SYNCHROTRON RADIATION AND NEUTRONS IN ART AND ARCHAEOLOGY CONFERENCE 2016

September 6th to 8th

The Art Institute of Chicago - 111 S Michigan Ave, Chicago
Hosted by the Northwestern University /Art Institute of Chicago Center for Scientific Studies in the Arts (NU-ACCESS) with major support from Argonne National Laboratories and the Society for Archaeological Science.
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SESSION SCHEDULE

Sept. 6th 2016

8.00 – 9.30  REGISTRATION AND COFFEE RECEPTION
9.30 – 10.00 OFFICIAL OPENING
10.00 - 12.20 SESSION I: INNOVATIVE SR-BASED METHODS AND ANALYTICAL PROCESSES
13.50 – 16.40 SESSION II: NEUTRON-BASED TECHNIQUES
16.40 – 18.00 POSTER SESSION - STOCK EXCHANGE ROOM
18.00 - 20.00 RECEPTION EVENT - GRAND STAIRCASE

Sept. 7th 2016

9.30 – 12.40 SESSION III: CONSERVATION AND ALTERATION
12.40-14.00 VISIT OF THE ART INSTITUTE MUSEUM
14.00 – 17.30 SESSION IV: PROCESSES AND CHAINES OPERATOIRES
17.30 – 18.30 RADIATION DAMAGE SESSION
19.30 – 23.00 DINNER – ORIENTAL INSTITUTE MUSEUM

Sept. 8th 2016

9.00 – 11.30 SESSION V: PALEONTOLOGY AND PALEO ENVIRONNEMENTS
11.30 – 12.30 ROUND TABLE – CLOSURE SESSION
AFTERNOON APS TOUR
Detailed Schedule

Tuesday, September 6

8.00-9.30 Registration and Coffee Reception

09.30-10.00 Official Opening

Session I: Innovative SR-based Methods and Analytical Processes

Chairman: V. Rose

10.00-10.20 Investigating the 3D arrangement of submicron pores in blanched easel oil paintings by X-ray phase contrast nanotomography
A. Genty-Vincent, A. Pacureanu, M. Eveno, J. Uziel, M. Cotte, P. Cloetens, N. Lubin-Germain, M. Menu

10.20-10.40 Revealing hidden text in rolled papyri
D. Baum, N. Lindow, V. Lepper, K. Mahlow, H.E. Mahnke

10.40-11.00 Degradation mechanisms of reinforcement iron rebars in monuments: Time-resolved X-ray microtomography of water percolation in corrosion layers
M. Jacot-Guillarmod, A. King, O. Rozenbaum, D. Neff, Claire Gervais

11.00-11.20 Following Pt in gold Byzantine tesserae: towards provenance and chronology with SR-XF
M. Radtke, E. Neri, U. Reinholz, M. F. Guerra

11.20-12.20 The quest of lost ancient literature. Synchrotron based techniques reveal the secrets of Herculaneum papyri: letters and ink composition.
Invited Speaker: V. Mocella

12.20-13.50 Lunch

Session II: Neutron-based Techniques

Chairman: K. Janssens

13.50-14.10 Characterisation of excavated Napoleonic artefacts from the Berezina battlefield in Belarus using neutron and x-ray techniques

K. Bajnok, G. Káli, A. Len
## Detailed Schedule

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<tr>
<th>Time</th>
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<th>Organizer and Details</th>
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<tbody>
<tr>
<td>15.30-16.00</td>
<td>Coffee Break</td>
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<tr>
<td>16.00-16.20</td>
<td>Neutron diffraction for cultural heritage studies: the Italian Neutron Experimental Station INES</td>
<td><em>A. Scherillo, A. Brunetti, F. Grazzi, A. Depalmas, M. E. Minoja, G. Salis, S. Orrù</em></td>
</tr>
<tr>
<td>16.20-16.40</td>
<td>Nondestructive study on metallurgical characteristics of traditional Japanese sword throughout the manufacturing process by pulsed neutron imaging</td>
<td><em>M. Tanaka, M. Isono, Y. Shiota, A. Uritani, Y. Kiyanagi</em></td>
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<tr>
<td>16.40-18.00</td>
<td>Poster session – Stock Exchange room</td>
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<tr>
<td>18.00-20.00</td>
<td>Reception event - Grand Staircase</td>
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### Wednesday, September 7

#### Session III: Conservation and Alteration

**Chairman: F. Casadio**

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<thead>
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<th>Event</th>
<th>Organizer and Details</th>
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<tbody>
<tr>
<td>10.30-10.50</td>
<td>The “corrosion” of historic stained glasses: an investigation using synchrotron radiation based x-ray fluorescence and X-ray absorption (XANES) spectroscopy</td>
<td><em>J. Hormes, W. Klysubun, G.-L. Bovenkamp-Langlois, T. Küpper, M. Kleine</em></td>
</tr>
<tr>
<td>10.50-11.10</td>
<td>Investigating the degradation of gelatin sized paper by iron gall ink with STXM analysis</td>
<td><em>A. Gimat, A. Michelin, P. Massiani, V. Rouchon</em></td>
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<tr>
<td>11.10-11.40</td>
<td>Coffee Break</td>
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**Chairman: L. D’ Alessandro**

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<th>Time</th>
<th>Event</th>
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<tbody>
<tr>
<td>11.40-12.00</td>
<td>Elemental and chemical heterogeneity of lead soaps in paint degradation</td>
<td><em>Y. K. Chen-Wiegart, J. Catalano, S. A. Centeno, A. Murphy, Y. Yao, N. Zumbulyadis, C. Dybowski, G. Williams, J. Thieme</em></td>
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**Detailed Schedule**

<table>
<thead>
<tr>
<th>Time</th>
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<th>Authors</th>
<th>Session</th>
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<tbody>
<tr>
<td>12.20-12.40</td>
<td><strong>Degradation of minium (Pb₃O₄) on the long and short term in material originating from a Red Shroud Mummy</strong></td>
<td>F. Vanmeert, K. Trentelman and K. Janssens</td>
<td>13</td>
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<tr>
<td>12.40-14.00</td>
<td><strong>Lunch</strong></td>
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<tr>
<td>14.40-15.00</td>
<td><strong>Pigments from Roman mural paintings from Germania Superior analyzed with SR-XRF</strong></td>
<td>R. Debastiani, R. Simon, T. Baumbach, M. Fiederle</td>
<td>16</td>
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<tr>
<td>15.00-15.20</td>
<td><strong>Evidence for a Buried Underslip on a Painted Athenian Ceramic from 5th Century BCE</strong></td>
<td>A. Mehta, T. Wang, J. Villanova, P. Sciau, C. Pantigny, E. Pouyet</td>
<td>17</td>
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<tr>
<td>15.20-15.50</td>
<td><strong>Coffee Break</strong></td>
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<tr>
<td>15.50-16.50</td>
<td><strong>Smart*Light: A Flemish-Dutch Table-top Synchrotron Light Source for Conservation Science</strong></td>
<td>Invited Speaker: J. Dik, X. Stragier, J. Luiten, K. Janssens</td>
<td>k4</td>
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<tr>
<td>16.50-17.10</td>
<td><strong>Deciphering information recorded in Ancient materials’ heterogeneity at the sub-microscale with synchrotron deep UV imaging</strong></td>
<td>M. Thouy, T. Séverin Fabiani, M. Réfrégiers, J.-P. Echard, L. Robbiola, B. Mille, L. Bertrand</td>
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<tr>
<td>17.10-17.30</td>
<td><strong>Using sulfur K-edge X-ray Absorption to Assess the Application of Heat in Historical Ultramarine Pigment Production</strong></td>
<td>K. Schnetz, A. Gambardella, R. van Elsas, M. Cotte, K. Keune</td>
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### Detailed Schedule

#### Radiation Damage Session

**Chairman: M. Walton**

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<tr>
<td>17.30-17.50</td>
<td>Computational X-Ray Fluorescence (XRF) Imaging using Dictionary Learning</td>
<td>O. Cossairt</td>
<td>RD1</td>
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<tr>
<td>17.50-18.10</td>
<td>Cultural Heritage X-ray Imaging at SLAC – Challenges and Strategies to Mitigate Radiation Effects</td>
<td>S. Webb</td>
<td>RD2</td>
</tr>
<tr>
<td>18.10-18.30</td>
<td>Monitoring and mitigating radiation damage during synchrotron examination of heritage materials</td>
<td>L. Bertrand</td>
<td>RD3</td>
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<tr>
<td>19.30-23.00</td>
<td>Dinner – Oriental Institute Museum</td>
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#### Thursday, September 8

#### Session V: Paleontology and Paleo-environments

**Chairman: L. Dussubieux**

<table>
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<th>Time</th>
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<th>Speaker(s)</th>
<th>Room</th>
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<tbody>
<tr>
<td>9.00-10.00</td>
<td>15 years of Synchrotron X-ray imaging in paleontology: Reasons of a success and new tendencies</td>
<td>Invited Speaker: P. Tafforeau</td>
<td>K5</td>
</tr>
<tr>
<td>10.00-10.20</td>
<td>Micro-environmental burial conditions involved in exceptional fossilization: insight from synchrotron X-ray spectroscopy and imaging</td>
<td>P. Gueriau, C. Mocuta and L. Bertrand</td>
<td>O20</td>
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<tr>
<td>10.20-10.50</td>
<td>Coffee break</td>
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<tr>
<td>10.50-11.10</td>
<td>Paleontological projects at the Advanced Photon source</td>
<td>C. Soriano</td>
<td>O21</td>
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<tr>
<td>11.10-11.30</td>
<td>Relation between the macroscopic Schreger pattern of elephant ivory and its mineralized collagen fiber matrix</td>
<td>M. Albéric, A. Gourrier, W. Wagermaier, P. Fratzl and I. Reiche</td>
<td>O22</td>
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<tr>
<td>11.30-12.30</td>
<td>Round Table – Closure session</td>
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<tr>
<td>12.30-13.30</td>
<td>Lunch</td>
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<tr>
<td>13.30-18.00</td>
<td>APS Tour</td>
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**Dr. Vito Mocella, National Research Council Rome**

Vito Mocella graduated (Laurea) in Electronic Engineering at the “Federico II” University of Naples in 1995, in 1999 he got the French Ph.D (Doctorat) in Physics working at European Synchrotron Radiation Facility (ESRF), Grenoble, France. From 1999 to 2001 he worked with Optics Group of ESRF and with SRI-CAT Group of the Advanced Photon Source, Argonne Illinois (USA). In 2002 he joined the National Council of Research (CNR) working on x-ray optics, photonic crystal and metamaterials. In November 2006 he has been nominated Cavaliere all’Ordine del Merito della Repubblica from the Italian President. In 2015 he joins the Management Board of the CNR.

**Dr. Letizia Monico, CNR-ISTM, University of Perugia**

Letizia Monico is a researcher at the CNR-ISTM and University of Perugia. Since receiving a joint Ph.D in Chemistry from the University of Perugia and Antwerp in 2012, she has established herself as a specialist for the study of the alteration processes and characterization of painting materials through vibrational and synchrotron-based X-ray microspectroscopies, with a focus on chrome yellow pigments. From 2010 till now, her research activities have summarized in 14 peer-review articles, a book-chapter, several short-communications and over 30 conference contributions. Her work about the darkening of chrome yellows has been awarded the Eric Samuel award (Oxford Instruments/Microscopy Society of America) and the SILS -SPECS prize.

**Dr. Paul Tafforeau, ESRF**

Paul Tafforeau is beamline scientist at the ESRF on the beamline ID19. In 2000 at the beginning of his PhD, he initiated the used of synchrotron microtomography for non-destructive investigations of fossils. This topic has regularly grown since then, and has now spread in many other synchrotrons all around the world. In 2004 he starts a post-doc at the ESRF, and then becomes beamline scientist in 2007 and scientist in charge of the palaeontology. In addition to the palaeontology related researches and development of X-ray synchrotron microtomography in general, his areas of interest involves also evolutionary biology and more recently archaeology.
Dr. Adrian Hillier, STFC Rutherford Appleton Laboratory

Adrian Hillier was awarded his PhD at University of St. Andrews in 1998, followed by a post-doc position. Afterwards he worked at the Institut Laue Langevin, Grenoble, France and then went on to a role at the ISIS pulsed neutron and muon facility as a muon instrument scientist. Currently, he is Muon Group Leader and has an active research programme investigating material properties using a wide range of techniques including muon-spin relaxation/rotation, elastic and inelastic neutron scattering, heat capacity and magnetization, resulting in nearly 150 publications. Recently at ISIS he has been developing elemental analysis techniques using negative muons. He collaborates with researchers from around the world on experiments which include investigating ancient swords and coins; irradiation of electronic components and fundamental magnetism and unconventional superconductivity.

Dr. Joris Dik, TU Delft

Joris Dik holds the Antoni van Leeuwenhoek Chair, Materials in Art and Archeology, at Delft University of Technology. He works on the development and application of innovative analytical concepts in the study of cultural heritage objects including fine art for a variety of diagnostic purposes. Joris received an M.A. (1997) in art history and classical archaeology from the University of Amsterdam, which included (1995-1996) graduate study at the J. Paul Getty Museum’s Conservation Institute in Los Angeles; a Ph.D. (2003) from the University of Amsterdam in chemistry, focusing on historical pigment technology. He was appointed full professor at TU Delft in 2011 and is a member of the Young Academy of the Netherlands Royal Academy of Arts and Sciences (KNAW).
LIST OF POSTERS

P01-DANTE: processing electronics with Ultimate Energy-Resolution and High-Count Rate Capability for micro and macro XRF mapping application
L. Bombelli, M. Manotti, R. Alberti, T. Frizzi, R. Mott, N. Barbi

P02-Optimizing Compositional Images of Daguerreotype Photographs Using a Laboratory X-ray Source and Post Processing Methods
J. M Davis and E. P Vicenzi

P03-High Definition X-ray Fluorescence Imaging of Cultural Materials at the XFM Beamline of the Australian Synchrotron

P04-Hard X-ray Fluorescence Imaging and micro X-ray Absorption Spectroscopy Facilities at SSRL
C. M. Krest (Roach), S. Webb

P05-Recent archaeological studies at the GSECARS 13-ID-E hard X-ray microprobe beamline at the Advanced Photon Source
A. Lanzirotti, M. Newville, M. Hunault, and R. Bianucci

P06-Development of combined XRF and XRD mapping for cultural heritage applications at CHESS
L. M. Smieska, A. R. Woll

P07-New approaches for the study of cultural heritage objects by means of neutron imaging methods
E. H. Lehmann, D. Mannes

P08-Old russian jewelries studies by means of neutron imaging method
A. V. Saprykina, A. N. Khokhlov, S. E. Kichanov, D. P. Kozlenko

P09-Neutron, Proton, and Ion Based Techniques for Heritage Materials: A Synergistic Approach at ANSTO

P10-Dechlorination of ferrous archaeological artefacts in subcritical conditions: understanding of the corrosion layer transformation thanks to a multi-scale characterisation

P11-Understanding Smalt Discoloration through Potassium K-edge XANES
M. Ganio, C. Schmidt Patterson, K. Trentelman

P12-Determining the Cause of Degradation of Landscape with Cowherd by Claude Lorrain Using X-ray Fluorescence Imaging and µ-X-ray Absorption Spectroscopy
C. Krest (Roach), J. L. Lazarte Luna, S. Kleiner, S. Webb, A. Mehta

P13-Towards an Electrochemical Sensor for Archaeological Wood: Simultaneous Electrochemistry and In-situ XAS speciation on Simulated Systems
E. Schofield, S. Tay, M. Koronfel, N. Al-Qahtani, G. Cibin, M. Ryan
P14-Saving the Dead Sea Scrolls: From the Molecular Properties of Collagen to Preservation Strategies of Ancient Parchments
R. Schuetz, J. Weaver, I. Rabin, A. Masic

P15- Probing the carbonatation process of Ca-based consolidants into limestone matrix by SR-based Ca K-edge XANES and micro-XRD investigations.
L. Monico, L. Cartechini, F. Rosi, W. De Nolf, C. Maurich, C. Miliani

P16-Visualizing Van Gogh’s use of the red dye Eosin via MA-XRF mapping of Br: possibilities and limitations

P17-From Lapis Lazuli to Ultramarine Blue: investigating Cennino Cennini’s recipe using Sulfur K-Edge XANES
M. Ganio, E. Pouyet, S. Webb, C. Schmidt Patterson, M. Walton

P18-Reflections of the Past: Uncovering the Chemical Mystery of Daguerreotypes
M.S. Kozachuk; T.K. Sham; R.R. Martin

P19-Characterization of applied brocades from Savoie duchy, France, by means of combined micro-analytical techniques
E. Pouyet, T. Guiblain, S. Cersoy, S. Champdavoine, M. Cotte, F. Lelong, P. Martinetto, P. Walter

P20-Dating metal objects by XRF tests: Pilot project with Metal finds from Nahariyya Excavations
K. Sari

P21-Investigation on Fire Gilding using XRF and NAA
R. Margreiter, K. Eberhardt, B. Niemeyer, M. Radtke, E. Strub

P22-Hidden elements: revealing the history of a whiteground lekythos through xray fluorescence spectroscopy
S. Sheffels

P23-Technology of production of manganese decorations

P24-Discrimination of complex layer structures from artworks coatings by μSR-FTIR and μSR-XRD
V. Beltran, N. Salvadó, S. Butí, T. Pradell, G. Cinque and J. Juanhuix

P25-Herbivorous or Carnivorous? An X-ray fluorescence analysis of a cracked tooth from the theropod dinosaur Troodon.
R. Feng, R. Sammynaiken, D. Brinkman

P26-Preliminary Analysis of Zn and S in Bone and Teeth Surrounding Pathological Lesions.
S.J. Naftel, E. Molto, TK. Sham, Y. Hu, Q. Xia

P27-Measuring crystal characteristics of intact archeological human second metacarpal bones as a function of individuals’ age at death
S.R. Stock, J.S. Park, I.G. Nielsen, S. Mays, H. Birkedal and J.D. Almer
Using Public Transportation

The Art Institute is located just one block east of the Loop and is easily accessible via the city’s Chicago Transit Authority (CTA). The Brown, Green, Orange, Pink, and Purple lines all stop above ground at Adams/Wabash, one block west of the museum. The Red and Blue lines stop underground at Monroe, just a few blocks away. A number of bus lines also stop in front of the museum. Currently, El fare is $2.25 per adult. Visit the Chicago Transit Authority’s website for route, schedule, and fare details.

Metra is Chicago’s commuter rail transit system. The Art Institute is accessible from both the Van Buren and Millennium stations, which are underground just one to two blocks south and north (respectively) along Michigan Avenue. Visit Metra’s website for route, schedule, and fare details.

Divvy is Chicago’s bike-sharing system with thousands of bikes and hundreds of stations across the city, intended to provide Chicagoans and visitors with an additional transportation option for getting around the city. There are several Divvy bike stations within walking distance of the Art Institute. For more information and pricing, please visit divvybikes.com.

Driving to the Art Institute via Expressways

From Indiana
Indiana toll road (90) to Chicago Skyway to Dan Ryan Expressway (90, 94) to Congress East (Loop exit). East on Congress to Congress Plaza (first light east of Michigan Avenue.) North (left turn) on Congress Plaza, which merges with Michigan Avenue. North on Michigan Avenue to Adams.

From South Suburbs
Dan Ryan Expressway (90, 94) to Congress East (Loop exit). East to Congress Plaza (first light east of Michigan Avenue). North (left turn) on Congress Plaza which merges with Michigan Avenue. North on Michigan Avenue to Adams.

From Wisconsin and North Suburbs
Edens Expressway (94) into Kennedy Expressway (90, 94) to Loop, exit Monroe Street east. East to Michigan Avenue.

From O’Hare Airport and Northwest Suburbs
Kennedy Expressway (90) to Loop, exit Monroe Street east. East to Michigan Avenue.

From West Suburbs
Eisenhower Expressway (290) east (290 becomes Congress Parkway in Loop) to Congress Plaza (first light east of Michigan Avenue). North (left turn) on Congress Plaza which merges with Michigan Avenue to Adams.

From Southwest Suburbs
Stevenson Expressway (55) to Lake Shore Drive (41). North to Jackson Blvd. West on Jackson (left turn) to Michigan Ave. North on Michigan to Adams.
Nearby Public Garages
These garages are located underground below the parks adjacent to the museum. Please call (312) 616-0600 for lot and rate information. Drop-offs are permitted at the Millennium Park entrance. A traffic pull out is available from the eastbound lanes of Monroe Street.

- **East Monroe Street** and **Millennium Park garages**
  (entrance at Columbus Drive and Monroe Street)
- Grant Park south garage
  (entrance at Michigan Avenue between Van Buren and Adams streets)
- Grant Park north garage
  (entrance at Michigan Avenue between Madison and Randolph streets)

Warning concerning Columbus Drive Street Parking

Both sides of Columbus Drive immediately east of the museum are “No Parking” zones from 4:00 to 6:00 p.m., and violators will be towed. Call (312) 744-7550 for towing information.

Accessible parking is located in the following garages near the Art Institute:

- Millennium Park garage (enter at Columbus Drive and Monroe Street), with 8’ clearance in limited sections and an elevator at the exit
- Grant Park north garage (enter at Michigan Avenue between Madison and Randolph), with 8’ 3” clearance in limited sections and an elevator at the exit
Art Institute Museum

For entry to the Art Institute of Chicago on all mornings please use the **Columbus Drive Entrance** on the East side of the building (facing the lake). The talk and poster sessions will be held into the *Chicago Stock Exchange Trading Room* of the Museum. However, the reception on Tuesday, September 6th will be held in the *Woman’s Board Grand Staircase* of the Museum - exit the museum on Columbus after the poster session and walk all the way around the museum to enter through the Michigan Ave. entrance.

A map of the museum has also been provided in the conference bags.
For more information about the museum please visit: [http://www.artic.edu/](http://www.artic.edu/)
Bus Pick-Up area

The pick-up area for bus departure from the Art Institute will be in front of the Modern Wing museum entrance (227 E Monroe St, Chicago, IL 60601).

Oriental Institute – Dinner on Sept. 7th

The dinner will be held at the Oriental Institute on Wednesday September 7th. For this occasion a bus will pick up attendees at 18.30 in front of the Art Institute Modern Wing – on Monroe street. The dinner will start at 19.15 in the Mesopotamia Gallery.

For more information about the Oriental Institute please visit: https://oi.uchicago.edu/

APS visit – Sept. 8th

An APS visit is organized from 13.30 to 18.00 on Thursday September 8th. A bus will pick up the attendees at 13.30 in front of the Art Institute Modern Wing – on Monroe street – to the APS facility. There, a 2hours visit is scheduled including :an introduction talk together with a visit of beamlines from sector 1, sector , sector 13, sector 26. The bus will leave Argonne at 17.00.

For more information about APS facility please visit: https://www1.aps.anl.gov/.
Local Organizing Committee

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International Advisory Board

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Dik, J. (Delft)

Janssens, K. (Antwerp)

Radtk, M. (Berlin)

Reiche, I. (Germany)

Susini, J. (Grenoble)

Pérez-Arantegui, J. (Zaragoza)

van Langh, R. (Amsterdam)

Wess, T. (Cardiff)
This conference was made possible through the generous support of:

[Logos for Argonne National Laboratory, XGlab, NU ACCESS, SAS, and Thermo Scientific]
O1-Investigating the 3D arrangement of submicron pores in blanched easel oil paintings by X-ray phase contrast nanotomography

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Blanching of easel oil paintings is a frequently observed alteration that can affect varnish and also paint layers, strongly altering the visual appearance of these paintings [1,2]. This alteration remains an important issue for the conservation, since the treatments currently used are not satisfactory. Investigations performed on micro-samples by field-emission gun scanning electron microscopy revealed a highly porous structure in the altered layers with a pore size ranging from few nanometers to few micrometers [1]. As our observations were limited to the sample surface or edge, we imaged the specimens by X-ray phase contrast nanotomography at the new ID16A-NI beamline of ESRF to investigate the 3D arrangement of the pores in the whole volume (ca. 100x100x100 µm\textsuperscript{3}) at the nanoscale. A set of five paint micro-samples collected from French and Flemish blanched paintings from 16\textsuperscript{th} to 19\textsuperscript{th} centuries has been imaged with a voxel size of 50x50x50 nm\textsuperscript{3}, at 17 keV. Three dimensional images were obtained from retrieved phase maps by tomographic reconstruction. After image segmentation, the size of the pores (typically ca. 200 nm to 4 µm), their morphology, spatial distribution in the stratigraphy and chemical environment can be determined (fig 1). Considering the pore size, the blanching can be explained by Mie light scattering [3]. The use of magnified holotomography [4] enables us to distinguish regions with similar and low electron densities (binder and pores probably filled with air) in presence of high density compounds (pigments). It shows that the pores are located inside the binder, which revealed that the degradation takes place in the organic matter. The current conservation treatments (solvents application and varnishing) are not efficient. The analyses of altered and restored samples from the same area revealed that the pores were not filled nor resorbed. These results constitute a major advance towards the understanding of the alteration. Further investigations are currently undertaken in two directions: 1/ to identify the physico-chemical phenomena involved in the pore formation (by small angle neutron scattering); 2/ to propose durable conservation treatments.

![Fig. 1 Detail of a reconstructed slice highlighting the presence of pores in the organic binder](image)

References

O2-Revealing hidden text in rolled papyri

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Our best sources for information about the culture of our predecessors are their writings. Some of these writings are hidden in rolled, folded or scrambled documents. Due to recent improvements with respect to sensitivity and resolution, a few spectacular disclosures of hidden texts were possible by x-ray tomography on heavily corroded metallic foils with imprinted writings and on parchment written with inks containing heavy elements, typically Fe. Most recently, even letters written with carbon ink could be identified in carbonized papyri by phase contrast tomography.

Besides the mere detection of the script, the reconstruction of the text as a whole poses a challenge to the mathematical treatment of the tomographic data set. In contrast to more homogeneous material, parchment, or even metal foils, the structure of papyrus poses further challenges. First, the stripes of the cut papyrus stems, which are arranged in two layers with the orientation of the stripes being orthogonal to each other, complicate the distinction between writings and substrate for iron gall ink. Second, virtual unfolding is hampered since the two layers often separate from each other.

To optimize the virtual unfolding, we have prepared sample papyri from modern material written with cinnabar (mercury red) and minium (lead red) for the best possible contrast in absorption tomography. The tomographic data of the rolled papyrus were acquired with the GE Phoenix Nanotom S at 50 kV. A preliminary virtual unrolling was done by manually setting points in just three slices of the CT scan. After interpolation over the total length, a 2D surface is defined that was subsequently unrolled into the 2D plane. This yielded the text part of which is shown in the figure. By improving the sensitivity as learned for this cinnabar sample, we hope to apply this procedure to a folded papyrus package from ancient Egypt in which iron gall ink has been identified by XRF.

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Fig. 1 (a) photo of the 9-cm long rolled papyrus, (b) tomographic view with markers for the rendering and reconstruction, (c) reconstructed text
O3-Degradation mechanisms of reinforcement iron rebar in monuments: Time-resolved X-ray microtomography of water percolation in corrosion layers

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Iron rebar have been used for centuries in stone monuments. Their corrosion seriously endangers the structural integrity of the monument in the long term and thus needs to be appropriately assessed and understood. Corrosion layers are constituted of different iron oxides and oxi-hydroxides, along with a significant porosity which plays a significant role in the corrosion process by allowing transport of electrolytes from outside to the vicinity of the metal core [1]. Previous investigations by X-ray microtomography have shown that this porosity forms a complex and anisotropic network with pores ranging from the micro- to the nano-scale [2]. Here we show that time-resolved X-ray microtomography allows to visualize the flow of water within the corrosion layers, a first step towards the quantification of important transport properties such as permeability and diffusion coefficients. Samples of corroded iron rebar from the cathedral of Metz were cut and embedded into resin to present a cavity on the top of the corroded surface where water mixed with a contrast product was added. X-ray microtomography images of 870nm voxel size were acquired by propagation phase contrast on the PSICHE beamline, with a pink beam of 63keV. After imaging of the dry sample, the contrast solution was added and tomography images were acquired every few minutes, allowing after suitable image processing the 3D time-resolved visualization of water percolation in the corroded layers (Figure 1). We further characterized the process by means of several metrics (chord distribution functions, Betti numbers and diffusion coefficient computations) and could evidence a two-step percolation dynamics and the influence of sub-resolution nanoporosity.

Fig. 1 Water percolation of the porosity over time (blue: immediate, red: 30-35 minutes) in the corrosion layer of an iron rebar from the cathedral of Metz. Red zones show pores not directly connected to the main porosity network, where water percolates only in a second stage.

References
O4-Following Pt in gold Byzantine tesserae: towards provenance and chronology with SR-XRF

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Gold mosaics, made from gold and glass, are one of the best expressions of Late Antique Byzantine and Early Islamic art. The gold alloys, whose composition seems to indicate that gold coins were re-used to fabricate the tesserae, can be used to provide information on the mosaics chronology. Monetary Byzantine gold is in fact characterized by the presence of Pt, which contents in the gold alloy change over time, but Pt must be measured in 0.2-0.4 μm thickness gold leaves that were beaten to be sandwiched between two glass layers.

To analyze this samples the D²XRF [1] set-up at the BAMline at the BESSY synchrotron in Berlin was used. The combination of a crystal for wavelength dispersion and an energy resolving single photon counting pnCCD allows the realization of this very simple wavelength dispersive detection system. With this system an MDL of 1 μg/g for the determination of Pt in Au under optimal conditions can be reached.

Gold leaf tesserae from nine archaeological sites, covering the period that goes from the 5th c. to the 8th c., were analyzed. The presence of Pt in the majority of the samples confirmed the re-use of coins. The Pt contents separate the samples in three groups, one of which having the same chemical characteristics as the Byzantine gold could be compared to dated coins for chronology. The higher Pt contents for one of other groups suggest access to Oriental supplies whilst its absence for the remainder group suggests recycling.

![Fig. 1 Spectra for the Aurubis Gold NA-Au-30 standard with 58 μg/g Pt.](image)

References
K1-The quest of lost ancient literature.
Synchrotron based techniques reveal the secrets of Herculaneum papyri: letters and ink composition.

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We present the first experimental demonstration of a non-destructive technique that reveals the text of a carbonized and thus extremely fragile Herculaneum papyrus. Buried by the famous eruption of Vesuvius in 79 AD, the Herculaneum papyri represent a unique treasure for humanity. Overcoming the difficulties of the other techniques we prove that x-ray phase contrast tomography technique can detect the text within scrolls, thanks to the coherence and high-energy properties of a synchrotron source [1]. This new imaging technique represents a turning point for the study of literature and ancient philosophy, disclosing texts that were believed to be completely lost. In order to improve the imaging technique we performed also an extensive experimental analysis of the ink composition, using a combination of synchrotron techniques at the ESRF, discovering the presence of metal in the ink of two Herculaneum papyrus fragments and proving that metals were used in ink several centuries earlier than previously believed [2],[3].

Fig. 1 X-Ray fluorescence map of the lead, from [3]

References
O5-Characterisation of excavated Napoleonic artefacts from the Berezina battlefield in Belarus using neutron and x-ray techniques

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An important collection of artifacts have been unearthed during preventative archaeological surveys from 2012 to 2014 around the village of Stoudienka in Belarus – the site of the Napoleonic army’s passage during the retreat from their Russian campaign in November 1812. Recovered objects (Fig.1), such as fragments of imperial eagles, brass plates and buttons with faint outlines of inscriptions and several lead bullets have resulted in historian’s needs for further characterisation to obtain otherwise uncertain information, for example their mode of destruction, their composition and dating.

The Belarus Academy of Science and the Centre d’Etudes Napoléoniennes collaborated with the Institute Max Von Laue Paul Langevin in a series of experiments using non-destructive neutron diffraction techniques available at the ILL on selected artifacts: For instance, mechanical deformation measurements on the strain imager SALSA provided insights into object biographies and neutron activation analysis was used to obtain clearer knowledge of fabrication processes.

Collaborations with other centers (HZB Germany and LLB France) in neutron radiography and tomography as well as complementary XCT analysis at the laboratory 3SR in Grenoble have revealed hidden details in certain objects and the identity of hitherto unrecognizable artifacts. Another advanced non-destructive technique - prompt neutron activation analysis – was carried out at UJF (Czech Republic) on a series of musket shots from Berezina and compared with similar shot recovered from the Waterloo battle site.

Fig. 1

N and X tomographies of eagle talons revealing corroded screw
Identification of Regimental arms on coins
Examining the internal structure of lead shot with NI
XCT of pen-knife
O6- Analysing clay of early medieval pottery wares with non-invasive Small Angle Neutron Scattering and Time-of-flight Neutron Diffraction

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Using non-invasive Small Angle Neutron Scattering (SANS) and Time-of-flight Neutron Diffraction (TOF-ND) for analysing the nanostructure of archaeological ceramic artefacts has no antecedent in Hungary so far, although it is not completely unknown in Europe [1, 2, 3, 4]. The two main objective of our research were to get information about the firing technique and provenance of the 4-5\textsuperscript{th} century A.D. archaeological settlement in Keszthely (Hungary) and deepen our knowledge about the limits and usefulness of these neutron analytical methods regarding ceramic samples. SANS measurements on ceramic samples have been performed at the Yellow Submarine and FSANS instruments at Budapest Neutron Centre. A series of control samples (tempered and not tempered versions of clay samples fired at 600, 700, 800 and 900 °C, and also tempered and not tempered versions of an unfired, dried sample) have also been measured at the same instruments. The first objective was to test the feasibility of the neutron measurements, as non-destructive methods for studying the structural features of archaeological objects made of ceramic. The intensity versus scattering vector (Q) curves obtained from the detector neutron counts, showed two different regions: at large Q values YS-SANS) the surface characteristics of the scattering – namely crystallites, pores, voids, amorphous inclusions – were obtained, while at small Q values (F-SANS) their average sizes could be obtained. High resolution time-of-flight neutron diffraction analysis applied in our study proved to be an appropriate and successful method to characterise the microstructure and determining the mineralogical composition of ancient pottery pieces without any sampling or special treatment, and based on that we can deduce either the firing conditions and the origin of the used raw material (provenance studies). A correlation between the firing temperature and the SANS curves was set up, showing that this method – as complementary measurements among e.g. X-ray and Neutron Diffraction, Scanning Electron Microprobe, X-ray Fluorescence etc. – is suitable for analysing the high temperature nanostructural behaviour of ceramics.

![Fig. 1 Intensity versus scattering vector SANS curves of early medieval ceramics from Keszthely (Hungary). Dots represents measured values and lines represents fitting models.](image_url)

References
K2-Bulk non-destructive elemental analysis using muons

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Elemental analysis is a process in which a sample is analysed for its composition. Often this is accomplished by destructive and damaging techniques. Clearly, such techniques are not desirable for valuable items (either scientific or monetary). A non-destructive, non damaging elemental analysis would be an extremely useful tool. Using negative muons, which emit a characteristic X-ray, could be such a tool.

Negative muons are like heavy electrons and replace an electron in the outer shell of an atom then travel to near the nucleus through the modified energy states of the atom. Each transition on this path produces an x-ray which is characteristic of the atom, which absorbed the muon, hence allowing this spectrum to reflect the atomic species (see Figure 1). The sensitivity of this technique is such that even light atoms can be detected and further the technique is open to be used as a depth analysis tool, since by varying the energy of the incident muon beam it is possible to change the depth of implantation for the negative muon. A significant advantage of muonic X-rays over those of electronic X-rays is the higher energy (0.1 - 8 MeV). These high energy muonic X-rays are emitted from the bulk of the samples without photon self-absorption and can be simply detected by a semiconductor detector. Over the years there has been sporadic use of negative muons as an elemental analysis tool, and a wide-ranging number of materials have been investigated, including Japanese coins[1], spinal columns[2], pig fat[3], tissue analysis[4] and ancient Chinese mirrors[5].

ISIS pulsed neutron and muon facility, UK is a primary high-flux source of pulsed muon beams. Recently, we have been developing elemental analysis using negative muons [6] and in this paper we will discuss the latest developments, recent results on archeological materials and the possible uses for the future.

References
O7- Neutron diffraction for cultural heritage studies: the Italian Neutron Experimental Station INES

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The Italian Neutron Experimental Station INES, located at the pulsed neutron source ISIS (U.K.), is a general-purpose neutron diffractometer that was built with a special care aiming to focus its use on cultural heritage related studies. Thanks to the high penetration power of thermal neutrons, archaeometric measurements performed through neutron diffraction allow us to determine bulk properties of the sample in a non-destructive way, in particular regarding phase analysis and microstructure. This opens up the possibility of scientific investigation on objects otherwise unsuitable, due to their cultural and/or historical importance. Here, we describe the INES instrument and present the results of some recent measurements, in particular on bronze objects from Sardinia, Italy.

Sardinian bronze metallurgy represents an important example concerning the study of the development of Bronze technology in an insular area located in the centre of Mediterranean sea, relatively isolated but with important links with the surrounding lands.

Three bronze swords of the "Monte Sa Idda" type, named after the important eponymous hoard found in the early 1900s in Sardinia, were studied through neutron diffraction using the INES instrument. The obtained data analyzed through Rietveld refinement allowed us to quantitatively determine the bronze composition, the casting procedure and the presence of thermal and mechanical interventions. Furthermore, neutron diffraction permitted to obtain the quantitative distribution of all phases (revealing dendritic segregation of the bronze in several parts of the samples) including the ones related to mineralization.

Two of the analyzed swords are from Monte Sa Idda-Decimoputzu while the third was found in the cave shrine of Pirosu-Santadi. A production date between 930 and 750 A.C. was proposed, into the III phase of the Atlantic Final Bronze Age.

The obtained results show a very specific procedure for sword forging: the bronze composition, the presence of dendritic segregation and the microstructure are very peculiar. A comparison with micro-structural characteristics of contemporary bronze artifacts produced in the other areas of the Mediterranean area adds important details about the development and exchange of knowledge in this geographic area.
O8- Nondestructive study on metallurgical characteristics of traditional Japanese sword throughout the manufacturing process by pulsed neutron imaging

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It’s getting clear that an image indicating the number density, the crystal structure, the preferred orientation, etc. can be obtained nondestructively by using the time-of-flight (TOF) energy analysis at a pulsed neutron source. Concerning the nondestructive methods, physical quantity like this can be obtained only by neutron. We have started our study to apply this method to analyze Japanese iron artifacts. It is said that traditional Japanese iron has good workability and does not rust easily. The reasons of these characteristics are derived from the raw materials, iron making technique, and iron manufacturing technique in ancient Japan. Also, the temperature and the frequency of forging decide the mechanical characteristics and the aesthetic value of Japanese iron artifacts. However, the details of the raw materials and traditional Japanese iron making and manufacturing techniques are not clear as they were mainly carried out in secret. Ten tamahagane steel samples manufactured by a contemporary sword smith which show the each manufacturing process of traditional Japanese sword have been investigated by pulsed neutron imaging. The purpose of this work is to evaluate their crystallographic texture and microstructure and to clarify the details of the traditional Japanese sword making techniques nondestructively. The experiment was carried out at Japan Proton Accelerator Research Complex (J-PARC). A 2D-PSD was used to get the spatial dependent TOF data. Each steel sample show a distinctive shape of Bragg edge (Fig.1) which tells information of the crystal structure, density, preferred orientation, and the lattice spacing. From the position of the edges, lattice constant and relative edge width were calculated. Those differences in microstructure remarkably reflect their material characteristics and the sword manufacturing techniques. Specifically, the differences of the carbon content of two kinds of raw material, tamahagane, grain refining and orientation variation by forge-welding, martensite formation by quenching, lattice spacing change by tempering were observed. It is concluded that by using pulsed neutron imaging, we can clarify the metallurgical characteristics and reveal the traditional Japanese sword making techniques nondestructively. We plan to use the results as a basic data and to extend our study towards a systematic measurement on Japanese swords.

Fig. 1 Neutron spectrum (the Bragg edge) of the sword sample after quenching.
K3-Darkening process of the chrome yellow pigments in paintings by Vincent van Gogh studied by means of synchrotron radiation-based X-ray spectromicroscopy, EPR and vibrational spectroscopy

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Chrome yellow (denoted below as CY) is a class of synthetic pigments often encountered in paintings of the late 19th-early 20th century, such as those by Vincent van Gogh. These materials are characterized by a different stoichiometry (PbCr1−xSxO4, 0≤x≤0.8) and crystalline structure (monoclinic/orthorhombic), with shades that range from the yellow-orange to the paler-yellow color with increasing amount of sulfate.[1-4] The CY darkening is a significant art conservation problem, threatening iconic masterpieces such as the famous Sunflowers by Van Gogh [1-2], that poses a challenge for designing and optimizing the long-time conservation strategies of such irreplaceable artworks.

SR-based microscopic X-ray fluorescence (µ-XRF) and Cr K-edge X-ray near-edge absorption structure (µ-XANES) spectroscopies in combination with electron paramagnetic resonance (EPR) investigations have permitted to establish that the CY degradation occurs via a CrVI→CrIII reduction, with CrV-intermediates that are formed through the interaction with the oil binder.[5-11] This reaction was found to be the main cause of darkening of a series of artificially aged CY model paints [5-8]; it was also encountered in a selection of CY-paint micro-samples taken from several Van Gogh paintings.[2,9-11] The stability of CY is affected by its stoichiometry and crystalline structure; moreover, the type of environmental conditions to which the pigment is exposed influence the formation of either CrIII- or CrV-species.[6-8] Various CY types were identified in over 20 Van Gogh paintings by SR-based microscopic X-ray diffraction (µ-XRD), Raman and infrared techniques.[2,3-4] Since only some of the CY varieties (the S-richest ones) have a composition/crystal structure that makes them prone to degradation, the results provide a first answer to the possible reasons of visible CY darkening only in selected areas of original paintings. Nevertheless, since CYs were often used in mixtures with other pigments (e.g., red lead, vermilion, zinc white and emerald green),[1-2] further research is ongoing to explore if/how these added pigments and the corresponding alteration compounds may influence the CYs stability and contribute to visible color change.

At the conference, we will give an overview of the findings arising from the study of artificially aged CY model paints and a series of Van Gogh paintings, such as Sunflowers (Van Gogh Museum, Amsterdam), by combining molecular spectroscopies and Cr-speciation methods. These results will be used for describing a digital reconstruction method of the original color of selected CY-painted areas.

References
O9-The “corrosion” of historic stained glasses: an investigation using synchrotron radiation based x-ray fluorescence and X-ray absorption (XANES) spectroscopy

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The corrosion of glass is a very complex process as it depends on external conditions as well as on the composition of the glass. While at least the basic mechanisms of the degradation process seem to be understood, there are still several open questions that should be answered for finding the “best” method for restoration (e.g. cleaning) and conservation of historic stained glass. There is also hardly any information about the influence of the corrosion on the glass-forming SiO\(_2\) – network. Both these issues are addressed in this contribution using synchrotron-radiation excited X-ray fluorescence (SR-XRF) and X-ray absorption near edge structure (XANES) spectroscopy. SR-XRF allows the determination of the elemental composition of the samples and XANES spectroscopy provides detailed information about the chemical speciation of the elements of interest and thus direct information about corrosion processes.

In this contribution, we present examples for the applications of SR-XRF and XANES experiments for the analysis of stained glasses and the corresponding corrosion products from different production times and origins: some glasses from the Cathedral in Paderborn (~ 12\(^{th}\) century), glasses from the Cathedral in Lester, (~ 13\(^{th}\) century) and glass from one window from the Cathedral in Seville (16\(^{th}\) century). In all cases spectra from the non-cleaned samples are compared with those from the cleaned samples for getting information about the efficiency of the various cleaning techniques. Parts of the glass from the Seville Cathedral, for example, were cleaned using 3 different techniques: 1. mechanically using a spatula, 2. “chemically” using EDTA, and 3. mechanically using diamond powder. In some cases the corrosion products that incur were collected and included into the investigation.

“In principle” XANES allows measuring Si-K-spectra that are sensitive to the coordination of the Si-atoms and thus to the short/medium range structure of the Si-O network making it possible to analyse (for the first time) also damages of the Si-O – network caused by the corrosion process. For fathoming these new opportunities Si-K-XANES spectra of several of the cleaned (pristine glass) and non-cleaned glass samples (marred network) and suitable reference compounds were measured. Figure 1 shows an example of these measurements.

![Fig. 1 Si-K-XANES spectra of the diamond cleaned Seville glass in comparison with the spectrum of crystalline SiO\(_2\).](image-url)
O10-Investigating the degradation of gelatin sized paper by iron gall ink with STXM analysis

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Iron gall inks have largely been used for writing since the middle age till the twentieth century. They contain a mixture of FeII sulfate and gall nuts extracts and can significantly damage the paper through acid hydrolysis and iron catalyzed oxidation [1]. These phenomena are not only governed by the chemistry of the "ink + cellulose" system, but also by the penetration of the ink within the paper sheet, and more precisely within the paper fibers (5 to 20 microns diameter). These fibers are initially highly permeable to water. The paper making process includes sizing, an operation that corresponds to the impregnation of paper with an adhesive (size) such as gelatin that makes it less permeable to water and thus suitable for writing.

In this contribution, physical and chemical interactions between gelatin, iron gall inks, and cellulose was investigated on the scale of a paper fiber by synchrotron-based STXM using FIB sections taken from paper fibers as already described in Rouchon et al [2]. In situ mapping of iron redox state (Fe L2,3-edge NEXAFS) showed some beam induced reduction phenomena that fortunately remained limited and did not jeopardize qualitative determination of the regions rich in FeII and FeIII. In addition, C K-edge NEXAFS measurements were performed to map the distribution of cellulose, gallic acid and iron gall ink precipitate. Finally, N K-edge NEXAFS was used to map gelatin distribution.

By this approach, it was shown that, when the fiber is not sized, ink components migrate in the inner part of the fiber. Low amounts of FeII are evenly distributed in the fiber while some Fe-rich spots are noticed in the lumen (center of the fiber) probably attesting of local precipitation phenomena occurring during drying. When the paper is sized, gelatin does not penetrate the fibers but forms instead an external layer that prevents migration of ink components in the inner part. It additionally favors conversion of FeII to FeIII, which gives some clue to understand the “positive” impact of gelatin in paper conservation.

References
O11-Elemental and Chemical Heterogeneity of Lead Soaps in Paint Degradation

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The formation of Pb, Zn, and Cu carboxylates (soaps) has caused visible deterioration of hundreds of oil paintings dating from the 15th to the 20th centuries. Through transport phenomena not yet understood, the free fatty acids in the oil binders migrate through the paint and react with pigments containing heavy metals, such as 2PbCO₃·Pb(OH)₂ (lead white) and Pb₂SnO₄ (lead-tin yellow type I), to form soaps that aggregate in protrusions, form surface crusts and/or cause increased transparency of the paint. To investigate the complex correlation among the elemental segregation, types of chemical compounds formed as a result of the natural aging process and their chemical states, degradation, and environmental conditions in paint films, we utilized the Sub-micron Resolution Spectroscopy (SRX) beamline at the National Synchrotron Light Source II. Sample cross-sections of paint removed from oil paintings were examined by X-ray fluorescence (XRF) microscopy and micro X-ray absorption near edge structure (μ-XANES) spectroscopy. XRF maps showed Pb and Sn segregation in the soap affected areas (Fig.1A-B.), whereas μ-XANES spectra gave further information on the chemical heterogeneity. The μ-XANES around the Pb-L3 absorption edge were also compared with standard powder compounds and synthetic paints aged under different environmental conditions, by which the Pb pigments and Pb soap compounds can be distinguished (Fig.1C). The ultimate aim of the present work is, to develop a detailed understanding of the mechanism of soap formation, and make recommendations for the conservation and preservation of the works affected.

Fig. 1 (A) Photomicrograph of a paint cross-section removed from the original frame in *The Crucifixion* (MMA# 37.92ab), ca. 1435-1440, by Jan Van Eyck. (B) XRF maps of the area shown by the yellow square in (A), showing areas where Sn is depleted due to soap formation. (C) Comparison of Pb μ-XANES spectra for Pb-containing pigments and Pb soaps.
O12-A Study of the effect of moisture and light on the stability of CdS-based yellow pigments

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The fading of CdS-based yellow pigments (Cd1-xZnxS) has been documented in artworks by Ensor [1], Van Gogh [2] and Matisse [3-5]. In all these cases, CdSO4 has been identified and interpreted as the result of a photo-oxidation of cadmium sulphides. Additional compounds have been detected, namely: (NH4)2Cd(SO4)2 in a Ensor painting [1], CdC2O4 (oxalate) and PbSO4 in the Van Gogh case, [2] and additionally CdCO3 and CdCl2 in masterpieces by Matisse [3-5].

However, apart from these observations on original paint micro-samples, knowledge about the underlying degradation mechanisms and the factors affecting the stability of this class of pigments remains fairly scarce.

At the conference, we will describe the results obtained from the study of a series of oil paint models made from historical CdS-based pigments of different stoichiometry, composition (with additives and/or synthesis residuals) and crystalline structure (hexagonal, cubic or amorphous) before and after accelerated aging either with moisture or visible light.

The combined use of FTIR and synchrotron radiation-based X-ray micro-spectromicroscopic methods (i.e. XRD, XRF, XANES) allowed for identification and mapping of secondary products in aged paints. Notably, depending on both the aging conditions and the nature of additives/synthesis residuals (e.g. Cl-species) present in the historical pigment formulations, the formation of Cd-oxalates, Cd-sulfates, or Cd-carboxylates, has been revealed.

References
O13-Degradation of minium (Pb$_3$O$_4$) on the long and short term in material originating from a Red Shroud Mummy

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Plumbonacrite, 3PbCO$_3$.Pb(OH)$_2$.PbO is a ‘missing link’ compound the pathway from the artists’ pigment minium (aka Red Lead) towards (hydro)cerrusite. The alteration mechanism, leading to a whitening of read lead involves (a) photo-reduction of Pb$^{4+}$ to Pb$^{2+}$, followed by (b) CO$_2$ capture by the resulting Pb$^{2+}$. Another form of minium degradation is blackening, due to the formation of $\beta$-PbO$_2$ (plattnerite). In addition, another Pb-compound giving rise to blackening is galena, PbS.

A combination of Raman spectrometry, SEM-EDX, synchrotron X-ray microdiffraction and X-ray tomography was used to examine sample material originating from a 2000 year old Roman-Egyptian “Red Shroud” mummy (P.J.Getty Museum, Los Angeles) that showed a superficial yellow-white discoloration. Throughout the red lead paint, spherical nodules (ca 50-100 µm in diameter) were observed.

XRPD line scans and distributions (recorded at the P06 beamline of the PETRA-III synchrotron facility) have revealed a strikingly large variety of Pb,Cl compounds inside and around these nodules: PbCl$_2$, Pb(OH)Cl, PbCl$_2$.PbCO$_3$, NH$_4$Pb$_2$Cl$_5$ next to $\alpha$- and $\beta$-PbO$_2$, minium, PbO, hydrocerrusite and cerussite as well as PbSO$_4$ and other sulfates are present. The nodules may be remnants of the minium production process (involving the roasting of litharge); however, some of these compounds are suspected to have formed in secondary reactions after the minium was applied on the mummy surface. Some of these were only very recently formed.

In this presentation, on the basis of the chemical alteration pathways described in the literature, a reconstruction of the (sequence of) reactions that is suspected to have taken place on the long and short term in this material, will be presented. If available already, also relevant XANES data will be shown.
O14- The combined use of in-situ and SR-based techniques for revealing artistic technology and relighting history - NU-ACCESS case studies

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The Northwestern University/Art Institute of Chicago Center for Scientific Studies in the Arts (NU-ACCESS) pursues objects-based and objects-inspired scientific research to advance the role of science within art history, curatorial scholarship, archaeology, and conservation. The art objects and historical materials studied through NU-ACCESS often come from a variety of institutions that do not have ready access to scientific instruments and/or have strict limitations on taking samples. Therefore the Center utilizes a variety non-invasive instruments that may be transported to remote locations (e.g., macro X-ray fluorescence, hyperspectral visible imaging, and Fourier transform infrared spectroscopy in reflectance mode).

However, many of the scientific questions being addressed require access to higher spatial resolutions (a few µm down to some tens of nm) and lower detection limits (down to a atomic percents) than typically available from these benchtop instruments. Bright and collimated synchrotron radiation (SR) sources extended the analytical possibilities.

Here, two research studies are presented that highlight the advantages of SR-based techniques. First, micro-X-ray Absorption Near Edge Spectroscopy (µXANES) and micro-X-ray Fluorescence (µXRF) at the Stanford Synchrotron Radiation Lightsource (SSRL) have been used to investigate the alchemical approach of medieval craftmans to extract ultramarine pigment from a mixture of resins and lapis lazuli rock. Second, analysis by fast SR µXRF performed at the Cornell High Energy Synchrotron Source (CHESS) revealed a hidden manuscript text from the cover of a 16th century book (Fig. 1). We compare and contrast these data collected at synchrotron to what is possible with conventional instrumentation.

![Visible picture of the 2D µXRF setup (using the MAIA detector-CHESS) used to perform the analysis of the recycled manuscript used to cover the early printed Northwestern Hesiod book](image1)

![Visible image of the book cover](image2)

![Fe K-line XRF map revealing hidden writing](image3)
O15-The Early Electrum Enigma: Shedding Light on the Invention of Coinage


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It is rare that an invention succeeds so perfectly that it permanently changes the way society operates, becoming so essential that one cannot conceive of life without it. Coinage has profoundly affected the lives and economies of individuals and states in immeasurable ways, and yet has remained remarkably unchanged for millennia. The coins produced in Sardis (modern Western Turkey) during the height of the Lydian empire (second half of the 7th century BC) are considered the earliest examples of true coinage with controlled metal content and valuation. These coins were made from electrum, an alloy of gold and silver. It is widely reported that the source(s) of the metals that were used to create these first coins was alluvial electrum from the Hermos and Pactolus Rivers (called the Gediz River in modern Turkey) eroded from Mount Tmolus close to the Sardis. The Lydian coins are of consistent composition (~54 % gold, ~44 % silver, and ~2 % copper) as determined by XRF analysis. From a geological perspective, such high quantities of silver in placer electrum are highly unusual, and examples of electrum nuggets of a size that could be used for coinage are extremely rare.

We have used the VLS-PGM and SXRMBA XPS end stations at the Canadian Light Source (CLS) to analyze the surface gold, silver, copper, and trace element content of Lydian coins. We have combined this surface sensitive analysis technique with the XRF mapping capabilities from the VESPERS beamline at the CLS and 20-ID beamline at the Advanced Photon Source (APS) to develop a picture of the processing methods used to mint these first coins. In addition we have used the Nikon XT225 microCT scanner at Sustainable Archaeology to visualize the coins’ internal structure. Finally we have performed rapid uXRF mapping using the Maia detector on the F3 beamline at the Cornell High Energy Synchrotron Source (CHESS) to provide whole coin images of trace element distributions. We are using these results in concert to address questions regarding the manufacture of these coins. Preliminary results indicate a much more sophisticated level of minting technology than currently accepted in the literature.
O16- Pigments from Roman mural paintings from Germania Superior analyzed with SR-XRF

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The decoration of houses and public buildings with mural paintings was commonplace in the whole Roman Empire in the first centuries. Even though these mural paintings generally have been going through the course of time as fragments in a pile of rubble they still can give clues about the kind and status of the buildings and owners reflected in the quality of the painting, the choice of pigments and the technical skill of the painter. Most of the Roman murals were painted using Fresco technique, in which the pigment is applied in the plaster still damp. The pigments are fixed by chemical reaction and a thin layer of CaCO\textsubscript{3} forms under them [1].

Fragments of mural paintings from south (Augusta Raurica) to north (Koblenz Stadtwald Remstecken) of the Roman province of Germania Superior from different kinds of settlements (\textit{vicus}, villas and colonies) were analyzed by means of synchrotron based scanning macro X-ray fluorescence (SR-MA-XRF). The research was focused on green, red and yellow pigments whose main and trace elements could be identified with this nondestructive technique. Those SR-MA-XRF measurements have been performed at FLUO beamline, ANKA Synchrotron Radiation Facility, in Karlsruhe, Germany.

Areas selected due to variations in color, shade and brushstroke were scanned in two dimensions and distribution maps of all accessible elements were obtained. These maps in combination with optical microscopy enabled us to segment the data, separate the contribution from pigments, impurities and plaster and quantify the respective concentrations of the elements.

Fe-based pigments were the most common pigment used in the analyzed fragments from Germania Superior. The main red pigment identified from buildings from Germania Superior was red ochre (Fe\textsubscript{2}O\textsubscript{3}). Red ochre was identified as single pigment used for the red color, and also mixed which chalk (CaCO\textsubscript{3}) or red lead (Pb\textsubscript{3}O\textsubscript{4}). In contrast, in the villa of Mülheim-Kärlich, located in north of the province, red lead was used as red pigment in a painting of a cold bath [2].

For green colorations green earth was used on the majority of sites. At some places we could identify a mixture of green earth and Cu-based pigments.

References
O17- Evidence for a buried underslip on a Painted Athenian Ceramic from 5th century BCE

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How new technologies emerge, and mature are of immense interests to a wide range of communities: from historians and sociologists to scientists and technologists.

In the late Bronze Age, in eastern Mediterranean, a technology for red-and-black decoration of pottery based on precise control of oxidation state and mineralogy of Fe-rich illitic clay preparations, through skilled control of nanoscale porosity began to emerge. This technology is still considered one of the milestones of technological achievement in human history and evolved to produce iconic black and red figure vessels, during the rise of the city-state of Athens. In early fifth century there was also an explosion in the volume of production and these ceramics were exported in large numbers to colonies and trading posts spread through-out the Mediterranean region.

In here, we examine a rectangular FIB pullout of a painted vessel produced during this period, and recently excavated from the long abandoned Greek trading post in port city of Lattara, in southern France. We combine X-ray micro and nano spectromicroscopy with nano tomography to obtain a detailed elemental, mineralogical, and porosity distribution from the surface into the body. Our results show a clear evidence of a partially oxidized underslip buried beneath the highly reduced upper black gloss layer. The existence of the underslip suggests two slip applications with a firing in-between, and raises the question what benefit did the underslip impart? Did the fired underslip provide a better surface for painting the upper layer decorations, did it allow a rapid second firing resulting in more reduced and thus blacker and glossier upper slip layer, or did it by using poorer quality material buried and hidden under a thinner higher quality material provided an economic benefit?
K4-Smart*Light: A Flemish-Dutch Table-top Synchrotron Light Source for Conservation Science

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Immediately after its discovery in 1895, X-ray radiation started to make an enormous contribution to the study of artwork. Notwithstanding major developments over the past century, there are three important intrinsic limitations to X-ray tubes - the conventional X-ray sources used in the lab: their relative low intensity, the poor coherence of radiation and the selective availability of X-ray energies. Since the late 1970s synchrotron sources have become available, which offer high-brilliance, coherent and energy-tunable X-rays, but these are only available at a limited number of specialized facilities worldwide, providing scarce beam time – at a high cost – outside the museum lab.

This contribution will discuss the future development and application of a revolutionary, compact, affordable and miniaturized alternative to a synchrotron facility – a tabletop Inverse Compton Scattering (ICS) source. The physical basis is the ICS process in which photons from a laser beam are bounced off a relativistic electron beam, turning them into X-ray photons through the relativistic Doppler effect. Already described theoretically decades ago, the enabling technology necessary to materialize such a source, has only very recently matured into robust components. Ultra-low-emittance electron guns, compact X-band accelerator technology and highpower pulsed lasers have become available only recently. This now brings the ICS source for in-situ applications of high-energy X-rays within our reach. In combination with the newest X-ray detectors (Medipix) the tabletop ICS source will constitute an extremely sensitive, on-site, non-destructive tool for imaging and analysis. It will combine (sub)micrometer spatial resolution with high analytical precision in structural and spectroscopic applications. We plan to use the ICS source where it will be most effective: in the museum conservation studio for the study of important artwork.

Fig. 1(left) Overview of the central components of the envisaged Smart*Light setup. On the left the low-emittance RF electron gun, in the middle two Xband LINAC sections (orange) and on the right the vacuum chamber where laser beam (blue) and electron beam (green) collide, generating a hard X-ray beam (purple). (right) X-ray brilliance as a function of X-ray energy for synchrotron bending magnet radiation (SR BM) such as available at the DUBBLE beamline at ESRF, the proposed Inverse Compton Scattering (ICS) Smart*Light source, the liquid-gallium X-ray tube developed by Excillum and a rotating anode tungsten X-ray tube.
O18-Deciphering information recorded in Ancient materials’ heterogeneity at the sub-microscale with synchrotron deep UV imaging

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Since pioneering works in the early 20th century, examination of cultural heritage artifacts and paleontological specimens under UV illumination has become an important tool to enhance spatial contrast between materials in order to evaluate their conservation state or to reveal otherwise invisible morphology, respectively [1,2]. This early work had to overcome significant instrumental constraints due to limitations in the sources, optics and the overall experimental setups.

Photoluminescence imaging developments in the deep ultraviolet by IPANEMA with the DISCO beamline of SOLEIL synchrotron offer a novel probe to visualize and study the heterogeneity of ancient materials at a micrometric scale on a wide variety of ancient materials, from organic varnishes applied on historical musical instrument [3,4] to semiconducting pigments [4,5], and corrosion phases.

In the course of a several-year program, instrumentation has been developed and adapted to better exploit the tunability and the stability of the synchrotron source. The full-field imaging setup at the DISCO beamline as built around an inverted microscope [6] in which optics have been optimized or tunability between 200 and 600nm. The full-field approach using detection in multiple spectral bands was thoroughly optimized with the aim of detecting low fluctuation of the photoluminescence signal at high spatial ‘dynamics’ in heterogeneous systems.

This paradigm shift in DUV micro-imaging allows probing intrinsic photoluminescence contrasts within historic materials at submicrometric scale over sample-or artifact-wide areas. This will be demonstrated on several important examples from cultural heritage and archaeology, in particular metallurgical artifacts, artists’ paint and coating materials.

References

O19-Using sulfur K-edge X-ray Absorption to Assess the Application of Heat in Historical Ultramarine Pigment Production

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The historical production of ultramarine pigment from lapis lazuli rock involves many steps. The procedure has been described in manuscripts dating back to the 14th century and can include a heat treatment of lapis lazuli, the incorporation of lapis lazuli powder in a beeswax resin mixture, storage in water and kneading in lye or water. During this process the mineral lazurite is purified, resulting in an intense blue pigment. Our research focuses on the questions whether the production steps affect the chemical composition of lazurite and whether there is a correlation with the degradation of ultramarine paint layers, known as ultramarine sickness.

Our investigation revealed that the elemental composition of lazurite and its silica-alumina β-cages stay intact upon heating to 750°C, while properties affecting e.g. separation yield and color vary with temperature. The variation in the blue color of lazurite is associated with changes in sulfur speciation inside the β-cages, which we studied by using sulfur K-edge X-ray absorption.

A series of lazurite particles, prepared by using four heat treatments on lapis lazuli rocks (i.e. no heat, 415, 600, and 750 °C), were studied with S-XANES. A heat treatment of lapis lazuli above 600°C seems to modify the spectral shape of the broad envelope between 2470 - 2475 eV, best described by increased peak intensity at 2470.7 eV, see included figure. Subsequently we investigated lazurite particles from three historical paintings painted during the middle of the 17th century (Still Life with a Golden Goblet by Pieter de Ring, Orpheus and the Animals by Paulus Potter and Woman Scouring Metal Ware by Jan Steen). We found an increased peak intensity at 2470.7 eV in the spectra of particles from Paulus Potter’s painting, see included figure, which may indicate that Potter used ultramarine pigment prepared from heat treated lapis lazuli. For comparison, spectra of lazurite particles from the two other paintings do not manifest this peak, indicating no heat treatment has been applied during the preparation of these pigments. Assuming that in all these cases pigments made from Afghanistan lapis lazuli were used, this would suggest that at the time these paintings were painted, different techniques were used to prepare ultramarine pigment.

![Fig. 1 Sulfur K-edge X-ray spectra (microbeam used) of ultramarine pigment produced from heated (red trace) and unheated lapis lazuli (dark blue trace) compared with spectra of lazurite particles taken from three historical paintings (orange and light blue traces).](image-url)
RD1- Spatial-Spectral Representation for X-Ray Fluorescence Image Super-Resolution

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Over the last few years X-Ray fluorescence (XRF) laboratory-based systems have evolved to lightweight and portable instruments thanks to technological advancements in both X-Ray generation and detection. Spatially resolved elemental information can be provided by scanning the surface of the sample with a focused or collimated X-ray beam of (sub) millimeter dimensions and analyzing the emitted fluorescence radiation, in a nondestructive in-situ fashion. The new generations of XRF spectrometers are used in the Cultural Heritage field to study the technology of manufacture, provenance, authenticity, etc. In particular, XRF has been extensively used to investigate historical paintings, capturing the elemental distribution images to reveal their complex layered structure, and witness the painting history from the artist creation to restoration processes.

As with other imaging techniques, high spatial resolution and high Signal-to-Noise Ratio (SNR) are desirable for XRF scanning system. However, the acquisition time is usually limited resulting in a compromise between dwell time, spatial resolution, and desired image quality. In the case of scanning large scale mappings, a choice may be made to reduce the dwell time and increase the step size, resulting in low SNR XRF spectra and low spatial resolution XRF images.

In this project, we propose a super resolution (SR) approach to obtain high resolution (HR) XRF images, with the aid of a conventional HR RGB image, as shown in Fig. 1. Our proposed XRF image SR algorithm can also be applied to spectral images obtained by any other raster scanning methods, such as Scanning Electron Microscope (SEM), Energy Dispersive Spectroscopy (EDS) and Wavelength Dispersive Spectroscopy (WDS). We model the spectrum of each pixel using a linear mixing model. Since there is no direct one-to-one mapping between the visible RGB spectrum and the XRF spectrum, and therefore the hidden part of the painting is not visible in the conventional RGB image, but it can be captured in the XRF image, we model the XRF signal as a combination of the visible signal (on the surface) and the non-visible signal (hidden under surface). For super-resolving the visible XRF signal, a coupled XRF-RGB dictionary is learned to explore the correlation between these two signals. The RGB dictionary is applied to obtain the sparse representation of the HR RGB input image, resulting in an HR coefficient map. Then the XRF dictionary is applied on the HR coefficient map to reconstruct the HR XRF image. For the non-visible part, we increase its spatial resolution by using a standard total variation regularizer. Finally, the HR visible and the HR non-visible XRF signals are combined to obtain the final HR XRF result. We do not explicitly separate the input LR XRF into visible and non-visible parts. Instead, we formulate the whole SR problem as an optimization problem. By alternatively optimizing over the coupled XRF-RGB dictionary and the visible / non-visible HR coefficient maps, the fidelity of the estimated HR output for both LR XRF input and HR RGB input signals is improved, thus resulting in better SR output.

![Fig.1 Proposed pipeline of spatial-spectral representation for X-ray fluorescence image super-resolution.](image-url)
RD2-Cultural Heritage X-Ray Imaging at SLAC-Challenges and Strategies to Mitigate Radiation Effects

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Synchrotron based techniques are widely used for analysis of complex materials, in part due to the high brilliance of the x-ray source and the tuneability of x-ray energy. These characteristics provide superior performance over traditional lab sources in the measurements of many techniques, from diffraction to spectroscopy. The ability to focus x-rays to micro-scale sizes allows for the probing of the structure and chemistry of many elements on this spatial regime. While the enhanced flux and brilliance is advantageous enables many analyses, it also creates problems with potential radiation damage of the material, which in the case of cultural heritage materials, presents unique challenges. In this talk, an overview of several case studies will be presented, along with the challenges faced in many of the cases when performing x-ray analyses on one-of-a-kind cultural heritage materials.

RD3-Monitoring and mitigating radiation damage during synchrotron examination of heritage materials

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Radiation damage, or radiation-induced side effect, is any undesirable change in the properties of a material caused by irradiation, in particular during the scientific examination of objects and samples. In the past years, several international and European programs, e.g. with the support of the International Atomic Energy Agency and European Commission IPERION CH, have started researching new ways to propose safer ion and photon beam experiments for heritage materials. We will review the progress of these developments and discuss opportunities for further collaborative work to address the monitoring and mitigation of such changes.
K5-15 years of Synchrotron X-ray imaging in palaeontology: Reasons of a success and new tendencies

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The first application of X-ray synchrotron microtomography on a fossil occurred at the end of 2000 on the beamline ID19 of the ESRF. This research field originally appeared quite esoteric or close to research of aliens to many “classical” users of synchrotron. Nevertheless, it rapidly developed and became one of the most visible topics of synchrotron imaging applications at the ESRF, but also out of the ESRF. Several other light sources are nowadays involved in imaging of palaeontological specimens, the most noticeable one being the SLS, or more recently APS.

Many reasons can be invoked to explain this success, but the main one is clearly the application of phase contrast imaging to fossils. Originally, monochromaticity was the key aspect to scan fossils in order to get rid of beam hardening artefacts. Nevertheless, phase contrast rapidly appeared as the key to reveal internal structures of fossils with a sensitivity level not achievable with conventional machines, especially on large specimens.

Few years ago, monochromatic beams were abandoned on ID19 for palaeontology and were replaced by high quality tuneable polychromatic beams. These configurations can cover energy range from 19 keV up to 300 keV, are perfectly stable, have nearly no defects in the wave front and high coherence level. Their bandwidths are narrow enough to make beam hardening not detectable in most of the cases. The high flux allowed by these direct beam configurations, coupled with specific detectors development, dramatically increased scanning speed and quality, as well as the maximum size of samples. The multi-scales approaches often used on fossils also strongly benefited from these developments.

New tendencies are emerging at different light sources by coupling microtomography with other techniques such as scattering, fluorescence or diffraction. Nanotomography also appeared recently as a powerful approach for palaeontology and should develop rapidly in the coming years.

Very recently, archaeology seems starting to follow a similar success story than palaeontology. Archaeologists have been using synchrotrons for a long time, but mostly for chemical or crystallographic purposes. Recent experiments performed at the ESRF clearly demonstrate this high potential for archaeology.
O20-Micro-environmental burial conditions involved in exceptional fossilization: insight from synchrotron X-ray spectroscopy and imaging

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Phosphatization is one of the major processes leading to exceptional fossilization of soft tissues. It is attributed to past microbial activity (microbial mat growth around carcasses). The most spectacular preservation occurs where tissues are phosphatized directly by very small apatite crystallites (often < 30 nm) [1]. In the last decades, experimental taphonomy has been used to identify the origin of this process by monitoring the decay pattern of an organism or assessing its chemical change during decay [1–3]. However, some fossils show extensive preservation of soft tissues inconsistent with decay experiments performed on extant analogues, as recently exemplified in the Cretaceous (~100 Myr) polychaete worm Rollinschaeta myoplena from Lebanon [4].

This emphasizes the need for an in-depth (geo)chemical characterization of fossils to reconstruct the (micro-)environmental and biological controls on decay and fossilization. While most geochemical analyses used today are destructive, require sampling and powder preparation, and often only provide average information, synchrotron-based local probe techniques like spectroscopy and imaging have proved to be invaluable non-invasive tools to studying heterogeneous samples such as paleontological specimens [5]. Micro-X-ray fluorescence (µXRF) allows imaging the distribution of metals and most rare earth elements (REEs) in flat fossils at the microscale [6]. Processed XRF spectra provide semi-quantitative local REE contents, and therefore an indirect assessment of the redox conditions through the so-called ‘cerium anomaly’ [7]. Micro-X-ray absorption spectroscopy (µXAS) allows direct access to the oxidation state of redox-sensitive elements such as Ce and Fe at histological length scales (several 10 µm).

Here, we report application of these techniques to well-preserved fossil fishes and crustaceans from the Cretaceous (~95 million years ago) of Morocco found in association with microbial mats. While anaerobic conditions were shown to rapidly establish in decaying carcasses [8], our analyses reveal slightly oxidative conditions of burial [7]. Instead of an anaerobic, reducing environment, an oxidizing microenvironment was formed inside the carcasses. This is consistent with decay experiments that showed that the complex chemical microenvironments generated by microbial mats turn oxic after initial anaerobic conditions [9]. µXRF and µXAS therefore show promise to characterize chemical microenvironments leading to exceptional preservation of fossils.

References
O21-Paleontological projects at the Advanced Photon source (ANL)

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Even Synchrotron radiation analysis have become more popular among paleontologists in the last years, there is still a large part of our community that does not consider these techniques to study fossil material, even the correct application and interpretation of these novel techniques can help resolving some major questions related with these materials.

In the last three years, several new experiments in paleontology research have been performed at the Advanced Photon Source, the only third generation synchrotron source at the US, and one of the more brilliant photon sources around the globe. Some of these projects have benefited from the imaging capabilities of the two tomographic beamlines, capable of producing scans from 3 microns to 70 nm of spatial resolution. Other projects have explored the fluorescence capabilities of the large field of view instrument, capable of detecting the presence of different elements in the surface of large objects from 30 to 5 microns of spatial resolution.

The projects developed at the APS during these last two years involve the study of different groups of plants from Mongolia, Panama or France, invertebrates in amber from all over the world, vertebrate bones and teeth and many more.
O22-Relation between the macroscopic Schreger pattern of elephant ivory and its mineralized collagen fiber matrix

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Elephantoidea (elephant and mammoth) dentin or ivory is a valuable biological material, which has been worked and used since prehistoric times to produce precious artefacts. These ivories are distinguishable from other biological materials by the so-called Schreger patterns on polished cross sections and are characterized by outstanding mechanical properties such as simultaneous hardness and elasticity. The special mechanical properties are related to the composite nature of ivory composed of poorly crystalline carbonated hydroxyapatite (HAP) and collagen type I as well as to a strong hierarchical structure. At the micro-scale, two networks can describe ivory: the tubular one formed by the odontoblast cells during ivory growth and a mineralized collagen fiber (MCF) matrix. These structural arrangements in ivory are still not well understood.

Therefore, we present here a combined study by means of circularly polarized light microscopy, scanning electron microscopy and synchrotron radiation small and wide angle X-ray scattering (SAXS and WAXS) analyses to get precise insights into the 3D arrangement of the MCF matrix of elephant ivory. This is of great importance to understand the origin of the so-called Schreger patterns that are used to identify ivory in modern and archaeological objects. Especially, SAXS and WAXS techniques have been commonly used over this last decade to study the organization and orientation of MCF of a wide range of biological materials including also archaeological biological materials.

Our results allow us establishing a new 3D model of the micro MCF arrangement in elephant ivory in relation to the macroscopic Schreger patterns. These findings provide new insights into the ivory structure and allow drawing conclusions on ivory working techniques and use for art and archaeological objects.

Fig. 1 a) Degree of MCF organization = % of MCF with the same orientation (ρ-profiles) from cement to pulp of the longitudinal plane of elephant ivory in black and of the transverse plane in grey. The mean SAXS signals are shown for the longitudinal and transverse plane. b) WAXS pattern of the longitudinal plane showing the orientation of the c axis of the HAP particles and therefore the orientation of the MCF.
P01-DANTE: processing electronics with Ultimate Energy-Resolution and High-Count Rate Capability for micro and macro XRF mapping application

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A growing number of X-ray spectroscopy applications (e.g. using synchrotron facilities or adopting a high-efficiency X-ray tube) require detection systems operating with high counting-rate capability. Such need is fundamental in order to reduce the time of the analysis whenever many spectra have to be acquired. Typical examples are XRF (X-Ray fluorescence) mapping of large surfaces or XAS (X-ray Absorption Spectroscopy) measurements, to make a few examples.

In order to meet these requirements, Silicon Drift Detectors (SDDs) are widely used. To achieve the full benefit from SDD advancements, the read-out electronics must provide short processing-time while adding a negligible contribution to the overall noise. A new digital pulse processor, named DANTE, has been developed taking these considerations into account. DANTE can be used coupled to X and Gamma-ray detectors equipped with CUBE (the CMOS preamplifier developed by XGLab) or with different pulsed-reset preamplifiers. DANTE is implemented on a single printed circuit board. It uses low power and is scalable for a multi-channel configuration.

Thanks to an accurate very low-noise design, DANTE provides excellent spectroscopic performance even at very high count-rates. Therefore, excellent energy resolutions of 138eV and 159eV FWHM have been achieved with peaking times of only 100ns and 32ns respectively. The combination of ultra-short peaking-time and effective pile-up rejection system enables the system to maximize throughput and minimize spectrum artifacts even when the input count-rate exceeds 3Mcps.

The CRONO instrument (also developed by XGLab) will be also presented as one example of DANTE usage. CRONO is a MACRO-XRF scanner specifically designed for in-situ elemental mapping. The detection head (which includes SDD detector, DANTE and X-Ray generator) is mounted on a motorized stage that allows for up to 60cm x 45cm scanning area. The typical measurement time ranges from few tens of minutes up to few hours depending on required spatial resolution, area size and contrast. Thanks to a proper design, the scanning on the sample can be performed with a linear speed up to 45mm/sec acquiring up to 50 complete spectra per second. XRF maps acquired from a painting are reported in the figure.

Fig. 1: Elemental mapping on a 50cm x 40cm painting, with 2mm spatial resolution; scanning time is 30 minutes. From the top-left, clockwise: visible picture, Pb-La, Ca-Kα, Ba-La.
P02-Optimizing Compositional Images of Daguerreotype Photographs Using a Laboratory X-ray Source and Post Processing Methods

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Microfocused X-ray fluorescence imaging was used to examine two 19th century daguerreotypes. The distribution of Hg-bearing nanoparticles beneath the Au gilding layer gives rise to contrast in the photographs. The sum image for Au + Hg M line X-rays is therefore a compositional image that mimics daguerreotype photograph contrast. Because the thickness of the Au and Hg on the surface represents a small fraction of the X-ray activation depth, the resulting sum images are not of high quality and are dominated by Poisson noise. This is true even for long collection times up to multiple days in length. Achieving superior contrast resolution by increasing the duration of data collection further is impractical. In this study, a new image processing technique based upon the Haar-Fisz algorithm and wavelet theory was used to improve the image quality of compositional maps (Davis and Vicenzi, 2016).

The digitally processed images show a reduction in noise without a loss of spatial resolution over the length-scale of photographic features. The Haar-Fisz denoising algorithm decreased the contribution of the Poisson noise in compositional images. Multiple resolution analysis improved image quality further. Features within the portraits are uniformly more recognizable in the final processed images relative to the raw X-ray images. Intensity line profiles that traverse midtone, highlight and shadow regions of the daguerreotype reveal that spatial resolution is not degraded by the image processing routines. Improvement in image quality is quantified by comparing the relative variance of the raw and Haar-Fisz processed imagery.

The use of a Haar-Fisz denoising transformation, coupled with multiple resolution analysis was found to improve the quality of low count X-ray images without impacting the spatial resolution at the scale of photograph features. The process can be implemented in freely available open-source software with a minimum of programming effort. Such digital post processing routines offset the need for longer acquisition times to achieve improved X-ray fluorescence image quality. Finally, because the Au + Hg map is insensitive to surface imperfections and tarnishing via atmospheric adsorption of sulfur, digitally processed images may be used to reconstruct photograph features in heavily disfigured daguerreotypes.

References
P03-High Definition X-ray Fluorescence Imaging of Cultural Materials at the XFM Beamline of the Australian Synchrotron

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The X-ray fluorescence microscopy (XFM) beamline at the Australian Synchrotron utilizes three separate probes for its scanning operations: a zone plate nanoprobe, the workhorse KB mirror microprobe and a recently installed “milliprobe” for large area (1.1×0.6 m²) elemental mapping down to the order of 10 micron spatial resolution. The majority of the XFM studies have been performed with the large solid-angle 384-element energy dispersive Maia detector array.[1] The Maia detector routinely operates with pixel dwell times on the order of one millisecond, and has the capability for imaging to around 10⁸ pixels with full XRF spectra saved per pixel.

There has been an increasing desire of users to examine large-sized cultural materials such as paintings, and historic objects such as the de Vlamingh pewter plate,[2] which have posed many new challenges for their analysis in a synchrotron setting. We have designed the milliprobe apparatus for the analysis of such varied materials.

Data will be presented on the XFM analysis of a wide range of cultural materials with spatial resolutions ranging from 400-nm for a Degas paint sample section measured on a zone plate system to 0.1-mm for a 16th century Tudor painting on the milliprobe apparatus.[3] The challenges associated for their analysis will be discussed.

The XFM/Maia detector combination and the large scanning area milliprobe apparatus have proven effective for the non-invasive analysis of cultural materials. The objects can be investigated in high definition while maintaining the context of the object, and the low dwell times minimize radiation dose to the sample. This has allowed great insights into the conservation of the materials, and in some cases has aided their preservation.

References
The X-ray fluorescence (XRF) imaging facility at the Stanford Synchrotron Radiation Lightsource (SSRL) consists of three beamlines, which cover a wide range of x-ray energies and beam sizes, allowing for the ability to conduct an extensive variety of experiments. As a facility, we cater to a broad range of users including those from the Biological, Environmental, and Material Science communities, which often require different beam line conditions based on sample composition. Needs can range from including varying sample sizes (5μM to 0.5m), varying resolution (<2μM to >200μM), and varying energy ranges (2100eV-20,000eV). These needs have been achieved with the utilization of three beam lines for microfocus activities:

1) Beamline 2-3: High spatial resolution (beam size ~2μM), good for spectroscopy/diffraction, accommodates medium to small sample sizes, ~5,000eV to ~20,000 eV, tomography
2) Beamline 10-2: Moderate resolution, (10μM – 200μM), high flux, rapid scanning, accommodates medium to large sample sizes, spectroscopy, ideal diffraction, ~5,000eV to ~20,000eV, tomography, confocal microscopy
3) Beamline 14-3: Low energy (~2,000 to ~4,500eV), high spatial resolution (~5μM beam size), good spectroscopy, accommodates small to medium sample sizes, Helium sample environment

These three beamlines are tied together via a cohesive suite of software developed by Sam Webb. All imaging beamlines at SSRL share the same suite of software to control the beamline as well as analyze the data. These programs also share the same look and many features as the bulk XAS lines for ease of transition between beamlines. The capabilities of the imaging facility are always expanding at SSRL, future directions include the addition of zone plates at beamline 10-2 allowing beam sizes < 100nM as well as a hexapod stage to allow for easy changes between optics and thus beam sizes.
P05-Recent archaeological studies at the GSECARS 13-ID-E hard X-ray microprobe beamline at the Advanced Photon Source

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Synchrotron-based X-ray fluorescence microscopy (XFM) has become a powerful tool for cultural heritage research that can provide non-destructive, high resolution quantification of trace element abundance, chemical form, and molecular and crystallographic structure at low concentrations and at µm length scales. The GSECARS hard X-ray microprobe at beamline 13-ID-E of the Advanced Photon Source enables cultural heritage researchers to answer a broad range of scientific questions that require spatially resolved chemical analysis to answer. Here we highlight two recent studies that have utilized its capabilities.

Hunault and co-workers (J. American Ceramic Society, 2016, 99:89-97) used the X-ray spectroscopic capabilities of the beamline to understand how Medieval craftsmen produced the unique colorations found in 12th-13th century stained glass windows. Such uniquely colored blue glass became intensively used in France in such the cathedrals of Chartres, the Holy Chapel of Paris and the basilica of Saint-Denis. While these potash- and soda-lime-stained glasses were blue-colored by addition of cobalt, the optical coloration cannot be accounted for by Co²⁺ alone. XAFS analysis Mn, Fe, and Cu K-edge in these glasses showed that it is Fe³⁺ in the glass that contributes to the blue color, modifying the optical absorption spectra due to tetrahedral Co²⁺.

Bianucci and co-workers (Int. Conf. Comparative Mummy Studies, Hildesheim, April 2016) used 13-ID-E to study mummified tissues collected from the Frankish Queen Arégonde (515?- around 580 AD), uncovered from Saint Denis’ Basilica in 1957. Of particular interest was whether the preservation of mummified lung tissue was the result Medieval embalming. XRF, XAFS and XRD analysis of the biological remains found the lung tissue to contain high levels of copper oxide. Biochemical analysis also showed the presence of benzoic acid and related compounds; commonly reported in the balms of Egyptian mummified bodies. Based on these analyses, and taking into account that Arégonde’s waist was surrounded by a copper alloy thick belt, the researchers speculate that the copper oxide in the lung is from weathering of the belt and that the preserving properties of copper combined with a spice based embalming treatment might have allowed her lungs to preserve.
P06-Development of combined XRF and XRD mapping for cultural heritage applications at CHESS

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Macroscopic X-ray Fluorescence (MA-XRF) is increasingly employed to noninvasively survey cultural heritage objects in order to infer material or pigment composition, distribution, and correlation from the local elemental concentrations. This approach can unambiguously identify some materials based on either the presence or co-location of particular elements. However, the broader utility of XRF is limited by its lack of direct information regarding material compounds, especially those that include light elements. The addition of x-ray diffraction to MA-XRF provides simultaneous probes of both elemental composition and crystalline structure, and has been demonstrated to be capable of resolving buried pigment layers in a painting [1]. In general, XRD benefits from much higher energy x-rays than are typically used for MA-XRF. However, the optimal x-ray energy will depend strongly on the particular sample of interest, as well as detector size and efficiency.

At CHESS, we are evaluating simultaneous macroscopic XRF and XRD mapping for the purpose of studying a 20\textsuperscript{th}-century painting on panel in the Herbert F. Johnson Museum Collection and a group of 13\textsuperscript{th}-15\textsuperscript{th} century illuminated manuscript fragments from the Cornell Library Rare and Manuscript Collection. We are particularly interested in assessing this combined mapping approach for the identification of trace minerals in copper-rich blue pigments in illuminated manuscript fragments. We are further interested in evaluating this method’s ability to determine the distribution of materials composed of lighter elements that are difficult or impossible to detect with MA-XRF, such as lazurite in illuminated manuscript fragments. Our preliminary results have shown that XRD mapping with 19.3 keV x-rays can effectively detect historic iron gall ink lettering on a parchment fragment. Our approach takes advantage of a 384-element Maia detector to quickly and efficiently collect backscattered XRF signal, while simultaneously collecting powder-like transmission XRD using an area detector.

References

P07-New approaches for the study of cultural heritage objects by means of neutron imaging methods

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Neutron imaging is applied as tool for non-destructive investigations alternatively or complementarily to the more common X-ray methods. Since the interacting mechanism of neutrons with matter is completely different from that with X-rays, the obtained transmission contrasts are diverse. Metals can be transmitted in much thicker layers while organic materials provide a high contrast already for small amounts.

Our team has long-term experience in collaboration with museum experts for dedicated studies of cultural heritage objects, on the macro-scale of about 40 cm sample size up to the micro-scale with highest possible resolution on the order of about 10 micro-meters. Next to the simple radiography approach, neutron tomography has become now a routine method on the different length scales.

The new approaches are on the one hand the selection of narrow energy bands of the used neutrons. This enables to tune contrast and transmission of the investigated materials. More important is to characterize the metal structure with respect to texture and grain size distribution in relevant studies.

On the other hand, we installed and combined X-ray imaging options into our beam lines NEUTRA and ICON in order to have the pixel/voxel wise comparison for the same object. This enables a data fusion process for the enhancement of the inherent sample properties.

The presentation will give technical details of our state-of-the-art user facilities and demonstrates their performance by selected examples of previous studies.

In particular, we will highlight the opportunities to study corrosion processes in metal artefacts best with neutrons (Fig.1).

![Fig. 1 Neutron tomography view of a corroded Roman find piece of the Aventicum (Switzerland) site (left); the slice indicates in the bright areas the corrosion as found with neutrons (middle), but not with X-rays (right).](image-url)
P08-Old Russian jewelries studies by means of neutron imaging method

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The neutron radiography and tomography methods are the powerful tool of non-destructive analysis, which demonstrates importance in industrial and scientific research. The fundamental difference in nature of neutrons interaction with matter compared to X-rays provides additional benefits to neutron methods, including sensitivity to light elements, notable difference in contrast between neighboring elements or isotopes, high penetration effect through metals or heavy elements. All these features make neutron radiography and tomography highly demanded tools with growing range of applications in industry, geophysics, paleontology, archeology and culture heritage investigations. A neutron radiography and tomography facility have been developed recently at the IBR-2 high flux pulsed reactor. The IBR-2 high flux pulsed reactor is one of the most powerful pulsed neutron sources in the world with the average power 2 MW, power per neutron pulse 1850 MW and neutron flux in pulse of \(5 \times 10^{15} \text{n/cm}^2/\text{s}\). The neutron radiography and tomography facility is placed on the 14th beamline of the IBR-2 high flux pulsed reactor. As scintillation screen, the \(^6\text{LiF}/\text{ZnS}\) scintillator of 0.2 mm thickness is used. The light is reflected out of the beam by a mirror and focused on CCD chip by an optical lens Nikon 50 mm 1:1.4D AF-Nikkor. The sample manipulator system is based on HUBER goniometer with x-, y-translation and z-rotation stages. The minimal rotational step is 0.02 deg. The imaging data are subtracted by the dark current image and are divided to the incident neutron beam by means of an ImageJ software. The tomographic reconstruction is performed by a H-PITRE program. The VGStudio MAX 2.2 software of Volume Graphics (Heidelberg, Germany) is used for the visualization and analysis of reconstructed 3D data. The evaluated spatial resolution for the field-of-view 20x20 cm\(^2\) is about 300 µm. The tomography experiments have been performed with rotation step of \(0.5^\circ\) and total number of measured projections was 360. The exposure time for one projection was 10 s and resulting measurements lasted for 4 h. Items of jewelry art of Old Russian time from ancient Russian city Tver were studied with use of this method. All the jewelry was made of silver and was greatly damaged by fire. All traces of gilding and blackening disappeared under temperature effects and also, those parts of jewelry which were connected by soldering were deformed. The Old Russian bracelet, heavily damaged by fire, and the kolt were studied by means of neutron tomography. We succeed to restore parts of gilding and blackening on a bracelet, what would be impossible by standard means of research (Fig. 1). Now we can say that a bracelet from Tver belongs to Kievan Old Russian jewelry school, which traditions ascended to the Byzantine Empire. Analogues of such bracelets can be seen in the museums of Moscow Kremlin, in the Historical and the Russian museums. Data obtained for a kolt (Fig. 2) is a great interest of restorers and researchers: we succeed to learn about the technique of connection of its separate details, and to reconstruct the number of separate elements used for its making (there are more than 50). Moreover, parts with different elemental composition were detected, allowing us to reconstruct the process of soldering of granules and filigree on the surface of a kolt. Undoubtedly, the data obtained not only allows optimizing the process of restoration of these items, but also provides us with new knowledge of the Old Russian technique of jewelry making and has a big exposition interest as well.

Fig. 1

Fig. 2
P09-Neutron, Proton, and Ion Based Techniques for Heritage Materials: A Synergistic Approach at ANSTO


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Over recent decades, nuclear methods have been established as an innovative and attractive investigative approach to characterise heritage materials. Providing a powerful and versatile way to look at the structure and dynamics of materials at the atomic level, they extract maximum information from an object without the need for sampling or invasive procedures.

ANSTO’s facilities offer a wide range of unique techniques for cultural heritage research. A suite of world-class neutron scattering instruments and the availability of neutron activation analysis at the OPAL research reactor, the Centre for Accelerator Science, the Australian Synchrotron, along with state-of-the-art electron microscopy facilities, analytical laboratories, and computing facilities constitute unique research infrastructure.

A cultural heritage project has been promoted across ANSTO to interface and synergize this suite of techniques and analytical capabilities with the needs of the cultural heritage community. In this presentation, current and future perspective on the integrated application of nuclear techniques for heritage materials will be discussed.

Recent studies, in collaboration with the cultural heritage community, include:

- Neutron diffraction and imaging techniques were applied to shed light on the manufacturing procedure developed to produce a particular variety of silver coins, called incuse, minted around 540 BC in the cities of Southern Italy.
- A set of Egyptian mummies were successfully dated and attributed by $^{14}$C accelerator mass spectrometry (AMS) analysis on small amounts of the wrapping material.
- The combination of Ion Beam Analysis (IBA), Neutron Activation Analysis (NAA) and X-ray Fluorescence Microscopy (XFM) helped in the characterization and study of provenance of Aboriginal pigments and artefacts.
- Synchrotron IR microscopy and spectroscopy investigated the degradation and conservation of acrylic emulsion paints, and the degradation of cellulose nitrate artefacts in museum collections.
P10-Dechlorination of ferrous archaeological artefacts in subcritical conditions: understanding of the corrosion layer transformation thanks to a multi-scale characterisation

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Dechlorination of ferrous archaeological artefacts is rendered necessary after excavation in order to remove chloride species present at the metal/corrosion layer interface. Indeed, when artefacts are exposed to air after a long period of burial they can suffer severe damages. This is due to the reactivation of the corrosion processes through the migration of those chlorides that provokes local acidification. In the conservation field, treatments are based on the immersion of the artefacts in alkaline bath in order to transform the chloride containing phases (akaganeite and β-Fe₂(OH)₃Cl). But specifically for artefacts of high dimensions the process can last from several months to years. An innovating approach based on treatment in subcritical conditions (180°C, 35 bars) allows to reduce by a factor of 10 the treatment duration. The optimisation of this treatment requires the determination of the reaction pathways between the initial corrosion layers and the transformed ones after treatment. Therefore synthetic phases representative of archaeological corrosion products formed in aerated environments (goethite, lepidocrocite, magnetite, akaganeite, maghemite) have been treated separately to study their transformation during the treatment. Specifically in-situ experiments under synchrotron radiation have been performed on akaganeite in order to determine the different transformation steps of this phase. The behaviour of two akaganeite, the first one obtained by laboratory synthesis and the second one from archaeological origin has been compared. Thanks to XANES at the Fe K-edge in sub-critical conditions it has been highlighted that depending on the heating rate the akaganeite transforms either in hematite or in a mix of goethite and hematite. High resolution X-ray diffraction under synchrotron has allowed to determine the evolution of the crystalline structure of the remaining akaganeite depending on the chloride content of this phase. Last the results show that the transformation kinetics depend on the origin of the precursor and that archaeological phases transform much slower than synthetic ones.
P11-Understanding Smalt Discoloration through Potassium K-edge XANES

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The blue pigment smalt is a finely ground cobalt-containing potash glass, made by mixing at high temperatures zaffera – a roasted cobalt ore – with a potash flux and sand. It is generally accepted that smalt was widely used in European oil paintings from the end of the 15th century onwards, although examples of its earlier use have recently been found. For example, in a Byzantine manuscript dating to the 13th century in the collection of the J. Paul Getty Museum, the use of smalt is associated with ultramarine blue.

Notably, the blue passages in the illuminations in the Getty manuscript are still a vivid blue color. The discoloration of smalt in oil medium, turning from a deep blue to a grey-yellowish color, is a well-known phenomenon [1-3]. Smalt is sensitive to humidity in a way typical of an alkali silicate glass: an ion exchange reaction between hydrogenated species (H+) originating from the atmosphere and the alkali (Na+ and K+) content of the glass resulting in potassium leaching. The depletion of potassium causes a reorganization of the atomic structure, and a change in the coordination symmetry of cobalt ions from tetrahedral (blue) to octahedral (colorless). Moreover, the interaction of the leached potassium ions with the oil binding medium promotes the formation of potassium soaps and salts.

However, little is known about the behavior of smalt when dispersed in other binding media other than oil. This study explores the aging process of smalt when dispersed in three different binding media: egg white, egg yolk and gum arabic. Using potassium K-edge XANES, fresh and artificially aged (60°C, 55-60 % RH) paint-outs are studied to investigate whether, and if so how, the different binding media affect the degradation process of smalt.

References
P12-Determining the Cause of Degradation of Landscape with Cowherd by Claude Lorrain Using X-ray Fluorescence Imaging and µ-X-ray Absorption Spectroscopy

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Landscape with Cowherd, from the Fine Arts Museums of San Francisco (FAMSF), (Fig. 1.) is attributed to Claude Lorrain and has the same composition as El Vado, an autographed Claude painting from El Prado Museum ca. 1644. The FAMSF’s painting exhibits blanching in the form of a white crystalline build up on the surface of the dark green foliage. Blanching is a common phenomenon observed in the complex green mixtures of Claude paintings. This study of Landscape with Cowherd seeks to determine the cause of the blanching and compare it to the degradation mechanism found in other paintings using X-ray Fluorescence Imaging and µ-X-ray Absorption Spectroscopy of dark green paint samples. Analysis at the Stanford Synchrotron Radiation Lightsource (SSRL) showed arsenic as a component in the green paint, suggesting the presence of orpiment and/or realgar. Still Life with Five Apricots by Adriaen Coorte from 1704, exemplifies the degradation of this pigment with exposure to light; arsenic species migrated and caused whitening as well as friable paint. (ref, MEHTA JAAS). A similar mechanism may be occurring in the blanched green paint of Landscape with Cowherd.

Preliminary results and analysis on a blanched green paint sample show multiple arsenic species, which could point to the degradation products causing the whitening (Fig. 2.) Figure 2 (top) shows a photomicrograph of the paint sample, which was captured from the area denoted with a blue dot on figure 1. Figure 2 (middle) is overlay of sulfur (red), arsenic (green) and lead (blue). Figure 2 (bottom) is obtained from cluster analysis of multi-energy edge mapping at 7 different energies through the arsenic K-edge. This ongoing analysis will include sulfur K-edge imaging and sulfur µ-XAS to determine speciation and help propose a mechanism of degradation observed in the painting.

References
P13-Towards an Electrochemical Sensor for Archaeological Wood: Simultaneous Electrochemistry and In-situ XAS speciation on Simulated Systems

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Waterlogged archaeological wood, such as that found in shipwrecks, can be damaged and potentially destroyed by the presence of sulfur. The sulfur originates from the formation of H₂S by sulfate reducing bacteria, which diffuses into the wood and forms reduced sulfur compounds. In the anaerobic burial conditions these species are not problematic, but exposure to oxygen causes the formation of sulfuric acid, leading to the degradation of the wood-cellulose and formation of stress producing mineral deposits. A further complication arises in that iron species in the wood (e.g. from original fixtures) can catalyse this acid formation. A key issue for conservators is to be able to determine the presence, concentration and, critically, the redox state of any sulfur species present. This is critical for both un-conserved and conserved materials as the latter historically have not received treatments to combat this problem. Currently the only mechanism for accurately assessing the sulfur is via synchrotron-based XAS which is often a challenge, given a typical museum’s limited resources, and the need to take samples of material to the beamline.

Electrochemical sensors have been developed to probe iron and sulfur biogeochemical processes in sediments and microbial mats. Hg/Au electrodes are used to perform local electrochemical measurements which can provide the fingerprint for the sulfur compounds. This seems like an ideal solution, however direct transfer of this technology to archaeological wood is not trivial. Strategies to develop the local environment need to be addressed; the electrodes need to be micro-scale to avoid too much interruption of the timber itself; interpretation of the data is complicated by the co-reacting species and potential losses in the electrode geometry. The systems also need to be validated against the current methodologies.

In this study, the chemical environment in marine archaeological wood is simulated in fresh oak and concurrent XAS and electrochemical measurements are taken to characterise the species present. This approach offers the possibility of on-line monitoring of museum artefacts. This would have a significant impact on the conservator’s ability to manage wooden and other organic artefacts, such as leather and paper, and provide timely intervention for treatment.

References
P14-Saving the Dead Sea Scrolls: From the Molecular Properties of Collagen to Preservation Strategies of Ancient Parchments

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Since their discovery in the late 1940s, the Dead Sea Scrolls have continually fascinated both scholars and the general public. While the texts of the Dead Sea Scrolls are crucial for understanding one of the most important periods for both the Jewish and Christian religions, the scrolls themselves contain much more information than simple text. They are physical objects and carry with them rich historical information regarding the ancient technologies used in their production as well as their alteration during their life in the desert caves in which they were stored. Furthermore, their traumatic post-discovery life led to significant alteration and deterioration as well as the introduction of foreign materials following numerous, and largely unsuccessful, preservation and restoration treatments. All this information is preserved and accessible in the form of the organic and inorganic compounds in the scroll’s material. In this work, we have applied advanced spectroscopic and microscopic methods to investigate collagen-based modern and ancient manuscript materials. By combining polarized Raman, synchrotron-based far infrared spectroscopy and X-rays scattering we have been able to directly investigate, in unprecedented detail, the changes in collagen structure during the deterioration in the fragments of the Temple Scroll, one of the most important documents of the Dead Sea Scrolls collection. Through advanced materials characterization and modeling we provide insights into the past, present and future of these valuable historical documents.
P15- Probing the carbonatation process of Ca-based consolidants into limestone matrix by SR-based Ca K-edge XANES and micro-XRD investigations.

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The application of consolidants is a common practice for the preservation of limestones used in cultural heritage monuments against outdoor weathering. In the past, consolidating products commonly used were based on synthetic organic polymers which generally exhibit some shortcomings in terms of mechanical efficacy, physico-chemical compatibility and stability over time (1). Recently, inorganic treatments involving the in situ formation of CaCO₃ [starting from nanometric Ca(OH)₂ dispersions or solution of calcium alkoxides], have proved to be more suitable due to their higher compatibility and stability with respect to synthetic polymers (2,3). The main issue of these Ca-based consolidants is the formation of different CaCO₃ phases which may range from amorphous deposits to crystalline systems composed of either vaterite, or calcite, or their mixtures (1-3). Amorphous CaCO₃ and vaterite are more soluble than calcite; moreover, differences in crystal structure between a calcitic substrate and vaterite could hamper an effective cohesion of the phases.

In this work, we exploited the structural selectivity, imaging capabilities and high lateral spatial resolution of SR-based Ca K-edge XANES (in scanning and full-field mode) and μ-XRD techniques to investigate at the micrometer scale the nature and distribution of CaCO₃ phases inside calcitic substrates treated with two Ca-based consolidants. Specifically we analyzed thin transversal sections of limestone specimens treated with a newly developed product (based on a solution of calcium acetocacetate and developed within the HEROMAT EU-project) and a commercial nanometric Ca(OH)₂ dispersion, both cured at different RH% values. The study permitted to obtain valuable information on the distribution and mineralogy of the newly formed CaCO₃ compounds inside the porosity of limestone.

References

Acknowledgments
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P16-Visualizing Van Gogh’s use of the red dye Eosin via MA-XRF mapping of Br: possibilities and limitations


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Eosin is a red dye that was frequently employed by Van Gogh. We could recently demonstrate its presence in paintings such as the various versions of Portrait of Joseph Roulin (F436, 1889; Museum of Modern Art and F439, 1889; Kröller-Müller Museum) and The Bedroom (F482, 1888; Van Gogh Museum), as well as in several flower pieces such as Irises (F678, 1890; Van Gogh Museum), Roses (F681, 1890; National Gallery of Art) and Sunflowers (F458, 1888; Van Gogh Museum) but also in earlier works such as Still-life with Apples and Pumpkins (F106, 1885; Kröller-Müller Museum) and Basket of Apples (F99, 1885; Van Gogh Museum). In these and other Van Gogh’s, the original red-pink colour has faded to a significant extent, altering the colour balance of the entire painting and creating an appearance quite different from that which the artist intended.

One of the forms of Eosin, called Eosin Y, contains four Br atoms per molecule. SEM-EDX analysis of cross-sections from photochemically faded Eosin-based oil paints showed that the spatial distribution of bromine is not affected by the fading. Since macroscopic XRF (MA-XRF) is able to reveal the distribution of Br on or just below the surface of paintings, it is a convenient manner of visualizing the original use of Eosin by Van Gogh. In this presentation, the possibilities and limitations of MA-XRF for doing this in different situations and paintings will be discussed. Insights derived from examining original Van Gogh paintings as well as (un)aged model samples are combined.

The ease with which Eosin can be detected via Br appears to vary. On the one hand, the presence of other pigments such as vermillion red and lead white, may render its detection more difficult, mainly as a result of the overlap between the XRF lines of Br, Hg and Pb. On the other hand the manner in which Van Gogh employed Eosin, either as a superimposed glaze on contours or mixed with other (white) pigments to obtain a pink-coloured painting, also influences the detection of the Br-XRF signals.

References
P17-From Lapis Lazuli to Ultramarine Blue: investigating Cennino Cennini’s recipe using Sulfur K-Edge XANES

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As one of the most desired and expensive artists’ materials throughout history, there has long been interest in determining the provenance of natural lapis lazuli. Much of the recent research has focused on studying the presence and distribution of lazurite [Na$_8$(Al$_6$Si$_6$O$_24$)S$_n$] and accessory minerals (including calcite (CaCO$_3$), pyrite (FeS$_2$), diopside (MgCaSi$_2$O$_6$) and wollastonite (CaSiO$_3$)) either in lapis lazuli rock of known provenance [1-3], or in ultramarine blue pigments [4, 5].

The traditional method of pigment extraction from lapis lazuli, as outlined by Cennini in the \textit{Craftman’s Handbook}, involves a lengthy purification process, which includes (1) finely grinding the raw rocks; (2) mixing with venice turps, mastic gum and beeswax; and (3) massaging under water. This process, combined with the hydrophilicity of the lazurite, causes the blue particles to pass into the water, while most of the accessory minerals are trapped in the wax/gum mass. The process produces several grades of pigment, each less saturated in color than the one before.

Here, we extend prior work [6] on the identification of provenance markers in lapis by using sulfur K-Edge XANES to investigate the sulfur environment within the aluminosilicate framework of lazurite during the extraction process of ultramarine blue pigment from raw lapis lazuli. The sulfur XANES fingerprint of samples from the different stages of Cennini’s extraction method, from the unrefined lapis lazuli rock to the third-grade purity pigment [1-3], were examined. All spectra shared a strong absorption peak at 2483 eV, attributable to sulfate present in the lazurite structure. However, intensity variations appeared in the pre-edge features: the minor peak at 2469.1 eV and the broad envelope of peaks between 2470 and 2475 eV. These specific features will be described and sulfur chemistries through the pigment preparation will be presented.

References
Invented in 1839 by Louis Daguerre, the daguerreotype was popular in Europe and North America between 1839 and 1860. This first form of the photographic image was produced by first exposing a silver coated copper plate to iodine vapour to produce a light-sensitive surface. Improvements were made to this process until it was supplanted by film-based photography. Daguerreotypes provide an important historical record of events during their period of their use however the technique remains poorly understood and chemical damages disfiguring many important daguerreotypes.

This work reports preliminary research using synchrotron-based techniques to elucidate the daguerreotype process and the chemistry involved in how these artifacts age so their conservation can be better managed. Synchrotron-based x-ray absorption near edge spectroscopy (XANES) was used to study a specially prepared daguerreotype plate. The results showed the presence of sulfur and chlorine, elements believed to be responsible for tarnish on daguerreian images. The analysis also shows the image particles to be comprised of gold and mercury and silver with a face centered cubic structure. Gold appears to be elevated in the bright areas. Furthermore, synchrotron and laboratory based X-ray photoelectron spectroscopy (XPS) has unveiled residual halides on the surface of the daguerreotype test plates.

This research provides us with valuable insight to the chemistry and composition of the image particles on the surface. Furthermore, the distribution and speciation of sulfur and chlorine will assist in defining the causation of tarnish on the plates. Continued analysis will be conducted in an effort to prevent further tarnish as well as preserve plates that have previously degraded.
P19-Characterization of applied brocades from Savoie duchy, France, by means of combined micro-analytical techniques

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Applied brocades are complex relief decoration applied on painted or sculpted support aiming at reproducing the gold or silver threads of precious fabrics. Original from Central Europe, in particular Low Countries from the beginning of the XIVth century [1], this complex decorative process rapidly spread to Southern Europe, e.g. France, Portugal and Spain [2] being widely used from the mid-XVth century to the mid-XVIth century.

The lacunar state of conservation of the applied brocade as well as the scattered documentation concerning this technique motivated the study and classification of an important number of applied brocades recently identified on a corpus of 7 sculptures from Savoie duchy, France, dated from 1460 to 1530.

In order to provide a complete characterization of the different types of applied brocades from overall to detail, an extended analytical protocol has been settled based on i) in-situ X-Ray Diffraction (XRD) and Fluorescence (XRF) analyses, completed by ii) the sampling of micro-fragments specifically prepared for the combination of visible and electronic microscopies with SR-based µ-Fourier Transform InfraRed, µ-XRF, and µ-XRD techniques.

This combination of techniques allowed both the identification and localization of the different ingredients and degradation products present into the complex stratigraphy of applied brocades. Consequently, ancient know-hows involved in the execution of applied brocade in Savoie area have been undiscovered, and conservation questions have been answered regarding the degradation of metallic tin foil, main element of the decoration.

Completed by stylistic and historic studies on applied brocade and brocade textile, this work helps in understanding the place of this production in an enlarged geographic and economical context.

References
An assemblage of 29 metal finds was discovered during salvage excavations conducted at Balfour Street in Nahariyya. The excavation, carried out on behalf of the Israel Antiquities Authority was directed by N. Getzov and Y. Lerer. This group of metal finds included: daily use objects (iron knives, fishing weights (lead) and nails), luxuries (two spatula and fibulae) and weapons (mainly Irano – Scythic arrowheads). The metal finds were dated by the excavators to the Persian period. This assemblage from Nahariyya is considered one of the well-dated metal groups from the Persian period: According to the excavators, the metal objects are assigned to two main periods: the finds from Stratum V–VI, are dated between the 6th till the beginning of the 5th century BCE, while finds from Stratum IV–II are dated to the 4th century BCE.

The main goal: in addition to typological examinations, all the objects went under chemical analysis in purpose, to check the possibility, of dating metal objects by chemical analysis (XRF).

Results: preliminary observation shows some differences in the chemical composition of the objects from 4th and 6th century B.C:

- **Objects dated to the 6th century B.C (mainly arrowheads) include Antimony (sb), that do not exist in the 4th century B.C objects tested in this research. Needles, made from tin bronze without any use of antimony.**

- **Spatula dated to the 4th century B.C include an amount of up to 11% of tin while a spatula dated to the 6th century B.C include an amount of less than 10% tin.** This 1% difference of tin is not significant. On the other hand, the amount of lead in the 6th century B.C objects (between 3% – 7%), is higher than the objects from 4th century B.C (less than 1% of lead).

- **Fibulae dated to the 6th century B.C include an amount of up to 12% tin, while the founds from the 4th century include an amount of less than 12% tin.**

- **The two fibulae dated to the 6th century B.C include an amount higher than 5% of lead, while most of the fibulae from 4th century include an amount that less that 1% Of lead.**

- **Two arrowheads from the inland (Tel Hadid) dated to the 5th century B.C include a high amount (7.4% - 14.3%) of antimony.**

The existence or absence of antimony can indicate the difference between local or imported objects, since the local minerals in Israel do not include antimony. These results, correlate with the historical resources describing the Persian conquest of the area in the 6th century B.C. This could suggest that arrowheads that include antimony belong to the foreign forces of the Persian army, while the other objects can be considered as local products.

The results of this research must be considered preliminary, due to the absence of good parallels: no such tests or research has been conducted yet in other sites, dated to the Persian period. In addition, in most archaeological sites excavated during the last century, the objects are generally dated to the Persian period without a possibility to determine a specific period such as the case of the Nahariyya excavation in 2005. These results, lead to the conclusion that such research should be completed. The first step is to create a data base from such archaeological excavation with good and exact dating. Only after completing the data base, the chemical analyses can be compared to determine the difference between periods and materials.
P21-Investigation on Fire Gilding using XRF and NAA

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Fire-gilding or amalgam gilding is a historical technique for the gilding of objects. The object to be gilded is coated with an amalgam (a solution of gold (Au) in mercury (Hg)). By heating, the largest part of the Hg is subsequently evaporated and there remains a gold layer, containing still traces of Hg.

The information on the used gilding technique might be crucial for the conservation and preservation of archaeological objects. Therefore, the main objective of this work is the detailed understanding of the behaviour of Hg under conditions of fire gilding. I.e. the understanding of the diffusion and evaporating behaviour of Hg, depending on parameters like substrate material (silver, copper, bronze, brass...), heating temperature and duration, and the resulting Hg depth profiles under these conditions. Secondary objective is the establishment of a measurement protocol for the unambiguous identification of different types of gilding, based solely on non-destructive methods, which can be applied to historical samples.

In a first step, fire-gilded samples have been prepared on different on Cu and Ag, respectively. Some of the gildings were produced by a professional goldsmith; another set of samples was produced under laboratory conditions. These samples have been examined with NAA (neutron activation analysis) and SR-XRF (synchrotron radiation induced X-ray fluorescence). First results of these measurements will be presented and discussed (Fig.1.).

![Fig. 1 Hg content of fire gilded samples, determined with both NAA and XRF (preliminary)
P22-Hidden elements: revealing the history of a whiteground lekythos through xray fluorescence spectroscopy

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A close scientific examination of an art object’s surface can also reveal clues about that particular object’s history. To this end, an Athenian whiteground lekythos was studied using xray fluorescence spectroscopy. The lekythos was attributed to the Reed Painter and is dated to 430 BCE, when this style of pottery and decoration was common for funeral vessels.

X-ray absorption measurements performed at the Stanford Synchrotron Radiation Lightsource provided an elemental mapping of the pigments on the white ground. The lack of copper indicates that the black pigments are carbonaceous, rather than Egyptian blue as originally speculated. Iron and arsenic were found in the red outlines, leading to the assumption that the lines were a red arsenic sulfide pigment (realgar). However, line scans revealed that the arsenic is not correlated with the sulfur. The arsenic is correlated with iron, suggesting that the pigment is a red iron oxide that absorbed arsenic. It is possible that the arsenic came from contaminated groundwater and was adsorbed onto the red iron oxide pigment and into the terracotta clay body itself, or that the iron oxide pigments were already contaminated with arsenic when they were applied. Mercury lines (with the appearance of brush strokes) around the hems of the figures’ garments and around the top of the grave stele indicate that additional decorations were present and have now become totally invisible to the naked eye. The most likely explanation for this is that the decorations were done with cinnabar, which degraded and left only trace amounts of mercury. Another possible explanation for the presence of mercury that is not correlated to sulfur is that gilding was once present on this lekythos, since an amalgam of gold is one way to apply and remove gold from a surface. Gilding was applied to lekythoi during this time period and earlier, though usually on raised decorations made with clay slip. Either way, the XRF analysis revealed decorations and details that have since been lost to years of degradation.

Fig. 1 Tricolor plot of mercury (red), arsenic (green), and sulfur (blue) overlaid on a rollout camera image of the lekythos surface.
P23-Technology of production of manganese decorations

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The use of manganese brown paints dates back to early Islamic times [1]. They were applied over lead and tin yellow or white glazes to draw contours and separate colours. Their use expanded to the Mediterranean regions reaching the Christian lands in Europe in the 13th century. The reaction of the manganese pigment with the glaze during firing, gives rise to the formation of various types of manganese containing microcrystallites, which have been identified by micro-XRD with synchrotron light in combination with SEM-EDS, such as kentrolite, Pb\textsubscript{2}Mn\textsubscript{2}(Si\textsubscript{2}O\textsubscript{7})O\textsubscript{2}, braunite, Mn\textsubscript{6}SiO\textsubscript{12}, haussmanite, Mn\textsubscript{3}O\textsubscript{4}, bustamite, (Ca,Mn)\textsubscript{2}Si\textsubscript{2}O\textsubscript{6}. The presence of these microcrystallites is certainly related to the materials used, methods of application and firing temperatures. However, little information about how the presence of specific crystallites and the technology are known.

In order to obtain information about the relationship between the presence and distribution of specific crystallites across the glaze and the methods of production a series of replication of manganese brown decorations which include the use of various manganese pigment mixtures, methods of application and firing temperatures are performed.

As the crystals formed are very small (10 to 50 μm) and appear distributed across the glaze thickness (200-300 μm) a combination of micro-analytical techniques including Optical Microscopy, SEM-EDS and μm-XRD are used. Polished thin cross sections of the glazes were obtained over a glass substrate; the thin sections (~30 μm thick) are mounted over a thick glass holder, and therefore, a high energy (30 keV), high brilliance and small probe size (=15x15 μm\textsuperscript{2}) and a CCD area detector are used in order to obtain maps of the crystalline compounds present in the decoration layers.

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P24-Discrimination of complex layer structures from artworks coatings by μSR-FTIR and μSR-XRD

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Either in the making or on subsequent restorations, the application of varnishes and colored or transparent layers to cover metal foils, has been constant practice throughout history. These coatings are thin (less than 30 μm thick) and often present a complex composition [1]. This could be because of the wide materials variety used, the artistic technique utilized which sometimes include more than one coating layer or the alteration processes associated or also to the subsequent restorations that may leave residues.

A thorough reference materials study is essential for the study, including their composition, degradation processes and identification of distinctive markers as often various substances coexist in the layers, but a good analytical procedure is also crucial.

Two requirements are essential, namely a very small beam (a few μm) and a suitable sample preparation (thin enough to work in transmission geometry which gives the maximum resolution and data quality). In particular the combination of μSR-FTIR and μSR-XRD together with SEM/EDS analyses is an optimal methodology to identify these compounds as well as their distribution across the multi-micro-layered samples. A good discrimination capability is the key to the understanding of the data. An optimal sample preparation method consist in slicing cross sections of the samples of 2 μm thickness for μSR-FTIR and 20 μm for μSR-XRD [2]. μSR-FTIR measurements have been performed at MIRIAM beamline B22 at Diamond Light Source with a slit size of 15x15 μm and 10x10 μm and μSR-XRD at Xaloc beamline at Alba Synchrotron with ~12 keV and 6x50 μm or 6x6 μm footprints.

Various case studies will be presented. Examples shown will include: the identification of older varnishes below synthetic resins associated to later restorations and analysis of metal foils coatings either containing mixed colorants or of multilayered structures.


References:
P25-Herbivorous or Carnivorous?

An X-ray fluorescence analysis of a cracked tooth from the theropod dinosaur Troodon.

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A cracked fossilized tooth from Troodon, a small theropod dinosaur, was collected from the Dinosaur Park Formation in Dinosaur Provincial Park, Alberta, Canada. Synchrotron micro X-ray fluorescence spectroscopy with 2-dimensionsal element mapping technique was used to investigate the elemental distribution within this tooth. In addition to the main elements P, Ca, and trace metal elements Mn, Fe, Ni, Cu, Zn appeared in the tooth, much higher yttrium concentration was observed in the cracks within the tooth. Considering the natural source of yttrium, a question was raised – is Troodon carnivorous or herbivorous? To understand environmental effects during the fossilization, a series of soil samples were collected from the different locations around the site where the fossilized tooth was collected. Their X-ray fluorescence spectra were measured for comparison. Detailed experimental study will be presented and discussed.
P26-Preliminary Analysis of Zn and S in Bone and Teeth Surrounding Pathological Lesions

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Working of the hypothesis that element distributions in tissues may be affected by nearby bacterial infections, the distribution of several elements including Zn and S were mapped in areas of bone adjacent to dental abscess lesions caused by anaerobic bacteria. Areas of healthy bone were mapped for comparison. The samples were drawn from several archaeological collections housed at the University of Western Ontario at the time of the study. The distribution of Zn and S do not correlate with the presence of the neighbouring lesion. However, Zn and S do show specific patterns of distribution not related to the pathology. Zn distribution appears to be related to areas of active bone deposition/formation within all the samples studied.

S K-edge XANES spectra show several oxidations states of S are present in the bone samples. The proportions of the oxidation sates vary within the sample. Together these studies highlight the potential of micro-XANES and XRF mapping in unravelling the chemical speciation and role of elements in bone biochemistry at the sub-tissue level.
P27-Measuring crystal characteristics of intact archeological human second metacarpal bones as a function of individuals’ age at death

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Bone consists of nanoplatelets of carbonated hydroxyapatite (cAp) embedded in a matrix of collagen. Mammalian bone is replaced during life, i.e., remodeled, and x-ray diffraction of powdered bone has shown cAp lattice parameters, crystallite size and microstrain change as the individual grows older. Destructive sampling, however, is rarely an option for bones from archeological collections, and use of high energy x-rays (E > 40 keV) allows all of the bone volume to be interrogated, even in human bones with diameters > 1 cm, and samples large ranges of reciprocal space, i.e., many hk.l reflections.

We report results of high energy x-ray scattering (wide angle – WAXS – and small angle – SAXS) obtained on human second metacarpal (Mc2) bones from Roman era and from medieval era Britain. Results from two Mc2 from each of three age (at death) cohorts are to those from a modern Mc2 and two synthetic hydroxyapatite (hAp) phantoms. We seek to answer the following questions:

1. How much has diagenesis altered the bone material and changed quantities measured by x-ray scattering (cAp lattice parameters; crystallite size, microstrain; collagen D-period)?
2. If diagenetic changes are minor or non-existent, do the above quantities change with age in Roman and medieval era populations, and are these changes similar to those observed for bone from modern sedentary populations?

WAXS and SAXS patterns were collected simultaneously (Sector 1, Advanced Photon Source, APS) using the Hydra detector array and a CCD detector, respectively, and 71.7 keV x-rays, a 50 μm wide beam and a 4.5 (6.5) m WAXS (SAXS) detector-sample separation. Each Mc2 (and phantom) was sampled at ~20 equally spaced positions across the distal metaphysis, with each series repeated after 180º rotation about the sample’s long axes. This allowed correction of geometric effects (irregular Mc2 cross-section, 1 mm < path length < 10 mm through bone). Rietveld refinement was applied to the WAXS patterns, and cAp lattice parameters and crystallite size and microstrain determined. From SAXS, collagen D-period was quantified. Intra- and interspecimen variations are discussed as well as conclusions about the questions mentioned above and recommendations for future work.