RAMAN INVESTIGATIONS ON TWO HISTORICAL OBJECTS FROM BASEL CATHEDRAL: THE RELIQUARY CROSS AND DOROTHY MONSTRANCE

By Henry A. Hänni, Benno Schubiger, Lore Kiefert, and Sabine Häberli

Two ecclesiastical objects of the late Gothic period (1350–1520) were investigated to identify the gemstones that adorn them. Both are from the treasury of Basel Cathedral (Basler Münster, Basel, Switzerland). To avoid potential damage, the identifications were conducted using only optical microscopy and Raman spectroscopy. Most of the mounted materials were found to be varieties of quartz, either as polished single pieces or as doublets with evidence of what may once have been dyed cement. Glass of various colors was also identified, as were peridot, sapphire, garnet, spinel, and turquoise.

In 1996, the SSEF Swiss Gemmological Institute investigated the adornments on two ecclesiastical objects from the treasury of Basel Cathedral: the Reliquary cross and the Dorothy monstrance (figures 1 and 2). These objects have been described previously with regard to their historical and cultural importance (Burckhardt, 1933; Barth, 1990), but not with regard to the materials themselves.

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Only rarely does a gemologist get the opportunity to examine the stones adorning historical religious items. The investigations of Meixner (1952), CISGEM (1986), Köseoglu (1987), Querré et al. (1996), Bouquillon et al. (1995), Querré et al. (1995), and Scarratt (1998) are notable exceptions. The prudence and concern of museum curators is undoubtedly a major reason why so many important historical and religious pieces of jewelry and other artwork lack precise descriptions of their materials. Another explanation is that the fancy names and historical terminology for gemstones in old inventories are often simply accepted, without taking into account

Figure 1. The Reliquary cross from the treasury of Basel Cathedral, Basel, Switzerland, is believed to have been manufactured around 1440. Fashioned from silver with rock crystal quartz, it is adorned with a variety of "stones"—including glass and quartz doublets, as well as natural gem materials. The 37 cm high piece is currently in the collection of the Historical Museum of Basel. Photo by P. Portner, Basel.

Figure 2. The Dorothy (also known as Offenburg, in honor of the donor) monstrance, another piece from the treasury of Basel Cathedral, is believed to have been manufactured around 1440 as well. The "stones" in this religious artifact, which is constructed from silver with partial gilt, also include glass and doublets, as well as various natural gem materials. It is 55 cm high and currently resides in the Historical Museum of Basel. Photo by P. Portner, Basel.

BOX A: RAMAN ANALYSIS

Laser Raman microspectrometry has a unique combination of properties that make it useful in tackling gemological problems. These properties include a high spatial resolution that permits the study of inclusions as small as one micrometer. With a high-power objective and spatial light filtering, the system can be focused to a point *inside* a sample. This allows the analysis of layered compounds or inclusions inside gemstones with minimal contribution from the main bulk species. In addition, the analysis is rapid, requires no sample preparation, and, most importantly, is (with a few known exceptions) damage-free.

The Raman effect is a light-scattering technique that uses a monochromatic light source (usually a visible laser). While most of the light focused on a sample is scattered and contains no useful information (so-called "Rayleigh," or elastic, scattering), a small amount, typically one photon in 10^6–10^8, is re-emitted after having lost some energy. This shifted, or "Stokes," radiation appears as lines in a spectrum that is characteristic for the substance under study. Most materials that the gemologist or mineralogist will encounter have a distinctive Raman spectrum, which is dependent on the material's crystal structure and atomic bonding. Even subtle changes within a single material, such as alterations in crystallinity and composition, often can be detected. However, the operator must be aware that Raman spectra can change depending on the orientation of the sample (just as color can change with pleochroism). Also, inclusions within fluorescent minerals (such as ruby) must be at or very near the surface, because of interference caused by fluorescence. The only major subset of materials that cannot be studied are metals and alloys.

Using the "extended scanning" facility, the operator can measure a complete spectrum from 100 up to 9000 cm^{-1} with a resolution of 2 cm^{-1}. This allows not only Raman measurements, but also simultaneous Raman and luminescence studies, to be performed between 520 and 1000 nm. The spectrum obtained can be identified by comparison with known spectra, which means that a large set of reference spectra is an important condition for the successful use of the method.

A number of references are available for basic descriptions of the technique (McMillan and Hofmeister, 1988; McMillan, 1989) and its mineralogical (Griffin, 1987; Smith, 1987; Malézieux, 1990; Ostertag, 1996) and gemological applications (Dhamelincourt and Schubnel, 1977; Delé-Dubois et al., 1980; Pinet et al., 1992; Schubnel, 1992; Lasnier, 1995; Hänni et al., 1997). Geologic and gemological applications of the Raman method were also discussed at the Georaman 96 Congress (as summarized by E. Fritsch in Johnson and Koivula, 1996) and the 2nd Australian Conference on Vibrational Spectroscopy (Kiefert et al., 1996).

contemporary nomenclature rules and the fact that gemstone names today agree (more or less) with modern mineralogical identifications. However, the scarcity of both analytical techniques and research organizations specialized in nondestructive methods may be the primary reason for so many vague descriptions of the materials used in such objects. The Louvre Museum in Paris is one of relatively few repositories that have a well-equipped analytical laboratory; at the Louvre, various microprobes are used to investigate a wide variety of very delicate, rare, historical objects (Querré et al., 1995).

The present article reports on the examination of two historical religious objects with two nondestructive means—microscopy and Raman spectroscopy—available at the SSEF. Specifically, this article describes the identification of cut "stones" used in Christian ceremonial objects of the 15th century, during the late Gothic period. The two religious artifacts—a reliquary cross (i.e., one that contains some aspect, or relic, of a holy person) and a monstrance (a transparent vessel, surrounded by metalwork)—were brought to SSEF for gem identification in 1996. Such unique objects should, of course, be tested only by techniques that ensure no risk of damage. Among the available techniques, visible-range spectroscopy does not provide characteristic data for many (especially colorless) materials. Fourier-transform infrared (FTIR) spectroscopy might be appropriate, but Raman microspectrometry better accommodates large objects (figure 3) and provides a more rapid analysis (see Box A). We combined Raman analysis with observation through a microscope to arrive at the results presented below. We hope that this article will give the gemologist dealing with antique objects information about a relatively new nondestructive method of identification. We also hope that more historians will take Raman spectroscopy into account when they are considering how to describe or catalogue pieces in their inventory with respect to the gem materials they contain.

HISTORICAL BACKGROUND

Places of worship in many cultures are characterized by magnificent construction and rich decoration as an expression of religious devotion. Such sacred places frequently are reservoirs for gifts and votive offerings from believers, some of whom may be quite wealthy. Such gifts can result in the accumulation of a significant treasury of gold, silver, and gems.

Both of the objects described here are part of the treasury of Basel Cathedral, in Basel, Switzerland. The Cathedral treasury is fascinating not only for the artistic quality and richness of its pieces, but especially for its long history (as described in Burckhardt, 1933; Barth, 1990). Through donations and, in the odd case, purchases during the 500 years from the early 11th century until the advent of the Reformation in the early 16th century, hundreds of examples of the handiwork of goldsmiths and other artisans were collected in the cathedral of the Bishopric of Basel. These incense burners, chalices, crosses, monstrances, and various other religious artifacts were the centerpieces during mass or other church ceremonies. The key piece in this collection, and also the oldest object (made in 1020), is the Golden altarpiece, which is now at the Cluny Museum in Paris. It previously belonged to Emperor Heinrich II of the Holy Roman Empire (973–1024).

Before the Reformation, Basel Cathedral had the richest church treasury in the region that is today southern Germany and Switzerland. The treasury was spared destruction during the Reformation when the members of the cathedral chapter hid the items in a cupboard in the vestry of the cathedral in 1528, right before they fled the city. The treasures remained hidden in the vestry, removed only occasionally for inventory, until 1827.

Subsequent local politics in Basel, however, finally led to the breakup of this collection. In 1833, Basel Canton divided into the half cantons of Basel-Stadt (city) and Basel-Land, and the ancient

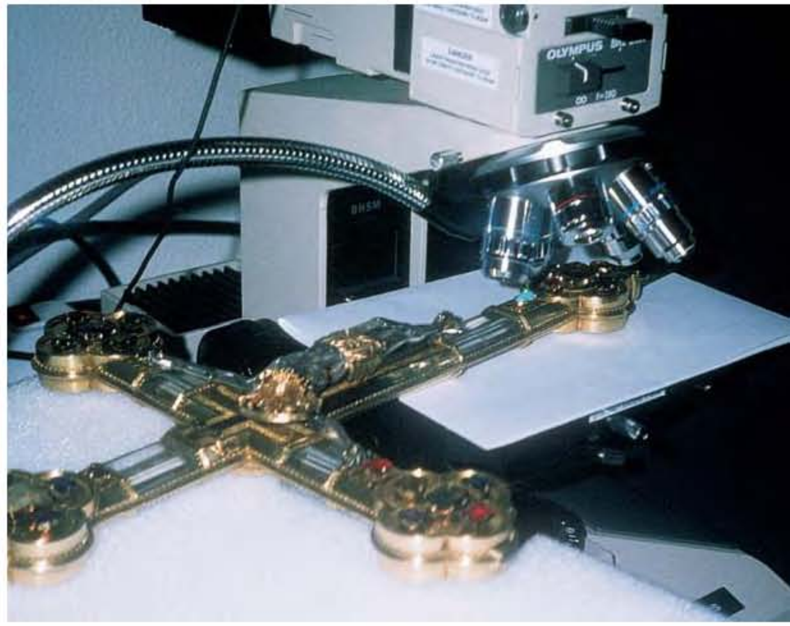


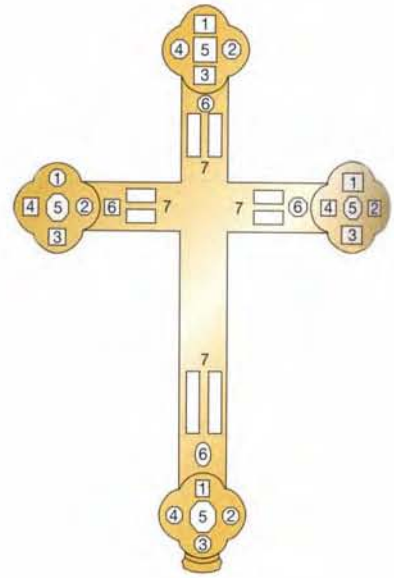
Figure 3. The Reliquary cross is shown here under the Raman microscope. To record the spectra of the different stones, the investigators had to carefully adjust the rather bulky object and direct the laser beam to the surface of the specific stone.

Cathedral treasury was likewise divided. The canton of Basel-Land received two-thirds of the treasury, which it sold at auction in its capital city Liestal in 1836. Whereas the city of Basel retained its share of the treasury items, the Basel-Land pieces were dispersed in many directions. Today, those pieces that have not been destroyed or lost can be found in museums in Berlin, Paris, London, New York, St. Petersburg, Vienna, and Zürich, as well as in Basel in the church of St. Clara. A large number are now in the Historical Museum of Basel, which over the last hundred years has purchased approximately two-thirds of the existing objects from the treasury, including the portion that remained with Basel-Stadt and 11 pieces that had been sold by Basel-Land. The Reliquary cross and the Dorothy (or Offenburg) monstrance (again, see figures 1 and 2), on which we conducted our gemological investigations, came from this collection. The Reliquary cross purportedly contains relics of St. Catherine and St. Jacob, whereas the monstrance is believed to contain a relic of St. Dorothy.

A precise dating of the two objects is not possible, because little information is available on the origin or history of the pieces. The first record of them is in the Cathedral treasury inventory of 1477. However, on the basis of stylistic features and what

TABLE 1. Physical properties of the gem materials set in the Reliquary Cross.

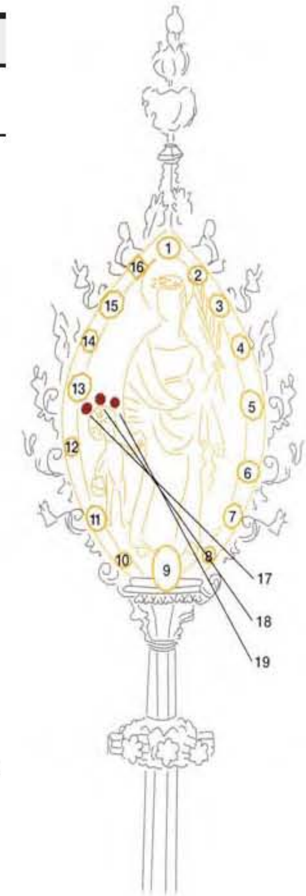
No.	Shape/cut	Color	Measurements (mm)	Internal features	Identification
A. Quatrefoil at left					
1	Octagonal, faceted	Violet	9.5 × 8.4	Color zoning	Amethyst
2	Octagonal, faceted	Yellow	11.8 × 9.6	Bubbles	Paste/glass
3	Rectangular, cut corners	Blue	9.6 × 8.0	Bubbles	Paste/glass
4	Rectangular, cut corners, domed table	Red	10.7 × 8.6	Tiny red particles in cement layer	Doublet with quartz top and dyed red cement
5	Octagonal, engraved man's head	Brown	18.2 × 11.8	Two-phase inclusions	Smoky quartz
6	Rectangular, cut corners	Red	9.6 × 8.0	Tiny particles in cement layer	Doublet with quartz top and dyed red cement
7	Colorless piece, drilled, with metal core	Colorless	25.5 × 22.8	Drilled, with metal core	Quartz
B. Quatrefoil on top					
1	Rectangular, domed table	Blue	9.2 × 7.7	Bubbles	Paste/glass
2	Octagonal, domed table	Violet	9.6 × 8.6	Color banding	Amethyst
3	Rectangular, domed table	Blue	9.1 × 7.7	Elongated bubbles	Paste/glass
4	Octagonal, cut corners	Violet	9.8 × 8.6	Two-phase inclusions	Amethyst
5	Rectangular, domed table	Yellow	17.1 × 13.9	Bubbles	Doublet with glass top
6	Octagonal, cut corners	Violet	8.8 × 7.0	Two-phase inclusions	Amethyst-quartz
7	Colorless piece, drilled, with metal core	Colorless	30.1 × 24.6	Drilled, with metal core	Quartz
C. Quatrefoil on right					
1	Rectangular, cut corners	Violet	8.7 × 6.5	Two-phase inclusions	Amethyst
2	Rectangular	Red	9.6 × 9.1	Bubbles and red	Doublet with quartz top particles in cement layer
3	Rectangular, domed table	Blue	9.6 × 8.6	Bubbles	Paste/glass
4	Rectangular, cut corners	Yellow	9.6 × 9.1	Bubbles	Paste/glass
5	Octagonal, cut corners, engraved woman's head	Brown	15.0 × 12.3	Two-phase inclusions	Smoky quartz
6	Octagonal, cut corners	Violet	10.2 × 7.0	Two-phase inclusions	Amethyst
7	Colorless piece, drilled, with metal core	Colorless	25.4 × 23.4	Drilled with metal core	Quartz
D. Quatrefoil on bottom					
1	Rectangular, cut corners, domed table	Red	9.7 × 7.5	Bubbles and red particles in cement layer	Doublet with quartz top and dyed red cement
2	Octagonal, cut corners	Violet	10.7 × 8.8	Two-phase inclusions	Amethyst
3	Octagonal, domed table	Yellow	12.8 × 10.2	Elongated bubbles	Paste/glass
4	Octagonal, cut corners	Violet	11.2 × 8.8	Color banding; inclusions	Amethyst
5	Octagonal, cut corners	Brownish yellow	23.5 × 21.4	Two-phase inclusions	Citrine
6	Oval, cabochon	Light greenish blue	11.8 × 7.5	Black veins	Turquoise
7	Colorless piece, drilled, with metal core	Colorless	42.9 × 24.4	Drilled, with metal core	Quartz



little is known of their history, both objects are believed to date from approximately 1440 (Burckhardt, 1933; Barth, 1990). Specifically, the style of the mold-made crucifix figure and the engraved foliage scrolls on the back of the cross are typical of this period. It is likely, too, that the donor of the Dorothy monstrance, Henmann Offenburg (1397–1459), had it made to hold a relic of Saint Dorothy that he brought from Rome after being knighted there in 1433.

TABLE 2. Physical properties of the gem materials set in the Dorothy monstrance.

No.	Shape/cut	Color	Measurements (mm)	Internal features	Identification
1	Polished pebble	"Olive" green	10.7 × 9.3	Slight turbidity	Peridot
2	Polished pebble	Colorless	6.3 diameter	Elongated bubbles	Paste/glass
3	Octagonal lozenge, sl. domed table	Blue	13.2 × 10.7	Spheric bubbles	Paste/glass
4	Octagonal, slightly domed table	Colorless	11.8 × 9.1	Cement layer, decomposed	Doublet with quartz top
5	Octagonal, slightly domed table	Blue	12.3 × 9.7	Spheric bubbles	Paste/glass
6	Round disc engraved goat	Orange	12.0 × 11.0	None observed	Chalcedony, var. carnelian
7	Octagonal, slightly domed table	Colorless	11.0 × 8.6	Cement layer, decomposed	Doublet with quartz top
8	Octagonal, slightly domed table	Blue	6.6 × 5.8	Elongated bubbles	Paste/glass
9	Oval, engraved woman's head	Cream and grey layers	13.5 × 21.5	Weak banding	Agate, layered onyx
10	Round cabochon	Green	6.0 × 5.5	Spherical bubbles	Paste/glass
11	Oval, unpolished	Black	14.0 × 10.0	None observed	Black chalcedony
12	Oval, cabochon	Light blue	9.5 × 8.3	Bubbles	Paste/glass doublet
13	Octagonal, slightly domed table	Blue	13.3 × 11.3	Bubbles	Paste/glass
14	Octagonal, slightly domed table	Colorless	11.1 × 8.6	Cement layer, decomposed	Doublet with quartz top
15	Octagonal, slightly domed table	Blue	14.2 × 11.1	Bubbles	Paste/glass
16	Rectangular, blocky	Violet	6.2 × 5.2	None observed	Amethyst
17	Oval, cabochon	Blue	5.0 × 4.0	Turbid growth layers	Sapphire
18	Octagonal, cabochon	Red	5.9 × 4.8	Rutile needles and mineral inclusions	Garnet
19	Round, cabochon	Pink	4.7 diameter	Mineral inclusions	Spinel



MATERIALS AND METHODS

The Reliquary cross and Dorothy monstrance both contain a variety of stones mounted in metal settings that are attached to the pieces (tables 1 and 2). The two pedestal-based objects are comparatively large, 37 cm and 55 cm high, respectively, and difficult to handle under a microscope. The settings of the stones as well as the fragility of the pieces themselves inhibit the use of a refractometer. To avoid any damage or contamination to those parts made of silver, all of the investigators wore cotton gloves.

For the microscopic examination, we used a Leica Stereozoom Binocular Microscope with a fiber-optic light source. The microscope was equipped with a camera enabling us to take photomicrographs with magnifications from 10× to 50×.

A handheld OPL spectroscope was used in connection with a fiber-optic light to analyze the blue stones that looked like a cobalt glass. Because the objects were so bulky, chemical analysis was not possible.

Conclusive identifications were made by taking Raman spectra of each of the "stones" in both objects and comparing the spectra to those in our reference data file. The spectra were obtained using a Renishaw Raman System 1000 equipped with a Peltier-cooled CCD detector, together with a 25 mW air-cooled argon ion laser (Spectra Physics; 514 nm) The laser beam was focused onto the sample, and the scattering was collected with an Olympus BH series microscope equipped with 10×, 20×, and 50× MSPlan objectives. Because most minerals have their characteristic Raman peaks between 100 and 1800 cm^{-1}, we measured spectra from 100 to 1900 cm^{-1} using the "extended scanning" facility (again, see Box A). A standard personal computer with GRAMS/386 software was used to collect and store

Figure 4. Four of the stones tested were found (by microscopy and Raman analysis) to be doublets with quartz tops and a layer of red cement. This stone, in the Reliquary cross, measures 10.7 × 8.6 mm.

the Raman spectra, as well as to analyze the data and compare the collected spectra to reference spectra stored in electronic files (Schubnel, 1992; Hänni et al., 1997).

The metals in the two objects were not analyzed, but the white metal is believed to be silver and the yellow appears to be gold-plated silver.

RESULTS

Description of the Objects. With few exceptions, the faceted "stones" in both objects are cut in symmetrical shapes (e.g., oval or octagonal). The style of cutting usually uses a slightly domed table and one step of parallel facets on the crown. In most cases, the cutting style could be identified only on the crown side; because the stones are held in closed-back settings, any fashioning of the pavilion generally was not visible. In some doublets, the pavilion was completely invisible from above because of the decomposed cement layer. For the most part, those "stones" that were not faceted—including turquoise, sapphire, spinel, and garnet—were cabochons.

Figure 5. Red pigment is seen here mixed in the cement of the doublet in figure 4. Magnified 60×

The Reliquary Cross. The partially gold-plated Reliquary cross (again, see figure 1) is in the Gothic style. The design of the mold-made crucifix and the stamped evangelical medallions on the reverse of the quatrefoil (four-lobed decorative motif) that terminates each arm of the cross has many similarities to comparable crucifixes of the same era. However, the use of rock crystal in the arms of the crucifix is unusual, if not singular. The presence of gem materials on the front of the cross gives the impression that this was a cherished object. On the back, at the intersection of the arms, a rock crystal capsule contains the relics of St. Catherine and St. Jacob, which can be seen through the transparent quartz window.

The Dorothy Monstrance. Crockets (in Gothic architecture, a crocket is an ornament that resembles an outward-curving leaf) frame the almond-shaped vessel like tongues of flame (again, see figure 2). The base, which consists of an eight-lobed foot, a smooth shaft, and a knob that resembles bundled rods, is more soberly treated.

A red niello coat of arms riveted to the door of the rear opening suggests that the monstrance was a gift from master craftsman Henmann Offenburg, of the Saffron guild of Basel. Restrained gilding on the front of this slender object creates a charming effect. The embossed figure of St. Dorothy in lavishly draped garments, hand-in-hand with the naked Christ child, appears to float within the mandorla (an almond-shaped halo of light enclosing the whole of a sacred figure). The preciousness of the object is enhanced by the fashioned stones and other ornamental materials set around the saint and by the cameo at her feet.

Identification of the Ornamental Materials. Tables 1 and 2 list the results of our testing on the stones in the Reliquary cross and Dorothy monstrance, respectively.

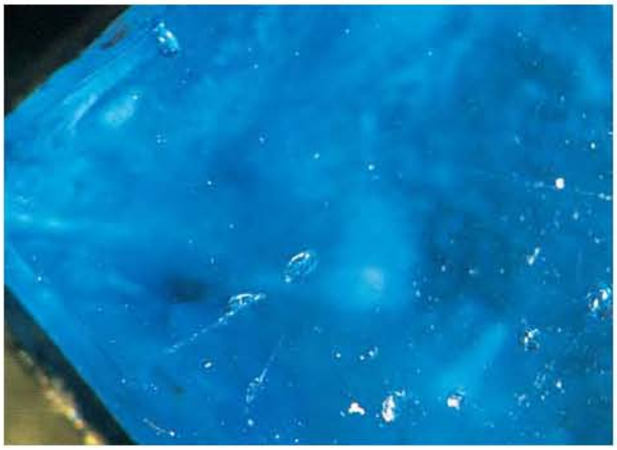


Figure 6. This piece of fashioned blue glass in the Reliquary cross showed the air bubbles typical of glass. Magnified 40×.

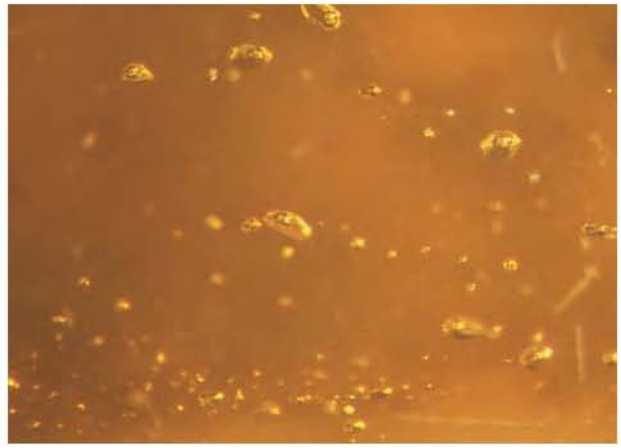


Figure 7. This yellow stone, set in the Reliquary cross, contains fluid and two-phase (fluid and gas) inclusions that are typical of crystalline quartz, in this case citrine. Magnified approximately 60×

Optical Microscopy. We identified many doublets (figure 4) and glass imitations in the Reliquary cross. Because all the gem materials are mounted in closed-back settings, in most cases we could not identify the pavilion material of the doublets. In some cases, however, gas bubbles were visible with magnification. The red doublets were found by microscopy to have quartz tops, with a cement layer that showed a red pigment mixed into the adhesive (figure 5). Probably due to their age, the cement layers in most of the doublets appeared to have dried out or shrunk, where air had entered the joining plane. The blue glasses showed air bubbles, either round or elongated (figure 6), that are typical of glass; with the spectroscope, we observed a weak cobalt spectrum.

Among the natural stones found, amethyst, citrine, and colorless quartz contained typical fluid and two-phase (fluid and gas) inclusions (figure 7). The turquoise cabochon (subsequently identified by Raman analysis) has a slightly greenish color that is typical of many turquoises seen today.

The Dorothy monstrance also contains a number of glass imitations (table 2), but it has some interesting natural stones as well. We identified peridot (figure 8), blue sapphire, red garnet, pink spinel (figure 9), and amethyst. A carnelian finely engraved with a goat (figure 10) suggests an interesting link to Greek art (Gray, 1983). An agate is engraved with the profile of a woman's head (figure

Figure 8. Raman analysis identified this 10.7 × 9.3 mm stone in the Dorothy monstrance as peridot.

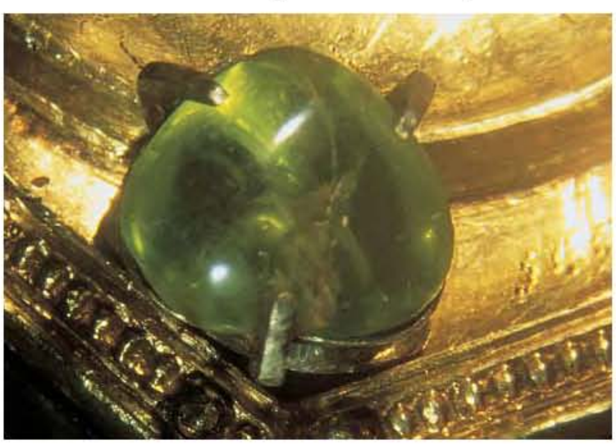


Figure 9. Blue sapphire, red garnet, and pink spinel were identified in the Dorothy monstrance. The center stone (garnet) is approximately 6 mm in longest dimension.

Figure 10. This intaglio engraved with the figure of a goat was found to be carnelian. From the Dorothy monstrance, it is approximately 11 × 12 mm.

Figure 11. This cameo, also part of the Dorothy monstrance, was fashioned from agate. It is approximately 21.5 × 13.5 mm.

11). Four colorless to slightly yellow quartz doublets with heavily decomposed cement layers are particularly interesting (figure 12).

Raman Analysis. For the most part, the Raman spectra simply confirmed the microscopic observations. Figure 13 shows typical spectra from samples of the quartz varieties (rock crystal, amethyst, citrine) that were present in the Reliquary cross and the Dorothy monstrance. These spectra do not differ greatly from one another, but the quartz spectrum itself is very distinct from other materials. Figure 14, in comparison, shows the Raman spectrum taken at the porous surface of a black cabochon (stone no. 11 of the Dorothy monstrance). In addition to a small peak at 461 cm^{-1}, the spectrum shows two broad peaks at 1355 and 1605 cm^{-1}. On the basis of the peak at 461 cm^{-1}, the stone was identified as chalcedony. The peak at 1605 cm^{-1} is seen in epoxy resins, such as those used for emerald treatments. To protect the pieces, a layer of varnish was applied to them around 1970; museum personnel removed this layer with acetone prior to these analyses. Because of the porous nature of the chalcedony, it is likely that the protective varnish was not completely removed by the cleaning process, which resulted in the peak at 1605 cm^{-1}. The broad peak at 1355 cm^{-1} is possibly due to carbon, present as the coloring agent.

Good spectra were also obtained from peridot, garnet (figure 15), and sapphire mounted in the Dorothy monstrance; whereas glass gives a relatively nonspecific spectrum, with broad bands varying from sample to sample. The spectrum of the spinel in the Dorothy monstrance (figure 16) and that of

Figure 12. A decomposed layer of cement is evident in this approximately 11.1 × 8.6 mm quartz doublet from the Dorothy monstrance.

the turquoise in the Reliquary cross showed high fluorescence and small, but characteristic, peaks.

In the pedestal to the Dorothy monstrance, the ends of the bundled rods are adorned with red and green enamel inlay (again, see figure 2). Although more precise characterization of this enamel is possible with Raman analysis, as recently demonstrated by Menu (1996), we did not pursue this because we were not equipped with reference data for enamel and its pigments.

DISCUSSION

We were surprised to find so many imitations, such as glass and doublets, in a historic piece of art with outstanding metal work. We cannot evaluate the significance of these imitations that today we call fakes. Blue (cobalt?) glass (figure 6) seems to have been a common substitute for sapphire. Red doublets (figure 4) might have been selected to mimic ruby. We believe that the near-colorless quartz and glass doublets once contained colored cement, but that the color faded over the centuries because of the organic dyes used at that time. Given that colorless glass and quartz usually exist in fairly large pieces, this seems to be the only explanation for such assemblages. In those cases where the cement layer still exhibited color, such as in the red stone A4 (figure 4) of the Reliquary cross, we recognized pigment powder.

Among the natural gemstones encountered, varieties of quartz (rock crystal, amethyst, citrine, smoky quartz, and chalcedony) were the most common. In central Europe, a few occurrences of such stones have been known for centuries. The spinel and sapphire, however, show inclusions and growth zoning that suggest a Sri Lankan origin (Hänni, 1994). Although many occurrences of red garnets in Europe have been known since ancient times, there was only very limited use of this material.

The turquoise and peridot probably originated from Near East deposits (Khorassan, Persia; and Zabargad, Egypt, respectively), since the pieces predate the discovery of America. Regarding the engraved carnelian and agate, we consider a Greek or Roman origin, dating from the classical age, as most probable, inasmuch as engraved gemstones from the classical Greek and Roman period were frequently recycled in the Gothic era. However, it is also possible that they were fashioned at approximately the same time as the objects themselves, because there was a resurgence of interest in engraved gems in the 15th century (Gray, 1983).

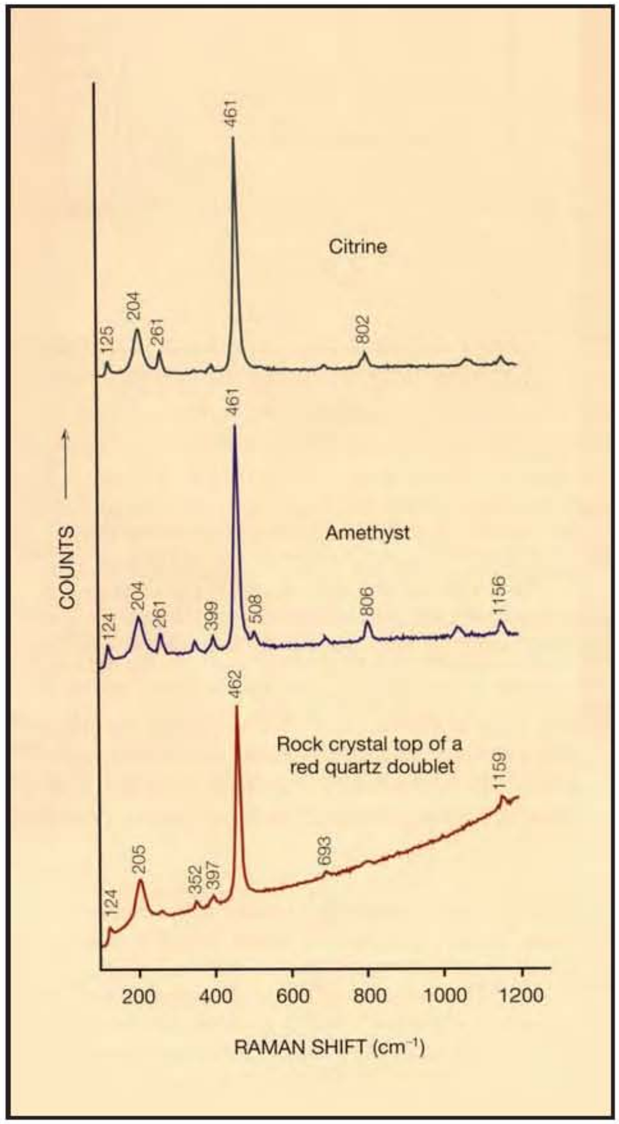


Figure 13. Note the similarities in the Raman spectra of the rock crystal top of a red quartz doublet (bottom), amethyst (middle), and citrine (top) set in the Reliquary cross. The most distinctive peak for quartz is at 461 (±2) cm^{-1}. Additional characteristic peaks are at 124, 204, and 261 cm^{-1}. Other peaks are less distinct and occur in different intensities, depending on the crystallographic orientation of the gem.

CONCLUSION

Our investigations of the Reliquary cross and Dorothy monstrance provided a great deal of information both on the gem materials used in these two 15th century religious objects and on the viability of Raman analysis for the characterization of

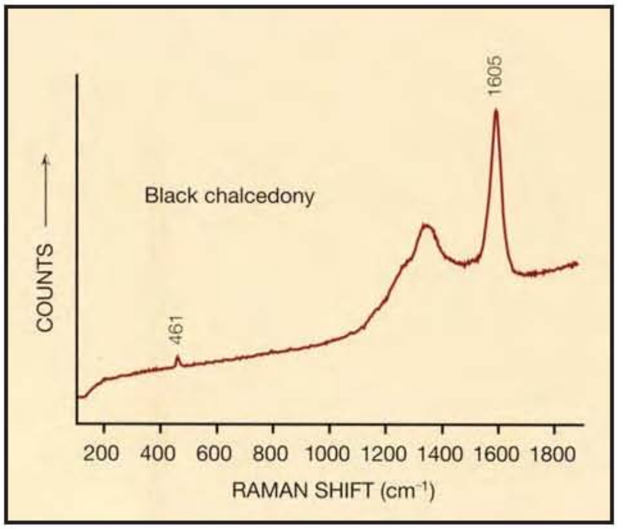


Figure 14. On the basis of the 461 cm^{-1} Raman peak, we identified this black opaque stone in the Dorothy monstrance as chalcedony. The peak at 1605 cm^{-1} is derived from residue of the varnish; whereas the broad peak at 1355 cm^{-1} may be due to the presence of carbon, which is the typical coloring agent for black chalcedony.

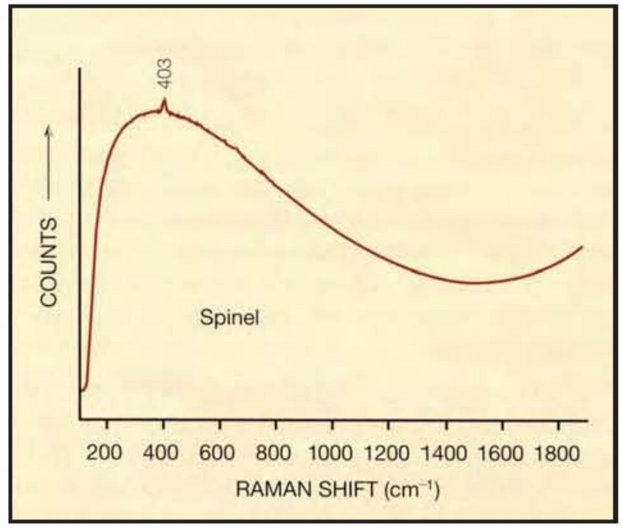
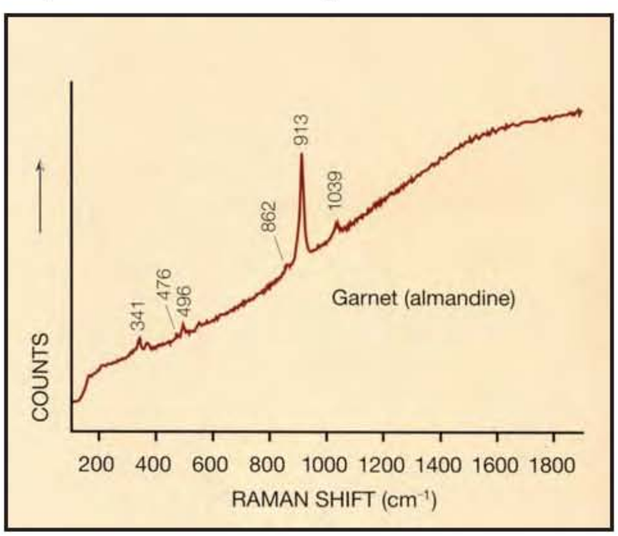


Figure 15. The Raman spectrum of a garnet set in the Dorothy monstrance shows its strongest peak at 913 cm^{-1}, with peaks of lower intensity at 341, 496, 862, and 1039 cm^{-1}. If we compare this spectrum with our reference spectra for garnet, the stone appears to be garnet with a high percentage of almandine.

such unique *objets d'art*. Although the metalwork appears to be quite fine, many of the "stones" in both pieces are actually colorless materials with a pigment backing, colored glass, or quartz doublets with a (presumably dyed) cement layer. Nevertheless, there are also some attractive natural gems, such as peridot, sapphire, garnet, spinel, and turquoise, as well as varieties of quartz. Raman analysis provided a manageable, relatively quick method for identifying these materials without any damage to either the gems themselves or the metal in which they were set.

Figure 16. Spinel generally shows a high Raman fluorescence at low wavenumbers, which is overlain by its distinct peaks at 403, 308, 663, and 765 cm^{-1}. The intensity of the peaks depends on the color of the spinel. In this Raman spectrum of a pink spinel set in the Dorothy monstrance, only the peak at 403 cm^{-1} is clearly visible.



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