Chapter 5
A Non-destructive Archaeometric Study of a Hellenistic Gold Jewel

Andrea Smeriglio, Giuseppe Elettivo, Simone Caputo, Maria Caterina Crocco, Joseph John Beltrano, Antonello Nucera, Marco Castriota, Vincenzo Formoso, Riccardo Cristoforo Barberi, Armando Taliano Grasso, Giada Chiodo, and Raffaele Giuseppe Agostino

Abstract The fonts on the technological processes used in the art of the ancient goldsmith are largely fragmentary and a continuous activity must be developed to describe those processes. Amongst them, the archaeometric studies recently are taken advantage of the innovative non-destructive techniques. Some of those allows to study

A. Smeriglio (✉) · S. Caputo · M. C. Crocco · J. J. Beltrano · A. Nucera · M. Castriota · V. Formoso · R. C. Barberi · R. G. Agostino
Dipartimento Di Fisica, STAR Lab IR, Università Della Calabria, Arcavacata Di Rende, (Cosenza), Italia
e-mail: andrea.smeriglio@unical.it

S. Caputo
e-mail: simone.caputo@outlook.it

J. J. Beltrano
e-mail: joseph.beltrano@unical.it

A. Nucera
e-mail: antonello.nucera@unical.it

M. Castriota
e-mail: marco.castriota@fis.unical.it

V. Formoso
e-mail: vincenzo.formoso@fis.unical.it

R. C. Barberi
e-mail: riccardo.barberi@fis.unical.it

R. G. Agostino
e-mail: raffaele.agostino@fis.unical.it

G. Elettivo
GE STONES, Rose, (Cosenza), Italia

Università Di Bari, Bari, Italia

A. T. Grasso · G. Chiodo
ArToMed-Lab Dipartimento Di Culture, Educazione E Società, Università Della Calabria, Arcavacata Di Rende, (Cosenza), Italia
e-mail: armando.taliano@unical.it

R. Furferi et al. (eds.), *The Future of Heritage Science and Technologies*,
Advanced Structured Materials 179, https://doi.org/10.1007/978-3-031-15676-2_5

the whole body of a finding in terms of both used materials and traces of the technological processes put in place in its production process. The aim is twofold: on the one hand, we need to reveal the techniques and their relationship to the specific cultural milieu and, on the other hand, we can attempt to describe the exchange of raw materials needed for the production of such jewellery. Our study concerns the complete description of an archaeological finding consisting in a piece of Hellenistic gold jewellery embedding a precious stone. It was likely manufactured in the Greek colony of Taranto and discovered in Serre Boscose location in Cariati municipality (CS), Italy. This is a hilly area known in ancient times as Hylias, which was centred around fortified brettia city of Pruìia of Terravecchia (CS). The gold jewel was examined by means of the X-ray microtomography at the μTomo experimental station of STAR-facility (University of Calabria) to recover its internal structure and describe the details of the metal processing. This imaging technique allowed us to acquire the volumetric model of the finding and to characterize its internal structure with a resolution of 10 microns. Furthermore, the X-ray fluorescence spectrometry was used to analyse the elements of the constituent materials whilst the Raman spectroscopy was used to characterize the precious stone.

Keywords Hellenistic jewel · X-ray μCT · XRF spectroscopy · Raman spectroscopy · Archaeometry

5.1 Introduction

The study of ancient goldsmithing has acquired, over the years, a scientific value that goes beyond the artistic and aesthetic of the objects. The jewel, to which the value of "historical document" is attributed [1], represents the ideology of the age and it is strictly related to the power symbology. In addition, it has an ornamental function representing an important expression of culture.

In October 2010, during a topographical survey carried out in Cariati municipality (CS)—as part of a research project on ancient human settlements in the territory in Serre Boscose location (Fig. 5.1)-, we found a golden disk that was probably part of an earring. The location is a hilly area, not far from the coast and the Nicà river's mouth, known in ancient times as Hylias. According to the Greek historian Tucidide, in the 413 B.C. This river marked the boundary between Kroton and Thurii [2]. Several traces of human activity have been found in this area from the first half of the Iron age to the late-Imperial period, even though the Hellenistic age was the most important for its development. In fact, during this period, buildings and necropolis were created on the hills. This defenceless agglomeration, which gravitated on the near fortified brettia city of Pruìia of Terravecchia (CS), was used to control seaport placed at the Nicà river's mouth, connecting the coast with the inland areas [3]. Anyway, there have been already found others jewellery's objects in this area, like a golden ring related to electrum alloy coins of Carthaginian and Syracusans origin. A closet recovered in 1957 contained silver's coins of Corinth and of the most important Magno-Greek mint [4]. Moreover, several gold's jewels have been found as part of female grave decoration [2].

The case of study consists of a golden round-shaped thin case (Ø 13 mm) with a twisted wire (Ø 0, 8 mm) which is welded on the outer edge. Next to it, there is a straight wire (Ø 0, 5 mm). The case inner bottom is decorated with an eight-petalled rosette which has a red gemstone in its centre. On the back there is a twisted threadlike ring that was used to attach a pendant to the disk, which was unfortunately lost. There are also visible traces of welding where likely the earring hanger was fixed. Finally, the case is slightly deformed and bruised as it can be noted in Fig. 5.2.

The documents regarding the round-shaped earrings with pendant typology, to which the artefact under investigation belong, provide a multitude of variant. It's possible to split the different types of earrings according to the relative position between the disk and the pendant and their size. Pier Giovanni Guzzo identified these

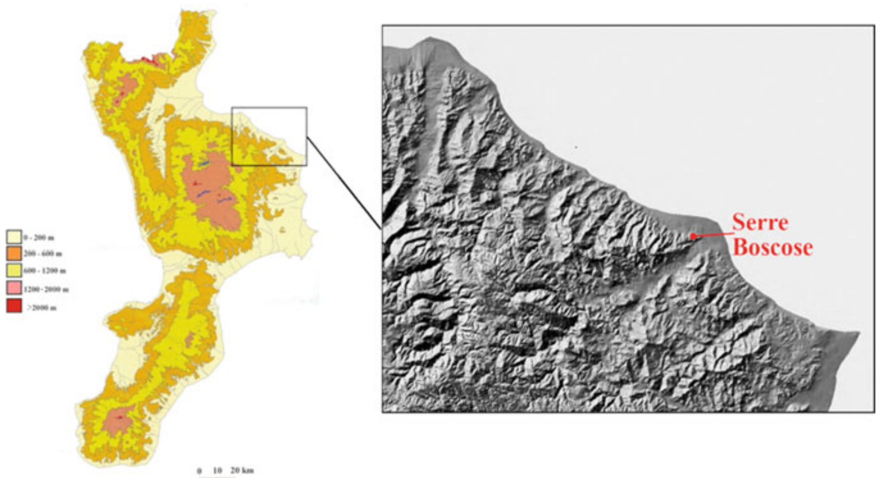

Fig. 5.1 Map of the Calabrian region in which Serre Boscose location is shown (in the inset)

Fig. 5.2 Back and front of the find under study

different variants in ten specific classes [5]. It's difficult to do a direct comparison with other manufacts of this type because they were made for a long period, until the Hellenism [6] and beyond. However, according to classification quoted above, our finding is part of class V type B2 [5]. Moreover, it is possible to perform a comparison with the gold's earring (n. inv. 1872.0604.562), that the British Museum bought from Alessandro Castellani in 1873 [7] and with the earrings kept in the Antikensammlung des Staatliche Museen of Berlins, that are made probably in Taranto between the III and the II century B.C. [8].

Some details, like the simple decoration and the presence of the red gemstone in its centre, suggests that the manufact found in Cariati belongs to the same period of the other earrings. In fact, it is known that the use of gemstones increases from the Hellenistic age to more recent times [6]. Probably the finding was produced in Taranto. Here have been found several gold jewels from the Hellenistic age, revealing the probable presence of goldsmith shops [9]. If this hypothesis is true, it confirms the relevant business relationships between the Bretti and the city of Taranto. There is evidence of this commercial interchange also in the period before the Hellenistic age [10] and in the period after the second Punic war, when, in 209 B.C., Taranto was conquered by Romans and so all its riches were confiscated [9].

The aim of this research is to expand the archeological investigation and to get more information about the manufacturing processes of the jewel. By means of non-destructive methodologies such as X-ray microtomography, X-ray fluorescence spectroscopy and Micro-Raman spectroscopy we have been able to study its morphology and the chemical composition of alloy and precious gem. The results allowed us to give hints on the production methodologies of the find.

5.2 Methods

5.2.1 X-ray Microtomography

The X-ray microtomography is a powerful technique to characterize the 3D microstructure of various samples. It is a non-destructive and non-invasive method that allows it to be applied in many research fields like biology, material science, cultural heritage [11, 12] and so on.

X-ray μ-CT investigations were performed at the μTomo experimental station of the STAR research infrastructure devoted to material science at the University of Calabria. The source features are well described in Lopez-Prat et al. [13]. In order to acquire the microtomographic images, the following parameters of X-ray source, detector and their relative position have been set: the voltage and current inside X-ray tube was 150 kV and 66 μA respectively, was selected a small focal spot (7 μm) and an 40 μm thick aluminium filter has been placed at the output of source to cutoff low energies. The distance between the source and the object was 100 mm whilst the distance between source and detector was 900. These distances imply a magnification value of 9 and equivalent pixel size of 5.55 μm. To perform the tomographic reconstruction, 1801 images were acquired every 0.2 degrees. The acquisition time was 2500 ms for each image.

5.2.2 X-ray Fluorescence Spectroscopy

Quantitative analysis to determine the composition of the various parts of the jewel was carried out using Bruker Artax 400 μXRF spectrometer located at the X-RAY laboratory of Biology, Ecology and Natural Science Department (DiBEST) of University of Calabria. Analysis was carried out at 50 kV, 700 μA, using the 0.2 mm collimator and with an acquisition time equal to 600 s. Quantitative analysis was carried out using pure element reference standard. Spectra were collected using the Artax Spectra 7® software.

5.2.3 Raman Spectroscopy

The Raman analysis was performed with a confocal Micro-Raman LABRAM by Jobin–Yvon Horiba scientific equipped with a long working distance objective 50 × and a Nd:YAG doubled laser source at 532 nm. A CCD detector was used cooled with a Peltier module 1024 × 256, dynamic range 16 bits and pixel dimensions of 27 μm. Spectral resolution was about 1 cm^{-1}.

5.3 Results and Discussion

The X-ray microtomography surveys allowed us to advance hypotheses on the jewel production method. The X-ray tomographic reconstruction reveal that the gold pendant is made by at least fourteen different pieces welded together. Some hidden parts in the artefact are impossible to be seen by a visual inspection. Already from the X-ray radiographic image in Fig. 5.3, it is easy to distinguish the various parts. Note that the red gemstone is nearly transparent to X-rays.

Each part of archaeological find has been better analysed by 3D rendering of the X-ray microtomographic reconstructions.

The external ring is a single wire coiled on itself to form a hollow tubular structure, as it is shown in Fig. 5.4.

Figure 5b shows the X-ray absorption intensity along the yellow line in transverse section reported in Fig. 5a. The graph shows a minimum on the centre and maxima on the edges of the wire. The minimum corresponds to the hole created by the wrapping of the gold wire. The diameter of the internal hole can be evaluated to be 0.4 mm.

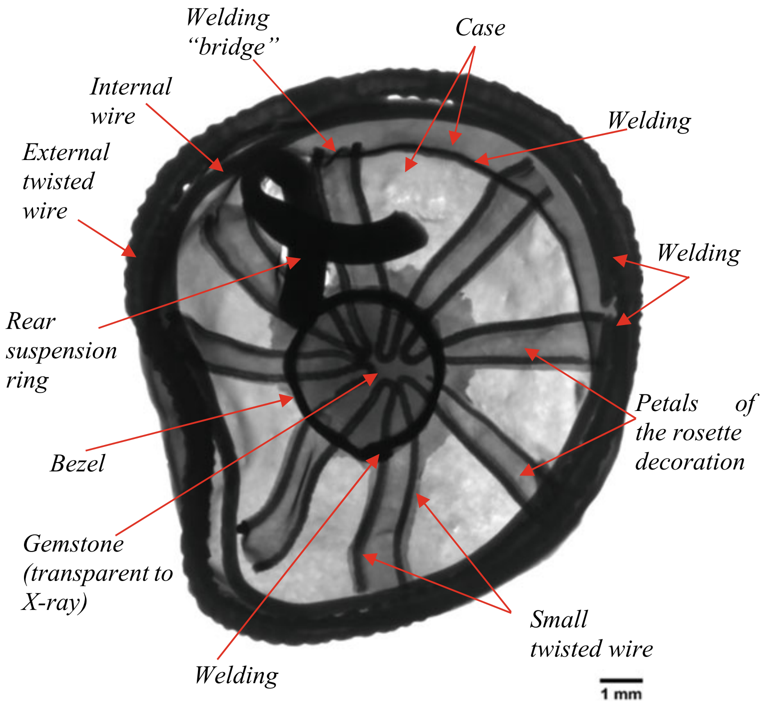

Fig. 5.3 X-ray radiography of the jewel in frontal projection. The arrows point to parts composing the earring

The same manufacturing technique was used to produce the wires placed on edges of the rosette petals. As a matter of fact, they present a hole along all their length as shown in Fig. 5.6. Moreover, the small wires welded on each petal are connected each other and welded together by a little "bridge" giving a greater stability to the whole structure. The intensity profile reported on the right of the lower panel of Fig. 5.6 was recovered along the yellow line in the virtual cut shown in false colours. The diameter of the hole is about 0.1 mm, whilst the diameter of twisted wire is about 0.4 mm.

The same manufacturing technique was used to make the solenoidal hollow wires welded on the rosette petals on the internal bottom of the case and on its external edge. They are produced with a single wire with a diameter of about 0.15–0.20 mm.

Lastly, the central bezel is made by a curved rectangular plate and welded to hold the red gemstone.

The XRF chemical investigation was performed to find out the composition of the metal as well as to follow any chemical difference in correspondence of the welding points.

Fourteen spectra in different positions on the artefact surface have been acquired, as it is shown in Fig. 5.7. Four spectra are recorded on the welding points (A1, A2,

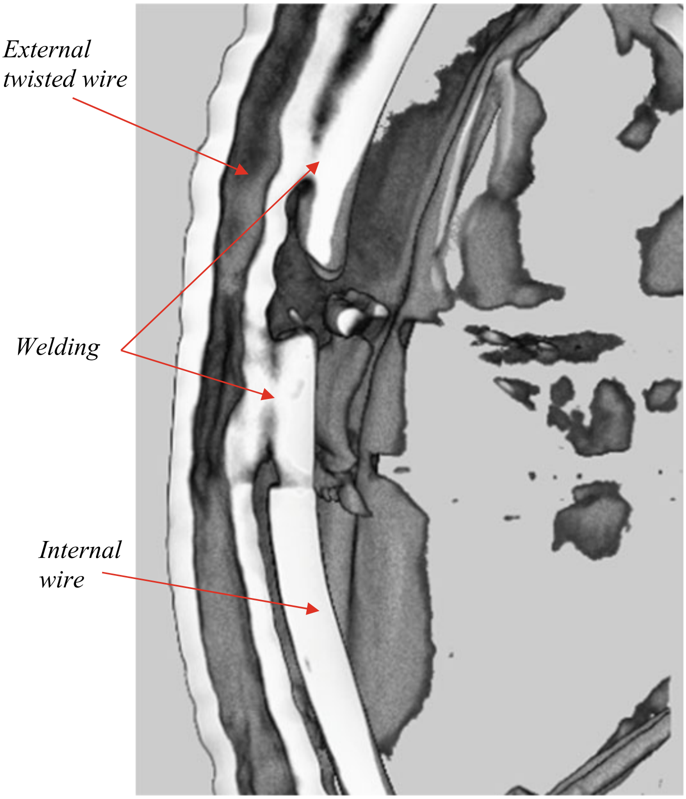

Fig. 5.4 Virtual cross section acquired by using volume viewer function on Imagej software in which the external and the internal ring are visible as well as two welding points

A3 and A4 points) whilst the other ten (B1–B10 points) in other significative areas of the jewel.

The acquired spectra tell us that the jewel is made of a gold-rich Au–Ag–Cu alloy. The fluorescence results have also unveiled that the welding spots were somehow richer in silver even though the difference in concentration are very low and the percentage averages composition overlap in the error bar. Thus, if any, a very similar alloy was used for the welding.

The concentration value of Au, Ag and Cu were normalized to 100 and they are reported in Table 5.1.

Usually, in ancient jewellery, was used three different types of welding and soldering processes: solid-state diffusion bonding with copper salt, which is used in the granulation technique [14], brazing and autogenous or fusion welding [15]. The latter was used to solder the various pieces of the jewel under investigation, using a punctual heating source like a blowpipe [16].

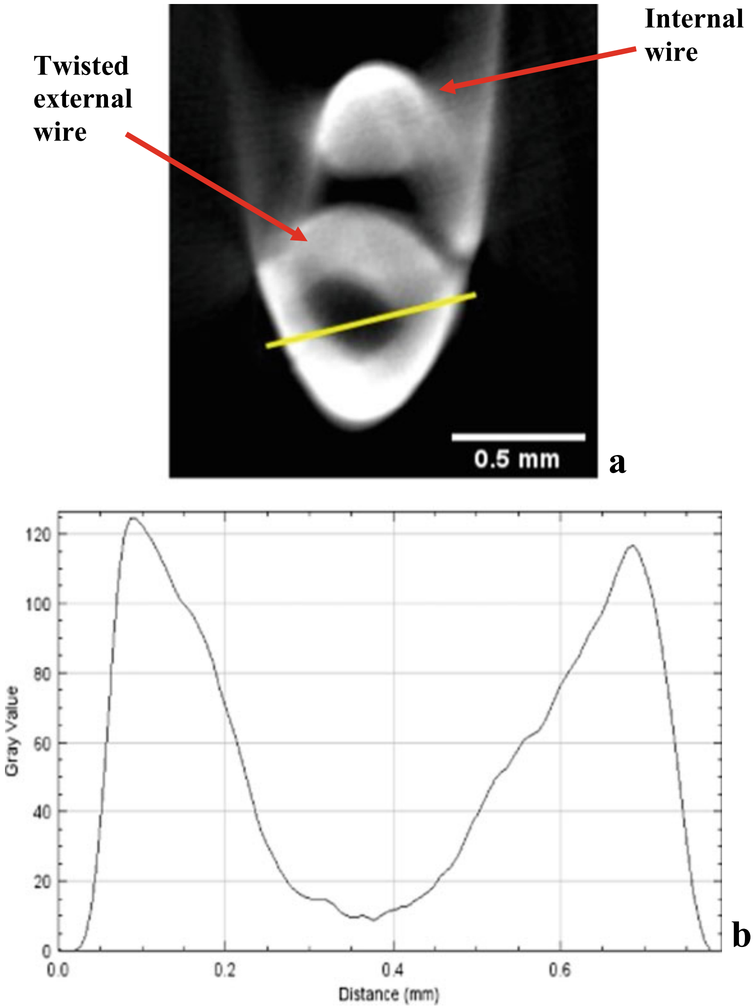

Fig. 5.5 **a** A particular of external wire shown on a single slice. The yellow line means the points at which is measured the intensity profile. **b** Histogram of greyscale's intensity

In Fig. 5.8, it is shown the representative Raman spectrum in the range between 300 and 1100 cm^{-1} collected on the red gemstone cast in a pendant.

Outside of such range (300 and 1100 cm^{-1}) there are non-detectable Raman features. As it can be seen in Fig. 5.8, the main bands fall at 355, 504, 555, 637, 856, 916 and 1048 cm^{-1}. In Table 5.2 is reported the attribution and the symmetry of the Raman modes of Fig. 5.8.

This pattern indicates that the gemstone is made by a mineral belonging to the family of the Garnets [17]. The general structural formula of the Garnets is $X_3Y_2(SiO_4)_3$, where it is possible to see the orthosilicate tetrahedral structure

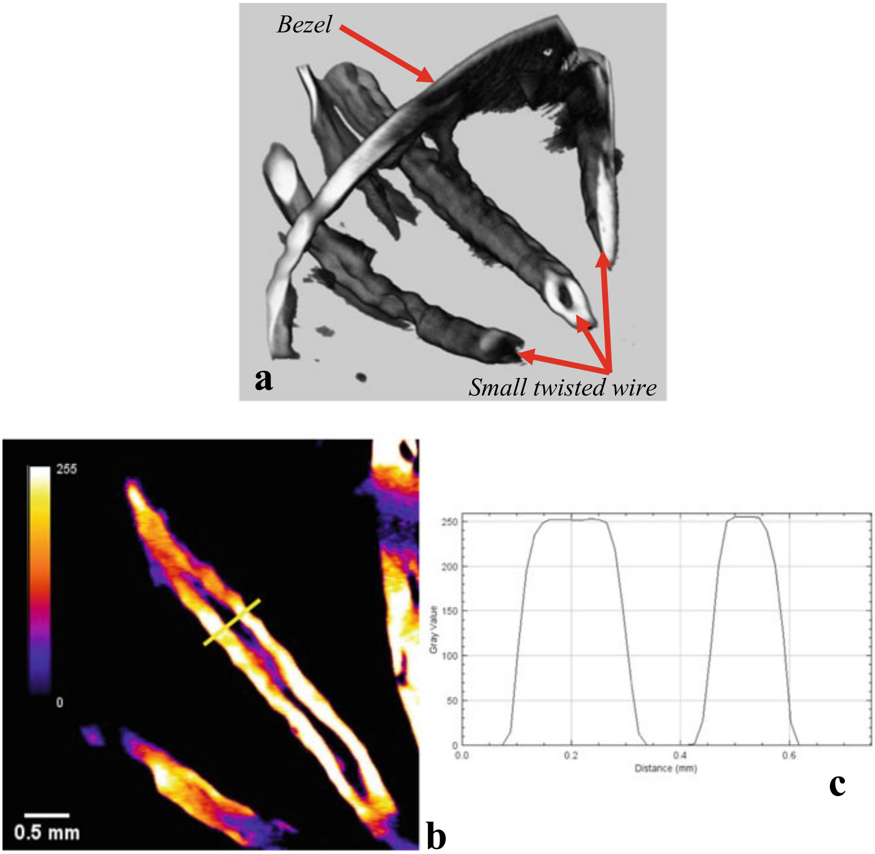

Fig. 5.6 Virtual cross section acquired by using volume viewer routine of the Imagej software in which is visible the tubular structure of the small twisted wire (**a**). In the lower panel, a closeup of small twisted wires is shown in false colors (**b**). The yellow line marks the line on which the intensity profile is extracted (**c**)

combined with bivalent and trivalent cations. In particular, the bivalent cations are Ca^{2+}, Mg^{2+}, Fe^{2+} and Mn^{2+} (indicated by the X) whilst the trivalent cations are Al^{3+}, Fe^{3+} and Cr^{3+} (indicated by the Y). Dependently from the cations involved in the structure, the garnets take different properties and different names. In particular, we have the isomorphic series denominated pyralspite when Y is aluminium (Al^{3+}): $Fe_3Al_2(SiO_4)_3$ (Almandine), $Mn_3Al_2(SiO_4)_3$ (Pyrope) and $Mg_3Al_2(SiO_4)_3$ (Spessartine). Indeed, if the X position is occupied by calcium cation (Ca^{2+}), the ugrandite isomorphic series is present: $Ca_3Fe_2(SiO_4)_3$ (Andratite), $Ca_3Al_2(SiO_4)_3$ (Grossular) and $Ca_3Cr_2(SiO_4)_3$ (Uvarotite).

On the basis of the attribution of the Raman bands, it is possible to state that the spectra of Fig. 5.8 indicated that the red gemstone in the pendant is a garnet made by a solid solution of Almandine ($Fe_3Al_2(SiO_4)_3$) and Pyrope ($Mn_3Al_2(SiO_4)_3$) [18].

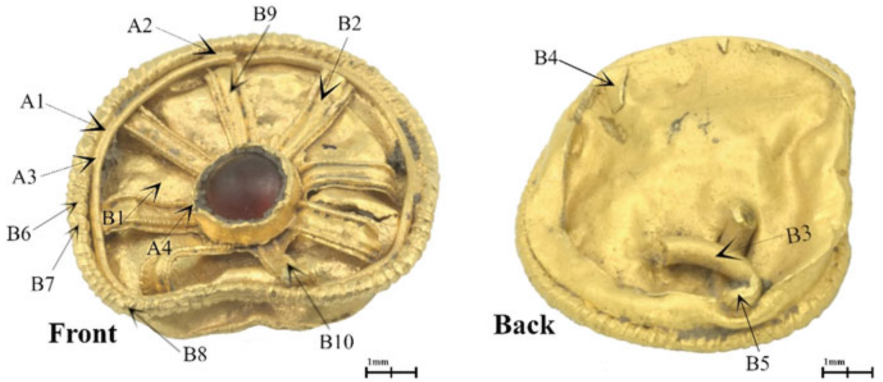

Fig. 5.7 XRF measuring points

Table 5.1 Concentration value of Au, Ag and Cu in percentage

	Au $l\alpha_{1-2}$ (conc. %)	Ag $k\alpha_{1-2}$ (conc. %)	Cu $k\alpha_{1-2}$ (conc. %)
A1	93.64	5.57	0.79
A2	93.06	5.96	0.98
A3	93.48	5.67	0.85
A4	94.16	4.92	0.92
A	93.58 ± 0.55	5.53 ± 0.52	0.89 ± 0.10
B1	94.83	4.20	0.97
B2	94.43	5.00	0.56
B3	93.11	6.10	0.79
B4	93.45	5.66	0.89
B5	93.42	5.71	0.87
B6	93.26	5.91	0.82
B7	93.17	5.88	0.95
B8	93.39	5.66	0.95
B9	94.35	5.22	0.43
B10	93.2	5.98	0.82
B	93.66 ± 0.86	5.53 ± 0.95	0.81 ± 0.27

During the Hellenistic period were used widely the Garnet to give more value to goldsmith's production [19]. The provenance of these gemstone was usually India and other eastern lands [19, 20].

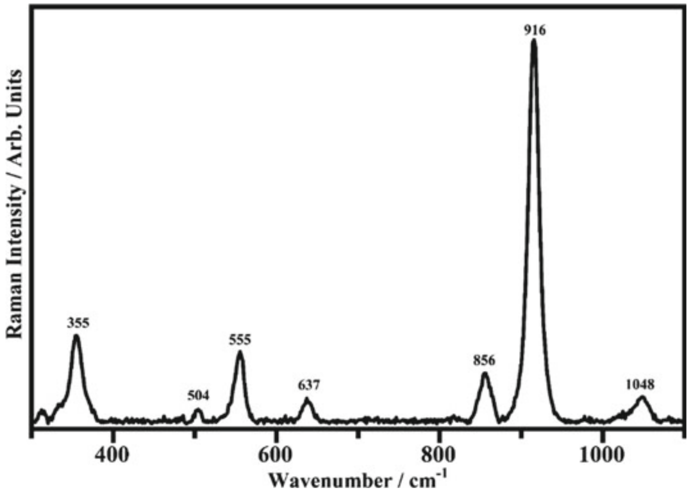

Fig. 5.8 Representative Raman spectrum in the range between 300 and 1100 cm^{-1} of red stone set in a pendant

Table 5.2 Attribution of the Raman bands of the representative spectra collected on the red stone set in a pendant and shown in Fig. 5.8

Wavenumber[a]/cm^{-1}	Raman mode and relative symmetry [14, 15]
355 (m)	Librational SiO_4^{4-}, F_{2g} mode
504 (vw)	Si–O Bending, F_{2g} mode
555 (m)	Si–O Bending, A_1 mode
637 (m)	Si–O Bending, F_{2g} mode
856 (m)	Si–O Stretching symmetric, F_{2g} mode
916 (vs)	Si–O Stretching symmetric, A_1 mode
1048 (m)	Si–O Stretching symmetric, F_{2g} mode

[a] *on bracket the relative intensity of the bands: m = medium; vw = very weak; w = weak; s = strong; vs = very strong*

5.4 Conclusions

An ancient gold earring has been studied by complementary physical methodologies through X-ray microtomography, XRF portable spectroscopy and Micro-Raman spectroscopy. These completely non-invasive and non-destructive methods methodologies have allowed to understand the constituent materials and the manufacture technology of the find. The results allow the identifying and describing of manufacturing methods used by Hellenistic goldsmiths to create amazing jewellery.

X-ray microtomography has been used to investigate the internal morphology of the jewel that is made by about fourteen different pieces welded together, some of which are impossible to see at naked eye. The solenoidal hollow wires welded on the rosette petals on the internal bottom of the case and on its external edge are coiled on themselves to form the hollow tubular structure using the strip-twisting technique. The technique of strip-twisting, best described by Oddy [21, 22], was very common in the Hellenistic jewellery [23] and involves cutting a strip of metal foil and wrapping it round an existing wire which is then removed. This helix is then tightened and gently extended by hand. The wires welded on the rosette petals are connected each other and welded together by a little “bridge” to gives it more stability.

Through the XRF chemical investigation we can confirm that the jewel is made of a gold-rich Au–Ag–Cu alloy. Furthermore, the fluorescence result has unveiled that a very similar alloy was used for the welding. This allows us to guess that the welding process was carried out forging by rapid fusion of discrete parts in contact by autogenous welding method without filler different material [24]. As the chemical composition of the earring is very similar to some Hellenistic jewels manufactured in Greek colony of Taranto and preserved at Archaeological Museum of Taranto [25], the investigated earring was likely manufactured there.

Micro-Raman spectroscopy has been used to investigate the red gemstone set in the pendant. The representative Raman spectrum and the relative assignment of the Raman features lead us to identify the composition of the gemstone as a Garnet.

Through surveys we furnished important data for the attribution of the nature of the constituent materials, which in turn may be considered a valid support for an eventual restoration. The information obtained from archaeological and archaeometric studies contributes to the discussion of the knowledge and technological capabilities of the Hellenistic goldsmiths and the spread of jewellery in the Magna Graecia area.

A more in-depth study of the raw materials used, including alloys and precious stones, could give an indication on their places of origin. Trade in Mediterranean area in Hellenistic period information could be provided, opening new topics about socio-cultural and anthropological aspects of Magna Graecia population.

Future investigation will be directed to further on the provenience of the raw materials used for the Hellenistic gold jewel making.

Funding
This research was funded by the Project STAR 2, PIR01_0008, Ministero dell’Università e Ricerca/Italian Ministry University and Research.

References

1. Guzzo PG (1992) Introduzione all'artigianato della Puglia antica, dall'età coloniale all'età romana. In: Mazzei M (ed) Oreficerie. Edipuglia, Bari, pp 161–180
2. Taliano Grasso A (2020) Approdi, rotte e naufragi lungo la costa meridionale del Sinus Tarentinus. In: Spadea R, Lo Schiavo F, Lazzarini ML (eds) Tra Ionio e Tirreno: orizzonti d'archeologia. Omaggio a Elena Lattanzi, pp 795–808
3. Marino D, Taliano Grasso A, Medaglia S, Nicoletti G (2017) Rocche protostoriche e abitati brettii tra Sila e mare Jonio. In: Atti Convegno Internazionale Centri fortificati indigeni della Calabria dalla protostoria all'età ellenistica, Università Federico II, Napoli 2014. Napoli, pp 97–130
4. Pennestri S (1983) Il ripostiglio di Cariati. AIIN 30:39–62
5. Guzzo PG (1993) Oreficerie dalla Magna Grecia. Ornamenti in oro e in argento dall'Italia meridionale tra l'VIII e il I secolo. Taranto, La Colomba
6. Lippolis E (2008) L'età classica ed ellenistica. In: Gandolfo L (ed) Pulcherrima Res. Preziosi ornamenti dal passato. Palermo, pp 143–191
7. Marshall FH (1911) Catalogue of the jewellery, Greek, Etruscan and Roman, in the Departments of Antiquities. British Museum, London
8. Schojer T (1984) Orecchini 129–137. In: De Juliis EM (ed) Gli ori di Taranto in età ellenistica, Catalogo della mostra (Milano-Taranto 1984–1986). Milano, pp 140–178
9. Guzzo PG (2014) Oreficerie dell'Italia antica. Rossano (CS)
10. Taliano Grasso A (2019) La ceramica argentata in Calabria. Orizz Rass di Archeol XX:27–46
11. Agostino RG et al (2016) Microtomographic studies as a tool in the identification of a new ceramic class: the metal-imitating pottery as grave goods among Brettians and Lucanians. Microchem J 126:138–148. https://doi.org/10.1016/j.microc.2015.12.007
12. Morigi MP, Casali F, Bettuzzi M, Brancaccio R, D'Errico V (2010) Application of X-ray computed tomography to cultural heritage diagnostics. Appl Phys A 100(3):653–661. https://doi.org/10.1007/s00339-010-5648-6
13. López-Prat M et al (2021) Architectural Terracruda sculptures of the Silk Roads: new conservation insights through a diagnostic approach based on non-destructive X-ray micro-computed tomography. Stud Conserv 1–13. https://doi.org/10.1080/00393630.2020.1862605
14. Nestler G, Formigli E (2010) Etruscan granulation: an ancient art of goldsmithing, Brynmorgen
15. Scrivano S et al (2013) Identification of soldering and welding processes in ancient gold jewellery by micro-XRF spectroscopy. X-Ray Spectrom 42(4):251–255. https://doi.org/10.1002/xrs.2482
16. Pacini A (2006) Appunti di bottega—Microsaldature nell'oreficeria antica, Don Chisci. San Quirico D'Orcia (SI)
17. Kolesov´ BAK, Geiger KA, Kolesov BA, Geiger CA (1998) O R I G I N A L P A P E R Raman spectra of silicate garnets. Phys Chem Miner 25:142–151
18. Culka A, Jehlička J (2019) A database of Raman spectra of precious gemstones and minerals used as cut gems obtained using portable sequentially shifted excitation Raman spectrometer. Raman Spectrosc 50(2):262–280
19. Spier J (1989) A group of Ptolemaic engraved garnets. J Walters Art Gall 47:21–38
20. Pappalardo L, Karydas AG, Kotzamani N, Pappalardo G, Romano FP, Zarkadas C (2005) Complementary use of PIXE-alpha and XRF portable systems for the non-destructive and in situ characterization of gemstones in museums. Nucl Instrum Methods Phys Res Sect B Beam Interact Mater Atoms 239(1–2):114–121. https://doi.org/10.1016/j.nimb.2005.06.184
21. Oddy A (1977) The production of gold wire in antiquity hand-making methods before the introduction of the draw-plate. Gold Bull 79–87
22. Oddy WA (2004) The manufacture of wire since the Bronze Age: a technological investigation using the microscope. Phys Methods Archaeom 257–267
23. Perea A, Gutiérrez-Neira PC, Climent-Font A (2018) Archaeometric investigation of a hellenistic golden funerary belt: a case study. Mediterr Archaeol Archaeom 18(3):1–16. https://doi.org/10.5281/zenodo.1461657

24. Karydas AG (2007) Application of a portable XRF spectrometer for the non-invasive analysis of museum metal artefacts. Ann Chim 97:419–432
25. Buccolieri A, Castellano A, Degl'innocenti E, Cesareo R, Casciaro R, Buccolieri G (2017) EDXRF analysis of gold jewelry from the Archaeological Museum of Taranto, Italy. https://doi.org/10.1002/xrs.2761