

# Applied Geochemistry & Luminescence on Cultural Heritage (GeoLuC)

*Maria Isabel Prudêncio*

The Group of Applied Geochemistry & Luminescence on Cultural Heritage (**GeoLuC**) is especially devoted to the **study of cultural heritage (immovable and movable assets), archaeological and geo-environmental contexts**, with a view to their compositional characterization, absolute dating and/or definition of conservation strategies, through the **application of nuclear methods**.

The GeoLuC group has an interdisciplinary approach to the study of both archaeological and geological contexts and materials, as well as of museum artworks, and other forms of cultural heritage expression in the framework of compositional / chronological procedures in a wide range of time records. Detailed geochemical studies for the understanding of the lanthanides, actinides and other trace elements behaviour in superficial environments are another major research domain.

The main research activities of GeoLuC during 2011 are summarised according to the following themes:

- Neutrons and ionizing radiation in Portuguese glazed tiles: establishing strategies of conservation.
- Dating, authenticity, materials and pigments: Portuguese Faience and Chinese Porcelain produced for the Portuguese market (XVI to XVIII centuries).
- Application of luminescence dating to the understanding of Iberian cultural evolution.
- Luminescence-dosimetric processes in quartz.
- Drained measurements for the constraint of time averaged water content.
- Casa do Governador da Torre de Belém: Haliectual resources industry in Roman times.
- Trace elements and natural radionuclide distribution associated to superficial weathering of uranium-rich veins of Central Portugal.
- Geochemistry, mineralogy and radiometric measurements of superficial environments in the Iberian Peninsula and Cape Verde islands - distinguishing geogenic and anthropogenic contributions.
- Nuclear methods for the characterization and preservation of cultural and natural heritage.

The main methodologies used comprise instrumental neutron activation analysis (INAA), X-ray diffraction (XRD) and luminescence (thermoluminescence and optically stimulated luminescence: TL and OSL) applied to archaeometry, geology and palaeoenvironmental 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.

During 2011, a new project started: "Luminescence-Dosimetric Processes in Quartz", Convénio Portugal, (FCT) / Itália, (CNR) 2011-2012. Two FCT projects were approved: (1) - VADOSE - Spatial Variation of Dose Rate in Soils and Sediments, PTDC/AAC-AMB/121375/2010; and (2) ROBBIANA - The Della Robbia sculptures in Portugal: History, Art and Laboratory, PTDC/HIS-HEC/116742/2010. GeoLuC has a total of seven financed projects.

Concerning organization of international conferences, for the first time the Iberian Congress on Archaeometry has done his edition (9<sup>th</sup>) in Portugal organized by the GeoLuC research group.

Three members of GeoLuC took leadership positions in international organizations. M. Isabel Dias become the President of the "Sociedade de Arqueometria Aplicada ao Património Cultural" (SAPaC); M. Isabel Prudêncio is vogal of the directive board of SAPaC. Christopher I. Burbidge is the Secretary of EURADOS WG10 "Retrospective dosimetry"

Among the published work (two book chapters articles, 12 articles in international journals; and two in Conference Proceedings), one article is in the Top 25 Hottest Articles - ELSEVIER: Earth and Planetary Sciences (July to September 2011).

The GeoLuC group's activities also include education and training of students from universities through supervision of M.Sc. and Ph.D. thesis and post-doctoral programmes.

---

## Research Team

### Researchers

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

### Students

A.L. RODRIGUES, Ph.D. student, FCT grant  
J. MUNGUR-MEDHI, Ph.D. student

### Technical Personnel

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

### Collaborators

M.A. GOUVEIA, Princ. (Retired)

## Neutrons and ionizing radiation in Portuguese glazed tiles (16<sup>th</sup>-18<sup>th</sup> cent.): establishing strategies of conservation

M.I. Prudêncio, M.A. Stanojev Pereira, S.I. Cabo Verde, M.I. Dias, J.G. Marques, L. Esteves<sup>1</sup>, C.I. Burbidge, M.L. Botelho, T. Silva, T.P. Silva<sup>2</sup>, M.O. Figueiredo<sup>2</sup>, M.B. Albuquerque<sup>3</sup>, S. Flor<sup>4</sup>, R. Carvalho<sup>4</sup>, M.J. Trindade, R. Marques

Neutron imaging techniques using the Portuguese Research Reactor have been applied to ancient glazed tiles to evaluate the efficiency of two methods of treatment with the consolidant Paraloid\_B-72: brushing and immersion in solution (Figure 1). Gamma rays have been used to inactivate microbiota with the determination of a minimum dose to attain the decontamination and a maximum dose to preserve the studied tiles. The determination and morphologic characterization of the bioburden of ceramic tiles of different origins (environment and location) was also a major goal. The overall aim is to contribute to the establishment of the best strategy for conservation of this type of cultural object.

Neutron tomography (NT) allowed the visualization of the penetration depth and distribution of polymer-based consolidants inside ancient tiles. Neutron attenuation in the hydrogen-rich consolidant is much greater than in the mineral constituents of the ceramics: this is registered as sharply contrasting signal levels (gray levels) in images generated from slices through the tomographs. NT indicates that the application of 10% Paraloid® B-72 in acetone solution by brushing produces a higher and more uniform impregnation of the consolidant in the tile than does immersion. The results obtained for the immersion technique indicate that this might be improved if the concentration of the resin were reduced.

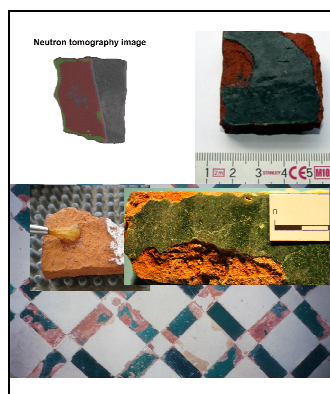


Fig. 1. Museu Nacional do Azulejo (MNA) glazed tiles (16<sup>th</sup> century): in situ, before and after resin treatment, and NT image.

The main goal of the microbiological studies was the determination and characterization of the microbial population of ceramic tiles located at the National Tile Museum – Lisbon. The analyzed samples belong to the ceramic tile panels “Grande Panorama de Lisboa” (XVIII century), one part exposed and other in reserve, and to “Quinta de Santo António” (XVIII century). The estimated tile samples average bioburden varied between 102 -103 colony forming unit (CFU) per 100 cm<sup>2</sup> of tile. The morphologic characterization of tiles isolates indicated a

heterogeneity/diversity of the microbial population. This could be related to the different environments that each of the panels are subjected, being the fraction of the panel in the warehouse (reserve) more protected than the exposed panel, which presents more signs of biodeterioration. Relatively to the filamentous fungi, considered one of the main agents of biodeterioration, were detected with a relative frequency between 3 to 8 %. The visual observation of these ceramic panels revealed colored green spots. In order to identify this pathology it was performed a microbiological culture of the green spot and it was isolated a filamentous fungi, identified as *Aspergillus fumigatus* (Figure 2). Preliminary results suggested that the green spot pathology corresponds to an excretion metabolite of the detected fungi.



Fig. 2 – *Aspergillus fumigatus*

### Published work:

Prudêncio, M.I., Stanojev Pereira, M. A., Marques, J.G., Dias, M.I., Esteves, L. Burbidge, C.I., Trindade, M.J., Albuquerque, M.B.. Neutron tomography for the assessment of consolidant impregnation efficiency in Portuguese glazed tiles (16th and 18th centuries). *Journal of Archaeological Science* (2011), doi:10.1016/j.jas.2011.11.010.

Silva, T.P., Figueiredo; M.O., Prudêncio, M.I., Ascertaining the degradation state of ceramic tiles: a preliminary non-destructive step in view of conservation treatments using gamma radiation. EMAC'11, Viena, Austria, 29 Sept - 1 October 2011, p. 39.

Prudêncio, M.I., Stanojev Pereira, M. A., Marques, J.G., Dias, M.I., Esteves, L. Burbidge, C.I., Trindade, M.J., Albuquerque, M.B.. Neutron tomography for the assessment of consolidant impregnation efficiency in Portuguese glazed tiles (XVII – XVIII centuries). TECHNART, Berlin, Germany, April 26 – 29, 2011.

T. Silva, S. Cabo Verde, C.I. Burbidge, A.C. Fernandes, M.L. Botelho, M.I. Dias, G. Cardoso e M.I. Prudêncio. Perfis de contaminação e inativação microbiana em azulejos. IX Congresso Ibérico de Arqueometria, CIA-IX, 26 -28 Outubro de 2011, Lisboa, Portugal.

M.A. Stanojev Pereira, M.I. Prudêncio, J.G. Marques, M.O. Figueiredo, M.I. Dias, T.P. Silva, L. Esteves, C.I. Burbidge, M.J. Trindade e M.B. Albuquerque. Tomografia de neutrões aplicada a azulejos do séc. XVII – visualização para caracterização, diagnóstico e optimização de técnicas de conservação. IX Congresso Ibérico de Arqueometria, CIA-IX, 26 -28 Outubro de 2011, Lisboa, Portugal.

<sup>1</sup> Museu Nacional do Azulejo, Rua da Madre de Deus n° 4,1900-312 Lisboa, Portugal

<sup>2</sup> Instituto Nacional de Engenharia, Tecnologia e Inovação, Estrada do Paço do Lumiar, 1649-038 Lisboa, Portugal

<sup>3</sup> Conservar-Inovar, Lda, Av. Duque de Loulé n° 77, 4° Dto, 1055-088 Lisboa, Portugal

<sup>4</sup> Rede Temática de Estudos de Azulejos (RTEACJMSS), Inst. de História de Arte (IHA-FLUL), Alameda da Universidade, Lisboa, Portugal

**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. Figueiredo<sup>1</sup>, T. Silva<sup>1</sup>, J.P. Veiga<sup>1</sup>, M.A. Matos<sup>2</sup>, A.M. Pais<sup>3</sup>, C. Burbidge, D. Franco, R. Marques, G. Cardoso, A. L. Rodrigues, A. Zink<sup>4</sup>

This project (PTDC/HAH/69506/2006) has focused on the interdisciplinary study of: (1) Portuguese faience (XVII - 1st half century. XVIII) and (2) Chinese porcelain made for the Portuguese market (sécs. XVI-XVII). Main objectives were achieved, and even exceeded, with a better definition of the morphological and decorative typologies associated productions and specific timelines and for both cases a definition of chemical and mineralogical composition (INAA and XRD) and the production technology (firing temperature and surface coating technique) was established together with a luminescence dating methodology. Still for Chinese porcelains it was difficult to establish TL and OSL dating due to their very thin thickness and hardness. Regarding non-destructive characterization on selected cobalt-rich blue glazes, XAFS results confirm that cobalt plays the dual role of chromophore and network-former in the blue glaze of CPOPM, the tetrahedral Co<sup>2+</sup> ions being responsible for a blue colouring, conversely non-colouring pseudo-octahedral Co<sup>2+</sup> ions occupy available coordination sites of the tetrahedral silica-rich glassy matrix.



- 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 the understanding of Iberian cultural evolution**

M. I. Dias, M.I. Prudêncio, C. Burbidge, G. Cardoso, D. Franco, R. Marques, A.L. Rodrigues, A.C. Valera<sup>1</sup>, A. M. Gama da Silva<sup>2</sup>, C. Odriozola<sup>3</sup>, V. Hurtado<sup>3</sup>, L. San Juan Garcia<sup>4</sup>, L. Oosterbeek<sup>5,6</sup>, P. Rosina<sup>5,6</sup>, C. Scarre<sup>7</sup>, A. Cruz<sup>6</sup>, P. Cura<sup>6</sup>, J. Sanjurjo<sup>8</sup>,



Research activities including participation in FCT projects (PTDC/HIS-ARQ/101299/2008; PTDC/CS-ANT/104333/2008), Ph.D. thesis (SFRH/BD/62396/2009) and post-graduation working programmes, in collaboration with national and international universities, regarding the study of Iberian cultural contexts of various chronologies and geological backgrounds, have been carried out. Several types of materials belonging to Portuguese and Spanish archaeological sites and museums have been studied by Luminescence methods, such as sediments, soils, mortars, heated clay structures, and ceramic and lithic artefacts. The chronology of funerary practises in prehistory is being examined through the dating of ceramics and sediments from the fills of negative archaeological features. Methods are being developed for the dating of rock art, based on the testing of raw materials used for pigments. Ancient mining activities and technologies are being analysed through testing of rocks for heating to aid their extraction, and dating of the accumulation of mining spoil (Figure 1).

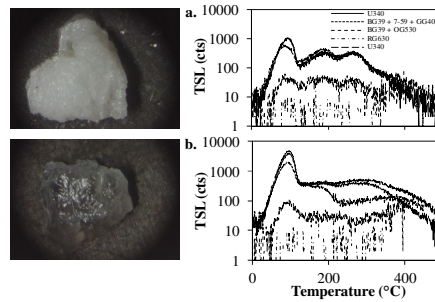
Fig. 1. Sample profile through a zone of phosphatic rock, thought to have been heated to facilitate the mining of Variscite

- <sup>1</sup> Era Arqueologia S.A. Portugal
- <sup>2</sup> FCT/UC, Univ. Coimbra, Portugal
- <sup>3</sup> ISCME, CSIC, Seville, Spain
- <sup>4</sup> Univ. Seville, Spain
- <sup>5</sup> Inst. Politécnico de Tomar, Portugal.
- <sup>6</sup> Museu de Arte Pré-Histórica de Mação, Portugal.
- <sup>7</sup> Durham Univ., Dep. of Archaeology. UK.
- <sup>8</sup> Inst. Universitario de Xeologia, Corunha, Spain

**Luminescence-Dosimetric Processes in Quartz<sup>1</sup>**

C.I. Burbidge, M. Martini<sup>1</sup>, A.L. Rodrigues, M.I. Dias, M.I. Prudêncio, M. Fasoli<sup>1</sup>, I. Villa<sup>1</sup>, A. Galli<sup>1</sup>

This project, begun in 2011, aims to establish a basis in international collaboration that will lead to the development of new understanding of the processes of trapping, transport and recombination of the electronic charges that produce dosimetric luminescence signals in natural quartz. These signals are associated with the compensation of substitutional defects by alkali ions in the quartz lattice. These are strongly affected by the formation mechanism and thermal and radiation history of the quartz, but the precise roles of - and effects on - the defects and ions remain unclear. Following discussion at inter-laboratory meetings, quartz crystals have been prepared from samples of Pegmatite (metamorphosed, Li rich) and Granite (plutonic). Differences are apparent optically and in their thermally stimulated luminescence (TSL) emissions. Future work will attempt to relate luminescence, structural and geochemical properties of the quartz, including following its transformation by heating to different temperatures in different atmospheres.



Examples of quartz crystals from a. Pegmatite and b. Granite, and their TSL emissions in different spectral regions in response to 50 Gv

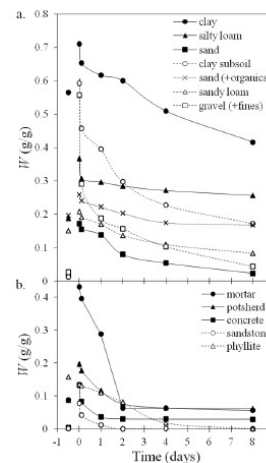
<sup>1</sup> Convénio Portugal (FCT) / Itália (CNR) 2011-2012. italia128584682220330. Processos Luminescentes-Dosimetricos no Quartzo

<sup>2</sup> Centro Universitario per le Datazioni Milano – Bicocca, Dipartimento di Scienza dei Materiali, Via Cozzi 53 20125 MILANO, Itália

**Drained measurements for the constraint of time averaged water content<sup>1</sup>**

C. I. Burbidge, G. Cardoso, D. C. W. Sanderson<sup>2</sup>, M. I. Dias

Accurate evaluation of the time averaged water contents of a sample and its environment are important for trapped charge dating methods. Optimization of estimates for time averaged water content, since the event to be dated, requires reconstruction of the hydraulic history of the sample in its burial or storage context. The literature offers no guide for obviously dry contexts, or for freely draining sediments. This work examined the use of field capacity or drained upper limit to constrain time averaged water content. Standard methods for laboratory evaluation of the drained upper limit are based on extraction of water from prepared material at controlled pressures, but an estimate can be obtained simply by draining. Results for 220 dating samples from a wide range of relevant soil, sediment and other types, taken from a variety of climatic and hydrological conditions, were compared with saturated and field water content values in terms of the samples' textural classification. Drainage for one or more days was found to yield useful values for the constraint of the average water content of a sample and/or its surroundings. This approach is simplest for samples taken in relatively dry conditions (as was shown to commonly be the case), where drained values provide a realistic upper limit for the time averaged water content, and the field water content can be reasonably assumed to represent the lower bound.



Examples of field, saturated and drained water contents for a variety of dating samples

<sup>1</sup> Presented at 13th International Conference on Luminescence and Electron Spin Resonance Dating, submitted to Radiation Measurements.

<sup>2</sup> Environmental Physics, SUERC, Rankine Avenue, Scottish Enterprise Technology Park, East Kilbride, G75 0QF, Scotland, UK

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

M.I. Dias, M.I. Prudêncio, R. Marques, M.A. Gouveia, D. Franco, C. Burbidge, C. Fabião<sup>1</sup>, S. Gabriel<sup>2</sup>, M. Coelho<sup>2</sup>, I. Filipe<sup>2</sup>



The CGTB will become a hotel preserving part of the ruins of the roman fish sauce factory and an exhibition of the research project (PTDC/HAH/74057/2006). A compositional study of amphorae sherds representative of the various classes found was performed and compared with ITN database of Lusitanian amphorae production centers (Sado estuary-six sites; Tagus basin-two in the estuary and one upper stream), suggesting that the majority of amphorae was produced in the Tagus basin. Quartz and feldspars (mostly alkali) are ubiquitous and the most abundant mineral phases. Diopside was observed in a few samples, in small amounts (formed during firing process?), anatase and hematite. Small amounts of carbonates are present in many samples (post-depositional processes?). Concerning clays illite is present in most of the samples.

<sup>1</sup> Fac. Letras, Univ. Lisboa. <sup>2</sup> Era Arqueologia S.A. Portugal

**Trace elements and natural radionuclide distribution associated to superficial weathering of uranium-rich veins of Central Portugal**

*M.J. Trindade, M.I. Prudêncio, M.I. Dias, R. Marques, M.A. Gouveia, D. Franco, C. Burbidge, G. Cardoso, F. Rocha<sup>1</sup>*

Research activities related to distribution of trace elements and natural radionuclides of the U and Th radioactive series in superficial environments of Central Portugal continued throughout the year of 2011, with special focus on weathering processes developed in uranium-rich aplite and dolerite veins, commonly presenting spheroidal weathering. The whole-rock geochemical and mineralogical study of the clay-rich materials (based on INAA and XRD), and specially the comparison between different decayed shells of the spheroidal weathering complexes, enabled better comprehension of the mobilization, distribution and re-precipitation/accumulation mechanisms of the uranium and related trace elements during sub-superficial weathering under oxidizing conditions. Results point to some degree of mobilization of the REEs from the altered primary minerals and its redistribution and incorporation into the alteration products (mainly clay minerals), the different degrees of mobility leading to fractionation among the REEs and development of Ce and Eu anomalies in the chondrite-normalized REE patterns. Most trace elements showed mobilization and subsequent integration in secondary phases, with the main exception of the alkalis and uranium that tended to be released from the spheroidal system.



<sup>1</sup>Univ. Aveiro, GeoBioTec

**Geochemistry, mineralogy and radiometric measurements of superficial environments in the Iberian Peninsula and Cape Verde islands - distinguishing geogenic and anthropogenic contributions**

*M.I. Prudêncio, M.I. Dias, R. Marques, F. Rocha<sup>1</sup>, E. Silva<sup>1</sup>, D. Franco, M.J. Trindade, C. Burbidge, G. Cardoso, A.L. Rodrigues, F. Ruiz<sup>2</sup>, M. Abad<sup>2</sup>, M.M.S. Cabral Pinto<sup>1,3</sup>, M.M.V.G. Silva<sup>4</sup>*

Geochemical, mineralogical and radiometric studies of superficial environments of the Iberian Peninsula and Cape Verde archipelago were performed. During 2011 a third field work campaign was conducted in the Fogo island according to the recommendations of the IGCP 259 (“International Geochemical Mapping”). A first campaign was done in Brava island. REE clearly differentiate soils of Santiago island with contrasting parent materials, particularly carbonatites-related one’s, associated with higher contents of Ba, Th and U. Total contents of Cs, As and Ga are associated with the finer soils. Concerning potentially pollutant elements, As contents increase with decreasing particle size, and high Cr contents were found in some soils. However, As is less available in the finer soils and extraction of Cr is low, limiting eventual environmental and health effects in the Santiago island.



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

**Nuclear methods for the characterization, dating and preservation of cultural and natural heritage**

*M.I. Prudêncio, M.I. Dias, C. Burbidge, M. J. Trindade, R. Marques, M.A. Gouveia, D. Franco, G. Cardoso, F. Rocha<sup>1</sup>, C. Odriozola<sup>2</sup>, L. Osterbeek<sup>3</sup>, J. Mungur-Medhi<sup>3</sup>, J. Sanjurjo<sup>4</sup>, A.C. Valera<sup>5</sup>, V. Hurtado<sup>6</sup>, L. San Juan Garcia<sup>6</sup>, L. Rebelo<sup>7</sup>, P. Brito<sup>7</sup>*



Neutron activation and luminescence techniques, complemented with XRD, support most of the research activities of the GeoLuC group. These nuclear methods were applied to cultural and natural heritage studies, most of them performed in the frame of research projects, and master and doctoral theses, as well as post-doctoral programmes. Service work for public and private institutions also makes up a significant part of the work conducted by GeoLuC. Compositional studies (mineralogical and chemical) and absolute dating (TL-OSL) are applied to geological and archaeological contexts and materials, contributing to answering questions related with provenance, production technology, ancient recipes and alteration pathways, weathering processes, and absolute chronology. Research work has also been conducted in the frame of the IAEA-TC Project RER/8/015 “Using Nuclear Techniques for the Characterization and Preservation of Cultural Heritage Artefacts in the European Region”, and in the frame of the IAEA technical meeting (TM-40771) “Applications of synchrotron radiation sources for compositional and structural characterization of objects in cultural heritage, forensics and materials science”.

<sup>1</sup> Univ. Aveiro, GeoBioTec; <sup>2</sup> ISCME, CSIC, Seville, Spain; <sup>3</sup> Inst. Politécnico de Tomar, Portugal; <sup>4</sup> Inst. Univ. de Xeologia, Corunha, Spain; <sup>5</sup> Era Arqueologia S.A. Portugal; <sup>6</sup> Univ. Seville, Spain; <sup>7</sup> IGM. INETI, Portugal