



Rare-earth element and stable isotope signatures of kaolin from a Pliocene lateritic weathering profile at mid-latitude region (Andalusia, Spain): Implications for paleoweathering and paleoclimatic reconstructions

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ABSTRACT

This study reports the impact of weathering on behavior of rare earth elements (REE) in a coastal lateritic profile developed on Pliocene sediments at mid-latitude location ($\sim 37^\circ$ N), in the Guadalquivir Basin (Spain). It also explores the stable isotope signature of kaolinite providing constraints on paleotemperature and isotopic composition of the ancient meteoric water. The paleoweathering profile (~ 20 m thick) comprises a white sandy clayey saprolite overlain by a red-mottled clay zone, which in turn is capped by a pisolitic ferricrete. The kaolinitic regolith was practically reduced to a mixture of kaolinite and quartz by intense chemical weathering under warm and seasonally humid climate.

The kaolinized material is markedly depleted in total REE (mean value of 77.30 mg kg^{-1} in the white saprolite and 72.70 mg kg^{-1} in the mottled zone) relative to the parent rock ($168.96 \text{ mg kg}^{-1}$). Development of acidic and oxidizing conditions promoted a suitable soil environment for REE release and leaching with percolating rainwater, leading to an apparent loss of REE from the profile (up to 87%). The parent rock-normalized REE patterns display concave-upward shapes tracing a remarkable depletion in middle REE (MREE), with no significant anomalies. The REE concentrations normalized against the North American Shale Composite (NASC) showed consistently similar fractionation patterns. The MREE-depleted signature (NASC-normalized ratios of La/Sm up to 3.32 and Gd/Lu as low as 0.45) probably arises from reductive dissolution of iron oxyhydroxide phases due to seasonal water saturation, as indicated from redoximorphic features.

The $< 2 \mu\text{m}$ kaolinite separates showed $\delta^{18}\text{O}$ values ranging from 17.3‰ to 20.0‰, and δD values between -71‰ and -60‰ . The $\delta^{18}\text{O}$ and δD mean values indicated a crystallization temperature of about 24°C , which is higher than the local present-day annual mean air temperature ($\sim 18^\circ\text{C}$). For the calculated temperature, the oxygen isotope fractionation factor between kaolinite and water ($\alpha_{k-w} = 1.0248$) implies that kaolinite formed in equilibrium with meteoric waters ($\delta^{18}\text{O} = -5.4\text{‰}$ and $\delta\text{D} = -33\text{‰}$) that closely reflect the regional meteoric precipitation.

The lateritic weathering profiles evolved during the mid-Pliocene warm period in the southwestern Iberian margin could be useful for predicting potential future environmental effects of increased atmospheric CO_2 on the Earth's critical zone.

1. Introduction

Paleoweathering profiles are a major record of Earth's surficial conditions because they represent fundamental events (climatic, tectonic, etc.) that assist in stratigraphical correlation and give precise information on past environmental conditions (Thiry et al., 1999). Within the context of the lateritic environment, deeply kaolinized profiles may have important implications for paleoclimatic and paleoweathering reconstructions. Kaolinization is a prominent weathering process in the intertropical rainy zone that usually leads to the

formation of large kaolin deposits on extensive lateritic mantles (e.g. Ambrosi and Nahon, 1986; Tardy and Roquin, 1992; Schaefer et al., 2008). In fact, kaolinite is an abundant clay mineral in paleosol profiles that formed in paleotropical sites (e.g. Sheldon and Tabor, 2009).

However, the stable isotope composition of kaolinite reveals that much of the kaolinitic regoliths formed under relatively cold conditions, suggesting that, contrary to classical interpretations, laterization and deep weathering phenomena are not solely the result of weathering in tropical or subtropical climates (Bird and Chivas, 1989). It has been also suggested that development of kaolinitic profiles at extra-tropical

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latitudes may be the result of a greenhouse warming induced by increased atmospheric CO₂ levels (e.g. Dowsett et al., 1992; Barron et al., 1993; Thiry, 2000; Krause et al., 2010). Thus, the areal distribution of kaolin means in effect the presence of a “cool” and “warm” kaolinization, one of moderate intensity in the humid mid-latitude climatic zone, and the other one much bigger in size and more variable in the mineral assemblage, typical of the humid tropical climate zones (Dill, 2016).

Ancient kaolinitic weathering surfaces currently exposed to non-tropical alteration conditions have been recognized in the southwestern corner of the Iberian Peninsula, both in Portugal (Marques et al., 1980–81; Abreu, 1990) and Spain (Rodríguez-Vidal et al., 1985; Núñez and Recio, 2007; Díaz del Olmo et al., 2010; Fernández-Caliani and Cantano, 2010). The Bonares profile is a relict paleosol formed on the kaolinized past landscape that has fortunately been preserved in the geological record of the Guadalquivir Basin (Spain). The kaolinization process was described by Fernández-Caliani and Cantano (2010) in terms of major and trace element distributions, excluding rare earth elements (REE), with the preliminary results being consistent with a lateritic weathering profile evolved under humid subtropical conditions during late Neogene time. The present paper revisits the issue by providing new insights from REE geochemistry and stable isotope data.

Research on geochemistry of REE in paleosol studies has gained considerable prominence over the last decade. This increasing interest is based on the fact that the REE patterns can be used as promising tracers of past water-rock interaction and soil formation processes (Minafík et al., 1998; Taunton et al., 2000; Laveuf et al., 2008; Vermeire et al., 2016), and they can aid in monitoring the impact of weathering on REE mobilization and fractionation (Öhlander et al., 1996; Laveuf and Cornu, 2009; Ma et al., 2011; Yusoff et al., 2013; Jin et al., 2017). Isotope geochemistry is another major contributor to paleoweathering studies. Stable isotope ratios of hydroxylated soil minerals can serve as a proxy for the temperature of formation and the isotopic composition of the water from which they crystallized, which in turn provide information about past surface air temperatures (Lawrence and Taylor, 1972; Delgado and Reyes, 1996; Tabor and Montañez, 2005; Clauer et al., 2015; Hall et al., 2015). Also, stable isotope analysis is usually applied in paleosol studies to reconstruct environmental and/or climatic conditions that prevailed at the time of soil formation (Savin and Hsieh, 1998; Girard et al., 2000; Yapp, 2000; Feng and Yapp, 2009; Sheldon and Tabor, 2009; Rosenau and Tabor, 2013).

The present study was specifically aimed at determining: (1) the effects of weathering on distribution, mobility and fractionation of REE in the lateritic profile of Bonares with a view to tracing the geochemical behavior of REE during the formation of the kaolin-enriched paleosol; and (2) the hydrogen and oxygen stable isotope ratios of kaolinite to constrain the isotopic composition of the local meteoric water and temperature of the ancient weathering system.

2. Geological setting and description of the profile

The Bonares lateritic profile is located at the northwestern margin of the Guadalquivir Basin, an ENE-WSW elongated basin developed during the Neogene and Quaternary between the external units of the Betic Cordillera and the Iberian Massif, in southwestern Spain (Fig. 1). This foreland basin occupies a strategic position for studying the interplay between lithospheric and surface processes, and may help in the understanding the tectonic and climatic factors controlling the connection between the Mediterranean Sea and the Atlantic Ocean (Larrasoña et al., 2013).

The paleoweathering profile developed over the locally named Bonares Sands Formation, which constitutes the last Neogene depositional sequence at the west end of the Guadalquivir Basin (Sierro et al., 1996). The formation is composed mainly of highly permeable arkosic sands, with gravel lenses and layers, representative of tidally-influenced foreshore sedimentation (Mayoral and Pendón, 1986–87), although the

upper formation probably was part of a braided fluvial system feeding deltaic and shallow-marine environments. An erosional surface or erosive unconformity separates these siliciclastic deposits from the underlying Huelva Sands Formation, which is characterized by fine-grained sands and sandy silts with large accumulations of mollusk shells of early Pliocene age (Civis et al., 1987). The Neogene formations appear unconformably overlaid by coarse-grained sands and gravels deposits conditioned by the Quaternary evolution of the fluvial network of the Tinto river, a naturally acidic system fed by subsurface biooxidation of sulfide orebodies (Gómez-Ortiz et al., 2014) and, additionally, severely affected by acid mine drainage (Galán et al., 2003).

The altitude of the area ranges between 120 and 140 m above sea level and the present climate is oceanic Mediterranean, with mean annual precipitation of about 525 mm, and mean annual temperature around 18.2 °C. The relative humidity remains moderately high (up to 80%) due to the proximity to the Atlantic Ocean.

The Bonares profile (Fig. 2) can be subdivided from bottom to top into four zones, with an overall exposed thickness of about 20 m at this location (Fernández-Caliani and Cantano, 2010):

- Zone I (parent material): it consists mainly of yellowish orange (10YR 7/6, Munsell color chart), fine to medium-grained sands displaying parallel lamination and gentle cross-bedding dipping in opposite directions.
- Zone II (10–12 m thick): a white (10YR 8/1) sandy clayey saprolite in which sedimentary structures of the parent rocks are still well preserved and recognized (Fig. 2a, b). This saprolitic horizon is referred to as lithomarge by Rodríguez-Vidal et al. (1985).
- Zone III (3–4 m thick): a mottled clay horizon showing a distinct contrast between brown-red colored (10R 5/8) and bleached (7.5YR 8/3) domains (redoximorphic features). In this horizon the original structure of the parent rock was completely obliterated (Fig. 2c). The mottled zone can be regarded as an old plinthic horizon similar to those found in lateritic profiles.
- Zone IV (0–1 m thick): the profile is capped by a purple-reddish (10R 3/2) duricrust paleosurface with a pisolitic structure (Fig. 2c), partially dismantled by erosive processes. In places, a soft clay layer occurs at the base of the duricrust. The remnants of the pisolitic duricrust can be seen only on highest parts of the present-day landscape.

3. Material and methods

The outcrops of the lateritic paleosol sampled for this study are located around Bonares, approximately 30 km east of Huelva (SW Spain), on the left bank of the Tinto river (Fig. 1). Seventeen kaolin samples were collected at different depths of the lateritic paleosol from three vertical cross-sections located at the following geographic coordinates (referred to UTM zone 29N): Section 1 (37°18'42"N–6°40'26"W), Section 2 (37°19'35"N–6°40'21"W) and Section 3 (37°19'55"N–6°38'52"W). Section 1 shows the upper-middle part of the lateritic paleosol, Section 2 exposes the saprolite horizon and the bedrock, while Section 3 is representative of the entire weathering profile. The sample PTB-1 was used as a proxy for the average composition of the parent rock from which the paleosol developed.

Particle-size distribution was measured by laser diffraction with a Mastersizer 2000 (Malvern Instruments). Mineralogical analysis was conducted by X-ray powder diffraction (XRD) on a Bruker-AXS D8-Advance diffractometer, using monochromatic CuK α radiation at 40 kV and 30 mA. Whole-rock random powders were scanned over a range of 3 to 65° 2 θ using a step size of 0.02° 2 θ and 0.6 s count time per step, after gentle grinding and homogenization. Sample aliquots were disaggregated by ultrasonic agitation in deionized water and the < 2 μ m size fraction was separated by wet sieving and centrifugation after dispersion. The clay separates were transferred to glass slides as oriented aggregates, air-dried, and then scanned from 1 to 30° 2 θ using a

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