

Environmental and Analytical Chemistry

Maria de Fátima Araújo

The activities of the Environmental and Analytical Chemistry Group (EAC) combine fundamental and methodological research related to **Elemental and Isotopic Analysis** as well as their applications in the fields of **Environmental Geochemistry, Isotope Hydrology, Oceanography** and **Archaeometry**.

Different facilities are available in our group: an **Energy-Dispersive X-Ray Fluorescence spectrometer**, two dedicated on-line **Isotope Ratio Mass Spectrometers** systems, equipped with elemental analysers, a **Tritium Laboratory**, a **Radiocarbon Dating Laboratory** and a **High Performance Liquid Chromatograph/ Inductively Coupled Plasma Mass Spectrometer** installed in a clean room facility.

Major achievements are summarized below:

Environmental Geochemistry and Oceanographic research was carried out under a multi-proxy approach, involving elemental, organic and isotopic analysis, sedimentology, geochronology and absolute dating. An evaluation of environmental changes on the NW Iberian coastal area, using geochemical approaches, showed an important input from terrestrial sources reaching a maximum at AD 1100-1200 and AD 1750-1850, time periods during which have occurred major flood events. Significant reduction in the terrestrial signature was detected in more recent times (ca. AD 1960-1985), contemporary with the construction of major dams on the Minho River.

Oceanographic studies concerning the marine reservoir effect (ΔR) were “completed” concerning two regions: Canary Islands and Cape Verde Archipelago. ΔR takes a positive weighted mean value of $+185 \pm 30$ ^{14}C yr for Canarian eastern islands (Fuerteventura and Lanzarote), while for central and western islands ΔR value is 0 ± 35 ^{14}C yr, in accordance with the hydrodynamic system off Canary Islands. Also, a first ΔR calculation was done for the Cape Verde Archipelago (ΔR weighted mean value of $+70 \pm 70$ ^{14}C). This value is in agreement with the oceanographic conditions of the region indicating the existence of a seasonal active upwelling regime.

Isotope Hydrology studies were realized taking into account the sustainable regional development and the appropriate use of the water resources and coastal management, based on several European and national directives. Investigations on the use of environmental isotopes hydrology in different systems has been continued, e.g. on the evaluation of geothermal potential and of seismo-volcanic hazard at Azores archipelago; on high mountain areas; on arid and semi arid zones and on gas geochemistry in CO_2 -rich thermomineral waters in the N Portugal and Spain.

Archaeometallurgical research was pursued by the characterization of metallic artefacts and production remains from Chalcolithic till Early Iron Age, recovered from different regions of the Portuguese territory. A Late Bronze Age metallurgical workshop was studied and evidences on bronze production by co-smelting were found (Entre Águas 5). Besides, the influence of the As contents on the thermo-mechanical properties of Chalcolithic artefacts (from V. Nova S. Pedro) was investigated. From the N territory, studies have shown evidences of a bronze metallurgy with higher Pb contents than contemporaneous bronzes from Central and Southern regions. Also, the characterization of Bujões/Barcelos axes, assumed to be linked with the production of the first bronzes in the Portuguese territory, showed they were manufactured in bronze, with rather uniform tin content and a low impurity pattern.

During the current year, a high-frequency Liquid Water Isotope Analyzer (LWIA - LGR DT-200) that quantifies $\delta^2\text{H}$ and $\delta^{18}\text{O}$ in multiple natural water sources, simultaneously, was installed reinforcing the isotope hydrology field. The installation of the IRMS, equipped with an elemental analyser (Sercon 20-20 EA-IRMS), has permitted relevant contributions in the palaeoenvironmental and archaeological fields. Provenance studies of Cu-based metal archaeological artefacts using Pb isotope ratios were initiated by Q-ICPMS.

The EAC group is highly engaged in education and training of M.Sc. and Ph.D. students in collaboration with different Universities. Technical services are available to Public and Private Institutions.

Research Team

Researchers

M.F. ARAÚJO, Princ, Group Leader
A.M.M. SOARES, Princ.
J.M. DE LA ROSA, Aux.
P. CARREIRA, Aux.
E. FIGUEIREDO, Post-Doc, FCT grant

Students

J. MARTINS, Ph.D. student, FCT grant
M. J. FURTADO, Ph.D. student, FCT grant
F. LOPES, Graduate student
I. PEREIRA, Graduate student

F. PEREIRA, Graduate student
P. PORTELA, Graduate student
S. GOMES, Graduate student

Technical Personnel

A. AMARO
D. NUNES
M. CORREIA
M. MATEUS, FCT grant (Since September)
P. VALÉRIO

Environmental changes in the Portuguese coastal area by organic geochemical approaches

A.M.M. Soares, J.M. Rosa, J.M. Martins, P. Portela, M.F. Araújo, F.J. González-Vila¹, F. Fatela², A.R. Pereira³

Objectives

Over the last 5000 yr different trends of sea level, climatic fluctuations, Bond events or humid episodes have been recorded in the Iberian Peninsula, as well as the increase of the human intervention in the landscape, particularly sensitive since the Middle Bronze Age, all imprinted in the filling-up of the alluvial plain estuaries. To assess the evolution of interface environments along the Portuguese coast, several estuaries presenting different characteristics (e.g. geologic, geomorphologic, climate, human occupation) were selected. Spatial and temporal distribution patterns on their sedimentological, geochemical and isotopic parameters provide evidence of the evolution, extension and impact of human activities, also allowing the identification of climatic events from recent to millennium time scales. The overall objectives of this work are the evaluation, in different coastal environments, of the fluvial and marine contribution to the sedimentary record, the responses to climatic events and the impact of land use changes. Several different estuarine environments are under investigation, from the Minho estuary, at the NW border with Spain till the Guadiana, delimiting the SE Spanish border.

To achieve the above mentioned goals several approaches are being applied focused on the study of the sedimentary organic matter (OM) on dated sequences. Sedimentary OM was characterized using several organic geochemical methods and indices, including elemental carbon, nitrogen and sulphur abundances (C, N, S), molar organic carbon to nitrogen and sulphur ratios (Corg/N; Corg/S), and stable organic carbon isotope values ($\delta^{13}\text{C}$; $\delta^{15}\text{N}$). Besides, the distributions of several lipid-biomarker's compounds were also evaluated to precisely identify OM sources and the relative contributions of autochthonous and allochthonous OM inputs to the sedimentary record over a wide range of temporal and spatial scales.

Results

During 2011, studies were mainly focused on the salt-marshes of the Minho and Mira estuaries located at the western coastal area and at the Guadiana river adjacent shelf.

Significant conclusions could be taken concerning the Minho estuary, summarized as:

(1) $\delta^{13}\text{C}$, TOC, TN, C/N and the distribution of biomarkers show that the OM is primarily derived from terrestrial sources, reaching the maximum terrestrial signature during the Little Ice Age.

(2) Samples corresponding to the period 1960–1985 presented low Corg/N ratio and heavier $\delta^{13}\text{C}$ values indicating a significant increase in the marine input. This is likely due to the drastic reduction in River discharge associated with the construction of several major dams.



(3) Alternations in the C/N and $\delta^{13}\text{C}$ values through the 18th and 19th centuries were consistent with fluctuations of the n-alkyl parameters. They reveal common intensive precipitation alternating with severe droughts recorded.

(4) High C/N and lipid content at approximately AD 1100 suggest punctual increase in the continental discharges, which is contemporary with major flood events reported at that period in the area.

(5) High TS and very low Corg/S values could be derived from the mining exploitation during the Roman domination.

(6) Changes in land use practices (deforestation and intensification of cultivation) have been identified during the Roma Period. Also, a significant increase was observed in the contribution of marine phytoplankton at AD 100–200, which may be related to the marine highstand reported by several authors during the early Roman Warm Period.

Selected publications

J.M. De la Rosa, M. Santos, M.F. Araújo (2011) Metal binding by Humic Acids extracted from recent sediments from the Southwest Atlantic coast of the Iberian Peninsula. *Estuarine Coastal and Shelf Sciences*, 93, 478-485.

J. M. De la Rosa, M. F. Araújo, J. A. González-Pérez, F. J. González-Vila, A. M. Soares, J. M. Martins, E. Leorri, R. Corbett, F. Fatela (2011). Organic matter sources to tidal marsh sediment over the last two millennia in the Minho River estuary (NW Iberian Peninsula). *Organic Geochemistry* (in press)

¹ IRNAS, CSIC, Seville, Spain; ² Lab. de Processos Costeiros, Centro e Dep. Geologia da FCUL, Lisboa, Portugal

³ Centro de Estudos Geográficos, IGOT, Univ. Lisboa

Secular variations on the sedimentary elemental composition in western Portuguese estuaries salt marshes*M.F. Araújo, I Pereira, J.M. Rosa, F. Fatela¹*

Elemental geochemistry and sedimentary analyses are being used as fundamental tools in the study of estuarine systems evolution. Several salt-marshes located in different estuaries along the W coast (Minho, Tagus and Mira rivers) were selected based on their protected settings, which allow higher accuracy in the assessment of specific temporal changes. The overall objectives of this current work are the recognition of recent environmental changes which have occurred at the main Portuguese estuaries and coastal lagoons, by multidisciplinary approaches to trace the history of the sedimentary record. Geochemical data of sediment cores collected in salt marshes from estuaries located along the W coastal region (Minho, Tagus and Mira) display the different characteristics on the Human occupation, lithology of each drainage basin and sea level. In general, variations on the elemental contents in the lithogenic/continental (e.g. Ti, Zr, K, Rb) are being related with stronger terrestrial sources (flood periods), whereas high Ca, Sr, Cl and Br are associated with a dominant marine contribution. Concerning the anthropogenic trace elements (e.g. Cu, Zn, As and Pb), enhanced values could be detected in the Minho and even more significant in Tagus, revealing the effects of Human occupation and industrialization levels. Mira sediment core presents in general, rather homogeneous elemental composition and no signs of anthropogenic influences, probably a consequence of a rather low human occupation along the times.

¹ Lab. de Processos Costeiros, Centro e Dep. de Geologia da FCUL, Lisboa, Portugal

The oceanic radiocarbon reservoir effect in regions affected by the NW Africa coastal upwelling system*A.M. Monge Soares, J.M. Matos Martins, P. Portela, A. Mederos Martín¹, J.L. Cardoso²*

The quantification of the oceanic (or marine) radiocarbon reservoir effect (ΔR) is essential not only to calibrate conventional radiocarbon dates from marine shell samples with reliability but also to provide information concerning the intensity of coastal upwelling in marine regions affected by this phenomenon. The NW Africa coastal upwelling system characterized by a complex and heterogeneous oceanographic pattern extends south to Cape Verde Islands in winter and north to the Iberian Peninsula in summer. The dominant oceanic current is the Canary Current, which marks the eastern boundary of the North Atlantic Ocean subtropical gyre. Research regarding that quantification issue has been done for the Atlantic Iberian coast, namely for the north-western and western Galician coast, Portuguese western coast and northern region of Gulf of Cadiz (the Barlavento and the Sotavento regions of Algarve and the Andalusian coast). The marine radiocarbon reservoir effect of two other regions – the Canary Archipelago and the Cape Verde Islands – has also been a matter of study in recent years. In this manner the variability in the ΔR around the Canary Islands was determined. ΔR takes a positive weighted mean value of $+185 \pm 30$ ^{14}C yr for eastern islands (Fuerteventura and Lanzarote), while for central and western islands the acceptable ΔR value is 0 ± 35 ^{14}C yr. These values are in accordance with the hydrodynamic system off the Canary Islands characterized by a coastal upwelling regime that affects the eastern islands but not the remaining islands. Archaeological excavations at São Vicente Island, Cape Verde Archipelago permitted the first calculation of the marine radiocarbon reservoir effect for this region. A ΔR weighted mean value of $+70 \pm 70$ ^{14}C yr was obtained. This value is in accordance with the previously published oceanographic conditions of the region indicating the existence of a seasonal active upwelling regime.

¹ Dep. de Prehistoria y Arqueología, Univ. Autónoma de Madrid, Campus de Cantoblanco, Madrid, Spain

² Univ. Aberta, Lisboa. Centro de Estudos Arqueológicos do Concelho de Oeiras (Câmara Municipal de Oeiras)

Isotope Hydrology and geochemistry*P.M. Carreira, D. Nunes, J.M. Marques¹, M.R. Carvalho², J. Espinha Marques³; A. Carvalho³; G. Capasso⁴, F. Grassa⁴, J.C. Nunes⁵*

Isotope Hydrology studies aiming to contribute to a better understanding of the dynamic evolution response of groundwater systems to Human influences such as industrial development associated with the growing of population and intensive agriculture activities. Groundwater resources have become progressively more endangered by accelerated modification of the natural conditions. Environmental isotopes represent an important tool for hydrological investigations, relevant for the management, protection and development of water resources. Under these objectives, work has been carried out in: i) Azores archipelago to characterize the chemical and isotopic composition of ground waters, fumaroles and gas emissions related with hydrothermal/geothermal systems and volcanologic/seismic settings; ii) arid and semi arid zones (recharge areas and seawater intrusion); iii) high mountain areas and iv) gas geochemistry in CO₂-rich thermomineral waters. These investigations are essential to the exploitation and future development of regional water resources and to the delimitation of protection areas.



¹ Dep. de Engenharia de Minas e Georrecursos, I.S.T., Lisboa, Portugal; ² Dep. de Geologia, Fac. Ciências da Univ. Lisboa, Lisboa, Portugal; ³ Fac. de Ciências, Univ. Porto, Portugal; ⁴ Ist. Nazionale di Geofisica e Vulcanologia, Palermo, Italy; ⁵ Dep. Geociências, Univ. Açores, Ponta Delgada, Portugal

Archaeometallurgy – Provenance, metal composition and manufacturing techniques

M.F. Araújo, P. Valério, E. Figueiredo, M.J. Furtado, F. Pereira, F. Lopes, S. Gomes, A.M.M. Soares, R.J.C. Silva¹

The study of ancient metallurgy has provided important information on past technologies and cultural spheres of interaction. Main studies involve elemental analysis and microstructural characterization made on metallic artefacts and production remains from Chalcolithic till Early Iron Age, recovered from diverse sites and regions of the Portuguese territory. In the Southern Portuguese territory, a study of circa 50 artefacts from Torre Velha 3 identified an early introduction of bronze in this region, dated to the second quarter/beginning of the third quarter of the 2nd millennium BC. Also, various studies on artefacts from Late Bronze Age and Early Iron Age sites (e.g. Entre Águas 5, Outeiro do Circo, Martes, Mangancha and Cabeço Redondo) have provided detailed information on metallurgical processes and metals. Discoveries of a Late Bronze Age metallurgical workshop with indications on bronze production by co-smelting of copper ore and cassiterite and the identification of an exceptional bronze nail with a gilded head by the attachment of a thin gold foil, both in Entre Águas 5 are worth to mention. In the Central Portuguese territory, detailed analysis on 53 artefacts from Vila Nova de São Pedro has highly improved the knowledge on Chalcolithic metallurgy. In this site, both copper and arsenical coppers have been identified for the manufacture of various types of artefacts. From the Northern Portuguese territory, analysis on various metallic artefacts and some metallurgical remains from the second quarter/beginning of the third quarter of the 2nd millennium BC and Late Bronze Age found at Fraga dos Corvos site have been made. Analyses have shown evidences of a bronze metallurgy with higher Pb contents than contemporaneous bronzes from Central and Southern territories. Also, 10 axes of Bujões/Barcelos from Central and Northern territories were characterized. So far, the analyses show that this type of axe, which is assumed to be linked with the production of the first bronzes, are manufactured in bronze alloy with rather uniform tin contents and a low impurity pattern. Finally, the first approach on metal provenance through the determination of Pb isotopes was initiated, with the analysis by ICP-MS of some artefacts from Fraga dos Corvos.

Finally, a study of the Chinese cash coins of the CCCM collection was finished permitting the establishment of the evolution on the composition and technological production features of the Cu-based coins during a large time period (300 a.C. - 1854 d.C.). Also, the presence of particular metallic phases conferring variable corrosion resistance to the artefacts were identified and associated to the abundance and distribution of specific elements.



¹ CENIMAT/I3N, Dep.Ciência dos Materiais, Fac.Ciências e Tecnologia, FCT, Univ. Nova de Lisboa, 2829-516 Caparica, Portugal