

# Synchrotron Radiation in Art and Archaeology



**ESRF-CNRS Joint Workshop**  
**9-11 February, 2005**

**Venue:** [CNRS](#) Grenoble, Auditorium  
([map](#))

## Scope

Materials - bones, artifacts, artwork,... - lie at the heart of both archaeology and art conservation. Synchrotron radiation techniques provide powerful new ways to interrogate these records of our physical and cultural past. In this workshop we will discuss and explore the current and potential applications of synchrotron science to problems in archaeology and art conservation.

Bringing together key members of the synchrotron community and experts in the disciplines of Archaeology, Archaeological Science, Art Conservation and Materials Science, the interdisciplinary workshop will report their latest research accomplishments, highlight ongoing projects, and catalyse new interactions between these fields.

## Previous related meetings:

- 1) SR in Archaeometry Workshop, Daresbury Laboratory, 19-20 November 1999 (M. Pantos)
- 2) SR in Art and Archaeology Workshop, Stanford Synchrotron Radiation Laboratory, Palo Alto, California, 18 October 2000 (N. Pingitore, R. Chianelli, H. Winick)
- 3) The First International Symposium on X-ray Archaeometry, 18-20th July 2002, Tokyo (Prof. Uda).

## Organising Committee

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M. Vendrell-Saz, Dept. Cristallografia i Mineralogia, Barcelona, Spain

## Poster Programme

**Wednesday, 9 February 2005**

14:00	<b>Registration</b>	
	<b>Welcome by</b>	
14:30	<b>Sine Larsen</b> , Director of Research, ESRF and <b>Michel Anne</b> , Director of Research, CNRS, Grenoble	
15:00	1st Introductory talk: <b>Hot Topics and Current Needs in Archaeology – or Why Isn't Everyone Using SR?</b>	<b>Alan M. Pollard</b> Oxford, UK
16:00	<i>Coffee break</i>	
16:30	2nd Introductory talk:	<b>Koen Janssens</b>

Non-destructive SR techniques: Current and future applications

Antwerp, Belgium

17:30 ***Bus departure to ESRF and ARC NUCLEART***

19:30 ***Wine and cheese at the ESRF mezzanine***

21:00 ***Bus departure from the ESRF to Grenoble downtown***

**Thursday, 10 February 2005**

*Session 1*

***Metals***

*Chair: Salvatore Siano (Sesto Fiorentino, Italy)*

09:00 Crystallographic texture analysis: A non-invasive metallographic technique in archaeometry

**Gilberto Artioli**  
Milano, Italy

09:30 Synchrotron x-ray diffraction and imaging of ancient Chinese bronzes: some questions waiting to be answered

**David C. Dunand**  
Evanston, Illinois, USA

09:50 Investigation on corrosion of iron archaeological artefacts using microfocused synchrotron X ray absorption spectroscopy

**Solemn Reguer**  
Saclay, France

10:10 Poster clips\* P01 - P07

10:30 ***Coffee break and Poster session***

*Session 2*  
***Ceramics, glazes and clays***  
*Chair: Maria Ondina Figueiredo (Caparica, Portugal)*

11:15	Lustre decoration of ceramics: Mechanisms of luster development	<b>Trinitat Pradell</b> Barcelona, Spain
11:45	Silver and copper in Renaissance lustre pottery: Nanoparticles, ions, and local environment	<b>Brunetto Brunetti</b> Perugia, Italy
12:15	Speciation of network modifiers (Na, K and Ca) and transition metals (Mn, Fe and Cu) in stained-glass windows of Tours and Strasbourg cathedrals (France)	<b>François Farges</b> Marne-la-Vallée, France
12:35	X-ray absorption spectroscopy and archaeological materials	<b>Andy D. Smith</b> Daresbury, UK
13:00	<b><i>Lunch</i></b> at the CNRS restaurant	

*Session 3*  
***Paintings, pigments and minerals***  
*Chair: Michel Menu (Paris, France)*

14:30	Radiation for the study of paintings: possibilities and limitations	<b>Arie Wallert</b> Amsterdam, The Netherlands
15:00	The investigation of oxidation and migration processes of inorganic compounds in ink corroded manuscripts	<b>Birgit Kanngiesser</b> Berlin, Germany
15:20	New minerals discovered in Palaeolithic black pigments by Transmission Electron Microscopy and micro-X-ray Absorption Near-Edge Structure	<b>Emilie Chalmin</b> Marne-la-Vallée, France
15:40	Poster clips* P08 - P14	

16:00

*Coffee break and Poster session*

*Session 4*

*Soft condensed matter (biology and molecular archaeology)*

*Chair: Jacques Duchêne (Grenoble, France)*

16:45

Sulfur spectroscopy and shipwrecks

**Magnus Sandström**  
Stockholm, Sweden

17:15

Mummified tissues and ancient cosmetic recipes  
analysed by infrared and X-ray micro-spectroscopies

**Marine Cotte**  
Grenoble, France

17:45

Synchrotron radiation analysis of parchment  
degradation

**Craig J. Kennedy**  
Cardiff, UK

18:05

X-ray microdiffraction and microfluorescence using  
synchrotron radiation as a new tool for investigating  
single archaeological textile fibres

**Martin Müller**  
Kiel, Germany

18:30

*Bus departure to the Musée Dauphinois*

19:00

**Visit of the Exhibition "Gens de l'alpe"**

20:00

*Workshop Buffet at the Musée Dauphinois*

22:30

*Bus departure to Grenoble downtown and ESRF Guesthouse*

**Friday, 11 February 2005**

*Session 5*

*Emerging SR techniques and their potential applications for cultural heritage*

*Chair: José Baruchel (Grenoble, France)*

09:00      Revealing the distribution of painting pigments      **Joris Dik**  
Delft, The Netherlands

09:30      Some applications of X-ray Synchrotron  
microtomography of non-destructive 3D studies of  
paleontological specimens      **Paul Tafforeau**  
Grenoble, France

10:00      Micro scanning X-ray diffraction study of Roman Terra  
Sigillata ceramics      **Philippe Goudeau**  
Poitiers, France

10:20      Poster clips\* *P15 - P21*

10:35      ***Coffee break and Poster session***

*Session 6a*  
***Combined strategies and complementary techniques***  
*Chair: Michel Anne (Grenoble, France)*

11:15      Applications of TOF neutron diffraction in  
archaeometry      **Winfried Kockelmann**  
Didcot, UK

11:45      Corrosion study of archaeological copper artefacts right  
after excavation and during their storage and  
stabilization processes      **Annemie Adriaens**  
Ghent, Belgium

12:15      Analysis of paint layers by light microscopy, scanning  
electron microscopy and synchrotron induced X-Ray  
micro-diffraction      **Manfred Schreiner**  
Vienna, Austria

12:35      A secret of Mayan alchemy: how to turn a colorant into  
a pigment      **Manuel Sanchez del Rio**  
Grenoble, France

13:00 *Lunch at the CNRS restaurant*

*Session 6b*  
***Non-destructive analysis and testing of museum objects***  
*Chair: Helena Wouters (Brussels, Belgium)*

14:30 [A multidisciplinary handshake between the humanities & sciences vis-à-vis Qumran and Dead Sea scrolls](#) **Jan Gunneweg**  
Jerusalem, Israel

15:00 [Synchrotron radiation on the traces of famous painters: XRF analyses of silverpoint drawings by Dürer, Holbein, Van Eyck and Rembrandt](#) **Ina Reiche**  
Paris, France

15:20 [Improved noninvasive microstructural analysis of fossil tissues by means of SR-microtomography](#) **Arnaud Mazurier**  
Poitiers, France

15:40 [Poster clips\\* P22 - P27](#)

16:00 ***Coffee break and Poster session***

*Session 7*  
***Round table and Closing remarks***  
*Moderators: Emmanuel Pantos (Warrington, UK) - Annemie Adriaens (Ghent, Belgium)*

16:45 Analytical techniques applied to the study of cultural heritage: limitations and challenges

17:30 ***Bus departure from the CNRS to the Museum of Grenoble***

18:00-19:00 **Visit of the Museum of Grenoble**

19:00-20:30     *Farewell Cocktail in the Museum Restaurant 'Le 5'*

**\*Poster clips**

Posters are expected to present **EITHER** a particular subject on archeology and materials of the cultural heritage, with emphasis on open questions and needs for synchrotron techniques **OR** a relevant synchrotron technique/method/beamline, which can be beneficial in present/future studies in Archaeology and Conservation Science.

The main author of each poster is given the opportunity to present the topic of his contribution in **3 minutes**, before a coffee break.

The posters presented orally in a session are attended and open to discussion during the coffee break which immediately follows.

# Hot Topics and Current Needs in Archaeology – or Why Isn't Everyone Using SR?

POLLARD A.M.

Research Laboratory for Archaeology and the History of Art, University of Oxford. UK.

The application of Synchrotron Radiation to archaeology dates back to 1986 [1] and has been subsequently documented on a dedicated website at Daresbury [<http://www.srs.ac.uk/srs/>]. The majority of the applications in the 1990s used SR as a source for X-ray fluorescence microanalysis on a variety of archaeological and historical materials, including glass [2,3] ink and paper [4], dental calculus [5] and bone [6]. This repertoire has since been expanded to include X-ray micro-diffraction on materials such as iron [7], bone, wood [8] and Egyptian cosmetics [9]. More recent applications have included Small Angle X-ray Scattering to study the alterations of shape and size of bone mineral crystals as a result of diagenetic and microbial attack [10].

It is probably true to say, however, that SR has not yet made a great deal of impact on archaeology. It is of fundamental importance to realise that archaeology is about *human behaviour*, not primarily about *material objects*. Thus, to an archaeologist, the analysis of archaeological material is only of interest when it can be interpreted in the context of human behaviour. Arguably, it has taken 20 years for archaeologists and SR specialists to begin to identify applications of the technique which genuinely use the potential of the tool to answer questions of archaeological significance. Some of this delay undoubtedly stems from the fact that archaeology, unlike the 'harder' scientific disciplines, until recently has not possessed a fully unified view of what constitutes a 'high priority' in research terms – in many ways it has operated as a humanities subject, with as many 'priorities' as there are practitioners!

This is gradually changing, and national research priorities are emerging – particularly in the context of the preservation of the cultural heritage, where major research thrusts over the next few years will include *Preservation of Archaeological Remains in-situ*, and, for maritime countries, the location, identification and preservation of submerged archaeological sites (including, but not exclusively, shipwrecks). Now that this dialogue has begun, we can anticipate a fruitful period of the application of SR techniques in archaeology.

## References

- [1] Harbottle, G., *et al. Nucl. Inst. and Methods B* **14**, 116, (1986).
- [2] Schofield, P.F., *et al. Glass Technology* **36**, 89, (1995).
- [3] Janssens, K., *et al. Nucl. Inst. and Methods B* **109/110**, 690, (1996).
- [4] Mommsen, H., *et al. Archaeometry* **38**, 347, (1996).
- [5] Capasso, D.J.T., *et al. Int. J. Osteoarch.* **5**, 282, (1995).
- [6] Janssens, K., *et al. Fresenius J. Anal. Chem.* **363**, 413, (1998).
- [7] Dillmann, P., *et al. J. de Phys. IV* **12**, 393, (2002).
- [8] Kuczumow, A., *et al. Spectrochim. Acta B* **55**, 1623, (2000).
- [9] Martinetto, P., *et al. Nucl. Inst. and Methods B* **181**, 744, (2001).
- [10] Wess, T.J., *et al. Fibre Diffraction Review* **36**, (2002).

# Non-destructive SR techniques: Current and future applications

JANSSENS K.

Department of Chemistry, University of Antwerp, Universiteitsplein 1, 2610 Antwerp, Belgium

Highly intense X-ray beams as produced at synchrotron radiation facilities, that often are also highly monochromatic and have a low divergence, are highly suitable tools for examining fragile, valuable and/or unique artefacts with minimal or no damage. Depending on the nature of interactions the impinging X-ray photons are subject to and the type of detectors that are employed to record the result of such interactions, information of different nature can be obtained on the materials or objects being investigated. This information can be about the major- and trace-level composition of the objects, about the chemical state of one or more atomic species that are present and/or about crystallographic phases on the materials.

Since the materials and objects encountered in the field of art-analysis, archaeology and conservation are often complex in shape, covered with alteration layers and/or may be highly heterogeneous, the use of X-ray micro beams is very often required to allow for the measurement of local rather than bulk properties. Elemental microanalysis down to the sub-ppm level is possible in two or three dimensions by means of conventional or confocal  $\mu$ -XRF (X-ray fluorescence analysis). Local chemical state determinations of selected (trace) constituents are possible by applying  $\mu$ -XAFS (X-ray absorption spectroscopy) while information on the presence of (sub)microscopically small crystalline phases can be obtained via  $\mu$ -XRD (X-ray diffraction) and  $\mu$ -SAXS (Small angle X-ray scattering). These methods usually employ X-ray photons with energies in the 0.5 to 30 keV range. Alternatively, entire objects may be bathed in highly-energetic synchrotron beams to allow high quality radiographic or tomographic imaging measurements, revealing the internal structure of these artefacts.

On the other side of the wavelength- or energy scale, also the infra-red radiation produced by synchrotron facilities is starting to be used for investigation of ancient materials in FT-IR (fourier-transform infra-red spectroscopy) microscopes adapted for this purpose.

In this introductory presentation, an overview of the above-mentioned SR-based methods will be given, briefly illustrated with examples taken from the recent literature, with special attention for the micro- or non-destructive aspects of each technique. Additionally, the complementarity between these SR-based techniques and (non-destructive) laboratory-based methods of investigation (such as the various forms of electron microscopy) will be discussed.

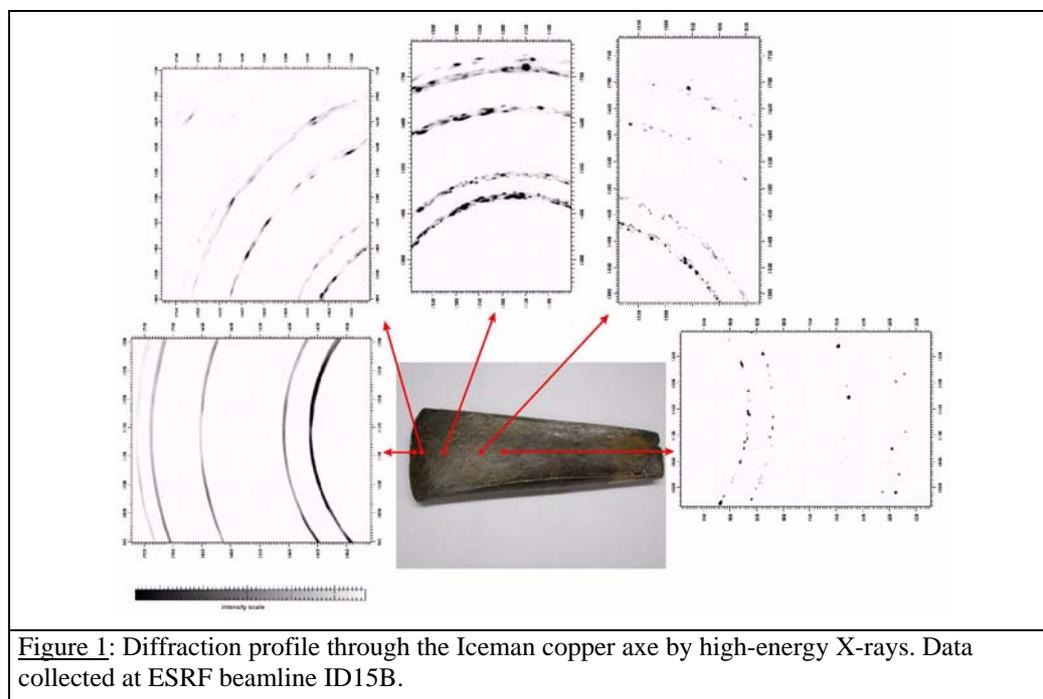
# Crystallographic texture analysis: A non-invasive metallographic technique in archaeometry

ARTIOLI G.

Dipartimento di Scienze della Terra, Università di Milano

Texture analysis by diffraction methods has greatly advanced in the last few years because of instrumental and computational developments, and it is now to be considered a routine tool for the analysis of crystallite orientation in a wide variety of natural and man-made materials, industrial products and archaeological samples [1]. The advances in the experimental measurements are mainly linked to the use of flexible experimental setups at large radiation sources, such as synchrotrons and neutron sources, which allow faster data collection, the use of samples of any size, and complete coverage of texture and reciprocal space. The developments in the data analysis are mainly related to the use of the full diffraction profiles in place of the single-peak methods. This produces pole figures and orientation distribution functions (ODF) that are statistically more significant and less prone to biases in the data analysis. Furthermore it opens the possibility of analysis of complex polyphasic materials, which are hard to characterize by other experimental techniques [2].

If high energy X-rays or neutrons are used as penetrating probes, the technique can effectively be used as a powerful non-invasive tool for the investigation of thick objects such as metal artefacts (Figure 1). The recent results obtained on prehistoric copper axes will be described as case study showing the potential of crystallographic texture analysis in archaeometry [3].



## References

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- [2] - G. Artioli, M. Dugnani, *Period. Mineral.* 73, 5-16, (2004)
- [3] - G. Artioli, M. Dugnani, T. Hansen, L. Lutterotti, A. Pedrotti, G. Sperl, Crystallographic texture analysis of the Iceman and coeval copper axes by non-invasive neutron powder diffraction. In: A. Fleckinger (ed.) "The Copper Age mummy. 2. New finds on the Iceman". Museo Archeologico dell'Alto Adige, Vol. 3, Folio Verlag, Bolzano, pp. 9-22, (2003)

# Synchrotron x-ray diffraction and imaging of ancient Chinese bronzes: some questions waiting to be answered

YOUNG M. L.<sup>1</sup>, CASADIO F.<sup>2</sup>, SCHNEPP S.<sup>2</sup>, MARVIN J.<sup>1</sup>, DUNAND D.C.<sup>1</sup>, ALMER J.<sup>3</sup>, FEZZAA K.<sup>3</sup>, LEE W.-K.<sup>3</sup> and D.R. HAEFFNER<sup>3</sup>

<sup>1</sup>Northwestern University, Evanston, IL, 60208, <sup>2</sup>The Art Institute of Chicago, Chicago, IL, 60603, <sup>3</sup>Argonne National Laboratory, Argonne, IL, 60439

Starting in the late 1960s, the study of early Chinese metallurgy, both from a scientific and archaeological perspective, has grown at an impressive pace. The collection of the Art Institute of Chicago comprises approximately 50 bronzes of outstanding artistic quality. The aim of this work was to test the ability of a range of synchrotron radiation (SR) x-ray techniques to answer specific art-historical questions in a non-destructive way. In particular, we apply both diffraction and imaging techniques using high-energy x-rays ( $E = 80$  keV). Such x-rays can penetrate several millimeters into bronze alloys containing several percent lead, and thus allow us to non-destructively interrogate bulk structures previously inaccessible with surface-sensitive techniques such as typical (lower-energy) laboratory x-ray sources. In addition, the high brilliance of synchrotron x-rays permits use of small beams for diffraction studies, as well as use of phase-enhanced imaging for higher contrast than traditional x-ray absorption methods. We have investigated fragments of a Chou dynasty vessel (*Hu*, 112-255 B.C.), which offer the unprecedented opportunity to compare compositional results obtained with traditional metallographic and SEM/EDX examination of cross sections with non destructive SR x-ray diffraction on whole fragments. We show that the transition from oxidation layers (patina) to bulk microstructure at the edge of the fragments can be mapped with approximately 20  $\mu\text{m}$  resolution. We have also investigated a Tripod Food Cauldron (*Ding*, 8<sup>th</sup> century B.C), non-destructively characterizing the metal composition, smooth and compact patina and core material contained in the foot. The latter was studied non-destructively using x-ray absorption and diffraction and compared with a destructively-cored piece of material. We have then focused on the inscription inside the vessel. Sometimes used by scholars to glean the history of a particular vessel, inscriptions are of paramount importance and in this particular case the style and content of the inscription had generated some debate as to whether it had been cast or carved. Combining x-ray diffraction data taken in proximity to and inside the characters (to evidence possible residual strain) with phase-contrast imaging allowed for a more complete picture of the processing. Finally, we examined a bronze Dagger Axe (*Ge*, 3<sup>rd</sup>/2<sup>nd</sup> century B.C.) with a silver-inlaid casing. The silhouette of the axe had been thought to be the casing placed over a weapon rather than the weapon itself due to the absence of a sharp tip. We have used diffraction to determine the spatial distribution of the composition and the probable processing method used to create the silver inlay. In addition, phase-contrast x-ray imaging provided a detailed view of the interior structure of the axe.

## Acknowledgements

Use of the Advanced Photon Source (APS) was supported by the U.S. Department of Energy (DOE), Office of Science, Office of Basic Energy Sciences, under Contract No. W-31-109-ENG-38.

# Investigation on corrosion of iron archaeological artefacts using microfocused synchrotron X ray absorption spectroscopy

REGUER Solenn<sup>1</sup>, DILLMANN Philippe<sup>1,2</sup>, MIRAMBET François<sup>3</sup>,  
SUSINI Jean<sup>4</sup>, LAGARDE Pierre<sup>5</sup>

1 LPS, Laboratoire Pierre Süe (CEA/CNRS), CEA Saclay

2 LRC CEA DSM 01-27 : IRAMAT UMR5060 CNRS

3 LRMH, Laboratoire de Restauration des Monuments Historiques

4 ESRF, The European Synchrotron Radiation Facility

5 LURE and SLS, Swiss Light Source

Synchrotron based micro X Ray Absorption Spectroscopy was used in the present study to obtain micro scale chemical information such as coordination and oxidation state of phases constituting corrosion products within archaeological iron artefacts buried in soil. This techniques were required in order to answer questions about iron corrosion process related to the presence of chlorine, particularly for restoration and conservation of metallic heritage application. Indeed, the deterioration after excavation of archaeological artefacts buried in soil is often associated to the presence of chlorine ions in corrosion products.

The samples available for X ray microprobe analyses are cross section from iron corroded objects coming from particular archaeological excavation sites dating from 12<sup>th</sup> to 16<sup>th</sup> century AD. Previously, various analytical techniques are employed to reveal morphological, compositional information of corrosion products; some others techniques are based on structural investigation of artefacts, such as  $\mu$ XRD and  $\mu$ Raman. [1-3] In this specific study, we present a number of case studies applying synchrotron-based micro absorption spectroscopy to iron artefacts. X-Ray Absorption Near Edge Structure ( $\mu$ XANES) was used to determine the spatial variation of the predominant Fe oxidation state and the corresponding crystallographic phase. The micro-XAS experiments reported here were conducted on the ID21 beam line at ESRF and on the LUCIA beam line at SLS. The analyses performed at Fe and Cl K-edge ( $\mu$ XANES) revealed the correlation between the Fe<sup>2+</sup> and Fe<sup>3+</sup> distribution in the corrosion products, and the evolution of the chlorine concentration. In addition to the presence of the well known beta iron hydroxide  $\beta$ -FeOOH: akaganeite, in iron corrosion product, we highlight the presence of an other important phase, the  $\beta$ -Fe<sub>2</sub>(OH)<sub>3</sub>Cl hydroxychloride. This result is particularly interesting because, to our knowledge, this phase has never been identified in archaeological artefacts corrosion products. These finding help to gain new insights concerning the influence of such phases in iron corrosion mechanism within their precise characterisation.

1 D. Neff, S. Reguer, L. Bellot-Gurlet, P. Dillmann and R. Bertholon, Structural characterization of corrosion products on archaeological iron. An integrated analytical approach to establish corrosion forms. *Journal of Raman Spectrometry*. 35 (Special Issue on the application of Raman spectroscopy in art and archaeology): p. 739-745.(2004)

2 S. Reguer, P. Dillmann and P. Lagarde. Studies of the corrosion mechanisms related to the presence of chlorine on the archaeological ferrous artefacts. Contribution of the local and structural characterisation. in *Eurocorr 2004.Nice*.(2004)

3 S. Reguer, P. Dillmann, F. Mirambet and L. Bello-Gurlet, Local and structural characterisation of chlorinated phases formed on ferrous archaeological artefacts by  $\mu$ XRD and  $\mu$ XANES. *Nuclear Instruments and Methods B*. p.(submitted)

# Luster decoration of ceramics: Mechanisms of luster development

PRADELL T.<sup>1</sup> & MOLERA J.<sup>2</sup>

<sup>1</sup>Dept. Física I Enginyeria Nuclear, UPC, Urgell 187 08037-Barcelona

<sup>2</sup>Dept. Física, UdG, campus Montiliví, Girona

Luster is a ceramic decoration showing golden or coppery metallic shine and that can exhibit purple and blue iridescence. The origin of this decoration goes back to early Islamic times, *i.e.* the 10th century AD, and followed the expansion of the Arabian culture through Spain and the rest of the western Mediterranean. Transmission Electron Microscopy performed showed that in all cases examined the luster appeared to be a nanosized metal-glass composite (metal nanoparticles appear embodied in a glassy matrix). The metal particle sizes range between 5 nm and 50 nm and form a layer of thickness varying between 100 nm to 1  $\mu\text{m}$ . A wide range of Cu to Ag ratio has been observed in the luster layers, ranging from pure silver to pure copper luster decorations, even in the same design. Their chemical composition is related to their color, yellow, green to brown for the silver rich lusters or orange, red to crimson for the copper rich lusters.

Luster is produced by direct application of a raw paint over a glazed ceramic which after firing in a reducing atmosphere results in the formation of the luster layer, the remaining paint (called cosela) is removed revealing the luster beneath. The composition of the lustre paint is therefore different from that of the final luster layer, and may vary widely. Typical recipes are a water (with some vinegar) suspension of a powder mixture containing about 50% of clay minerals mixed with iron oxides, copper or/and silver compounds and a sulfur containing compound. In particular, cinnabar (HgS) was found in the 13<sup>th</sup> century AD workshop from Paterna. Firing in reducing atmosphere is necessary to produce the transformation of the copper and silver compounds to metallic copper and silver. The question arising from these studies is how such nanostructures are formed. The mechanism should first the introduction of the copper and/or silver into the glassy matrix and then they must be reduced to achieve its metallic state. Moreover, chemical analysis of medieval luster showed a clear inverse correlation between the metal components of the luster decorations (Cu and Ag) and the presence of Na and K in the glaze. This result allows us to infer that a possible mechanism for the introduction of Cu and Ag into the glaze may be the ion exchange between the alkali ions originally present in the glaze and the metal cations present in the powder luster paint during the firing. However, the luster and glaze of these samples are quite weathered, and the loss of alkalis is very typical. I will present the laboratory reproductions of luster following the original Paterna recipes which will give insight in the exact mechanisms involved in the luster development.

# Silver and copper in Renaissance lustre pottery: nanoparticles, ions, and local environment

BRUNETTI B.<sup>1</sup>, D'ACAPITO F.<sup>2</sup>, MAURIZIO C.<sup>2</sup>, MAZZOLDI P.<sup>3</sup>, PADOVANI S.<sup>3</sup>, SGAMELLOTTI A.<sup>1</sup>.

<sup>1</sup> INSTM, Centro S.M.A.Art, Dipartimento di Chimica, Università di Perugia, 06123 Perugia, Italy

<sup>2</sup> INFN, GILDA CRG, ESRF, BP 200 F-38043, Grenoble, France

<sup>3</sup>INFN, Dipartimento di Fisica, Università di Padova, 35131 Padova, Italy

Lustre pottery decorations are characterised by the presence of copper and silver nanoparticles dispersed in the more external layers of the glaze[1-3]. Following this finding, a study has been carried out on several original gold and red lustre samples, with the objective to better understand the lustre manufacturing technique and chromatic properties. Preliminary measurements were carried out by several techniques (XRF, SEM, TEM, Vis-NIR) [1], then EXAFS measurements were carried out at ESRF, on the BM8 beamline GILDA [2,3].

XRF and SEM-EDS measurements confirmed that gold and red lustre decorations are characterised by Ag and Cu. However, surface plasmon resonances in Vis absorption spectra indicated that, for gold lustre, metallic silver nanoparticles are mainly responsible of the colour while, in case of red lustre, responsible of colour are copper nanoparticles [1].

EXAFS measurements confirmed these observations. In most cases of gold and red lustre samples, copper and silver were found as metals, however, they have been also found in oxidised forms. Oxidised copper atoms were  $\text{Cu}^+$  and  $\text{Cu}^{2+}$ , with a large prevalence of  $\text{Cu}^+$  [2,3]. The observed simultaneous presence of metallic and ionised copper and silver are consistent with a lustre formation mechanism where the first step is an ion-exchange between copper and silver ions of the original lustre recipe, and the alkali ions present in the glaze (on average, total  $\text{Na}^+$  and  $\text{K}^+$ : 5-15% wt) [1-4].

Regarding the chromatic properties, only the fraction of reduced silver and copper are mainly responsible of the colour. This fraction can be low and variable case by case, depending on used recipes, reductive conditions and temperature of the kiln. It has been found that even the metallic Ag/Cu measured ratio cannot be in all cases simply and univocally correlated with the colour.

## References

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- [2] S. Padovani, C. Sada, P. Mazzoldi, B. Brunetti, I.Borgia, A.Giulivi,A.Sgamellotti, F. D'Acapito, G. Battaglin, *J. Appl. Phys.* **93**, 158 (2003)
- [3] S. Padovani, I. Borgia, B. Brunetti, A. Sgamellotti, A. Giulivi, F. D'Acapito, P. Mazzoldi, C. Sada, G. Battaglin, *Appl. Phys. A* **79**, 229 (2004).
- [4] T.Pradell, J. Molera, 2004, private communication.

# Speciation of network modifiers (Na, K and Ca) and transition metals (Mn, Fe and Cu) in stained-glass windows of Tours and Strasbourg cathedrals (France)

FARGES F.<sup>1,2</sup>, ETCHEVERRY M.P.<sup>1,3</sup>, FLANK A.-M.<sup>4</sup>, LAGARDE P.<sup>4</sup>, MARCUS M.A.<sup>5</sup>, SCHEIDEGGER A.M.<sup>6</sup>, GROLIMUND D.<sup>6</sup>, PALLOT-FROSSARD I.<sup>3</sup>

<sup>1</sup> Laboratoire des Géomatériaux, Université de Marne-la-Vallée, France.

<sup>2</sup> Department of Geological and Environmental Sciences, Stanford University, USA

<sup>3</sup> Laboratoire de Recherche des Monuments Historiques, Champs-sur-Marne, France

<sup>4</sup> SOLEIL, CNRS, Saclay, France (currently at SLS, Switzerland)

<sup>4</sup> Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, USA

<sup>5</sup> Paul Scherrer Institut (PSI), Villigen-PSI, Switzerland

A series of XIVth century medieval glasses from Tours and Strasbourg cathedrals stained-glass windows were studied by  $\mu$ -XRF and  $\mu$ -XAFS at the K-edge of Na, K, Ca, Mn, Fe and Cu, in order to understand first the origins of the color of the red glasses (Tours), as well as to study the formation of surface weathered phases for both sites. These red flashed glasses are composite: The red part of the glass consists of a multitude of micrometer-thick dark-reddish layers that are intercalated between some greenish layers. The red-green composite is layered on a gre. This composite (1 mm thick maximum) covers a much thicker layer (about 2 mm) of a greenish glass support. Na, K, Ca, Mn and Fe K-edges were measured at the LUCIA beamline, using beryl and Si(111) double crystal monochromators and a beam size of  $\sim 15 \times 15 \mu^m$ . Cu K-edge XAFS and XRF (K-As) data were collected at the 10.3.2 beamline (ALS, Berkeley, USA) using a Si(111) monochromator and a  $8 \times 8 \mu m$  spot size. Special care was taken to ensure that the X-ray beam did not photo-reduced the samples.

The intensity of red color of the flashed glasses from Tours is directly correlated to the Cu-content at the probed area, Furthermore, the measurements reveal that the greenish glass is enriched in Fe and Mn. Cu speciation within the red regions indicates the presence of linear Cu(I) complexes, such as observed in cuprite ( $Cu_2O$ ). No evidence for metallic Cu was found in any of these (which?) glasses. Reference glass samples were synthesized at variable oxygen fugacities and confirm the above results. In the greenish regions, Cu is highly depleted. Nevertheless, Cu speciation remained unchanged (2-coordinated Cu(I) complexes). On the inner glass surface (exposed to the inside), a weathered and pale green layer covering the red glass area is detected. Its origin is still unknown, but this weathered layer is enriched in Cu(II) and as well as in Na, K, Mn and Fe. The outer side of the glass shows different signs of weathering, made of craters enriched in Fe that is present as ferrihydrite. On the outer side of the glasses from Strasbourg, a black layer of unknown is present. In this layer, Mn is present as a birnessite-type oxy-hydroxide, whereas Fe is present as ferrihydrite-type compounds. Mn is highly correlated to Na, suggesting the presence of a sodic-birnessite. Surprisingly, the Mn redox in the Strasbourg sample changes as a function of the depth of the weathered layer from  $\sim IV$  to from  $\sim III$ .

For the first time, Na K-edge  $\mu$ -XAFS spectra are reported the (LUCIA beamline at SOLEIL/SLS). The data suggest a variety of changes in Na speciation for Na present the non-corroded glasses and Na present in the weathered layers. As for K-edge data of K and Ca, the reduction of Na K-edge XANES data is challenging because of the difficulty to perform accurate *ab-initio* XANES calculations, which are mandatory to perform reliable assignments. Therefore, much work is still needed to fully conclude the above spectroscopic information, especially in the weathered layers.

# X-ray absorption spectroscopy and archaeological materials

SMITH A.D.<sup>1</sup>, PRADELL T.<sup>2</sup>, JONES M.<sup>3</sup>, GLIOZZO E.<sup>4</sup>, MEMMI-TURBANTI I.<sup>4</sup>,  
MOLERA J.<sup>5</sup>, VENDRELL M.<sup>5</sup>, MCCONACHIE G.<sup>3</sup>, SKINNER T.<sup>6</sup>, KIRKMAN  
I.W.<sup>1</sup>, PANTOS E.<sup>1</sup>

<sup>1</sup>CCLRC–Daresbury Laboratory; <sup>2</sup>ESAB-CEIB, Universitat Politecnica de Catalunya; <sup>3</sup>Mary Rose Trust, Portsmouth; <sup>4</sup>Dept. Earth Sciences, Univ. Siena, Italy; <sup>5</sup>Dept. Cristallografia i Mineralogia, Universitat de Barcelona; <sup>6</sup>National Museums of Scotland, Edinburgh

X-ray absorption spectroscopy (XAS) is a powerful tool in materials science for determining local atomic structure and chemistry. It can equally well be applied to ancient materials to better understand their manufacture and preservation. A review of recent XAS studies is presented, illustrating the use of soft and hard x-ray spectroscopy at *L* and *K* absorption edges to elucidate archaeological problems.

Copper based salts have been used throughout islamic and medieval periods to create gold like lustre finishes on ceramic goods. X-ray spectroscopy at the copper *K*-edge has been used to identify copper oxidation and the ratio of copper metal to oxide as a function of copper/silver content. The technique can be applied to both genuine artifacts and modern reproductions, enabling tests to be performed to verify the original manufacture process and the chemistry involved<sup>[1]</sup>. Using microfocussed beams has enabled these measurements to be made across the pattern of particular decorations, yielding information on the natural variation of the decoration.

Iron based black gloss ceramics predate the copper lustreware, and was much in evidence in ancient Greece. Soft X-ray XAS at the Fe *L*-edge has been used to highlight the different oxidation states evident in different finishes of black gloss. Comparisons with reference spectra of known oxidation state has enabled grouping of artifacts of similar appearance and provided insights into their respective provenances<sup>[2]</sup>.

Waterlogged archaeological wood is known to contain relatively large quantities of sulphur. Without proper treatment this sulphur can be catalysed to acid, with obvious damaging consequences. Whilst the pathway for this reaction is not yet well understood, x-ray spectroscopy of the S *K*-edge is proving important in determining the oxidation state of sulphur in recovered timbers from vessels such as the Mary Rose<sup>[3]</sup>.

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# Radiation for the Study of Paintings: Possibilities and Limitations

WALLERT A.

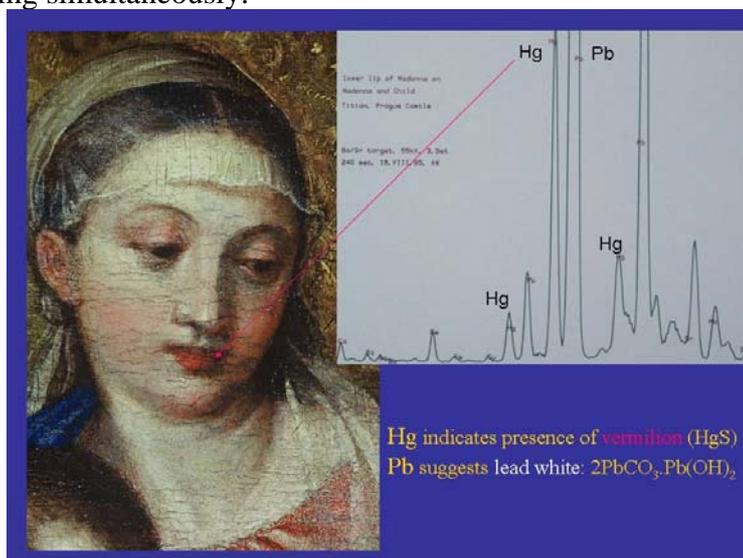
Department of Paintings, Rijksmuseum Amsterdam

Approaches in the scientific examination of paintings may vary from high-resolution electron microscopy or advanced neutron activation research to old-fashioned micro chemical tests and conventional polarized light microscopy, answering questions that may vary from technical conservation issues to scholarly problems of attribution. The case studies presented deal with paintings of important old masters like Lievens, Titian, de Heem, and Rembrandt. For the examination of such masterpieces non-destructive techniques are usually preferred. Non-sampling techniques can reveal a wealth of information on the support, lead containing pigments, underdrawings and the identity of some pigments.

One of the most important non-sampling techniques is conventional x-radiography. It allows the analyst to literally look through a painting, as the x-ray absorbing compounds such as lead-containing paints, puttied retouchings and nails in the support can be visualized.

Pigments on the surface can be studied by particle induced x-ray emission (PIXE) analysis based on the energies of x-rays emitted upon irradiation with high energy particles.

Similar information can be obtained with x-ray fluorescence (XRF) spectroscopy where the sample is excited by irradiation with x-rays. PIXE and XRF can analyse only a single spot in the painting simultaneously.



Many different measurements are needed to analyse different areas of one painting. Both techniques do not yet allow for satisfactory analysis of larger areas or the whole painting in a spatially resolved manner. They cannot be classified as imaging techniques. This is a serious disadvantage since the chemical properties of adjacent areas can be completely different. Painting materials in traditional paints contain many impurities, resulting in difficulties in the interpretation of spectra. The interpretations are further complicated because in the techniques of the old masters, generally several paint layers were applied for larger coloured areas, for smaller details, shadow regions and highlights. In the study of such multi-layered paint systems it is impossible to physically separate these thin (between 1 and 100  $\mu\text{m}$  thick) and inhomogeneous layers and analyse them individually.

Synchrotron radiation can be used to overcome some of the problems encountered with conventional methods. A few possible solutions to address some important questions in technical art history are discussed.

# The investigation of oxidation and migration processes of inorganic compounds in ink corroded manuscripts

KANNGIESSER B.<sup>1</sup>, HAHN O.<sup>2</sup>, WILKE M.<sup>3</sup>, NEKAT B.<sup>3</sup>, MALZER W.<sup>1</sup>, ERKO A.<sup>4</sup>

<sup>1</sup>Institut für Atomare Physik und Fachdidaktik, Technische Universität, Berlin, Germany

<sup>2</sup>Bundesanstalt für Materialforschung und -prüfung, Berlin, Germany

<sup>3</sup>Institut für Geowissenschaften, Universität Potsdam, Potsdam, Germany

<sup>4</sup>Berliner Elektronenspeicherring-Gesellschaft für Synchrotronstrahlung mbH, Berlin, Germany

Archives and museums around the world contain a vast number of hand-written documents, music compositions and also drawings that were executed in iron gall ink, the most important in Western history.

Different decomposing reactions with and by the environment (especially with the organic matrix of the paper) are leading to changes in the ink colour and, occasionally, to iron gall ink corrosion. This process consists of two principal mechanisms: the acid hydrolysis by formation of sulphuric acid and the catalytic oxidation by mobile transition of metal ions, above all the major element iron. They end in a complete degradation of the paper. Therefore, non-destructive investigation are of great importance.

We studied the oxidation and migration processes of inorganic compounds in ink corroded material with a combination of micro X-ray fluorescence analysis (micro-XRF) and micro X-ray absorption near edge structure spectroscopy (micro-XANES) on two historical manuscripts in comparison to self-made well-defined iron gall ink samples.

With elemental mapping by micro-XRF of the historical documents, the correlation of the minor elements in the ink (Zn and Cu) to the major element Fe was investigated. It was found that the minor elements occur relatively in higher amounts in the outer regions of the ink spot, indicating that the mobility of non-iron metal ions through the paper is higher than that of iron ions.

Along concentration profiles of Fe, micro-XANES measurements were carried out in order to determine the oxidation state and the local environment. They reveal a spatial dependence of the Fe<sup>2+</sup>/Fe<sup>3+</sup> ratio only in manuscripts in an advanced state of ink decomposition process, whereas the samples with lower degree of corrosion and the model inks showed a nearly constant Fe<sup>2+</sup>/Fe<sup>3+</sup> ratio.

Comparison of the Cu-XANES profiles from an original, a model ink and reference samples (CuSO<sub>4</sub> and CuO) showed that Cu is not only present as sulphate but also as oxide in the historical manuscript. The higher hazardous potential for Cu-bearing inks is shown in time-series of micro-XANES measurements.

With micro-XANES it is possible to show in situ the catalytic activity of Cu-ion in iron gall inks as an enforcement of the photo reduction of iron.

The combination of micro-XRF and micro-XANES is a step forward in the understanding of this complicate and complex paper degradation process.

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# New minerals discovered in Paleolithic black pigments by Transmission Electron Microscopy and micro-X-ray Absorption Near-Edge Structure

CHALMIN E.<sup>1,2,3</sup>, VIGNAUD C.<sup>3,4</sup>,  
FARGES F.<sup>2,5</sup>, SUSINI J.<sup>6</sup>, MENU M.<sup>3</sup>

<sup>1</sup> Labo. de Géophysique Interne et Tectonophysique, UMR CNRS 9995, Grenoble, France

<sup>2</sup> Labo. des Géomatériaux, Université de Marne la Vallée, FRE CNRS 2455, Marne la Vallée, France

<sup>3</sup> Centre de Recherche et de Restauration des Musées de France, UMR CNRS 171, Paris, France

<sup>4</sup> Labo. Interfaces et Systèmes Electrochimiques, UPR CNRS 15 and Univ. P et M Curie, Paris, France

<sup>5</sup> Dept. of Geological and Environmental Sciences, Stanford University, Stanford, USA

<sup>6</sup> ESRF, Grenoble Cedex 9, France.

Paleolithic artists used two main colors: red (iron oxide: hematite or red ochre) and black (charcoal or manganese oxides). These pigments could be prepared in different ways, by grinding, by mixing with an extender and/or a binder or by heating, in order to enhance the properties of painting matter. Physicochemical analyses attempt to determine the nature of the matter and its preparation mode, and to get an idea of its provenance.

This work deals with black pigments and more particularly with manganese oxides. The different phases of manganese oxides can be distinguished using their elemental composition, their structure and the oxidation state of the Mn ion (II, III, IV). The present study is limited to two main families: simple ( $\text{MnO}_2$  type) and composite ( $\text{Ba}_x\text{Mn}_y\text{O}_z$  type) manganese oxides.

Transmission electron microscopy (TEM) was performed to identify the specific phase of manganese oxide and to study structural transformation during heat-treatment. As a complementary technique, Mn K-edge  $\mu$ -XANES (X ray absorption near-edge structure) spectroscopy was used, for its element specific sensitivity to redox and local structures. The spectra were collected on ID21, using Si(111) double crystal monochromator and a Fresnel focusing device.

Using this combined approach of TEM and  $\mu$ -XANES, archaeological samples of black painting matter were analyzed. The complex mixtures of manganese oxides studied here belong to the caves of Ekain (Basque country, Spain), Labastide and Gargas (Hautes-Pyrénées, France) and as well as to black “crayons” from the cave of Combe Saunière (Dordogne, France). From these analyses of painting matters, several conclusions are drawn concerning the technical level of Paleolithic artists:

- for the first time, the distinction between natural phase mixtures and mixtures of anthropogenic origin is possible.
- new minerals, never identified before in archaeological context, have been discovered in these painting samples.
- however, black heated pigments have never been found in the studied rock painting samples, in contrast to heated red hematite, that was evidenced mainly in prehistoric funeral context.

Consequently, the sometimes-unusual mineralogy found in these pigments suggests that some of the manganese ores are coming from geological settings that are sometimes relatively far away from the Dordogne and Basque region such as in Ariège.

# Sulfur Spectroscopy and Shipwrecks

SANDSTRÖM M.

Structural Chemistry, Stockholm University, SE-106 91 Stockholm, Sweden

Wooden marine archaeological artefacts can be of great historical and cultural value, even though conservation of the complex material, degraded waterlogged wood infested with sulfur and iron compounds, is a difficult task. The anoxic conditions predominating at the seabed and in bottom sediments have often enabled high levels of preservation, as for the 17<sup>th</sup> century Swedish warship *Vasa* (Figure 1). Synchrotron-based sulfur K-edge x-ray absorption near edge structure (XANES) spectroscopy has made sulfur speciation possible for natural samples, and revealed when applied on the *Vasa* that totally several tonnes of reduced sulfur compounds had unexpectedly accumulated in the hull timbers, now with oxidation processes giving rise to severe acidity [1], see <http://www.fos.su.se/~magnuss/>.

For a number of historical shipwrecks XANES analyses, combined with x-ray fluorescence line scans along core samples, show that sulfur and iron compounds often have penetrated into the wood, reacted and accumulated in large quantities. Recent x-ray microprobe studies indicate that bacterially produced hydrogen sulfide formed iron sulfides and organosulfur compounds in the wood by different reaction pathways, aided by wood-degrading bacterial activity. Oxidation of the iron sulfides probably is the main cause of acidity in the wood, while the organosulfur compounds may be more resistant to oxidation. For lasting conservation, acid-forming sulfur compounds in the wood should be removed, if possible together with extraction of iron ions with a new efficient soluble chelate [2, 3]. For each unique marine archaeological object sulfur and iron scanning microprobe spectroscopy can be used to assess the need of specially adapted conservation procedures, to monitor the efficiency of the removal processes and the stability of the compounds remaining in the wood.

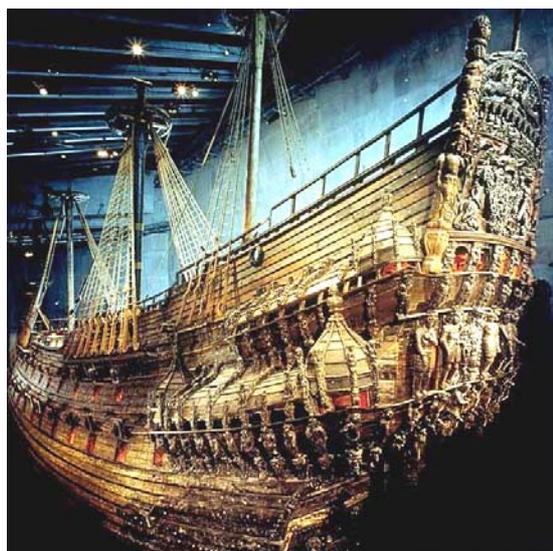


Figure 1: The *Vasa* after conservation treatment on display in the Vasa Museum.

Photo: Hans Hammarskjöld, the Vasa Museum

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# Mummified tissues and ancient cosmetic recipes analysed by infrared and X-ray micro-spectroscopies

COTTE M.

ESRF ID21

Some organic materials may present an exceptional resistance to degradation even after many centuries. Among them, pieces of human tissues from mummies as well as cosmetics are sometimes discovered in tombs. They are very precious samples and may provide a lot of information about the way of life contemporaneous of the funeral, as well as the chemical long time evolutions that may occur.

We will present two types of examples: mummified tissues and ancient cosmetics. Infrared (IR) and X-ray spectroscopies are well-suited methods to study such samples, which are often composed of a mixture of organic and inorganic materials. The chemical probing of these two techniques is completely different due to the two distinct wave-number domains used. IR micro-spectroscopy offers images of the molecular groups, whereas X-ray analyses reveal the atomic composition. Hence, the complementarity of these two methods is helpful. For the two techniques, the synchrotron radiation provides a good trade-off between duration, spatial resolution and spectral quality of the acquisitions.

Concerning the mummified tissues, some samples are in an amazing conservation state. The main constituents (lipids and proteins) as well as the protein secondary structure present a similar distribution to the one observed on modern samples. A beginning of degradation seems to appear in the middle of the hair, the medulla. X-ray fluorescence, IR and XANES spectroscopies converge on the same result: the identification of a calcium phosphate which could be formed via long term reactions.

The analysis of some ancient cosmetics revealed the presence of some lead soaps. IR spectroscopy can sometimes be used to identify the precise nature of these soaps and their distribution may be indicative of the process of the cosmetics. These lead compounds are considered, nowadays, as potentially toxic. We have reconstructed ancient recipes to study the interactions between these pharmaceutical preparations and skin. X-ray fluorescence enables to follow the diffusion of lead inside transversal cross-sections of skin, treated by different mixtures and analyse the resistance of *stratum corneum* to the penetration of exogenous substances. IR micro-spectroscopy is less sensitive, and may not detect so low concentrations, but, conversely, it can give information about the supramolecular organisation of the molecules.

These two examples demonstrate the usefulness of combining IR and X-ray spectroscopies to better understand the short and long term interactions between organic materials and minerals.

# Synchrotron radiation analysis of parchment degradation

KENNEDY C.J., WESS T.J.

Structural Biophysics Group, School of Optometry and Vision Sciences, Cardiff University, Cardiff, UK

Parchment contains important historical information, from text written on the surface to the structure of the material itself. Whilst deterioration of historical parchments is often attributed to harsh storage conditions, other factors may also accelerate the decay of the collagen structure within parchment, such as harsh cleaning techniques.

X-ray diffraction is a technique capable of non-destructively describing the condition of the structure of collagen within parchment. As such, this technique has been used on valuable documents such as the Dead Sea Scrolls [1]. Recent advances in synchrotron radiation technology has led to more detailed analysis of the parchment structure.

Microfocus X-ray diffraction and fluorescence using a compound refractive lens has allowed for surface-to-surface analysis of cross-sections of parchment samples [2]. Up to 200 images can be taken in a single cross sectional scan of a 300  $\mu\text{m}$  thick parchment section, providing X-ray diffraction analysis of features present only in specific areas of the parchment, such as at the surface. Using this technique, the degradation of collagen through cross sections, the orientation of collagen fibrils, the presence of lipids and minerals and the effects of ink have been described. This analysis has demonstrated that parchment is not a uniform structure in cross-section. The collagen is aligned in the plane of the parchment, with lipids packed between collagen fibrils, suggesting specific lipid-protein interactions, polymorphs of calcite are distributed randomly throughout the cross-sections. Collagen at the parchment surface is damaged in regions immediately underneath writing, suggesting that the ink corrodes the parchment structure.

Microfocus X-ray diffraction coupled with conventional synchrotron radiation analysis has been used to describe the effects of conservation treatments on the collagen structure within parchment. Conventional treatments as well as the new technique of laser cleaning have been analysed by these methods [2,3]. Surface cleaning of parchments with erasers or sponges appears not to adversely affect the structure of the collagen; however, when these are coupled with relaxing techniques such as the use of isopropanol or ultrasonic humidifiers, surface damage of collagen becomes apparent. Laser cleaning using long wavelengths and low energy levels appear not to damage the collagen structure in parchment; however, using ultraviolet wavelengths of light or excessively high energy levels appear to induce gelatinisation of the collagen at the parchment surface.

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# X-ray microdiffraction and microfluorescence using synchrotron radiation as a new tool for investigating single archaeological textile fibres

MÜLLER M., MURPHY B. M., ROBERTS M. A. \*, BURGHAMMER M.<sup>1</sup>, RIEKEL C.<sup>1</sup>,  
GUNNEWEG J.<sup>2</sup>, PANTOS E.\*

Institut für Experimentelle und Angewandte Physik, Universität Kiel, Germany, \*Daresbury Laboratory,  
Warrington, UK, <sup>1</sup>ESRF, Grenoble, France, <sup>2</sup>Archaeometry, The Institute of Archaeology, The Hebrew  
University of Jerusalem, Israel

The classical approach to identify archaeological textile fibres is via optical and electron microscopy. Optical microscopy readily reveals the handedness of spun yarns. The shape of the fibres allows for the discrimination between animal and plant fibres. However, degradation may have changed the outer appearance and shape of textile fibres. In particular, the small differences between plant fibres of the bast fibre family (flax, hemp, jute, ramie) are usually not visible with microscopic techniques.

Intact textile samples can be investigated by means of synchrotron X-ray diffraction. These non-destructive techniques yield diffraction diagrams with sharp and intense powder rings from the fine adhering mineral particles. If larger beams (of the order of 0.2 mm in diameter) are used, the fibre material (cellulose or wool) produces broad diffuse rings due to the small crystallites in the material and an averaging effect over many fibres. X-ray microbeam diffraction [1], a technique with a beam size of typically 2 to 5 µm, overcomes this difficulty by providing a microscopic spatial resolution. A highly intense focused synchrotron radiation microbeam allows one to collect fibre diffraction patterns from fractions of single fibres in a few seconds. The high internal orientation of textile fibres makes the discrimination of the contributions of soil particles and fibres to the diffraction patterns straightforward.

We measured single threads of textile samples from the Caves of Qumran (inhabited by the Essenes from around 50 BC to 70 AD) [2,3] and from the Cave of the Letters (hiding place for Jews in the second revolt against the Romans around 135 AD), both located in the Dead Sea area, at the ESRF Microfocus Beamline ID13. The archaeological fibre diffraction patterns in comparison with modern reference samples made the identification of cellulose fibres and wool and in particular for the first time of different types of cellulose bast fibres possible.

Another difficult part of the analysis of archaeological textiles concerns the way they were dyed. From the textiles found in the Cave of the Letters, X-ray fluorescence spectra were recorded simultaneous to X-ray diffraction patterns. The position-resolved analysis yields elemental distributions across the fibre diameter [4]. In a preliminary analysis, adhering soil particles can be identified as well as elements that are homogeneously distributed in the fibres. Those may be associated with dyes or mordants used in the dyeing process.

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# Revealing the Distribution of Painting Pigments

Joris DIK

Laboratory of Materials Science, Delft University of Technology, Rotterdamseweg 137, 2628 AL Delft, The Netherlands

The visible surface of a painting hides many important traces of the painting process. The substructure of a painting may include initial sketches of the composition of a painting, modifications made during the actual painting stage, as well as abandoned compositions covered by a different painting. The visualization of such hidden layers provides information on the condition, genesis and authenticity of an artwork.

Laboratory-based imaging techniques include x-ray radiography and infra-red reflectography. Main drawback are the insensitivity of x-rays to light element pigments and the limited penetration of infra-red radiation.

Using monochromatic x-rays and/or neutrons at large facilities, such as the ESRF and ILL, obstacles of traditional imaging can be overcome. The first example shows the use of neutron irradiation and subsequent autoradiography in the imaging of a discoloured pigment. This allowed to make a digital reconstruction of the original appearance of a discoloured painting. The second technique concerns the use of x-ray K-edge imaging of paintings. An example of this technique is presented and its potential is discussed.

# Some applications of X-ray Synchrotron microtomography for non-destructive 3D studies of paleontological specimens

TAFFOREAU P.<sup>1</sup>, BOISTEL R.<sup>2</sup>, BOLLER E.<sup>1</sup>, BRAVIN A.<sup>1</sup>, BRUNET M.<sup>4</sup>,  
CHAIMANEE Y.<sup>5</sup>, CLOETENS P.<sup>1</sup>, FEIST M.<sup>6</sup>, HOSZOWSKA J.<sup>1</sup>, JAEGER J.-J.<sup>6</sup>,  
KAY R. F.<sup>7</sup>, LAZZARI V.<sup>6</sup>, MARIVAUX L.<sup>6</sup>, NEL A.<sup>3</sup>, NEMOZ C.<sup>1</sup>, THIBAUT X.<sup>1</sup>,  
VIGNAUD P.<sup>4</sup>, ZABLER S.<sup>8</sup>

<sup>1</sup>European Synchrotron Radiation Facility (Grenoble, France)

<sup>2</sup>Laboratoire de Neurobiologie de l'Apprentissage de la Mémoire et de la Communication (Orsay, France),

<sup>3</sup>Museum National d'Histoire Naturelle (Paris, France)

<sup>4</sup>Laboratoire de Geobiologie Biochronologie et Paleontologie Humaine (Poitiers, France)

<sup>5</sup>Department of Mineral Resources (Bangkok, Thailand)

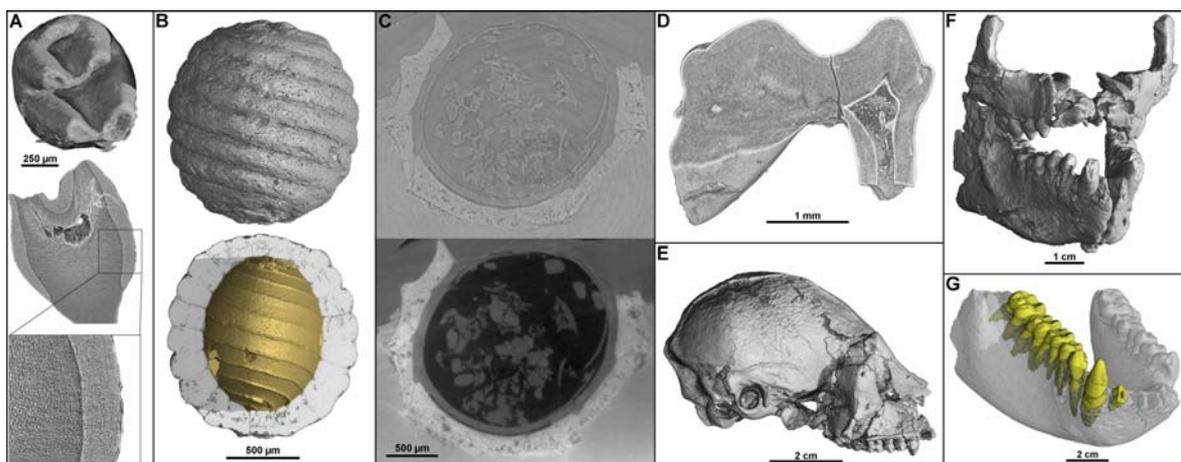
<sup>6</sup>Institut des Sciences de l'Evolution (Montpellier, France)

<sup>7</sup>Department of Biological Anthropology and Anatomy (Duke, USA)

<sup>8</sup>Hahn Meitner Institute (Berlin, Germany)

Among the numerous applications of the X-ray Synchrotron microtomography, paleontology is a recent newcomer.

Studies of external morphological characters are not sufficient for paleontologists to extract all the important data about fossil organisms. Observations of internal structures become more and more necessary, but they have to be non-destructive in most of the cases. Conventional microtomography allows numerous investigations. But the best microtomographic images are obtained using a third generation synchrotron, as the ESRF, which provides a lot of supplementary information. Firstly, beam intensity allows very high spatial resolutions and exceptional contrast when compared with industrial microtomographs. Secondly, monochromaticity permits to avoid beam hardening that is frequently strong for paleontological samples. Thirdly, coherence leads to new imaging techniques: phase contrast radiography, phase contrast microtomography and holotomography. These methods appear to be successful for fossils presenting high mineralization or low densities contrasts. Figure 1 shows some examples, at different scales, of applications of X-ray synchrotron microtomography in paleontology.



**Figure 1:** **A:** Rodent molar. Phase contrast reveals enamel and dentine microstructure. **B:** Fossil charophyte algae showing a virtual 3D cast of the gyrogonite. **C:** Comparison between absorption and holotomography on a fossil charophyte. **D:** Fossil primate molar. Phase contrast enhance the enamel-dentin junction. **E:** Fossil skull of a South-American primate. **F:** Virtual 3D reconstruction of the jaws of an Asiatic fossil primate. **G:** Mandible of an ancestor of modern orang-utans from Thailand. Right teeth have been virtually pulled off.

# Micro scanning X-ray diffraction study of Roman Terra Sigillata ceramics

SCIAU P., GOUDEAU P.<sup>1</sup>, TAMURA N.<sup>2</sup>, DOORYHEE E.<sup>3</sup>

CEMES - UPR 8011 CNRS (Toulouse, France),<sup>1</sup> LMP - UMR 6630 CNRS – Université de Poitiers (France)

<sup>2</sup> ALS – LBNL (Berkeley, USA), <sup>3</sup> Laboratoire de Cristallographie - UPR 5031 CNRS (Grenoble, France)

*Terra Sigillata* is the most famous fine ware of the Roman period. This class of pottery appeared in the mid-first century BC in Italy. From the Augustan period (27 BC – 14 AD), it has been widely spread within and outside the Italian Peninsula and branches were established in Pisa and in the south of Gaul. Among the southern Gaul workshops, *La Graufesenque* was the most important. During the first century AD, this workshop produced vast quantities of the sigillata pottery, which were sold all over the Roman Empire, mainly in Gaul, Great Britain, Germany and Spain [1].

The success of this pottery was due in great part to the brightness and colour of the gloss. However, up to now few studies were devoted to this topic. Also in order to better understand the origins and elaboration process of these ceramics, a study of the microstructure of the Gaul *sigillata* slip has been carried out by  $\mu$ -beam X-ray diffraction.

The XRD experiments were carried out at the beam line 7.3.3 of the Advanced Light Source (Berkeley, USA) by successively scanning a white and monochromatic X-ray beam over the sample surface with a submicron spot size [2]. Simultaneously, the main chemical species Fe were located by their X-ray fluorescence emission. The diffraction diagrams were recorded with a 2D CCD detector. The phase, the size range and the orientation distribution of the grains are determined for the Fe host phase and for the other main crystalline constituents.

The different populations of crystallites were also imaged by TEM and their chemical composition estimated by EELS.

The gloss is mainly formed of  $\mu\text{m}$ -sized quartz, with smaller hematite and corundum crystallites embedded in a glassy matrix. The matrix does not contain any colouring agent. The colour of hematite crystallites usually varies from black to red, depending both on the Al/Fe ratio and on the crystallite size. In the sigillata, hematite is red, due to the presence of Al and to the submicronic grain size. In the case of corundum, we observe a light yellow colour to these crystals in relation with the presence of iron. Both the hematite and corundum crystal populations are homogeneously dispersed in the matrix and they give, together, the red-orange colour to the sigillata. The diffraction 2D diagrams show that corundum is composed of nanocrystallites. This phase is formed during the firing and its structural and chemical features can be imparted to the elaboration process of the ceramic.

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# Applications of TOF Neutron Diffraction in Archaeometry

KOCKELMANN W.

Rutherford Appleton Laboratory, ISIS Facility, Chilton, OX11 0QX, UK

Neutron radiation is a versatile diagnostic probe for collecting information from the interior of large, undisturbed museum objects or archaeological findings. Neutrons penetrate through coatings and corrosion layers deep into centimetre-thick artifacts without substantial attenuation, a property that makes them ideal for non-destructive testing for which sampling is impractical or unacceptable. A particular attraction of neutron techniques for archaeologists and conservation scientists is the prospect of locating hidden materials and structures inside objects.

Intense neutron beams are presently produced by either nuclear fission (reactors) or spallation (high-energy accelerator-driven sources). Archaeometric studies at the ISIS spallation source at the Rutherford Appleton Laboratory are based on time-of-flight (TOF) neutron diffraction which is a direct method for examining all structural aspects of cultural heritage objects [1-3]. With the existing suite of instruments at ISIS, a full structural characterisation of a wide class of materials such as pottery, pigments, marble artefacts and metal objects can be achieved. The abundance of mineral and metal phases, the crystal structure of each of the phases, the grain sizes and grain orientations, microstructures as well as micro- and macro stresses in materials can be examined. A particular promising application of neutron diffraction is texture analysis for recording the grain orientation distribution [4,5]. The crystallographic texture is critically dependent on the past mechanical and/or thermal treatment of an artefact. Thus, texture analysis provides important clues to the deformation history, and may therefore help to uncover historic production steps. Moreover, if the making techniques are known, texture maps may help to distinguish genuine from fake objects.

TOF neutron diffraction allows for a time-efficient collection of the texture maps, the pole figures. On a powder diffractometer like GEM at ISIS a large portion of orientation space is covered without sample rotations. A combined phase, structure and texture analysis of a bulky object of complex shape can be achieved in a single measurement in a matter of minutes, an important aspect if the short-term radio-activation of a unique object is to be kept to a minimum. Decay times of induced radioactivity levels, which depend on the isotopic compositions and the irradiation times, are typically in the order of minutes for ceramics and up to several days for objects containing elements such as silver or copper.

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# **Corrosion study of archaeological copper artefacts right after excavation and during their storage and stabilization processes**

ADRIAENS A., DE RYCK I.\* , LEYSSENS K.

Ghent University, Department of Analytical Chemistry, Krijgslaan 281-S12, 9000 Ghent, Belgium

\*University of Antwerp, Department of Chemistry, Universiteitsplein 1, 2610 Antwerp, Belgium

This paper describes the use of microbeam analysis techniques for the chemical characterization of corrosion compounds on ancient bronze objects. They include optical microscopy, SEM-EDX, TOF-SIMS, SR-FTIR, SR-XRD, and XANES. The objective is to investigate which combination of analysis methods is most suitable for this type of application, taking into account aspects such as limited sampling and the ability of obtaining spatial information.

In a second part of the presentation the attention is focused on archaeological copper artefacts recovered from wet saline environments. They are often stored in tap water and stabilized in sodium sesquicarbonate solutions. Modification of the natural patina and development of active corrosion can occur during these processes. This implies that monitoring of storage/stabilisation processes is necessary. The focus of the study consists of examining how corrosion potential ( $E_{corr}$ ) measurements can contribute in providing information on the effectiveness of storage and stabilisation treatments. This paper reports on the  $E_{corr}$  versus time plots of artificially prepared copper coupons (covered or not with corrosion layers) immersed in tap water and a sodium sesquicarbonate solution. Synchrotron radiation XRD measurements were performed in parallel to understand the reactions that take place during the immersion processes.

# **Analysis of paint layers by light microscopy, scanning electron microscopy and synchrotron induced X-Ray micro-diffraction**

HOCHLEITNER, B., SCHREINER, M.

Institute of Science and Technology in Art, Academy of Fine Arts, Vienna, Austria

DRAKOPOULOS, M., SNIGIREVA, I., SNIGIREV, A.

ESRF - European Synchrotron Radiation Facility, Grenoble, France

The most common way to analyze paint layers is the preparation of a cross-section of properly sampled specimens, where the sequence of all layers is preserved. The examination of the cross-section by light microscopy and UV-fluorescence microscopy provides frequently sufficient information about the structure of the paint layers, grain size and grain size distribution of the various pigments as well as varnish layers or organic binding media. However, for the identification of individual pigments present in the various paint layers additional investigations of the cross-section are necessary. Scanning electron microscopy (SEM) combined with energy dispersive x-ray microanalysis (EDX) has been used widely to obtain information about the elements present in the pigments as well as their distribution in the different layers. Single pigments can be identified by comparing their colour and elemental composition with standard materials known to be used in the present or past for painting artefacts.

However, many inorganic materials and some of the most interesting pigments can occur in different crystalline structures.  $\text{CaCO}_3$  – chalk, which has been often used as filler in the ground layer, e. g. can occur in the modification of calcite as well as aragonite. Therefore, x-ray diffraction analysis has been proved to be a valuable tool for the examination of the paint layers too. With common XRD it is rather difficult to carry out those investigations of specific pigments, as the thickness of the paint layers is in the range of several tens micrometers or even below. Therefore, synchrotron induced x-ray micro-diffraction at ID22 of the ESRF could be used in the present work, where the step scan resolution can be much smaller than the thickness of the paint layers.

The sample investigated consisted of 7 layers in total, whereby a thin layer of pure gold was suspected to be the uppermost layer. The sequence of the various paint layers as well as the distribution of the elements present in the pigments could be obtained from the cross-sectioned specimen. Additionally, synchrotron induced x-ray micro-diffraction analysis (XRD) enabled the identification of the crystalline structure of the pigments used for the painting. Traversing the sectioned sample through a focused x-ray beam with a size of  $2\ \mu\text{m}$  allows microscopic resolved analysis of the crystalline constituents within the diverse paint layers. By this, it is possible to attribute the usage of various pigment minerals within the paint layers, even including a  $2\ \mu\text{m}$  thick gold layer at the surface.

# A secret of Mayan alchemy: how to turn a colorant into a pigment

SANCHEZ DEL RIO M.<sup>1,2</sup>, MARTINETTO P.<sup>3</sup>, DOORYHEE E.<sup>3</sup>, SUAREZ M.<sup>4</sup>,  
SODO A.<sup>1</sup>, REYES-VALERIO C.<sup>5</sup>, HARO PONIATOWSKI E.<sup>2</sup>, PICQUART M.<sup>2</sup>,  
LIMA E.<sup>2</sup>, REGUERA E.<sup>6</sup>

[1] European Synchrotron Radiation Facility, BP 220, F-38043 Grenoble Cedex, France

[2] Universidad Autónoma Metropolitana Iztapalapa, Mexico 09340 D.F., Mexico

[3] Laboratoire de Cristallographie, CNRS, BP166 F-30842 Grenoble, France

[4] Universidad de Salamanca, Departamento de Geología, E-37008 Salamanca, Spain

[5] Instituto Nacional de Antropología e Historia, Mexico D.F., Mexico

[6] Universidad de La Habana, 10400 La Habana, Cuba

Colorants used in antiquity are organic molecules extracted from plants and animals. They cannot be used in many artworks because they are not very stable over the years. They fade with light, age, pollutants and some of them react with other chemicals (oil, resins, substrates, etc.) of the artwork. Pigments made from minerals are very stable and always preferred for many artistic techniques (mural paint, oil paint, polychromatic pottery, etc.). The Maya have succeeded in “mineralizing” the indigo, the most common blue colorant well known by many ancient civilizations, by embedding it in a very particular clay mineral (palygorskite).

We present a review of recent studies about this pigment, known as Maya blue. We tested the stability of the pigment against acids, and performed synchrotron experiments (XRD, XANES) aiming to determine the structure of the pigment and palygorskite.  $\mu$ -XRD and  $\mu$ -XRF investigations performed at ESRF on archaeological mural samples of Maya blue suggest that the Maya also created a green pigment (the “Maya green” of Bonampak) with the same ingredients used in Maya blue. The synchrotron studies are being complemented by other laboratory techniques (FTIR, Raman and NMR) with the aim of understanding how indigo interacts with palygorskite, and why this compound is so stable.

# **A multidisciplinary handshake between the humanities & sciences vis-à-vis Qumran and the Dead Sea scrolls**

GUNNEWEG J.

Archaeometry, the Institute of Archaeology, The Hebrew University of Jerusalem

The famous Dead Sea scrolls that were found in 1947 at Qumran point to a group of people, the “Essenes” who were surrounded by 850 manuscripts of biblical, sectarian and non-religious writings. In 1998, interdisciplinary laboratory research has started between material scientists, museum curators and archaeologists to obtain the utmost information from what the manuscripts as well as the Qumran artefacts may demonstrate from the past, as well as how to preserve this piece of cultural heritage for the centuries to come.

The Dead Sea scrolls are not only of great importance for understanding the biblical texts we have, but also what went on in the period of time that coincided with the dawn of Christianity.

Instrumental Neutron Activation Analysis<sup>[1]</sup> provided the origin of the scroll jars and the interactions of the sectarian “Essenes” with other Jews between 50BC-70AC. Petrography and Thermoluminescence combined with Magnetic Susceptibility confirmed the NAA results. Microscopy, SEM and Synchrotron X-Ray Diffraction<sup>[2]</sup> was used to identify the threads of textile wrappings that covered the scrolls as well as clothe that was worn 2000 years ago. A successful tentative was made to identify the used pigments of the yarns by High Performance Liquid Chromatography too, especially with regards to the use of Indigo that will now be verified by Raman microscopy and Synchrotron XRD at the ESRF in Grenoble where we are analyzing Bar Kochba textiles.

The date for the scrolls, the settlement and the cemetery was provided by AMS Carbon 14 that was applied to textiles, wood and date kernels, whereas the date for pottery was obtained by Thermoluminescence. Further research was done on the DNA of the parchment of the scrolls. Sr 87/86-ratio research will start on the diet of the Qumran population, whereas isotope analysis of the bones will explain why they died young.

The photographed fragments of the scrolls undergo an intensive cleaning and conservation process before they will be studied and re-exhibited.

Unbiased scientific cooperation with multidisciplinary data bases assembled in European or global framework is a sine qua non if historians and museum curators must show modern man what his ancestors accomplished and with what consequences.

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# Synchrotron radiation on the traces of famous painters: XRF analyses of silverpoint drawings by Dürer, Holbein, Van Eyck and Rembrandt

REICHE, I., BERGER, A.\*, BEVERS, H.<sup>1</sup>, DUVAL, A., GÖRNER, W.\*, KETELSEN, T.<sup>2</sup>, MERCHEL, S.\*, RADTKE, M.\*, RIESEMEIER, H.\*, ROTH, M.<sup>1</sup>

Centre de Recherche et de Restauration des Musées de France (C2RMF) - UMR 171 du CNRS,  
Palais du Louvre, F-75001 Paris, France, corresponding author: [ina.reiche@culture.gouv.fr](mailto:ina.reiche@culture.gouv.fr)

\* Bundesanstalt für Materialforschung und –prüfung (BAM), D-12205 Berlin, Germany

<sup>1</sup> Kupferstichkabinett, Staatliche Museen zu Berlin - Preußischer Kulturbesitz,  
10785 Berlin, Germany

<sup>2</sup> Kupferstich-Kabinett, Staatliche Kunstsammlungen Dresden, 01067 Dresden, Germany

In our days, artists have a large panoply of drawing materials at their disposal. But when you search for drawing materials used by Renaissance's artists in Europe only little information is available. Nearly no ancient drawing instruments are conserved. Therefore, the only possibility to get insights into former drawing techniques is the analysis of the drawings themselves.

The use of silverpoints for drawing is one of the most delicate and precious drawing techniques. In some primary work, about seventy drawings by mainly Italian, but also Flemish and German artists were analysed using external beam micro-Proton induced X-ray emission ( $\mu$ -PIXE) in order to get more information on this drawing technique and to define new criteria for comparison of drawings of unknown origin [1]. In the frame of a French-German cooperation, about 25 further drawings were investigated using spatially resolved Synchrotron induced X-ray fluorescence (SR-XRF) analysis at the BAMline at BESSY. Indeed, the analysis of drawings requires particular attention because the study has to be fully non-destructive and extremely sensitive. The metal alloy on the paper does not exceed some hundreds of  $\mu\text{g}/\text{cm}^2$ . Therefore, surface sensitive  $\mu$ -PIXE and SR-XRF are particularly well suited for the analyses of silverpoint drawings.

Here, we report new analyses of a series of silverpoint drawings that were made by Albrecht Dürer [2], Jan van Eyck [3] and even Rembrandt as well as those originating from the workshop of Hans Holbein the Elder. The latter drawings show the specificity that they were realised with metal points but also highlighted with red and white pigments and overdrawn with inks or gouaches. Various inscriptions and lead strokes are also present. The investigated drawings are kept today in the drawing cabinets of the State Museums of Berlin and of the State collections of Dresden.

The study of these drawing series permits to differentiate the drawing materials, to better understand the drawing technique and to give new insights into the genesis of some drawings.

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# Improved noninvasive microstructural analysis of fossil tissues by means of SR-microtomography

MAZURIER A., VOLPATO V., BRAVIN A.\* , MACCHIARELLI R.

Lab. de Géobiologie, Biochronologie et Paléontologie humaine, UMR 6046 CNRS, Université de Poitiers, 40 av. du Recteur Pineau, 86022 Poitiers, France, \*European Synchrotron Radiation Facility, ID17 Beamline, Grenoble, France

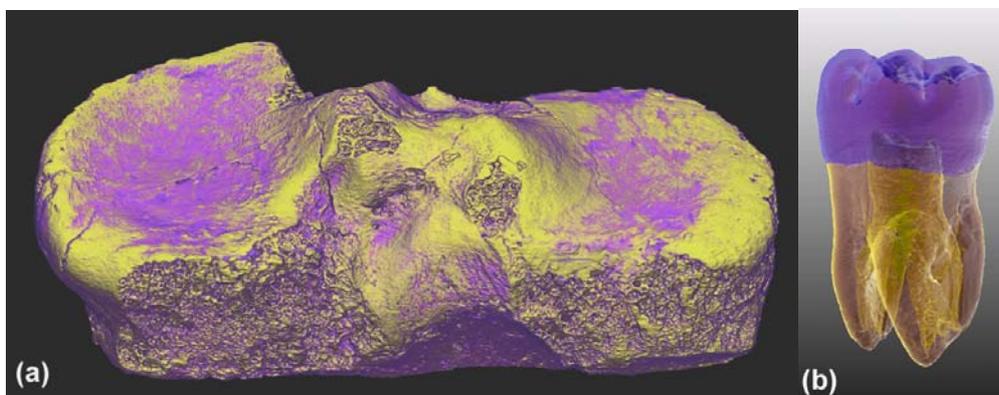
State of the art in paleobiology foresees the use of nondestructive investigative approaches on the usually scarce and fragmentary fossil record. X-ray microtomography ( $\mu$ CT) allows the extraction, at a high spatial resolution (tens of microns), of hidden structural information from dental and bony fossil specimens. In particular, synchrotron radiation microtomography provides a unique source of monochromatic and high photon flux x-ray beam which, in comparison to the commercially and industrially available  $\mu$ CTs equipments, guarantees higher signal-to-noise ratio imaging.

While  $\mu$ CT applications in paleontology and (paleo)biology are still limited, in order to detail large-size fossil specimens at high spatial resolution ( $<50\mu\text{m}$ ), we have experienced the ESRF ID17 medical beamline within two related research lines.

The first line concerns the quantitative assessment of the inner normal/abnormal bone architecture for the reconstruction of postural/locomotory patterns in fossil taxa (Figure 1a). This innovative approach bases on the dynamic interplay between the cortical and trabecular bone structures and their biomechanical environment, where normal bone mostly builds and remodels in response to mechanical demands.

The second research line is designed to detail major dental structural features (Figure 1b) such as, among the others, the enamel thickness topographic variation. This represents a key variable in (paleo)primatology and (paleo)anthropology because of its value as indicator of dietary habits and in taxonomic assessment and phylogenetic reconstructions. The methodological issue of the degree of repetitivity and replicability of the measurements with respect to the conventional radiographic and histological approaches is also considered.

Through the example of the ongoing “*The-Neanderthal-Tools*” European project, the relevance of this kind of methodology for the documentation, analysis, and safeguard of the (paleo)biocultural record will be illustrated.



**Figure 1:** 3D reconstructions of (a) a tibia of a Neanderthal from La Ferrassie, France and (b) a molar of a Neanderthal from La Chaise de Vouthon, France