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TERRAS RARAS NOS SEDIMENTOS PLIOCÉNICOS ENTRE OS RIOS VOUGA E MONDEGO (PORTUGAL)

RARE EARTH ELEMENTS IN THE PLIOCENE SEDIMENTS BETWEEN RIVERS VOUGA AND MONDEGO (PORTUGAL)

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Abstract

The geochemistry of Pliocene muddy sediments is determined to address the main phases that carry the rare earth (REE). Three different facies, related to floodplain and swamp-lake deposition, and two sectors were considered. It was found that the heavy REE concentration is substantially higher in swamp-lake than in floodplain sediments. Though clay minerals host part of the REE, xenotime and monazite must be the main carrying minerals. Other phases (e.g. organic matter) in swamp-lake facies must retain an important part of the REE, in particular the heavy REE. The REE concentrations in the two sectors are not substantially different, suggesting that provenance was similar.

Keywords: Geochemistry, REE, Facies, Hosting phases

Resumo

A geoquímica de sedimentos argilosos do Pliocénico é usada para determinar as principais fases transportadoras de terras raras. Foram consideradas 3 fácies, associadas a sedimentação em planície de inundação e em pântano-lago, e dois sectores. A concentração de terras raras pesadas é substancialmente maior nos sedimentos de pântano-lago que nos de planície de inundação. Ainda que os minerais de argila integrem parte das terras raras, o xenótimo e a monazite são os principais minerais a transportar aqueles elementos. Outras fases (p. ex. matéria orgânica) em sedimentos de pântano-lago devem reter uma parte significativa das terras raras, em particular das terras raras pesadas. As concentrações de terras raras nos dois sectores não são muito diferentes, sugerindo que a proveniência era similar.

Palavras chave: Geoquímica, REE, Facies, Fases de suporte

Introduction

Geochemistry, as other compositional features, of clastic sediments may be useful in identifying source rock, weathering and climatic conditions, tectonic regime, sorting process during transport and sedimentation and post-depositional reactions. In what regards to rare earth elements (REE), because these elements tend to be immobile during weathering and integrated in the sedimentary deposits they are usually considered good indicators of sediment provenance (Taylor and MacLennan, 1985). However, several researchers suggested that REE fractionation is affected by exogenous process, like weathering and sorting (Cullers et al., 1987; McLennan, 1989; Nesbitt et al., 1990; Lopéz et al., 2005).

In this work we present the geochemistry of distinct mud-sediments (facies) from the Pliocene units between the Mondego River and Aveiro in order to identify the main phases that host the REE in these sediments.

Geological setting

The studied area is influenced by the limit between the Variscan Iberian Massif, with Palaeozoic and Precambrian metasedimentary rocks and the West Iberia coastal margin, with diverse Mesozoic clastic and carbonate rocks (Fig. 1). This limit is defined by a N-S to NNW-SSE trending wide deformation zone, with complex internal geometry that has been referred to as the Porto-Tomar shear mega-domain (Pereira, 1987; Dias & Ribeiro, 1993; Chaminé et al., 2003). An elongated sub-basin that reaches 10 km wide and 50 km long develops to the east of the Cértima valley. It contains a Plio-Pleistocene alluvial succession (up to 70 m thick) related to a north to northwest-directed axial drainage and lateral alluvial fans. West of the Cértima valley the Pliocene-Pleistocene succession is thinner (~ 10m). The eastern sub-basin is separated in the NE sector (with Plio-Pleistocene cover more continuous and only Precambrian units of Central Iberian zone to the east) and SE sector (with Plio-Pleistocene cover more fragmentary and distinct Paleozoic and Precambrian units to the east) sectors. Today, the landscape is characterized by the presence of a north-directed trunk drainage defined by the River Cértima.

The Pliocene succession is part of a siliciclastic unit that extends throughout the Western Portuguese Margin with an overall trend of decreasing marine influence both up-section and east-wards (Cunha et al., 1993). The lower part of the succession (unit U1) consists mainly of fine-grained sands deposited in inner shelf to coastal environments. The remaining succession (units U2A, U2B and U3) comprises mainly alluvial deposits (Dinis, 2006). The samples studied in this work are from unit U2B.

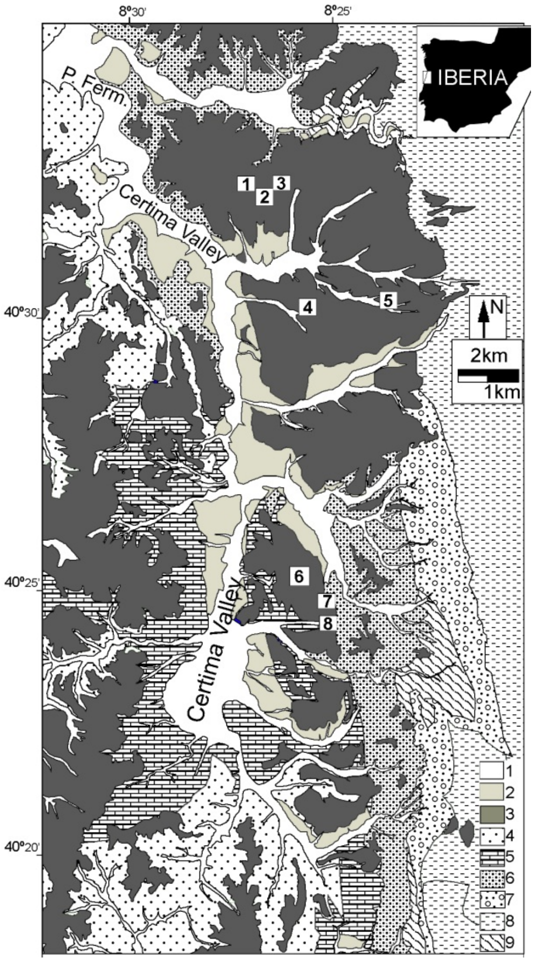

Fig. 1 – Geological map of the study area. Numbered white squares indicate the location of sampled sections. P. Ferm.: Pateira de Fermentelos present-day lake. 1: Holocene; 2: Pleistocene terraces; 3: Pliocene-Pleistocene; 4: Cretaceous; 5: Jurassic; 6: Triassic; 7: Carboniferous; 8: Central Iberian Zone; 9: Ossa-Morena Zone.

Unit 2B evolves gradually from unit 2A and is partially its lateral equivalent. The thickness of U2B is variable, reaching 50 m in some subsiding sectors. It comprises fine-grained floodplain and swamp-lake mud, sometimes articulated with peat-lignite, and coarse-grained stream channel and alluvial fan sediments. The depositional system included a north–directed trunk drainage and multiple points of lateral alluvial supply.

Sediment description (facies)

Only fine-grained sediments are considered in this work. The most common facies (facies 1 and 2) are massive, horizontally laminated or ripple laminated muddy sediments with yellow, red or purple colors. They may have mottled appearance and mud-cracks. Laminated facies 1 usually integrate thin (< 0.2 cm) laminas of mud and fine sand while facies 2 tend to be composed of thicker sediment divisions (< 15 cm). Facies 2 define wedge-shape sediment bodies that usually became coarser and thicker towards the channel fill facies, where they can rich 0.5 m. Facies 1 constitute thicker sediment bodies (up to 5 m) with tabular, lens or wedge shape.

Another type of mud sediments (facies 3) is characterized by meter thick grey beds, usually with vegetal remains, that may show thin horizontal lamination. In association with facies 3 occur lignite and peat beds. These sediment beds tend to have lens geometry, not visible in outcrop but recognizable from the analysis of boreholes. The peat-lignite beds can reach 3 m thick and are usually found between facies 3.

Facies 1 and 2 intercalated with coarse-grained sediments are interpreted as floodplain deposits. The ripple and horizontal laminations, with divisions of different grain-sizes suggest that they result from settling of particles transported by recurrent overbank currents of variable energy. The mottled appearance is due to pedogenetic processes in the floodplain. Concerning facies 2, the wedge shape, coarser grain-size and thicker divisions, and given the proximity to channel fill facies, these sediments must be related to higher energy conditions and sedimentation rates that occurred closer to the channels, possibly in association to crevasse splays or levees. The fine-grained grey sediments (facie 3) articulated with peat-lignite beds must be related to deposition from suspension in low energy lake or swamp-marsh environments. These environments developed preferentially in tectonically depressed sectors, in places of floodplain enlargement, upstream of uplifted structural blocks. The Pateira de Fermentelos constitutes a present day analogue of these environments (Fig. 1).

Methods

The majority of the samples were collected from boreholes. The location of the studied sections and the stratigraphic position of the samples is represented in figures 1 and 2, respectively. A few samples collected in old outcrops during previous works and presently stored at the LNEG (S. Mamede Infesta) were also considered.

Most elements were determined XRF (X-Ray Fluorescence spectroscopy). Homogenized powders of samples were previously digested with a mixture of HF, HNO_3 and $HClO_4$. REE content was determined by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) in Plio-Pleistocene sediments (27 selected samples) and the possible source rocks. Samples were mixed with Na_2O_2 and sintered at 480±10 ºC for 30 minutes. After cooling, the sinter residual was gently removed from with ultra-pure water into a 50 ml polypropylene tube, where 3 drops of concentrate HCl and 2 ml of concentrate HNO_3 were added. Before ICP-MS quantification this solution was diluted 1:10 with 2% HNO_3 blank solution. The precision of elemental determinations (XRF and ICP-MS) is < 3%, with the exception of Lu (7%).

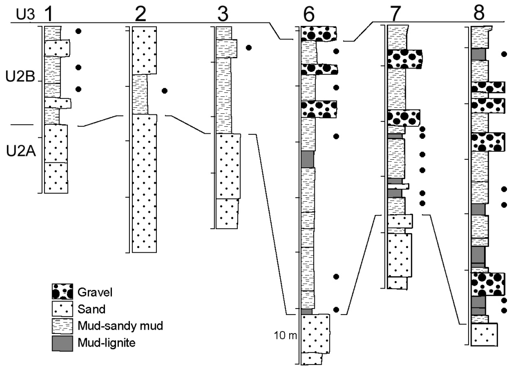

Fig. 2 – Simplified borehole logs with vertical position of the analysed samples (black dots). Borehole locations in Fig. 1.

Results

The different facies have comparable SiO_2 (60-76%), Al_2O_3 (15-23%), K_2O (2-3%) and TiO_2 (0.7-1.2%). Coarser-grained sediments (facies 2) have higher SiO_2 and lower Al_2O_3 contents. Swamp-lake sediments have slightly lower Fe content (mean of 2.7%) than coarser grained floodplain sediments (mean of 4.1%). Floodplain samples of sector SE tend to have lower Al_2O_3 and higher Fe concentrations (means of 18.5% and 4.6%, respectively) than samples of the NE sector (means of 20.6% and 3.5%, respectively); however, the variability in major elements is high, particularly in the NE sector. All sediments are depleted in Na_2O, which can be lower than the detection limit of the analytical methodology.

Regarding trace elements, the concentration of Y is generally lower in the floodplain (7-23 ppm, mean of 13.4 ppm) than in swamp-lake facies (19-32 ppm, mean of 26.7 ppm). Among floodplain facies, sediments from the SE sector tend to be richer in Y than those from the NE sector. Th concentration is highly variable, but the mean values in floodplain and swamp-lake facies are comparable. REE concentrations are generally higher in the swamp-lake sediments (131-300 ppm, mean of 201.5 ppm) than in the floodplain sediments (62-218 ppm, mean of 134.2 ppm). The sum of heavy REE (HREE) concentrations is higher in swamp-lake sediments (12-15 ppm) than in floodplain (5-12 ppm). Floodplain sediments from the SE sector tend to be richer in HREE than floodplain sediments from the NE sector.

The pattern of distribution of REE is relatively homogeneous (Fig. 3). The Chondrite-normalized REE show slight enrichment in light REE (LREE), which tend to be more fractionated in the coarser sediments (mean La_N/Yb_N ratios of 22.2 for facies 2, 9.8 for facies 1 and 9.3 for facies 3).

The patterns reveal flatter HREE (Gd_N/Yb_N between 1.16 and 2.39), and more fractionated LREE (La_N/Sm_N between 2.18 and 5.97). A Eu negative anomaly is detected in all samples (0.56<Eu/Eu*<0.77). The anomaly is higher in lower sediments of unit U2B, at the transition to unit U2A. The Ce anomaly can be either slightly positive or negative (0.74<Ce/Ce*<1.21).

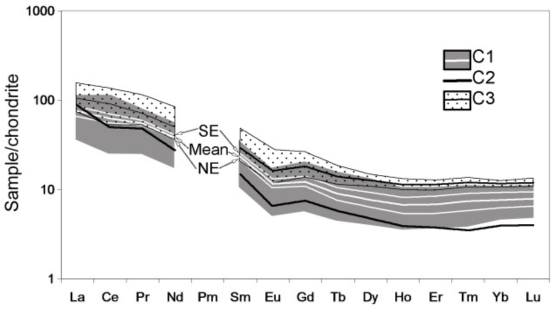

Fig. 3 – Chondrite-normalized REE patterns of different mud facies of unit U2B. Range and mean values are represented for facies 1 and 3. SE and NE indicate facies 1 mean values in these two sectors.

Discussion

The analysis of the correlations of REE with other elements and compositional features helps to understand which mineral phases host REE (Table 1). Zircon and Ti-minerals (ilmenite and rutile) were found in the heavy fraction (Dinis and Soares, 2007), but Zr and TiO_2 do not correlate with REE, indicating that these minerals must have minor contribution to the REE geochemistry. The lesser concentrations of REE in the coarser-grained sediments (facies 1 and 2) must be attributed to dilution by quartz, and some retention in clay minerals. This hypothesis is supported by the tendency for REE retention in illite (Cullers et al., 1975; Cullers et al., 1987; Taylor and McLennan, 1985; Condie et al., 1995). However, due to the absence of correlation REE-K_2O in most facies and sectors, the majority of the REE must be present in different mineral phases.

REE and LREE in floodplain facies (1 and 2) strongly correlate with Th (except for the NE sector) and Y, indicating that an important proportion of the REE must occur in monazite and xenotime. Because HREE correlates better with Y than with Th one can assume that the HREE incorporation in monazite is less important than in Y-bearing minerals. Regarding swamp-lake sediments (facies 3), the absence of correlation REE-Y and REE-Th and the negative correlation HREE-K_2O indicate that other phases must be involved in REE geochemistry. Because REE can be adsorbed in organic matter (Gotze and Lewis, 1994; Aubert et al., 2004; Xu and Han, 2009) and the swamp-lake sediments are characterized by an association with lignite beds (facies 4), it may be considered that an important part of the REE is hosted by organic compounds. Organic matter adsorption also justifies the higher HREE concentration (Fig. 3), as organic matter tends to be richer in these elements (Aubert et al., 2004).

The limited differentiation between sectors is probably related to homogeneous provenance. Although the SE sector has several Paleozoic units beside the Precambrian of Central Iberian Zone in its eastern basin edge, the Precambrian rocks must have played an important role in supplying sediment to the Pliocene of the SE sector. The Precambrian units also probably contributed as sediment sources to the younger Paleozoic formations of the region.

Table 1 – Most relevant correlation coefficients between REE and other compositional features in the different facies and sectors. Bold values indicate correlations significant at 99% probability and the other at 95% probability.

		K_2O	CIA	Th	Y
Total	REE			**0.49**	**0.73**
	LREE			**0.51**	**0.70**
	HREE	0.39			**0.93**
Facies 1	REE			**0.72**	**0.74**
	LREE			**0.73**	**0.71**
Total	HREE				**0.90**
Facies 1	REE				0.78
	LREE				0.77
NE	HREE				0.70
Facies 1	REE			**0.90**	**0.81**
	LREE			**0.91**	**0.79**
SE	HREE			0.65	**0.91**
Facies 3	REE		0.91		
	LREE		0.91		
Total	HREE				
Sector	REE			**0.72**	**0.72**
SE	LREE			**0.72**	**0.69**
	HREE			0.56	**0.92**
Sector	REE				**0.78**
NE	LREE				0.77
	HREE				

Conclusions

The mineralogical and geochemical signals are partially determined by depositional conditions. Swamp-lake sediments usually have higher REE content (131-300 ppm) than floodplain sediments (62-218 ppm); the differences between facies are more pronounced in HREE content (12-15 ppm in swamp-lake vs. 5-12 ppm in floodplain). Most REE in floodplain sediments is hosted in Y and Th-bearing minerals, but a significant part of the REE are probably associated with clay minerals. Other phases (e.g. organic matter) must be associated with REE in swamp-lake sediments.

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