

Applied Geochemistry & Luminescence on Cultural Heritage (GeoLuC)

M. Isabel Prudêncio

The Group of Applied Geochemistry & Luminescence on Cultural Heritage (GeoLuC) is especially devoted to the **study of the Portuguese cultural heritage materials and geo-environmental contexts**, through the **application of nuclear methods**.

The GeoLuC group has an interdisciplinary approach to the study of archaeological and geological contexts and materials. The study of artworks from museums is also an important activity. Origin, composition, technique of manufacture, and age, are the issues of primary importance when examining cultural assets. Analysis of these complex materials, such as pottery, minerals, stones and mortars, is based on field geology, geochemistry, mineralogy and luminescence dating. Detailed geochemical studies for the understanding of the lanthanides, actinides and other trace element behaviour in superficial environments is also a major research domain of the GeoLuC group.

The main research activities of GeoLuC group during 2009 are summarised according to the following themes:

- Dating, authenticity, materials and pigments: Portuguese Faience and Chinese Porcelain produced for the Portuguese market (XVI to XVIII centuries)
- Application of luminescence dating to understanding Iberian cultural development
- Luminescence dating of coastal geomorphological development in Portugal and Mozambique
- Casa do Governador da Torre de Belém (Tagus estuary): Halieutical resources industry in Roman times
- Distribution of trace elements and natural radionuclides of the U and Th radioactive series in superficial environments

- Applied geochemistry to the study of superficial environments in the Iberian Peninsula and Cape Verde islands - distinguishing geogenic and anthropogenic contributions

- Development of nuclear methods and applications in the archaeometry of cultural heritage assets

The main methodological approaches of the GeoLuC group comprise instrumental neutron activation analysis (INAA), X-ray diffraction (XRD) and luminescence (thermoluminescence and optically stimulated luminescence: TL and OSL) applied to archaeometry, environmental geology and paleoenvironmental reconstruction. The research is developed through financed projects, protocols, collaboration with national and international laboratories and universities, and contracts/services with private and public institutions.

Methodological testing and development of neutron activation analysis and luminescence measurements are an ongoing task, having the potential to offer a number of insights into the dating and elemental composition of different types of samples and environments.

The GeoLuC group's activities also include education and training of students from national and international universities through supervision of MSc and PhD thesis. Our students participate in the entire research programme, including: field work and sampling, sample preparation for several types of analytical techniques, irradiations and measurements, and data management and interpretation. Thus, they become able to conduct projects in fundamental and applied research.

The research team has been involved in several post-graduate and masters degree courses in universities, as well as national and international seminars and workshops.

Research Team

Researchers

M. I. PRUDÊNCIO, Princ., Group Leader
M. I. DIAS, Invited Aux.
C. BURBIDGE, Aux. (Contract)
M. J. TRINDADE, Pos-Doc, FCT grant

Students

A. JORGE, PhD student, U. Sheffield grant
S. VILELA, MSc student
J. MUNGUR-MEDHI, MSc student
A. L. RODRIGUES, FCT grant

Technical Personnel

L. FERNANDES
R. MARQUES
D. FRANCO
G. CARDOSO

Collaborators

M. A. GOUVEIA, Princ. (Retired)

Dating, authenticity, materials and pigments: Portuguese Faience and Chinese Porcelain produced for the Portuguese market (XVI to XVIII centuries)

M.I. Dias, M.I. Prudêncio, M.O. Figueiredo¹, T. Silva¹, J.P. Veiga¹, M.A. Matos², A.M. Pais³, C. Burbidge, D. Franco, R. Marques, G. Cardoso, A. Zink⁴

Two main subjects are addressed in this FCT project: one topic aims a better knowledge of early Portuguese faience (XVII-XVIII), and the other is focused on the Chinese porcelain ordered for the Portuguese market (XVI-XVII). The general aspects to be considered in both cases are related with chronological precision, identification and differentiation of production centres and technologies, including characterisation of surface coatings (glazes and pigments). Fig.1.

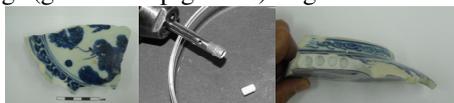


Fig.1 Sampling of ceramic pastes for analytical approaches.

Newly obtained results (INAA/XRD): (i) good chemical based identification of Portuguese faience, clearly differentiating Coimbra (Cluster 1) and Lisbon faience productions (Cluster 2 and 3), and two compositional groups for Lisbon (Fig.2)-occidental and oriental Lisbon production centers; (ii) no special correlation between stylistic/ decoration and compositional group. Faience with “rendas” (lace), usually assigned to Coimbra, but also found in Lisbon, present a geochemical pattern similar to one of Lisbon’s production. So, chemical composition confirms that this decorative style was also produced in Lisbon, imitating Coimbra; (iii) chemical homogeneity found for each compositional group may reflect the use of standardised raw materials and probably also recipes.

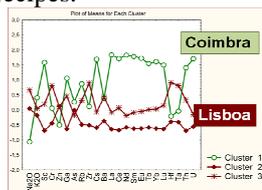


Fig.2 Geochemical groups for Lisbon and Coimbra faience.

New obtained results (TL-OSL): (i) prolonged HCl treatment of cores taken from high fired ceramics enables the extraction of powders for preparation according to mineralogy and grain-size; (ii) of all available signals, equivalent dose determination using the 110 °C TL “Simplified” PreDose response requires minimal sample material (Fig.3); (iii) due to the saturating form of the dose response from these samples, conventional linear extrapolations from laboratory dose response tend to overestimate absorbed dose and hence age, while saturating exponential fits often produce underestimates; (iv) an “Additive and Regenerative Predose” protocol has been proposed in an attempt to overcome problems relating to extrapolation (v) OSL signals appear to

have been affected by light exposure in these thin ceramics.

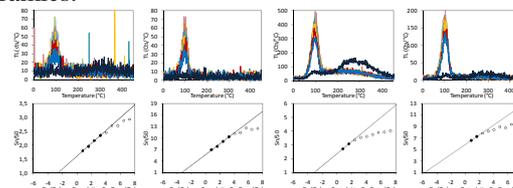


Fig.3 110°C TL PreDose on porcelain and faience

Newly obtained results of non-destructive characterisation on selected cobalt-rich blue glazes to ascertain the speciation state of the chromophore element. Co K-edge X-ray absorption spectra by irradiation of glazes at ESRF in Grenoble/France show: (i) edge energy indicates metal present in divalent state; (ii) theoretical modelling of XANES spectra from two model compounds - CoAl_2O_4 with spinel-type structure and Co_2SiO_4 with olivine-type structure was performed; (iii) these simulations and the deconvolution of the EXAFS region using IFEFFIT program corroborate a mean coordination number higher than four for the first shell of oxygen atoms around Co^{2+} ions. The presence of lead and arsenic, plus the relative contents of manganese, iron, cobalt and copper, confirms previous dating by Art Historians based on stylistic features.

Published work:

M.O.Figueiredo, T.P.Silva, J.P.Veiga, M.I.Dias (2009), “Speciation state of cobalt in blue glazes: a XAFS study on XVI century Chinese blue-and-white porcelains”, Nuclear Instruments and Methods in Physics Research B. Manuscript nr. GSRA0R1.

M.O.Figueiredo, T.P.Silva, J.P.Veiga, M.I. Prudêncio, M.I.Dias, M.A.Matos, A.M.Pais (2009), “Blue pigments in XVI-XVII cent. glazes: a comparative study between Portuguese faiences and contemporary Chinese porcelains manufactured for the Portuguese market”, Symp.3 LASMAC, XVIII Internat. Materials Research Congress, México, CD-ROM S3-29.

M.I.Dias, A.Pais, A.L.Rodrigues, R.Marques, M.I.Prudêncio (2009). Chemical characterization of Portuguese faience from 16th-18th century: a preliminary neutron activation study. Book of Abstracts, EMAC’09, UCL, British Museum, London, p. 65.

C.I.Burbidge, A.L.Rodrigues, M.I.Dias, M.I.Prudêncio, G.Cardoso, in press. ‘Optimisation of preparation and measurement protocols for luminescence dating of small samples from a suite of porcelains and faiences’, Mediterranean Archaeology and Archaeometry.

¹ CENIMAT, UNL. 2829-516 Caparica, Portugal.

² MNaz. Rua da Madre de Deus 4. 1900-312 Lisboa, Portugal.

³ IPCR. Rua das Janelas Verdes, 37. 1249-018Lisboa, Portugal. 1

⁴ CNRS, Musee du Louvre, Paris, France

Application of luminescence dating to understanding Iberian cultural development

M. I. Dias, M.I. Prudêncio, C. Burbidge, G. Cardoso, D. Franco, R. Marques, A.C. Valera¹, C. Fabião², C. Odriozola³, V. Hurtado³, L. San Juan Garcia⁴, L. Osterbeek^{5,6}, C. Scarre⁷, J. Munghur Medhi^{6,8}, A. Cruz⁶, P. Curá⁶, J. Garcia Gazolaz⁹, J. Sesma⁹, D. Mosquera¹⁰, J. Sanjurjo¹⁰, S. M. Espino¹¹, C. Bento¹², A. Silva¹², T. Gomes¹²

Luminescence dating of sediments, mortars, heated clay structures and ceramic artefacts, is being conducted in both research and service contexts. Samples from museums and archaeological sites across Iberia are being measured to develop and test chronological frameworks for cultural development, exchange, and population dynamics. Studies of prehistoric human occupation and activity are focussing on the Upper Ribatejo, Lower Alentejo, and Navarra regions. At such sites dating is being combined with luminescence profiling of sedimentary sequences to provide additional stratigraphic context for the dating results, to enhance understanding of archaeological site formation processes. Cultural chronologies established or tested have related to the Roman, Medieval and Post-Mediaeval periods: analysis of materials such as the roman “concrete”, lime mortar, porcelain and faiança has required substantial methodological testing and development. Some artefacts have been found to actually be modern.



¹ Era Arqueologia S.A. Portugal

² Fac. Letras, Univ. Lisboa

³ ISCME, CSIC, Seville, Spain

⁴ Univ. Seville, Spain

⁵ Inst. Politécnico de Tomar, Portugal.

⁶ Museu de Arte Pré-Histórica de Mação, Portugal.

⁷ Durham Univ., Dep. of Archaeology. UK.

⁸ Fundação Ernesto Lourenço Estrada, Abrantes, Portugal

⁹ Dep. de Cultura y Turismo, Pamplona, Navarra, Spain

¹⁰ Inst. Universitario de Xeologia, Corunha, Spain

¹¹ Arqueoiberia Estudios, S.L. Madrid, Spain

¹² Colecção Berardo, Portugal

Luminescence dating of coastal geomorphological development in Portugal and Mozambique

C. Burbidge, M. I. Dias, M.I. Prudêncio, G. Cardoso, D. Franco, R. Marques, L. Rebelo¹, P. Brito¹, D. Mosquera², J. Sanjurjo².

Luminescence dating is being applied as part of ongoing research programs into the chronologies of coastal geomorphological development in Portugal, Galicia and Mozambique, in the Holocene and through the late Pleistocene. Dating of Holocene dunes has been technically straightforward. This has enabled the establishment of a chronology for the formation and mobilisation of the Troia spit, presently the subject of major tourist infrastructure development. It has also resulted in a series of dates for recent dune activation on the Mozambican coastal plain. Analysis of older sands from Mozambique and Galicia has been more technically challenging. Methodological testing and development related to these challenges has so far produced one technical publication, and has the potential to offer a number of insights into the dating of “old” samples by luminescence methods.



¹ IGM. INETI, Portugal

² Inst. Universitario de Xeologia, Corunha, Spain

Casa do Governador da Torre de Belém (Tagus estuary): Haliutical resources industry in Roman times

M.I. Dias, M.I. Prudêncio, R. Marques, M.A. Gouveia, D. Franco, C. Burbidge, C. Fabião¹, S. Gabriel², M. Coelho², I. Filipe²

A multidisciplinary FCT project is running in the archaeological site of the fish-salted factory of the Casa do Governador da Torre de Belém - CGTB, Lisbon, Portugal, which aims to understand one of the most important economic activities of the coastal areas of the Roman Province of Lusitania, the salted fish and salsamenta production, exported in amphorae to other areas of the Roman Empire. The CGTB will become a hotel and will preserve a part of the ruins of the roman factory and an exhibition of the research project. Compositional study of samples from amphorae finds is an ongoing task. Chemical composition was obtained by INAA by using the RPI as neutron source, and mineralogical composition was obtained by XRD. Significant chemical differences were found so far, pointing to the use of diverse raw materials. The comparative study with our database including Lusitania production centers suggests that the majority of amphorae were produced in the Tagus basin. Also luminescence dating (OSL) of in situ sediments is running for a better definition of the chronostratigraphic sequence of both human occupation levels and fluvial deposits, contributing to the establishment of a palaeoenvironmental scenario.



¹ Fac. Letras, Univ. Lisboa

² Era Arqueologia S.A. Portugal

Distribution of trace elements and natural radionuclides of the U and Th radioactive series in superficial environments

M.J. Trindade, M.I. Prudêncio, M.I. Dias, R. Marques, M.A. Gouveia, D. Franco, J. Sanjurjo¹, D. Mosquera¹, J. R. Vidal Romani¹

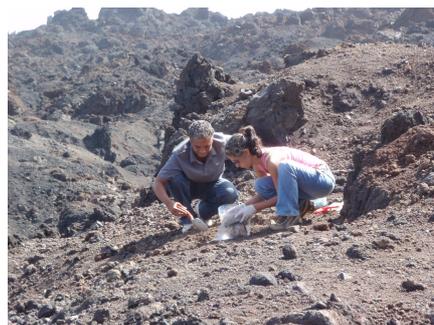
The distribution/mobility of trace elements and natural radionuclides of the uranium and thorium radioactive series are being studied in superficial environments in order to determine the causes of radioactive disequilibrium in the U- and Th-series decay. This study may have impact in various research areas, mainly in soil formation and evolution; study of the post-depositional alteration processes in sedimentary series and weathering profiles, especially the ones developed in granitic terrains; palaeoenvironmental investigations; and the study of the impact of radioactive disequilibrium on luminescence (OSL) dating of Quaternary sedimentary deposits, contributing to better constrain geological and anthropogenic events. In 2009 especial attention was paid to the study of secondary manganese oxyhydroxides formed during alteration of consolidated dunes, and their capacity in co-precipitate actinides and lanthanides.



¹Inst. Univ. de Xeologia, Corunha, Spain

Applied geochemistry to the study of superficial environments in the Iberian Peninsula and Cape Verde islands - distinguishing geogenic and anthropogenic contributions

M.I. Prudêncio, M.I. Dias, R. Marques, D. Franco, M.J. Trindade, F. Rui¹, M. Abad¹, F.Rocha², E.Silva², M.M.S. Cabral Pinto^{2,3}, M.M.V.G. Silva⁴



Geochemistry and mineralogy studies were applied to superficial environments (soils and sediments) of the Iberian Peninsula and Cape Verde archipelago. Concerning Cape Verde, a detailed study of topsoils (regolith) from Santiago and Fogo islands is an ongoing project aiming a contribution for the construction of the Geochemical Atlas of these islands. The evaluation of both geogenic and anthropogenic contributions (particularly the total contents of trace elements) is a major goal. During 2009 a first sampling campaign in the Fogo island occurred. The results obtained so far for soils formed in the semi-arid climate of Cape Verde suggest the presence of chemical elements in different forms/ availability. Rare earth elements (REE) and thorium were found to be good indicators of the parent rock lithology, particularly for carbonatites. The preferential incorporation of LREE (after the breakdown of primary minerals) in Fe/Mn oxides and in clay minerals, as well as the preferential incorporation of HREE in carbonates (calcite or dolomite) was found.

¹ Univ. Huelva, Spain; ² Univ. Aveiro, GeoBioTec; ³INIDA – Inst. Nac. Inv. Des.Ag., Santiago, Cabo Verde; ⁴ Univ. Coimbra

Development of nuclear methods and applications in the archaeometry of cultural heritage assets

M.I. Prudêncio, M.I. Dias, C. Burbidge, M. J. Trindade, R. Marques, M.A. Gouveia, D. Franco, G. Cardoso, A. Jorge¹, P. Day¹, F. Rocha², C. Odriozola⁴, L. Osterbeek⁵, J. Mungur-Medhi⁵, J. Sanjurjo⁶, A.C. Valera⁷, V. Hurtado⁸, L. San Juan Garcia⁸

INAA (using the RPI), together with luminescence techniques support most of the research activities of the GeoLuC group. These nuclear methods were applied to several archaeometric studies, most of them performed in the framework of master and doctoral thesis, as well as post-doctoral programmes. During 2009 the compositional database of ancient ceramics was increased. Study of objects from excavations and museums, including their origin, technique of manufacture, age and conservation was done. Public and private institutions often requested the group for services of both laboratories. The quality of the analytical procedures of INAA is periodically controlled through the analyses of international standards and inter-calibrations with other laboratories, in order to maintain and increment their good performance. The Luminescence Dating Laboratory participates in international comparisons, particularly with the IUX, Coruña, Spain. These studies unlock information from ancient materials, such as provenance, mainly pottery, technique of manufacture, firing technology, ancient recipes and alteration pathways, as well as absolute chronology, in an Iberian perspective.

¹ Univ. of Sheffield – Dep. of Archaeology and Prehistory, England; ² Univ. Aveiro, GeoBioTec; ³ Univ. Bordéus, France; ⁴ ISCME, CSIC, Seville, Spain; ⁵ Inst. Politécnico de Tomar, Portugal; ⁶ Inst. Univ. de Xeologia, Corunha, Spain; ⁷ Era Arqueologia S.A. Portugal; ⁸ Univ. Seville, Spain