RAMAN SPECTROSCOPY OF FOUR ANTIQUE GEMS (FROM THE COLLECTIONS OF THE SLOVAK NATIONAL MUSEUM – ARCHAEOLOGICAL MUSEUM IN BRATISLAVA)

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1. Introduction

Mineralogical composition of ancient gems has been identified by Raman spectroscopy. The use of Raman spectroscopy to study archaeological materials has a long tradition mainly because it is a non-destructive technique and does not require removal of samples to be analyzed. In this way, various materials have been examined, ranging from gemstones, through pigments and glass to ceramics [1].

2. Experimental material and methods

Four antique gems were analyzed by Raman spectroscopy, three of them set in rings, and one free gem. The gems imbedded in rings were analyzed without any treatment and without touching the precious archaeological material.

Raman measurements were conducted in Raman spectrometer DILOR-JOBIN YVON-SPEX, type LabRam. The samples were placed on a micrometric manipulator of a confocal microscope (Olympus BX-40), and visualized, by means of a camera, on a monitor. The excitation source is a He-Ne laser (632.8 nm, 15 mW). The scattered radiation is focused onto the entrance slit of a grid monochromator (600 and 1800 grooves/mm), the spectral range was 450 nm to 1.05 μm. The spectrometer is equipped with an air-cooled CCD detector with a resolution of 1.3 cm^{-1}. The spectra were processed by the software package LabSpec. The spectrometer was calibrated to the 520.7 cm^{-1} band of single crystalline silicon. The measurements were performed at room temperature. The focused beam had a diameter of approx. 2 μm, the time of data collection varied from 20 to 200 seconds depending on the intensity of Raman scattering and fluorescence. The achieved spectra were compared with the database RRUFF [2].

Figure 1 shows a massive gold ring widened to a front plate with an inlayed oval light red gem (AP 44 419). The gem is engraved with a nude human figure holding a helmet in the right hand, and a subject with an extended ending (perhaps a mace) in the left hand. The metal part of the ring is undecorated. The archaeological finding dated to the second half of the 3rd century is from the Castle Hill in Bratislava [3].

Figure 2 shows a convex gem (AP 44 749) of rubiginous colour with an image of standing goddess Fortuna holding a steer in the left hand and a horn of plenty in the right one. The finding is from the Castle Hill in Bratislava, above the Church of St. Nicholas, and dated from the middle of the 2nd century. The gem is part of the collection of findings dated to the La Tene period until the 20th century [4].

Fig. 1 *Gold ring with a gem (registration number AP 44 419) decorated with a human figure. Its Raman spectrum is shown in Fig. 3, top curve.*

Fig. 2 *Gem with goddess Fortuna (registration number AP 44 749). Its Raman spectrum is shown in Fig. 3, bottom curve.*

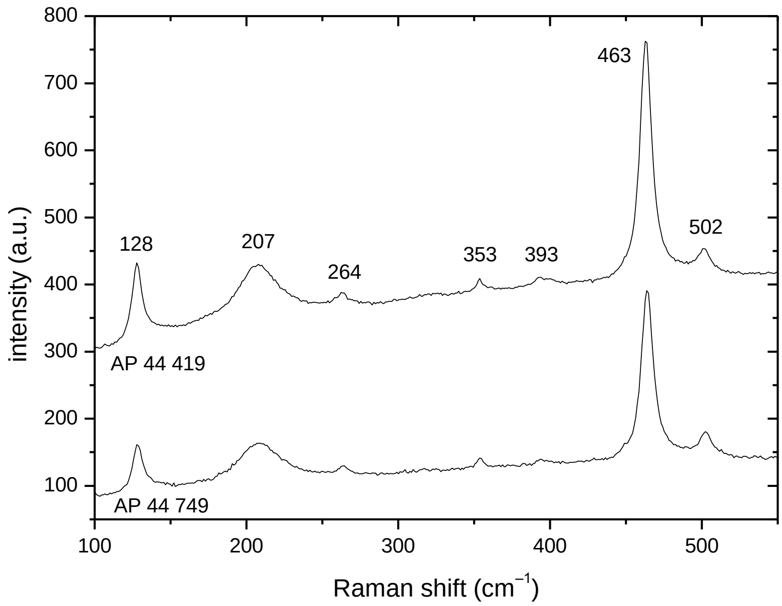

Fig. 3 *Raman spectra of the gems shown in Figs. 1 and 2. The bands centred at approx.* 463 *and* 502 cm^{-1} *prove the presence of quartz and moganite.*

In Fig. 4 there is a ring from an Old Hungarian tomb. The antique gem (AP 17 343) made of a red stone was secondarily imbedded in a medieval ring of white metal. The gem is decorated by a bust of a woman, viewed from the left profile, holding a round subject, probably an apple. The finding dated to the second century.

Figure 5 shows a bronze ring with a sleeve. In the broader part of the ring there is a dark red gem with a parrot sitting on a sprig. The finding comes from the backfill of a hole in Bratislava-Rusovce and is dated to the first half of the 2nd century [5].

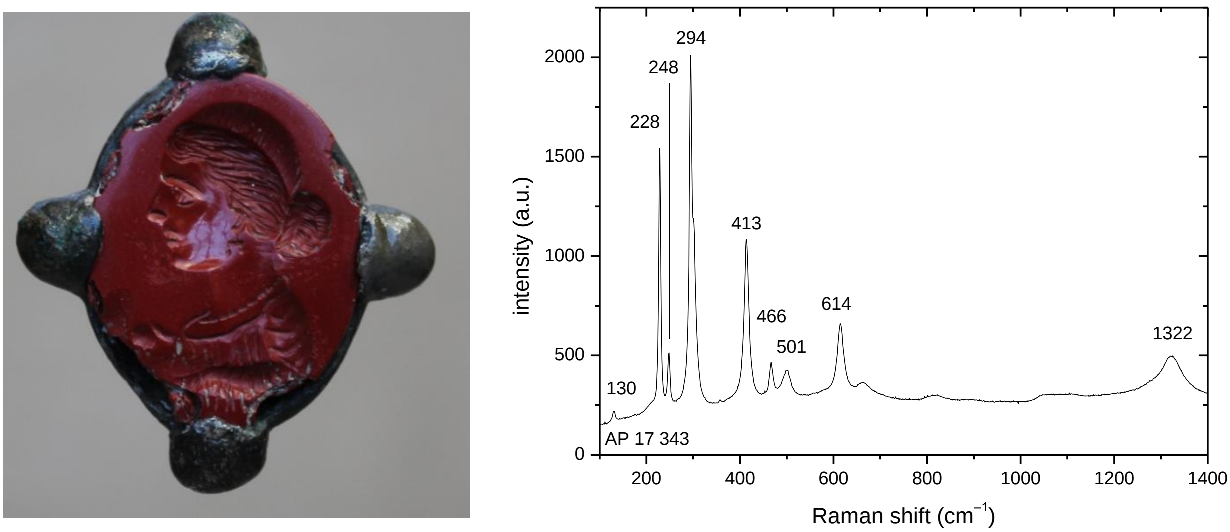

Fig. 4 *Ring from an Old Hungarian tomb with a secondarily imbedded gem (registration number AP 17 343) with an image of a woman, and its Raman spectrum (hematite).*

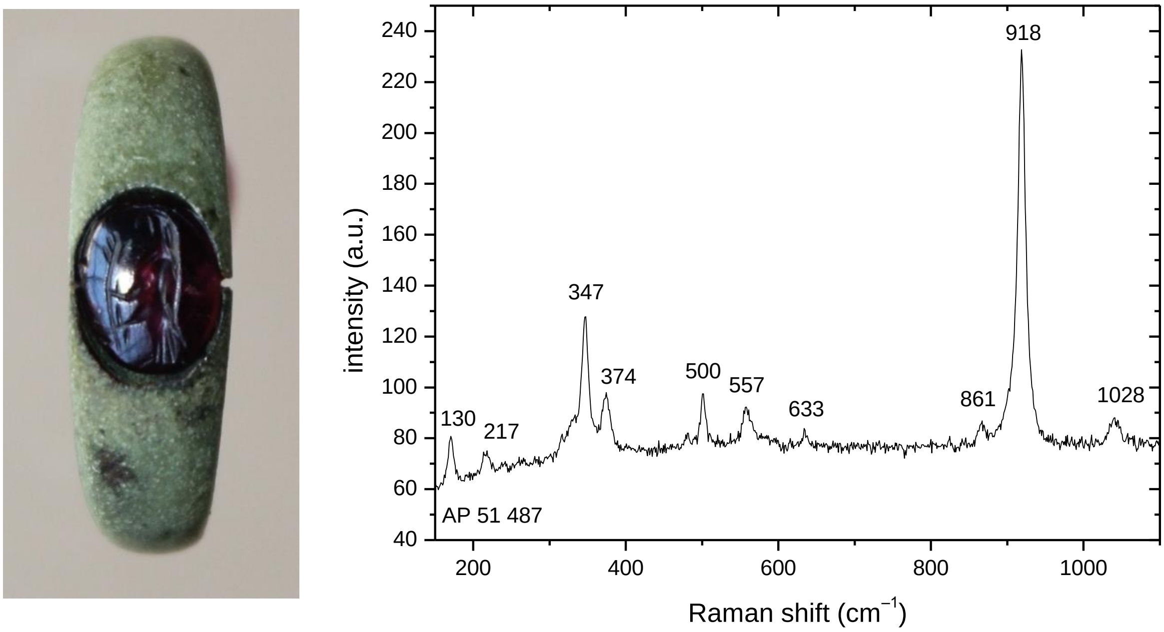

Fig. 5 *Bronze ring with a dark red gem (AP 51 487) with an image of a parrot. Vibrational bands in the Raman spectrum belong to almandine but also those belonging to pyrope and spessartine components were identified.*

3. Results and discussion

The Raman spectrum (Fig. 3) of gem AP 44 419 with a dominant vibrational band centred at 463 cm^{-1} and bands at 393, 353, 264, 207 and 128 cm^{-1} identifies α-quartz (trigonal SiO_2). The band at 502 cm^{-1} is the only visible band of moganite (monoclinic SiO_2) and corresponds to Si-O-Si vibration. The identified minerals are characterized by almost the same vibrational bands and the presence of quartz can be reliably established not only through the dominant band at 463 cm^{-1} but also by the band at 353 cm^{-1} [6]. Macroscopic appearance of the gems (red colour, hardness) corresponds to a microcrystalline variation of SiO_2 – chalcedony, more accurately carnelian. Carnelian belongs to fibrous varieties of quartz which do not create typical crystals but usually spherical, kidney- or stalactite-shaped formations. Sometimes they form a solid filling of the cracks and cavities in rocks. Gem AP 44 749 has similar macroscopic characteristics, corresponding to carnelian, and Raman spectrum (Fig. 3, bottom curve) of α-quartz and moganite. As with the previous gem, the Raman spectrum is affected by photoluminescence, which is likely to reflect the presence of ferrous compounds. The reddish-orange or brownish-orange colour is due to the traces of ferric oxide, hematite (Fe_2O_3). However, haematite was not observed in the Raman spectra of gems AP 44 419 and AP 44 749.

On the basis of the macroscopic characteristics of gem AP 17 434, particularly of its strikingly red colour, it was assumed that the gem was made of jasper. The gem is damaged at its edges and the fracture surfaces do not show the seashell fracture typical for the microcrystalline variety of quartz. Another type of raw material used to manufacture the gems was confirmed by Raman spectroscopy. The Raman spectrum does not correspond to quartz or to quartz-and-moganite association, different varieties of SiO_2, including jasper. The identified vibrational bands (Fig. 4) are centred at 228, 248, 294, 413, 466, 501, 614 and 1322 cm^{-1}, which excludes jasper quite unambiguously and confirms hematite (Fe_2O_3) [7, 8].

Gem AP 51 487 in the bronze ring has a strikingly dark red colour and is transparent. The colour is not typically carnelian, therefore this material can be immediately ruled out. As for the colour, minerals from the group of garnets come into consideration. Dark red garnets usually belong to the group of pyralspites, such as pyrope, almandine and spessartine, or to the ugrandite group, andradite. The obtained Raman spectrum was compared with the spectrum of almandine (rruff.info/almandine-R040076), pyrope (rruff.info/pyrope-R040159) and spessartine (rruff.info/spessartine-R050063), but also with spectra of almandine from Tyrol (Austria) and historical site Alabanda (Turkey) [9]. The identified vibrational bands centred at 347, 374, 500, 557, 633, 861, 918 and 1028 cm^{-1} correspond also to almandine, but also to spessartine and pyrope. Variability in the positions of the vibrational bands is due to the chemical composition of the garnet. These minerals are namely not ”chemically pure”. Chemical nature of the analyte corresponds best to almandine but also spessartine (Mn) and pyrope components (Mg) affect the Raman spectrum.

4. Conclusion

Three antique gems set in rings and one free antique gem were analyzed using non-destructive Raman spectroscopy with the aim to identify precisely the mineralogical composition of material. In gems AP 44 419 and AP 44 749 Raman spectroscopy identified the association of quartz and moganite, which is typical for microcrystalline varieties of SiO_2. Considering the colour, it is a variety of carnelian. The Raman spectrum of gem AP 17 343 corresponds to hematite. The spectrum of gem AP 51 487 corresponds to almandine but some vibrational bands also reflect the presence of pyrope and spessartine components. The origin of particular raw materials of the gems could not be identified on the basis of mineralogical composition. Therefore only those localities are named which, from the depositional or historical views, may have provided quality raw materials for the manufacture of the antique gems. The most important results of the work is identification of the material of gem AP 17 343. The Raman spectrum identified hematite, which corrects the description of this gem in the collection of the Slovak National Museum.

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