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Geochemical and mineralogical characterization of a Lower Cretaceous sedimentary profile from central Algarve (Portugal)

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Abstract

Geochemical and mineralogical studies were carried out in Cretaceous sedimentary rocks from a profile of the central Algarve (Portugal), with the aim of contributing to the analysis of paleoenvironmental variations, during Cretaceous, in the Algarve Basin. Major and trace analysis provided information on the provenance, sedimentary history and geochemistry of the Cretaceous sediments. The clay assemblage (illite/kaolinite) and high Zr/Rb ratios point to a strong continental influence and early diagenesis. The chemical variability for most elements is concordant with variations in the grain-size distribution, with the exception of some transition trace elements. There is a strong relationship between the levels formed under more reducing conditions (richer in organic matter) and higher positive anomalies of transition elements like Zn, Co, U, As and Sb. These observations enhance the role of organic activity in modifying the chemical composition of rocks. The mineralogical content, as the presence of reduced sulfur species (pyrite), and some field observations suggest the preservation of different redox regimes in the sedimentary column, denoting paleoenvironmental variations.

Keywords: Sedimentary profile; Geochemical anomalies; Redox environment; Sulfate reduction; Paleoenvironmental variations

1. Introduction

The Algarve sedimentary basin, located in South Portugal, is a large basin elongated in the E–W direction and comprising sediments from Triassic to Quaternary ages. The sedimentary filling began as a consequence of a distensive phase (“rifting”) initiated between the Upper Triassic and Liassic (Mougenot et al., 1979). The basin Cretaceous sedimentation is characterized by important facies variations and sedimentary discontinuities. Occidental and central Algarve has sedimentary characteristics of more shallow waters than the oriental, predominating detritic deposits (conglomerates, arenites and argillites) over carbonate sediments.

2. Material and methods

Chemical and mineralogical characterization of clay deposits from the Algarve have been carried out by members of the Instituto Tecnológico e Nuclear (ITN) with the general objective to study the distribution of such deposits and, in a more detailed scale, their local variations. In that later perspective, were taken 8 samples from a sedimentary column of about 12 m, of a Cretaceous clay exploration (Vales no. 5) in the Algoz

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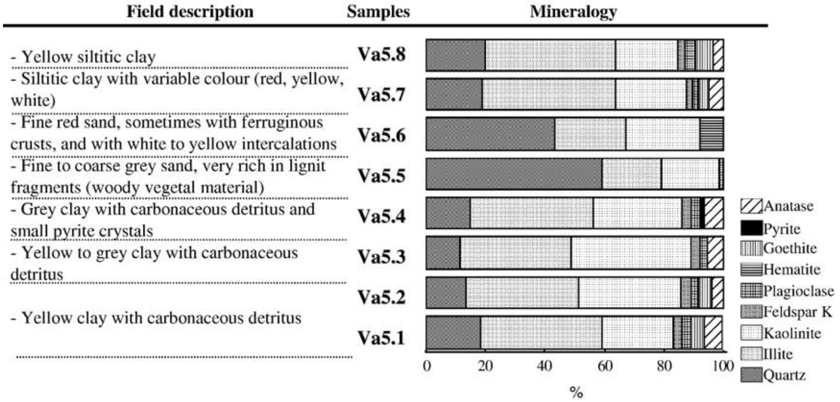

Fig. 1. Field sample description and bulk rock and clay mineralogy (represented by the columns sequential/stacked plot) along the sedimentary profile.

region, central Algarve. A summary description of the samples is given in Fig. 1.

Chemical analyses were performed by X-ray Fluorescence (major elements) and by the Instrumental Neutron Activation Analysis method (trace elements) developed at ITN (e.g. Prudêncio et al., 1986).

X-ray powder diffraction (XRD), using Cu-Kα radiation, was the method selected for the mineralogical analysis of the bulk rock and clay fraction. Oriented mounts were prepared by settling a suspension of the <2 μm grain-size fraction (separated by settling in distilled water), air-dried, glycolated and heated at 300 and 500 °C.

3. Results

3.1. Mineralogy

Fig. 1 represents a semi-quantification of the principal minerals encountered in the studied sediments. With the exception of the more quartz-rich coarser samples, Va5.5 and Va5.6, as suggested in Fig. 2A, there is a predominance of the clay minerals illite and kaolinite in similar proportions. Accessory minerals are more abundant in the finer samples, and they include K feldspar, plagioclase, goethite, anatase, hematite and rarely pyrite. The principal Fe-bearing mineral is goethite, which is present in half of the samples. In the samples without goethite, one of them, the gray clay Va5.4, contains pyrite and another one, the red sand Va5.6, contains hematite.

3.2. Geochemistry

Analyzed samples have high values of chemical index of Weathering (CIW), which average values vary from 96 (clay samples) to 78 (sand samples). These high CIW values, due to the general depletion in Na_2O and CaO relatively to the upper crust (e.g., Rollinson, 1993), suggest severe alteration on land of these source rocks.

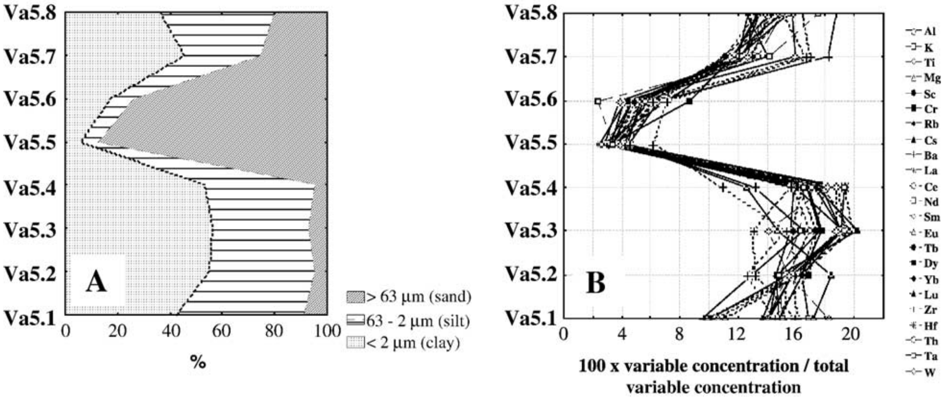

Fig. 2. (A) Area sequential/stacked plot of the particle size distribution; (B) multiple line plots (variables) showing chemical composition variability, along the sedimentary profile.

The comparison of the grain-size distribution along the profile and the chemical composition (Fig. 2), indicate that the variability for most elements is related to variations in granulometry. This distribution pattern is observed for Al, K, Ti, Mg, Sc, Cr, Rb, Cs, Ba, REEs, Zr, Hf, Th, Ta and W, suggesting their general enrichment in the finer samples. Similar result is obtained through cluster analysis, using Pearson coefficient, enhancing a high correlation between Al (indicator of clay fraction) and most of such elements.

The variability of the elements with a more independent distribution relatively to grain-size is represented in Fig. 3. The red sand sample (Va5.6) is the richest in Fe, and also has high values of Br (correlated with Fe, $r=0.91$) and As (uncorrelated with Fe). The gray clay sample, Va5.4, is enriched in Zn and Co (strongly correlated, $r=0.98$) and U. Elements such as Mn and Ga are enriched in the yellow clay, Va5.2, and others, like Si, Na, P and Sb, are little variable across the profile.

The patterns of rare earth elements (REE) normalized to chondrites show enrichment in LREEs ($La_N/Yb_N=4.80–9.28$), a negative *Eu* anomaly ($Eu/Eu^*=0.64–0.73$), and a weak *Ce* anomaly ($Ce/Ce^*=0.87–0.93$), which are typical of sediments and similar for all samples, differing in the relative proportion of the total REEs content.

4. Discussion

The clay assemblage of the rocks can give important constrains about the proximity of the source area and the diagenesis evolution in the study of sedimentary basins (Millot, 1964). Illite and kaolinite, and some unidentified mixed layers, are the only clay minerals present in the studied sediments. Illite is a ubiquitous mineral, while the presence of kaolinite is mostly connected with relative proximity to exposed areas (Ortega, 1995). Similar conclusions are reached using the Zr/Rb ratio (1.2–3.7), as indicator of the relative proportions of detritial and non-detritial fractions in the sediments. Because Zr is mostly present as zircon and is a heavy metal very resistant to weathering, the high Zr/Rb values are suggestive of a great influx of detritial materials in the Algarve basin during Lower Cretaceous.

The presence of pyrite in Va5.4 is indicative of sulfate and organics because the formation of stable pyrite requires an anoxic sedimentary environment, where reduced iron Fe(II) can exist in solution. The sequence of alternating organic-rich and organic-poor layers in the sedimentary record allows us to put forward some paleoenvironmental considerations. In the profile under study it can be found relicts of different redox regimes, where the enrichment in reduced sulfur species, like it occurs in Va5.4, indicates episodes of sulfate reduction and, iron (hydr)oxide-enriched layers, as represented in Va5.6, indicate boundaries of oxic and suboxic sediments (e.g., Van Santvoort et al., 1996).

Microbial activities can exert enormous influences on the biogeochemical cycles of elements, interconverting species that display remarkably different behaviors like, for example, arsenic. In well-oxygenated waters, As(V) is the dominant species and may forms strong complexes on Fe (hydr)oxides. Under slightly reducing conditions As(V) is reduced to As(III), which sorbs less strongly to Fe (hydr)oxides. The reduction of As(V), arsenate, to As(III), arsenite, by microorganisms is widely referred in the literature.

Fig. 3 shows that the most oxidized sediments, represented by the Va5.6 sample, are the richest in As, probably incorporated in hematite; as the redox potential decreases, a reductive dissolution of Fe(III) (hydr)oxide minerals may occur before As reduction, causing As(V) release in solution. These could explain why there is less As in the levels containing goethite

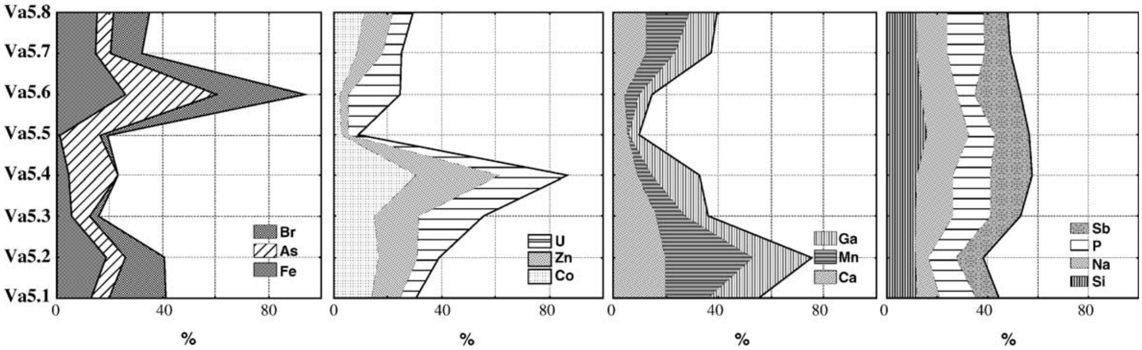

Fig. 3. Area sequential/stacked plots showing abundance variations of some chemical elements along the sedimentary column.

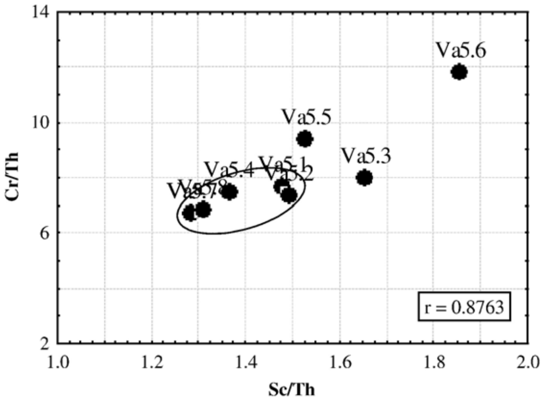

Fig. 4. Sc/Th vs. Cr/Th diagram for the eight samples of the studied Cretaceous sedimentary column, enhancing compositional variations of the source area.

(Va5.1, Va5.2, Va5.7, Va5.8); below the anoxic boundary and in association with sulfate reduction, the formation of sulfide minerals like pyrite is possible, which can incorporate reduced arsenic. These conditions are represented in Va5.4 sample, which contains pyrite but no goethite or hematite, and where higher As concentration is again observed.

Besides As, microorganisms may influence the distribution of other elements. For example, Ortega et al. (1991), studied the Toarcian sedimentation of central Italy and identified sub-environments, in the general shallow marine paleoenvironment, that enable the deposition of black shales with important positive anomalies in As, Zn, Co, Cu As, Pb, V, Cr, Ba.

The bivariate plot Sc/Th vs. Cr/Th (Fig. 4) can be used as indicator of sediment source composition. These ratios point to an overall more mafic composition of the source of the red sand (Va5.6), contrasting with the upper layer sediments of more felsic composition. Although some chemical differences between samples may be caused by differences in source area composition, as suggested in Fig. 4, these do not explain all chemical variability. In fact, if we focus on the clay samples that derived from a similar source, it is possible to observe some important chemical variations. In particular the gray sample Va5.4, generated under anoxic conditions, is characterized by significant positive geochemical anomalies in the trace elements Co, Zn, U, As, Sb and total REE content (mostly LREE), which clearly distinguishes it from the more oxygenized clay sediments. The higher trace element anomalies of the level in which maximum anoxic conditions were reached, represented by Va5.4 sample, is evidenced comparing their values (underline) and the mean values for the other clay samples (italic) that lye within the circle defined in Fig. 4: Co-27/*11*, Zn-117/*43*, As-23/*8*, Sb-1.7/*1.0*, $\sum$REE-213/*118*, U-9/*3*.

5. Conclusions

The studied sedimentary profile, corresponding to a small sample of the Cretaceous filling of the Algarve basin, put in evidence the proximal character of the continental source that suffered intense weathering and the early state of the diagenesis process. Some geochemical anomalies were detected which appear to be due to microbiological activity in anoxic environments.

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