



# Occurrence and environmental constraints of gray monazite in red soils from the Campo de Montiel area (SW Ciudad Real province, south central Spain)

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## Abstract

Monazite ((Ce, La, Nd, Th) PO<sub>4</sub>) is a rare and strategic mineral that occurs naturally as an accessory and minor mineral in diverse igneous and metamorphic rocks. This mineral does not frequently form mineable ore deposits and it has different typologies, including those formed by endogenous processes (generally “yellow monazite” mineralizations) and those formed by exogenous processes (“gray monazite” mineralizations). The mineral is an important ore of Rare Earth Elements (REEs), which have been identified by the European Union as critical raw materials. Monazite can be considered a weathering-resistant mineral, and the mobility of the REE and associated elements is low. The study reported here concerns a mineralogical and geochemical assessment of the occurrence and risks associated with the presence of concentrations of monazite in a typical, well-developed, and representative red Mediterranean soil, in order to establish the associated risk with their future mining. The results confirmed that monazite ore is particularly poor in radioactive elements, and it is concentrated in the most surficial soil horizons. The chemical mobility of REEs present in the soil, as assessed by selective extraction with ammonium acetate in acidic media, follows the order Y > Dy > U > Tb > Gd > Eu > Sm > La > Th > Ce. The mobility of REEs contained in monazite proved to be higher than that of the REE compounds in the upper horizons of the soil profile suggesting the immobilization in other REE-containing minerals, while light REEs show lower mobility rates than heavy REEs, due to an immobilization of LREE by sorption with iron oxy-hydroxides. Further studies are required in order to obtain better speciation data for REEs in soils aimed to identify soluble and insoluble compounds.

**Keywords** Monazite · REE · Red Mediterranean soils · Selective extraction · Central Spain

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## Introduction

Rare Earth Elements (REEs) are a group of chemical elements with common characteristics due to their similar electronic configuration. The term is approximately equivalent to “lanthanides,” since the term REE includes this group of chemical elements plus Y and Sc. Some actinides (U and Th) can also be considered forming part of this group since they often appear together in nature. Despite the chemical similarities, each of these elements has unique applications in modern industry, such as aerospace and defense, nuclear, automobile, high-temperature superconductors, fiberoptic cables, computers, and mobile phones, as well as in steel and in pigments for ceramics (Du and Graedel 2013). These wide-ranging applications make REEs of great economic interest. Furthermore, given the economic interest, the low production rates worldwide, the high importance to the EU economy, and the high

supply risk, these elements have been defined by the European Union as critical raw materials (CRMs) (EU 2017).

Monazite ((Ce, La, Nd, Th) PO<sub>4</sub>) is one of only two REE ores (together with bastnaesite, a carbonate, Jordens et al. 2013). It is a rare and strategic mineral that occurs naturally as an accessory and minor constituent in igneous and metamorphic rocks such as granite, pegmatite, schist, shales, and gneiss. In addition, this ore can only be found in two types of profitable ore deposits: (i) a variety of hydrothermal deposits characterized by the occurrence of the so-called yellow monazite and (ii) concentrations of detrital nodules of millimeter size (“gray monazite,” as defined by Donnot et al. 1973). These latter deposits are associated primarily with Ordovician shales, with secondary concentrations produced through the supergene processes in recent sediments formed over the aforementioned shales. Yellow monazite appears as the main REE ore in the huge Bayan Obo (China) deposit, which was formed due to metasomatism of carbonatites in a subduction-related environment (Ling et al. 2013), as well as in breccia pipes associated with Mesoproterozoic volcanic-plutonic rocks of the St. Francois Mountains in southeastern Missouri, USA (Aleinikoff et al. 2016). The yellow monazite described by Aleinikoff et al. (2016) contains U and Th concentrations in the range 5000–12,000 and 100–3000 ng g<sup>-1</sup>, respectively, with exceptional values reaching more than 220,000 and 5400 ng g<sup>-1</sup>, respectively. Gray monazite was discovered as detritic grains of this mineral and is abundant in stream sediments in the context of European Hercynian Massifs (Donnot et al. 1973; Burnotte et al. 1989), as well as in the Spanish Massif (Vergara 2019). Indeed, a number of authors have already studied these monazite detrital deposits (Overstreet 1971; Donnot et al. 1973; Rosenblum 1974; among others). In general, these authors interpret the concentrations found as being a consequence of the previous release of the nodules from other rocks that contain the elements in question, followed by their detrital accumulation. However, the ultimate origin of these materials, most probably as nodules disseminated in the aforementioned Ordovician shales, has not yet been investigated, and it is therefore difficult to interpret the situation. Salgueiro et al. (2020) identified the criteria to interpret these nodules as being synsedimentary, thus suggesting an origin linked to direct precipitation from seawater.

The studied concentrations of monazite are of interest for mining, particularly given the CRM status of these elements. However, there are significant social concerns about the exploitation of these resources, in particular regarding the possibility of mobilization of radioactive elements (U, Th) contained in the monazite. On the other hand, monazite can be considered a weathering-resistant mineral in which the mobility of the REEs and associated elements is low; only under severe conditions, such as in the context of sulfide-mining areas, does the mobility of REEs increase with respect to their generally accepted low mobility (Fernández-Caliani et al. 2009; Pérez-

López et al. 2015; Edahbi et al. 2018). Lintjewas and Setiawan (2017) considered the question of the mobilization of these elements from minerals under weathering conditions and they noted that, as supported by Cocker (2012), during pedogenesis a relative enrichment of REEs in the weathering products in relation to bedrock is pronounced in horizon B. Jin et al. (2017) studied the mobility of these elements during the weathering of shales and reported different degrees of mobility depending on the climatic conditions as well as mineralogical differences and different organic matter contents. The mobility of REEs in the environment depends on the parent material, as well as on geochemical and biological processes (Zhang et al. 2001; Hu et al. 2006; Cidu et al. 2013). Mineral weathering can be considered an important source of elements for the soils (Price 1995), but REEs can still be incorporated in secondary minerals such as smectite, sericite, kaolinite, alunite, epidote, gypsum, or anhydrite, and these REEs remain immobilized, even after the weathering of primary minerals (Palacios et al. 1986; Fulignati et al. 1999; Gnandi and Tobschall 2003; Moldoveanu and Papangelakis 2012). Jones (1997) and Cao et al. (2001) described higher mobility rates for La, Ce, Gd, and Y with low pH and redox potential.

The ecotoxicology of REEs and associated elements has been reviewed by González et al. (2014, 2015). In particular, Gonzalez et al. (2014) discussed concerns about these elements in terrestrial environments, and they concluded that conspicuous effects have not been described in terms of the effects that REEs have on living beings, although the subject still requires more detailed study. Gonzalez et al. (2015) studied the effects that these elements have on aquatic organisms, and they concluded that any negative effects require concentrations in the media that can only be reached in hotspots associated with industrial processing or usage. Another important question to bear in mind is the contents of radioactive elements (U, Th) in REE minerals (Weng et al. 2014). In this respect, García-Tenorio et al. (2018) assessed the radiological impact of the presence of monazite as well as on the mining operations to be carried out in this area. It was concluded that the monazite deposit studied did not have any radiological impact on the surroundings or on the public, and that activities involving the extraction of the raw material and the subsequent remediation of the mined area should be exempt from radiological regulation according to European Union legislation. However, chemical analysis of the monazite ore was not performed in that study.

The aim of the study reported here was to perform a preliminary assessment of the risks associated with the presence of concentrations of monazite in soils in formation, in the context of future mining works of these critical raw materials. This goal was achieved by considering the composition of the ore, the interactions with soil components, and, in particular, its precise contents in radioactive elements (U, Th). The mobility and availability of these REEs and associated elements contained in this mineral was also evaluated.

## Materials and methods

### Characteristics of the studied area

The area of interest is in the municipalities of Torrenueva and Torre de Juan Abad, both in the Campo de Montiel area in La Mancha region (south central Spain). From a geological point of view, this area corresponds to the southern limit of the Iberian Hercynian Massif, a Paleozoic domain characterized by the presence of metasedimentary sequences that include quartzites and shales affected by the Hercynian orogeny. This orogeny produced a relatively simple structuration of the area dominated by lax folds of kilometric scale and faults that produce short/medium lateral displacements (generally < 1 km). This regional geology conditions a characteristic Appalachian-style geomorphology with quartzitic mountain ranges up to 300–500 m. Above the base level of the valleys, and valleys excavated in the Ordovician shales formations, a general WNW-ESE trend was observed. The general study area is located in the core of a Hercynian anticline with Armorican quartzite forming the limbs of the enclosing structure, which is delimited by the higher areas of the Chiriví, Peña Parda, and Matamulas hills. Two valleys are excavated in Ordovician shales, with sporadic croppings in the area, and these have a characteristic gray color, but generally, they are overlaid with recent (Plio-Quaternary) colluvial and alluvial materials. These black shales have classically been considered the source of the monazite concentrated in the recent soils and sediments (Donnot et al. 1973; Burnotte et al. 1989, among others). The whole area that has been explored for this mineral occupies terrains with low slopes (below 5%) and they occupy a maximum extent of 1500 ha (Fig. 1), although the area of

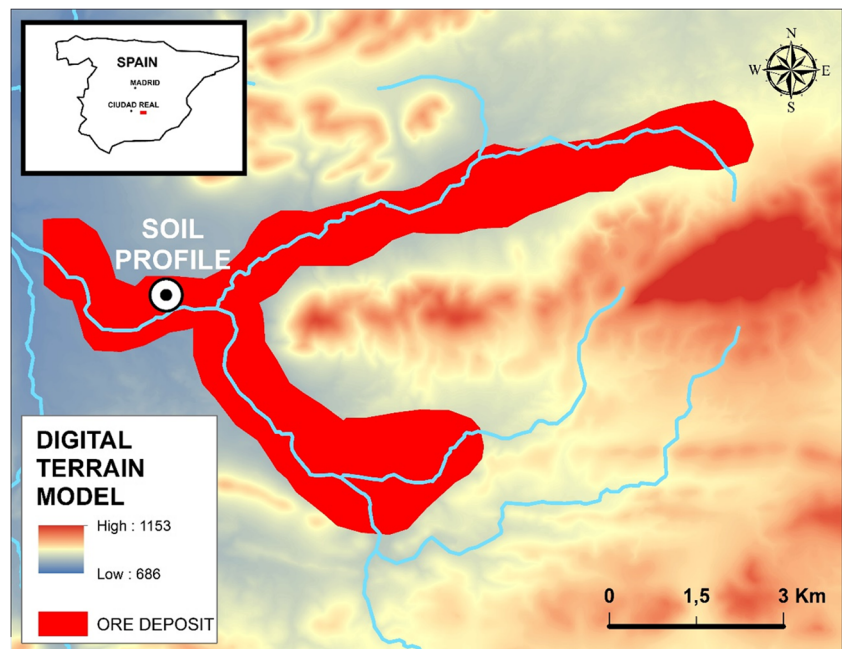
highest interest is restricted to less than 400 ha. In this area, more than 1000 soil profiles were carried out by the mining company, what has allowed the selection of a representative area for this research, as being one of intermediate-to-rich in REEs contents, as well as with a typical soil.

The regional and local climate is Mediterranean, warm and temperate, categorized as Csa by the Köppen–Geiger classification, and the average annual precipitation is 458 mm yr<sup>-1</sup> with a mean temperature of 14.7 °C (5.8 °C in winter months and 25.6 °C in summer months). The summers are usually hot and dry, winters are cold and dry, and the rainy periods are concentrated in spring and autumn.

### Pedological features

The soils that host the monazite concentrations correspond to red Mediterranean soil typology. Reifenberg (1952), Kubierna (1953), and Durand (1959) described these as relict soils, which would have developed under much more humid climates than those observed today, mostly during the late Tertiary and early Pleistocene periods. More recently, authors such as Lamouroux (1971) and Verheyne (1973) discarded these explanations and proposed that the genesis could still be active today and that old red soils are in equilibrium with the present-day prevailing Mediterranean climate. Furthermore, the question of whether red Mediterranean soil is dominant or not in the Mediterranean region has not been resolved during soil surveys; many specific soil-forming processes are related to the location (Mediterranean basin) and climate (Mediterranean type) (Yaalon 1997). Characteristically, the processes that produce this type of soil include clay illuviation and rubefaction, which occur in soils

**Fig. 1** Location of the soil profile in relation with the ore body of gray monazite



with higher evapotranspiration than water infiltration (Fedoroff and Courty 2013).

According to a preliminary report by Higuera et al. (2016), the soils described in the studied area can be classified as Alfisols and Inceptisols (Soil Survey Staff 2006), which correspond to Luvisols and Cambisols (FAO-ISRIC-ISSS 2006). In particular, the studied profile corresponds to a Typical Rhodoxeralf (Soil Survey Staff 2006) or Rhodic Luvisol (FAO-ISRIC-ISSS 2006).

### Soil characterization and sampling

The profile analyzed in this study is considered as representative of the area based on the preliminary study by Higuera et al. (2016). The soil profile was excavated with a backhoe excavator to a depth of around 1 m. For descriptive and sampling purposes, four main horizons were distinguished in the profile and these are related to differential weathering: Ap (0–15 cm) – Bt (15–75 cm) – C (75–90 cm) – R (> 90 cm). On the basis of field observations, the Ap horizon is of ocric type since it does not show the characteristics of the rest of the epipedons. The most important pedological characteristic of the studied profile is the presence of a textural B horizon of some 60 cm in thickness (15–75 cm in the profile) that has thick argillic coatings and an intense red color. In this Bt horizon, the hue is more reddish than 5YR, and the chroma is higher than 3.5, which is the characteristic of this type of soil (Bech et al. 1997). Furthermore, all of the soil profiles display hues of 2.5YR, with values between 3 and 6 and chroma values between 4 and 6. Torrent et al. (1983) and Boero and Schwertmann (1989), among others, attributed the red color of these soils to the abundance of hematite, and the preservation of the red color in deep horizons can be considered an indication of the prevalence of conditions that favor the preservation of hematite stability over long periods in these reactive sites. The C horizon appears as a chaotic mélange of strongly weathered shales with decimetric quartzite blocks, while the R horizon comprises even bigger quartzitic boulders. The limits between horizons are gradual, and the presence of moderate proportions of a gravel fraction along the profile favors good drainage conditions. The texture varies from loam to clay-loam, which has favored the development of a strong structure constituted by subangular blocks with prismatic tendency in the Bt argillic horizon.

The sampling strategy involved obtaining representative samples from the described horizons, with seven samples taken every 15 cm directly from the ditch open to recognize soil horizons: Ap1 (0–15 cm), corresponding to the Ap horizon; Bt1 (15–30 cm), corresponding to the upper part of the Bt horizon; Bt2 (30–45 cm) and Bt3 (45–60 cm), corresponding to the intermediate part of the Bt horizon; Bt4k (60–75 cm), corresponding to the lower part of the Bt horizon in transition to the C horizon; C (75–90 cm), corresponding to the C horizon;

and R (> 90 cm), corresponding to the R horizon, as represented in the bottom of the soil profile. Approximately 2 kg of soil was taken for each sample, using a gardener shovel to collect it, and washing it with deionized water between samples. These soil samples were stored in polyethylene bags, taken to the laboratory, and dried at room temperature for 15 days. The samples were then sieved to separate and discard the fraction > 2 mm; the fraction < 2 mm was disaggregated, homogenized, and split to give two aliquots of some 100 g each. One aliquot was used directly for the determination of physicochemical soil parameters and enzymatic activity; the second aliquot was ground to less than 100 µm in an automatic agate mortar Retsch RM100 for 2 min and was used to multielemental determinations by EDX-XRF.

### Analytical methods

The physicochemical parameters of the soil samples included the determination of reactivity (pH), salts contents (electrical conductivity, EC), and soil organic matter (SOM) contents. The reactivity and electrical conductivity were measured on a 1/5 soil suspension in deionized water after shaking for 60 min at 95 rpm. One hour after decantation, the measurements were made on a CRISON model GLP-22 pH meter and a Crison model GLP-32 conductivimeter, respectively. Contents of SOM were determined by the method described by Walkley and Black (1934).

Dehydrogenase activity was analyzed to characterize the activity of the soil microbial community, which is an effective indicator of soil quality changes (Kumar et al. 2013), using the same aliquot as for pH, EC, and SOM. Samples were then homogenized and stored at –20 °C to avoid altering the enzymatic activity (Peoples and Koide 2012). Dehydrogenase activity was measured spectrophotometrically according to the modified triphenyl tetrazolium chloride (TTC) method initially described by Casida et al. (1964), using a Biochrom Libra S60 spectrophotometer. Three repetitions were performed for each sample, and the results are given per gram of dry soil.

The chemical composition of individual monazite grains was analyzed by an electron microprobe technique at the laboratories of the University of Oviedo. The equipment used was a CAMECA SX-100 electron microprobe that incorporated five WDS spectrometers. In order to allow accurate measurements, a voltage of 20 kV (100 nA) was used under a 1–2-µm diameter beam. The original idea of these analyses was to determine the chronological (absolute) age of this mineral by applying the U-Th-Pb method (Montel et al. 1996; Sánchez et al. 2011; Aleinikoff et al. 2016); however, this could not be carried out because of the low Th contents in the studied monazite.

The mineralogical composition of the soil was studied by X-ray diffraction (XRD) using both the random powder method for the bulk mineralogical composition and oriented aggregates with the aim of identifying the clay minerals. These oriented

aggregates were examined as air-dried samples and then examined again following various treatments, such as solvation with ethylene glycol and heating to 550 °C. The X-ray diffractometer used was a SIEMENS D-5000 with a Cu anode, operated at 30 mA and 40 kV using divergence and reception slits of 2 and 0.6 mm, respectively. The XRD profiles were measured in 0.04 2θ goniometer steps for 3 s. Measured patterns were qualitatively and quantitatively analyzed using the Match v.3 and Fullprof software for Rietveld analysis, respectively (Rietveld 1967; Moore and Reynolds 1997).

The concentrations of major oxides and trace elements (excluding REEs, U, and Th) in the soil samples were determined by Energy Dispersion X-Ray Fluorescence Spectroscopy (EDXRF) (Panalytical Epsilon1 device). Samples were analyzed as pressed tablets for 22 min in two sample replicates, and thereafter, an adjustment between XRF spectra and model spectra was applied prior to element quantification. These adjustments were made as a package for all of the samples to ensure that precision was maintained.

The total REE contents were determined after digestion of the samples in aqua regia (9 mL HCl + 3 mL HNO<sub>3</sub>) in a Milestone Ethos 1 microwave furnace. The resulting solution was sent to a commercial laboratory (ALS Laboratories, Seville, Spain) for the determination of REEs and associated elements (Ce, Dy, Eu, Gd, La, Ni, Pb, Tb, Th, U, Y, and Sm) using the ICP-MS technique.

Assessment of the mobility of elements in geological samples (soils, sediments, minerals) is usually carried out by means of selective extraction techniques (Sondag, 1981; Gleyzes et al.

2002; Monteiro et al. 2016). In this respect, there are numerous different possibilities for the application a variety of extractants, but the application of these to REEs is scarce and/or poorly documented. Prieto-García et al. (2019) applied sequential extraction to REEs contained in soils, but negative results were obtained in terms of the extraction of these elements. Therefore, based on the affinity of these elements for carboxylic acids (Alguacil and Rodríguez 1997), from the most common extractants used for potentially toxic elements, we selected ammonium acetate plus acetic acid in this study. The extraction was applied to samples with a 1:20 solid/liquid ratio, with 1 M NH<sub>4</sub>Ac at pH 4.5 obtained by addition of glacial acetic acid. Samples were stirred for 2 h at room temperature prior to analysis. As for the total contents, extracts were sent to ALS Laboratories, Seville, to determine the concentrations of REEs and associated elements by the ICP-MS technique.

## Results and discussion

### Monazite composition

The results of the electron microprobe analysis (EPMA) on individual grains of monazite are presented in Table 1. Comparison of the data obtained in this study with compositions of monazite crystals/grains from other types of mineral deposits shows some differences. Firstly, silica contents are significantly higher in the Spanish monazite than that in others. This finding can be explained by the presence of small

**Table 1** Chemical compositions of individual monazite grains. Data from this study (Montiel field) is presented as the mean value (*n* = 42 analyses, % wt) followed by the minimum and maximum

Deposit	Montiel field (Spain)	Bayan Obo (China) <sup>1</sup>	Mountain Pass (USA) <sup>1</sup>	Floresta Azul (Brazil) <sup>2</sup>	Erzebrige (Germany) <sup>2</sup>	Lala (China) <sup>2</sup>	Korsnas (Finland) <sup>5</sup>	US Atlantic coastal plane <sup>6</sup>
Type	Placer (eluvial)	Carbonatite	Carbonatite	Alkaline complex	Granite	IOCG	Skarn	Placer (alluvial)
SiO <sub>2</sub>	3.83 (0.11–35.43)	0.62	0.61	1.20	L47	0.21	2.60	0.33
P <sub>2</sub> O <sub>5</sub>	26.36 (12.24–28.64)	29.77	29.91	28.45	28.12	31.51	25.7	29.86
Y <sub>2</sub> O <sub>3</sub>	0.46 (0.30–0.60)	0.16	ND	ND	1.29	0.66	0.14	1.75
Ce <sub>2</sub> O <sub>3</sub>	31.58 (21.14–36.76)	34.24	34.13	33.85	33.15	36.41	33.8	29.24
La <sub>2</sub> O <sub>3</sub>	10.79 (4.62–17.99)	18.23	18.33	17.30	14.22	15.51	18.6	14.03
Nd <sub>2</sub> O <sub>3</sub>	14.79 (7.90–21.64)	10.19	10.43	10.30	9.42	11.94	11.5	12.01
Sm <sub>2</sub> O <sub>3</sub>	2.71 (0.89–7.15)	1.17	1.06	1.10	1.76	ND	1.2	2.21
Pr <sub>2</sub> O <sub>3</sub>	3.75 (2.52–4.46)	3.59	2.73	3.30	2.85	ND	3.9	2.97
Gd <sub>2</sub> O <sub>3</sub>		0.76	ND	ND	1.13	ND	0.43	1.46
Dy <sub>2</sub> O <sub>3</sub>		0.18	ND	ND	0.26	NO	0.06	0.32
ThO <sub>2</sub>	0.07 (0–0.62)	1.18	2.52	3.80	7	0.22	0.15	4.67
UO <sub>2</sub>	0.05 (0.01–0.13)	0.16	ND	ND	1.55	ND	0.05	0.44

Source of bibliographic data: (1) Chen et al. (2017); (2) Alves Santos et al. (2018); (3) Förster (1998); (4) Chen and Zhou (2015); (5) Papunen and Lindsjö (1972); (6) Bern et al. (2016)

ND not determined

quartz mineral inclusions within the monazite, which should also be present at the sub-microscopic scale. This explanation is more likely than a high rate of replacing P by Si (huttonite substitution), which would also give rise to a higher presence of Th in the monazite (Schulz et al. 2007). Regarding REE<sub>2</sub>O<sub>3</sub> data, the monazite described here had low Ce and La values (slightly lower in the case of Ce but more markedly so in the case of La, with a mean La<sub>2</sub>O<sub>3</sub> value of 10.79%). In contrast, the monazite is enriched in Nd (14.79% Nd<sub>2</sub>O<sub>3</sub>), which strengthens its potential economic interest. In any case, the most noteworthy characteristic of the studied monazite is its very low Th and U contents, which are far below the common values found in other monazites (by up to 7%, as explained by the isomorphism between Th and lanthanides). High Th (and U) levels are also considered to be harmful in REE metallurgy from monazite ores, so this property is advantageous in terms of a possible future mining project.

### Edaphological characterization

The results of the edaphological characterization of this profile are provided in Table 2. Soils close to the surface are neutral and have very low contents in salts, while the deeper levels are moderately alkaline and have slightly higher salts contents. The organic matter content is low, which is common for this semiarid area, and the values decrease with depth. Data on dehydrogenase activity can be considered normal for a semi-dry land area; in comparative terms, the Almadenejos Hg mining and metallurgical precinct and the San Quintín Pb-Zn-Ag mining areas, both decommissioned and located in the same geological and regional context, show DHA values between 55.48 and 91.96 µg TPF g<sup>-1</sup> d<sup>-1</sup> in bordering agricultural soils (Higuera et al. 2017). The dehydrogenase enzyme does not reside in extracellular locations in the soil and, as such, its activity is considered to be an accurate indicator of the oxidative degradation process of organic matter, which is directly related to the soil quality (Campos et al. 2018). This enzymatic activity is often used as a measure of any disruption caused by pesticides, trace elements, or management practices

due to its sensitivity to anthropogenic disturbances (Kumar et al. 2013). The results obtained in this study followed the general trend of decreased soil dehydrogenase with increasing soil depth—a phenomenon that is due to the reduction in the presence of microorganisms as depth increases (Bhattarai et al. 2015).

### Mineralogy and geochemistry of the profile

Minerals identified in the soils by XRD included quartz as the most abundant phase, along with feldspar, iron oxides (hematite and maghemite), and clay minerals, including mainly illite/muscovite and kaolinite (Tables 2 and 3). Ordovician shales, which are the origin of the studied soils, are easy to weather, and therefore, this association is expected from the process of weathering of shale-rocks during pedogenesis. It can be seen from the results in Table S1 that quartz is the most abundant mineral, and it is particularly frequent in the topsoil (as a consequence of accumulations of quartzitic clasts redistributed in the general area due to agricultural practices) and in the R horizon, characterized as stated previously by the presence of quartzite boulders. In the rest of the profile, the abundance of quartz is minimal in the most surficial part of the Bt horizon, with an increased abundance with depth towards the C horizon. Phyllosilicates as a group are more abundant than quartz, except for the Ap and R horizons, and they are particularly abundant at the bottom of the Bt horizon and in the C horizon. Concerning the phyllosilicate distribution (Table S2), illite and kaolinite are the most abundant phases, with the former being more frequent in the deeper horizons followed by the surficial horizons. This finding shows that illite could be the primary clay mineral in the shales and kaolinite is the newly formed mineral.

### Soil geochemical composition

The soil geochemistry was analyzed by XRF (Table S3) and the most abundant major component is SiO<sub>2</sub>, which ranges from 26 to 36% with an average of 30%; Al<sub>2</sub>O<sub>3</sub>, ranging

**Table 2** Main edaphological parameters of the soil profile

	pH (H <sub>2</sub> O)	EC (µS.cm <sup>-1</sup> )	SOM (%)	DHA (µg TPF g <sup>-1</sup> d <sup>-1</sup> )
Reference	7.6	8.1		
Ap (0–15)	7.1	47.7	2.3	91
Bt1 (15–30)	7.2	39.8	1.7	48
Bt2 (30–45)	7.4	35.7	0.9	19
Bt3 (45–60)	7.8	63.4	1.1	n.a.
Bt4 (60–75)	8.1	105.4	1.3	n.a.
C (75–90)	8.2	115.0	0.8	n.a.
R (>90)	8.2	100.8	0.2	n.a.

n.a. indicates not analyzed

**Table 3** Concentrations of REE and associated elements in the soil profile. All values in mg kg<sup>-1</sup>

	Y	La	Ce	Sm	Eu	Gd	Tb	Dy	Th	U
Ap (0–15)	26.19	228.58	572.42	58.86	9.18	27.18	2.43	8.46	16.92	1.79
Bt1 (15–30)	27.36	252.92	655.18	70.65	11.73	33.21	2.97	9.81	18.27	1.71
Bt2 (30–45)	19.26	118.76	265.51	26.64	4.51	14.04	1.44	5.38	14.13	1.08
Bt3 (45–60)	19.81	106.23	237.63	23.67	3.96	12.33	1.26	5.22	13.68	0.99
Bt4 (60–75)	18.63	111.15	242.07	21.15	3.69	11.52	1.26	5.04	13.41	0.99
C (75–90)	14.94	68.85	154.42	15.48	2.68	8.64	0.91	3.87	12.51	1.08
R (> 90)	15.66	50.31	98.58	9.63	1.71	6.21	0.81	3.78	12.87	1.44
Average	20.26	133.83	317.97	32.30	5.35	16.16	1.58	5.94	14.54	1.30
Est. deviation	4.81	77.31	211.46	23.11	3.67	10.07	0.81	2.31	2.19	0.35
Aver. CLM	17.9	23.6	57.7	6.9	n.d.	n.d.	n.d.	n.d.	9.6	3.8

Aver CLM: average concentrations for Castilla-La Mancha soils (Jiménez-Ballesta et al. 2010)

between 15 and 19% (17% average); and Fe, with total Fe in the form of Fe<sub>2</sub>O<sub>3</sub> ranging from 7 to 11% (10% average). Trace element concentrations, and in particular heavy metals and metalloids (As, Ba, Cu, Cr, Ni, Pb, Rb, V, Zn, and Zr), are systematically higher than the average concentrations of these elements in agricultural soils from the region (Bravo et al. 2019). This finding is probably due to a contribution of mafic volcanic materials from the Calatrava Volcanic Field, which is located very close to the study site.

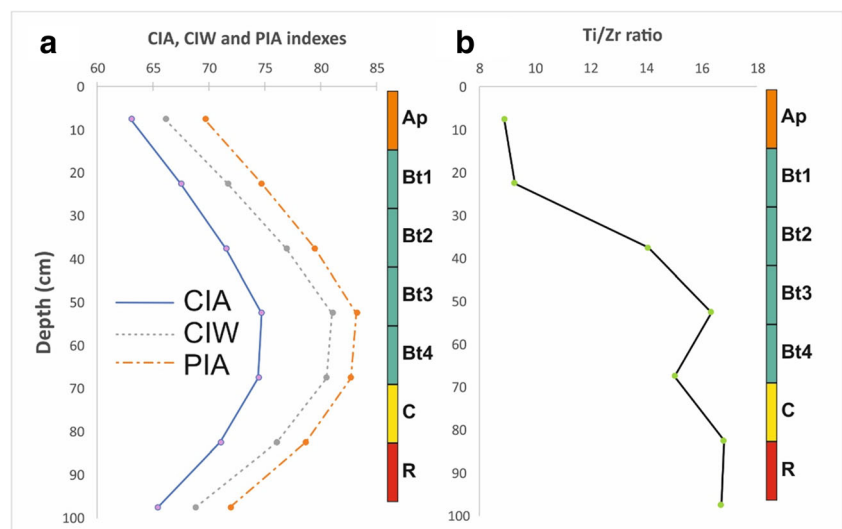
The major elements composition allowed the degree of weathering along the soil profile to be estimated by considering the following indexes:

- (a) Chemical index of alteration, CIA = 100 (Al<sub>2</sub>O<sub>3</sub>/(Al<sub>2</sub>O<sub>3</sub> + CaO + Na<sub>2</sub>O + K<sub>2</sub>O) (Nesbitt and Young 1982);
- (b) Chemical index of weathering, CIW = 100 (Al<sub>2</sub>O<sub>3</sub>/(Al<sub>2</sub>O<sub>3</sub> + CaO + Na<sub>2</sub>O) (Harnois 1988);
- (c) Plagioclase index of alteration, PIA = 100 (Al<sub>2</sub>O<sub>3</sub> - K<sub>2</sub>O/(Al<sub>2</sub>O<sub>3</sub> + CaO + Na<sub>2</sub>O - K<sub>2</sub>O) (Fedo et al. 1995).

These indexes provide a quantitative measure of the depletion of mobile (Ca, Na, K) versus immobile (Al) elements during chemical weathering, which mainly reflects the degree of muscovite alteration. In sedimentary rocks, the CIA can vary from around 35–55 (values for fresh igneous rocks) to 100 (for kaolinite), which represents the highest degree of weathering (e.g., Nesbitt and Young 1982). McLennan et al. (1983, 1993) and Mongelli et al. (1996) stated that the CIA and CIW are interpreted in the same way, with values of 50 for unweathered upper continental crust and roughly 100 for materials that are highly weathered and whose alkali and alkaline-earth elements have been completely removed. The values obtained for these indexes in the studied profile are shown in Fig. 2a. Ranges and averages: CIA 63–75%/70%, CIW 70–83%/77%, and PIA 66–81%/74%. The different indexes indicate an intermediate degree of weathering of the original materials, which is markedly higher for the Bt horizon (Fig. 2a).

Additionally, the Ti/Zr ratio was calculated because incremental weathering favors a rise in this parameter due to

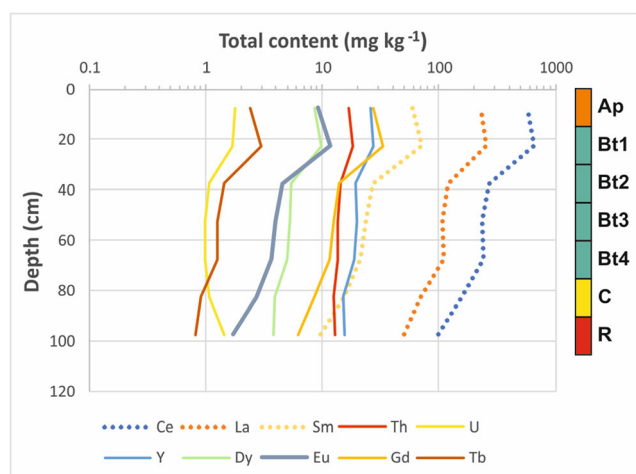
**Fig. 2** Variability of the different weathering indexes (CIA, CIW, and PIA, %) and the Ti/Zr ratio along the profile



oxidation and lixiviation of zirconium (Taylor and McLennan 1995; Critelli et al. 2008; Zaghoul et al. 2010; Gu et al. 2002). As shown in Fig. 2b, this ratio is much higher in the deeper horizons—particularly below the Ap horizon, which includes the higher monazite concentrations. On this basis, we consider that this ratio is locally affected by the anomalous composition of trace metals produced by the presence of the monazite mineralization.

### REE concentrations in the profile

The total concentrations of REEs in the soil profile (see Table 3 and Fig. 3) indicate that in this profile, the maximum concentrations are located in the first 30 cm, i.e., the Ap horizon and the upper part of the Bt horizon, with the concentrations decreasing markedly in the deeper horizons. This trend is almost negligible for Th and Y, and is weak for U. Comparison of the REE values for the profile (and particularly those of the topsoil) with average data for the region (Jiménez-Ballesta et al. 2010) shows that La, Ce, and Sm are strongly enriched, while other comparable elements (Y, U, and Th) have similar concentrations or even lower ones (e.g., U). The low concentrations of these three elements in monazite (Table 1) explain the absence of a relationship between the presence and abundance of the nodules and their concentrations in both the topsoil and in lower levels of the soil profile. As far as this question is concerned, it is also evident that the generalized presence of REEs, in variable concentrations, is not linked directly to the presence of monazite; other mineral phases can be present in common soils and this explains the variable concentrations of these elements. Another important aspect is that the most probable source of REEs in the upper horizons of the soil profile is the weathering of the monazite nodules present in the C and R horizons, but there is a second possibility, namely incorporation from the phosphate-based



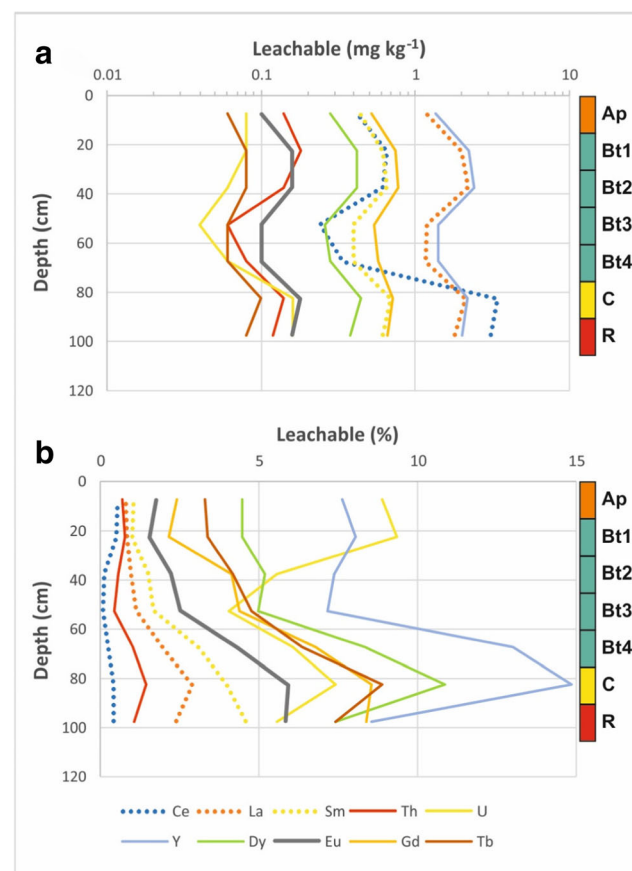
**Fig. 3** Variations of total concentrations of REEs and associated elements in the soil profile

fertilizers commonly used in agriculture. Although the background REE concentrations referenced by Jiménez-Ballesta et al. (2010) could be attributed to the upper continental crust levels, the possibility that a minor proportion comes from fertilizers cannot be ruled out.

### Mobility of REEs in the soil profile

The selective extraction technique using ammonium acetate at pH 4.75 was employed with the aim of assessing the mobility of the REE and associated elements included in the monazite concentrated in the soil profile. This reagent and this acidic medium were used in order to simulate extreme environmental conditions and the corresponding lixiviation risk. Furthermore, it is important to note that soils contain REEs in variable concentrations and chemical/mineralogical forms. Therefore, in our case, not all of the REEs extracted using this technique can be attributed to extractions from the monazite nodules present in this profile.

The results show the following order for the mobility of the studied elements:  $Y > Dy > U > Tb > Gd > Eu > Sm > La > Th > Ce$  (Table S4 and Fig. 4a). Alguacil and Rodriguez (1997)



**Fig. 4** Distribution of the extracted values expressed as absolute concentrations (a) and percentages of the total concentrations (b) along the soil profile



found a similar order, with Y being the most mobile element, Gd showing an intermediate mobility, and La and Ce being the most mobile elements in absolute terms but the least mobile in relative terms. In the soil profile, the distribution of the extraction values, expressed as absolute concentrations and percentages of the total concentrations, is shown in Table S5 and in Fig. 4a and b, respectively. It can be seen from these figures that, for all of the analyzed elements, absolute mobility is higher in the most surficial and in the deepest horizons, and much lower in the intermediate horizon (Bt). In relative terms, and due to the higher abundance of these elements in the most surficial levels, their relative mobility is much higher in the deeper horizons. In this case, only U shows contrasting behavior when compared with the rest of the elements, with the maximum mobility in the most surficial levels probably related with the highly oxidative conditions prevailing in topsoil, which favor the formation of oxidized compounds of this element and provide much higher mobility.

A remarkable finding is that the lowest mobility values are located in horizons A and B of the soil, where one would expect that the REEs appear not only in the form of the original nodules but also as a proportion of compounds newly formed by the evolution processes of the soil. A clear exception is U, but the mobility of this element is linked to environmental conditions, mainly oxidizing/anaerobic conditions. In the aerobic conditions of the studied topsoil, U can form relatively soluble compounds with organic matter and/or iron oxy-hydroxides, which explains the differences in their behavior. On the other hand, REEs seem to have more affinity for clay-rich horizons, where they form more stable and less soluble compounds. The question arises as to what are these compounds that decrease the solubility of REE. One would not expect this to be organic matter, a typical source of negative charges in soil horizons but easily extracted with ammonium acetate (Beckwith and Butler 1993). In this context, sorption to iron oxy-hydroxides present in the studied soils can explain the low mobility in the A and B horizons. Another remarkable fact is that light rare earth elements (LREEs) have lower mobility rates than heavy rare earth elements (HREEs) in the studied soils. This is because LREEs have greater affinity with the clayey soil fraction, while HREEs appear to be more frequently linked with the coarse soil fraction (Caspari et al. 2006). One might expect that HREEs would appear in the form of unaltered monazite in the coarse fraction, i.e., in the monazite nodules probably present in the C and R soil horizons, while LREEs would immobilize by sorption with iron oxy-hydroxides (Pang et al. 2002). In this scenario, REEs from phosphate-based fertilizers play an unknown role in the mobility rates found in agricultural soils. In terms of risk assessment, these low mobility rates of LREEs eliminate human risk by soil ingestion. It would

be necessary to carry out further investigations aimed to obtain data about the bioavailability of REEs in relation to agronomic crops, in order to assess this human uptake route. Another topic of interest in this sense is the need to perform better speciation studies about REEs in soils in order to identify soluble and insoluble compounds.

## Conclusions

The studied soil profile was located in an area characterized by the presence of concentrations of monazite in deep red soils and corresponds to a red Mediterranean soil. This soil is classified as Rhodoxeralf or Rhodic Luvisol after the most widely used edaphological classifications. The soil was formed from gray shales and quartzites of Ordovician age. This soil, and in particular its well-developed Bt horizon, shows an intermediate degree of weathering, as demonstrated by the CIA, CIW, and PIA specific indexes.

In the most surficial horizons, the soil includes high concentrations of gray monazite, but these concentrations decrease markedly in deeper horizons.

The general chemical characteristics of this monazite are compatible with the typology of REE ore deposits of gray monazite, including very low concentrations of U and Th, as confirmed in this study and in previous studies that showed the low radioactive activity of concentrations of these nodules.

The mobility of REEs contained in monazite proved to be higher than REE compounds in the upper horizons of the soil profile. The data obtained suggests the immobilization of these elements in other REE-containing minerals, which are common constituents of regional soils. While LREEs show lower mobility rates than HREEs, LREEs can be immobilized by sorption with iron oxy-hydroxides and HREEs coming from the monazite nodules probably present in the C and R soil horizons. Further studies are required in order to obtain better speciation data for REEs in soils in order to identify soluble and insoluble compounds.

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and research: PLH, JAC, and CGN; methodology: JME, RA, and JACG; resources/funding: PLH.

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## Compliance with ethical standards

**Conflict of interest** The authors declare that they have no conflict of interest.

**Ethical approval** Pablo L. Higuera, Full Professor, PhD, as responsible of the manuscript entitled “Occurrence and environmental constraints of gray monazite in red soils from the Campo de Montiel area (SW Ciudad Real province, south central Spain),” authored by myself and Prof. Raimundo Jiménez-Ballesta, PhD; José María Esbrí, PhD; Prof. Rosario García-Giménez, PhD; Eva María García-Noguero, PhD; Rodrigo Álvarez, PhD; Jesús Daniel Peco; Carolina García-Noguero and Juan Antonio Campos-Gallego, PhD. On behalf of the rest of coauthors, with this statement I warrantee that:

- The manuscript has not been submitted to more than one journal for simultaneous consideration.
- The submitted work is original and has not been published elsewhere in any form or language (partially or in full).
- This is not a single study splitted up into several parts to increase the quantity of submissions and submitted to various journals or to one journal over time.
- The results have been, to our intention, presented clearly, honestly, and without fabrication, falsification, or inappropriate data manipulation of any kind.
- No data, text, or theories by others are presented as if they were ours. Proper acknowledgements to other works have been done: summarized and/or paraphrased, quotation marks (to indicate words taken from another source) are used for verbatim copying of material, and permissions secured for material that is copyrighted.

**Consent to participate** Pablo L. Higuera, Full Professor, PhD, as responsible of the manuscript entitled “Occurrence and environmental constraints of gray monazite in red soils from the Campo de Montiel area (SW Ciudad Real province, south central Spain),” authored by myself and Prof. Raimundo Jiménez-Ballesta, PhD; José María Esbrí, PhD; Prof. Rosario García-Giménez, PhD; Eva María García-Noguero, PhD; Rodrigo Álvarez, PhD; Jesús Daniel Peco; Carolina García-Noguero and Juan Antonio Campos-Gallego, PhD. On behalf of the rest of coauthors, with this statement I warrantee that all authors whose names appear on the submission:

1. made substantial contributions to the conception or design of the work and/or the acquisition, analysis, or interpretation of data.
2. drafted the work or revised it critically for important intellectual content;

3. approved the version to be published; and
4. agree to be accountable for all aspects of the work in ensuring that questions related to the accuracy or integrity of any part of the work are appropriately investigated and resolved.

**Consent to publish** Pablo L. Higuera, Full Professor, PhD, as responsible of the manuscript entitled “Occurrence and environmental constraints of gray monazite in red soils from the Campo de Montiel area (SW Ciudad Real province, south central Spain)”, authored by myself and Prof. Raimundo Jiménez-Ballesta, PhD; José María Esbrí, PhD; Prof. Rosario García-Giménez, PhD; Eva María García-Noguero, PhD; Rodrigo Álvarez, PhD; Jesús Daniel Peco; Carolina García-Noguero and Juan Antonio Campos-Gallego, PhD. On behalf of the rest of coauthors, with this statement I warrantee that this manuscript does not contains any individual person’s data in any form (including any individual details, images or videos).

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