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Synchrotron X-ray diffraction of bole layers from Portuguese gilded baroque retables



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ABSTRACT

Studies based on a scientific approach to materials and techniques used in Portuguese gilded retables from the Baroque are very scarce and focus particularly on works with erudite features and on the characterization of the superficial gold leaf. The conservation and appearance of gilded surfaces, however, depended on the qualities of the clayey ground layer underneath, which is the bole. Colour and texture are closely related to its mineralog-ical composition.

Boles were healing clays. Red to orange varieties could also be used for gilding, usually agglutinated with animal glue when the gold surface was meant to be burnished. Armenian was the name used to identify the best quality material.

Microsamples collected from erudite and popular gilded retables, respectively belonging to the city of Oporto and its rural surroundings, were selected for elemental and mineralogical characterization. It was intended to shed light on the characteristics of boles used in Portuguese retables and to understand if there are any differences between materials used in works of distinct artistic quality.

Elemental analysis was performed through SEM–EDS. SR-XRD was used for phase identification, performed with a six-circle diffractometer at the DIFFABS beamline of SOLEIL Synchrotron. Portuguese clay standards of identifiable composition and provenance were also analysed.

The results suggest that boles are mainly kaolinitic, with variable amounts of illite and smectite. Gypsum was used as an extender. Although the proportions of the main clay minerals are similar in erudite and popular works, in Oporto homogeneity is clearly higher.

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1. Introduction

Most studies of Portuguese baroque retables, or altarpieces, which represent a type of artwork of primary importance in Portugal, have been developed in the scope of Art History projects. For this reason, it is still not possible to characterize regional working procedures and their evolutionary processes. The gilding process of these wooden pieces was generally based on the application of a series of layers of coarse gypsum (nowadays anhydrite), fine gypsum (nowadays mainly dehydrate calcium sulphate and accessorial anhydrite), and a red layer to orange thin clay material, which is the so-called bole. All of these were usually agglutinated with animal glue (collagen-based binder) when the gold surface was meant to be burnished (Le Gac et al., 2009; Bidarra et al., 2009; Sandu et al., 2012; Barata et al., 2012; Cardoso, 2013; Antunes et al., 2014). According to documental sources, small proportions of gypsum could be mixed with the bole (Alves, 2002). For non-burnished gilding (matte gilding), bole could be replaced by mixtures of pigments agglutinated with drying oils (Pacheco, 2001).

Of all the materials used to produce gilded surfaces, boles are the least known. They were never systematically studied and there are few published studies including boles mineralogical composition (Hradil et al., 2003; Grygar et al., 2003; Salvado et al., 2014; Chao et al., 2014). For both ethical and conservation principles, it is not possible to remove samples from gilded works with areas greater than 1 to 3 mm². The small thickness of bole layers, usually below 40 µm, usually limits its analysis to the identification of the elemental composition.

Boles were healing clays administered mainly orally as "antacids", gastrointestinal protectors and antidiarrhoeaics (Wilson, 2003; Carretero and Pozo, 2010). The red to orange varieties were also used in water gilding, as a ground, and generally sold by apothecaries who also traded other artists' materials (Cruz, 2009, 2013).

Traditionally, the expression 'Armenian bole' was used in art treatises and work contracts to designate the highest quality material,





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in accordance with the best-known origin (Armenia) or simply to identify the purpose for which it was used, as it happened with other artists' materials (Kirby et al., 2010). The designation 'Armenian' follows oral tradition and literature based namely on Theophrastus, Dioscorides and Pliny the Elder, references which were still in use in the 18th century (Chambers, 1753). Probably due to its high cost, however, boles from other origins must have been used. Besides, some historical written sources suggest that apothecaries usually used the same label for boles with different origins or mixtures and that few people would be able to distinguish between them (Cruz, 2009, 2013; Hill, 1748). Works written by naturalists from the 16th to the 18th centuries, which in some cases may be considered early geologists (Agricola, 1955), provide valuable information on these healing clays and its uses, and relate them to the same material used by artists as a ground for gilding (Biringuccio, 1990; Diderot and d'Alembert, 1751). It is also cleared that these boles could be extracted in other regions, namely in Portugal, where good quality boles were obtained (Henriques, 1726; Hill, 1751: Costa, 1757).

In order to clarify the composition of the boles used in Portuguese retables, a number of pieces from Oporto dioceses were chosen for a first systematic study. With the objective of understanding if there are any differences between the materials used in works of distinct artistic quality, seventeen erudite retables were selected from the city of Oporto, a very important artistic centre during the Baroque and where the best artists opened their workshops, and sixteen popular works came from the rural surroundings of the dioceses (Fig. 1). All works were produced between the final quarter of the 17th century and the third quarter of the 18th century.

The main objectives of this research were to identify the crystalline phases in bole layers and, simultaneously, to understand how the results provided by the different analytical techniques available could be complemented. Following a methodology usually applied in Geosciences, the goal is to answer some questions raised by Conservation and Art History, such as if artistic quality has any relation to the materials and techniques used; if the materials used in rural areas were the same that were available in the main trade centres; or if a relationship can be established between these boles and common Portuguese red clays, as suggested by historical documents.

In the present paper, an approach based on the use of micro X-ray diffraction under synchrotron radiation (SR-XRD) to identify the phases constituting the bole is proposed. After chemical analysis undertaken through scanning electron microscopy with X-ray energy dispersive spectrometry (SEM–EDS) on a set of samples taken from each retable under research, one representative sample of the burnished areas of each work was selected to be analysed through SR-XRD. This experiment constitutes the first systematic study of the bole's mineralogical composition. Phase identification of bole layers by conventional XRD is not possible due to the small sample area and its thickness. On the other hand, aged protein binders used in burnished areas usually make samples become very friable, which does not allow for the separation of bole layers from the calcium sulphate underneath by mechanical means, as well as making the use of μ XRD difficult or even not possible.

2. Materials and methods

2.1. Historical samples

Samples were collected from representative areas of the burnished gilded decoration of two groups of works. The first group, labelled E, concerns seventeen erudite retables selected from the city of Oporto and focus on the best artistic quality. The second group, labelled P, corresponds to sixteen popular works selected from smaller churches and chapels located in the rural surroundings of the dioceses.

Samples have an area of 1 to 3 mm^2 and the bole layers show a thickness of 5 to 100 μ m.

They were embedded in acrylic resin (Tecnovit 4004) and transverse sections were cut for analysis. As usual, each transverse section (cross section) was polished in order to allow multilayer structure observation.



Fig. 1. Left: Saint John the Baptist church main retable, in Oporto (1735); right: lateral retable of Ancede chapel (first half of the 18th century).

2.2. Reference samples

As standards, four different clays collected from known Portuguese deposits with clearly different compositions were used: ALV from Alvarães (mainly kaolinitic), TAV from Taveiro (kaolinitic-illitic), BUS from Bustos (mainly illitic with kaolinite and smectite in variable proportions) and CH from Chaves (with smectite, illite and kaolinite in approximate proportions). These clays were analysed through SEM– EDS and XRD in the scope of this research.

Fraction under 63 μ m was obtained by wet sieving. After testing its suitability for gilding through the preparation of several models, grain fraction under 63 μ m was also selected for SR-XRD analysis to be compared to the material used in the bole layers of the works under research.

Fraction under 2 μ m, commonly used for the identification of main clay mineral composition, was extracted from a distilled water suspension and sedimented over glass slides (oriented aggregates).

2.3. Analytical techniques and methodology

All historical samples were observed as cross sections using an Olympus binocular microscope, model BX41, equipped with a digital ProgRes CapturePro 2.7 camera with infinity corrected optical system (OM). This approach revealed the traditional sequence of gypsum, bole and gold leaf applied over the wooden support.

Elemental analysis of boles was undertaken on a selection of 64 cross sections (two samples from each retable) coated with carbon, using a scanning electron microscope HITACHI 3700 N coupled with a Bruker AXS X-Flash 5010 X-ray energy dispersive spectrometer and a XFlash 5010 Silicon Drift Detector, under high vacuum, at Hercules Laboratory. Images were obtained in backscattering (BSE) and secondary electron modes (SE). A 20 kV acceleration voltage and a current intensity of about 0.1 mA were applied during acquisition times from 120 to 300 s. Considering the fact that these are multiphase materials, EDS spectra were collected from areas and point analyses were kept only for particles that represented exceptions to the main composition.

SEM–EDS analysis of clay standards and models, prepared both as cross sections and powders, were performed with Hitachi SEM, model SU-70, with B-U Bruker QUANTAX 400 EDS, using the same experimental conditions, at RNME – Pole, University of Aveiro.

Looking for differences and similarities among both groups, statistical methods using EDS results, such as correlation matrixes and principal component analysis (PCA) were also performed with Statgraphics Centurion 16.1 software. Data matrixes were prepared taking the elemental mass concentration for correlations and using logarithms for PCA. Significant correlation coefficients were considered for a confidence interval of 95%.

XRD was employed for the characterization of the four clay standards, both for <63 μ m powders and <2 μ m oriented aggregates. A MP Philips/Panalytical diffractometer equipped with a conventional X-ray tube (Cu K α radiation with the wavelength 1. 5405 Å, 50 kV, 30 mA, point focus) was also used. Diffraction patterns were recorded in the 2 θ interval from 5° to 65° for fraction <63 μ m and from 5° to 20° for fraction <2 μ m with a step of 0.02° per second.

The characteristic peaks of the minerals constituting each clay reference were identified in diffractograms corresponding to both <63 μ m and <2 μ m fractions. Semi-quantification of main clay minerals was computed for its relative proportion determination using reflecting powers methodology, as proposed by Schultz and Thorez (Schultz, 1964; Thorez, 1976). Qualitative and semi-quantitative mineralogical analyses followed the method described by Martins et al. (2007); for the semi-quantification of the identified main minerals, peak areas of the specific reflections were calculated and weighted by empirically estimated factors according to Galhano et al. (1999) and Oliveira et al. (2002). SR-XRD was used for phase identification of boles in a selection of 34 representative cross sections, one from each retable belonging to both groups E and P.

The four clay standards were analysed as randomly oriented powders.

SR-XRD was performed with the 6 + 2 circles diffractometer of the DiffAbs beamline at SOLEIL Synchrotron facility (France). The main optical set-up is equipped with two long mirrors (50 nm Rh-coated Si) on either side of a fixed-exit double crystals Si (111) monochromator that offers an energy range of 3–23 keV. A second optical set-up using two mirrors in Kirkpatrick Baez geometry allowed for work with a microbeam ($10 \times 10 \,\mu m$). Because of measurements in reflection mode on the cross sections, the beam footprint on the sample was about 10 $\mu m \times$ 200 μm , according to the imposed incident angle (less than 3°), which corresponded roughly to the areas previously analysed through EDS. The cross sections were oriented in such a way that the bole layers were aligned parallel to the beam direction, in order to cover an area as large as possible but along the thin layers. The excitation energy was fixed at 7 keV (wavelength at 1.77 Å), just below the Fe K line edge, to avoid signal disturbance by fluorescence. A twodimensional detector, a camera CCD Rayonix SX165, was used to collect XRD images with an acquisition time of 600 s. For each 2D XRD image, the Debye-Sherrer diffraction rings were circularly integrated using homemade script and ImageI software to obtain the diffraction pattern.

Although the CCD detector limited the possible range of angles between 5° to 25° 2 θ (Cotte et al., 2008; Chadwick et al., 2012), its use made it possible to reach the main objective of detecting the predominant clay minerals in the bole layers. Semi-quantification for determining the proportion of the main clay minerals was computed using the reflecting powers method mentioned above.

3. Results and discussion

The first observation through OM revealed the traditional sequence of gypsum, bole and gold leaf used in burnished gilded areas. In both erudite and popular works bole layers generally show a homogeneous red to orange matrix, 5 to 100 µm thick, apparently without additives (Fig. 2).

Through SEM images, the same homogeneity was observed in most samples, as well as its plate like and much smaller particles, when compared to the gypsum underneath (Fig. 3).

The sequence of gypsum, bole and gold layers was observed, but only through SEM it is possible to distinguish base coarse gypsum



Fig. 2. OM image of a typical cross section of a gilded area (amplification of $100 \times$): a) gypsum; b) bole; c) gold leaf.



Fig. 3. SEM (BSE) images of cross section E14 (left) and cross section P82 (right): a1) coarse gypsum; a2) fine gypsum; b) bole; c) gold leaf.

(mainly composed of anhydrous calcium sulphate with particles of heterogeneous sizes and shapes) from upper fine gypsum (mainly finely grounded calcium sulphate dihydrate). The mineralogical composition of gypsum layers was supported by XRD analysis in the context of this research.

3.1. EDS

The chemical results are very similar among both groups of works. As expected, bole is mainly composed of Al, Si and Fe, elements that form the structure of iron-rich clay minerals. Fe should be related to the red to orange colour, which is suitable for producing a warm colour contrast with the gold leaf placed above. The atomic ratio between Al and Si is 0.8 in average, which suggest that main components are 1:1 structure clay minerals such as kaolinite. Ti is frequent in Portuguese kaolin deposits, replacing Si in the structure of kaolinites or in the form of anatase. K suggests the presence of illite and, given the low concentration of Na, detected in only half of the samples, the main feldspar should be K. Mg also suggests the existence of smectite (Table 1).

The atomic concentrations of Ca and S are, on average, two times higher in rural samples than in the ones from Oporto, which points out to a higher content of calcium sulphate in rural works. Although traces of gypsum may occur in some clay deposits, the higher concentrations detected in historical samples suggest that it has been added intentionally as recommended by historical literature (Alves, 2002). In addition, in both groups the atomic ratio between Ca and S is above 2.0, suggesting that Ca may be also present in the structure of other minerals, such as carbonates.

Table 1

Normalized mass concentrations [norm. wt.%] for representative samples from the two groups: E47 and P40.

Element	Sample E47	Sample P40	
	[norm. wt.%]	[norm. wt.%]	
0	44.8	42.2	
Al	8.8	10.1	
Si	12.4	13.3	
S	0.5	0.2	
K	1.1	0.9	
Ca	0.5	0.6	
Fe	4.0	5.2	
Ti	0.4	0.4	
Mg	0.4	0.4	
Na	0.0	0.2	
Р	0.00	0.02	
Cl	0.00	0.03	

When regarding the correlation matrixes obtained for the total set of historical samples (Table 2), the strong correlation between Al and Si suggests that boles are mainly composed of aluminosilicates something that was supported by mineralogical analysis which pointed out to a dominance of kaolinite. The significant correlation between Al and K suggests the presence of illite, also supported by mineralogical analysis. Considering the significant correlation between Fe and Al it is likely that Fe makes part of the aluminosilicates' structure.

A strong positive correlation between Ca and S indicates the presence of calcium sulphate mixed with the bole as observed above.

However, there seem to be some differences between the bole composition of the two groups, which become clear only when comparing correlation matrixes prepared separately for each group of samples (Table 3).

In Oporto (group E), the strong correlation between K and Al, K and Si and K and Fe suggests the presence of illite. Significant correlation between Fe and Al may be related to the presence of Fe in aluminosilicate structure.

In the rural surroundings (group P), correlation coefficients between Si and K and Al and K are lower than what is observed in Oporto, which suggests that illite is less important in rural bole composition. The significant correlation coefficient between Ti and Al may be related to the presence of kaolinite, something that don't happen in the group from Oporto. The dominance of kaolinite in popular works may be suggested by the negative correlation between Fe and K and a not relevant correlation between Al and Fe. Contrary to what was observed in the group from Oporto, in rural areas Fe is apparently more related to iron oxides and less related to aluminosilicates' structure.

Through correlation matrixes, there is no clear evidence of smectite in any of the groups. The positive correlation between Al and Mg in Oporto may suggest that smectite could be present, but only through mineralogical analysis was it possible to confirm.

There is a significant positive correlation between Mg and Na in rural works, however with no connection to Al and Si, which suggests that Na may be present in other minerals, such as carbonates, either as a minor component or as a result of material alterations posterior to the gilding process.

Still in respect to differences and similarities within each group, when observing the results of principal component analysis a different variable distribution becomes visible, which is consistent with the interpretation of the correlation matrixes (Fig. 4): in Oporto there is an association between K, Ti and Fe and the elements that represent aluminosilicates (Al and Si). In rural areas K and Fe are not clearly associated to Al and Si and Ca and S are more clearly separated from other elements.

Apparently, the majority of boles used, especially in the popular works (group P), have a closer composition to clay standard ALV, which corresponds to the most kaolinitic standard. Also in group P,

Table 2	
Correlation matrix for the two groups of samples.	

	Si	Al	Fe	Mg	К	Ca	Na	Ti	S
Si		0.8082	0.0531	0.0911	0.5330	-0.3923	-0.2088	0.2150	-0.3249
Al			0.2980	0.0936	0.5231	-0.1755	-0.2003	0.1738	-0.1599
Fe				-0.2042	-0.0013	0.2651	-0.2064	0.2176	0.2411
Mg					0.0664	-0.0956	0.3600	-0.1985	-0.0420
K						-0.0609	0.1096	0.1103	-0.2372
Ca							0.0513	-0.1456	0.7991
Na								-0.0349	0.0328
Ti									-0.0798
S									

Significant correlation coefficients for a confidence interval of 95% are bold.

some samples are closer to the other three standards, something which is not observed in group E.

Although it is not possible to propose additional divisions in any of the main groups based on chemical results, the dispersion of samples seem to be slightly higher in rural works when compared to the ones from Oporto. The outermost samples correspond to the ones where higher concentrations of Ca and Fe were detected, probably related respectively to gypsum and iron oxides used as additives.

Although EDS results allow to establish a differentiation between popular and erudite groups and to propose a higher homogeneity in the bole composition of erudite works, chemical analysis cannot support by itself the main objective of this research, which is the mineralogical characterization of boles used in gilded baroque retables.

3.2. SR-XDR

SR-XRD results showed that in historical samples most boles are mainly kaolinitic, with variable proportions of other clay minerals, such as illite, smectite and chlorite. Other silicates, such as quartz and feldspars, and gypsum were also detected (Fig. 5).

Diffractograms show peaks with different shapes and varying definition degrees, corresponding to a mixture of minerals with different degrees of crystallinity, as it is typical of common Portuguese red clays, with varying proportions of kaolinite, illite and smectite (Gomes, 2002). Simultaneously, it should also be consistent with the composition of most geophagic material known (Wilson, 2003; Carretero and Pozo, 2010).

Only through mineralogical analysis did it become possible to confirm that the strong correlation between Al and Si corresponds to the presence of clay minerals as main components, besides other silicates that are usually associated to clays.

Correlations between Al and K may thereby be related either to kaolinitic or kaolinitic-illitic boles. The detection of other clay minerals, such as smectites, even when present in significant proportions, is only possible through mineralogical analysis, something that, in this study, could only be achieved through SR-XRD, in view of the characteristics of the samples available.

In thinner samples or in cross sections where top surface was not perfectly parallel to the base, diffractograms showed a broad hump (diffusion), probably caused by the resin, which prevented the detection of some phases. For this reason main clay mineral composition was determined for 14 erudite and 10 popular samples (Table 4).

There are similarities between the bole clay composition of the two groups, concerning both qualitative and semi-quantitative features, with the predominant clay mineral being usually kaolinite. Kaolinites have globally neutral charge, something that is appropriate for a material that should form stable suspensions and not offer resistance to being spread over a surface, in order to produce a compact thin layer. In addition, animal glue should act as a protective colloid, increasing suspension stability and particle bonding (van Olphen, 1963; Bergaya et al., 2006; Giese and van Oss, 2002).

Another observation provided by these experiments was the comparison between SR-XRD and XRD results obtained for the four clay references. It was noted that semi-quantification calculated through XRD diffraction patterns obtained for the <2 μ m oriented aggregates (usually used for main clay mineral identification) and through the respective SR-XRD patterns obtained for the <63 μ m powders present comparable results (Table 5).

The high sensitivity of SR-XRD for detecting phases in low concentration (Latella and O'Connor, 1997) is well-known. Even if semiquantification values are used for only an approximate characterization, in this experiment that is a particularly important observation, since it means that results obtained from historical samples may be used for the identification of the main clay minerals present in bole composition, something that is essential for understanding its technological performance. The systematic identification of boles used in burnished gilded wooden works had never been achieved before due to the small quantities of samples available and also to its friability.

Table 3 Correlation matrixes for group E (upper half) and group P (lower half).

	Si	Al	Fe	Mg	К	Ca	Na	Ti	S
Si		0.8943	0.3793	0.2327	0.6764	0.1556	-0.1620	0.1881	0.3566
Al	0.7350		0.5192	0.2142	0.7912	0.1515	-0.1524	0.0851	0.3696
Fe	-0.2232	0.1065		0.0609	0.5371	0.0420	-0.1894	-0.0062	0.2784
Mg	0.0191	-0.0134	-0.3375		0.0585	0.1969	0.2578	-0.1592	0.3413
К	0.4352	0.3503	-0.3747	0.1785		-0.1376	-0.1952	0.1601	0.1497
Ca	-0.6798	-0.3907	0.2200	-0.1157	-0.1706		0.0050	-0.2655	0.7401
Na	-0.2786	-0.2760	-0.2864	0.5306	0.2948	0.0450		0.0875	-0.1106
Ti	0.2544	0.3158	0.4701	-0.2523	0.0591	-0.2189	-0.2355		-0.0813
S	-0.5648	-0.3824	0.2018	-0.1063	-0.3866	0.7998	0.0583	-0.1394	

Significant correlation coefficients for a confidence interval of 95% are bold.



Fig. 4. PCA: projection of components 1 and 2 for group E and respective variables, corresponding to 51.8% of total variance (top); projection of components 1 and 2 for group P and respective variables, corresponding to 49.5% of total variance (bottom).

4. Conclusions

Boles used in the preparation of the gilded retables under research correspond in most cases to common red clays. According to the known composition of main Portuguese deposits, it is possible that the boles used in the retables under research have been extracted in Portugal, apparently supporting historical references. However, a systematic study of the possible deposits under the same experimental conditions is still to be done.

Only through SR-XRD was it possible to confirm bole characterization and its clay mineral-based composition. Boles are mainly kaolinitic, illite and smectite being usually present in lower concentrations. These features make bole a suitable material to be used as a ground for gilding, for small plate like particles, low plasticity, resistance to moisture variations and warm colour.

The results do not allow for a division into groups beyond the one that seems to be clear through chemical analysis between erudite and popular works. A higher heterogeneity in composition of boles used in popular works was detected, when compared to erudite works. Although clay mineral composition is similar between the two groups of works, chemical results suggest that, in rural areas, artists may not always have had access to the same suppliers available in the main trade centres or that mixtures of different materials might be more frequent when away from the most important cities.

There is gypsum in almost every sample, added as an extender, but its concentration is generally higher in rural works, as in the case of the iron content. Heterogeneity seems actually to be mostly related to additives, such as gypsum, probably used to increase smoothness, and iron oxides, for colour control.

The similarity between semi-quantification calculated for diffraction patterns corresponding to fraction <2 µm, obtained through XRD, and fraction <63 µm, obtained through SR-XRD, is of great importance for this study. SR-XRD has proved to be a precious technique for the identification of boles in historical microsamples, leading to the first systematic mineralogical characterization of boles used in burnished gilded works and opening possibilities for future research.

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Fig. 5. SR diffractograms of bole layers from sample E64 (top) and P84 (bottom).

Table 4
Semi-quantification calculated for main clay minerals present in historical samples.

	Kaolinite	Illite	Smectite
E4	76	16	7
E14	51	-	49
E20	49	24	27
E28	88	8	4
E38	77	15	8
E39	87	8	5
E46	69	23	8
E64	54	43	3
E82	54	-	46
E84	67	11	22
E102	57	6	37
E114	82	13	5
E122	36	24	40
E110	48	14	38
P39	59	-	41
P47	54	44	2
P72	65	22	13
P84	79	14	7
P100	44	-	56
P108	73	14	13
P113	41	41	17
P116	72	-	28
P128	47	14	38
P137	87	-	13

Table 5

Comparison between semi quantification for the 4 clay references analysed through XRD and SR-XRD.

	XRD slides < 2 µm			SR-XRD powder < 63 μm		
	Illite	Kaolinite	Smectite	Illite	Kaolinite	Smectite
ALV	20	79	-	15	83	1
TAV	47	49	2	29	66	3
BUS	36	46	17	53	35	11
CH	26	47	26	39	22	38

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