# Chemical and Radiopharmaceutical Sciences Unit



## **Chemical and Radiopharmaceutical Sciences**

Maria Isabel Prudêncio

The Chemical and Radiopharmaceutical Sciences Unit (CRSU) is designed to provide a catalyst and support network for enhancing research and expertise in the synthesis and characterization of inactive and radioactive compounds, cultural materials, geological and biogenic materials, and hydrological resources. Its activities focus on Health, Nuclear Sciences, Catalysis, Materials, Environment, Cultural Heritage, Earth Sciences, and Natural Heritage applications.

National and international projects, many with the scientific coordination of Unit members, mainly financed by the FCT and EC, are in course. Seven new projects financed by FCT started in 2011 (four coordinated by CRSU members). Additional funding was obtained through protocols, contracts, and services with private and public institutions.

CRSU members are the Portuguese representatives in the Management Committees of COST Actions, designated counterparts of IAEA projects, and provided expertise through IAEA in thematic areas like Health, Chemistry, Cultural Heritage, and Hydrology. Expertise was also provided in other national and international institutions particularly, Nuclear Medicine Centres, INFARMED, and international Science Foundations, and as members of Advisory Boards of International Journals and Conferences.

Research interests have been extended to molecular magnetism namely in the framework of the European Network of Excellence *MAGMANet*, and participation in the European Institute of Molecular Magnetism.

Cultural Heritage activities of CRSU members were significantly enhanced during 2011 through Presidency of the Directive Board of the international "Sociedade de Arqueometria Aplicada ao Património Cultural" (SAPaC).

The International Conference - *IX Iberian Congress* on Archaeometry - was held for the first time in Portugal (Lisbon), and the Workshop on Strongly Correlated Electron and Complex Systems – from intermetallics to molecular materials was held in ITN, both organized by CRSU members. numerous publications, some articles being in high index factor journals, as well as through the active participation in international conferences, including invited talks. A letter in Science was published in the scope of 2011- International Year of Chemistry -, concerning the origin of the names of chemical elements.

Education and training at Undergraduate, M.Sc., Ph.D. and Post-doctoral levels is one major achievement at CRSU. Four Ph.D. theses and four BSc theses were completed. A strong participation in advanced education activities in collaboration with universities is being done, such as the Coordination of the Master Course Biomedical Inorganic Chemistry (ITN/UL), and the Coordination of Radiopharmaceutical Chemistry in the Master Course Pharmaceutical and Therapeutic Chemistry/FFUL.

Also of note was the CRSU participation in the commemoration of the 50th Anniversary of the Portuguese Research Reactor, where our activities based on the use of the nuclear reactor on Cultural Heritage and Earth Sciences were presented.

The activities are developed by five experienced multidisciplinary research groups: (i) Applied Geochemistry & Luminescence on Cultural Heritage; (ii) Environmental and Analytical Chemistry; (iii) Inorganic and Organometallic Chemistry; (iv) Radiopharmaceutical Sciences; and (v) Solid State.

Collaborations among CRSU groups increased in 2011, particularly to study the magnetic properties of and uranium complexes layered lanthanide hydroxides. In addition, collaborative links with other ITN units were strengthened for the characterization, pathologies diagnosis and establishment of conservation strategies of artworks, for biological decontamination of cultural objects, for dosimetry, ultra-trace elements determination in and environmental and biological research. Collaborations with international research institutions were strengthened.

During 2011 a high frequency Liquid Water Isotope Analyzer (LWIA - LGR DT-200) was installed, reinforcing the isotope hydrology field.

The dissemination of results was conducted through

Staff Researchers M.I. PRUDÊNCIO, Princ. (Agreg.) A. PAULO, Princ. A.M.M. SOARES, Princ. A.P. GONÇALVES, Princ. I. SANTOS, Princ. (Agreg.) J. MARÇALO, Princ. J.C. WAERENBORGH, Princ. LD G. CORPELA Princ.	F. MARQUES, Aux. F. MENDES, Aux. (Contract) G. MORAIS, Aux. (Contract) I.C. SANTOS, Aux. J.B. BRANCO, Aux. J.M. CARRETAS, Aux. J.M. DE LA ROSA, Aux. (Contract) J.P. LEAL, Aux. L. MARIA, Aux. (Contract) L.C.J. PEREIRA, Aux. M.C. OLIVEIRA, Aux. M.I. DIAS, Aux. (Invited) M.P. C. CAMPELLO, Aux. P. CARREIRA, Aux. S. RABAÇA, Aux. (Contract) T. ALMEIDA GASCHE, Aux.	Admin. & Techn. Personnel A. CRUZ A. RODRIGUES A.J. AMARO A.J. SOARES D. ANDRÉ D. FRANCO E. CORREIA G. CARDOSO I. FRAZÃO L. FERNANDES M. CORREIA M.F. MARQUES P. VALÉRIO P.M. REIS R. MARQUES
M. ALMEIDA, Coord. M.F. ARAÚJO, Princ. V. GAMA, Princ. C. BURBIDGE, Aux. (Contract) C. FERNANDES, Aux. C.C.L. PEREIRA, Aux. (Contract) D. BELO, Aux. (Contract) E.B. LOPES, Aux.		

## 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 geoenvironmental 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: Halieutical 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.

#### 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

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 postdoctoral programmes.

#### **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 polymerbased 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 inactivação 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>&</sup>lt;sup>1</sup> Museu Nacional do Azulejo, Rua da Madre de Deus nº 4,1900-312 Lisboa, Portugal

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

<sup>&</sup>lt;sup>3</sup> Conservar-Inovar, Lda, Av. Duque de Loulé nº 77, 4º Dto, 1055-088 Lisboa, Portugal

<sup>&</sup>lt;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.



CENIMAT, UNL. 2829-516 Caparica, Portugal.
MNAz. Rua da Madre de Deus 4. 1900-312 Lisboa, Portugal.
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



Examples of quartz crystals from a. Pegmatite and b. Granite, and their TSL emissions in different spectral regions in response to  $50~{\rm Gv}$ 

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.

<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 daing 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>&</sup>lt;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

## **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**.

Different facilities are available in our group: an Energy-Dispersive X-Ray Fluorescence spectrometer, two dedicated on-line Isotope Ratio Mass Spectrometers systems, equipped with elemental analysers, a Tritium Laboratory, a Radiocarbon Dating Laboratory and a High Performance Liquid Chromatograph/ Inductively Coupled Plasma Mass Spectrometer installed in a clean room facility.

Major achievements are summarized below:

**Environmental Geochemistry** and **Oceanographic** research was carried out under a multi-proxy approach, involving elemental, organic and isotopic analysis, sedimentology, geochronology and absolute dating. An evaluation of environmental changes on the NW Iberian coastal area, using geochemical approaches, showed an important input from terrestrial sources reaching a maximum at AD 1100-1200 and AD 1750-1850, time periods during which have occurred major flood events. Significant reduction in the terrestrial signature was detected in more recent times (ca. AD 1960-1985), contemporary with the construction of major dams on the Minho River.

Oceanographic studies concerning the marine reservoir effect ( $\Delta R$ ) were "completed" concerning two regions: Canary Islands and Cape Verde Archipelago.  $\Delta R$  takes a positive weighted mean value of +185±30 <sup>14</sup>C yr for Canarian eastern islands (Fuerteventura and Lanzarote), while for central and western islands  $\Delta R$  value is 0±35 <sup>14</sup>C yr, in accordance with the hydrodynamic system off Canary Islands. Also, a first  $\Delta R$  calculation was done for the Cape Verde Archipelago ( $\Delta R$  weighted mean value of +70±70 <sup>14</sup>C). This value is in agreement with the oceanographic conditions of the region indicating the existence of a seasonal active upwelling regime.

**Isotope Hydrology** studies were realized taking into account the sustainable regional development and the appropriate use of the water resources and coastal management, based on several European and national directives. Investigations on the use of environmental isotopes hydrology in different systems has been continued, e.g. on the evaluation of geothermal potential and of seismo-volcanic hazard at Azores archipelago; on high mountain areas; on arid and semi arid zones and on gas geochemistry in CO2-rich thermomineral waters in the N Portugal and Spain.

Archaeometallurgical research was pursued by the characterization of metallic artefacts and production remains from Chalcolithic till Early Iron Age, recovered from different regions of the Portuguese territory. A Late Bronze Age metallurgical workshop was studied and evidences on bronze production by co-smelting were found (Entre Águas 5). Besides, the influence of the As contents on the thermo-mechanical properties of Chalcolithic artefacts (from V. Nova S. Pedro) was investigated. From the N territory, studies have shown evidences of a bronze metallurgy with higher Pb contents than contemporaneous bronzes from Central and Southern regions. Also, the characterization of Bujões/Barcelos axes, assumed to be linked with the production of the first bronzes in Portuguese territory, showed they were the manufactured in bronze, with rather uniform tin content and a low impurity pattern.

During the current year, a high-frequency Liquid Water Isotope Analyzer (LWIA - LGR DT-200) that quantifies  $\delta^2$ H and  $\delta^{18}$ O in multiple natural water sources, simultaneously, was installed reinforcing the isotope hydrology field. The installation of the IRMS, equipped with an elemental analyser (Sercon 20-20 EA-IRMS), has permitted relevant contributions in the palaeoenvironmental and archaeological fields. Provenance studies of Cu-based metal archaeological artefacts using Pb isotope ratios were initiated by Q-ICPMS.

The EAC group is highly engaged in education and training of M.Sc. and Ph.D. students in collaboration with different Universities. Technical services are available to Public and Private Institutions.

#### Research Team Researchers

M.F. ARAÚJO, Princ, Group Leader A.M.M. SOARES, Princ. J.M. DE LA ROSA, Aux. P. CARREIRA, Aux. E. FIGUEIREDO, Post-Doc, FCT grant

#### Students

J. MARTINS, Ph.D. student, FCT grant M. J. FURTADO, Ph.D. student, FCT grant F. LOPES, Graduate student I. PEREIRA, Graduate student F. PEREIRA, Graduate student P. PORTELA, Graduate student

S. GOMES, Graduate student

#### **Technical Personnel**

A. AMARO D. NUNES M. CORREIA M. MATEUS, FCT grant (Since Sepember) P. VALÉRIO

# Environmental changes in the Portuguese coastal area by organic geochemical approaches

A.M.M. Soares, J.M. Rosa, J.M. Martins, P. Portela, M.F. Araújo, F.J. González-Vila<sup>1</sup>, F.Fatela<sup>2</sup>, A.R.Pereira<sup>3</sup>

#### Objectives

Over the last 5000 yr different trends of sea level, climatic fluctuations, Bond events or humid episodes have been recorded in the Iberian Peninsula, as well as the increase of the human intervention in the landscape, particularly sensitive since the Middle Bronze Age, all imprinted in the filling-up of the alluvial plain estuaries. To assess the evolution of interface environments along the Portuguese coast, several estuaries presenting different characteristics (e.g. geologic, geomorphologic, climate, human occupation) were selected. Spatial and temporal distribution patterns on their sedimentological, geochemical and isotopic parameters provide evidence of the evolution, extension and impact of human activities, also allowing the identification of climatic events from recent to millennium time scales. The overall objectives of this work are the evaluation, in different coastal environments, of the fluvial and marine contribution to the sedimentary record, the responses to climatic events and the impact of land use changes. Several different estuarine environments are under investigation, from the Minho estuary, at the NW border with Spain till the Guadiana, delimiting the SE Spanish border.

To achieve the above mentioned goals several approaches are being applied focused on the study of the sedimentary organic matter (OM) on dated sequences. Sedimentary OM was characterized using several organic geochemical methods and indices, including elemental carbon, nitrogen and sulphur abundances (C, N, S), molar organic carbon to nitrogen and sulphur ratios (Corg/N; Corg/S), and stable organic carbon isotope values ( $\delta^{13}$ C;  $\delta^{15}$ N). Besides, the distributions of several lipid-biomarker's compounds were also evaluated to precisely identify OM sources and the relative contributions of autochthonous and allochthonous OM inputs to the sedimentary record over a wide range of temporal and spatial scales.

#### Results

During 2011, studies were mainly focused on the saltmarshes of the Minho and Mira estuaries located at the western coastal area and at the Guadiana river adjacent shelf.

Significant conclusions could be taken concerning the Minho estuary, summarized as:

(1)  $\delta^{13}$ C, TOC, TN, C/N and the distribution of biomarkers show that the OM is primarily derived from terrestrial sources, reaching the maximum terrestrial signature during the Little Ice Age.

(2) Samples corresponding to the period 1960–1985 presented low Corg/N ratio and heavier  $\delta^{13}$ C values indicating a significant increase in the marine input. This is likely due to the drastic reduction in River discharge associated with the construction of several major dams.



(3) Alternations in the C/N and  $\delta^{13}$ C values through the 18<sup>th</sup> and 19<sup>th</sup> centuries were consistent with fluctuations of the n-alkyl parameters. They reveal common intensive precipitation alternating with severe droughts recorded.

(4) High C/N and lipid content at approximately AD 1100 suggest punctual increase in the continental discharges, which is contemporary with major flood events reported at that period in the area.

(5) High TS and very low Corg/S values could be derived from the mining exploitation during the Roman domination.

(6) Changes in land use practices (deforestation and intensification of cultivation) have been identified during the Roma Period. Also, a significant increase was observed in the contribution of marine phytoplankton at AD 100–200, which may be related to the marine highstand reported by several authors during the early Roman Warm Period.

#### Selected publications

J.M. De la Rosa, M. Santos, M.F. Araújo (2011) Metal binding by Humic Acids extracted from recent sediments from the Southwest Atlantic coast of the Iberian Peninsula. Estuarine Coastal and Shelf Sciences, 93, 478-485.

J. M. De la Rosa, M. F. Araújo, J. A. González-Pérez, F. J. González-Vila, A. M. Soares a, J. M. Martins, E. Leorri, R. Corbett, F. Fatela (2011). Organic matter sources to tidal marsh sediment over th 1 e past two millennia in the Minho River estuary (NW Iberian Peninsula). Organic Geochemistry (in press)

 <sup>&</sup>lt;sup>1</sup> IRNAS, CSIC, Seville, Spain;
<sup>2</sup> Lab. de Processos Costeiros, Centro e Dep. Geologia da FCUL, Lisboa, Portugal
<sup>3</sup> Centro de Estudos Geográficos, IGOT, Univ. Lisboa

## **Secular variations on the sedimentary elemental composition in western Portuguese estuaries salt marshes** *M.F. Araújo, I Pereira, J.M. Rosa, F. Fatela'*

Elemental geochemistry and sedimentary analyses are being used as fundamental tools in the study of estuarine systems evolution. Several salt-marshes located in different estuaries along the W coast (Minho, Tagus and Mira rivers) were selected based on their protected settings, which allow higher accuracy in the assessment of specific temporal changes. 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 data of sediment cores collected in salt marshes from estuaries located along the W coastal region (Minho, Tagus and Mira) display the different characteristics on the Human occupation, lithology of each drainage basin and sea level. In general, variations on the elemental contents in the lithogenic/continental (e.g. Ti, Zr, K, Rb) are being related with stronger terrestrial sources (flood periods), whereas high Ca, Sr, Cl and Br are associated with a dominant marine contribution. Concerning the anthropogenic trace elements (e.g. Cu, Zn, As and Pb), enhanced values could be detected in the Minho and even more significant in Tagus, revealing the effects of Human occupation and industrialization levels. Mira sediment core presents in general, rather homogeneous elemental composition and no signs of anthropogenic influences, probably a consequence of a rather low human occupation along the times.

<sup>1</sup> Lab. de Processos Costeiros, Centro e Dep. de Geologia da FCUL, Lisboa, Portugal

**The oceanic radiocarbon reservoir effect in regions affected by the NW Africa coastal upwelling system** *A.M. Monge Soares, J.M. Matos Martins, P. Portela, A. Mederos Martín<sup>1</sup>, J.L. Cardoso<sup>2</sup>* 

The quantification of the oceanic (or marine) radiocarbon reservoir effect ( $\Delta R$ ) is essential not only to calibrate conventional radiocarbon dates from marine shell samples with reliability but also to provide information concerning the intensity of coastal upwelling in marine regions affected by this phenomenon. The NW Africa coastal upwelling system characterized by a complex and heterogeneous oceanographic pattern extends south to Cape Verde Islands in winter and north to the Iberian Peninsula in summer. The dominant oceanic current is the Canary Current, which marks the eastern boundary of the North Atlantic Ocean subtropical gyre. Research regarding that quantification issue has been done for the Atlantic Iberian coast, namely for the north-western and western Galician coast, Portuguese western coast and northern region of Gulf of Cadiz (the Barlavento and the Sotavento regions of Algarve and the Andalusian coast). The marine radiocarbon reservoir effect of two other regions – the Canary Archipelago and the Cape Verde Islands – has also been a matter of study in recent years. In this manner the variability in the  $\Delta R$  around the Canary Islands was determined.  $\Delta R$  takes a positive weighted mean value of  $+185\pm30$  <sup>14</sup>C yr for eastern islands (Fuerteventura and Lanzarote), while for central and western islands the acceptable  $\Delta R$  value is 0±35 <sup>14</sup>C yr. These values are in accordance with the hydrodynamic system off the Canary Islands characterized by a coastal upwelling regime that affects the eastern islands but not the remaining islands. Archaeological excavations at São Vicente Island, Cape Verde Archipelago permitted the first calculation of the marine radiocarbon reservoir effect for this region. A  $\Delta R$  weighted mean value of  $+70\pm70^{14}C$ yr was obtained. This value is in accordance with the previously published oceanographic conditions of the region indicating the existence of a seasonal active upwelling regime.

Dep. de Prehistoria y Arqueologia, Univ. Autónoma de Madrid, Campus de Cantoblanco, Madrid, Spain
<sup>2</sup> Univ. Aberta, Lisboa. Centro de Estudos Arqueológicos do Concelho de Oeiras (Câmara Municipal de Oeiras)

#### Isotope Hydrology and geochemistry

*P.M.* Carreira, D. Nunes, J.M. Marques<sup>1</sup>, M.R. Carvalho<sup>2</sup>, J. Espinha Marques<sup>3</sup>; A. Carvalho<sup>3</sup>; G. Capasso<sup>4</sup>, F. Grassa<sup>4</sup>, J.C. Nunes<sup>5</sup>

Isotope Hydrology studies aiming to contribute to a better understanding of the dynamic evolution response of groundwater systems to Human influences such as industrial development associated with the growing of

population and intensive agriculture activities. Groundwater resources have become progressively more endangered by accelerated modification of the natural conditions. Environmental isotopes represent an important tool for hydrological investigations, relevant for the management, protection and development of water resources. Under these objectives, work has been carried out in: i) Azores archipelago to characterize the chemical and isotopic composition of ground waters,



fumaroles and gas emissions related with hydrothermal/geothermal systems and volcanologic/seismic settings; ii) arid and semi arid zones (recharge areas and seawater intrusion); iii) high mountain areas and iv) gas geochemistry in CO2-rich thermomineral waters. These investigations are essential to the exploitation and future development of regional water resources and to the delimitation of protection areas.

<sup>&</sup>lt;sup>1</sup> Dep. de Engenharia de Minas e Georrecursos, I.S.T., Lisboa, Portugal; <sup>2</sup> Dep. de Geologia, Fac. Ciências da Univ. Lisboa, Lisboa, Portugal; <sup>3</sup> Fac. de Ciências, Univ. Porto, Portugal; <sup>4</sup> Ist. Nazionale di Geofísica e Vulcanologia, Palermo, Italy; <sup>5</sup> Dep. Geociências, Univ. Açores, Ponta Delgada, Portugal

#### Archaeometallurgy - Provenance, metal composition and manufacturing techniques

M.F. Araújo, P. Valério, E. Figueiredo, M.J. Furtado, F. Pereira, F. Lopes, S. Gomes, A.M.M. Soares, R.J.C. Silva<sup>1</sup>

The study of ancient metallurgy has provided important information on past technologies and cultural spheres of interaction. Main studies involve elemental analysis and microstructural

characterization made on metallic artefacts and production remains from Chalcolithic till Early Iron Age, recovered from diverse sites and regions of the Portuguese territory. In the Southern Portuguese territory, a study of circa 50 artefacts from Torre Velha 3 identified an early introduction of bronze in this region, dated to the second quarter/beginning of the third quarter of the 2<sup>nd</sup> millennium BC. Also, various studies on artefacts from Late Bronze Age and Early Iron Age sites (e.g. Entre Águas 5, Outeiro do Circo, Martes, Mangancha and Cabeço Redondo) have provided detailed information on metallurgical processes and metals. Discoveries of a Late Bronze Age metallurgical workshop with indications on bronze production by co-smelting of copper ore and cassiterite and the identification of an exceptional bronze nail with a gilded head by the attachment of a thin gold foil, both in Entre Águas 5 are worth to mention. In the Central Portuguese territory, detailed analysis



on 53 artefacts from Vila Nova de São Pedro has highly improved the knowledge on Chalcolithic metallurgy. In this site, both copper and arsenical coppers have been identified for the manufacture of various types of artefacts. From the Northern Portuguese territory, analysis on various metallic artefacts and some metallurgical remains from the second quarter/beginning of the third quarter of the 2<sup>nd</sup> millennium BC and Late Bronze Age found at Fraga dos Corvos site have been made. Analyses have shown evidences of a bronze metallurgy with higher Pb contents than contemporaneous bronzes from Central and Southern territories. Also, 10 axes of Bujões/Barcelos from Central and Northern territories were characterized. So far, the analyses show that this type of axe, which is assumed to be linked with the production of the first bronzes, are manufactured in bronze alloy with rather uniform tin contents and a low impurity pattern. Finally, the first approach on metal provenance through the determination of Pb isotopes was initiated, with the analysis by ICP-MS of some artefacts from Fraga dos Corvos.

Finally, a study of the Chinese cash coins of the CCCM collection was finished permitting the establishment of the evolution on the composition and technological production features of the Cu-based coins during a large time period (300 a.C. - 1854 d.C.). Also, the presence of particular metallic phases confering variable corrosion resistance to the artefacts were identified and associated to the abundance and distribution of specific elements.

<sup>&</sup>lt;sup>1</sup> CENIMAT/I3N, Dep.Ciência dos Materiais, Fac.Ciências e Tecnologia, FCT, Univ. Nova de Lisboa, 2829-516 Caparica, Portugal

## Inorganic and Organometallic Chemistry

#### Joaquim Marçalo

The activities of the Group encompass the synthesis, characterization and reactivity studies of inorganic, organometallic and intermetallic compounds of the actinides and lanthanides. The main objectives of the work are to understand the role of the electronic structure and the size of the f-elements in the properties of their compounds, and to find new applications for these elements. Chemical properties are evaluated by stoichiometric reactions and by homogeneous and heterogeneous catalytic studies. Gas-phase ion chemistry studies, using advanced MS techniques, are undertaken with the same goal. Energetics is also examined using calorimetry, thermal analysis and MS.

Relevant facilities maintained by the Group are a laboratory for catalytic studies, a laboratory for handling the more radioactive actinides, a laboratory for calorimetric studies and thermal analysis, and two select mass spectrometers, a FTICR instrument with EI and LDI sources and a QIT with ESI, n-ESI and APCI sources. The QIT is part of the National Mass Spectrometry Network (RNEM).

Gas-phase chemistry/mass spectrometry studies expanded in 2011. ESI-QIT/MS was used to investigate several aspects of the coordination chemistry of lanthanides and actinides, and a few fundamental gas-phase properties of these elements, including size, effective charge and oxidation state stability. New thorium species, namely, polysulfide ions and cluster carbide ions were synthesized and characterized by LDI-FTICR/MS.

The investigation of the organometallic chemistry of the actinides continued. New Th(IV) and U(IV) complexes with  $[salan-R_2]^{2^-}$  (R = Me, <sup>t</sup>Bu) ligands, notably, the alkyl derivatives  $[An\{salan-$ <sup>t</sup>Bu<sub>2</sub> $\}_2(CH_2SiMe_3)_2]$ , were prepared and characterized. Studies on the chemistry of U(III) anchored on the  $\{tacn-Me_2SiN(Na)Ph\}$  ligand were restarted and the reactivity with redox-active substrates explored. Collaboration with the Solid State Group was initiated to study the magnetic properties of uranium complexes. In a collaboration with CICECO, U. Aveiro, several new materials were synthesized, namely, uranyl and uranyl-Eu MOFs with phosphonate ligands, and layered lanthanide hydroxides (LLHs) of Eu and Tb 2,6-naphthalene-dicarboxylate with intercalated anions, and their luminescence properties are under study. The magnetic properties of a Dy LLH and its intercalation product with 2,6-naphthalenedicarboxylate anions were evaluated, in а collaboration with the Solid State Group.

The study of important environmental issues such as the activation and valorisation of  $CH_4$  and  $CO_2$  as valuable C1 feedstocks continued. For the first time, the conversion of  $CH_4$  using N<sub>2</sub>O as oxidant either for the production of syngas or C2 hydrocarbons over fblock elements based catalysts, namely, over KCl-LnCl<sub>3</sub> (Ln = La, Ce, Sm, Dy, Yb) eutectic molten salts, was studied and published. A new work plan was started that comprises the synthesis of binary intermetallic compounds nanoparticles, containing, in particular, f-block elements, and the study of their catalytic behavior for the elimination of primary gaseous pollutants such as  $CO_2$  and N<sub>2</sub>O.

The study of the energetics of organic, inorganic and organometallic molecules was pursued. The Therminfo database (www.therminfo.com) underwent an upgrade of its structure and soon is expected to include some 20 000 new entries. The experimental study of alkaline, alkaline-earth, silicon and lanthanide polyalkoxides continued as well as the study of some of their properties.

Collaborations continued with other research groups within and outside ITN in different areas. Of note is the continued collaboration with OMNIDEA (AeroSpace Technology and Energy Systems) Lda..

A significant part of the activity of the Group was the training of research students. Some of the Group members were involved in undergraduate and post-graduate university teaching. The financial support for the work was mostly from FCT, via research projects and Ph.D. and Post-Doc grants..

## Research Team

Researchers J. MARÇALO, Princ., Group Leader C.C.L. PEREIRA, Aux., Contract J.B. BRANCO, Aux. J.M. CARRETAS, Aux. J.P. LEAL, Aux. L. MARIA, Aux., Contract T. ALMEIDA GASCHE, Aux. B. MONTEIRO, Post-Doc, FCT Grant

#### **Technical Personnel**

A. CRUZ A.J. SOARES V. SOUSA, FCT grant

#### Students

A.C. FERREIRA, Ph.D. student, FCT grant A.F. LUCENA, Ph.D. student, FCT grant J.M. VITORINO, Ph.D. student, FCT grant (FCUL) M.M. VARELA, Ph.D. student (FCUL) S.C. LEAL, Ph.D. student, FCT grant (FCUL)

C. LOURENÇO, Research student E. MORA, Research student P.G. ROSADO, Research student

Collaborators

A. PIRES DE MATOS, Coord. (Retired) N. MARQUES, Princ. (Retired)

## Mass Spectrometry Studies of the Coordination Chemistry of Lanthanides and Actinides

J. Marçalo, J. M. Carretas, A. F. Lucena, C. Lourenço, B. Monteiro, L. Maria, I. Paiva, J. K. Gibson<sup>1</sup>, M. C. Michelini<sup>2</sup>, L. Berthon<sup>3</sup>

#### Objectives

The coordination chemistry of the lanthanides (Ln) and actinides (An) is a topic of current interest as related to Ln/An separations within advanced nuclear fuel cycles. We intend to explore the differences and similarities in the chemistry of trivalent Ln and An at a fundamental level, contributing to the clarification of An(III)/Ln(III) selectivity in Ln/An separations. We also expect to widen the knowledge of the physical and chemical properties of elementary actinide species which is essential to enhance the fundamental understanding of these elements

#### Introduction

Electrospray ionization quadrupole ion trap mass spectrometry (ESI-QIT/MS) is used to investigate several aspects of the coordination chemistry of lanthanides and actinides. These studies range from the characterization of new f-element complexes to the examination of fundamental gas-phase properties of lanthanides and actinides [1]. The experimental



studies are accompanied by theoretical calculations of selected systems.

#### Results

(1) The complexation of the new neutral ligands bisand tris[3-(2-pyridyl)pyrazolyl]methane to Ln(III) and Am(III) nitrates and chlorides was probed. MS spectra showed that displacement of the anions did not occur for nitrate, as only  $[M(NO_3)_2L]^+$  ions were formed, while for chloride formation of  $[MCIL]^{2+}$  ions could be observed. Collision induced dissociation (CID) in the QIT indicated a tetradentate coordination mode for both ligands.

(2) The relative affinity of N- and O-donor bases to Ln(III) and Am(III) ions in the gas phase and in solution was assessed. Competitive CID experiments in the QIT, involving  $[M(NO_3)_2(L^1)(L^2)]^+$  ions, where L were mono- and bidentate heterocyclic N-donor bases or monodentate O-donor bases, revealed the relative gas-phase affinities of the bases and the relevant gas-phase factors behind the observations. Comparison of the relative intensities of

 $[M(NO_3)_2(L^1)_2]^+$  and  $[M(NO_3)_2(L^2)_2]^+$  ions in MS spectra indicated different relative affinities of L that may result from a combination of solution and gasphase properties of the L bases.

(3) The size/effective charge of Ln(III) and An(III) ions in the gas phase was evaluated. Solutions with pairs of Ln(III), Y(III), Pu(III) and Am(III) nitrates or chlorides readily yielded, in the negative ion mode,  $[M^1M^2X_7]^-$  species. CID experiments in the QIT resulted in the preferential formation of  $[MX_4]^-$  for the smaller, more charge dense metal ions. Intriguingly, in the gas phase, Y(III) appears to be closer to Gd(III) than to Ho(III) in terms of ionic size/effective charge, while both Pu(III) and Am(III) seem to be closer to their Ln(III) congeners.

(4) CID experiments in the QIT involving  $[(UO_2)MX_n]^-$  ions, where M = alkaline-earth metal (n = 5) or lanthanide (n = 6), and X = nitrate or chloride, allowed to examine the effective charge of U in the uranyl ion  $(UO_2^{2^+})$  in the gas-phase. Preferential formation of  $[(UO_2)X_3]^-$  for the cases of the alkaline-earth metals and the larger Ln was observed. These results indicate that, in the gas phase, the uranyl ion is more similar to a trivalent metal ion than to a divalent, in agreement with solution chemistry studies and theoretical calculations.

(5) The relative stability of the III/IV oxidation states of Ln and An ions in the gas phase was investigated. CID of  $[M(NO_3)_x]^-$  ions in the QIT, where M = Sc, Y, Ln, produced  $[M(O)(NO_3)_3]^-$  for M = Ce, Pr, Nd and Tb (Ln with more accessible oxidation state IV), while  $[M(OH)(NO_3)_3]^-$  ions dominated for most of the remaining metals; the much smaller Sc yielded both fragment ions. In the cases of Pu, Am and Cm, all having an accessible oxidation state IV, only  $[M(O)(NO_3)_3]^-$  ions were observed. Gas-phase reactions with the background water present in the QIT [2] were examined in detail to unravel the diverse behavior of the f-element ions and the formation of  $[M(OH)(NO_3)_3]^-$  by hydrolysis of  $[M(O)(NO_3)_3]^-$ .

#### **Published work**

J. Marçalo, A.F. Lucena, C. Lourenço, B. Monteiro, L. Maria, J.M. Carretas, P. X Rutkowski, J.K. Gibson, Mass Spectrometry of Rare Earths—From Compound Characterization to Fundamental Gas-Phase Properties, *XXIV. Terrae Rarae 2011*, Karlsruhe, Germany, October 2011.

P. X Rutkowski, M.C. Michelini, T.H. Bray, N. Russo, J. Marçalo, J.K. Gibson, Hydration of Gas-Phase Ytterbium Ion Complexes Studied by Experiment and Theory, *Theor. Chem. Acc.* 129 (2011) 575-592.

<sup>&</sup>lt;sup>1</sup> Lawrence Berkeley National Lab. (Berkeley, CA, USA). <sup>2</sup> U. Calabria (Arcavacata di Rende, Italy).

<sup>&</sup>lt;sup>3</sup> CEA-Atalante (Marcoule, France).

#### Gas-Phase Chemistry and Thermochemistry of Elementary Actinide Molecules

J. Marçalo, C. C. L. Pereira, A. F. Lucena, A. Pires de Matos, A. P. Gonçalves, J. K. Gibson<sup>1</sup>, L. Andrews<sup>2</sup>

Gas-phase chemistry studies, using advanced mass-spectrometry techniques (LDI-FTICR/MS and ESI-QIT/MS), are conducted to search for new elementary actinide species and reactions, and investigate their chemical and thermochemical properties.

We used FTICR/MS to study the reactions of  $An^{2+}$  ions (An = Th, Np, Pu, Am, Cm) with COS; in the case of Th<sup>2+</sup>, the sequential formation of ThS<sub>n</sub><sup>2+</sup> ions, with n = 1-4, was observed. Theoretical studies performed by C. J. Marsden (Univ. Paul Sabatier, Toulouse, France) indicated that the Th polysulfides, as the previously studied U analogues, are mostly of the metallacycle type.

A  $ThC_4$  compound, obtained by high-temperature synthesis, was investigated by LDI-FTICR/MS and formation of  $Th_mC_n^{\ +}$  cluster ions,



for m = 1-6, was observed. ThC<sub>4</sub> was also studied by matrix-isolation spectroscopy at the U. Virginia but no neutral ThC<sub>x</sub> species could be identified.

<sup>1</sup> Lawrence Berkeley National Lab. (Berkeley, CA, USA). <sup>2</sup> U. Virginia (Chalottesville, VA, USA).

#### f-Element Chemistry with Multidentate Nitrogen and Oxygen Donor Ligands

L. Maria, M. A. Antunes, B. Monteiro, E. Mora, A. Cruz, J. Marçalo, J. M. Carretas, N. Marques, I. C. Santos, L. C. Pereira<sup>1</sup>, M. Almeida, M. Mazzanti<sup>1</sup>

The main goal of this research is to develop new coordination environments for the f-elements, with the purpose of creating new reactive centres with unusual reactivity patterns, providing the opportunity to study fundamental organometallic chemistry and also to synthesize new compounds with potential interest in organic synthesis and



catalysis. In this context, the study of the coordination chemistry of the diamino bis(phenolate) ligands  $[salan-R_2]^{2-}$  (H<sub>2</sub>salan-R<sub>2</sub> = N,N'-bis(2-hydroxybenzyl-3,5-di-R)-1,2-dimethylamino-methane; R = Me (L<sub>1</sub>), <sup>t</sup>Bu (L<sub>2</sub>)) toward the actinides Th and U was continued. This family of ligands allowed the stabilization of mono and bis-substituted complexes of the type [An{salan-R<sub>2</sub>}Cl<sub>2</sub>Y] (An = Th, U; Y = dme, bipy) and [An{salan-R<sub>2</sub>}2]. Reactivity studies of [An{salan-<sup>t</sup>Bu<sub>2</sub>}2Cl<sub>2</sub>Y] were performed, showing that this system is able to stabilize the monomeric alkyl complexes [An{salan-<sup>t</sup>Bu<sub>2</sub>}2(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>2</sub>] for both Th and U (Fig. 1). The formulation of the actinide complexes was based in NMR

experiments, ESI-QIT/MS and X-ray diffraction analysis. Studies on the coordination chemistry of U(III) anchored on a functionalised triazacyclononane (tacn) ligand, {tacn-Me<sub>2</sub>SiN(Na)Ph}, were restarted. Some years ago we found out that the U(III) complex [U{tacn-Me<sub>2</sub>SiN(Na)Ph} (1), which displays a trigonal prismatic coordination sphere with a free axial coordination position, was a good platform to access higher oxidation states. Thus, we started to explore the electron transfer reactions of 1 with redox-active substrates such as organic azides and azobenzene.

Aiming at the study of the magnetic properties of uranium complexes, particularly in terms of single-moleculemagnet behavior, we have initiated a project in collaboration with the Solid State Group of UCQR. In this context, the cationic U(III) compound  $[U(Tp^{Me2})_2(bipy)]I$  was prepared and structurally characterized.

<sup>1</sup> INAC, CEA-Grenoble (France).

#### f-Element-Based Luminescent and Magnetic Materials

C. C. L. Pereira, B. Monteiro, J. Marçalo, L. C. Pereira, M. Almeida, D. Ananias<sup>1</sup>, F. A. A. Paz<sup>1</sup>

In a collaboration with CICECO of U. Aveiro, several materials were synthesized with the aim of studying their photophysical and photochemical properties. Metal-Organic Frameworks (MOFs) based on uranyl and uranyl-europium with phosphonate ligands, and layered lanthanide hydroxides (LLHs) of general formula

 $Ln_8(OH)_{20}Cl_4 \circ nH_2O$  (Ln = Eu, Tb), with 2,6naphthalene-dicarboxylate anions intercalated inside the gallery are presently being evaluated as luminescent materials (Figure 1).

The magnetic properties of a dysprosium LLH and its intercalation product with 2,6-naphthalenedicarboxylate anions were also evaluated, in a collaboration with the Solid State group of UCQR-ITN.

*f-Block Elements as Catalysts for the Elimination of Primary Gaseous Pollutants (CO<sub>2</sub>, N<sub>2</sub>O and CH<sub>4</sub>)* J. B. Branco, A. C. Ferreira, T. Almeida Gasche, A. Rego<sup>1</sup>, A. Ferraria<sup>1</sup>, A. P. Gonçalves

We continue to study important environmental issues such as the activation and valorisation of methane and carbon dioxide as valuable C1 feedstocks, namely through the catalytic partial oxidation of CH<sub>4</sub> (POM reaction) using O<sub>2</sub> or N<sub>2</sub>O as oxidant. The study of the partial oxidation of methane (POM) over KCI-LnCl<sub>3</sub> (Ln=La, Ce, Sm, Dy, Yb) eutectic molten salts was undertaken. The main reaction products were hydrocarbons (> 70%, except for K-Ce).

The catalytic performance is clearly dependent on the rare earth ions properties and the factors that seem to contribute to the variation of the activity and selectivity along the lanthanide series are the mobility and the oxidative character of the rare earth trivalent ions in the



potassium chloride melt. The activity increases with the molten salts eutetic melting temperatures and the selectivity to hydrocarbons decreases with the oxidative character of rare earth ions. To our knowledge, this is the first time that POM was studied over chloride based rare earth molten salts.

<sup>1</sup>Technical Univ. of Lisbon/IST, IN and Centre for Molecular Physical Chemistry.

#### **Binary Intermetallic Compounds Nanoparticles: Synthesis and Catalytic Behavior** J. B. Branco, A. C. Ferreira, T. Almeida Gasche, J. P. Leal, A. Rego<sup>1</sup>, A. Ferraria<sup>1</sup>

A new work plan that comprises the synthesis of binary intermetallic compounds (IC) nanoparticles containing,



in particular, f-block elements and the study of their catalytic behavior for the elimination of primary gaseous pollutants such as carbon dioxide and nitrous oxide was started in 2011. This approach will enable the synthesis of nanoparticles at temperatures significantly lower than those used by traditional high temperature solid state chemistry and, predictably, with different chemical and physical properties. Moreover, the combination of the unique properties of the f elements with the ability to control the shape and size of the nanoparticles will bring benefits to the expected catalytic properties of these materials. Several approaches were already tried, such as the polyol and bioreduction methods. Nanoparticles of Cu, La, LaNi, LaCu<sub>2</sub>, SmCo<sub>5</sub> and DyFe<sub>3</sub> were obtained. XRD, SEM

and TEM measurements were performed to characterize the ICs.

<sup>1</sup>Technical Univ. of Lisbon/IST, IN and Centre for Molecular Physical Chemistry.

#### **Conversion of Methane by Non-Thermal Plasma**

N. R. Pinhão, A. Janeco, J. B. Branco

The conversion of methane by a non-thermal plasma produced by DBD (dielectric barrier discharge) was studied using mixtures of  $CH_4/O_2$  and  $CH_4/CO_2$  with a rare gas (helium or argon). The main products obtained were  $H_2$ , CO,  $C_2H_6$  and  $C_3H_8$  but traces of other hydrocarbons, carbon deposition and the formation of condensable products (e.g. ethanol) were also detected. The dependence of the conversion, selectivities and abilities on the rare

nature and concentration, gas specific input energy (S), type of electric excitation plasma power (sinusoidal pulsed or supplies) and synergies with both commercial and home-made catalysts was studied. It was found that helium has a significant influence on the discharge, decreasing the breakdown voltage increasing the rate and of conversion of CH<sub>4</sub> and CO<sub>2</sub>.



#### Molecular Energetics of Organic, Inorganic and Organometallic Compounds

J. P. Leal, T. Almeida Gasche, P. G. Rosado, J. M. Vitorino<sup>1</sup>, M. E. Minas da Piedade<sup>1</sup>, J. A. Martinho Simões<sup>1</sup>, R. Borges Santos<sup>1</sup>, R. Melo, L. Botelho, A. Teixeira<sup>2</sup>, A. Falcão<sup>2</sup>

The main objective of this research is to collect energetics data, rationalize it in a systematic way and explore connections between energetics and structure of molecules (both inorganic and organic compounds). Special

importance was given to f-element compounds (both in solid state and in solution). To achieve this goal, lanthanide and actinide (organometallic and intermetallic), alkaline and alkaline-earth compounds, hydrocarbons and ionic liquids were studied.

During 2011, an extended revision of Therminfo database (<u>www.therminfo.com</u>) was undertaken. The main goal is to make the database structure more flexible and also enlarge its size (from the previous 3000 compounds to around 25000). The nature of ionic liquids in the gas phase continued to be studied by using FTICR/MS. The study of metallic polyalkoxides continued and in



addition to alkaline and alkaline-earth metals, lanthanide and mixed (lanthanide and silicon) polyalkoxides where synthesised, characterized and studied. The degradation/decomposition mechanism of acetovanillone and sculetine were studied by using pulse-radiolysis and mass spectrometry (ESI-QIT/MS).

<sup>1</sup>Centro de Química e Bioquímica, FCUL. <sup>2</sup> Large-Scale Informatics Systems Lab., FCUL.

#### **Gas-Phase Studies of d-Transition Metal Species**

M. C. Oliveira<sup>1</sup>, J. Marçalo, C. Lourenço<sup>1</sup>, M. Santos, J. K. Gibson<sup>2</sup>, M. C. Michelini<sup>3</sup>



We have been examining the gas-phase chemistry and thermochemistry of transition metal oxide ions by FTICR/MS, to provide fundamental chemical models to complex multi-charged systems and obtain new thermodynamic data for ionic and neutral species containing these elements.

The study of gas-phase oxidation reactions of Ta<sup>2+</sup> was completed and the properties of TaO<sup>2+</sup> and TaO<sub>2</sub><sup>2+</sup> were inspected by experiment and theory. Formally "hypervalent" TaO<sub>2</sub><sup>2+</sup> was shown to be a dioxide, {O-Ta-O}<sup>2+</sup>, based on density functional theory (DFT) results. It was found that TaO<sub>2</sub><sup>2+</sup> oxidizes CO to CO<sub>2</sub> and that it acts as a catalyst in the oxidation of CO by N<sub>2</sub>O; TaO<sub>2</sub><sup>2+</sup> also activates H<sub>2</sub> to form TaO<sub>2</sub>H<sup>2+</sup>. The study of gas-phase oxidation reactions of Hf<sup>2+</sup> was initiated and the formation of HfO<sup>2+</sup> and HfO<sub>2</sub><sup>2+</sup> were observed. DFT computations showed that "hypervalent" HfO<sub>2</sub><sup>2+</sup>, unlike TaO<sub>2</sub><sup>2+</sup>, is a peroxide.

<sup>1</sup> Centro de Química Estrutural, IST.<sup>2</sup> Lawrence Berkeley National Lab. (Berkeley, CA, USA). <sup>3</sup> U. Calabria (Arcavacata di Rende, Italy).

### Gamma Irradiated Membrane Systems for Bioapplications

L. M. Ferreira, M. H. Casimiro<sup>1</sup>, J. P. Leal

Membranes using polyethylene as backbone polymer and HEMA as grafting molecule, produced through irradiation on a <sup>60</sup>Co source, were synthesized and the corresponding properties extensively studied. The

prepared films were characterized through nuclear microprobe techniques. Qualitative analysis showed a random and non homogeneous distribution of contaminant elements, independent of the grafting degree, suggesting the existence of several sources of contamination at different stages of their preparation.



Results also suggest that this "phased" contamination occurs simultaneously with mechanisms of agglomeration/entrapment of impurities during the gamma induced copolymerization reaction. Moreover, quantitative data showed that all contaminants found in the copolymeric films are natural contaminants of their reagents of preparation, although at concentrations without toxicological hazard, which points to a low cytotoxic potential of the films.



#### **Glass Science with Applications in Art Studies**

A. Pires de Matos<sup>1</sup>, C. Queiroz<sup>2</sup>, A. Ruivo<sup>2,3</sup>, F. Lopes, R. C. Silva

In 2011 A. Pires de Matos continued as Senior Researcher in the Research Unit VICARTE - "Glass and Ceramics for the Arts", and work was developed by members of ITN, VICARTE - FCT/UNL and REQUIMTE - FCT/UNL in the development of new materials for artistic

applications and in archaeology of Marinha Grande glasses.

Studies on thin layer deposition on glass continued using the spray pyrolysis technique. The first experiments with copper acetate in methanol and water gave origin to a thin layer deposition of copper oxide which after heating at about 600°C gave origin to nanoparticles of copper. They were analysed by X-ray fluorescence and by Rutherford Backscattering. The deposition on the tin side of the float glass and on the other side were studied.

The studies of Marinha Grande glasses continued and a special attention was given to the 18th century arcana of Guilherme



Stephens. The study of the four arcanes available was completed. The recipes used for coloured glass were discussed while interpreting the chemical nomenclature used.

<sup>1</sup> IOC Group/UCQR-ITN & VICARTE, FCT-UNL. <sup>2</sup> VICARTE, FCT-UNL. <sup>3</sup> REQUIMTE, FCT/UNL.

## **Radiopharmaceutical Sciences**

Isabel Rego Santos

The *Radiopharmaceutical Sciences Group* (RSG) developed and implemented expertise and facilities to carry on basic/applied oriented research and technology transfer *on specific halogen and metal-based nuclear tools for SPECT and PET molecular imaging and targeted radiotherapy*. The group is multidisciplinary with knowledge on synthetic chemistry, bioconjugation, radiochemistry, animal and cell studies, and molecular biology. Such background enables the RSG to deal with problems of modern Radiopharmaceutical Sciences, to provide education and training at different levels and to act as key partner in several research projects.

The main achievements during 2011 were:

#### **Financial Support:**

In collaboration with other Institutions, five new projects were funded by FCT: three coordinated by RSG /ITN and two by FFUL and FCUL.

#### **Research:**

For targeted-specific imaging and/or therapy, we pursued the design of molecular or nanoparticlesbased multifunctional radio-platforms to target biomarkers related with cancer and neurodegenerative diseases. The radiolabeled targeting agents included peptides, antibody fragments or small molecules.

**1** – For SLND, the first specific nanocompound labeled with  $fac-[^{99m}Tc(CO)_3]^+$  was isolated. As a result of the superior *in vitro* and *in vivo* pre-clinical data, human evaluation is underway, coordinated by IAEA.

**2-** From the designed peptide-based complexes, an excellent *in vivo* targeting of MC1R, for melanoma detection, was achieved using a cyclic melanocortin analog.

**3** - In close cooperation with the University of Porto and Institute Rocasolano/Madrid, Molecular Modelling and NMR studies have been performed. A clear understanding of the effect of the metal–core on the targeting vector was accomplished. 5 - Within the framework of running projects, between RSG and different Health-related Research Centres, we continued our efforts to design novel bone- and amyloid aggregates-targeting compounds.

#### **Education and Training**

#### **1-Graduation**:

Radiopharmacy teaching at ESTeSL and at Faculty of Pharmacy/University of Lisbon.

#### 2-Post-graduation:

a) Coordination of the Master Course Biomedical Inorganic Chemistry: Diagnostic and Therapeutical Applications (ITN/UL). Coordination and teaching of Radiochemistry and Biomedical Inorganic Chemistry in the same M.Sc. course.

*b)* Coordination and teaching of Radiopharmaceutical Chemistry in the Master Course Pharmaceutical and Therapeutical Chemistry/FFUL.

c) Teaching of Chemical Systems and Reactivity in the  $2^{nd}$  Cycle of Chemistry, FCUL.

d) Teaching at the Master in Pharmaceutical Sciences, Lusófona University.

e) Teaching at the Master in Human Molecular Biology, Faculty of Sciences/UL

e) Teaching at the Master Course in Nuclear Medicine, ESTeSL.

#### High School/Universities Visits: 14

#### **Expertise Provided:**

Nuclear Medicine Centers, INFARMED, IAEA, Science Foundations (Portuguese, Canadian, USA, South Africa, Argentina, Uruguay and Chile), International Conferences and International Journals.

#### **Publications:**

International Journals–17; Proceedings–1; Communications–20; Invited Lectures and Seminars: 5.; Ph.D. thesis: 3; BSc thesis: 2; Reports – 2.

#### Research Team Researchers

I. SANTOS, Princ., (Agreg.), Group Leader A. PAULO, Princ. J.D.G. CORREIA, Princ. C.FERNANDES, Aux. F. MARQUES, Aux. F. MENDES, Aux. contract G. MORAIS, Aux. contract L.GANO, Aux. M.C. OLIVEIRA, Aux. M.P.C. CAMPELLO, Aux. P. RAPOSINHO, Aux.

#### Students

M. CORREIA, Post-Doc, FCT grant PSANIUNES, Post-Doc, FCT grant (until July) S. GAMA, Post-Doc, FCT grant B. OLIVEIRA, Ph.D. student, FCT grant C. MOURA, Ph.D. student, FCT grant E. PALMA, Ph.D. student, FCT grant F. SILVA, Ph.D. student, FCT grant M. MORAIS, Ph.D. student, FCT grant S. CUNHA, Ph.D. student, FCT grant T. ESTEVES, Ph.D. student, FCT grant F. TOSCANO, M.Sc. student I. RODRIGUES, M.Sc. student

L. CORTE-REAL, M.Sc. student P. MENDES, M.Sc. student

F. VULTOS,

S. MONTEIRO,

J. CASTRO, Undergraduate student

R. GOMES, Undergraduate student S. BARROS, Undergraduate student

S. BRITES, Undergraduate student

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#### **Technical Personnel**

A.RODRIGUES E. CORREIA

## Multifunctional Re(I)/<sup>99m</sup>Tc(I) Tricarbonyl Complexes for Cell-Specific Nuclear Targeting

Teresa Esteves, Fernanda Marques, António Paulo, José Rino<sup>1</sup>, Prasant Nanda<sup>2</sup>, C. Jeffrey Smith<sup>2</sup>, Isabel Santos

#### Objectives

The demand for more selective therapeutic approaches makes Auger emitters, such as  $^{99m}$ Tc, an important resource in radionuclide therapy. In this field, we are studying new multifunctional  $^{99m}$ Tc(I)–based frameworks for receptor-specific nuclear targeting.

#### Results

The multifunctional structures designed comprise: i) a pyrazolyl - diamine chelator to stabilize the metal fragment ii) a DNA intercalating moiety to ensure a close proximity of the radionuclide to DNA iii) a bombesin (BBN) analogue to provide specificity towards cells expressing the gastrin releasing peptide receptor (GRPr) (Fig. 1).



Fig.1. Trifunctional tricabonyl metal complexes

The new trifunctional Re and <sup>99m</sup>Tc tricarbonyl complexes were prepared, characterized and studied with GRPr-positive PC3 human prostate tumor cells. Taking advantage of the fluorescence properties of the intercalator, the live-cell uptake of the Re-BBN conjugates was evaluated by time-lapse confocal microscopy imaging, and quantified using the <sup>99m</sup>Tc-congeners. From the evaluated complexes the ones containing an intercalator of the acridine orange type and the BBN analogue GGG-BBN[7-14] (Fig. 2) have shown the highest cellular internalization and a remarkably high nuclear uptake.



Fig. 2. Chemical structure of a tricarbonyl complex bearing GGG-BBN[7-14] and acridine orange.

Figure 3 shows the significant nuclear uptake of the cell-specific Re complex shown in Figure 2, which has been quantified as 10% using the  $^{99m}$ Tc congener.



Fig.3. Live-cell uptake of the Re complex, visualized by time-lapse confocal microscopy imaging. Images acquired at 5, 15, 30 and 60 min after incubation with PC3 cells (single cell fluorescence distribution)

Altogether, our data show that the AO intercalator and the metal fragment are co-localized in the nucleus, indicating that they remain connected despite the eventual lysosomal degradation of the metallated peptides.

These complexes are the first examples of <sup>99m</sup>Tc bioconjugates that combine specific cell targeting with nuclear internalization, a crucial issue in the potential usefulness of <sup>99m</sup>Tc in Auger therapy.

#### **Published work:**

T. Esteves, C. Xavier, S. Gama, F. Mendes, P. D. Raposinho, F. Marques, A. Paulo, J. C. Pessoa, J. Rino, G. Viola and I. Santos, Tricarbonyl M(I) (M = Re, <sup>99m</sup>Tc) complexes bearing acridine fluorophores: synthesis, characterization, DNA interaction studies and nuclear targeting, *Org. Biomol. Chem.*, 2010, **8**, 4104–4116.

T. Esteves, F. Marques, A. Paulo, J. Rino, P. Nanda, C. J. Smith, I. Santos, Nuclear targeting with cell-specific multifunctional tricarbonyl M(I) (M is Re, 99mTc) omplexes: synthesis, characterization, and cell studies, *J. Biol Inorg Chem*, 2011, **16**, 1141-1153.

T. Esteves, Complexos de Elementos Emissores de Radiação  $\gamma$  e de Electrões Auger para Diagnóstico e/ou Terapia do Cancro, Tese de Doutoramento, Faculdade de Ciências, Universidade Lisboa, 2011.

<sup>&</sup>lt;sup>1</sup> IMM, Fac. de Medicina da Univ. de Lisboa, Av. Prof. Egas Moniz, 1649-028 Lisboa, Portugal.

<sup>&</sup>lt;sup>2</sup> Univ. of Missouri, School of Medicine, USA

### MC1R-Targeting Properties of <sup>99m</sup>Tc(I)-Labeled Cyclic α-MSH analogs

M. Morais, P. D. Raposinho, M. C. Oliveira, I. Santos, M. A. Jiménez,<sup>1</sup> D. Pantoja-Uceda,<sup>1</sup> J. D. G. Correia



Aimed at the *in vivo* targeting of the Melanocortin 1 Receptor (MC1R) for melanoma imaging, we have synthesized novel cyclic  $\alpha$ -MSH analogs containing a thioether or amine bridge within the main ring, as well as their respective metallated (<sup>99m</sup>Tc/Re) derivatives **1/1a** and **2/2a**. The receptor binding affinity of the peptide conjugates was not significantly affected by metallation with the organometallic core *fac*-[Re(CO)<sub>3</sub>]<sup>+</sup>. The cellular uptake of **1** and **2** are comparable to those previously described for other <sup>99m</sup>Tc(CO)<sub>3</sub>-labeled  $\alpha$ -MSH analogues.

These encouraging results prompted us to evaluate the *in vivo* MC1R-targeting properties of 1 and 2 in a B16F1 melanoma-bearing mouse model. Additionally, the conformational preferences of the cyclic peptides in solution were also investigated by nuclear magnetic resonance spectroscopy.

<sup>1</sup> Inst. Química-Física Rocasolano, Consejo Superior de Investigaciones Científicas, Serrano 119, 28006 Madrid, Spain.

#### Radiolabelled neuropeptide Y analogues for Y1 receptor-targeting in breast cancer

P. Antunes, P. Raposinho, C. Fernandes, I. Rodrigues, I. Santos



The use of radiolabeled analogs of the Neuropeptide Y (NPY) has recently emerged as a promising approach for *in-vivo* targeting of the highly expressed Y1 receptors in breast cancer. Based on the smallest and

selective Y1R agonist [Pro<sup>30</sup>, Nle<sup>31</sup>, Bpa<sup>32</sup>, Leu<sup>34</sup>]NPY(28-36) (NPY1), several short NPY1 derivatives conjugated to DOTA or to a pyrazolylbased bifunctional chelator (pzNN) were labeled with <sup>67</sup>Ga and <sup>99m</sup>Tc, respectively. The corresponding cold Ga/Re



congeners were also synthesized and characterized. The *in vivo* stability, as well as the pharmacokinetic profile of these radiopeptides was determined in healthy mice. Cellular uptake studies, using MCF-7 human breast cancer cells expressing Y1R, were also performed. Among <sup>99m</sup>Tc-labeled complexes, the most promising one, <sup>99m</sup>Tc-pzNN-GluNPY1,

were also performed. Among <sup>39III</sup>Tc-labeled complexes, the most promising one, <sup>39III</sup>Tc-pzNN-GluNPY1, presented good cellular uptake (7.6  $\pm$  0.2 % at 1h p.i.) that was inhibited (46%) by Y1R-saturation with the endogenous NPY, indicating a receptor-mediated cellular uptake.

#### Albumin binding-domain fusions to improve protein pharmacokinetics

J. D. G. Correia, M. Morais, L. Gano, I. Santos, C. S. C. Cantante<sup>1</sup> J. M. B. Gonçalves<sup>1</sup>

The main goal of this research project is to assess whether the fusion of an albumin-binding domain of protein H of Streptococcus pyogenes to a Small Domain Antibody (SDA) anti-TNF will increase serum half life of the resulting fusion protein. Thereby, improving its pharmacokinetic properties and, consequently, enhancing the therapeutic potential. We have labelled the SDA alone and the fusion protein with *fac*- $[^{99m}Tc(CO)_3]^+$  and, after purification by gel-filtration chromatography, we have evaluated the biodistribution profile of  $^{99m}Tc(CO)_3$ -SDA in mice. Preliminary results indicated that the radiolabeled SDA alone cleared rapidly from blood without accumulation in any particular organ except the kidneys. Evaluation of the biological profile of the radiolabeled fusion protein is underway.



<sup>1</sup> Unidade dos Retrovírus e Infecções Associadas, Fac. de Farmácia da Univ. de Lisboa, Portugal.

#### $^{99m}$ Tc(CO)<sub>3</sub>-Mannosylated Dextran Derivatives for Sentinel Lymph Node Detection M. Marais, V. Arano<sup>1</sup>, L. D. G. Corraia, M. Marting, <sup>2</sup> S. Paraira, <sup>2</sup> J. Santos

M. Morais, Y. Arano,<sup>1</sup> J. D. G. Correia, M. Martins,<sup>2</sup> S. Pereira,<sup>2</sup> I. Santos

Sentinel lymph nodes (SLN) are the first lymph nodes to receive lymphatic flow as well as metastatic cells from the primary tumor sites. In cases of breast cancer or melanoma, sentinel lymph node detection (SLND) is followed by excision and biopsy of the SLN to detect the presence of metastasis. Accurate SLND is a key issue

for tumor staging, evaluation of the extension of surgery, and establishment of the most adequate therapy. Recent studies have shown that receptor-binding mannosylated nanocarriers provide selectivity for mannose receptors on lymph node macrophages. Therefore, we have synthesized and fully characterized the first class of  $^{99m}$ Tc(CO)<sub>3</sub>-mannosylated dextran derivatives with superior biological features for SLN detection. The SPECT/CT studies in mice confirmed that those radiolabeled polymeric nanoparticles are retained in the first lymph node allowing its clear visualization.



<sup>1</sup> Graduate School of Pharmaceutical Sciences, Chiba Univ., Chiba, Japan. <sup>2</sup> CICECO, Univ. de Aveiro, Portugal



F.Silva, A. Zambre<sup>1</sup>, A. Paulo, R. Kannan<sup>1</sup>, I. Santos



Nanoscience is poised to make significant contributions to both molecular imaging and molecular medicine. Among different nanoparticles, AuNPs play pivotal roles in the design and development of nanoscale tumor specific imaging agents. Searching

for multifunctional AuNPs suitable for PET imaging, we have synthesized AuNPs coated with a Di-Thiolated-DTPA (DTDTPA) chelator and a Bombesin

(BBN) peptide. BBN-Au-DTDTPA constructs bearing different amounts of BBN have been prepared. All the conjugates showed excellent stability under physiological conditions, displaying also Gastrin Releasing Peptide receptor (GRPr) specificity. Radiolabelling of BBN-Au-DTDTPA with <sup>64</sup>Cu, as well as

biodistribution studies in PC-3 xenographs bearing mice are currently in progress.

<sup>1</sup> Dep. of Radiology, Univ. of Missouri, USA.

**Cationic organometallic complexes as radioactive probes for tumoral detection** *F. Mendes, L. Gano, C. Moura, C. Fernandes, A. Paulo, I. Santos* 



 $^{99m}\text{Tc-DMEOP}$  and  $^{99m}\text{Tc-TMEOP}$  are promising radiotracers for myocardial perfusion imaging. We have shown that these ethercontaining tris(pyrazolyl)methane  $^{99m}\text{Tc}(I)$  complexes are able to

accumulate in a variety of human cancer cell lines, but there is a significant reduction of their tumor uptake due to multidrug resistance (MDR). To overcome this drawback, we have synthesized and evaluated <sup>99m</sup>Tctricarbonyl complexes



(**Tc1-Tc6**) containing triphenylphosphonium derivatives and stabilized by different bifunctional chelators. In general, these phosphonium-containing  $^{99m}$ Tc complexes showed moderate cellular and mitochondrial uptake, which are dependent on the mitochondrial membrane potential. These features indicate that these complexes are promising for the design of radioactive probes to target the mitochondria of neoplastic tissues.





**Novel** <sup>99m</sup>**Tc(I)-labeled multi-functional bone-seeking molecules for bone imaging and targeted therapy** C. Fernandes, E. Palma, S. Monteiro, P. Mendes, J. D. G. Correia, L. Gano, L. Costa<sup>1</sup>, S. Casimiro<sup>1</sup>, I. Santos



drug bioavailability at the desired site, reducing their toxicity. This fact encouraged the design of new complexes bearing a bisphosphonate (BP) to deliver radiation and a cytotoxic agent for the treatment of bone metastasis. Toward this goal we started the synthesis and evaluation of Re and <sup>99m</sup>Tc tricarbonyl complexes bearing bisphosphonates in

different positions of the bifunctional chelator. So far, the best biological data were obtained with the <sup>99m</sup>Tc tricarbonyl complex bearing a BP in the 4-position of the pyrazolyl ring. This complex presents a fast blood clearance and high bone uptake. Notably, the target to non target ratios are



MDP Aln-4pz

Active targeting of therapeutic agents to bone metastasis may improve

considerably higher than the ones obtained for <sup>99m</sup>Tc-MDP, the gold standard for bone imaging in nuclear medicine.

<sup>1</sup>Unidade de investigação Aplicada em Oncologia Clínica, IMM, Fac. de Medicina da Univ. de Lisboa, Lisboa, Portugal.

## Targeting of Nitric Oxide Synthase with M(I)-complexes (M = <sup>99m</sup>Tc, Re): A structure-activity study

B. L. Oliveira, F. Mendes, P. D. Raposinho, I. Santos, J. D. G. Correia, M. Correia,<sup>1</sup> T. Santos-Silva,<sup>1</sup> M. J. Romão,<sup>1</sup> A. Ferreira,<sup>2</sup> C. Cordeiro,<sup>2</sup> A. P. Freire,<sup>2</sup> I. S. Moreira,<sup>3</sup> P. A. Fernandes,<sup>3</sup> M. J. Ramos<sup>3</sup>

Aiming to probe NOS *in vivo* we have introduced  $\text{Re}^{99\text{m}}\text{Tc}(\text{CO})_3$ -complexes containing L-Arg derivatives with high *in vitro* and *in vivo* affinity for the enzyme. Towards a structural understanding of the affinity of the

complexes to the enzyme we combined experimental (X-ray, protein:ligand) and computational approaches (Docking and Molecular Dynamics simulations) to achieve that goal. We have cloned, expressed, and purified the iNOS oxygenase domain, and assayed its enzymatic activity. Currently, co-crystallization, pre-incubation and soaking techniques are being explored to obtain single, well diffracting crystals of the desired Re(I)-complexes:iNOS constructs. The MD simulations showed that metal center plays a key role in the organization/orientation of the complexes inside the active pocket of iNOS. The increased complementarity of shape and charge of the rhenium complexes justify their better affinity when compared with the corresponding free ligands.



<sup>1</sup> REQUIMTE/CQFB, Dep. de Química, Fac. de Ciências e Tecnologia, Portugal

<sup>2</sup> Centro de Química e Bioquímica, Dep. de Química e Bioquímica, Fac. de Ciências da Univ. de Lisboa, Portugal.

<sup>3</sup> REQUIMTE, Dep. de Química, Fac. de Ciências da Univ. do Porto, Portugal.

**Radiolabeling of biomolecules with DOTA like chelators for tumor targeting** S. Cunha, F. Vultos, C. Fernandes, C. Oliveira, M. P.C. Campello, L. Gano, I. Santos



Seeking for new probes for *in vivo* targeting of tumours we have pursued our research efforts on the synthesis of macrocyclic complexes of trivalent radiometals, using different strategies to couple selected biomolecules

(e.g. small peptides and estradiol derivatives). In the case of estradiol derivatives, two  $^{67}$ Ga/<sup>111</sup>In-complexes with a  $16\alpha$ -DOTA-estradiol

chelator (L1) have been evaluated. Both complexes have a neutral charge and exhibit high stability under physiological concentrations of apotransferrine and in human blood serum. Preliminary biological studies indicate high *in vivo* stability, rapid clearance from main organs and fast overall excretion. Cellular uptake studies in MCF-7 cells suggest a moderate uptake via an estrogen receptor-mediated process.



#### Metal-based anti-cancer agents – new mechanisms of action

S. Gama, F. Mendes, F. Marques, A Casini,<sup>1</sup> J. Rino,<sup>2</sup> J. Coimbra,<sup>3</sup> A. Paulo, T.S. Morais,<sup>4</sup> A.I. Tomáz,<sup>4</sup> M.H. Garcia,<sup>4</sup> I. Santos



The search for anti-cancer metal-based drugs constitute an interesting and emerging research field. In this area, Pt-, Cu-, Ru- and Au-based complexes are being investigated as therapeutic agents. In order to get a better insight on the mechanism of action of several promising complexes, we have studied their uptake on cancer cell lines, and DNA or target proteins interactions

by confocal microscopy, ICP-MS, gel electrophoresis and functional assays. Our studies



Live imaging of cancer cells after incubation with a Pt(II) complex

against a range of human tumour cell lines. Moreover, we have demonstrated that interaction with DNA and/or inhibition of novel protein targets are involved in their mechanism of action.

<sup>1</sup>Institut des Sciences et Ingénierie Chimiques, Ecole Polytechnique Fédérale de Lausanne, Suiça; <sup>2</sup>IMM, Fac. de Medicina da Univ. de Lisboa, Portugal; <sup>3</sup>Lab. Central de Análises, Univ. de Aveiro, Portugal; <sup>4</sup>Dep. de Química e Bioquímica, Fac. de Ciências, Univ. de Lisboa, Portugal

#### Radiofluorinated benzazole derivatives for *in vivo* imaging of amyloid aggregation

have shown that a set of Pt and Ru-based complexes are potent cytotoxic agents

G. Morais, A. Paulo, E. Palma, C. Oliveira, I. Santos, T. Kniess,<sup>1</sup> R. Bergman,<sup>1</sup> A. Abrunhosa,<sup>2</sup> H. Miranda,<sup>3</sup> T. Outeiro<sup>3</sup>C. Oliveira,<sup>4</sup> C. Pereira<sup>4</sup>



In the course of our efforts to identify small, planar and highly conjugated compounds to interact with the  $\beta$ -sheet structure of  $\beta$ -amyloid aggregates, we have introduced new fluorinated/radiofluorinated styryl benzazole (**A**) and aryl benzimidazole (**B**) derivatives. These two families of compounds started

to be evaluated as radioprobes (<sup>18</sup>F) for PET imaging of protein aggregates, implied in neurodegenerative disorders such as Alzheimer's disease (AD). So far, such evaluation involved the measurement of the binding affinity towards different types of amyloid aggregates, as well as biodistribution



studies in healthy animal models. *In vivo* and *ex vivo* studies in animal models of AD are underway for the more promising  $^{18}$ F-labeled compounds.

<sup>1</sup> PET-center, Helmholtz-Zentrum Dresden-Rossendorf, Dresden, Germany, <sup>2</sup> ICNAS; Univ. de Coimbra, Coimbra, Portugal;

<sup>3</sup> IMM, Fac. de Medicina da Univ. de Lisboa, Portugal; <sup>4</sup>CNBC, Univ. Coimbra, Portugal

#### Iodination, radioiodination and biological evaluation of a Kyotorphin derivative

M. C. Oliveira, C. Neto, L. Gano, I. Santos, S. Sá Santos<sup>1</sup>, M. M. B. Ribeiro<sup>1</sup> and M. Castanho<sup>1</sup>

The neuropeptide Kyotorphin (KTP) is potently analgesic when delivered directly to the central nervous system. However, its inability to cross the blood-brain barrier (BBB) precludes its possible clinical use. A new KTP-

derivative (KTP-amide or KTP-NH<sub>2</sub>) with enhanced lipophilicity and good analgesic ability after systemic delivery was mono-radioiodinated with I-125 (MIK-<sup>125</sup>I). MIK-<sup>125</sup>I was obtained in high radiochemical purity after RP-HPLC purification. *In vivo* stability data suggested fast de-iodination in rat blood, kidney and liver homogenate. *In vitro* radiochemical studies also indicate fast degradation in human serum. Biodistribution studies in healthy rats indicate predominant hepatobiliary excretion. The relatively high level of radioactivity in stomach probably reflects enzymatic



degradation. The low brain uptake suggests that only a small fraction of MIK-<sup>125</sup>I was able to cross the BBB.

<sup>&</sup>lt;sup>1</sup> Unidade de Bioquímica Física, Inst. de Medicina Molecular, Fac. de Medicina de Lisboa, Lisboa, Portugal.

## Solid State

#### Manuel Leite de Almeida

The Solid State Group has developed during the past years a broad range of expertise in complementary areas of solid state science and focused, under a global on selected new materials approach, with unconventional electrical and magnetic properties. The nature of the group is multidisciplinary combining expertise ranging from the synthetic chemistry of both molecular materials with transition metal complexes and intermetallic compounds, to many different specialised solid state characterisation techniques. Among the more relevant facilities developed, operated by and maintained in the group, are a high temperature laboratory with crystal growth techniques (Czochralski, Bridgman and float zone), X-ray diffraction (single crystals and powder), EPR and Mössbauer spectroscopy, measurements of magnetisation by SQUID, Faraday and extraction techniques and AC-susceptibility, different electronic transport measurements and heat capacity, in a broad range of temperature and magnetic field.

The use of all these specialised characterisation techniques, often requiring low temperatures down to 0.3 K and high magnetic fields up to 18 T, lead to the development of facilities and expertise in cryogenics, unique in Portugal. The group was responsible for the installation at ITN in 1991 of a helium liquefier, which since then remained the only liquefaction centre operational in Portugal, serving also many users outside ITN. The liquefaction capability was upgrade in 2010 by the installation of a new liquefier with expanded capacity and enhanced efficiency.

The rare combination of the **preparative chemistry** expertise with the specialised **solid state physics** techniques enables the group to deal with different problems of modern materials science. Thanks to the valuable techniques developed, the group often act as a key partner of many national and international research projects. His activities have been centered in strategic selected type of materials, namely:

- Molecule based conducting and magnetic materials.

- Intermetallic compounds with *f*-elements.

Specific ongoing research projects are described in more detail in the following sections.

The group has an established tradition of research on **molecular conductors** since its origin at Sacavém. The two chain compounds, originally reported more

than 3 decades ago, remain an important topic of research due to their unique properties. This research has recently focused on a new fundamental aspects of crystallogenesis studied namely by AFM and magnetic field studies of the Peierls and spin-Peirels ground states. The chemistry of bisdithiolene complexes and related TTF donors, namely substituted with coordinating groups as building blocks for multifunctional materials is a another topic of research that has been pursued.

The interests of the group have been extended during the last years to molecular magnetism namely in the framework of the European Network of Excellence MAGMANet and the resulting participation in the European Institute of Molecular Magnetism. The combination of spin crossover (SCO) compounds with other conducting and magnetic functionalities was a topic pursued in the context of the development of new multifunctional and nanostructured materials. The detailed study of a two-step SCO transition associated with symmetry breaking in the crystal structure was an important recent achievement. A major development of the group during 2011 in the molecular magnetism field was the discovery of Single Molecule Magnet behaviour in mononuclear U compounds, which have been prepared and characterised in collaboration with the Organometallic Chemistry Group of this research Unit at ITN.

The research on **intermetallic compounds**, initiated in 1992 with emphasis on the study of phase diagrams of the type (f-element)-(d metal)-(p-element) and on new compounds with strongly correlated electronic behaviour and complex magnetic structures, has been recently extended to borides and thermoelectric materials with special emphasis on conducting glasses based o Cu-Ge-Te.

The application of Mössbauer spectroscopy to different fields was pursued with large emphasis in the development of novel ferrite materials with mixed ionic-electronic conductivity for applications in alternative energy sources.

A significant output of the group continued to be the **training and education of young scientists** which always plays a major role in its projects and the collaboration in undergraduate and pos-graduate University courses.

#### Research Team Researchers

M. ALMEIDA, Coord., Group Leader V. GAMA, Princ. J.C. WAERENBORGH, Princ. A.P. GONÇALVES, Princ. E.B. LOPES, Aux. L.C.J. PEREIRA, Aux. I.C. SANTOS, Aux. D. BELO, Aux. contract S. RABAÇA, Aux. contract M.A. ANTUNES, FCT grant M. AFONSO, Post-Doc, ITN grant S. DIAS, Post-Doc, FCT grant P.I. GIRGINOVA, Post-Doc, FCT grant E. TSIPIS, Post-Doc, FCT grant Y. VERBOVYTSKYY Post-Doc, FCT grant.

#### Collaborators

A. CASACA. Adjunct Professor, ISEL R.T. HENRIQUES, Assoc. Professor, IST

#### Students

A. NEVES, Ph.D. Student, FCT grant. A. CERDEIRA, Ph.D. Student, FCT grant. M. HENRIQUES, Ph.D. Student, FCT grant B. VIEIRA, Ph.D. Student, FCT grant S. OLIVEIRA, Ph.D. student FCT grant R. SILVA, BIC grant (since May) J.T. COUTINHO, BIC grant (since March) R. FREITAS, BIC grant (since March) T. MENDES (since February)

## Single Molecule Magnetic Behavior in mononuclear U(III) Complexes

M. A. Antunes, L. C. J. Pereira, J. T. Coutinho, I. C. Santos, M. Mazzanti<sup>1</sup>, J. Marçalo, M. Almeida

#### Objectives

The main goal of this project is to develop new uranium complexes as discrete molecules that display single molecule magnetic (SMM) behaviour and to establish magneto-structural correlations enlightening the role of the 5f electrons in stronger magnetic exchange environments. These studies are expected to enlighten the origin of the low temperature magnetic relaxation mechanisms and improve the design of new compounds with higher relaxation barriers.

#### Results

We focused our work on the study of the cationic U(III) mononuclear complex  $[U(TpMe_2)_2(bipy)]$  I which was obtained by the addition of 2,2'-bipyridine to  $[U(TpMe_2)_2I]$  resulting in the displacement of the iodide and the formation of the cationic uranium(III) complex as a dark-green crystalline solid.

This compound was isolated in good yield and characterized by IR and NMR spectroscopies, and its molecular structure determined by single-crystal X-ray diffraction. The metal coordination geometry can be best described as distorted dodecahedral (Fig.1).



Fig. 1. Molecular structure of [U(TpMe<sub>2</sub>)<sub>2</sub>(bipy)] I.

The arrangement of the donor atoms around the uranium atom approximates a C<sub>2</sub> symmetry, which is consistent with the solution NMR data. The U-N-(TpMe<sub>2</sub>) distances range from 2.524(4) to 2.653(4) Å and are typical of other similar  $[U(TpMe_2)_2X]$  compounds.

Studies of its magnetic properties revealed that the compound is paramagnetic but shows at low temperatures a frequency dependence of the magnetization with a blocking temperature of 4.5 K, and at lower temperatures, a slow relaxation of magnetization characteristic of a single-molecule-magnet behaviour. According to the AC susceptibility data the relaxation time follows an activated Arrhenius law characteristic of a single process with a pre-exponential factor of  $\tau_0 = 1.4 \times 10^{-7}$  s and an energy barrier for the relaxation of  $E_{\rm ff} = 18.2$  cm<sup>-1</sup>. These results demonstrate a slow magnetic relaxation of the same order of magnitude as that observed in other well-known SMMs such as Fe<sub>8</sub> and a few recently described lanthanide compounds. Below 3 K, a

deviation from the Arrhenius law is observed, which is attributed to the onset of a relaxation regime by quantum tunneling. However slow magnetisation cycles at 0.3 K do not show quantum tunnelling steps in spite of an hysteresis without coercivity.

This was only the third example of a U compound with such behaviour. The difference in the relaxation barrier with respect to the previously reported compounds showing SMM behaviour suggest that small variation in the uranium coordination sphere can significantly affect the relaxation. Further experimental and theoretical studies of this and of related compounds, including the precursor compound [U(TpMe<sub>2</sub>)<sub>2</sub>I], presently under way, are expected to more clearly establish magneto-structural correlations.



Fig.2 Temperature dependence of the real ( $\chi$ ', inset) and imaginary ( $\chi$ '') components of the AC susceptibility under 0.05 T (left). Plot of ln( $\tau$ ) vs T<sup>-1</sup> with a fitting to the Arrhenius law (right).

#### Published or in press work (selected)

M.A. Antunes, L.C.J. Pereira, I.C. Santos, M. Mazzanti, J. Marçalo, M. Almeida  $[U(Tp^{Me2})_2(bipy)]^+$ : A Cationic Uranium(III) Complex with Single-Molecule-Magnet Behavior, *Inorg. Chem.* **50** 9915-9917 (2011).

J.T. Coutinho, M.A. Antunes, L.C.J. Pereira, I.C. Santos, M. Mazzanti, J. Marçalo, M. Almeida, Single-Molecule-Magnet behaviour in U compounds, *Workshop on Strongly Correlated Electron and Complex Systems; From Intermetallics to Molecular Materials*, ITN, Sacavém, Portugal, 10–11 November 2011 (oral).

M.A. Antunes, L.C.J. Pereira, I.C. Santos, M. Mazzanti J. Marçalo, M. Almeida,  $[U(Tp^{Me2})_2(bipy)]^+$ : A Cationic Uranium(III) Complex with Single-Molecule-Magnet Behaviour,  $5^{th}$  EuCheMS Conference on Nitrogen Ligands, Granada, Spain, 4-8 September 2011 (poster).

L.C.J. Pereira, J.T. Coutinho, M.A. Antunes, I.C. Santos, M. Mazzanti, J. Marçalo, M. Almeida, SMM behaviour in Uranium mononuclear complexes:  $[U(Tp^{Me2})_2(bipy)]^+$ ,  $3^{rd}$  European Conference on Molecular Magnetism-ECMM 2011, Paris, France, 22-26 November 2011 (poster).

<sup>1-</sup> Lab. de Reconnaissance Ionique et Chimie de Coordination, UMR-E 3 CEA/UJF, FRE3200 CNRS, INAC, CEA, 38054 Grenoble, France.

**Studies on the Electrochemical Growth of** (**Per**)<sub>**n**</sub>[**Au**(**mnt**)<sub>**2**</sub>]. *M. Afonso, R. Silva, M. Matos*,<sup>*l,*</sup> *A. S. Viana*,<sup>*2*</sup> *M. Almeida* 

The electrocrystallisation has been widely applied to obtain single crystals of many charge transfer salts. However in spite of its success this technique has been regarded as an art based mainly on empirical evidence, there is lack of fundamental studies and its application of to perylene compounds has several limitations. Therefore a study was initiated aiming at understanding the factor governing the nucleation and electrochemical growth of perylene compounds.

The first stages of the electrocrystalization of  $(\text{Perylene})_2[\text{Au}(\text{mnt})_2]$  salt from dichloromethane on gold, platinum and highly orientated pyrolytic graphite (HOPG) were investigated by cyclic voltammetry



and atomic force microscopy. This was one of the rare microscopic studies on the electrocrystallisation of a molecular system. It was found that the crystal growth occurs from adsorbed films, of dithiolate on gold or platinum, and of perylene on HOPG, after an homogeneous nucleation process and in spite of low current densities it is controlled by the low diffusion of the species towards the growing surface.

1- Instituto Superior de Engenharia de Lisboa, Lisboa, Portugal and Instituto de Telecomunicações, Av. Rovisco Pais, Lisboa, Portugal 2- CQB, Faculdade de Ciências da Universidade de Lisboa, P-1749-016, Lisboa, Portugal

#### Magnetic field-dependent Peierls and spin-Peierls ground states in (Perylene)2[Pt(mnt)2]

E.L. Green,<sup>1</sup> L.L. Lumata,<sup>1</sup> J.S. Brooks,<sup>7</sup> P.L. Kuhns,<sup>2</sup> A.P. Reyes,<sup>2</sup> J.Wright,<sup>2</sup> S.Brown,<sup>2</sup> M. Almeida, M. J. Matos,<sup>3</sup> R. T. Henriques.

 $Per_2[Pt(mnt)_2]$  consists of segregated perylene and  $Pt[mnt]_2$  chains that undergo a charge density wave (CDW) and spin-Peierls (SP)-transition (respectively) below 8 K. Fundamental questions involve what drives the transitions and the nature of the coupling between the two chains. The T-B phase diagram, based on electrical transport (which is only sensitive to the conductivity in the perylene chains), has previously been mapped out up to 42 T. In this work, proton NMR was used to probe the behavior of the localized spin  $\frac{1}{2}$  Pt moment on the  $[Pt(mnt)]_2$  chains. By measuring relaxation rates and spectra at high fields and low temperatures, we were able to map out the SP phase boundary. Results indicate that the SP transition occurs at a lower temperature than the CDW boundary determined from transport, suggesting that the lattice instability on the perylene drives the dimerization of the platinum moment.

1 - National High Magnetic Field Laboratory / Florida State University, Tallahassee FL 32310, USA

2- Department of Physics, University of California Los Angeles, Los Angeles CA 90095, USA

3- Instituto de Telecomunicações, Av. Rovisco Pais, Lisboa, Portugal

#### Symmetry breaking two-step spin crossover in [Fe<sup>III</sup>(nsal<sub>2</sub>trien)]SCN

B.J.C. Vieira, J.T. Coutinho I.C. Santos, L.C.J. Pereira, J.C. Waerenborgh, M. Almeida, D. Belo, V. Gama



In spin crossover (SCO) complexes the spin state of the transition metal can be often switched between the low-spin (LS) and high-spin (HS) states by the application of an external perturbation such as temperature, pressure or light. The bistability between the HS and LS states is promising for the application of SCO complexes as molecular memories and switches. In this context we studied the incorporation of SCO cation, [Fe<sup>III</sup>(nsal<sub>2</sub>trien)]<sup>+</sup> in hybrid (conducting or magnetic) materials in order to use the switchability of the SCO phenomena. For [Fe(nsal<sub>2</sub>trien)]SCN we observed the existence of a two-step SCO transition  $(T_{1/2} = 142 \text{ and } 260 \text{ K})$  associated with symmetry breaking in the crystal structure, where the (single site) HS and LS isostructural phases are separated by an

intermediary (Int) phase with two distinct Fe<sup>III</sup> sites (one in HS and the other LS). This is quite unusual and only the second example of a Fe<sup>III</sup> based complex showing this type of behaviour, and the first one that was structurally characterized in the HS, LS and Int phases. This behaviour is quite interesting due to increased switching possibilities, involving three states and enabling larger information storage capacity.

Single component molecular metals based on thiophenedithiolenes

A.I.S. Neves, E.B. Lopes, J. T. Coutinho, L.C.J. Pereira, I.C. Santos R. T. Henriques, M. Almeida, D. Belo

This project aims to enlarge the number of compounds and the knowledge about the family of single component molecular metals (SCMM) based on thiophenic units. Three complementary lines of research were followed. First the technological applications of  $[Au(\alpha-tpdt)_2]$ ,  $(\alpha-tpdt= 2,3-$ thiophenedithiolate) by processing it has a topmost conductive layer of transparent and flexible bilayer films with polycarbonate. This was achieved by using the reticulate doping technique and, depending on the synthetic



parameters, it was possible to obtain either semiconductor or metallic films. Secondly the number of complexes based on the previously reported thiophene-tetrathiafulvalene-dithiolene ligands was enlarged, by preparing the Cu and Co complexes. These neutral complexes display room temperature conductivities of ~0.1 S/cm. Finally we started the study of new family of transition metal complexes based on the substituted thiophenic ligand 3-methyl-2,3-thiophenedithiolate ( $\alpha$ -m tpdt). We could obtain the neutral Au and Ni complexes with this ligand, which display some solubility in usual organic solvents, which opens new possibilities concerning processing, of these compounds that show a semiconductor behaviour.

#### Chiral bisdithiolene complexes

S. Dias, J.D. Wallis<sup>1</sup>, M. Almeida

Introduction of chirality into molecular conducting materials is currently a topic of large interest but most of the work published so far has been on TTF derivatives and their charge-transfer salts. Chiral transition metal bisdithiolene complexes, which are the inorganic coordination analogs of the TTF donors, have been a lot less studied.



Based on the synthesis of the ligand (5S,7S)-5,7-dimethyl-6,7-dihydro-5H-1,3-dithiolo[4,5-b]-1,3-dithiepine-2one a series of monoanionic complexes based on this chiral ligand and with the general formula  $[M(ddd)_2] (nBu_4N)$  could be obtained with different transition metals (M = Ni, Au, Pd, Fe). Single crystals suitable for X-ray diffraction of the gold complex  $[Au(ddd)_2](nBu_4N)$  were obtained. The complex adopts a chair conformation, forming zig-zag chains alternating anion and cation with no S<sup>...</sup>S short-contacts between them. This works opens the possibility to prepare new charge transfer solids based on these complexes, as magnetic or electroactive species, which is currently being explored.

<sup>1</sup>School of Science and Technology, Nottingham Trent University, Nottingham, UK.

#### Electrocrystallisation of (DT-TTF)<sub>n</sub>[M(mnt)<sub>2</sub>]; The M=Pd salt

R. A. L. Silva, M. L. Afonso, I. C. Santos, D. Belo, R. Freitas, E. B. Lopes, J. Coutinho, L. C. J. Pereira, R.T. Henriques, M. Almeida, C. Rovira<sup>1</sup>

The charge transfer salts based on the organic donor dithiophenetetrathiafulvalene (DT-TTF) and transition metal bis-maleonitriledithiolate  $M(mnt)_2$  were previously explored with different transition metals M=Au, Ni, Cu, Pt, Co and Fe. The first four metals lead to a family of isotructural compounds with formula (DT-TTF)<sub>2</sub>[M(mnt)<sub>2</sub>] presenting strongly paired stacks of partially oxidized donor molecules (DT-TTF)<sub>2</sub><sup>+</sup>, which for diamagnetic anions (M=Cu, Au) were the first examples of organic spin ladder systems. Other structures and stoichiometries (n=1) have been observed not only for Fe and Co with dimerised anions but also for Cu, depending on the growth conditions. The compounds with M=Pd remained until recently unexplored and we could describe the new compound (DT-



 $TTF)_2[Pd(mnt)_2]$ , obtained by electrocrystallisation in dichloromethane, that has been fully characterised as single crystal. The structure is of a distinct type, with fully oxidised donor molecules forming dimerised stacks, responsible for semiconducting properties. Donors chains form layers alternating with layers of reduced  $[Pd(mnt)_2]^2$  anions sitting side by side almost perpendicular to the donors, and forming magnetic chains.

<sup>1 -</sup> Instituto Ciència de Materials de Barcelona, CSIC, Spain

Progresses in the study of the series of transition metal cianobenzenodtiolate complexes  $[M(cbdt)_2]$ 

A. Cerdeira, S. Rabaça, P. I. Girginova, I. C. Santos, L. C. J. Pereira, R. T. Henriques, D. Simão,<sup>1</sup> M. Almeida



The study of the series of complexes  $[M(cbdt)_2]$  with different different transition metals (M=Zn, Fe, Co, Ni, Au, Cu, Pd) previously initiated based on the synthesis of the new dcbdt ligand, as dithiol, was pursued in 2011 with significant synthetic, structural and magnetic characterization progresses. A new alternative synthesis of these complexes  $[M(cbdt)_2]$  complexes, more convenient to obtain the complexes in more reduced forms, was developed starting from the 4cyanobenzene-1,3-dithiole-2-thione a compound that was described for the first time. This synthesis allowed a better characterization of the complexes in the dianionic state. Among them the dianionic Co complex became relevant because it is a rare case where as a powder

its EPRspectrum presents in addition to a rhombic g-anysitropy an hyperfine structure typical of I = 7/2 <sup>59</sup>Co with a component  $a_{0x} = 8.6$  mT. These complexes were explored as building blocks for complex magnetic structures using the secondary coordination through the N atom. Several Ni(cyclam) salts with the [M(cbdt)<sub>2</sub>] anions M=Cu, Au and Ni, were obtained. However with the Cu anion structures where the Ni ions are also coordinated by acetonitrile molecules rather than the nitrile group of the ligands are onserved.

1 Inst. Superior Técnico, Univ. Técnica de Lisboa, Lisboa, Portugal.

#### One-dimensional Ln coordination polymers with Single-Chain Magnet behaviour

P. I. Girginova, L. C. J. Pereira, J.T. Coutinho, M. Almeida

Molecular systems displaying slow relaxation of magnetisation at low temperatures and behaving as magnets have been a central topic of interest in contemporary molecular magnetism. An important class of materials with such behaviour are one-dimensional magnetic systems with magnetic anisotropy which have been classified as Single Chain Magnets

In this context we decide to explore different lanthanide-containing one-dimensional coordination polymers and prepared a series of three isostructural compounds based on picolinic (pic) and glutaric acid (glu)  $Ln(glu)(pic)(H_2O)_2$ , where Ln = Gd III (1), Tb III (2) and Dy III (3). These compounds were structurally characterized by single-crystal (2) and X-ray powder diffraction (1,3), elemental analysis, infrared spectroscopy and thermoanalytical measurements (1,2). The structure of these compounds was found to be identical with the one of the previously reported analogous compound with Sm, where the rare earths ions are arranged in double chains bridged by the two type of ligands as steps and rungs of a ladder. Their magnetic properties were characterised by both static magnetisation and AC-susceptibility. All the three compounds present weak ferromagnetic interactions between lanthanide cations. AC susceptibility at low temperatures reveals a significant frequency dependence and slow relaxation of the magnetisation under applied DC field for compounds (1) and (3). These results qualify these Gd and Dy compounds as "Double Chain Magnets", a new structural type of molecular magnets.

#### Study of Ternary Phase Diagrams based on f and d elements

A.P. Gonçalves, Y. Verbovytskyy, J.C. Waerenborgh, M. Almeida, M. Dias, M.S. Henriques, P.A. Carvalho<sup>1</sup>, A. Ferro<sup>1</sup>, R. Vilar<sup>1</sup>, O. Tougait<sup>2</sup>, M. Pasturel<sup>2</sup>, H. Noël<sup>2</sup>

The main objective of this research line is to explore (*f*-element)-(*d*-metal)-X ternary phase diagrams in order to establish the phase relations and identify, synthesise and characterise new ternary intermetallic compounds. Fundamental information for the pure compounds synthesis and growth of single crystals is also expected to be obtained. Under this project novel ternary phases  $EuZn_{2-x}Ga_{2+x}$ ,  $EuZn_{2-x}Al_{2+x}$ ,  $Eu_2Zn_{14.32}Al_{2.68}$  and  $Eu_3Zn_{17.68}Al_{4.32}$ , from the Eu-Zn-(Al,Ga) systems, have been synthesized.  $EuZn_{2-x}Al_{2+x}$  and  $Eu_2Zn_{14.32}Al_{2.68}$  and  $Eu_3Zn_{17.68}Al_{4.32}$ , and  $Eu_2Zn_{14.32}Al_{2.68}$  and  $Eu_3Zn_{17.68}Al_{4.32}$ , and  $Eu_2Zn_{14.32}Al_{2.68}$  and  $Eu_3Zn_{17.68}Al_{4.32}$ , adopt



the rhombohedral  $Th_2Zn_{17}$  and the tetragonal  $Ce_3Zn_{22}$ -type structure, respectively. 15 new representatives from the R-Zn-Ga systems (R=Y, Lu, Gd-Tm), with BaAl<sub>4</sub>, La<sub>3</sub>Al<sub>11</sub> and BaHg<sub>11</sub> structure types, were also studied.

1 IST, Univ. Técnica de Lisboa, Portugal.

<sup>2</sup> Lab. Chimie du Solide et Inorganique Moléculaire, UMR CNRS 6511, Univ. Rennes 1, France.

#### Superconductivity in TiNiSi-type structure compounds

A.P. Gonçalves, L.C.J. Pereira, E.B. Lopes, M.S. Henriques, J.C. Waerenborgh, M. Almeida, L. Havela<sup>1</sup>, O. Tougait<sup>2</sup>, H. Noël<sup>2</sup>, J.S. Brooks<sup>3</sup>, A. Kiswandhi<sup>3</sup>, D. Kristovska<sup>3</sup>, E. Steven<sup>3</sup>



The peculiar behaviour of in several uranium intermetallics (as  $UGe_2$ , UIr, URhGe and UCoGe), showing a coexistence of ferromagnetism and superconductivity, raised the question about the main mechanism responsible for the pairing. In 2011 the study of the superconducting ferromagnet UCoGe compound was started. Its angular dependent magnetoresistance was studied in detail at 40 mK under fields up to 18 T in a single crystal sample with a low residual resistivity ratio. A ferro-to-ferrimagnetic transition near 9 T that depends only on the field component along the uniaxial magnetic *c* axis is observed in both transport and susceptibility measurements.

<sup>1</sup> Department of Condensed Matter Physics, Faculty of Mathematics and Physics, Charles University, 12116 Prague, Czech Republic.

<sup>2</sup> Lab. Chimie du Solide et Inorganique Moléculaire, UMR CNRS 6511, Univ. Rennes 1, France.

<sup>3</sup> National High Magnetic Field Laboratory, Florida State University, Tallahassee, Florida, USA.

#### Magnetic and strongly correlated electron behaviour in intermetallics

A.P. Gonçalves, J.C. Waerenborgh, L.C.J. Pereira, E.B. Lopes, M. Dias, M.S. Henriques, S. Sério, M. Almeida, L. Havela<sup>1</sup>, O. Tougait<sup>2</sup>, H. Noël<sup>2</sup>

The understanding of the magnetic and strongly correlated electron behaviour of intermetallics containing f-elements (in particular the role of f-electrons) has been subject of a long-term project in the Solid State group.

The physical properties of selected compounds from the Yb-Zn-(Ga,In) systems were studied in 2011. A diamagnetic behaviour was observed for the YbZn<sub>8.3–9.2</sub>Ga<sub>2.7–1.8</sub>, YbZn<sub>x</sub>Ga<sub>4-x</sub> and Yb<sub>3</sub>Zn<sub>11-x</sub>Ga<sub>x</sub> phases, whereas YbZn<sub>0.7</sub>In<sub>1.3</sub> shows a paramagnetic behavior with antiferromagnetic-like interactions. The calculated magnetic moment of this last compound points to a mixed valence state of Yb. The study of uranium intermetallics was also continued. UZn<sub>12</sub> was previously



reported as a non-magnetic heavy fermion. However, our studies made on single crystals clearly indicate an antiferromagnic transition at  $T_N = 5.0(2)$  K. The paramagnetic magnetoresistivity isotherms of UZn<sub>12</sub> can be fairly well superimposed onto each other using Schlottmann's scaling for the single-ion Kondo model.

<sup>1</sup> Department of Condensed Matter Physics, Faculty of Mathematics and Physics, Charles University, 12116 Prague, Czech Republic.

#### New materials for thermoelectric applications

E.B. Lopes, A.P. Gonçalves, G. Delaizir<sup>1</sup>, C. Godart<sup>1</sup>, J. B. Vaney<sup>2</sup>, B. Lenoir<sup>2</sup>, A. Piarristeguy<sup>3</sup>, A. Pradel<sup>3</sup>, J. Monnier<sup>1</sup>, P. Ochin<sup>1</sup>

The synthesis and characterization of new thermoelectric systems with high figure of merit are of fundamental importance to their potential application in environment friendly energy sources. During 2011 we continued the studies on electrically conducting glasses prepared by melt-spinning. We explored in more detail the compositions of the already studied  $Cu_{x+y}As_{20-x}Te_{80-y}$  ( $0 \le x \le 20$ ;  $0 \le y \le 10$ ) family, and extended these studies to other  $Cu_{x+y}A_{20-x}Te_{80-y}$  (A = Ga and Si) systems. As a general trend we observed that the increase of the copper concentration decreases the electrical resistivity while the increase of tellurium increases the Seebeck coefficient. Nevertheless  $Cu_{30}As_{15}Te_{55}$  remains the best composition with a power factor of 106  $\mu$ WK<sup>-2</sup>m<sup>-1</sup>. Structural studies of the  $Ge_{20}Te_{80}$ ,  $Ge_{15}Cu_8Te_{77}$  and  $Ge_{15}Cu_5Te_{80}$  glasses made by X-ray diffraction and extended X-ray absorption fine structure measurementsb show that the lower Cu content samples both Ge and Te obey the 8–N rule and the structure is built up of GeTe<sub>4</sub> tetrahedra connected via Te–Te bonding or shared Te atoms connected to two Ge atoms. In  $Ge_{15}Cu_8Te_{77}$  the coordination number of Te is higher than 2 and significant Cu–Cu bonding exists..

<sup>&</sup>lt;sup>2</sup> Lab. Chimie du Solide et Inorganique Moléculaire, UMR CNRS 6511, Univ. Rennes 1, France.

<sup>&</sup>lt;sup>1</sup>CNRS, ICMPE, CMTR, 2/8 rue Henri Dunant, 94320 Thiais, France

<sup>&</sup>lt;sup>2</sup> Institut Jean Lamour (IJL), Nancy Université, Parc de Saurupt, 54042 Nancy

<sup>&</sup>lt;sup>3</sup> Institut Charles Gerhardt (ICG), UMR 5253 CNRS, Université de Montpellier 2, 34095 Montpellier

#### SOLID STATE

#### Materials for solid oxide fuel cells and dense ceramic membranes

J C Waerenborgh, E. Tsipis, V. V. Kharton<sup>1</sup>, E.N. Naumovich<sup>1</sup>, A. Yaremchenko<sup>1</sup>, M. V. Patrakeev<sup>2</sup>, M.F.Lu<sup>1,3</sup>

Materials based on iron-containing oxides with perovskite-derived structures attract significant attention for energy-related electrochemical technologies, such as electrodes of solid oxide fuel cells (SOFC) or ceramic membranes for conversion of natural gas and biogas. Experimental information on Fe states on ferrite-based mixed conductors surfaces and on their role in fuel oxidation processes is still very scarce. A study by conversion electron Mössbauer spectroscopy on the electrode surface layers of model electrochemical cells, comprising porous  ${}^{57}$ Fe-enriched (La<sub>0.9</sub>Sr<sub>0.1</sub>)<sub>0.98</sub>Cr<sub>0.6</sub>Fe<sub>0.3</sub>Mg<sub>0.1</sub>O<sub>3- $\delta$ </sub> electrodes and lanthanum gallate solid electrolytes, revealed that the predominant state of Fe cations remained trivalent irrespective of the oxygen partial pressure in surrounding atmosphere and polarization, whilst oxygen coordination of Fe<sup>3+</sup> decreased on lowering electrode potential. This work suggests that Fe-substituted chromites and their derivatives may provide a stable operation of intermediate-temperature SOFC anodes. A promising method to optimize the thermomechanical properties of mixed-conducting ceramics is the fabrication of composites. Additions of alumina to  $SrCo_{0.8}Fe_{0.2}O_{3-\delta}$  and yttria-stabilized zirconia to  $SrCo_{0.4}Fe_{0.6}O_{3-\delta}$  were known to enhance dimensional integrity and mechanical strength, respectively. An investigation of  $(SrFeO_{3-\delta})_{1-x}(SrAl_2O_4)_x$  and  $(SrCo_{0.8}Fe_{0.2}O_{3-8})_{1-x}(SrAl_2O_4)_x$  composites was therefore performed. The overall performance of SrFeO\_3-based composite membranes for energy-related applications, was found to be always better than the performances of  $Sr(Co,Fe)O_{3-\delta}$ -based materials. The latter materials are promising mainly for high-purity oxygen separation in oxidizing atmospheres, essentially free of carbon dioxide.

1 Dept. de Engenharia Cerâmica e do Vidro, UIMC, Universidade Aveiro, 3810-193 Aveiro, Portugal.

2 Institute of Physicochemical Problems, Belarus St. University, Minsk, Rep. of Belarus.

Mössbauer spectroscopy in Materials Science

J C Waerenborgh, E. Tsipis

As referred in previous reports a Mössbauer spectroscopy facility was developed in ITN in order to support local research projects. The acquired expertise has been, in the last years, able to assist other national or foreign research institutions in the framework of joint research projects. Presently, in the ITN Mössbauer laboratory  $\gamma$ -ray transmission with the sample in the 300-1.4 K temperature range, and backscattering as well as conversion electron spectra may be obtained. In 2011 studies were performed in the areas of



environmental samples (Fe speciation during weathering of volcanic top soils in semi arid climates, Cabo Verde), archaeometry (production technology of late roman grey ceramics), materials science (new moleculebased multifunctional materials; hydrogenation of intermetallics, namely UFeGe) in collaboration with the Department of Geosciences, Univ. Aveiro; Instituto de Ciencia Molecular, Univ. of Valencia, and Dep. Geodinámica y Paleontología, Univ. Huelva, Spain; Faculty of Mathematics and Physics, Charles University, Prague, Czech Republic; Faculty of Physics, Univ. of Science and Technology, Kraków, Poland.

<sup>3</sup> Key Laboratory of Rare Earth Chem. Physics, Changchun Institute of Applied Chemistry, Changchun 130022, People's Republic of China