

Sediment Geochemistry on the Portuguese Continental Shelf

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Objectives

Run-off and sediment load carried by rivers through estuaries to the continental shelf has been drastically modified because of a range of anthropogenic activities: damming, mining and urbanisation. Among them are the large river basins of the West Iberian margin (Minho, Douro, Tejo and Guadiana), which have been differently influenced by such effects.



At the North, Minho and Douro drainage basins are large and have strong industrial, agricultural and population implantation. At the Western region flows the Tagus river, the largest in Iberian Peninsula, in which estuary is concentrated one of the highest industrialised areas in the country. The Guadiana river basin runs along the SW Iberian region drains an arid mining area (Iberian Pyrite belt) and presents extreme annual climate variability and high inter-annual flow variability. River mouths are: 1. directly exposed to incident dominant waves (Douro and Guadiana) and 2. a protected river mouth (Tejo).

The geochemical characterisation of sediments along whole the Portuguese Continental Shelf in regions adjacent to those river basins is being used to evaluate the consequences caused by the changes that occurred during the last millenia in the basins. An interdisciplinary approach is being carried out

combining mineralogy, nanoplankton, meteorology, climate, oceanography, dating, sedimentology and historical aspects.

Results

Geochemical characterisation of the collected sediment core indicates that the Douro basin is apparently the main source of the shelf fine sediments, although these sediments do not present any signals of anthropogenic contamination. However, in this region, sediments pass through many remobilisation and mixing processes during a long transport until being deposited in the shelf.

Southwards, at the continental shelf adjacent to the Tagus estuary, the anthropogenic (Cr, Cu, Zn and Pb) contamination and specific lithological influences (Al, Ca and Sr) of the drainage basin are clearly identified. Tejo estuary is located in a region with a strong industrial, agricultural and population implantation and the polluted sediments are fastly deposited due to the continental shelf geomorphology.

At the Southwestern Iberian Continental Shelf, the temporal and spatial elemental distribution patterns were established along the shelf between the Guadiana and Tinto/Odiel rivers.

An enrichment in some metals such as Ni, Cu, Zn, As and Pb indicating an anthropogenic source was determined along the mid and out shelf sediments. Variations seem to be dependent on the shoreline distance and bathymetry/ latitude. The heavy metal enrichment can be associated to sulphide minerals related to the presence of the Iberian Pyrite Belt and/or to the mineral wastes of industrial plants.

Downcore profiles on metal concentrations showed a clear enrichment/contamination at the top levels followed by a gradual decrease. Anthropogenic continental influence is visible down to 40-80 cm at which depths, geochemical background values are reached.

Published, accepted or in press work

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Sources of fine organic matter on the Southwestern Iberian continental shelf

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Objectives

Geochemical isotopic parameters used as environmental tracers can be an important tool to assess the sources and destiny of sediment material deposited on the Portuguese shelf. The recent implementation of an elemental analyser coupled to the mass-spectrometer for light isotopes has enlarged the studies on sediment geochemistry and hydrology.

The main study involved the elemental (organic carbon and total nitrogen) and isotopic ($\delta^{13}\text{C}$) record of fine-sized particulate organic matter in



Southwestern Iberian continental shelf sediments

Our major goal was the evaluation of the contribution of terrestrial organic matter in marine

sediments, particularly associated with the sediment load carried by the large Iberian river basins: Douro, Tagus and Guadiana.

Results

Main study has been carried out on shelf sediments from the SW Iberian, in surficial and core samples collected at the influenced area of the Guadiana river.

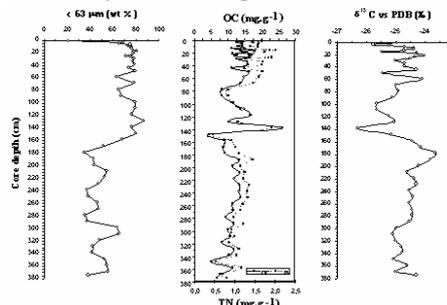
Surficial sediments - The lowest $\delta^{13}\text{C}$ and the highest OC/TN ratios (OC/TN = 9.4 ± 0.9 ; $\delta^{13}\text{C}$ = $-26.2 \pm 0.2\text{‰}$) of the most inner shelf sediments (adjacent to the Guadiana river) reflect organic matter derived from terrestrial C_3 plants. In contrast, evidence of a changing source of organic matter is revealed both by the regular increasing trend of $\delta^{13}\text{C}$ values toward the outer shelf, and by the lowest OC/TN ratios for sediment below 70 m water depth (OC/TN = 8.8 ± 0.2 ; $\delta^{13}\text{C}$ = $-24 \pm 0.3\text{‰}$).

Core 5 - The down-core variation of grain-size distribution ($<63\mu\text{m}$) indicates that fine fraction percentage decreases from 100% at the top to 55% at the bottom, suggesting a major change in sediment supply composition. The regular increase of OC and TN through the core suggests a gradual increase in

fine-sized organic matter supply during the last centuries. Evidence of changing source of organic matter is also shown by the $\delta^{13}\text{C}$ values, ranging from -21.3‰ to -24.9‰ .

Core 8 - The down-core variation of grain-size distribution indicates that fine fraction percentage is predominant ($75 \pm 5\%$) above 170cm depth, contrasting sharply with the values displayed in the deeper part ($45 \pm 10\%$). This later depth corresponds to a major change in sediment supply composition. The regular increase of OC and TN toward the core top suggests a gradual increase in fine-sized organic matter supply. Evidence of changing source of OM is also shown by the $\delta^{13}\text{C}$ values, ranging from -26.3‰ to -23.7‰ .

Terrestrial versus Marine sources of fine-sized organic matter - The negative correlation between $\delta^{13}\text{C}$ values and OC/TN ratios from cores 5 and 8 indicates that the terrestrial source end-member is best approximated by core 8 samples, which have the most



depleted in ^{13}C and nitrogen (high OC/TN) fine organic matter. The marine end-member would have an isotopic signature approached by the most enriched in ^{13}C and nitrogen core 5 samples. Assuming constant $\delta^{13}\text{C}$ end-member values for marine (-20‰) and terrestrial (-27‰) fine-sized organic matter supply along both cores, we can make a semi quantitative estimate of the continental contribution. According to our estimates, 55 to 90% and 20 to 70% of fine-sized organic matter is derived from terrestrial sources, respectively in core 8 and 5.

Studies on elemental and isotopic composition to assess the origin of organic matter are being extended to other regions of the Portuguese shelf and to environmental pollution studies due to agriculture.

Published, accepted or in press work

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Geochemical Palaeoenvironmental Patterns in the Minho and Douro Estuaries

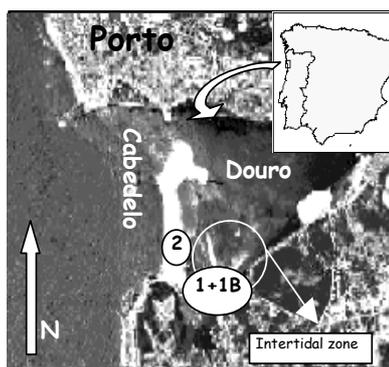
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Objectives

A study on the stratigraphic succession of the sedimentary record of Douro estuary is being carried out aiming the recognition and distinction of the environmental changes, which have occurred during the Late Quaternary. Chemical and mineralogical variations in sediment fragments down to -40m depth are used to characterise the sediment distribution patterns and allow to recognise and evaluate some temporal changes occurred during the last 14000 years.

Results

This work is based on the study of three cores, which were obtained by rotary drilling in the Douro estuary: one in the barrier (core 2) known as Cabedelo and two in the back-barrier (cores 1 and 1B, 50 cm apart), inside de S. Paio Bay.



The core 2 is divided in two units – SED1 and SED2. The lower unit (SED1), comprised between the core bottom and ~-34m and aged between 13750 and 10310 BP, consists of a muddy sand/sandy mud sequence. SED2, comprised between ~-34m and -20m and aged between 10310 and 8930 BP, is constituted by a mud and sandy mud sequence.

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In both units, sediment major and minor elemental composition is in general similar to published values for the mean crust, mean sediment and average shale. The most striking differences are the low contents in Ca and Sr, which is a consequence of the major occurrence of granitic rocks in the region, also confirmed by the high negative correlation with the Zr contents.

Downcore elemental distribution of some lithogenic elements revealed a slight downcore (corresponding to SED1 levels) increase in some lithogenic elements (Al and K), usually associated with the finer grain size fractions. Calcium contents is in general below 0.40%, although considerably higher concentrations have been measured at the sections (-20.53 to -22.74m, corresponding to the upper levels of SED2) in which a slight increase of carbonates was determined. At a much deeper layer (39.46m), considerable higher concentrations of Ca and Zr were measured. Ca values must probably relate to the increase of plagioclases and/or smectites, whereas Zr values may be the signature of the fluvial detrital supply. The Ca increasing tendency in the upper layers of SED2 unit reflects a marine influence, corroborating the results obtained by the calcareous nannoplankton analyses.

The REE distribution patterns usually reflect the provenance of sedimentary rocks, since REE are not easily fractionated during sedimentation. The average shale-normalised REE distribution patterns determined along the unit SED 2 exhibit a strong Eu negative anomaly and are slightly LREE enriched. At the lower section the REE patterns become comparable, probably due the homogeneity of sedimentary materials. The Eu depletion in sedimentary rocks is due to chemical fractionation related to production of K-rich granitic rocks, which typically possess negative Eu-anomalies.

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Geochemistry of lagoonal, estuarine and interdune depressions' sediments

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Objectives

The Portuguese coast shows great environmental diversity, which also contrast in genesis, evolution, morphology and response to forcing factors. Among these environments, sedimentary basins are most suitable to yield geological record of their behaviour at different time-scales. Studies are concentrated in lagoons, estuaries and interdune depressions of the SW coast and related watersheds – Mira River, Albufeira, Melides, Santo André lagoons and Sancha interdune depression. The main objectives are: 1) at macroscale, to establish the evolutionary patterns of these environments since the Late Glacial; to define geochemical signatures for different marine and terrestrial contributions; to evaluate changes in sediment sources; to delineate local fossil background values; 2) at mesoscale, to characterize bottom sedimentation in the last centuries; to understand accumulation of heavy metals resulting from anthropic influence and to quantify enrichment factors; 3) at microscale, to map geochemical parameters and to identify sediment and contamination sources. Geochemical studies integrate a multidisciplinary approach, with sedimentology and paleoecology.

Results

The results presented have been obtained in the scope of one PhD thesis (ongoing), three graduate projects (one concluded¹ and two ongoing) and a report of an 8th semester undergraduate course².

At *macroscale*, the study of two long cores - MIGM (Melides) and MIRA (Mira River) have been initiated and one - LSA6A (Sancha) – is concluded. In the latter, two units (II and III) have been defined overlying basal aeolian sand (Unit I). Unit II consists predominantly of organic debris with interbedded mud, suggesting close dependence to the water level. Unit III is exclusively made of minerogenic mud, in agreement with increase in Al, Si, K and Ti.

At *mesoscale*, the study of five short cores - LA11 and LA19 (Albufeira); LM6 (Melides); LSA7 and LSA11 (Santo André) have been initiated.

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At *microscale*, the study of bottom sediments from Albufeira and Santo André lagoons and Sancha interdune, as well as sediment of Santo André's tributaries is concluded. The analyses of Melides' bottom sediments have been initiated. At Albufeira and Santo André and Sancha systems, major elements reflect directly textural characteristics: coarser minerogenic materials settle near the margins and barrier and show highest concentrations of Si (>30%), whereas finer sediments deposited in the depocenters and are enriched in Al. At Albufeira and Santo André, Ca and Sr reflect essentially bioclastic content and are higher near the tidal inlet, where marine influence is more important, regardless the substrate. At Santo André only Pb seems to indicate incipient contamination. Results obtained in fluvial sediment are in agreement with the different lithologies cut by streams: Cascalheira – high Si (sourced in paleozoic quartzite); Ponte, Badoca, Azinhal, Forneco – high Ca and Mg (sourced in Mesozoic carbonates); Ponte – higher Mn (related to shales rich in manganese)⁴.

The Sancha interdune depression is a peculiar environment: bottom sediment shows normal values of Si and Al but null concentrations of Ca and lower Sr (<100ppm), probably as a result of essentially acidic organic muddy sediment; one relevant result refers to unusually high concentrations in Fe (17%) that can be related with underground leaching and remobilization in acidic environment, followed by precipitation of Fe-oxide films in oxidic conditions near surface. Also, the Cu, Zn and Pb contents higher than the Average Shale, may suggest anthropogenic influence in this system.

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¹ Lab. Processos Costeiros, Dept. Geologia FCUL.

Groundwater Resources as Indicators and Archives of Palaeoclimatic Changes

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Objectives

The scarcity of fresh water, degradation of its quality and increasing demands has fostered interest in isotope methods as tools to characterise and manage freshwater resources. In the last decades, the groundwater resources have become progressively more endangered, by accelerated modification of their natural conditions due to industrial development, associated with the growing of population and intensive agriculture. Recharge of groundwater is one critical aspect in water resource management and environmental isotopes are of a great importance to determine both the area and rate of recharge. The origin of different groundwater systems located at the North and Southeast of Portugal is being determined by using isotopic and geochemical parameters. The characterisation of deep aquifers and the relation with shallow groundwater is being carried out, as well as, the definition of groundwater characteristics with respect to environmental issues.

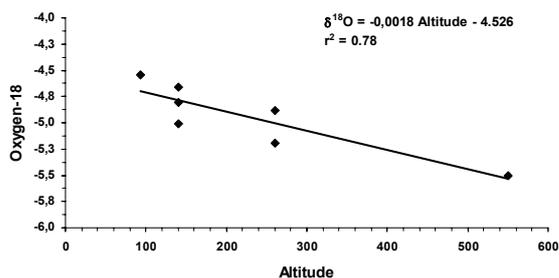


Fig.1. Estimation of the altitude gradient in Caldas de Monção.

Published, accepted or in press work

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Results

Our main study areas are located at NE Portugal, namely, Caldas de Monção geothermal mineral water, Caldelas and Gerês Spas and in SE Portugal, at Cabeço de Vide mineral waters. At Caldas de Monção the isotopic gradient estimated for $\delta^{18}\text{O}$ is -0.18‰ per 100m of altitude, pointing to a recharge altitude for the thermomineral system between the 300m and 600m and a mean altitude value around 400m a.s.l., south of Caldas de Monção (Fig.1).

The $\delta^{13}\text{C}$ determinations carried out on the TDIC of Caldas de Monção thermomineral system were in the range of -7.06‰ in AC1 borehole and -6.25‰ in AC2 borehole. These results suggest that the CO_2 origin can be explained by a mixing between atmospheric CO_2 and deep-seated - upper mantle CO_2 . The apparent groundwater ages obtained for AC2 and AC1 thermomineral waters were 14.11 ± 1.69 ka BP and 18.56 ± 2.32 ka BP, respectively.

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² Centro Geologia, FCUL.

Groundwater resources assessment by anthropogenic and natural contamination sources

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Objectives

Concerted prevention and control may remedy pollution of surface waters. However after the infiltration of pollutants in the groundwater, they may be retained within aquifers, being very difficult to clean them up. We have been studying the quality of groundwater sources for Human supply, through the identification and quantification of pollution sources traced by environmental isotopes ($\delta^{13}\text{C}$, $\delta^{15}\text{N}$, $\delta^{18}\text{O}$, $\delta^2\text{H}$ and ^3H). Isotope data may assess the vulnerability of groundwater to surface pollution by determining how rapidly it moves and where it is being recharged. The origin of pollution in surface waters can be sorted into natural, industrial, agricultural or domestic. Besides, isotopic techniques may identify incipient pollution, providing an early warning before chemical and/or biological indicators.

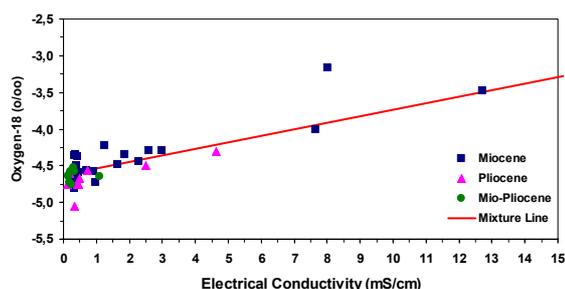
Results

Agricultural practices and highly industrialised areas must be seen as new inputs of pollution to the environment (sediments and hydrological domains), through demographic density increase and growing of contamination. Also seawater intrusion process in coastal areas due to overexploitation of the groundwater systems can lead to the degradation of the water quality.

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5. P.G. Fernandes, P.M. Carreira, M.O. Silva, Anthropogenic inputs traced by hydrogeochemical features in Sines coastal aquifers - SW Portugal, *Séminaire International Isotopes et Ressources en Eau*, Marrakech, Maroc, 30 September–1 October (2004) 18-19.

The Sado-Sines coastal aquifers (systems located at coastal regions) have been exposed to increasing salinisation and pollution.



The first consequence is usually associated with the effects of seawater intrusion due to overexploitation of the groundwater system and by sea-salt spray. Besides, different anthropogenic activities including domestic wastes, agriculture and industry are inducing the degradation of the water quality. In the Sines basin, anthropogenic contamination of the groundwater systems by fertilisers was detected.

Studies carried out in the Sado Miocene Aquifer reveal a strong increase of the groundwater mineralization, which lead to the degradation of these natural resources. The isotopic results have demonstrated that the salt increase is related with seawater encroachment in Setubal and Troia areas.

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National Network for Isotopes in Precipitation

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Objectives

Interpretation of the isotopic composition in terrestrial water (groundwater resources and superficial waters) requires knowledge about the meteoric water that feeds them: rain and snow. Their isotopic composition is quite variable in time and space and depends on climate, geography, nuclear fallout and also other factors. For more than a decade we have been participating in the Global Network for Isotopes in Precipitation (GNIP) in a close collaboration with the Isotope Hydrology Section of the IAEA. The work carried out aims to provide basic isotope data (²H, ³H and ¹⁸O), for hydrological investigations, by determining the temporal and spatial variations of these environmental isotopes.

Results

The results obtained under a CRP Project allowed the study of the air masses transport in some parts of the Mediterranean Basin

The correlation between the water vapour samples and precipitation events is not always clear, probably due to different characteristics of the sampling periods, although a general similar evolution can be observed. The large depletion in the isotopic composition found in vapour and rain event samples is associated with the depressions over Atlantic (in front of the Portuguese coast – Mid North Atlantic) or over the British Islands, crossing Portugal mainland (W to E). The atmospheric weather depressions induce a progressive depletion both in rain and water vapour (Fig. 1).

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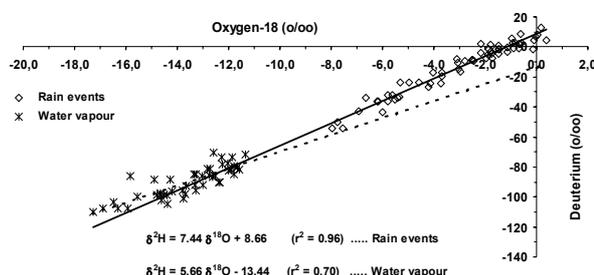


Fig. 1. $\delta^{18}\text{O}$ versus $\delta^2\text{H}$ in atmospheric water vapour and daily precipitation events

Regional variations in the ³H content (monthly data) between littoral and interior stations are probably a result of the oceanic dilution of the tritium content in the atmospheric water vapour (Fig. 2).

All the obtained isotopic results are compiled and gathered in the IAEA Data Base and disseminated via IAEA publications to be used in international hydrogeological and climatologic studies (www.iaea.org/programs/ri/gnip/gnipmain.htm).

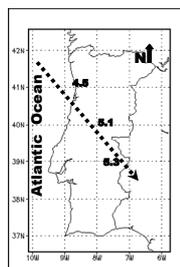


Fig. 2. Tritium concentration (TU) from coastal towards the hinterland stations. Dilution effect by oceanic water masses.

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Archaeometallurgy–Provenance, Technology and Use of Metallic Artefacts

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Objectives

This area intends to comprehend the technological and social conditions of metallic artefact production and circulation in the pre-history of Portugal. The work combines analytical and archaeological studies concerning, in particular, the Chalcolithic and Bronze Ages from the Portuguese territory. Elemental composition of metallic artefacts provide significant information regarding the technology and evolution of metal fabrication, as well as, the amounts of metal production, circulation and socio-economic implications in the dynamics of the Pre-historic Age peoples of Portugal.



Results

The archaeometallurgical studies carried out concerned mainly two important areas of the Portuguese territory: the Estremadura and Beira Alta.

Penedo do Lexim – The work carried out in the last years regarding this settlement, located 40 km up north of Lisbon and occupied since the 4th millennium BC till the Bronze Age, led to important conclusions: (i) the copper artefacts appeared only during the Full Chalcolithic Age and constitute merely a minor percentage of the recovered materials, pointing out to the reduced importance of the metallurgy in this society. Contrary, during the Bronze Age, the increasing weight of the metallurgical operations is well characterised by the binary and ternary bronzes

recovered, which compose the principal material remains from this period.

Castro de Pragança – The large collection of metallic artefacts analysed confirmed the occupation of this site during the Bronze and Iron Ages. The collection proved to be composed of copper, arsenical copper, bronze and leaded bronze materials, with the preponderance of the bronze materials. The majority of the analysed artefacts are related with Late Bronze Age productions, being composed mainly by weapons and tools. The presence of high leaded bronzes suggests the trade of materials with regions up to the north of the Portuguese territory, probably exchanged by tin, which was a very common item in the area.

Castro da Senhora da Guia de Baiões – This site constitutes one of the central places in the Baiões/Santa Luzia Cultural Group, with the most important collection belonging to the Portuguese Late Bronze Age. Although some bronze artefacts with high lead contents were identified, the majority of the artefacts recovered were bronze alloys. The Late Bronze Age Atlantic typology of those artefacts is not consistent with the chemical composition, since the “Atlantic Bronzes” are usually made of leaded bronze alloys. In this settlement, the investigation has shown a more complex situation, where both Atlantic and Mediterranean traditions co-existed.

Castro da Senhora das Necessidades – The socketed spearhead recovered here constitutes exactly one of the exceptions to the predominance of the binary bronze alloys in the Baiões/Santa Luzia Cultural Group. This artefact is composed by a ternary bronze (~5% of Pb), alloys very common in France and in the British Islands. However, in our case the ternary alloy, associated with the typological diversity characteristic of the spearheads, were understand as the result of a local metallurgical production with a weak circulation between the different areas of the Portuguese territory.

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