Revista de la Sociedad Geológica de España 25 (1-2)

MAGNETIC PROPERTIES IN A LOESS-PALEOSOL SEQUENCE OF CÓRDOBA, ARGENTINA

Propiedades magnéticas en una secuencia de paleosuelos desarrollados en Loess en Córdoba, Argentina

Sabrina Rouzaut[1,3], María Julia Orgeira[2], Carlos Alberto Vásquez[2], Graciela L. Argüello[3] and Jorge A. Sanabria[3]

[1,3]*Becaria FONCyT .srouzaut@efn.uncor.edu*
[2]*Dpto. Ciencias Geológicas FCEN, UBA, IGEBA. Ciudad Universitaria Pab. II, Nuñez, Buenos Aires*
[3]*Cátedra de Pedología. Escuela de Geología. F.C.E.F.y N. UNC. Vélez Sarsfield 1611. CP 5016. Córdoba. Argentina*

Abstract: *In order to understand pedogenic processes and their relation with changes in magnetic mineralogy and paleoclimate conditions, a study of magnetic properties was carried out in Corralito area, Córdoba province, Argentina. In this contribution the hysteresis parameters at room temperature and the variation of magnetic susceptibility with temperature were analyzed. The area is situated in central semi-arid region of Argentina (mean annual precipitation of 700 mm and mean annual temperature of 17ºC). The section comprises loess layers with one buried soil and three paleosols. An extensive period of soil formation recorded in one of the mentioned paleosol can be correlated with Marine Isotopic Stage 5 (MIS 5) and other two paleosols could be related with Marine Isotopic Stage 3 (MIS 3).Changes in magnetic parameters suggest that paleosol III and the buried soil are characterized by depletion of detrital magnetic minerals, while the other paleosols the magnetic signal is the opposite.According to the interpretation of the obtained results the actual climatic conditions seems to be similar to those prevailing during MIS 5, while MIS 3 seems to be more humid.*

Keywords: *Magnetic Properties, Paleosols, Quaternary*.

Resumen: *Con el objeto de comprender la relación entre los procesos pedogenéticos, los cambios en la mineralogía magnética y las condiciones del paleoclima, se llevó a cabo un estudio de las propiedades magnéticas en Corralito, Córdoba, Argentina. En esta contribución se presentan los resultados del análisis de los parámetros magnéticos obtenidos a partir de ciclos de histéresis a temperatura ambiente y de la variación de la susceptibilidad magnética con la temperatura. La zona está situada en la región central semiárida de la Argentina (con una precipitación media anual de 700 mm y una temperatura media anual de 17 º C). La sección está compuesta por loess, con un suelo enterrado y tres paleosuelos interdigitados. Un extenso período de formación del suelo registrado en uno de los paleosuelos mencionados se puede correlacionar con estadío isotópico 5 (MIS 5) y otros dos paleosuelos podrían estar relacionados con estadio isotópico 3 (MIS 3). Los cambios en los parámetros magnéticos sugieren que paleosuelo III y el suelo enterrado se caracterizan por un decrecimiento de minerales magnéticos detríticos, mientras que los otros paleosuelos la señal magnética es lo contraria lo que implica un enriquecimiento de estos minerales. De acuerdo con la interpretación de los resultados obtenidos el MIS 5 tuvo condiciones climáticas similares a las actuales, mientras que el MIS 3 habría sido más húmedo.*

Palabras clave: *Propiedades magnéticas, Paleosuelos, Cuaternario.*

Rouzaut, S., Orgeira, M.J., Vásquez, C.A., Argüello, G.L. and Sanabria, J.A. (2012): Magnetic properties in a loess-paleosol sequence of Córdoba, Argentina. *Revista de la Sociedad Geológica de España*, 25 (1-2): 57-65.

Loess and paleosol alternation indicates changes between dry and wet periods, and in addition, paleosols are among the most important geoindicators to elucidate climatic and environmental changes in continental environments.

Studies of environmental magnetism in the Chinese loess and paleosols sequences were used as proxies of the climatic change during the Quaternary. (Maher and Thompson, 1995).

Several mechanisms, were proposed in order to find the relationship between the climatic changes, pedogenetic processes and magnetic properties. Most of those theories were elaborated to understand the classical China loess-paleosol sequences, but they fail when applied of the behavior of the magnetic signal in the loess-paleosol sequences of Argentina. In the following paragraphs, a brief description of the most used models is summarized.

A widely accepted model for the precipitation of ultrafine magnetite in soils is the so-called "fermentation mechanism" proposed by LeBorgne (1955), Mullins (1977), and Dearing *et al.,*(1996), and then refined by Maher (1998). It requires the oxidation of Fe^{2+}(aq) at near-neutral pH, to produce a magnetic material that is very similar in chemical composition, morphology and grain size. First, Fe^{2+} ions are released by weathering of Fe bearing silicates during repeated wetting and drying cycles. Fe^{2+} ions oxidize rapidly to Fe^{3+} in presence of oxygen, and Fe^{3+} hydrolysis induces the precipitation of poorly crystalline oxyhydroxides such as ferrihydrite. Ferrihydrite is easily reduced during episodic anaerobicity caused by organic matter respiration, leading to the precipitation of magnetite and other Fe (II) minerals.

But, other hyphoteses have been proposed. Begét *et al.,* (1990) and Kukla (1987, 1988, 1990) presented, based on their studies of the Alaskan loess, that atmospheric input of iron oxides would have been diluted by weakly magnetic dust at times of rapid loess accumulation.

Heller *et al*., (1991) proposed that the magnetic properties of the paleosols are climatically-controled by chemical alteration. They proposed topsoil decalcification and carbonate reprecipitation downwards as a means of iron oxide concentration.

Maher (1998) proposed that the soil enhancement is the conversion of weakly magnetic iron oxides; these operations are ruled by factors like temperature, soil moisture, redox conditions, organic matter and mainly by bacterial activity. This bacterial activity according to this author may play a key role in the production of ultrafine-grained magnetite.

Orgeira *et al.,* (2010) elaborated a model based in a climatic index, which was able to explain the variation of magnetic signals in different climatic environments, and this was improved by Orgeira *et al*., (2011).

Boyle *et al.,* (2010) proposed that the formation of secondary ferrimagnetic minerals requires parent material rich in Fe and that the main control variables are precipitation and temperature, in that order. However, Orgeira *et al.,* (2011) suggest that the initial amount of Fe minerals is not a first order control on the pedogenic magnetic signal.

The hypothesis used in the present contribution considers the following processes. The formation of pedogenic magnetite is conditioned by a well-drained soil, pH between 5 and 8, the presence of organic matter and cation exchange capability. Also weathering of primary Fe minerals and formation of secondary ones is sensitive to the relation pH-Eh .The redox conditions induced by water table oscillations lead to magnetite dissolution and depletion of secondary Fe oxides. The depletion of magnetite is also promoted by organic ligands present in the upper soil horizons and pore water silica (Orgeira *op.cit*. 2011). In these cases, the volcanic glass, usually present in the Pampean plain, is an important factor that modulates the magnetic signal. High contents of pore water silica from the volcanic glass, allow the ferromagnetic depletion. According to Sayago *et al.,* (1999) and Etchichury and Tófalo (2004), among others, the Pampean loess is characterized by the abundance of plagioclase (20 to 60%), quartz and volcanic glass fragments (20 to 30 %), while loess in the pre-Andean region is composed by 25-27% quartz, 6-10% plagioclase and volcanic glass. Those authors, among others, attribute the composition of the loess to Patagonian explosive volcanism, and subsequent weathering by glaciations. In the profile studied in Corralito the presence of volcanic glass was also detected.

The idea of a pedogenetic threshold driven by soil water balance was used by Orgeira and Compagnucci (2010) to explain magnetic enhancement and depletion in different loessic soils of the world. They proposed that a climatic index, PWS (potencial water storage) is related with the magnetic signal in loess-paleosols sequences. Soils and paleosols with positive PWS belong to a reductive environment and generate the depletion of detritic magnetic minerals; this trend is also valid for soils with no evidence of waterlogging or gleyzation, like the ones in SE of China and our Pampean plain.

On the contrary, negative PWS, preserves ferrimagnetic minerals and under certain environmental conditions, new magnetic nanoparticles are formed on the soils. This process produces magnetic enhancement in soils of Europe, Asia and North Africa.

According to this hypothesis, Córdoba is in a climatic threshold. PWS is near zero. Neither generation nor depletion of magnetic particles should be expected.

Geological Setting

The town of Corralito (Fig.1) is located in the Tercero Arriba Department of Córdoba province (Lat 32º 0.5'45"S-Long 64º10' 30"W) at 87 Km from Córdoba city, and it can be reached after driving along the national road Nº 36 and then taking a secondary road to arrive to the site (Fig. 1)

The sampled profile (Fig. 2) for the magnetic study is a 12 m gully that was originated in the late 70's by intense rains and as a consequence of the lack of farming practices, along with soy bean agriculture (Argüello *et al.,* 2006)

The gully is located in the Undulated Tilted Platform at 455-477 meters above sea level (Kemp *et al.,* 2006).The main climatic characteristics of the area are temperature and precipitation. The thermal regime of the area is considered as mesothermal with a warm Summer, as indicated by temperature records. The annual average is 17ºC, the thermal minimum lies around 10.5ºC and occurs between June and July and the maximum mean temperature is 23.5ºC in January.

The Normal Annual precipitation is 789 mm. Two seasonal cycles are distinguished during the hydrologic year, one for the Summer (October to March), in which the mean rainfall is 82 mm/month; and other for the Winter from

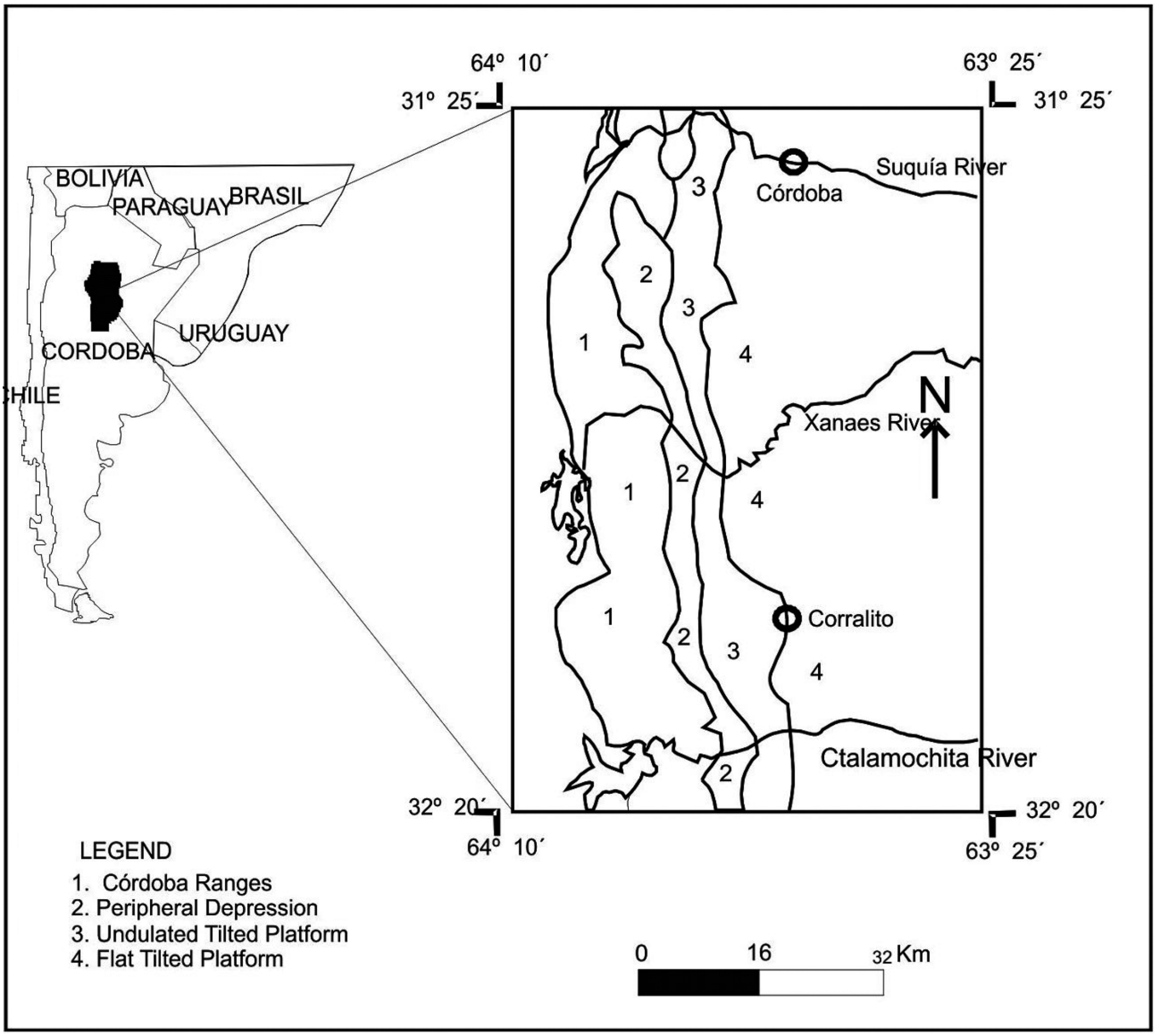

Fig. 1.- Location Map.

April to September where the rainfall remains below 50 mm/month.

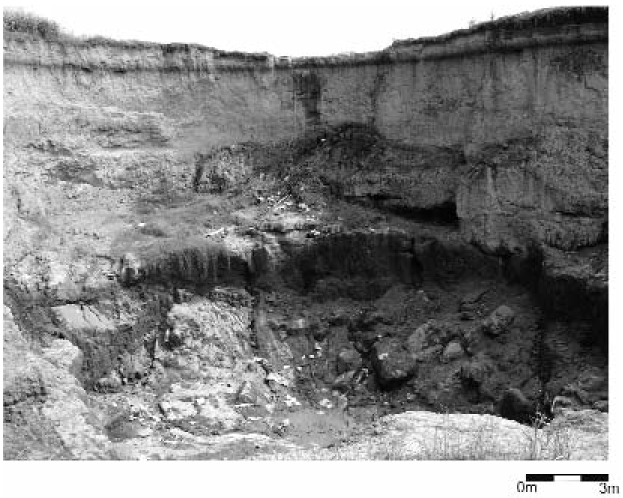

Fig. 2.- The interbedded loess and paleosols of Corralito.

The studied profile is integrated by Pampean Formation and Cordobense Formation (Fig. 3). The Pampean Fm. corresponds to a well-selected silty loam, assigned to eolian deposits. This formation includes isolated lenticular silty deposits with horizontal stratification which are interpreted as ephemeral streams; and massive silty levels, with fragipans, mostly in the upper part of the unit. Above this level there are calcretes with, angular clastic cores. In this unit, fossils such as; *Mesotherium cristatum* (Notoungulata,Typotheria, Mesotheriidae), and fragments of mandible, carpus and metacarpus assigned to *Neolicaphrium Recense* (Litoptherna, Protheriidae), among others, were found. The fossils found are genera and species of mammals that are somehow represented even nowadays. For example, *Hippidion cf.* principale (Perissodactyla, Equiidae), *Ctenomys sp*. (Rodentia, Ctenomydae), among others.

The Cordobense Fm. according to its granulometry and massive deposits corresponds to eolian deposits. This formation has silty sediments interbedded with fluvial lenticular bodies, with abundant carbonate dispersed in the matrix.

The top of the unit corresponds to the present soil, which is partly eroded and covered by recent storm deposits.

The luminescence studies carried out by Frechen *et al.,* (2009) the age of the loess paleosol sequence corresponds to Late Pleistocene. Paleosol III at the bottom was dated 115±21 ka and the youngest sediment - 13.8±2.1 ka old-corresponds to the buried soil.

A brief geological description of the studied profile is presented below, these descriptions are according to Schoeneberger *et al*., (2002), C horizons represent the loessic deposits.

Present Soil

The thickness of the present soil is from 0 cm to -170 cm.

Ap: From 0 cm to -40 cm. Dark grayish-brown (10 YR 3/2) when wet, silty loam, subangular blocky structure, medium, moderate to weak, friable when moist, slightly plastic and slightly adhesive, and abrupt, smooth lower limit.

Bw: From -50 cm to -80cm. Dark yellowish brown (10 YR 3/4) wet, silty loam to silty clay loam; irregular prismatic structure, moderate, that breaks into subangular blocks, friable when moist, slightly plastic and slightly adhesive, common, medium clayhumic coatings and lower boundary gradual and smooth.

BC: From -90 cm to -150 cm. Brown to dark brown (7,5 YR 4/2) when wet, silty loam, subangular blocky structure, medium, moderate friable when moist, non plastic, non-adhesive; remnants of fine clay coatings; abrupt smooth lower boundary.

Ck: From -160 cm to-170 cm. Brown to dark brown (7,5 YR 4/4) if wet, silty loam, massive, very friable when moist, non plastic, non-adhesive abundant powdery calcium carbonate in the soil mass.

Buried soil

The thickness of the buried soil is from -180 cm to -400 cm.

Ab: From -180 cm to -190 cm. Moist color 10 YR 2/3, dry 10 YR 3/3, silt loam, subangular blocky structure, coarse to medium, moderate, strong, field. Field pH 6.5; lower boundary clear, smooth.

Btbk1: From -200 to -220 cm. Its upper limits are abrupt smooth. Moist color 10 YR 3 / 2, dry: 7.5 YR 5/3, silty loam; prismatic structure composed by medium and coarse subangular blocks, moderate to strong, common medium clay-humic coatings (organo argillans), pH at the field: 6.5; lower boundary clear, smooth.

Ckb: From -230 cm to -400 cm. Its upper limits are abrupt smooth. Moist color 7.5 YR 4/5, dry 7.5 YR 7/3, silty loam, massive, abundant disseminated $CaCO_3$; cemented, bioturbated; field pH 8.2 to more; contact to paleosol is clear and smooth.

Paleosol I

The extension of the Paleosol I is from -410 cm to -660 cm.

2Btbk: From -410 cm to -570 cm. Its upper limits are abrupt smooth. Dry Color 7.5 YR 6 / 5 and moist 7.5 YR 5 / 6. Structure with irregular prism, medium to coarse, strong. Consistency when dry, firm. Few fine carbonatic concretions, abundant, fine, medium clay- humic coatings. pH field estimation is over 7.

2BCbk: From -580 cm to -660 cm. Its upper limits are diffuse and smooth. Dry color 7.5 YR 7/4, and moist color 7.5 YR 6/4. Subangular blocky structure medium to coarse, moderate. Dry consistency firm. Common carbonates. Abundant fine clayskins. Fragipan lenses. Field pH estimation over 7. This horizon corresponds to the loess deposit in Fig. 3.

Series	Formations	Loess-paleosol sequence	IRSL(ka)
Pleistocene	Cordobense Fm	Present Soil	
		Loess	
		Buried soil	
		Loess	32.7±6.7
	Pampeam Fm	Paleosol I	
		Loess	
		Paleosol II	66.1±9.4
		Loess	
		Paleosol III	115±21
		Loess	

Fig. 3.- Corralito schematic profile.

Paleosol II.

The thickness of the Paleosol II is from -670 cm to -920 cm.

3Btbk1: From -670 cm to -860 cm. The upper limits are diffuse, smooth. Dry Color 7.5YR 7 / 4 and moist 7.5YR 5 / 6. Composed by irregular prisms, medium, coarse, strong. Consistency is firm when dry, common carbonates and abundant clay-humic coatings, medium to fine. Field pH over 7. The prisms break into smaller prisms and sub-angular blocks. High porosity can be observed with naked eye. Laterally, the horizon has abnormalities such as Mn mottles and mottles of fragipan boulders, which determine a great lateral variability within distances as short as 3 or 4 meters.

3BCb: From -870 cm to -890 cm. Its upper limits are diffuse, smooth. Dry color 7.5 YR 7/4 and moist color 7.5 YR 6/6. Structure, subangular blocks, medium to coarse, firm. Dry consistence slightly firm. Common carbonates, few fine clayskins. Field pH over 7.

3Ckb: From -900 cm to -920 cm. Its upper limits are difuse and smooth. Dry Color 7,5 YR 8 / 3 and moist color 7,5 YR 6 / 4. Bulk dry consistence is friable. Abundant $CaCO_3$ disseminated and few carboate concretions. Field pH over 7. This horizon corresponds to the loess deposit in Fig. 3

Paleosol III.

The thickness of the Paleosol III is from -930 cm to -1120 cm.

4Btbk1: From -930 cm to -960 cm. Its upper limits are diffuse and smooth. Dry color

7. 5 YR 7 / 6 and wet color is 7.5 YR 5 / 6. Coarse moderate to strong irregular prisms. Dry consistence is firm. Few disseminated carbonates. Scarce fine clay-humic coatings. Color 7.5YR 4/4. Field pH over 7.

4BCbk: From -970 cm to -1120 cm. Its upper limits are diffuse, smooth. Dry color is 7.5 YR 6 / 6 and moist color is 7.5 YR 5 / 6. Subangular blocky, is moderate to strong. Consistence when dry firm. Few carbonates disseminated. Scarce fine clayskins. pH at the field is over 7. This horizon corresponds to the loess deposit in Fig. 3.

Calcium carbonate percentage was measured in collected samples along the studied profile. As it is shown in Fig. 4 values lesser than 5% were obtained.

Taking into account IRSL ages (115±21 ka to 92.1±14.7 ka, Frechen *et al.,* 2009) obtained from the lowest loess sediment of the studied profile, the stratigraphic oldest paleosol, paleosol III (PIII) (Fig. 4) could be assigned to the MIS 5. This paleosol is covered by a loess deposit which indicates arid and cold climate conditions; IRSL age 66.1±9.4 ka suggests that this loess deposit could be correlated with the MIS 4. Following this correlation, the pedocomplex integrated by paleosol II and I could be assigned to the MIS 3 (Fig. 4) The overlying loess deposits with luminiscense data of around 32.7 ka could be correlated with the MIS 2. Finally, the parent material of the buried soil has ages between 18.9±2.4 ka and 13.8±2.1 ka; this luminescence data allow their assignment to Lateglacial loess.

Magnetic Measurement Methodology

One hundred and twelve samples were taken using an aluminium shovel after cleaning the first 50 cm of the profile in order to take out the weathered material. Vertical equidistance between samples was 10 cm. In the lab, samples were dried up at room temperature and stored into plastic boxes. The susceptibility measurement was carried out with Bartington MS2 at two frequences: 470 Hz and 4700 Hz. The hysteresis cycles were obtained with a Vibrating

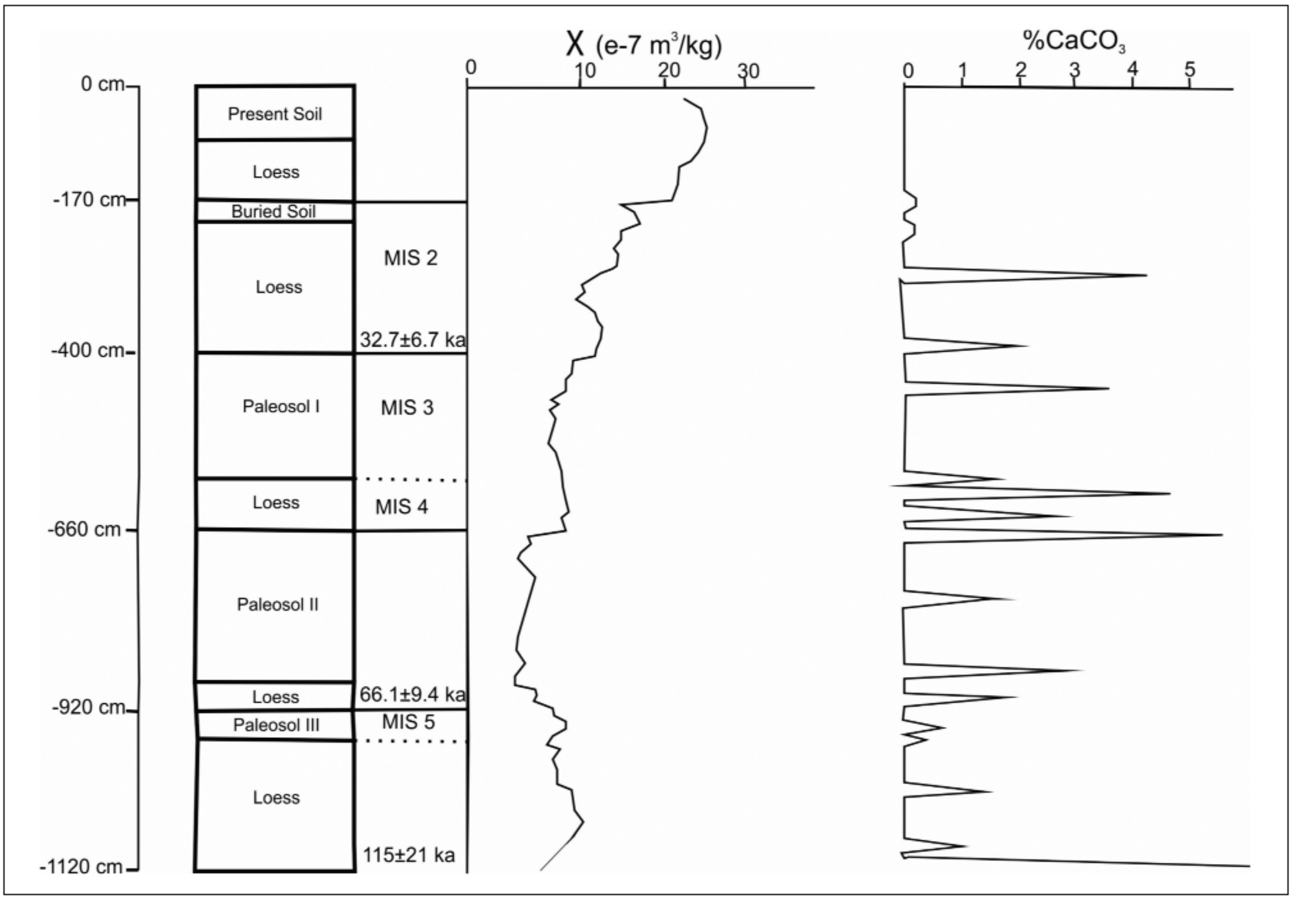

Fig. 4.- Schematic column and Magnetic Susceptibility X (e-7 m3/kg) vs. Calcium Carbonate percentage.

Sample Magnetometer Molspin, with a maximum field near 1 Tesla. The variation of magnetic susceptibility with temperature was measured with an AGICO Kappabridge MFK1-FA; the frequency used was 976 Hz and the maximum amplitude of the applied field was 200 A/m. The experiments were carried out at high and low temperature. During high temperature experiments the samples were heated from room temperature up to near 970 K and then cooled to room temperature; all the process was under Ar atmosphere to prevent air oxidation; in low temperature experiment, the samples were heated from near 73 K to room temperature.

Analysis and Discussion of the results

Field evidence (Fig. 4) shows well developed paleosols horizons with a medium thickness of two meters; they indicate wet and warm climatic conditions during their formation. This is supported by the structure of the Bt horizon. The present soil shows a Bw horizon; this may be related to a shorter development period or the present climatic conditions are more drier than the past ones.

The Bt horizons indicate the pedogenic process of eluviation-iluviation, and humid climatic conditions alternated with a dry season. During the dry season the soil cracks, it let the clay, enter in the profile. In the wet season it travels down the profile forming the coatings. The coatings are clayhumic, which indicates that there was an A horizon in the top of the Bt.

Also, these horizons have $CaCO_3$, which is not common in present soils; it could come from the loess mantles above these Bt horizons. The percentage of $CaCO_3$ does not surpass 5%, which could indicate semiarid conditions in the source area.

The Ck horizon from the paleosol I (PI) has fragipans and together with the Mn mottles of Bt horizon from paleosol (PII) represents wet periods with hydromophic conditions in the profile. The thickness from PI y PII indicates humid conditions, wetter than today. PI corresponds to MIS 3, and PIII corresponds to MIS 5.

The variation of the magnetic hysteresis parameters, magnetic susceptibility (X), magnetization of saturation (Ms), remanent magnetization of saturation (Mrs), coercivity (Hc) and coercivity of the remanence (Hcr), are shown in Fig. 5.

Values of Hc range between 4-7 mT and Hcr between 35-37 mT, indicate magnetite or titano poor magnetite as the main ferromagnetic carriers. A more detailed observation of these parameters allows distinguishing different values of X, Ms and Mrs in each of the intervals of loess-paleosol, as if the paleosol would basically inherit magnetic minerals from parent material.

The Day plot (Fig. 6) results suggests a mixture of SD titano poor magnetite with small SP grains. (Dunlop, 2002).

Fig.7 and Fig. 8. represent the magnetic susceptibility vs. temperature. Fig. 7 shows results from samples collected in the present soil; 7a from B horizon and 7b from C horizon. Fig. 8 represents the behaviour of paleosols; 8a shows the behaviour of a sample collected in B horizon and 8b from the C horizon. As it can be seen in both figures, in all the analized levels at high temperatures, the variations in B horizons and in C horizons were similar. Curie temperatures related with titano poor magnetite and magnetite, were observed. Increases in the high temperature curves (Fig. 7

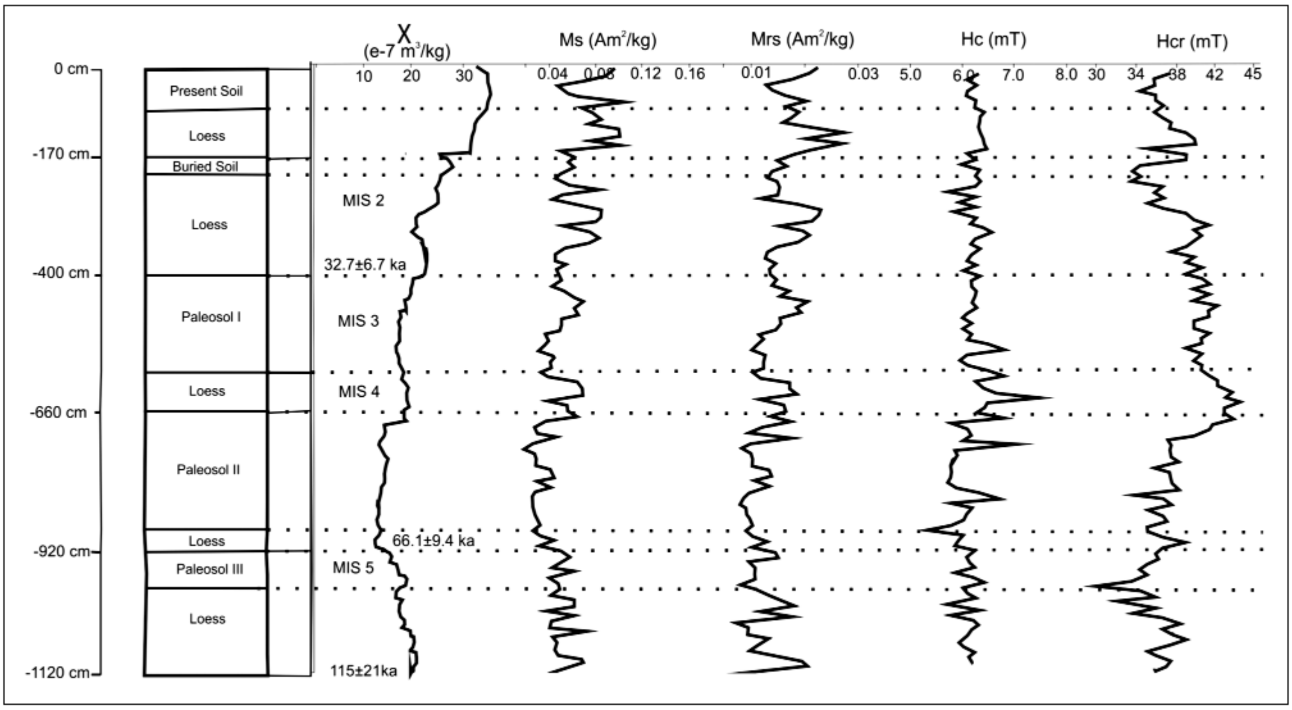

Fig. 5.- Magnetic properties of the Corralito profile. Magnetic Susceptibility (X, e-7 m3/kg); Saturation Magnetization (Ms, Am2/kg); Remanent Saturation Magnetization (Mrs, Am2/kg); Coercivity (Hc, mT); Remanent coercivity (Hcr, mT).

and Fig. 8) could be associated with generation of magnetite during the heating process in anoxic environment.

The results of low temperature do not show significant features, and it can be interpreted as magnetite or titano poor magnetite.

Although the variations of magnetic parameters along the profile (Fig. 5) are not relevant, there are some tendencies that can be identified.

The upper part of the profile, from a depth of 400 cm to the top, shows a tendency of increasement of extensive

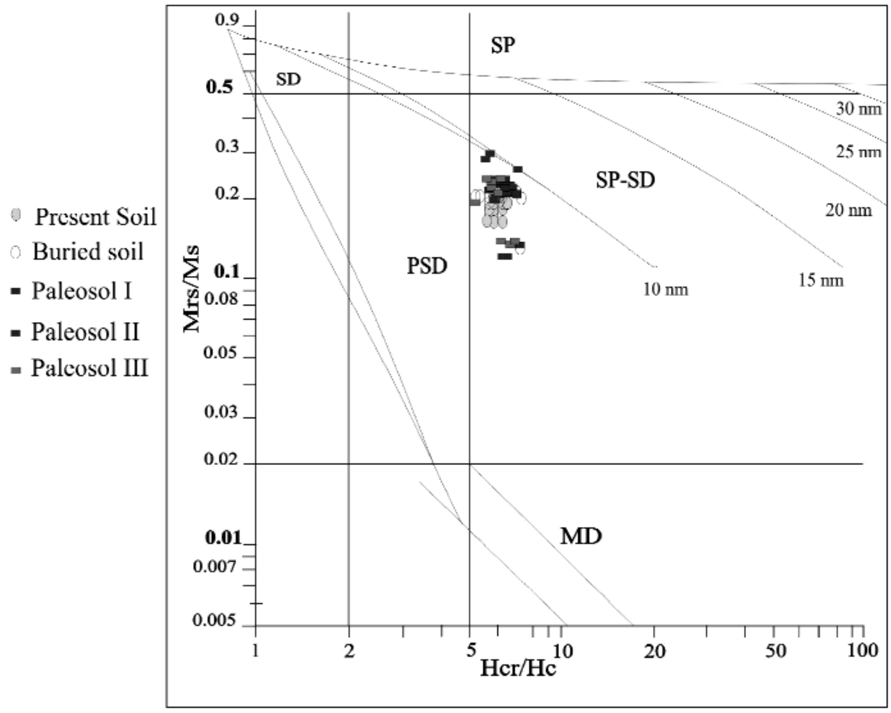

Fig. 6.- Day plot modified by Dunlop (2002).

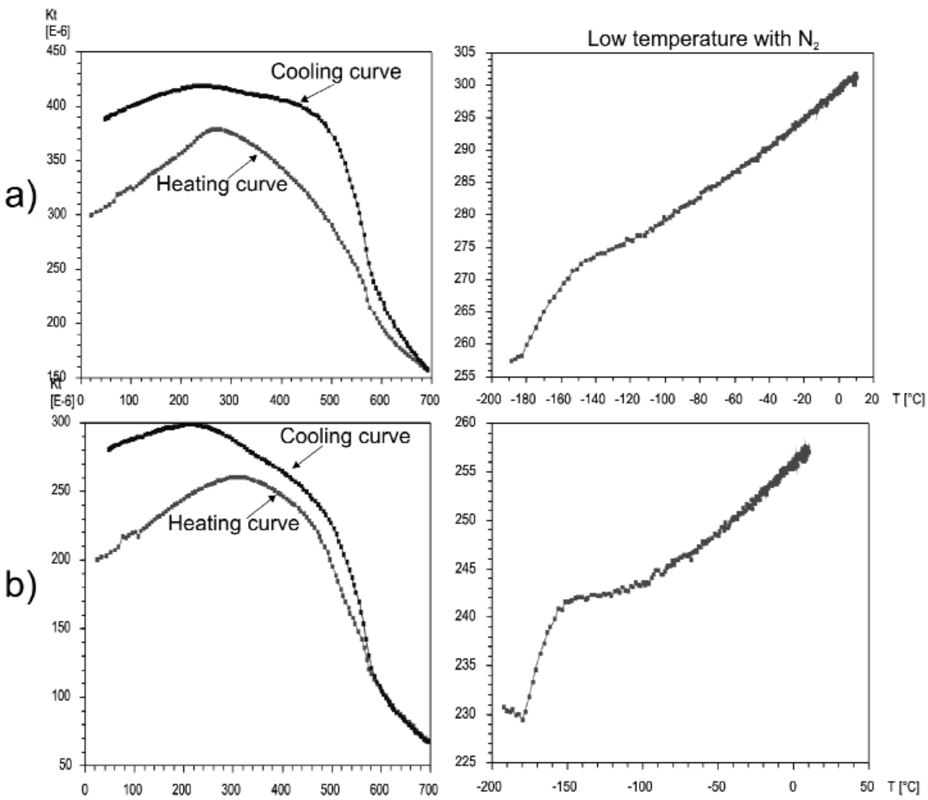

Fig. 7.- Variation of the magnetic susceptibility (Kt E-6) vs. low and high temperature (ºC) of the present soil. a-Corresponds to the B horizon and b- Corresponds to the C horizon (loessic parent material).

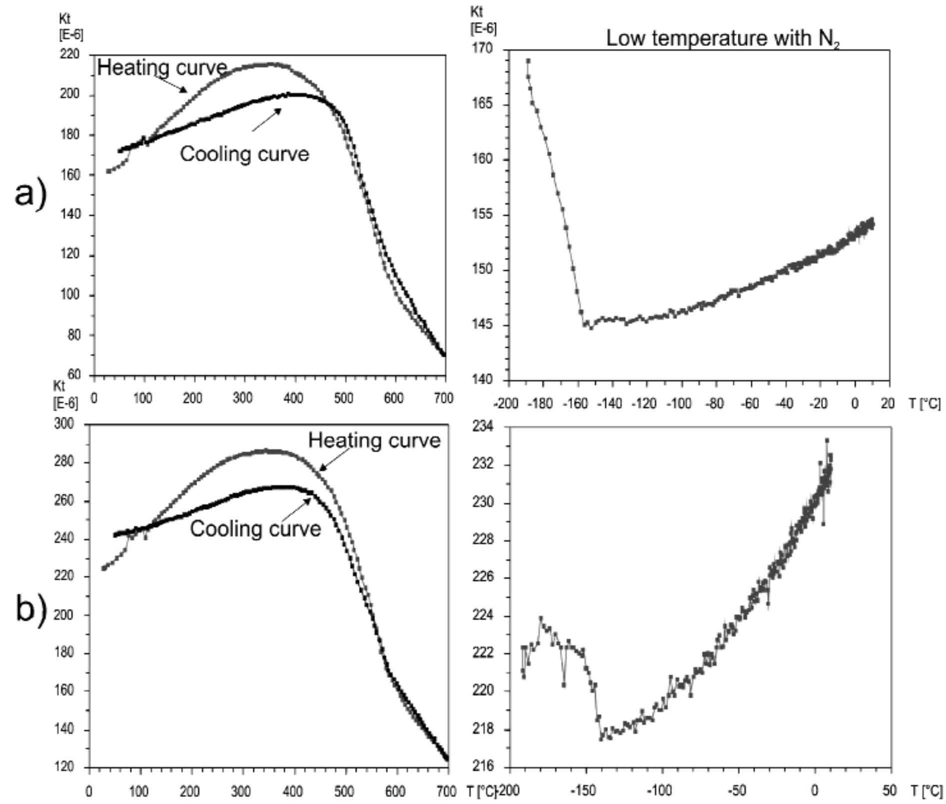

Fig. 8.- Variation of the magnetic susceptibility (Kt E-6) vs. low and high temperature (ºC) of a Paleosol. a-Corresponds to the B horizon and b- Corresponds to the C horizon (loessic parent material).

magnetic parameters (mainly in X, Fig. 5). It could be related with an increase of the concentration of magnetic particles or an increase of grain size of them. This last option could be supported by the slight decrease of the coercivity of the remanence. This could indicate changes in the source area and / or in the intensity of the wind. Further studies should be performed to confirm this suggestion.

Morover, in paleosols some observations can be done. The variation of the magnetic susceptibility (Fig. 5) shows smooth enhancements in paleosol III (PIII), in the buried soil and in the present soil with respect to the below parent material. This could be related to a slight concentration of particles due to eluviation during pedogenesis. There is no evidence of generation of superparamagnetic particles.

In opposition of the trend mentioned above, paleosol I (PI) shows a decreacement of this magnetic parameter; because no changes in coercivity parameters (Hc and Hcr) were observed, this decreacement could be represent less amount of magnetic minerals, probably due to depletion during pedogenetic proocesses. Paleosol II (PII) maintains similar magnetic behaviour related with its parent material.

Similar tendencies to the susceptibility can be observed in Mrs, while Ms does not show any particular trend.

Taking into account Orgeira *et al.,* (2011) model, the similar magnetic behaviour of PIII, buried soil and present soil can be attributed to similar climatic conditions or a similar storage of water in the soil during pedogenesis. As a consequence of dry winter periods which generate a negative water storage preservation of magnetite is possible even with the presence of volcanic glass; this is supported by field evidences that show arid climate condition as present times.

PI, characterized by depletion of ferrimagnetic minerals, could have developed under a climate wetter than present time. It also could be a consequence of a greater amount of volcanic glass. Particulary, this paleosol shows field evidence of humid conditions through the presence of fragipan, which also indicates hydromorphic conditions in the profile.

Finally, according to the interpretation of the obtained results the actual climatic conditions seems to be similar to those prevailing during MIS 5.

Conclusions

The obtained magnetic properties indicate the presence along the profile of detrital magnetite and titanomagnetite, poor in Ti.

Enhancement in the magnetic signal is detected in PIII (114 ka, MIS 5), the buried soil and present soil, which could indicate similar climatic condition for the time periods related with their genesis. On the other hand, PI, characterized by depletion of ferrimagnetic minerals, could have developed under more humid climate conditions than present time, associated with a higher storage of water in the soil. It also could be a consequence of the presence of volcanic glass.

According to the interpretation of the obtained results the actual climatic conditions seems to be similar to those prevailing during MIS 5.

Acknowledgement

We would like to thank to the projects PICT 0382/07 and PIP 747/10 which allow us to develop the present research. We also would like to thank to the referees for their suggestions which help us to improve our paper.

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Manuscrito recibido el 14 de Octubre de 2011.
Aceptado el manuscrito revisado el 29 de Marzo de 2012.