

# GILDED SILVER PLATES OF THE GREAT SHRINE OF ST MAURICE – AG ALLOY – HIGH MEDIEVAL TIMES

Artefact name	Gilded silver plates of the Great Shrine of st Maurice
Authors	Romain. Jeanneret (Abbaye de St-Maurice, Saint-Maurice, Valais, Switzerland)
Url	/artefacts/1176/

## ≡ The object

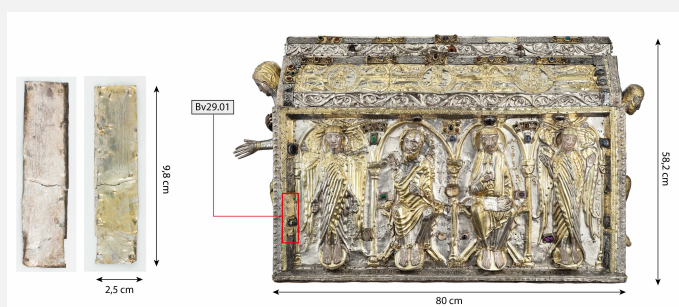


Fig.1: Front and reverse sides of the gilded plate Bv29.01 and its location on the Great Shrine of saint Maurice,

Credit ABSM, R.Jeanneret.

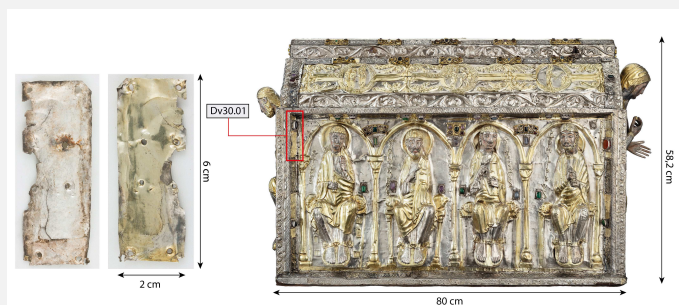


Fig.2: Front and reverse sides of the gilded plate Dv30.01 and its location on the Great Shrine of saint Maurice,

Credit ABSM, R.Jeanneret.

## ≡ Description and visual observation

Description of the artefact	These two pieces are part of 44 gilded or partially gilded silver plates of the Great Shrine of saint Maurice with evidence of earlier decoration. These gilded plates are found re-used as backgrounds for set gems and filigree plates.
Type of artefact	Religious goldsmithing
Origin	Northern continental Europe
Recovering date	Around 1160
Chronology category	High medieval times

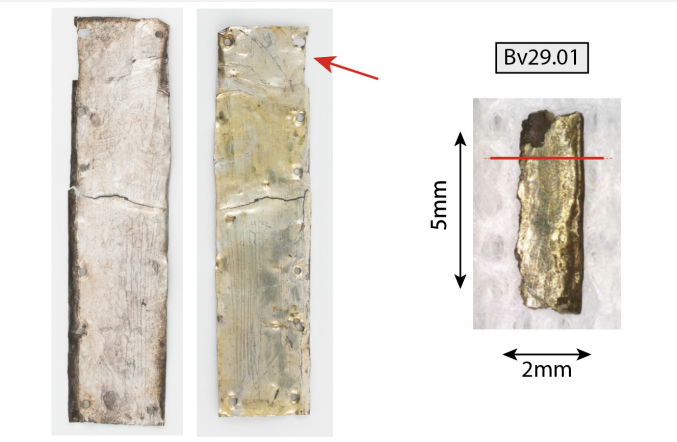
chronology tpq	1150	A.D. ▼
chronology taq	1170	A.D. ▼
Chronology comment	Identified as re-used from a Romanesque relief dated around 1160	
Burial conditions / environment	Indoor atmosphere	
Artefact location	Abbaye de St-Maurice (Jeanneret Romain), Saint-Maurice, Valais	
Owner	Abbaye de St-Maurice (Jeanneret Romain), Saint-Maurice, Valais	
Inv. number	Inv.2_Bv29.01 & Dv30.01	
Recorded conservation data		

Complementary information

The plates are a re-use of gilded reliefs, traces of which can still be found on the Great Shrine. The traces of the ancient decorations are similar to some of the ornaments still present, such as the mandorla of Christ, columns of the apostles, floral decorations, and ribbons flanking the medallions of the genesis present on the roof of the shrine.

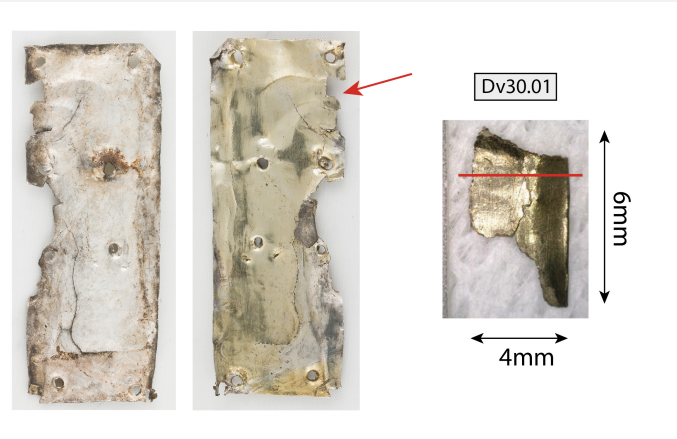
For more information on the Great Shrine of saint Maurice see Nathania Girardin, 2015.

Study area(s)



Credit ABSM, R.Jeanneret.

Fig. 3: Location of the loose analysed fragment of gilded plate Bv29.01 and its sampling area. Size of the sample: 5 x 2 mm,

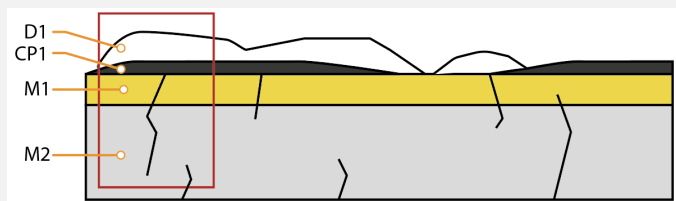


Credit ABSM, R.Jeanneret.

Fig. 4: Location of the loose analysed fragments of gilded plate Dv30.01 and its sampling area. Size of the sample: 6 x 4 mm,

## Binocular observation and representation of the corrosion structure

None.



Credit ABSM, R.Jeanneret.

Fig. 5: Stratigraphic representation of the corrosion structures of both gilded plates Bv29.01 and Dv30.01 by macroscopic and binocular observation with indication of the corrosion structure (before conservation treatment) used to build the MiCorr stratigraphy of Fig. 6 (red rectangular),

## MiCorr stratigraphy(ies) – Bi

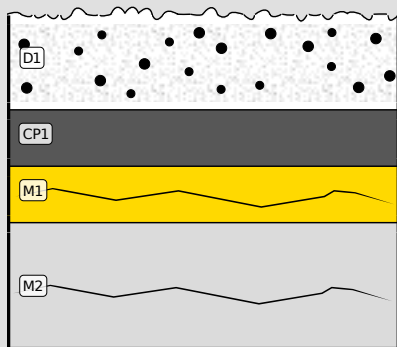
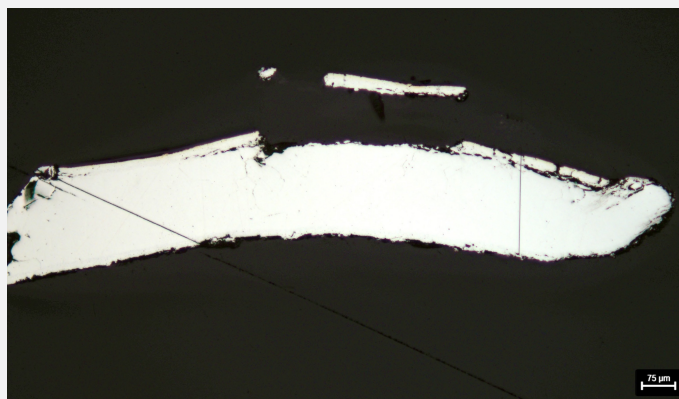


Fig.6: Stratigraphic representation of the corrosion structures of the both Bv29.01 and Dv30.01 gilded plates (before conservation treatment) observed macroscopically under binocular microscope using the MiCorr application with reference to Fig. 5. The characteristics of the strata are only accessible by clicking on the drawing that redirects you to the search tool by stratigraphy representation. Credit ABSM, R.Jeanneret.

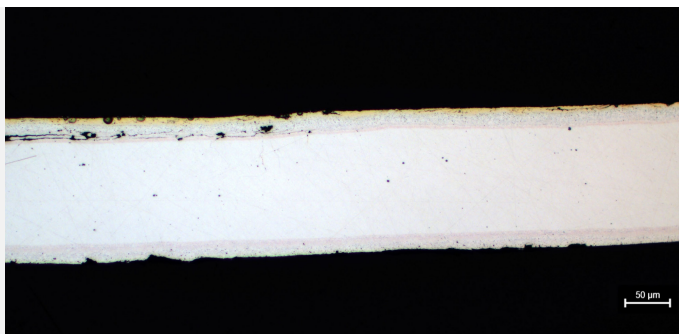
## Sample(s)



Credit HEI Arc, S.Ramseyer.

Fig.7: Micrograph of the cross-section of the sample taken from gilded plate Bv29.01 (Fig.3),

Fig.8: Micrograph of the cross-section of the sample taken from gilded plate Dv30.01 (Fig.4),



*Credit HEI Arc, S.Ramseyer.*

<b>Description of sample</b>	Samples of gilded plates fragments embedded (Figs. 7 & 8). These are transversal cuts as shown on Fig. 3 & 4.
<b>Alloy</b>	Ag alloy
<b>Technology</b>	Hammered, annealed, repoussé, gilded and cold worked
<b>Lab number of sample</b>	
<b>Sample location</b>	Abbey of St Maurice, Saint-Maurice, Valais
<b>Responsible institution</b>	Abbey of St Maurice, Saint-Maurice, Valais
<b>Date and aim of sampling</b>	18.09.2020

#### Complementary information

The plates Bv29.01 and Dv 30.01 are from the same decoration as the genesis reliefs. Intact examples of this can be found on the Great Shrine's roofs (Figs. 1 and 2). The plates have been cut out of the gilded areas and cold worked for reuse as gilded plates under gemstones and filigrees.

#### ✧ Analyses and results

##### *Analyses performed:*

##### **Non-invasive approach**

- XRF with handheld portable X-ray fluorescence spectrometer (NITON XL3t 950 Air GOLDD+, Thermo Fischer®). Precious mode, acquisition time 60s.

##### **Invasive approach (on samples)**

- Optical microscopy: the sample is polished, then it is observed with a numerical microscope LEICA DMLM in bright field.

- Metallography: the polished sample is etched in an oxygenated ammoniacal solution (10mL NH<sub>3</sub> 25%+5mL H<sub>2</sub>O<sub>2</sub> 6%+10mL (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> 20%) and observed by optical microscopy in bright field.

- SEM-EDS: the sample is coated with a carbon layer and analyses are performed on a SEM-EDX JEOL equipped with a silicon-drift EDS Oxford detector with an accelerating voltage of 20 kV and probe current from a 1 to 10nA (to reveal the microstructure).

#### ✧ Non invasive analysis

During a portable p-XFR analysis campaign, the ungilded sides of the plates were studied. The result of this analysis seems to indicate a silver alloy with about 1-2 wt%Cu. Trace elements such as gold and lead were also found.

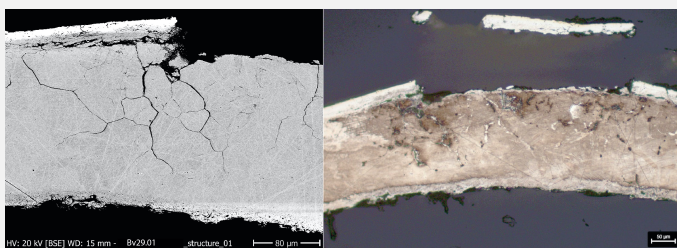
## Metal

The metal of the plates is silver with a low percentage of copper (about 1-2wt%). The plates are gilded only on their visible side (Figs. 7 and 8). The gilding was studied in cross-section by EDS analysis using a composition line (Figs. 10 & 12). The results are similar for both plates and indicate a presence of mercury bound to both gold and silver and decreasing as we get away from the interface. These results are consistent with what has been studied by Kilian Anhauser on mercury gilding samples reproduced in the laboratory (Anhauser, 1999) and on medieval gilded silver (Schweizer & Degli Agosti, 2007).

SEM images (Figs. 10 and 12) show that the metal surface of the underlying metal is slightly porous. This suggests a surface enrichment due to the repoussé work and successive annealing. This is reinforced by the etching of the two samples (Figs 9 & 11) indicating a very different reaction between the first 25 microns and the core of the alloys. Despite these differences, the composition line (Figs 10 & 12) analysis shows no variation in copper content.

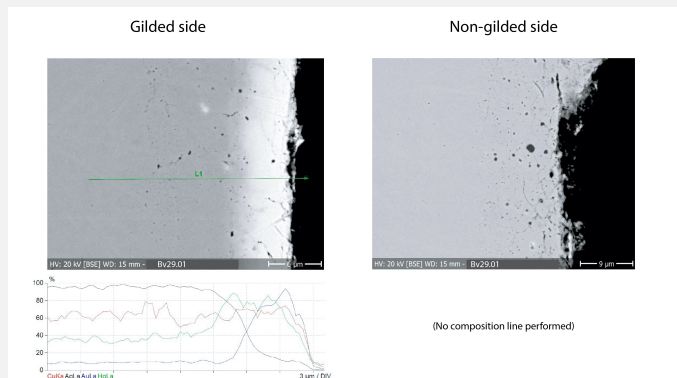
Under the Dv30.01 gilding, there is a pink layer about 10um thick visible on the micrograph (Fig.8). While this may appear to be a highly enriched copper layer, it is not confirmed by composition line analysis. This layer is also found on the non-gilded side, indicating that it is maybe related to the gilding process. This is not clearly visible on plate Bv29.01.

The grain structure of the silver core (large polygonal grains, which may indicate recrystallization of the material(s)) is only visible in the SEM, BSE mode, and by increasing the beam intensity to 10nA (Figs. 9 and 11).



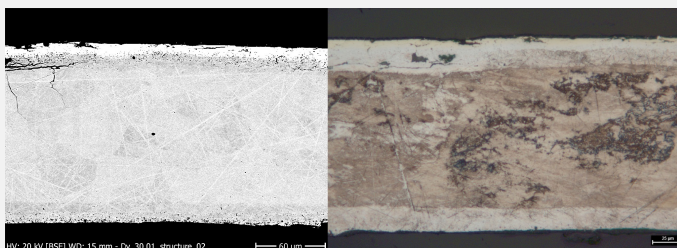
Credit HEI Arc, S.Ramseyer & HE-Arc CR, C.Degrigny.

Fig. 9: SEM image (BSE mode, current 10nA) and micrograph of sample etched of the cross-section of the sample taken from gilded plate Bv29. 01 revealing partly the microstructure,



Credit HEI Arc, S.Ramseyer

Fig.10: SEM images (BSE mode) and EDS analysis by line of composition of the cross-section of the sample (gilded side only) taken from the gilded plate Bv29.01,

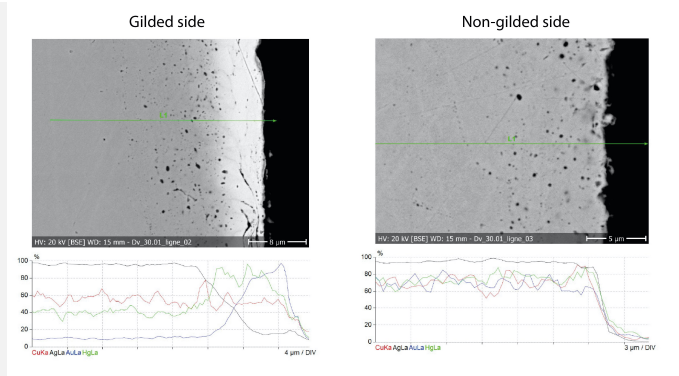


Credit HEI Arc, S.Ramseyer & HE-Arc CR, C.Degrigny.

Fig. 11: SEM image (BSE mode, current 10nA) and micrograph of sample etched of the cross-section of the sample taken from gilded plate Dv30.01 revealing partly the microstructure,

Fig.12: SEM images (BSE mode) and EDS analyses by line of composition of the cross-section of the sample (both sides) taken from the gilded plate Dv30.01,





Credit HEI Arc, S.Ramseyer

Microstructure	Recrystallized structure with large grains
First metal element	Ag
Other metal elements	Cu, Au, Hg

#### Complementary information

None.

#### Corrosion layers

The gilded metal is covered with a thin layer of brown to black tarnish on which deposits of cleaning products are detected. This tarnish on top of the gilding has been analyzed using Linear Sweep Voltammetry in the cathodic domain which showed a  $\text{Ag}_2\text{S}$  reduction peak. Other works on tarnished gilded silver have shown the same results (Jeanneret & al. 2016).

The majority of cracks are due to cold work. It is possible that this phenomenon was amplified and/or followed by intergranular corrosion. Nevertheless, the mercury-enriched interface seems to have suffered the most from cold working leading to loss of local adhesion of the gilding. This could be explained by differences in the ductility of the different metal layers. Some of the cracks reach the center of the metal (Figs. 9 & 11).

On the reverse side of the plate, protected from the environment, only the edge is tarnished.

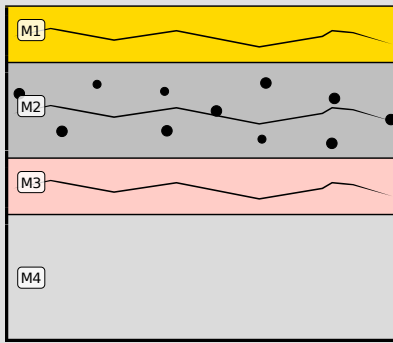
Corrosion form	Passive
Corrosion type	Silver tarnishing

#### Complementary information

None.

#### MiCorr stratigraphy(ies) – CS

Fig.13: Stratigraphic representation of the sample taken from Dv30.01 in cross-section using the MiCorr application. The characteristics of the strata are only accessible by clicking on the drawing that redirects you to the search tool by stratigraphy representation. Credit ABSM, R. Jeanneret.



### ✧ Synthesis of the binocular / cross-section examination of the corrosion structure

The observation in cross-section does not allow the identification of the surface deposits observed under the binocular microscope. This is due to the fact that the observations of the object are made before treatment while the fragment analyzed in cross-section has been treated (degreasing and reduction of tarnish). An intergranular corrosion may also have developed and increased the cracking.

The pinkish stratum (M3) and porous layer (M2) are clearly visible on the micrograph (Fig. 8) but compositional line analysis did not demonstrate any difference from the metal.

The analysis of the cross-section reveals the diffusion of mercury between the gilding and the silver, which is of course not visible under the binocular microscope.

### ✧ Conclusion

The metal is a gilded silver alloy with a low copper content (about 1-2wt% Cu). As suspected, by naked-eye observation, it consists of a mercury gilding. The EDS analysis in line of composition shows well the presence of mercury at the interface between silver and gold and its diffusion in both metals.

Its corrosion layers are typical of gilded silver with a very thin tarnish that has not been analyzed but is considered to be a mixture of silver sulfide and chloride. We did not observe any copper corrosion on the surface during voltammetric measurements. As with other silver gilded pieces treated by electrolytic reduction (Jeanneret, R. 2016), it seems that the copper does not diffuse through the gilding, unlike silver.

The metallographic study shows a microstructure that is difficult to interpret as indicated below. Etching indicates a difference in reaction between the surface layer of about 30µm and the core of the silver alloy. This suggests a surface enrichment prior to gilding since the gold layer appears on top. The lack of difference in copper percentage shown by the EDS line of composition may be due to the original low content of copper within the alloy.

The several cracks on the two plates are the result of metal strain after cold work. This is the result of flattening the original repoussé reliefs to re-use its gilded surfaces as background plates for gems and filigree of the Great Shrine of saint Maurice. An intergranular corrosion may also have developed and increased the cracking.

### ✧ References

#### References on object and sample

1. Girardin, N. (2015). La châsse de saint Maurice. In: Mariaux, P.A dir., L'abbaye de Saint-Maurice d'Agaune 515-2015. Volume 2 - Le trésor. Ed. Infolio. Gollion, 73-85.

#### References on analytic methods and interpretation

2. Anheuser, K. (1999). Im Feuer vergoldet. Geschichte und Technik der Feuervergoldung und der Amalgamversilberung. AdR Schriftenreihe zur Restaurierung und Grabungstechnik Band 4. Stuttgart.
3. Jeanneret, R., Degryny, C., Fontaine, C. and Tarchini, A. (2016). Using the Pleco: Electrolytic Treatment of Metal Components on Artefacts. Conference: METAL 2016, proceedings of the ICOM-CC Metal WG interim meeting. New

Dehli.

4.Schweizer, F. & Degli Agosti, M. (2007). Plaques en argent repoussé et ornements de moulures. In Schweizer, F. & Witschard, D. La Châsse des enfants de saint Sigismond. Ed. Somogy, 153-179.

5.Wanhill, R. (2013) Stress corrosion cracking in ancient silver, Studies in Conservation, 58:1, 41-49, DOI: 10.1179/2047058412Y.0000000037.