tau/\tau_{\rm o}))/(\mu_{\rm o}M_{\rm S}H_{\rm K}) \tag{1}$$

where, τ is the experiment time, $\tau_o \approx 10^{-9}$ s is the atomic reorganization time and μ_o is the vacuum magnetic permeability.

Classic thermal relaxation theory of Néel (1949) predicts a relationship between thermal relaxation energy kTand the blocking volume $V_{\rm B}$ (Dunlop and Ozdemir 1997; Blanco-Mantecón and ÓGrady 1999),

$$\frac{\partial M(T)}{\partial T} = f(V(T_{\rm B})) \frac{\partial V(T_{\rm B})}{\partial T_{\rm B}}$$
(2)

with

$$V(T_{\rm B}) = V_{\rm B} = CT_{\rm B} \tag{3}$$

and

$$C = \frac{2k\ln(\tau/\tau_{\rm o})}{\mu_{\rm o}H_{\rm K}M_{\rm S}} \tag{4}$$

and finally

$$\frac{\partial M(T)}{\partial T} = Cf(CT_{\rm B}) \tag{5}$$

Following Worm (1998), we assume a minimum coercivity of $\mu_0 H_c \approx 20$ mT for nearly spherical SD magnetite particles. Since $H_{\rm K} \approx 2.09 \ H_{\rm c}$ for randomly oriented Stoner– Wohlfart particles (Stoner and Wohlfart 1948), we assume $\mu_0 H_K \approx 40 \text{ mT}$ as an estimate for the minimum microcoercivity of the pedogenic SP particles. Then, with $M_{\rm S} = 480$ kA/m, measurement time $\tau \approx 60$ s and T = 300 K, calculations from equations (3) and (4) give $V_{\rm B} = 1.02 \times 10^{-23} \,\mathrm{m}^3$ and the grain size diameter D = 27 nm, which is in agreement with the SP-SSD limit at this temperature (e.g. Carter-Stiglitz et al. 2002; Dunlop and Ozdemir 1997; Jackson and Worm 2001). Equations (3) and (5) show that blocking temperatures and blocking volumes have the same distribution function, which is proportional to temperature derivative of magnetization; therefore, we can infer the volume distribution with this derivative.

Blanco-Mantecón and O'Grady (1999) showed that artificial magnetite nanoparticles have a lognormal distribution of sizes. The same distribution is generally observed in a variety of synthetic magnetites of different grain sizes. In the absence of data for the shape of the grain size distribution in pedogenetic magnetite, we assume that the lognormal distribution is:

$$f(V) = \frac{\text{Mo}}{\sqrt{2\pi}} \sigma^2 V \exp\left[-\frac{\ln}{2\sigma^2} (V/V_{\rm m})^2\right]$$
(6)

where f(V) defines the contribution of all the particles of volume V to the total magnetization Mo, σ is the standard deviation and $V_{\rm m}$ the median volume. Since blocking volume and blocking temperature are proportional to each other, an assemblage with a lognormal distribution of grain sizes has a lognormal distribution of blocking temperatures. The assumption of a lognormal distribution was confirmed on the example of paleosol sample TPQ73, where the blocking temperature distribution has been calculated from the first derivative of thermal demagnetization curves during zero field cooling (ZFC) of a SIRM (2.5 T) imparted at 10 K (Fig. 1a, b). The empirical distribution of blocking temperature matched the lognormal distribution which has a median blocking temperature of 26 K, corresponding to $V_{\rm m} \approx 1.16 \times 10^{-24} \,\mathrm{m}^3$ (4). A second minor peak in the distribution of blocking temperatures around 100 K is an artifact of the Verwey transition. The median diameter of the assumed spherical SP particles is 13 nm. In sediments from the same region, Orgeira et al. (2003) obtained a slightly larger diameter around 15 nm, from susceptibility measurements as a function of temperature and frequency.



Fig. 1 a Normalized magnetic temperature remanence decay curve (Mn) of TPQ73 sample; b normalized derivative of magnetic temperature remanence decay curve (Mn) of TPQ73 sample fitted with a lognormal distribution whose parameters are shown in the graph

Methodology

Low temperature magnetic measurements were interpreted with a phenomenological model, based on lognormal grain size SP distribution of synthetic magnetite particles (El-Hilo et al. 2002). The SP concentration was estimated using ZFC curves.

Nine samples, belonging to present soils from two localities of Buenos Aires Province, were analyzed (Table 1). These soils developed from the same parental material, the Pampean loess assigned to Buenos Aires formation. One additional paleosol sample taken from the Tapalque area (Buenos Aires Province) developed on reworked loess was included in the analysis.

The measurement of the hysteresis parameters and of room temperature susceptibility at low field was performed with a vibrating sample magnetometer (VSM) MicroMag (Princeton Measurements Corporation). The room temperature frequency dependence susceptibility χ_{fd} %

Table 1 Samples studied in this contribution

Sample	Description	
TPQ73	Tapalque paleosol	
R19	Veronica- poorly drained	
R210	Veronica- poorly drained	
R213	Veronica- poorly drained	
R310	Veronica- well drained	
R38	Veronica- well drained	
AP15	Zarate- poorly drained	
AP18	Zarate- poorly drained	
SZ10	Zarate- well drained	
SZ14	Zarate- well drained	

measurements were carried out with a Bartington susceptibilimeter at two frequencies (470 and 4700 Hz). ($\chi_{fd}\% = [(\chi_{If} - \chi_{hf})/\chi_{If}] \times 100$, where χ_{If} and χ_{hf} are the low- and high frequency values, respectively)

Anhysteric remanent magnetization (ARM) measurements were performed with a homemade coil system that provides a direct magnetic field of 114 μ T. The applied alternating field was of 100 mT and the magnetization measurements were made in a 2 G cryogenic magnetometer system.

Low temperature magnetization was measured with a Quantum Design MPMS XL SQUID magnetometer. The samples were cooled in zero magnetic field from room temperature to 20 K, then a 2.5 T magnetic field pulse was applied and the magnetization was measured in zero field, while warming to room temperature.

Results and discussion

The parent material of Pampean plain soils contains minerals of volcanic origin transported by SW-NE winds from the Patagonia region (Clapperton 1993). The pedogenic process is characterized by a sequence of iron-reducing and oxidizing reactions: according to Orgeira and Compagnucci (2006), a hypothesis for the origin of the magnetic signal in pedogenic horizons of Pampean plain is assumed. First, detrital minerals undergo weathering processes. Some of these processes affect the ferrimagnetic detrital minerals. The iron made available by weathering processes could, under certain conditions, precipitate pedogenic SP/SD particles. Part of the soluble ferrous iron ions dissolves in the soil and is eventually reoxidized, turned into ferrihydrite, goethite or hematite forms, depending on the specific chemical conditions (e.g. Faure 1998; MacBride 1994; Buol et al. 1991).

The ferrimagnetic SP fraction seems to be one of the most important magnetic indicators of pedological processes.

Several parameters have been proposed to distinguish this fraction from the detrital signal. The most popular is the frequency dependence of room temperature (RT) susceptibility $\chi_{fd\%}$. More quantitative methods are based on the analysis of ZFC curves and on the measurements of magnetic susceptibility as a function of temperature.

A strictly quantitative estimation of the pedogenic SP fraction is based on the subtraction of the detrital contribution from the magnetic signal. This task is difficult to perform for the studied samples, because of the strong concentration of detrital ferrimagnetic minerals. Owing to this characteristic, a method to accomplish this task has been proposed; it is based on the blocking temperature distribution of the pedogenic SP minerals.

It is assumed that pedogenic SP particles have a lognormal distribution of blocking temperatures based on the studies carried out on some synthetic samples of magnetite (Blanco-Mantecón and ÓGrady 1999; Kim et al. 2001, Kiss et al. 1999). Using this assumption, the contribution of SP particles was separated from the titanomagnetite (TM) background, which has different characteristics (i.e. they cannot be fitted to a lognormal distribution and/or have a sharp Verwey-like transition) (Moskowitz et al. 1998; Brachfeld and Banerjee 2000; Lagroix et al. 2004). Due to this, it is not possible to infer the distribution of volumes and microcoercivity from low-temperature alone. A value for the microcoercivity was assumed in order to calculate the distribution of volume from the blocking temperatures.

The shape anisotropy can affect, among other things, the magnetization vs. temperature curve (Kliava and Berger 1999); therefore, the magnetization curve is determined by the size and shape of magnetic nanoparticles. Otherwise, Berger et al. (2001) showed that the distributions of particle volumes, regardless of the shape, are well described by a lognormal function.

ZFC curves, measured systematically for the studied paleosol and soil samples, are represented in Figs. 1a and 2a. The loss of remanence between 10 and 50 K indicates the presence of SP particles. Note that the effect is higher in Zarate samples AP18, AP15, SZ10 and SZ14. The step near 118 K in the same samples is caused by Verwey transition in magnetite.

The normalized derivative of magnetization versus temperature and the lognormal fitting are shown in Figs. 1b and 2b. When Fig. 2b is compared with the lognormal fitting of Fig. 1, the samples, exhibit a blocking temperature $T_{\rm B}$ near 20 K, excluding samples R210 (which is not represented in the figure) and AP18 which have $T_{\rm B}$ near 30 K, indicating higher blocking volume. The magnetic coercivity field is assumed $\mu_{\rm o}$ $H_{\rm C} \approx 20$ mT for all the samples, therefore, in samples AP18 and R210, the blocking volume is $V_{\rm B} \approx 2 \times 10^{-24}$ m³, and the media diameter $D_{\rm m} \approx 16$ nm. In the rest of the samples, the



Fig. 2 a Low temperature thermal demagnetization of saturation of isothermal remanent magnetization, $M_{\rm rs}$, imparted at 10 K in a 2.5 T field; **b** derivative of normalized magnetization decay (Mn), showing a blocking temperature $T_{\rm B} \approx 20$ K in samples, SZ14, AP15, SZ10, R19, R213, R310 and R38. Sample AP18 shows a blocking temperature near 30 K

blocking volume is $V_{\rm B} \approx 8.9 \times 10^{-24} \text{ m}^3$, and the media diameter is $D_{\rm m} \approx 12 \text{ nm}$.

In low temperature thermomagnetic runs, the titanomagnetites and SP particles show similar curves (Moskowitz et al. 1998). In order to distinguish between them, the low temperature variation of magnetic susceptibility and the saturation of isothermal remanent magnetization (SIRM) were analyzed.

The low temperature variation of susceptibility was used in order to establish the Ti-content of detrital titanomagnetite grains. It was compared with titanomagnetites curves from Moskowitz et al. (1998). The magnetic susceptibility of the soils is controlled mainly by ferrimagnetic and paramagnetic signal. To disregard the paramagnetic signal the following equation was applied:

$\chi_{\rm ferri}(T) = \chi - \chi_{\rm para}(T),$

where $\chi_{\text{para}}(T) = \chi_{\text{para},293}$ 293/*T*, and $\chi_{\text{para},293}$ is the susceptibility at 293 K

The variation of ferrimagnetic susceptibility with temperature is shown in Fig. 3; the shape of the curve can be attributed to SP particles plus ferrimagnetic non-SP minerals. A visual comparison with published data (Moskowitz et al. 1998; Richter and van der Pluijm 1994; Thompson and Oldfield 1986) suggested that studied samples are controlled mainly by titanomagnetite with low Ti-content.

On the other hand, the low temperature SIRM variation can be controlled by the titanomagnetites or the SP fraction (Moskowitz et al. 1998; Brachfeld and Banerjee 2000). In order to establish which of them is the predominant cause, the results from soil samples were compared with TM0, TM28 and TM 41 (Moskowitz et al. 1998). The curves are shown in Fig. 4 and show significant differences between the soil samples and TM28–TM41. According to that, the low temperature SIRM behavior in the studied Argentinean soils seems to be controlled by SP grains rather than by titanomagnetites. Therefore, the lognormal model of SP distribution can be applied to these soils.

Grain size of magnetic SP particles of chemical origin follow a lognormal distribution, while those of biogenic origin does not (Kopp 2007). Therefore, the present results indicate a chemical origin of the SP grains.

The concentration of superparamagnetic particles with grain size close to 15 nm is linearly correlated with ferrimagnetic susceptibility (Fig. 6a). This correlation could indicate that the pedogenetic processes that produce SP



Fig. 3 Normalized ferrimagnetic susceptibility versus temperature curves for selected samples. Ferrimagnetic susceptibility, χ_{ferri} , was obtained subtracting the paramagnetic component according to $\chi_{\text{ferri}} = \chi_{\text{bulk}} - \chi_{\text{para293}} \times 293/T$. Linear correlation is shown with a correlation coefficient R = 0.99825



Fig. 4 Normalized SIRM for the selected samples compared with TM0, TM28 and TM41, data taken from Moskowitz et al. (1998)

particles are driven by pH, Eh, the environmental condition (i.e. temperature, humidity, rainfall) and by the amount of detrital ferrimagnetic mineral which is an important source of iron (Orgeira et al.2007) Measurements from a large number of samples indicate an upper limit for $\chi_{fd} \approx 15$ per cent (Stephenson 1971; Thompson and Oldfield 1986; Dearing et al. 1996). Eyre (1997) and Worm (1998) demonstrated that χ_{fd} % depends strongly on the grain sizes distribution of SP particle, being maximal for a narrow distribution of volumes, with a corresponding mean blocking temperature, close to room temperature for sediments with SP particles.

A very wide distribution of volumes or a set of SP particles with blocking temperatures $T \ll 300$ K are both characterized by a vanishing χ_{fd} % that leads to an underestimation of the SP fraction. A χ_{fd} % at frequencies lower than 5 kHz, in fine-grained material is indicative of the presence of superparamagnetic grains and if susceptibilities are measured at several frequencies *f*, the curvature of the χ versus log *f* curves should yield approximate information on the width of the distribution (Fig. 5). Wide distributions have nearly linear χ versus log *f* curves; these distributions can be related to low χ_{fd} % values regardless the presence of superparamagnetic grains (Worm 1998). In such cases, low temperature measurements are more reliable to detect the presence of superparamagnetic grains.

The room temperature magnetic parameters, mean values and standard deviation for Verónica and Zarate soils are shown in Tables 2 and 3. Paramagnetic susceptibility was obtained from the high-field slope of the hysteresis loop. The ferrimagnetic susceptibility is obtained by subtracting the paramagnetic susceptibility from the bulk susceptibility.



Fig. 5 Susceptibility versus logarithm of frequency, for selected samples, showing linear behavior

Changes in the χ_{para}/χ_{ferri} ratio can be due to variations in paramagnetic or ferrimagnetic content. In order to establish which of them is the constant fraction, the standard deviation of ferrimagnetic and paramagnetic susceptibility was calculated. Low (high) standard deviation values are indicative of uniformity (variability) in the

 $M_{\rm s}$ (A m²/kg)

 $M_{\rm rs}$ (A m²/kg)

 χ_{tot} (m³/kg)

 $\chi_{\text{para}} (\text{m}^3/\text{kg})$

 χ_{ferri} (m³/kg)

0.0795

0.012

 9.26×10^{-7}

 9.05×10^{-8}

 8.33×10^{-7}

0.037

0.005

 3.87×10^{-7}

 2.30×10^{-9}

 3.84×10^{-7}

content of the correspondent fraction, respectively (Table 3). In both soils (Veronica and Zarate), the mean paramagnetic susceptibility has low standard deviation while the mean ferrimagnetic susceptibility shows a relative high standard deviation; therefore, changes in $\% \chi_{para}/\chi_{ferri}$ shown in Table 2, can be attributed mainly to changes in concentration of ferrimagnetic minerals, while iron bearing paramagnetic minerals are constant.

The ARM measurements are shown in Table 4. The susceptibility of ARM, χ_{ARM} , the bulk susceptibility, χ_b and the χ_b/χ_{ARM} ratio, that ranged between 0.2 and 0.12, are in agreement with SP grain sizes or particles in the single domain (SD)-pseudosingle domain boundary (PSD) (Liu 2004). Due to the low SP concentration (Table 5), roughly 30% of the total, the χ_b/χ_{ARM} ratio is driven by SD/PSD fraction.

The Figs. 6a and b show a linear correlation between the concentration of ferrimagnetic minerals and SP generation. This correlation is plausible, since it is often reflected in rocks. Noticeably, the best correlation coefficient (0.98) is shown in a plot of χ_{ferri} versus SP, followed by a correlation coefficient of 0.96 for M_{rs} versus SP, and a correlation coefficient of 0.85 for M_{S} . Considering the increasing sensitivity of M_{rs} and ARM to fine grains, it seems that the finer fraction of ferrimagnetic minerals is correlated with SP. This is supported by the no correlation of χ_{para} versus

Sample	$M_{\rm s}$ (A m ² / × 10 ⁻	$M_{\rm rs}$ (A m ² /kg) $\times 10^{-2}$	$B_{\rm c}~({\rm mT})$	$B_{\rm cr}~({\rm mT})$	$\begin{array}{l} \chi_b \ (m^3/kg) \\ LF \times \ 10^{-6} \end{array}$	$\chi_{\rm para} \ ({\rm m}^3/{\rm kg}) \ imes \ 10^{-8}$	$\begin{array}{l} \chi_{ferri} \\ (m^3/kg) \\ \times \ 10^{-6} \end{array}$	χ _{para} /χ _{ferri} %
R19	1.33	1.86	10.43	34.16	1.47	9.21	1.37	6.70
R310	0.868	1.32	10.48	32.98	0.998	8.71	0.911	9.56
R38	0.853	1.26	10.08	33.44	1.04	9.31	0.945	9.85
R213	0.581	0.984	11.55	36.10	0.659	9.01	0.569	15.84
R210	0.343	0.611	11.31	35.11	0.463	9.01	0.373	24.16
SZ14	0.986	1.53	12.1	26.2	1.40	6.52	1.33	4.90
SZ10	1.05	1.61	10.8	20.5	1.33	6.32	1.26	5.00
AP15	1.58	2.42	11.2	29.3	1.80	7.19	1.73	4.16
AP18	1.35	2.16	12.6	35.5	1.91	5.59	1.85	3.02
Paramet	ers	Veronica mean	SD	Variał	oility Zarate	e mean	SD	Variability
$\overline{B_{\rm c}}$ (mT)		10.8	0.6	0.06	11.7	(0.8	0.07
$B_{\rm cr}~({\rm mT})$)	34.6	1.3	0.04	27.9	(5.3	0.23
χ _{para} /χ _{fer}	_{ri} %	13.2	7	0.53	4.27	(0.9	0.21

0.47

0.42

0.42

0.03

0.46

0.124

0.0193

 1.61×10^{-6}

 6.41×10^{-8}

 1.55×10^{-6}

0.027

0.0043

 2.88×10^{-7}

 $6.59\,\times\,10^{-9}$

 2.91×10^{-7}

0.22

0.22

0.18

0.10

0.19

Table 3 Mean values, standard
deviation (SD) and variability
(Variability = SD/Mean) of
magnetic parameters in
Veronica and Zarate samples

Table 2 Magnetic parametersfor samples at room temperature

Table 4 χ_{ARM} normalized ARM susceptibility obtained with a 114 µT direct magnetic field and 100 mT peak of alternating magnetic field

Sample	χ_{ARM} (m ³ /kg)	χ _b /χ _{ARM}	
R19	7.33E-06	2.01E-01	
R310	6.81E-06	1.47E-01	
R38	6.89E-06	1.51E-01	
R213	4.65E-06	1.42E-01	
R210	3.69E-06	1.25E-01	
SZ14	1.13E-05	1.24E-01	
SZ10	1.07E-05	1.24E-01	
AP15	1.17E-05	1.54E-01	
AP18	1.22E-05	1.57E-01	

 $\chi_b/\chi_{ARM},$ bulk susceptibility divided by χ_{ARM}

Table 5 SP/total for all the samples and SP concentration

Sample	SP/total	$\frac{\text{SP} (\text{A m}^2 / \text{kg})}{\times 10^{-3}}$	$\chi_{\rm ferri} \ ({ m m}^3/{ m kg}) \ imes \ 10^{-7}$	Average pH
R19	0.268	3.76	13.7	8.74
R210	0.283	1.67	3.73	7.9
R213	0.293	2.41	5.69	7.9
R310	0.337	3.41	9.11	6.4
R38	0.283	3.12	9.45	6.4
AP18	0.332	6.21	18.5	8.98
SZ10	0.291	4.46	12.6	7.6
SZ14	0.285	4.90	13.3	7.6

The SP/total does not show noticeably variations along the profiles, while SP concentration show differences between waterlogged and non-waterlogged soils that are different in Zarate and in Veronica

SP (Fig. 6c). This observation suggests a selective weathering of finer grain fraction of detrital ferrimagnetic minerals, due to increased surface/mass ratio.

Conclusions

The presence of detritic PSD titanomagnetite with low titanium content ranging between TM 28 and TM40 has been established.

One of the most important magnetic characteristics of these sediments is the lack of a typical frequency dependence of susceptibility between 470 and 4,700 Hz at room temperature. The χ_{fd} % factor at room temperature is close to 2%; this could be related to a wide grain size distribution. The curves of χ versus log *f* for selected samples show a linear relation, indicating a wide volume distribution. The linear decreasing of χ ferrimagnetic with temperature, before the Verwey transition, is consistent also with broad distribution. Therefore, the low frequency dependence of the susceptibility can be attributed to wide grain size



Fig. 6 a Linear fit of ferrimagnetic susceptibility vs. SP content. The linear fit has a very good correlation coefficient R = 0.96; **b** saturation magnetization M_s versus SP content shown a linear correlation with R = 0.85; **c** paramagnetic susceptibility vs. SP content, the figure shows no correlation

distribution and mixing of a superparamagnetic fraction with a multidomain magnetite, indicated by the Verwey transition. The linear correlations of SP content with ferrimagnetic susceptibility and with $M_{\rm S}$ suggest that ferrimagnetic minerals drive the SP generation.

It is well known that the paramagnetic minerals (like clays, amphiboles and pyroxenes) are transformed during the first weathering steps. However, new minerals are generated with similar magnetic properties and, as a consequence, the variation of the paramagnetic susceptibility is null.

Finally, it can be concluded that SP magnetic grains, in the Pampean plain, are generated by inorganic processes in adequate environmental pH and Eh of the soils.

Acknowledgments The authors thank the Consejo Nacional de Investigaciones Científicas y Tecnológicas (CONICET) from Argentina, the Universidad de Buenos Aires, Argentina, and Instituto de Física Arroyo Seco (IFAS) from Universidad Nacional del Centro de la Provincia de Buenos Aires (UNCPBA), Buenos Aires, Argentina. We wish to thank Mr. Emanuel Fabian Vasquez, who kindly helped with the manufacture of the apparatus and with the measurements of ARM. This work was supported by PIP 636/98, PIP 5659/05 from CONICET (Argentina) and UBACYT X236 (Argentina).

References

- Banerjee SK, Hunt CP (1993) Separation of local signals from the regional paleomonsoon record of the Chinese Loess Plateau: a rock-magnetic approach. Geophys Res Lett 20(9):843–859
- Bidegain JC, Evans ME, van Velzen J (2005) A magnetoclimatological investigation of Pampean loess, Argentina. Geophys J Int 160:55–62
- Brachfeld SA, Banerjee S (2000) Rock-magnetic carriers of centuryscale susceptibility cycles in glacial-marine sediments from the Palmer Deep, Antartic Peninsula. Earth Planet Sci Lett 176:443– 455
- Blanco-Mantecón M, O'Grady K (1999) Grain size and blocking distributions in fine particle iron oxide nanoparticles. J Magn Magn Mater 203:50–53
- Berger R, Bissey J-C, Kliava J, Daubric H, Estournés C (2001) Temperature dependence of superparamagnetic resonance of iron oxide nanoparticles. J Magn Magn Mater 234:535–544
- Buol SW, Hole FD, McCracken J (1991) Soil genesis and classification. The Iowa State University Press, Iowa
- Carter-Stiglitz B, Jackson M, Moskowitz B (2002) Low-temperature remanence in stable single domain magnetite. Geophys Res Lett 29(7):1029–1033
- Clapperton C (1993) Quaternary geology and geomorphology of South America. Elsevier, Amsterdam, p 779
- Dearing JA, Dann RJL, Hay K, Lees JA, Loveland PJ, Maher BA, O'Grady K (1996) Frequency-dependent susceptibility measurements of environmental materials. Geophys J Int 124:228–240
- Dunlop DJ, Özdemir Ö (1997) Rock magnetism fundamentals and frontiers. Cambridge University Press, Cambridge
- El-Hilo M, O'Grady K, Chantrell RW (2002) Fluctuation fields and reversal mechanisms in granular magnetic systems. J Magn Magn Mater 248:360–373
- Eyre JK (1997) Frequency dependence of magnetic susceptibility for populations of single-domain grains. Geophys J Int 129:209– 211
- Faure G (1998) Principles and application of geochemistry. 2nd edn. Prentice Hall, New Jersey

- Hunt PC, Banerjee SK, Han J, Solheid PA, Oches E, Sun W, Liu T (1995) Rock-magnetic proxies of climate change in the loesspalaeosol sequences of the western Loess Plateau of China. Geophys J Int 123:232
- Jackson M, Worm H (2001) Anomalous unblocking temperatures, viscosity and frequency-dependent susceptibility in the chemically-remagnetized Tranton limestone. Phys Earth Planet Inter 126:27–42
- Jordanova D, Jordanova N (1999) Magnetic characteristics of different soils types from Bulgaria. Studia Geoph Geod 43:303–368
- Kiss LB, Söderlung J, Niklasson GA, Granqvist CG (1999) New approach to the origin of lognormal size distributions of nanoparticles. Nanotechnology 10:25–28
- Kim DK, Zhang Y, Voit W, Rao KV, Muhammed M (2001) Synthesis and characterization of surfanct-coated superparamagnetic monodispersed iron oxide nanoparticles. J Magn Magn Mater 225:30–36
- Kliava J, Berger R (1999) Size and shape distribution of magnetic nanoparticles in disordered systems: computer simulations of superparamagnetic resonance spectra. J Magn Magn Mater 205:328–342
- Kopp RE (2007) The identification and interpretation of microbial biogeomagetism. Ph.D. Thesis, Division of Geological and Planetary Sciences, California Institute of Technology
- Lagroix F, Banerjee SK, Jackson M (2004) Magnetic properties of the Old Crow tephra: identification of a complex iron titanium oxide mineralogy. J Geophys Res 109:B01104
- Liu Q (2004) Grain sizes of susceptibility and anhysteretic remanent magnetization carriers in Chinese loess/paleosol sequences. J Geophys Res 109:b3–B03101
- MacBride J (1994) Environmental chemistry of soils. Oxford University Press, Oxford
- Maher BA, Thompson R (eds) (1999) Quaternary climates, environments and magnetism. Cambridge University Press, Cambridge
- Moskowitz B, Jackson M, Kissel C (1998) Low-temperature magnetic behavior of titanomagnetites. Earth Planet Sci Lett 157:141–149
- Neel L (1949) Théorie du traînage magnétique des ferromagnétiques en grains fins avec applications aux terres cuites. Ann Geophys 5:99–121
- Orgeira MJ, Compagnucci R (2006) Correlation between paleosolsoil magnetic signal and climate. Earth, Planets and Space (EPS), Special Issue "Paleomagnetism and Tectonics in Latinamerica" 58(10):1373–1380
- Orgeira MJ, Walther AM, Tófalo R, Vásquez CA, Berquó T, Favier Dubois C, Boehnel H (2003) Environmental magnetism in paleosols developed in fluvial and loessic Holocene sediments from Pampean Plain (Argentina). J South Am Earth Sci 16:259– 274
- Orgeira MJ, Walther AM, Vasquez CA, Di Tommaso I, Alonso S, Sherwood G, Yuguan H, Vilas JF (1998) Mineral magnetic record of paleoclimatic variation in loess and paleosol from the Buenos Aires formation (Buenos Aires, Argentina). J South Am Earth Sci 11:561–570
- Orgeira MJ, Pereyra FX, Vásquez C, Castañeda E, Compagnucci R (2007) Environmental magnetism in present soils, Buenos Aires Province, Argentina. J South Am Earth Sci (in press)
- Petrovsky E, Kapicka A, Jordanova N, Boruvka L (2001) Magnetic properties of alluvial soils contaminated with lead, zinc and cadmium. J Appl Geophys 48:127–136
- Richter C, van der Pluijm BA (1994) Separation of paramagnetic and ferrimagnetic susceptibilities using low-temperature magnetic susceptibilities and comparison with high field methods. Phys Earth Planet Inter 82(52):113–123
- Stephenson A (1971) Single domain grain distributions. I. A method for the determination of single domain grain distributions. Phys Earth Planet Inter 4:353–360

- Stoner EC, Wohlfarth EP (1948) A mechanism of magnetic hysteresis in heterogenous alloys. Philos Trans R Soc Ser A 240:599–642
- Terminiello L, Bidegain JC, Rico Y, Mercader RC (2001) Characterization of Argentine loess and paleosols by Mössbauer spectroscopy. Hyperfine Interact 136:97–104
- Vasquez CA, Walther AM, Orgeira MJ, Di Tomasso I, Alonso MS, Lippai H, Vilas JF (1998) Magnetic properties and envi-

ronmental conditions: study of a palaeosol of the Chaco-Pampean plain (Argentina). Quat South Am Antarct Penins 11:195–202

Worm HU (1998) On the superparamagnetic-stable single domain transition for magnetite, and frequency dependence of susceptibility. Geophys J Int 133:201–206