

UPPER CRETACEOUS CLAYEY LEVELS FROM WESTERN PORTUGAL (AVEIRO AND TAVEIRO REGIONS): CLAY MINERAL AND TRACE-ELEMENT DISTRIBUTION

ROSA MARQUES^{1,3,*}, M. ISABEL DIAS^{1,3}, M. ISABEL PRUDÊNCIO^{1,3}, AND FERNANDO ROCHA^{2,3}

¹ Instituto Tecnológico e Nuclear, Estrada Nacional 10, 2686-953 Sacavém, Portugal

² Universidade de Aveiro, Departamento de Geociências, Aveiro, Portugal

³ GeoBioTec Research Centre, Universidade de Aveiro, Aveiro, Portugal

Abstract—Clay-rich deposits of Upper Cretaceous levels in the Taveiro (Reveles and S. Pedro) and Aveiro (Bustos) regions of west-central Portugal are economically and environmentally important, but detailed chemical and mineralogical characterization is lacking. The purpose of this study was to partially fill that gap by correlating the trace-element geochemistry (particularly the rare earth elements, *REE*) with the mineralogy of both the whole rock and of the <2 μm fraction along selected stratigraphic levels of the formations. The results will help the ceramics industry in the region and will be important in paleoreconstruction environmental studies.

Mineralogical and chemical characterizations were carried out using X-ray diffraction (XRD), X-ray fluorescence (XRF), and instrumental neutron activation analysis (INAA). The following clay-mineral associations were identified: (1) at Reveles – smectite, illite, and kaolin minerals; (2) at S. Pedro – kaolin minerals and illite; and (3) at Bustos – illite, kaolin minerals, and mixed-layer illite-smectite. The distribution of trace elements in the <2 μm fraction depended on the clay mineralogy, suggesting that the trace elements were incorporated in, adsorbed to, or even replaced major elements in the clays, as follows: (1) first-row transition elements, particularly Zn and Ga, were enriched when smectite predominated; (2) As, Rb, and Cs were enriched in this fraction of the S. Pedro deposit, the only one with Fe (oxyhydr)oxides and a high proportion of illite; and (3) *REE* were more concentrated when kaolin minerals predominated. Eu was enriched in the <2 μm fraction, which was due to preferential incorporation in the Fe (oxyhydr)oxides and/or carbonates.

Key Words—Clay Minerals, Geochemistry, *REE*, Trace Elements.

INTRODUCTION

The elemental composition and ratios of shales and sandstones have been used in numerous studies to infer provenance and tectonic environments (Cullers, 2002; Cox *et al.*, 1995; Cullers and Beredsen, 1998; Wronkiewicz and Condie, 1990). Rare earth elements (*REE*), Th, Sc, and other trace elements have been considered the most immobile elements during weathering, transport, deposition, and diagenetic processes (Cullers *et al.*, 1997). In general, such studies have been carried out based on the chemical and mineralogical composition of the whole rock. In this work, besides the whole rock, the <2 μm fraction from two main formations of west-central Portugal (Aveiro and Taveiro) was characterized from a geochemical and mineralogical point of view.

Previous studies of this region have included chemical, mineralogical, and technological characterizations of the clayey deposits from these same formations, which aimed to reconstruct sedimentary processes and to identify potentially new raw materials for distinct

applications, such as for the ceramics industries (ancient and contemporaneous) and for use in barriers in waste landfills (Prudêncio *et al.*, 1989; Rocha, 1993; Rocha and Gomes, 1995; Galhano *et al.*, 1999; Santos, 1998; Santos *et al.*, 2000; Coroado, 2000).

In the present study, new, more detailed and improved chemical and mineralogical characterizations of the whole-rock samples and of the <2 μm fractions from representative clay deposits from the Taveiro and Aveiro formations (Upper Cretaceous levels) were performed, comprising a new data set with enhanced understanding for application to paleoenvironmental reconstruction of the Lusitanian basin, as well as describing better the raw materials for the regional ceramics industry. The clay bodies studied were located in the western margin of Iberia, known as the Lusitanian basin, where the break-up of Pangea developed a complex NNE–SSW-oriented system of graben structures (Dinis *et al.*, 2008; Azeredo *et al.*, 1998; Proença Cunha and Pena dos Reis, 1995). In western Portugal, these Cretaceous sediments are mainly siliciclastics and consist of fluvial and deltaic coastal marine systems, as well as of extensive deposits of shallow-marine carbonate platforms, both open and rimmed. Two main phases characterize these deposits, the first corresponding to the infill of the Lusitanian basin during the late rifting stage

* E-mail address of corresponding author:

rmarques@itn.pt

DOI: 10.1346/CCMN.2011.0590307

(Berriasian–Cenomanian), and the second (post-Cenomanian) corresponding to a low subsidence rate and dominated by fluvial deposits with occasional marine intercalations. The later deposits (Campanian–Maastrichtian) corresponding to the Taveiro formation consist of yellowish coarse clastics of quartz sandstone and a reddish and brown sequence of lutites with nodular calcareous crusts. The interfingering of these two facies can be interpreted as having been deposited in alluvial fans, including many mud-flow beds, lakes, and highly sinuous rivers, with a general fining upward trend and a complex architecture (Dinis *et al.*, 2008). Such an environment provided the conditions for the deposition of sediments with a clay mineralogical assembly dominated by two main associations in the clay fraction: kaolin minerals and illite; and, smectite, kaolin minerals, and illite (Marques, 2007).

The origin of the ‘Argilas de Aveiro’ formation is related to a regression which occurred during the second phase of the infill of the Lusitanian basin, and the formation consists of marly–sandy clays, resulting from intensive and rapid weathering and erosion affecting the rejuvenated continental areas in a temperate climate. Previous work (Rocha, 1993) on the paleoreconstruction of the overall sedimentation phenomena of the Lusitanian basin in this western sector suggested sedimentary deposition in a flat region with channels of fresh to brackish waters (low hydrodynamics) and the development of a barrier island-tidal flat system. This sedimentary environment consisted of three main domains with diverse mineralogical associations, one characterized by clayey–sandy sediments containing the illite and kaolin minerals association, with pyrite in some layers, corresponding to a central-east supra-tidal area with anoxic episodes; a second consisting mainly of illite-rich sediments deposited on a tidal flat, developed in a central-west lagoonal area; the third domain is represented by clayey smectite-rich sediments in the meridional margin. The large illite content is a distinctive feature of this formation; the illite, as a rule, is highly degraded and shows irregular interstratifications (Rocha, 1993).

Previous studies, including chemical analysis of the whole rock and also of the $<2\ \mu\text{m}$ fraction of sediments (Taveiro formation) revealed a positive correlation between the *REE* contents and the clay minerals, in particular kaolin minerals and light *REE* (*LREE*) (Prudêncio *et al.*, 1989), and a positive correlation between illite and Cs (Prudêncio and Cabral, 1988). In the $<2\ \mu\text{m}$ fraction a smaller negative Eu anomaly than in the corresponding whole-rock sample was observed. The greater proportion of Eu in the fine fraction has been explained by a greater incorporation of Eu in clay minerals compared to the other middle *REE* (*MREE*) (Prudêncio *et al.*, 1989).

Though the various studies in the Upper Cretaceous deposits from the Taveiro and Aveiro formations provide

an overview of the sedimentation phenomena in the Lusitanian basin, a lack of detailed information persists. For this reason three clayey deposits of these Upper Cretaceous levels were selected for study: the Reveles and S. Pedro deposits in the Taveiro region, belonging to the so-called ‘Argilas e arenitos de Taveiro’ formation, and the Bustos deposit in the Aveiro region from the so-called ‘Argilas de Aveiro’ formation. Detailed analysis of geochemical behavior of the trace elements (the *REE* in particular) along the selected levels in the deposits and correlations with the clay mineralogy were carried out. The geochemistry of major, minor, and trace elements, and the mineralogy of the whole rock and the $<2\ \mu\text{m}$ fraction of these sedimentary deposits are also discussed.

EXPERIMENTAL

Sampling and sample preparation

Seven clay samples were collected from the Taveiro and Aveiro regions (see map, Figure 1). In Taveiro, two clayey deposits were sampled – three samples were taken from an old quarry in Reveles (RVL-50, RVL-51, and RVL-52), which were from different stratigraphic layers, and two from S. Pedro (SP-50 and SP-51). In the Aveiro region, two samples were collected from Bustos (BST-51 and BST-52).

The whole-rock portion of the samples was the $<2\ \text{mm}$ fraction (obtained by dry sieving). About 100 g of the whole rock sample was dried, weighed, and dispersed in H_2O , then the $<63\ \mu\text{m}$ silt-size fraction was separated by wet sieving. The resulting suspension was fractionated into the 20–63 (coarse silt), 2–20 (fine silt), and $<2\ \mu\text{m}$ (clay) fractions by sedimentation according to Stokes’ law (Moore and Reynolds, 1997). The whole-rock and fractionated samples were air dried, then ground and homogenized in agate mortars for analysis.

Mineralogical composition

The mineralogical compositions of the whole-rock samples and of the $<2\ \mu\text{m}$ fractions were determined by XRD, using a Philips Pro-Analytical diffractometer with $\text{CuK}\alpha$ radiation.

Randomly oriented samples of whole-rock powders were prepared by filling front-loading XRD mounts (Moore and Reynolds, 1997; Kleeberg *et al.*, 2008). The samples were scanned at a rate of $1^\circ/20\ \text{min}$ from 2° to $70^\circ 2\theta$.

Oriented specimens of the $<2\ \mu\text{m}$ fraction were prepared by air drying a small amount of dispersed suspension onto a glass slide (Moore and Reynolds, 1997). To help identify the clay minerals, in addition to the sample preparations described above, ethylene glycol-solvated (8 h) samples and samples heated at 550°C for 2 h were also prepared using well known methods (Thorez, 1976; Brindley and Brown, 1980;

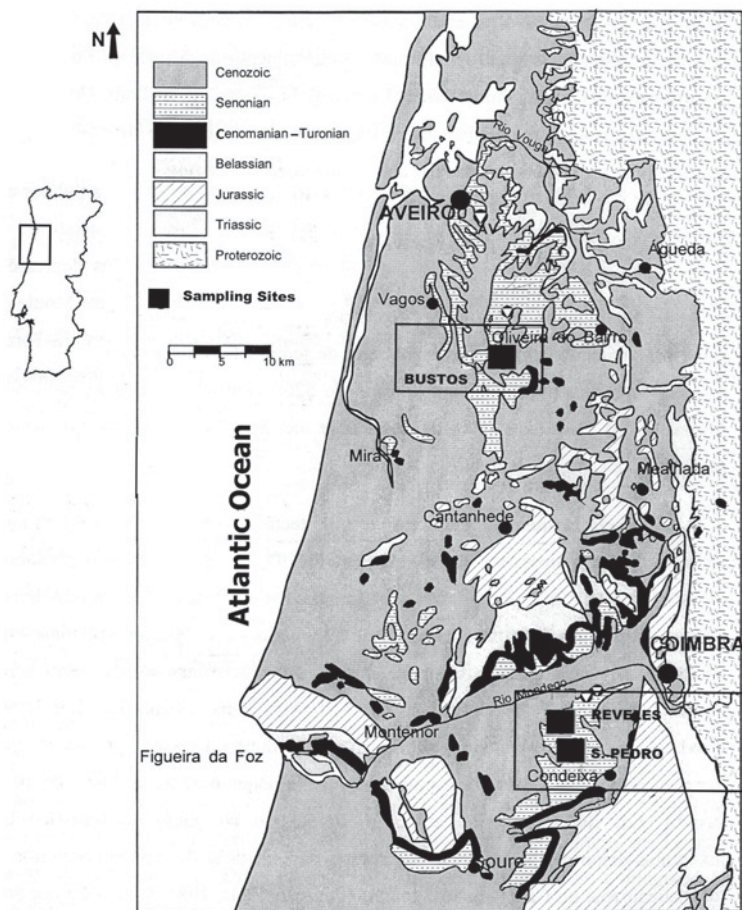


Figure 1. Sampling location of the Taveiro (Reveles – RVL; S. Pedro – SP) and Aveiro (Bustos – BST) formations (figure adapted from Santos *et al.* (2000)).

Moore and Reynolds, 1997). Mineral proportions in the whole rock and the $<2 \mu\text{m}$ fraction (in the ethylene glycol-solvated state) were estimated semi-quantitatively based on XRD peak areas (Schultz, 1964; Rocha, 1993) calculated and weighted with empirically estimated factors, according to Galhano *et al.* (1999) and Oliveira *et al.* (2002).

Chemical analysis

The amounts of major and minor elements (as oxides – SiO_2 , Al_2O_3 , Fe_2O_3 tot, MnO , MgO , CaO , Na_2O , K_2O , TiO_2 , and P_2O_5) were determined by X-ray fluorescence spectroscopy (XRF), using a Philips PW1410/00 spectrometer. Further details of the analytical method can be found in Terroso (2005).

Concentrations of the trace elements were obtained by instrumental neutron activation analysis (INAA). Approximately 200 mg of each dried sample and standard was weighed in polyethylene vials and irradiated together for 6 h in the core grid of the Portuguese Research Reactor, with a neutron flux of $3.6 \times 10^{12} \text{ n cm}^{-2} \text{ s}^{-1}$. The concentrations of Sc, Cr, Co, Zn, Ga, As, Rb, Zr, Sb, Cs, Ba, La, Ce, Nd, Sm, Eu, Tb, Yb, Lu, Hf,

Ta, W, Th, and U were determined. Sediments GSS-4 and GSS-5 from the Institute of Geophysical and Geochemical Exploration from the People's Republic of China were used as standards (Govindaraju, 1994). Measurement and processing of the gamma spectra followed the methods of Prudêncio *et al.* (1986) and Gouveia *et al.* (1992). The spectral interference by U fission products in the determination of Ba, REE, and Zr was corrected in accordance with Gouveia *et al.* (1987) and Martinho *et al.* (1991).

Multivariate statistical analysis

A statistical approach was adopted to understand the chemical data (especially trace-elements behavior) for samples collected from the selected stratigraphic levels and to make correlations with the clay mineralogical assemblages. Chemical data from whole-rock samples were submitted to multivariate statistical analysis performed with the *Statistica* program (Statsoft, 2008), using the chemical contents and also the element/Sc ratios as variables. Scandium was selected as a divisor to normalize chemical data, due to the conservative behavior of this element in superficial environments

Table 1. Grain-size distribution of the samples from Reveles (RVL), S. Pedro (SP), and Bustos (BST) obtained by wet sieving and sedimentation.

| | Wet sieving | | Sedimentation | |
|--------|--------------------------|----------------------------|---------------------------|-------------------------|
| | <63 μm (%) | 20–63 μm (%) | 2–20 μm (%) | <2 μm (%) |
| RVL-50 | 36 | 5 | 15 | 16 |
| RVL-51 | 32 | 7 | 13 | 12 |
| RVL-52 | 79 | 17 | 34 | 28 |
| SP-50 | 89 | 14 | 35 | 40 |
| SP-51 | 86 | 15 | 38 | 33 |
| BST-51 | 98 | 1 | 22 | 75 |
| BST-52 | 99 | 3 | 22 | 74 |

(Prudêncio *et al.*, 2006; Dias and Prudêncio, 2008). Joint-tree and k-means clustering methods were performed.

RESULTS AND DISCUSSION

Grain-size distribution

The proportions of the different grain-size fractions in the Taveiro formation (Table 1) revealed that the <63 μm fraction of S. Pedro deposit was large (86% and 89%), as well as that from sample RVL-52 (79%). The other two samples from Reveles contained smaller proportions of the <63 μm fraction (32% and 36%). Note that the two samples from S. Pedro and sample RVL-52 were distinguished by a large proportion of the 20–63 μm fraction (14–17%) and the 2–20 μm fraction (34–38%) compared to the other studied samples. In the Aveiro formation, samples from the Bustos deposit were less sandy than others, with a <63 μm proportion of ~98%.

The distribution of the >63 μm , 20–63 μm , 2–20 μm , and <2 μm fractions (Figure 2) revealed the differences

among the three deposits. Samples from Bustos, for example, contained the largest <2 μm fraction (74% and 75%), followed by S. Pedro (33% and 40%), and then sample RVL-52 (28%). The other two Reveles samples were dominated by coarser particles (Table 1).

Mineralogical composition

The mineral proportions found in the whole-rock samples of the three deposits (Table 2, Figure 3) revealed quartz as the dominant mineral in the Reveles and S. Pedro deposits (Taveiro), while phyllosilicates dominated in samples from Bustos (Aveiro). Besides quartz, phyllosilicates and alkali feldspars also occurred in significant amounts in Reveles. Sample RVL-52 contained a larger amount of phyllosilicates and a smaller amount of alkali feldspars compared to the other samples from the same deposit, in agreement with the grain-size distribution (Table 1). S. Pedro samples consisted mainly of quartz and phyllosilicates; trace amounts of alkali feldspars and hematite were also found. Bustos samples consisted mainly of phyllosilicates, in agreement with the grain-size distribution, followed by quartz, traces of alkali feldspars, and calcite.

In the <2 μm fraction, illite and kaolin minerals were present in all of the samples studied (Table 3, Figure 4). In the Reveles deposit, smectite was also found in amounts varying from 29% to 71%. In the <2 μm fraction of the S. Pedro samples, besides the clay minerals found (kaolin minerals and illite), Fe (oxyhydr)oxides also occurred. In Bustos, mixed-layer illite-smectite was also found (3–17%).

Chemical composition

Whole-rock samples. Chemical analysis (major, minor, and trace element) of the whole-rock sample (Table 4)

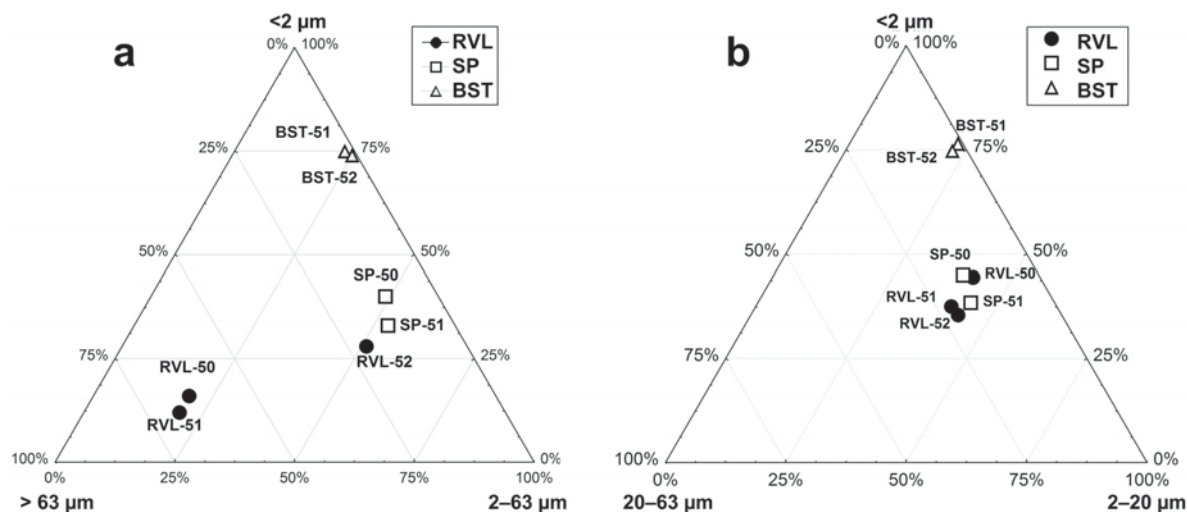


Figure 2. Granulometric distribution of Reveles (RVL), S. Pedro (SP), and Bustos (BST) samples: (a) >63 μm , 2–63 μm , and <2 μm ; and (b) 20–63 μm , 2–20 μm , and <2 μm .

Table 2. Semi-quantitative mineralogical composition (%) obtained by XRD of whole-rock samples from Reveles (RVL), S. Pedro (SP), and Bustos (BST) deposits.

| Peak (Å) | Quartz 3.34 | Phyllosilicates 4.45 | Alkali feldspars 3.24 | Calcite 3.03 | Hematite 2.68 |
|----------|----------------|-------------------------|--------------------------|-----------------|------------------|
| RVL-50 | 58 | 20 | 22 | | |
| RVL-51 | 50 | 23 | 27 | | |
| RVL-52 | 49 | 48 | 3 | | |
| SP-50 | 79 | 19 | 1 | | 1 |
| SP-51 | 66 | 32 | 1 | | 1 |
| BST-51 | 22 | 76 | 2 | | |
| BST-52 | 17 | 78 | 3 | 2 | |

revealed differences in chemical compositions among samples from the various regions. Concerning major and minor elements concentrations, the main differences found are: (1) Taveiro formation – samples from Reveles deposit, particularly RVL-50, contained more MnO and MgO and RVL-51 more P₂O₅. All Reveles samples were richer in Al₂O₃, Fe₂O₃, and TiO₂, than those from S. Pedro. The two S. Pedro samples studied were similar in terms of most major and minor element contents, except for Na₂O; (2) Aveiro formation – the Bustos deposit clearly differed from the deposits of the Taveiro region, with much smaller SiO₂ contents and greater concentrations of all the other major and minor elements, particularly Al₂O₃, MgO, and K₂O. The two Bustos samples studied were similar in composition, except in the case of CaO content, which was greater in sample BST-52 where calcite was detected.

The tree-cluster analysis of the whole-rock samples, using the major and minor element concentrations as variables, Pearson's correlation as the similarity coefficient, and the UPGMA method (Statsoft, 2008), showed

a clear differentiation between the three deposits, as can be seen in the resulting hierarchical tree (Figure 5a). However, when trace-element contents were included in the data matrix, sample RVL-52 clustered with the S. Pedro samples (Figure 5b), in agreement with the similarities found in the grain-size distribution (Table 1) as well as in the proportion of K-feldspars present (Table 2). In this way, the trace-element content was a better reflection of the grain size and mineralogy than were the major and minor elements (Figures 2, 3). After normalization of the chemical contents to Sc, *i.e.* using the element/Sc ratio as variables, the results obtained by k-means clustering showed the same similarity between the RVL-52 sample and the S. Pedro deposit (Figure 6). This method revealed which variables contributed the most for differentiation of the groups. For the Taveiro formation, the S. Pedro and RVL-52 samples were clustered due to a general depletion of the elements studied except for Sb. The other two samples from Reveles (the coarser ones) were the more enriched in all elements other than Mg, Ca, Sb,

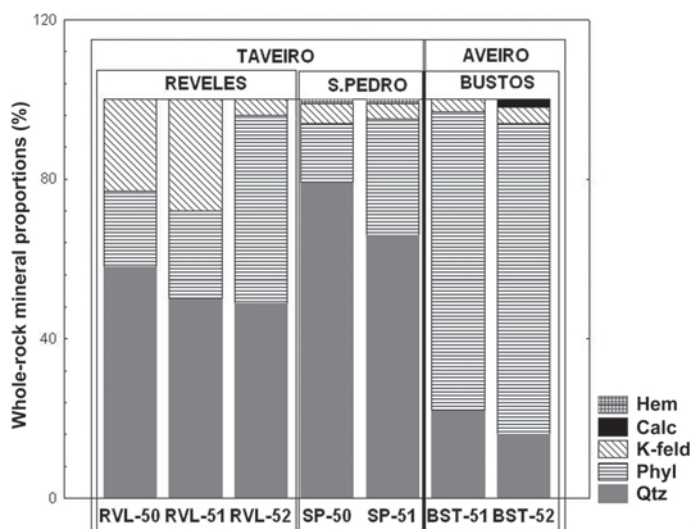


Figure 3. Whole-rock mineral proportions (%) in samples from the Taveiro (Reveles – RVL and S. Pedro – SP) and Aveiro (Bustos – BST) formations.

Table 3. Semi-quantitative clay mineral compositions (%) obtained by XRD in the $<2 \mu\text{m}$ fraction of samples from Reveles (RVL), S. Pedro (SP), and Bustos (BST) deposits.

| Peak (\AA) | Smectite 17 | Illite 10 | Kaolin minerals 7 | Illite-smectite 20–28 |
|-----------------------|----------------|--------------|----------------------|--------------------------|
| RVL-50 | 49 | 34 | 17 | |
| RVL-51 | 71 | 21 | 8 | |
| RVL-52 | 29 | 48 | 23 | |
| SP-50 | | 45 | 55 | |
| SP-51 | | 36 | 64 | |
| BST-51 | | 78 | 19 | 3 |
| BST-52 | | 50 | 33 | 17 |

and especially enriched with respect to Cs and W. The Bustos samples were clearly differentiated from all the others, especially by *REE* depletion and enrichment in Mg, Ca, Ga, Cs, and W.

In this way, normalization to Sc was a useful tool for differentiating the studied clay levels, among and within the deposits. Reveles samples can be distinguished from those of the S. Pedro and Bustos deposits by an enrichment in Zn, Zr, Ba, *REE*, Hf, and Th (Figure 7). The Bustos deposit was enriched in Cs and W and the S. Pedro deposit in Sb. Within the Reveles deposit, chemical differences were found among the stratigraphic layers, particularly for Mn, Mg, Ca, K, Co, As, Ta, and U.

$<2 \mu\text{m}$ fraction

The trace-element distribution patterns in the $<2 \mu\text{m}$ fraction of the Reveles, S. Pedro, and Bustos samples (Table 5) were compared to the patterns of the whole-rock samples (Figure 8). In general Sc, Cr, Co, Zn, Ga, As, and Cs were enriched in the $<2 \mu\text{m}$ fraction. Hf and Zr were depleted in all samples. In the Reveles deposit, a greater enrichment of these elements, especially Zn and Ga, was

observed, particularly in the samples with greater proportions of smectite (Table 3), suggesting the preferential incorporation of Zn and Ga in the crystal structure of this clay mineral. Such substitution could then yield a change in negative layer charge of the smectite.

The $<2 \mu\text{m}$ fraction of the S. Pedro samples were enriched with respect to all trace elements, especially As, Rb, and Cs. Note that these samples contain a large proportion of illite (36–45%) and the only ones containing Fe (oxyhydr)oxides. The large amounts of Rb and Cs can be explained by their adsorption on or incorporation in the structure of illite (Prudêncio and Cabral, 1988; Zachara *et al.*, 2002; Setti *et al.*, 2004). The sorption characteristics of Cs in micaceous minerals such as illite may be important and a model for sorption of Cs in illite was proposed by Bradbury and Baeyens (2000). In this model, three types of sites for Cs uptake are contemplated, which differ distinctly from one another in their capacities and affinities. The sites are denoted as “frayed edge,” “type II,” and “planar.”

For the enrichment of As in the S. Pedro samples, the adsorption/desorption and oxidation/reduction of As at

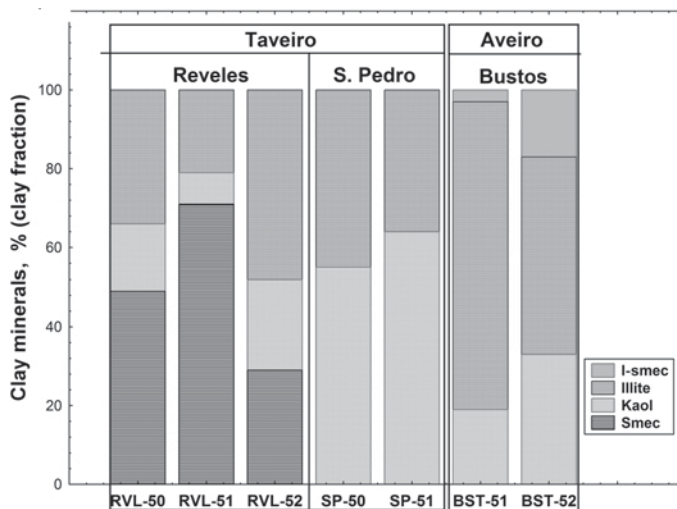


Figure 4. Proportions of clay minerals (%) in the $<2 \mu\text{m}$ fraction of samples from the Taveiro (Reveles – RVL and S. Pedro – SP) and Aveiro (Bustos – BST) formations.

Table 4. Chemical contents of major (%), minor (%), and trace elements ($\mu\text{g/g}$) obtained by XRF and INAA for whole-rock samples of the Taveiro (Reveles – RVL and S. Pedro – SP) and Aveiro (Bustos – BST) formations, *REE* fractionation, and Ce and Eu anomalies.

| | RVL-50 | RVL-51 | RVL-52 | SP-50 | SP-51 | BST-51 | BST-52 |
|------------------------------------|--------|--------|--------|-------|-------|--------|--------|
| SiO ₂ (%) | 75.78 | 74.69 | 75.75 | 80.59 | 80.07 | 57.61 | 56.89 |
| Al ₂ O ₃ | 11.68 | 13.14 | 13.95 | 8.94 | 8.77 | 19.89 | 19.55 |
| Fe ₂ O ₃ tot | 3.86 | 5.09 | 3.06 | 1.32 | 1.56 | 6.08 | 4.79 |
| MnO | 0.11 | 0.02 | 0.01 | 0.02 | 0.02 | 0.03 | 0.03 |
| MgO | 1.36 | 0.24 | 0.22 | 0.81 | 0.95 | 2.83 | 2.70 |
| CaO | 0.42 | 0.01 | 0.01 | 0.32 | 0.45 | 0.54 | 1.64 |
| Na ₂ O | 0.23 | 0.17 | 0.18 | 0.68 | 0.22 | 0.62 | 0.47 |
| K ₂ O | 2.26 | 1.54 | 1.34 | 2.47 | 2.35 | 4.42 | 4.22 |
| TiO ₂ | 0.95 | 0.83 | 0.84 | 0.51 | 0.48 | 0.80 | 0.73 |
| P ₂ O ₅ | 0.05 | 0.08 | 0.04 | 0.04 | 0.04 | 0.08 | 0.09 |
| Sc ($\mu\text{g/g}$) | 4.71 | 4.03 | 8.39 | 10.9 | 10.4 | 13.6 | 12.4 |
| Cr | 30.1 | 26.8 | 52.7 | 68.9 | 61.7 | 70.5 | 63.1 |
| Co | 10.1 | 4.18 | 10.7 | 3.85 | 2.33 | 13.5 | 13.5 |
| Zn | 23.8 | 21.9 | 47.7 | 37.3 | 29.7 | 59.6 | 46.9 |
| Ga | 6.89 | 8.11 | 13.0 | 16.0 | 13.5 | 25.0 | 20.7 |
| As | 1.10 | 2.09 | 7.04 | 15.1 | 12.7 | 19.4 | 5.88 |
| Rb | 95.7 | 94.1 | 103 | 78.7 | 76.9 | 236 | 232 |
| Zr | 208 | 201 | 321 | 198 | 231 | 119 | 130 |
| Sb | 0.42 | 0.544 | 1.12 | 2.16 | 1.69 | 0.994 | 0.707 |
| Cs | 3.74 | 3.47 | 5.53 | 6.3 | 7.01 | 21.8 | 21.9 |
| Ba | 223 | 216 | 354 | 233 | 231 | 245 | 189 |
| La | 23.9 | 22.1 | 38.8 | 35.6 | 42.3 | 37.5 | 39 |
| Ce | 47.8 | 42.1 | 79.2 | 66.3 | 76.9 | 69.3 | 72.9 |
| Nd | 24.6 | 20.9 | 37.4 | 34.8 | 41.7 | 31.3 | 36.6 |
| Sm | 4.51 | 3.76 | 6.85 | 6.67 | 7.82 | 5.8 | 6.92 |
| Eu | 0.832 | 0.642 | 1.18 | 1.28 | 1.55 | 0.986 | 1.14 |
| Tb | 0.638 | 0.496 | 0.897 | 0.889 | 1.05 | 0.726 | 0.895 |
| Yb | 2.33 | 1.95 | 3.17 | 3.26 | 3.59 | 2.67 | 2.83 |
| Lu | 0.325 | 0.282 | 0.477 | 0.46 | 0.504 | 0.36 | 0.393 |
| Hf | 6.41 | 6.69 | 10.4 | 7.39 | 7.93 | 4.89 | 4.75 |
| Ta | 0.912 | 0.99 | 1.64 | 1.55 | 1.63 | 2.72 | 2.55 |
| W | 1.35 | 1.37 | 2.48 | 2.57 | 2.83 | 5.47 | 4.88 |
| Th | 7.49 | 7.52 | 12.2 | 10.1 | 11.7 | 15.7 | 15.8 |
| U | 2.46 | 1.57 | 2.37 | 3.37 | 3.41 | 3.18 | 4.95 |
| (La/Yb) _{ch} | 6.22 | 6.87 | 7.42 | 6.62 | 7.14 | 8.51 | 8.35 |
| Ce/Ce* | 0.88 | 0.85 | 0.91 | 0.83 | 0.80 | 0.85 | 0.84 |
| Eu/Eu* | 0.57 | 0.54 | 0.54 | 0.60 | 0.62 | 0.54 | 0.52 |

$\text{Ce/Ce}^* = 3\text{Ce/Ce}_{\text{ch}} / (2\text{La/La}_{\text{ch}}) + (\text{Nd/Nd}_{\text{ch}})$; $\text{Eu/Eu}^* = 3\text{Eu/Eu}_{\text{ch}} / (2\text{Sm/Sm}_{\text{ch}}) + (\text{Tb/Tb}_{\text{ch}})$; $(\text{La/Yb})_{\text{ch}} = (\text{La/La}_{\text{ch}}) / (\text{Yb/Yb}_{\text{ch}})$

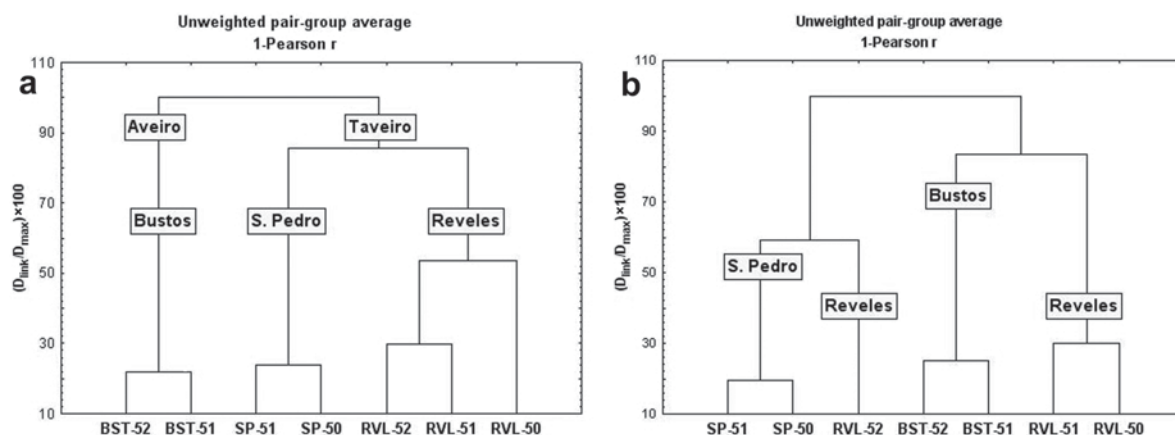


Figure 5. Phenogram resulting from tree-cluster analysis of whole-rock samples, using as variables the major- and minor-element concentrations (a), and the major-, minor-, and trace-element concentrations (b).

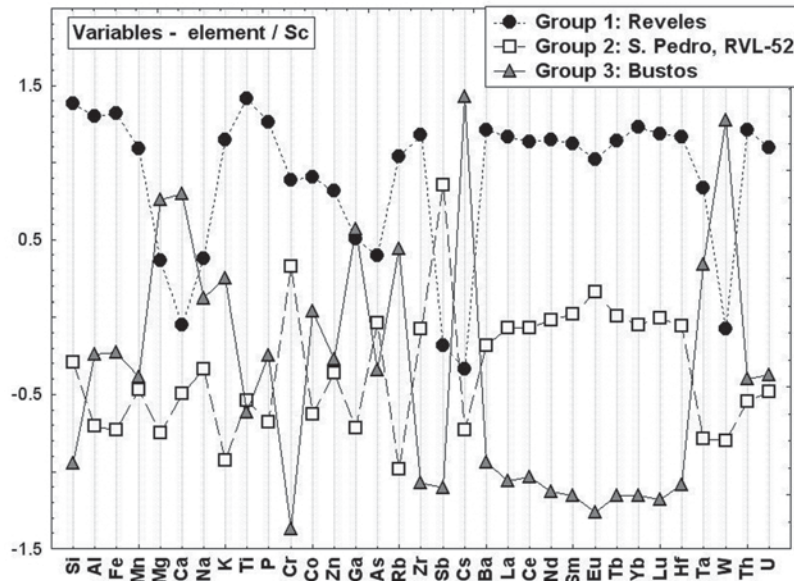


Figure 6. Plot of means for each cluster obtained by the k-mean clustering method, using as variables the total-element concentration normalized to Sc of the whole-rock samples from the Taveiro (Reveles – RVL and S. Pedro – SP) and Aveiro (Bustos – BST) formations.

clay surfaces has been suggested to be influenced by the presence of impurities, such as Fe oxides, in the clays (Lin and Puls, 2000). In fact, the S. Pedro samples are the only ones in the present study where goethite and hematite occur in both the whole-rock samples and in the $<2 \mu\text{m}$ fraction.

The Aveiro formation (Bustos samples) is dominated by the $<2 \mu\text{m}$ fraction ($\approx 75\%$), so few differences were observed between the trace-element contents of the $<2 \mu\text{m}$ fraction and the whole-rock samples. However, some differences occur between the two Bustos samples.

BST-52 contains larger amounts of Zn and Ga compared with BST-51, due to their incorporation into the smectite of the mixed-layer illite-smectite, which was confirmed by XRD to be present in a greater proportion in this sample.

In the three deposits studied no positive relation between Hf and Zr concentrations and REE was established in the $<2 \mu\text{m}$ fractions, suggesting the presence of a significant proportion of REE in the clay minerals, Fe (oxyhydr)oxides, or heavy minerals (except zircon).

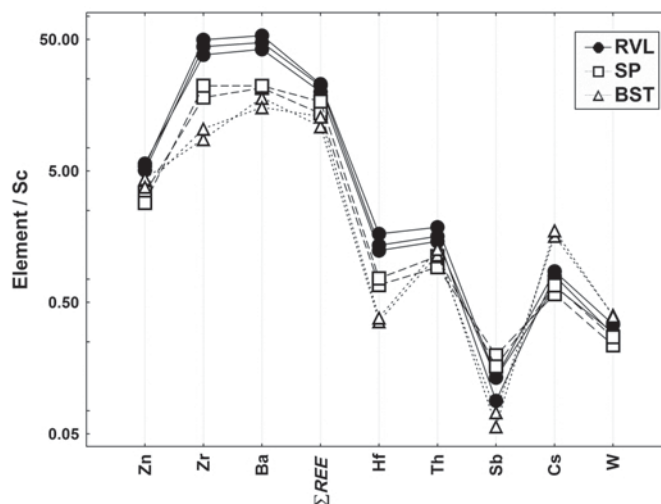


Figure 7. Differentiation between samples from the Taveiro (Reveles – RVL and S. Pedro – SP) and Aveiro (Bustos – BST) formations using selected elements normalized to Sc.

Table 5. Chemical contents of trace elements ($\mu\text{g/g}$) obtained by INAA for $<2 \mu\text{m}$ fractions of samples from the Taveiro (Reveles – RVL and S. Pedro – SP) and Aveiro (Bustos – BST) and Aveiro formations, *REE* fractionation, and Ce and Eu anomalies.

| | RVL-50 | RVL-51 | RVL-52 | SP-50 | SP-51 | BST-51 | BST-52 |
|-----------------------|--------|--------|--------|-------|-------|--------|--------|
| Sc | 12.5 | 9.21 | 13.1 | 24.7 | 22.8 | 15.2 | 14.5 |
| Cr | 82.6 | 59.3 | 79.0 | 179 | 146 | 80.7 | 74.8 |
| Co | 11.0 | 8.83 | 11.6 | 8.30 | 4.23 | 15.3 | 15.9 |
| Zn | 105 | 74.2 | 63.8 | 72.5 | 44.2 | 60.2 | 66.0 |
| Ga | 21.5 | 12.2 | 14.1 | 25.4 | 23.1 | 19.0 | 29.5 |
| As | 1.87 | 4.29 | 12.0 | 43.9 | 29.0 | 19.2 | 6.30 |
| Rb | 111 | 76.8 | 122 | 189 | 198 | 267 | 273 |
| Zr | 90.5 | 66.3 | 112 | 151 | 182 | 102 | 123 |
| Sb | 0.445 | 0.476 | 1.46 | 4.67 | 2.92 | 0.980 | 0.712 |
| Cs | 6.54 | 4.39 | 7.63 | 17.0 | 19.7 | 26.7 | 26.8 |
| Ba | 176 | 139 | 182 | 481 | 502 | 165 | 183 |
| La | 22.9 | 15.9 | 22.6 | 39.3 | 61.0 | 33.5 | 36.6 |
| Ce | 46.8 | 32.1 | 47.8 | 80.4 | 118 | 59.1 | 65.1 |
| Nd | 23.3 | 12.5 | 25.8 | 38.9 | 71.4 | 28.3 | 31.6 |
| Sm | 4.74 | 3.03 | 4.28 | 8.83 | 12.5 | 4.74 | 6.01 |
| Eu | 1.17 | 0.877 | 1.01 | 2.07 | 2.82 | 0.849 | 1.07 |
| Tb | 0.593 | 0.391 | 0.559 | 1.19 | 1.63 | 0.589 | 0.806 |
| Yb | 1.68 | 1.10 | 1.58 | 3.41 | 4.24 | 2.02 | 2.31 |
| Lu | 0.218 | 0.166 | 0.233 | 0.484 | 0.651 | 0.258 | 0.319 |
| Hf | 2.62 | 1.79 | 2.82 | 5.17 | 4.85 | 3.53 | 3.58 |
| Ta | 0.849 | 0.79 | 1.09 | 1.73 | 1.92 | 2.67 | 2.61 |
| W | 1.62 | 1.11 | 2.03 | 3.94 | 4.39 | 5.72 | 5.63 |
| Th | 7.68 | 6.19 | 8.85 | 14.5 | 16.9 | 13.9 | 14.9 |
| U | 2.03 | 0.776 | 1.20 | 6.28 | 5.13 | 2.80 | 3.94 |
| (La/Yb) _{ch} | 8.26 | 8.76 | 8.67 | 6.98 | 8.72 | 10.1 | 9.60 |
| Ce/Ce* | 0.90 | 0.93 | 0.90 | 0.90 | 0.82 | 0.81 | 0.81 |
| Eu/Eu* | 0.78 | 0.91 | 0.74 | 0.73 | 0.71 | 0.57 | 0.56 |

$$\text{Ce/Ce}^* = 3\text{Ce/Ce}_{\text{ch}}/(2\text{La/La}_{\text{ch}}) + (\text{Nd/Nd}_{\text{ch}}); \text{Eu/Eu}^* = 3\text{Eu/Eu}_{\text{ch}}/(2\text{Sm/Sm}_{\text{ch}}) + (\text{Tb/Tb}_{\text{ch}}); (\text{La/Yb})_{\text{ch}} = (\text{La/La}_{\text{ch}})/(\text{Yb/Yb}_{\text{ch}})$$

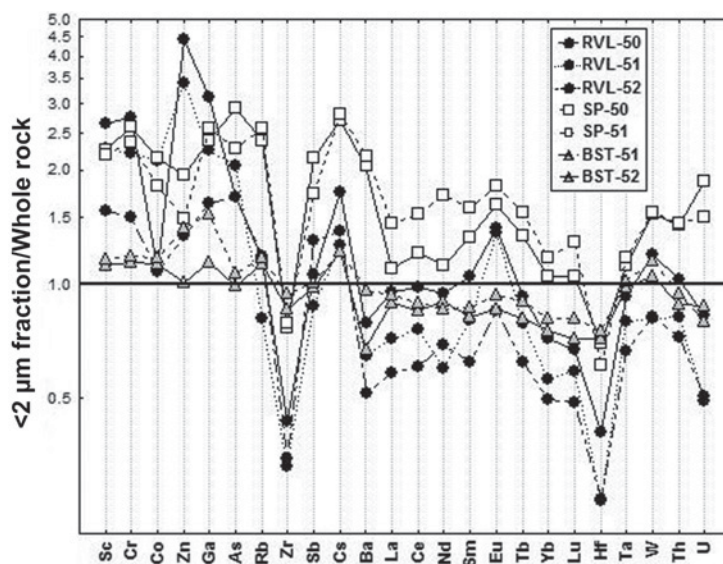


Figure 8. Trace-element distribution in the $<2 \mu\text{m}$ fraction relative to the respective whole rock of samples from the Taveiro (Reveles – RVL and S. Pedro – SP) and Aveiro (Bustos – BST) formations.

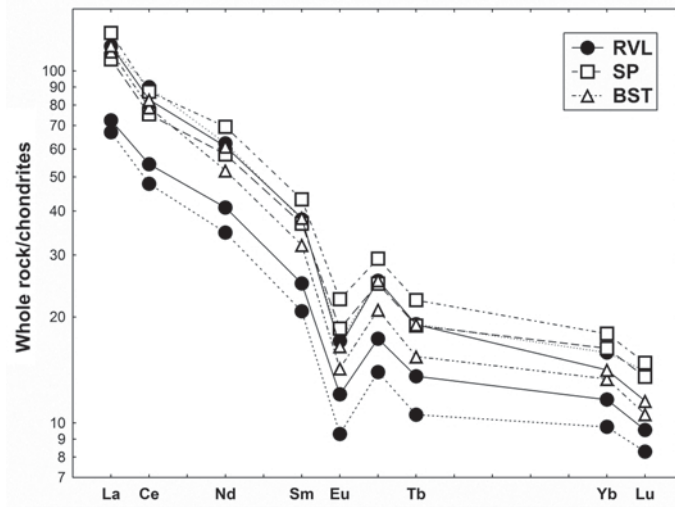


Figure 9. *REE* distribution patterns in whole rock relative to chondrites (Haskin *et al.*, 1971) of samples from the Taveiro (Reveles – RVL and S. Pedro – SP) and Aveiro (Bustos – BST) formations.

REE

Chondrite-normalized *REE* patterns for the whole-rock samples (Figure 9) were characterized by a differentiation between *LREE* and heavy *REE* (*HREE*), and to different extents by negative Ce and Eu anomalies (Table 4). The *REE* patterns for the whole-rock samples normalized to PAAS from the three studied deposits (Figure 10) revealed that all samples have negative Ce anomalies. The *REE* distribution patterns of the Reveles samples were similar, except for the *REE* contents which were greater in RVL-52, especially *MREE* and *HREE*,

than in the other samples. All the RVL samples had negative Eu anomalies. Samples from the S. Pedro deposit exhibited a clearly different behavior compared with the other samples, with evident enrichment of all *REE* (except Ce) relative to PAAS. The Aveiro formation samples, especially the BST-52 sample, revealed an enrichment in *MREE* and a negative Eu anomaly.

The *REE* patterns of the <2 μm fractions compared to the respective whole-rock samples showed a generally positive Eu anomaly (Figure 11). The larger amount of Eu incorporated into the fine fraction may be due to the

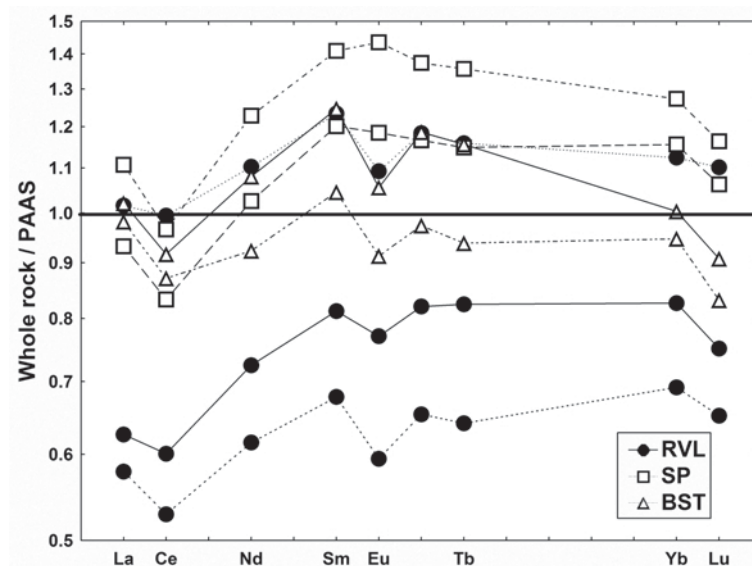


Figure 10. *REE* distribution patterns in whole rock relative to PAAS (McLennan, 1989) of samples from the Taveiro (Reveles – RVL and S. Pedro – SP) and Aveiro (Bustos – BST) formations.

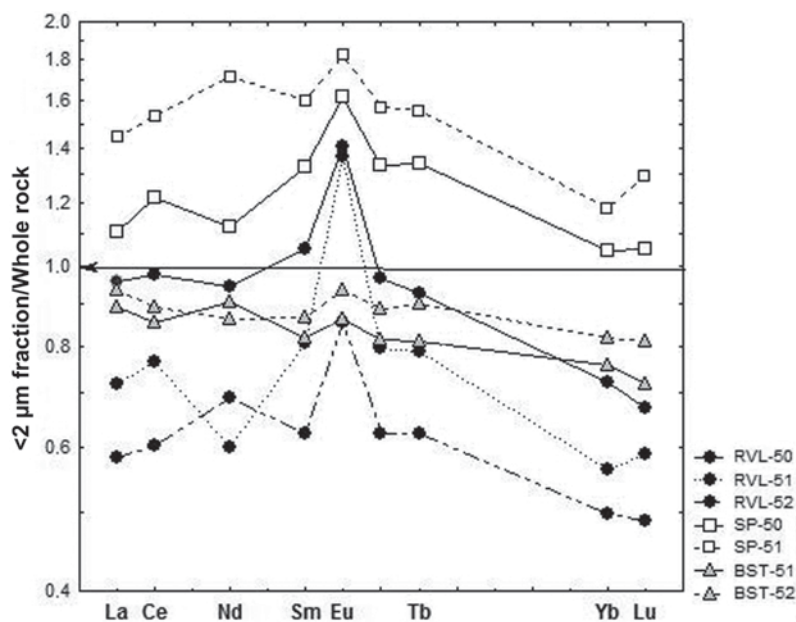


Figure 11. REE distribution patterns in the $<2 \mu\text{m}$ fraction relative to whole rock of samples from Taveiro (Reveles – RVL and S. Pedro – SP) and Aveiro (Bustos – BST) formations.

alteration of feldspars, leading to a greater release of Eu^{2+} , which is oxidized and incorporated into the clay minerals or other phases such as Fe oxides or carbonates.

The two samples of the S. Pedro deposit were the only ones enriched in all REE in $<2 \mu\text{m}$ fraction, especially LREE and MREE, which can be explained by their incorporation in the kaolin minerals (the dominant clay minerals in these samples) and in the Fe (oxyhydr)oxides detected, as argued elsewhere (Prudêncio *et al.*, 1989; Papoulis *et al.*, 2004; Compton *et al.*, 2003).

CONCLUSIONS

In the present study, selected clayey levels of the Upper Cretaceous from the Taveiro and Aveiro formations of west-central Portugal were differentiated by granulometric, mineralogical, and geochemical criteria, providing a detailed explanation of the behavior of trace elements and correlation with the $<2 \mu\text{m}$ fraction.

Samples from the Bustos deposits are the finer ones, with larger amounts of phyllosilicates associated with quartz and traces of K-feldspars. The S. Pedro samples have a similar bulk mineralogical association, but with larger amounts of quartz. Hematite also occurs in these samples. Significant differences were found within the Reveles deposit, mainly in terms of the greater proportions of feldspars in the coarser samples.

The clay mineral associations clearly differentiated the three deposits studied. Illite and kaolin minerals occur in different proportions in all of the samples studied. The presence of smectite distinguishes the Reveles deposit, and the occurrence of mixed-layer

illite-smectite distinguishes the Bustos deposit. Iron (oxyhydr)oxides were only detected in the S. Pedro samples.

The geochemical behavior of trace elements in the $<2 \mu\text{m}$ fraction relative to the whole rock suggests that REE are essentially concentrated in phyllosilicates or Fe (oxyhydr)oxides, particularly in samples rich in kaolin minerals. Europium is enriched in the $<2 \mu\text{m}$ fraction of all samples. The first-row transition elements studied are also concentrated in this fraction. In the presence of smectite, even in mixed-layer minerals, a greater enrichment of Zn and Ga was found, indicating a preferential incorporation of these elements in smectite due to preferential charge conditions for adsorption of metal cations. In samples with large proportions of illite and Fe (oxyhydr)oxides, As, Rb, and Cs enrichments were verified. The presence of impurities in clays, such as Fe (oxyhydr)oxides, may enable the adsorption/desorption and oxidation/reduction of As at clay surfaces. The uptake of Cs may be explained by the so-called “frayed-edge sites,” which are predominantly accessible to cations with low hydration energies, *e.g.* K and Rb, and that these cations, particularly K, compete most effectively with Cs for these sites.

This work contributes to a better understanding of the geochemistry and mineralogy of both the whole-rock and $<2 \mu\text{m}$ fractions from selected levels of Upper Cretaceous clay deposits of Taveiro and Aveiro formations, achieving a better characterization of these clays, which is so important to the regional ceramics industry. The distribution of the elements, especially trace elements, in the $<2 \mu\text{m}$ fraction relative to the whole rock and its correlation with clay minerals may also have

an important role in further paleoreconstruction studies of the Lusitanian basin (west margin of Iberia).

REFERENCES

- Azeredo, A., Ramalho, M., and Wright, V.P. (1998) The Middle-Upper Jurassic disconformity in the Lusitanian basin, Portugal: preliminary facies analysis and evidence for palaeoclimatic fluctuation. *Cuadernos de Geologia*, **24**, 99–119.
- Bradbury, M.H. and Baeyens, B. (2000) A generalised sorption model for the concentration dependent uptake of caesium by argillaceous rocks. *Journal of Contaminant Hydrology*, **42**, 141–163.
- Brindley, G.W. and Brown, G. (1980) *Crystal Structures of Clay Minerals and their X-ray Identification*. Monograph 5, Mineralogical Society, London.
- Compton, J.S., White, R.A., and Smith, M. (2003) Rare earth element behavior in soils and salt pan sediments of a semi-arid granitic terrain in the Western Cape, South Africa. *Chemical Geology*, **201**, 239–255.
- Coroado, J.P.P.F. (2000) Propriedades cerâmicas das argilas das unidades litoestratigráficas Argilas de Aveiro e Argilas de Tomar. PhD thesis, University of Aveiro, Portugal.
- Cox, R., Low, D.R., and Cullers, R.L. (1995) The influence of sediment recycling and basement composition on evolution of mudrock chemistry in the southwestern United States. *Geochimica et Cosmochimica Acta*, **59**, 2919–2940.
- Cullers, R.L. (2002) Implications of elemental concentrations for provenance, redox conditions, and metamorphic studies of shales and limestones near Pueblo, CO, USA. *Chemical Geology*, **191**, 305–327.
- Cullers, R.L. and Berendsen, P. (1998) The provenance and chemical variation of sandstones associated with the Mid-continent rift system, USA. *European Journal of Mineralogy*, **10**, 987–1002.
- Cullers, R.L., Bock, B., and Guidotti, C. (1997) Elemental distributions and neodymium isotopic compositions of Silurian metasediments, western Maine, USA: Redistribution of the rare earth elements. *Geochimica et Cosmochimica Acta*, **61**, 1847–1861.
- Dias, M.I. and Prudêncio, M.I. (2008) On the importance of using scandium to normalize geochemical data preceding multivariate analyses applied to archaeometric pottery studies. *Microchemical Journal*, **88**, 136–141.
- Dinis, J.L., Rey, J., Cunha, P.P., Callapez, P., and Pena dos Reis, R. (2008) Stratigraphy and allogenic controls of the western Portugal Cretaceous: an updated synthesis. *Cretaceous Research*, **29**, 772–780.
- Galhano, C., Rocha, F., and Gomes, C. (1999) Geostatistical analysis of the influence of textural, mineralogical and geochemical parameters on the geotechnical behaviour of the “Argilas de Aveiro” formation (Portugal). *Clay Minerals*, **34**, 109–116.
- Gouveia, M.A., Prudêncio, M.I., Freitas, M.C., Martinho, E., and Cabral, J.M.P. (1987) Interference from uranium fission products in the determination of rare earths, zirconium and ruthenium by instrumental neutron activation analysis in rocks and minerals. *Journal of Radioanalytical and Nuclear Chemistry*, **2** (Articles 14), 309–318.
- Gouveia, M.A., Prudêncio, M.I., Morgado, I., and Cabral, J.M.P. (1992) New data on the GSJ reference rocks JB-1a and JG-1a by instrumental neutron activation analysis. *Journal of Radioanalytical and Nuclear Chemistry*, **158**, 115–120.
- Govindaraju, K. (1994) Compilation of working values and sample description for 383 geostandards. *Geostandards Newsletter*, **18**, 1–158.
- Haskin, L.A., Helmmke, P.A., Paster, T.P., and Allen, R.O. (1971) *Activation Analysis in Geochemistry and Cosmogeochimistry* (A.O. Brunfelt and E. Steinnes, editors). Universitetsforlaget, Oslo, pp. 201–218.
- Kleeberg, R., Monecke, T., and Hillier, S. (2008) Preferred orientation of mineral grains in sample mounts for quantitative XRD measurements: How random are powder samples? *Clays and Clay Minerals*, **56**, 404–415.
- Lin, Z. and Puls, R.W. (2000) Adsorption, desorption and oxidation of arsenic affected by clay minerals and aging process. *Environmental Geology*, **39** (7), 753–759.
- Marques, R. (2007) Geoquímica e mineralogia de argilas do Cretácico de Taveiro e Aveiro, Portugal. MSc thesis, University of Aveiro, Portugal, 109 pp.
- Martinho, E., Gouveia, M.A., Prudêncio, M.I., Reis, M.F., and Cabral, J.M.P. (1991) Factor for correcting the ruthenium interference in instrumental neutron activation analysis of barium in uraniumiferous samples. *Applied Radiations and Isotopes*, **42**, 1067–1071.
- McLennan, S.M. (1989) Rare earth elements in sedimentary rocks: influence of provenance and sedimentary processes. Pp. 169–200 in: *Geochemistry and Mineralogy of the Rare Earth Elements* (I.R. Lipin and G.A. McKay, editors). Reviews in Mineralogy, **21**, Mineralogical Society of America, Washington, D.C.
- Moore, D.M. and Reynolds, R.C. (1997) *X-ray Diffraction and the Identification and Analysis of Clay Minerals*, 2nd edition. Oxford University Press, New York, 378 pp.
- Oliveira, A., Rocha, F., Rodrigues, A., Jouanneau, J., Dias, A., Weber, O., and Gomes, C. (2002) Clay minerals from the sedimentary cover from the Northwest Iberian shelf. *Progress in Oceanography*, **52**, 233–247.
- Papoulis, D., Tsolis-Katagas, P., and Katagas, C. (2004) Monazite alteration mechanisms and depletion measurements in kaolins. *Applied Clay Science*, **24**, 271–285.
- Proença Cunha, P. and Pena dos Reis, R.P.B. (1995) Cretaceous sedimentary and tectonic evolution of the northern sector of the Lusitanian basin (Portugal). *Cretaceous Research*, **16**, 155–170.
- Prudêncio, M.I. and Cabral, J.M.P. (1988) Rare earths and other trace elements in Cretaceous clays from Central Portugal. *Journal of Radioanalytical and Nuclear Chemistry*, **123**, N°1, 309–320.
- Prudêncio, M.I., Gouveia, M.A., and Cabral, J.M.P. (1986) Instrumental neutron activation analysis of two French geochemical reference samples – basalt BR and biotite Mica-Fe. *Geostandards Newsletter*, **X**, 29–31.
- Prudêncio, M.I., Figueiredo, M.O., and Cabral, J.M.P. (1989) Rare earth distribution and its correlation with clay mineralogy in the clay-sized fraction of Cretaceous and Pliocene sediments (central Portugal). *Clay Minerals*, **24**, 67–74.
- Prudêncio, M.I., Sequeira Braga, M.A., Oliveira, F., Dias, M.I., Delgado, M., and Martins, M. (2006) Raw material sources for the Roman Bracaraense ceramic (NW Iberian Peninsula). *Clays and Clay Minerals*, **54**, No. 5, 639–651.
- Rocha, F.T. (1993) Argilas aplicadas a estudos litoestratigráficos e paleoambientais na bacia sedimentar de Aveiro. PhD thesis, University of Aveiro, Portugal.
- Rocha, F. and Gomes, C. (1995) Paleoenvironmental reconstruction of the Aveiro region during Cretaceous based on clay mineralogy. *Cretaceous Research*, **16**, 187–194.
- Santos, M.H. (1998) Potencialidades de argilas portuguesas para o uso como materiais de selagem em sistemas geoambientais de confinamento de resíduos. MSc thesis, University of Aveiro, Portugal.
- Santos, M.H., Rocha, F., and Gomes, C. (2000) Assessment of some relevant properties of the “Argilas de Taveiro” formation (Coimbra, Portugal) in order to be used as liners

- in land-fills. *Geociências*, Revista Universidad Aveiro, **vol 14**, fasc (1/2).
- Schultz, L.G. (1964) Quantitative interpretation of mineralogical composition X-ray and chemical data for the Pierre Shale. *Geological Survey*, 391 pp.
- Setti, M., Marinoni, L. and López-Galindo, A. (2004) Mineralogical and geochemical characteristics (major, minor, trace elements and *REE*) of detrital and authigenic clay minerals in a Cenozoic sequence from Ross Sea, Antarctica. *Clay Minerals*, **39**, 405–421.
- Statsoft, Inc. (2008) *Statistica* (data analysis software system), version 8.0. www.statsoft.com.
- Terroso, D. (2005) Argilas/Lamas e Águas Termais das Furnas (Açores): avaliação das propriedades físicas e químicas relevantes para a utilização em Peloterapia. MSc thesis, University of Aveiro, Portugal.
- Thorez, J. (1976) *Practical Identification of Clay Minerals*. G. Lelotte, Dison, Belgium.
- Wronkiewicz, D.J. and Condie, K.C. (1990) Geochemistry and mineralogy of sediments from the Ventersdorp and Transvaal Supergroups, South Africa: cratonic evolution during the early Proterozoic. *Geochimica et Cosmochimica Acta*, **54**, 343–354.
- Zachara, J.M., Smith, S.C., Liu, C., Mckinley, P., Serne, R.J., and Gassman, P.L. (2002) Sorption of Cs^{+} to micaceous subsurface sediments from the Hanford site, USA. *Geochimica et Cosmochimica Acta*, **66**, 193–211.

(Received 2 November 2009; revised 14 September 2011; Ms. 371; A.E. J.W. Stucki)