

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**.

Research is developed by a multidisciplinary team constituted by Analytical and Environmental Chemists, Geologists, Biologists and Conservation scientists. Different facilities have been implemented and are maintained by the team: **Energy-Dispersive X-Ray Fluorescence, Light Isotope Mass Spectrometers, Radiocarbon Dating, Tritium Unit and High Performance Liquid Chromatograph/Inductively Coupled Plasma Mass Spectrometer**.

Major achievements were obtained in the different research fields.

Environmental Geochemistry and Oceanographic research was carried out under a multi-proxy approach, including sedimentology, geochronology, absolute dating and paleoecology. Research focused in Sedimentary Geochemistry aimed at the palaeoenvironmental reconstruction along the Holocene on the Portuguese coastal area, in particular at the coastal lagoon of Pederneira and at the salt marshes of some main Portuguese estuaries. Particularly, new studies on Organic Geochemistry have contributed to evaluate the metal binding capacity of humic acids and to assess the origin of organic matter in sedimentary records related to sea level changes. Oceanographic studies concerning the marine reservoir effect, based on **Radiocarbon Dating** of pairs of samples (terrestrial and marine) were enlarged and new data were added the previously obtained allowing for the first time the quantification of ΔR for the Sotavento region of Algarve (Southern Portuguese coast), for the last 3000 yr.

Isotope Hydrology research studies have been developed aiming at to contribute to a sustainable regional development and appropriate use of the water resources. Investigations were carried out in different

environments, mainly Arid and Semi Arid Zones and Gas Geochemistry in CO₂-rich Thermomineral Waters, including the geothermal potential evaluation and the seismo-volcanic hazard assessment at Azores archipelago. These investigations have significantly contributed to the exploitation and development of regional water resources and to the delimitation of protection areas.

Archaeometallurgical research was focused on materials characterization, involving different analytical techniques (EDXRF, micro-XRF, optical metallography, XRD and SEM-EDS) of Cu based artefacts and other remains recovered in different archaeological sites from the whole Portuguese territory. Results have shown that reduction, alloying and recycling operations were probably undertaken in several sites, and that artefact shaping was performed by diverse methods. Obtained results could demonstrate the co-existence of both local and Orientalising signatures of bronze metallurgy during Early Iron Age. Study of the Macao Scientific and Cultural Center Museum Chinese copper cash was focused on the correlation of alloy elemental composition with metallic phases. Current observations showed that minor elements (Sn, Sb, Fe and As) are structurally significant in these coins since they tend to associate affecting the corrosion resistance of the alloy.

The EAC group continued highly engaged in education and training of MSc and PhD students in collaboration with different Universities. Technical services are also available to Universities and to Public and Private Institutions.

Recently, in the sequence of the approval for financing by FCT a new large research project (resulting from the merging of 3 proposals) was initiated aiming at the comprehension of the Early Metallurgy in the Portuguese Territory (PTDC/HIS-ARQ/110442/2008). On the overall, the project main goal is to investigate the metallurgical evolution from Chalcolithic to Late Bronze Age and also during the Orientalizing period in the Portuguese territory.

Research Team

Researchers

M.F. ARAÚJO, Princ. Group Leader
A.M.M. SOARES, Princ
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Students

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I. PEREIRA, Graduate student, FCT grant
P. PORTELA, Graduate student, FCT grant

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Collaborators

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Archaeometallurgy – Provenance, technology and use of metallic artefacts

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

Objectives

Archaeometallurgical research is being based on the chemical and structural characterization of archaeological metallic artefacts, tools and other materials employed in the metallurgical process as well as by-products that were originated during metallurgical operations. Studies have been mainly focused in archaeological materials from the Portuguese territory. Another current investigation in the archaeometallurgical field is being dedicated to the understanding of the production of ancient Chinese coins with diverse compositions, from the Macau Scientific and Cultural Centre collection.

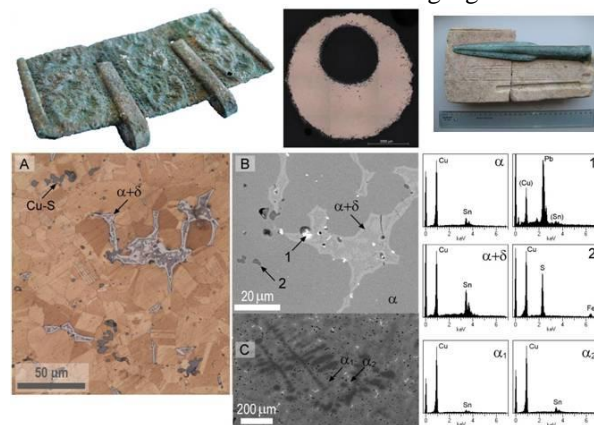
The main used techniques are EDXRF, optical metallography, XRD, SEM-EDS, digital X-radiography and radiocarbon dating aiming at the investigation of the evolution of ancient metallurgical operations, artefact production and corrosion processes (fundamental for conservation strategies).

Results

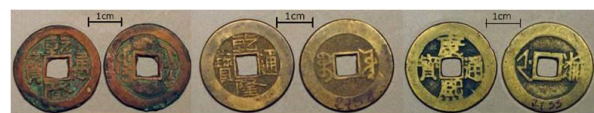
A large amount of archaeometallurgical data regarding metallic artefacts of various typologies and diverse materials related to metallurgical operations has been gathered and discussed. Artefacts and archaeological remains were recovered from diverse important archaeological sites (e.g. Baiões/Santa Luzia, Medronhal, Fraga dos Corvos, Escoural, Castro de Pragança). The overall results have shown that during the Chalcolithic period relatively pure coppers were at use (with exception for the presence of As), and that during Late Bronze age binary bronze with relatively constant tin contents (average of ~13wt.%) and impurities as Pb, As and Sb was the main material used. Unalloyed copper was used sporadically to produce particular items whenever the properties of this metal could be an advantage. Differing from other Western European regions, ternary bronzes seem to have a later appearance, i.e. during Iron Age. The shaping of large and more complex artefacts (e.g. spear heads, axes, closed rings) was made in moulds with only some final thermo-mechanical processing being needed. On the other hand, smaller and simpler items were produced by shaping pre-defined forms, as cast bars, through thermo-mechanical processes that could be very intense, as those that include various cycles of deformation and annealing.

Particular studies were dedicated to the important collection of copper-based artefacts belonging to the Orientalising settlement of Quinta do Almaraz. Its particular location (Tagus estuary) has favoured human occupation since the Neolithic period. Studied

artefacts were mainly composed by Cu-Sn alloys, systematically exhibiting rather low Sn contents (~2.2 to 8.8 %), despite the presence of few unalloyed coppers and leaded bronzes (Pb > 2 %). Relatively high Fe contents (~0.2 to 0.9 %) point to the use of efficient smelting furnaces. Manufacture operations consisted of hammering and annealing operations regardless of their typologies. Comparison with neighbouring Early Iron Age collections allows detection of both local and Orientalising signatures.



More recently the study of the emblematic collection of Vila Nova de S. Pedro settlement, internationally recognized has one of the most representative of metallurgical activities during Chalcolithic has been initiated in order to establish the first metallurgical steps in the prehistory of the Portuguese Estremadura.



Finally, the study of Chinese cash coins showed they are mainly brass and bronze coins with varied amounts of lead. Phase elemental composition and digital X-radiography allowed the observation of Pb globules susceptible to trans-globular corrosion in certain environments. Pb is immiscible in Cu-based alloys, being distributed in globules, which seem susceptible to trans-globular corrosion in certain environments. Preliminary-XRD analysis allowed to identify an Sb-rich phase (in some brass coins) similarly to previously identified Sn-rich phase; and the [Fe,As] rich phase. It was found these elements – Sb,Sn and Fe,As – tend to associate due to their similar properties and affect the corrosion resistance of the alloy. These results contribute to evaluate the importance of minor elements in the promotion of microstructural changes in Cu-based alloys, relevant to the conservation of this type of artefacts.

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Metal binding by humic acids in recent sediments from the SW Iberian coastal area*J.M. Rosa, M. Santos, M.F. Araújo, F.J. González-Vila¹*

The concentrations of Cu, Zn, Cr, Ni, Pb, As, Mn and Co were determined by ICP-MS in recent sediments from the Huelva littoral and in their humic acid (HA) fractions, in order to evaluate distribution and binding capacity of heavy metals to HAs. In addition, elemental composition and $\delta^{13}\text{C}$ values were determined to appraise the sources of organic matter in the area. The study involved the comparison of selected samples taken from different environments including the estuary of the Guadiana River, the main fluvial system of the region, the Tinto and Odiel system and shelf sediments. A significant positive correlation was found for Co, Zn, As and Pb in bulk sediments, suggesting a common origin of all of those elements, the mining activities and pyrite deposits located hinterland. On the other hand, results for Cr, Mn, Co and Ni pointed to the basic rocks from the low basin of the Guadiana River as their main source. Elemental (C, N) and isotopic ($\delta^{13}\text{C}$) analysis of sediments indicated a significant contribution of autochthonous plankton in coastal shelf sediments, whereas estuarine and riverine sediments showed major contribution of terrestrial biomass. Geochemical values for respective HAs suggested a greater terrestrial contribution in estuarine and marine OM than bulk sediments, which evidenced the influence of coastal currents and sediment fluxes. Concentration of trace metals in HAs followed the sequence $\text{Cu} \gg \text{Zn} > \text{Cr} > \text{Ni} \geq \text{Pb}$. Humic Acids sequester considerable amounts of Cu and Zn contributing to reduce the bioavailability of these contaminants. Low levels found in HAs for Mn and As suggested the formation of stable complexes with pyrite and the preferential binding of Cu and Zn in HAs.

¹ IRNAS, CSIC, Seville, Spain**Geochemical record of environmental changes in Portuguese estuaries and coastal area***M.F. Araújo, J.M. Rosa, S. Moreira¹, A.M.M. Soares, M.C. Freitas¹, F. Fatela¹, F.J. González-Vila²*

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 and sedimentological data of a sedimentary sequence (Lagoa da Pederneira) allowed its palaeoenvironmental reconstruction and four stratigraphic units have been identified related to diverse environments mainly related to climate and sea level rise. Final lipidic extracts of dried sections of cores (1 m depth) collected in the estuaries (Minho, Lima and Mira) were analysed by gas chromatography-mass spectrometry (GC-MS). The variability observed in the biomarkers downcore distribution allowed to identify the origin in the organic matter supply (terrestrial/marine). Sections of top-most cores were characterized by the presence of a complex mixture of polysaccharides, lignin derived compounds, fatty acids and a greater abundance of n-alkanes. The dominance of n-alkanes with a distribution biased toward higher chain lengths (n-C25 to n-C33) together with an odd-over-even predominance and the presence of lignin compounds indicate of a terrestrial higher plant origin. However, this dominance of terrestrial markers disappears in the deeper sections (e.g. Minho river) suggesting a greater marine contribution in ancient times.

¹ Laboratório de Processos Costeiros, Centro e Departamento de Geologia da FCUL, Lisboa, Portugal² IRNAS, CSIC, Seville, Spain**The variability of the marine radiocarbon reservoir effect in Southern Atlantic Iberian Coast***A.M. Monge Soares, J.M. Matos Martins, P. Portela, A. M. Arruda¹*

The quantification of the marine radiocarbon reservoir effect (ΔR) is essential in order to calibrate conventional radiocarbon dates from marine shell samples with reliability. Also, the quantification of this parameter can provide information concerning the intensity of coastal upwelling in marine regions influenced by this phenomenon.

Previous research regarding these issues has been done for the Atlantic Iberian coast. Nevertheless, new data were added to these research allowing for the first time the quantification of ΔR for the Sotavento region of Algarve (Southern Portuguese coast), for the last 3000 yr. A ΔR weighted mean value of -65 ± 30 ^{14}C yr was obtained for the Sotavento region. This area can be considered as a transition zone between an area influenced by the prolongation of the western coastal upwelling system in the southern Portuguese coast, the Barlavento region of Algarve ($\Delta R = +65 \pm 20$ ^{14}C yr), and an area where the upwelling regime is absent, the Andalusian coast ($\Delta R = -135 \pm 20$ ^{14}C yr).

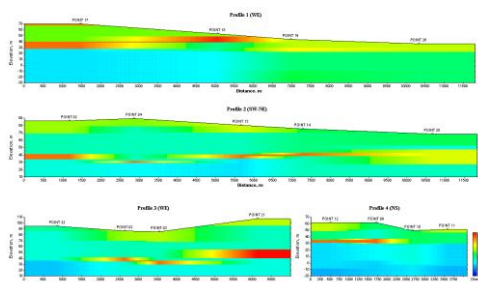
These values are in accordance with the oceanographic conditions present in Southern Atlantic Iberian coast, and suggest a consistent oceanographic pattern in the region for the last 3000 yr.

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Arid /semi arid zones hydrology

P.M. Carreira, D. Nunes, F. Monteiro Santos¹, J.M. Marques², Hans Eggenkamp², M. F. Ben Hamouda³

Overexploitation of coastal aquifers and pollution are among the main problems related to groundwater resources assessment and management in Tunisia. Brackish groundwater for agriculture and human supply is being provided to numerous parts of the region, as the only type of available water. The salts income to the groundwater systems could be derived from seawater intrusion (overexploitation of the systems- very touristic area), from salt dissolution (evaporitic minerals within the basin sediments), and from marine aerosols. A field work campaign was carried out in order to sample groundwater to determine ²H, ¹³C, ¹⁸O, ³⁵Cl and ³H content. The isotopic results obtained together with geophysical survey will help to clarify this problem.



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Groundwater isotopic geochemistry applied in geothermal potential evaluation and the seismic-volcanic hazard assessment

P.M. Carreira, D. Nunes, J.M. Marques¹, M.R. Carvalho², G. Capasso³, F. Grassa³, J.C. Nunes⁴

Three sampling campaigns were performed in Azores archipelago in order to: i) characterize the chemical and isotopic composition of ground waters, fumaroles and gas emissions related with hydrothermal/geothermal systems and volcanologic/seismic settings. A continuous-flow GC/IRMS technique has been developed to analyses $\delta^{15}\text{N}$ values for molecular nitrogen in gas samples. The method was tested on magmatic and hydrothermal gases as well as on soil gas samples. The analysis of nitrogen isotope composition may be prone to atmospheric contamination mainly in samples with low N_2 concentration; based on the simultaneously determined $\text{N}_2/^{36}\text{Ar}$ ratios and assuming that ^{36}Ar content in crustal and mantle-derived fluids is negligible with respect to ^{36}Ar concentration in the atmosphere. Besides, ^{35}Cl sampling campaign was performed in order to identify the origin of Cl in the groundwater systems (mantle or sea water mixing).



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