

# 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 environmental contexts**, through the **application of nuclear methods**, geochemistry and mineralogy.

The GeoLuC group has an interdisciplinary approach to the study of archaeological and geological contexts, and objects from excavations and museums. The origin, technique of manufacture, and age are the main issues in studying cultural assets. The study of these complex materials, such as pottery, minerals, stones and mortars, include field geology, nuclear and physical methods, geochemistry and mineralogy.

The GeoLuC research activities during 2008 were developed as follows:

- Composition and internal dosimetry of natural quartz grains
- Thermoluminescence (TL) and Optically stimulated luminescence (OSL) applied to dating geological and archaeological contexts
- Luminescence applied to Portuguese Faience and Chinese Porcelain produced for the Portuguese market (XVI to XVIII centuries): Dating, authenticity, materials, pigments
- Casa do Governador da Torre de Belém (Tagus estuary): Halieutical resources industry in Roman times
- Portuguese clays – geochemical and mineralogical characterization with a view to technological applications
- Archaeometry of Cultural Heritage Assets
- Applied geochemistry to the establishment of natural background of superficial environments: Iberian Peninsula and Atlantic islands

- Elemental distribution, radioisotopes and radioactive equilibrium of actinides and other trace elements in superficial environments
- Nuclear methods of analysis: development and application of luminescence techniques and neutron activation analysis

The main methodological approaches of the GeoLuC group comprise instrumental neutron activation analyses (INAA), X-ray diffraction (XRD) and luminescence (thermoluminescence and optically stimulated luminescence: TL and OSL) applied to archaeometry, environmental geology and paleoenvironmental reconstruction. SEM-EDS and Mössbauer are also commonly used. The application of these methodologies unique in Portugal, is crucial for solving archaeological and geological problems. The research is developed through financed projects, protocols, collaboration with national and international laboratories and universities, and contracts/services with private and public institutions.

Under the National Scientific Infrastructure Programme, the Project REEQ/590/CTE/2005, “Palaeoenvironmental Reconstruction using Chemical Analysis and Single-Grain Luminescence Dating. A non-biostratigraphical approach” ended, and the equipments for INAA and TL-OSL are in full operation.

The GeoLuC group activities also include education and training of students from national and international universities. Our students participate in the entire research work, 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 accomplish projects in fundamental and applied research.

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## Research Team

### Researchers

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

### Students

A. JORGE, Ph.D. student, U. Sheffield grant  
C. CAPITÃO-MOR, M.Sc. student  
S. VILELA, M.Sc. student  
J. MUNGUR-MEDHI, M.Sc. student  
A. CALADO, M.Sc. student  
A. L. RODRIGUES, FCT grant

### Technical Personnel

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

### Collaborators

M. A. GOUVEIA, Princ. Researcher (Retired)

## Composition and internal dosimetry of natural quartz grains

C.I. Burbidge, M.I. Dias, M.I. Prudêncio, L.P. Rebêlo<sup>1</sup>, G. Cardoso, P. Brito<sup>1</sup>

### Objectives

As part of continuing studies to improve our understanding of luminescence behaviour in samples for dating, differences in signal levels obtainable from natural and laboratory irradiated grains of Mozambican quartz were investigated to evaluate:

- Average impurity concentrations and the composition of localised inclusions.
- TL and OSL signals contributing to the ~380 nm emission from these grains.
- The potential of  $\alpha$  radiation to induce additional OSL signal beyond that produced by  $\beta$  irradiation, in both compact crystalline quartz (the surfaces of acid-etched grains), and in milled quartz with large numbers of defects exposed on grain surfaces.

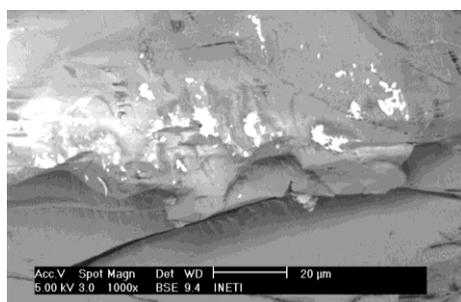


Fig. 1. BSE image of Iron Oxide inclusions in etch pits on the surface of a quartz grain.

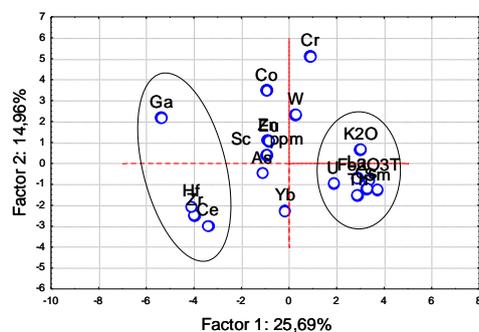


Fig. 2. PCA of INAA results indicating “Substitutional” (Zr) and “Structural” (Fe) groupings.

### Results

OM, SEM, XRF and INAA, indicate the presence of various types of quartz and mineralogical inclusions. A spatial association of Th and U with Fe in structural defects was observed. Fe concentrations and inclusion sizes indicated that internal  $\alpha$  dose rate would affect the defects that contained these impurities but would be insignificant to the bulk quartz.

A broad range of optically sensitive TL peaks were observed. The TL results suggested a preheating regime (260°C/30s) to minimise the effect of the observed inclusions and defects on absorbed dose determinations by OSL. Growth in OSL with dose from whole grains preheated in this way approached saturation by 332 Gy of  $\beta$  irradiation ( $^{90}\text{Sr}/^{90}\text{Y}$ ) and by

4 kGy of  $\alpha$  irradiation ( $E \approx 3.5$  MeV, approximate natural soil spectrum average, using converted dose rate from  $^{241}\text{Am}$ ). This indicated  $\alpha$ -efficiency ( $k_{\text{eff}}$ ) at saturation of around 0.08. However, the OSL decay curves contained a small “medium” component. Structural defects introduced by milling the grains, produced a larger “medium” component with a similar decay rate under optical stimulation, which exhibited high saturation doses ( $>32$  kGy $\alpha$ ,  $>8.4$  kGy $\beta$ ) and  $\alpha$ -efficiency ( $k_{\text{eff}} = 0.34$ ). Dose normalised signals from the milled material greatly exceeded those obtained from the whole grains as they approached saturation.

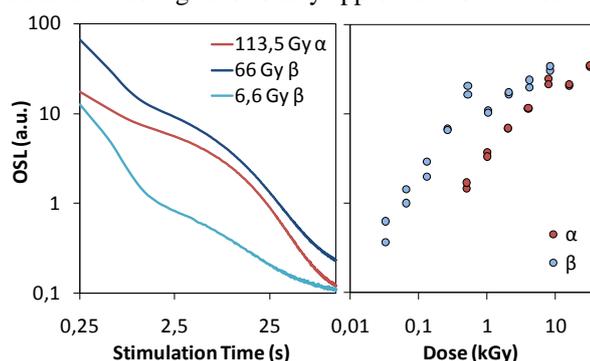


Fig. 3. Milled quartz: OSL decays and growth in signal with dose following  $\alpha$  and  $\beta$  irradiation.

### Conclusions

It is inferred that the presence of structural defects within a quartz crystal, similar to those produced by milling, can produce OSL components that grow to signal levels and doses exceeding those from the crystalline quartz. Samples exhibiting high saturation doses may therefore contain higher numbers of structural defects and vice versa, but the contribution to total OSL signal is expected to be small in general. When the whole crystal is irradiated, growth of these minor components at high doses may be masked by effects on signals from the bulk material, such as radiation quenching. In the present study though, such defects were found to host  $\alpha$ -emitting impurities. High localised dose rates in nature could enhance signals from these locations without affecting the bulk crystal, making natural signal levels difficult to reproduce in the laboratory. However, association of internal  $\alpha$  activity with Fe indicates potential for removal of the most  $\alpha$  affected grains by magnetic separation.

### Published work

Burbidge, C.I., Dias, M.I., Prudêncio, M.I., Rebêlo, L.P., Cardoso, G.O., Brito, P. Internal  $\alpha$  activity: localisation, compositional associations and effects on OSL signals in quartz approaching  $\beta$  saturation, *Radiation Measurements (in press)*

<sup>1</sup>DGM, INETI

**Thermoluminescence (TL) and Optically stimulated luminescence (OSL) applied to dating geological and archaeological contexts, archaeological artefacts and art objects**

*M. I. Dias, M.I. Prudêncio, C. Burbidge, A. L. Rodrigues, D. Franco, G. Cardoso, R. Marques, D. Mosquera<sup>1</sup>, J. Sanjurjo<sup>1</sup>, L. Rebelo<sup>2</sup>, A. Martins<sup>3</sup>, L. Osterbeek<sup>4</sup>, A.C. Valera<sup>5</sup>, C. Odriozola<sup>6</sup>, V. Hurtado<sup>7</sup>, L. San Juan Garcia<sup>7</sup>*

TL and OSL absolute dating methods were applied to diverse geological and archaeological contexts from Iberian Peninsula, as well as artefacts (ceramics and lithics) on behalf of some running projects (Grices, FCT), contracts and services with national and international institutions. These studies specially aim to contribute for a better definition of the chrono-stratigraphic sequence of human occupation and/or of geological environments. Absolute dating of archaeological artefacts and authenticity tests applied to art objects was also performed. An inter-calibration program is running with Luminescence Laboratory of Instituto de Xeologia da Univ. La Coruña. Methodology involved includes physical and chemical characterization techniques (SEM, INAA, XRF and XRD), and luminescence dating techniques.



<sup>1</sup> Inst. Universitario de Xeologia, Corunha, Spain

<sup>2</sup> IGM. INETI

<sup>3</sup> Univ. Évora

<sup>4</sup> Inst. Politécnico de Tomar, Portugal.

<sup>5</sup> Era Arqueologia S.A. Portugal

<sup>6</sup> ISCME, CSIC, Seville, Spain

<sup>7</sup> Univ. Seville, Spain

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

*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. Zink<sup>4</sup>,*



Portuguese faience and Chinese porcelain produced for the Portuguese market (XVI to XVIII centuries) are being studied on behalf of an FCT project, including: (i) chemical (INAA) and mineralogical (XRD) characterization of the ceramic body; (ii) characterization (XRF and synchrotron radiation techniques) of surface coatings (glazes and pigments); (iii) TL and OSL of the ceramic body. Different composition of the ceramic raw materials may be inferred from mineralogical data. Substantial sensitisation effects were noted in the luminescence measurements. These may limit application of conventional additive and regenerative luminescence techniques, but aid the use of predose sensitisation measurements. Absorbed doses of 1-5 Gy indicate high radioactivity and/or signals from fine grains, which absorb  $\alpha$  radiation as well as  $\beta$  and  $\gamma$ . Ongoing analysis of sample composition and geochemistry will elucidate these issues. Further investigation of luminescence emissions in relation to the mineralogical assemblage will be undertaken.

<sup>1</sup> CENIMAT, UNL Campus de Caparica. 2829-516 Caparica, Portugal.

<sup>2</sup> Museu Nacional de Arte Antiga. Rua das Janelas Verdes. 1249-017Lisboa, Portugal.

<sup>3</sup> Inst. Português de Conservação e Restauro. Rua das Janelas Verdes, 37. 1249-018Lisboa, Portugal. 1

<sup>4</sup> CNRS, Musée du Louvre, Paris, France

**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. Fabião<sup>1</sup>, S. Gabriel<sup>2</sup>, M. Coelho<sup>2</sup>, I. Filipe<sup>2</sup>*

The study of archaeological artefacts of the production unity of fish resources transformation identified in Casa do Governador da Torre de Belém, located in the Tagus estuary, has as main purpose the chronological and functional space characterization, in order to integrate this specific site in the sphere of the production of fish-processing products in the Tagus Estuary and in a larger spectrum in the Sado Estuary, Algarve and Andalusia. This study is an FCT running project. A typological classification of the ceramics was done by the archaeological team, and some were chosen for the archaeometric approach, namely the geochemical characterisation of amphorae paste (INAA) and mineral phases (XRD) identification. Sampling collection of sediments and paleosoils (human occupation) for luminescence dating was also performed, as well as in situ measurements of environmental radioactivity (gamma measurements).



<sup>1</sup> Fac. Letras, Univ. Lisboa

<sup>2</sup> Era Arqueologia S.A. Portugal

**Portuguese clays – geochemical and mineralogical characterization with a view to technological applications**

*M.J. Trindade, R. Marques, M.I. Dias, M.I. Prudêncio, D. Franco, M.A. Gouveia, F. Rocha<sup>1</sup>, J. Coroado<sup>2</sup>*

Clay raw materials from the Meso-Cenozoic basins (Algarve and Lusitania) of Portugal are being characterized in the granulometric, geochemical and mineralogical point of view. The main goals are: (i) detailed characterization of basin sediments, particularly of clayey levels, which enable valuable palaeoenvironmental interpretations and reconstruction of the evolutionary history of the depositional environments; (ii) in addition, compositional transformations of clays with firing are study to better assess estimates of maximum firing temperatures of local ancient ceramics and to establish geochemical and mineralogical reference groups and fingerprinting clay raw materials for comparison with contemporaneous and ancient ceramics in archaeometric studies.



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

<sup>2</sup> Inst. Politécnico de Tomar, Portugal. GeoBioTech

**Archaeometry of Cultural Heritage Assets**

*M.I. Dias, M.I. Prudêncio, M.A. Gouveia, D. Franco, R. Marques, A. Jorge<sup>1</sup>, P. Day<sup>1</sup>, P. Francisco<sup>2</sup>, F. Rocha<sup>2</sup>, A. Calado<sup>3</sup>, C. Odriozola<sup>4</sup>, J. Mungur-Medhi<sup>5</sup>, J. Sanjurjo<sup>6</sup>, A.C. Valera<sup>7</sup>, V. Hurtado<sup>8</sup>, L. San Juan Garcia<sup>8</sup>*

Nuclear methods of analyses were applied to several archaeometric studies, namely pottery of a wide range of chronologies. Most of these studies were done in the framework of master and doctoral thesis, as well as post-doctoral programmes. Study of objects from excavations and museums, including their origin, technique of manufacture, age and conservation was done. These studies unlock information from ancient materials, such as provenance of raw materials, mainly pottery, technique of manufacture, firing technology, ancient recipes and alteration pathways, in an Iberian perspective.



<sup>1</sup> Univ. of Sheffield – Department of Archaeology and Prehistory, England;

<sup>2</sup> Univ. Aveiro, GeoBioTec

<sup>3</sup> Univ. Bordéus, France

<sup>4</sup> ISCME, CSIC, Seville, Spain

<sup>5</sup> Inst. Politécnico de Tomar, Portugal

<sup>6</sup> Inst. Universitario de Xeologia, Corunha, Spain

<sup>7</sup> Era Arqueologia S.A. Portugal

<sup>8</sup> Univ. Seville, Spain

**Applied geochemistry to the establishment of natural background of superficial environments: Iberian Peninsula and Atlantic islands**

*M.I. Prudêncio, M.I. Dias, R. Marques, D. Franco, M.J. Trindade, J.C. Waerenborgh, F. Ruiz<sup>1</sup>, M. Abad<sup>1</sup>, F.Rocha<sup>2</sup>, E.Silva<sup>2</sup>*

Geochemistry, crystal chemistry and mineralogy are applied to the study of superficial environments (present day and paleoenvironments). The establishment of natural background and evaluation of potential anthropogenic influence, particularly in the trace elements contents, is a major goal. The geochemistry of the earth surface, principally the distribution and behavior of rare earth elements (REE) and other trace elements in secondary natural systems, and the alterations due to pollution actions in sediments and soils, have been applied in Azores Island and Cape Verde archipelago, as well as in different geomorphological/geological units of the Iberian Peninsula.



<sup>1</sup> Univ. Huelva, Spain;

<sup>2</sup> Univ. Aveiro, GeoBioTec

**Elemental distribution, radioisotopes and radioactive equilibrium of actinides and other trace elements in superficial environments**

*M.J. Trindade, M.I. Prudêncio, M.I. Dias, R. Marques, M.A. Gouveia, D. Franco, J. Sanjurjo<sup>1</sup>, D. Mosquera<sup>1</sup>, J. R. Vidal Romani<sup>1</sup>*

Natural radioactive elements, mainly from the actinide series, are being studied in superficial environments such as soils resulting from weathering of different types of rocks, predominantly granites, and in sedimentary formations. The study of radioisotopes and radioactive equilibrium in addition to elemental concentrations distribution, enable a more accurate investigation of the mobility of elements in different geological contexts. The comparison of actinides behaviour with other trace elements, lanthanides in particular, and with mineralogy, helps on tracing sedimentary processes like weathering, sedimentary calibration and source area homogeneity. Special attention is paid to the most abundant natural radionuclides (<sup>232</sup>Th, <sup>238</sup>U, <sup>235</sup>U, <sup>40</sup>K). Another important application of this study is in the determination of annual palaeodoses received by geological materials to be dated by luminescence.



Another important application of this study is in the determination of annual palaeodoses received by geological materials to be dated by luminescence.

<sup>1</sup> Inst. Universitario de Xeologia, Corunha, Spain

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**Nuclear methods of analysis: development and application of luminescence techniques and neutron activation analysis**

*M.I. Prudêncio, M.I. Dias, C. Burbidge, M. J. Trindade, R. Marques, M.A. Gouveia, D. Franco, G. Cardoso*

Instrumental neutron activation analysis is a well-established method within this group since the seventies. Based on the use of the RPI (nuclear research reactor unique in the Iberian Peninsula), this analytical method together with luminescence techniques (complemented with other methods) supports most of the research activities of the GeoLuC group. 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 the good performance of the laboratories. The Luminescence Dating Laboratory participates in international comparisons, particularly with the IUX, Coruña, Spain. The luminescence and neutron activation laboratories were reinforced with new equipment on behalf of the national Re-equipment Program by FCT (CONC-REEQ/590/2001) and are fully running.