

Mélanie Machowski<sup>1</sup>, Helena Calvo del Castillo<sup>1</sup>, Cécile Oger<sup>1,2</sup>, David Strivay<sup>1</sup>

1 I.P.N.A.S., Centre Européen d'Archéométrie, Université de Liège, Belgium. Contacting authors : mmachowski@student.ulg.ac.be, hcalvo@ulg.ac.be  
2 Bibliothèque, Faculté de Philosophie et Lettres, Université de Liège, Belgium

## Introduction

The Nizet Manuscript is a XVIIIth century book conserved at the University of Liège (Belgium). It contains the genealogy of four families coming from Verviers (Belgium) and is illustrated with many heraldries and some drawings. The metallic colours used to imitate gold and silver have induced an important degradation of the paper, particularly in the case of the silver imitation, which leads to the propagation of the stains on several folios. Moreover, both metallic pigments are also degraded and sometimes present a colour different from the original one.

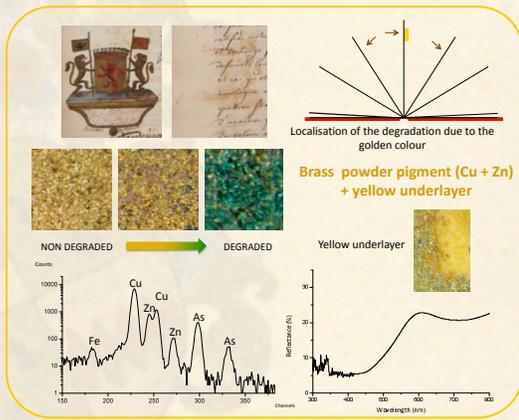
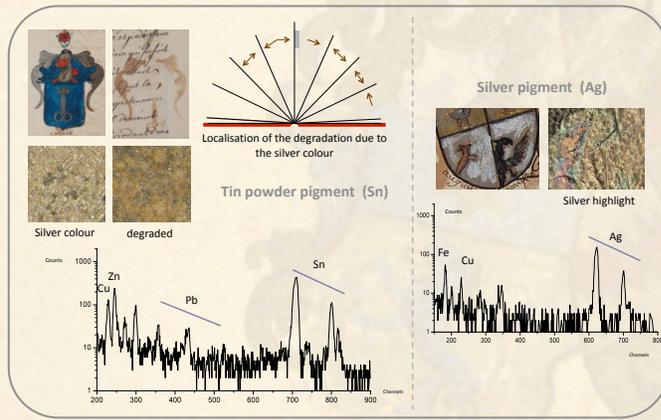
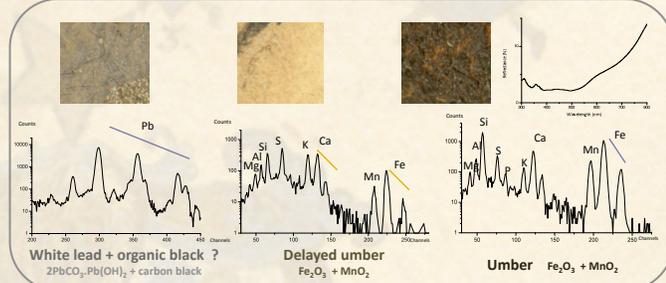
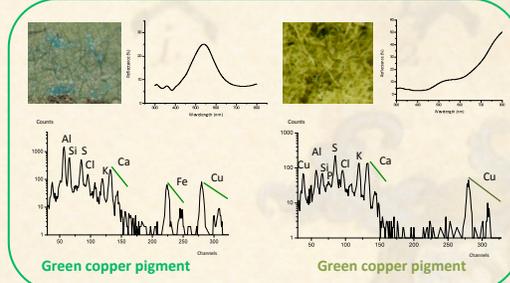
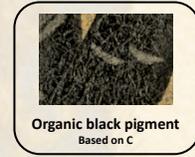
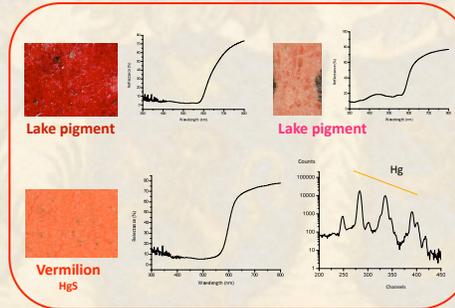
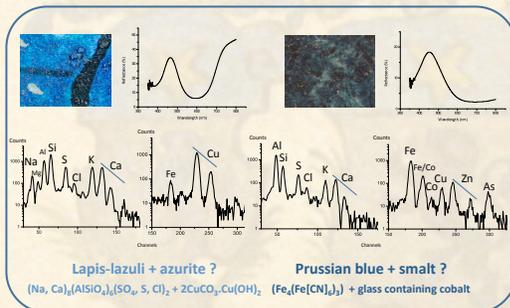
## Aims of this research

- 1) Identification of the palette used to do the heraldries.
- 2) Identification and explanation of the mechanisms of degradation of the paper.

## Analytical techniques

- Macroscopic observation, observation under UV light.
- Stereomicroscope Olympus SZX9 9.5X- 85.5X.
- UV-visible spectroscopy: StellarNet EPP2000C, UV-Vis Hamamatsu light source
- PIXE: IPNAS Cyclotron, 3MeV proton beam,  $i \leq 0.5$  nA, beam  $\Phi = 0.8$  mm. Working distance 13mm. Si(Li) Sirius e2V detector (low energy) supplied with He flux and, Ultra LEGE GU0035P Canberra with 50 $\mu$ m Al absorber (high energy) each @ 40° to beam direction.
- EDXRF mapping: Portable EDXRF device, Moxtek Magnum X-Ray tube Ag anode @ 35k & 200 $\mu$ A, beam  $\Phi = 1$  mm. Working distance 21mm, Ketek GmbH SDD placed @ 49° to beam direction.

## First results



## First conclusions

- 1) Identification of some pigments, currently used at the XVIIIth century<sup>1</sup>.
- 2) The XRF mapping showed no migration of ions of both metallic pigments.
- 3) Regarding the metallic degradation phenomenon:
  - i. The *Kupferfraß* phenomenon<sup>2</sup> could explain the degradation induced by the brass pigment (golden colour is based on copper and zinc).
  - ii. The tin content must play a role in the paper degradation induced by the silver colour. We assume there are interactions between the pigment, the binder and the paper.
  - iii. Influence of the ink on the degradation must be explored, as it accentuates the formation of the stain and the discoloration of both metallic pigments.

## Future work

Molecular analyses (Raman and FTIR) will be done to identify all the pigments and understand the role of tin in paper degradation processes.

Whereas copper and iron degradation of paper have been thoroughly studied, the role of tin remains an unexplored subject in the scientific literature.

**Acknowledgments:** Aymeric Holsbeek, Mathieu Clar, Saïd Rakkaa (IPNAS technicians), Thomas Dupuis, François-Philippe Hocquet and Grégoire Chêne (colleagues).  
**References:** 1 *Artists' Pigments* (3 vol.), 2 BANIK, G., STACHELBERGER, H., MAIRINGER, F., VENDL, A., PONTALHO, J., *Analytical Investigations of the Problem of "Kupferfraß" in Illuminated Manuscripts*, in *Mikrochimica Acta [Wien]*, 1 (1981), p. 49 – 55.