

# Critical elements in Lower Cretaceous paleosols (SE Iberian Range, NE Iberia): concentration and distribution

Elisa Laita (1\*), Blanca Bauluz (1), Alfonso Yuste (1), Alejandro Lorenzo (1)

(1) IUCA-Departamento de Ciencias de la Tierra. Universidad de Zaragoza, 50009, Zaragoza (España)

\* corresponding author: [laita@unizar.es](mailto:laita@unizar.es)

**Keywords:** Critical elements, laterites, paleosols, weathering.

## INTRODUCTION

The intense chemical weathering processes that lead to the formation of aluminum-rich rocks (e.g., laterites) results in the economic enrichment of critical metals (Freyssient et al., 2005; Butt & Cluzel, 2013). This group includes the Rare Earth Elements (REE), Sc, V, Co, Ga, Sr, Nb, Hf, Ta, and W. These metals are crucial in the green energy, aerospace, medical, automotive, or electronic industries (Goodenough et al., 2017). Therefore, the study of the mineral phases hosting the critical elements in laterites is crucial. For this reason, this work focuses on the geochemical characterization of Lower Cretaceous lateritic profiles from NE Iberia with two aims: to evaluate the concentration of major and trace elements and its relationship with the weathering processes, and to determine which mineral phases control the distribution of the critical elements.

## DESCRIPTION OF THE LATERITIC SAMPLES AND METHODS

The studied samples come from paleosols developed on sedimentary rocks of Lower Cretaceous (early Barremian). Four continental profiles located in the SE part of the Iberian Range (NE Iberia), that were previously investigated by Laita et al. (2020) have been analyzed. According to these authors, the paleosols can be classified as laterites and developed *in situ* through the chemical weathering of lacustrine mudstones and marlstones. The lower levels of the profiles are formed by red clays (RC) containing abundant ferruginous pisoids and macropisoids, whereas the middle and upper levels correspond to ochre and violet clays/marls (OVC) with few or no pisoids. Authigenic kaolinite, beidellite, goethite, hematite, anatase, rutile, ilmenite and diasporite and detrital quartz and illitic phases are detected in the matrix of the paleosols, whereas pisoids and macropisoids are mainly formed by authigenic kaolinite, hematite, goethite, and ilmenite and detrital quartz. An upward decrease in the authigenic kaolinite and pisoids content towards the top of the profiles, coinciding with an increase of detrital quartz and illitic phases, and the presence of authigenic beidellite, reflect a decrease in the chemical weathering intensity towards the top related to a change from warm and humid to cooler and drier conditions (Laita et al., 2020).

A total of 30 samples from different paleosol levels included in the four profiles have been selected for the geochemical study. Seventeen samples correspond to the RC, eight to OVC and five to macropisoids. Chemical analyses of major and trace elements of bulk samples were performed at Actlabs Laboratories (Canada). Major elements and some trace elements (V, Sr, Ba, Sc, Be) were determined by inductively coupled plasma-optical emission spectroscopy (ICP-OES), and the rest of the trace elements were analyzed by inductively coupled plasma-mass spectrometry (ICP-MS).

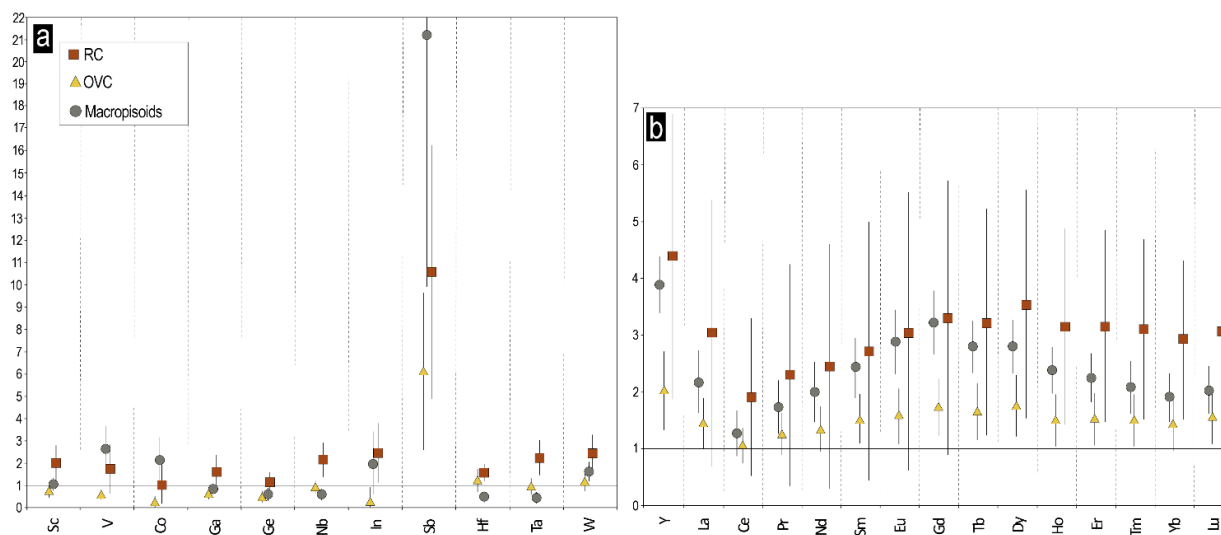
## MAJOR AND CRITICAL ELEMENTS DURING WEATHERING

The Si concentrations normalized to the Upper Continental Crust (UCC) showed an enrichment in the OVC and a depletion in the RC, indicating that there is an increase in the Si content to the top of the profiles. The RC are enriched in Al and present higher Fe and Ti content than the OVC, while the later has a higher K and Mg content. This is consistent with the higher kaolinite, hematite, and goethite content of the RD and the higher quartz, illitic phases and smectite content of the OVC reported by Laita et al. (2020). The macropisoids are enriched in Fe, Mn, Ti, and P reflecting the presence of certain phosphates and Mn-, Fe-, and Ti-rich minerals.

The critical elements concentration (from Sc to W, excluding REE) is higher in the lower levels of the profiles (RC: 302.14 ppm) and the macropisoids (360.77 ppm) than in the upper levels (OVC: 107.80 ppm) (Figure 1a). Normalized concentrations to the UCC indicate that both the laterites and the macropisoids are enriched in light rare earth elements (LREE) (RC: 301.81 ppm; OVC: 161.23 ppm; macropisoids: 223.01 ppm) and in heavy rare earth elements (HREE) (RC: 129.04 ppm; OVC: 60.51 ppm; macropisoids: 110.53 ppm) (Figure 1b). The (La/Sm) average values (RC: 4.85; OVC: 3.93; macropisoids: 3.76), and the (Gd/Yb) average values (RC: 1.53; OVC: 1.71; macropisoids: 2.40) show that the lower levels exhibit higher LREE fractionation than the upper levels and the macropisoids, whereas the pisoids exhibit higher HREE fractionation. This indicates that the HREE are less mobile than the LREE during weathering.

Average CIA values of the RC are higher (CIA=98) than those from the OVC (CIA=85). CIA values of the four profiles decrease to the top, which coincides with a decrease in the critical elements content, indicating that the concentration of critical elements in the studied laterites increases with weathering. The decrease in the CIA confirms the decrease in chemical weathering intensity previously detected.

All the critical elements present good positive correlation with Fe and Ti, indicating that Fe and Ti-bearing minerals can be acting as scavengers for these metals. For certain elements, the correlation is also acceptable for P in the macropisoids. On the other hand, the critical elements display a negative correlation with K, but they have a good positive correlation with Al. This is reflecting that, during the lateritization process, the critical elements are mainly associated to Fe and Ti oxides (hematite, goethite, anatase, rutile, and ilmenite), as well as to authigenic clay minerals (kaolinite).



**Fig 1.** a) Average of critical elements (from Sc to W, excluding REE) normalized to the UCC, b) average of REE normalized to the UCC. RC=red clays; OVC=ochre and violet clays/marls.

## REFERENCES

- Butt, C.R.M. & Cluzel, D. (2013): Nickel Laterite Ore Deposits: Weathered Serpentinites. *Elements*, **9**, 123–128. DOI: 10.2113/gselements.9.2.123.
- Freyssient, P.H., Butt, C.R.M., Morris, R.C., Piantone, P. (2005): Ore-forming processes related to lateritic weathering. in “Economic Geology One Hundredth Anniversary Volume”, J.W. Hedenquist, J.F.H. Thompson, R.J. Goldfarb, J.P. Richards, eds. Society of Economic Geologists, 681–722.
- Goodenough, K.M., Wall, F., Merriman, D. (2017): The Rare Earth Elements: Demand, Global Resources, and Challenges for Resourcing Future Generations. *Nat. Resour. Res.*, **27**, 201–216. DOI: 10.1007/s11053-017-9336-5.
- Laita, E., Bauluz, B., Aurell, M., Bádenas, B., Canudo, J.I., Yuste, A. (2020): A change from warm/humid to cold/dry climate conditions recorded in lower Barremian clay-dominated continental successions from the SE Iberian Chain (NE Spain). *Sediment. Geol.*, **403**, 105673. DOI:10.1016/j.sedgeo.2020.105673.