



## GEOCHEMISTRY OF A LATE QUATERNARY LOESS-PALEOSOL SEQUENCE IN CENTRAL ARGENTINA

### GEOQUÍMICA DE UNA SECUENCIA DE LOESS-PALEOSUELOS DEL CUATERNARIO TARDÍO EN EL CENTRO DE ARGENTINA

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#### Abstract

A loess-paleosol sequence in central Argentina was geochemically analyzed. Corralito I sequence (32°00'7" S, 64°11'08" W, 469 m a.s.l.) is composed by three paleosols and a buried soil separated by loess layers. Weathering indices (CIA, CIW, LWI), elemental ratios ( $\Sigma\text{Bases}/\text{Al}_2\text{O}_3$ , Rb/Sr, CaO/TiO<sub>2</sub>, Na<sub>2</sub>O/TiO<sub>2</sub>), and mean annual paleo-precipitation indices (MAPPs) were calculated in order to obtain a weathering insight and to probe geochemical paleoclimatic proxies. The results indicate an incipient weathering degree throughout the sequence, without significant geochemical differences between paleosols and the loess mantles. Moreover, geochemical paleoclimatic proxies (MAPPs) do not detect a significant paleoprecipitation variability for the time period recorded in the studied loess-paleosol sequence.

**Keywords:** Weathering, Paleoclimatic indices, Corralito I sequence, Córdoba.

#### Introduction

Loess-paleosol sequences are important continental archives of climate change during the Quaternary (e.g., Kühn et al., 2013). Thus, several tools can be used as variables or proxies to reconstruct paleoclimatic conditions. In this sense, the inorganic geochemical composition of loess and paleosols are particularly valuable as a record of paleoclimatic cycles as it reflects paleo-weathering conditions. A loess-paleosol sequence, named Corralito I, located in Córdoba Province, central Argentina (32°00'7"S, 64°11'08"W, 469 m a.s.l., Fig.1), was studied here with the aims of determining its geochemical composition, analyzing the weathering signature, and probing the use of different geochemical tools as proxies of paleoclimatic conditions. The studied sequence is about 11 m thick and is constituted by a sequence of three paleosols (identified as paleosol III, paleosol II, and paleosol I) and a buried soil, interlayered with loess mantles (loess III, loess II, loess I, and B loess, Fig. 1). The buried soil is covered by layered sediments about 1 m thick where human refuse was recognized. Corralito I sequence was previously described, sampled, and morphologically analyzed by Rouzaut and Orgeira (2017 and references therein). The pedological processes recognized in the whole sequence are melanization, decarbonation-carbonation, and clay illuviation (Rouzaut et al., 2015). Frechen et al. (2009) established, by means of luminescence methods, a Late Pleistocene - Holocene age for Corralito I sequence. An age of 115 ± 21 ka was attributed to the base of paleosol III (i.e., loess III), whereas an age of 13.8 ± 2.1 ka was determined for the base of the buried soil (i.e., B loess). The current climate in the region is mesothermal, typically continental; mean annual precipitation for the record period 1960-2015 is 815 mm.

#### Materials and methods

From the base to the top of Corralito I sequence, 10 samples were selected to determine elemental concentrations (Table 1). Clay illuviation processes have been inferred in the paleosols and in the buried soil by the presence of clay coatings on ped faces, which allowed classifying them as Bt horizons (Rouzaut et al., 2015). All samples were air-dried, crushed and passed through a 2 mm sieve. Organic matter and carbonates were removed by conventional methods. Major oxides and some trace elements (Sc, V, Ba, Sr, Y and Zr) were measured by ICP-OES; other trace elements were determined by ICP-MS. Several chemical alteration

indices were calculated to assess weathering: the CIA (Chemical Index of Alteration, Nesbitt and Young, 1982); the CIW (Chemical Index of Weathering, Harnois, 1988) and the LWI (Loess Weathering Index), defined by Yang et al. (2006) as a proxy for chemical weathering intensity of loess deposits. Likewise, some elemental ratios, such as  $\Sigma\text{Bases}/\text{Al}_2\text{O}_3$  (Retallack, 2001),  $\text{Rb}/\text{Sr}$ ,  $\text{CaO}/\text{TiO}_2$ ,  $\text{Na}_2\text{O}/\text{TiO}_2$ , were also used with the same purpose.

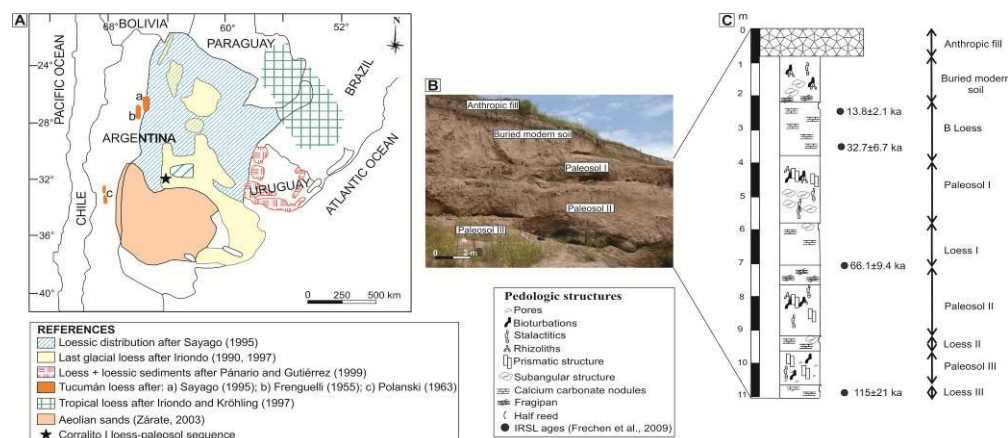


Figure 1. A) Loess and loessic sediments distribution in Argentina according to several authors (modified from Zárata, 2003) and location of Corralito I loess-paleosol sequence. B) Field photograph of the sequence

As a proxy of paleoclimatic conditions we calculated different climo-function proposed by Sheldon et al. (2002) and Sheldon and Tabor (2009), all based on major geochemistry to quantify mean annual paleo-precipitation (MAPP). According to these authors, the most robust function is that defined as:  $P \text{ (mm yr}^{-1}\text{)} = 221e^{0.0197(\text{CIA}-K)}$ . In this case we used the CIW since, by definition, it is equivalent to the CIA-K. The other proxies for paleo-precipitation defined by Sheldon et al. (2002) are based on the Retallack (2001) ratio:  $P \text{ (mm yr}^{-1}\text{)} = -259.3 \text{ Ln} (\Sigma\text{Bases}/\text{Al}_2\text{O}_3) + 759$ , and on the molar ratio  $\text{CaO}/\text{Al}_2\text{O}_3$  (C):  $P \text{ (mm yr}^{-1}\text{)} = -130.9 \text{ Ln} (C) + 467$ . The last function is specific for Mollisols.

## Results and discussion

Weathering indices and elemental ratios calculated for Corralito I sequence (Table 1) denote incipient chemical alteration throughout the analyzed loess-paleosol sequence. Although CIA values of the paleosols (~60) are slightly higher than those of the loess mantles (~58), the difference is not significant. The buried soil exhibits the highest value (CIA = 68). The other calculated indices, i.e., the CIW and LWI show similar results (Table 1). Interestingly, the Rb/Sr ratios, which represent leaching behavior during weathering, with Rb being less mobile than Sr, are in concordance with CIAs, denoting the incipient alteration of feldspars (Table 1). On the other hand, the  $\Sigma\text{Bases}/\text{Al}_2\text{O}_3$  ratio has also been used to identify base-rich soils (ratio >0.5, e.g., Alfisols) from base-poor soils (<0.5, e.g., Ultisols) (Sheldon and Tabor, 2009). The  $\Sigma\text{Bases}/\text{Al}_2\text{O}_3$  values in the studied loess-paleosol sequence range between 0.71 and 1.06 (Table 1), implying base-rich paleosols, also suggesting incipient chemical alteration. Fig. 2 shows the classical ternary plot  $\text{Al}_2\text{O}_3\text{-CaO+Na}_2\text{O-K}_2\text{O}$  (A-CN-K) for the studied loess-paleosol sequence. Accordingly with the calculated weathering indices, Fig. 2 shows that the loess and paleosols of Corralito I exhibit an early Ca and Na removal stage, as the weathering trend is parallel to the A-CN line in the plot and close to the feldspar line. Furthermore, paleosols cluster around loess samples, showing that the incipient weathering signature of the paleosols resembles that of the loess mantles. Table 1 also shows the mean annual paleo-precipitation indices (MAPPs) calculated for the Corralito I sequence. Besides, these climo-functions were also applied to B-horizons of present soils of a catena developed from loess deposits in the piedmont of Sierra Chica de Córdoba (Table 1; from Pasquini et al., 2017). The MAPP for the paleosols, calculated using the equation based on CIA-K (Sheldon and Tabor, 2009), ranges between 814 and 897  $\text{mm yr}^{-1}$ , whereas a MAPP variable between 761 and 811  $\text{mm yr}^{-1}$  was estimated for the loess, suggesting slightly wetter conditions during paleosols formation (Table 1). The same MAPP index calculated for the Bt-horizons of present soils shows values of 812  $\text{mm yr}^{-1}$ ; (Table 1), which are similar to those calculated for the loess-paleosol sequence.

Table 1. Weathering indices, elemental ratios and paleo-precipitation indices calculated for Corralito I

Sample	CIA	CIW	LWI	$\Sigma$ Bases/	CaO/	Na <sub>2</sub> O/	Rb/Sr	MAPP <sup>a</sup>	MAPP <sup>b</sup>	MAPP <sup>c</sup>
<b>Buried modern soil</b>										
CORI BS	68	75	9.30	0.71	2.61	2.84	0.53	--	--	--
<b>B Loess</b>										
CORI B-Loess	61	68	11.57	0.89	3.74	3.93	0.36	845	787	662
<b>Paleosol I</b>										
CORI PI-1	59	66	12.95	1.01	4.28	4.17	0.34	814	755	645
CORI PI-2	59	67	12.74	0.99	4.17	4.23	0.39	822	761	651
<b>Loess I</b>										
CORI PI Loess I	56	63	14.99	1.05	5.36	5.41	0.32	761	745	628
<b>Paleosol II</b>										
CORI PII-1	60	67	13.08	0.99	4.39	3.90	0.43	836	762	647
CORI PII-2	59	67	12.63	0.93	3.95	4.90	0.48	834	777	669
<b>Loess II</b>										
CORI PII Loess II	57	65	13.41	0.97	4.28	5.75	0.42	795	767	661
<b>Paleosol III</b>										
CORI PIII	62	71	11.66	0.87	3.25	3.97	0.48	897	793	691
<b>Loess III</b>										
CORI PIII Loess III	59	65	12.88	0.99	4.50	4.12	0.37	811	761	640
<b>Bt-horizons of</b>										
								812	760	625

MAPP<sup>a</sup> (mm yr<sup>-1</sup>) = 221.1e<sup>0.0197(CIA-K)</sup>, from Sheldon and Tabor (2009)

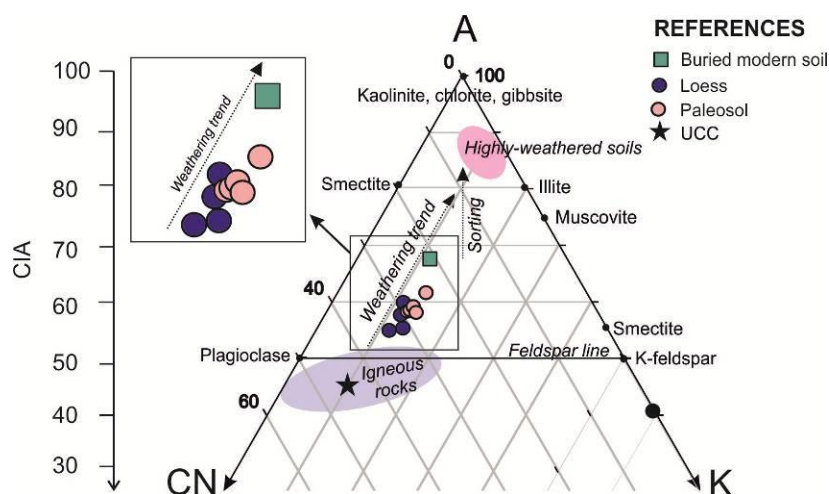


Figure 2. Al<sub>2</sub>O<sub>3</sub>-CaO+Na<sub>2</sub>O-K<sub>2</sub>O ternary diagram showing the paths of weathering. The field of igneous rocks, the upper continental crust (UCC, Mc Lennan, 2001) and highly weathered soils (Caspari et al., 2006) are plotted as a reference. The supplementary vertical axis of CIA is also included.

Furthermore, the mean annual precipitation calculated for the paleosols as well as for the Bt-horizons of present soils by means of this function, is in concordance with the present-day mean annual precipitation in the region (i.e., mean of 815 mm for the last 60 years), indicating that this climo-function is accurate for the region. So, the geochemical tools probed here do not allow identifying significant paleoclimatic changes throughout the studied sequence, since the calculated MAPPs do not show substantial differences between the three analyzed paleosols.

## Conclusions

The analysis of the loess-paleosol sequence Corralito I, based on geochemical proxies, evidences an incipient degree of weathering throughout the sequence. The weathering indices (CIA; CIW; LWI), elemental ratios ( $\Sigma$ Bases/Al<sub>2</sub>O<sub>3</sub>, CaO/TiO<sub>2</sub>, Na<sub>2</sub>O/TiO<sub>2</sub>, Rb/Sr), and the A-CN-K diagram indicate that the weathering signature in the paleosols resembles that of the loessic mantles, and it is coherent with a weathering-limited regime that would have prevailed in the region. Geochemical proxies do not detect a significant paleoprecipitation variability for the time period recorded in the studied loess-paleosol sequence, evidencing that the climatic conditions



for the region during the Late Pleistocene - Holocene could have been similar than the present ones, with contrasting seasons inferred by the pedogenetic processes observed in the profile.

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