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Raman Investigation of Precious Jewelry Collections Preserved in Paolo Orsi Regional Museum (Siracusa, Sicily) Using Portable Equipment

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Abstract

This work is a part of a large scientific project aimed at highlighting the potential of portable Raman equipment in characterizing jewelry materials preserved in museums, carried out in collaboration with gemologists and archeologists. In detail, we report the results of a measurement campaign performed for the study of gems and jewels preserved in the well-known *Medagliere* section at the Paolo Orsi Regional Museum of Siracusa (Sicily). The studied materials consist of exquisite examples of engraved loose gems and really rare examples of Hellenistic–Roman jewels, mainly coming from relevant Sicilian archaeological sites. Portable Raman measurements have been carried out using two instruments equipped with different excitation wavelengths. The obtained results have allowed for a complete characterization of the studied gemological materials, also suggesting sometimes misclassification for some valuable objects and gems.

Keywords

Gems, jewels, Medagliere, museum collection, portable Raman spectrometry, Siracusa

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Introduction

Among the collections preserved in the well-known *Medagliere* section in the Paolo Orsi Regional Museum of Siracusa is a noteworthy and valuable quantity of gems and jewels. These materials mainly date back to the Hellenistic and the Roman Age and come from both private collections and archaeological excavations.

A large number of the preserved artifacts were acquired from the museum under the directorship of Paolo Orsi, from 1888 to 1930.[1] Among these is a large range of 700 engraved loose gems bought in 1890 from the private collection of Marchese Corrado Di Lorenzo di Castelluccio. The collection mainly consists of quartz gems of different varieties, whose attribution is already questioned as noted in archive documents.[2,3] Particularly interesting, both from historical and archaeological points of view, are materials coming from several archaeological sites explored in Siracusa during the last centuries; the historical sources testify in fact to the development of a particularly flourishing goldsmith industry during the third century BC, a period characterized by intense cultural and commercial exchanges between the city and the Hellenistic areas.[4]

Even if documentation about these artifacts were available, some of these objects were acquired by the museum in a non-systematic way (i.e., from archaeological surveys or private donations); therefore, several attribution problems, mainly related to the composition of gems set in finished jewelry, their authenticity, and dating have arisen over the

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time. The recent development and application of analytical techniques able to give reliable information on mineral composition in fast, noninvasive, and nondestructive methods,[5–8] an archaeometric investigation of gemological materials was performed.

The most powerful among these methods is Raman spectroscopy. The Raman technique has in fact been successfully applied in characterizing jewels and gems, obtaining much information on studied materials (i.e., composition, provenance, genesis, and treatments) over a relatively short time and without sample preparation.[9] Moreover, the availability of high-resolution portable systems that allow in situ measurements represents an important advantage for unmovable and highly valuable art objects.

Therefore, within the framework of a scientific collaboration among the Universities of Catania, Parma, Prague, and Gent, a portable Raman measurement campaign has been carried out on a selection of valuable artifacts preserved in the collections at the Paolo Orsi Museum of Siracusa. The main aim of this work is to complement and support the archaeological interpretations and characterize and evaluate two sets of precious objects, namely loose gems and jewels, selected by the curators due to their questionable classification.

The problem of the gemological classification of SiO_2 varieties

One of the problems related to the classification and exhibition of gemological materials in museums is related to their correct nomenclature. A current example is represented by gems made from quartz varieties, widely present in the studied sets of objects. In fact, usually, in the archive documents, no rigorous nomenclature of quartz varieties has been used for the archaeological description. According to the gemological and mineralogical classification, quartz is usually distinguished in macrocrystalline and micro- or cryptocrystalline varieties depending on the compositional, structural, and textural features exhibited using optical microscope observation.[10,11] In detail, the term macrocrystalline is referred to varieties that develop visible crystals or are made of large inter-grown crystals (e.g., rock crystal, amethyst, aventurine, citrine, etc.); otherwise, microcrystalline varieties exhibit tiny crystal grains that are visible in an optical microscope (crystals less than 30 μm in size), while cryptocrystalline ones are characterized by a very finely fibrous and sub-microscopic texture.[10,12,13] For cryptocrystalline stones, chalcedony is the type name, but this has been divided into several optically distinct types characterized by different impurities and colors, whose etymology is often derived from antiquity.[14] Among these, the most diffused in gemology are represented by agate (characterized by concentric layers in a wide varieties of colors),[14] sardonyx and onyx (a reddish-black and white-and-black banded varieties, respectively),[14] carnelian (characterized by a reddish color due to ferric iron oxides),[14] and jasper (a mixture of different types of microcrystalline quartz with impurities of other minerals that give the colors).[14]

In this context, the recent discovery of a new monoclinic polymorph of microcrystalline quartz, named moganite,[15–17] permits important considerations. Pure moganite is really rare; usually, it occurs as intergrowth in several varieties of microcrystalline quartz, especially in agate and chalcedony.[18] The proportion of moganite with respect to quartz is variable and it is considered a key crystallographic features able to distinguish microcrystalline quartz varieties coming from different geological areas.[19]

On the basis of the abovementioned, it is clear that a correct nomenclature attribution needs in-depth investigation of the microstructural and microtextural features of a quartz gem; however, this study is not always easy and immediate using a classical gemological method (e.g., microscope observation), especially in the case of gems mounted in settings or materials preserved in a museum, for which handling has to be minimized. In this framework, the use of Raman spectroscopy is highly valuable, as the ability of the method to distinguish polymorph and detect the presence of impurities in quartz, often responsible of the color of the gems and, therefore, allowing the correct nomenclature of the gemological material.

Materials

Among the really valuable objects preserved in the collections of Paolo Orsi Museum, 21 loose gems and 20 gems in exquisite and precious settings were selected and investigated due to several attribution problems related to them. Details on sample ID, catalog number, shape, weight, color, optical features, and provenance information of all studied samples are reported in Table 1.

In particular, the selected loose gems were acquired by the museum at the end of the nineteenth century from local antique dealers and private proprieties. For this set of objects, several difficulties in obtaining certifications or certain source information occurred; therefore, a attribution and archaeological hypotheses have to be verified and supported by in-depth studies. Overall, the selected gems exhibit a variegate repertoire of color, shape, and esthetic features; from a macroscopic point of view, a large number of them are transparent to translucent in appearance with an elliptical shape. Moreover, the samples are engraved with images related to mythological or war theme (samples 1–10, 12, 13, 16, 17, 21),[20] as well as human faces (sample 14) and animal subjects (sample 11). In some cases (samples 15, 18, and 20), inscriptions are also visible.

Referring to the jewels, the studied set consists of numerous objects acquired by the Museum and coming from relevant archaeological excavations carried out in several Sicilian sites. The more interesting sources are represented by the

Table 1. Sample IDs, catalog number, aesthetical and dimensional features (i.e., color, optical properties, dimension, weight, and shape), provenance, and archaeological description of studied jewels and gems. Moreover, the main Raman peaks (in cm^{-1}) and attribution of the studied gemological materials are reported.

Sample ID	Catalog number	Color	Optical properties	Dimension and weight	Shape/object	Provenance	Archaeological description	Main Raman features (cm^{-1}) (785 nm)	Attribution
Loose gems									
1	15226	violet	transparent	15 mm; 1.3 g	elliptic	acquired	Eros engraved on amethyst	208, 355, 463, 807, 1081	amethyst
2	16509	yellow-brown	opaque	12 mm; 0.4 g	elliptic	acquired	soldier engraved on agate	Only fluorescence	–
3	21118	violet	transparent	16 mm	elliptic	acquired in Taranto	Eros holding a horn of plenty engraved on amethyst	209, 355, 463, 809, 1160	amethyst
4	30153	yellow	transparent; enriched of sub-millimetric dark inclusion	10.5 mm	elliptic	acquired in 1909	mythological subject engraved on emerald	465, 505	chalcedony
5	24251	red	transparent	11.5 mm	elliptic	Lentini	women on a set engraved on carnelian	219, 465, 502	chalcedony
6	22726	red	transparent	11 mm	elliptic	Siracusa	Eros and Psyche engraved on carnelian	217, 465, 502	chalcedony
7	18808	orange-red	transparent	13 mm	Little angel head	Lentini	carnelian	209, 465, 500	chalcedony
8	37206	pale pink	translucent	19 mm; only a fragment	elliptic	Palazzolo Acreide	fragmentary sample; cameo representing Hercules.	214, 465, 504	chalcedony
9	30145	red	transparent	10 mm	elliptic	acquired in 1909	Zeus engraved on carnelian	214, 466, 504	chalcedony
10	23390	orange-reddish	transparent	13 mm	elliptic	acquired in Taranto	soldier engraved on carnelian	466	chalcedony
11	24469	pale pink	transparent	23 mm; 5.4 g	elliptic	Grammichele	roe deer engraved on agate	214, 358, 464, 502, 790, 1069, 1166	chalcedony
12	15062	yellow-brownish	opaque; enriched of sub-millimetric dark inclusion	13 mm	elliptic	Pantelleria; acquired in 1895	Eros engraved on carnelian	462	chalcedony
13	38868	yellow-pale brown	transparent	12 mm	elliptic	Tindari	Hermes and a child Dionysus engraved on carnelian	465	chalcedony
14	43353	pale pink	opaque	8 mm	head of a men	Palazzolo Acreide	black man engraved on amethyst	Broad band centered at ~1500	glass
15	17269	orange	transparent	13.6 mm; 0.6 g	elliptic	acquired	two butterflies and inscription engraved on carnelian	467, 502	chalcedony
16	36267	red	transparent	14 mm	elliptic	acquired in 1915	soldiers engraved on carnelian	214, 365, 465, 502	chalcedony
17	36271	orange	transparent	8 mm	elliptic	acquired in 1915	nude man engraved on jasper	Only fluorescence	–
18	18860	pale brown	opaque	11 mm	polygonal	acquired	pendant representing the symbol of Sicily	286, 712, 1086	calcite

(continued)

Table 1. Continued

Sample ID	Catalog number	Color	Optical properties	Dimension and weight	Shape/object	Provenance	Archaeological description	Main Raman features (cm^{-1}) (785 nm)	Attribution
19	13372	banded; from orange-yellow to pale yellow	transparent	12 mm	elliptic	acquired	Pegaso engraved on onyx	465, 502, 804	jasper
20	30152	pale brown	opaque	13 mm	elliptic	acquired in 1909	feather and inscription "GRI" engraved on jasper	Only fluorescence	–
21	17631	pale brown	opaque	18 mm	elliptic	acquired in 1897	Dionysus engraved on onyx[28]	465	chalcedony
Jewels									
25	8398	red-orange	transparent	12 × 9 mm	ring	S. Giuliano- Siracusa	Neptune engraved on a carnelian	465, 504	chalcedony
26	8533	dark brown	transparent	7 mm; 2.6 g	ring	acquired in Siracusa	gold ring; Ares engraved on onyx	465	chalcedony
27	12376	red-orange	transparent	15 mm	ring	acquired in Siracusa	gold ring; cameo	464	chalcedony
28	18521	red-orange	transparent	7 mm	ring	acquired in Lentini	gold ring	465, 504	chalcedony
29	20144	green	translucent		ring	acquired from an archaeological excavation carried out in Agrigento	emerald	223, 465, 503	green chalcedony
31	8534	pale orange	transparent	8 mm	ring	S. Giuliano- Siracusa	little angel engraved on carnelian	465, 502	chalcedony
32	25675	white	opaque		pendant	Collection Castelluccio	cameo with engraved soldier	209, 365, 465, 803, 1160	α-quartz
33	59–600	dark red	translucent	11 × 16 mm	ring	Morgantina archaeological site (*Casa di Ganimede*)[25]	Gold ring; cabochon gem	360, 559, 639, 861, 918, 1050	garnet
34	56–1669	dark red	translucent	50 mm	earring	Morgantina archaeological site[24]	Pendant with garnet	360, 556, 639, 860, 918, 1050	garnet
36	55079	red	transparent	13 × 9 mm	ring	Hellenistic Mausoleum Siracusa[23]	gold ring; two fishes engraved on garnet	360, 558, 641, 860, 918, 1050	garnet
37	55080	red	transparent	12 × 14 mm	ring	Hellenistic Mausoleum Siracusa[23]	gold ring; Agatocle head engraved on carnelian	209, 465, 501, 802, 1161	chalcedony
38	82015	green	transparent	6 × 6 mm	ring	found in Taormina in 1979 from De Luca private proprieties	gold ring with emerald	685, 1070	emerald
39	3515–99958	dark green	opaque	33 × 28 mm	necklace	from the archaeological excavation carried out at the Ospedale Civile in Siracusa in 1969[22]	gold necklace with a dog engraved on a glassy pendant	Broad band centered at ~1500	glass
41	32141	dark red	translucent	15 mm; 5.4 g	ring	from a tomb in C.da Cittadella in Morgantina[26]	gold ring with red gem	360, 559, 645, 860, 918, 1050	garnet
42	45907	red-orange	transparent	12 × 9 mm	ring	acquired in Lentini[29]	silver ring with carnelian	465, 504	chalcedony

(continued)

Table 1. Continued

Sample ID	Catalog number	Color	Optical properties	Dimension and weight	Shape/object	Provenance	Archaeological description	Main Raman features (cm^{-1}) (785 nm)	Attribution
43	32944	red-orange	transparent	3 × 6 mm	ring	archaeological excavation in C.da Dammusi, Siracusa[21]	gold ring with carnelian	465, 504	chalcedony
44	102803	dark red	transparent	13 × 17 mm	ring	found in Tindari, 1983	gold ring; soldier engraved on garnet	Broad band centered at ~1500	glass
45	102798	red	transparent	21 mm, 4.235 g	earring	unknown	gold earring with antelope shape and three red gems	365, 560, 860, 918, 1050	garnet
48	25882	pale violet	transparent	12 × 14 mm	ring	Collection Castelluccio	gold ring with Cesar engraved on amethyst	Broad band centered at ~1500	glass
60	1577	red	transparent	33 cm	necklace	from the tomb 3 Frudà in Naxos[27]	gold necklace with spherical elements and red gems	361, 557, 860, 918, 1047	garnet

archaeological sites explored in Siracusa. Noteworthy is a jewelry set found in a tomb dating to the end of the fourth century BC and attributed to a young women (C. da Dammusi, Siracusa);[21] among the objects composing the set, namely earrings, a necklace, and a ring, the latter one (sample 43) was selected for analysis because of its the interesting beetle-shape, that suggests the diffusion of Egyptian design in the Greek goldsmith art. Another interesting object is represented by a gold necklace with pendant (specimen 39),[22] in which the diffused Roman loyalty symbol of a crouched dog is engraved. The sample was acquired by the Museum after the archaeological excavations carried out in the building area of the Civil Hospital during the 1960s. From the well-known Hellenistic Mausoleo of Siracusa,[23] two exquisite gold rings (specimens 36 and 37) with engraved red-orange gems have been selected for the analyses.

Beside the artifacts coming from Siracusa, several interesting objects came from the archaeological excavations carried out by the American Archaeological Mission in Morgantina in 1950s. This campaign highlighted numerous precious artifacts and coins. Among the jewels discovered in the site, an interesting pendant (sample 34) and two fashionable gold rings (specimens samples 33 and 41) have been selected for the scientific investigations.[24–26]

Finally, the archaeological site of Naxos represents another relevant source of interesting materials, both from artistic and archaeological points of view. Of the Naxos jewels, a gold necklace composed of 123 gold links and four set, red gems, discovered in the necropolis area and dated back to the fourth–third centuries BC,[27] has been included in the analyzed set. For further details on provenance, archaeological contexts, manufacture features, and dating hypotheses (as noted in the documentation) for the other samples,[28,29] see Table 1.

Experimental

Two portable instruments equipped with different wavelengths excitation sources have been used: a portable Enwave Optronics (Irvine, CA) EZRAMAN-I-DUAL and a handheld RockHound (DeltaNu, now SciAps, Laramie, WY) Raman spectrometer.

The DeltaNu instrument is equipped with a 785 nm diode laser, 120 mW maximum output power, and a thermoelectrically cooled charge-coupled device (CCD) detector that allows Raman spectra ranging from 200 to 2000 cm^{-1} to be obtained with a spectral resolution of 8 cm^{-1}. It is connected via a USB cable to a laptop, allowing a remote control of input and output settings. The EZRAMAN-I-DUAL Raman system (Enwave Optronics, Irvine CA) is a portable dual laser instrument.[30] It is a fiber optic-based spectrometer equipped with a near-infrared diode laser (785 nm) and a green Nd:YAG laser (532 nm) and a thermoelectrically cooled CCD detector. The optical fibers have interchangeable lenses and adjustable power controller for each laser (maximum output power 400 mW and 100 mW for the 785 nm and the 532 nm lasers, respectively). Different gratings are used with different spectral range/spectral resolution for each laser: 100–3200 cm^{-1}/7 cm^{-1} for the near-infrared laser and 100–2350 cm^{-1}/6 cm^{-1} resolution for the green laser. The spectrometer can use 230 V AC or an internal or external Li battery. A laptop, present in the case, is connected to the spectrometer. Both spectrometers have been calibrated using a polystyrene bead before each experimental session.

The measurements conditions were similar for both instruments: all measurements, consisting of 10–15 accumulations of 2–3 s each, were carried out in situ by shielding the specimen and instrument output lens with a black cloth in order to minimize spectral interference from room light. The Raman probe was focused at a few millimeters of distance from the probe lens. In the chosen configurations, the laser spot was around a tenth of a millimeter in diameter to obtain a real space resolution in the range of a few millimeters. Due to the relatively large spot size, the laser power per area unit was too weak to induce any undesired effect or damage, even on organic or photosensitive materials, with both laser lines.

As a result of the really short time available for performing the measurements, mainly due to limits of access to some sections of the museum, the Enwave system was set to operate with the 532 nm laser. In order to compare the different excitation source in the identification of gems and support the eventually questioned attribution that arose using the DeltaNu instrument, the last one equipped only with the 785 nm laser.

Data processing the acquired Raman spectra using both instruments have not been subjected to any data manipulation or processing techniques and are reported generally as collected, with the aim to highlight the potential of the technique in the fast and on-site identification of gemological materials. In fact, as the instruments can be connected via a USB cable to a laptop, Raman spectra were simultaneously visualized, allowing a real time identification of materials during the measurement campaign carried out in collaboration with the Museum curators. The identification was compared with standard spectra present in the libraries of the authors.

Results and discussion

Loose gems

The obtained results for the set of loose gems are summarized in Table 1, whereas the main Raman bands (in cm^{-1}) that allowed the mineralogical identification are reported. Raman measurements have been collected using the 785 nm excitation source of the DeltaNu instrument, obtaining in almost all cases successful results. In order to compare spectra acquired with a different laser and in cases of really high fluorescence signals, the 532 nm line of the Enwave instrument was used in support of the DeltaNu.

The main problem related to this set of materials was related to the classification of the gems and their correct nomenclature. The Raman measurements performed on samples have allowed us to distinguish mono- and macro/microcrystalline varieties of quartz, as well as some artificial gems.

As detailed in the set of examined gems, only two transparent and translucent violet-pale pink samples (e.g., 1 and 3) exhibit the typical Raman spectrum of pure α-quartz (peaks at ~207, 355, 465, 798, 1065, and 1160 cm^{-1}; Figure 1),[31] classifying these gems as amethyst (monocrystalline variety of quartz). Samples 8 and 11, too, were classified as amethyst for the first time due to their aspect and to their Raman spectra typical of quartz. Nevertheless, the two gems are better classified as violet chalcedony due to the presence in the spectra of the sharp mode at 502 cm^{-1} assigned to moganite (see Figure 1).[18]

Among the gems exhibiting a transparent, homogenous, and orange-red/pale-brown color, samples 5, 6, 7, 9, 10, 13, 15, 16, and 21 have been identified as quartz, as suggested by the typical strong Raman band at 465 cm^{-1} visible in all spectra (Figure 2). The intense reddish color of gems determined an archive classification as carnelian. However, the absence of any bands related to iron oxides in the Raman spectra does not support this hypothesis. Therefore, for this set of materials the more general nomenclature of chalcedony has to be preferred.

For samples 4, 12 (both specimens really heterogeneous in color and exhibiting numerous inclusions), and 19 (characterized by the typical banded features of jasper), the typical quartz Raman modes have been identified, allowing them to be classified as chalcedony (see Figure 2, where sample 4 is reported as example). Even if the portable Raman equipment is able to give back information on the eventually presence of impurities, as in the case of moganite detected in almost all chalcedony samples, for an in-depth investigation on the composition of inclusions a laboratory micro-Raman instrument should be mandatory. However, this aspect is out of the scope of this work, focused on the potential of Raman spectroscopy in classifying gemological materials in on-site conditions in the framework of Museums contexts.

In addition to the quartz varieties previously identified, the analysis performed on the opaque and pale-brown sample labeled as 14 (see Figure 3) reveals the artificial nature of this gem; in fact, the inspection of the Raman spectrum highlights the presence of not well-structured Raman bands suggesting a glass nature for it. The obtained results determine a re-attribution for this sample, previously classified as amethyst. Referring to the interesting polygonal gem labeled as sample 18, whose composition was unknown, it has been identified as calcite as testified by the main Raman modes detected at 286, 712, and 1086 cm^{-1} (Figure 3).

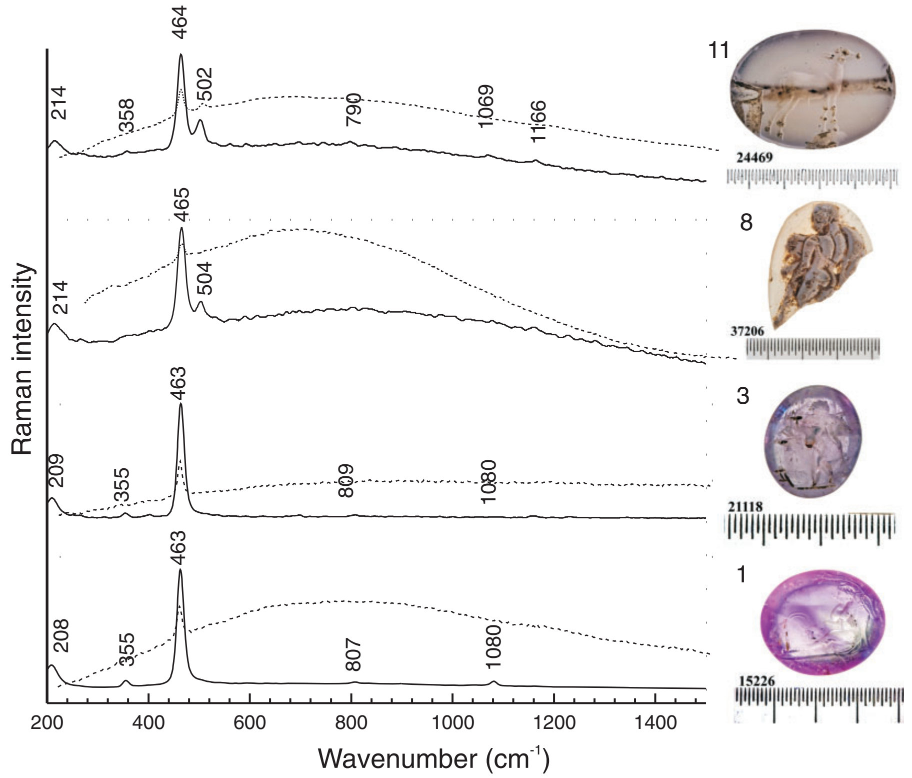

Figure 1. Pictures and Raman spectra collected on violet/pink specimens labeled as 1, 3, 8, and 11 using 785 nm (solid line) and 532 nm (dashed line) excitation lines, as examples of α-quartz and chalcedony gems.

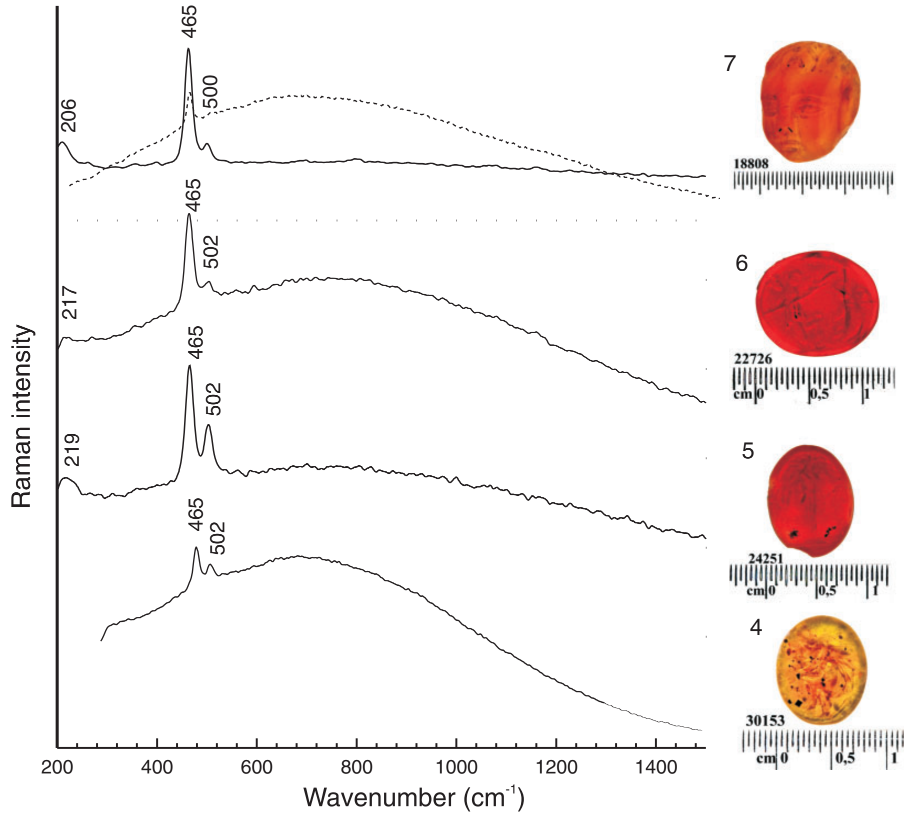

Figure 2. Pictures and Raman spectra collected on orange/red specimens labeled as 4, 5, 6, and 7 using 785 nm (solid line) and 532 nm (dashed line) excitation lines, as examples of chalcedony.

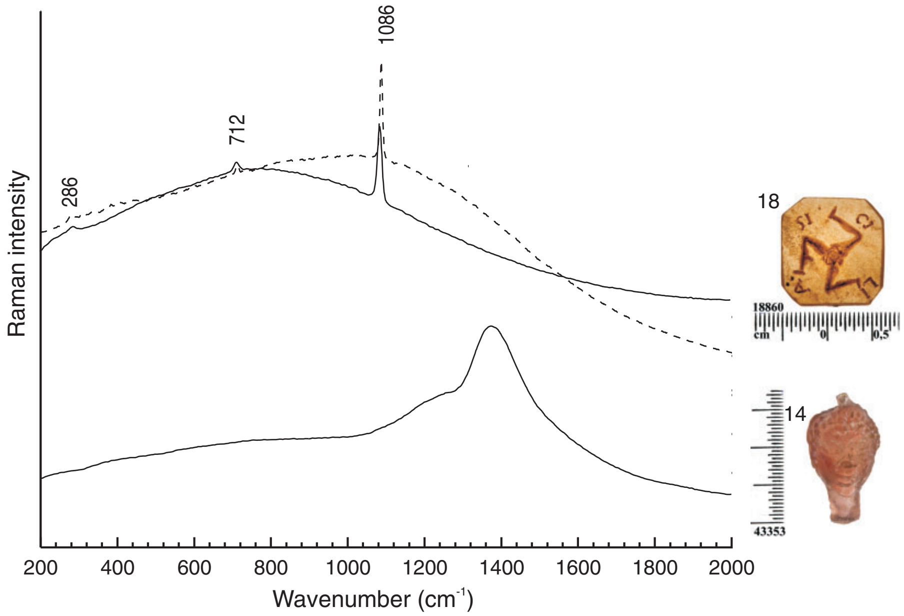

Figure 3. Pictures and Raman spectra collected on samples 14 and 18 using 785 nm (solid line) and 532 nm (dash line) excitation lines, as examples of gems obtained from less valuable materials.

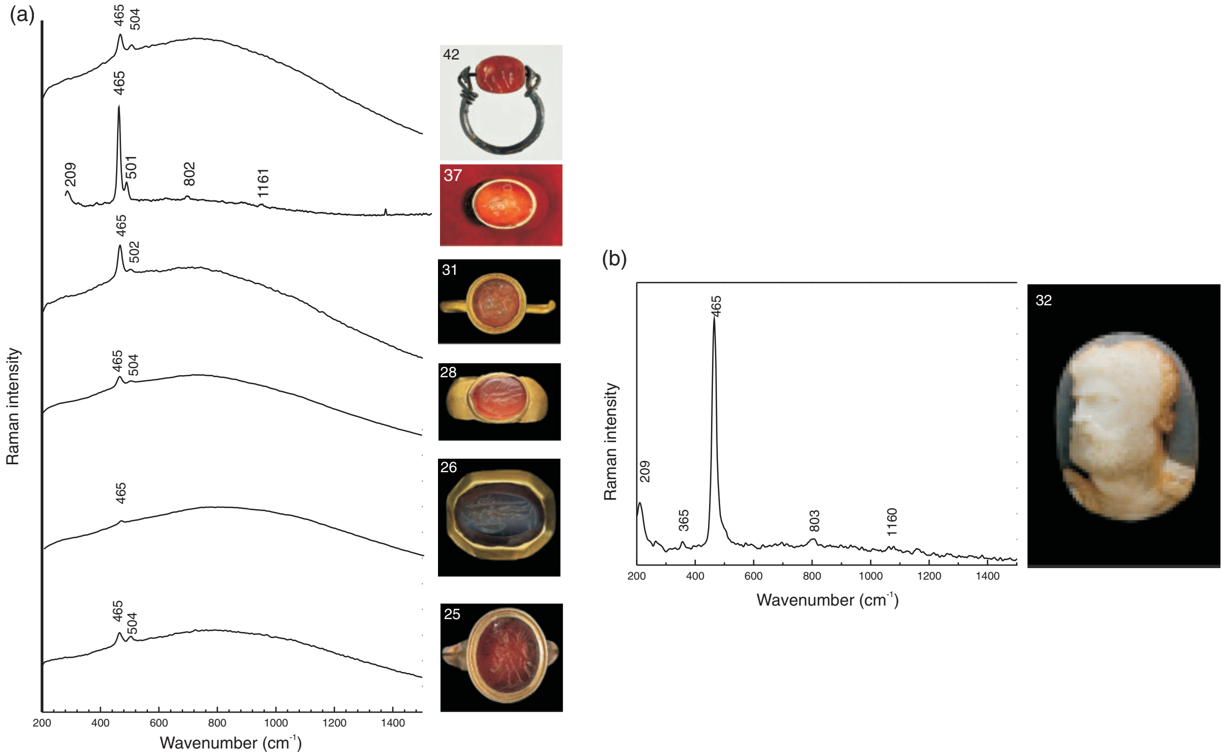

Figure 4. Pictures and Raman spectra (785 nm excitation) of (a) gems set in rings and identified as chalcedony and (b) a fashionable monocrystalline quartz gem engraved as cameo.

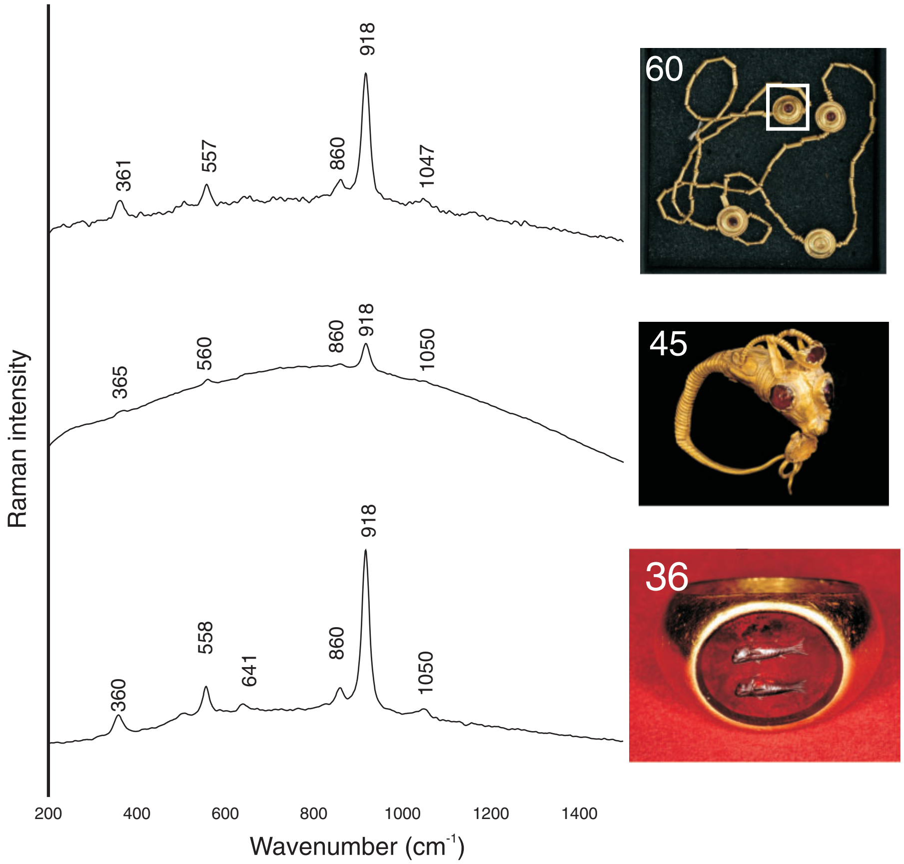

Figure 5. Pictures and Raman spectra of some red gems set in ancient jewels identified as garnets, as examples. Spectra have been collected using 785 nm excitation line.

Finally, for samples labeled as 2, 17, and 20, only fluorescence signals were collected using the 785 nm excitation source; therefore, measurements were collected also using the 532 nm line in order to solve the questionable results. However, also using a different excitation source means no attribution has been obtained for these gems.

Hellenistic–Roman jewels

The second set of gemological materials analyzed consists of Roman and Hellenistic jewels, selected by the curators for their questionable attribution. The Raman analyses were performed using the 785 nm line that allowed the immediate identification of the composition of the gems set in jewels. Overall, several quartz varieties, garnets, emeralds, and glass materials were identified. The main Raman bands (in cm^{-1}) with the relative attribution of materials are reported in Table 1.

In detail, the majority of red-orange gems analyzed (specimens 25, 26, 27, 28, 29, 31, 32, 37, 42, and 43) were identified as quartz varieties characterized a small amount of moganite in some cases, as suggested by the typical bands of quartz at 465 cm^{-1} and the small bands at ~500 cm^{-1} (Figure 4a). These results classified them as chalcedony. Raman spectra of pure α-quartz were acquired only in the case of the beautiful white-and-black engraved cameo, labeled as sample 32 (see Figure 4b).

Referring to the red/dark-red gems analyzed (specimens 33, 34, 36, 41, 45, and 60), the Raman spectra acquired exhibited the typical features of garnet (Figure 5), a gem widely used in ancient and modern goldsmith art and usually classified by the curators of the historical collection as almandine. However, the spectra collected on this class of gems showed significant differences with respect to almandine garnet, especially in the 300–400 cm^{-1} range. In fact, almandine is expected to show a resolved doublet with the main peak at 343 cm^{-1}, while our spectra show a single peak at higher wavenumbers ($\approx$360 cm^{-1}), suggesting a pyrope composition for them. In order to better estimate this aspect, a routine based on a Matlab software called Miragem that was successfully employed on portable Raman measurements on garnets.[32] According to the results obtained using Miragem, all investigated garnets consist of prevalent pyrope, between 70% and 80% in the different gems, with a second major term represented by spessartine and an estimated uncertainty of ±10%. Noteworthy is that the Raman spectra collected on all the analyzed garnets exhibited similar features and

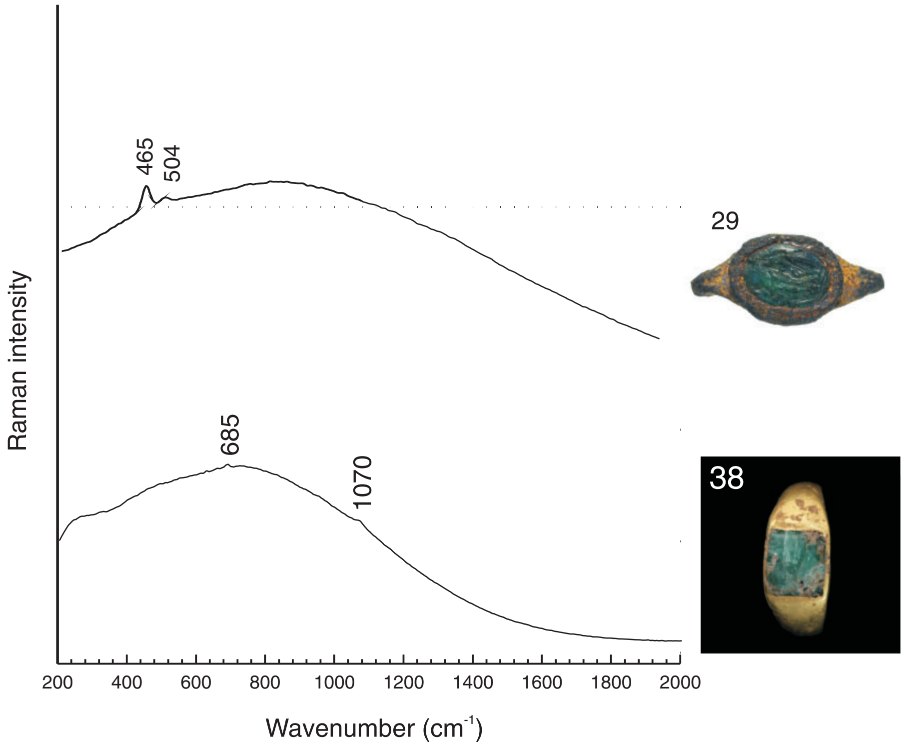

Figure 6. Pictures and Raman spectra (785 nm excitation) of green gems set in gold rings believed to be emeralds; the inspection of Raman spectra collected on samples allow to classify the specimen 29 as green chalcedony and the specimen 38 as emerald.

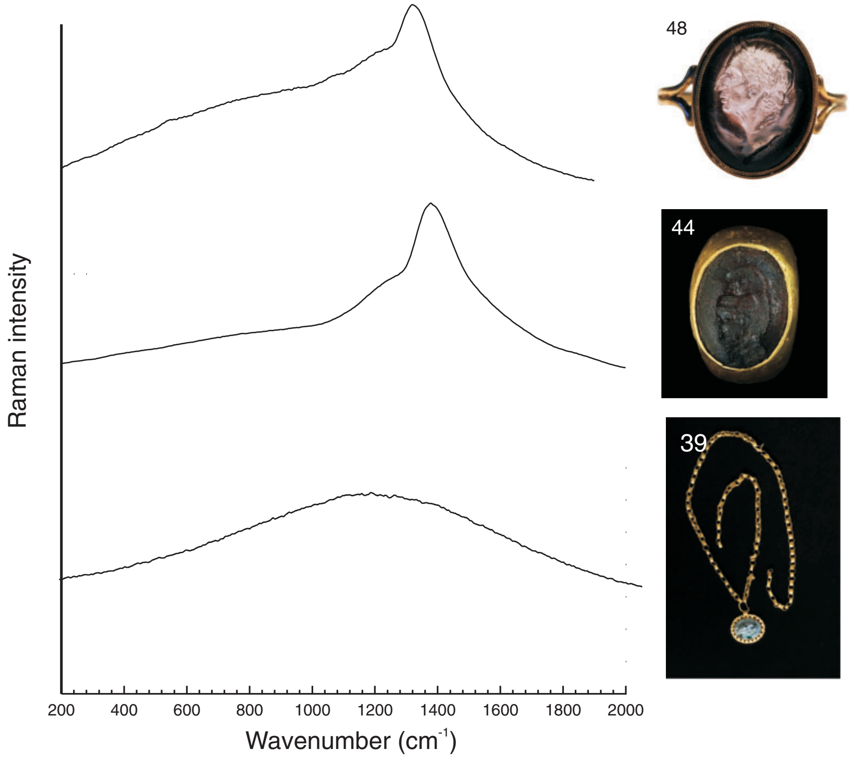

Figure 7. Pictures and Raman spectra (785 nm excitation) of some glass materials identified (samples 39, 44 and 48), as examples of artificial gems used in ancient jewelry.

comparable composition, suggesting a possible common origin for them.

Among the studied jewels, two samples have been classified by the curators and the documented sources as precious and valuable emeralds (see Table 1 and Figure 6). However, only in the case of the exquisite gold ring coming from Taormina (sample 38) does the Raman spectrum confirm the use of an emerald. In fact, the two main bands of beryl are visible at 685 and 1070 cm^{-1}.[33] Otherwise, the other green gem has been identified as green chalcedony (sample 29).

Finally, less valuable and artificial gems were identified among the analyzed objects (Figure 7). In the case of jewels labeled as samples 39 and 44, the analytical results confirm their previous attribution as glass materials. Otherwise, worthy of note is the case of the fashionable gold ring with Caesar engraved on a gem (sample 48), believed to be a precious and really valuable amethyst. The Raman spectrum collected on the gem, however, highlights the typical not-structured Raman bands of glass.

Conclusions

The short time required for a single measurement allowed for an impressive number of identifications using two different instruments. As expected, working with a higher excitation wavelength (785 nm) means that a lower fluorescence background was observed, because photons with lower energy are less likely to excite electronic states that are able to produce photo-luminescence. As a consequence, better spectra for the identification of the mineral species were obtained. Apart from fluorescence, the use of the two instruments, equipped with a different excitation wavelength, produced very similar results.

On the basis of the acquired Raman spectra, we confirmed the previous identification of 31 gems, three gems previously unclassified were identified, while the classification of seven gems was corrected. Only for three samples belonging to the loose gems set, the compositional attribution was not possible; in fact, only a strong fluorescence signal was obtained using both the 785 nm and the 532 nm excitations. In some cases, we re-attributed gems of great archaeological relevance, as in the cases of the pendant with a man head (sample 14) and the gold ring with Caesar engraved (sample 48), believed to be amethyst and now classified as glass.

Overall, the measurement campaign confirms the use of a large variety of precious and non-precious materials in the Hellenistic and Roman jewelry in Sicily; silica varieties are really predominant and are mainly represented by chalcedonies that are, usually characterized by moganite impurities. Only in rare cases, the pure monocrystalline variety of quartz has been recognized. In addition to these, more valuable gems such as garnets and emeralds have been identified. With garnets, the possibility to estimate their composition has allowed a similar origin hypothesis for these gems.

In conclusion, the obtained results suggest that even if the systematic use of portable Raman instruments cannot substitute the competence and knowledge of archaeologists and art historians, it could help to speed up the classification procedure of gems in the case of new findings, allowing a fast and on-site identification of gemological materials.

Conflict of Interest

None declared.

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