

Highlight #7: DISORDERED AND MULTISCALE MATERIALS and METHODOLOGIES

Revealing the techniques of medieval artists by X-ray analyses

Cultural Heritage Sciences are developing a strong interest in understanding the skills and techniques used by early craftsmen and artists. A rapidly growing number of scientific investigations are now yielding a wealth of information on the history of art and techniques. These investigations also benefit the fields of restoration and conservation by providing detailed knowledge of the materials used and their degradation over time.

As part of the "PATRIMALP" project (a Cross Disciplinary Programme of the IDEX Université Grenoble-Alpes) several teams covering art history, physico-chemistry, numerical sciences and art restoration are involved in the study of painted works bearing specific decorations called "applied brocades" produced in the Duchy of Savoy at the end of the Middle Ages. These artefacts are of scientific interest for each of the disciplines involved, thus promoting interdisciplinarity.

The applied brocades are decorations in light relief which aimed at imitating, on a painted or sculpted support, the silks embroidered with gold or silver threads worn by the nobility during medieval times. Originating in northern Europe, this complex polychrome decoration technique quickly spread to works produced in the rest of Europe during the xvth and xvith centuries. Analyzing these decorations which consist of a complex stacking of materials of different natures (organic, inorganic, metallic...) and different crystalline states and thicknesses, often covered by late overpainting, pose a real materials-science challenge (Fig. 1).

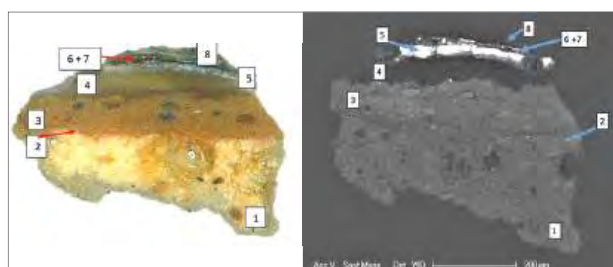


Fig. 1: Typical stratigraphy of a half-mm size brocade sample (at top: optical microscopy; below: electron microscopy), from the 15th century Pietà of Montrottier castle, Lovagny, France. Layer compositions from combined analyses are:

- 1) gypsum
- 2) vermillion
- 3) second filling layer: saponified oil and pigments
- 4) first filling layer: beeswax
- 5) tin oxides
- 6) organic glue
- 7) gold foil and silver chloride
- 8) highlighting, organic layer

Our strategy was to perform systematic non-invasive investigation of a large corpus of 17 statues from the Savoy Duchy, using a portable instrument combining X-ray fluorescence and X-ray diffraction. Based on these analyses, selected micro-samples could then be taken and submitted to non-destructive synchrotron tomographic measurements, providing more precise and detailed information. These data were complemented with optical and Scanning Electron Microscopy observations and infrared and Raman spectroscopy on sacrificed micro-samples.

Our first X-ray measurements were made on a portable instrument from the Laboratoire d'Archéologie Moléculaire et Structurale (Paris). We then developed our own instrument, called "MobiDiff", which is now used in several collaborative research projects within PATRIMALP (Fig. 2).



Fig. 2: Analysis of the polychromy of a medieval sculpture (Saint Jean Baptiste, early xvith century, Musée Savoisien, Chambéry) using our X-Ray instrument "MobiDiff".

Our investigations show the variations of the materials used, and their stacking within a brocade, which could reveal the knowhow of local workshops or craftsmen and provide markers to follow the diffusion of artworks at the regional scale. For example, the material used to fill the tin foil relief and to transfer it to its support was often found to consist of two distinct layers, one being made of beeswax, the other of saponified oil and pigments. In some cases, the gilding was made of zwischgold, a mixture of gold and silver, rather than pure gold. We could also observe the effect of time to heavily degrade the original brocades: the tin metal foil is always observed as a mixture of tin oxides (romarchite and cassiterite), while the silver metal from the zwischgold gilding is transformed to silver chloride and sulfide. These observations help to reconstruct the original appearance of the decorations (which may be hardly detectable today) using computer graphics, and thus provide crucial information to the restorers.

This work was presented in the exhibition: "Pietà - Dans l'atelier des sculpteurs savoyards à la fin du Moyen Âge" at the Musée-Château, Annecy, from December 2021 to March 2022.

We dedicate this article to Alain Prat, who died in October 2021, in appreciation of his valuable work on the design and the construction of the MobiDiff instrument.

Reference

P. Martinetto, N. Blanc, P. Bordet, S. Champdavoine, F. Fabre, T. Guiblain, J.-L. Hodeau, F. Lelong, O. Leynaud, A. Prat, E. Pouyet, E. Uher, Ph. Walter, "Non-invasive X-ray investigations of medieval sculptures: New insights on "applied tin-relief brocade" technique", *J. Cultural Heritage* 47, 89 (2021).