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ANALYTICAL STUDY AND CONSERVATION OF ARCHAEOLOGICAL TERRA SIGILLATA WARE FROM ROMAN PERIOD, TRIPOLI, LIBYA

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ABSTRACT

The aim of the present paper is to study the chemical and the mineralogical composition of an archaeological pottery ware shred which was found in the excavation belongs to the Roman period (250A.D). It was found and stored in the National Museum in Tripoli the capital of Lybia. Its type was found to be a Terra Sigillata ware, bright-red, polished pottery used throughout the Roman Empire from the 1st century B.C to the 3rd century A.D. To perform this study, several analytical instruments were used; including X-ray diffraction (XRD), optical microscopy (OM), scanning electron microscopy (SEM), thermal analysis (TG) and differential thermal analysis (DTG) and Fourier transform infrared spectroscopy (FTIR). The texture of the pottery was made of fine quartz and the fracture color is red due to the presence of Hematite (Fe_2O_3). The firing temperature of the ware is high, subsequently; the hardness of the pottery is quite high. The dish was made with a mould In addition to analytical studies, restoration treatments were carried out on the dish including; mechanical and chemical cleaning, bonding and replacement and coloring processes.

KEYWORDS: Pottery, Terra Sigillata, Roman period, Analytical techniques, Restoration

1. INTRODUCTION

Terra Sigillata is the name that describes fine tableware produced in the Roman period and characterized by a red sintered slip obtained from a suspension of very fine clay of suitable composition deposited before firing at the surface of the body.(Guarino, et.al., 2011). The combination of firing conditions with grain size and composition of the clay led to the development of a high sintered coating (Lopez, 2007). The production of Terra Sigillata began in Central Italy in the 1st century B.C. and from there it spread to many areas of the Roman Empire being popular until the 5th century A.C. Figure 1 shows a map of the locations of Terra Sigillata industry in the world in ancient times. (WWW.ceramic today.com/links/wood firing).

Hispanic Terra Sigillata is the pottery that was produced in what is today Spain. The manufacturers can, in favourable cases, be identified by stamps (Sigillum) of origin on the underside of ceramic wares. Sometimes not only the production place is identified, but also the name of the craftsman involved. Terra Sigillata is an example of a large-scale industrial pottery production in Roman times (Lo´pez, 2005). These ceramics, usually decorated with raised motifs and standardized shapes, were quickly established as semi-luxury dishes, in-between common pottery and luxury metal tableware (bronze or silver), replacing Campanian crockery with black slips inspired from the Greek tradition. The use of models to produce decorated shapes, links Sigillata to the Greek vases of M´egara or Samos from III and II century BC. Such pottery also comes under the name of Vasa Samia, mentioned in ancient texts. Sigillata can be distinguished from the Hellenistic (Sciau, 2008).

Productions by its surface gloss due to the verification of the clay slip produced under an oxidizing atmosphere, which induces slip vitrification without iron reduction. The control of the oxidizing atmosphere during firing allowed the development of the Sigillata technique) Riccardi, 1998) (Fig.2). Some forms of pottery pots Terra Sigillata found in international museums, (Fig. 3) Are the most important forms of pottery Terra Sigillata. (Fig.4) shows some of the most important forms of pottery Terra Sigillata displayed at the National Museum in Tripoli, Libya.

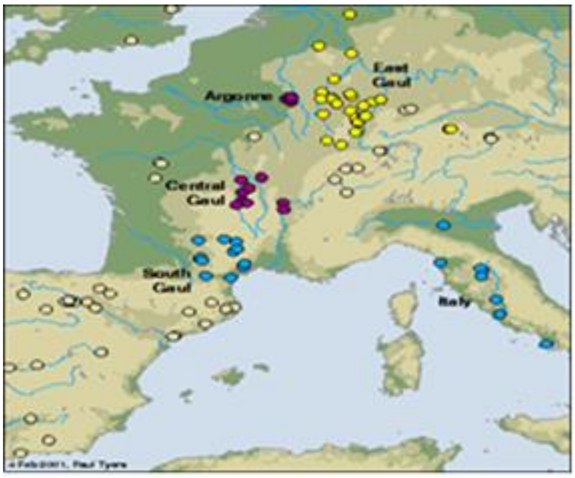

Figure 1.The locations of Terra Sigillata industry in ancient world

The success of Sigillata ware was mainly due to the brightness and the red color aspect, which is derived from the nature and the microstructure of its slip. Previous studies have shown that Sigillata slips of La Graufesenque were obtained from a non-calcareous clay while the local calcareous clay was used for the bodies. During firing the slips are vitrified and develop a specific microstructure containing submicrometric hematite and nanometric corundum crystals homogeneously dispersed in a vitreous matrix (Kiiskinen, 2013)

Quartz crystals of micrometric size are also present, but with a more heterogeneous distribution. No transition metals have been detected in the vitreous matrix, which is probably transparent. Similar conclusions have been reached for products from the Montans workshop. Recent results concerning the smaller south Gaul centre of Espalion (Aveyron) indicate that this is also the case for other Gallic workshops. It seems that the slips of major south Gaul production centres have a particular type of microstructure, which differs from that of the Italian slips found at the site of La Graufesenque by the massive presence of corundum Nano crystals (30%–50% of the crystallized part) and the almost entire absence of spinel crystals (< 2%). The Italian slips are composed of a transparent vitreous phase, which contains also quartz and hematite crystals. However, the proportion of spinel exceeds 30% and corundum was not detected (Mariana, 2010)

Figure 2. Some pottery forms of Terra Sigillata found in international museums

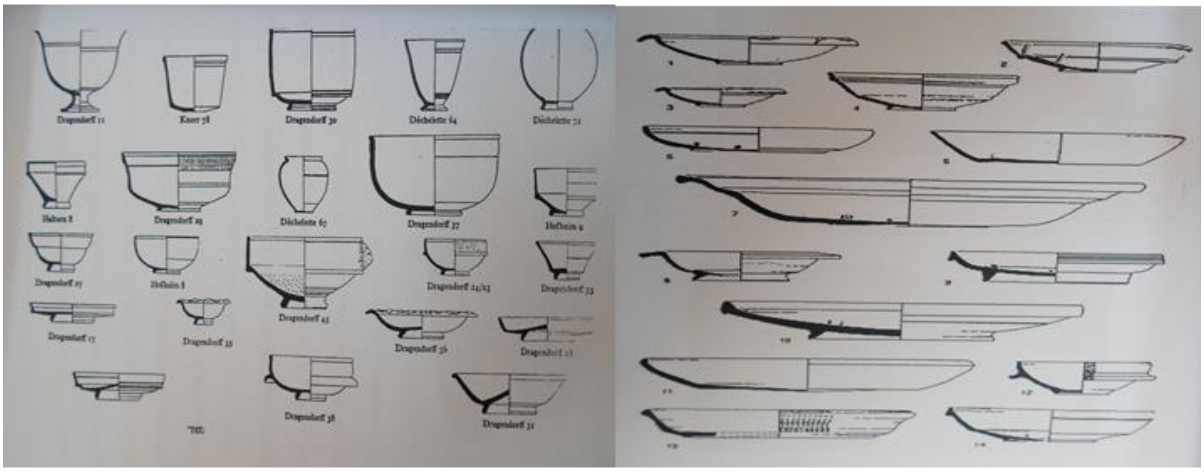

Figure 3. The Most important forms of pottery Terra Sigillata

Figure 4. Some of the most important forms of pottery Terra Sigillata displayed at the National Museum in Tripoli, Libya.

2. METHODS (PLM, XRD, SEM, FTIR, THERMAL ANALYSIS)

The samples under study had been found in digs in the ancient city of Tripoli limits were stored at the National Museum, which was known as the Museum of the red brigades in Tripoli,which is the Libyan capital.

It consists of six medium size shreds including a base part (Fig. 5, a-b-c). It is red in colour and its thickness is about 2mm with incised at the outer part of the ware and a stamp on the base.

Figure 5 (3a,b,c). The Condition of deterioration of the dish.

The samples were examined by naked eye as well as using magnifying lenses ×10 to identify the type of component in the fabric of the ware. lenses ×10 to identify the type of component in the fabric of the ware.

The sample was studied using a NIKON ECLIPSE ME 600 PLM microscope equipped with an Olympus e-410 digital camera. The magnification varied from x100 to x400 depending on the size of the samples. Microscopic examinations in transmitted light were made on thin sections, cut across the thickness of the dish, using a Leica Zoom 2000 microscope equipped with an Olympus e-410 digital camera in order to determine different typologies of the body and the slip and the strong similarities between the internal cohesion(body) and the surface layer (slip).

XRD measurements provide information about the relative quantities of the different mineral phases present within a material and thus, give compositional information about the raw material.

Preliminary analysis by X–ray powder diffraction (XRD) allowed the identification of major crystalline Phases in the pottery body. XRD was performed with an X' Pert PRO Analytical diffract meter equipped with conventional X-ray tube (Cu-Kα) Radiation (k = 1.5406 Å) with power condition 45 KV and 40 MA. The XRD patterns were measured in the range of 4 to 70° (2θ) with the step size of 0.02° and 30s counting per step at room temperature (25°C).

The SEM was used to determine micro textural and micro chemical features of the body by ESEM microscope (model Philips XL 30 ESEM). The analytical conditions are 25 – 30 KeV accelerating voltages, 1-2mm beam diameter and 60 – 120 second counting times. Minimum detectable weight concentration from 0.1 to 1 wt%.. All analyses were carried out at the laboratories of the Nuclear Materials Authority (NMA), Cairo, Egypt.

Thermal analysis is a powerful tool for the characterization of pottery which allows concluding the chemical and the phase composition.

There is a very important characterization method used for the control of the reaction process sand of the properties of the materials obtained. The thermal analyses were performed with a TGA/SDTA 851 Mettler Toledo equipment, in a temperature range 35–1200 °C (10 °C min^{-1}) in an air stream with a heating rate of 5 °C min^{-1}, using alumina crucible.

Fourier transform IR spectroscopy FTIR spectra were collected using a Perkin Elmer Spectrum GX spectrometer, equipped with a diffuse reflectance unit It was possible to use the drift accesory with the powdered pure substance, thereby allowing for a better and easier analysis. The resolution was 4 cm^{-1} and 64 scans were obtained and averaged. The background spectrum was obtained against an aluminum plate. Transmittance percentage (%) was collected in the range of 4000–400 cm^{-1}.

3. RESULTS

Visual examination does not reveal the presence of any different elements. The slip and the body are homogenous with subtle variations in the ratios of line intensities in the body and slip can be seen. This might indicate changes in the proportions. It should be noted that compositional results are qualitative because standards for these archaeological materials are not available (Schleicher, 2008).

Figure 6 shows the part of the pottery General view of the pottery dish; and detail of the body and slip by optical image

The XRD analysis for the pottery body suggests the presence of many minerals. The results indicate that this clay has the presence of a high proportion of silica as a part of the composition of a metal. Hematite, (Fe_2O_3) red iron oxide, gives the red color to the body.

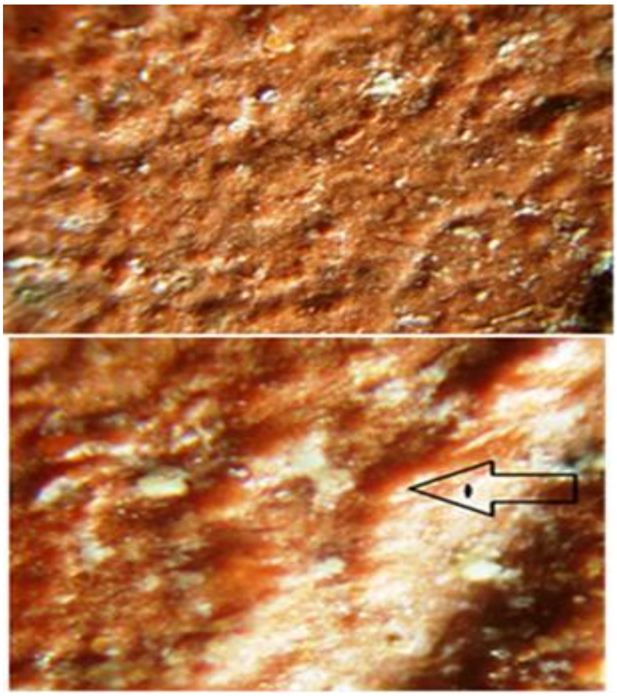

Figure 6. Part of the pottery by optical microscopy image.

The final color of pottery depends on the chemical state of iron which is completely oxidized in the case of hematite. It also works as a strong aid in melting.(Schleicher, 2008). In addition to quartz inside the clay, which works as an additive, mullite ($Al_2 O_3.2 SiO_2$), albeit ($NaAlSi_3O_8$) and Ilite ($KAl_2Si_3AlO_{10}$) were also found.

The phase transformations of the two natural illitic clays, clearly demonstrates the necessity of performing measurements during firing. Phase assemblage for the Gallo-Roman Sigillata in dicates a firing temperature higher than 1000 ^oC. (Guarino, 2011).

The firing temperatures estimated from the crystalline phase, are in good agreement with those that can be deduced from the microstructures of the slips and pastes. Low-gloss coating Granada pottery that it also seems to contain a vitreous fraction might confirm the high firing temperature higher (Iordanidis, 2009). Table 1 shows X-ray diffraction pattern of the sample of the pottery; the sample of salt contains calcite as a major beside quartz.

From the SEM images, the internal structuring composition of the fabric of pottery could be determined. Homogeneity with the appearance of no gaps or plant debris was apparent. The properties of the clay differ from one type to another according to the difference in chemical composition. This in addition to water greatly affects the degree of firing and the characteristics of the clay used (Riccardi, 1998)

Table 1 X-ray diffraction pattern of part of the pottery

Minerals	Pottery sample	
	Mineral	Chemical Formula
	Quartz	SiO_2
	Hematite	Fe_2O_3
	Albite	$Na AlSi_3O_{10}$
	Ilite	$KAl_2Si_3AlO_{10}$
	Mullite	$Al_2 O_3. 2 SiO_2$

SEM micrographs were taken of fresh fracture sections. The images were shown in (Fig 7). They were obtained by using secondary electrons and they reveal morphological differences between slip and body. A high sintered slip of about 20μ m can be seen in the sample. It describes the homogeneity and cohesion between particles and accuracy in the thickness of the surface layer with a thickness ranging between 19.8 and 22.2 μm.

The TGA curve (Fig.8), indicates that the degree of heat may exceeded 1000-1050 ° C. It consists of three phases; the first phase at 50–70 ^oC related to the evolution of the physically adsorbed water by the particles. The second phase at 300–400 ^oC, with a large exothermic peak around 325 ^oC due the organic matter decomposition was observed for all studied samples. The last phase at 400–450 ^oC on which the total weight loss is in the 1–3% range. This peak could be responsible for Kaolinite whose hydroxylation is seen at 400–450 ^oC. Meta-kaolinite is generated by losing the hydroxyl groups.

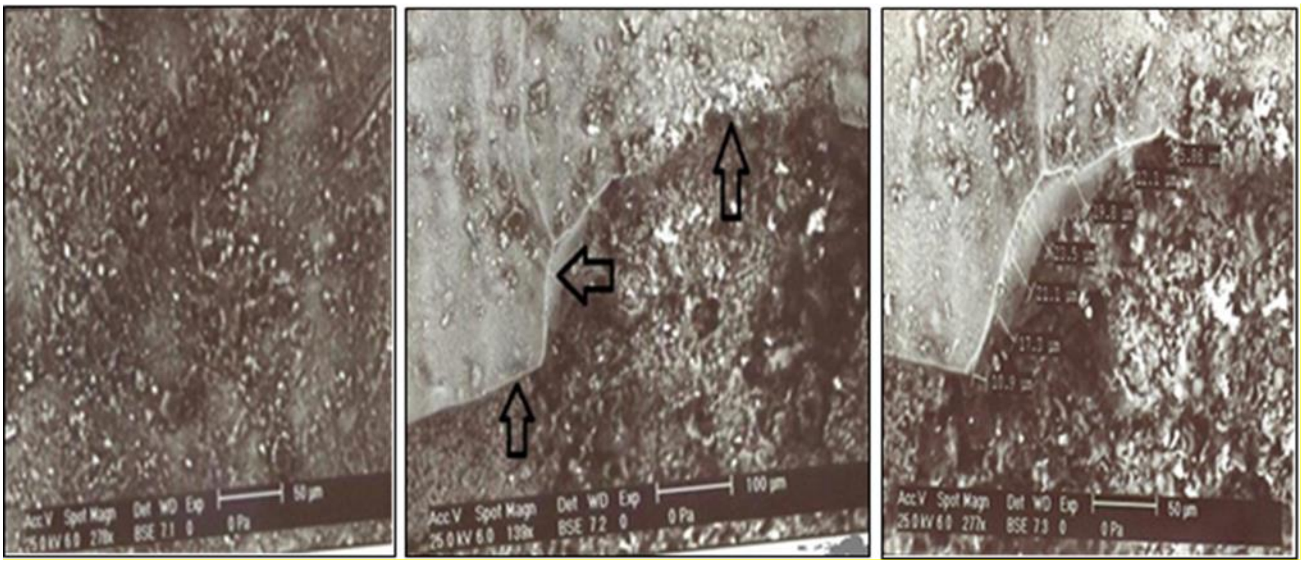

Figure 7. The red part of the pottery SEM images

The FTIR spectrum was used to confirm wither the gloss of the ware are resulting from the presence of organic coating. And the results confirm that no organic coating was added to the ware, therefore, the silica with the high temperature are responsible of this gloss. (Fig.9). The FTIR spectra of (a) the original slip (b) the silica reference sample(c) the original pottery (d)the kaolinite reference sample and meta-kaolinite transforms comprising mullite whice forms at 1000-1100° C, a transition alumina phase and silica (Riccardi, 1998).

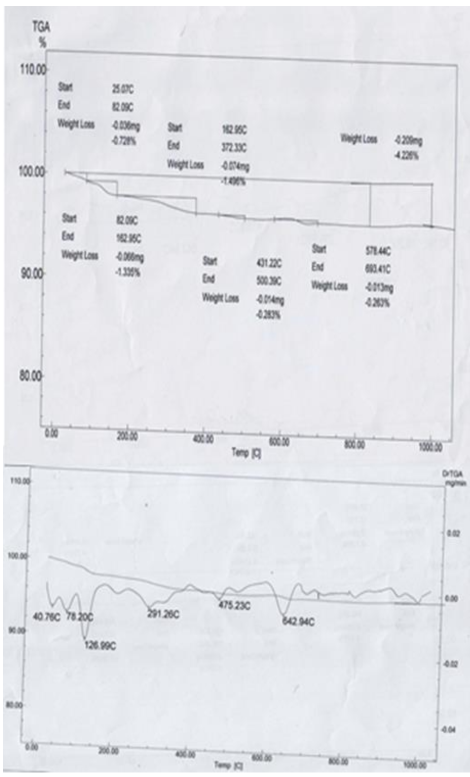

Figure 8. TGA results for the analyzed sample

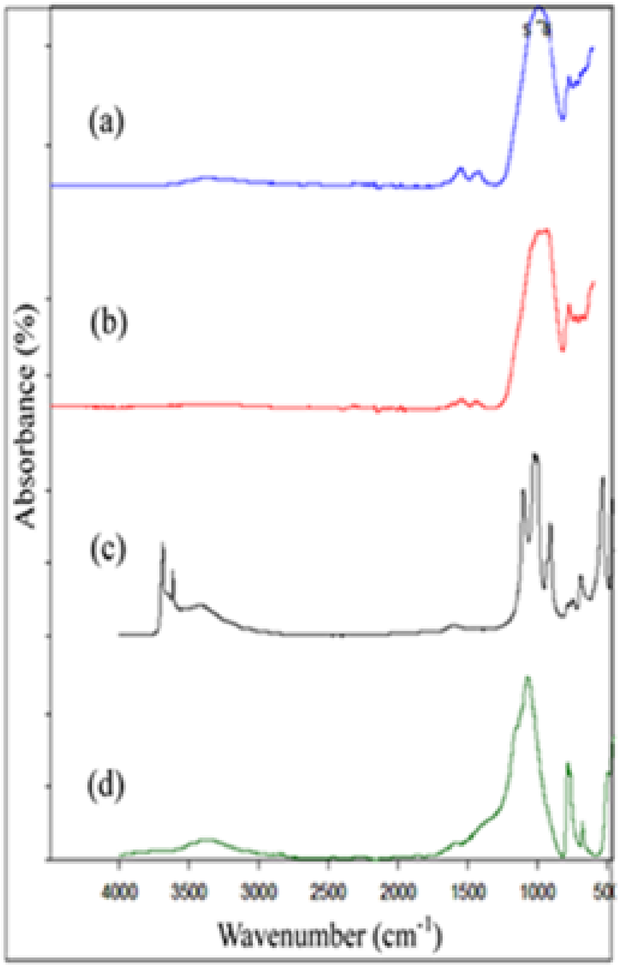

Figure 9. FTIR spectra of (a) the original slip (b) the silica reference sample(c) the original pottery (d)the kaolinite reference sample

4. TREATMENT AND CONSERVATION METHODS FOR THE SELECTED OBJECT

The pottery dish has some problems, such as the presence of dust and some parts of adherent surface. So, mechanical cleaning was done using brushes and scalpels to remove stick and loose dust.

The use of distilled water has given good results in the cleaning and removal of dust conjoined walls. Also a mixture of water and ethyl alcohol and purified with a 1:1 ratio were used. For the treatment of non-soluble salts we must begin with mechanical means, especially micro-devices that give vibrations, then acids, where the nitric acid 10% for the removal of the carbonate sediments (Buys, 1996). A useful mixture for removing calcareous deposits is ethylene diaminetetra - acetic acid (EDTA) (Davison, 1999). Figure 10 shows the cleaning prosses. The ware separated into 6 parts, after testing a number of adhesives, paraloid B 72 dissolved in acetone 15% was chosen (Vaz, 2008). The ware under study has lost a part of the base and the body. With the presence of the rim, the completing of the whole shape of the ware became easier. The reconstruction was performed in the manner similar to the way of the shaping of the proposed deliberate and simple access to a part similar to the original part.

Figure 10. View of the cleaning

Figure 11. The dish during joining parts and reconstruction

5. USED MATERIAL IN THE RECONSTRUCTION

Some experiments were done to gain an access paste that can give specifications which closely resemble its original pottery form and allow the formation similarly. These materials need moulding, give a smooth ,sleek surface far away from of the original surface and that manufactured manually. Hence, Elastic that can be manually shaped was color or that can be re-colored, either during or after processing. This elastic dough could be recovered with less mechanical force than the original body. Moreover, it does not affect the archaeological piece chemically because it is made of natural materials, mostly like pottery, phenolic microballons with red color 70%, Pottery powder (a crushed mature and smooth pottery, grog) with red color 30%, admixed with paraloid B.72 in 20% acetone. It was mixed with water until dough became elastic noticeable to don't leave marks of the fingers, particularly from outside, as in the configuration ability. (Vaz, 2008).

The used type is thermal mud burns on a high degree of temperature. Phenolic microballons does not shrink with the speed hardening 3.4% (Rahim, 2011)

The missing parts of the piece under study were formed by the free hand formation archaeological piece. It was noted that it is inseparable from the archaeological piece after completing the restructuring and dryness. Follow-up on the pieces during drying at room temperature, whose defects may appear in the completed portion, must be done.

It contracts taken into account proper care to level surface to the hilt. Figure 10 shows the dish during joining parts and reconstruction.

Some coloring experiments were made with pieces of the dried dough to reach the appropriate color using acrylic reversible colors. The color complementary part of the artefact, and diluted water emulsion had used red acrylic color. Figure 12 shows the dish after completion and coloring.

Figure 12. The dish after completion and coloring

6. CONCLUSION

The petrographical and mineralogical analyses and their analytical data allowed not only the characterization of the pottery ware, but also the formulation of some hypotheses regarding its specific manufacturing techniques. Technology, manufacture, materials used of the Terra Sigillata located in Lybia region could be summarized as follows. It was also found that the texture of the pottery was made using rich clay with silica that is characterized with a large quantity of medium to coarse plant residues which is suitable for manufacturing these types of ware. The quartz present in the ceramics could have a double origin; it could have been added as a temper, or it could have formed during the annealing from the decomposition of the clay silicates (Bersani, 2010).

The dish was shaped by moulding, and its red colors is due to the presence of iron oxides mainly hematite and the effect of temperature in the burning. The hardness of the pottery is very high. From the morphological and mineralogical studies, we could indicate that the reached temperature was high enough for silicates formations. The thermal analysis shows that the degree of heat may burn exceeded 1000-1100°C. (Maniatis 1981)

The dish was fully restored using some conservation materials and scientific methodologies, including cleaning, construction, completion and coloring using traditional materials such as grog and phenolic microballoons and finely colored by natural color red wash with acrylic paints.

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