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The Chiaravalle Cross: Results of a Multidisciplinary Study

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Abstract: The Chiaravalle Cross, a masterpiece of Mediaeval goldsmithery, went under restoration in 2016. This was a unique opportunity to undertake an in-depth multidisciplinary study. Several issues were addressed, as for example the chronology of the Cross, lacking any official document about it. The scientific investigations included in situ and laboratory measurements, and the analyses, part of a multidisciplinary protocol, completely characterized the gemstones adorning the Cross, the cameos, the gold, silver, jasper and glass parts, to derive indications on their provenance, authenticity and dating issues. All the results were shared with the whole collaboration of experts, which included art historians, a restorer, a conservator, a scholar in ancient glyptic, gemologists, archaeometallurgists, physicists and scientists in a very fruitful exchange of knowledge. This work is an example of a real multidisciplinary research, gathering good practices in the study of a complex piece of art.

Keywords: Chiaravalle Cross; multidisciplinary protocol; gemstones characterization; ^{14}C dating; SEM measurements; Raman Spectroscopy; XRF analyses; cameos study

1. Introduction

The Chiaravalle Cross, a mediaeval jewelry masterpiece, is a processional cross made of silver and gold laminas, combined to filigrees, gemstones, cameos and red jasper plates. This piece from the Museo del Duomo's collection was restored during "Restituzioni 2016" [1]. Ancient documents on the Chiaravalle Cross are rare,[1] inaccurate and contradictory. In the late 19th century other scholars

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1 The Cross has been mentioned in a Braidense manuscript [2], in the works of Count Giulini [3] and in the pages of Longobardic Antiquities [4], chapter VIII.

added different conflicting interpretations.[2] Finally, in the twentieth century, having cleared the field of erroneous attributions to earlier times, the Cross was recognized as a work of Venetian art that could be inserted into a large group of masterpieces of goldsmithery, dated to the end of the 13th century. In particular, the Chiaravalle Cross is acknowledged as a work of art executed in Venice at the end of the 13th century [6], likely commissioned by the archbishop of Milan Ottone Visconti (who died in 1295). However, some decorations (like one angel statue and some gems) seem to have been produced after this period.

The chronological attribution was one of the important research aspects, but the rich decoration and complex iconography of this piece of art deserved further insights. The production and manufacturing techniques of a complex piece of art like the Chiaravalle Cross involve much expertise, and in order to derive a comprehensive knowledge many different multidisciplinary skills are required. Metalworking and decoration techniques used in the production of jewelry can, for example, give indications on the period of fabrication, while the choice for different materials suggests information on the provenance of an ancient object of unknown origin. Several scientific investigations were applied during the restoration of the Cross, including in situ and laboratory measurements, addressing different materials. The analyses, part of a multidisciplinary protocol, completely characterized the gemstones adorning the Cross, the cameos, the gold, silver, jasper plates and glass parts, to derive indications on materials provenance, conservation status and authenticity issues [7].

The Cross was under restoration at Franco Blumer laboratory (Bergamo, Italy): this was an invaluable circumstance to undertake selected and focused scientific analyses. A multidisciplinary study was carried out, including neutron and nuclear analysis, gemological analysis, Raman characterization, X-ray fluorescence (XRF) and scanning electron microscope (SEM) measurements, whose main results will be discussed below.

This project gathered many different experts and all the contributors shared their findings in a very fruitful collaboration, resulting in an in-depth knowledge of the masterpiece in order to clarify several open questions as stated above.

2. Materials and Methods

The Cross is a precious jewelry masterpiece of rather complex construction, as can be seen from the pictures (see Figure 1). The core of the Cross is a walnut wooden structure covered on the front with 12 plates of red jasper, on which the main figures of the crucified Christ, of the Virgin and of Saint John the Evangelist were applied, all made of lost wax-cast silver, finely chiselled, gilded with mercury amalgam. The filigree in gilded silver entirely surrounds the outline and it is adorned with jeweled settings (cameos, transparent and opaque colored gemstones). The perimeter thickness of the Cross is entirely covered by a smooth and shiny silver sheet made in a single segment, fixed by nails. On the back there are embossed, chiselled and gilded silver laminae, covered with natural quartz lenses, ialine variety (commonly known as "rock crystal"). Many other details, visible before and after the restoration, are available in [1] as well as the restoration report by F. Blumer (see contributions by F. Blumer in [1], and [7], pp. 237–271).

The restorer had access to the inner part of the artefact, since a few parts were dismounted to perform a better cleaning. In some cases, few fragments were available for the analysis. The use of non-destructive and non-invasive analysis was very important for the whole study. However, for dating analyses some very small fragments were used. We will focus on three different types of analysis: (a) radiocarbon dating, (b) gemological study and (c) SEM measurements. Further analyses were carried out, mainly neutron-based techniques, whose details can be found elsewhere [8,9]. Concerning the golden filigree, this deserves a particular attention, since the materials used and the

[2] See for example [5], p. 54. Many other interpretations on the origin of the Cross followed, as described by the historic-artistic notes in [1].

techniques of fabrication were very peculiar. Therefore, an in-depth study performed both by SEM and particle-induced X- and gamma-ray emission (PIXE and PIGE) is still ongoing and it will be the subject of a presentation at the forthcoming IBA2019 congress (Antibes, October 2019 [10]).

(**a**) (**b**)

Figure 1. The Chiaravalle Cross: (**a**) front; (**b**) rear. High-resolution images, before and after the restoration, are available in [1]. The codes are relevant mainly for the identification of different gems placements.

2.1. Radiocarbon Dating

^{14}C-AMS (radiocarbon accelerator mass spectrometry) dating was performed at the CIRCE laboratory (Caserta, Italy). Three samples were made available for the analysis: two pieces of wood (few grams, from two different locations on the Cross) and some stucco coming from the rear of a gem setting. In particular, we coded samples from the wood as RC442 (coming from the node of the Cross, at its bottom part, FZ region-see Figure 1a,b) and RC443 (coming from the central part of the Cross), while RC439 specimen was the stucco one (taken from the rear of jasper in R1, see Figure 1b). The samples were prepared in the CUDAM laboratory (University of Milano-Bicocca).

The measurements have derived the ratios C14/C12 and C13/ C12 for carbon isotopes, extracted by chemical and physical treatments from the specimens. From these data, the percentage of modern carbon (pMC) has been derived, and the conventional age (tRC) calculated. This age has been calibrated from OxCal v.4, calibration curve INTCAL04 [11] to obtain the calendar age.

2.2. Gemological Study

To identify and characterize all the gemstones set in the Chiaravalle Cross, we used the standard gemological tools [12]. The gems dimensions, when possible, have been measured using a digital dimensiometer, Presidium model, with a tolerance of ±0.01 mm. The setting prevented the direct detection of gemstones weights by the scale method. The estimated carat weights were obtained on the basis of the dimensions and known average density. On the unremovable stones, the observations have been performed by the achromatic aplanatic 10× triplet gemological loop; while the partially unset stones allowed the dark field microscope analysis. We used a Leica S6E optical microscope with 16× ocular and 0.63–4.0× magnification.

The species and the variety identification were obtained crossing the refractometer analysis, where applicable, with the optical observation. The standard gemological tests were completed by fluorescence analysis exciting the gemstones with long wave (365 nm) and short wave (354 nm) light sources.

For the main 17 gemstones set in the front of Chiaravalle Cross, the limitations imposed by the mounting in the characterization performed by the standard methods were undertaken by applying a portable spectrometer of new generation: XRAMAN, made by XGlab company [13]. This instrument is able to perform in situ, fast and non-contact combined elemental and molecular analyses, by the complementary EDXRF (energy-dispersive X-ray fluorescence) and Raman techniques. The XRF system is fully integrated into a compact detection head and is equipped with a 20 mm^2 fast silicon drift detector (SDD) and digital readout electronics. The exciting source is a high-efficiency and compact 50 kV X-ray tube, 200 μA (max 10 W) with Rh anode. The X-ray tube is coupled with three automatically software-selectable different collimators between 0.5 mm and 2 mm and a set of X-ray filters to improve low detection limit capability in special applications. Usual measuring conditions for XRF were the following: X-ray tube 50 kV, 80 μA current, and acquisition time 30 s. Regarding the Raman system, the instrument is equipped with a cooled CCD detector with 6–7 cm^{-1} of resolution and 100–4000 cm^{-1} analytical range. The excitation source is a compact 785 nm stabilized laser source with output power regulable from 0 to 500 mW. Common measuring conditions were power 400 mW and acquisition time 180 s. However, the length of the measurements (for both XRF and Raman spectra) could be different in order to acquire a good statistic.

Thanks to the XRAMAN alignment system, made by a couple of lasers (axial and focal) and a micro-camera, able to observe a 2×2 cm^2 area at 10× magnification, the tests were performed at 1 cm distance, without any direct contact between the gemstones and the instrument. The analyzed area corresponds to about 1 mm diameter with perfect coincidence for both techniques.

2.3. Scanning Electron Microscope (SEM) Measurements

A scanning electron microscope (SEM) equipped with an energy-dispersion (EDS) detector was used in a non-invasive approach, i.e., without any treatment of the artifact, to study some elements of the Cross (like glass, filigrees, collets, embossed sheet and figures in relief). Their sizes, though large, could be easily housed in the sample chamber.

The instrument used is a TESCAN Mira XMU series, coupled with an EDAX system in EDS, and the operating conditions for the collection of images and microanalysis were as follows: beam acceleration voltage: 20 KV; beam current: 40 mA; working distance: 15.8 mm; counting for microanalysis: 100 s; correction factor for microanalysis: ZAF; analysis area 100×100 μm^2.

The study has returned images in high resolution, both in secondary electrons (SE) and in back-scattered electrons (BSE) of the surfaces, of the texture of the material, of the relations (microstructures) between the different metal alloys and crystalline and/or amorphous phases.

EDS measurements, when conducted on morphological surfaces, should be considered purely indicative of the chemical composition of the sample, since it is possible that, during the measurement, a direct proportionality between the signal output from the sample and the counts to the detector is not guaranteed, due to the lack of flatness of the surface.

3. Results

3.1. Radiocarbon Dating Results

The following results were obtained for the pMC and conventional dates, with relative errors and ranges of the probable dates within 1σ and 2σ (between 68% or 95% confidence level).

Code	pMC	tRC (years BP)	Calibrated Date (±1σ)	Calibrated Date (±2σ)
RC439	97.10 ± 0.36	236 ± 30	1645–1800 AD	1530–present
RC442	90.28 ± 0.34	822 ± 30	1190–1260 AD	1165–1265 AD
RC443	89.51 ± 0.34	890 ± 30	1050–1205 AD	1040–1220 AD

A better visualization of the results is displayed in Figure 2. As reported in the previous section we coded samples from the wooden core as RC442 (node of the Cross) and RC443 (central part of the Cross), while RC439 specimen was the stucco one (R1 gem position, see Figure 1b).

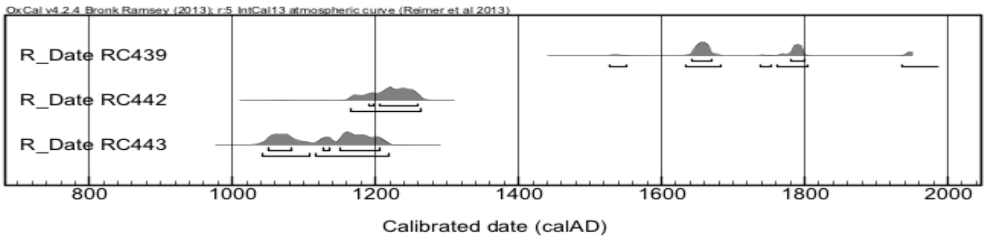


Figure 2. Scheme for the results of ^{14}C dating, displaying the probability for the dates of the different specimens.

We can thus underline from the age of the wooden part that the central part of the Cross was not fabricated before 1040 AD (considering the wider probability range of dates: 1040–1220 AD) and the node of the Cross was not fabricated before 1165 AD (considering the wider probability range of dates: 165–1265 AD). If we consider the node and the central part of the Cross fabricated at the same time, the chronological attribution of the Cross should be in the shortest range, that is 1165–1265 AD. We stress that these dates represent a lower limit: indeed, the wood could have been cut at those dates, but we do not know the exact date of fabrication of the Cross. We know that the piece of art has been produced later than the cut of the wooden part (later than 1165–1265 AD), while the age obtained for the stucco sample is a modern age.

3.2. Gemstones Characterization

On the Chiaravalle Cross are set a total of 985 gemstones, assigned 533 on the front and 452 on the rear. On the basis of the dimensions it was possible to classify this large number of stones as reported in Table 1.

Table 1. Overview of front and rear distribution of central and lateral gemstones on the Chiaravalle Cross. In this table, the average of the estimated carat weights ranges are also reported.

Front	Rear
420 lateral gemstones (0.40–0.60 ct [1])	420 lateral gemstones (0.40–0.60 ct [1])
96 central gemstones (1.00–3.00 ct [1])	15 central gemstones (0.80–3.00 ct [1])

[1] Due to the limitations imposed by the mounting, the carat weight ranges are estimated.

As displayed in Figure 3, we could summarize the gemological items shown in Figure 1: the main gemstones are the 34 stones, 10 cameos included, set as centre of the round motif; the central gemstones are the 111 stones set as centre of the half-moon motif plus the stones surrounding the Christ icon on the front; the lateral term refers to the smaller gemstones decorating the circular and the half-moon motif as well. The lateral and the central gemstones are all oval cabochon or irregular oval cabochon, while the main gemstones present more variety in shape and cutting style.

Figure 3. The terms used to describe the stones are clarified in this image, corresponding to the right arm magnification and reporting several examples: in purple circle, green circles and blue circles are reported the position of one main gemstone, two central gemstones and two lateral gemstones, respectively.

On the basis of the data reported in Table 1, it is possible to observe a difference in the distribution between the front and the rear of the Cross. The higher number of the front central stones is ascribable to the line motif surrounding the Christ icon, not present on the rear where the bas relief are surrounded by the filigree.

Due to the large number of central and lateral gems, these gemstones have been also classified on the basis of their species and their colors (Table 2).

Table 2. This table reports the distribution of the lateral and central stones set in the front (a) and in the rear (b) of the Chiaravalle Cross, in relation to the main color categories.

	(a) FRONT		
	Red	**Blue**	**Green–Yellow–Other**
LATERAL	mainly garnets and spinels; rare rubies	mainly sapphires; rare iolite and moonstones [1], artificial glass	beryls, few emeralds included, tiger eye quartz [1], artificial glass
CENTRAL	mainly rubies	sapphires, few lapis, rare artificial glass	artificial glass, amethysts and chalcedonies
	(b) REAR		
	Red	**Blue**	**Green–Yellow–Other**
LATERAL	mainly garnets and spinels; rare rubies	mainly sapphires; rear iolite and moonstones [1] artificial glass	green beryls and few emeralds, tiger eye quartz [1], artificial glass
CENTRAL	rubies and spinels	sapphires and artificial glass	artificial glass, amethysts and moonstones[1]

[1] Gem with optical phenomena.

The characterization data of the 34 main gemstones are reported in Table 3. To match the correct position of the gemstones set on the Chiaravalle Cross, Table 3 reports the codes used to identify the stones in Figure 1.

Table 3. Identification of the main 34 gemstones set in the Chiaravalle Cross. Due to the limitation imposed by the mounting, the dimensions have been rounded off and "Not Applicable (NA)" has been indicated when it was not possible to carry out the identification.

Code	**Dimensions (mm)**	**Shape and Cut**	**Transparency**	**Color**	**Identification**
F1	35.7 × 29.3 × 2.8	oval cameo	translucent	brown and white	chalcedony, sardonyx variety
FDD1	32.4 × 23.5 × 2.4	hexagonal tablet	translucent	blue and white	trapiche sapphire

Table 3. *Cont.*

Code	Dimensions (mm)	Shape and Cut	Transparency	Color	Identification
FDE1	15.8 × 12.4 × 2.7	irregular cabochon	translucent	green	artificial glass
FDF1	30.5 × 21.7 × 2.8	hexagonal tablet	translucent	blue and white	trapiche sapphire
FDL1	33.1 × 25.6 × NA	oval cameo	opaque	brown and white	chalcedony, sardonyx variety
FDP1	20.6 × 16.7 × NA	cushion cameo	translucent	brownish green	artificial glass
FDQ1	17.0 × 15.8 × 2.3	oval tablet	opaque	orangy brown	Artificial mixture
FDR1	NA	square cameo	translucent	greenish blue	chalcedony
FDV1	27.6 × 24.0 × NA	cameo	translucent	brown and white	chalcedony, sardonyx variety
FSV1	36.6 × 30.0 × 4.4	cameo	translucent	brown and white	chalcedony, sardonyx variety
FSR1	22.8 × 14.8 × 3.4	oval cameo	translucent	green	artificial glass
FSQ1	15.4 × 13.7 × NA	oval tablet	opaque	blue	lapis simulant
FSP1	NA	oval cameo	translucent	brownish green	artificial glass
FSL1	NA	cameo	opaque	bluish green	artificial glass
FSF1	NA	hexagonal tablet	translucent	blue and white	trapiche sapphire
FSE1	15.0 × 11.5 × 2.5	irregular cabochon	translucent	green	artificial glass
FSD1	31.9 × 23.3 × 2.7	hexagonal tablet	translucent	blue and white	trapiche sapphire
R1	32.8 × 27.4 × 2.1	oval tablet	opaque	red	jasper
RDD1	29.3 × 18.6 × 7.2	irregular cabochon	translucent	white	chalcedony, agata variety
RDE1	13.4 × 11.1 × 4.3	irregular tablet	opaque	orangy brown	jasper
RDF1	26.0 × 23.7 × 3.0	irregular cabochon	transparent	green	artificial glass
RDL1	19.2 × 17.2 × 4.0	cushion cameo	translucent	green and brown	artificial glass plus greek tar
RDP1	24.6 × 17.8 × 4.2	oval cabochon	transparent	green	artificial glass
RDQ1	17.3 × 14.1 × 4.8	tumbled	opaque	green and white	chalcedony, plasma variety
RDR1	19.9 × 14.7 × 3.3	irregular cabochon	translucent	orangy white	chalcedony
RDV1	27.8 × 23.3 × 4.1	rectangular cabochon	opaque	brownish red	jasper
RSV1	33.7 × 25.0 × 5.0	oval tablet	opaque	red	jasper
RSR1	13.0 × 12.5 × 3.5	oval tablet	opaque	brown and white	chalcedony/jasper
RSQ1	14.8 × 13.3 × 4.1	round tablet	opaque	brown	jasper
RSP1	24.7 × 20.4 × 6.4	cushion cabochon	opaque	green and brown	jasper

Table 3. *Cont.*

Code	Dimensions (mm)	Shape and Cut	Transparency	Color	Identification
RSL1	20.9 × 17.3 × 6.2	irregular triangular cabochon	opaque	brownish green	chalcedony-jasper
RSF1	25.2 × 23.5 × 4.3	oval tablet	opaque	brown	chalcedony-jasper
RSE1	13.0 × 11.5 × 4.2	irregular tablet	opaque	orangy brown	jasper
RSD1	22.1 × 14.4 × 6.3	irregular cabochon	translucent	white	chalcedony, agata variety

As already observed for lateral and central stones, the front and the rear of the Cross result different for quality and preciousness of the gem materials set, favoring the front. Considering for example the cameos distribution, 9 are set on the front while only one on the rear.

Where the standard gemological tests were not enough to complete the identification of the main gemstones, the XRAMAN instrument was used, in order to complete the characterization by the chemical and Raman data.

When the laser source of the XRAMAN instrument was focused on the surface of one of the four sardonyx cameos reported in Figure 4a–d, a Raman spectrum as reported in Figure 4e was recorded, showing bands at 208, 350, strong 466 with a second weak peak at 500 cm^{-1}, consistent with chalcedony—crypto-crystalline quartz—mineral phase [14]. These cameos are different from the other six, one in bluish-green chalcedony (FDR1) and the other five in artificial glass.

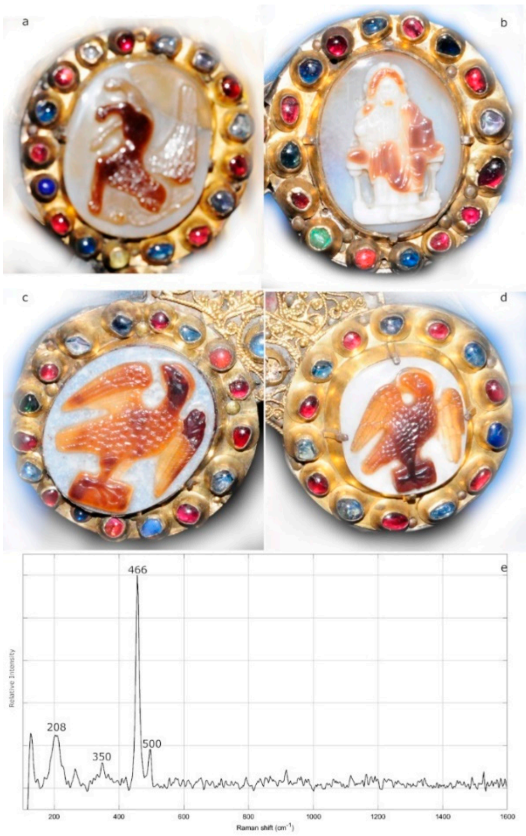


Figure 4. The four sardonyx cameos ((**a**) F1, (**b**) FDL1, (**c**) FDV1, (**d**) FSV1) and the corresponding Raman spectrum (**e**), showing the bands consistent with the chalcedony mineral phase. High-resolution images can be seen in [1].

The same technique was applied to confirm the identification of the FSQ1 gemstone as lapis simulant (Figure 5). The Raman spectrum acquired on the FSQ1 gemstone did not display any band at 544 cm^{-1} (usually considered diagnostic for lazurite mineral phase [15]), or calcite bands or other typically lapis minerals bands. The band at 1316 cm^{-1} is the only Raman feature visible in the spectrum of the FSQ1 gemstone and this band, especially when it is present without the 544 cm^{-1} band, corresponds to the Raman feature of the synthetic ultramarine pigment [16]. On the other hand, the XRF spectrum has recorded barium and zirconium traces, not reported for the natural lapis-lazuli chemical composition [17]. For better clarity, we report that in the XRF spectrum the presence of the Au peaks (at ~9.7 and 11.4 keV) and the broad Rh Compton (~19 keV) peak are visible.

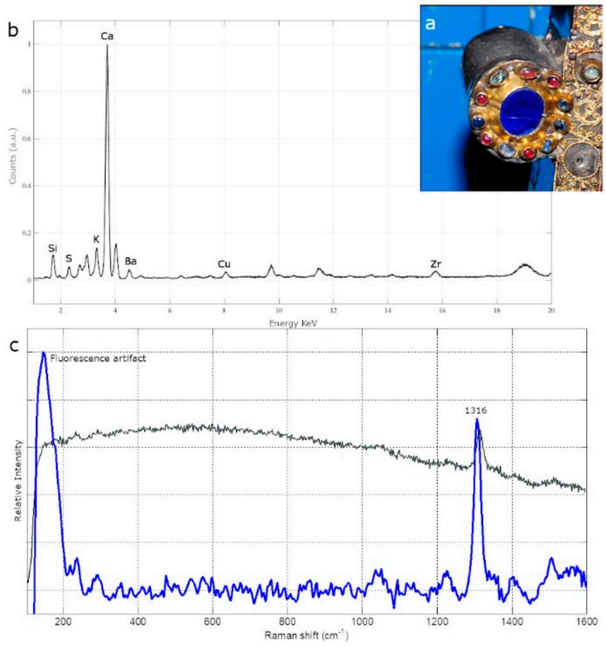


Figure 5. (**a**) lapis simulant FSQ1, (**b**) the chemical composition X-ray fluorescence (XRF) spectrum, and (**c**) the Raman spectrum. Note the presence of barium and zirconium, commonly found in the mixtures, and the absence of the lazurite and calcite bands in the Raman spectrum.

Due to their relative rarity, one of the most important gemological observation regards the presence of four magnificent trapiche sapphires, set in the front and characterized by hexagonal shape tablet cut. In Figure 6, sapphires detailed images are reported with the corresponding Raman and XRF spectra. The Raman bands at 416 cm^{-1} and 749 cm^{-1} are ascribable to the corundum mineral phase [15] and the bands at 185 and 246 cm^{-1} are correlated to the vibrational modes of the blue chromophore group in sapphire variety [18]. Moreover, by the XRF analyses it was possible to detect aluminum, iron, small trace of titanium and gallium as the mainly elements of the gemstones' chemical composition [19]. The inclusions responsible for the "white star" visible on the surface of the trapiche sapphires, have been characterized as feldspar group minerals [20].

Among the gemstones, 10 are carved in relief (cameos). They can be divided into two groups. The first consists of six specimens (Figure 1: FSL1, FSP1, FSR1, FDR1, FDP1, RDL1). The group can be dated to the mid-Byzantine period (dynasty of the Komnenoi; late 11th century), owing to peculiar iconographies, (Christ Pantokrator, the Virgin Hagiosoritissa—two specimens—Christ in the well dated iconography of the Akra Tapeinosis, saint Peter and, possibly, saint Paul; its upper half is missing), styles and inscriptions (mostly the cameo with saint Peter, showing the typical 11th-century remake of the epigraphic "uncial BR" style). All of the six cameos are in monochrome glass, except for one, in bluish chalcedony. The second group consists of four cameos, all in two-layered sardonyx (Figure 1: F1, FSV1, FDV1, FDL1; Figure 3). They can be ascribed to the atelier working at the Norman court of the Hautevilles in Palermo (second half of the 11th century), owing to comparisons with artifacts in different media, regarding the rendering of the lion head; the ordering of the feathers on the eagle's body; details in the pose, draperies, nimbus of the Pantokrator. During the 12th century at the court of the Hautevilles, in fact, a multi-ethnic atelier was active in the arts of luxury: among these, glyptic flourished again in the West, after a span of at least four centuries, merging the skillfulness of gemstone carvers from Fatimid Egypt and iconographic models from Byzantium, with no traces of cultural conflicts (see an extended discussion and wide literature on both groups in Gagetti, E., "Minute imagini scolpite nelle pietre". L'ornato glittico della Croce di Chiaravalle, in [7], pp. 123–183).

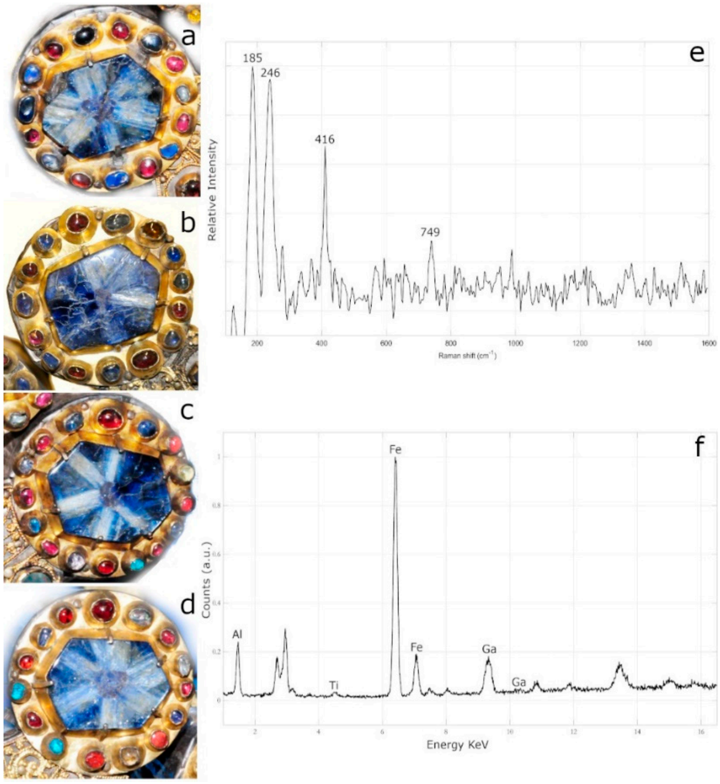


Figure 6. The marvelous four trapiche sapphires ((**a**) FSD1, (**b**) FSF1, (**c**) FDD1, (**d**) FDF1) and the corresponding Raman (**e**) and XRF (**f**) spectra.

Finally, the XRAMAN instrument was focused on the red platelets constituting the background of the front, recording a spectrum with a double bands at 466 cm^{-1} and 504 cm^{-1}, ascribable to jasper—crypto-crystalline quartz—mineral phase [14], while the bands at 227, 294, 407 and 610 cm^{-1} are typical for the hematite phase [21], responsible for the jasper red color [19].

3.3. SEM Results

The analysed glass-gems belong to the plate coded RDD1 (Figure 7A) and seem to be original. Figure 7B shows the BSE image of gem-glass 3. The collet is intact and shows no sign of deformation, as reported by the restorer. Moreover, in the southern portion of the collet it is possible to observe the presence of a boilish material, inserted between the glass and the collet, which can be interpreted as the glue used for fixing the gem. The observations reported for collet 3 can also be extended to the other collets.

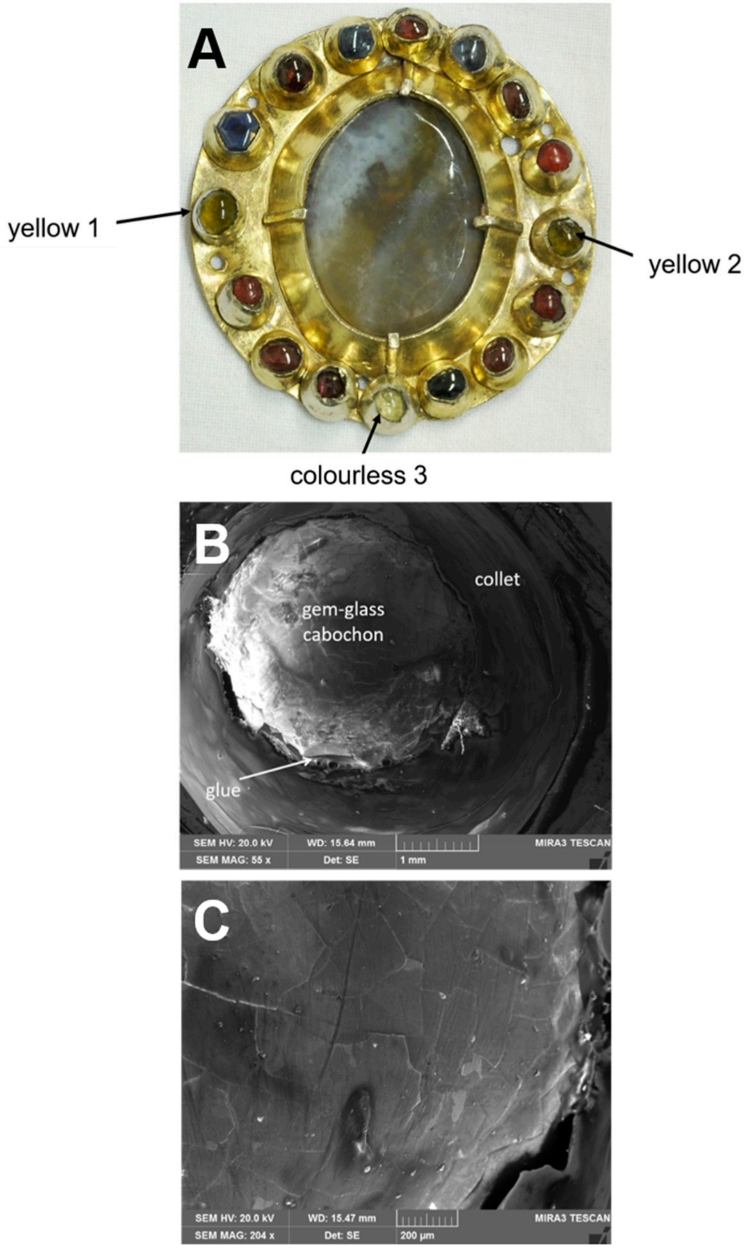


Figure 7. The gem-glass in the plate RDD1. (**A**) RDD1 plate with the positions of the gem-glass analyzed (Table 4); (**B**) BSE image of collet 3; (**C**) back-scattered electrons (BSE) image of the surface of gem-glass 3.

The glass shows limited surface alterations. This is testified by the tiny flakes that detach from the surface of the glass, indicating a beginning of degradation (Figure 7C). The presence of this thin layer of alteration has not allowed to obtain compositional data completely adherent to the composition of the intact glass, but they represent an average between the composition of the intact glass and the layer of alteration. Therefore, the data obtained and reported in Table 4 are to be considered as indicative of the composition of the glass.

Table 4. Chemical composition (semi-quantitative analysis) of gem-glass in RDD1 plate.

	Colourless 3	Yellow 2	Yellow 1
Na_2O	1.4	1.3	1.5
MgO	3.4	3.3	3.9
Al_2O_3	0.8	0.6	0.6
SiO_2	64.7	64.9	64.0
P_2O_5	0.7	0.9	1.2
PbO	17.7	18.6	19.2
Cl_2O	0.7	0.6	0.6
K_2O	6.1	6.1	5.8
CaO	3.2	2.9	2.5
MnO	0.2	0.1	0.0
FeO	0.6	0.4	0.2
CuO	0.6	0.4	0.4

The values shown in Table 4 represent the average of 5 measurements, carried out on the same decorative element, on areas of $20 \times 20\ \mu m^2$. The gem-glass is a silicates glass. The flux used seems to be a mixed-alkali flux, containing both sodium (Na_2O) and potassium (K_2O), while the stabilizer has a Ca-rich composition. The stabilizing component (CaO) as well as Na_2O are deficient compared to the optimal formula for glass production, but the lack of these components is undoubtedly to be attributed to surface leaching effects (Figure 7C). Magnesium (MgO) is present in percentages equal to 3–4 wt %. This component can be related both to the composition of the flux, probably ash, and to the stabilizer (use of mixed carbonates CaO/MgO).

The glass colorants are Fe (FeO in Table 4) and probably Cu (CuO in Table 4), even if the measured values of Cu are at the limit of the sensitivity of the instrument. The presence of small amounts of chlorine (Cl_2O) and phosphorus (P_2O_5) can be justified by the presence of dust deposits. The measurements also indicate important values for Pb (PbO).

The metal was analyzed in portable XRF and at SEM–EDS in order to obtain a mapping of the chemical compositions of the alloys in relationship with the type of decoration and the moulding technique. The main objects under investigation are located on the front of the Cross: the cherub, the two angels, the Christ, the foils and collets, and the filigrees (Figure 8A,B); 46 analyses have been collected. The measurements obtained express the average composition between the composition of the surface gilding and that of the silver. Although we are aware that these data could be strongly conditioned by the thickness of the gilding, which may not be constant on the different elements analyzed, the representation of the ratio between the three main components of the metal alloys, shown in the ternary diagram in Figure 8, indicates different ratios Au/Ag depending on the analyzed decorative element. For each type, the compositions are quite homogeneous. The copper (Cu) content rarely exceeds 10 wt %.

The embossed sheet, observed at SEM in secondary electrons (SE), shows on the surface the presence of a thin homogeneous layer (see Figure 9), which is distinguished as weaving from the underlying metal of the foil. This is an evidence of the presence of a gold leaf. The table in Figure 9 shows the measurements carried out on the individual grains of the alloy. The main metal is silver (Ag), with the presence of gold (Au) in values between 3 and 5 wt %. Minor elements are tin (Sn), iron (Fe), zinc (Zn) and copper (Cu). The presence of abundant mercury (Hg) indicates how the gold leaf was installed on the foil. However, the observation at SEM is not diagnostic to identify the technique followed for gilding because the leaf can be "amalgamated" or applied directly to the surface where the mercury has been brushed (see [22] and Cucini, C. "Note di tecnologia sulla fabbricazione della filigrana veneziana del Duecento" in [7], pp. 185–203), cold or hot. Full-surface observations of the plate show no signs of junction or overlapping of gold leaves (see Blumer, F. "Il restauro" in [7], pp. 237–271), but it is also possible, for the gilding on silver, that the workpiece has been heated after polishing the surface, in order to obtain a better adhesion of the leaf to the substrate (see [22] and Cucini, C. "Note di tecnologia sulla fabbricazione della filigrana veneziana del Duecento" in [7], pp. 185–203).

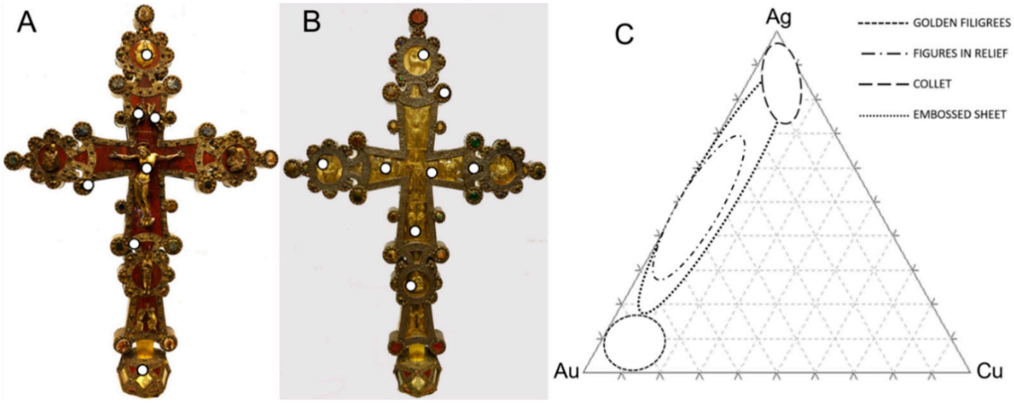


Figure 8. XRF measurements. (**A**,**B**) indication of the objects analyzed on the front (**A**) and on the back of Cross; (**C**) ternary diagram Ag—Au—Cu.

	1	2	3	4	5	average
Ag	45.4	46.7	52.1	49.0	55.9	49.8
Sn	0.9	0.6	0.9	1.3	0.9	0.9
Sb	0.0	0.0	0.0	0.3	0.0	0.1
Fe	0.2	0.4	0.5	1.2	0.6	0.6
Cu	0.0	0.3	0.1	4.3	1.9	1.3
Zn	0.2	0.4	0.2	0.3	0.3	0.3
Au	5.2	3.4	2.8	3.3	1.3	3.2
Hg	48.1	48.2	43.5	40.4	39.0	43.8

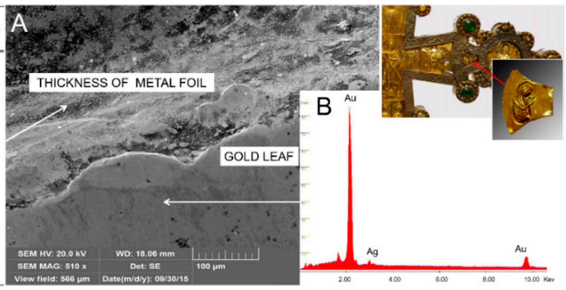
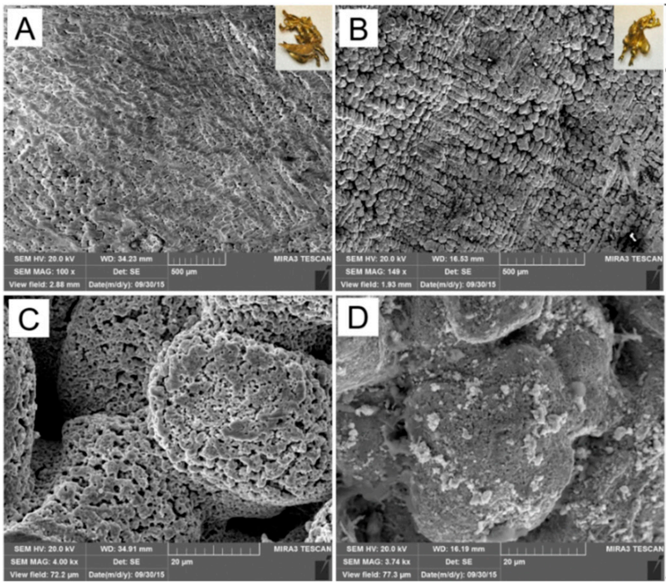


Figure 9. Textures and chemical composition of alloys of embossed sheet. (**A**) secondary electron images of sheet; (**B**) energy-dispersive X-ray spectroscopy (EDS) spectrum of gold leaf. The table shows the microchemical data and average alloy.

The angels placed in the central part of the Cross clearly show two very different aspects, both in style and size (Figure 1A). This raised doubts about their relative ages, also in connection to the realization of the Cross. The measurements were therefore directed to understand their composition but also to verify their affinities and differences in texture. Figure 10A,B highlight the differences of the two objects: The left angel (1), the smallest, shows a finer grain (each grain is about 20 µm) and the shape of the grains seems rather irregular so as their arrangement (Figure 10A), while the right angel (2) has grains whose dimensions are included between 30 and 40 µm (Figure 10B), better formed and with more regular dispositions. The observation at higher magnifications (Figure 10C,D) also puts in evidence that the smallest angel (right (2)) has a greater porosity, with micrometric pores, while the larger angel (left (1)) has a diffuse submicrometric porosity. The composition of the metal alloy is very similar for both objects (see the table in Figure 10). The composition of the right angel is different from that of the left angel. The major components of the metal alloy are silver (Ag) and gold (Au), but their ratio varies from 0.85 for the left angel to 3.7 for the right angel. There are minor elements such as tin (Sn), antimony (Sb), iron (Fe) and zinc (Zn). The presence of mercury (Hg) is undoubtedly linked to the existence, on the surface, of gilding.



	left (1) average	right (2) average
Ag	34.14	58.19
Sn	0.39	1.39
Sb	0.04	0.62
Fe	0.31	0.55
Cu	1.83	2.26
Zn	0.18	3.31
Au	40.09	15.65
Hg	23.01	17.32

Figure 10. Textures and chemical composition of alloys of central angels statues. (**A**,**C**) secondary electron images of left (1) angel; (**B**,**D**) secondary electron images of right (2) angel. The table shows the average alloy composition of each angel.

4. Discussion

The Chiaravalle Cross is a processional cross that came from the abbey of Chiaravalle (close to Milan, Italy). Several non-destructive (or micro-invasive) techniques were used, tailored to this case study. Wood, stucco, gems, cameos, and metals were deeply investigated and many interesting considerations can be derived.

Lacking any indication on the date of the production of this artefact, since no documentation has been found until now, we obtained by radiocarbon dating a date in agreement with the current attribution of this masterpiece to the late 13th century, since for the wooden part of the Cross we derived an age not earlier than 1165–1265 AD. Concerning the modern date of the stucco behind a jasper gem, this could be related to a different chronological placement but also to a later restoration improving the adhesion of the gem setting. Yet, two previous restorations were recorded: the first in 1539 when the Cross was found again after having been stolen in 1521, and the second in the 17th century [7] (p. 240). In addition, F. Blumer reported a recent restoration too, finding a small paper with the inscription “Agostino Figini orafo—Milano, restaurò anno 1950” (literally meaning “Agostino Figini goldsmith—Milan, did restore in 1950 AD”, see the restoration report in [1] and Blumer, F. “Il restauro” in [7], pp. 239, 262–263).

Regarding the characterization of the gems on the Chiaravalle Cross, it is possible to focus the attention on several discussion points. First of all, on the basis of the statistical data reported in Tables 1–3 it has been possible to observe differences in the number, quality, dimensions and color of the gemstones between the front and rear of the Cross. The dominant red color is the first sensation observing the front of the Cross, hand in hand with the preciousness of the gem materials.

Considering all the differences found between the front and the rear, it is possible to deduce a deep planning ability beyond this magnificent opera. The gemstones come from several parts of the world, as it was known during the 13th century. Due to that the gemstones set could be considered as a symbol of the commercial links existing from Italy, Venice particularly, to the Asian regions. A proof for these facts is the presence of the four trapiche sapphires, probably from Burma or Ceylon.

The four trapiche sapphires open an interesting window regarding where are they from and how old they are. In the modern market the trapiche corundum, rubies and especially sapphires, are very rare gemstones. Regarding the geographic origin, the first trapiche rubies arrived on the market from MongHsu mines, Myanmar (Burma), around 1995 and subsequently from the Vietnam mines, as described by Schmetzer, et al. [23,24] and Garnier, et al. [25]. About sapphires, the discovery of the trapiche variety is a recent fact, too and the rare ones found are typically from modern and magmatic geographic origin, such as Madagascar, Australia, Montana mines [20]. Due to that and to the limitations imposed by the mounting, using only the gemological applicable methods it is not possible to give a unique answer to these questions, but crossing all the other knowledge obtained on the Chiaravalle Cross during this work, several hypotheses could be formulated. On the basis of the data obtained analyzing the metal and particularly the settings, it is possible to define them as original and untouched; however, since we could not date the fabrication age of all the decorative parts, we cannot be sure about the chronological arrangement of the four trapiche sapphires. However, the cut and the inclusion pattern observed on them suggest that the trapiche sapphire tablets could have been cut from the same, big, hexagonal "barrel"-shaped rough stone. Therefore, considering the edge and all the gemological characteristics, the four trapiche sapphires could come from only two geographic areas: Burma or Ceylon, actually known as Myanmar and Sri Lanka, respectively.

Regarding the cameos, on the basis of the gemological analyses, it is possible to identify three type of materials: sardonyx, chalcedony and artificial glass, divided into two groups (see results). Both groups are older than the creation of the Cross, and reused on it because felt as "ancient" and then "precious"—a phenomenon well known since the Early Middle Ages[3]—as demonstrated by the fact that a cameo from group (a), lacking its upper half, has been nonetheless maintained on the Cross, even if integrated with colophony, as stated after autoptical examination and experimental remake by the conservator F. Blumer (see his report in [1]) and moved from the front to the rear side of the precious artifact.

The natural untreated lapis-lazuli gemstone is a complex and variable mixture of minerals, commonly constituted by lazurite and sodalite with minor amount of calcite, nosean, hauyna and pyrite [28]. No bands corresponding to these typically associated mineral phases were observed in the Raman analysis of FSQ1. Moreover, the chemical spectrum of FSQ1 presents barium and zirconium traces not reported for natural lapis-lazuli chemicals [17]; a chemical composition as reported in Figure 4b is compatible with a mixture used to create a gemstone imitation [29]. The presence of the imitation of lapis on the Cross is not a surprise, because the use of lapis-lazuli simulants or dyed are common and well known in the gemstones on the market, also from ancient ages [30]. Due to that, the presence of lapis imitation is easily explicable thanks to the observations made on the metal setting during the restauration process; indeed, Blumer [7] indicates a settings alteration corresponding to FSQ1 and FDQ1 gemstones. The presence of this modern lapis could be compatible with the restoration in 1950 documented by Blumer (see the restoration report in [1] and Blumer, F. "Il restauro" in [7], pp. 239, 262–263).

The red jasper on which the crucifix has been fixed was macroscopically identified as likely coming from Giuliana, province of Palermo, Sicily (see [7], pp. 207–209). This source of beautiful green, yellow and red jaspers was known since the Hellenistic period and much exploited in Roman and Baroque times when it was exported throughout the Italian peninsula [31]. This information, together with the connection to the atelier working at the Norman court of the Hautevilles in Palermo (for some cameos provenance) opens new scenarios for the Cross production, linking the acknowledged golden filigree fabrication in Venice to some peculiar materials provenance from Sicily.

The analytical data collected on the transparent glass-gems, although only indicative of their chemical composition, indicate the main components of the glass recipe: SiO_2 as a vitrified, mixed-alkali as a flux, CaO as a stabilizer. The yellow color of two of the three gems is due to the presence of FeO; the colorless glass-gem has been obtained by adding manganese to the vitrifiable mixture [32].

[3] For a large variety of objects (liturgical and not) reusing ancient cameos and intaglios see [26] For examples of glyptic reuse still in the Late Middle Ages, see [27].

We cannot forget that each ancient artefact is the testimony of a series of gestures and actions (*chaine operatoire*), whose sequence often comes to us incomplete and devoid of operational details sometimes fundamental to the success of the object. The ancient artefact also comes to us with the overprint of its entire "life path", including the use, ordinary maintenance and extraordinary maintenance [33]. The presence of lead (Table 4) found in the glass could be also attributed to the polishing phases of the fake gemstone, as reported in technical cookbooks [34,35] certainly known in the early Middle Ages and, therefore, may not be a component of the glass recipe.

Finally, concerning metal objects we observed, they are made of an alloy of silver, containing copper and gold as minor elements. The proportions between these elements seem to show a correlation with the technique of realization of the single decorative elements (Figure 8). A striking result followed the observations and measurements on the two central angels' statues, confirming the hypothesis that the realization of the two artefacts could have taken place in different times and probably in different workshops.

Other metallic processional crosses were characterized in the literature [36,37], but this is the first really multidisciplinary study, addressing different materials and fabrication techniques, published as a journal paper. The study of a complex masterpiece like the Chiaravalle Cross has taken advantage from the exchange of knowledge and skills in the field of gemology, gliptic, restoration, art history, physics, and archaeometallurgy.

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