CULTURAL AND NATURAL HERITAGE WORKSHOP

ESRF – Grenoble, France

22-24 January 2020

Abstract Booklet

This project has received funding from the European Union’s Horizon 2020 research and innovation programme under grant agreement No 870313.

Organising Committee

Marine Cotte, **ESRF Grenoble**

Pierre-Olivier Autran, **ESRF Grenoble**
Camille Berruyer, **ESRF Grenoble**
Nils Blanc, **Institut Néel, CNRS Grenoble**
Catherine Dejoie, **ESRF Grenoble**
Paul Tafforeau, **ESRF Grenoble**

Workshop Assistant

Katherine Fletcher, **ESRF Grenoble**

Special thanks

Chantal Argoud, **ESRF Grenoble**
Kirstin Colvin, **ESRF Grenoble**
Anne-Françoise Maydew, **ESRF Grenoble**
Ewa Wyszynska, **ESRF Grenoble**

Contact email

heritage-ebs@esrf.fr

Contents

CULTURAL AND NATURAL HERITAGE WORKSHOP

22-24 January 2020

Practical Information

ESRF site map

TUTORIAL MEETING ROOMS

★1 X–ray Tomography: *Science Building SB036*

★2 X-ray Diffraction Phase Identification: *LOB 1-45*

★3 PyMca ROI Imaging: *Auditorium*

Coffee breaks

On the Mezzanine & ground floor of the ESRF Central Building

Lunches

In the ESRF canteen – please show your Workshop badge at the cash till

Your site badge

You have been given a visitor **BADGE** at the site entrance: this badge is strictly personal.
Due to the strengthened security measures,
you must wear your badge at all times on site over the whole period of the event.
It is your pass for the site entrance and, on site, for the Guesthouse and the canteen.
This badge does not give you access to the Experimental Hall; due to the EBS machine, access to the Experimental Hall is completely forbidden.

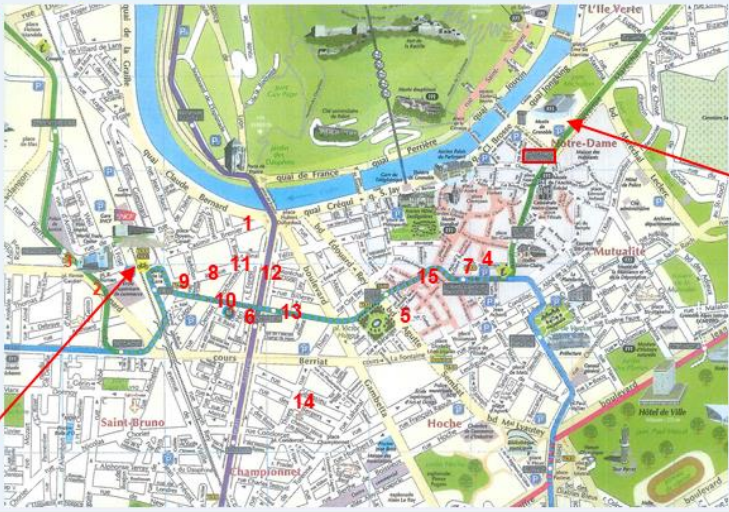
Hotels in Grenoble City Centre

ESRF
Tram B Terminus “Oxford” (formerly Presqu’Ile)

Tram B

HOTELS

1 Hotel Ibis Gare
2 Novotel Centre
3 Hotel Europole
4 Grand Hôtel
5 Hotel Angleterre
6 Royal Hotel
7 Hotel de l’Europe
8 Hotel de l’Institut
9 Hotel Terminus
10 Hotel des Alpes (Kyriad)
11 Hotel Gloria
12 Hotel Ibis Style
13 Touring Hotel
14 Hotel Splendid
15 Hotel Ibis Centre



Train Station (SNCF)

Grenoble Museum
Tram B stop “Notre Dame-Musée”

TAXI GRENOBLOIS
+33 (0)4 76 54 42 54

For further information, please contact Katherine Fletcher
ESRF Central Building – Room 008, ground floor near side doors – Tel. +33 (0)4 76 88 20 31

CULTURAL AND NATURAL HERITAGE WORKSHOP

22-24 January 2020

ESRF The European Synchrotron — ESRF-EBS Extremely Brilliant Source — STREAMLINE

Afternoon and Evening events

Wednesday 22 January	Thursday 23 January	Friday 24 January
Poster Clips **17:30 to 18:30** *followed by* **Poster Session & Buffet Dinner** **18:30 to 20:30** Ground floor and mezzanine of the ESRF Central Building	**Grenoble Museum** **18:15 to 20:00** General public conference and private access *followed by the* **Workshop Dinner** **20:00 – 22:00** « Patio » of the Grenoble Museum *Transport to Grenoble is organised at 17:10 – see below*	**Visit of Grenoble Street Art** **16:00 to 18:00**

Transport from ESRF to Grenoble on Thursday & Friday: Tram « B »

Meet on ground floor of the ESRF Central Building, by the main doors
We will provide single tram tickets - valid 1 hour - and accompany you to the tram terminus
Trams leave the terminus "Oxford" (previously "Presqu'Ile") approx. every 5 minutes
Thursday (Grenoble Museum): 11 stops to "Notre-Dame – Musée", 20 minutes
Friday (Street Art): your guide will accompany you to Fontaine or into the centre of Grenoble to your starting point

Tram Map of Central Grenoble

1 ★ Tram B Terminus "Oxford" (or "Presqu'Ile")

2 ★ Tram B stop "Notre Dame - Musée" Grenoble Museum

TAXI GRENOBLOIS
+33 (0)4 76 54 42 54

For further information, please contact Katherine FLETCHER
ESRF Central Building – Room 008, ground floor near side doors – Tel +33 (0)4 76 88 20 31

Cultural and Natural Heritage ESRF-EBS workshop

22-24 January 2020

Wednesday 22 January

09:00-09:30	REGISTRATION FOR PARTICIPANTS ATTENDING THE INTRODUCTION (OPTIONAL)
OPTIONAL INTRODUCTION FOR NEWCOMERS	
09:30-09:35	**Welcome and introduction** (M. Cotte, Scientist at the ESRF)
09:35-10:00	**The ESRF in a few words** (J. Susini, Director of Research, ESRF)
10:00-10:25	**Basic principles of X-ray tomography** (P. Tafforeau, Scientist at the ESRF)
10:25-10:45	*Coffee break*
10:45-11:10	**Basic principles of X-ray diffraction** (C. Dejoie, Scientist at the ESRF)
11:10-11:35	**Basic principles of X-ray spectroscopy** (M. Cotte, Scientist at the ESRF)
11:35-12:00	**Applying via peer-reviewed proposals & writing good proposals** (J. McCarthy, Head of User Office)
11:30-13:30	REGISTRATION FOR PARTICIPANTS NOT ATTENDING THE INTRODUCTION
12:00-13:30	*Lunch at the EPN campus restaurant*

OFFICIAL LAUNCH OF THE WORKSHOP	
13:30-13:45	**Welcome and introduction to EBS** (F. Sette, Director General, ESRF)
13:45-14:00	**Scopes and objectives of the workshop** (M. Cotte, Scientist at the ESRF)
SESSION I – PALAEONTOLOGY I ***(Chairperson: S. Sanchez)***	
14:00-14:40	**10 Years of Synchrotron and Sediba** Lee BERGER, University of the Witwatersrand, Johannesburg
14:40-15:00	**Synchrotron X-ray imaging enables 3D quantification of bone microstructures across fossil and modern bird-line archosaurs** Dennis VOETEN, Department of Organismal Biology, Uppsala University
15:00-15:40	**Digging virtually into large fossils using synchrotron X-ray microtomography** Vincent FERNANDEZ, Natural History Museum, London
15:40-16:10	*Coffee break*
SESSION II - MATERIALS, PROCESSES AND CHAÎNES OPÉRATOIRES I ***(Chairperson: M. Cotte)***	
16:10-16:50	**Cultural Heritage & Synchrotron Radiation: Quo Vadis?** Koen JANSSENS, Faculty of Science, University of Antwerp
16:50-17:10	**Colour Enamels in the Modernist Catalan stained glasses from Barcelona** Marti BELTRAN, University of Catalonia, Barcelona
17:10-17:30	**Complementary use of SR and neutrons for heritage study at NRC "Kurchatov institute"** Elena TERESCHENKO, National Research Centre “Kurchatov Institute”, Moscow
17:30-18:30	Poster clips
18:30-20:30	Poster session and buffet dinner *(apéritif dinatoire)*

Thursday 23 January

SESSION III – CONSERVATION AND ALTERATION ***(Chairperson: V. Gonzalez)***	
09:00-09:40	**Probing the degradation mechanisms of artists' pigments by different 2D XANES-based approaches** Letizia MONICO, CNR-SCITEC, Perugia
09:40-10:00	**The criticality of synchrotron techniques in developing new conservation strategies to characterise and stabilise marine archaeological artefacts** Eleanor SCHOFIELD, Mary Rose Trust, HM Naval Base, Portsmouth
10:00-10:20	**3D Visualization of the Effect of Light Aging on Orpiment Pigment Particles** Fréderique BROERS, Rijksmuseum Amsterdam, Conservation and Science, Amsterdam
10:20-10:50	*Coffee break*
SESSION IV - MATERIALS, PROCESSES AND CHAINES OPERATOIRES II ***(Chairperson: N. Blanc)***	
10:50-11:30	**Structural studies of historical inorganic pigments using synchrotron radiation: capacities and future applications** Victor GONZALEZ, Science Department, Rijksmuseum, Amsterdam
11:30-11:50	**Shed light on the schematic paintings of Savoy: the use of µXRD to understand the painted wall** Emilie CHALMIN, University Savoie Mont Blanc, CNRS, EDYTEM (UMR 5204)
11:50-12:10	**Burning before painting: Synchrotron Radiation X-ray and Micro-XRF based Characterisation of rock art pigments from Karim Cave, Sangkulirang-Mangkalihat site, East Borneo, Indonesia** Moh Mualliful ILMI, Institute of Technology, Bandung
12:10-13:40	*Lunch at the EPN campus restaurant*
SESSION V - INKS AND PAPYRUS ***(Chairperson: C. Dejoie)***	
13:40-14:00	**Structural and spectroscopic analyses of ancient black pigments from Roman archaeological sites** Maria Cristina GAMBERINI, University of Modena, Department of Life Science
14:00-14:20	**Elephantine: Challenges and first results on papyrus research** V. LEPPER and H.-E. MAHNKE, Ägyptisches Museum und Papyrussammlung Berlin
14:20-14:40	**Retrieval of the lost literature from the Herculaneum Papyri with the XRF Microscopy** Luxi LI, Advanced Photon Source APS
SESSION VI - DEEP LEARNING ***(Chairperson: A. Goetz)***	
14:40-15:00	**Visibility Enhancement of Heritage Materials Through Deep Learning** James BRUSUELAS, University of Kentucky, Computer Science Department
15:00-15:20	**Automated Segmentation of Microtomography Imaging Using Machine Learning** Johann BRIFFA, University of Malta
15:20-15:50	*Coffee break*
SESSION VII - PALAEONTOLOGY II ***(Chairperson: V. Fernandez)***	
15:50-16:30	**Three-dimensional virtual bone histology of early tetrapods revealed by synchrotron light** Sophie SANCHEZ, Uppsala University, Department of Organismal Biology
16:30-16:50	**A lost world in sausage-shaped packages: synchrotron microtomography of fossil droppings as a tool for investigating ancient ecosystems** Per AHLBERG, Department of Organismal Biology, Uppsala University
16:50-17:10	**X-ray Raman scattering: A hard X-ray probe for the study of cultural and natural heritage** Rafaella GEORGIOU, IPANEMA c/o synchrotron SOLEIL
Transfer to Grenoble Museum	
18:30-20:00	Social programme: General public conference & private access at the Grenoble Museum
20:00-22:00	Workshop Dinner: Patio of Grenoble Museum

Friday 24 January

TUTORIALS (2) / PRACTICAL (1)	
09:00-10:00	PyMca ROI Imaging & Phase identification / Tomography
10:00-10:30	*Coffee break*
BEAMLINES POST ESRF-UPGRADE PHASE 2	
10:30-10:50	**Introduction** (J. Susini, Director of Research, ESRF)
10:50-11:10	**X-ray tomography beamlines** (P. Tafforeau, Scientist at the ESRF)
11:10-11:30	**X-ray diffraction beamlines** (C. Dejoie, Scientist at the ESRF)
11:30-11:50	**X-ray spectroscopy beamlines** (M. Cotte, Scientist at the ESRF)
11:50-12:10	**ILL** (J. Beaucour, C. Mondelli, ILL)
12:10-13:30	*Lunch at the EPN campus restaurant*
BEYOND INSTRUMENTS AND DATA COLLECTION	
13:30-13:40	**Introduction** (M. Cotte, Scientist at the ESRF)
13:40-14:10	**Access models** (J. McCarthy, Head of User Office)
14:10-14:25	**Proprietary research** (E. Mitchell, Head of Business Development Office, ESRF)
14:25-14:50	**Data policy and data management** (A. Goetz, Head of Software Group)
14:50-15:30	Discussion and Conclusions
End of the Workshop	
16:00-18:00	Social programme: Visit of Grenoble street art

LIST OF SPEAKER ABSTRACTS

10 Years of Synchrotron and sediba

L.R. Berger

Phillip Tobias Chair in Palaeoanthropology, Evolutionary Studies Institute, The University of the Witwatersrand, Johannesburg, South Africa
Lee.Berger@Wits.ac.za

In 2010 the first synchrotron images of the 2-million-year-old *Australopithecus sediba* fossils, from the Malapa site in South Africa were made at the European Synchrotron Radiation Facility (ESRF) in Grenoble France. The resulting data, along with that from subsequent scanning efforts, have been used in a large number of scientific and popular publications and resulted in many significant and important discoveries. This original synchrotron data continues to play an important part in research to this day. The data from these scanning efforts also produced many important images that have improved the outreach work around *Au. sediba*, ensuring quality transmission of scientific information to both the Academy and the public. This work conducted a decade ago, still provides the gold standard for imaging of these fossils. Over a decade of testing alternate methods of imaging including high resolution scanning using both industrial and military grade micro-focus computed tomography on fossils and large blocks of breccia containing hominid fossils, has demonstrated that synchrotron scanning continues to be the gold standard for imaging of the material from Malapa and thus likely other southern African Plio-Pleistocene aged fossil-bearing sites. These results hold promise for significant future discoveries and work using synchrotron radiation, particularly if beam lines can be developed that can take larger and heavier fossils, and rocks containing fossils.

Synchrotron X-ray imaging enables 3D quantification of bone microstructures across fossil and modern bird-line archosaurs

D.F.A.E. Voeten[1,2], P. Tafforeau[2], and S. Sanchez[1,2]

[1]Uppsala University, Subdepartment of Evolution and Development, Department of Organismal Biology, Evolutionary Biology Centre, Norbyvägen 18A, 752 36 Uppsala, Sweden. [2]European Synchrotron Radiation Facility, 71 Avenue des Martyrs, CS-40220, 38043 Grenoble Cedex, France

dennis.voeten01@upol.cz

The origin and early establishment of feathered flight (> 150 million years ago) ultimately allowed one group of dinosaurs to negotiate the end-Mesozoic mass extinction event (~ 66 million years ago). Although early birds diversified into the most speciose living tetrapod clade, many crucial evolutionary adaptations to early dinosaurian flight remain unresolved.

Fossilised bone represents a valuable archive that not only recorded macromorphological adaptations, but also registered microstructural indicators for life history, metabolic activity, and biomechanical optimisation. Osteohistological thin sectioning still grants unparalleled resolution, colour information, and cross-polarised details. However, destructive sampling prevents inclusion of high-profile fossils and microscopic slides only cover a limited depth.

We sampled a representative assemblage of fossil and modern archosaurs with propagation phase-contrast synchrotron X-ray micro-computed tomography, which is nondestructive, at the beamlines BM05, ID17, and ID19 of the ESRF. Vascular infrastructures that evolved under the influence of niche-specific physiological constraints were visualised in 3D. Their orientation was quantitatively characterised along the avian ancestry (**Fig. 1**) to identify structural signatures associated with archosaurian physiological and locomotory flexibility.

Ongoing improvement of the ESRF synchrotron, including implementation of the Extremely Brilliant Source, continues to expand the possibilities for nondestructive visualisation of materials. The new beamline BM18 will fuel innovative applications for high-energy, hierarchical multi-scale imaging of most fossil tissues and materials. In this context, our example not only offers insight into bone structural adaptations to archosaurian flight but will also serve future (palaeo-) biological and material science studies.

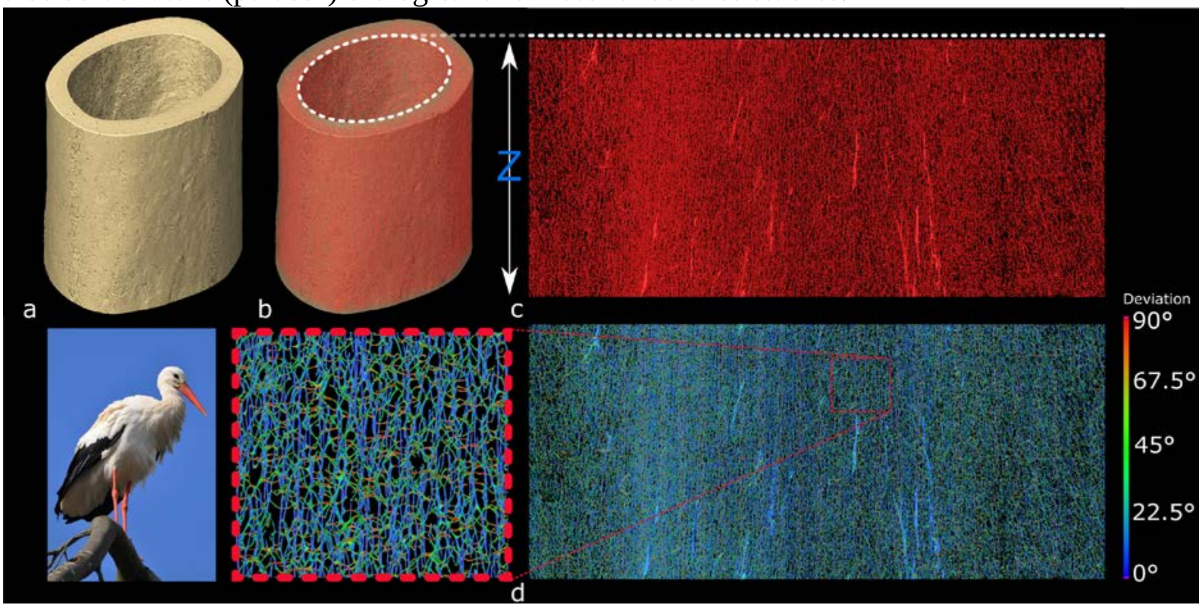


Figure 1: The ulnar mid-diaphysis (a) of the stork *Ciconia ciconia* and its vascular mesh (b). We virtually 'unrolled' the vascular mesh (c) and visualised and quantified local deviations from the bone long axis (d).

Digging virtually into large fossils using synchrotron X-ray microtomography

V. Fernandez[1], K. Chapelle[2], J. Choiniere[2], V. Radermacher[2]

Natural History Museum, Imaging and Analysis Centre, Cromwell Road, SW7 5 BD, London, UK, [1]European synchrotron radiation facility, 71 rue des Martyrs, 38000 Grenoble, France, [2]Evolutionary Studies Institute, University of the Witwatersrand, Yale Rd, Johannesburg, 2000, South Africa,
v.fernandez@nhm.ac.uk

Palaeontologists have become regular users of X-ray computed tomography (CT) facilities to study fossils in a non-destructive way. Beyond the conservation aspect, X-ray CT offered the possibility to study samples in 3 dimensions, gaining extra information. The use of synchrotron radiation as a source was driven by specific characteristics. The brilliance, parallel geometry, and coherence of the beam participated in opening new opportunities compared to laboratory sources. At its debut, synchrotron light source experiments focussed mostly on small fossils, benefiting of the partial spatial coherence of the beam to use propagation phase contrast micro-CT. The increase in sensitivity from this technique allowed to show fossils that remained invisible with classical absorption based micro-CT [1-3]. Characterisation of large sample was challenging. While the synchrotron light is considerably more brilliant than laboratory sources, the energy available still limited sample to 15 cm in diameter, providing they were not abnormally dense (i.e., compared to common sedimentary rocks). The development of optics and other imaging protocols progressively allowed for horizontal field of view up to 25 cm, gradually introduced larger specimens. Combining the advantages of several beamlines (i.e. BM05, ID17 and ID19 at the ESRF), it was first possible to image specimens up to 25 cm in width and near 60 cm in length in their entirety, and then to focus on a region of interest at higher resolution [4,5]. The limit was hit with a large fossilised burrow cast enclosing skeletal material inside. The cast of the terminal chamber was excavated in two blocs of roughly 25x30x35 cm in size. For such a size, it was possible to either image each bloc individually on ID17 with a Germanium detector, but with a resolution so low that bones were almost invisible; or using the more coherent and more energetic beam of ID19 to reach 25 µm resolution and see the bones, limiting the analysed volume to a diameter of ~80 mm. While the equipment and synchrotron beam available before the EBS upgrade allowed the imaging of numerous iconic fossils (including several small sized dinosaurs and *Archaeopteryx*), the new ESRF-EBS and the new BM18 beamline should once more push this limits several steps further.

References

[1] - P. Tafforeau, R. Boistel, E. Boller, A. Bravin, M. Brunet, Y. Chaimanee, P. Cloetens, M. Feist, J. Hoszowska and J.J. Jaeger. Applied Physics A: Materials Science & Processing **83** (2), 195-202 (2006).
[2] - M. Lak, D. Néraudeau, A. Nel, P. Cloetens, V. Perrichot and P. Tafforeau. Microscopy and microanalysis **14** (3), 251-259 (2008).
[3] - V. Fernandez, E. Buffetaut, E. Maire, J. Adrien, V. Suteethorn and P. Tafforeau. Microscopy and microanalysis **18** (01), 179-185 (2012).
[4] - A. Cau, V. Beyrand, D.F.A.E. Voeten, V. Fernandez, P. Tafforeau, K. Stein, R. Barsbold, K. Tsogtbaatar, P.J. Currie and P. Godefroit. Nature **552** (7685), 395 (2017).
[5] - D.F. Voeten, J. Cubo, E. De Margerie, M. Röper, V. Beyrand, S. Bureš, P. Tafforeau and S. Sanchez. Nature communications **9** (1), 923 (2018).

Cultural Heritage & Synchrotron Radiation: Quo Vadis?

Koen Janssens

Faculty of Science, University of Antwerp, Belgium
koen.janssens@uantwerpen.be

Synchrotron radiation is being used to an increasing extent to examine cultural heritage (CH) materials and artefacts. In this presentation, an attempt will be made to provide an overview of activities during the last five years and to highlight some trends. As the basis of this presentation, a number of recently reviews will be used,[1-3] as well as the scientific programmes of the last few editions of the Synchrotron Radiation in Art and Archaeology (SR2A) conference.

Broadly speaking, synchrotron radiation based investigations of cultural heritage materials can be divided into two categories: those mainly targeted towards imaging, usually with the aim of better understanding the build-up, the creation process and/or the current state of conservation of specific CH artefacts. Such imaging can be executed at different length scales but usually involves the macroscopic level, as most CH artefacts have 'human' dimensions, i.e., in the cm-m range.
To complement such studies, in a second category of investigations, the materials that comprise CH artefacts, but no longer the artefacts as a whole, are the focus of attention. In many cases, next to (minute samples of) original artefacts, attention is devoted to series of self-synthesized modern equivalents (mock-ups) that have been prepared in well-controlled laboratory circumstances. The combined study of original and mock-up samples of this kind usually serves to experimentally verify one or more hypotheses on the (ancient) manufacturing technology employed to produce a particular CH material and/or to study the way this material responds to physical and chemical agents during the course of its lifetime.

References

[1] K. Janssens, M. Cotte, The use of XAS and related methods in Cultural Heritage investigations. International Tables for Crystallography, Vol. I, Chapter 8.16 (in press, 2019).

[2] M. Cotte, A. Genty-Vincent, K. Janssens, J. Susini, Applications of synchrotron X-ray nano-probes in the field of cultural heritage - Application des nano-faisceaux de rayons X synchrotron dans le domaine du patrimoine, Comptes Rendus Physique 19 (2018) 575-588. https://doi.org/10.1016/j.crhy.2018.07.002

[3] K. Janssens and M. Cotte, Using Synchrotron Radiation for Characterization of Cultural Heritage Materials, in: E. J. Jaeschke et al. (eds.), Synchrotron Light Sources and Free-Electron Lasers, https://doi.org/10.1007/978-3-319-04507-8_78-1, Springer Nature Switzerland AG 2019.

Colour Enamels in the Modernist Catalan stained glasses from Barcelona

M. Beltran[1], T. Pradell[1]

[1]Physics Department and Barcelona Research Centre in Multiscale Science and Engineering, Universitat Politècnica de Catalunya, Campus Diagonal Besòs, Av. Eduard Maristany, 10-14 08019 Barcelona, Spain

marti.beltran@upc.edu

Modernist stained glasses are a beautiful and fragile component of our Cultural Heritage. During the last years of the 19th century Catalonian glass makers were strongly influenced by the beauty of the large medieval and renaissance glasses that decorate the walls of churches and developed a new style that combines the use of glasses of different textures either coloured or transparent, but also made extensive use of enamels, consisting of a thin coloured glass layer fixed over a transparent base glass. The colour is given by the addition of metallic ions or of micrometric/nanometric pigment particles to the glass phase. In particular, Modernist enamels have been found to have a lead-zinc borosilicate glass (30-40 mol%PbO, 10-30 mol%B_2O_3 and 0-20 mol%ZbO) which has a low softening temperature (between 580 °C and 620 °C), adequate to fix the enamel to the base glass without affecting its mechanical integrity [1] and which are fairly stable to water corrosion. The applied enamels form a thin layer measuring from a few to some tens of micrometers. Due to its functional use as a windows of buildings the stained glasses have been exposed to the weathering and to the effects of the solar exposure for more than 100 years and today we can observe an evident degradation in some of them. The aim of this paper is to present the results of the research we have done from a collection of historical modernist stained glasses produced by the most important modernist workshops from Barcelona in close collaboration with J. Bonet Vitralls S.L., a company dedicated to the production and retoration of stain glass. LA-ICP-MS has been performed to determine the chemical composition of the enamels and SEM and micro-XRD to determine the micro and nanocrystalline compounds present in the layers, including the original pigment particles, reaction compounds produced during the fixing of the enamels to the base glass and the compounds formed due to the alteration/weathering of the enamels. The identification of the micro and nanocrystalline compounds present in the enamels together with the weathering compounds formed gives clues about their role in the degradation of the layers. Finally, it is also important to determine the presence of compounds which may compromise the stability of the decorative layers in order to propose strategies for its conservation.

References

[1] - M. Beltrán, F. Brock and T. Pradell, "Thermal properties and stability of Catalan Modernist blue and green enamels", *International Journal of Applied Glass Science*,Vol 10, Issue 3, 414-425 (2019).

Complementary use of SR and neutrons for heritage study at NRC "Kurchatov institute"

Elena Tereschenko[1,2], Alexei Veligzhanin[1], Konstantin Poduretz[1], Ekaterina Kovalenko[1], Roman Svetogorov[1], Pavel Kashkarov[1], Ekaterina Yatsishina[1]

1 National Research Centre "Kurchatov Institute", Moscow, Russia
2 Federal Scientific Research Centre "Crystallography and photonics" Russian Academy of Sciences, Moscow, Russia
tereschenko_EY@nrcki.ru

The variety of cultural heritage objects and the wide range of the solved tasks determine a diverse sets of methods that should be used for the researches. The complementary combination of synchrotron and neutron diagnostic methods as well as a number of laboratory methods (including electron microscopy, mass-spectrometry, optical spectrometry and else) allows to realize the mostly complete study of such objects.

The most striking instances of the comprehensive studies on exhibits from the old museum collections of the State Historical museum and The Pushkin State Museum of Fine Arts and the new archaeological finds will be presented.

The selection of methods for the study of artifacts was determined not only by the characteristics of the materials (metals, ceramics, stones, etc), the preservation state surface and inner structure of the objects, the possibility of microprobe sampling, but also the concrete historical targets.

The studies are partially supported by grants (RSF 17-18-01399, RFBR – 17-29-04144, 17-29-04201, 17-29-04129)/

Probing the degradation mechanisms of artists' pigments by different 2D XANES-based approaches

L. Monico,[1,2,3] M. Cotte,[4,5] K. Janssens,[3] W. De Nolf,[4] A. Romani,[2,1] C. Miliani.[2,6]

[1] CNR-Scitec, c/o Department of Chemistry, Biology and Biotechnology, University of Perugia, via Elce di Sotto 8, 06123 Perugia (Italy).
[2] SMAArt Centre and Department of Chemistry, Biology and Biotechnology, University of Perugia, via Elce di Sotto 8, 06123 Perugia (Italy).
[3] AXES, Department of Chemistry, University of Antwerp, Groenenborgerlaan 171, 2020 Antwerp (Belgium).
[4] ESRF, 71 Avenue des Martyrs, 38000 Grenoble (France).
[5] L.A.M.S., CNRS UMR 8220, Sorbonne Université, UPMC Univ Paris 06, 4 place Jussieu 75005, Paris (France).
[6] CNR-ISPC (Istituto CNR di Scienze del Patrimonio Culturale), via Cardinale Guglielmo Sanfelice 8, 80134 Napoli (Italy).
letizia.monico@cnr.it

In the field of Heritage Science, chemical analysis are made complicated by the fact that objects consist of multilayered and heterogeneous networks composed of organic and inorganic compounds with amorphous and/or crystalline structures that undergo chemical transformations over time. In this context, the use of synchrotron radiation (SR)-based X-ray micro-spectroscopic methods, such as μ-XRF, μ-XANES and μ-XRD, has grown within the last decade due to their ability to provide elemental and molecular speciation information with spatial resolution down to the (sub)micrometer length scale. [1-3]

Currently, technological research perspectives call for a time acquisition reduction in order not only to render the 2D/3D mapping of large areas more feasible but also to avoid/minimize possible damages of samples induced by the exposure to SR X-ray beams.

Usually, three 2D XANES-based approaches are employed to gather chemical speciation information:
i) analysis of one or more regions of interest by recording μ-XRF maps at a few different energies around the absorption edge of a specific element combined with the acquisition of a series of single-point XRF-mode μ-XANES spectra at a limited number of spots;
ii) full-spectral XANES imaging in XRF-mode (using either traditional ED-XRF or fast X-ray detectors);
iii) transmission-mode full-field XANES imaging.

These approaches have found a wide range of applications, such as the investigation of degradation mechanisms of different artists' pigments and of manufacturing processes of ceramics. [4-11]

In this contribution, the advantages and drawbacks of the three above-mentioned 2D XANES-based approaches in the context of the degradation processes of various artists' pigments, including chrome yellows, cadmium yellows and Prussian blues, will be presented. In particular, XANES/XRF data obtained at ESRF-ID21 beamline [3] from the investigation of artificially aged mock-up paints and paint micro-samples from original paintings will be discussed. These results will be integrated with those recorded directly at the surface of the paintings by means of non-invasive portable equipments.

References:
[1] K. Janssens, G. Van der Snickt, et al. Non-Invasive and Non-Destructive Examination of Artistic Pigments, Paints, and Paintings by Means of X-Ray Methods. In: *Analytical Chemistry for Cultural Heritage. Topics in Current Chemistry Collections.* Mazzeo R. (Ed.) Springer, Cham, **2017**, pp. 77-128.
[2] L. Bertrand, S. Bernard, et al. Emerging Approaches in Synchrotron Studies of Materials from Cultural and Natural History Collections. In: *Analytical Chemistry for Cultural Heritage. Topics in Current Chemistry Collections.* Mazzeo R. (Ed.), Springer, Cham, **2017**, pp. 1-39.
[3] M. Cotte, E. Pouyet, et al., *J. Anal. Atom. Spectrom.* **2017**, *32*, 477.
[4] L. Monico, K. Janssens, et al., *Angew. Chem. Int. Edit.* **2015**, *127*, 13923.
[5] L. Monico, K. Janssens, et al., *J. Anal. At. Spectrom.* **2015**, *30*, 613.
[6] L. Monico, K. Janssens, et al., *Anal. Chem.* **2014**, *86*, 10804.
[7] L. Monico, L. Sorace, et al., *ACS Omega* **2019**, *4*, 6607.
[8] E. Pouyet, M. Cotte, *Appl. Phys. A: Mater. Sci. Process.* **2015**, *121*, 967.
[9] L. Monico, A. Chieli, et al. *Chem. Eur. J.* **2018**, *24*, 11584.
[10] F. Meirer, Y. Liu, et al. *J. Anal. At. Spectrom.* **2013**, *28*, 1870.
[11] T. Wang, T.Q. Zhu, et al. *Anal. Chim. Acta* **2016**, *928*, 20.

The criticality of synchrotron techniques in developing new conservation strategies to characterise and stabilise marine archaeological artefacts

E. J. Schofield[1]

[1]Mary Rose Trust, HM Naval Base, College Road, Portsmouth, PO1, 3LX
e.schofield@maryrose.org

Marine archaeological artefacts exhibit properties which differ from their original material due to a combination of degradation, the incorporation of foreign species from the seawater, and their experience post-excavation. These induce chemical, biological and mechanical changes which fundamentally change the material and its stability. Displaying these artefacts is only possible when we understand the material properties, which in turn gives us the ability to develop new and tailor-made conservation treatments.

This talk will focus on two particularly challenging materials to conserve; marine archaeological wood and iron [1]. Both were recovered, in abundance, from the *Mary Rose*, Henry VIII's warship which was recovered in 1982 after 437 years under the seabed. Foreign species lodged in the materials can have a deleterious effect when the material is dry. In the case of marine archaeological iron this is the presence of chlorine from the salt in seawater [2], whereas in the wood it is due to deposits present from the seawater (e.g. S, Fe, Zn) and corroded artefacts [3]. Synchrotron based x-ray analysis has been critical in gleaning information on the degradation processes at play and the products formed. It has allowed the tracking of these species as they chemically transform over time and determining how they are distributed throughout the artefacts. An overview will be given of the suite of techniques used, our present understanding of the degradation mechanisms at play and the new targeted conservation treatments currently being developed.

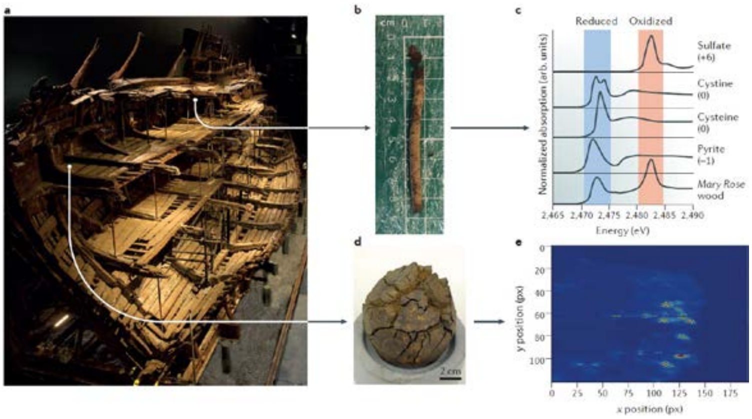


Figure 1: The Mary Rose hull (a) sampled (b) to record the change in sulfur using x-ray absoprtion Spectroscopy (c) and a cannnonball (d) used to map Cl via x-ray fluoresence mapping (e)

References
[1] Schofield, E. J., "Illuminating the past: X-ray analysis of our cultural heritage" *Nat. Rev. Mater.* 3, 285-287, 2018
[2] Simon, H., Cibin, G., Robbins, P., Day, S., Tang, C., Freestone, I., and Schofield, E. "A Synchrotron-Based Study of the *Mary Rose* Iron Cannonballs" *Angewandte Chemie International Edition*, 57(25), Pages 7390-7395, 2018
[3] Schofield, E. J., Sarangi, R., Mehta, A., Jones, A. M. and Chadwick, A. V. "Nanotechnology and Synchrotron light in the service of Henry VIII: preserving the *Mary Rose*" *Materials Today*, Vol 14 (7-8) Pages: 354-358 2011

3D Visualization of the Effect of Light Aging on Orpiment Pigment Particles

F.T.H. Broers[1], F. Meirer[2], J. Nelson Weker[3], K. Janssens[4] and K. Keune[1,5]

[1]Rijksmuseum Amsterdam, Conservation and Science, Amsterdam, The Netherlands, [2]Inorganic Chemistry and Catalysis, Debye Institute for Nanomaterials Science, Utrecht University [3]Stanford Synchrotron Radiation Lightsource, SLAC National Accelerator Lab, CA 94025, USA [4]Department of Chemistry, AXES Research Group, University of Antwerp, Antwerp, Belgium
[5]Van 't Hoff Institute for Molecular Sciences, University of Amsterdam
f.broers@rijksmuseum.nl

Photo degradation of pigments used in (oil) paintings is unfortunately rather common. One of the classes of pigments that is known to photodegrade are arsenic sulphide pigments. The photo degradation of orpiment (As_2S_3) and realgar (As_4S_4) leads to the formation of arsenolite (As_2O_3) and other degradation products [1][2]. The exact degradation pathway is not yet clear and also the migration of arsenic degradation products throughout the multiple layers of a painting is not yet understood [3]. To understand the complete degradation pathway, in this study we focus on the effect of artificial light ageing on pigments particles on a nanometric scale.
The alteration of orpiment pigment particles due to light is visualized using Transmission X-ray Microscopy (TXM). The measurements were performed at beamline 6-2c at the Stanford Synchrotron Radiation Lightsource. It was clearly observed that the structure of the pigment particle had changed. These results are supported by Scanning Electron Microscopy (SEM) images in which a clear difference is seen between the area that was exposed to light and the area that was not exposed. For the TXM experiment, multiple field of views had to be recorded using mosaic imaging. The multiple field of views were afterwards stitched using the Mosaic Image Stitcher in TXM-Wizard software [4]. After aligning and reconstruction of the tomographic data in TXM-Wizard, the data was visualized in 3D using the AVIZO software package. As TXM was performed at different energies around the As K-edge, information on the 3D distribution of arsenic degradation species was obtained.

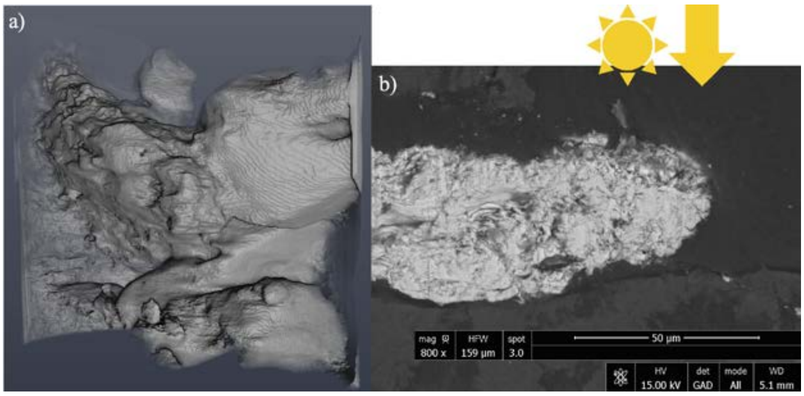


Figure 1: a) 3D visualization of light aged As_2S_3 pigment particles obtained by TXM shows an alteration in the morphology of the pigment particles b) SEM image of light aged As_2S_3 pigment particles in Paraloid B-72 resin. Left side of the pigment particles were covered by PTFE tape, blocking direct illumination.

References

[1] - A. Wallert, Maltechnik Restauro **90**, 45–58 (1984).
[2] - K. Trentelman and L. Stodulski, Analytical Chemistry **68**, 10 (1996).
[3] – K. Keune et al., J. Anal. At. Spectrom. **30** ,813–827 (2015).
[4] - Y.Liu et al., J. Synchrotron Rad. **19**, 281–287 (2012).

Structural studies of historical inorganic pigments using synchrotron radiation: capacities and future applications

Victor Gonzalez

Science Department, Rijksmuseum, Amsterdam, The Netherlands
v.gonzalez@rijksmuseum.nl

Omnipresent in paintings since the Antiquity, inorganic pigments are key materials of art history. Collecting accurate chemical information on them is thus essential today to achieve a better understanding of ancient pictorial practices, as well as to develop new conservation strategies. However, this objective faces a major scientific challenge: historical pigments are materials of high complexity. They were often obtained in the past through elaborate synthesis procedures, then mixed and used following the artists' know-how, which might no longer be known today. Finally paintings are dynamic systems: chemical interactions within paint layers can result in the *in-situ* formation of non-original crystalline compounds.

Among the multiple techniques available at synchrotron facilities, X-ray Diffraction (XRD) is particularly suited for the study of inorganic pigments. Relying on the analytical power of synchrotron radiation, XRD indeed enables to discriminate between the multiple inorganic products present in complex paint stratigraphies at the micrometric scale, but also to provide detailed information on their composition and microstructure. These results not only allow insights into the ancient artistic processes but also yield precious assets for the long term preservation of paintworks.

This talk will present recent research performed at several Synchrotron facilities, especially the ESRF, aimed at revealing the ancient syntheses of inorganic pigments, and deciphering the potential degradation mechanisms affecting historical pictorial matter. The communication will notably illustrate the complementarity of structural data collected using various analytical configurations, among them High-angular resolution XRD and High-angular resolution XRD.

Finally, by presenting some future challenges with potential ground-breaking impact in the study of historical artifacts, the communication will attempt to trigger discussion on the expectations from the Cultural Heritage community regarding the ESRF-EBS.

Shed light on the schematic paintings of Savoy: the use of µXRD to understand the painted wall

E. Chalmin[1], F. Kergoulay[2], A. Chassin de Kergommeaux[1], P. Martinetto[2], N. Blanc[2], N. Boudet[2], C. Defrasne[3]

[1] Univ. Savoie Mont Blanc, CNRS, EDYTEM (UMR 5204), Le Bourget du Lac cedex, France, **emilie.chalmin-aljanabi@univ-smb.fr**
[2] Univ. Grenoble Alpes, CNRS, Grenoble INP, Institut Néel, 38000 Grenoble, France
[3] Univ. Aix Marseille, CNRS, Ministère de la Culture, LAMPEA (UMR 7269), Aix-en-Provence, France

Schematic prehistoric rock paintings, extending across the Iberian Peninsula to the Italian Piedmont, are mainly attributed to the Neolithic period from the archaeological context, whereas absolute dating has never been realized on the mineral pigments. The Rocher du Chateau (1750 m, Bessans, Savoie, France) is one of the western Alps sites which presents schematic paintings and appears as a key site to address chronological issue, due to the presence of coloring matter discovered during excavation and dating back to 4600-4000 BC. This context provides an unique opportunity to conduct an integrated study and to investigate the coloring matter used in the paintings.
One of the limitations of this study is due to the weathering process affecting the rock surface before and after the application of the paint. The presence of the mineral accretions or crusts limits the access to the coloring matter, either during *in situ* analysis (such as portable Raman) or during the analysis of micro-samples. However understanding these weathering processes makes it possible to respond to two challenges: (i) to distinguish the components of the pictorial material, (ii) to evaluate the possibility of dating the concretions and to propose a chronological interval for the realization of the paints.
A combined approach has been developed on the Rocher du Château site using both *in situ* methods and analyses of micro-samples and excavated coloring matter [1]. To understand the complex stratigraphy of the micro-samples and to identify the mineral accretion, the use of the µXRD based on synchrotron radiation remains essential to identify crystalline phases in very small, fragile and complex objects. Thanks to the brightness of the micro-beam and the absence of preparation, the ID22 and D2AM beamlines of ESRF are very suitable to characterize the thinness (< 5µm) of the painting layers and the complex mixture of some coloring matter from the excavation. The anthropogenic origin of this complex mixture is confirmed by the presence of charcoal mixed with large muscovite, small rounded quartz, and potentially hematite.
Finally, we highlighted and explained here the taphonomic processes of the painted rock wall and determined the geological origin of coloring matter. This appears to be essential in order to reinforce comparisons between rock paintings and dated excavated pigments and other pigmented materials.

This work is supported by the French National Research Agency in the framework of the Investissements d'Avenir program (ANR-15-IDEX-02, CDP Patrimalp) and the DRAC (Direction régionales des affaires culturelles) Auvergne-Rhône-Alpes.

References

[1] - Defrasne, C., E. Chalmin, L. Bellot-Gurlet and E. Thirault 2019. "From archaeological layers to schematic rock art? Integrated study of the Neolithic coloring materials at the Rocher du Château (Western Alps, Savoy, France)." Journal of Anthropological and Archaeological Sciences on line.

Burning before painting: Synchrotron Radiation X-ray and Micro-XRF based Characterisation of rock art pigments from Karim Cave, Sangkulirang-Mangkalihat site, East Borneo, Indonesia

M. M. Ilmi[1,†], N. Nurdini[1], P. Setiawan[2], Ismunandar[1,‡], G. T. M. Kadja[1,3,*]

[1]Division of Inorganic and Physical Chemistry, Institut Teknologi Bandung, Bandung Indonesia.
[2]Visual Communication and Multimedia, Institut Teknologi Bandung, Bandung, Indonesia.
[3]Research Center for Nanosciences and Nanotechnology, Institut Teknologi Bandung, Indonesia.
[†]**ilmi.kimia@gmail.com**, [‡]ismu@chem.itb.ac.id, *kadja@chem.itb.ac.id,

Borneo island, Indonesia is a home for thousands of rock art depicted on the cave wall with various of motifs and hues. Leang Karim cave, located in Sangkulirang-Mangkalihat karst, East borneo displayed interesting rock art images with pigment varies from light red to purple. This different colour of pigment may due to different properties of pigment. This work try to introduce a scientific technique using combined synchrotron radiation X-ray including powder diffraction (SR-XRD) and X-ray absorption near edge spectroscopy (XANES) and micro-XRF to determine the components, composition, and electronic properties of the rock art pigment material. Chemical component characterization by using SR-XRD assigned that hematite is main component of pigment material with the presence of calcite and gypsum as cave wall minerals. The diffractogram of purple sample show sharper hematite peak due to higher crystallite size and lower crystallite strain. From chemical composition analysis by using micro-XRF, purple sample showed higher iron oxide content compared to another samples. The identification of electronic properties of pigment material was carried out using XANES which showed that the deconvolution of pre-edge peak of purple reveals that the $4T_{1g}$ peaks are relatively becomes lower than $4T_{2g}$ due to shift of favourable transition condition. This phenomena was found when the hematite compound was heated above temperature of 900ºC. It was responsible to the distortion of octahedral symmetry of the crystal system and change favourable transition condition. Analysis of Linear Combination Fitting on Pre-edge region of Fe K-edge XANES spectra of each sample showed the pure composition of the hematite phase (~100%). As result, we conclude that each pigment consist of hematite phase with different crystallite properties. According to XRD and Fe K-edge XANES analysis of KBL sample showed higher crystallite size and distorted crystallite structure due to temperature treatment (by burning) of pigment material.

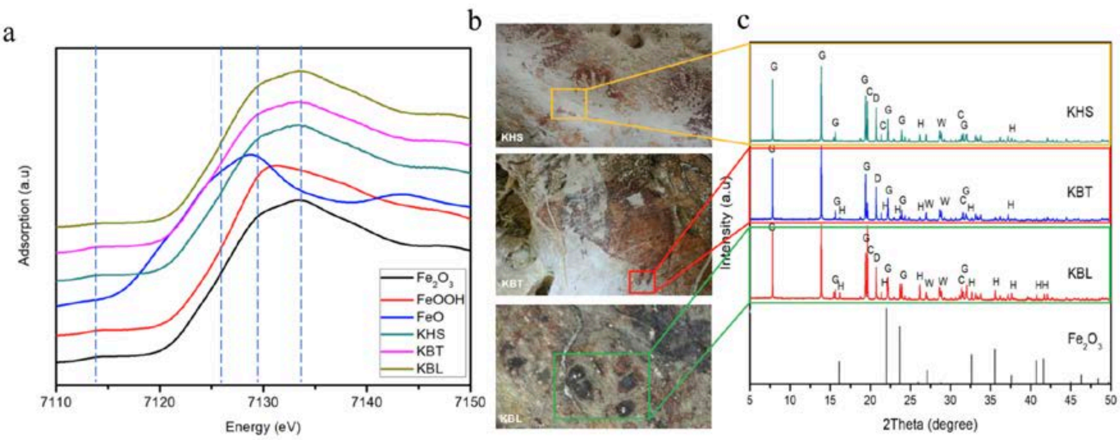


Figure 1. Pre-edge region of Fe K-edge XANES spectra (a), sampling spot of each pigment (b), X-ray diffraction pattern of each pigments (c).

Structural and spectroscopic analyses of ancient black pigments from Roman archaeological sites

M. C. Gamberini[1]*, P.-O. Autran[2,3,4], Cecilia Baraldi[1], C. Dejoie[2], P. Martinetto[3,4] and P. Walter[5]

[1]Department of Life Science, University of Modena and Reggio Emilia, Via Campi 103, Modena, Italy
[2]European Synchrotron Radiation Facility, 71 Avenue des Martyrs, 38000 Grenoble, France
[3]Univ. Grenoble Alpes, Inst NEEL, 25 rue des Martyrs BP 166, 38042 Grenoble, France
[4]CNRS, Inst NEEL, 25 rue des Martyrs BP 166, 38042 Grenoble, France
[5]UPMC Univ Paris 06, CNRS, UMR 8220, Laboratoire d'archéologie moléculaire et structurale (LAMS), Sorbonne Universités, F-75005 Paris, France
mariacristina.gamberini@unimore.it

The aim of our project is to identify and describe the structure of the main phases found in ancient pigments dating from the Roman period, in particular from Italian and Sicilian archaeological sites. We focus in particular on black pigments possibly used as cosmetics, paintings or inks. Several black powders from different contexts have been considered: 15 samples from Italy, Salinas Museum (Palermo), 12 from Mozia island, 2 from Baglio museum (Marsala), 5 from Ercolano excavation and 31 found in Pompeii [1] The samples were found in different types of containers (cylindrical theca atramentaria, unguentaries and aryballoi), and analysed in order to characterize their elemental and structural composition. To do so, a multi-analytical approach was adopted, which involved the use of Fourier-transformed infrared spectroscopy, Raman, X-ray fluorescence and X-ray powder diffraction.

High resolution X-ray powder diffraction and X-ray fluorescence were performed on the ID22 beamline at the ESRF. Taking advantage of the high flux of the synchrotron, a batch of the most relevant samples, in sealed capillaries, was measured to identify the crystalline phases using complementary information from both diffraction and fluorescence signals. The diffraction data analysis indicates that the crystalline part corresponds mainly to quartz, calcite, gypsum or other non-black minerals. The black powders show a composition based mostly on the presence of carbon black. The additional inorganic components may give an indication of the everyday use of the pigments as writing inks, cosmetics or painting material [2]. Furthermore, the composition profile of the samples could be a starting point for reflection to link the content to the type of its container.

Keywords: FTIR, Raman spectroscopy, X-ray powder diffraction

References

[1] A multi-analytical approach for the characterization of powders from the Pompeii archaeological site", C. Canevali, P. Gentile, M. Orlandi, F. Modugno, J.J. Lucejko, M.P. Colombini, L. Brambilla, S. Goidanich, C. Riedo, O. Chiantore, P. Baraldi, C. Baraldi, M.C. Gamberini; Anal Bioanal Chem 401 (2011) 1801–1814
[2] Cersoy S., Martinetto P., Bordet P., Hodeau J.-L., Van Elslande E. and Walter Ph. (2016) – Identifying and quantifying amorphous and crystalline content in complex powdered samples: application to archaeological carbon blacks, *J. Appl. Cryst.* 49, 585-593, doi: 10.1107/S1600576716003551

Elephantine: Challenges and first results on papyrus research

V. Lepper[1,2] and H.-E. Mahnke[1,3,4]

[1]Ägyptisches Museum und Papyrussammlung, Berlin, Germany, [2]Humboldt Universität zu Berlin, Germany, [3]Freie Universität Berlin, Germany, [4]Helmholtz-Zentrum Berlin, Germany
vlepper@princeton.edu, **hemahnke@zedat.fu-berlin.de**

The ERC Project "Localizing 4000 Years of Cultural History. Texts and Scripts from Elephantine Island" is based at the Ägyptisches Museum und Papyrussammlung, Staatliche Museen zu Berlin, which houses one of the largest papyrus collections from Elephantine. Today, several thousand papyri and other manuscripts from Elephantine are spread throughout more than 60 institutions in 24 different countries. Their texts are written in various languages and scripts, including hieroglyphs, hieratic, demotic, Aramaic, Greek, Coptic and Arabic. 80% of these manuscripts are unpublished. No other settlement in Egypt has been so well documented over such a long period through texts. Its inhabitants comprise a multi-ethnic, multicultural and multi-religious community, which has left behind large amounts of written material, which provides evidence of everyday life from the Old Kingdom up to the era following the Arab conquest. First results of this project will be presented, including access to hidden text due to fading of the ink and revealing texts from folded papyri by virtual unfolding.

The texts are made accessible in an online database, allowing the identification of joins between fragments from different collections. Through international cooperation, the "papyrus puzzle" can thus be solved – with the help of cutting-edge methods from the digital humanities, natural sciences and mathematics.

In cooperation with Tobias Arlt (TU Berlin); Daniel Baum, Hans-Christian Hege, Felix Herter, Norbert Lindow (ZIB); Ingo Manke (HZB); Marc Etienne (Musée du Louvre), Eve Menei (Paris); Tzulia Siopi (ÄMP SPK).

O 15

Investigations of the elemental evidences in Art and Archaeology with the X-ray Fluorescence Microscopy at APS

Luxi Li*[1], Zou Finfrock[1,2], Evan Maxey[1], Evan Saitta[3], Vito Mocella[4]

[1]Advanced Photon Sources, Argonne National Laboratory, 9700 Cass Ave., Lemont, IL 60439, USA; [2]Canadian Light Source Inc. 44 Innovation Boulevard Saskatoon, SK S7N 2V3 Canada; [3] Field Museum of Natural History in Chicago, 1400 S. Lake Shore Dr., Chicago, IL 60605, USA. [4] Italian National Research Council, Via Ulisse Aldrovandi, 16, 00197 Roma, RM, Italy.

***luxili@anl.gov**

The Synchrotron Radiation X-ray Fluorescence Microscopy (XFM) is an indispensable non-destructive method to study the material elemental information. High energy X-ray beam is used to excite the inner shell electron, leaving a vacancy in the atomic structure. To stabilize the atom, an outer shell electron will fill in the vacancy and emit an X-ray photon with a characteristic energy respectively to the element species. Therefore, by detecting energy and the intensity of the emitted X-ray photons, one can identify and quantify the elements in the materials. XFM has high sensitivity and it is well-suited to study trace elements. XFM is a scanning probe technique. The sample is illuminated with an X-ray beam, which an energy dispersive detector is located perpendicular to the X-ray beam direction to measure a full spectrum to resolve the elemental information within the sample illumination volume. While the sample is raster-scanned, one can retrieve the 2D projective elemental information in the material. Combining the raster-scanning strategy with the computerized- tomography, one can probe 3D elemental information. The confocal XFM is another approach to study elemental information in 3D fashion. In this presentation, I will share the current XFM beamline capabilities and demonstrate with a few case studies of XFM application in the Art and Archaeology that are currently ongoing in the Microscopy Group in the Advanced Photon Source, Argonne National Laboratory.

Visibility Enhancement of Heritage Materials Through Deep Learning

J. Brusuelas, S. Parker, S. Parsons, C. Chapman, W. Seales

University of Kentucky Computer Science Department
james.brusuelas@uky.edu

Tomography has become common as a way to see and analyse the internal structure of heritage materials. The brilliance of a synchrotron source gives precise control over incident energies and reduces the time scale for the collection of tomographic images at high spatial resolution, making it a very desirable technique for analysis of heritage samples.

Some of the subtlest features, however, require more than mere data collection in order to be teased out and examined. When the raw materials in a heritage object are similarly radiodense, it can be challenging to simply identify features-of-interest. Carbon inks and pigmentations on damaged writing substrates, such as the papyrus sheets used in the construction of ancient bookrolls, are examples.

We have proposed the use of deep learning techniques, in conjunction with large-scale tomographic "reference libraries," in order to enhance synchrotron-based data acquisition and improve the visibility of difficult-to-see features [1]. This approach fits into our broader software pipeline for "virtual unwrapping" as a useful tool for reading texts from tomographic data without physical restoration [2]. In this talk we will discuss not only our initial results from the application of a deep-learning framework for experimentation in this context, but also our intentional collection and management of important metadata and a custom software setup that we designed to allow the training of our deep learning algorithms within "containers" using cloud-based computational resources.

To provide an expanded scope to the promise and challenge of deep learning methods applied to cultural heritage artifacts, we will present the details of our computational approach and the tradeoffs involved with its practical deployment. Specifically, we will address the challenge of building a supervised reference library and training large scale networks with tomographic data at a massive scale. The computational and representational requirements lead to protocols at scan time that emphasize massive data collection in favor of over-collection, as opposed to tuning and pruning "by sight" without the guidance of a fully trained supervised system. We will present results from recent sessions scanning Herculaneum material at Diamond Light Source, the United Kingdom's national synchrotron light source facility, as well as results obtained on other heritage materials using several different tomographic environments.

References

[1] – Parker CS, Parsons S, Bandy J, Chapman C, Coppens F, Seales WB (2019) From invisibility to readability: Recovering the ink of Herculaneum. PLoS ONE 14(5): e0215775. https://doi.org/10.1371/journal.pone.0215775

[2] – Seales WB, Parker CS, Segal M, Tov E, Shor P, Porath Y (2016) From damage to discovery via virtual unwrapping: Reading the scroll from En-Gedi. Science Advances 2(9): e1601247.

Automated Segmentation of Microtomography Imaging Using Machine Learning

J.A. Briffa, M. Tanti, A. Muscat, R. Farrugia, K. Scerri, G. Valentino, A. Solé[1], P. Tafforeau[1], A. Gotz[1], C. Berruyer[1]

Affiliation: University of Malta, Msida MSD 2080, Malta, [1]European Synchrotron Radiation Facility,
johann.briffa@um.edu.mt

X-ray microtomography using synchrotron radiation can be used to capture volumetric scans at high resolution, and can image soft tissues in the absence of contrast agents thanks to the phase contrast effect. One application is in Egyptology, where animal mummies are scanned and manually segmented into textiles, organic tissues, balm resin, ceramics and bones [1]. This process is very time consuming, taking several weeks even for a small animal mummy.

In the ASEMI (Automated SEgmentation of Microtomography Imaging) project we are developing artificial intelligence techniques to automatically segment volumetric microtomography images, labelling textiles, organic tissues and bones. We use features that combine the voxel intensity, 3D texture and shape to determine the class of every voxel while enforcing continuity across slices. The objective of this approach is to reduce the time required to segment a volume from a few months to a few days or even hours. This would enable the analysis of several related artefacts from museum collections, which is currently not possible for practical reasons. In this presentation we report on our progress to date, showing examples of our automatic process, an analysis of the principal challenges, and our plans for further work.

The ASEMI project is a collaboration between the University of Malta and the European Synchrotron Radiation Facility, and has received funding from the ATTRACT project funded by the EC under Grant Agreement 777222.

References

[1] Porcier S M, Berruyer C, Pasquali S,Ikram S, Berthet D and Tafforeau P. *Wild Crocodile Hunted to Make Mummies in Roman Egypt: Evidence from Synchrotron Imaging*. Journal of Archaeological Sciences. 2019; 110:105009

Three-dimensional virtual bone histology of early tetrapods revealed by synchrotron light

Sophie Sanchez

Department of Organismal Biology, Evolutionary Biology Centre, Uppsala University, Uppsala, Sweden
sophie.sanchez@ebc.uu.se

Early tetrapods appeared a bit less than 400 million years ago. They were the first vertebrates to exhibit limbs. The fin-to-limb transition has intrigued researchers for decades. Biologists have demonstrated the diversity of developmental patterns in modern vertebrate appendages (e.g. zebrafish, mouse), assuming that they are representative of the group they belong to (respectively, ray-finned fish and tetrapods). However, long-bone microstructures in these models are highly derived and do not reflect their original function. Until the recent development of virtual palaeohistology at the European Synchrotron Radiation Facility (ESRF), molecular and morphological studies carried out on extant taxa could only rely on partial historical information to address questions of interaction and functional roles within long bones. Indeed, no histological study (with the exception of one), based on destructive classical methods, could be conducted on the precious and rare fossils of stem tetrapods. In the framework of international collaborations, we were recently able to study the limb bone histology of the famous early-tetrapod *Acanthostega* and the lobe-finned fishes *Eusthenopteron* and *Hyneria* in three dimensions (3D) using both propagation phase contrast and tomo-diffraction at the ESRF. I will demonstrate how crucial the synchrotron light has been to reveal a completely unexplored field of our palaeontological heritage and shed new lights on the origins of our limb bone microstructure. With the new developments of the X-ray beamlines BM18, ID15 and ID19 at the ESRF, virtual palaeohistology will become the only cutting-edge, non-destructive 3D imaging method able to reveal the bone microstructure of large and dense fossil tetrapods to answer key evolutionary questions.

A lost world in sausage-shaped packages: synchrotron microtomography of fossil droppings as a tool for investigating ancient ecosystems

P. E. Ahlberg, M. Qvarnström, H. M. Byrne, M. A. D. During, G. Niedzwiedzki

Department of Organismal Biology, Uppsala University, Norbyvägen 18A, SE-752 36, Sweden
per.ahlberg@ebc.uu.se

Fossilised excrement, known as coprolites, are not uncommon in the fossil record. It has long been known that they contain inclusions such as bones and scales that give clues to the diet of the producer. However, until now they have received little attention from scientists, largely because it is very difficult to get an overview of their contents by means of traditional techniques. These techniques involve either sectioning the coprolite, which gives only a two-dimensional cross-section view of a small part of the content, or macerating the entire coprolite, which destroys the internal spatial organisation and damages the contents. We have pioneered full 3D visualisation of coprolite contents by propagation phase contrast synchrotron microtomography (PPC-SRμCT), performed at ESRF beamline ID19. The results are remarkable [1-4]: fully visualised contents in vertebrate coprolites of Devonian to Triassic age (approximately 382 to 201 million years old) include foraminifera, beetle wing cases, crushed clam shells, a partly articulated fish, and skull bones of a previously unknown tetrapod (Figure 1).

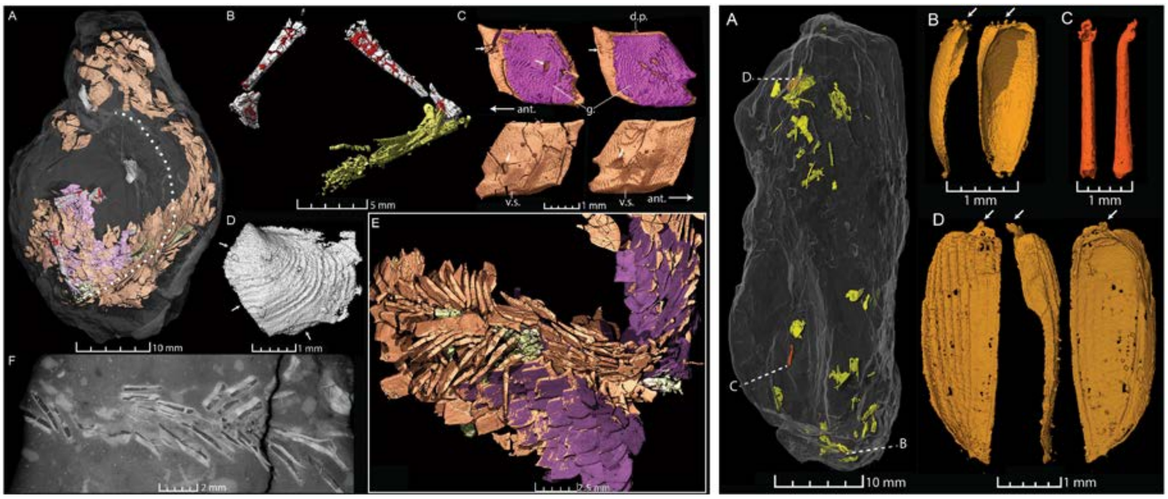


Figure 1: Fish remains and a clam shell (left) and beetle remains (right) from two Late Triassic coprolites [1].

The quality of the data creates wholly new possibilities for reconstructing the food webs of ancient ecosystems, which until now have been largely based on educated guesswork, and for understanding the lifestyles of individual coprolite producers [2-4].

References

[1] - M. Qvarnström, G. Niedzwiedzki, P. Tafforeau, Z. Zigaite and P.E. Ahlberg, *Scientific Reports* **7,** 2723 (2017).

[2] - M. Qvarnström, P.E. Ahlberg and G. Niedzwiedzki, *Scientific Reports* **9**, 925 (2019).

[3] - M. Qvarnström, E. Elgh, K. Owocki, P.E. Ahlberg and G. Niedzwiedzki, *PeerJ* **7**, e7375, 1-12 (2019).

[4] - M. Qvarnström, J.V. Wernström, R. Piechowski, M. Talanda, P.E. Ahlberg and G. Niedzwiedzki, *Royal Society Open Science* **6**, 181042 (2019).

X-ray Raman scattering: a hard X-ray probe for the study of cultural and natural heritage

Rafaella Georgiou[1,2], Pierre Gueriau[3], Christoph J. Sahle[4], Alessandro Mirone[4], Rachel S. Popelka-Filcoff[5], Sylvain Bernard[6], Romain Garrouste[7], Dimosthenis Sokaras[8], Uwe Bergmann[8], Jean-Pascal Rueff[3,9] & Loïc Bertrand[1,2]

[1] IPANEMA, CNRS, ministère de la culture, UVSQ, Université Paris-Saclay, Gif-sur-Yvette, France.
[2] Synchrotron SOLEIL, l'Orme des Merisiers, Gif-sur-Yvette, France.
[3] Institute of Earth Sciences, University of Lausanne, Géopolis, Lausanne, Switzerland.
[4] ESRF–The European Synchrotron, Grenoble, France.
[5] College of Science and Engineering, Flinders University, Adelaide, SA, Australia.
[6] Muséum National d'Histoire Naturelle, Sorbonne Université, Institut de Minéralogie, de Physique des Matériaux et de Cosmochimie (IMPMC), Paris, France.
[7] Institut de Systématique Evolution Biodiversité (ISYEB), MNHN / CNRS / Sorbonne Univ. / EPHE / Univ. Antilles, Muséum National d'Histoire Naturelle, Paris, France.
[8] Stanford PULSE Institute, SLAC National Accelerator Laboratory, Menlo Park, CA, USA.
[9] Sorbonne Université, CNRS, Laboratoire de Chimie Physique–Matière et Rayonnement, LCPMR, Paris, France.

rafaella.georgiou@synchrotron-soleil.fr

Deciphering the chemical nature of carbon-based compounds in ancient materials is now possible in three dimensions [1]. We use X-ray Raman imaging (XRI), a novel synchrotron-based hard X-ray technique first proposed by Huotari et al. [2], to visualize at each point the chemical composition of a 53-million-year-old ant preserved in amber (Fig. 1A). The 3D XRS-based imaging highlights the presence of two distinct chemical fingerprints in the exoskeleton (Fig. 1B): the first being molecular signatures of chitin, the main structural component of insect's exoskeleton and the second aliphatic carbons, a product of burial diagenetic transformation of the original chemistry of the organism. The results point to the importance of complete characterization of paleontological specimens, at a global scale, to provide information about the specimens' biochemistry, molecular evolution, and chemical interactions between the organism and the depositional setting.
The capabilities of X-ray Raman spectroscopy also provide new insights in the analysis of organic materials in cultural heritage studies [3]. We use carbon K-edge XRS-based spectra towards characterizing chemical fingerprints of native resins from a historical collection. This study opens new perspectives on non—invasive identification and statistical clustering of organic materials based on their plant genera, with the potential to identify resins on Aboriginal Australian cultural heritage materials.

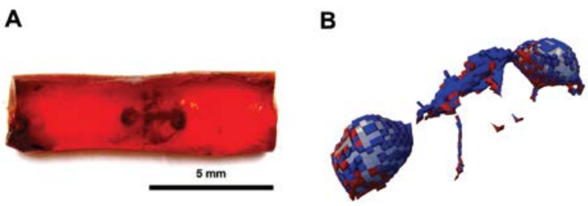


Figure 1: XRS 3D carbon K-edge speciation mapping of an Eocene ant (ca. 53 Mya) entrapped in Oise amber

References

[1] Georgiou et al. "Carbon speciation in organic fossils using 2D to 3D x-ray Raman multispectral imaging." Science advances 5.8 (2019): eaaw5019.

[2] Huotari et al. "Direct tomography with chemical-bond contrast." Nature materials 10.7 (2011): 489.

[3] Gueriau et al. "Noninvasive Synchrotron-Based X-ray Raman Scattering Discriminates Carbonaceous Compounds in Ancient and Historical Materials." Analytical chemistry 89.20 (2017): 10819-10826.

FULL LIST OF POSTERS

P1	A. Abdrabou *(student)*	Investigation of ancient Egyptian polychrome wooden artifacts by the combined use of imaging and handheld XRF spectroscopy
P2	M. Alfeld	Smart*Light – An Inverse Compton Source for Cultural Heritage
P3	I. Allegretta	Combining µXRF and µCT for the characterization of meteorites: the case of NWA8657 shergottite
P4	V. Antunes	Iberian ties: technical and ideological evolution from Zurbarán to Baltazar Gomes Figueira and Josefa d' Óbidos
P5	T. Arlt	Accessing inks on Egyptian papyri using synchrotron X-ray techniques
P6	P.O. Autran *(student)*	Structural investigation of black inks from Ancient Egyptian papyri
P7	E. Avranovich Clerici *(student)*	Macro and Micro-level X-Ray powder diffraction mapping of Giotto and Cimabue fresco fragments from Assisi Cathedral
P8	C. Berruyer *(student)*	Egyptian animal cult investigated with Synchrotron light: Mummies from the Grenoble Natural History Museum
P9	V. Beyrand	Multiphase progenetic development shaped the brain of flying archosaurs
P10	O. Bonnerot	Are X-rays safe for manuscripts' materials?
P11	M.C. Caggiani	Insight into Ancient Roman polychrome surfaces: investigation campaign at "Parco Archeologico del Colosseo" (Rome, Italy)
P12	Z. Chahardoli *(student)*	A Technical Investigation On a 20th Century Oil Painting by Jules Gustave Lempereur
P13	D. Chen	The origin of teeth and tooth replacement revealed by 3D synchrotron virtual palaeohistology
P14	T. Christiansen	A study of scarlet inks from an ancient Egyptian temple library under synchrotron lights
P15	L. Cortella	50 years' experience of gamma irradiation for remedial conservation of cultural heritage at ARC-Nucléart
P16	C. Costantino *(student)*	Lead calcium phosphates in Cultural Heritage objects: an integrated analytical approach for studying their origin and formation
P17	P. Dararutana	X-ray tomographic microscopy study of ancient ceramics from Thailand archaeological site
P18	J. Debrie *(student)*	Comparative study of Messinian fossil stromatolites and modern analogs from Sardinia: deciphering paleogeobiological archives
P19	T. De Kock	Conceptualizing a 4D laboratory X-ray CT dataset of stone weathering
P20	M. During	Synchrotron X-ray imaging of sturgeons and paddlefishes from Tanis, North Dakota (USA), reveals End-Cretaceous seasonality
P21	A. Fedrigo	X-ray or neutron imaging?
P22	E. Figueiredo	A XANES study of the Sn K-edge in slag by-products from tin smelting experiments

P23	D. Geffard-Kuriyama	The TRIPHON 3D platform
P24	M. Ghirardello *(student)*	Micro-Photoluminescence Imaging of intact and degraded Cadmium Yellow paint cross-sections
P25	L.C. Giannossa	Gold application on gilded and enamelled glass objects from Southern Italy
P26	A. Gojska	Compatibility of spectroscopic techniques in comparative measurements of historical Polish coins
P27	S. Harding	Synchrotron Circular Dichroism spectroscopy: a brief review of its potential for investigations of interactions in archaeological wood systems
P28	G. Lanzafame	Geopolymers: innovative green materials for cultural heritage conservation-restoration
P29	M. Larsson Coutinho	Co and Cu K-edge XANES study of the glazed tiles from the Fronteira Palace (Lisbon, Portugal)
P30	L. Li	Investigations of the elemental evidences in Art and Archaeology with the X-ray Fluorescence Microscopy at APS
P31	E. Maryanti *(student)*	The synchrotron radiation based investigation of prehistoric rock art from Saleh cave, Borneo island, Indonesia
P32	J. Mirao	Characterization of colour changes in limestone sculptures using X-ray based methods
P33	E. Mista-Jakubowska *(student)*	A possibility of detection of chemical soldering in medieval jewellery
P34	L. Nodari	An unusual CN stretching in Prussian Blue painted materials
P35	C. Noirot *(student)*	Oxidation-reduction effects on copper colour in glasses and glazes
P36	N. Nurdini *(student)*	Physicochemical Identification Based Synchrotron Radiation of Prehistoric Pigments in Tewet Cave, Sangkullirang-Mangkalihat Site, Borneo Island-Indonesia
P37	S. Raneri	Synchrotron micro-XRF imaging and micro-XANES spectroscopy at the new PUMA beamline at SOLEIL
P38	E. Sozontov	Ancient manuscripts research using radiations of different spectral ranges and complementary techniques
P39	A. Trosseau *(student)*	Informative potential of Fe and Mn K edge X-ray absorption spectroscopy for the distinction of pictorial layers from the wall support of prehistoric decorated caves and rock shelters
P40	V. Vaskaninova	Synchrotron tomography as a perfect tool to successfully imagine large and flattened fossils
P41	J.P. Veiga	From ceramics and glasses to mortars and stones: using synchrotron radiation to study cultural heritage
P42	P. Wils	Is it worth spending so much time? A comparative study on micro-CT segmentation techniques for quantitative investigations of bone.

Investigation of ancient Egyptian polychrome wooden artifacts by the combined use of imaging and handheld XRF spectroscopy

A. Abdrabou , Gilan Sultan, Hussein.M.Kamal

Grand Egyptian Museum- Conservation Centre, Ministry of Antiquities, Egypt
ahmed_abdrabou87@yahoo.com

The scientific analytical techniques of artifacts, belonging to museum collections in particularly unique objects such as King Tutankhamun collection (18^{th} dynasty 1347-1337BC, in ancient Egypt) which emphasize the necessity of working with noninvasive techniques, have gained much interest in the last years.

In this study, we demonstrate the ability of combining imaging techniques and hand held XRF as a very efficient and non-destructive method for analyzing the polychrome layers and previous applied materials for a number of wooden objects belong to King Tutankhamun.
In the first step, Multispectral techniques [visible-reflected (VIS), ultraviolet-induced visible luminescence (UVL), Visible-induced visible luminescence (VIVL), ultraviolet-reflected (UVR), infrared-reflected (IRR) and infrared-reflected false colour (IRRFC)] and optical microscopy were applied to gather information and to provide evidences on the distribution of original and previous applied materials on the polychrome surfaces. In the second step of our work, we analyzed the selected areas with hand held X-ray fluorescence spectroscopy (XRF). The materials of the previous restoration interventions were studied by Fourier Transform Infrared Spectroscopy (FTIR).

The results showed that the application of a protocol based on imaging techniques combined with data obtained from single-spot techniques such as X-ray fluorescence spectroscopy (XRF) allowed the characterization of a remarkable number of pigments and some previous restoration materials and mapping of their distribution on original and retouching areas of the surface without sampling. However, complete characterization of some polychrome layers required the use of other techniques such as XRD and FTIR spectroscopy.

References

[1] A. Abdrabou, N. E l Hadidi, S. Hamed and M. Abdallah, Journal of Archaeological Science: Reports 21, (2018).
[2] A. Abdrabou, M. Abdallah, I. A. Shaheen and H. M. Kamal, INT J CONSERV SCI 9, 1(2018).
[3] J. Dyer and S. Sotiropoulou, Herit Sci, (2017)
[4] A. Abdrabou, M. Abdallah, M. H. Kamal, Conservar Património 26 (2017).
[5] S. Bracci, O. Caruso, M. Galeotti, R. Iannaccone, D. Magrini, D. Picchi, D. Pinna and S. Porcinai, Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 145 (2015).
[6] A. Cosentino, Conservar Património 21(2015).
[7] J. Dyer, G.Verri and J. Cupitt, The British Museum, (2013).

Smart*Light – An Inverse Compton Source for Cultural Heritage

M. Alfeld, H.L. Castricum, P.H.A. Mutsaers[1], J. Dik, K. Janssens[2], O.J. Luiten[1]

Delft University of Technology, 3mE – MSE, Delft, the Netherlands, [1]Eindhoven University of Technology, Applied Physics, Coherence and Quantum Technology, Eindhoven, the Netherlands. [2]University of Antwerp, Department of Chemistry, AXES research group, Antwerp, Belgium **m.alfeld@tudelft.nl**

X-ray techniques are very well suited for the investigation of cultural heritage objects, as they allow to look below the surface of an objects and identify chemical species without causing visible alteration in it.

Many techniques, such as X-ray radiography, XRF and XRD are available on site, making use of X-ray tubes. However, more powerful techniques, such as phase contrast imaging, K-edge imaging and fast scanning XRD imaging are in practice limited to Synchrotron Radiation (SR) sources. Consequently, they are only available for short beam times and require sampling or the transport of an object over vast distances.

The Smart*Light project aims to bridge the gap between X-ray tubes and Synchrotron sources by using the inverse Compton effect: photons in the IR range, scattered back by a electron beam gain energy and can be enhanced to the X-ray level.

Inverse Compton Sources are compact and can be installed on site, e.g. in a shielded cellar of a museum and thus allow for the application of advanced X-ray techniques near the common storage place of an object.

This contribution will summarize the design and expected performance of Smart*Light at the first experiment (expected Fall 2020) and in later upgrades as well as possible applications on cultural heritage objects.

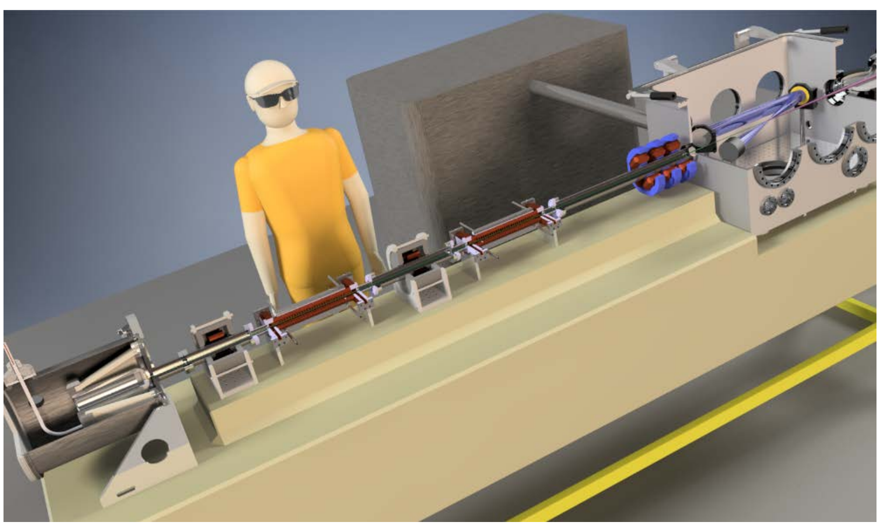


Figure 1: Artistic impression of Smart*Light.

Combining µXRF and µCT for the characterization of meteorites: the case of NWA8657 shergottite

Ignazio Allegretta[1], Carlo Porfido[1], Giorgio S. Senesi[2], Paola Manzari[3], Olga De Pascale[2], Roberto Terzano[1]

[1]Dipartimento di Scienze del Suolo, della Pianta e degli Alimenti, Università degli Studi di Bari "Aldo Moro", Via Amendola 165/A, 70126, Bari, Italy, [2]CNR - Istituto per la Scienza e Tecnologia dei Plasmi (ISTP) – Sede di Bari, Via Amendola 122/D, 70126, Bari, Italy, [3]Agenzia Spaziale Italiana, via del Politecnico, 00133, Roma, Italy

ignazio.allegretta@uniba.it

Meteorites are rocks coming from different parts of the solar system, e.g. Moon, Mars, asteroid belt, comets and probably Mercury, which reach the Earth surface after interaction with atmosphere. Their study can provide important information on their native celestial body and consequently on the solar system. Due to their rarity and importance, the use of non-destructive and non-invasive methods is essential for their study, in order to preserve the samples.

X-ray based techniques are very useful in this context since they can provide chemical and microstructural information of the sample without altering it.

In the present work micro X-ray fluorescence spectroscopy (µXRF) and high resolution micro X-ray computed tomography (µCT) were combined in order to characterize meteorites. In particular, a fragment of the Northwest Africa 8657 (NWA8657), classified as shergottite, was investigated. Analysis were led with laboratory equipement.

µCT can distinguish between maskelinite (a plagioclase) and pyroxenes (Figure 1A) which have two different densities (2.7 and 3.9 g/cm^3) and quantify them. Correlating the intensities of Si and Al (Figure 1B) three Al/Si ratios belonging to three different aluminosilicates could be discriminated. The blue group is associated to maskelinite, while the other two groups are connected to pyroxenes. The red group is also associated with a higher concentration of Mg (Figure 1D) which could be imputed to the presence of enstatite while the green one contains only Fe (Figure 1E) and could be recognized as ferrosillite. Other phases like phosphates, jarosite, sulphates and sulphides were also recognized combining the two techniques.

The present approach can be used for the chemical and microstructural characterization of meteorites.

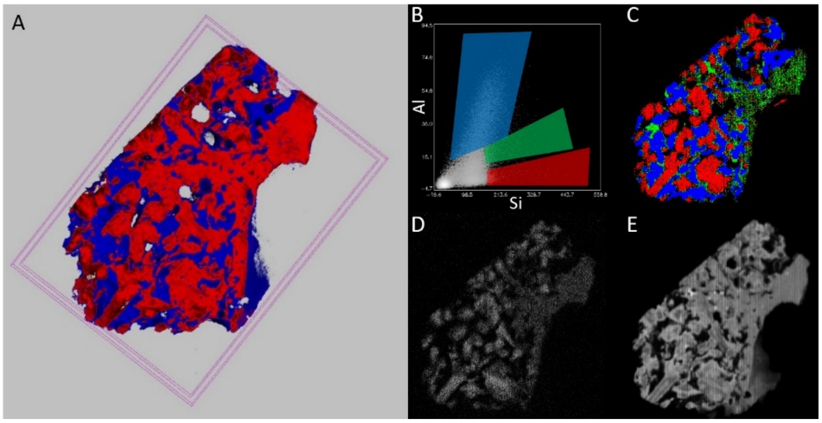


Figure 1: µCT (A) distinguished between maskelinite (blue) and pyroxenes (red). Al/Si scatterplot (B) allowed identifying the distribution (C) of maskelinite (blu), enstatite (red) and ferrosillite (green). Mg (D) and Fe (E) maps allowed recognizing the two pyroxenes.

Iberian ties: technical and ideological evolution from Zurbarán to Baltazar Gomes Figueira and Josefa d' Óbidos

V. Antunes[a,b] S. Valadas[c], A. Candeias[c], J. Mirão[c], A. Cardoso[c], S. Pessanha[b], M. Manso[b,d,] M. L. Carvalho[b]

a. ARTIS-Instituto História da Arte, Faculdade de Letras, Universidade de Lisboa (ARTIS-FLUL), Alameda da Universidade, 1600-214 Lisboa
b. LIBPhys-UNL, Laboratório de Instrumentação, Engenharia Biomédica e Física da Radiação, Departamento de Física, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, 2829-516, Caparica, Portugal
c. Laboratório HERCULES, Escola de Ciências e Tecnologia, Universidade de Évora, Largo Marquês de Marialva 8, 7000-676 Évora, Portugal
d. Faculdade de Belas-Artes, Universidade de Lisboa, Largo da Academia Nacional de Belas-Artes, 1249-058 Lisboa, Portugal
vanessahantunes@gmail.com

In the seventeenth century, the art of the protobaroque in Portugal thrives at a stage when the profession of painter asserts itself in the face of the work of a craftsman. The search for the imitation of the natural (including natural earth materials) is explored in the effects of light by the new generation of painters, of which Baltazar Gomes Figueira and, later, Josefa d' Óbidos stand out. These artists work in naturalistic ways, which surpass and oppose the counterreformation models employed by the last generation of Mannerist painters in Portugal. Alongside the traditional painting of religious character is the evolution of other genres - such as Portrait, Landscape and Still Life, a reflection of the economic and ideological vitality of the time. Protobaroque painting emerges under the Castilian political domination, reflecting the modernity of the beginning of the Spanish "Siglo d'Oro", assumed by the Portuguese painters during the first half of the seventeenth century. Some of them lived and learned to paint in Seville, as is the case of Baltazar Gomes Figueira. Zurbarán has a profound influence on the so-called Óbidos painting workshop, including the work of Baltazar Gomes Figueira as well as his daughter, Josefa d'Óbidos. The painting of *Agnus dei* created by Zurbaran was the inspiration for the making of father and daughter paintings, afterwards, in Portugal. In this work we study and compare the materials and technique of three *Agnus dei* paintings, one made by Zurbarán, a second assigned to Baltazar Gomes Figueira, and a third assigned to Josefa d'Obidos, his daughter and follower. The analytical study was achieved by the complementary information given by the techniques of μ-Raman and μ-FTIR in combination with XRF, μ-XRD, and SEM-EDS. Assessment to these results the evolution between Zurbarán an Baltazar, and father and daughter materials and technique in Óbidos painting workshop, one of the most important Portuguese workshops of the 17th century.

References

[1] Antunes, V., Influencias ibéricas en la terminología de los materiales - breves apuntes. ICOM-CC 16th triennial conference, 19 a 23 de Setembro de 2011, in ICOM-CC 16th triennial conference, Book of Abstracts, International Council of Museums (ICOM), Editor. 2011, Critério, produção gráfica,Lda.: Lisboa

[2] Serrão, V., A Pintura Proto-Barroca em Portugal, 1612-1657, in Faculdade de Letras. 1992, Universidade de Coimbra: Coimbra

Accessing inks on Egyptian papyri using synchrotron X-ray techniques

T. Arlt[1], H.-E. Mahnke[2,3,4], T. Siopi[2], E. Menei[2,5], I. Manke[4], U. Schade[4], V. Lepper[2,6]

[1]Technische Universität Berlin, Germany, [2]Ägyptisches Museum und Papyrussammlung, Berlin, Germany, [3]Freie Universität Berlin, Germany, [4]Helmholtz-Zentrum Berlin, Germany, [5]Visiting conservator, 75002 Paris, France, [6]Humboldt Universität zu Berlin, Germany, **arlt@tu-berlin.de**

In the Egyptian Museum and Papyrus Collection, Berlin, a multitude of papyrus manuscripts are stored. As part of the “Elephantine” project, funded by an ERC starting grant, we attempt to gain access to hidden text. Most of the fragments are very fragile, deformed, with some rolled or folded [1]. Papyri from the Old and Middle Kingdom were typically written with carbon ink. Consequently, these fragments show no absorption sensitivity for hard X-rays. Also, other inks, i.e. ferrous or plumbiferous inks, have been used in those times. Latter inks provide a sufficient sensitivity for absorption edge radiography and tomography in order to distinguish between writing and base material. This technique was applied using synchrotron X-rays at the BAMline at BESSY II [2].

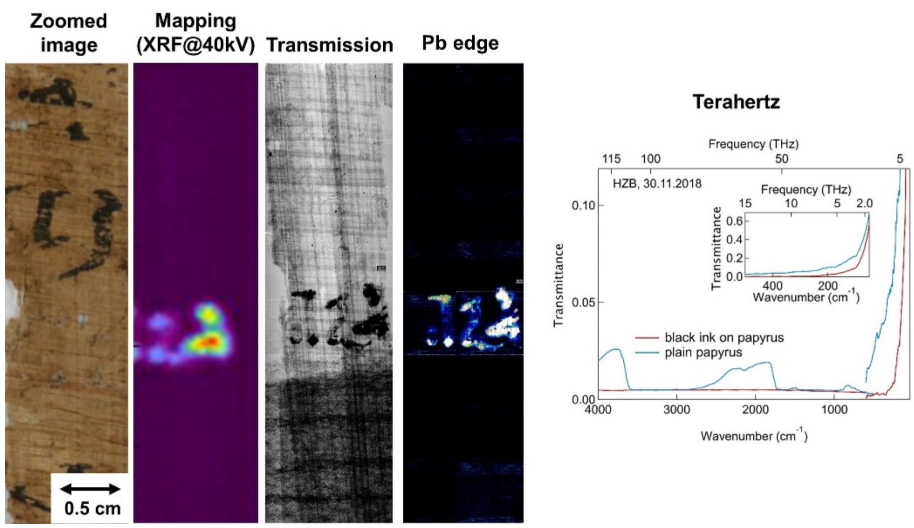


Figure 1: Method development to access hidden text.

Due to the low contrast between carbon ink and the papyrus substrate and the low absorption edges of carbon in the range of soft X-rays, methods related to those techniques do not work for carbon-based inks. Recently, THz radiography, applied to planar fragments turned out as a suitable methodology which enables to access text written with carbon ink as well (see the right part in the figure and [3]). Moreover, X-ray scattering techniques could be an alternative approach for detecting carbon ink writings on ancient papyri. First results, which were generated at PETRA III P03, will be presented.

References

[1] H.-E. Mahnke, T. Arlt, D. Baum, H.-C. Hege, F. Herter, N. Lindow, I. Manke, T. Siopi, E. Menei, M. Etienne, V. Lepper, Journal of Cultural (2019), in press, DOI: 10.1016/j.culher.2019.07.007.

[2] T. Arlt, H.-E. Mahnke, T. Siopi, E. Menei, C. Aibéo, R.-R. Pausewein, I. Reiche, I. Manke V. Lepper, Journal of Cultural Heritage, 39 (2019) 13-20, DOI: 10.1016/j.culher.2019.04.007.

[3] J. Labaune, J.B. Jackson, S. Pagès-Camagna, I.N. Duling, M. Menu, Gérard Mourou, Applied Physics A, 100(3), (2010), 607-612, https://doi.org/10.1007/s00339-010-5693-1.

Structural analysis of black inks from Ancient Egyptian papyri

P.-O. Autran[1,2,3], C. Dejoie[1], P. Bordet[2,3], J.-L. Hodeau [2,3], P. Walter[4], and P. Martinetto[2,3]

[1]European Synchrotron Radiation Facility, 71 Avenue des Martyrs, 38000 Grenoble, France
[2]Univ. Grenoble Alpes, Inst NEEL, 25 rue des Martyrs BP 166, 38042 Grenoble, France
[3]CNRS, Inst NEEL, 25 rue des Martyrs BP 166, 38042 Grenoble, France
[4]Laboratoire d'Archéologie Moléculaire et structurale, LAMS, Sorbonne Université, CNRS, 4 place Jussieu, 75005 Paris, France
pierre-olivier.autran@esrf.fr

Starting as early as the fourth millennium B.C., Egyptian writings on papyrus spread knowledge all around the Mediterranean Sea. Carbon-based pigment from Egyptian period were used as a base for ink manufacturing dedicated to writing [1]. Although a large number of papyri have been collected during archaeological excavations, the complexity of the amorphous nature of black inks limits our understanding of Old Egyptian writing techniques. Recent studies on papyri fragments from both Herculanum and ancient Egypt showed the presence of metallic element such as copper and lead, their origin remains unanswered [2,3].

The purpose of this study is to get a better understanding of the process of black ink manufacturing in Ancient Egypt. For this, the investigation focuses on tracking the origin of amorphous carbon as well as any traces of metallic elements in a corpus of fragments of papyrus. These fragments were made available by the Champollion Museum, located in Vif, under the responsibility of the department of Isère. In order to analyze the structure of the ink deposited on the surface of the fragments, only non-destructive techniques are suitable. Synchrotron X-ray diffraction and fluorescence techniques associated with the pair distribution function were performed at the ESRF on ID22 and ID11 beamlines. Complementary analyzes of Raman and infrared spectroscopy have also been used to try to reveal the presence of binders in the ink. Finally, scanning electron microscopy has been exploited to compare the microstructure of ink deposits with a series of standards.

The first results of scanning electron microscope imaging show a great similarity between the ink deposited on the surface of the papyrus and the lampblack, obtained by collecting the residue of organic compound combustion. The X-ray diffraction demonstrates the presence of a structure in correlation with the ink deposited on the papyrus. X-ray fluorescence indicates a low contrast of metallic elements between the ink-covered areas and empty areas. Finally, the microscopy techniques remain to be better examined. Combining X-ray analysis, spectroscopy and imaging data is essential to clarify the nature of cultural heritage materials.

References

[1] Lucas A. and Harris J. R., Ancient Egyptian materials and Industries, *Dover Publications Inc*., (1962) 338-366.
[2] Brun, E. et al. Revealing metallic ink in Herculaneum papyri. *PNAS* **113(14)**, (2016) 3751–3754
[3] Christiansen et al., The nature of ancient Egyptian copper-containing carbon inks is revealed by synchrotron radiation based X-ray microscopy, *SREP* **7-15346**, (2017).

Macro and Micro-level X-Ray powder diffraction mapping of Giotto and Cimabue fresco fragments from Assisi Cathedral

Ermanno Avranovich Clerici,(1) Steven De Meyer,(1) Geert van der Snickt,(1) Letizia Monico,(2) Costanza Miliani, (3) Koen Janssens (1), J. Thieme(4)

(1) University of Antwerp, Department of Chemistry, AXES Research group, Groenenborgerlaan 171, Antwerp, Belgium
(2) CNR-Scitec, via Elce di Sotto 8, 06123 Perugia, Italy
(3) CNR-ISPC (Istituto CNR di Scienze del Patrimonio Culturale), via Cardinale Guglielmo Sanfelice 8, 80134 Napoli, Italy
(4) SRX Beamline, NSLS-II, Brookhaven National Labotatory, Upton NY 11973, USA
Ermanno.AvranovichClerici@uantwerpen.be

Cimabue (1240 – 1302) was an Italian painter and designer of mosaics from Florence. He is famous for breaking away from the Italo-Byzantine painting style. According to Vasari, he was the teacher of Giotto (1267 – 1337), the first artist of the Italian Proto-Renaissance. Cimabue went to Assisi to paint several large mural paintings at the new Basilica of Saint Francis and his pupil Giotto accompanied him.[1] The paintings of Cimabue in Assisi are generally in very poor condition. The white areas painted by the master today appear blackened as for example in the painting of the Crucifixion. In the 1997 earthquake, a portion of the vault of the Upper Basilica collapsed. Several fragments of the Cimabue mural paintings that show discolorations were collected after the earthquake and conserved.

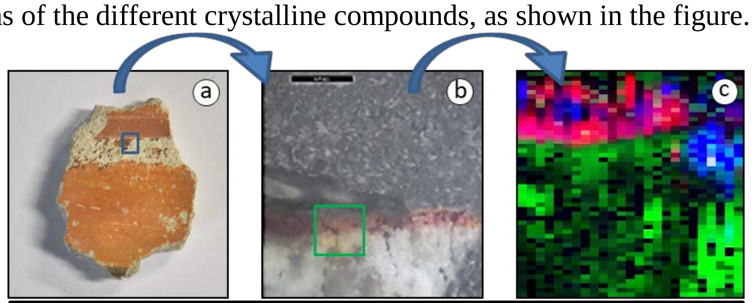
Several fresco fragments of the Upper Basilica belonging to Cimabue and Giotto have been chosen for examination with the aim of explaining the conversion process that triggers the oxidation of lead white to plattnerite (β-PbO_2). While in mural paintings, the blackening of lead white has been frequently noticed and attributed to the formation of plattnerite, the mechanism and primary cause of this oxidation process remains unclear.[2]

Experimental evidence suggests that chlorine is the main contributor in this blackening process. If Cl is present in the hypochlorite form, the following reaction may take place:

$Pb^{2+} + OCl^- + 2OH^- \rightarrow Cl^- + PbO_2 + H_2O$

An extensive investigation of the fresco fragments is being performed to confirm the starting hypotheses and provide insights into the painting techniques and material use of Cimabue and Giotto.

Reflection mode MA-XRPD scans on the fragments themselves are combined with SR-based microscopic XRPD scans in transmission geometry to identify the different pigments and degradation products formed over the paintings. The discriminating capability of this method allows to collect highly specific distributions of the different crystalline compounds, as shown in the figure.



a) Photograph of the fragments analyzed. The blue rectangle indicates where the sampling was performed
b) Cross sectional micrograph of the scanned area
c) RGB Distribution map Plattnerite β-PbO_2, Laurionite PbOHCl & Calcite $CaCO_3$

References

[1] G. Vasari: Le vite de' più eccellenti pittori, scultori e architettori, (1568)
[2] M. Vagnini, R. Vivani, E. Viscuso, M. Favazza, B.G. Brunetti, A. Sgamellotti, C. Miliani: Investigation on the process of lead white blackening by Raman spectroscopy, XRD and other methods: Study of Cimabue's paintings in Assisi. Vibrational Spectroscopy, 98, 41-49 (2018).

Egyptian animal cult investigated with Synchrotron light: Mummies from the Grenoble Natural History Museum

Camille Berruyer[1,2], Philippe Candegabe[3], Paul Tafforeau[1]

[1] European Synchrotron Radiation Facility, 71 Avenue des Martyrs, 38000 Grenoble
[2] ArchéOrient (UMR 5133), Maison de l'Orient et de la Méditerranée Jean Pouilloux, 7 rue Raulin 69365 Lyon
[3] Muséum d'Histoire Naturelle de Grenoble, 1 rue Dolomieu, 38000 Grenoble
camille.berruyer@esrf.fr

For more than a millennium, between New Kingdom and Roman Periods, ancient Egyptian mummified millions of animals. Nevertheless, only a very small fraction of these mummies reached us and, even less, in reasonably good preservation state. Nowadays, archaeologist studies again old museum's collections with new technologies for a better understanding of this special industry. On this respect, X-ray microtomography, especially when using synchrotron light, can bring a non-destructive and non-invasive direct access to the internal structures of these precious specimens.

Through a large research project, dozens of animal mummies have been scanned at the ESRF, mostly on the BM05 beamline. Among these, we scanned all the specimens conserved at the Natural History Museum of Grenoble, for both research and conservation purposes. As the majority of old collections, the information about provenance and history of these mummies has been lost. Despite its relatively modest number of specimens, the Grenoble collection through its proximity with the ESRF and goodwill of the museum team, brings valuable information about votive animal mummies. Among the most noticeable specimens, we will present mummies made from complete single animals such as cats, dog and ibises. A crocodile mummy that includes only a head and a large bone from two different animals, and a "falcon" mummy that is made with a raptor head, but that does enclose in fact a baby marine bird.

This poster will present an overview of this collection and the preliminary results that were obtained through the collaboration between the museum and the ESRF.

Multiphase progenetic development shaped the brain of flying archosaurs

V. Beyrand[1,2], D.F.A.E. Voeten[1,2], S. Bureš[2], V. Fernandez[1,3], J. Janaček[4], D. Jirák[5,6], O. Rauhut[7], P. Tafforeau[1]

Affiliation : [1]European Synchrotron Radiation Facility, 71 Avenue des Martyrs, CS-40220, 38043, Grenoble, France, [2]Department of Zoology and Laboratory of Ornithology, Palacký University, 17.listopadu.50, 77146, Olomouc, Czech Republic, [3]Imaging and Analysis Centre, National History Museum, Cromwell Rd, London, UK, [4]Department of Biomathematics, Institute of phisiology of the Czech academy of Sciences, Vídeňská 1083, 142 20, Prague 4, Czech Republic, [5]MR Unit, Department of Diagnostic and Interventional Radiology, Institute for Clinical and Experimental Medicine, Vídeňská 1958/9, 142 21, Prague 4, Czech Republic, [6]Institute of Biophysics and Informatics 1st Medicine Faculty, Charles University, Salmovská 1, 120 00, Prague 2, Czech Republic, [7]Department for Earth and Environmental Sciences and GeoBio-Center, SNSB-Bayerische Staatssammlung für Paläontologie und Geologie, Ludwig-Maximilian-University Munich, Richard-Wagner-Str.10, 80333, Munich, Germany

vincent.beyrand@gmail.com

Archosaurs is one of the vertebrate group with the longest history and the oldest origin. Through their long evolutionary history, they developed a large variability of size, morphological features and locomotion behaviours. Flight is a particular behaviour that has been developed twice independently by archosaurs during their evolution. As a complex locomotory behaviour, flight requires advanced cognitive capabilities in order to deal with all the information necessary for a proper locomotion. As the center of processing of information and selection of appropriate response, brain is an important structure to study in order to understand how cerebral capacities in archosaurs evolved in parallel of flight evolution. Because of its position at the root of birds, *Archaeopteryx* from the Jurassic of Germany, is a very important taxon as it is considered as the oldest form having developed active flight capabilities in the avian lineage. The study of the features showed the different *Archaeopteryx* specimens add information on how flight capabilities evolved in birds. Another important point of this evolutionary history is the mechanism leading to the appearance of cerebral features related to flight. In this respect, *Haslzkaraptor escuillei*, a small dromaeosaur from the Cretaceous of Mongolia, is a key specimen, showing brain characters very similar to *Archaeopteryx*, despite the fact that it was clearly not a flying animal and probably not having flying ancestors.

Along archosaurs evolution toward flying forms, endocasts show an increase of coiling as well as of infilling level by the brain itself. Basal archosaurs such as crocodiles show an elongated and low-filled endocast, reflecting the primitive condition observed in lepidosaurian. Non-maniraptoriform dinosaurs and then Maniraptoriforms show two successive events of coiling increase, but only small maniraptoriforms suggest an increase of infilling. In crocodiles and non-maniraptoriforms dinosaurs, coiling and low infilling are independent from body size, contrary to maniraptoriforms for which small specimens do present a higher filling level than large sized specimen, for similar coiling values. Finally, birds show a total decoupling of those two characters and size. This general pattern is observed during crocodilian embryonic development, for which coiling and infilling decrease along ontogeny. This suggest a serie of progenetic events, associated with a general size reduction, along archosaurs lineages toward flying forms which was leading to cerebral shape unlocking the cerebral capabilities for flight in birds and pterosaurs.

Are X-rays safe for manuscripts' materials?

O. Bonnerot[1,2], I. Shevchuk[2], L. Gaser[3], A-L. Dupont[4], V. Rouchon[4], Z. Cohen[1], I. Rabin[1,2]

[1] Bundesanstalt für Materialforschung und -prüfung, Unter den Eichen 44-46 12203 Berlin, [2]Center for the Study of Manuscript Cultures, University of Hamburg, Warburgstraße 26, 20354 Hamburg, [3]Deutsches Elektronen-Synchrotron, 22603 Hamburg, [4]Centre de Recherche sur la Conservation, Muséum d'Histoire Naturelle, CNRS USR 3224, 36 rue Geoffroy Saint-Hilaire, 75005 Paris
olivier.bonnerot@bam.de

In the last decade, applications of X-rays to the study of manuscripts significantly spread in both diversity and extent. They range from writing material analysis, mostly with X-ray fluorescence (XRF), permitting non-invasive characterization of inks and pigments used [1], to the investigation of the origin of writing supports [2]. In addition, XRF mapping has proved to be an invaluable tool for recovering erased text [3]. Finally, computed-tomography (CT) has shown potential in virtually unrolling rolls, making text readable without using damaging mechanical methods [4]. Despite their growing use, little attention has been paid to the side effects of such analytical tools. We observed irreversible parchment colour changes during some experiments on dead-sea scrolls with synchrotron radiation sources. Furthermore, partial photo-reduction of iron under high intensity beam during X-ray absorption near edge structure spectroscopy (XANES) measurements of iron-gall ink on paper has been reported several times [5,6]. Such phenomena have mostly been overlooked so far, although there is an increasing awareness of the necessity to study them. We conducted experiments at the Deutsches Elektronen-Synchrotron (DESY) facilities to investigate X-ray induced structural alteration of paper and parchment to see whether the presence of absorption centres (ink and pigments) has an impact. In addition to better understanding degradation processes, we are aiming to define an appropriate methodology of analysis of manuscripts with a tolerable risk of damage. The first results concerning X-ray induced damage of cellulose materials have already been presented at the Synchrotron Radiation and Neutrons in Art and Archaeology (SR2A) [7]. We are focusing here on the results on parchment materials.

References

[1] - O. Hahn, B. Kanngiesser, and W. Malzer, Studies in Conservation **50**, 23-32 (2005).
[2] - I. Rabin and O. Hahn, Analytical Methods **5**, 4648-4654 (2013).
[3] - L. Glaser and D. Deckers, Manuscript Cultures **7**, 104-112 (2015).
[4] - W. B. Seales, C. S. Parker, M. Segal, E. Tov, P. Shor, and Y. Porath, Science Advances **2**, e1601247 (2016).
[5] - B. Kanngießer O. Hahn, M. Wilke, B. Nekat, W. Malzer, and A. Erko, Spectrochim. Acta, Part B **59**, 1511-1516 (2004).
[6] - G. Banik, G. Kolbe and J. Wouters, Actes des quatrièmes journées internationales d'études de l'ARSAG, 205–217 (2002).
[7] - A. Gimat, S. Schoeder, M. Thoury, S. Paris-Lacombe, V. Rouchon, I. Rabin, L. Glaser, and A.-L. Dupont, SR2A (2018).

Insight into Ancient Roman polychrome surfaces: investigation campaign at "Parco Archeologico del Colosseo" (Rome, Italy)

G. Barone[1], M.C. Caggiani[1], A. Coccato[1], P. Mazzoleni[1], A. Russo[2]

[1]Department of Biological, Geological and Environmental Sciences, University of Catania, Italy
mariacristina.caggiani@unict.it
[2]Parco Archeologico del Colosseo, Rome, Italy

The project "Non-destructive analytical studies at Parco Archeologico del Colosseo (Rome, Italy)" aims at investigating the raw materials and technology employed by the Romans for the decoration of sculptures, *terracotta* and walls. In this framework, archaeometric investigations were carried out on the wall paintings of the recently discovered "Sphinx Room" at Domus Aurea and on marbles with polychrome and gilding traces (Figure 1). The two sculptures analysed are a male statue and a basket (*cista*), found during Palatino excavations [1].

The employed methodological strategy favoured the use of portable non-invasive instrumentation such as handheld X-Ray Fluorescence (hXRF), portable Raman spectroscopy and Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS). Where possible, micro-fragments of pictorial material were sampled and subjected to Raman and Infrared spectroscopy with laboratory instrumentation.

Figure 1: Details of male statue, *cista* and Sphinx Room vault during *in situ* analysis.

Gilding traces and pigments including white, earth tones, bright pink, different shades of green, blue and black were characterized. The combination of the information gained by the elemental and molecular techniques with portable and laboratory instrumentation allowed to confirm the colour palette traditionally identified for Roman paintings [2, 3]. Notwithstanding, the colours obtained by mixing different pigments based on the same key-elements should be further investigated, studying their distribution and the oxidation state of iron, copper and lead by means of X-Ray Absorption Spectroscopy (XAS), including chemical mapping.

References

[1] - M.A. Tomei, M. Filetici (eds.) Domus tiberiana, scavi e restauri 1990-2011 Electa, Milano (2011).
[2] - A. Paradisi et al., Archaeometry **54**, 6 (2012).
[3] - M.L. Amadori et al., Microchemical Journal **118** (2015).

A Technical Investigation on a 20th Century Oil Painting by Jules Gustave Lempereur

Z. Chahardoli[1], J. Shen[1], G. Zhang[1], A. Chevalier[1,2]

[1] Faculty of Science for the Conservation - Restoration of Cultural Heritage, School of science, University of Bologna, Ravenna, Italy [2] Atelier Chevalier, 4/6, rue Larrey, 75005 Paris, France
zohreh.chahardoli@studio.unibo.it

This paper focuses on the results provided by the scientific analysis of an oil painting by Jules Gustave Lempereur (1902–1985). Paint materials used in the creation of the said painting exhibit some degree of decay over time. This investigative study was carried out to analyze the presence of some damage on canvas, paint layer and varnish. To study and identify the materials employed by the artist, previous restorations and the products of their degradation processes samples were analyzed using optical microscopy, Multispectral Imaging (VIS-UV-IR), X-Ray Fluorescence (XRF) and Fourier-Transform Infrared Spectroscopy in attenuated total reflectance (FTIR-ATR).

The study at hand highlights the varied degradation of the two varnishes (old varnish mastic, and new varnish dammar), which demonstrated yellowing, alteration of thermal and spectroscopic features and changes in surface morphology and viscoelasticity. This study reveals, *inter alia*, that the white pigment consisted of calcium carbonate, red pigment stemmed from madder lake and green pigment was possibly created with a mixture of cobalt blue (cobalt (II) oxide-aluminum oxide) with yellow ochre (limonite). Key data gathered in this study sheds a new light on the nature of the constituent materials and the state of retouched areas which in turn facilitated elaboration of correct conservation measures along with suitable restoration interventions.

Refrences

[1] B. Hochleitner, V. Desnica, M. Mantler, M. Schreiner. Atomic Spectroscopy **58**, 641-649 (2003)
[2] K. Şerifaki, H. Böke, Ş. Yalçın, B. İpekoğlu. Materials Characterization **60**, 303–311, (2009)
[3] D. Comelli, A. Nevin, A. Brambilla, I. OsticioliG. Valentini, L. Toniolo, M. Fratelli, R. Cubeddu, Applied Science A **23**, (2011)
[4] F. C. Izzo, B. Ferriani, K. J. Van den Berg, H. Van Keulen, E. Zendri, Journal of Cultural Heritage **15**, 557–563 (2014)

The origin of teeth and tooth replacement revealed by 3D synchrotron virtual palaeohistology

D. Chen[1], S. Sanchez[1,2], P. Tafforeau[3], V. Vaškaninová[1,4], T. Märss[5], H. Blom[1], P.E. Ahlberg[1]

[1]Department of Organismal Biology, and [2]SciLifeLab, Uppsala University, Uppsala, Sweden, [3]European Synchrotron Radiation Facility, Grenoble, France, [4]Institute of Geology and Palaeontology, Faculty of Science, Charles University, Prague, Czech Republic, [5]Estonian Marine Institute, University of Tartu, Estonia
donglei.chen@ebc.uu.se

The origin and evolution of vertebrate dentitions has long been a cardinal question for comparative morphologists. To understand the organisation and development of fossil dentitions it is essential to examine their histology (microscopic tissue structure). This has traditionally been done by cutting thin sections that can be examined under the light microscope. However, while teeth are generally abundant in the fossil record, dental materials from the earliest vertebrates are very rare and too precious to be sectioned. Furthermore, thin sectioning does not reveal the three-dimensional organisation of the tissues, and thus gives a misleading impression of the structure. Propagation phase-contrast synchrotron microtomography (PPC-SRμCT) scans performed at ESRF beamline ID19 have revealed a variety of early dentitions from the Late Silurian to the Early Devonian periods, approximately 410 to 425 million years old. The details of the subtle embedded microstructures modelled in 3D revealed the true growth pattern hidden inside.

Radotina and *Kosoraspis* are among the most primitive jawed vertebrates and shed surprising light on the origin of teeth. In *Radotina*, teeth are already added lingually but have not been integrated to a specific jawbone. The most primitive form of tooth-bearing bones is found in *Kosoraspis*, where the jaw bones carry alternate tooth files but consist of multiple short pieces. The teeth of *Radotina* and *Kosoraspis* were not shed. Tooth shedding by basal resorption (where the base of the tooth is dissolved away before it drops out, as happens with our own milk teeth) first evolved in the so-called stem osteichthyans, the common ancestors of all later bony fishes and land vertebrates including ourselves. In the Silurian stem osteichthyans *Andreolepis* and *Lophosteus* [1-3]. Both genera have a primary non-shedding dentition that resemble that of *Kosoraspis*. But it is later overgrown by dermal odontodes and thus invisible in surface view; this non-shedding dentition gives rise to the later shedding dentition, where teeth are repeatedly replaced by basal resorption. These data, which could only be obtained by PPC-SRμCT with sub-micron resolution, give us an extraordinarily vivid insight into the biology of tooth growth and replacement more than 400 million years ago, and promise to illuminate the evolution of the linear tooth rows of modern osteichthyans.

The unique ability of ESRF to perform high-resolution spot PPC-SRμCT on large specimens, which will be further enhanced on the new BM18 beamline, creates great potential for investigating not only small isolated bones but large articulated specimens in this way. This has made possible the study of *Radotina* and *Kosoraspis*, and is further illustrated by an ongoing study of *Megamastax*, another Silurian stem osteichthyan related to *Andreolepis* and *Lophosteus* but much larger and more complete.

References

[1] - H. Botella, H. Blom, M. Dorka, P.E. Ahlberg and P. Janvier, Nature **448**, 583-586 (2007).
[2] - D. Chen, H. Blom, S. Sanchez, P. Tafforeau and P.E. Ahlberg, Nature **539**, 237-241 (2016).
[3] - D. Chen, H. Blom, S. Sanchez, P. Tafforeau, T. Märss and P.E. Ahlberg, Royal Society Open Science **4**, 1-21 (2017).

A study of scarlet inks from an ancient Egyptian temple library under synchrotron lights

T. Christiansen[1], M. Cotte[2, 3], W. de Nolf[2], E. Mouro[2], J. Reyes[2], S. de Meyer[4], N. Salvado[5], V. Gonzales[6], P.E. Lindelof[7], K. Mortensen[7], K. Ryholt[1], S. Larsen[8]

[1]Department of Cross-Cultural and Regional Studies (ToRS), Egyptology Section, University of Copenhagen, Denmark, [2]The European Synchrotron Radiation Facility (ESRF), Grenoble, France, [3]Laboratoire d'archéologie moléculaire et structurale (LAMS), University of Sorbonne, Paris, France, [4]Department of Chemistry, University of Antwerp, Belgium, [5]Departament d'Enginyeria Química, Escola Politècnica Superior d'Enginyeria de Vilanova y la Geltrú (EPSEVG), Polytechnic University of Catalonia (UPC), Barcelona, Spain, [6]Rijksmuseum, Science Department, Amsterdam, Netherlands, [7]The Niels Bohr Institute (NBI), University of Copenhagen, Denmark, [8]Department of Chemistry, University of Copenhagen, Denmark.

tc.msc546@gmail.com

A hitherto unindentified complex composition was recently brought to light by syncrotron-based X-ray microscopy in red inks inscribed on papyri from the only institutional library to survive from ancient Egypt – the Tebtunis temple library. X-ray fluorescence (XRF) mapping revealed the presence of iron (Fe) and lead (Pb) compounds in the majority of 12 red inks that were analyzed at the ESRF on beamline **ID 21**. The iron-based compounds in the inks could be assigned to ocher, notably due to the co-localization of Fe with aluminum (Al), and the detection of hematite by micro X-ray diffraction (µXRD). Using the same techniques together with micro Fourier transformed infrared (µFTIR) spectroscopy analyses, the Pb was shown to be bound to fatty carboxylate and phosphate groups, thereby contesting the naïve and generic hypothesis that primarily associates the presence of Pb in ancient Mediterranean red pigments with minimum (Pb_3O_4) or other red/orange crystalline phases such as itharge (PbO) and massicot (PbO). XRF maps performed at higher resolution accentuated a peculiar distribution and co-localization of Pb, phosphorus (P) and sulfur (S), which were present at the micrometric scale as a sort of diffused "coffee rings" surrounding the ocher in the red letters, and at the sub-micrometric scale concentrated in the papyrus cell walls (fig. **1**). These elements and their co-localization support the use of Pb (mixed with a lipid binder) as a drying agent in ancient Egyptian and Mediterranean inks – as it was later employed during the development of oil painting in 15th century Europe – and not as a pigment.

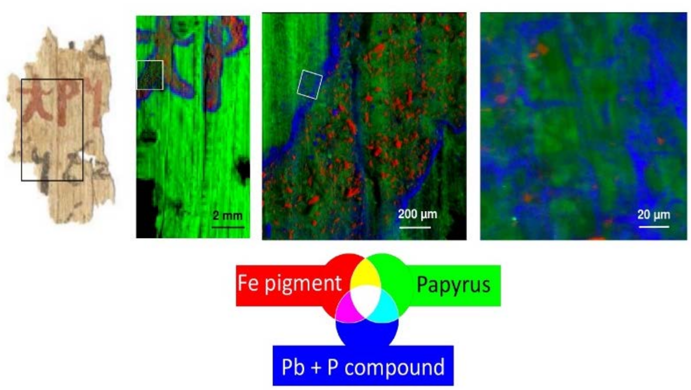


Figure 1: Macro- and µXRF maps showing the distribution of ocher/Fe (red) and the co-localization of Pb and P (blue) in a red ink inscribed on an Egyptian papyrus (green). The papyrus fragment derives from the Tebtunis temple library and forms part of a long astrological treatise (P. Carlsberg 89) that date to 1st century CE.

50 years' experience of gamma irradiation for remedial conservation of cultural heritage at ARC-Nucléart

Laurent Cortella, Christophe Albino, Quoc-Khoi Tran, Karine Froment

ARC-Nucléart, CEA Grenoble, 17, rue des Martyrs, 38054 Grenoble Cedex 9, France
laurent.cortella@cea.fr

Gamma irradiation processing is used for remedial conservation since the 70's in ARC-Nucléart, Grenoble, France. It can arrest biological degradation and, when necessary, consolidate the most fragile artefacts using radio-curable resin. From that time, it has been continuously used on a very wide variety of artefacts.

Insect eradication is the most common treatment, 500 Gy being the threshold to reach the required deterministic effects leading to their systematic death. For fungicide purposes, doses up to 10 kGy reduce in statistical way the worst contamination to an acceptable level, the one that can be encountered in "healthy" museum or storage room. Potential side effects has always been considered with particular attention. Apart from some rare contraindications, experience has shown that the technique can be applied safely on a very large range of material.

For consolidation, densification of porous material with radio-curable consolidant is obtained after classical vacuum / pressure impregnation. Styrene / unsaturated-polyester resin is used, cross-linking being the way it hardens. The achieved consolidation is particularly efficient and stable, but irreversible. However, it is occasionally justified in some relevant cases.

These techniques continue to save many cultural heritage artefacts. From the last decade, international collaborations, notably through IAEA[1], help us to improve our understanding and control of side effects and to diversify our techniques. ARC-Nucléart, as a pioneer of these techniques, help also to their dissemination for a worldwide used.

Figure 1: Irradiation of polychrome wooden sculptures (Angels and Apostles, 17th c., Le Pègue, France) for insect eradication.

References

[1] - IAEA, Uses of ionizing radiation for tangible cultural heritage conservation. IAEA Radiation Technology Series N°6. International Atomic Energy Agency, Vienna (2017).

Lead calcium phosphates in Cultural Heritage objects: an integrated analytical approach for studying their origin and formation

Authors: C.Costantino[1], L.Monico[1,2], A.Romani[1,2], V.Gonzalez[3], A.van Loon[3], T.Christiansen[4], S.Larsen[5], M.Eveno[6], N.Salvado[7], S.Buti[7], K.Keune[3,8] and M. Cotte[9, 10]

[1]SMAArt Centre and Department of Chemistry, Biology and Biotechnology, University of Perugia, Perugia, Italy; [2]CNR-SCITEC, Perugia, Italy;[3]Rijksmuseum, Science Department, Amsterdam, The Netherlands;[4] Department of Cross-Cultural and Regional Studies (ToRS), Egyptology Section, University of Copenhagen, Copenhagen, Denmark;[5]Department of Chemistry, University of Copenhagen, Copenhagen, Denmark;[6]Centre de Recherche et de Restauration des Musées de France (C2RMF), Paris, France;[7]Departament d'Enginyeria Química, Escola Politècnica Superior d'Enginyeria de Vilanovai la Geltrú (EPSEVG), Polytechnic University of Cataloni, Spain;[8]Van't Hoff Institute for Molecular Sciences, University of Amsterdam, The Netherlands;[9]ESRF, Grenoble, France;[10]CNRS, Laboratoire d'archéologie moléculaire et structurale, LAMS, Sorbonne Université, Paris, France.

claudio.costantino@studenti.unipg.it

Lead calcium phosphates have been reported in few historical artistic materials, such as paintings and inks. Theorigin of these compounds is not completely understood. Some authors propose that they are present as a natural pigment **[1]**, while others attribute them to degradation reactions **[2]**.
Interestingly, other researches in the field of environmental science have focused on the reactivity of hydroxyapatite [$Ca_{10}(PO_4)_6(OH)_2$; hereinafter named "HA"] for the treatments of toxic metal in different environmental matrices **[3]**. They showed that HA can immobilize Pb^{2+}ions, giving rise to a series of solid solutions of lead and calcium phosphate [$Pb_xCa_{(10-x)}(PO_4)_6(OH)_2$], where Pb^{2+} ions are mostly occupying Ca^{2+}sites. If Pb^{2+} ions are substituting all the calcium available in the structure, a compound called "hydroxypyromorphite" ($Pb_{10}(PO4)_6(OH)_2$) is obtained **[4]**.
The present project aims to investigate the spectroscopical properties of different solid solutions and the physico-chemical and environmental conditions that promote the formation of lead calcium phosphates in various kind of cultural heritage objects, and to define how they may evolve over time.
As a first step, a series of lead calcium hydroxyl phosphates of different Pb:Ca stoichiometry will be synthesized according to previous studies. Then, characterized by means of SEM-EDX, FT-IR, Raman and UV-Visible spectroscopies as well as a number of X-ray methods (with conventional and synchrotron radiation sources), including XRF, XRD and XANES spectroscopy at the P K- and Ca K-edges.
As a second step, the physico-chemical stability of these synthesized compounds will be assessed by studying the effect of pH and different binding media. Furthermore, accelerated aging experiment will be performed for evaluating the influence of moisture, light and/or temperature on their reactivity.
In parallel, mock-up paints and ink model samples will be prepared in laboratory to verify and compare the composition and morphology of the synthesized lead calcium phosphates with those found in different original artworks.

References

[1] Bearat H., "Les pigments à base de plomb en peinture murale romaine", Proceeding of the 1995 LCP Congress Montreaux **1995**, pp. 547-555.
[2] Rémazeilles C., Conforto E., "A Buried Roman Bronze Inkwell – Chemical Interactions with Agricultural Fertilizers", Studies in Conservation, **2008**, Vol. 53, pp. 110-117.
[3] Laperche V., Traina S.J., et al., "Chemical and Mineralogical Characterizations of Pb in a Contaminated Soil: Reactions with Synthetic Apatite", Environmental Science and Technology, **1996**, Vol. 30, pp. 3321-3326.
[4] Mavropoulos E., Rocha N.C.C., et al., "Characterization of phase evolution during lead immobilization by synthetic hydroxyapatite.", Materials Characterization, **2004**, Vol. 53, pp. 71-78.

X-ray tomographic microscopy study of ancient ceramics from Thailand archaeological site

K. Won-in[1], P. Pakawanit[2], P. Dararutana[3]

[1]Department of Earth Sciences, Faculty of Science, Kasetsart University, Bangkok 10900 Thailand,
kritwonin@gmail.com
[2]Synchrotron Light Research Institute, Muang District, Nakhon Ratchasima 30000 Thailand,
[3]Retired Army Officer, Royal Thai Army, Bangkok 10900 Thailand

Archaeological studies for ceramics focus on some topics such as dating, provenance and technology seem to be an important information about the development of ceramics manufacturing throughout history [1-2]. In this paper presents the results of the X-ray tomographic scans of potsherd samples of ancient ceramics from Ban Muang Bua archaeological site in Roi Et province (northeastern Thailand), which dated around 1500 BC to 500 AD. These ceramics are one of the Thung Kula Ronghai cultural group which are produced as burial goods for funeral offerings or used as the burial jars, daily used ceramics, and low-fire earthenware [3]. The study is performed with an X-ray tomographic device (BL1.2W) at the Synchrotron Light Research Institute (SLRI), Thailand. The tomographic investigations revealed the internal configuration of the samples. Based on the X-rays images resulting from these scans, hints about the techniques used in the manufacturing of the artifacts were obtained, as well as some indications useful for conservation and restoration purposes.

References

[1] C. Chaivari, S.E. Martini and M. Vandini, Quaternary Sci. Reviews. **20**, 967 (2001).
[2] D. Barilaro, et.al., Vibrational Spectroscopy. **42**, 381 (2006).
[3] *Re-cataloging SEACM Prehistoric Ceramic Collection*, Southeast Asian Ceramics Museum Newsletter, Vol. IX, No. 3, Feb.-May 2016, pp. 1-4.

Conceptualizing a 4D laboratory X-ray CT dataset of stone weathering

T. De Kock, J.Dewanckele[1], M.A.Boone[1]

PProGRess/UGCT, Ghent University, Krijgslaan 281/S8, 9000 Gent Belgium
[1]T TESCAN XRE, Bollebergen 2B box 1, 9052 Zwijnaarde, Belgium
tim.dekock@ugent.be

Time-lapse and dynamic X-ray computed tomography (µCT) create a large amount of 3D datasets to study specific processes. Here, we show a conceptual way to visualize the course of such process on a single, reference 3D dataset. Therefore, we define the time step where a voxel in the 3D dataset changes (defined here as flip point), and rebuilt a new 3D dataset containing this time step information in its pixel value. As such, a 3D representation can be made of the 4D process (Fig. 1).

We test this tool on a continuous time-lapse dataset of limestone weathering and the formation of a gypsum crust [1]. Scans were acquired with a TESCAN UniTOM^{HR} (custom configuration). The raw data was processed using the batch reconstruction module and the flip point detection tool in the XRE Acquila 4D toolkit.

The limestone sample is exposed to a closed atmosphere above a $H_2SO_{3(aq)}$ solution during the course of 4 days whilst being continuously scanned with µCT. The development of a gypsum crusts coincides with the dissolution of calcite matrix and is a continuous process in time. Here, application of the flip point detection creates a single 3D dataset consisting of time-step labelled voxels representing either calcite dissolution or gypsum precipitation. Therefore the kinetics of the process can be studied by analysis of the newly built flip point volume (Fig. 1).

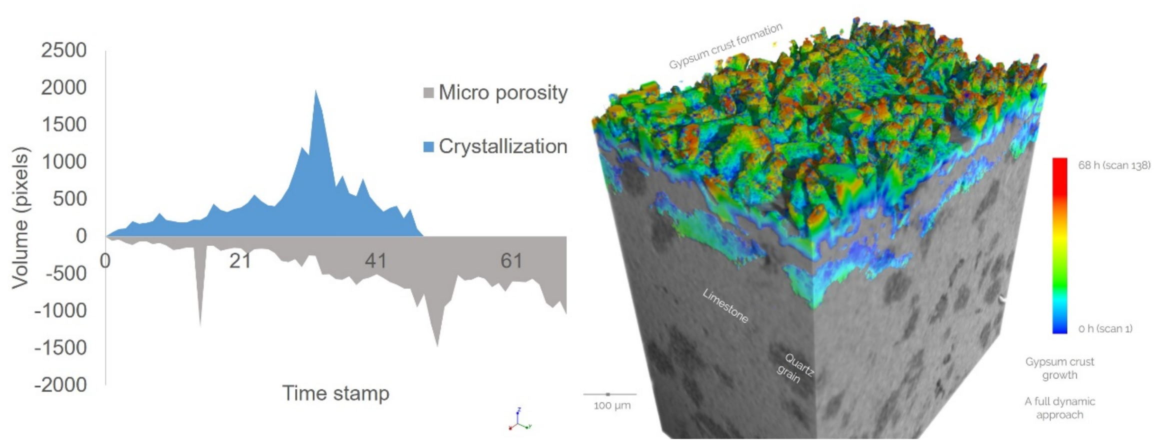


Figure 1: Representation of the kinetics of crystallization and dissolution (micro porosity) in function of time (left) and 4D time colour coded representation (right).

References
[1] T. De Kock, T., J. Van Stappen, J., G. Fronteau, M.A. Boone, W. De Boever, F. Dagrain, G. Silversmit, L. Vincze, V. Cnudde, Talanta **162**: 193-202 (2017).

Comparative study of Messinian fossil stromatolites and modern analogs from Sardinia: deciphering paleogeobiological archives

J. Debrie[1], K. Benzerara[1], J.P. Saint-Martin[2]

[1]IMPMC, UMR 7590 SU, CNRS, MNHN, IRD, 75252 Paris
[2]CR2P, UMR 7207 SU, CNRS, MNHN, Département Histoire de la Terre, 75005 Paris
juliette.debrie@upmc.fr

The unexpected discovery of stromatolites, ie macroscopically laminated carbonate rocks formed by diverse microbial communities, in small coastal ponds in Western Sardinia [1] provides new keys to understand the formation of modern microbialites in a lagoon environment. This kind of environment is extreme since it seasonally experiences severe evaporation and hence broad variations of salinity from seawater-like to hypersaline conditions. Some authors have suggested that fossil stromatolites of the Messinian period (~ 6 Ma ago), a time when the Mediterranean Sea extensively evaporated, experienced similar environmental conditions [2]. However, this remains debated. We believe that information about paleoenvironmental conditions typical of this kind of environment can be recorded by these rocks. Therefore, our objective is to compare the chemical and mineralogical composition of stromatolites formed in the Messinian with modern stromatolites from Sardinia.

I will present my PhD research project aiming at studying the mineralogy, chemistry, and microstructures of modern and fossil stromatolites from the macro- to the nano-scale. Several analyses have already been carried out: bulk X-ray diffraction (XRD), optical microscopy, confocal laser scanning microscopy (CLSM) and scanning electron microscopy (SEM) coupled with elemental analysis by energy dispersive X-ray spectrometry (EDXS). Some auto-fluorescence has been detected in the modern stromatolites with spatial variations in its spectral properties. The origin of this fluorescence could be organic and/or mineral. More in-depth analyses, including fluorescence lifetime microscopy (FLIM), will be used in correlation with other micro-analyses to better understand what paleoenvironmental and/or paleobiological information is carried by these fluorescence properties.

References

[1] - J.P. Saint Martin and S. Saint Martin, Saint Martin S. GeoEcoMarina **21**, 35-53 (2015a)
[2] - E. Perri, L. G. Chanu, A. Caruso, M. Cefal, G. Copelliti, M. Tucker, Marine and Petroleum Geology **88** 235-250 (2017)

Synchrotron X-ray imaging of sturgeons and paddlefishes from Tanis, North Dakota (USA), reveals End-Cretaceous seasonality

M.A.D. During[1,2], R.A. DePalma[3,4] J. Smit[1], C. Berruyer[5], D. F. A. E. Voeten[2,5], P. Tafforeau[5], H.J. L. van der Lubbe[1,6]

[1]Geology and Geochemistry Cluster, Vrije Universiteit Amsterdam, De Boelelaan 1117, 1081HVAmsterdam, the Netherlands, [2]Uppsala University, Subdepartment of Evolution and Development, Department of Organismal Biology, Evolutionary Biology Centre, Norbyvägen 18A, 752 36 Uppsala, Sweden, [3]Department of Geology, University of Kansas, Lawrence KS, United States of America.[4]Palm Beach Museum of Natural History, Wellington FL, United States of America. [5]European Synchrotron Radiation Facility, 71 Avenue des Martyrs, 38000 Grenoble, France.[6]School of Earth and Ocean Sciences, Cardiff University, Main Building, Park Place, Cardiff, CF10 3AT, United Kingdom

palaeomelanie@gmail.com

The Chicxulub impact on the Yucatán Peninsula (~66 Ma) obliterated ~75% of all species. As such, the Cretaceous-Paleogene (K-Pg) mass extinction was among the most selective extinction events in the history of life on Earth. The timing of impact relative to their seasonal cycles likely influenced survival of latest-Cretaceous biota. However, until now, impact timing was constrained on a millennial timescale, and the season of impact remained unclear. Here, we demonstrate that the bolide responsible for the K-Pg mass extinction struck during boreal spring. This impact was geologically recorded by impact spherules, shocked quartz, and a global iridium anomaly. Seiche deposits preserving mass-death assemblages of fishes with impact spherules lodged in their gill rakers was recently discovered (Tanis, North Dakota, USA). Using non-destructive propagation phase-contrast synchrotron X-ray micro-computed tomography at beamline BM05 of the ESRF, tektites were only encountered in the gill region but are notably absent elsewhere in the fossils. Synchrotron microtomographic osteohistology delivered high-resolution growth records from dermal bone of sturgeons and paddlefishes. These data resolved continuous annual cyclicity during the final years of the Mesozoic. The periosteal surfaces preserve an unfinished growth zone with a $\delta^{13}C$ value of -2.5 ‰, intermediate between winter minima of -3.3‰ and summer maxima of - 1.3‰. Our high-resolution records thereby demonstrate that the fish perished in spring. Annual cyclicity, including timing and duration of reproduction, ingestion, and metabolic activity, strongly varies across biota. Seasonal sensitivity to the effects of both ejecta re-entry and wildfires, and reduced insolation and acidic precipitation induced by sulfuric aerosols, will have substantially influenced relative biotic survival rates across the K-Pg boundary.

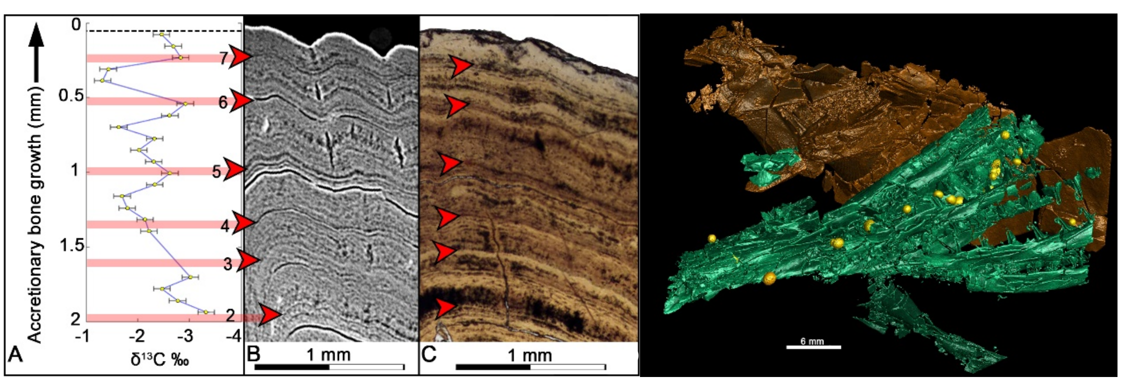


Figure 1: A, Paddlefish $\delta^{13}C$ ‰ vs. VPDB. B, µCT 0.1mm thick slab (4.35 µm voxel size). C, Cut thin section. **Arrows** indicating LAGs. D, The tektites in the gill rakers behind the suboperculum at 13.67 µm.

X-ray or neutron imaging?

A. Fedrigo[1]

[1]STFC, United Kingdom, **anna.fedrigo@stfc.ac.uk**

X-rays imaging is generally the first choice for examination of museum objects for their availability and easy application. But where X-rays fail or cannot deliver specific information, such in case of dense materials like bulky metals, neutron imaging methods will be successful at most times, delivering contrasts and penetration data that are not accessible for X-rays. Neutrons also deliver contrast between many neighbouring elements in the periodic system, often rendering contrast between very similar materials. In addition, neutron imaging provides high contrast for hydrogen containing phases, which can be easily located even in the presence of heavy atoms.

Neutron tomography can also be applied in combination with X-ray tomography in a bi-modal approach [1]. The different interactions of X-rays and neutrons with matter allow us to exploit the complementary information of both modalities: X-rays interact mainly with the electrons of an atom (the more electrons an atom has the higher the probability of interaction), whereas neutrons are electrically neutral particles that interact with the atomic nuclei.
Bi-modal imaging can provide a wealth of information on multi-phase objects. A bi-modal imaging approach can provide a more detailed and quantitative understanding of the structural and chemical composition compared to standard single mode imaging methods, as X-ray and neutron interaction with matter results in different attenuation coefficients with a non-linear relation.

The work covers various examples of neutron imaging and bi-modal imaging investigations of museum objects [2–4].

References

[1] - A.Fedrigo *et al*., Investigation of a Monturaqui Impactite by Means of Bi-Modal X-ray and Neutron Tomography, *J. Imaging* **4**(5), 72 (2018)
[2] - A. Fedrigo *et al.*, Neutron imaging study of ‘pattern-welded’ swords from the Viking Age. *Archaeol. Anthropol. Sci.* **10**(6), 1249–1263b (2018)
[3] - F.Salvemini *et al*., Reveals the Secrets of Composite Helmets of Japanese Tradition, The *European Physical Journal Plus* **128**(8), 87 (2013)
[4] - A. Fedrigo *et al.*, Integrated approach between neutron diffraction and elemental imaging through Neutron Resonance Transmission Imaging, preliminary results on Chinese bimetallic sword fragments, *J. Anal. At. Spectrom.* (2019)

A XANES study of the Sn K-edge in slag by-products from tin smelting experiments

E. Figueiredo[1] , M. Larsson Coutinho[2], T. Pena da Silva[3], E. Salas-Colera[4], J.P. Veiga[1]

[1] CENIMAT/i3N – Centro de Investigação em Materiais, Departamento de Ciência dos Materiais, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, 2829-516 Caparica, Portugal.
[2] Laboratório Hercules,Universidade de Évora, 7000-809 Évora, Portugal.
[3] LNEG (National Laboratory for Energy and Geology), Mineral Resources and Geophysics Research Unit, Estrada da Portela, Apartado 7586, 2610-999 Amadora, Portugal.
[4] SpLine, Spanish CRG Beamline, European Synchrotron Radiation Facility (ESRF), Grenoble, France
esf@fct.unl.pt

Tin was a very important alloying element in Western Europe in the production of bronze (Cu-Sn alloy) since the second millennium BC (Bronze Age), when most metallic artefacts were made of this alloy.

Smelting experiments using cassiterite collected in the NW Iberian territory were made to produce tin in a very simple and small scale manner, using a small open pit structure to reproduce what could have been the manufacturing process of tin in prehistoric times.

Chemical and structural analysis of the products by XRF, SEM-EDS and XRD were made to achieve a detailed knowledge of the characteristics of the materials [1]. Additionally, an X-ray absorption near-edge structure region (XANES) study was performed on three types of slags previously identified (Type 1, Type 2 and Type 3) to obtain information on the oxidation state of Sn. The analyses were made at the European Synchrotron Radiation Facility (ESRF) at the beamline SpLine BM 25A (5-45 keV).

Keywords**:** Cultural Heritage, Synchrotron Radiation, XANES, Tin, Slags, Archaeometallurgy

Acknowledgments: Project Iberian Tin (PTDC/HAR-ARQ/32290/2017), funded by FEDER through the Lisboa Regional Programme and POCI and National Funds through FCT (Fundação para a Ciência e Tecnologia).

[1] E. Figueiredo, A. Lackinger, B. Comendador Rey, R.J.C. Silva, J.P. Veiga, J. Mirão (2017). An experimental approach for smelting tin ores from Northwestern Iberia, Materials and Manufacturing Processes 32(7-8), 765-774. https://doi.org/10.1080/10426914.2016.1244837

The TRIPHON 3D platform

D. Geffard-Kuriyama[1], M. Bellato[1]

Affiliation: [1]UMS 2700 Acquisition et Analyse de Données (2AD) CNRS MNHN, **digef@mnhn.fr**

3D imaging, chemical or structural analyses require sample preparation protocols that can be very restrictive when analyzing cultural and natural heritage artifacts.

MultiJet Printing (MJP) is an advanced high-resolution polymer 3D printing technology that offers a way of optimising these scientific analyses. A *3D Systems ProJet MJP 2500+* printer has been recently acquired by the MNHN of Paris [1].

Our workflow focuses on conceptualizing, designing and printing 3D supports or moulds to fit the shape of objects of interest. We use 3D digital scanning and/or computerised 3D modelling to replicate and create unique fixtures, perfectly supporting and securing any object of natural and heritage sciences. We will focus on first trials and on using this technique to support different branches of the MNHN in optimising scientific analyses. By designing different supports molded to our scanning and lab equipments, we can better position and firmly secure objects.

We will also be able to offer TRIPHON services for other uses, such as in designing more protective packaging for shipping, or to meet specific exhibition needs. We will have new samples of 3D printed objects available on the poster.

Figure 1: Tryphon Tournesol, 3D printer first « inventor »

.

References

[1] - D. Geffard-Kuriyama and M. Bellato. The TRIPHON 3D project – Computerised replication technique for nonstandard supports. Heritage2019 : Scientific Symposium - Frontiers in Heritage Science, Feb 2019, PARIS, France. hal-02274070.

Micro-Photoluminescence Imaging of intact and degraded Cadmium Yellow paint cross-sections

M. Ghirardello[1], M. Refregiers[2], D. MacLennan[3], C. Schmidt Patterson[3], K. Trentelman[3], A. Nevin[4], G. Valentini[1] and D. Comelli[1]

[1]Politecnico di Milano, Physics Department, Piazza Leonardo da Vinci 32, 20133, Milano, Italy
[2]Synchrotron SOLEIL, DISCO Beamline, BP48 Saint-Aubin F-91192 Gif-sur-Yvette cedex, France
[3] Getty Conservation Institute, Science Department, 1200 Getty Center Drive, Los Angeles, California 90049, United States
[4] University of Gothenburg, Göteborg, Vaestra Goetaland, Sweden
marta.ghirardello@polimi.it

UV-visible induced luminescence is one of the first tools employed by conservator and restorers to analyse artworks in a non-destructive and non-invasive way. Recently, due to the development of more quantitative analysis techniques such as multi-spectral imaging spectroscopy and fluorescence lifetime imaging [1], photoluminescence (PL) techniques have been proposed to provide more specific information on the characteristic of the material analysed.

In this field, synchrotron DUV photoluminescence micro-imaging studies have proved to be a useful technique to characterize different types of materials. In particular, the approach has been successfully tested to probe crystalline defects in zinc white pigments, showing that materials homogeneous at macroscale are highly heterogeneous at micro and sub-micro scale [2]. More recently, the technique has been applied to identify the coexistence of two cuprous oxide phases in an ancient amulet and to monitor the processes of metal soap formation in paint films [3,4].

In this work, highly-resolved PL micro-imaging using DUV excitation (SOLEIL synchrotron, DISCO beamline) has been employed to characterize degraded and preserved Cadmium Sulphide paint cross-sections from Pablo Picasso's painting *Femme*.
Previous Time Resolved Photoluminescence (TRPL) spectroscopy analyses of the painting have demonstrated that the degraded CdS paint have a strong and peculiar optical emission from trap states, ascribed to a higher density of surface crystal defects [5]. The use of synchrotron micro-imaging confirms the changing of the PL properties in the degraded paint layer with respect to the preserved one and instead reveals a complex sub-micrometric spatial heterogeneity of the optical emission of the altered CdS paint films.
In the future, other X-ray-based SR studies will be applied to evaluate the crystalline phases present in the paint films and the possible existence of CdS nanocrystal grains [6].

The research leading to these results has received a financial support by the Access to Research Infrastructures activity in the H2020 Framework Programme of the EU (IPERION CH Grant Agreement n. 654028).

References

[1] M. Thoury, et al., Analytical chemistry 83.5: 1737-1745 (2011).
[2] L. Bertrand, et al., Analyst 138.16: 4463-4469 (2013).
[3] M. Thoury, et al., Nature communications 7: 13356 (2016).
[4] M. Thoury, et al., Metal Soaps in Art. Springer, Cham, 211-225 (2019).
[5] D. Comelli, et al., Analytical chemistry 91.5: 3421-3428 (2019).
[6] B.D.A. Levin, et al., arXiv preprint, arXiv:1909.01933 (2019).

Gold application on gilded and enamelled glass objects from Southern Italy

M.C. Caggiani[1], L.C. Giannossa[2,*], R. Laviano[3,*], A. Mangone[2,*]

[1]Department of Biological, Geological and Environmental Sciences, University of Catania, Italy, [2]Department of Chemistry, University of Bari Aldo Moro, [3] Department of Earth and Geoenvironmental Sciences, University of Bari Aldo Moro, [*] Interdepartmental Centre "Research Laboratory for Diagnostics of Cultural Heritage", University of Bari Aldo Moro, Italy

lorenacarla.giannossa@uniba.it

A group of gilded and enamelled glass, dating back to 13th - 14th century, was recently found in Melfi's Castle, a Frederick II fortress in Southern Italy. This production is comparable both with more recent Mamluk Syrian and Egyptian objects and with much more ancient Roman enamelled glass.

As far as the gildings are concerned, several different ways to apply gold on a glass/ceramic substrate are documented but they can be summarized in gold foil or "liquid" gold with or without heating. Special attention is given to the adhesion agents that allowed a certain resistance of the decoration for which different mechanisms were suggested.

The general objective of this study is to draw conclusions on possible commercial and cultural exchanges, while its specific aims can be summarized as such:

1) investigating the technological processes employed to apply gilding and understanding adhesion agents;

2) detecting the presence of tracing elements to hypothesize the provenance of gold.

Up to now, Raman spectroscopy, SEM-EDS analyses and OM observations were carried out on the enamels, whose pigments/opacifiers compositions were determined, and on the gildings. Gildings observations highlighted an irregular particle-like morphology that did not resemble that of a foil. As far as a possible medium or sub-layer working as a gluing agent is concerned, in our samples the experimental evidences are complex and diversified: 1) a frequent presence of manganese under and over the gildings, as well as an occasional presence of lead associated to the underlying manganese, was detected; 2) in few cases a red iron- and lead-rich enamel basis was observed directly below the gilding without a manganese intermediate layer; 3) in two samples gold was observed immersed into the red enamel, or into a green, lead based enamel; 4) in all samples Raman spectroscopy highlighted the occurrence of either amorphous carbon or an organic substance among the gold particles, occasionally found also in the manganese layer associated to gold.

For the elemental analyses, nowadays, the most accepted techniques are (LA)ICP-MS and IBA. However, (LA)ICP-is (micro)destructive and IBA techniques, despite being totally non-invasive, have inadequate detection limits for certain elements. In literature, as well as on ancient glass objects [1], SR-XRF studies on metallic objects are reported, aimed to the determination of the provenance of metals [2,3].

We believe that micro-analyses through SR-XRF associated to elemental mappings of the cross sections would be the optimal methodology to accomplish both our goals, thanks to the micronic spot and the high sensitivity fundamental to the resolution of the exposed problems.

References

[1] P. Fredrickx et al., X-Ray Spectrom. **33** (2004).
[2] M.F. Guerra et al., Nuclear Instruments and Methods in Physics Research B **266** (2008).
[3] A. Vasilescu, B. Constantinescu, Romanian Reports in Physics, **63**, 4, (2011).

Compatibility of spectroscopic techniques in comparative measurements of historical Polish coins

A. M. Gójska, E. A. Miśta, K. Trela

[1] National Centre for Nuclear Research, ul. A. Soltana 7, 05-400 Otwock, Poland
Aneta.Gojska@ncbj.gov.pl

The ED-XRF (energy-dispersive X-ray fluorescence) compact system was used to analyze selected Polish historical coins. The compact X-ray tube developed in the National Centre for Nuclear Research (NCBJ) was used as an X-ray source in the system designed for the ED-XRF studies. The XRF spectra were recorded with the Amptek SDD spectrometer. The elemental compositions of two historical Polish coins have been determined using above mentioned system and the results were compared to those obtained with WD-XRF method. Other techniques such as SEM-EDX and XRD were also included into this work for comparison. The experimental data show that the X-ray system with transmission type X-ray tube with silver anode operating at 50kV/30µA which was developed in NCBJ together with the Amptek SDD spectrometer is an effective tool for chemical composition analyze of historical coins and can be successfully used in archaeometry**.**

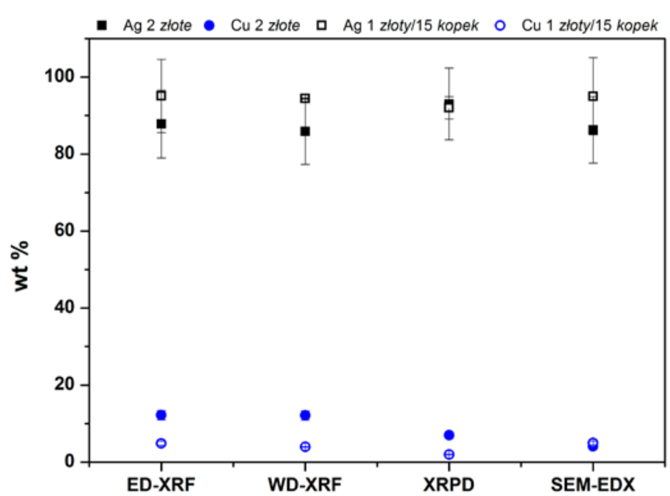


Figure 1. The comparison of the elemental composition of coins obtained by use of four spectroscopic methods: ED-XRF, WD-XRF, SEM-EDX, XRD.

Synchrotron Circular Dichroism spectroscopy: a brief review of its potential for investigations of interactions in archaeological wood systems

Mary K. Phillips-Jones[1], Stephen E. Harding[1,2]

[1]National Centre for Macromolecular Hydrodynamics, School of Biosciences, University of Nottingham, Sutton Bonington, Leicestershire LE12 5RD, UK and [2]Kulturhistorisk Museum, Universitetet i Oslo, Postboks 6762, St. Olavs plass, 0130 Oslo, Norway

mary.phillips-jones@nottingham.ac.uk

Synchrotron circular dichroism (SCD) is widely used to study chiral molecules, in particular proteins in solution and in thin amorphous dry films [1,2]. In the near-UV region (250 – 340 nm) it reports on tertiary structural conformational changes in proteins revealed through changes in the environments of aromatic amino acid residues, whilst measurements in the far-UV region (180-260 nm) reveal protein folding and secondary structure composition e.g. [2,3]. A unique strength of SCD spectroscopy is its higher photon flux and extended vacuum UV region down to 125nm[2], the latter being particularly useful for obtaining spectral measurements of sugars, oligosaccharides and complex polysaccharides including cellulose [4,5]. The technique is of high sensitivity and excellent for measurements of conformational changes induced upon addition of ligands and changes in solvent conditions. However, thus far it has not been extensively used to investigate celluloses, hemicelluloses, lignin and other related complex systems, perhaps because of the claimed lack of optical activity of the lignins [6] and the more specialised requirements of vacuum UV conditions. However, interactions of celluloses, hemicelluloses and lignin with chiral ligands have been more recently studied [7]. With the development of next-generation consolidants including molecules that interact with specific remnant molecular structures in archaeological wood [8,9], here we indicate the potential of using SCD to investigate polymerisation and networking interactions involving consolidants of the future in aqueous and non-aqueous systems.

We are grateful to the Diamond Light Source Ltd. (Oxfordshire, UK) for beamtime and to the ‘Saving Oseberg’ team (Oslo, Pisa and Nottingham).

References

[1] - S.M. Kelly, T.J. Jess and N.C. Price, Biochimica et Biophysica Acta **1751**, 119 (2005).
[2] - G. Siligardi, R. Hussain, S.G. Patching and M.K. Phillips-Jones, M.K. Biochimica et Biophysica Acta Biomembranes **1838**, 34 (2014).
[3] – S.G. Patching, S. Edara, P. Ma, J. Nakayama, R. Hussain, G. Siligardi and M.K. Phillips-Jones, Biochimica et Biophysica Acta Biomembranes **1818**, 1595 (2012).
[4] - W.C. Johnson, Advances in Carbohydrate Chemistry & Biochemistry **45**, 73 (1987).
[5] – K. Matsuo, Biomedical Spectroscopy & Imaging **6**, 111 (2017).
[6] - J. Ralph, J. Peng, F. Lu, R.D. Hatfield and R.F. Helm, Journal of Agricultural & Food Chemistry **47**, 2991 (1999).
[7] - A. Yamaguchi, K. Isozaki, M. Nakamura, H. Takaya and T. Watanabe, Scientific Reports **6**, 21833 (2016).
[8] - Z. Walsh, E.-R. Janeček, J.T. Hodgkinson, J. Sedlmair, A. Koutsioubas, A., D.R. Spring, M. Welch, C.J. Hirschmugl, C. Toprakcioglu, J.R. Nitschke, M. Jones and O.A. Scherman, Proceedings of the National Academy of Sciences USA **111**, 17743 (2014).
[9] - E. McHale, C.C. Steindal, H. Kutzke, T. Benneche and S.E. Harding, Scientific Reports **7**, 46481 (2017).

Geopolymers: innovative green materials for cultural heritage conservation-restoration

G. Barone[1], M.C. Caggiani[1], A. Coccato[1], F. Di Benedetto[2], C. Finocchiaro[1], M. Fugazzotto[1,3], G. Lanzafame[1], P. Mazzoleni[1], R. Occhipinti[1], A. Stroscio[1]

Affiliation: [1]Dep. of Biological, Geological and Environmental Sciences, University of Catania, Italy; [2]Dep. of Earth Sciences, University of Firenze, Italy, [3]Dep. of Humanities, University of Catania, Italy

gabriele.lanzafame@unict.it

Geopolymers are inorganic polymeric materials obtained by mixing of solid aluminosilicate precursors with an alkaline solution (NaOH and Na_2SiO_3 mixed in various ratios) plus other constituents such as fibers or aggregates [1,2]. These materials resemble artificial rocks or ceramics and have been recently proposed as substitutes for conventional materials in interventions of conservation-restoration of built heritage [3]. The precursors used in their production are raw materials of different nature, including industrial waste (ceramic tiles, bricks), volcanic (ash, ghiara paleosoil, pumices) and sedimentary rocks (clays, calcarenites). These products represent an innovative tool in terms of recycle and sustainability, since their production is carried at low temperature, involves the re-use of waste material from human activity and produce low emission of CO_2 and energy consumption in comparison with Portland cements [3,4].

The Advanced Green Materials for Cultural Heritage (AGM for CuHe) project (PNR fund with code: ARS01_00697; CUP E66C18000380005), currently carried at University of Catania (Italy), aims to formulate geopolymers using local (Sicilian) raw materials as precursors. Volcanic rocks, together with industrial waste materials are widely available in Sicily, and show promising perspectives in terms of chemical, mineralogical, mechanical and aesthetic compatibility with the local built heritage. As an example, bricks and tiles can be used as geopolymer precursors for substitution, consolidation and repairing of brick masonries of archaeological interest, since they are compatible with the wall substrates. On the other hand volcanic stones can be used in the geopolymers production since they mimic the traditional materials used in the Etnean area.

The process of geopolymers production requires a wide characterization of the involved materials in order to evaluate their chemical, textural and mechanical features. This is achieved by a multi-analytical approach (XRD, XRF, FT-IR, Raman spectroscopy, SEM-EDS, XAS, mCT, mechanical tests) in order to optimize the formulation design and to evaluate mechanical properties and chemical stability of the final product for use in conservation-restoration intervention on historical buildings. These techniques have their best application at Synchrotron Light facilities. As few examples, mCT is fundamental for investigating the inner structure of the finite product and relate its texture to mechanical properties. Element specific techniques such as XAS and μXAS are instead employed in the close control of the fate of selected elements (among others, mainly Fe), crucial to attain controlled aesthetical properties and to monitor potential release of polluting species during the future alteration of such materials.

References

[1] J. Davidovits, J. Therm. Analys. **37**, 1633-1656 (1991).
[2] A. Palomo and F. Glasser , British Ceramic. Trans. J. **91**, 107-112 (1992).
[3] M. Clausi et al., App. Clay Sci. **132**, 589-599 (2016).
[4] G. Habert, C. Ouellet-Plamondon, RILEM Tech. Lett. **1**, 17-23 (2016).

Co and Cu K-edge XANES study of the glazed tiles from the Fronteira Palace (Lisbon, Portugal)

M.L. Coutinho[1], T. Pena[2], E. Figueiredo[3], M. Rolim[3], E. Sales-Colera[4], J.P. Veiga[3]

[1]IFAA and Laboratório Hercules, Univerisdade de Évora, Largo Marquês de Marialva, 8, 7000-809 Évora, Portugal
[2] Unidade de Recursos Minerais e Geofísica, Laboratório Nacional de Engenharia e Geologia, 7586 Alfragide, Portugal
[3]Centro de Investigação de Materiais, CENIMAT/I3N, Faculdade de Ciências e Tecnologia, Universidade NOVA de Lisboa, Quinta da Torre, 2829-516 Caparica, Portugal
[4] SpLine, Spanish CRG Beamline, European Synchrotron Radiation Facility (ESRF), Grenoble, France Times
mathildal@gmail.com

The Fronteira Palace located in Lisbon was built during the second half of the seventeenth century. The Palace is known for its unique azulejos (Portuguese glazed tiles) dated from the 17th and 18th century which were profusely used both in the interior of the palace and on its magnificent formal gardens. The gardens have a unique cladding of high relief lustre tiles combined with blue-and-white tiles adorning the Gallery of the Kings (Figure 1). Samples of azulejos from Gallery of the Kings, were characterized in a previous work by PIXE [1]. They display a silica alkali-lead glass or silica alkali glass and chromophores based on Co for the blue colouring and Cu for the red-lustre effect [1]. In fact, the analyses showed that the colourless glaze has a lead-alkali silicate composition and a copper-rich lustre overlay, in agreement with the Manise lustreware production (Spain) after the XVII century [2]. To achieve a comparison between manufacturing techniques and pigments used samples were characterized using X-Ray Absorption Spectroscopy. XANES techniques can provide information on the structural behaviour of transition metals in the vitreous matrix - namely, their bonding state and coordination environment, providing relevant information regarding the Co and Cu as chromophores [3][4].

Figure 1: Gallery of the kings in the gardens of the Fronteira Palace (A), detail of a Lustre tile (B).

References

[1] – S. Teixeira A.M. Lima, L.C. Alves; R.C. Silva, M. Vilarigues, M.F. Macedo, M.L. Coutinho In 5th International Conferene Yococu 2016. (Abstract)

[2] – A. Polvorinos, M. Aucouturier, A. Bouquillon, J. Castaing, J. Camps. Archaeometry **53**, 490, 2011.

[3] – M.O Figueiredo, T.P. Silva, J.P. Veiga. Journal of Electron Spectroscopy and Related Phenomena **185** (3–4), 97, 2012.

[4] – W. Klysubun , C. A. Hauzenberger, B. Ravel, P. Klysubun ,Y Huang ,W. Wongtepa, P. Sombunchoo.. X-Ray Spectrometry, **44**(3) 116, 2015.

The synchrotron radiation based investigation of prehistoric rock art from Saleh cave, Borneo island, Indonesia

E. Maryanti[1], M.M. Ilmi[1], N. Nurdini[1], G.T.M. Kadja[1,2,], P. Setiawan[3], Ismunandar[1]

Division of Inorganic and Physical Chemistry, Institut Teknologi Bandung, Jl, Bandung, Indonesia[1], Research Center for Nanosciences and Nanotechnology, Institut Teknologi Bandung, Bandung , Indonesia , Visual Communication and Multimedia, Institut Teknologi Bandung, Bandung , Indonesia[2]

evimaryanti82@students.itb.ac.id

Indonesia is a country whose prehistoric rock images with hundreds of sites and varied of motifs. Kalimantan Island (Borneo), one of islands in Indonesia, has prehistoric rock images created during the Pleistocene era based on Uranium analysis dating of a reddish-orange figurative painting of an animal known to be a minimum age of 40 ka and dark purple hand stencil aged around 21-20 ka [1]. In this research, synchrotron X-Ray Diffraction was carried out to determine the major and minor phases of reddish-orange pigment of bull foot image and purple hand stencil from Saleh Cave, East Kalimantan. The analysis showed that both samples contained hematite (α-Fe_2O_3) as the main component of pigment, with gypsum ($CaSO_4.2H_2O$) and calcite ($CaCO_3$) as rock component of the image substrate. However, the purple pigment showed sharper peak corresponds to hematite phase which may suggest more crystalline phase. Mapping element analysis using X-Ray Fluorescence showed a greater distribution of Fe elements in the reddish-orange bull foot pigment. In addition, the two pigment samples show the distribution of Al and Si elements which can be derived from clay material.

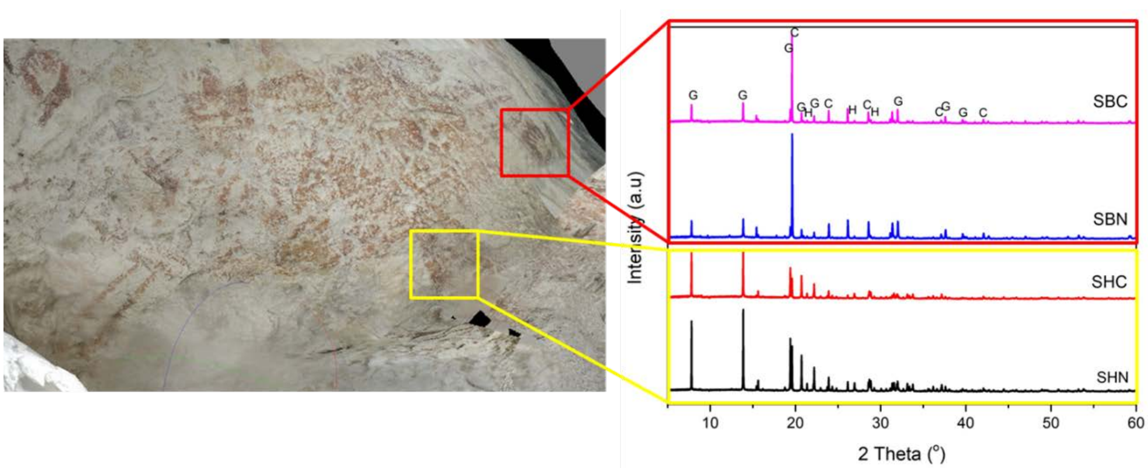


Figure 1: Sampling spot and Diffractogram of pigment

References

[1] – M. Aubert, P. Setiawan, A.A. Oktaviana, A. Brumm, P.H. Sulistyarto, E.W. Saptomo, B. Istiawan, T.A. Ma’rifat, V.N. Wahyuono, F.T. Atmoko, J.-X. Zhao, J. Huntley, P.S.C. Tacon, D.L. Howard & H.E.A. Brand, Nature **564**, 254-257 (2018).

Characterization of colour changes in limestone sculptures using X-ray based methods

L. Dias[1], A. Candeias[1,2], A. T. Caldeira[1,2], J. Mirão[1,3]

[1]HERCULES Laboratory, University of Évora, Portugal, [2]Chemistry Department, Sciences and Technology School, University of Évora, Portugal, [3] Geosciences Department, Sciences and Technology School, University of Évora, Portugal

jmirao@uevora.pt

Since the ancient times, natural stone has been the material selected to construct cultural heritage assets due to its beauty and durability. However, like all materials, stone may suffer inexorable deterioration, caused by several factors, either external or internal. The main degradation promotors that may easily affect indoor limestone are soluble salts, water and biodeteriogenic agents which can induce physical and chemical deterioration, leading in extreme cases to the loss of sculptors' original intention.

The limestone sculptures selected are dated from the 15th and 16th centuries and are currently exposed inside the National Museum of Ancient Art, Lisbon, Portugal. They have two main types of pathologies affecting their chromatic characteristics, namely white and red staining, in addition to the loss of some original material.

The analytical approach allowed the characterisation of several alteration products formed on the sculptures' surface, which can potentiate the structural damages of the sculptures and are probably related to their colour alteration. Using complementary analytical techniques, it was possible to state that the white hues and loss of material are mainly related with the formation of efflorescence (Fig.1a) and microbial development. On the other hand, the reddish hues seem to be related with the of iron oxides' concentration (Fig.1b) and formation of carotenoids.

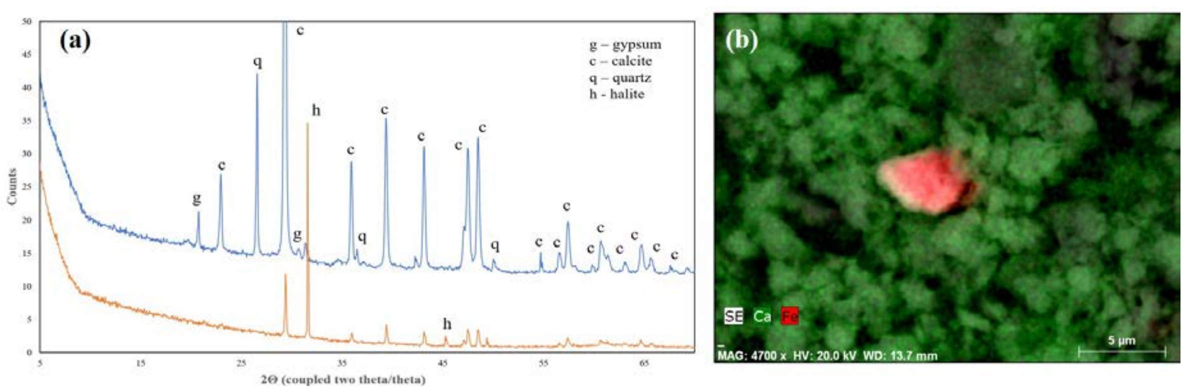


Figure 1: Detection of alteration products using µ-DRX (a) and SEM-EDS (b).

A possibility of detection of chemical soldering in medieval jewellery

Ewelina A. Miśta-Jakubowska[1], Aneta Gójska[1], Renata Czech Błońska[2], Władysław Duczko[2], Krystian Trela[1]

[1]National Centre for Nuclear Research, Andrzeja Sołtana 7, 05-400 Otwock, Poland
[2]Institute of Archaeology and Ethnology, Polish Academy of Sciences, Al. Solidarności 105, 00-140 Warsaw, Poland
Ewelina.Mista@ncbj.gov.pl

The aim of this presentation is to discuss some technological details of medieval jewellery on the basis of studies on lunula-type ornaments from a hoard in Obra Nowa, Wielkopolskie Voivodeship, Central Poland (fig.1). The most important research problems are the types of soldering which were applied in order to attach ornamentation details (granules and wire) to the surface of the artefacts in question (fig. 2). Types of solders which were in use in Antiquity and in the Middle Ages were discussed. Five fragments of silver lunulas were examined using optical light microscopy, SEM-EDX, micro-Raman spectroscopy and XRD. Results produced by a combination of these methods confirmed the use of chemical soldering in the ornament of the discussed artefacts. In conclusion, it was said that the presence of individual elements in the solder may have been due to different reasons, such as the use of certain types of ores or of metal from re-melted dirhams.

Fig. 1. Studied lunulas from the Obra Nowa hoard: obverse and reverse

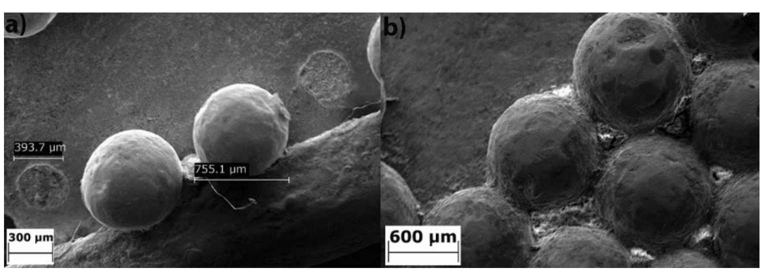


Fig. 2. a) Lunula 2261, obverse and b) Lunula 2262, obverse. SEM-SE images of cloud-shaped soldering region located between granules

Retrieval of the lost literature from the Herculaneum Papyri with the X-ray Fluorescence Microscopy

Luxi Li[1], Zou Finfrock[1,2], Emmanuel Brun[3], Daniel Delattre[4], Vito Mocella[5]

[1]Advanced Photon Sources, Argonne National Laboratory, 9700 Cass Ave., Lemont, IL 60439, USA; [2]Canadian Light Source Inc. 44 Innovation Boulevard Saskatoon, SK S7N 2V3 Canada; [3] Inserm U1216, F-38000 Grenoble, France; [4] INRS-Institut de Recherche et d'Histoire des Textes, 75016 Paris, France;
[5] CNR-IMM Italian National Research Council, Via P. Castellino 111 , 80131 Napoli, Italy.
luxili@anl.gov; **vito.mocella@cnr.it**

The Herculaneum papyri in an ancient library buried by the eruption of Mount Vesuvius were recovered 260 years ago. The papyrus scrolls are highly carbonized during the volcano eruption and have become extremely fragile and disformed. The papyri appear to be black either in a full roll or in fragments. It is impossible to open them and read the text without damaging them irreparably. In order to read the content in the scrolls without unrolling them, The X-ray Phase Contrast Tomography was applied to reveal a ~~few~~ characters and few words from in-situ measurements [1]. In this work, we are using a different approach, the X-ray Fluorescence Microscopy (XFM) to study the intrinsic element contrast. The Synchrotron Radiation X-ray Fluorescence Microscopy (XFM) is an indispensable non-destructive method to study the material elemental information. High energy X-ray beam is used to excite the inner shell electron, leaving a vacancy in the atomic structure. To stabilize the atom, an outer shell electron will fill in the vacancy and emit an X-ray photon with a characteristic energy respectively to the element species. Therefore, by detecting energy and the intensity of the emitted X-ray photons, one can identify and quantify the elements in the materials.

The ink used to write in the papyri may contain Hg, Pb, or Fe, and the papyrus materials contain K and one can even identify the waiving pattern of the papyrus fibre[2]-[3]. An artificial sample of papyrus with multiple layers and with Greek letters written on it was scanned by XFM with the confocal setup. One managed to measure the 2D elemental maps and at multiple depths into the sample with 30μm depth resolution. Letters from individual layers can be clearly identified by the Pb maps. Then a few fragments of the Herculaneum papyri are scanned with confocal XFM identifying some letters within fragments containing multiple layers. The fragments are also scanned with X-ray Fluorescence Tomography for the technique comparison.

References

[1] Vito Mocella, Emmanuel Brun, Claudio Ferrero, Daniel Delattre, Nat. Comm. 6, 5895 (2015).
[2] Emmanuel Brun et al, PNAS 13-14, 3751–3754 (2016).
[3] Tack et al, Scientific Reports **6**, 20763 (2016)

An unusual CN stretching in Prussian Blue painted materials

Luca Nodari[1], Martina Zuena[1], Stefano Legnaioli[2], Beatrice Campanella[2], Vincenzo Palleschi[2], Patrizia Tomasin[1]

[1]ICMATE-CNR, Corso Stati Uniti 4, 35127 Padova, Italy; **luca.nodari@cnr.it**
[2]ICCOM-CNR, Via G. Monuzzi 1, 56124 Pisa, Italy

The present project deals with the study of the influence of the manufacturing process in the composition of the Prussian Blue (PB), a popular dark-blue pigment, widely used from ca. 1720 to the 1970's. PB, is a mixed valence compound and it can be obtained in two forms: insoluble (IPB) $Fe_4[Fe(CN)_6]_3 \cdot xH_2O$ or soluble (SPB) $KFe[Fe(CN)_6] \cdot yH_2O$. The presence of a CN^- group, bounded to both Fe(II) and Fe(III) ions, results in a well recognizable stretching band,□□(CN), in both infrared and Raman spectroscopy. This sharp absorption is commonly used as marker for the pigment identification [1] and, when shifted, it can be representative of alteration processes [2,3]. For instance, PB, identified in *Superficie lunare* (1969) by L. Turcato, shows an unusual □(CN) split in two components: one at ≈2085 cm^{-1}, characteristic of PB [4] while the other, at ≈2050 cm^{-1}, typical of ferrous ferrocyanide complexes. In general, literature data [2,3] report that these complexes can be representative of the PB photoreduction. On the contrary, in our case study, a thorough spectroscopic characterization (by means of *in-situ* Raman and ERFTIR and successively by □-ATR, and □-Raman) identified the presence in the pictorial layer of hydrate Fe(II) sulphate, rozenite, and an ammonium ferrous ferrocynide complex, typical of the indirect production methodology [5,6]. In order to understand if the presence a reaction intermediate, such as ammonium ferrous ferrocynide complex, could mislead the evaluation of alteration process, an experimentation on different mock-ups was projected. The mock-ups were prepared applying on different substrates both commercial PB paint tubes and laboratory formulations. Here the investigations on *Superifice Lunare* are briefly reported and the results of the starting materials characterization (by means of Infrared, Raman and Mössbauer spectroscopies) are presented and discussed. In the data discussion a special attention will regard the effect of the substrate on the □(CN) ERFTIR signal and the presence of manufacturing intermediate on the commercial formulations. Moreover, preliminary results on the effects of accelerate ageing will be presented.

References

[1] L. Samain, G. Silversmit, J Sanyova, B. Vekemans, H. Salomon, B. Gilbert, F. Grandjean, G. J. Long, R. P. Hermann, L. Vincze and D. Strivay, J. Anal. At. Spectrom., **26**, 930 (2011)
[2] L. Samain, B. Gilbert, F. Grandjean, G. J. Long, and D. Strivay, J. Anal. At. Spectrom., **28**, 4, 524, (2013).
[3] C. Gervais, M.A. Languille, S. Reguer, M. Gillet, S. Pelletier, C. Garnier, E.P. Vincenzi and L. Bertrand, J. Anal. At. Spectrom., **28**, 10, 1600 (2013).
[4] M. Zuena, S. Legnaioli, B. Campanella, V. Palleschi, P. Tomasin, M.K. Tufano, F. Modugno, J. La Nasa, L. Nodari, submitted to Microchem J, (2019)
[5] J. Kirby, National Gallery Technical Bulletin, **14**, 62 (1993).
[6] J. Kirby and D. Saunders, National Gallery Technical Bulletin, **25**, 73 (2004).

Oxidation-reduction effects on copper colour in glasses and glazes

C. Noirot, L. Cormier

Sorbonne Université, CNRS UMR7590, MNHN, IRD, Institut de minéralogie, de physique des matériaux et de cosmochimie (IMPMC), 4 place Jussieu, 75005 Paris, France. **cecile.k.noirot@gmail.com**

In glasses or ceramic glazes, copper can either produce a blue to green colour, or form a vivid red known as "pigeon-blood" or "liver red", due to the formation of copper-rich nano-particles. Understanding the mechanisms for these colourations can help control colour formation, but also reveal ancient manufacturing processes, in medieval stained glasses for instance.

On the one hand, blue to green hues obtained with cupric ions largely depend on the glass composition and heat treatment. The reason for the colour variation was investigated through EPR spectroscopy and optical absorption spectroscopy. It could be shown that redox effect alone can not account for hue variations. The research pointed towards an effect linked to inter-valence charge transfers, varying with Cu^{2+}/Cu^{+} equilibrium and with copper concentration.

On the other hand, reductive atmosphere during firing can lead to the formation of copper-rich nanoparticles. Both $Cu_{(0)}$ and Cu_2O nano-crystals can lead to a red hue, which makes the origin of the colour controversial. We present the PhD research project aiming at understanding the mechanisms of colour formation through *in situ* XAS, optical absorption spectroscopy, and electronic imaging, during the development of colour.

Figure 1: "Pigeon-blood" porcelain glaze by France Franck [1].

References

[1] – Ph. Sciau, L.Noé, Ph. Colomban, Ceramic International 42 (2016) 15349-15357.

Physicochemical Identification Based Synchrotron Radiation of Prehistoric Pigments in Tewet Cave, Sangkullirang-Mangkalihat Site, Borneo Island-Indonesia

N. Nurdini, E. Maryanti[1], M. M. Ilmi, P. Setiawan[2], Ismunandar, G. T. M. Kadja[3]

Division of Inorganic and Physical Chemistry, Institut Teknologi Bandung, Jl. Ganesha No. 10, Bandung 40132, Indonesia, [1]On leave from Department of Chemistry, Universitas Bengkulu, Jl. Wr. Supratman, Kandang Limun, Kota Bengkulu, Bengkulu 38371, Indonesia, [2]Visual Communication and Multimedia, Institut Teknologi Bandung, Jl. Ganesha No. 10, Bandung 40132, Indonesia, [3]Research Center for Nanosciences and Nanotechnology, Institut Teknologi Bandung, Jl. Ganesha No. 10, Bandung 40132, Indonesia

nadyanurdini71@gmail.com

Rock art research based on Uranium-series dating of calcium carbonate deposits in Indonesian Borneo Island showed that rock art emerges at around the same time as the earliest forms of artistic expression appear in Europe (45,000–43,000 calibrated years bp) [1]. Tewet cave, one of limestone cave in East Borneo Island, possessed negative hand stencils in reddish to purple hues that can be investigated the chemical and mineralogical composition of pigments. The scientific approach using Synchrotron based X-Ray characterization (X-Ray Diffraction and X-Ray Absorption Near Edge Structure) and further analysis using X-Ray Fluorescence, Scanning Electron Microscopy and Fourier Transform Infrared would give better understanding of pigment origin used of rock art in Indonesia. The results of this research indicated haematite was main composition in pigment with gypsum and calcite were primarily mineral in substrate. The difference of hues between the samples were caused by different average particle sizes of the mineral pigment. The larger particles absorbed longer light wavelength and scattered shorter light wavelength that will appeared as purple, as smaller particles generated reddish hue. Purple hue that produce by larger particle size occured by heating treatment of pigment source as evidence from younger period of Pleistocene [2].

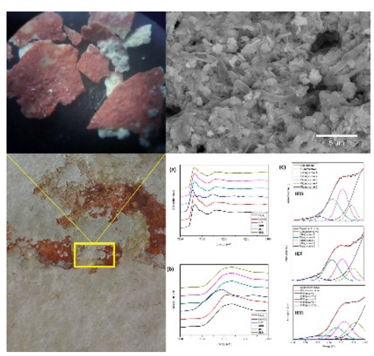


Figure 1: Optical properties of reddish hue of hand stencil in Tewet Cave, Indonesian Broneo Island (a) 40x magnification (b) 5000x magnification from (c) hand stencils figure on site; with (d) XANES spectra of Tewet cave pigments.

References

[1] - M. Aubert, P. Setiawan, A. A. Oktaviana, A. Brumm, P. H. Sulistyarto, E. W. Saptomo, B. Istiawan, T. A. Ma’rifat, V. N. Wahyuono, F. T. Atmoko, J. X. Zhao, J. Huntley, P. S. C. Taçon, D. L. Howard and H. E. A. Brand, Nature, **564**, 254-257 (2018).

[2] - A. Hunt, P. Thomas, D. James, B. David, J. M. Geneste, J. J. Delannoy and B. Stuart, Microchemical Journal, **126**, 524-529 (2016).

Synchrotron µ-XRF imaging and µ-XANES spectroscopy at the new PUMA beamline at SOLEIL

Alessandra Gianoncelli[1], Simona Raneri[2], Tulin Okbinoglu[3], Sebastian Schoeder[3]

[1]Elettra Sincrotrone Trieste, Strada Statale 14, km 163.5 in Area Science Park I-34149 Basovizza-Trieste, Italy, [2]University of Pisa, Department of Earth Sciences, Via Santa Maria, 53, 56126, Pisa, Italy,; [3]Synchrotron SOLEIL, PUMA beamline, Saint-Aubin BP48, F-91192 Gif-sur-Yvette cedex, France

alessandra.gianoncelli@elettra.eu; **simona.raneri@unipi.it**

Archaeometry is a scientific discipline which aims at characterizing, studying, preserving and/or dating archeological materials by applying scientific analytical techniques. Such analyses allow to retrieve historical and artistic information about the past and can be performed with standard instrumentation, devoted to a specific technique, or with dedicated instrumentation built to better satisfy the requirement of archeological/artistic artefacts.

This is the case of PUMA, standing for French for "Photons Utilisés pour les Matériaux Anciens”, a hard X-ray imaging beamline at SOLEIL synchrotron optimized for the scientific communities of the heritage sciences. It is equipped with a 2D imaging end-station which offers a resolution of several microns with elemental (XRF), chemical (XANES) and structural (XANES and XRD) contrast.

In the this work, we present the first analyses performed at the newly opened-to-users PUMA beamline on three set of samples, namely decorated ceramics [1], painted architectural terracottas [2] and natural stones treated with conservation products [3].

The first and recent results obtained on the analyzed samples are here presented to highlight the potential offered by this new beamline in characterizing different kind of archaeological materials, highlighting possible research outcomes and new challenges in cultural heritage studies.

References

[1] A. Gianoncelli et al., Program Booklet TechnArt 2019, 57, (2019) https://www.uantwerpen.be/images/uantwerpen/container51136/files/TechnArt2019_Programme-booklet.pdf.

[2] G.V.M. Spagnolo, Quaderni dell'istituto di archeologia della Facoltà di Lettere e Filosofia dell’Università di Messina **6**, 55, (1991).

[3] S. Raneri et al., Materials Characterization **56**, 109853, (2019).

Ancient manuscripts research using radiations of different spectral ranges and complementary techniques

E. Sozontov, N. Presnyakova, A. Pakhunov[1], A. Demkiv, G. Peters, E. Greshnikov, P. Gaidukov[1], E.Yatsishina, M. Kovalchuk

National Research Centre "Kurchatov Institute," Moscow, Russian Federation
[1] Institute of Archaeology, Russian Academy of Sciences, Moscow, Russian Federation
esozontov@yahoo.com

The analytical diagnostics of objects of art and cultural heritages becomes more and more demanded in the modern multidisciplinary research. The element mapping, detailed studying of process of writing and formation of a color contrast of letters on the birch bark manuscripts was a main goal and motivation of this research. Multispectral visualization of the hidden textual fragments of the birch bark letter of the 14th century and hidden textual fragments on medieval parchment was also objective of this research.

Synchrotron based SAXS and scanning X-ray fluorescence experiments were carried out at the Kurchatov Synchrotron Radiation Facility, NRC Kurchatov Institute, Moscow, Russia. A set of complementary techniques has been used: the samples were investigated with a scanning electron-ion microscope Versa 3D (FEI) equipped with energy-dispersive X-ray spectrometer (SEM-EDS) under the low-vacuum (40–200 Pa) mode, optical microscopy and profilometry, multispectral photography, Fourier transform infrared spectroscopy (FTIR). These experiments were carried out at the NBICS Center, NRC Kurchatov Institute.

One object of our study was birch bark manuscript of the 14th Century found during excavation in Veliky Novgorod, Russia in October 2016 by an expedition of the Institute of Archaeology, Russian Academy of Sciences (Moscow). It was supposed, that letters are written by ink, that was extremely rare because usually letters was scratched on a birch bark. Another objects of study were textual fragments of medieval parchment manuscript. The text was written by the red color ink.

Textual fragments of ancient parchment and birch bark manuscript, including hidden textual fragments, are elementally mapped and digitally imaged with scanning synchrotron based X-ray fluorescence and multispectral imaging techniques. The collagen structure of the parchment are diagnosed using synchrotron based small-angle X-ray scattering technique.

We carried out, detailed studying of process of writing and formation of a color contrast of letters on birch bark manuscript. We conclude that the letters could have been written on the birch bark using mechanical pressing of the writing instrument during the writing process without using specially prepared ink. The color (light-brown) contrast of letters is connected with the process of natural pigmentation by natural organic pigments, as a result of mechanical destruction of the suberin cell walls structure. To the best of our knowledge, this is the first comprehensive analytical research of a birch bark manuscript as a written cultural heritage object.

Acknowledgments: The reported study was partially supported by the RFBR (project no. 17-29-04476 ofi-m) and was partially supported by the NRC "Kurchatov Institute".

Informative potential of Fe and Mn K edge X-ray absorption spectroscopy for the distinction of pictorial layers from the wall support of prehistoric decorated caves and rock shelters

A. Trosseau, I.Reiche

PSL, ENSCP, IRCP UMR 8247 CNRS - Centre de recherche et de restauration des musées de France
antoine.trosseau@chimieparistech.psl.eu

Prehistoric decorated caves and rock shelters still retain many secrets, about their purpose, the authors of the art or their aspect back in prehistoric times. Our knowledge is progressing step by step by answering precise research questions. Physicochemical analysis allows exploring these questions [1-4]. Therefore, colouring matter composing cave art is an important study subject by means of a physicochemical approach. Indeed, the questions of their nature, their alteration processes, and the raw material sourcing provide information on the cave or shelter context and the cultural behaviour of their former occupants [5]. Elemental analysis is a fairly widespread mean to investigate the colouring matter of cave art and rock shelters, and non-destructive in-situ approaches are generally applied because of the necessity to avoid sampling [3, 6-9]. These analyses are limited because Fe-based pigments, which are common in this context, cannot be easily distinguished from the iron naturally present in the wall support [8]. Thus, chemical speciation of Fe- and Mn-based compounds is needed to overcome this difficulty. We think that there is still an unexplored informative potential of synchrotron techniques to get access to improved information on the chemical composition of the colouring matter used in cave art [10]. This presentation aims at sounding a new research hypothesis: the potential of X-ray absorption spectroscopy (XAS) at the Fe and Mn K edge on archaeological micro-samples to allow a better distinction of the pictural layer from the wall support. This would support the better interpretation of in-situ analysis performed in prehistoric decorated caves and rock shelters.

References

[1] - J. Monney, J.J. Delannoy, D. Genty, J. Hellstrom, S. Jaillet, E. Kaltnecker, N. Lateur, C. Moreau, M. Philippe, B. Sadier, S. Stocchetti and H. Valladas, Paleo **25**, 41–50, (2014).
[2] – M.P. Pomiès, M. Menu and C. Vignaud, Journal of the European Ceramic Society **19**, 1605–1614, (1999).
[3] – L. Beck, H. Salomon, S. Lahlil, M. Lebon, G. P. Odin, Y. Coquinot and L. Pichon, Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms **273**, 173–177, (2012).
[4] – F. Lévêque and V. Mathé, Les nouvelles de l'archéologie **36** ,19–23, (2015).
[5] – H. Salomon, C. Vignaud, Y. Coquinot, L. Beck, C. Stringer, D. Strivay and F. D'Errico, Archaeometry **54**, 698–722, (2012).
[6] – R. S. Popelka-Filcoff, E. J. Miksa, J. D. Robertson, M. D. Glascock and H. Wallace, Journal of Archaeological Science **35**, 752–762, (2008).
[7] – M. Lebon, L. Pichon and L. Beck, Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms **417**, 91–95, (2018).
[8] – M. Gay, K. Müller, F. Plassard, J.-J. Cleyet-Merle, P. Arias, R. Ontañón and I. Reiche, Journal of Archaeological Science: Reports **10**, 878–886 (2016).
[9] – M. Gay, F. Plassard, K. Müller and I. Reiche, Journal of Archaeological Science: Reports, In press.
[10] - M. Gay, M. Alfeld, M. Menu, E. Laval, P. Arias, R. Ontañón and I. Reiche, J. Anal. At. Spectrom **30**, 767–776, (2015).

Synchrotron tomography as a perfect tool to successfully imagine large and flattened fossils

V.Vaškaninová[1,2], P.E. Ahlberg[1], B. Ekrt[3]

[1] Department of Organismal Biology, Uppsala University, Norbyvägen 18A, SE-752 36 Uppsala, Sweden
[2] Institute of Geology and Palaeontology, Charles University, Albertov 6, 128 43 Praha, Czech Republic
[3] Department of Palaeontology, National Museum, Václavské náměstí 68, 115 79 Praha, Czech Republic
va.vaska@gmail.com

Acanthothoracid fish belong among the most primitive jawed vertebrates and may have a major impact on our understanding of early vertebrate evolution. Potentially the most important acanthothoracid collection in the world is the Lochkovian (Lower Devonian, approximately 415 million years old) material from the Czech Republic. However, it is problematic to study. The specimens contain semi-articulated heads and trunks with parts of the posterior body embedded in large blocks of dark, fine-grained limestone. The colour contrast of the limestones is very low and they don't respond well to mechanical or chemical preparation. These specimens are extremely important because the anatomy of the cheek, gill arches, shoulder and pelvic girdle are all poorly known or completely unknown in early vertebrates. The only non-destructive method able to image these specimens is phase contrast synchrotron microtomography (PPC-SRμCT) at ID19 beamline of ESRF. This powerful beam capable of high energies is by far the best tomographic facility in the world for vertebrate fossil specimens of this size. Most of the scans proved to be very informative; the scanning characteristics of the limestone are excellent, with high bone-rock contrast and little background noise. One observation of particular importance is the discovery of tooth-bearing jaw bones (Figure 1). The dentitions in our specimens combine features seen in bony fishes and cartilaginous fishes in an unexpected manner.

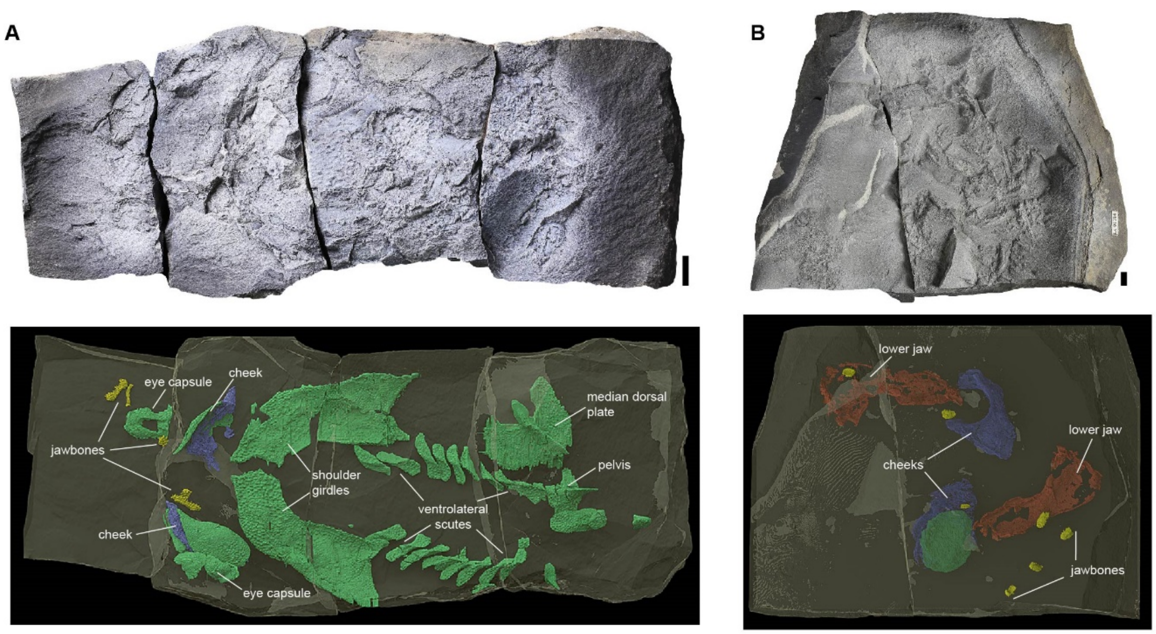


Figure 1: **A,** Specimen of *Kosoraspis* (above) and a partly modelled scan (below) showing jawbones, the postcranial skeleton and the first articulated pelvic girdle ever seen in a basal gnathostome. **B,** Specimen of *Tlamaspis* (above) and partly modelled scan (below) showing the upper and lower jaws with associated jawbones. Dermal bones in green, perichondral bones in violet and red, jawbones in yellow. Voxel size of scans 24.59 µm. Scale bar equals 10 mm.

From ceramics and glasses to mortars and stones: using synchrotron radiation to study cultural heritage

João Pedro Veiga[1], Teresa Pereira da Silva[2], Mathilda Larsson Coutinho[3]

[1] CENIMAT/I3N – Centro de Investigação em Materiais, Departamento de Ciência dos Materiais, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, 2829-516 Caparica, Portugal.
[2] LNEG (National Laboratory for Energy and Geology), Mineral Resources and Geophysics Research Unit, Estrada da Portela, Apartado 7586, 2610-999 Amadora, Portugal.
[3] Laboratório Hercules,Universidade de Évora, 7000-809 Évora, Portugal.
jpv@fct.unl.pt

Keywords: Cultural Heritage, Synchrotron Radiation, Mortars, Binders, Stones, Glasses, Ceramics, Porcelains, Minerals

The use of Synchrotron Radiation to study cultural heritage, either through objects with museum interest or materials from historical monuments is no longer a novelty. Advanced non-destructive characterization techniques to understand degradation phenomena, ageing mechanisms and ancient manufacturing techniques is now a well-established trend.
Profiting from the properties of synchrotron radiation and using large scale facilities such as ESRF (European Synchrotron Radiation Facility, Grenoble, France), BESSY (Berliner Elektronenspeicherring-Gesellschaft für Synchrotronstrahlung, Berlin, Germany) and former LURE (Laboratoire pour l'Utilization du Rayonement Synchrotron, Orsay, France), it was possible to study a great diversity of materials and objects of cultural value from different ages and provenances through X-rays.

Synchrotron radiation sources available at these large-scale facilities provide powerful chemical and structural characterization tools such as micro X-ray fluorescence and X-ray absorption spectroscopies (XANES and EXAFS).

Different case studies will be presented regarding the variety of materials studied by a group of Portuguese researchers from the past two decades (ceramics, glasses, inorganic pigments and lithologic materials).

JP Veiga acknowledges funding from the European Institute of Innovation and Technology (EIT) a body of the European Union, under the Horizon 2020, the European Framework Programme for Research and innovation, through EIT Raw Materials “MineHeritage” Project (PA 18111).

Is it worth spending so much time? A comparative study on micro-CT segmentation techniques for quantitative investigations of bone.

Alexandra HOUSSAYE[1], Patricia WILS[2]

1 : UMR 7179 CNRS / Muséum national d'Histoire naturelle, Département Adaptations du vivant, 57 rue Cuvier CP-55, 75005 Paris, France
2 : UMS 2700 CNRS / Muséum national d'Histoire naturelle, 57 rue Cuvier, 75005 Paris
patricia.wils@mnhn.fr

Bone inner structure is of great interest in vertebrate evolution studies, because it is known to bear a strong functional signal and is often well conserved in fossils. Micro-computed tomography (μCT) is a widespread and non-destructive technique that provides three-dimensional density images of both fossil and modern bones. Scanning parameters can substantially vary between the data acquisitions pending on the X-ray beam (e.g. clinical or laboratory CT scanner, synchrotron radiation -SR- μCT), the object size and chemical composition. This results in huge differences in the contrast quality between the osseous tissue and other materials constituting the bone (soft tissues or infilling sediment in fossil specimens for instance).

The trabecular architecture of the bone requires a segmentation technique in order to be described. Various approaches exist, from manual to fully automatic, and choosing one is a trade-off between time, accuracy, reproducibility and robustness to poor-contrasted images. We here evaluate different segmentation methods: manual segmentation, half mean height thresholding (1), local thresholding (2) and MIA Clustering (3) for both laboratory and SR μCT, modern and fossil taxa, complete bones or regions of interest. We measure the impact on the quantitative analysis of the trabecular bone using the BoneJ plugin (4) of ImageJ (5) and then discuss the optimal segmentation strategies.

References

1. Spoor, C. F., Zonneveld, F. W., & Macho, G. A. (1993). Linear measurements of cortical bone and dental enamel by computed tomography: applications and problems. *American journal of physical anthropology*, *91*(4), 469-484.
2. Landini, G., Randell, D. A., Fouad, S., & Galton, A. (2017). Automatic thresholding from the gradients of region boundaries. *Journal of microscopy*, *265*(2), 185-195.
3. Dunmore, C. J., Wollny, G., & Skinner, M. M. (2018). MIA-Clustering: a novel method for segmentation of paleontological material. *PeerJ*, *6*, e4374.
4. Doube, M., Kłosowski, M. M., Arganda-Carreras, I., Cordelières, F. P., Dougherty, R. P., Jackson, J.S.,& Shefelbine, S. J. (2010). BoneJ: free and extensible bone image analysis in ImageJ. *Bone*, *47*(6), 1076-1079.
5. Schindelin, J., Rueden, C. T., Hiner, M. C., & Eliceiri, K. W. (2015). The ImageJ ecosystem: An open platform for biomedical image analysis. *Molecular reproduction and development*, *82*(7-8), 518-529.

LIST OF PARTICIPANTS

Name	First Name	Laboratory	Country
AHLBERG	Per E.	Uppsala Univ. - Evolutionary Biology Centre	SWEDEN
AHMED ABDRABOU IBRAHIM			
ALI	Ahmed	Grand Egyptian Museum	EGYPT
ALBANO	Michela	University of Pavia	ITALY
ALFELD	Matthias	Delft University of Technology	NETHERLANDS
ALLEGRETTA	Ignazio	University of Bari	ITALY
ANTUNES	Vanessa	LIBPhys	PORTUGAL
ARGOUD	Chantal	ESRF	FRANCE
ARLT	Tobias	Technische Universitaet Berlin	GERMANY
ATWOOD	Robert	Diamond Light Source	UNITED KINGDOM
AUTRAN	Pierre Olivier	ESRF	FRANCE
AVRANOVICH CLERICI	Ermanno	University of Antwerp	BELGIUM
BAUVOIS	Stefanie	University of Antwerp	BELGIUM
BEAUCOUR	Jerome	Institut Laue-Langevin - ILL	FRANCE
BELLATO	Marta	Museum National Histoire Naturelle, Paris	FRANCE
BELTRAN	Marti	UPC university	SPAIN
BERGER	Lee	University of Witwatersrand	SOUTH AFRICA
BERNAUDAT	Florent	ESRF	FRANCE
BERRUYER	Camille	ESRF	FRANCE
BERTRAND	Loïc	IPANEMA USR 3461 CNRS/MCC	FRANCE
BEYRAND	Vincent	ESRF	FRANCE
BILON	Rebecca	Museum d'Histoire Naturelle, Grenoble	FRANCE
BIOLCATI	Veronica	University College Cork - UCC	IRELAND
BLANC	Nils	Institut Neel	FRANCE
BONNEROT	Olivier	BAM- Federal Institute for Materials Research	GERMANY
BORDET	Pierre	CNRS - UJF - Institut Neel	FRANCE
BOUDET	Nathalie	CNRS/UGA UPR2940	FRANCE
BRIFFA	Johann	University of Malta	MALTA
BROERS	Fréderique	Rijksmuseum Amsterdam	NETHERLANDS
BRUNELLI	Michela	DUBBLE CRG (NL)	FRANCE
BRUNSWIC	Lea	CEA Marcoule	FRANCE
BRUSUELAS	James	University of Kentucky	USA
BURGHAMMER	Manfred	ESRF	FRANCE
CAGGIANI	Maria Cristina	University of Catania	ITALY
CANDEGABE	Philippe	Museum d'Histoire Naturelle, Grenoble	FRANCE
CATTERSEL	Vincent	University of Antwerp	BELGIUM
CHAHARDOLI	Zohreh	University of Bologna	ITALY
CHALMIN	Emilie	Edytem	FRANCE
CHAPMAN	Christy	University of Kentucky	USA
CHECHOTKINA	Olha	Institute of Archaeology RAS	RUSSIA
CHEN	Donglei	Uppsala Univ. - Evolutionary Biology Centre	SWEDEN
CHICHE	Joëlle	Museum d'Histoire Naturelle, Grenoble	FRANCE
CHRISTIANSEN	Thomas	CCRS	DENMARK
COLOMBO	Marco	TU Darmstadt	GERMANY
COLVIN	Kirstin	ESRF	FRANCE
CORMIER	Laurent	Sorbonne Universite - IMPMC	FRANCE
CORTELLA	Laurent	CEA Grenoble	FRANCE
COSTANTINO	Claudio	Universita di Perugia - CRM - ISTM	ITALY

Name	First Name	Laboratory	Country
COTTE	Marine	ESRF	FRANCE
D ACAPITO	Francesco	LISA/BM08 CRG	FRANCE
DARARUTANA	Pisutti	Royal Thai Army	THAILAND
DE KEYSER	Nouchka	University of Antwerp	BELGIUM
DE KOCK	Tim	Ghent University	BELGIUM
DEBRIE	Juliette	CNRS UMR 7590 - IMPMC	FRANCE
DEJOIE	Catherine	ESRF	FRANCE
DELEU	Nina	University of Antwerp	BELGIUM
DUAN	Peiquan	The Palace Museum	CHINA
DURAND	Claudie	Museum d'Histoire Naturelle, Grenoble	FRANCE
DURING	Melanie	Vrije Universiteit Amsterdam	NETHERLANDS
EMELYANOV	Andrey	Institute of Archaeology RAS	RUSSIA
ENGOVATOVA	Asya	Institute of Archaeology Russian Acagemy of S	RUSSIA
FABRE	Frederic	CEA Grenoble	FRANCE
FEDRIGO	Anna	STFC Rutherford Appleton Laboratory	UNITED KINGDOM
FERNANDEZ	Vincent	Natural History Museum London	UNITED KINGDOM
FIGUEIREDO	Elin	New University of Lisbon	PORTUGAL
FLETCHER	Katherine	ESRF	FRANCE
GAMBERINI	Maria Cristina	University of Modena and Reggio Emilia	ITALY
GARROUSTE	Romain	MNHN	FRANCE
GAUTHIER	Catherine	ICM	FRANCE
GEFFARD-KURIYAMA	Didier	Museum National Histoire Naturelle, Paris	FRANCE
GEORGIOU	Rafaella	IPANEMA USR 3461 CNRS/MCC	FRANCE
GHIRARDELLO	Marta	Politecnico di Milano	ITALY
GIACOBBE	Carlotta	ESRF	FRANCE
GIANNOSSA	Lorena Carla	Universita di Bari	ITALY
GOETZ	Andrew	ESRF	FRANCE
GOJSKA	Aneta	National Centre for Nuclear Research	POLAND
GOLOVLEVA	Olga	Mendeleev University	RUSSIA
GONZALEZ	Victor	Rijksmuseum Amsterdam	NETHERLANDS
GRESHKO	Michael	National Geographic	USA
GRIMA	Matthew	Heritage Malta	MALTA
GUILLAUME	Alix	Alix Guillaume	FRANCE
HARDING	Stephen	University of Nottingham	UNITED KINGDOM
HENNIG	Christoph	ROBL - CRG	FRANCE
HODEAU	Jean Louis	CNRS	FRANCE
IACCONI	Clemence	CNRS	FRANCE
ILMI	Moh Mualliful	Institut Teknologi Bandung	INDONESIA
IMPALLARIA	Anna	Istituto Nazionale di Fisica Nucleare INFN	ITALY
JANSSENS	Koen	University of Antwerp	BELGIUM
KEUNE	Katrien	University of Amsterdam	NETHERLANDS
LA BELLA	Michela	Universita di Firenze	ITALY
LA PORTA	Alice	University of Manchester	UNITED KINGDOM
LACAZE	Yannick	ESRF	FRANCE
LANZAFAME	Gabriele	University of Catania	ITALY

Name	First Name	Laboratory	Country
LARSSON COUTINHO	Mathilda	Universidade de Evora	PORTUGAL
LI	Luxi	Argonne National Laboratory	USA
LOCKER	Tobias	Universite Grenoble Alpes	FRANCE
MAHNKE	Heinz-Eberhard	Freie Universitaet Berlin	GERMANY
MARCHETTI	Andrea	University of Antwerp	BELGIUM
MARCUCCI	Giulia	University of Milano Bicocca	ITALY
MARTIN	Jeremy	CNRS	FRANCE
MARTINETTO	Pauline	CNRS/UGA UPR2940	FRANCE
MARYANTI	Evi	Institut Teknologi Bandung	INDONESIA
MATTIELLO	Sara	Parma University	ITALY
MAYDEW	Anne-Françoise	ESRF	FRANCE
MC CARTHY	Joanne	ESRF	FRANCE
MEDNIKOVA	Maria	Institute of archaeology RAS	RUSSIA
MEZGER	Markus	MPI fuer Polymerforschung	GERMANY
MIRAO	Jose	University of Evora	PORTUGAL
MISTA-JAKUBOWSKA	Ewelina	National Centre for Nuclear Research (NCBJ)	POLAND
MOCELLA	Vito	CNR - IMM - Sezione di Napoli	ITALY
MONICO	Letizia	CNR	ITALY
MOURO	Elouan	University of Freiburg	GERMANY
NDAHIMANA	Jean De Dieu	INSTITUTE OF NATIONAL MUSEUMS OF RWANDA	RWANDA
NODARI	Luca	CNR	ITALY
NOIROT	Cecile	CNRS - Universite Paris 6 et 7	FRANCE
NURDINI	Nadya	Institut Teknologi Bandung	INDONESIA
OLIVEIRA	Ana Leticia	IFRJ	BRASIL
OOI SU YIN	Su Yin	Universidade de Evora	PORTUGAL
ORTEGA SAEZ	Natalia	University of Antwerp	BELGIUM
PARADOL	Guilhem	INP Grenoble - MINATEC	FRANCE
PERREAU	Michel	IUT Paris Diderot	FRANCE
PINTO	Ariane	CNRS - CEMES	FRANCE
RACK	Alexander	ESRF	FRANCE
RANERI	Simona	University of Pisa	ITALY
REGUER	Solenn	Synchrotron Soleil	FRANCE
REICHE	Ina	CNRS UMR 8247 - Chimie ParisTech	FRANCE
REYES HERRERA	Juan	ESRF	FRANCE
RICHARDS	Liam	University College London	UNITED KINGDOM
ROZAY	Anne Sophie	INSA ROUEN NORMANDIE	FRANCE
SALAVIALE	Celine	UCB Lyon 1 - CNRS UMR 5570	FRANCE
SANCHEZ	Sophie	Uppsala Univ. - Evolutionary Biology Centre	SWEDEN
SAPRYKINA	Irina	Institute of Archaeology RAS	RUSSIA
SCHOFIELD	Eleanor	The Mary Rose Trust	UNITED KINGDOM
SEDLAK	Jane	CNRS UMR 8247 - Chimie ParisTech	FRANCE
SERAL-ASCASO	Andres	Universidad de Zaragoza - CSIC	SPAIN
SETTE	Francesco	ESRF	FRANCE
SOLE JOVER	Vicente Armando	ESRF	FRANCE
SOZONTOV	Evgeny	NRC Kurchatov Institute	RUSSIA

Name	First Name	Laboratory	Country
STULCOVA	Anna	IPANEMA USR 3461 CNRS/MCC	FRANCE
SUSINI	Jean	ESRF	FRANCE
TAFFOREAU	Paul	ESRF	FRANCE
TANTI	Marc	University of Malta	MALTA
TERESHCHENKO	Elena	FSRC Crystallography & Photonics - RAS	RUSSIA
TOMASIN	Patrizia	CNR	ITALY
TROSSEAU	Antoine	Centre de Recherche et de Restauration	FRANCE
TWILLEY	John	Stony Brook University	USA
VAN DER SNICKT	Geert	University of Antwerp	BELGIUM
VASKANINOVA	Valeria	Charles University	CZECH REPUBLIC
VEIGA	Joao Pedro	Universidade Nova de Lisboa	PORTUGAL
VOETEN	Dennis	Palacky University	CZECH REPUBLIC
WILS	Patricia	Museum National Histoire Naturelle, Paris	FRANCE