Lanthanides in granulometric fractions of Mediterranean soils. Can they be used as fingerprints of provenance?

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Summary

There is geochemical interest in the lanthanides because they behave like a group that is closely related to the parent materials during surface processes, although they also undergo fractionation as a result of supergene dynamics. We analysed lanthanide concentrations (ICPms) in the granulometric fractions fine sand, clay and free forms of clay (FFclay-CDB and FFclay-Ox: extracted with citrate-dithionite-sodium bicarbonate and with ammonium oxalate, respectively) from a soil chronosequence of Mediterranean soils. There was a relative enrichment of heavy rare earth elements (HREE) in the clay fraction and its free forms with respect to fine sand. The clay free forms behaved as scavengers of lanthanides, and oxidative scavenging of cerium (Ce) in FFclay-CDB was also detected. Lanthanide concentrations (lanthanum to gadolinium in fine sand; terbium to lutetium in clay) varied with soil age, and chronofunctions were established. There was a strong positive collinearity between most of the lanthanide concentrations. Furthermore, the value of the correlation index (Pearson’s r) of the concentrations between couples of lanthanides (rCLC) decreased significantly with increasing separation between the elements in the periodic table; this has never been described in soils. Several geochemical properties and indices in the fine sand and clay soil fractions and in the geological materials of the Guadalquivir catchment showed, on the one hand, a genetic relation between them all, enabling the lanthanides to be used as fingerprints of provenance; on the other hand, fractionation between fine sand and clay showed these are actively involved in soil lanthanide dynamics.

Highlights

- Are lanthanides from fine sand and clay genetically related to the geological materials?
- Lanthanide concentrations of fine sand and clay fit chronofunctions
- Pearson’s r of lanthanide couples decreases when separation increases in the periodic table
- Free forms of clay are scavengers of lanthanides and concentrate HREE and cerium

Introduction

Quantities of rare earth elements (REE) (lanthanoids: 57-71Ln, and scandium 21Sc and yttrium 39Y) in the Earth’s crust are of the order mg kg\(^{-1}\), and show some characteristic periodic behaviour such as: (i) light REE (LREE), low atomic weight (\(A_r\)) (lanthanum La to samarium Sm), are more abundant than heavy REE (HREE) (holmium Ho to lutetium Lu) (British Geological Survey, 2011) (medium REE, MREE: samarium Sm to dysprosium Dy, have an intermediate \(A_r\); Rollinson, 1993) and (ii) a strong linear correlation between their concentrations has been reported; in European soils, \(r > 0.7\) (Salminen, 2005).

The chemical signatures of the parent rock assemblages in a tectonic province can persist in the daughter sediments produced, and are thus preserved in the corresponding sedimentary deposits (Rollinson, 1993). It has been suggested (Blundy & Wood, 2003) that the trace elements (<0.1% by weight, as in the case of lanthanides) exhibit passive behaviour during supergene processes, resulting in their being excellent tracers of the source area of sediments and soil materials. Wang et al. (2017) described them as ideal tracers of origin in aeolian research. Consequently, the geochemical interest in the lanthanides is because of their close relation...
with the source area. This feature can be used in paleoenvironmental studies of sedimentary origin and tectonic setting (Chen et al., 2014; Och et al., 2014), and in soil studies such as pedogenic tracers (Laveuf & Cornu, 2009). The concentrations of REE in soil have been shown to depend not only on the lithology over which they develop, but also there are soil processes that induce internal fractionation or anomalies (Laveuf & Cornu, 2009). The Ln patterns, where the abundance of each Ln relative to that of a chondrite or shale is plotted on a logarithmic scale against the atomic number, or the geochemical ratios between lanthanides (e.g. HREE/LREE, lanthanum/ytterbium (La/Yb), samarium/ytterbium (Sm/Yb), and so on, or the cerium and europium anomalies (Ce/Ce* and Eu/Eu*, respectively)) are used for studying the provenance of geological materials (as fingerprints) and for analysing pedogenic intensity (Rollinson, 1993; Moreno et al., 2006; Mongelli et al., 2014). In soil lanthanide dynamics, another process to add to inheritance and pedogenic action is aeolian contribution. Aeolian processes are common in Mediterranean soils (Delgado et al., 2003).

Relatively little is known about lanthanide behaviour in soil (Chen et al., 2014); therefore, their dynamics in different soil environments need to be analysed (Laveuf et al., 2012). Studies of REE concentrations of granulometric fractions of soils, including sands (2000–50 μm) (Aide & Smith-Aide, 2003; Marques et al., 2011) or in free forms, or in soil chronosequences are even more scarce (Chang et al., 2016; Martín-García et al., 2016).

The aim of the present study was to examine lanthanide concentrations in the fine sand and clay fractions and the free forms of clay from a soil chronosequence from the River Guadalquivir (southern Spain) (a soil chronosequence is a series of soils that differ in their degree of profile development because of differences in age, while other soil-forming factors remain relatively constant). Other novel aspects investigated in this study are: (i) the effect of soil age, including the formulation of chronofunctions, (ii) the correlations between concentrations, (iii) the use of lanthanides as fingerprints of provenance compared with geological samples from the same soil zone and (iv) the contribution to the soil of lanthanides from aeolian materials.

In previous studies we have shown how the soils of the Guadalquivir behave like an ideal chronosequence, in which a considerable number of components and properties fitted significantly to chronofunction equations (Calero et al., 2008, 2009, 2013). In addition, Martín-García et al. (2016) have studied the geochemistry of the clay fraction (including some aspects of lanthanides).

The present study can be included in the collection of soil chronofunction studies, which, at present, are few.

**Materials and methods**

**Setting and soils**

Geographically, the Guadalquivir River (640-km long) drains an area of 68,300 km². It rises in the Baetic Cordillera at a height of 1400 m before flowing into the Atlantic Ocean. It is the most important fluvial system in the southern Iberian Peninsula. From a geological point of view, the Guadalquivir-Cenozoic Basin was developed between the Iberian Massif (passive margin) to the north and the Baetic Cordillera (active margin) to the south (Figure 1). From a sedimentological point of view their fluvial alluvia are gravels with some stone-free sandy silt layers. The source rocks for this alluvium are lithologically diverse and include: to the north, igneous rocks (such as granite, granodiorite, rhyolite, tonalite, andesite, gabbro and intrusive rocks) and metamorphic rocks (mainly shales) from the Iberian Massif (Central Iberian Zone, mainly Los Pedroches batholith and Santa Elena pluton, and the Iberian Massif) (Larrea et al., 1992, 1994, 1995; Carracedo et al., 1997; Pin et al., 2002; Pascual et al., 2008); to the south and west, sedimentary materials such as limestones, marly limestones, marls and dolomites from the External Baetic Zones of the Baetic Cordillera (Martínez-Ruiz, 1994), metasedimentary rocks (schist and gneiss) from the Internal Baetic Zones (Torres-Ruiz et al., 2003) and Quaternary sediments from the Guadalquivir Depression, a Cenozoic Basin (Jiménez-Espinosa et al., 2016).

The study area is in the middle reaches of the Guadalquivir River, near the town of Andújar on a transect of 3.7 km along the river between 3°50′–4°3′W and 38°0′–38°2′N (Figure 1). The soils selected (Table 1) developed on four Quaternary terrace surfaces (P1, P2, P3 and P4: Luvisols and Calcisols) and a floodplain (P5: Fluvisol) with ages ranging from 600 to 0.3 ka (Calero et al., 2008). Fresh point bar sediments (PM) in the river were also selected. Currently, the climate is hot in the Mediterranean with mean annual rainfall of 650 mm and a mean annual temperature of 18°C. The vegetation is mainly anthropogenic because the flat surfaces have been cultivated since time immemorial (nowadays olive groves, wheat and cotton).

The solum of the older terrace soils (pre-Holocene soils: P1, P2 and P3) (Table 1) shows Bt horizons (with clay illuviation features such as clay cutans), red Munsell colours, relatively deep thickness, clayey textures (> 30% clay) and evidence of leaching of carbonates (and accumulation, in P2). Thus, the older soils have the largest values of Harden’s profile development index (between 44.8 for P1 and 39.6 for P3; Table 1). In the Holocene soil P4, brunification and some leaching and accumulation of carbonates has also been detected. The soil P5 had no evident evolution features. In the fine sand fraction (Table 1), quartz was the main mineralogical component in P1, P2 and P3 (≥ 58%, mean value), whereas the carbonates, calcite and dolomite were the main components in P4 and P5 (≥ 44%, mean value of total carbonates). Other phases present were phyllosilicates (illite, brammallite, chlorite, kaolinite and various mixed-layer phases), feldspars (potassium feldspar and plagioclases, both abundant in P3) and iron (hydr)oxides (goethite and haematite). The point bar sediment PM showed a more balanced composition of quartz and carbonates (30 and 40%, respectively).

**Materials and lanthanide analyses**

Lanthanide concentrations of the fine sand fraction (50–250 μm) of 24 samples (belonging to soil horizons and point bar sediment, PM) were determined by inductively coupled plasma–mass spectrometry.
spectrometry (ICP–MS) using an Agilent 7700x (Santa Clara, CA, USA) instrument at the Natural History Museum (London, UK) after lithium metaborate fusion in a Pt–Au crucible, and the resulting flux was dissolved in 10% HNO₃. Calibration was performed using certified reference materials (CRM) prepared in the same way. Further analytical details are given in Gregory et al. (2017). As study material, we also used the concentrations of lanthanides from the clay fraction and the free forms of clay after extraction with citrate-dithionite-bicarbonate (FF_{clay-CDB}) or with ammonium oxalate (FF_{clay-Ox}), measured previously by Martín-García et al. (2016). The FF_{clay-CDB} is conventionally assumed to be a measure of the total pedogenic free forms (crystalline and poorly crystalline forms), whereas FF_{clay-Ox} is a measure of poorly crystalline forms; mainly iron, but with appreciable quantities of Al and Ti.

We grouped lanthanides following Rollinson (1993) into light (LREE: La to Nd), medium (MREE: Sm to Dy) and heavy rare earth elements (HREE: Ho to Lu). Lanthanide concentrations were normalized to (i.e. divided by) the CI chondrite, considered to represent the bulk earth composition, of McDonough & Sun (1995), and then the Ce/Ce* and Eu/Eu* anomalies were calculated \( Ce/Ce^* = Ce_N/(La_N \times Pr_N)^{1/2} \); \( Eu/Eu^* = Eu_N/(Sm_N \times Gd_N)^{1/2} \); the subscript \( N \) shows that the value was normalized by the chondrite used. It makes sense to calculate both anomalies because \( Eu^{3+} \) and \( Ce^{3+} \) might be in another valency (\( Eu^{2+} \) and \( Ce^{4+} \)) and thus be involved in different reactions from those of the rest of the trivalent lanthanides (\( Ln^{3+} \)) (i.e. separate from the group behaviour). The ratios \( La_N/Yb_N, Sm_N/Yb_N, HREE_N/LREE_N \) and \( MREE_N/LREE_N \) were also calculated; all establish the degree of fractionation of LREE from MREE and HREE (La is a representative of LREE, Sm of MREE and Yb of HREE) during geochemical processes.

Statistical analysis

The statistical analysis was carried out using the IBM SPSS v.22.0 software package. The Kolmogorov–Smirnov and Shapiro–Wilk tests were used to determine the normality of data, and the results were considered statistically significant if \( P \) was less than 0.05. Statistical analyses were carried out after data were transformed.

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| Profile (Terrace No) | Soil classification\(^b\) | Age / ka | PDI \(^c\) | Fine earth fraction \(< 2\) mm | Clay fraction \(< 2\) μm | Mineralogy \((\text{XRD}) / \%\) |
|---------------------|-----------------------------|----------|-------------|---------------------|----------------------|-------------------------------|
|                     |                             |          | Fine sand /% | Clay /% | CEC / cmol\(_k\) kg\(^{-1}\) | FFC\(_{\text{CDB}}\) /% | CaCO\(_3\) eq /% | FF\(_{\text{clay-CDB}}\) /% | FF\(_{\text{clay-Ox}}\) /% | FFC\(_{\text{Ox}}\) /% | phy | qz | fd | feox | Ca | do | phy | qz | fd | feox | Ca |
| P1 (Terrace 1)      | Cutanic Luvisol/Palexeralf  | 600\(^d\) | (7.2) | (9.6) | (0.14) | (0.4) | (1.8) | (0.44) | (0.9) | (0.83) | (0.06) | 29 | 61 | 6 | 3 | 1 | 86 | 8 | 1 | 5 | 0 |
| P2 (Terrace 2)      | Lixic Calcisolo/Haploxeralf | 300\(^d\) | (5.5) | (13.4) | (0.23) | (0.1) | (2.8) | (0.36) | (19.4) | (0.35) | (0.06) | 18 | 58 | 12 | 3 | 9 | 87 | 5 | 2 | 4 | 2 |
| P3 (Terrace 3)      | Cutanic Luvisol/Haploxeralf | 70\(^d\) | (7.5) | (9.2) | (0.09) | (0.2) | (7.7) | (0.34) | (0.0) | (0.28) | (10) | 6 | 58 | 31 | 2 | 3 | 89 | 6 | 2 | 3 | 0 |
| P4 (Terrace 4)      | Haplic Calcixerert          | 7\(^d\) | (8.5) | (6.8) | (0.25) | (0.4) | (6.1) | (0.48) | (7.1) | (0.43) | (0.05) | 14 | 30 | 9 | 3 | 14 | 30 | 87 | 3 | 2 | 2 | 6 |
| P5 Flood plain      | Haplic Fluvioxeralf         | 0.3\(^d\) | (3.4) | (8.2) | (0.19) | (0.1) | (3.3) | (0.11) | (19) | (0.15) | (0.11) | 20 | 26 | 6 | 2 | 29 | 17 | 88 | 3 | 1 | 1 | 7 |
| PM\(^e\)            |                             | 0        | 16.3 | 21.6 | 1.76 | 84 | 87 | 0.78 | 23.5 | 1.06 | 0.60 | 17 | 30 | 10 | 3 | 33 | 7 | 85 | 3 | 2 | 1 | 9 |

\(^a\)From Calero et al. (2009) and Martín-García et al. (2016).
\(^b\)World Reference Base for Soil Resources/Soil Taxonomy.
\(^c\)Pre-Holocene.
\(^d\)Holocene.
\(^e\)Parent material: Fluvial sediment ‘point bar’.

PDI, profile development index (Harden, 1982); OC, organic carbon; CEC, cation exchange capacity; FFC\(_{\text{CDB}}\), citrate-dithionite-bicarbonate extractable free forms in the fine earth fraction \((\text{Fe}_2\text{O}_3 + \text{Al}_2\text{O}_3)\); FF\(_{\text{clay-CDB}}\), citrate-dithionite-bicarbonate extractable free forms in the clay fraction \((\text{Fe}_2\text{O}_3 + \text{Al}_2\text{O}_3 + \text{TiO}_2)\); FF\(_{\text{clay-Ox}}\), ammonium oxalate extractable free forms in the clay fraction \((\text{Fe}_2\text{O}_3 + \text{Al}_2\text{O}_3 + \text{TiO}_2)\); CaCO\(_3\) eq, calcium carbonate equivalent; phy, phyllosilicates (illite, smectite, mixed-layer phases, kaolinite, chlorite, brannmlite); qz, quartz; fd, feldspar; feox, iron (hydr)oxides (goethite, hematite); ca, calcite; do, dolomite.
logarithmically if this was necessary. The matrix of Pearson’s product-moment correlation coefficients ($r$) and, in some cases, the coefficients of determination ($R^2$) were obtained. The coefficient of determination ($R^2$) was obtained to determine the fit of the least squares regressions.

Results and discussion

Lanthanides in the fine sand fraction

The series of lanthanides in fine sand showed very variable values, ranging from around 0.05 to 65 mg kg$^{-1}$ (Table 2). The order of abundance was $\text{Ce} > \text{La} > \text{Nd} > \text{Pr} > \text{Sm} > \text{Gd} > \text{Dy} > \text{Er} > \text{Yb} > \text{Eu} > \text{Ho} > \text{Tb} > \text{Tm} > \text{Lu}$, identical to that of the mean of the Earth’s crust (Rollinson, 1993; British Geological Survey, 2011), so that $\Sigma\text{LREE} > \Sigma\text{MREE} > \Sigma\text{HREE}$ (Table 3). Lanthanide concentration increased with depth in the profile (Table 2). The P1 horizons contained most $\Sigma\text{Ln}$ (Table 3). The $\Sigma\text{LREE}$ increased with age ($\text{P1} > \text{P2} > \text{P3} > \text{P4} > \text{P5} > \text{PM}$) and profile P4 was the richest in $\Sigma\text{HREE}$ and Dy (e.g. horizon 4C2 had the largest concentration). The ratios $\text{MREE}_n/\text{LREE}_n$ and $\text{HREE}_n/\text{LREE}_n$ were smaller in pre-Holocene than Holocene soils and PM (Table 3).

The concentrations of lanthanides ($\Sigma\text{Ln}$) were related to those of phyllosilicates, as proposed by Mongelli et al. (2014). In the fine sand of the present study, this was determined as:

$$\Sigma\text{Ln} \ (\text{mg kg}^{-1}) = 1.85 \times \text{Phyllosilicates} \ (%)$$

$$+ 59.08 \ (n = 24; r = 0.538; P < 0.01).$$

In addition, the abnormally large concentrations of Dy and HREE in 4C2 of profile P4 (Table 2) reaffirm the presence of the lithological discontinuity detected morphologically by Calero et al. (2008, 2009). A possible explanation might be a change in the mineralogical composition of the major species (phyllosilicates, quartz, feldspars, iron oxides, calcite and dolomite) compared with the other horizons of the profile. However, this mineralogical change was not detected (table 4 on page 471 of Calero et al., 2009). Therefore, it must be assumed that the change is in the mineral phases ($< 1\%$), which are those having an important role in lanthanide concentration (Kerr & Rafuse, 2012). Thus, the excess of Dy and HREE in geologic materials might be a result of the presence of minerals such as thoriteite, with the formula (Sc, Y)Si$_2$O$_7$, which can show detectable concentrations of Dy, Ho, Er, Tm, Yb and Lu (Guastoni et al., 2012), or xenotime, with the formula (HREE, Y)PO$_4$. However, verification of this would be beyond the scope of the present study.

The chondrite-normalized profiles (Figure 2a) always had values > 1 (i.e. larger quantities than in the reference meteorite), a common tendency in soil materials (Hu et al., 2006). Figure 2(a) also indicates a pronounced relative abundance of LREE, shown by a steep slope that flattens out in such a way that after Ho (region of the HREE) it is almost horizontal. The P1 horizons, with more lanthanides, occupy the highest positions on the graph and the 4C2 horizon of P4 is V-shaped because of its large Dy and HREE concentrations.

No notable Ce/Ce* anomaly was detectable (Figure 2a, Table 3), with values very close to unity (all horizons between 0.93 and 1.04). The mean values of Ce/Ce* per profile increased with soil age, probably as a result of alteration processes in the soil material (Huang & Gong, 2001). In the present study, the alteration could be related to decarbonation of the fine sand (decrease in calcite and dolomite content through leaching) (Table 1), as shown by the moderate negative correlation in fine sand between Ce/Ce* and the sum of calcite + dolomite, % ($r = -0.530, n = 22, P < 0.01$), which accords with the results of Wen et al. (2014), in their case with $r = -0.403$ and $P < 0.01$.

According to its lanthanides, the fine sand fraction has evolved geochemically rather than being inert.

Lanthanides in the clay fraction and clay free forms

In the clay fraction, the order of abundance of $\Sigma\text{Ln}$ (mean values per profile in mg kg$^{-1}$) is: $\text{P3} > \text{P2} > \text{P4} > \text{P1} > \text{P5} > \text{PM}$ (Table 3), with no obvious trend regarding age or when compared with the fine sand fraction (Table 3). Aide & Smith-Aide (2003) and Marques et al. (2011) reported that the lanthanides are concentrated in the fine fractions, < 50 µm (silt and clay); in the present study, this was not clear in P1 and P5. This might be a result of the differences in phyllosilicate content because these were always larger in the clay (Table 1), and in P1 and P5 this would suggest searching for the presence of lanthanide-rich minerals (e.g. zircon) in fine sand; again, this is beyond the scope of the present study. Moreover, in the clay fraction, as occurred in the fine sand, there was a relation between $\Sigma\text{Ln}$ and phyllosilicates ($n = 35, r = 0.566, P < 0.001$). Considering the complete population (clay + fine sand), this correlation was not significant.

The clay of the pre-Holocene soils (P1, P2 and P3) contained more $\Sigma\text{HREE}$ than that of two of the Holocene soils (P4 and P5) and PM. Furthermore, the clay of these pre-Holocene soils also had more $\Sigma\text{HREE}$ than the corresponding fine sand (Table 3). The clay free forms ($\text{FF}_{\text{clay-CDB}}$ and $\text{FF}_{\text{clay-Ox}}$) generally contained fewer lanthanides ($\Sigma\text{Ln}$) than the fine sand and clay fractions (Table 3). However, calculation of $\Sigma\text{Ln}$ in $\text{FF}_{\text{clay-CDB}},$ assuming that all proceed from the mineral phases that constitute the free forms (in $\text{FF}_{\text{clay-CDB}}$ it was mainly goethite, haematite and poorly crystalline forms of Fe; in $\text{FF}_{\text{clay-Ox}}$ it was poorly crystalline iron, mostly ferrihydrite; Martín-García et al., 2016), provided striking new evidence of REE accumulation in iron free forms. Thus, $\text{FF}_{\text{clay-CDB}}$ of P1, with $\Sigma\text{Ln}$ of 39.82 mg kg$^{-1}$ attributable to 5.61% of $\Sigma\text{Ln}$ ($\text{Fe}_{\text{Ox}} + \text{Al}_{\text{Ox}} + \text{TiO}_2$; Table 1), suggests that iron (hydr)oxides ($\text{FF}_{\text{clay-CDB}}$) had $\Sigma\text{Ln}$ of 709.8 mg kg$^{-1}$. When the calculation was carried out with PM (1.06% $\text{FF}_{\text{clay-CDB}}$ ($\text{Fe}_{\text{Ox}} + \text{Al}_{\text{Ox}} + \text{TiO}_2$; Table 1) and 9.60 mg kg$^{-1}$ of $\Sigma\text{Ln}$) the goethite + haematite had 905.7 mg kg$^{-1}$. These values of $\Sigma\text{Ln}$ can be attributed to the special characteristics of these iron (hydr)oxides: small particle size and neofomed in the soil, absorbing Ln at their surface, which might even have been buried during the growth of the iron (hydr)oxide.
Table 2 Lanthanide content (mg kg\(^{-1}\)) in the soil fine sand fraction (50–250 \(\mu\)m)

|     | La  | Ce  | Pr  | Nd  | Sm  | Eu  | Gd  | Tb  | Dy  | Ho  | Er  | Tm  | Yb  | Lu  |
|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| P1  | Ap  | 24.93 | 53.69 | 6.37 | 23.03 | 4.14 | 0.66 | 2.92 | 0.35 | 1.87 | 0.32 | 0.97 | 0.14 | 0.93 | 0.15 |
| Bt  | 29.55 | 64.30 | 7.58 | 28.09 | 5.29 | 0.93 | 4.03 | 0.52 | 2.97 | 0.51 | 1.49 | 0.21 | 1.50 | 0.22 |
| Btg2| 31.78 | 66.50 | 7.97 | 29.82 | 5.66 | 1.05 | 4.22 | 0.53 | 3.05 | 0.53 | 1.56 | 0.23 | 1.56 | 0.22 |
| 2Btg3| 26.21 | 54.91 | 6.69 | 25.06 | 4.91 | 0.95 | 3.51 | 0.42 | 2.37 | 0.40 | 1.29 | 0.17 | 1.29 | 0.19 |
| P2  | Ap  | 10.79 | 21.59 | 2.51 | 9.08 | 1.66 | 0.34 | 1.13 | 0.21 | 1.49 | 0.21 | 1.50 | 0.21 | 1.50 | 0.22 |
| Btg1| 18.82 | 37.44 | 4.66 | 17.06 | 3.18 | 0.64 | 2.53 | 0.34 | 1.95 | 0.38 | 1.05 | 0.15 | 0.99 | 0.15 |
| Btg2| 17.09 | 32.75 | 3.73 | 13.26 | 2.35 | 0.50 | 1.67 | 0.21 | 1.23 | 0.23 | 0.67 | 0.11 | 0.68 | 0.10 |
| Mean| 25.85 | 48.96 | 6.04 | 22.56 | 4.28 | 0.80 | 3.20 | 0.40 | 2.25 | 0.46 | 1.19 | 0.17 | 1.09 | 0.18 |
| P3  | Ap  | 11.97 | 22.72 | 2.96 | 10.72 | 2.06 | 0.37 | 1.47 | 0.19 | 1.12 | 0.21 | 0.63 | 0.09 | 0.59 | 0.09 |
| Btg1| 18.01 | 35.02 | 4.41 | 15.35 | 3.73 | 2.83 | 1.13 | 0.56 | 0.20 | 2.08 | 0.92 | 1.51 | 0.66 | 0.29 | 0.35 |
| Btg2| 17.66 | 35.20 | 4.20 | 15.35 | 3.73 | 2.83 | 1.13 | 0.56 | 0.20 | 2.08 | 0.92 | 1.51 | 0.66 | 0.29 | 0.35 |
| Mean| 18.01 | 35.78 | 4.41 | 15.85 | 3.35 | 3.05 | 0.64 | 0.46 | 0.05 | 2.19 | 0.52 | 1.76 | 0.56 | 0.34 | 0.11 |
| P4  | Ap  | 11.21 | 21.74 | 2.80 | 10.43 | 2.10 | 0.45 | 1.63 | 0.22 | 1.34 | 0.26 | 0.78 | 0.11 | 0.65 | 0.10 |
| Btg1| 12.53 | 24.01 | 3.06 | 11.32 | 2.23 | 0.47 | 1.76 | 0.24 | 1.47 | 0.29 | 0.84 | 0.12 | 0.71 | 0.11 |
| Btg2| 16.78 | 34.21 | 4.07 | 15.25 | 2.99 | 0.58 | 2.54 | 0.34 | 2.03 | 0.39 | 1.17 | 0.19 | 1.11 | 0.17 |
| Mean| 18.01 | 35.78 | 4.41 | 15.85 | 3.35 | 3.05 | 0.64 | 0.46 | 0.05 | 2.19 | 0.52 | 1.76 | 0.56 | 0.34 | 0.11 |
| P5  | Ap  | 11.21 | 21.74 | 2.80 | 10.43 | 2.10 | 0.45 | 1.63 | 0.22 | 1.34 | 0.26 | 0.78 | 0.11 | 0.65 | 0.10 |
| Btg1| 12.53 | 24.01 | 3.06 | 11.32 | 2.23 | 0.47 | 1.76 | 0.24 | 1.47 | 0.29 | 0.84 | 0.12 | 0.71 | 0.11 |
| Btg2| 16.78 | 34.21 | 4.07 | 15.25 | 2.99 | 0.58 | 2.54 | 0.34 | 2.03 | 0.39 | 1.17 | 0.19 | 1.11 | 0.17 |
| Mean| 18.01 | 35.78 | 4.41 | 15.85 | 3.35 | 3.05 | 0.64 | 0.46 | 0.05 | 2.19 | 0.52 | 1.76 | 0.56 | 0.34 | 0.11 |

a Weighted to horizon thickness (standard deviation in parentheses).
This proves that iron (hydr)oxides act as lanthanide scavengers. Our values were small considering that Onac et al. (1997) reported Σ(La, Ce, Sm, Nd) greater than 2000 mg kg\(^{-1}\) in coatings of ferromanganese (hydr)oxides.

The 2ΣLn in the clay free forms (FF\(_{\text{clay-CDB}}\) and FF\(_{\text{clay-Ox}}\)) tended to increase with soil age because they were more abundant in pre-Holocene soils than in Holocene soils and PM (Table 3).

The chondrite-normalized patterns (Figure 2b) showed that in most cases the clay was within the range of concentrations of fine sand. The profiles of FF\(_{\text{clay-CDB}}\) (Figure 2c) differentiate clearly between the pre-Holocene soils (P1, P2, P3) and the Holocene soils (P4, P5) and PM, which had smaller concentrations. The ratio HREE\(_N\)/LREE\(_N\) in the clay fraction (Table 3) was greater than in the fine sand (except in P4). Laveuf & Cornu (2009) stated that during pedogenesis the LREE are less readily complexed by fluids than the HREE and that the latter accumulate in alteration products such as phyllosilicates, which are more abundant in the clays than in the fine sand. Furthermore, the HREE\(_N\)/LREE\(_N\) index was greater in FF\(_{\text{clay-CDB}}\) and FF\(_{\text{clay-Ox}}\) (neoformed iron (hydr)oxides) than in fine sand or clay, which was in accord with Pédro et al. (2015), who reported that the iron (hydr)oxides precipitated during alteration have a greater affinity for HREE than for LREE. This all suggests fractionation of the Ln by granulometric fractions (and mineralogy), with the HREE being concentrated in the clay, FF\(_{\text{clay-CDB}}\) and FF\(_{\text{clay-Ox}}\).

The values of the Ce/Ce\(_N\) anomaly of the clay fraction (0.94–1.14) (Table 3, Figure 2a) were also similar to those of the fine sand. In FF\(_{\text{clay-CDB}}\) all these values were positive (1.03–1.62), indicating a relative accumulation of Ce in the iron (hydr)oxides also reported by Pédro et al. (2015); in FF\(_{\text{clay-Ox}}\) the range was wider (0.86–2.22) and erratic again.

### Behaviour of lanthanides in relation to soil horizon evolution and time

The lanthanide concentrations exhibited very different behaviours in the fine sand and clay fractions with regard to the morphological evolution of the soil horizons, measured with the horizon development index (HDI) (Harden, 1982) (Table 4). Positive linear correlations with \(P < 0.01\) were typical of the clay fraction, whereas...
Figure 2 Chondrite-normalized concentrations of lanthanides (logarithmic scale) in: (a) the soil fine sand fraction (50–250 μm) (all horizons; this study), (b) the soil clay fraction (<2 μm) (mean profile, this study), (c) free forms from the soil clay fraction (mean profile, this study) extracted with citrate-dithionite-bicarbonate (FF\textsubscript{clay-CDB}), (d) free forms from the soil clay fraction (mean profile, this study) extracted with oxalate (FF\textsubscript{clay-Ox}), (e) acid igneous and magmatic-like rocks from the Guadalquivir catchment (Larrea \textit{et al.}, 1992, 1994, 1995; Carracedo \textit{et al.}, 1997; Pascual \textit{et al.}, 2008), (f) alkaline igneous rocks from the Guadalquivir catchment (Larrea \textit{et al.}, 1995; Pin \textit{et al.}, 2002), (g) sedimentary rocks from the Guadalquivir catchment (Martínez-Ruiz, 1994; Jiménez-Espinosa \textit{et al.}, 2016), (h) metasedimentary rocks from the Guadalquivir catchment (Torres-Ruiz \textit{et al.}, 2003) and (i) Sahara–Sahel materials (Moreno \textit{et al.}, 2006) and Spanish topsoil (Locutura \textit{et al.}, 2012). The shaded area (b to i) and the area with horizontal lines (c to i) enclose the upper and lower margins of the mean values per profile of the fine sand and clays (a and b).
there was no significant correlation with the fine sand. Thus, lanthanide concentration in clay increases with horizon evolution, particularly in HREE, which are those with the strongest correlations (P < 0.001; r = 0.656, 0.705, 0.727 and 0.656 for Tm, Yb, Lu and ΣHREE, respectively). The clay free forms FF\textsubscript{clay-CDB} showed the same behaviour as the clay fraction, with the correlations being even more significant (P < 0.001), possibly because of the previously mentioned role of iron (hydr)oxides (goethite and haematite, principal constituents of the FF\textsubscript{clay-CDB}) as scavengers of the lanthanides liberated during alteration of the soil minerals. The ratio Ce/ΣLn (Pédrot \textit{et al.}, 2015) in FF\textsubscript{clay-CDB} was correlated (P < 0.05) with HDI (r = 0.416; n = 35), suggesting the relative enrichment of Ce in FF\textsubscript{clay-CDB} in the most morphologically evolved horizons.

Evidence has already been provided to illustrate the dependence of the lanthanides in the present study (properties ΣLn, ΣLREE, ΣHREE, Ce/Ce\textsuperscript{*}, MREE\textsubscript{N}/LREE\textsubscript{N} and HREE\textsubscript{N}/LREE\textsubscript{N}) on age groups of soils: pre-Holocene (P1, P2 and P3) and Holocene (P4, P5 and PM). To quantify these relations better, we calculated the correlation matrix of lanthanide concentration with soil age (Table 5). The behaviour was different: the fine sand showed a linear relation with time \((y = ax + b)\) and a quadratic relation with time \((y = ax^2 + bx + c)\) in LREE and part of MREE (La to Gd), and ΣLn, whereas the clay fraction was fitted well by logarithmic functions \((y = a\ln x + b)\) in HREE and another part of MREE (Tb to Lu) and ΣHREE. For the fine sand, this suggests that the concentrations of lanthanides from La to Gd did not attain a stable state (identified by the logarithmic model). On the other hand, the concentrations in clay of lanthanides from Tb to Lu did attain a stable state. Furthermore, the chronofunctions with strong correlations spanned from La to Gd in fine sand and were present from Gd (not included) in the clay, suggesting the ‘gadolinium breaking effect’ (Chi \textit{et al.}, 2006). The latter is the infringement of the monotonic change of properties of lanthanide compounds according to the atomic number, attributed to a variation in the electron configuration of the lanthanides occurring in the gadolinium.

When the problem of soil age is considered from the point of view of LREE and HREE fractionation, estimated by the indices HREE\textsubscript{N}/LREE\textsubscript{N} and La\textsubscript{N}/Yb\textsubscript{N} (Table 5), it can appear that this process depends markedly on age, with the HREE concentration increasing with time, for example in soil clay:

\[
\text{La} / \text{Yb} = -5.2 \times 10^{-3} \times \text{age (ka)} + 10.39; \quad n = 6; R^2 = 0.870; P < 0.01.
\]

However, a stable state was not attained for either fine sand or clay because the correlations never fitted the logarithmic functions.

### Relations between lanthanide quantities

Although concentrations of elements of the lanthanide series were different in all the fractions analysed (Tables 2 and 3, Figure 2a–d), many changes in a parallel way in the samples showing a strong positive collinearity (large r\textsubscript{CLC}, where r\textsubscript{CLC} are the correlation coefficients between ‘couples of lanthanide concentrations’) (Figure 3).

In the fine sand, the r\textsubscript{CLC} varied between 0.998 (P < 0.001) and 0.477 (P < 0.001). In the clay fractions (total clay, FF\textsubscript{clay-CDB} and FF\textsubscript{clay-Ox}) r\textsubscript{CLC} was even larger, ranging from 0.998 to 0.896 (both with P < 0.001). Salminen (2005) stated that in European soils ‘all REE in soil are strongly correlated among themselves, with all correlation coefficients higher than 0.7’. However, in the present study, more than a third of the r\textsubscript{CLC} of the fine sand were below 0.7.

Furthermore, r\textsubscript{CLC} had (Figure 3) the largest values between couples of adjacent lanthanides in the periodic table (e.g. \textit{go}Nd vs. \textit{go}Pr; 0.998 in fine sand, > 0.945 in clay, FF\textsubscript{clay-CDB} or FF\textsubscript{clay-Ox}). This fact was previously reported for igneous materials (Kerr & Rafuse, 2012) and shales (Noack \textit{et al.}, 2015), but never demonstrated for soil.

In addition, r\textsubscript{CLC} became progressively weaker with increasing separation between the elements in the periodic table (e.g. in fine sand, r\textsubscript{CLC} of 57La with the adjacent 58Ce was 0.997, with 66Dy, 0.622 and with 71Lu, at the other extreme, 0.524). This behaviour has never been described previously in geologic materials, and is related to chemical periodicity (adjacent Ln have similar ionic radii, atomic mass and a +3 valence, and will behave similarly in the crystal structure of the minerals). This behaviour of r\textsubscript{CLC} enables a bivariate diagram to be produced (Figure 4) showing the r\textsubscript{CLC} of any couple of lanthanides against their differences in standard atomic weight (\(\Delta A_i\)), with a negative collinearity (P < 0.001). The \(A_i\) (expressed in decimals) was used because it differentiates more

\[\text{Table 4 Matrix of linear correlations (Pearson’s } r\text{) between lanthanides content and horizon development index (HDI)}^a\]

| Lanthanide content | Soil fine sand\(^b\) (n = 24) | Soil clay\(^a\) (n = 35) | FF\textsubscript{clay-CDB}\(^a\) (n = 35) | FF\textsubscript{clay-Ox}\(^a\) (n = 35) |
|-------------------|-----------------|-----------------|-----------------|-----------------|
| La                | 0.314           | 0.557           | 0.718           | 0.367           |
| Ce                | 0.317           | 0.579           | 0.765           | 0.483           |
| Pr                | 0.297           | 0.565           | 0.745           | 0.442           |
| Nd                | 0.257           | 0.551           | 0.746           | 0.409           |
| Sm                | 0.192           | 0.572           | 0.766           | 0.503           |
| Eu                | 0.031           | 0.526           | 0.745           | 0.467           |
| Gd                | 0.020           | 0.567           | 0.741           | 0.516           |
| Tb                | −0.077          | 0.564           | 0.746           | 0.454           |
| Dy                | −0.203          | 0.589           | 0.745           | 0.527           |
| Ho                | −0.227          | 0.594           | 0.740           | 0.373           |
| Er                | −0.267          | 0.614           | 0.730           | 0.403           |
| Tm                | −0.227          | 0.656           | 0.724           | 0.431           |
| Yb                | −0.213          | 0.705           | 0.746           | 0.484           |
| Lu                | −0.219          | 0.727           | 0.741           | 0.517           |
| ΣLn               | 0.252           | 0.575           | 0.762           | 0.537           |
| ΣLREE             | 0.304           | 0.569           | 0.761           | 0.461           |
| ΣMREE             | 0.007           | 0.571           | 0.753           | 0.519           |
| ΣHREE             | −0.240          | 0.656           | 0.739           | 0.454           |

Statistical significance: P < 0.05; P < 0.01; P < 0.001. 

\(^a\)HDI and lanthanides values from Martín-García \textit{et al.} (2016).

\(^b\)Lanthanides values from Table 2. 

FF\textsubscript{clay-CDB}: citrate-dithionite-bicarbonate extractable free forms in clay fraction; FF\textsubscript{clay-Ox}: ammonium oxalate extractable free forms in clay fraction.
Figure 3 Matrix of Pearson correlation coefficients of couples of lanthanide concentrations (r_{CLC}) in the Mediterranean soils studied: (a) the soil fine sand fraction (50–250 μm), (b) the soil clay fraction (<2 μm), (c) free forms extracted from the soil clay fraction with citrate-dithionite-bicarbonate extract (FF_{clay-CDB}) and (d) free forms extracted from the soil clay fraction with oxalate (FF_{clay-Ox}).

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Table 5 Correlation ($R^2$, coefficient of determination) between lanthanide contents and geochemical ratio with soil age ($n = 6$). Selected chronofunctions (s).

| Lanthanide properties | Soil fine sand$^b$ | Soil clay$^c$ | FFclay-CDB$^{ac}$ | FFclay-Ox$^{ac}$ |
|-----------------------|-------------------|--------------|------------------|------------------|
|                       | Linear (s) | Logarithmic (ln) | Quadratic | Linear (s) | Logarithmic (ln) | Quadratic | Linear (s) | Logarithmic (ln) | Quadratic |
| La                    | 0.794      | 0.643         | 0.824      | 0.005      | 0.469         | 0.241      | 0.211      | 0.526         | 0.429     |
| Ce                    | 0.803      | 0.616         | 0.841      | 0.004      | 0.486         | 0.391      | 0.106      | 0.494         | 0.524     |
| Pr                    | 0.785      | 0.593         | 0.835      | 0.011      | 0.496         | 0.229      | 0.183      | 0.501         | 0.381     |
| Nd                    | 0.787      | 0.555         | 0.854      | 0.014      | 0.506         | 0.194      | 0.215      | 0.523         | 0.389     |
| Sm                    | 0.752      | 0.494         | 0.859      | 0.058      | 0.607         | 0.192      | 0.251      | 0.563         | 0.410     |
| Eu                    | 0.823      | 0.323         | 0.945      | 0.083      | 0.624         | 0.188      | 0.324      | 0.593         | 0.444     |
| Gd                    | 0.613      | 0.416         | 0.796      | 0.092      | 0.645         | 0.168      | 0.329      | 0.588         | 0.440     |
| Tb                    | 0.365      | 0.389         | 0.578      | 0.086      | 0.664         | 0.208      | 0.241      | 0.554         | 0.378     |
| Dy                    | 0.127      | 0.237         | 0.372      | 0.102      | 0.676         | 0.224      | 0.195      | 0.546         | 0.364     |
| Ho                    | 0.016      | 0.155         | 0.176      | 0.099      | 0.674         | 0.230      | 0.171      | 0.520         | 0.326     |
| Er                    | 0.001      | 0.094         | 0.189      | 0.153      | 0.743         | 0.300      | 0.130      | 0.490         | 0.298     |
| Tm                    | 0.000      | 0.100         | 0.134      | 0.207      | 0.764         | 0.365      | 0.122      | 0.471         | 0.314     |
| Yb                    | 0.025      | 0.154         | 0.181      | 0.314      | 0.865         | 0.493      | 0.126      | 0.491         | 0.329     |
| Lu                    | 0.010      | 0.144         | 0.142      | 0.411      | 0.893         | 0.500      | 0.163      | 0.510         | 0.364     |
| ΣLn                   | 0.762      | 0.596         | 0.819      | 0.013      | 0.523         | 0.285      | 0.165      | 0.526         | 0.446     |
| ΣLREE                  | 0.796      | 0.608         | 0.841      | 0.006      | 0.493         | 0.301      | 0.150      | 0.516         | 0.464     |
| ΣMREE                  | 0.582      | 0.438         | 0.760      | 0.080      | 0.638         | 0.191      | 0.265      | 0.570         | 0.407     |
| ΣHREE                  | 0.010      | 0.126         | 0.176      | 0.207      | 0.805         | 0.386      | 0.136      | 0.496         | 0.317     |
| HREE$_N$/LREE$_N$      | 0.324      | 0.070         | 0.462      | 0.752      | 0.068         | 0.906      | 0.293      | 0.255         | 0.830     |
| Ln$_N$/Yb$_N$          | 0.533      | 0.412         | 0.870      | 0.850      | 0.171         | 0.865      | 0.300      | 0.003         | 0.325     |

s: Selected linear chronofunctions from fine sand fraction:

- $La$ (mg kg$^{-1}$) = 0.022 × age (ka) + 14.17
- $Ce$ (mg kg$^{-1}$) = 0.050 × age (ka) + 27.75
- $Pr$ (mg kg$^{-1}$) = 0.006 × age (ka) + 3.46
- $Nd$ (mg kg$^{-1}$) = 0.021 × age (ka) + 12.80
- $Sm$ (mg kg$^{-1}$) = 0.004 × age (ka) + 2.52
- $Eu$ (mg kg$^{-1}$) = 0.001 × age (ka) + 0.47
- $ΣLn$ (mg kg$^{-1}$) = 0.107 × age (ka) + 68.15
- $ΣLREE$ (mg kg$^{-1}$) = 0.099 × age (ka) + 58.19

Statistical significance: $P < 0.05$; $P < 0.01$.

$^a$Lanthanide values from Table 1.

$^b$Soil age values from Table 2.

$^c$Lanthanide values from Table 3 and Martín-García et al. (2016).

$FF_{clay-CDB}$, citrate-dithionite-bicarbonate extractable free forms in clay fraction; $FF_{clay-Ox}$, ammonium oxalate extractable free forms in clay fraction.

precisely between couples than $Z$ (expressed in units) and is more independent of valency than effective ionic radii (IR). However, $A_i$ and $Z$ and IR are equivalent magnitudes, with strong collinearity (Table 6).

The equation of the straight line $ΔA_i$ against $r_{CLC}$ shows different values from its slope ($m$), depending on the granulometric fraction: (i) fine sand, $m = -0.0170$ and (ii) clay, $-0.0021$, $FF_{clay-CDB} -0.0015$ and $FF_{clay-Ox}, -0.0051$. Thus, $m$ becomes a granulometric differentiating characteristic.

In Figure 4(c) ($FF_{clay-CDB}$), the behaviour of $Ce$ is interesting because it shows slightly stronger correlation with the elements furthest from $A_i$ (Ce against Tb to Lu: $0.955 < r_{CLC} < 0.968$; mean = 0.963; $σ_{m-1} = 0.005$) than with those nearest (Ce against La to Gd: $0.947 < r_{CLC} < 0.960$; mean = 0.954; $σ_{m-1} = 0.006$), and is thus related better to the HREE than LREE. This is because of $FF_{clay-CDB}$ being free from forms of iron (goethite and haematite) where the process of oxidative scavenging of Ce takes place: part of the Ce$^{3+}$ adsorbed on to Fe (hydroxides oxidizes to Ce$^{4+}$, producing a preferential desorption of the remaining Ce$^{3+}$ (Bau, 1999; Pédrot et al., 2015), and the Ce$^{4+}$ accumulated in the $FF_{clay-CDB}$ behaves similarly to the HREE (Pédrot et al., 2015). Further evidence for this is the preferential fractionation of Ce and HREE in $FF_{clay-CDB}$ described in the samples. Furthermore, Figure 4(c) shows a change in tendency of the $r_{CLC}$ values in the correlations between Ce and Gd (0.951) and Ce a Tb (0.964), once again suggesting the gadolinium breaking effect (Chi et al., 2006).

Evidence for fractionation and fingerprints of provenance

The La – 5×Sm – 10×Yb triangle (Figure 5) shows the population of the fine sand and clay plotted close together as a cluster...
Figure 4 Relations between differences in atomic weight ($\Delta A_r$) and Pearson correlation coefficients of couples of lanthanide concentrations ($r_{CLC}$) in: (a) the soil fine sand fraction (50–250 $\mu$m), (b) the soil clay fraction (<2 $\mu$m), and (c) free forms extracted from the soil clay fraction with citrate-dithionite-bicarbonate (FFclay-CDB). The black circles represent correlations with Ce and (d) free forms extracted from the soil clay fraction with oxalate (FFclay-Ox). In all cases: $n=91$; $P<0.001$.

Table 6 Chemical and physical properties of lanthanides

| Name         | Chemical symbol | Atomic number (Z)$^a$ | $A_r$/mol$^b$ | Valency$^c$ | Effective ionic radii ($IR$/pm)$^d$ |
|--------------|-----------------|-----------------------|---------------|-------------|----------------------------------|
| Lanthanum    | La              | 57                    | 138.9         | 3           | 116.0                           |
| Cerium       | Ce              | 58                    | 140.1         | 3, 4        | 114.3                           |
| Praseodymium | Pr              | 59                    | 140.9         | 3           | 112.6                           |
| Neodymium    | Nd              | 60                    | 144.2         | 3           | 110.9                           |
| Promethium   | Pm              | 61                    | –             | –           | –                               |
| Samarium     | Sm              | 62                    | 150.4         | 2, 3        | 107.9                           |
| Europium     | Eu              | 63                    | 152.0         | 2, 3        | 106.6                           |
| Gadolinium   | Gd              | 64                    | 157.3         | 3           | 105.3                           |
| Terbium      | Tb              | 65                    | 158.9         | 3, 4        | 104.0                           |
| Dysprosium   | Dy              | 66                    | 162.5         | 3           | 102.7                           |
| Holmium      | Ho              | 67                    | 164.9         | 3           | 101.5                           |
| Erbium       | Er              | 68                    | 167.3         | 3           | 100.4                           |
| Thulium      | Tm              | 69                    | 168.9         | 3           | 99.4                            |
| Ytterbium    | Yb              | 70                    | 173.1         | 2, 3        | 98.5                            |
| Lutetium     | Lu              | 71                    | 175.0         | 3           | 97.7                            |

$^a$There is strong collinearity between $A_r$ and Z and IR: $Z = 0.3640 \cdot A_r + 7.1654$, $r = 0.997$; $IR = -0.4787 \cdot A_r + 180.6$, $r = 0.991$ ($n=14$, $P<0.001$). In the case of IR, the equivalence is a result of the periodic rule known as ‘lanthanide contraction’.

$^b$The chondrite-normalized profiles of lanthanide concentration (Figure 2) also appear to show the genetic relation ‘fine-sand with clay’ and ‘fine-sand + clay with parent rock’. Fine sand and clay (Figure 2a,b) have profiles that are close together and the profiles of igneous (Figure 2e,f), sedimentary (Figure 2g) and metasedimentary (Figure 2h) rocks are included in the shaded area representing our samples.

Similarly, mean values of fine sand and clay of $\Sigma$(La, Ce, Nd, Sm, Eu, Yb, Lu) (only these seven Ln were analysed in all the studies on the geological materials of the Guadalquivir basin) (Figure 6) are within the mean values of the rocks of the Guadalquivir catchment area, although closer in value to those of the sedimentary and alkaline igneous rocks than to the others. The ratio of $La_N/Yb_N$ (Figure 6) further emphasizes this tendency; the values for our samples form a cluster with a range of 7.2–15.7, within the range of the geological materials of the source area (range 3.3–20.4). The fine sand (range 9.8–15.7) had larger values than the clays (range 7.2–11.0) and would be closer to acidic igneous than sedimentary rocks. Notwithstanding this difference between fine sand and clay, it seems more likely that the fractionation of the lanthanides, rather than different source areas for the two fractions, resulted in the fine sand having a larger concentration of La than Yb. The $\Sigma$(La, Ce, Nd, Sm, Eu, Yb, Lu) (Figure 6) also shows that our samples have smaller values than the Sahara–Sahel materials or even the Spanish soils (both possible aeolian source areas). In contrast, $La_N/Yb_N$ values do not explain the differences between our samples and the Sahara–Sahel materials or the Spanish soils as they are all between 6.9 and 14.3 (except clay of P1 and fine sand of P2, which are close).
The ratio of Sm$_N$/Yb$_N$ functions in a similar way to La$_N$/Yb$_N$ (Figure 7). The fine sand had larger values than the clay. When La$_N$/Yb$_N$ was plotted against Sm$_N$/Yb$_N$ the points were aligned as expected because they have a common denominator, and La and Sm correlate well with each other (Figure 3). However, three families of points can be defined to which linear functions fitted well: (i) igneous rocks, (ii) sedimentary and metamorphic rocks (metasedimentary) and (iii) our fine sand and clay samples. The linear functions fitted to these families of points suggest a lithological relation. Furthermore, the family of points for fine sand...
Lanthanides in a Mediterranean soil chronosequence

Figure 7 Plot of LaN/YbN against SmN/YbN for soil fine sand and clay fractions (mean profile values) and all values for rocks from the Guadalquivir catchment (igneous, sedimentary and metasedimentary rocks; Larrea et al., 1992, 1994, 1995; Martínez-Ruiz, 1994; Carracedo et al., 1997; Pin et al., 2002; Pascual et al., 2008; Jiménez-Espinosa et al., 2016). Symbols used are the same as in Figure 5; the numbers in the circles correspond to soil profile numbers, and P corresponds to point bar sediment (PM). The lines (and adjacent equations) correspond to the relations for the population of samples of fine sand and clay fractions (continuous), the igneous rocks (dots) and the sedimentary and metasedimentary rocks (dots and dashes).

Figure 8 The Eu/Eu* values (mean and, in some cases, standard deviation) for soil fine sand and clay fractions (mean profile) and rocks from the Guadalquivir catchment (igneous, sedimentary and metasedimentary rocks), Sahara–Sahel materials and Spanish topsoil.

sand and clay is between the lines of the igneous and sedimentary + metamorphic rocks, indicating that both materials could act as parent materials. However, in this case, in contrast to Σ(La, Ce, Nd, Sm, Eu, Yb, Lu), the straight line is closer to the igneous rocks, including its slope value.

The Eu/Eu* anomaly had similar values for fine sand and clay (Table 3, Figure 8); in fact, the correlation between Eu/Eu*_{fine sand} and Eu/Eu*_{clay} was positive and significant ($r = 0.560$; $n = 24$; $P < 0.01$). Furthermore, the anomaly was always negative ($< 1$), a characteristic shared with the materials from the possible source areas (including aeolian) (Figure 8). The relative homogeneity of values between our soil and parent rocks (Figure 8) indicated that this geochemical ratio can be inherited from the sediment source and the weathering processes do not seem to have changed it (Mongelli et al., 2014).

So far, we have not confirmed a genetic relation between our soil and the aeolian contributions from the Sahara–Sahel or Spanish soils (Figure 6). We focus now on the surface horizons (Ap) of our soils and the point bar sediment (PM), which, because they occupy the upper levels of the profile, are more likely to receive these contributions (Figure 9). Our samples form a group, although differentiated between fine sand and clay because of fractionation of the lanthanides (between LREE, concentrated in fine sand, and HREE, relatively concentrated in soil clay). Outside the group, the Sahara–Sahel materials occur at the lower edge of Figure 9 because these are richer in Yb and the genetic relation cannot be confirmed. However, the spot for Spanish soils was included in the cluster of our soil material because surrounding Spanish soils could have provided materials to the Guadalquivir catchment. Nevertheless, the problem is complex because in the Ap the lanthanide concentration

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Figure 9 Plot of (a) Ce/Ce* against SmN/YbN and (b) LaN/YbN versus SmN/YbN for soil fine sand and clay fractions from Ap horizons (the numbers in the circles correspond to soil profile numbers) and PM (the letter P in the circle corresponds to point bar sediment PM) and Sahara–Sahel materials (Moreno et al., 2006), and Spanish topsoil (Locutura et al., 2012).

of fine sand decreased (Table 2), whereas it increased in clay (Martín-García et al., 2016).

Conclusions

The free forms of clay (FF\textsubscript{clay-CDB} and FF\textsubscript{clay-Ox}) showed a relative accumulation of lanthanides, with values > 700 mg kg\textsuperscript{-1} (with respect to the mass of free form), thus demonstrating their role as scavengers of lanthanides.

Soil age (pre-Holocene versus Holocene) affects the behaviour of the lanthanides in all the fractions studied: in the fine sand $\Sigma$LREE concentration increased in the oldest soil, as did $\Sigma$HREE in the clay and its free forms. Furthermore, chronofunctions were formulated between lanthanide concentration and soil age from La to Gd in fine sand and from Tb to Lu in clay. These chronofunction results tended to support the granulometric fractionation cited, and, indirectly, provided data to confirm the presence of a ‘gadolinium breaking effect’.

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