Evaluation of Conservation State by Analysis of Imperial Gates' Constituent Materials Belonging to Aşchileu Mic Wooden Church, Cluj County

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In order to preserve and restore the Imperial Gates belonging to the wooden church of Aşchileu Mic, Cluj County, the scientific expertise of the wooden support and of the painting materials (ground, pigments) with FTIR, XRF spectroscopy and DSC thermal analysis was performed. FTIR spectroscopy and DSC methods offer information about the wooden support whereas XRF and FTIR methods were employed for painting materials structural characterization. These structural data can be correlated with the artistic, theological and historical analysis of this religious patrimony object. After obtaining information about wooden support and painting materials the Imperial Gates were 3D digitized using state of the art laser scanning technology. The digital 3D model obtained was restored in virtual environment and converted to an interactive 3D model which can be used for cultural heritage digital dissemination.

Keywords: Orthodox Imperial Gates, spruce fir wood, painting materials, FTIR, XRF spectroscopy, DSC thermal analysis, 3D virtual restoration

Aşchileul Mic is a village from the northern side of Cluj County (Hungarian name *Kisesküllö;* German name *Klein-Schwalbendorf*), situated near the Salaj County border. The first documenting comes from the XIII century, when it was mentioned in the *Gesta Hungarorum* writing, chapters XXIV-XXVII, from the *Scriptores Rerum Hungaricorum* work written by *Anonymus*, the scrivener of king Bella III of Hungaria. The chronicle describes event from the 10th century, when the community from the village area, together with Gelu's army, pledged allegiance to Tuhutum and admitted him as a leader. The place of the oath of allegiance was called *Esculeu* in Hungarian (Aschileu) [1, 2].

The old church was build from 1762 to 1767 and the titular saints were the Holy Archangels Michael and Gabriel. There was another small church that existed in the village which could not accommodate all the people and was later donated to the Sava parish from Palatca township in the year 1796 [3].

The church (fig. 1) is built from timber in the specific style of the Maramureş region. It is nave shaped and measures 13.5 meters in length and 7 meters in width. Above the narthex there is a 20 meters high steeple and its spire is guarded by four small towers which give a distinct architectural note to the construction.

It is believed that the imperial doors were made sometime between the church construction and the painting of the church interior (1767-1806). They are decorated on the upper part with the Annunciation icon and on the lower part with the four Evangelists' icons (Matthew, John, Luke and Mark).

Fig.1.The restored old church

Fig. 2. Imperial Gates (The Annunciation – top, Matthew (man), Luke (bull), John (eagle) Mark (lion)

Several papers [4-13] were dedicated to the scientific investigation of some religious art objects like. Till now, to our knowledge, there are no papers devoted to the Imperial Gates from wooden churches. The aim of this paper was to investigate the wooden support of the Imperial Gates and the painting materials in order to preserve and restore them.

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mg/kg		Ca	Fe	Cu	As	Ag	Au	Hg	Pb
Aureole	Luke	17726	2315	101	106	620	2307	90	256
Attre (red)	John	16769	1230	246	10896	<LOD	<LOD	3537	53116
Attre (green)	John	48326	1911	7613	6093	<LOD	<LOD	387	27524
Bird (red)		66488	10994	220	5461	<LOD	<LOD	7883	27781
Background (yellow)		14246	1468	432	22231	<LOD	<LOD	1382	123558
Dress (red)(inf.)	Luke	21141	15772	331	16301	<LOD	<LOD	73394	73512
Hair (black)		52717	5172	305	1712	537	<LOD	299	6968
The Mother of Jesus (red)		13252	933	199	9876	<LOD	<LOD	55409	39360
Frame (green)	John	51661	2692	10805	145	1103	<LOD	26	279
Red	Mark	11003	2346	205	7132	<LOD	<LOD	53090	27378
Book	Mark	96338	3697	150	1440	<LOD	<LOD	239	5853
Attre (green)		69279	1784	22028	4603	<LOD	<LOD	318	21654
Frame (green)	Luke	50911	3612	23569	156	735	<LOD	32	314
Frame (green)	Matthew	65559	5933	17880	214	735	<LOD	<LOD	377

Table 1
XRF RESULTS

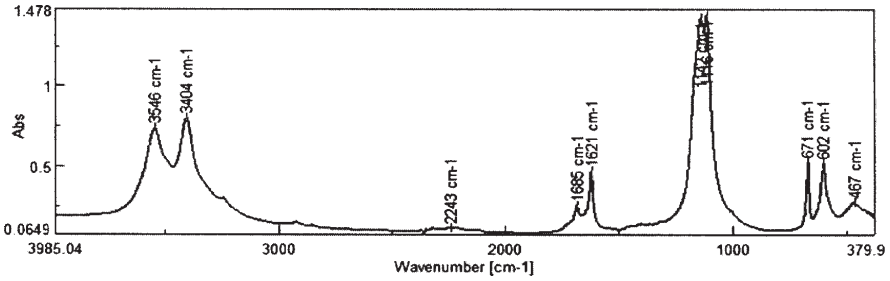

Fig. 3. FTIR spectrum of black pigment, 4000-350 cm^{-1} spectral domain

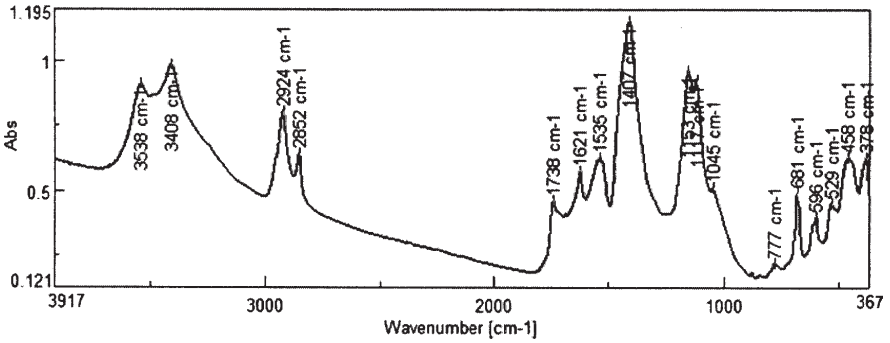

Fig. 4. FTIR spectrum of red pigment, 4000-350 cm^{-1} spectral domain

Experimental part

FTIR spectra were registered with a resolution of 4 cm^{-1} using a JASCO 6100 FTIR spectrometer in the 4000 to 400 cm^{-1} spectral domain by employing KBr (KBr pure spectral powder) pellet technique. The spectra were processed by Spectral Analysis software [5-11]. X-ray fluorescence measurements were performed using an INNOV-X Alpha-6500 portable instrument (35 kV voltage, 15 μA intensity, 3 mm filter, Be window, 2 square mm spot size and PIN Si detector). Integration time was set for 60 seconds, in two consecutive runs of 30 s each. Differential scanning calorimetry (DSC) was carried out by means of a Shimadzu DSC-60 calorimeter, the sample being heated in the range of 20–550°C with a heating rate of 10°C/min in crimped aluminum sample cell [14-16].

The purge gas was nitrogen purged of 60 mL/min. For data collection the Shimadzu TA-WS60 and TA60 2.1 software programs were employed. In order to obtain a 3D model and texture of the Imperial Gates, a ViuScan scanner was used. The main objective of digitization of the Imperial Gates was to obtain an accurate 3D model for digital restoration and dissemination to the general public in an interactive way in digital environment. For the primary digitization a laser scanner that is able to acquire in the same time the 3D shape and texture was employed. After the first phase of digitization the result was processed with CAD instrument (Catia V5) and 3D Modeling & Rendering Software (3D Studio Max) to obtain a 3D model which can be used in web environment or in virtual / augmented reality application.

Results and discussions

The results obtained by XRF spectroscopy measurements are presented in table 1. The chemical elements with higher concentrations are as follows: Ca, Fe, Cu, As, Pb, Hg, Au, Ag. This fact showed that the employed materials to paint the Imperial Gates could be: gypsum, red lead (Pb_3O_4), red mercury (HgS), iron red (Fe_2O_3), realgar (red As_2S_2), green malachite ($CuCO_3.Cu(OH)_2$), auripigment (yellow As_2S_3), lead white ($2PbCO_3.Pb(OH)_2$ silver white), silver sheet, gold sheet, iron bolus.

FTIR analysis confirmed XRF results, so the material employed for ground was gypsum (fig. 3). One can observe

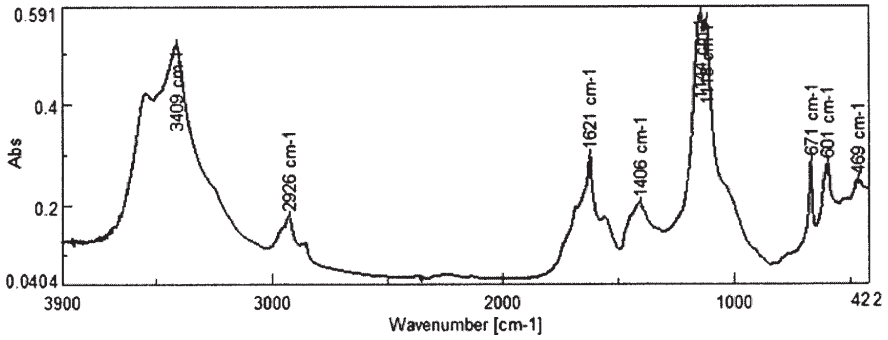

Fig. 5. FTIR spectrum of green pigment, 4000-350 cm^{-1} spectral domain

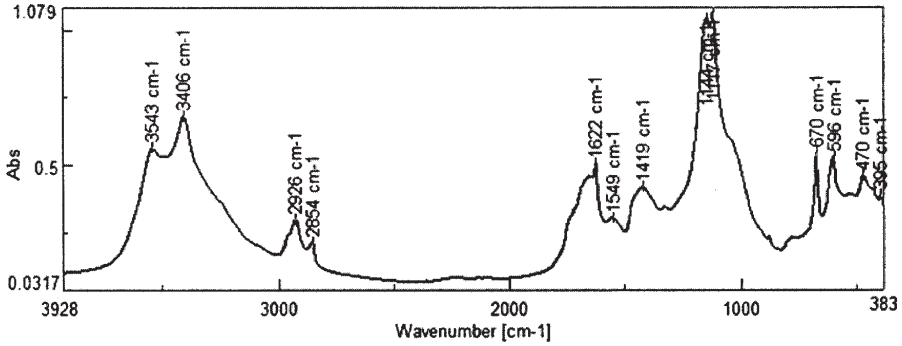

Fig. 6. FTIR spectrum of dark blue pigment, 4000-350 cm^{-1} spectral domain

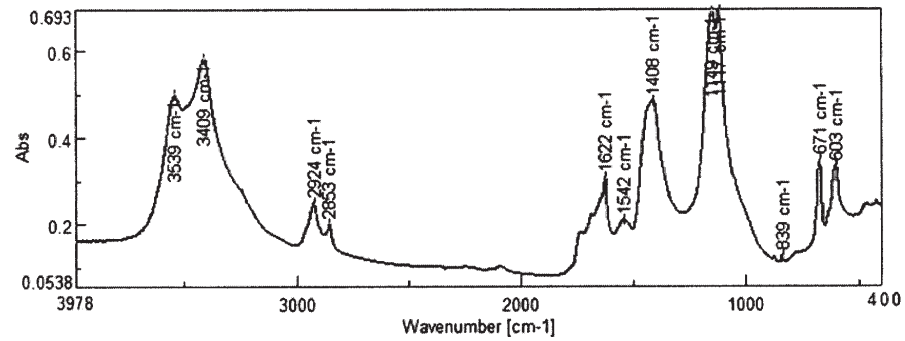

Fig. 7. FTIR spectrum of open blue pigment, 4000-350 cm^{-1} spectral domain

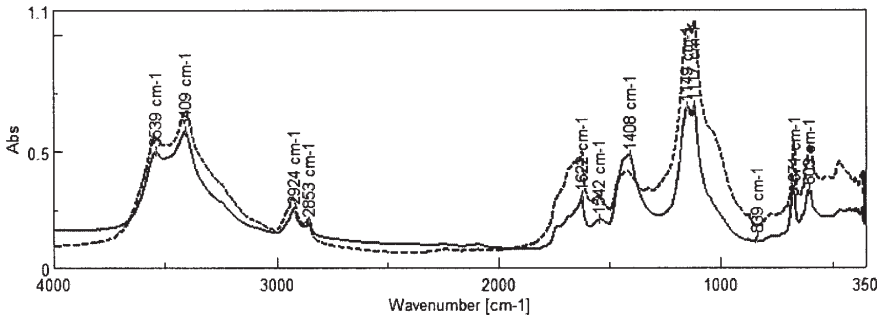

Fig. 8. FTIR spectra of solid line-open blue and dash line-dark blue painting materials, 4000-350 cm^{-1} spectral domain

that black color is due to carbon black (lack of characteristic absorptions), gypsum (characteristic bands at 3545, 3408, 1621, 1153, 1120, 672, 613 and 596 cm^{-1}) [7-13].

The composition of red material, (fig. 4), is: lead minium (529 and 458 cm^{-1} bands), lead carbonate (1407 and 876 cm^{-1}), SiO_2 (1045 cm^{-1}), gypsum, egg yolk (2924, 2852, 1738, shoulder at ~1645, 1535 cm^{-1}) [7-13].

The green sample (fig. 5) contains gypsum, carbonate (1406 cm^{-1}), SiO_2 (1040 and 469 cm^{-1}), probably malachite (1453 and 1407 cm^{-1}), XRF data showing copper [7-13].

This sample contains azurite (fig. 6, absorptions at 3416, 1458 and 1409 cm^{-1}), gypsum (3539, 3409, 1622, 1149, 1117, 671 and 603 cm^{-1}), egg yolk (2924, 2853, 1644, 1542 cm^{-1}) and lead carbonate (1408 cm^{-1}) [7-13].

The open blues sample (fig. 7) contained: azurite that absorbs at 3416, 1458 and 1409 cm^{-1}, gypsum (3539, 3409, 1622, 1149, 1117, 671 and 603 cm^{-1}), egg yolk (2924, 2853, 1644 and 1542 cm^{-1}) and lead carbonate (1408 cm^{-1}) [7-13].

From the analysis of superposed spectra, (fig. 8) (open blue-line, dark blue-dash line), one can conclude that: open blues sample contained more carbonate and less gypsum than dark blue sample, being diluted with lead white. The characteristic absorptions of azurite can be located at: 3416, 1458 and 1409 cm^{-1} [7-13].

Wood essence identification

If one compares the FTIR spectra of Imperial Gates wood and of standard spruce fir wood, (fig. 9), one can decide based on specific absorptions in the 1200-800 cm^{-1} spectral domain that spruce fir is the wooden essence employed for Imperial Gates [7-13].

Wood essences "health"

In order to determine the wooden "health" status, the crystallinity indexes (defined as [14] $I_{cr}^{1} = A_{1377}/A_{669}$, $I_{cr}^{2} = A_{1109}/A_{690}$ or as $TCI = A_{1378}/A_{2925}$ and $LOI = A_{1426}/A_{895}$) were determined. Lignin to cellulose ratios, defined [15] as $(L/C)_1 = A_{1506}/A_{1738}$, $(L/C)_2 = A_{1506}/A_{1158}$ or $(L/C)_3 = A_{1506}/A_{895}$ and $(L/C)_4 = A_{1506}/A_{1377}$ were calculated for wooden samples in

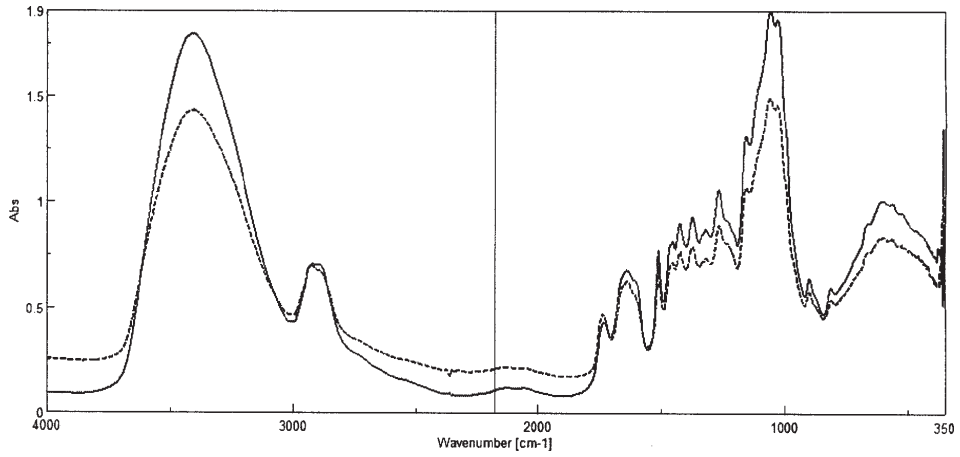

Fig. 9. FTIR spectra of wooden samples, 4000-350 cm^{-1} spectral domain (Legend: UI - Aschileul Mic Imperial Gates wood-solid line; spruce fir standard–dash line)

Sample	I^1_{cr}	LOI	$(L/C)_1$	$(L/C)_3$
Historical wooden support	1.04	1.20	1.79	1.20
Modern fir spruce wood	1.05	1.34	1.47	1.19

Table 2
"HEALTH" STATUS OF FIR SPRUCE WOODEN SAMPLES

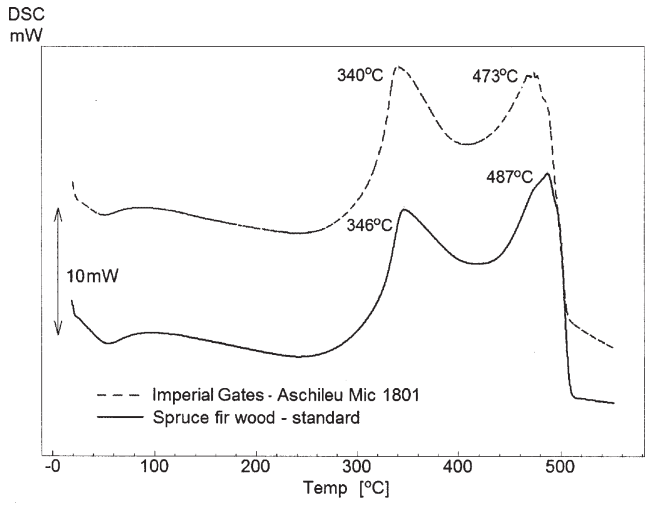

Fig. 10. DSC curves for Imperial Gates wood sample and for spruce fir wood standard, respectively

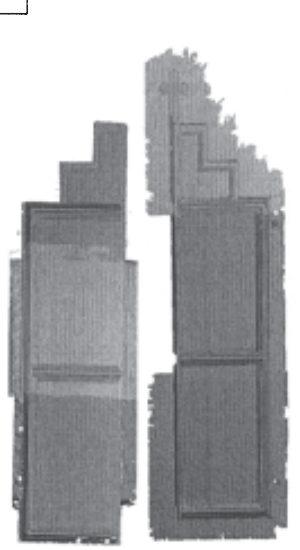

Fig. 11. Splitting the scanning volume: each Imperial Gate was separated in there segments

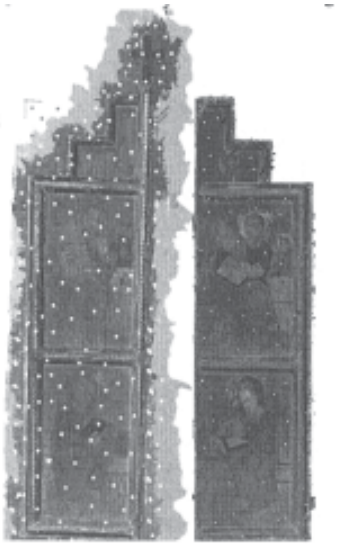

Fig. 12. Primary result of digitization (left) and intermediary processed model (right)

agreement to already established definitions. These definitions are used only as a measure of their change during time. Table 2 contains these parameters determined for historical and modern wood essences (lime and spruce fir ones).

The crystallinity is decreased for historical wood as compared to modern one, especially for spruce fir wooden essence; see I^1_{cr} and LOI values, (table 2). Consequently, the amorphous content is increased for historical lime wood as compared to modern lime wood, (table 2). The cellulose content is decreased in time more rapidly than lignin one for this wood essence, *i. e.* the cellulose consumption is faster that lignin one, see $(L/C)_1$ and $(L/C)_3$ behaviour [14,15].

DSC analysis

Wood is a polymeric material that consists in two major chemical components: lignin (18–35%) and carbohydrate (cellulose and hemicellulose) (65–75%) [14-17].

The thermal characteristics of wood depend on its moisture content, age and conservation status. Because of its complex structure and interaction of components in wood, it is difficult to distinguish the decomposition processes corresponding to each component [14-17].

Investigating thermal decomposition of wood [16, 17], cellulose shows two exotherms at around 350 and at 510°C, respectively [17, 18], (fig. 10). Most of the studies on the thermal properties of lignin proposed that lignin decomposition begins at ~ 280°C, the maximum rate occurring between 350 and 450°C and the completion of the reaction occurs between 450 and 500°C [17, 19]. DSC analysis of standard fire wood shows two exotherms (fig. 10), between 290 and 390°C with peak maximum at 346°C and between 435 and 500°C with peak maximum at 487°C, assigned to amorphous polysaccharides and to mixtures of native lignin and polysaccharides decomposition, respectively [18-24].

3D virtual restoration

After analyzing the Imperial Gates and scanning volume it was concluded that the optimal solution for digitization is to divide the scanning volume in three parts to get the best resolution and accuracy of the resulted 3D model. The splitting of Imperial Gate is presented in figure 11, each sector being scanned with an accuracy of 50 *m*. In figure 12 the primary results of scanning (left) and an intermediary processed 3D model (right) are presented.

The primary processing of 3D model is followed by correction and restoration of wooden support; this was done in CAD software (Catia V5). In this stage the wooden support was reconstructed piece by piece, a sequence of the process is showed in figure 13.

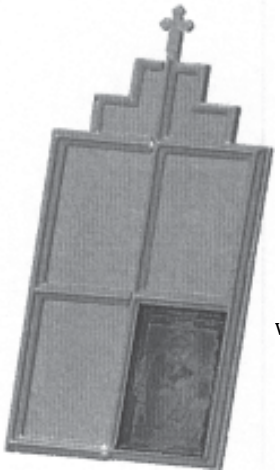

Fig. 13. CAD processing of wooden support

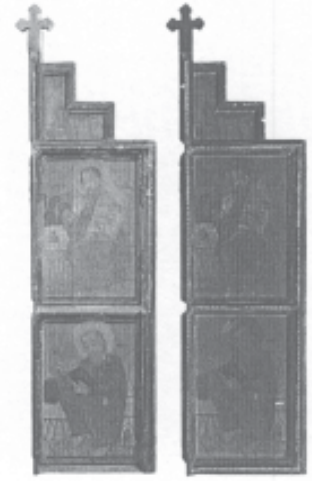

Fig. 14. Processing the painted layer

Fig. 15. Imperial Gates in 3DPD

The digitized painted layer was processed in photo editor to refresh the colors and repaint a small area for improving the visual aspect. In the figure 14 the result of this operation can be seen. For dissemination of 3D model two different file types were taken in consideration: 3DPDF and web embedded 3D model (Sketchfab).

In both solutions (pdf and Sketchfab) the user has three possibilities of interaction with 3D model: zoom, pan and rotate. Also it is possible to change the display mode from render to wireframe mode.

Both employed solutions were chosen because they are compatible with *Europeana* data base, probable the world largest collection of cultural heritage objects in digital format.

Conclusions

One can conclude that the employed materials for Imperial Gates wooden church from Aşchileul Mic, Cluj County, having the titular saints the Holy Archangels Michael and Gabriel, are as follows:

- spruce fir for wooden support;
- gypsum for ground;
- pigments: lead red (Pb_3O_4), red mercury (HgS), iron red (Fe_2O_3), realgar (red As_2S_2), malachite ($CuCO_3 \cdot Cu(OH)_2$), auripigment (yellow As_2S_3), lead white ($2PbCO_3 \cdot Pb(OH)_2$ silver white), azurite ($2CuCO_3 \cdot Cu(OH)_2$), carbon black;
- silver foil, gold foil;
- iron bolus;
- egg yolk as binder;
- animal glue for grounds.

The digitization and digital restoration of the Imperial Gates using laser scanning technology is feasible. The result of laser scanning can be processed and convert to a format which can be used for dissemination in digital environment. The digitized Imperial Gates that are subject of this paper can be seen on-line on the (http://usiimparatesti.granturi.ubbcluj.ro/3D.html) project website.

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