Alteration of gildings on mediaeval mural paintings

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Abstract

Numerous metallic decorations are found on Romanesque mural paintings. Generally, the metallic leaf has not survived on the wall due to poor environmental conditions provoking their degradation. However traces of fixing agents (mordants) can be detected by UV fluorescence. On the suspected ancient gilded zones, when samples are taken away, analysis by FTIR and SEM/EDS allows us to define the kind of metal (Sn, Au, Ag …) and the gilding technique.

Furthermore, alterations of gilded mural paintings have been observed on experimental samples made by a restorer following the recipes of mediaeval treatises. The samples were submitted to accelerated ageing and colour change analyzed.

Keywords: Gildings, wall paintings, alteration, accelerated ageing

Introduction

Numerous examples of gilding have been found on mediaeval mural paintings. These metallic decorations were applied a secco, by means of an organic binder, which explains their fragility and poor preservation. The gilding techniques in the Middle Ages are described in ancient treatises [Théophile, XIIthC., Cennino Cennini, XIVth.]. There are mainly two techniques: by distemper and by mixtion. In the first case, the pigment is mixed with a proteinic organic binder (glue) which allows the metallic leaf to adhere to the wall. In the second technique, the metallic leaf is fixed by means of a lipidic binder (linseed oil) with added siccative (litharge, red lead, lead white).

The gildings are fragile elements with often only traces remaining. They are sensitive to the numerous factors of degradation, in particular their environment, to which they have been subjected for centuries, and hence these traces of gilt are today difficult to reveal. Mostly, only the layer containing the organic binder is detectable through its fluorescence [Mounier et al., 2009]. Indeed fluorescence indicates the addition, by means of an organic binder, a restoration or a gilt detail. In this last case, several metals may have been employed: gold, silver, or tin. We can also find several metals on the same painting, in order to organize into a hierarchy the elements of the iconography or to create diversified metallic effects [Mounier et al., 2009]. Sometimes, the gold is placed over a tin or silver leaf and also with silver leaf on tin [Mounier and Daniel, 2010].

The causes of the loss of gildings are numerous and connected to the state of preservation of the building (thermo-hygrometric conditions, light, micro-organisms, pollution). We count mainly two causes of change: physical (salt crystallizations which lead to the desquamation of the pictorial layers and the metallic leaves) and chemical (the organic binder degrades and loses its adhesive properties or the metal, in particular silver, deteriorates or darkens). It is these causes which we wish to illustrate here through examples.

Furthermore gilding methods have been recreated according to ancient recipes and their changes reproduced through accelerated ageing of samples and their colour change measured.

Experimentation

Sites

Various sites (churches, chapels, and castles localized in Aquitaine between the 12thC and the 16thC century) where the gilding was identified on murals were chosen (Table 1). The sampling allowed for comparison of the various gilding techniques and to examine their alteration.

Experimental samples

Seven types of gilding were realized according to recipes described in ancient texts (fig 1). Three series serve as references; one is intended for hydro-thermal and the other UV ageing.

Analytical methods

• Colorimetry
The colorimetric study records chromatic variations before and after ageing. The measurements are made in diffuse spectral reflectance and expressed in the colorimetric space CIEL*a*b* 1976, by means of a portable spectrocolorimeter, HunterLab Miniscan XE Plus (model D/8 - S), according to illuminating standard D65 and an observation angle of 10 °. Thirty points are made on the surface of the sample.

Site	Date	Location on the painting	Gilding Metal	Alteration
Chapel of the ancient abbey home in Moissac (Tarn-et-Garonne)	XIIth C.		**Mixtion**	
		Haloes of the Christ and evangelists	Tin	Loss of the metal leaf
Occidental portal of the cathedral Saint-Etienne in Cahors (Lot)	XIIIth C.		**Mixtion**	
		Flowers, fleurs-de-lys	Tin	Blackened Sn
		Haloes	Gold	Traces of gold
Funeral paintings of the Sainte-Anne chapel in the Saint-André Cathedral in Bordeaux (Gironde)	XIVth C.	Sun, rose button	Gold	Loss of gold
		Crown of the Virgin	Silver	Blackened silver
		Stars	Tin	Blackened tin
Saint-Sauveur church in Saint-Macaire (Gironde)	XIVth C.	Broadsword of Apocalypse god	Silver	Blackened silver
Altarpiece of the church of Audignon (Landes)	XVth C.	Apostles symbols	Gold, Tin	Rests of gold, Blackened tin
		Clothes, jewels	Gold	
		Crown	Gold	
		Haloes	Gold	
Oratory of the La Roque Castle in Meyrals (Dordogne)	XVth to XVIth C.	Stars Haloes of the Christ and the Virgin Brooch	Gold, Silver, Tin Gold Silver	Gold well preserved Blackened silver and tin

Table 1 : Presentation of sites from 12th to 16th century in Aquitaine

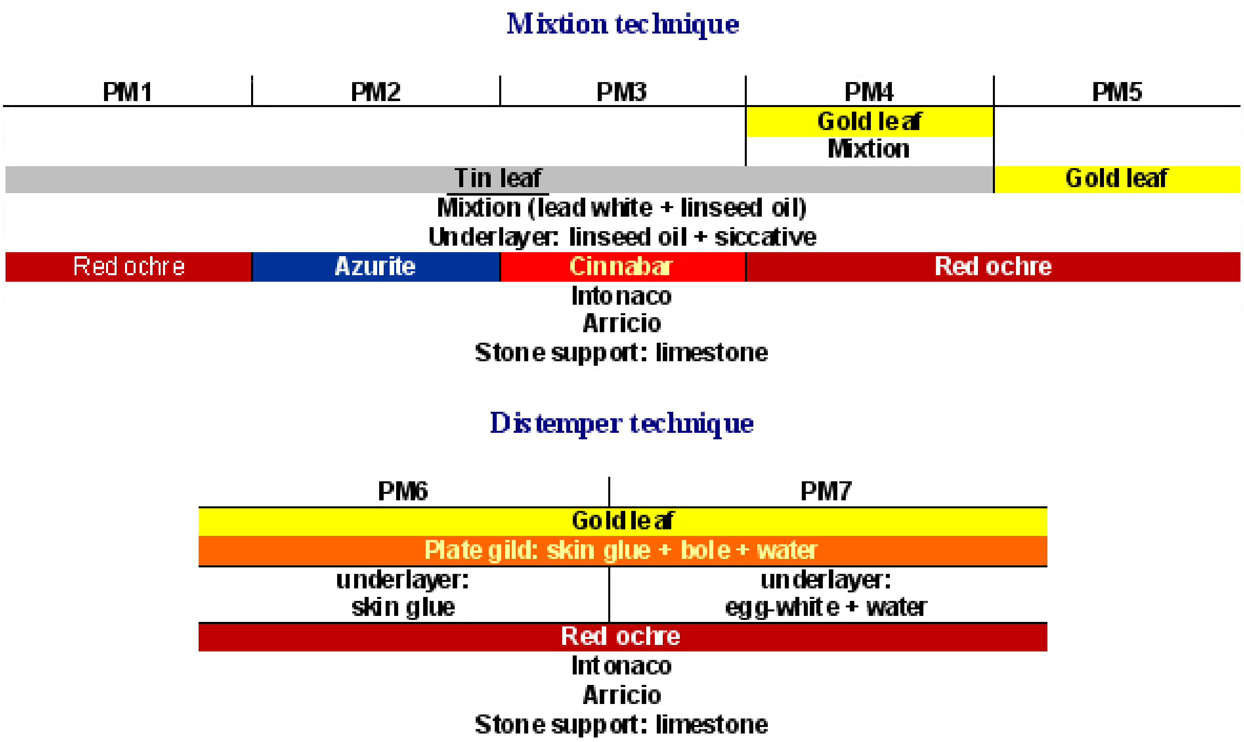

Figure 1. Representation of stratigraphic layers of gildings re-created according to mediaeval recipes of mixtion and distemper techniques.

SEM/EDS

The elementary analyses are achieved by means of an energy dispersive X-ray spectrometer (EDXS, INCA Oxford 300) coupled with a scanning electron microscope (SEM, Jeol JSM-6460LV). The possibility of working under a low vacuum (15 Pa to 20 Pa) eliminated the need to coat the samples which were either analyzed directly, or embedded in a resin (Sody 33), cut transversely and polished to study the layer sequence of mortar, pigments and metallic leaf.

- Raman and FTIR spectroscopy

All the pigments were identified by Raman spectrometry Renishaw RM 2000 with a confocal microscope Leica DMLM, which permits a large range of magnifications for the analysis and a CCD detector. In this study we used an x50 objective and a red laser (633 nm).
The analysis of organic binders was carried out by infrared spectroscopy (FTIR Nicolet Nexus) in attenuated total reflectance (ATR).

Accelerated ageing

Samples were subjected to hydro-thermal and UV light ageing, and compared with reference samples. Ageing conditions already used recently in a study on the alterations of pigments in murals paintings were chosen [Aze, 2005]. Samples underwent 90 cycles of 8 hours each, every cycle being constituted by a succession of 4 climatic phases of a duration of 90 minutes each, with linear transitions of 30 minutes (fig. 2).

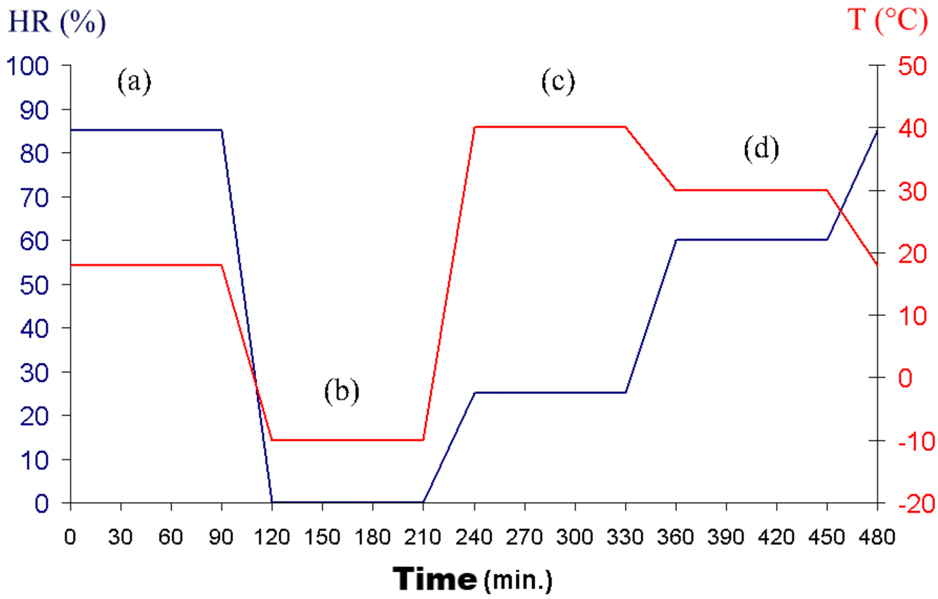

Figure 2. Hygrothermal ageing. Presentation of a cycle of 8 hours with different phases: High humidity (HR=85 %, T=18°C); Low temperature (HR=0 %, T =-10°C); dry heat HR=25 %, T=40°C); wet heat (HR=60 %, T=30°C).

At the same time as the thermo-hygrometric ageing, we observed the evolution of materials through UV light ageing. The device (QUV-Panel of Q-LAB) supplies UVB centred around 313 nm. These wavelength have been used in the study cited above [Aze, 2005] . The ageing lasts 400 hours (more than 16 days) with a constant temperature of 45°C. The spectral irradiance is 1.4 $W.m^{-2}.nm^{-1}$ for a distance of 3,2 cm of the sample with regard to the UV tubes.

Results

Partial or total loss of the gildings

If on certain sites, the gilding no longer survives, and the remnants are invisible to the naked eye only a pigmented layer, mixed with the organic binder remains. These gilt remnants can be detected by fluorescence of the organic binder or by the examination of the surface presenting a thicker aspect. The surviving visible layer is often yellow or red under removed gold leaf or white-grey under tin leaf.

In the Chapel of the ancient abbatial house of Moissac (12thC, Tarn-et-Garonne), zones formerly gilded are located on the haloes of Christ and on the symbols of the evangelists. The metallic leaf has completely disappeared and the coloured layer is very damaged. A white-grey layer is applied to a yellow layer. The aspect is rather thick, and in this zone, only the haloes remain, indicating that they were not applied by the simple fresco technique but by means of an organic binder. The identification of this oil was established by FTIR. It is an oil, mixed with lead white to obtain a mordant, the function of which is to glue the tin leaf. A layer of yellow ochre is directly applied to the wall and serves as support [Mounier, 2006].

This total loss of the metallic leaf can be explained by the conditions of preservation. The variations of humidity and temperature lead to the fragility of fillers and separate the gilts from their support. Furthermore, the crystallization of soluble salts concentrates in the underlying layer in the metallic leaf. Oxalates, in particular, crystallize in the layer where the binder is present, which explains the eventual loss of the metal [Lluveras et al., 2008].

Alteration of the metallic leaves

- Gold

Generally, if the gilt did not disappear, the gold leaf is rather well preserved even if tarnished. In the Saint-André Cathedral of Bordeaux, on the rose buttons located at the end of the beams of the sun representing the glory of God, a gold leaf is employed. It is stuck on a layer of lead white, itself on a under layer of cinnabar and red ochre.

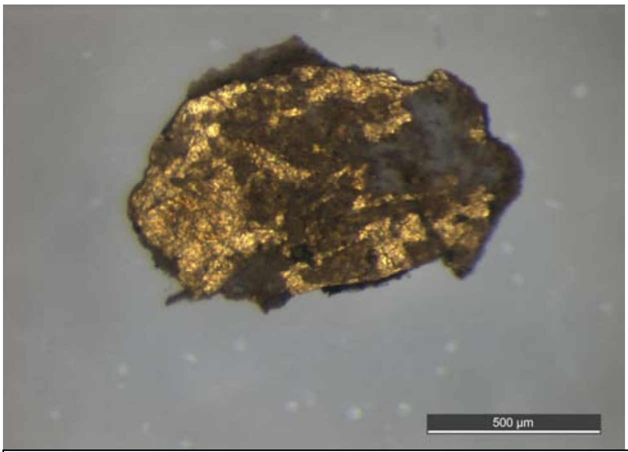

Fig. 3 – Sample taken from the crown of King David on the altarpiece of Audignon. Picture by optical microscopy (x50). We see by places the brilliant and matt gold leaf with zones where the under layer is visible.

Fig. 4 – Sample taken from a star on the murals of the La Roque castle in Meyrals. View by optical microscopy (x12). On the surface, we see mainly a thick, black layer and, on the surface, gold particles.

The altarpiece of the church Sainte-Marie in Audignon (15th C, Landes) which closes the central apse of the present church presents a great variety of polychromies and gilts. The gold leaf is well preserved and visible in numerous places (haloes, crowns, clothes, jewels, attributes (keys, armors and ciborium), pinnacles (fig. 3).

The metal has lost its reflective properties and the leaf is similar to a yellow brown layer. In the oratory of the castle La Roque in Meyrals (16thC, Dordogne), gold gildings are visible on haloes. Some are still very brilliant and the others more matte. The gold leaves from the haloes are stuck with a lipidic binder on a mixtion layer constituted of lead based pigments, minium and lead white or on a yellow ochre.

- Silver

Gildings with silver leaves are always very badly preserved. It is very rare to find the brightness of this metal surviving. Most of the time, the silvery zones become black, with thick and cracked faces (fig. 4). It is the localization of these black zones that indicate the possibility of the presence of gilding. The silver deteriorates mainly in the presence of hydrogen sulphide, an acid produced by the degradation of proteins containing sulfur (oil, natural gas) present in the atmosphere. It forms silver sulphide (Ag2S) which becomes black rather quickly. The chlorine is always associated with the silver, in our results, to form silver chloride (AgCl). The chlorine can come from salts that crystallize in poor conditions of preservation or by unadapted restoration treatments [Duran and al., 2008]. To avoid the blackening of the silver, a varnish layer is often applied, but with time it no longer performs its protective function [Martin and al., 1998].

This type of alteration is present on the funerary paintings of the Saint-Anne chapel of the cathedral Saint-André of Bordeaux (14thC, Gironde). In situ, we observe black zones on the beams of the sun because the silver is altered to black silver sulphide. On the crown of the Virgin, only the mixtion layer remains. It is thanks to the fluorescence of the binder under UV that our sampling was facilitated and allowed the identification of a gilding. Silver was identified on the sun's rays and on the Virgin's crown in the lower register of paintings. Silver was applied to an orange layer of red lead and red ochre. The metallic leaves were stuck by means of a lipidic binder.

On the paintings of the Saint-Sauveur church in Saint-Macaire (14thC, Gironde), remnants of a silver leaf were localized on the two-edged sword which the God of the Apocalypse holds in his mouth. It was nevertheless invisible to the naked eye, because only a grey layer can be observed. The silver leaf is adhered with an oil mordant, containing red ochre and lead white on a white layer of calcite and lead white.

- Tin

The problem of blackening also arises for tin gilding. In the cathedral of Saint André of Bordeaux black stars strewn across the bottom of decorations contain tin, present on a green under layer containing copper and lead based pigments. The alteration product of the tin is not identified but we assume that the tin could be transformed into romarchite (SnO), certainly because of the lipidic binder used to adhere the metal [Duran et al., 2008].

On the portal of the cathedral of Saint-Etienne in Cahors (17thC, Lot), ancient gilts were discovered behind a lintel on the portal of the occidental facade of the cathedral dated to the 17thC. The paintings include figures, golden haloes and musical instruments. Under the lintel, flowers and fleur-de-lys show metallic remnants, identified as tin. The pictorial layers are thin and heavily erased in places. The floral decorations present a black grey layer on the surface, a red sub layer for the flowers and blue for the fleur-de-lys. The black layer represents what remains of a deteriorated tin leaf [Czerniak et al., 2007].

This metallic leaf is adhered with a lipid binder (revealed by IRTF) over a layer of azurite, lead white or on a preparatory layer of lead white and yellow ochre for the fleur-de-lys (fig. 5). The tin in the hexalobe flowers, adhered with an oil mixed with cinnabar on a layer of lead white [Mounier et al., 2009].

On the altarpiece of the church of Audignon (15thC, Landes), tin was also identified in black zones (stained glasses, keys, armour). Tin foils are put on a layer composed of minium.

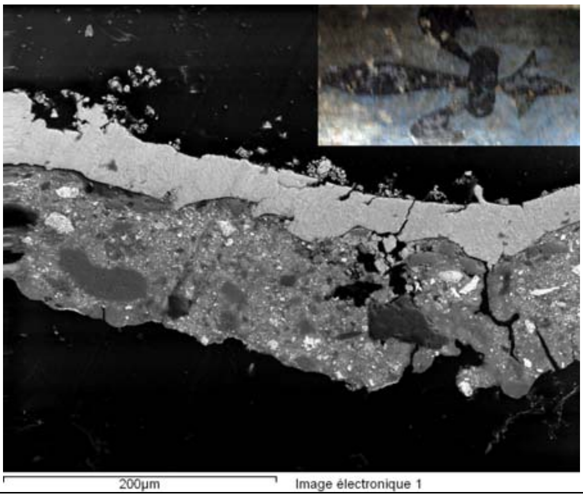

Fig. 5 - SEM image of a sample taken on a fleur-de-lys from the facade of the cathedral of Cahors. The picture shows a thick tin foil (light gray) on the stratigraphic cross section.

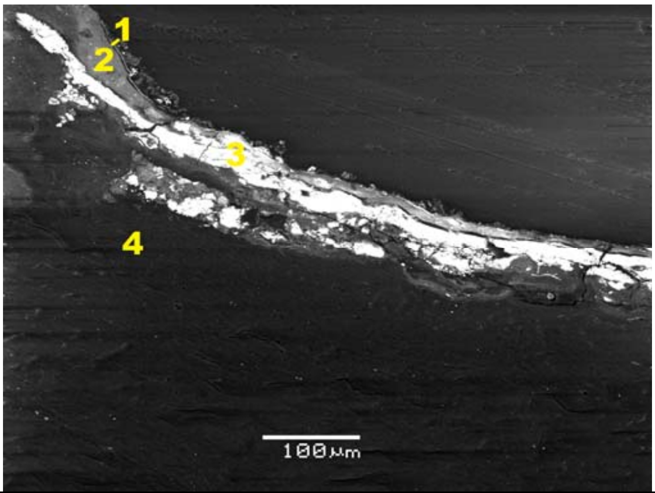

Fig. 6 - SEM image in mode (BSE (back scattering electrons) (x190) of the sample taken from a star on the mural paintings of the La Roque castle in Meyrals. We see here 4 zones: 1- silver leaf (1 in 2 µm) altered in silver sulphide; 2 - binding layer which allows to stick both metal leaves; 3 - tin leaf (15-20µm); 4 - wax layer.

Sometimes, we find a superimposition of metallic leaves. In the oratory of the La Roque castle in Meyrals (16thC, Dordogne), other traces of metal become black. They are visible on remnants of stars, which strew the bottom of the scenes in the vault and on the brooch of the angel's tunic. Generally the stars have fallen off and we only observe their white "ghost", the drawing that indicates their place. The analysis of samples taken from the paintings shows a technique similar to the "zwischgold" technique: a leaf of silver adhered to a thicker tin leaf (fig. 6) but that now appears as a black star (fig. 6). Gold was detected on the surface but it is difficult to determine whether this was metal leaf or gold paint (gold ground into a medium). A thick layer of wax provides a convex effect to give some relief to the star.

Evolution of the colour of gilts during accelerated ageing

- Reference samples of gildings

The measurements of colour done on the references samples of gilding shows a higher dispersion of the chromatic coordinates for gold leaf samples (gold leaf and "zwischgold") than for tin gilded samples. This difference can be explained by the difference of thickness between tin and gold leaves (fig.7). Tin foils, thicker (between 120 and 250 microns) do not allow the transmission of the under layer colour to contribute to the colour of the gold. However the much thinner gold leaves do allow the under layer to contribute and their fragility also means there can be breaks through which the under layer is measured rather than the gold.. The dispersion is higher on b* (which represents the optical ratio yellow/blue) than on a* (green/red axis).

- Effect of hydrothermal and UV artificial ageing on the colour of gildings

The global variation of the superficial colour of samples can be described by the total colour difference ΔE*, calculated from the average chromatic coordinates, taking for reference the measures made on the reference samples.

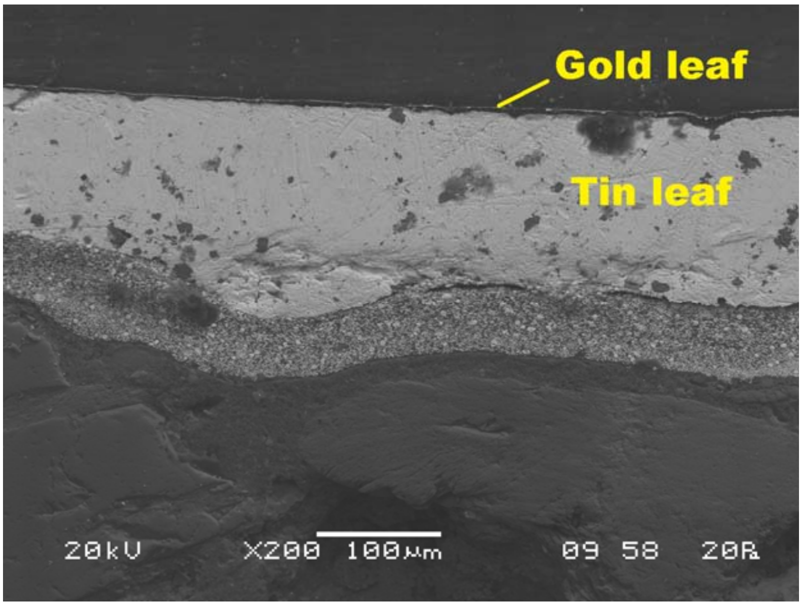

Fig. 7 - SEM image in mode (BSE (back scattering electrons) of a gilt sample («zwischgold" realized by mixtion) showing the difference of thickness between the gold leaf (some microns) and the tin leaf (120 to 150 microns).

The effect of the artificial ageing on the lightness (L*) is not significant. On the other hand, we can measure the variations of coordinates a* and b* which are principally a function of chemical changes on the metallic leaves.

We can note that the ageing under UV did not affect the colour of gilts. On the other hand, the effects are more pronounced after hydrothermal ageing. The aged samples became more yellow (b* increases), in particular samples gilded with gold. The increase of b* is particularly sensitive for the samples of gilt PM4 and PM5 (Table 1), both realized with gold on mixtion. The gold leaf allows the colour of the under layer to show through, with a yellowing of the layer with mordant evident on these two samples. The colour change in these two gold samples are the most significant and relevant (ΔE* up to 4) (fig. 8).

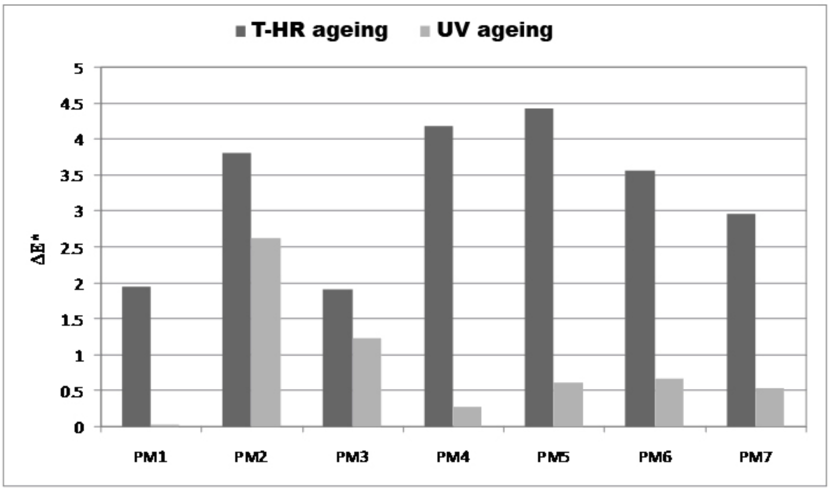

Fig. 8 – Colour difference ΔE between the reference and hygrothermal (dark gray) or UV aged (light gray). We notice higher colour difference for the hygrothermal aged samples.*

The measurements of color on the samples of gilding put in evidence the participation of the under layer in the gilt for samples realized with gold because of its extreme thinness. The measures thus correspond to the combination of the color of the gold leaf and that of its layer support.

Conclusions

For most of the sites, the presence of ancient gildings was revealed by observations of the surface of paintings and by means of the fluorescence of the binders used to adhere the metallic leaves. The gold leaf is the one that resisted best.

The metallic decorations on mural paintings have been made, on the whole, according to the mixtion technique. Oil was identified. Sometimes wax is present, in particular on stars, corresponding to the techniques described in ancient treatises.

The study of the ageing of the binders shows that the more the oil ages, the more the fluorescence becomes yellow [Mounier et al., 2009]. The UV lamps used in situ allow for the suspect presence of an organic binder, even gildings.

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