

THE PHYSICS OF PARCHMENTS

Experimental and historical approaches

A multidisciplinary workshop

University of Namur
Arsenal, Salle « Le Grenier »
Rue Bruno 11 - 5000 Namur – Belgium

28 & 29 November 2019

Useful information

Wifi name (SSID): unamur_events

Wifi password: Parchm3nts

Academics may also use EDUROAM

Contact e-mail during the conference: karin.derochette@unamur.be

Mobile phone: +32 478 441 117

Website: <http://www.pergamenum21.eu/>

Foreword

In the frame of the University of Namur **Pergamenum21** project, the conference will gather for the first time in Belgium experts in scientific and historical studies on parchments. It will be interdisciplinary and international, with speakers from United Kingdom, Germany and France.

The focus will be on the physics of the parchment material and the synergy between experimental and historical approaches, at the boundary between sciences and humanities. The sessions will be organized according to the different disciplines and techniques involved (history, bio-archaeology, physical optics, analytical methods, conservation and restoration), with emphasis on synergies between these approaches.

The conference will favour networking of various projects currently running across Europe, where researchers of a relatively small but active community just begin to know each other and to collaborate.

Scientific committee

- Matthew COLLINS (Copenhagen Univ., Denmark & Cambridge Univ., United Kingdom)
- Olivier DEPARIS (UNamur)
- Angel M. FERNANDEZ ALVAREZ (UNamur)
- Xavier HERMAND (UNamur)
- Jean-François NIEUS (UNamur)
- Etienne RENARD (UNamur)
- Nicolas RUFFINI-RONZANI (UNamur & Université Versailles-Saint-Quentin, France)
- Johan WOUTERS (UNamur)

Organizing committee

- Paul BERTRAND (UCLouvain)
- Catherine CHARLES (UNamur)
- Olivier DEPARIS (UNamur)
- Karin DEROCHETTE (UNamur)
- Xavier HERMAND (UNamur)



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Thursday 28 November 2019 programme

12:30 Welcome & registration

12:50 Prof. Olivier Deparis (UNamur, Belgium)

| Introduction

Plenary session | Chairman T. Falmagne (Luxembourg National Library, LU)

13:00 Prof. Matthew Collins (University of Cambridge, UK)

| Medieval libraries as archives of domestication

14:00 Dr Nicolas Ruffini-Ronzani, Prof. Xavier Hermand, Prof. Olivier Deparis (UNamur, Belgium)

| Autopsy of a scriptorium: Orval parchments put to the test of bio-archaeology

14:45 *Coffee break*

Session "Analytical techniques" | Chairman: Johan Wouters (UNamur, Belgium)

15:00 Dr Laurianne Robinet (CRC, FR)

| Retrieving knowledge from the Chartres fire-damaged medieval manuscripts

15:45 Angel M.F. Alvarez (UNamur, Belgium)

| Animal species identification in parchments using Principal Component Analysis (CPA)

16:30 *Coffee break*

Session "Conservation & Restoration" | Chairman: Catherine Charles (UNamur, Belgium)

16:45 Dr Lieve Watteeuw (KUL, Belgium)

| Historical Parchment Restoration. Reflections on materials, techniques and degradation

17:30 Prof. Andrea Pataki - Hundt (Cologne Institute for Conservation Sciences, DE)

& Rest. M.A. Marie Kern (LWL Museum, Munster, DE)

| Accelerated Ageing of Parchment - investigation of a low-heat approach

19:30 *Gala dinner*



Friday 29 November 2019 programme

08:45 Welcome coffee & croissants

Session "Imaging techniques" | Chairman: Laurianne Robinet (CRC, FR)

09:00 Gaël Latour (Univ. Paris-Saclay, FR)
| The potential of nonlinear optical microscopy to non-invasively quantify the degradation state of historical parchments

09:40 Julie Bouhy (UNamur, BE)
| Imaging birefringence in parchments

10:10 Dr Andreas Janke (University of Hamburg, DE)
| Multispectral Imaging of Medieval Music Manuscripts

10:50 *Coffee break*

Session "Animal skins" | Chairman: Matthew Collins (University of Cambridge, UK)

11:10 Dr Annelise Binois (Université de Paris Panthéon-Sorbonne/Université de Copenhague)
| Exploring past animal disease through the biological study of parchment

11:55 Dr Richard Thomas (University of Leicester, UK)
| The changing size and shape of livestock in medieval and post-medieval England

12:40 *Lunch break*

Session "Historical studies" | Chairman: François Bougard (IRHT Paris)

14:00 Prof. Jean-François Nieuws (UNamur, Belgium)
| Medieval parchment charters : Orval and beyond

14:45 Dr Richard Thomas (University of Leicester, UK)
| Zooarchaeological evidence for a possible parcheminerie at Green Shiel, Lindisfarne

15:30 Zina Cohen (BAM, Berlin & EPHE Paris, FR)
| Parchment production from Antiquity to Medieval time using Jewish manuscripts from the Dead Sea Scrolls and from the Cairo Genizah

16:15 *Coffee break*

16:30 Round table & discussions

17:00 **Concluding remarks | Paul Bertrand (UCL, Belgium)**

17:30 *Farewell drink*

INVITED SPEAKERS



Dr. Annelise BINOIS-ROMAN is a French zooarchaeologist currently employed as an assistant lecturer in Environmental Archaeology at the University of Paris 1 Panthéon-Sorbonne and as a post-doctoral fellow on the ERC Beasts-to-Craft project at the University of Copenhagen. After graduating as a veterinarian from the École Nationale Vétérinaire d'Alfort (France) in 2004 and working as a mixed-practice vet for six years, she turned to archaeology, obtaining an MSc (2011) and a PhD (2017) in Environmental Archaeology at the University of Paris 1 Panthéon-Sorbonne.

At the crossroads between her degrees, her doctoral dissertation focused on the identification and diagnosis of mass mortality events in archaeological livestock in Europe, especially in the Roman and Medieval periods.

Her research interests encompass all topics pertaining to animal health and disease in past societies, including, but not limited to, animal paleopathology. Her current project aims at exploring the physical and molecular traces of past animal disease in medieval parchments, in order to document livestock health in the Middle Ages and its impact on parchment production and trade.

Julie BOUHY is physicist, graduated (2017) from the University of Namur, Belgium. She carries on a PhD work on the optics of parchments in the physics department of the University of Namur.

She develops optical methods for characterizing structural properties of parchments. Her current interest are in the study of optical birefringence.



Prof. Matthew COLLINS FBA is a Niels Bohr Professor at the University of Copenhagen and professor of biomolecular archaeology at the University of Cambridge.

Formerly he worked at University of York where he founded BioArCh, a collaboration between the departments of biology, chemistry and archaeology (BioArCh: Biology Archaeology, Chemistry).

His research focuses on the persistence of proteins in ancient samples, using modelling to explore the racemization of amino acids and thermal history to predict the survival of DNA and other molecules. Using a combination of approaches (including immunology and protein mass spectrometry) his research detects and interprets protein remnants in archaeological and fossil remains.

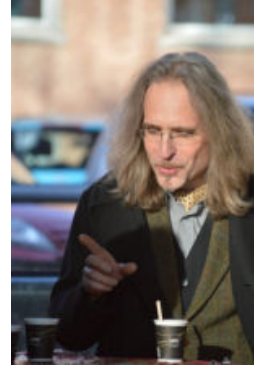
With former PhD student Dr Mike Buckley he developed ZooMS (Zooarchaeology by Mass Spectrometry), a way to rapidly identify bone and other collagen based materials using peptide mass fingerprinting.

In 2014, he was elected a Fellow of the British Academy, the United Kingdom's national academy for the humanities and social sciences.

Prof. Olivier DEPARIS is Professor in physics at the University of Namur, Belgium. He is member of the Namur Institute of Structured Matter (NISM) and the Heritages-Transmissions-Inheritances Institute (PaTHs).

Since 1993, he develops both theoretical and experimental researches in photonics, with an increasing interdisciplinary character for the last 15 years.

His present researches encompass light-matter interactions in living organisms, photonic crystals, solar light harvesting devices, bioinspired materials, multifunctional nanostructured coatings and parchment studies.



In 2014, he set up a transdisciplinary research group (Pergamenum21) at the University of Namur dedicated to parchment studies. In 2017, he received a grant from the Foundation Roi Baudouin to carry researches on a selection of manuscripts and charters of the Orval Abbey, Belgium.



Dr. Ángel FERNANDEZ was born in Santiago the Chile. He earned a dual doctorate between the University of Angers (France) and the Federico Santa María University from Valparaíso (Chile) in 2016.

Currently, he is a postdoctoral researcher at the physics department of the University of Namur, Belgium, where he carries on researches in photonics applied to parchments, under the frame of a transdisciplinary project entitled Pergamenum21.

In December 2018, King Baudouin Foundation rewarded his research with the Jean-Jacques Comhaire prize.

Dr Andreas JANKE is a musicologist (postdoctoral researcher) at the Centre for the Study of Manuscript Cultures in Hamburg, Germany.

He has worked on liturgical books and music manuscripts containing polyphonic settings of the Ordinarium Missae up to ca. 1430.

Other interests are the music of the Trecento and the recovery of music in damaged manuscripts.



Marie KERN is a graduate of the education program for Conservation and Restoration of Artworks on Paper, Archive- and Library materials at the State Academy of Art and Design in Stuttgart, where she obtained her Bachelors (2013) and Master Degree (2015).

From 2015, she worked as a postgraduate intern at the paper conservation department of the Staatsgalerie Stuttgart.

She is now employed as a conservator for paper-based artworks at the LWL Museum für Kunst und Kultur in Münster, North Rhine Westfalia.



Gaël LATOUR is an Associate Professor at Paris-Sud University. He works on the development of optical imaging techniques for the characterization of the biological tissues but also for the investigation of cultural heritage artefacts. During his PhD, he developed an experimental full-field OCT setup dedicated to the characterization of paintings and music instruments. Since few years, he is working on nonlinear optical microscopy to characterize collagen mainly in biological tissues (skin, cornea, tendon...) but also in cultural heritage artefacts. One part of his study is to establish the interest and the potential of nonlinear microscopy to investigate artworks (music instruments, parchments...) in close collaboration with conservation scientists.

Prof. Jean-François NIEUS is Senior Research Associate of the Belgian National Fund for Scientific Research (F.R.S.-FNRS) at the University of Namur, where he chairs the research centre *PraME – Pratiques médiévales de l’écrit* (member of the research institute *PaTHs – Patrimoines, transmissions, héritages*). His main focus is on secular governance in the high Middle Ages, primarily in northern France and the “Low Countries”, with a particular emphasis on the development of pragmatic literacy in the field of princely lordship and signorial administration.



Dr. Laurianne ROBINET was trained in chemistry and then specialized in analytical chemistry in France. She carried out a PhD research on the deterioration of historic glass between universities in France and in Scotland. As a conservation scientist, she has worked in different museums and conservation laboratories in France and in UK before joining the Research Center for Conservation (CRC) based at the Natural history museum in Paris in 2011, where she is in charge of the leather and parchment department. Her research interest concerns the characterization and the conservation of skin-based artefact, in collaboration with scientists from different fields, conservators and curators, as well as the development of non-invasive techniques.

Dr. Nicolas RUFFINI-ROZANI is a postdoctoral researcher in medieval history at the University of Versailles – Saint-Quentin-en-Yvelines (France) and a member of the “Pratiques médiévales de l’écrit” research centre at the University of Namur. He obtained his PhD in 2014 at the University of Namur, where he also worked as a postdoctoral fellow of the FNRS until 2017. His current projects are carried in collaboration with scientists from different fields and curator of medieval collections. They are dealing with the analysis of the composition of medieval writing materials, such as parchment, iron-gall inks (“EVAS project”, supported by the DIM “Matériaux anciens et patrimoniaux”), and seal matrixes (“ADEMAT project”, supported by the Fondation des Sciences du Patrimoine). He is also deeply interested in medieval literacy, political history, and digital humanities.



Dr. Richard THOMAS is an archaeologist based at the University of Leicester with expertise in zooarchaeology (the analysis of animal bones from archaeological sites).

His research centres on the study of human-animal relations, primarily in the medieval and early modern period and palaeopathology (the study of animal health, disease and injury).



Prof. Dr. Andrea PATAKI-HUNDT acts since 2017 as professor at the Cologne Institute for Conservation Sciences (CICS) at the TH Köln at the book and paper conservation programme.

From 1998 to 2017, she was research assistant of the conservation laboratory at the graduate conservation education programme for conservation of works of art on paper, archive- and library materials at the State Academy of Art and Design Stuttgart, where she also obtained her diploma (1997) and her PhD (2005).

In the year 1998 she was an advanced fellow at the Walters Art Museum Baltimore, support by the Academic Exchange Programme (DAAD). From 2007 to 2009 she conducted a two-year postdoctoral research programme funded by the Landesstiftung Baden- Württemberg. In spring 2008 she was invited as a museum guest scholar at the J. Paul Getty Museum, Los Angeles. She gives lectures for students and professionals national and worldwide in the fields of aerosol application, adhesives and parchment conservation.

Prof. Lieve WATTEEUW is head of the Book Heritage Lab – KU Leuven and senior staff of Illuminare, Centre of the study of Medieval Art. She is conservator of graphic materials and art historian. Her academic activity is concentrated on medieval manuscript illumination, book production, prints and drawings, art-technical research, and conservation-preservation of graphic materials.

Prof. Watteeuw lectures at the Faculty of Arts and the faculty of Theology and coordinates the research on the Codex Eyckensis, the BRAIN ArtGarden, Fingerprint Projects and the 3Pi Project (FWO, Diagnosis of Papyrus – Parchment – Paper Manuscripts through Advanced Imaging).



ABSTRACTS FOR TALKS

Medieval libraries as archives of domestication

Matthew COLLINS

*Niels Bohr Professor of Palaeoproteomics University of Copenhagen, CSS, Øster Farimagsgade 5, Bygning 7.101,
(Floor 1 Rm 1), 1353 København K, Denmark*

*McDonald Professor of Palaeoproteomics, University of Cambridge, McDonald Institute for Archaeological
Research, 2.4 West Tower, Downing St, Cambridge CB2 3ER, UK*

Of all the crosses of sheep Mr. Coke has tried, none strikes him so much as that of a New Leicester tup and a Norfolk ewe (Note, some years back). In 1803 I found his opinion changed; from much experience; so that he prefers the cross of a South Down ram on a Norfolk ewe to that of a Leicester ram." (Young, 1813).

County reports from the Board of Agriculture 1793–1822 document the enthusiasm with which gentleman farmers in Britain explored the effects of crossbreeding regional landraces. It was Robert Bakewell's realization a little more than a decade earlier that, by keeping males and females separate and breeding 'in-and-in', he could retain preferential traits and remove less desirable characters.

Parchment, a secondary product of domestication, derived from the skins of animals define the frontier between Western European history and prehistory. Turned into parchment they became the primary medium for our knowledge of pre-modern Western European culture. They were the most extensively used and best-preserved writing material in Europe before the piecemeal adoption of paper in the late Middle Ages and the early Modern Era.

With the object in hand, Jiří Vnouček's craftsman's eye can recognize the skill of the skinner and parchmenier, and can virtually reassemble the hide to estimate the size (age) of the animal. What else can we learn? The distribution of hair follicles suggests fleece type and breed, whilst medullation of the fibers or the wounds from parasites can both give clues to the season of slaughter. The biomolecules (DNA and proteins) in skins inform on species, type/breed, and sex of the animals used.

As well as being storehouses of assembled medieval knowledge, parchment can be considered as archives of domestication and animal management.

Autopsy of a scriptorium: Orval parchments put to the test of bio-archaeology

Nicolas RUFFINI-RONZANI, Xavier HERMAND, Olivier DEPARIS

University of Namur, Belgium

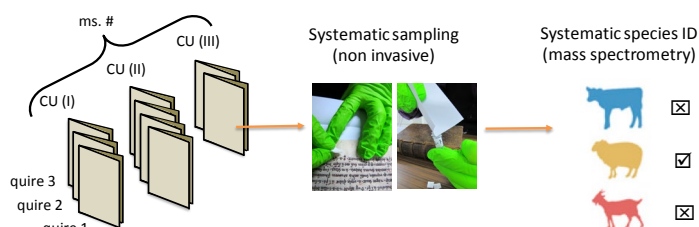
The Orval project, supported by the Fondation Roi Baudouin, is a collaborative transdisciplinary research project on parchments from the Orval Cistercian Abbey (1131). The goal is to explore the modes of production of manuscripts book and charters in the Middle Ages by comparing results of classical scholar studies and experimental sciences, in particular in the field of bio-archaeology. The question of the animal species used to produce medieval parchments is the first to be addressed here. From which species were Orval manuscripts and charters made of? Do we observe chronological



evolutions, differences between manuscripts produced in Orval's scriptorium (mainly active in the thirteenth century) or those acquired by the Abbey through purchases, donations, or legacies? Can we establish links between the types of skin used for parchment production and codicological characteristics or codices' contents? In other words, can we do an autopsy of the Orval scriptorium? Fullness and coherence of the available corpus motivated our choice of Orval's parchments for such a systematic study. With 85 manuscripts and 59 charters written on parchment, Orval's collection is one of the top-ten best-preserved medieval library collections in the Belgian area. Moreover, several manuscripts are regarded as major pieces by both historians and art historians (for instance, the autograph manuscript of the *Gesta episcoporum Leodiensium* written by Giles of Orval). About $\frac{3}{4}$ of the Orval corpus, representing 68 manuscripts, was made available for the study thanks to a cooperation agreement with the Luxemburg National Library where most of today remaining manuscripts of Orval library are preserved. All these manuscripts were previously subject to a codicological expertise by Thomas Falmagne (cf. full catalogue of Orval manuscripts published in 2017). Detailed bibliographical notes are available therein for each manuscript together with consensus date and provenance.

In this communication, only the results we obtained on manuscripts are reported, those obtained on charters are left for another communication. The 68 manuscripts, forming together 118 codicological units, were sampled using a non-invasive triboelectric sampling method originally developed at the University of York (BioArCh laboratory). Systematic sampling was realized at the level of manuscript quires, one sample (recto of the first folio of a quire came from the same skin).

A sample consisted of collagen-containing eraser crumbs collected by gentle rubbing of the parchment near the folio edges. The total number of samples amounted to 1491. This led to the largest data set reported so far on a single medieval corpus. Samples were analyzed by



proteomic methods for animal species identification based on collagen peptide analysis using mass spectrometry (MS) instruments. All the samples, except those from ms. #22 (catalogue index), were analyzed (peptide mass fingerprinting) using a high-throughput MALDI-TOF MS instrument at BioArCh laboratory. Samples of ms. #22 as well as samples from all charters were analyzed (peptide sequencing) at MaSUN facility (University of Namur) using a LC-ESI MSMS instrument. The results of the analyses were recorded in a database and scripts were written in order display species ID information (at the quire level) according to codicological unit labels and manuscript catalogue indexes. These results were then interpreted from an historian's perspective.

By focusing on the use of parchment in connection with the animal species, some specific features of the manuscripts produced in the scriptorium of Orval in the first and the second third of the thirteenth century will be examined. A first question we will address is whether manuscripts attributed to Orval by scholars are different from manuscripts made in other scriptoria during the same period. In addition, we will try to identify some general trends in the way the medieval ecclesiastical institutions made use of different types of parchment in their manuscript production. This will imply to examine several features of the manuscripts (types of quires, "consistency" of the codicological units, size of the manuscripts, etc.) in the light of parchment species statistical data.

Retrieving knowledge from the Chartres fire-damaged medieval manuscripts

Laurianne ROBINET

Centre de Recherche sur la Conservation des Collections(CRCC), Paris, France

On May 26, 1944, during an allied bombing on the city, a fire irremediably destroys almost half of the manuscript collection of the Chartres library. Of the 518 original medieval manuscripts, at least 215 survived the fire but remained in very variable states, from almost intact to entirely calcined.

Considering the fragility of the fragments, a digitization campaign was started in 2006, so the documents could be available again for research. However, in some manuscripts the alteration by the fire and the water caused the writings to become partly or totally unreadable, preventing their study.

For that reason, historians working on these documents raised the need for a simple imaging solution that would improve the readability of the manuscripts and could be implemented in the digitization process.

In 2017, a project explored the use of different analytical techniques and recent scientific developments to retrieve information from these heavy altered documents. The presentation will discuss the different technical approaches carried out on the Chartres fire-damaged medieval manuscripts to recover writings legibility, characterize the degradation state of parchment and to identify the animal species.

Despite the advanced degradation state, this work demonstrates that current scientific techniques can still retrieve many information from these manuscripts that were believed to be lost, therefore opening new research horizons.

Animal Species Identification in Parchments using Principal Component Analysis (PCA)

Ángel Martín FERNANDEZ ALVAREZ¹

¹ *Department of Physics & Heritages, Transmissions, Inheritances (PaTHs) Institute,*

University of Namur, Belgium.

angel-martin.fernandez@unamur.be

Amongst the most fascinating documents from the cultural heritage are parchments. They are made from processed animal dermis and used as writing support during centuries. The identification of the animal species is a fundamental information for both scholars and conservators [1]. In order to obtain such information, analytical methods based on genetics (proteomics) are used, with increasing progresses towards non-invasive protocols [2]. With less reliability, visual inspection often fails in the correct identification of the animal species, especially in historical parchments.

In this context, we introduce a non-invasive and novel optical method for identifying animal species in parchments. It is based on the processing and analysis of parchments spectra. Moreover, it is easy, straightforward to implement, robust and reliable [3]. It is noteworthy to mention that the method enables animal species identification in parchments without resorting to any molecular level analysis. Rather, it achieves the identification unveiling the “optical fingerprint” of each species via the processing of light scattering spectroscopic data with principal component analysis (PCA) [3]. The method was validated by performing proteomics analysis over 20 historical parchments [3].

The purpose of this talk is to present the new method and investigate two different representations of principal component analysis for identifying animal species in parchments.

[1] S. Fiddyment, et al. “Animal origin of 13th-century uterine vellum revealed using noninvasive peptide fingerprinting,” *PNAS* 112, 15066-15071 (2015).

[2] M. Teasdale et al., “The York Gospels: a 1000-year biological palimpsest,” *R. Soc. Open Science* 4, 170988 (2017).

[3] A. M. Fernandez Alvarez, J. Bouhy, M. Dieu, C. Charles and O. Deparis, “Animal species identification in parchments by light,” *Sc. Rep.* 9, 1825 (2019).

Historical parchment restoration.

Reflections on Materials, Techniques and Degradation

Lieve WATTEEUW

KU Leuven, Illuminare, Center for the Study of Medieval Art, Belgium

In the 20th century, a number of new techniques developed for the restoration / preservation of medieval parchment manuscripts using new synthetic substances. The aim was to protect and stabilize the text, but after several decades, they were drastic side effects, which severely damaged the original parchment material. In the early 20th century, for example, there was the new technique of Zaponizing parchment and archival documents. These methods were particularly hopeful as a method against the acidity of the inks and the degradation of parchment by microorganisms. The technique was developed around 1890 by the chemist dr. E. Schill in the Hygiënisch chemisch Laboratorium of the Prussian War Ministry. After the Second World War, the use of PVC (polyvinyl chloride) was propagated as a new material for the restoration of medieval documents (Mipofolie). Several medieval charters and the 8th century Codex Eyckensis were laminated in the 1950s with the best intentions. However, the rapid aging of the PVC with darkening and hardening put manuscript in serious danger 40 years later. The removal of the PVC foil and the conservation treatment with the parchment pulp technique took four years, while lamination itself probably lasted only several hours in 1957. A third case study is the treatment of a large 15th century architectural design of the St. Pieters Church in Leuven, on a hot vacuum table in 1962, with a dramatic shrinkage of the parchment as result when the temperature was raised to 35°C.

The lack of knowledge of parchment as a very specific material led in the 20th century to improper restoration treatments. They were affecting the structure, physic stability and esthetic appearance of the parchment documents fundamentally.

Accelerated Ageing of Parchment - investigation of a low-heat approach

Marie KERN, Andrea PATAKI-HUNDT, and Jan WOUTERS with contributions by Daniel P. KIRBY

Accelerated or artificial ageing experiments, which strive to simulate the gradual deterioration of materials over time under laboratory conditions, are of special interest to conservators, as they help to understand relevant degradation processes and even predict their long term stability. However, most common setup of dry or moist thermal ageing is difficult to apply to protein based materials such as parchment, due to its inherent sensitivity to heat.

Therefore, an attempt was made to establish an ageing setup that uses only moderate heat and replaces extreme temperatures with electromagnetic radiation (light ageing) and alternating relative humidity as an accelerating factor for the artificial degradation of parchment samples.

Samples of conservation grade limed goat parchment and “artificial” reconstituted parchment made from a cast suspension of bovine collagen fibres; powdered carbonate and a dispersing agent (methylhydroxyethylcellulose) were first subjected to 240 h of light ageing at 1,01 w/m², followed by 120h of dynamic climate ageing at either 30° or 50°C, with rH alternating between 35 % and 75 % every 8 hours.

As parchment retains the complex, collagen-based fibre structures of the animal skin, increasing degradation may affect any level – from the molecular to the macroscopic - within its discrete structural hierarchy. Changes in the materials were therefore observed at different structural levels, using selected analytical tools introduced in the 2017 IDAP (Improved Damage Assessment of Parchment) – project which are commonly available or easily conducted by conservators¹: VIS-Colorimetry, visual fibre assessment of fibre morphologies² (visible markers of deterioration, only performed on the goat parchment), determination of maximum moisture absorption capacity (hygroscopy and porosity of fibres and the fibre network), and shrinkage temperature determined by the MHT-method³ (amount of intact intrafibrillar bonds). In addition, an extract was analysed by MALDI-TOF PMF to gauge its potential in detection molecular degradation.

Both ageing cycles resulted in visible discolouration, an increase of the appearance of morphologies recently linked to oxidative degradation (30°C cycle) and fibres in advanced stages of degradation (50°C cycle). Moisture absorption capacity was slightly increased, though significant differences were found between individual sample pieces. The decrease of hydrothermal stability confirms the increasing loss of stabilizing intrafibrillar bonds with the shrinkage temperature reduced by over 10°C (30° cycle) and to room temperature (50°C cycle) for the goat and up to 9 °C for the reconstituted parchment. PMF analysis indicated an increased desamination of the collagen chain after light ageing as well as the potential formation of collagen degradation products, though the general applicability of this type of analysis to ageing studies will require further research. Though degradation markers were more pronounced with the addition of moderate heat (50°C), the samples aged at close to natural temperatures (30°C) showed the same tendencies. The observations point to oxidative degradation as the main cause of degradation.

The study confirms that photo-induced accelerated ageing at moderate temperatures could prove a viable alternative to thermal ageing for parchment and other heat sensitive organic materials. Though the main degradation process was not identified within the scope of the project, more recent research by the Polish Institute of World Art Studies, Academy of Fine Arts in Warsaw⁴ on the long time stability of different sources of parchment fibres for reconstituted parchment using a similar ageing protocol has confirmed oxidation as the main degradation factor by NIR spectroscopy and amino acid analysis.

¹ IDAP – Improved Damage Assessment of Parchment – Assessment, Data Collection and Sharing of Knowledge, R. Larsen (ed.), Luxemburg: The European Commission, 2007: 17–21

² Nielsen, K.: Visual damage assessment. In: IDAP – Improved Damage Assessment of Parchment – Assessment, Data Collection and Sharing of Knowledge, R. Larsen (ed.), Luxemburg, 2007: 45–51.

³ Larsen, R., Poulsen, D. and Vest, M.: The hydrothermal stability (shrinkage activity) of parchment measured by the micro hot table method (MHT). In: *Microanalysis of Parchment*, René Larsen (Hrsg.), London: Archetype Publications, 2002a: 55–62.

⁴ Liszewska, Weronika: *New methods of leafcasting in the conservation of historic parchments*, Polish Institute of World Art Studies, Academy of Fine Arts, Warsaw 2017

The potential of nonlinear optical microscopy to non-invasively quantify the degradation state of historical parchments

Gaël LATOUR

Université Paris-Sud, Université Paris-Saclay, Orsay, France

Laboratoire d'Optique et Biosciences, Ecole polytechnique, CNRS, INSERM, Palaiseau, France

Parchment is made from an untanned animal skin, which is preserved by liming, scraping and drying under tension. Parchment is very sensitive to heat and water, which causes in extreme case the denaturation of collagen, its main constituent, to gelatin. The measurement of the shrinkage temperature, by differential scanning calorimetry (DSC) or the micro-hot table (MHT) method, is commonly used in the cultural heritage field to assess the degradation state of collagen-based materials. However, these techniques are invasive, as they require a sample, and destructive, which is an issue in the case of some historical artifacts. The aim of this work is to demonstrate the potential of nonlinear optical (NLO) microscopy, also called multiphoton microscopy, to investigate in a non-invasive and quantitative way the conservation state of historical parchments.

NLO microscopy enables three-dimensional (3D) imaging with micrometer-scale resolution based on an intrinsic optical sectioning. A key advantage is its multimodal capability. Two-photon excited fluorescence (2PEF) signals are emitted by a wide range of materials (fluorophores) in historical artifacts with specific absorption and emission fluorescence spectra [1]. SHG signals are specific for dense and well aligned structures such as fibrillar collagen, and vanish for centrosymmetric materials such as gelatin. Accordingly, SHG microscopy provides structural information about the 3D organization of the fibrillar collagen within parchments [2,3]. Notably, it enables *in situ* non-invasive assessment of parchment degradation, which is characterized by the loss of the SHG signal and the onset of a 2PEF signal [2].

In order to quantify intermediate states of degradation, we further implement polarization-resolved SHG (P-SHG) microscopy: the SHG intensity is recorded as a function of the linear polarization orientation of the excitation for each pixel of the image. P-SHG microscopy provides two quantitative information: the main orientation and the degree of orientation disorder at the submicrometer scale. P-SHG images are acquired in a set of modern parchments that were artificially degraded by exposure to dry heat for increasing duration. The degradation state of the collagen in these parchments is assessed using DSC. P-SHG data are in good agreement with DSC measurements and prove to be a complementary investigation tool that requires no sampling. Most importantly, P-SHG is shown to reveal the earliest states of degradation.

Based on these results, this approach is used for the investigation of historical parchments from the Chartres's library, that were exposed to fire and then water as a result of a bombing at the end of the 2nd World War. The visual states of the manuscripts are heterogeneous and P-SHG shows its interest for the local characterization of their conservation states. Moreover, these analyses were also performed to compare restored and unrestored parchments in this collection.

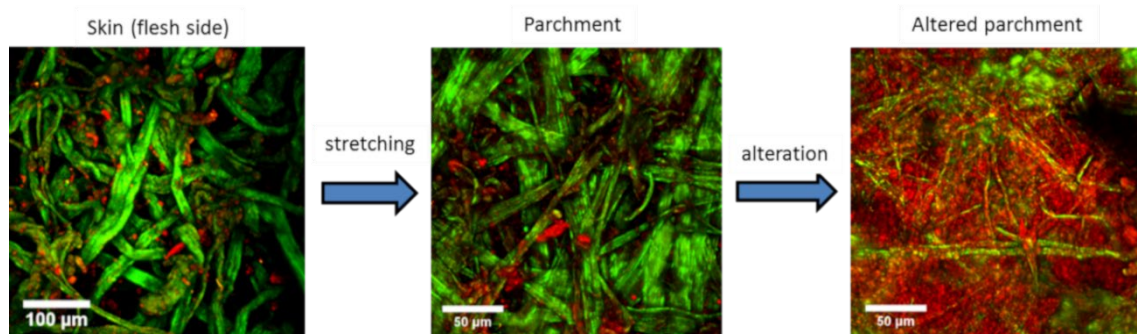


Figure 1: NLO imaging of skin, parchment and altered parchment (flesh side). Two-photon excited fluorescence (2PEF) is shown in red color and second harmonic generation (SHG) in green color.

References

[1] G. Latour et al., *Opt. Express* **20**, 24623 (2012)

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Adapted polarizing microscopy technique for the determination of birefringence patterns in parchments

Julie BOUHY¹, Angel Martin FERNANDEZ ALVAREZ², Catherine CHARLES³, Olivier DEPARIS²

¹Namur Institute of Structured Matter (NISM) ²Heritages, Transmissions, Inheritances (PaTHs) Institute & Department of Physics, University of Namur, Namur, Belgium

³Moretus Plantin University Library, University of Namur, Namur, Belgium.
julie.bouhy@unamur.be

1. Introduction

Conventional as well as nonlinear (SHG or TPEF) optical microscopies are used to investigate the physical properties of soft tissues (arteries, ligaments, skin, muscles) and hard tissues (cartilage, bones) in which collagen plays structural and mechanical functions [1]. Specific collagen fibers assemblies dictate the tissue's properties, such as cornea's transparency, skin's elasticity, bones and tendons' strength. Collagen-based tissues are optically anisotropic and, as such, exhibit both intrinsic and form birefringences. Intrinsic birefringence arises from the tropo-collagen molecules whereas form birefringence originates from hierarchical organization at the macromolecular level (fibrils and fibers). As a matter of fact, birefringence can be used as a tissue's structural indicator. For instance, the determination of the collagen fibers' network structure under normal and pathological conditions is used to find connections with diseases [2]. Another example is the modification of the three-dimensional dermal birefringence due to aging [3]. Polarized light microscopy has long been used to investigate birefringence patterns in biology and medicine, as well as in other domains, such as geology (petrography), materials science (photoelasticity), etc. Most studies use polarized light microscopy to assess qualitatively the collagen arrangements in various tissues. Recently, the technique was expanded to allow quantitative birefringence measurements [4,5]. Compared to conventional optical microscopy, polarized light microscopy offers the advantage of high image contrast, as light transmission through non-birefringent regions is completely blocked in crossed-polarizers configuration.

2. Parchment conservation issues

Parchment originates from the dermis of animal skin, which has been treated to obtain a strong, durable writing support. Its strength results from the organization of a complex network of parallel collagen fibers. Various factors modify this structure, hence, the parchment's optical properties. For instance, gelatinization, a severe degradation often encountered in historical parchments, is responsible for the collapse of the fibrous network, hence the disappearance of birefringence. Parchment is also particularly subject to mechanical stresses from different origins: stress of the skin related to the animal life, stress due to the manufacture process, and stress due to parchment's usage. Uneven stress inherited from skin causes the collagen fibers to have preferential orientations, for instance, along the spine or near the legs. During the manufacture process, drying of the wet skin under tension on a frame changes the initial orientation of collagen fibers. Once the parchment is prepared, its use as a writing support induces structural modifications (bends, damages). Storage conditions (vertical or horizontal book position, relative humidity, pollutants) have also significant impact. The study of the resulting birefringence patterns is interesting for conservators and curators since it can help them determining the state of parchment's degradation, and understanding the impact of repairs techniques. The goal of the present study is to measure the spatial distribution of birefringence (retardance and slow axis orientation) in parchments. For this purpose, we adapted a technique originally developed by Shribak and Oldenbourg [4], which involves single-wavelength measurements of two-dimensional birefringence and image processing algorithms. The method, which relies on the use of five polarization settings and image processing, allows extraction of both birefringence magnitude and slow axis orientation in each pixel. The non-invasive and contactless features of this technique are advantageous in the context of parchment studies.

3. Experimental set-up

The experimental set-up is built around a polarizing optical microscope (BX53-P, Olympus) with polarizing condenser removed and a mirror added in order to redirect the laser beam toward the sample and a polarization-grade plane achromat objective (Fig.1). The birefringence measurement requires a stable, bright and monochromatic light source, here a 633-nm HeNe laser (HNLS008R-EC, Thorlabs). In the original set up [4], a high-pressure mercury arc lamp was used with an interferential filter (12-nm bandwidth) to obtain a quasi-monochromatic light at 546 nm. In general, the choice of the wavelength depends on the sample's absorption and fluorescence properties. In the case of parchments, the absorption is lower at 633 nm than at 546 nm.

4. Application to parchment studies

Parchments conserved at the Moretus Plantin university library (Namur, Belgium) were made available for the study. Among them, an English deed (1682) was examined (Fig. 1). Preliminary observations of damages (Fig. 1a,b) and bends (Fig. 1c,d) were made using the unmodified microscope in transmission mode and crossed-polarizers configuration. In the damages zone, strong changes of birefringence patterns were observed as the sample stage was rotated (Fig. 1a,b) whereas, in the bend zones, no such patterns were observed (Fig. 1c,d). A bend (e.g. the lowest horizontal bend, thick arrow) was identified as a stripe on the image by focusing alternately inside and outside the bend. Outside this stripe, on both sides of it, brighter and colorful birefringence patterns were observed and changed upon rotation. The absence of such patterns in the bend could be due to damages of the parchment's fibrous structure upon folding, which would result in a loss of anisotropy, hence birefringence. Interestingly, a reduced contrast between inside and outside of the bend stripe was noticed in less severe bends. This trend still needs to be confirmed quantitatively by performing spatially resolved birefringence measurements.

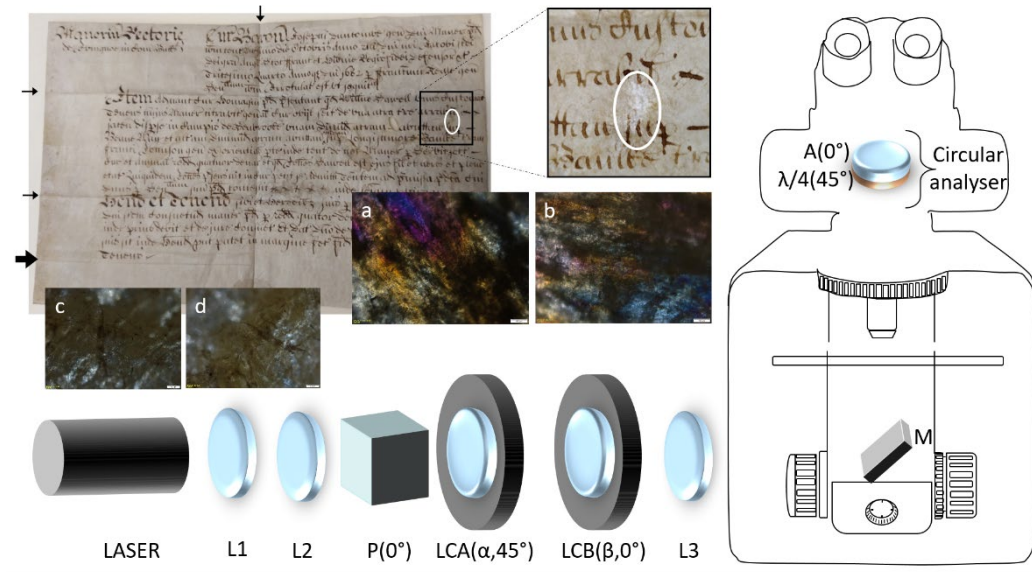


Fig. 1. A 633-nm He-Ne laser light beam is collimated by two lenses L1 and L2, and elliptically polarized by a linear polarizer (P) and two voltage-controlled liquid crystal compensators LCA and LCB, with slow axes at 45° to each other. Five elliptical polarizations are set by tuning liquid crystals retardation values. The beam is focused by a lens (L3) on the sample (S) and redirected by a mirror (M) towards the circular analyzer, made of a quarter wave-plate ($\lambda/4$) and a linear analyzer (A). The five microscope images obtained are processed in order to extract sample's birefringence pattern. The photograph of the historical parchment under test shows bends (indicated by arrows) and damages (circle). Inset: polarized light microscopy images of damage (a,b) and lowest horizontal bend (c,d).

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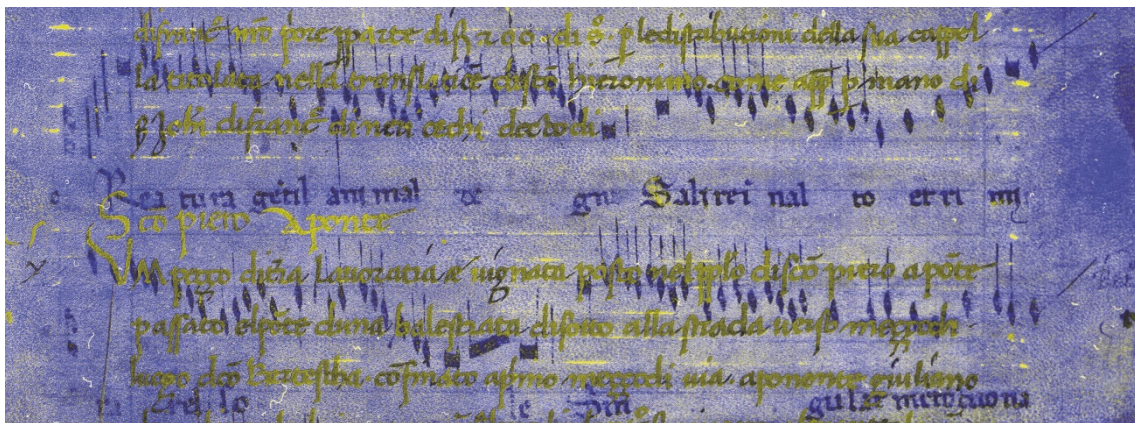
Multispectral Imaging of Medieval Music Manuscripts

Andreas JANKE

University of Hamburg, Germany

Medieval parchment manuscripts with notated music have been erased just as other manuscripts, but so far no palimpsest research has established itself within musicology that goes beyond the study of individual fragments or manuscripts.

For a long time, only a few aids were used to make lost music visible again. It was only through the use of state-of-the-art multispectral photography that previously unreadable music manuscripts could be analyzed, deciphered and finally used for editions and performances.



In my paper, I will present the basic procedure of multispectral imaging and then demonstrate the advantages and limitations of this method with different examples. In addition, difficulties will be discussed that musicologists face when working with recovered music palimpsests. Among them are testimonies that were written between the end of the 9th century and the 15th century, with different notation systems, as well as different liturgical and secular genres.

Exploring past animal disease through the biological study of parchment

Annelise BINOIS

Université de Paris Panthéon-Sorbonne, University of Copenhagen

Just as our scars tell of some of our life events, animals skins can record evidence of past disease through the presence of lesions, of scars and of pathogen remains. The analysis of parchment can therefore provide a source of invaluable information for the understanding of past livestock health and disease.

This paper presents a historical overview of the nature, symptoms and chronology of the main diseases of cattle and sheep in the Medieval and Post-Medieval periods, and explores what evidence they may have left behind in the skins of their victims and whether those skins could have been used by the parchment industry.

The analytical methods best suited to each type of evidence and the issues that can be encountered are then discussed. We conclude by presenting a research project aiming to investigate the impact of the 1279-1280 scab epidemic on British parchment production.

The changing size and shape of livestock in medieval and post-medieval England

Richard THOMAS

University of Leicester, United Kingdom

Over the past 40 years, the analysis of animal bone measurements from archaeological sites in England with medieval and early modern occupation has incrementally shed new light on spatial and temporal variation in the size and shape of domestic livestock. These studies have revealed increases in livestock size occurring from the 14th to the 18th centuries; but the picture is complex.

There is a great deal of regional variation, with outlying sites generally experiencing later developments than central localities. The earliest evidence for size change in cattle occurs in the early 14th century and may reflect restocking practices following the outbreaks of murrain in the first half of that century. Subsequent size increases in livestock size may have occurred as a consequence of the changing agricultural emphasis and/or innovatory practice in the wake of the Black Death and the increasing commercialization of animal farming, as the food requirements of an expanding urban centers.

By the later 17th century, there was a growing understanding of the principles of heredity and more careful selection of breeding stock was advocated by some authors; however the emphasis appears to have remained on crude size rather than any specific characteristic of productivity. This changes from the 18th century, and is evidenced in the zooarchaeological record by a decrease in animal bone size.

This paper presents a review of the zooarchaeological evidence for changing livestock size and shape change in England from the 13th century to the 19th century, and interprets the evidence within its social and economic context.

Medieval parchment charters: Orval and beyond

Jean-François NIEUS, Nicolas RUFFINI-RONZANI

University of Namur, Belgium

Charters (or deed, acta) remained the standard mean for recording legal transactions throughout the Middle Ages. Millions of them have been preserved all over Europe, especially for the period after 1100. They represent a major source of information for medieval historians, who have been carefully calendaring and studying them for centuries (a dedicated scientific discipline, called “diplomatics”, was created in the seventeenth century).

From the seventh century onwards, charters and related administrative documents were exclusively written on parchment. Even after the introduction of paper in Europe in the thirteenth and fourteenth centuries, parchment remained the most appropriate writing support for legal documents, thanks to its much greater solidity and durability. However, very little is known to this date about the animal species used for making charter parchment, or about the specific treatments that the preparation of charter parchment possibly necessitated (in other words, was it different from book parchment?). Medieval textual sources do not help (or nearly so), and, apart from isolated initiatives in the 1980s, modern scholarship failed to investigate the issue further.

This presentation will be twofold. In the first part, we will discuss the common views on charter parchment conveyed by diplomatic manuals, and reframe the (few) available data on the animal species that were used in various periods/regions/milieus, as provided by both tentative visual assessments (essentially made in the 1980s and 1990s) and proteomic analyses (since 2015). In the second part, we will present the results of new proteomic analyses conducted on a sample of 59 original charters from Orval Abbey written between 1173 and 1363 (mostly from the thirteenth century). Evidence on the evolution of the thickness of charter parchment through time will also be commented on.

Zooarchaeological evidence for a possible Parchmenerie at Green Shiel, Lindisfarne

Richard THOMAS, Petur HANSEN, Matilda HOLMES, Sian HOLMES, Deirdre O’SULLIVAN

University of Leicester, United Kingdom

The site of Green Shiel is located on the island of Lindisfarne off the west coast of Northumberland. The site is thought to be contemporary with the early monastic complex established in AD 635 by King Oswald, which became renowned following the creation of a shrine to St Cuthbert and later, the production of the Lindisfarne Gospels, until it was abandoned in the 9th century.

Excavations at the site between 1984 and 1997, by a team from the University of Leicester, revealed five linked buildings close to the north shore. Dating evidence is restricted to several 9th century coins (c. AD 835-71), but the site is thought to have been occupied between the 7th and 9th centuries.

Initially, the complex was interpreted as monastic farmstead; however, preliminary analysis of the animal bone assemblage entertained the possibility that this could have been used to produce vellum from calf skins for the scriptorium.

In this paper, we present a fuller analysis of the faunal remains and reconsider the evidence.

Parchment production from Antiquity to Medieval time using Jewish manuscripts from the Dead Sea Scrolls and from the Cairo Genizah

Z. COHEN^{1,2,3}, I. RABIN^{2,3}

¹ *Ecole Pratique des Hautes Etudes (EPHE), Laboratoire SAPRAT, 4-14 rue Ferrus 775014 Paris, France*

² *Bundesanstalt für Materialforschung und -prüfung (BAM), Unter den Eichen 87, 12205 Berlin, Germany*

³ *Universität Hamburg UHH, Alsterterrasse 1, 20354 Hamburg, Germany*

The discoveries of two major collections of Hebrew manuscripts have changed our knowledge of Antique and Medieval Jewish world and deepened our understanding of the manuscripts' production. Although these two collections are not equally well-known outside of the scholarly world, they possess several similarities that invite comparison. These two collections, namely, the Dead Sea Scrolls and the Cairo Genizah, contain a large number of Jewish manuscripts but are separated by at least a thousand years. The first one dates to the period between the 3rd century BCE and 1st century CE, while the second corresponds to a broader time period from the 9th to the 19th century CE. Among several other subjects of interests, the study of these manuscripts offers an opportunity to understand and compare the production of writing materials during these two periods.

As a part of the Qumran project conducted at the BAM Federal Institute for Materials Research and Testing in Berlin between 2007 and 2010, the Berlin scientists succeeded in reconstructing the treatment of hides and discovered that at least two distinct de-hairing techniques co-existed at the beginning of the common era. One method involved de-hairing with inorganic salts and led to the production of pale parchments that resemble Medieval parchment and might have even be its predecessor. The second technique involved de-hairing with the help of vegetable matter. In these cases, the resulting parchment was usually tanned, whereby it was not possible to clarify whether tannins were already present in the de-hairing mixture or applied to the surface only. The latter type of the parchment was, in fact, a hybrid between parchment (since it was dried under tension) and leather (the tanning was quite considerable). In contrast, a single de-hairing method by means of lime solution existed in the Middle Ages.

This reconstruction of workmanship concerning animal hides in Antiquity raised doubts about the applicability of the current definition of parchment, which is based on a production technique known from the Middle Ages only, to the antique skin-based materials. In the Genizah, we have found so far only two types of skin-based writing supports: non-tanned parchment and leather. Interestingly, only scrolls were found to be written on leather.

In this presentation, we will illustrate and compare the parchment production techniques in Antiquity and the Middle Ages building a bridge between these two periods.

ABSTRACTS FOR POSTERS

Iron-Gall Inks in Fourteenth-Century Chartres: The EVAS Project

Nicolas RUFFINI-RONZANI

University of Namur, Belgium

Thanks to new non-invasive processes, it is now possible to “enter” the medieval writing materials and to determine their physicochemical properties.

In 2018, the EVAS project (“Évaluer l’activité d’un scriptorium”, funded by the DIM “Matériaux Anciens et Patrimoniaux”) aimed at developing some non-invasive analysis techniques of iron-gall inks (or “black inks”) which were used in medieval manuscripts.

A corpus of fourteenth-century registers and rolls from the city of Chartres (France) was examined and analysed by researchers from the Centre de recherche sur la Conservation, the Institut de Recherche et d’Histoire des Textes, and the University of Versailles – Saint-Quentin.

By revealing which metallic sulphates were used to make black inks and in which proportions, XRF-analysis has made it possible to distinguish between different inks that look similar.

This is a new way for understanding the writing process of documents, and thus the organization of the medieval chanceries. The objective of the poster is to present the methods and the results of the research.

Evaluation of the effects of the X-rays irradiation on collagen matrix: a new proposed disinfection method

M. VADRUCCI¹, Cristina CICERO^{2,3}, G. De BELLIS^{2,3}, F. MERCURI⁴

1|Particle Accelerator for Medical Application Laboratory, Italian National Agency for New Technologies, Energy and Sustainable Economic Development ENEA, via E. Fermi, 45, 00044, Frascati, Italy.

2|Department of Astronautical, Electrical and Energy Engineering (DIAEE), Sapienza University of Rome, via Eudossiana 18, 00184, Rome, Italy.

3|Research Center for Nanotechnology applied to Engineering (CNIS), Piazzale Aldo Moro 5, 00185, Rome, Italy.

4|Department of Industrial Engineering, University of Rome Tor Vergata, via del Politecnico 1, 00133, Rome, Italy

Bio-deterioration is a frequent preservation problem for library materials. Microorganism can cause a series of damages on the writings supports and specifically, in the case of parchment, they can cause chemico-physical alterations inducing chromatic alteration or discolouration of the collagenous support. In the worst case they can affect the surface layers of the membrane sheet causing the loss of the precious written text and decorative apparatus of which the parchment is the vehicle. During the centuries, different disinfection treatments have been made up to preserve bio-deteriorated library materials such as biocides, chemicals, UV and γ radiation. However, these various treatments can result to be toxic and unsafe because of their capability to affect the chemico-physical integrity of the collagen molecule inducing irreversible deterioration. Recently, the use of the X-ray radiation, to reduce and inhibit the microbial growth has been proposed proving to be proficient, at suitable doses, in reducing the microbial growth without altering the structural stability of the collagen molecule. An experimental apparatus designed at ENEA (Frascati), namely the REX irradiation facility, has been employed to treat a series of biodeteriorated parchment samples demonstrating to be efficient to stop the microbiological activity [1,2].

In order to evaluate the damaging effects of the X-rays irradiation on parchment, different techniques have been employed. At first, a series of parchment samples, irradiated with increasing doses of X-rays, have been investigated by the Light Transmitted Analysis (LTA). This analysis allows to evaluate the preservation condition of the parchment by analyzing the so called hydrothermal denaturation of its fibers, a phenomenon related to the thermal unfolding of the collagen proteins. LTA measurements provides the value of the characteristic “denaturation temperature” for each specimen providing a parameter characteristic of its preservation conditions [3].

In order to evaluate the effect of the irradiation treatment on parchment’s structure at the nanoscale, two microscopy techniques, namely Atomic Force Microscopy (AFM) and Scanning Electron Microscopy (SEM), have been employed. The use of these two microscopic techniques helped in the characterization of the surface effects of the radiation on the collagen networking enabling the characterization of morphological and structural changes eventually induced by the radiation treatment.

These results obtained by this study endorse the possibility to use the X-rays radiation to recovering biodeteriorated parchments since it reduce the bio-deterioration while, at specific doses of irradiation, it preserves the collagen structure.

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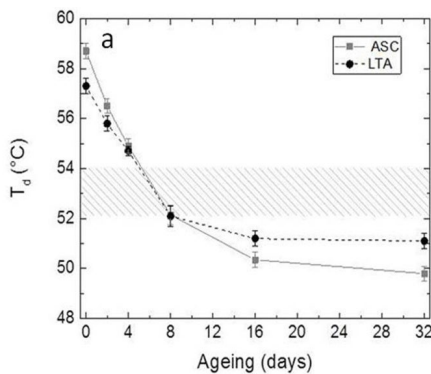
Adiabatic Scanning Calorimetry, Light Transmission and Imaging analysis of Collagen Deterioration in Parchment

U. ZAMMIT, C. CICERO, F. MERCURI, S. PAOLONI, N. ORAZI, C. GLORIEUX* and J. THOEN*

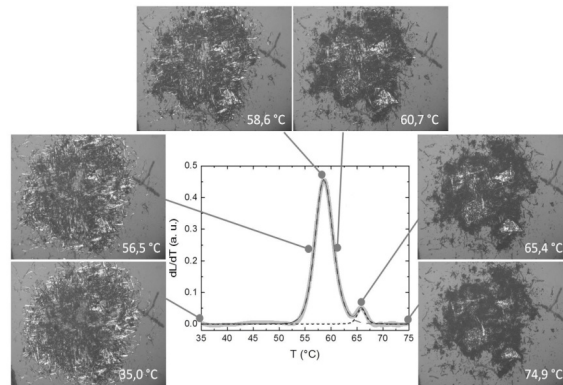
Dipartimento Ingegneria Industriale - Universita' di Roma 'Tor Vergata' - Rome – Italy

*Soft Matter and Biophysics, Department of Physics and Astronomy, KU Leuven, Celestijnenlaan 200D box 2416, B-3001 Leuven, Belgium

A new characterization technique, Light Transmission Analysis (LTA)¹, is presented for the study of the deterioration in several artificially aged modern parchment samples together with measurements by Adiabatic Scanning Calorimetry (ASC)², a very sensitive and reliable method for such kind of study. The technique consists in measuring the temperature dependence of the light transmitted through the sample and then by performing its temperature derivative. This results in peaked features similar to those found for the specific heat. The comparison of the results obtained by the two techniques led to the validation of LTA as a novel simple method capable of recording the entire collagen denaturation path of the investigated samples. In fact, the values of the parchment denaturation temperature, T_d , determined by the two techniques were found to be very similar and so was the trend of the change of T_d with the ageing.



Denaturation temperature Vs ageing for the native collagen population. The striped band



Polarization microscopy imaging for non-aged parchment fibres during the collagen denaturation stages

Moreover, polarization microscopy imaging could also be performed simultaneously with the optical transmission characterization, and enabled us to perform a direct correlation of the morphology changes of the parchment with the different stages of the collagen denaturation.

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PARTICIPANTS LIST

Name	First name	Affiliation	E-Mail Address
BARROS	Elisa	Atelier du Papier	elisa.rands@gmail.com
BELLA	Rania	UMons	Rania.BELLA@student.umons.ac.be
BENAZET	Elena		elena-benazet@outlook.com
BERTRAND	Paul	UCL	paul.bertrand@uclouvain.be
BINOIS	Annelise	University Paris 1 Panthéon-Sorbonne	abinois@gmail.com
BONAERT	Sibylle	Etudiante UNamur	sibbonaert@hotmail.com
BOUHY	Julie	UNamur	julie.bouhy@unamur.be
BURRIDGE	Claire	The British School at Rome	cpsb2@cam.ac.uk
CHARLES	Catherine	UNamur	catherine.charles@unamur.be
CHEVALIER	Gaëlle	La Cambre	gaellechevalier1204@gmail.com
COHEN	Zina	BAM & EPHE & Hamburg University	zina.cohen@outlook.fr
COLLINS	Matthew	University of Cambridge, UK	matthew@palaeome.org
DE GROOT	Henk	UL retired (Inden witten Hasewint)	zhdg@xs4all.nl
DEBRY	Laura	KIK-IRPA preventive conservation	lauradebry@hotmail.com
DEMOLDER	Juliette	ULiège	j.demolder@hotmail.be
DEPARIS	Olivier	UNamur	olivier.deparis@unamur.be
DEROCHETTE	Karin	UNamur	karin.derochette@unamur.be
DIEU	Marc	UNamur	marc.dieu@unamur.be
DING	Yang	UNamur	yang.ding@unamur.be
DUBUISSON	Bastien	University of Luxembourg - UNamur	bastien.dubuisson@uni.lu
FALISE	Eugénie	ARTBEE Conservation sprl	eugenie.falise@gmail.com
FALMAGNE	Thomas	Bibliothèque nationale Luxembourg	t.falmagne@ub.uni-frankfurt.de
FEDERICI	Carlo	University Ca' Foscari Venezia	cfederici@unive.it
FERNANDEZ ALVAREZ	Ángel	UNamur	angel-martin.fernandez@unamur.be
FRANÇOIS	Juliette	ENSAV La Cambre	Info@juliettefrancois.be
FRIPPIAT	Thierry	UNamur	thierry.frippiat@unamur.be
GERSTEN	Tatiana	Bibliothèque royale de Belgique	tatiana.gersten@kbr.be
HERMAND	Xavier	UNamur	xavier.hermand@unamur.be
HOUSSIAU	Laurent	UNamur	laurent.houssiau@unamur.be
JANKE	Andreas	University of Hamburg	andreas.janke@uni-hamburg.de

Name	First name	Affiliation	E-Mail Address
KERN	Marie	LWL Museum für Kusnt und Kultur	Marie.Kern@gmx.de
LADOUCE	Mathieu	mathieu.ladouce@student.unamur.be	UNamur
LATOURL	Gaël	Université Paris-Sud	gael.latour@u-psud.fr
LEBECQUE	Fiona	Archaeological Society of Namur	fiona.lebecque@lasan.be
LOBET	Marie	UNamur	marie.lobet@unamur.be
MERCURI	Fulvio	University of Rome "Tor Vergata"	mercuri@uniroma2.it
MINEO	Emilie	UNamur	emilie.mineo@unamur.be
MORGANE	Plateau	KU Leuven / freelance	morgane.plateau@kuleuven.be
MORTIAUX	Nathan	UNamur	nathan.mortiaux@student.unamur.be
MOUCHET	Sébastien	UNamur & University of Exeter	sebastien.mouchet@unamur.be
NIEUS	Jean-François	UNamur	jean-francois.nieus@unamur.be
NOLMANS	Axelle	UNamur	axelle.nolmans@unamur.be
PAPIN	Elodie	CRULH - Université de Lorraine	elodie.papin@univ-lorraine.fr
PASCALICCHIO	Francesca	Free researcher, ex-icrcpal	franci.pasca@libero.it
PATAKI-HUNDT	Andrea	Technical University Cologne	andrea.pataki@th-koeln.de
PIGNOT	Matthieu	UNamur	matthieu.pignot@unamur.be
PILO	Thomas	UMons	thomas.pilo@student.umons.ac.be
POUMAY	Yves	UNamur	yves.poumay@unamur.be
RAES	Martine	UNamur	martine.raes@unamur.be
RENARD	Etienne	UNamur	etienne.renard@unamur.be
ROBINET	Laurianne	CRC	lrobinet@mnhn.fr
ROY	Nicolas	UNamur	nicolas.roy@unamur.be
RUFFINI-RONZANI	Nicolas	University of Versailles	nicolas.ruffini@unamur.be
RUZZIER	Chiara	UNamur	chiara.ruzzier@unamur.be
RYDER	Tina	University of Colorado	Christina.Ryder@colorado.edu
SIERRA CASTILLO	Ayrton	UNamur	ayrton.sierracastillo@unamur.be
SOLIDORO	Cristina	University of Bologna	cristina.solidoro2@unibo.it
STRIVAY	David	ULiège	dstrivay@uliege.be
THOMAS	Richard	University of Leicester	rmt12@leicester.ac.uk
THYS	Noé	La Cambre	noellethys@gmail.com
VADRUCCI	Monia	ENEA	monia.vadrucci@enea.it
VAN DER VLIST	Ed	Koninklijke Bibliotheek	ed.vandervlist@kb.nl
VAN GEYTS	Estelle	ENSAV LA CAMBRE	estelle.vangeyts@lacambre.be
VANDOOREN	Pauline	La Cambre	paulinevandooren9@gmail.com
VOUE	Michel	UMons	michel.voue@umons.ac.be
VNOUCEK	Jiri	The Royal Danish Library	jiv@kb.dk
WANG	Tao	UNamur	tao.wang@student.unamur.be
WAROQUIER	Romain	UNamur	romain.waroquier@unamur.be
WATTEEUW	Lieve	KU Leuven	lieve.watteeuw@kuleuven.be
WOUTERS	Johan	UNamur	johan.wouters@unamur.be
YERDAY	Noam	La Cambre	noambathel@hotmail.fr
ZAMMIT	Ugo	University of Rome "Tor Vergata"	zammit@uniroma2.it



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The physics of parchment :
experimental
and historical approaches

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