Geofísica Internacional
ISSN: 0016-7169
silvia@geofisica.unam.mx
Universidad Nacional Autónoma de México
México

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Geofísica Internacional, vol. 50, núm. 1, enero-marzo, 2011, pp. 9-22
Universidad Nacional Autónoma de México
Distrito Federal, México

Geofísica Internacional (2011) 50-1: 9-22

Original paper

Magnetic parameter analysis of a climosequence of soils in the Southern Pampean Region, Argentina

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Received: May 21, 2009; accepted: September 29, 2010; published on line: December 17, 2010

Resumen

En este trabajo se utilizan parámetros de magnetismo de rocas en el estudio de diferentes tipos de suelos desde Caleu-Caleu, en la provincia de La Pampa hasta Tres Arroyos, en la provincia de Buenos Aires, Argentina. A partir de los datos obtenidos se puede observar que en todos los sitios analizados hay un incremento de la concentración de minerales ferrimagnéticos en el solum, determinados como titano-magnetita. El incremento de minerales magnéticos es estimado en forma simple mediante la utilización de la susceptibilidad magnética. Parámetros magnéticos indicadores de tamaño de grano tales como la susceptibilidad anhistérica y la susceptibilidad dependiente de la frecuencia versus profundidad, indican que existe un patrón de comportamiento que refleja una disminución del tamaño de grano magnético en los horizontes superiores de los suelos. Este comportamiento magnético es más evidente en el sector de mayor humedad relativa del área estudiada. Los suelos constituyen una climosecuencia, con condiciones de mayor sequía al oeste de la transecta y tipos de suelos Torripsammentes y Haplustoles arídicos. Condiciones de mayor humedad relativa impuestas hacia el este de la transecta generaron el desarrollo de Argiustoles y Argiudoles. El comportamiento de los parámetros magnéticos parece reflejar el grado de desarrollo pedogenético en la región estudiada, caracterizada por una temperatura media anual de 14 ºC y un régimen de lluvia entre 400 mm/año y 800 mm/año. Los datos obtenidos indican la existencia de un patrón de comportamiento magnético opuesto al obtenido en suelos del norte de la pradera pampeana.

Palabras clave: Argentina, suelos, parámetros magnéticos, incremento magnético

Abstract

Magnetic parameters of different soil types from Caleu-Caleu, La Pampa, Tres Arroyos, Buenos Aires province, Argentina show an increase in ferrimagnetic mineral concentrations in the solum. Titanomagnetites are major magnetic minerals in the soils. The distribution patterns of grain size dependent magnetic parameters, anhysteric susceptibility and frequency dependent susceptibility versus depth reflect changes to smaller grain sizes, especially single domain, in the upper soil horizons. This magnetic behavior is more evident in the humid than in the dry region. These soils represent a climosequence, where drier conditions are represented towards the west of the transect and were classified as Torripsamment and aridic Haplustoll types. Higher relative humidity conditions towards the east of the transect yield a development of Argiustolls and Argiudolls. The behavior of magnetic parameters appears to reflect the degree of pedogenesis reached in the area with a mean annual temperature around 14 ºC and a rainfall ranging between 400 to 800 mm/year. The data indicate a new magnetic pattern, opposite of that obtained in soils in the north of the Pampean prairie.

Key words: Argentina, soils, magnetic parameters, magnetic enhancement.

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Introduction

The present contribution is a first approach to a more ambitious project aiming to differentiate soil types developed around the 38º South Latitude in the southern Pampean Region of Argentina, by applying rock magnetic parameters. The soil transect to be investigated stretches from the drier west in La Pampa province to the more humid east in the Buenos Aires province; for this reason it may be considered as a climosequence of soils which is 600 km long. In order to document the main trend of magnetic parameters along the transect, five representative soils from Caleu-Caleu (La Pampa) to Tres Arroyos (Buenos Aires) are reported here.

Rock magnetic parameters applied in the study of soils and sediments are important tools for the investigation of their magnetic mineralogy. Soil magnetism, in particular, is receiving increasing attention as a source of climatic and environmental information. The influence of climate, especially rainfall, is clearly reflected in magnetic parameters according to Maher (1998, 2002). However a careful study must be carried out to interpret the magnetic signal and the link between soil magnetism and climate, particularly because the soils are complex bodies which result from the interaction of several factors contributing to their development. These factors include parent material, relief, time, organisms and climate. In several studies, the variation of magnetic parameters registered in soils has been attributed to different factors such as bacterial activity, poor or bad drainage, topographic position of soils, parent materials, soil erosion, soil age or pollution (Maher 1986; Jordanova *et al.* 1997; Jordanova and Jordanova 1999; Hanesch and Petersen 1999; de Jong *et al.* 2000; Dearing *et al.* 2001; Royall 2001; Kapicka *et al.* 2003; Chaparro *et al.* 2002; Hanesch and Schölger, 2005).

Studying recent soils, Bartel *et al.* (2005), found that the susceptibility values of Argiudolls in the north of the Buenos Aires province were depleted in A and Bt horizons compared to parent material (C horizon). These results are in agreement with those obtained by Bidegain *et al.* (2005, 2007) in loess/paleosols sequences of the same area and by Orgeira *et al.* (2008) in Argiudolls. The mentioned authors found that susceptibility values decrease in paleosols and increase in the parent material (loess) while the lowest values were obtained in gleyed horizons. According to the previous works, the development of soils under relatively high humidity (1,000 mm/year) will produce the decrease of the magnetic values on top soils. This is due to the alteration of magnetic minerals and the new building of paramagnetic ones as lepidocrocite, akaganeite, goethite in those levels (Bidegain 1998).

Ortega *et al.* (2004) and Rivas *et al.* (2006) studying paleosols developed on volcaniclastic parent materials in Mexico found that susceptibility values were lower in paleosols than in the parent material. The authors attributed this magnetic behavior pattern to a destructive process of primary and secondary magnetic components in paleosols.

The focus of this study is on magnetic parameters variations through a transect of soils in the southern Pampean Region. The analysis of data indicates a model of behavior that differs considerably from those ones previously realized in the northern Pampean Region. For this target several of the conventional magnetic parameters were applied to samples collected from the most representative soils. Some of the parameters refer to the magnetic concentration such as susceptibility (χ) and IRM (isothermal remanent magnetization). Other parameters, as frequency dependent susceptibility (χfd), and anhysteric susceptibility (χarm) were applied to estimate magnetic grain size. The values of coercivity of remanence (Bcr) were referred to the magnetic mineralogy of profiles, and thermal demagnetization was used in order to investigate the presence of different mineral phases. The main soil forming factors acting in the differentiation of soil properties along the transect are climate and the parental material. The former is related to rainfall which varies between 450 mm/year (west) and 800 mm/year (east), thus favoring the major development of soil to the east of the studied region. The latter varies according to the winds from Cordillera de los Andes. Wind energy decreases from west to east and grain size of sediments decreases also in the same direction. This has also been demonstrated by Lüters (1982), who did his research on the pedogenesis of soils in the region. Both climate and parent material as main factors have been acting during the development of soils along the transect longer than any other soil forming factor. However, we have considered not only the records of the parent material but particularly the way pedogenesis has affected the magnetic minerals.

Materials and methods

Area and soils descriptions

The studied area is located in the south-eastern part of La Pampa province and southern part of Buenos Aires Province, between 38º-39º S. and 64-60º W, in the southern of Pampean Region, Argentina (Fig. 1). This region is a huge slightly undulating plain, constituted by aeolian unconsolidated Quaternary sediments (Moscatelli, 1991). They mainly comprise the sandy to silty loess which, as a mantle, covers the landscape overlying Plio-Pleistocene silts and calcretes. The calcrete layers (2Ckm) are shallow

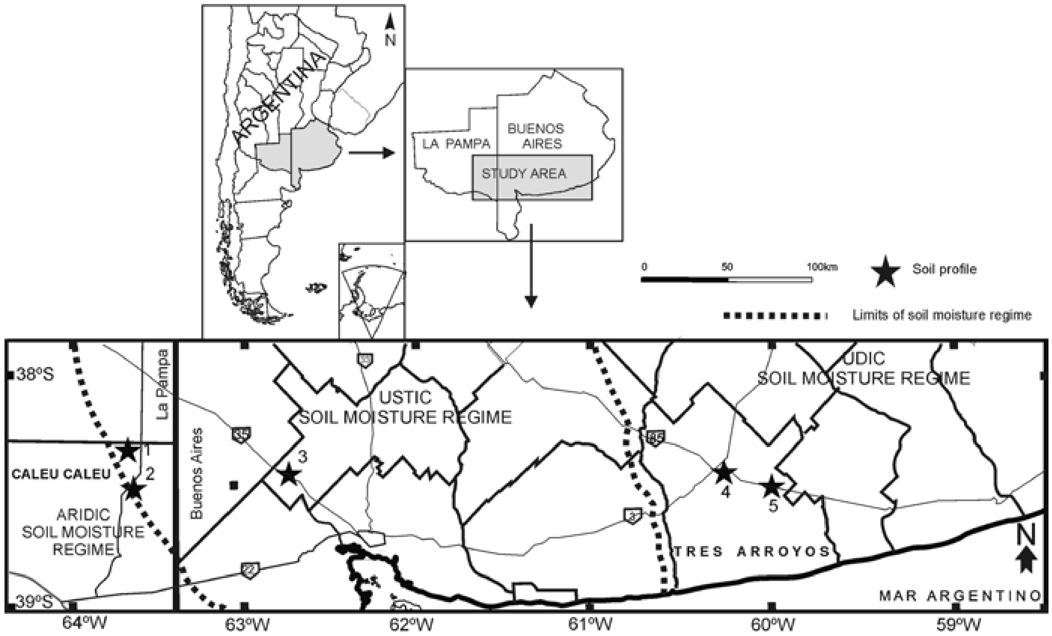

Figure 1. Map showing the location of the study area as well as the approximate limits of soil moisture regime. Solid symbols denote soils profile used for magnetic analyses.

and the parent material and soil horizons show generally short sections of about 1 meter.

The parent material of soils show similar mineralogical characteristics along the transect, with a predominance of minerals of volcanic origin as lithic fragments and volcanic glass; illite is the main clay mineral (Lüters, 1982). The lithologic grain size is coarse in the western than in the eastern of the transect studied. The soils sampled in the western were developed under semiarid climate and the soils from the eastern part were developed under sub humid climate. Considering the period between 1961 and 1990 the mean annual rainfall in the west of the studied area was around 400 mm while in the east was 796 mm. For the same period the mean annual temperature was 14-15 ºC. The potential annual water deficiency is about 300 mm in the west and it decreases towards the east, records between 229 and 255 mm of water deficiency have been mentioned in the locality of Tres Arroyos for the period 1970-1990 (Daitsch *et al.*, 2007). The vegetation is represented by perennial sparse bushes and sparse "caldén" trees in the west (La Pampa province), while the areas studied in the east (Buenos Aires province) are covered by grass. The use of land is mainly extensive livestock in the west and the agricultural production increases towards the east.

Five zonal soils were selected for the present contribution by using the map of soils, scale 1:500,000 (Atlas de suelos de la República Argentina, 1990). They were one Entisol and four Mollisols corresponding to different soil moisture regimes, going from aridic/ustic in soils P1 and P2 to udic in soils P4 and P5. The selected Soil P3 corresponds to an ustic moisture regime intermediate between the aridic and udic regime. These soils were described according to the norms of soil descriptions proposed by Etchevehere (1976) and classified according to the denomination proposed by "Soil Taxonomy" (Soil Taxonomy, 1999) as ustic Torripsamment (P1), aridic Haplustoll (P2), lithic Argiustoll (P3) and typic Argiudolls (P4 and P5). As a consequence of the climatic gradient, less evolved soils show a C-C2 horizons sequence as in the case of Torripsamment ones; A-AC-Ck horizons sequence are characteristic of aridic Haplustoll while the higher evolved soils (Argiudolls) present a A-Bt-BC-C sequence.

The texture of horizons in the less evolved soils in the west has a high proportion of the sand fraction which ranges between 86 and 96% in soils P1 and P2. With the increase of rainfall to the east of the transect translocation and neoformation of clay minerals occurs and the development of Bt horizons is more evident (Argiustoll and Argiudolls soils). The texture is sandy clay loam in the A and Bt horizons of the lithic Argiustoll soils. The more evolved Argiudolls soils (P4 and P5) show a clay loam texture in Bt horizons and a loam texture in the A, BC and C horizons. The physical and chemical properties of soils are summarized in Table 1.

Table 1. The physical and chemical characteristics of soils used in the study.

Soil Profile	Horizon (upper and lower Boundaries, cm)	Munsell Color (wet)	Texture (pipette method)	Structure	pH (H_2O)	Clay content (%)	OM (%)
P1	C 0-5	10YR3/3	Sand	Bl vw	6.3	-	1.3
	C_2 5-80	10YR3/4	Sand	Bl vw	7	-	
P2	A 0-19	10YR3/3	L. sand	Bl m	7.2	1.7	2
	AC 19-37	10YR4/3	Sand	Bl m	7.8	1.1	1.2
	Ck 37-75		Sand	Bl w	8	1.2	
P3	A 0-21	10YR3/3	Scl	Bl m	6	22.3	2.7
	Bt 21-33	10YR3/4	Scl	Bl m	6.8	28	1.3
	BCk 33-45	10YR4/4		Bl w	7.5		
P4	A 0-15	10YR3/1	L	Gr m	6.1	24.6	5.3
	AB 15-32	10YR3/2	L	Bl m	6.2	24.7	4.2
	Bt 32-55	10YR3/4	Clay loam	Pr m	6.3	35.1	1.1
	BC 55-75	10YR4/4	Clay loam	Pr/Bl m	6.6	31.9	0.6
	C 75-100	10YR5/4	L	Bl w	-		
P5	A	10YR3/1	L	Bl m	5.8	23.2	2.5
	Bt	10YR4/3	Clay loam	Pr m	6.2	35	1.4
	BC	10YR4/4	L	Pr/Bl m	-	25.7	0.7
	C	10YR5/4	L	Bl w	7.1	17.6	

Scl sand clay loam; L loam; Bl Blocky; Gr granular; Pr prismatic; vw very weak; m moderate; OM: organic matter.

Sampling and magnetic measurements

After a detailed differentiation of soil horizons by conventional edaphological methods, volumetric susceptibility (k) was measured *in situ* using a Bartington MS2 device with MS2F dual frequency sensor. In each profile, these measurements were repeated at least twice along the same line in the soils profile every 5 to 10 cm. These data obtained in the field were valuable for a better definition of boundaries between horizons. According to this first approach, representative samples to be measured in laboratory were collected from each horizon. The sampling was performed by using plastic boxes of 8 cm^3 and the material thus collected was air dried before laboratory work. The magnetic susceptibility was measured in each sample at low (470 Hz=χ lf) and high (4,700 Hz=χ hf) frequencies with a Bartington MS2B device in order to obtain the value of frequency dependent susceptibility (χfd), calculated as χfd(%)=(χ lf – χ hf)/ χ lf, with the aim of estimating the SP (superparamagnetic) particle contribution (Evans and Heller, 2003).

Stepwise acquisition of isothermal remanent magnetization (IRM) and determination of the value of saturation (SIRM) was performed by using a pulse magnetometer Model IM10-30 of ASC Scientific. Each sample was magnetized by exposing it to steadily increasing fields from 13 up to 1,000 mT and the remanent magnetization after each step was measured using a spinner fluxgate Molspin magnetometer. The IRM measurements were performed on representative samples from all horizons of the five different soil profiles. In addition, back field was applied using the same pulse magnetometer in order to have the coercivity of remanence spectrum of minerals, i.e. the Bcr values. The back field applied was up to 300 mT in all the samples in order to obtain the S ratio ($IRM_{-0.3T}$/ $SIRM_{-1T}$), which helps in the differentiation of high coercivity minerals (hematite-goethite) from low coercivity ones (magnetite-maghemite).

Applying AF and a low bias field, the ARM values were also obtained for all the samples. The ARM measurements were the first to be performed in the laboratory and carried out with the corresponding device for ARM, the Molspin demagnetizer and the mentioned spinner magnetometer for obtaining the values in each step. An alternating field of 100 mT was applied on all the samples as well as a direct bias field of 90 μT and the susceptibility of anhysteric remanent magnetization (χarm) was calculated. These measurements were performed taking into account previous contributions (Maher 1988) which mentioned that the relative variation in the content of single domain (SD) magnetite can be approximated by χarm values. To avoid particle movement during measurement cycles, sodium silicate was used in the laboratory for fixing the particles.

Susceptibility measurements at low temperature were carried out from 14 K to 300 K using a Lakeshore AC susceptometer in the Department of Physics of La Plata University. Low temperature susceptibility measurements allow us to investigate the presence of different mineral phases as to determine the transition temperatures (Verwey and possibly Morin transitions).

Stepwise thermal decay curves of isothermal remanent magnetization were used for magnetic phase identification through the determination of the Curie temperature. The samples considered in the present work were demagnetized from room temperature up to 700 °C using a TD-48 ASC Scientific furnace.

Other non-magnetic measurements were also performed in order to obtain extra information like mineral shape and composition. For that purpose a Philips 505 Scanning Electron Microscope (SEM) with a standard tungsten filament was used. The samples were covered with a 15nm Au layer; the acceleration potential was of 20kV. Simultaneously, energy dispersive spectroscopy (EDS) analyses of the grains were obtained using a light element energy dispersive spectrometer in conjunction with the SEM.

The organic matter (OM) content in the soils was determined in A horizons by the Walkley–Black wet digestion method (Schlichting *et al.*, 1995). Soil pH was measured using an Orion 701 A pH meter at a 1:2.5 soil: water ratio.

Results

Magnetic parameters

The χlf, χfd and χarm variation along the profiles of soils corresponding to those ones with lower (west) and higher (east) pedogenetic evolution is indicated in Figs. 2 and 3. The χlf values vary from 250 to 291 x 10^{-8} m^3/kg in soil P1 (Fig. 2a), from 406 to 563 x 10^{-8} m^3/kg in soil P2 (Fig. 2b), from 356 to 609 x 10^{-8} m^3/kg in soil P3 (Fig. 3a), from 383 to 558 x 10^{-8} m^3/kg in soil P4 (Fig. 3b) and from 384 to 581 x 10^{-8} m^3/kg in soil P5 (Fig. 3c). According to the data the lowest ferromagnetic contribution corresponds to the soil P1.

The magnetic susceptibility pattern indicates a progressive enhancement upwards as a general trend, i.e. from the C horizon to the epipedon. The pedogenetic origin of the magnetic signal seems also to be consistent with the fact that the highest susceptibility values are obtained in the top soils. The latter is more relevant due to the increasing of organic matter in the A horizons which is diamagnetic.

Similar behavior was found when considering the χarm data, although the difference in percentage of A horizon compared to C horizon is more remarkable for χarm values than for the low frequency susceptibility ones. Corresponding

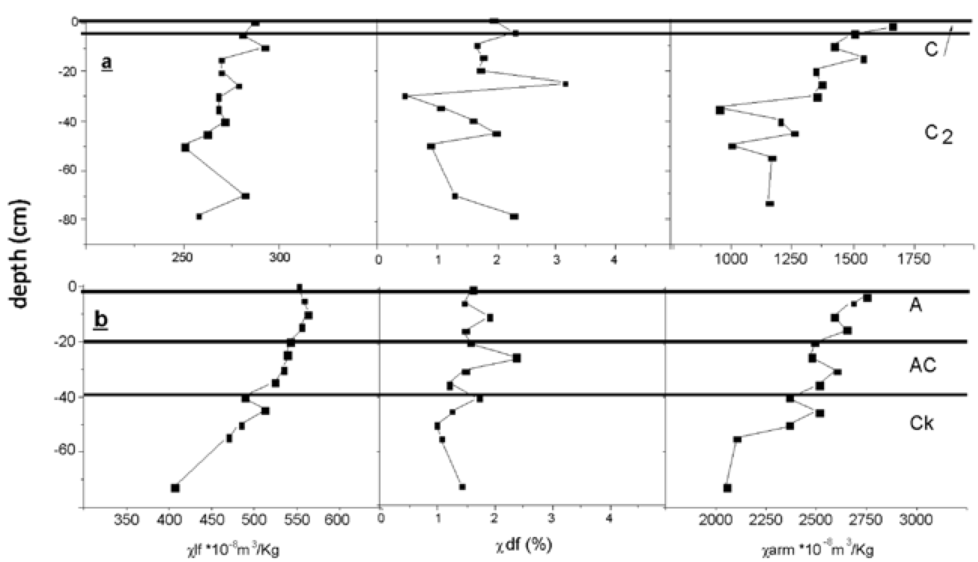

Figure 2. Magnetic properties for the soils of semiarid climate: ustic Torripsamment P1 (a) and aridic Haplustoll P2 (b). The horizontal lines show boundaries between horizons.

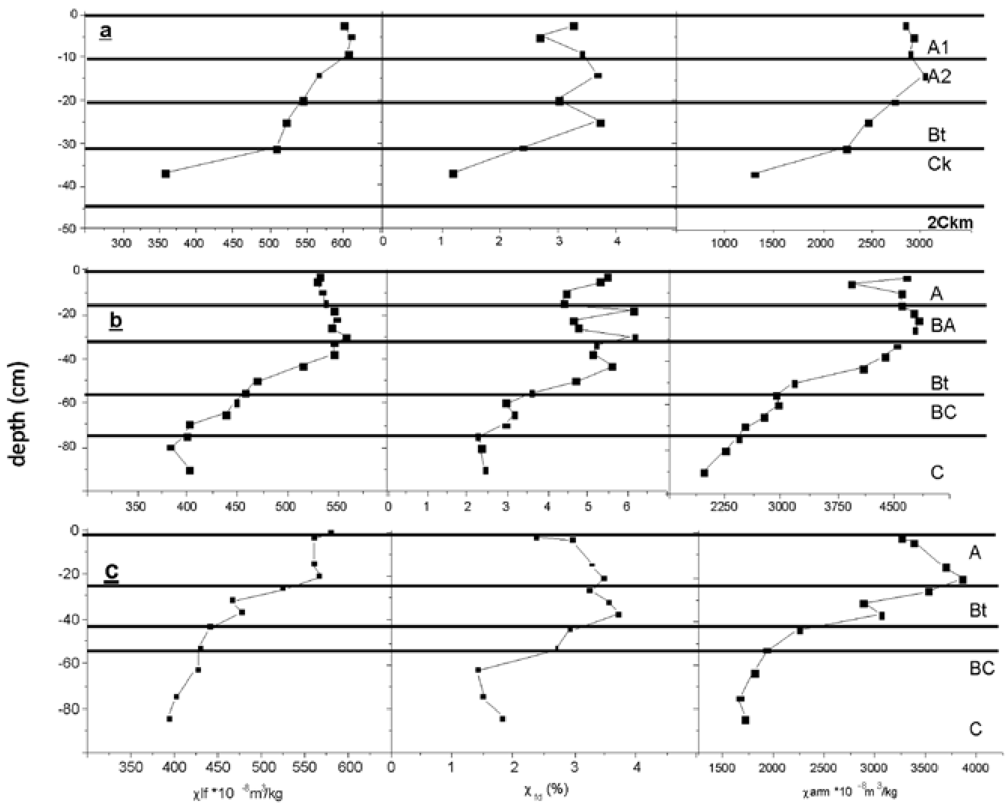

Figure 3. Magnetic properties for the soils of subhumid climate: Lithic Argiustoll P3 (a) and Typic Argiudolls P4, P5 (b, c). Soil horizons are indicated at right.

χfd values increase in the uppermost horizons but this is not so remarkable as to indicate an important contribution of SP particles.

Table 2 shows mean values of χlf and χarm for C and A horizons of each soil and the percentage increase rate when using the values of C horizon as reference. The χlf of the upper horizons were, in average, between 7 and 18% higher than those of the corresponding parental materials in soils P1 and P2, and between 30 and 37% in soils P3, P4 and P5. The increases of χarm were, in all cases, higher than those recorded when using low frequency susceptibility. They increase to maximums of 99% in profiles P4 and P5. Both parameters show higher increases in the increasing direction of soil evolution, i.e. from Entisol to Mollisols, and also into the Mollisols from aridic Haplustoll to Argiudolls. A significant linear relationship between χlf and χarm was found in all soils, suggesting that χlf is influenced by SD grains, while χfd% shows almost no correlation with χlf, except in soil P4 (R^2:0.95, $p<0.01$), where both SP and SD grains contribute to the increase of χlf (Table 2).

Magnetic mineralogy

The IRM acquisition curves show a similar behavior in all the samples analyzed of the studied profiles. The fast increase of magnetization between 0 and 100 mT is noteworthy (Fig. 4), 90 to 94% of SIRM is reached for a peak field of 200 mT. Besides, applying backfields to the SIRM of samples, values of Bcr between 30-45 mT are obtained.

These results suggest a dominance of ferrimagnetic minerals of low coercivity like (titano)-magnetite. Furthermore, the S ratio, ranging between 0.90 y 0.96, support previous analyses. S values increase in the topsoil, suggesting that the increase of χlf is produced mainly by (titano)-magnetite or maghemite. Fig. 4 shows the details of the backfield applied on the samples around the Bcr, suggesting that the values are closely related to the degree of pedogenesis, i.e. a higher degree of pedogenesis produces a lower Bcr. The most developed soil P5 produces lower Bcr than the less developed ones P1 and P2. Moreover, in each profile the Bcr is always lower in the horizons which are more affected by pedogenesis (soil solum) than in the

Table 2. Mean values of χlf and χarm for C and A horizons of studied soil and the increase rate.

Location	Soil Classification	Soil Profile	χ_{lf} horizon C (mean, 10^{-8} m^3/kg)	χ_{lf} horizon A (mean, 10^{-8} m^3/kg)	Enhancement (%)	Linear regression χ_{lf} – χ_{fd} R^2 (P)	χ_{arm} horizon A (mean, 10^{-8} m^3/kg)	χ_{arm} horizon C (mean, 10^{-8} m^3/kg)	Enhancement (%)	Linear regression χ_{lf} - χ_{arm} R^2 (P)
Caleu-Caleu	Ustic Torripsamment	P1	268	286	6.7	0.076 (NS)	1530	1120.3	36	0.385 (P=0.023)
Caleu Caleu	Aridic Haplustoll	P2	472.3	557.24	18	0.16 (NS)	2660.24	2270.3	17.3	0.85 (P= 0.0001)
Tornquist	Lithic Argiustoll	P3	450	584.6	29.9	0.60 (P<0.023)	2877.4	1750	64.4	0.93 (P<0.0001)
Tres Arroyos	Typic Argiudoll	P4	396.2	541.4	36.6	0.95 (P=0.0001)	4565.2	2292.3	99	0.826 (P=0.0001)
Tres Arroyos	Typic Argiudoll	P5	413.4	567.2	37.2	0.302 (NS)	3543.2	1777.6	99.3	0.883 (P=0.0001)

parental material. Conversely in less evolved soils towards the west (P1 and P2), Bcr values do not show conspicuous differences between horizons (Fig. 5) suggesting that this parameter is a suitable tool to compare different degrees of pedogenesis in the area.

The increase of Bcr towards deeper levels was previously mentioned in Argiudolls developed over Holocene loess from La Plata city, northern of Buenos Aires province, studied by Bartel *et al.* (2005). Avramov *et al.* (2006) attributed the lower Bcr in paleosoils respect to parental loess to the presence of pedogenic submicron particles with sizes close to the SP-SD boundary, which show magnetically soft behavior.

The Bcr of the studied soils shows an opposite trend than χarm values, with R^2:0.77, R^2: 0.66 and R^2: 0.505 (p<0.01 in all cases) for Argiudolls, Torripsamment and Haplustoll aridic respectively. The Argiustoll soil showed a no significant negative correlation (R^2: 0.25; p: 0.2). The general coercivity behavior could lead to the

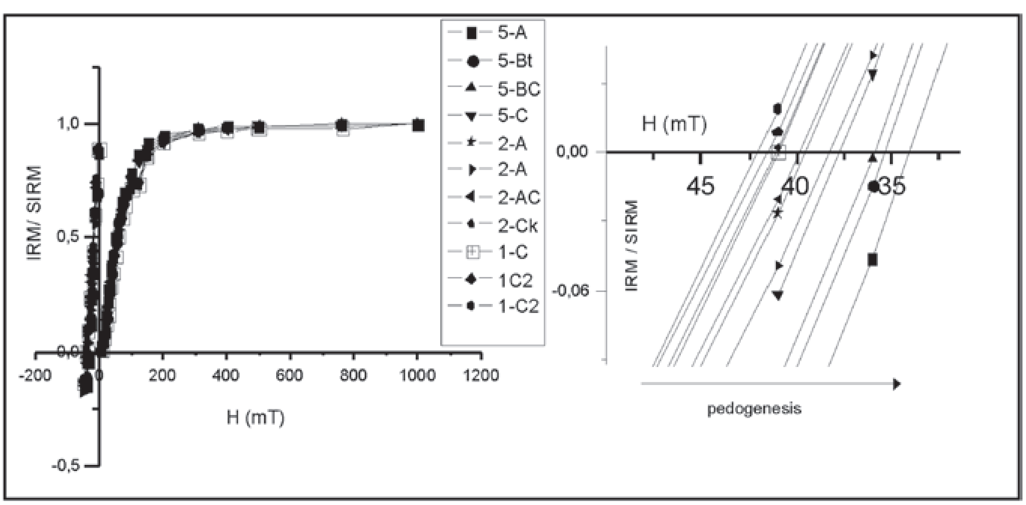

Figure 4. IRM acquisition curves for selected samples from different horizons of the studied profiles. The detail at right shows the variation of Bcr related to pedogenesis degree.

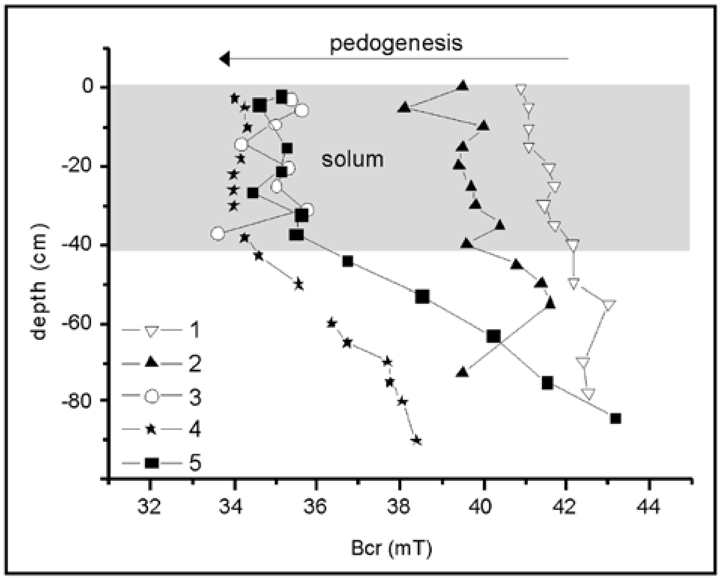

Figure 5. Variation of coercivity of remanence (Bcr) versus depth in the studied soils. A decrease of Bcr values in solum is observed in more developed soils (P3, P4 and P5) respect to less evolved ones (P1 and P2).

interpretation that there is a higher amount of multi domain (MD) particles in the top soils. However this does not appear to be the case mainly due to the values of χarm, χlf and χfd%. The data thus obtained suggest that the decrease in coercivity in the more pedogenized horizons is associated with the smaller magnetic grain size.

A set of selected samples from A respect to C horizon was exposed to thermal demagnetization in order to find mineralogical differences responsible for the magnetic parameters obtained. Around 580 ºC, 4.1-4.5% of magnetic remanence remains in the A horizons and 3-9% in the C horizons. According to the unblocking recorded temperature magnetite is the mean carrier of remanence or more specifically titanomagnetite with small dosage of Ti. However an oxidative process seems to be present due to the behavior of the curves at Curie point (575 ºC) and due to the fact that the almost complete demagnetization is achieved at 685 ºC in all samples (Fig. 6). At this temperature remains only 0.1 to 0.8% of the initial magnetization. According to this technique a similar result is obtained in A and C horizons, indicating that there are not a significant mineralogical differences along the profiles in terms of ferromagnetic contributors.

Van Velzen and Dekkers (1999a) argue that low-temperature oxidation (maghemitization) causes an increase of Bcr values of magnetite

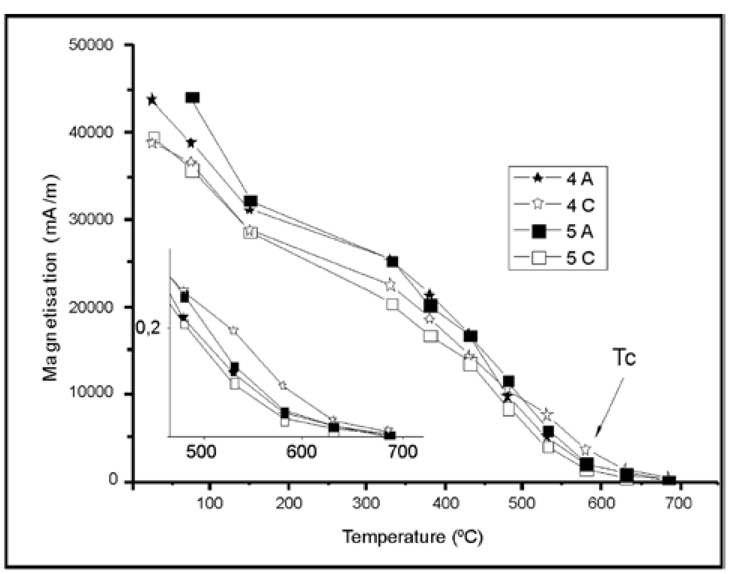

Figure 6. Stepwise thermal decay curves of the SIRM for Argiudolls.

grains in the nature. When magnetite is affected by this form of oxidation, an oxidized shell (Fe_2O_3) is formed around an unoxidized core by a very slow diffusion of the Fe^{+2} to the grain surface. According to the authors, the effects of low temperature oxidation can be removed after heating up to 150 ºC, because the diffusion constant of Fe-ions in the crystal is higher at 150 ºC which reduces the oxidation gradient between the reduced core and the oxidized grain surface, removing the stress and the enhanced (natural enhanced) coercitivities. Bidegain *et al.* (2007), by applying this treatment, found that the coercivity of remanence falls after heating the samples of loess and paleosols belonging to the Pleistocene loess of Argentina and refers this phenomenon to the secondary oxidation.

In order to check this, a set of samples belonging to A and C horizons of soils were analyzed before and after heating up to 150 ºC. Table 3 shows the result obtained after heating the samples for 30 minutes. The results indicate that the magnetic grains of the different horizons are slightly affected by low-temperature oxidation which is more evident in the C horizon of P2 and P3 soils. The decreasing in Bcr values in the most devolved soils (Argiudolls) is similar in both horizons (A respect to C) or even more significant in A horizons. In order to improve the study of the carriers of magnetic parameters, low temperature susceptibility measurements were also performed.

Measurements of susceptibility at low temperature are a useful tool for magnetic mineral identification in the context of soil and paleosols studies. The magnetic behavior of magnetite and magnetite with low substitution of other elements has been widely studied because it exhibits the Verwey transition which represents the structural phase transition that occurs at 110 to 120 K. The iron (Fe) substitution by Al and Ti and even a low degree of uniform oxidation lowers the temperature at which the magnetic transition occurs (Van Velzen and Dekkers, 1999b).

Fig. 7 shows Verwey transition around 120 K in samples belonging to P2 and P4 soils. This property seems to indicate that the major contributor of the magnetic parameters is magnetite or more exactly magnetite with minor Ti substitution ($x<0.04$). Low temperature susceptibility measurements do not indicate any other ferromagnetic mineral than magnetite and it was not possible to clearly detect the Morin transition of hematite. The increase of susceptibility at low temperature shows a similar behavior than low frequency susceptibility - in the sense of differences in the records between A and C horizons- and this is particularly noticeable in the more developed soils P4. The enhancement of susceptibility from C to A horizons is also revealed by this way as it is indicated with the arrows in both soils in Fig.7.

Hand magnet separation from C and A horizons indicates the presence of lithogenetic sub rounded grains in every profile, mainly in the sizes ranging between coarse silt and very fine sand (20-100 μ). The EDX spectra show the presence of titanomagnetite with low titanium substitution in all examined crystals. Fig. 8 shows an example obtained when analyzing the samples of soil P2.

Table 3. Bcr of A and C horizons measured before and after heating up to 150 ºC.

Profile/horizon	B_{cr} (MT) before heating	B_{cr} (mT) after heating	change (mT)
1C	41,56	41,52	-0,04
2A	41,5	41,41	-0,09
2C	41,85	41,72	-0,23
3A	35,75	35,5	-0,25
3B	35,39	34,7	-0,69
4A	34,23	33,8	-0,43
4C	38,01	37,9	-0,11
5A	35,71	35,24	-0,47
5C	40,14	39,62	-0,52

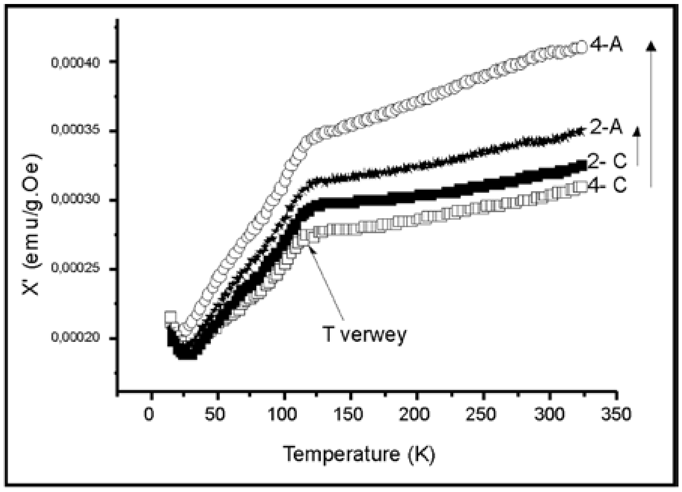

Figure 7. Susceptibility at low temperature for A and C horizons from P2 (Aridic Haplustoll) and P4 (Typic Argiudoll). The Verwey transition at ~120 K for every sample suggests the presence of magnetite.

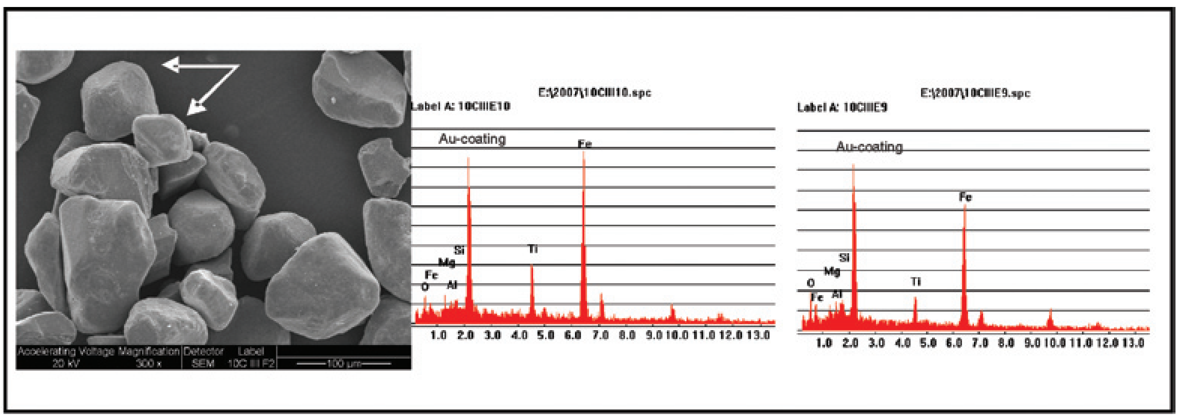

Figure 8. SEM image of a magnetic concentrate from C horizon of P2 soil. The general subrounded aspect of the grains is observed. EDX spectra of octahedral specimens at right (showed with arrows in the photograph) indicate a titanomagnetite compound. Si, Mg and Al appear as impurities.

Finally, it is important to point out that there is not extra contribution of magnetic minerals due to human activities such as industrial pollution. Industrial Fe-rich spherules or any other anthropogenic particles were not found in any uppermost soil horizons analyzed by microscopy. Besides, no coal – fired power plants, potential source of magnetic fly-ash, exist in the region.

Magnetic grain size

In general, χfd% values are lower than 4%, suggesting that the magnetic properties of these soils are not controlled by SP particles (<0.01 μ). However, the values of χfd obtained indicate detectable SP particles concentrations (Dearing *et al.*, 2001) in P3, P4 and P5 soils. The A and Bt horizons are particularly associated to the highest values (Fig. 2 and 3). Relatively high χfd for P4 (rise to 6%) may suggest the presence of relatively more SP magnetite of pedogenic origin, compared to other soils. It should be pointed out that the previously mentioned authors stated that detectable SP particles corresponded to χfd values of 2%.

The magnetic grain size of the samples was also analyzed by using the approaches of King *et al.* (1982) and Thompson and Oldfield (1986). The former shows that the smaller magnetic particles (<0.1 μ) correspond to the A and B horizons of Argiudolls (P4–P5), while the coarser grain sizes (0.1-1 μ) correspond to the parent material of these soils plus all horizons of the P1, P2 and P3 soils. Fig. 9a shows that the samples less affected by the pedogenesis, i.e. those from the parent materials and all the samples of soil P1 cluster in the area of lower Karm and Klf values (circle in Fig.9a). The increase in the degree of pedogenesis, indicated in the figure by the arrow, seems to be clearly related to the magnetic grain size.

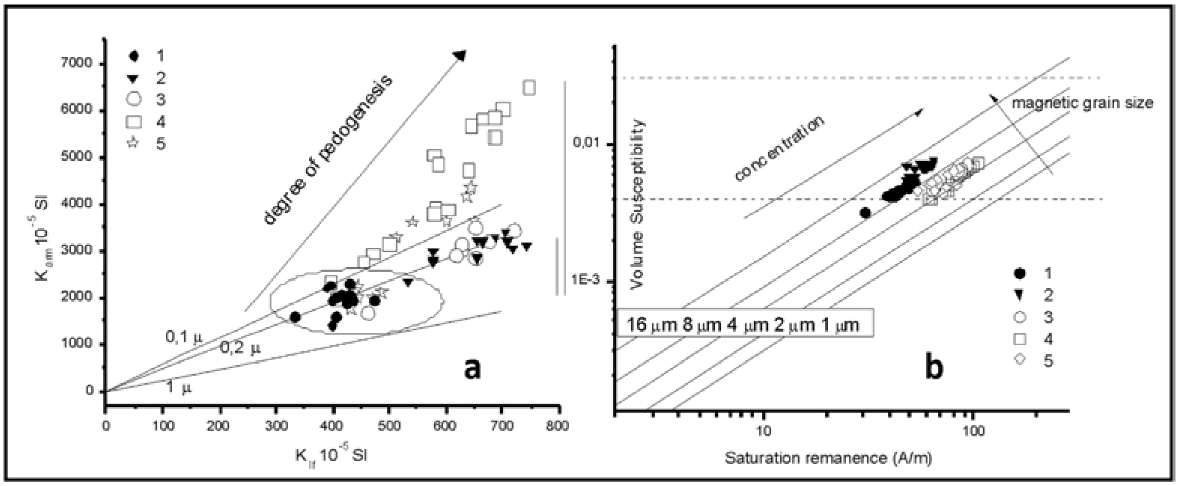

Figure 9. **a)** Klf versus Karm values of samples were represented according to King *et al.* (1982). Within each profile of soil a gradual increase of Karm and Klf from C horizons (less pedogeneized; dashed circle) to A and Bt horizons (top right) is obtained. Soils with higher pedogenetic development (P4 and P5) show higher Karm (finer magnetic grain size). The relation between the values of K versus the values of MRIS is indicated in the plot.
b) According to Thompson and Oldfield (1986). There are differences of magnetic grain size between samples from less developed soils (P1 and P2) and more developed ones (P3, P4 and P5). The coarser grain sizes are found in the former.

Assuming predominance of magnetite, the same differentiation can be observed in Klf versus MRIS plot. The samples belonging to the less developed soils P1 and P2 show grain size between 8-16 μ, while samples of soil P3-P4-P5 show finer magnetic grain size, 4-8 μ (Fig. 9b). The concentration of magnetite is estimated between 0.1 and 1% in all the samples. In spite of the different way used for estimate the grain size, the results are consistent with the other parameters.

Discussion

Taking into account the results, several characteristics of the soils from the southern Pampean Region of Argentina can be listed:

- Most of the soils of the studied climosequence - between 400 to 800 mm/year- show a pattern of enhancement of χlf, χarm and χfd values towards upper horizons.

- The increase of magnetic parameters is conditioned by the degree of pedogenesis. Consequently, Torripsamment soils (drier zone) show lower magnetic values than Argiudolls soils (humid zone).

- The increase of magnetic values is recorded in the first centimeters of the soils, in the A and Bt horizons, mostly in A horizon which is a more biologically active horizon than the underlying ones. In deeper horizons and particularly in the BC horizon the variation of χlf is lower; the values are closer to those of the parental material particularly in more evolved soils.

- The changes in magnetic grain size dependent parameters (χfd% and χarm) are observed in the first 40 cm, below this depth the values decrease abruptly, suggesting that fine particles, especially DS, are responsible for the upwards increasing of the magnetic values.

- Bcr decreases towards upper horizons A and B in every soil. The highest difference between these horizons and the parental material is observed in the most developed soils, showing that this parameter is a good proxy of pedogenesis intensity in the studied area.

The pattern of magnetic records in the soils of the area studied seems to be similar to the obtained one by Maher *et al.* (2003). After analyzing recent soils in the Russian loess (with a rainfall ranging between 300 to 500 mm/year), the authors, indicate that the magnetic susceptibility in the soils increases upwards. Similar results have been mentioned in a climosequence of soils developed in loess of the Great Plain (US), with a range of rainfall between 500 mm/year to 1,000 mm/year, by Geiss and Zanner (2007). An opposite pattern has been reported in the north humid Pampean Region with rainfall of 1,000-1,100 mm/year by Bartel *et al.* (2005). A depletion of susceptibility values on top soils has also been mentioned in subtropical regions with higher mean annual precipitation (1,300 mm/year) by Lu *et al.* (2008). The authors refer this behavior to the destruction of primary magnetite.

Different processes, which can be responsible of magnetic enhancement in soils, are considered by Singer *et al.* (1996). One of these processes includes preferential accumulation of ferromagnetic minerals in the upper horizons, due to the leaching of less resistant minerals. Translocation and solubilization of minerals that could contribute to the preferential accumulation of ferromagnetic ones-like magnetite, which is one of the most resistant mineral under weathering conditions-, require considerably high humidity in the environment.

The melanization (A horizon) and the clay translocation (Bt horizon) are relevant pedogenetic processes. The intensity of these processes increases from P1 soil to P5 soil; particularly the clay translocation which is absent in P1 and P2 soils, weak in P3 and relatively strong in P4 and P5 soils. Pazos (1984) found a high illuviation degree in Bt horizons of Argiudolls from southern of Buenos Aires province in the same area of the soils labelled P4 and P5. The soils labelled P3, P4 and P5 have similar percentage of total clay in the A horizons but the clay content increases in Bt horizons. According to the texture analysis carried out for the present contribution, the clay content in P3, P4 and P5 was 25.7, 42.5 and 58% higher in Bt horizons respect to A horizons, respectively. This suggests that a process of preferential accumulation of ferrimagnetic minerals in A horizons of these soils is highly possible.

The concentration of calcium carbonate increases downwards in the soils studied, however, its maximum concentration in the C horizons (3%) seems to be low to affect the magnetic signal.

Dearing *et al.* (1996) mention other processes related to partial dehydration and reduction of ferrihydrite in the presence of Fe^{+2} and subsequent formation of secondary ferrimagnetic oxides (magnetite). Fe^{+2} is released to the environment during the metabolic respiration of Fe reducing bacteria, that use ferrihydrite and other iron hydroxides like terminal electron receptors (Evans and Heller 2003). In this respect mention be should made of the research carried out by Cabria *et al.* (2006) who observed ferrihydrite in organic-mineral associations in superficial horizons of Argiudolls in the Pampean Region at 37º47′ S, 58º18′ W.

The Argiudolls P4 and P5 exhibit a strong positive relationship between χarm and the organic matter content, implying that higher levels of OM coincide with stronger χarm values. This significantly positive correlation (R^2: 0.98, p: 0.008 in soil P4, R^2: 0.93, p: 0.035 in soil P5) suggests that the biomineralization of ferrimagnetic oxides could explain part of the recorded magnetic increase, at least in Argiudolls. On the other hand, χarm shows no significant correlation with the OM content in the less developed soils. As an example of the previous, in P2 soil from the western La Pampa province, the correlation between χarm and OM was R^2: 0.77, p: 0.31.

Another plausible mechanism producing enhancement of magnetic values in the top soils is the more recent input of wind blown dust rich in ferrimagnetic minerals. However, the good correlation between the magnetic values and the pedological horizons favors the interpretation that the increase of values has a pedogenetic origin.

Furthermore, it should be pointed out that there is no extra contribution from human activities as industrial pollution. Fe-rich spherules, typical particles of anthropogenic origin, were not found in any uppermost soil horizons. Besides, no coal–fired power plants, potential source of magnetic fly-ash, exist in the region. As mentioned above, the absence of spherical particles with grain size higher than DS, which are commonly associated with anthropogenic pollution (Hanesch and Petersen 1999, Fialová *et al.* 2006), allow us to discard industrial pollution as the origin of the magnetic enhancement at top soil.

The magnetic data reported indicate that the soil in the studied area from semiarid to subhumid climate show an opposite pattern of magnetic behavior than this one reported from the north of the humid Pampean Region.

Conclusions

- The soils developed in the southern Pampean Region of Argentine integrate a climosequence with precipitation rates from 400 to 800 mm/year. The pattern of magnetic susceptibility indicates an enhancement in the top soils that is independent of the lithology.

- Titanomagnetite with low Ti substitution are the main carrier of magnetic parameters in the studied soils. The highest increase of magnetic susceptibility is found in soils of higher pedogenetic development (Argiudolls). χlf shows an enhancement of 37% which seems to be associated with higher concentration of fine magnetic particles, especially SD estimated by χarm.

- SP particles are detectable in every soil, especially in A and B horizons, although χfd (lower than 6%), suggests that the contribution of SP particles is low.

- Pedogenesis depletes the coercivity of remanence. The more developed soils towards east show the major decrease in Bcr values in the solum. This could be attributed to pedogenetic sub-micron magnetite with sizes closer to the SP-SD boundary with a magnetic soft behavior.

Acknowledgements

The authors wish to thank the Facultad de Ciencias Exactas y Natrulaes, Universidad de la Pampa, Instituto de Física Arroyo Seco (UNCPBA), CONICET and LEMIT (CIC) for the support of the research. We are greatly indebted to Dr. R. Mercader and F. Sives for the low temperature measurements and also to the reviewers of the present contribution.

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