Identification of gilding techniques on Roman marble sarcophagi

Eliana Siotto[a]

[a] *Visual Computing Lab - ISTI CNR, Pisa, Italy*

Abstract

Several Roman marble sarcophagi (2nd-4th centuries AD) have been investigated in a first systematic research effort to detect (pigments and) gilding techniques employed in the Imperial Rome. A comparative study has performed on a conspicuous group (no. eighty) of Roman sarcophagi identified in the Vatican Museums, the Capitoline Museums and the National Roman Museum collections. A focused in situ campaign of non-invasive analytical investigations have performed by multispectral imaging, spectroscopic and elemental analysis, followed by aimed micro-invasive techniques. As for the main issue of the gilding and its application techniques, the microscopy still remains one of the most efficient tools for their characterization. Therefore, some micro-samples of three sarcophagi chosen as case studies were examined by means of Optical Petrographic Microscopy (OPM) and Scanning Electron Microscope and Energy Dispersive X-Ray Spectrometer (SEM-EDS). The results of archaeological data and scientific analyses show that the leaf gold was applied by two different techniques. In the most attested method, the gold leaf was applied on a ground layer of colour (yellow and/or red ochre, Egyptian blue, etc.); on the other hand, in the other technique, the gold leaf was applied directly onto the marble surface or more probably on top of a thin ground layer of kaolin.

Keywords: Gilding techniques, Roman sarcophagi, Purplish substance, Colloidal gold, Optical petrographic microscopy, SEM-EDS

1. Research Aim

The purpose of this work is to present the original results concerning the gilding of Roman marble sarcophagi. The study of ancient gilding (and colour) on the surface of marble (architecture, sculpture, etc.) is extremely topical and of great general interest, but significant limits to knowledge and progress are due to complexity and uncertainty. The results collected by this transdisciplinary study on the identification of two techniques used to apply the gold leaf on the marble surface and, above all, the nature of the purple substance (i.e. colloidal gold) are innovative in archaeology and they could be relevant both for better conservation and awareness of marble artefacts, and to foster a constructive debate.

2. Introduction

Roman marble sarcophagi have been systematically studied from a typological, stylistic and iconographic point of view since the late 19th century. This has given rise to an extensive scientific production and a great corpus that although it is an invaluable resource, the series encourages an emphasis on form and content without unfortunately considering polychromy and gilding (among the endless bibliography see [1],[2],[3],[4],[5],[6],[7]). Conversely, the studies of polychromy on Roman marble sarcophagi are less than ten over the course of a century. Moreover, the attention on the gilding characterization was often given lower consideration (for an interpreted excursus see [8],[9]). Indeed, among these papers only Cagiano De Azevedo [10] reports his focussed comments on the used gilding technique on the so-called 'Gesico sarcophagus preserved at the National Archaeological Museum of Cagliari. Unfortunately, this work cannot aid us to improve our gilding knowledge on Roman sarcophagi because he believed that archaeology was sufficient to distinguish the process of applying gilt to a marble surface without scientific analyses [10]. The gilding was also mentioned by Swoboda [11], Pietrogrande [12], Gütschow [13], Reuterswärd

[14], Philippot [15], and Sörries and Lange [16] but only as well as symbolic or stylistic topics. Differently, some interesting data have come from a recent and systematic investigation of the polychrome and gilded sarcophagus with bucolic scenes at the Vatican Museums (inv. no 31485) carried out by Liverani [17], and the sarcophagus with garlands at the Ny Carlsberg Glyptotek of Copenhagen (inv. no. IN 2468) examined by Sargent [18]; together dating around AD 300. However, a special mention goes to Bourgeoise and Jockey [19],[20], who have deeply investigated the gilding of Hellenistic marble sculptures from Delos. This brief overview highlights the necessity that has motivated this first systematic investigation about the ancient (colour and) gilding on Roman marble sarcophagi identified in the Vatican Museums, the Capitoline Museums and the National Roman Museum collections [8],[9]. Careful examination of their surfaces - with naked eyes and through a magnifying glass or portable stereomicroscope - has underlined that among eighty polychrome sarcophagi investigated, including many unpublished examples, only twelve (or perhaps fifteen) preserve traces of original gilding with may or may not be associate with a purplish substance, which seems attributable to the transformation of gold leaf into colloidal gold (see Sections 5 and 6). In a case study among these sarcophagi (Tabs. 1 and 2), the gold leaf has been identified only thanks to a micro-sampling performed to recognise the techniques used to apply the colour [8],[9]. Therefore, this fortunate discovery reinforces the hope to identify new traces of gilding on other sarcophagi with more deep investigation that is in progress [9].

3. Materials

The examined sarcophagi with gilding or purplish substance cover the time period from the beginning to the end of the 3rd century AD and with no relation to a specific subject or iconographic theme (Tabs. 1 and 2). As a matter of fact the gilding is visible on the historical, mythological and Dionysian sarcophagi, and again on the sarcophagi with Muse, marine subjects, Victories and Cupids holding a shield or clypeus, scenes of private life, and also on the pastoral, bucolic and Christological sarcophagi [9]. The preserved gilding is mainly discernible on the protruding areas of the curls of hair and beards, the hair of animals, the rolled volumes or scrolls (*volumina*), the backs of garment folds, and the background drapes (*parapètasma*). Here and on the clothing and the *volumina*, gold was applied in a uniform manner with a linear shape; the width of the gilded strip and the thickness of the substrate are variable [9]. On the other hand, gold appears to have been applied in a non-uniform manner, as a sort of hatching aimed at creating a 'light vibration' effect, on the curls of hair, beards, torch flames, altars and censers (*thymiatèria*), manes and tails of lions and horses, sheep and goat fleeces, and sea waves [9]. The golden fragments are visible in the form of small flakes with a thickness of a few ten-thousandths of a millimetre on top of the colour layers with a thickness of a sub-millimetre. The main difficulties in characterizing the technique used to apply the gold leaf on the marble surface are, on the one hand, the justified hesitation in taking micro-samples to perform micro-invasive diagnostic analysis (which are mainly based on optical petrographic microscopy-OPM and scanning electron microscopy-SEM), and on the other, the lack of knowledge on the topic which is limited to a few isolated artefacts [17],[18],[19],[20]. However, three golden sarcophagi among these (Tabs. 1 and 2) have been chosen as case studies to perform comparative survey between the results of scientific analyses and archaeological information in order to characterize the techniques used to apply the gold leaf onto the marble surface. Specifically, the so-called 'Annona sarcophagus' (see Subsection 3.1) and the sarcophagus with the myth of Phaedra and Hippolytus (see Subsection 3.2) represent those sarcophagi where the gold leaf seems applied on top of a dark yellow tending towards brown-reddish layer (Tab. 3); while the so-called 'Acilia sarcophagus' (see Subsection 3.3) denote the sarcophagi were the gilding seems applied directly onto the marble surface or on top of a thin coat (Tab. 3).

3.1. The 'Annona sarcophagus' (MNR inv. no. 40799)

The first selected case study is the sarcophagus with *dextrarum iunctio* and personification, better known as 'Annona sarcophagus' (National Roman Museum in Palazzo Massimo inv. no. 40799). This rectangular sarcophagus without lid (Fig. 1) is decorated only in the frontal part with allegorical characters: *Portus*, *Annona*, *Concordia* (behind a married couple making a *dextrarum iunctio*), *Genius Senatus*, *Abundantia*, and *Africa*, from the right to the left of the sarcophagus.

Chest and lid type	Iconographic theme	Colours (pigments and dyes)	Purplish substance	Gilding	Dating	Discovery	Museum inv. no.
'Acilia sarcophagus'; *lenòs* without lid	*Processus consolaris*	Red (haematite, pink madder lake); VIL shows Egyptian blue	A great amount of purplish substance is penetrated into the marble surface and coexists with gold leaf	A great amount of gold is visible on the marble surface and with purplish substance	Second quarter of the 3rd cent. (AD 230-240)	1950 Acilia (Rome)	**MNR 126372**
Parallelepiped chest with gable lid and chunky acroteria corner	Phaedra and Hippolytus	Red made of iron oxides and hydroxides	Few traces are visible with gold leaf on the Theseus and left handmaid hair	A great amount of gilding is visible on top of a dark yellow to brown layer by direct visual inspection (DVI)	End of the 3rd cent. (c. AD 290)	1931 via Muzio Attendolo in Rome	**MNR 122444**
'*Plotinus*'s sarcophagus'; front of *lenòs*	Muses and Philosophers	Red and black probably attributable to red ochre and carbon black	A great amount of purplish substance is visible on the figures hair and bear. It is penetrate into the marble surface	DVI has not detected gilding traces	Third quarter of the 3rd cent. (AD 260-270)	1808 from the Canovas excavation: Servilii tomb on the via Appia, Rome	MV 9504
Parallelepiped chest without lid	Woman portrait among Cupids of seasons, shepherds and Muses	Red and blue: presumable red ochre and Egyptian blue		A possible gold trace has been identified on the left Cupids chlamys by DVI	End of the 3rd cent. (c. AD 300)	unknown	MV 31465
Parallelepiped chest with lid and acroteria corner	Dionysian procession	Red and yellow presumable ochres		Gilding traces were mentioned by [12]. At present we have not detected any traces by DVI	Third quarter of the 2nd cent. (AD 160-170)	1930 near the Rome-Pisa railway bridge	MC 1378
Parallelepiped chest with lid and acroteria corner	Dionysus and Ariadne	Red and yellow ochres, gypsum, Egyptian blue, and possible pink madder lake and carbon black		Some gold traces are occasionally identified by OPM analysis	End of the 2nd cent. (c. AD 200)	1936 via Labicana, Rome	MNR 124682
Lenòs sarcophagus without lid	Clypeus portrait among marine creatures	Red, red tending towards cyclamen, dark yellow and blue colours probably attributable to red and yellow ochres, pink madder lake, and Egyptian blue		A great amount of gilding is visible on top of a clear layer by DVI	First quarter of the 3rd cent. (c. AD 280)	1937 Villa Borghese, Rome	MC 2403
Parallelepiped chest with lid	Victories holding a clypeus and sacrifice Cupids	Red, red tending towards cyclamen, dark yellow and blue colours probably attributable to red and yellow ochres, pink madder lake, and Egyptian blue. Presence also of white and black		A great amount of gilding is visible on top of a dark yellow to brown layer by DVI	Middle 3rd century AD	1904 Lungotevere near the Farnesina, Rome	MNR 23894

Table 1: List of polychrome sarcophagi with gilding and/or purple substance identified with direct visual inspection (DVI) or optical petrographic microscopy (OPM) in the Vatican Museum (MV), the Capitoline Museum (MC) and the National Roman Museum (MNR) collections. Bold highlights sarcophagi chosen as case study that underwent in-depth diagnostic investigation.

Chest and lid type	**Iconographic theme**	**Colours (pigments and dyes)**	**Purplish substance**	**Gilding**	**Dating**	**Discovery**	**Museum inv. no.**
Parallelepiped chest with slab lid	Cupids holding a clypeus; *Oceanus* and *Tellus*; Chiron and Achilles	Red ochre and probably red cinnabar; Egyptian blue and black-based carbon		Gilding traces were mentioned by Sapelli (1981). At present we have not detected any traces by DVI	Third quarter of the 3rd cent. (c. AD 260)	1946 via Casilina Loc. Torraccia, Rome	MNR 124735
Two unmatched fragments of parallelepiped chest	Cupid seasons	Possible red ochre	Vanish traces of purplish colour are visible into the marble surface	DVI has not detected gilding traces	Second half of the 3rd cent. AD	unknown	MNR storages 115723, 115724
'Annona sarcophagus'; parallelepiped chest without lid	*Dextrarum iunctio* and personifications	Red ochre, red ochre mixed with possible pink madder lake, Egyptian blue and white lime	Few traces of purplish substance are visible together with gold leaf on the Annona hair	A great amount of gilding is visible on top of a dark yellow to brown layer on the hair and over the colours on the *parapètasma*	Last third of the 3rd cent. (AD 270-280)	1877 (few years before) via Latina, Rome	**MNR 40799**
Fragment of lid	Figure on biga (a two-horse chariot)	DVI has not detected colour traces	Purplish traces are visible into the marble surface	DVI has not detected gilding traces	End of the 3rd century AD	1935 from Wilpert collection	MV 31591
'Lateranense no. 150 sarcophagus'; parallelepiped chest with lid	Bucolic scenes (chest) Hunting hare and portrait (lid)	Red and yellow ochres, Egyptian blue	Dark purple substance visible on and under gold leaf by OPM are identified as varnish of vegetable resin [17]	The pure gold leaf was applied on a kaolin layer through albumin binder; in some areas it is on top of the red or blue layers [17]	End of the 3rd cent. (c. AD 300)	1818 Tor Sapienza, Rome	MV 31485
'*Iulius Achilleuss* sarcophagus'; *lenòs* with lid	Bucolic and pastoral scenes (*lenòs*) Cupids on chariots (lid)	Red and yellow ochres, Egyptian blue and probably bright pink madder lake	Few traces of purplish substance coexist with gilding	A great amount of gilding is visible on top of red and blue	Last third of the 3rd cent. (AD 270-275)	1939 Via Imperiale, Loc. Vigna Casali, Rome	MNR 125802
'Polychrome slab'	Christological scenes of the New Testament	Yellow-ochre and red-hematite; green was blue probably attributable to Egyptian blue; white still non identified		A great amount of gilding is visible on top of colours	Towards the end of the 3rd or the beginning of the 4th century (AD 290-310)	1860 from Kircker Museum	MNR 67606, 67607

Table 2: List of polychrome sarcophagi with gilding and/or purple substance identified with direct visual inspection (DVI) or optical petrographic microscopy (OPM) in the Vatican Museum (MV), the Capitoline Museum (MC) and the National Roman Museum (MNR) collections. Bold highlights sarcophagi chosen as case study that underwent in-depth diagnostic investigation.

Figure 1: The images show the 'Annona sarcophagus' and the sampling point of the micro-sample no. *40799-C* (National Roman Museum, Rome, inv. no. 40799. Photo: author).

Figure 2: The images show the sarcophagus with the myth of Phaedra and Hippolytus and the sampling point of the micro-sample no. *122444-2* (National Roman Museum, Rome, inv. no. 122444. Photo: author).

The sarcophagus was discovered with its fragmented lid in a modest tomb in via Latina, Rome some years before 1877 [21],[9]. It is dated at the last third of 3rd century, c. AD 270-280 [21],[22]. Direct visual inspection shows a great amount of polychromy and gilding only cited in the academic literature [21],[22]. Regarding the colour, the analytical investigation has showed the presence of pigments and dyes (unknown until now) representatives of the ancient painting techniques of the Mediterranean area: red and yellow ochres, haematite, Egyptian blue, pink madder lake and white lime. The apparent simultaneous use of two pictorial techniques identified may have been one or more ancient re-paintings. It is also interesting that the 'Annona sarcophagus' seems to have completely polychrome figurative elements [23],[9]. Traces of original gilding are discernible on the upper surface of the *parapètasma* and clothes, and on the protruding areas of the curls of hair and beard, the flame of the *thymiatèrion* and in some attributes of the personifications. Gold is visible on top of red and blue of the *parapètasma* and clothes; while on the beard and hair it seems applied on a dark yellow to reddish ground coat (see Subsection 6.1). On the *parapètasma* and clothing, gold was applied in a uniform manner with a linear shape; on the other hand, gold appears to have been applied in a non-uniform manner, as a sort of hatching aimed at creating a 'light vibration' effect, on the curls of hair, beard and flame of the *thymiatèria*. A purple colour substance is also visible in association with the gold on the hair of the *Annona* personification similarly to the 'Acilia sarcophagus' (see Subsection 3.3 and 6.3).

3.2. Sarcophagus of Phaedra and Hippolytus (MNR inv. no. 112444)

The second case study is the sarcophagus with myth of Phaedra and Hippolytus (National Roman Museum Baths of Diocletian inv. no. 112444). The sarcophagus (Fig. 2), in rectangular chest with gable lid covered by rosette-shaped ending tiles and chunky acroteria corner on the front, was carved in Rome by artists from Asia Minor at the end of the third century, c. AD 290 [24]. The sarcophagus is decorated, in high relief and only on the front; Phaedra and Hippolytus have unfinished portrait head, designed to receive the physiognomic features of the deceased [25].

The sarcophagus was found in via Muzio Attendolo near Largo Preneste, Rome in 1931 [24]. It presents a great amount of red and gilding traces on the relief and on the acroterial corner masks of the

lid [9], until now neglected from the academic studies ([24] with previous bibliography, [25], [7] with selected bibliography). Specifically, a whitish substance characterized by fine granules size is visible with the naked eye or through a magnifying glass in the prominent and recessed areas of the figures, the flesh, the background and the masks. It was probably applied as a ground layer of red colour that in other areas appears applied directly onto the marble surface. There is also the presence of earthy fouling, probably accumulated during the burial [9]. The gilding is preserved on the hair of the acroterial masks, on the protruding areas of the hair and beard of the figures, the hooves of the horse and, again, on the button of the coat and the eagle head of Hippolytus' sword and the Cupid wings [9]. Similar to the 'Annona sarcophagus', the gold leaf appears applied, especially on the hair and beard, on top of a dark yellow tending towards brown-reddish coat (see Subsection 6.2). This sarcophagus was also selected as a case study to understand the nature of a purple substance co-present with the gilding (see Subsection 3.3 and 6.3).

3.3. The 'Acilia sarcophagus' (MNR inv. no. 126372)

The third case study is the famous 'Acilia sarcophagus' (National Roman Museum in Palazzo Massimo inv. no. 126372) with *processus consularis* (Fig. 3). It was found at Acilia (Rome) and is generally dated at the second quarter of the 3rd century AD [26], [27] or, more recently, at the last quarter of the 3rd century AD [28]. The 'Acilia sarcophagus' was analysed in order to clarify the gilding technique used and to characterise the nature of the purplish substance [9]. In fact, the sarcophagus has been known to scholars since 1950 the year of its discovery due to the abundant presence of a purplish substance commonly interpreted as a 'bole' or 'mordant' for gilding ([26] referring to [12]; a theory also found in [29],[14],[27],[30]). Gilding is discernible on the upper surface of the togas and their *sinus*, the scrolls and on the protruding areas of the curls of hair and beards of the figures. Gold was applied in a uniform manner with a linear shape on the togas, sinus and scrolls; on the other hand, on the curls of hair and beard gold appears to have been applied in a non-uniform manner, as a sort of hatching aimed at creating a 'light vibration' effect [9]. The gold is co-present with a purple substance penetrate into the marble surface and a blue powdered substance (see Subsection 6.3).

Figure 3: The images show the 'Acilia sarcophagus' and the sampling points of the micro-samples no. *126372-A/E/F* (National Roman Museum, Rome, inv. no. 126372. Photo: author).

4. Methods

The first preliminary action in the study of Roman golden sarcophagi were the historical and iconographic research on one hand, and a careful examination by fixed magnification (2x) Olympus VMF stereo-microscope mounted on a tripod on the other hand. Moreover, we have performed some non-invasive analysis (e.g. VIL and UVL multispectral imaging) fallowing by micro-invasive investigations, namely optical petrographic microscopy (OPM) and scanning electron microscopy with energy dispersive x-ray spectroscopy (SEM-EDS), in order to acquire information on the techniques used to apply the gold leaf onto the marble surface (see Subsections 3.2 and 3.3). To this purpose, three small and representative micro-samples, namely *40799-C*, *122444-2* and *126372-F* samples (Figs. 1 - 3), were chosen respecting the criteria of minimum invasiveness in collaboration with the Museums restorers.

4.1. In situ microscopy and documentation

A fixed magnification (2x) Olympus VMF stereomicroscope mounted on a tripod was used to image details of golden sarcophagi. A reflex Nikon D80 and a Nikon Coolpix P340 were used to macro-digital imaging acquisition.

4.2. Optical petrographic microscopy (OPM)

Optical microscopy has allowed a preliminary examination of the micro-samples, which were investigated with a Wild Heerbrugg M10 stereomicroscope with variable magnification. The crushed-grain samples were then observed by means of Leitz Orthoplan-pol microscope equipped with a

PloemOpak filter cubes (excitation filter BP 340-380nm) in reflected and intersecting light, on dark field and after excitation by UV light, Hg lamp, UV filter 330-380nm and 450-490. Usual magnifications were from 4x to 40x, and 63x oil immersion. Morphological traits of gold leaf and individual pigment granules on prepared crushed-granules were examined in intersection polarised light in parallel (PPL) and crossed (XPL) nicols. The polarizing microscope was interfaced to a PC using a Canon EOS 5D digital camera.

4.3. SEM-EDS

Subsequently, the sample of the 'Acilia sarcophagus' was also examined by scanning electron microscopy with energy dispersive x-ray spectroscopy (SEM-EDS) using a SEM ZEISS EVO MA 15 with EDS Oxford Inca ENERGY 250 X-Act microanalysis instrument.

4.4. Archaeological and historical researcher

At the same time, archival and literature searches have performed to help us in the understanding the preservation and restoration history of the case studies and solve doubts about the application techniques of gold leaf on the marble surface. Obviously, the search started by evaluating the description of the sarcophagi in the historical archive and in the catalogue of the National Roman Museum.

5. Results

To detect the different techniques used to apply the gilding (see Section 3), we have taken a *40799-C* micro-sample from the 'Annona sarcophagus' (see Subsection 5.1). It seems to correspond to a very similar substance visible on the *122444-2* micro-sample took from the sarcophagus with the myth of Phaedra and Hippolytus (see Subsection 5.2). We have also performed a micro-sampling from the 'Acilia sarcophagus' (see Subsection 5.3). The first two micro-samples (*40799-C* and *122444-2*) are made up of minute flakes and granules, while the third micro-sample (*126372-F*) is powdery. Therefore, we have been able to examine only the crushed-grains type prepared by OPM. The *126372-F* sample presenting a more complex situation was also examined by SEM-EDS.

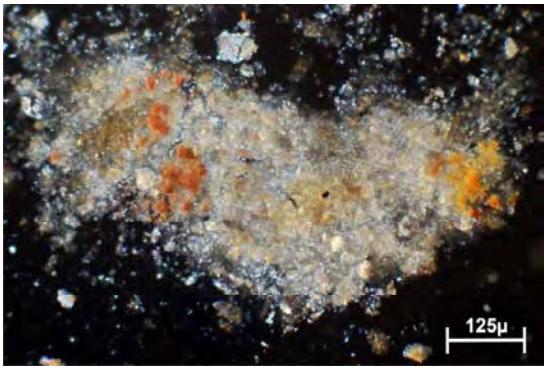

Figure 4: Micro-photo of the crushed-grains of the micro-sample no. *40799-C* in reflected light and crossed nicols (XPL), 10x lens and 125 length scale, which shows iron oxides and hydroxides and gold foil with non-homogeneous and riddled with holes feature (Photo: C. Gratziu, A. Moscato).

5.1. The 'Annona sarcophagus' (MNR inv. no. 40799)

The dark yellow almost brown micro-sample named *40799-C* was taken from a lock of hair at the back left of the *Annona* head (Fig. 1). It appears as small flakes. Sample no. *40799-C OPM reader*. The crushed-grains preparation is made almost entirely of calcite particle size ranging from micro-crystalline to coarse meso-crystalline. In 45° spot and reflected light frequent yellow-orange and, more rarely, bright red patches are observed. Their optical features are those of iron oxides and hydroxides. The gold leaf is characterized by non-homogeneous and riddled with holes feature (Fig. 4).

5.2. Sarcophagus of Phaedra and Hippolytus (MNR inv. no. 112444)

The dark yellow almost light brown micro-sample named *122444-2* was taken from a projecting area of Theseus hair lock (Fig. 2). It is composed of few granules. Sample no. *122444-2 OPM reader*. Minuscule fragments of gold leaf are visible in the crushed-grains preparation by 90° spot and reflected light to the polarizing microscope. A chalky matrix is associated with them. The optical microscope resolution limit (63x oil immersion) does not allow the characterization of other tiny elements dispersed in the matrix and which give a yellowish-orange colour when they are observed by 45° spot and reflected light (Fig. 5).

ANALYTICAL TECHNIQUES	INVESTIGATED ISSUES	SAMPLES OR MEASURE POINTS	ADDITIONAL INFORMATION	EXAMINED SARCOPHAGUS
OPM	Material composition	The micro-sample no. *40799-C* was taken from a lock of hair at the back left of the *Annona* head. It appears as small flakes	Directly inspection with naked eyes and through portable stereoscope has showed that (i) gold leaf appears applied on top of a dark yellow to reddish ground coat on the upper surface of the *parapètasma* and clothes, and on the protruding areas of the curls of hair and beard, the flame of the *thymiatèrion* and in some attributes of the personifications; (ii) purple substance is also discernible in association with the gold; (iii) gilding is visible either on top of red and blue colours, or on top of a dark yellow to reddish ground coat	Annona sarcophagus (MNR inv. no. 40799)
	Gold leaf characterization			
	Nature of purple substance			
	Degradation processes			
	Stratigraphy			
Raman	Materials composition	*Ibidem*		
VIL	Egyptian Blue mapping	Performed on all the relief surface		
UVL	Materials composition	Performed only on selected areas		
OPM	Material composition	The micro-sample no. *112444-2* was taken from a projecting area of Theseus hair lock; it is composed of few granules	Directly inspection with naked eyes or through magnifying glass has showed that (i) gold leaf appears applied on top of a dark yellow to reddish ground coat on the hair of the acroterial masks, on the protruding areas of the hair and beard of the figures, the hooves of the horse and, again, on the button of the coat and the eagle head of Hippolytus sword and the Cupid wings; (ii) a purple substance is also discernible in association with the gold	Sarcophagus of Phaedra and Hippolytus (MNR inv. no. 112444)
	Gold leaf characterization			
	Degradation processes			
	Stratigraphy			
Raman	Materials composition	*Ibidem*		
OPM	Material composition	The micro-sample no. *126372-F* was taken from a hidden area of the sinus of the figure with toga. It is powdery material mixed with marble	Directly inspection with naked eyes and through portable stereoscope has showed on the top of supposed stratigraphy a spread white substance, under it a bright blue substance, and under it the gilding appears always co-present with the purple substance. They seem applied directly onto the marble surface	Acilia sarcophagus (MNR inv. no. 126372)
	Gold leaf characterization			
	Nature of purple substance			
	Degradation processes			
	Stratigraphy			
Raman	Materials composition	*Ibidem*		
VIL	Materials composition	Performed on all the relief surface		
Ibidem	Nature of purple substance	*Ibidem*		
UVL	Materials composition	Performed only on selected areas		
Ibidem	Nature of purple substance	*Ibidem*		
SEM-EDS	Compositional and textural aspects	The micro-sample no. *126372-F* is powdery material mixed with marble, which was taken from a hidden area of the sinus of the figure with toga		
	Gold leaf characterization			
	Nature of purple substance			
	Degradation processes			
	Stratigraphy			

Table 3: The table shows an overview of the analytical techniques used to resolve the issues investigated and, on the other hand, the micro-samples and data detected by direct visual inspection of selected Roman marble sarcophagi to identify the gilding techniques used.

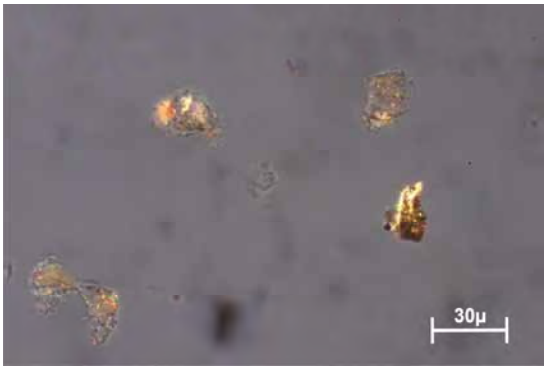

Figure 5: Micro-photo of the crushed-grains of the micro-sample no. *122444-2* in reflected light and parallel nicols (PPL), 40x lens and 30 length scale, which shows iron oxides and hydroxides and gold foil with non-homogeneous and riddled with holes feature (Photo: C. Gratziu, A. Moscato).

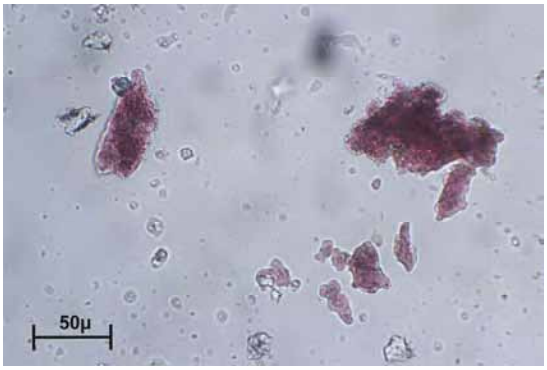

Figure 6: Micro-photo of the crushed-grains of the micro-sample no. *126372-F* in reflected light and parallel nicols (PPL), 25x lens and 50 length scale, which shows elements that appear transparent and an overall pinkish colour with fine dots ranging from bright red to brown within them (Photo: C. Gratziu, A. Moscato).

5.3. The 'Acilia sarcophagus' (MNR inv. no. 126372)

A micro-sampling in a hidden area near the *sinus* of the figure with toga attributed to Gordian III by Bianchi Bandinelli [26] was performed in order to understand the gilding application techniques and the nature of purplish substance often visible along the gilding or where it was (Fig. 3). Other two similar micro-samples (*126372-A* and *126372-E* were taken later from the toga of the same figure to deep the investigation [8],[9]. During the sampling activity, the purplish substance has appeared without thickness and strongly cohesive to the marble likewise to a fluid and thin brushwork. Therefore, its sampling was very hard: it is not coming away as flakes but as powdery material mixed with marble. It was also possible to identify the presence of intense blue material, which has never been mentioned in the academic literature [26], [29], [14], [27], [30], [28]. It is visible along the lines made of gilding on the projecting parts of garments (*togae*) and scrolls (*volumina*). In particular it appears between the gold leaf and a whitish substance, with OPM analysis has turned out to be modern [9]. Furthermore, the bright blue material has a powdery consistency to the sharp scalpel contact.

Sample no. *126372-F OPM reader*. We identified several marble crystals and small pieces of gold leaf in the crushed-grains prepared. The crystals of marble appear as aggregated with cataclastic structure sometimes very thin. The gold leaf is easily identifiable as such by 90° spot and reflected light viewing, and it has a bluish shade in transmitted light and PPL nicols. It is characterized by a non-homogeneous and riddled with holes feature and, in some cases, it appears directly overlapped to the crystals of marble. We also noted the presence of some additional elements that appear transparent and an overall pinkish colour with fine dots ranging from bright red to brown within them, in transmitted light and PPL nicols (Fig. 6). They are virtually extinct in XPL nicols, while they show orange fluorescent when viewed through ultraviolet light. These material optical characteristics seem attributable to a red lake. The purple element is instead ascribable to altered gold fragments if observed at 90° spot and reflected light (Fig. 7).

Sample no. *126372-F SEM-EDS reader*. The qualitative analysis of micro-sample, performed at SEM Zeiss EVO MA 10 with EDS microanalysis, indicates both a low presence of characteristic elements of ochres (such as iron, magnesium and potassium), and a high concentration of silicon, aluminium and calcium. Although they are into ochres, their high percentage compared to that of the iron can suggest a possible presence of kaolin. The measurement also shows a rather high peak of sulphur. The gold leaf is very thin (about 50nm), characterized by a non-homogeneous and riddled with holes feature (Fig. 8).

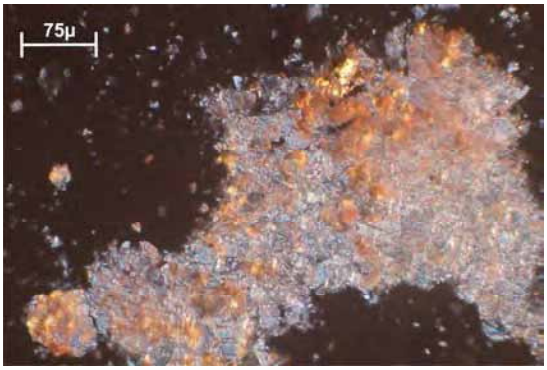

Figure 7: Micro-photo of the crushed-grains of the micro-sample no. *126372-A* in reflected light, spot 90° and crossed nicols (XPL), 16x lens and 50 length scale, which shows the purple substance with a metallic appearance like that the gold leaf (Photo: C. Gratziu, A. Moscato).

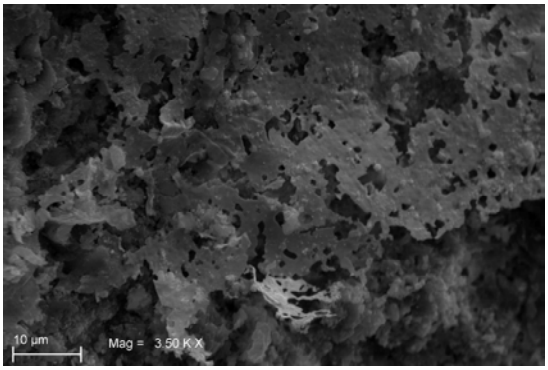

Figure 8: The SEM image of the micro-sample no. *126372-F* shows a thin gold leaf characterized by non-homogeneous and riddled with holes feature (Photo: A. Bertagnini).

6. Discussion

6.1. Remarks about the 'Annona sarcophagus' (MNR inv. no. 40799)

Traces of original gilding are visible with the naked eyes or through stereomicroscope on the upper surface of the *parapètasma*, on clothes, on hair, on the flame of the *thymiatèrion* and in some attributes of the personifications. It appears laid in systematic efforts with solid lines (approx. 1 cm wide) over the red and blue traces of the *parapètasma* (Fig. 3); on the other hand, on the beard and hair it seems applied on top of a dark yellow to reddish ground coat. A purple colour substance is also discernible in association with the gold on the hair of the *Annona* personification (Fig. 1). It is very similar to the purple substance detected on the marble surface of the 'Acilia sarcophagus' (see Subsection 6.3). The crushed-grains prepared does not allow us to see the stratigraphic sequence and provide an exact interpretation of data, however the yellow-orange and bright red granules related to iron hydroxides and oxides seem to confirm that in this case the gold leaf was applied on a ground layer made of ochres. In addition, we are in presence of uncommon corrosion process of the gold leaf that has turned into colloidal gold particles of purplish colour (see Subsection 6.3). In some *parapètasma* areas, the gold leaf is applied on few preserved blue traces that the recent investigation through non-invasive Visible-induced Infrared Luminescence-VIL imaging revealed made of Egyptian blue pigment proving the OPM result [23], [9].

6.2. Remarks about the sarcophagus of Phaedra and Hippolytus (MNR inv. no. 112444)

The gilding is preserved on the hair of the acroterial masks, on the hair and beard of the figures, on the manes and hairs on the hooves of the horse; and, again, on the button of the coat and the eagle head of Hippolytus' sword, and the Cupid wings. Similar to the 'Annona sarcophagus' the gold appears applied especially on the hair and beard on top of a dark yellow tending towards brown-reddish coat. In addition, a direct inspection with the naked eye and through magnifying glass has also detected a purplish substance co-present with the gilding. The reading of the crushed-grains of a micro-sample by polarizing microscope has demonstrated that also in this case the gold leaf is deteriorated and has turned into colloidal gold particles. Therefore, the purple colour substance is colloidal gold and not a mordant substance to fix the gold leaf as usually considered in the academic literature (see Subsection 6.3). Furthermore, the gold leaf is associated to a gypsum matrix with dispersed granules that give it a yellow-orange colour. These may represent the traces of yellow and red ochre commingled. This would lead us to think that the gold leaf was applied onto a coloured layer like as 'bole' technique or, perhaps, over a secondary painting [9].

6.3. Remarks about the 'Acilia sarcophagus' (MNR inv. no. 126372)

Traces of original gilding are discernible on the upper surface of the scrolls, the togas and their sinus in a uniform appearance and linear shape of approx. 0.5 cm wide. On the other hand, gold appears

to have been applied in a non-uniform manner, as a sort of hatching aimed at creating a 'light vibration' effect on the curls of hair and beard. The purplish substance and blue material are co-present to gilding or where the gold was at the beginning. The analyses results performed until now reveal that the gold leaf has a non-homogeneous and riddled with holes feature probably due to degradation phenomena [31]. That correspond to the transformation of the gold leaf in colloidal gold, that is "a colloidal suspension of sub-micrometric gold particles in a fluid that takes on an intense red colour (for particles smaller than 100nm) or a dirty yellow (for larger particle size)" [32], [33]. The purple element is also ascribable to altered gold fragments if observed in OPM at 90° spot and reflected light (see Subsection 5.3). The results seem also to highlight that the gold leaf was applied directly onto the marble or, more likely, onto a thin layer of kaolin with a possible egg white. They also confirm that the purple substance is gold which had been transformed into colloidal gold, rather than being a bole or mordant for gilding as hitherto assumed in the academic reading [more details in [9]]. Heinrich Piening [34] also comes to a similar conclusion on the purple element by UV-VIS spectroscopy, analysing some preserved traces on the so-called 'Artemide of Copenhagen' at the Ny Carlsberg Glyptotek of Copenhagen (inv. IN 481). The UV-VIS-spectrum seemed not to be produced by a dyestuff but showed a remarkable similarity to gold purple, a synthetic pigment made of gold and tin, which is known as 'Purple of Cassius'. Excluding that it may be the purple of Cassius [35], [36], Piening attributes the triggering of the corrosion process of gold leaf to magnesium oxide (MgO) or tin (Sn) which based on his analysis are in the marble. Therefore, the production of nano gold particles would be triggered by the dissolution of such chemical elements due to the humidity [34]. Piening's experimentation is interesting and meritorious, but the conclusions that come to him pose some perplexity. Dolomite marbles may contain magnesium oxide in a variable percentage but hardly enclose tin, though this is not impossible. Therefore, in a natural context, the transformation of gold into colloidal gold due to the dissolution of these chemical elements for humidity is not entirely convincing [9]. On the other hand, it is very likely that the process has been triggered by a microbiological attack when the sarcophagus was still underground and ongoing analysis will allow me to confirm or refute this original hypothesis [9]. Investigations are currently underway also on the powdery material of intense blue colour observed over the gold, so it is not possible to express it with assurance. Hematite granules and a red madder lake may have been used to paint the edges of the togas, the scrolls, the hair and facial features as evidenced by the residues of polychrome traces [9].

7. Conclusions

The presented work yielded better knowledge of gilding techniques used on Roman marble sarcophagi (see Tables 1 and 2) and confirms the complexity of this topic (see Table 3), which requires a combined approach, involving data integration obtained through various analytical techniques to be solved. However, the integration of macroscopic and microscopic examinations results on one hand, and archaeological and historical information on the other hand, enabled me to identify the two methods used to apply the gold leaf. The technique we have the most evidence for was to put the fine gold leaf on top of a coloured layer made of iron oxides and hydroxides used separately or mixed together or of Egyptian blue or, again, of madder rose lake mixed with other pigments. Sometimes, between the gold leaf and the polychrome layer there was also a thin coat of kaolin, which is often more difficult to identify in polished sections. In the other technique, a fine gold leaf appears to have been applied directly onto the marble surface or on a possible thin layer of kaolin using an organic adhesive of protein or oil-resinous nature. The first technique was found in the 'Annona sarcophagus' (see Subsection 6.1) and in the sarcophagus with the myth of Phaedra and Hippolytus (see Subsection 6.2). The same method seem also used on the sarcophagus with Victories holding a clypeus and Cupids that performing a sacrificial rite preserved in the National Roman Museum Baths of Diocletian inv. no 23894 [9]. This technique has also probably used in the sarcophagus with myth of Dionysus and Ariadne at the National Roman Museum Baths of Diocletian inv. no. 124682, where the gold has been identified only thanks to a micro-sampling performed to recognise the techniques used to apply the colour [9]. Additionally, Tables 1 and 2 show that in some sarcophagi only the colloidal gold is still visible and which is also visible in same sarcophagi characterised by the gold leaf applied on top of a layer of colour [9]. To conclude, colloidal gold is also visible in some Hellenistic, Roman and

Medieval marble sculptures and in some Roman sarcophagi re-painted and gilded (or re-gilded) in medieval time, when they have been re-used as, for example, those exposed in the Camposanto Monumentale of Pisa [9].

8. Acknowledgements

I wish to thank the Soprintendenza Speciale per il Colosseo e l'Area Centrale di Roma and the directors of the National Roman Museum, Dr. Rita Paris and Dr. Rosanna Friggeri, who facilitated this research and allowed me the permission to publish the results. Special thanks are due to Prof. Corrado Gratziu (University of Pisa), Alessandra Moscato (Gra-Al Lab Srl in Pisa) and Dr. Antonella Bertagnini (National Institute of Geophysics and Volcanology in Pisa) for the OPM and SEM-EDS analyses. I am also grateful to Dr. Giovanna Bandini, Debora Papetti and Silvia Borghini for the sampling activity at the National Roman Museum in Rome. This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors.

References

[1] C. Robert, et al., Die antiken Sarkophag-Reliefs, Deutsches Archäologisches Institut, Berlin, 1880-.
URL http://ancientworldonline.blogspot.it/2012/06/online-corpus-of-ancient-sarcophagi.html

[2] R. Garrucci, Storia dell'arte cristiana nei primi otto secoli della Chiesa, G. Guasti, Prato, 1872-1881 (especially vol. 5 - Sarcofagi ossia sculture cimiteriali, 1879).

[3] J. Wilpert, I sarcofagi cristiani antichi, Città del Vaticano, Roma, vol. I 1929, vol. II 1932, vol. III 1936.

[4] F. W. Deichmann, G. Bovini, H. Brandenburg, Repertorium der christlichantiken Sarkophage. I. Rom und Ostia, F. Steiner, Wiesbaden, 1967.

[5] F. Gerke, Die christlichen Sarkophage der vorkonstantinischen Zeit, W. de Gruyter & co., Berlin, 1940.

[6] G. Koch, H. Sichtermann, Römische Sarkophage, G. H. Beck, München, 1982.

[7] P. Zanker, C. B. Ewald, Living with Myths: The Imagery of Roman Sarcophagi, Oxford University Press, Oxford, 2012.

[8] E. Siotto, Nuove tecnologie per lo studio della policromia sui sarcofagi romani: proposte per una standardizzazione metodologica, Ph.D. thesis, University of Pisa (2013).
URL https://etd.adm.unipi.it/t/etd-10212013-143152/

[9] E. Siotto, La Policromia sui Sarcofagi Romani. Catalogo e Risultati Scientifici (foreword by G. Koch), Studia Archaeologica 220, L'Erma di Bretschneider, Roma, 2017.

[10] M. Cagiano de Azevedo, La doratura del sarcofago di Gesico, in: BRest, Vol. 31-32, Ministero per i beni e le attivit culturali, 1957, pp. 167–170.

[11] H. Swoboda, Zur altchristlichen Marmorpolychromie Fragmente, in: RömQSch, Vol. III, Herder, 1889, pp. 134–157.

[12] A. L. Pietrogrande, Sarcofago policromo con raffigurazione bacchica, in: Bullettino della Commissione archeologica comunale di Roma, Vol. LX, L'Erma di Bretschneider, 1932, pp. 177–215.

[13] M. Gütschow, Das Museum der Prätextat-Katakombee, in: Rendiconti, Atti della Pontificia Accademia Romana di Archeologia, Vol. IV of III, Memorie, Tip. poliglotta vaticana, 1938, pp. 26–267.

[14] P. Reuterswärd, Studien zur Polychromie der Plastik. Griechenland und Rom, Svenska Bokförtaget, Stockholm, 1960.

[15] P. Philippot, Sur la polychromie de sarkophages romains du IIIe siècle, in: A. Knoepfli, H. J. Albrecht (Eds.), Von Farbe und Farben. Albert Knöpfli zum 70. Geburtstag, Manesse-Verlag, Zürich, 1980, pp. 279–282.

[16] U. Lange, R. Sörries, D. Procla-Platte, Eine polychrome Loculus-Verschlussplatteaus der anonymen Katakombe van der Via Anapo in Rom, in: Antike WeltZeitschrift für Archäologie und Kulturgeschichte, Vol. 21, Zabern-Verlag, 1990, pp. 45–56.

[17] P. Liverani, New Evidence on the Polychromy of Roman Sculpture, in: V. Brinkmann, O. Primavesi, M. Hollein (Eds.), Circumlitio. The polychromy of antique and medieval sculpture, Proceedings of the Johann David Passavant Colloquium, Hirmer, Munich, 2010, pp. 290–302.

[18] M. L. Sargent, Metropolitan Roman Garland Sarcophagus, in: J. S. Østergaard (Ed.), Tracking Colour: The polychromy of Greek and Roman sculpture in the Ny Carlsberg Glyptotek. Preliminary Report 3, Copenhagen, 2011, pp. 14–34.
URL http://www.trackingcolour.com/publications/preliminary-reports

[19] B. Bourgeois, P. Jockey, D'or et de marbre. Les sculptures hellénistiques dorées de Délos, in: BCH, Vol. 128-129, cole franaise d'Athnes, 2004-05, pp. 331–349.

[20] B. Bourgeois, P. Jockey, La dorure des marbres grecs. Nouvelle enquête sur la sculpture hellénistique de Délos, in: JSav, De l'Imprimerie Royale, 2005, pp. 253–316.

[21] A. Aquari, Di due sarcofagi scoperti recentemente nella vigna Aquari fuori la Porta Latina, in: BComm, Vol. V, L'Erma di Bretschneider, 1877, pp. 146–159.

[22] L. Musso, R. Friggeri, II,1. Sarcofago dell'Annona (inv. n. 40799), in: A. Giuliano (Ed.), Museo Nazionale Romano. Le sculture esposte Aule delle Terme, Vol. I.8, De Luca, Roma, 1985, pp. 46–51.

[23] E. Siotto, G. Palma, M. Potenziani, R. Scopigno, Digital study and Web-based documentation of the colour and gilding on ancient marble artworks, in: R. Scopigno, G. Guidi (Eds.), Digital Heritage International Congress 2015, Vol. I, Granada, 2015, pp. 239–246. doi:https://doi.org/10.1109/DigitalHeritage.2015.7413877.

[24] L. Musso, I,4. Sarcofago con raffigurazione del mito di Ippolito (inv. n. 112444), in: A. Giuliano (Ed.), Museo Nazionale Romano. Le sculture esposte Aule delle Terme, Vol. I.8, De Luca, Roma, 1985, pp. 12–17.

[25] P. Liverani, Tradurre in immagini, in: V. Brinkmann, O. Primavesi, M. Hollein (Eds.), Römische Bilderwel-

tenradurre, Kolloquium der Gerda Henkel Stiftung am Deutschen Archäologischen Institut Rom, Heidelberg, 2007, pp. 13–26.

[26] R. Bianchi Bandinelli, Sarcofago da Acilia con designazione di Gordiano III, in: BdA, Vol. 39, Istituto Poligrafico dello Stato, 1954, pp. 200–220.

[27] A. Sapelli, 182. Sarcofago con scena di processus consularis da Acilia (inv. n. 126372), in: A. Giuliano (Ed.), Museo Nazionale Romano. Le Sculture, Vol. I.1, De Luca, Roma, 1983, pp. 298–304.

[28] C. Reinsberg, Die Sarkophage mit den Darstellungen aus dem Menschenleben. Vita Romana-Sarkophage, Vol. I.3 of Die antiken Sarkophag-Reliefs, Deutsches Archäologisches Institut, Berlin, 2006.

[29] G. Pesce, Sarcofagi romani di Sardegna, L'Erma di Bretschneider, Roma, 1957.

[30] M. Sapelli, La lastra policroma con scene cristologiche del Museo Nazionale Romano. Osservazioni su struttura e tecnica, in: G. Koch (Ed.), AktendesSymposiums 'Frühchristliche Sarkophage', Mainz am Rhein, 2002, pp. 187–206.

[31] D. B. Craig, B. D. Anderson, Handbook of corrosion data, ASM International, 1997.

[32] C. N. R. Rao, G. U. Kulkarni, P. J. Thomasa, P. P. Edwards, Metal nanoparticles and their assemblies, in: Chem. Soc. Rev., Vol. 29, The Royal Society of Chemistry, 2000, pp. 27–35. doi:10.1039/A904518J.

[33] V. Reddy, Gold nanoparticles: synthesis and applications, in: Synlett, Vol. 11, Thieme, 2006, pp. 1791–1792. doi:10.1055/s-2006-944219.

[34] H. Piening, Gold to purple. Violet traces on Antique Marble, Tech. rep., Bayerische Verwaltung der staatlichen Schlösser, Gärten und Seen (2014).
URL http://www.stiftung-archaeologie.de/Heinrich%20Piening%20Gold%20to%20purple%202014.pdf

[35] H. Gay-Lussac, Ueber den Cassius schen Goldpurpur, in: Annalen der Physik, Vol. 101, 8, Wiley-VCH, 1832, pp. 629–630.

[36] M. Faraday, The bakerian lecture: experimental relations of gold (and other metals) to light, in: Philos. Trans. R. Soc. London, Vol. 147, 0, The Royal Society, 1857, pp. 145–147.