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 and geo-environmental contexts**, with a view to their characterization and/or conservation, through the **application of nuclear methods**.

The GeoLuC group has an interdisciplinary approach to the study of archaeological and geological contexts and materials, as well as of museum artworks. Provenance, production technology and chronology are the main goals of the archaeometric research. During 2010 an innovative multidisciplinary project was initiated, on the diagnosis of pathologies and mechanisms of degradation, and conservation strategies for Portuguese Cultural Heritage, using non-destructive techniques. Detailed geochemical studies for the understanding of the lanthanides, actinides and other trace element behaviour in superficial environments are another major research domain of the GeoLuC group. Geochemistry and luminescence were applied for the reconstruction of coastal palaeoenvironments of dune systems from Iberian Peninsula and Africa.

The main research activities of GeoLuC group during 2010 are summarised according to the following themes:

- kGy dosimetry using OSL and TTOSL signals from quartz.
- RADIART - Diagnosis, decontamination and conservation of cultural heritage: neutrons and ionizing radiation in artwork.
- 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 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.
- 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 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 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.

Methodological testing and development of neutron activation and luminescence analyses are an ongoing task, having the potential to obtain more detailed insights into the elemental composition and chronology/dosimetry of different types of materials 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 and post-doctoral programmes. 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 the participation and organization of national and international conferences.

Research Team

Researchers

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

Technical Personnel

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

Students

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

Collaborators

M. A. GOUVEIA, Princ. (Retired)

kGy dosimetry using OSL and TTOSL signals from quartz

Burbidge, C.I., Cabo Verde, S.I., Fernandes, A.C.,
Prudêncio, M.I., Botelho, M.L., Dias, M.I., Marques, J.G., Cardoso, G.

Luminescence signals have been identified that permit the retrospective evaluation of absorbed doses in quartz up to tens of kGy: an order of magnitude beyond the maximum conventionally measured with this ubiquitous natural dosimeter. This work is part of a new project investigating the use of neutrons and ionizing radiation for diagnosis, decontamination and conservation of heritage materials (PTDC/HIS-HEC/101756/2008-RADIART).

Subsamples from historic ceramic tiles have been ^{60}Co gamma irradiated for the purposes of biological decontamination at CHIP (ITN), accompanied by Perspex dosimeters and quartz from a geological sample known to exhibit thermally-transferred optically-stimulated luminescence (TTOSL). OSL and TTOSL signals from quartz grains were measured (Fig. 1; -L1) using different preheats, and following re-irradiation with a ^{90}Sr/^{90}Y beta source at GeoLuC (-L2). OSL from 10 Gy test doses was measured following each high dose cycle (T1, T2). Reduction of the dynamic range of signal levels using linear modulation (LMOSL) was novelly applied for the avoidance of detector saturation effects without reducing detector sensitivity. Fits to gamma responses (Fig. 2) were interpolated through those to beta responses, to evaluate the effectiveness of retrospective dose evaluation for different signal integrals, preheat combinations, and dose intervals. OSL signals evident at short stimulation times, conventionally used for dosimetry and dating, exhibited inconsistent behaviour at high doses. High preheats reduced the significance of rapidly saturating and/or negative components in dose response (Fig. 2), and preferentially removed OSL and TTOSL signals evident at longer stimulation times (Fig. 1). Remaining signals yielded more accurate retrospective dose determinations. TTOSL signals evident at short stimulation times increased proportionally to dose between 1 and 30 kGy when a 300 °C preheat was applied (Fig. 2, arrow). Doses were underestimated by 13-20%: refinement of the measurement protocol should improve accuracy, but results already enable general assessment of radiation exposure.

This work has identified elements of OSL and TTOSL signals that can be used; following severe preheats, to retrospectively evaluate doses of tens of kGy.

GeoLuC is developing research in Retrospective Dosimetry with the European Radiation Dosimetry Group and with UPSR, ITN. Burbidge became a full EURADOS member in 2010: Working Group 10 is supporting attendance at meetings to develop the knowledge and contacts of GeoLuC. GeoLuC is contributing knowledge of luminescence dating and its research community. This has contributed to an international survey designed to stimulate knowledge exchange between physical and biological dosimetry practitioners.

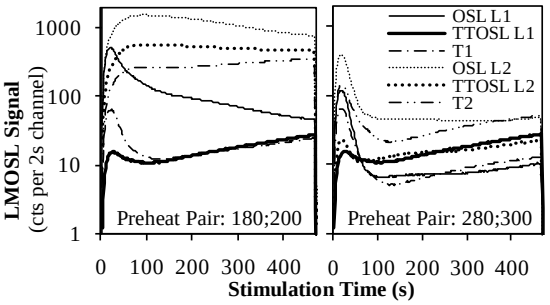


Fig. 1. LMOSL signals from quartz, for weak and severe preheats applied to -L1 and -L2 measurements, following doses of 1 kGy.

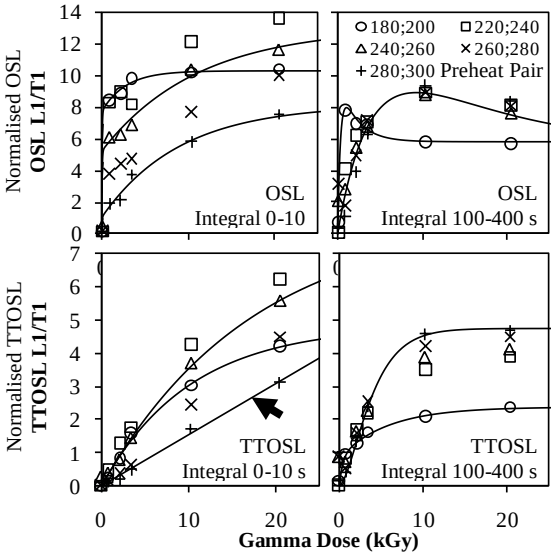


Fig. 2. Dose response characteristics of different OSL and TTOSL signal intervals for different preheats (OSL; TTOSL in °C/30 s).

Published work

Burbidge, C.I., Cabo Verde, S.I., Fernandes, A.C., Prudêncio, M.I., Botelho, M.L., Dias, M.I., Cardoso, G. (submitted) kGy dosimetry using OSL and TTOSL signals from quartz. Radiation Measurements.

Burbidge, C.I., Fernandes, A.C., Cabo Verde, S.I., Prudêncio, M.I., Botelho, M.L., Dias, M.I., Cardoso, G., Osvay, M. (2010) Retrospective dosimetry of ceramics irradiated for bio-decontamination and conservation of cultural heritage. In: EPRBioDose 2010, ISS and IRSN, Mandelieu La Napoule (France), pp. 170.

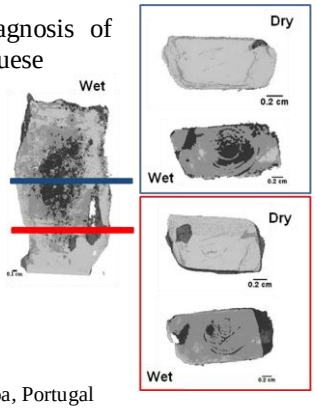
Burbidge, C.I., Fernandes, A.C., Cabo Verde, S.I., Prudêncio, M.I., Botelho, M.L., Dias, M.I., Cardoso, G., Osvay, M., Rocha, F. (2010) Comparison of OSL and TTOSL signals from quartz, for retrospective dosimetry in bio-decontamination and conservation of cultural heritage. In: UK Luminescence and ESR meeting 2010, University of Oxford, UK, pp 27.

Prudêncio, M.I., Silva, T.P., Dias, M.I., Marques, J.G., Figueiredo, M.O., Esteves, L., Albuquerque, M.B., Botelho, M.L., Trindade, M.J., Burbidge, C.I., Marques, R. (2010) Non-destructive and micro-invasive techniques for cultural heritage diagnostics - a case study of glazed tiles from Portuguese historical buildings. In: 38th International Symposium on Archaeometry, Tampa, Florida.

Trompier, F., Ainsbury, L., Burbidge, C., Kulka, U., Romm, H., Rothkamn, K., Roy, L., Whitehouse, C.A., Fattibene P. EURADOS survey for physical dosimetry methods in emergency preparedness and population triage. In: EPRBioDose 2010, ISS and IRSN, Mandelieu La Napoule (France), pp. 1

RADIART - Diagnosis, decontamination and conservation of cultural heritage: neutrons and ionizing radiation in artwork

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



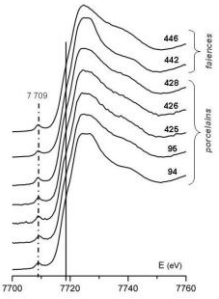
This project consists of an innovative multidisciplinary approach to the diagnosis of pathologies and mechanisms of degradation, and to the conservation of Portuguese Cultural Heritage, by the use of non-destructive techniques. The main outputs expected are the establishment of procedure protocols for (1) inner structure visualization by NT and for (2) non-toxic radiation treatments of artworks. Compositional characterization of ceramic body and mortars (XRD and INAA) and of glazes (XRD and XRF) were performed in some types of glazed tiles from the XVII century, namely form the Madre de Deus church, Lisbon, and from the N. Srª dos Aflitos church, Elvas. Experiments of gamma irradiation for biological decontamination were performed. Visualization of physical structures in the interior of tile fragments was obtained by neutron tomography.

[1] Instituto Nacional de Engenharia, Tecnologia e Inovação, Estrada do Paço do Lumiar, 1649-038 Lisboa, Portugal
[2] Museu Nacional do Azulejo, Rua da Madre de Deus nº 4,1900-312 Lisboa, Portugal
[3] Conservar-Inovar, Lda, Av. Duque de Loulé nº 77, 4º Dto, 1055-088 Lisboa, Portugal
[4] 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[1], T. Silva[1], J.P. Veiga[1], M.A. Matos[2], A.M. Pais[3], C. Burbidge, D. Franco, R. Marques, G. Cardoso, A. L. Rodrigues, A. Zink[4]

Co-*K* edge XANES spectra collected from blue glaze of PF and CPOPM



Two main subjects were addressed in this FCT project through the same methodological approach applied to the early Portuguese faience PF (XVII – 1st half XVIII cent.) and to the Chinese porcelain ordered for the Portuguese market CPOPM (XVI-XVII cent.). 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 CPOPM 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 Co2+ions being responsible for a blue colouring, conversely non-colouring pseudo-octahedral Co2+ 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[1], C. Fabião[2], C. Odriozola[3], V. Hurtado[3], L. San Juan Garcia[4], L. Osterbeek[5,6], J. Mungur-Medhi[5,]6, C. Scarre[7], J. Munghur Medhi[6,8],A. Cruz[6], P. Cura[6], J. Garcia Gazolaz[9], J. Sesma[9], D. Mosquera[10], J. Sanjurjo[10], S. M. Espino[11], C. Bento[12], A. Silva[12], T. Gomes[12]

Research activities including PhD thesis 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. Special attention has been paied to the in situ measurements of gamma radiation within profiles of sedimentary/archaeological stratigraphy to provide additional information for the dating results, as well as to a better correlation with lithology.

[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

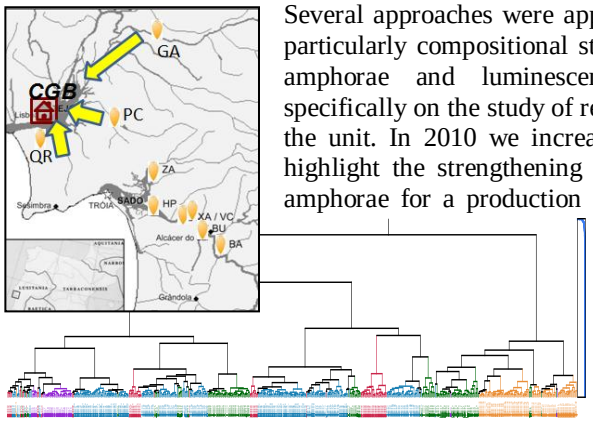
C. Burbidge, M. I. Dias, M.I. Prudêncio, G. Cardoso, D. Franco, R. Marques, L. Rebelo[1], P. Brito[1], D. Mosquera[2], J. Sanjurjo[2].

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. An additional 17 samples are being dated from Mozambique. These represent a shift of focus between islands in the coastal dune cordon: now Bilene. Most of the samples contain relatively large doses for dating using conventional OSL signals from quartz. Methodology developed for the measurement of such samples is now stable: interest in extending the possible range of measurements to even higher doses/ages has fed into the work presented on kGy dosimetry. Work at Troia is now drawing to completion: an additional 24 samples received in 2010 are aimed at filling gaps in the chronological data obtained to date, and at achieving sedimentary levels predating the formation of the spit. It is aimed to develop Portuguese coastal studies on the neotectonics of older coastal formations.

[1] IGM. LNEG, Portugal
[2] Inst. Universitario de Xeologia, Corunha, Spain

***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[1], S. Gabriel[2], M. Coelho[2], I. Filipe[2]



Several approaches were applied in this FCT interdisciplinary project: archaeometry, particularly compositional studies (chemical and mineralogical, INAA and XRD) of amphorae and luminescence dating; archaeozoology; archaeology, focusing specifically on the study of recovered artifacts, and building of the 3D virtual model of the unit. In 2010 we increased the number of classes to be sampled. New results highlight the strengthening of the trend previously observed, pointing most of the amphorae for a production in the Tagus basin. Having been most 20/21 = Dressel Class 14 supplied by the river upstream kilns (Garrocheira), some Dressel 20/21 = 14 by the Tagus estuary kilns of P. Cacos, and other types distributed by P. Cacos and Q. Rouxinol kilns. Recent results suggest the existence of amphorae of unknown origin, with high contents of LREE, Hf and Th, ponting to the use of materials related to more acid lithologies (granites?). Luminescence studies confirm the Roman age of the fish tank and indicate a Chalcolithic date for the paleosol on which it was built.

[1] Fac. Letras, Univ. Lisboa
[2] Era Arqueologia S.A. Portugal

Distribution of trace elements, especially lanthanides and actinides, in superficial environments of Portugal

M.J. Trindade, M.I. Prudêncio, M.I. Dias, R. Marques, M.A. Gouveia, D. Franco, J. Sanjurjo[1], D. Mosquera[1], J. R. Vidal Romani[1], F. Rocha[2]

Detailed geochemical studies on lanthanides, actinides (U and Th) and other trace elements' behaviours have been applied to superficial environments around Portugal. These studies have been complemented with mineralogical analysis and field radiometric measurements by portable gamma-ray detectors. This research contributes to the study of the post-depositional alteration processes (weathering) in vertical sedimentary profiles, with ultimate impact and application in soil formation and evolution studies, palaeoenvironmental investigations, and luminescence dating of Quaternary sediments. During 2010, our study was mostly focused on the variation of mineral and chemical composition in several size fractions (2 mm-63 μm, 63-20 μm, 20-2 μm and > 2 μm) of residual clays of dolerites, granites and slates from Central Portugal, a region known by its richness in uranium. The main aim was the understanding of the chemical changes that occur during the weathering of rocks in the formation of the various residual clays, especially the chemical patterns associated to uranium and other actinides and lanthanides mobilization.

[1] Inst. Univ. de Xeologia, Corunha, Spain; [2]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, D. Franco, M.J. Trindade, C. Burbidge, G. Cardoso, A.L. Rodrigues, F. Rui[1], M. Abad[1], F. Rocha[2], E. Silva[2], M.M.S. Cabral Pinto[2,3], M.M.V.G. Silva[4]

Geochemical, mineralogical and radiometric studies of superficial environments (soils and sediments) of the Iberian Peninsula and Cape Verde archipelago were performed. During 2010 a second field work campaign in the Fogo island was conducted. The results obtained so far showed that soils developed on carbonatites are clearly distinguished by high contents of K, Rb, Cs, W, Th and rare earth elements (REE). The main mineral compounds identified in Fogo topsoils are pyroxenes, feldspathoids, magnetite-maghemite, titanomagnetite, zeolites and phyllosilicates. The soil developed in carbonatites shows a distinct mineralogical association, with calcite, micas, phyllosilicates, and feldspars. Quartz and micas are found throughout the studied soils of this volcanic island, derived most probably from particulate deposition from the atmosphere, transported by wind from North Africa (Sahara).

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

Nuclear methods for the characterization 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, A. Jorge[1], P. Day[1], F. Rocha[2], C. Odriozola[4], L. Osterbeek[5], J. Mungur-Medhi[5], J. Sanjurjo[6], A.C. Valera[7], V. Hurtado[8], L. San Juan Garcia[8]

INAA (using the RPI), together with luminescence techniques 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 framework of 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. Neutron activation analysis and luminescence methods are applied to palaeoenvironments and ancient materials studies, contributing to answering questions related with provenance, production technology, ancient recipes and alteration pathways, weathering processes, as well as absolute chronology, with an Iberian focus. Research work has also been conducted in the framework of the IAEA-TC Project RER/8/015 - Using Nuclear Techniques for the Characterization and Preservation of Cultural Heritage Artefacts in the European Region.

[1] Univ. of Sheffield – Dep. of Archaeology and Prehistory, England; [2] Univ. Aveiro, GeoBioTec; [3] Univ. Bordeaux, 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