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The relic and reliquary of St. John the Baptist in Siena (Italy) and their gems



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ABSTRACT

Gems, especially from remote areas, were highly demanded and valued in Byzantine times, often used for sacred Imperial purposes. Because of their imperishable nature, they were often re-used over time and many of them passed, one way or another, from East to Western Europe. The history of the gems set in Byzantine relics that survived in medieval Europe is often impossible to reconstruct. The exceptional opening of the relics of St. John the Baptist in Siena, 200 years after the last inspection, has made it possible to study the magnificent gems that adorn it. Spinels, rubies, sapphires and other gems from oriental geographies, along with high quality glasses used together regardless of their monetary value, were identified in the relic and its reliquary case through gemological analysis and portable Raman spectroscopy, once again demonstrating the vital contribution of the trans-disciplinary approach in the study of ancient art goldworkings.

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1. Introduction

1.1. Oriental gems in Byzantium

The term "Byzantine gems" refers to gems characterized by exceptional beauty and rarity coming from exotic geography and traded in Byzantium to become part of important art pieces, mainly related to imperial or religious adornments [1–7]. Overall, the study of gems mounted in Byzantine goldworkings appears quite challenging [8]; in fact, despite the numerous evidence, only in some cases gems can still be found in their original settings [9], due to the unfortunate well-known practice of removing and remounting them in other jewelry. In literature, the description of the majority of "Byzantine gems" is based only on naked eye observation, so that the real paths of these gems, namely both their geological and geographical origin and their provenance from the East of the Empire, can only often be hypothesized [8].

When studying "Byzantine gems", the close relation between materiality and appearance in the Byzantine tradition has to be considered; it was traduced by Bosselmann-Ruickbie [8] in the concept of *sympathetic magic*, which finds comparisons in

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numerous texts related to the Crusades (e.g., Robert de Clarì and the foundation of the renewal policy of Abbot Suger) [10]. The symbolism of Byzantine gems seems to be linked to both imperial and religious power; in fact, it is well known that the Emperor hold the primatum in selecting the most beautiful, big and rare gems coming to Byzantium for adorning imperial or religious objects [1–3], while redistributing the less interesting in term of beauty and rarity to the gem market also destined to the West of the Empire. This may explain why, until the theft associated with the Crucides, the most meaningful examples of rare and big oriental gems that reached Western Europe from Byzantium were those mounted on Byzantine relics and reliquaries [11]. These were part of an intense traffic of non-economic exchange between kings and were used as personal gifts and diplomatic offers brought from the East to the West by imperial recipients and ecclesiastics personalities, who attributed great spiritual significance and priceless value to them, also because of their restricted accessibility [12]. It was only after the fall of Constantinople in 1204 - and even more so after the fall of the Byzantine Empire in 1453 that the practice of exchanging precious objects donated to notables changed drastically; at that time relic, reliquaries and other adornments reached the West through theft and a fairly organized (also illegal) trade [12]. In these circumstances, a larger number of rare and big gems, which until then had been reserved for the Byzantine Emperor's entourage and for imperial use, reached the

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Fig. 1. (a) The right arm of St. John the Baptist and (b) its 15th century case.

West, where they were often removed from Byzantine goldworks to be mounted on other objects, thus determining an increasing difficulty in tracing their "provenance" [13].

1.2. St John the Baptist right arm and its case

The relic of the right arm of St John the Baptist is preserved at the Siena Cathedral (Italy). Usually kept in a sacred room, once a year, about five days before the festivity on 24th of June, it is transferred to the Cathedral altar, where it is placed for the faithful's visit [14].

The relic became part of the Cathedral's treasure in 1464, when Pope Pius II, Aeneas Silvius Piccolomini, donated it to the Cathedral of his native city a few months before his death. The Pope had received the arm as a diplomatic gift from Thomas Paleologus, despot of the Peloponnese (renamed Morea by the Crusaders) and the last descendant of the imperial family of Constantinople [11]. The Pope's donation of the sacred relic to the Cathedral of Siena took place on 6 May 1464, during a ceremony described in the donation certificate [14].

Based on some hypothesis, the relic had left Constantinople at least two centuries before its arrival in Siena; in fact, looking at the inscription "*St John the Forerunner's right arm cover me, Sava the Serbian Archbishop*" that surrounds the image of St John at the end of the arm, the scholar Danica Popović identified in "Sava" the first Serbian Archbishop, Sava Nemajic; according to Danica Popović, Sava brought the relic from Constantinople to Serbia once appointed Archbishop in 1219 [15]. The relic is contained in a series of bracelets which make it possible to view the relic itself, a practice typical of the Byzantine tradition, while in the Latin West the relics were usually closed in cases and hidden to the faithfuls' view [15].

Nowadays, the relic is closed in a modern 17th- century case, while on its arrival in Siena a special case was commissioned to Francesco D'Antonio using both loose and already mounted gems (Fig. 1b) [15].

2. Research aim

Tracing the journey of "Byzantine gems" mounted in Byzantine goldworking realized around Constantinople and traveling from the East to the West is a rather challenging task. Nevertheless, it seems fundamental to a better understanding of the ancient trade and commercial/non-commercial exchanges between Byzantium and the other Western countries, closely linked to the history of the Empire and underlying the privileged position of Constantinople before its defeat.

For the first time, we herewith report the results of a diagnostic campaign carried out on the gems of the right arm of St John the Baptist. Gems on both the relic and its 15th cent. reliquary were analysed by traditional gemological analysis and with the support of Raman spectroscopy to identify their mineral identity and obtain clues on their geological origin [16–20]. In fact, the application of a multi-methodological approach to investigate the identity and provenance of gems mounted in ancient jewelry has indeed proved to be a powerful tool [21–26]. The final aim is to contribute to the literature on Byzantine gems, which is rarely based on analytical studies and mainly on naked-eye observation. It will also provide useful comparative data for future research.

3. Material and methods

3.1. The bracelets and the gems on the relic of St. John the Baptist

The right forearm of St John the Baptist, including the hand, is covered from the elbow to the wrist by a multi-piece gold and silver armour-jewel, designed to strengthen and protect the more fragile and vulnerable parts of the relic (Fig. 2). The different parts of the armour were made separately and joined together after being placed on the fingers and wrist with small folded pins. A Senese addition with a Latin inscription *"Piissima Albertia Rincherii cura laminis aureis communitum"* clearly testifies that it was commissioned by the Opera del Duomo of the Siena Cathedral [14,15].

The bracelets decorating the relics are adorned with gems (Fig. 2); they are not all contemporary [15]. The elbow is covered by a golden element engraved with the figure of St. John the Baptist; this is enriched by the inscription in Slavonic and is decorated by two registers of filigree.

Connected to the end-cover, a large bracelet made up of four sub-bracelets, each about 2 centimeters wide, stand out; the subbracelets are framed by rows of small pearls that are strung together with silver thread. The bracelet is decorated with filigree and six gems, of which three blue, one colorless, one green and one brown, all into prong settings.

A second bracelet, delimited by two rows of pearls, is in rose gold and richly decorated with filigree exhibits two gems in prong settings, one red and one blue, alternated with big, rounded pearls.



Fig. 2. Gems, metals, and adornment of the sacred relic of St. John the Baptist.

Between the first arm section and the second bracelet, there is another bracelet, much larger in diameter than the arm and without any ornamentation; according to the documents, it is a kind of handle for the manipulation of the relic when it is in the hands of the faithful¹.

The third bracelet, quite similar to the second, is characterized by a traditional golden color and by the presence of only two bezels, one of which is empty and the other with a blue gem.

Finally, the fourth bracelet is completely different from the others. It is made of a silk cloth decorated with numerous small pearls and octagonal red gemstones; based on material and style, it was probably added between the 15th and 16th century to cover the gap between the Byzantine bracelets and the Senese armour [15].

3.2. The 15th cent. reliquary case

The reliquary was made in the 15th-century to contain the holy relic after its arrival in Siena [14]; it has a parallelepipedal shape with a pyramidal lid (Fig. 3).

It is made of silver using different goldsmith techniques; it is embossed, chiseled, engraved and some parts are gilded, some others are made with the technique of lost wax [14]. Glass panels on the side of the case and on the lids might have enabled the faithfuls to admire the relic during its exposition. On the two long sides, a central embossed and chiseled element divides the glass panels into two parts; at the top of these two elements, a carnelian cameo with the face of Christ (on the front) and an engraved blue gemstone with the figure of the Pantocrator (on the back), which engraved images find comparisons with Byzantine tradition [8,27], stand out. The large glass panels are decorated at the top with a frieze running along the entire length of the case, in which chased and engraved cherubs alternate with folded pin pearls and gemstones; this frieze is repeated around the medallion of the Madonna and Child in chased and engraved silver on a champlevé enamel placed on the front of the lid. On the back there is another medallion made from a large engraved and painted motherof-pearl plate with the head of the Baptist in the center of the

¹ The official document (AOMS 33 (37), c. 69v.) states that "in medio autem lacerti cingulum ex auro frigio quo, cum attollitur, comprehendi possit" [in the middle of the arm a filigree gold band with which, when raised, it can be grasped]

long-embossed bas-relief frieze on the base of the case. The base of the reliquary is adorned with a frieze running around its entire circumference, engraved and chiseled with the Stories of St. John the Baptist, whose composition clearly shows artistic inspiration from Donatello, and in particular from the panels of the Baptismal Altar in Siena Cathedral. The reliquary case has zoomorphic feet, feathered to match the corners of the base and anchored with pins. The four corners of the base are decorated with silver angels in a circle. They hold cornucopias with holes in the tops. Inventories show that in the past they were adorned with gems on their heads and hands, and we can assume that the holes contained bezels with gems to simulate a flame. There are two locks with two keys on the lid of the case. The locks are decorated with a small pyramid. This imitates a diamond crystal. The bottom of the case is entirely covered with engraved silver tiles. They are held in place by nails in the middle of each tile, imitating a very fine coffered ceiling.

3.3. Experimental

Mineral identity of gemstones have been determined directly in situ by mobile instrumentation without any sample preparation or artefact handling. Gemstones were characterised by Raman spectroscopy using a portable i-Raman® Plus instrument (BWTEK, USA) equipped with a diode laser source emitting at 785 nm. Spectra were acquired between 80 and 3300 cm⁻¹ with a spectral resolution of ~ 3.5 cm⁻¹ @ 614 nm; the exposure time was set at 10 s per acquisition and a laser power below 2.5 mW.

A Dino-Lite model AM4113ZT digital microscope equipped with 8 white LEDs, with the possibility of working with the LEDs off or on, was used for the gemological analyses. The microscope has a magnification of $10-70\times$, $200\times$ equipped with an anti-reflection lens. It has a CMOS type sensor and a resolution of 1.3 megapixels (1280×1024). Inclusions and other details useful for identification were observed and recorded by microscope observations.

A UV LED lamp (@365 nm) was used to check the gemstones fluorescence and the presence of gem treatments.

4. Results and discussion

Gems on both relic and reliquary case were inspected visually and using portable instruments. On the relic, nineteen gems are



Fig. 3. Gems, metals, and adornment of the XV cent reliquary case.

Table 1

Summary of results on gems analysed on the relic by gemmological and Raman spectroscopic investigations. vs = very strong and s = strong bands in the Raman spectrum. The analysis points are specified in Fig. 4.

Gem ID	Main macroscopic features	Inclusions	Raman bands (cm ⁻¹)	Identification
#1	Shape: irregular Color light blue Dimension (mm): 13,08 x 9,13	Natural inclusions (liquid feather, milky wisps)	236-255-290 424-554 (vs)-575 (s)-670-970	Cordierite (iolite)
#2	Shape: irregular Color: colorless Dimension (mm): no measurement available due to limited access into the case	Gas bubbles	Broad bands	glass
#3	Shape: irregular Color: green Dimension (mm): no measurement available due to limited access into the case	Gas bubbles	Broad bands	glass
#4	Shape: irregular Color: red Dimension (mm): 11 x 6.1	Strong UV fluorescence, natural inclusion (iron stain, crystals)	405 (vs)-663-760	Spinel
#5	Shape: irregular Color: blue Dimension (mm): no measurement available due to limited access into the case	Gas bubbles	Broad bands	glass
#6	Shape: irregular Color: blue Dimension (mm): 18,93 x 12,38	Natural Inclusions (liquid feather, crystals)	378-416(vs)	Corundum, blue variety, sapphire
#7	Shape: octagonal Color: red Dimension (mm): 7,03 x 8,31	Gas bubbles	Broad bands	glass

present decorating the bracelets; however, due to reasons that are clearly related to its sacredness, the relic cannot be removed from the reliquary case for a full examination of the bracelets and only seven gems - accessible to the microscope and the Raman probe - have been inspected by both gemological and analytical methods (Table 1, Fig. 4).

4.1. The first bracelet

The first bracelet is the most decorated and complex in its composition. The first part is completely closed, while the larger part has a hinged opening system to allow it to be slipped over the sacred relic. On this bracelet three gems were analyzed, namely one blue, one green, and one colorless.

Regarding gem#1, it has a violetish shade, milky wisps, and internal cracks; it presents a strong pleochroism and a greasy lustre [28]. Raman analysis revealed bands at 236, 255, 290, 424, 554 (vs), 575 (s), 670, 970 cm⁻¹ typical of cordierite (iolite) [18] (Figs. 4b, 5a).

In Byzantine tradition, the blue-coloured gems were linked to heaven and air, and consequently became the emblem of the heavenly virtues that the saints contemplated in their earthly existence [29].

In antiquity sapphire and iolite were credibly used without distinction and might be identified with the Pliny's *water hyacinth* [30]. It is thus credible that ancient iolite came from the same secondary deposits where sapphires were found and traded at that time, namely Sri Lanka and Myanmar [31]; unfortunately, there are only few examples of iolite identified in ancient artifacts used along with sapphire (e.g., the Treasure of Guarrazarr) [32].

The other two gems, #2 and #3 - one green and the other colorless - show elongated bubbles and other micro internal fea-

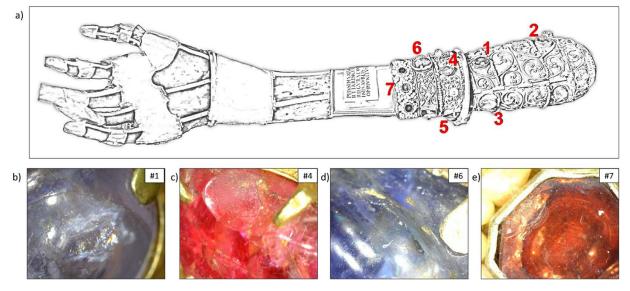


Fig. 4. Drawing of the arm of St. John the Baptist and picture if some gems (Magnification of 25X). a) #1 cordierite; b) #4 spinel; c) #6 sapphire; d) #7 glass.

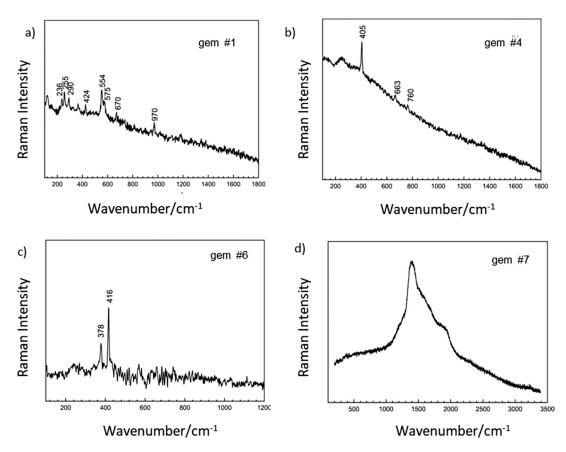


Fig. 5. Clockwise, Raman spectra collected on gems #1 cordierite, #4 spinel, #6 sapphire, #7 glass as an example of the variety of gemstones identified on the relic.

tures in the form of curved striations, suggesting the fingerprint of glass, according to the Raman spectra collected on the gems clearly showing the luminescence of glass under 785 nm excitation source [33–35].

The presence of glass used together with natural rare gemstones, regardless of their economic value, was quite common, as described in lapidaries, where glass is often associated with metals, stones, and gems [36].

4.2. The rose gold bracelet and its "Balas ruby"

In this bracelet the occurrence of a special red gem, irregular in shape, stand out; gemstone #4 has an intense red color and, despite its pebbly nature, shows good transparency and typical crystal habit. There are some brown-reddish stains, probably due to iron inclusions, and small cracks on the surface. The observation under the UV lamp shows an exceptional hot pink fluorescence,

Table 2

Summary of results on gems analysed on reliquary case by gemmological and spectroscopic investigations.

Gem ID	Color	Inclusions and other characteristics	Raman bands (cm^{-1})	Identification
#1, #8, #9, #12, #14, #16, #19, #24, #28, #32, #34, #37, #38, #39,#44, #45, #50, #53, #57, #61, #66, #69, #73, #76, #77	blue	Natural inclusions (long needles, liquid feathers, solid inclusions such pyrite, bands color zoning, particle clouds of short needles)	380, 420 vs, 650, 750	Corundum, blue variety, sapphire
#7, #10, #18, #63	red	Hot pink fluorescence; natural inclusions (dark included crystals, liquid feathers, silk, color swirl)	385, 424 (vs), 650, 750 (in some cases only the vs 420 and 770 bands have been detected)	Corundum, red variety, ruby
#30	transparent	Triplet, colored cement layer	420 (vs) + broad band	Corundum + glass
#2,#3 #4, #11, #20, #25, #26, #31, #33, #35, #56, #58, #59, #62, #68, #70, #74, #78, #81	red	Very strong hot pink fluorescence, Natural inclusions (needles, zircon halo,iron stains)	410 (vs), 670, 780	Spinel
#17	brownish red	Colored striae, microcrystalline pattern	470 (vs)	Quartz (carnelian)
#22 #41	yellow		130, 212, 470 (vs)	Quartz (Citrine)
#6	red		350, 555, 910 (vs)	Garnet (pyrope [47])
#60, #65, #71, #72, #	yellow, green		Broad bands	Glass
#5, #13, #15	green	Natural inclusions (dark crystals, multiphase inclusions, healed fissures)	No signal	Beryl (Emerald)
#21, #40, #42, #43, #46, #47, #48, #49, #52, #54, #64, #67	yellow, green, red		130, 212, 470 (vs) + broad bands	Quartz + glass
#27, #29, #36	red	Different refraction of tho materials, dried glue traces,	410 (vs), 670, 780 + broad bands in #27 + calcite (band at 1086)	Spinel + glass Spinel + calcite

already suggesting some clues on its mineral identity; it was confirmed by the Raman analysis which reveals the typical spectral bands of spinel (405, 663, 760 cm-1, Figs. 4c, 5b [37]).

The term spinel started to be used only from 1500 for identifying some red octahedral crystals coming from Myanmar [31] without clearly distinguishing this mineral family from rubies (this distinction arrived only at the end of 18th cent [38]. Before this date, spinels from Badakshan (nowadays northern Afghanistan and Tajikistan) were regularly traded as a special variety of rubies, used under the name of balas or balas rubies [31,39]. Since the 11th cent., the Badakshan mines were the source of exceptionally large waterworn spinels and some were the exclusive property of kings and emperors [40,41].

Based on the size, the internal characteristics (namely, color zoning, bluish hint, secondary healed fractures, iron oxide stains in cracks, dense zone clouds) and UV fluorescence a provenance from Badakshan might be suggested [42,43].

Gemstone #5 shows the typical microscopic features of glass, such as elongated vesicles and curved striations, according to the broad Raman bands and intense luminescence of glass under 785 nm excitation source [33–35].

4.3. The golden bracelet and its sapphire

This bracelet is very similar to the previous one, except for the color of the gold and the presence of only two bezels, one of which is empty. The Raman analysis of the blue gemstones #6 revealed the typical bands of corundum sapphire (378, 416 cm⁻¹, [18]) (Figs. 4d, 5c)

The sapphire has a cabochon cut, it is semi-transparent and light blue in color, with internal characteristics as long slender rutile silk, rectilinear healed fractures, and bands color zoning reconductible to light -blue Sri Lanka sapphires of metamorphic origin [44], funding similarities with the sapphire present on the reliquary of St. John the Baptist kept in the Cathedral of Monza [45]. In 12th–13th cent. similar pale-blue sapphires are attested in oriental geographies and on goldworks mounted in Byzantium, where we know that these peculiar Sri Lankan sapphires were regularly traded [31,39]

4.4. The 16th century bracelet and its red glass

The last bracelet, although it is decorated with real pearls, is very different from the others, especially for the presence of textile instead of a metal plate. It is also decorated with many small pearls around octagonal red stones. According to Danica Popović, this bracelet "obviously does not belong to the older part" [9]. In our opinion, the style of the bracelet, the cut of the gems and the type of materials would indicate a dating between the 15th and 16th centuries [46], suggesting that it was added later as a link between the ancient bracelets and the modern armour. Here, the gems are made of glass; they are quite transparent and of an intense deep red color, with numerous bubbles typical of glass materials; no fluorescence under UV has been observed. Raman analysis confirms the gemological observation giving back a luminescence typically to glass (gem #7, Figs. 4e, 5d) [33–35].

It is worth noting that the surface of the red gemstones appears to be abraded, which is typical of glass stones used in everyday life or personal jewelry, in contrast to an object designated to a devotional use and specifically made for the relic. This feature would support the hypothesis that the bracelet was a gift to the relic (likely an *ex-voto*) or, in any case, an object of reuse.

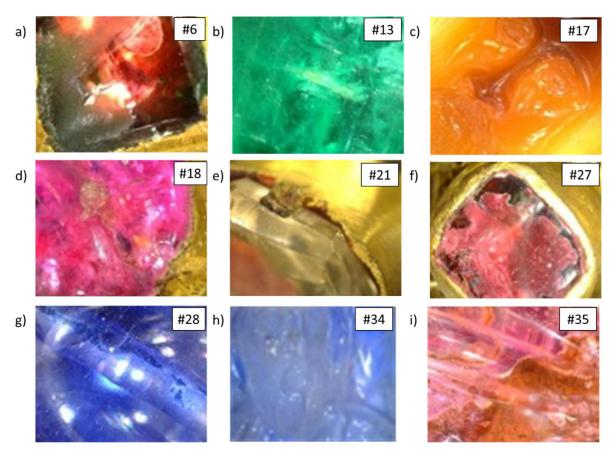


Fig. 6. Some of the gems of the reliquary. a) #6 garnet, b) #13 emerald, c) #17 carnelian, d) 18# ruby, e) #21 doublet quartz and glass, f) #27 spinel and calcite dublet, g) #28 sapphire, h) #34 engraved sapphire, i) #35 spinel. Magnification of 40X (b-e, g-i); 30X (a); magnification of 25X(f).

4.4. The 15th cent reliquary case

Most of the gems studied on the reliquary are natural and, when examined under the microscope, suggest that some of them have been subjected to enhancement treatment. In fact, the internal characteristics of some gems show the evidence of back foiling, back coating (sometimes in association) and assembled gems, as doublets and triplets.

The official documents relating to the commissioning of the reliquary list the gems purchased for its realization, including pearls and natural gems both loose and already mounted in their settings, a practice that was quite common. A summary of the typologies of gems identified on the reliquary case, together with their microscopic and physical characteristics, the analyses carried out and the main results are given in Table 2 and Fig. 6. Raman spectra representative of the various gems analysed and identified are given as examples in Fig. 7.

Looking at the sapphires, the color is purplish light blue, and no gem treatments were observed; the natural inclusions visible under the microscope show no sign of modification often caused by enhancement treatments.

As discussed, in the Byzantine tradition blue gemstones symbolize heaven and were associated with the figure of Christ Pantocrator; indeed, a beautiful light blue corundum (gem #34) with the typical Byzantine iconography of Christ - namely the shape of the face, the noise, the inscriptions - is visible on the reliquary case [14]. The style of the setting, which is completely different from that of the other gems, would suggest a Byzantine manufacture [9,14]. It is noteworthy that the microscopic observation shows that the gem is back foiled, and color coated, a treatment often used to enhance the brilliancy and the light color of the

sapphire [17,48,49]. Regarding the possible origin of the sapphire, the pale-blue color, the internal characteristics (bands color zoning, long "silk", particle clouds of short needles), as well as the size and clarity of the crystal, would suggest a Sri Lankan origin [44,50].

The emeralds, which are also mentioned in the official document that lists the gems used to make the reliquary case, are all of a bright green color and no signs of gem treatment have been observed; Raman spectroscopy indicated only a strong luminescence signal unfortunately due to the use of 785 nm excitation source; the gemological analysis revealed internal characteristics (multiphase fluid inclusions, healed fissure as a veil like aspect) compatible with a provenance from Pakistan or Afghanistan [51–53]. In antiquity, since Roman times, emeralds were known from Egypt, Austria, Pakistan, Afghanistan, and Russia [39,51–53], even if there is no clear evidence of use of Austrian emeralds in ancient jewels [53].

Red gems include both rubies and spinels, very similar in color and in shape of crystals, and were set without distinction. They are clearly identified based on their characteristics under dichroscopic observation and the Raman spectroscopic fingerprint (see Table 2 and Fig. 6). Both gem types are characterized by a very bright red color and a particularly intense UV fluorescence; these characteristics and the specific features observed under the microscope (iron stains, color in swirls, silk, solid crystals), might suggest a Burmese origin [54]; it is worth noting that burmese rubies (and spinel associated to these gems in secondary deposits) were present in Europe since 13th century [31].

On some spinels and rubies, traces of gold have been also observed; these traces might be the sign of heat treatments carried out into crucibles often used for gold smelting [55], or simply the residues of gilding.

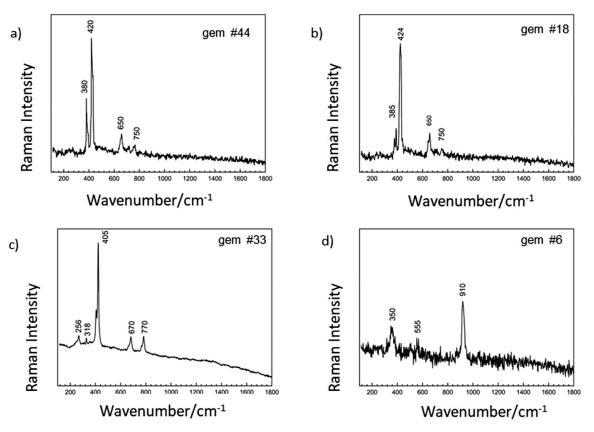


Fig. 7. Raman spectra collected on #44 blue corundum, sapphire, #18 red corundum, ruby, #33 red spinel, and #6 garnet, as an example of the variety of gemstones identified in the reliquary case.

Overall, among treatments, metal foiling and back-coating has been observed in some rubies, in garnets and, rarely, in some sapphires [17,48,49]. Finally, both quartz and glass were found in the lower part of the reliquary case; based on advanced style of cut and the modern type of glass, namely highly refractive glass [13], they could be considered later substitutions to replace lost gemstones. It is noteworthy that glass and natural gems are used together in replacements.

5. Conclusions

The extraordinary opening of the relic of St. John the Baptist and the authorization of this research have provided the unexpected opportunity to study the gems used to enrich the artwork, offering new information in support of its traditional attribution to Byzantine workshop.

The combined multi-disciplinary approach, based on gemology and analytical studies, revealed the presence of gems mainly provenancing from oriental regions, testifying that they passed through Byzantium when the city was the gem emporium of the West [39]. Among the gems identified, the big red spinel and the beautiful blue sapphire on the relic deserve special mention, both for their size, color and quality, and the proposed origin from Tajikistan and Sri Lanka, respectively. A Sri Lankan provenance might be supposed also for the blue cordierite (iolite), credibly traded at that time along with sapphires.

The presented results reinforce the relic Byzantine attribution and at the same time confirm that the gems mounted on the bracelet are original and credible in their original settings. In fact, due to the high devotional value of the relic, they are supposed to be not replaced, robbed or substituted over time. Another interesting aspect is the contextual use of natural rare and common gems together with vitreous simulants, which once again demonstrates the equal use of these different materials in ancient jewelry, regardless of their current economic value.

Finally, in the reliquary case, the gemological and manufacturing characteristics of some of the gems indicate a Byzantine provenance, as per for the beautiful sapphire engraved with the Christ Pantocrator that, based on microscopic features and comparative studies, could have a Sri Lanka origin.

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References

- [1] A. Toynbee, Costantino Porfirogenito e il suo Mondo, Firenze, Sansoni, 1987.
- [2] I.I. Reiskii, Constantini Porphyrogeniti De Cerimoniis Aulae Byzantinae, I, II, Bonn, Sagwan, 2018.
- [3] B. Cavarra, Lavorazione ed uso dell'oro nell'Impero Bizantino, in: Rendiconti della Accademia Nazionale delle Scienze detta dei XL, 2002, pp. 48–68.
- [4] K. Harrison, Byzantine Carved Gemstones: Their Typology, Dating, Materiality, and Function, Harvard University, Graduate School of Arts & Sciences, 2015 Doctoral Dissertation.
- [5] L. Bellosi, L'Oro di Siena, Il tesoro di Santa Maria della Scala, Milano, Skira, 1996.
- [6] H.R. Hahnloser, R. Polacco, La Pala d'Oro. Il tesoro di San Marco, Canal & Stamperia, Venezia, 1994.
- [7] T. Hackens, R. Winkes Gold Jewelry: Craft, Style and Meaning from Mycenae to Constantinopolis, Neuve, Brown Louvain-La, 1983.
- [8] A. Bosselmann-Ruickbie, The symbolism of Bizantine gemstones- Gemstones in the first Millenium AD, in: A. Hilgner, S. Greiff, D. Quast (Eds.), Gemstones in the First Millenium: Mines, Trade, Workshops and Symbolism, Conference Proceedings, Mainz, 2017, pp. 293–306.
- [9] I. Baldini, Lippolis, L'Oreficeria nell'Impero di Costantinopoli tra IV e VII secolo, Edipuglia, Bari, 1999.
- [10] J. Schlosser, La Letteratura Artistica, Firenze, La Nuova Italia, 1977.

- [11] A. Paolicchi, Dall'Oriente alla Toscana Preziose Devozioni, Firenze, Sillabe, 2020.
- [12] H.A. Klein, in: Eastern Objects and Western Desires: Relics and Reliquaries between Byzantium and the West, 58, Dumbarton Oaks Papers, 2004, pp. 283–314.
- [13] S. Martiniello, A. Capitanio, C. Sciuto, S. Legnaioli, S. Raneri, Synopsis of a treasure. A transdisciplinary study of medieval gold workings biographies, Open Archeol. 9 (2023) 20220336, doi:10.1515/opar-2022-0336.
- [14] E. Cioni, G. Fattorini, Francesco D'Antonio II reliquiario del braccio di San Giovanni Battista, Oreficeria a Siena al tempo di Pio II, Silvana, Milano, 2021.
- [15] D. Popović, The Siena Relic of St Jhon the Baptist's right arm, Zograf 41 (2017) 77–94, doi:10.2298/ZOG1741077P.
- [16] D. Bersani, P.P. Lottici, Raman spectroscopy of minerals and mineral pigments in archaeometry, J. Raman Spectrosc. 47 (5) (2016) 499–530, doi:10.1002/jrs. 4914.
- [17] S. Karampelas, L. Kiefert, D. Bersani, P. Vandenabeele, Gems and Gemmology: An Introduction for Archaeologists, Art-Historians and Conservators, Springer Nature, Basel, 2020.
- [18] A. Culka, J. Jehlička, Identification of gemstones using portable sequentially shifted excitation Raman spectrometer and RRUFF online database: A proof of concept study, Eur. Phys. J. Plus 134 (2019) 130, doi:10.1140/epjp/ i2019-12596-y.
- [19] S. Raneri, G. Barone, P. Mazzoleni, D. Bersani, Non-destructive spectroscopic methods for gem analysis: a short review, in: IMEKO TC-4 International Conference on Metrology for Archaeology and Cultural Heritage, MetroArchaeo, 2020, pp. 501–506.
- [20] H.G. Edwards, P. Vandenabeele, P. Colomban, Jewellery and gemstones, Raman Spectroscopy in Cultural Heritage Preservation, Springer International Publishing, Basel, 2022.
- [21] T. Calligaro, The origin of ancient gemstones unveiled by PIXE, PIGE and μ -Raman spectrometry, in: M. Uda, G. Demortier, I. Nakai (Eds.), X-rays for Archaeology, Springer Dordrecht, 2005, pp. 101-112. https://doi.org/10.1007/1-4020-3581-0
- [22] T. Calligaro, S. Colinart, J.-P. Poirot, C. Sudres, Combined external-beam PIXE and μ-Raman characterisation of garnets used in Merovingian jewellery, Nucl. Instrum. Methods Phys. Res. Sect. B 189 (1–4) (2002) 320–327, doi:10.1016/ S0168-583X(01)01078-3.
- [23] T. Calligaro, J.-P. Poirot, G. Querré, Trace element fingerprinting of jewellery rubies by external beam PIXE, Nucl. Instrum. Methods Phys. Res. B 150 (1999) 628–634, doi:10.1016/S0168-583X(98)01004-0.
- [24] M.F. Guerra, T. Calligaro, A. Perea, The treasure of Guarrazar: tracing the gold supplies in the Visigothic Iberian Peninsula, Archaeometry 49 (2007) 53–74, doi:10.1111/j.1475-4754.2007.00287.x.
- [25] P. Périn, T. Calligaro, F. Vallet, J.-P. Poirot, D. Bagault, Provenancing Merovingian garnets by PIXE and micro-Raman spectrometry, in: J. Henning (Ed) Post-Roman towns, trade and settlement in Europe, Byzantium 1, Berlin, New York, de Gruyter,2007, pp. 69-76
- [26] M.P. Riccardi, L. Prosperi, S.C. Tarantino, M. Zema, Gemmology in the service of archaeometry, EMU Notes Mineral. 20 (2019) 345–366, doi:10.1180/EMU-notes. 20.9.
- [27] E. Cioni, Scheda F.31, in: M. Seidel (Ed.), Da Jacopo della Quercia a Donatello, 2010 Le arti a Siena nel primo Rinascimento, 24 Ore Cultura, Milano.
- [28] W. Schumann, Gemstones of the World, 5th ed., Union Square & Co, New York, 2013.
- [29] A. Boezio de Boodt, Gemmarum et Lapidum Historia, Laon, 1636.
- [30] G. Plinio S, Storia Naturale, 2000 (Vol. Libro XXXVII), a cura di C. Lefons, Livorno, Sillabe.
- [31] J.M. Ogden, Gem Knowledge in the Thirteenth Century: The St. Albans Jewels, J. Gemmol. 37 (8) (2021) 816–835.
- [32] J.S. Cozar, C. Sapalski, Estudio de los meteriales gemológicos del Tesoro de Guarrazar, Boletin del Instituto Gemológico Espanol 37 (1996) 5–18.

- [33] P. Colomban, Raman μ -spectrometry, a unique tool for on-site analysis and identification of ancient ceramics and glasses, MRS Online Proceed. Lib. 852 (2004) 210–224, doi:10.1557/PROC-852-008.3.
- [34] S. Kamura, T. Tani, H. Matsuo, Y. Onaka, T. Fujisawa, M. Unno, New probe for porcelain glazes by luminescence at near-infrared excitation, ACS Omega 6 (2021) 7829–7833, doi:10.1021/acsomega.1c00322.
- [35] M.A. Fikiet, D. Tuschel, V.V. Ermolenkov, I.K. Lednev, Clarifying glass luminescence at near-infrared excitation, Appl. Spectrosc. 74 (2) (2020) 187–192, doi:10.1177/0003702819879109.
- [36] M. Beretta, The art of counterfeiting glass, Counterfeit, Imitation, and Transmutation in Ancient Glassmaking, Science History Publications, Sagamore Beach, 2009.
- [37] V. D'Ippolito, G. Andreozzi, D. Bersani, Raman fingerprint of chromate, aluminate and ferrite spinels, J. Raman Spectrosc. 46 (2015) 1255–1264.
 [38] F. Cesbron, P. Lebrun, J.Le Cléac'h, F. Notari, C. Grobon, J. Deville, Corundum and
- [38] F. Cesbron, P. Lebrun, J.Le Cléac'h, F. Notari, C. Grobon, J. Deville, Corundum and spinel: history, crystallography, mineralogy, gemology, deposits, uses, Synthesis Mineraux & Fossiles, Hors- Serie 15 (2002).
- [39] Y. Bruni, F. Hatert, P. George, H. Cambier, D. Strivay, A gemmological study of the reliquary crown of Namur, Belgium, Eur. J. Mineral. 33 (2021) 221–232, doi:10.5194/ejm-33-221-2021.
- [40] R.W. Hughes, V. Pardieu, G. Soubiraa, D. Schorr, Moon over the Pamirs: chasing ruby and spinel in Tajikistan, Guide 25 (6) (2006) 8–13.
- [41] R.W. Hughes, The rubies and spinels of Afghanistan: A brief history, J. Gemmol. 24 (4) (1994) 256–267.
- [42] J.I. Koivula, R.C. Kammerling, Examination of a gem spinel crystal from the Pamir Mountains, Zeitschrift der Deutschen Gemmologischen Gesellschaft 38 (2/3) (1989) 85–88.
- [43] V. Pardieu, T. Farkhodova, Spinels from Tajikistan. The gem that made famous the word "Ruby", Color 43 (2019) 30–33.
- [44] A.C. Palke, S. Saeseaw, N.D. Renfro, Z. Sun, S.F. McClure, Geographic origin determination of blue sapphire, Gems Gemol. 55 (4) (2019) 536–579, doi:10. 5741/GEMS.55.4.536.
- [45] V. De Michele, G. Manzini, Munera Imperalia, IGI, Sesto San Giovanni, 1993.
- [46] S. Macioce, Ori nell'arte. Per una storia del potere segreto delle gemme, Logart press, Roma, 2007.
- [47] D. Bersani, S. Andò, P. Vignola, G. Moltifiori, I.G. Marino, P.P Lottici, V. Diella, Micro-Raman spectroscopy as a routine tool for garnet analysis, Spectrochim. Acta A 73 (3) (2009) 484–491, doi:10.1016/j.saa.2008.11.033.
- [48] K. Nassau, Gemstone Enhancement, Oxford, Butterworth Heinemann, 1996.
- [49] H.A. Hanni, Short notes on some gemstone treatments, J. Gemmol. Assoc. Hong
- Kong (1998).
 G. Giuliani, D. Ohnenstetter, A.E. Fallick, L. Groat, A. Fagan, The geology and genesis of gem, corundum deposit, in: L.A. Groat (Ed.), Geology of Gem Deposit, Mineralogical Association of Canada, Québec, 2014, pp. 23–78.
- [51] D. Schwarz, V. Pardieu, Emeralds from the Silk Road countries a comparison with emeralds from Colombia, Color 12 (2009) 38–43.
- [52] T. Calligaro, J.C. Dran, J.P. Poirot, G. Querrè, J. Salomon, J.C. Zwaan, PIXE/PIGE characterisation of emeralds using an external micro-beam, Nucl. Instrum. Methods Phys. Res. Sect. B 161-163 (2000) 769–774, doi:10.1016/ S0168-583X(99)00974-X.
- [53] M. Nikopoulou, S. Karampelas, E. Gaillou, U. Hennebois, F. Maouche, A. Herreweghe, L. Papadopoulou, V. Melfos, N. Kantiranis, D. Nectoux, A. Delaunay, Non-Destructive study of Egyptian emeralds preserved in the collection of the museum of the Ecole des Mines, Minerals 13 (2023) 158, doi:10.3390/ min13020158.
- [54] R.W. Hughes, Ruby & Sappire a Collector Giude, Gem and Jewelry Institute of Thailand, Bangkok, 2014.
- [55] Al-Beruni, The Book Most Comprehensive in Knowledge on Precious Stones, Adam Publisher, New Delhi, 2007 Translated from the Arabic and with foreword by H.M. Said.