RAMAN SPECTROSCOPY OF GEMSTONES ON THE NECKLACES FROM ANCIENT GRAVES AT THE CASTLE OF DEVÍN

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1. Experimental material

The subjects of Raman and X-ray analyses were the beads from two necklaces found in ancient graves from the 11th and 12th centuries at the Castle of Devín. One of the necklaces (Fig. 1), consisting of 23 beads, was found in tomb 12/1980. Inside the grave, an incomplete skeleton of a woman was found, oriented in the west – east direction. The skull, shoulder blades and lower limbs were preserved in good condition. The grave contained a rich inventory: a silver ear-ring at the left side of the skull, a necklace between the shoulder blades and a ring on the right side at the height of the right hand. The other necklace, consisting of six stones (Fig. 2), was found in grave 145/1985 in which, similarly like in the first grave, a woman's skeleton was discovered. The stones were found below the mandible. All beads are drilled through axially. Results from systematic excavations performed between 1980 and 1987 were evaluated by Plachá and Divileková [1].

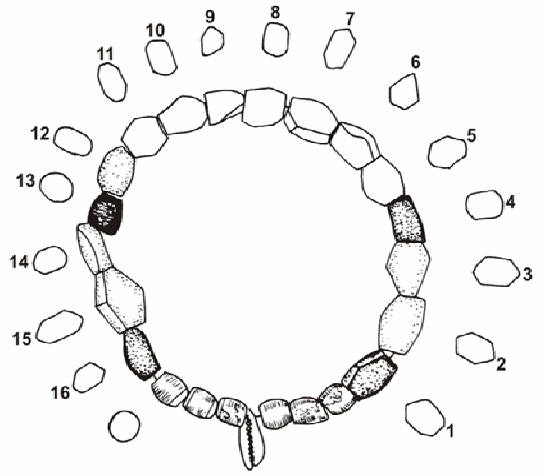

Fig. 1: *Necklace from grave* 12/1980*, registration number of the founding* 5241*, contains* 23 *stones:* 1 *shell of a cone snail Cypraea Moneta and* 22 *beads, out of which* 15 *are of fluorite,* 1 *of amber (stone No.* 13*) and* 6 *ball-shaped glass beads with a gold foil (non-numbered).*

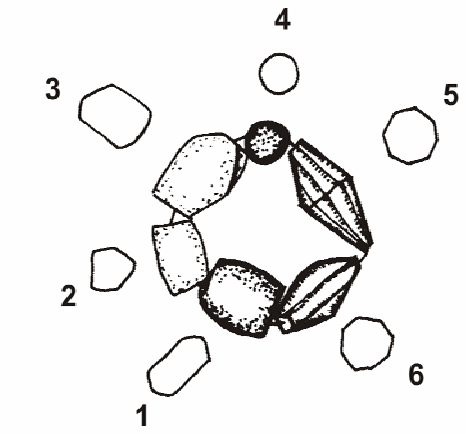

Fig. 2: *Necklace from grave* 145/1985*, registration number of the founding* 5521*, contains* 6 *stones, out of which stones* 1 *to* 3 *are of fluorite, and stones* 4 *to* 6 *are of carnelian.*

2. Experimental methods

Mineralogic identification of violet facetted gemstones was performed by X-ray diffraction and Raman spectroscopy. Raman spectroscopy has been chosen for studying these findings because it is a simple and non-destructive analytical method, it does not require any special sample preparation or invasive sample removal. The beads were analyzed without any pre-treatment or touching. Raman spectra of the beads were taken in a Dilor-Jobin Yvon-Spex apparatus, type LabRam with a confocal microscope Olympus BX-40, He-Ne laser excitation source (wavelength 632.8 nm), grid monochromator (650 nm to 1.05 μm) and a CCD detector with a resolving power of 1.3 cm^{-1}. The diameter of the laser beam was approx. 2 μm, the time of spectrum collection varied from 20 to 200 seconds in dependence on the intensities of Raman scattering and fluorescence. The recorded spectra were compared with the data from the integrated database of Raman spectra, X-ray diffraction and chemistry for minerals. In particular, fluorite (CaF_2) was compared with [2] and quartz (SiO_2) with [3].

So as to avoid destruction of the gemstones, no powder samples could be prepared for X-ray diffraction analysis. Therefore the beads were analyzed by X-ray diffraction using the Göbel mirror, which allows to analyze samples with irregular surfaces. The X-ray diffraction analyses were performed using a Bruker D8 ADVANCE X-ray diffractometer at the Department of Mineralogy and Petrology, Faculty of Natural Sciences, Comenius University, using Cu Kα radiation with a Ni filter, at acceleration voltage 40 kV and current 40 mA and a scan speed of 0.1° Θ per second.

The second type of stones, the reddish orange stones Nos. 4 to 6 of the necklace from grave 145/1985, were analyzed only by Raman spectroscopy.

3. Results and discussion

The material of violet beads was identified by both of the methods as fluorite. X-ray patterns at various orientations of bead No. 12 of the necklace from grave 12/1980 exhibited the presence of diffraction maxima revealing interplanar spacings d_{111}=0.312 nm and d_{220}=0.193 nm, which corresponds to fluorite.

Selected Raman spectra of the violet beads are shown in Fig. 3. The spectra were evaluated using the database of Raman spectra and published data [4]. The fluorescence background is a natural manifestation of the optical properties of the mineral – fluorite. The reddish orange beads were identified by Raman spectroscopy as quartz – carnelian, which is in accordance with our visual expectation that all reddish orange beads contain the red fibrous variety of quartz – chalcedony. In bead No. 4 of the necklace from grave 145/1985 we identified also another mineral – moganite. Raman spectra of carnelian (α-quartz) with inclusions of moganite are shown in Fig. 4. The experimentally achieved Raman spectra are in accordance with published data [5].

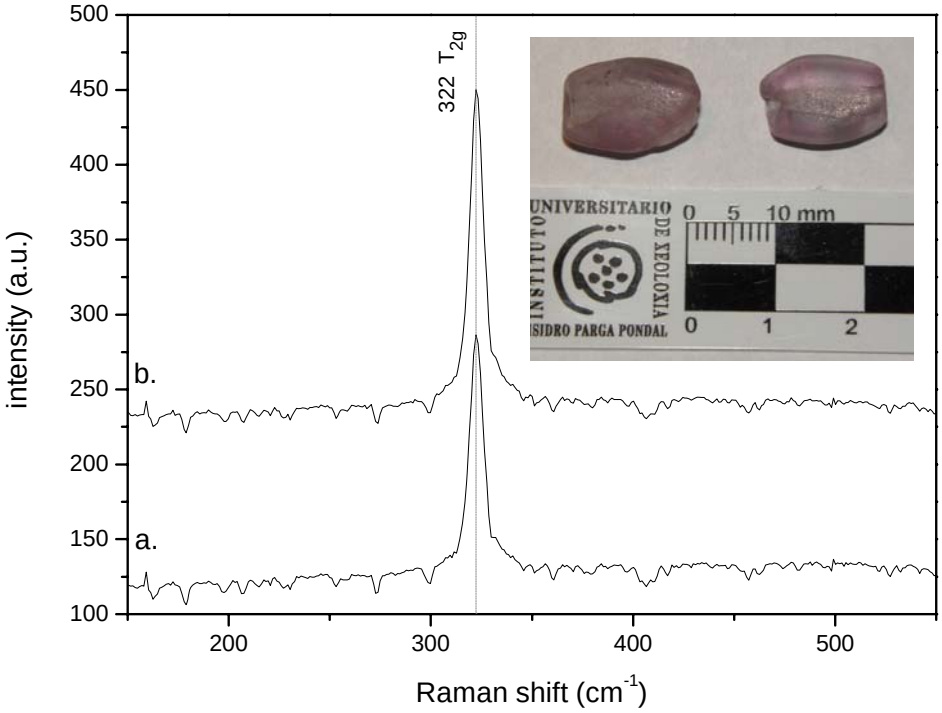

Fig. 3: *Raman spectra* (a) *and* (b) *corresponding to fluorite, recorded at two different places on bead* No. 3 (*the left bead in the inset*) *of the necklace from grave* 145/1985. *The Raman band at* 322 cm^{-1} *is a triple degenerated vibration of* F^- *anion sublattice with respect to stationary cations. This means that three vibrations have the same frequency with respect to standing* Ca^{2+} *cations and cannot be resolved* [4].

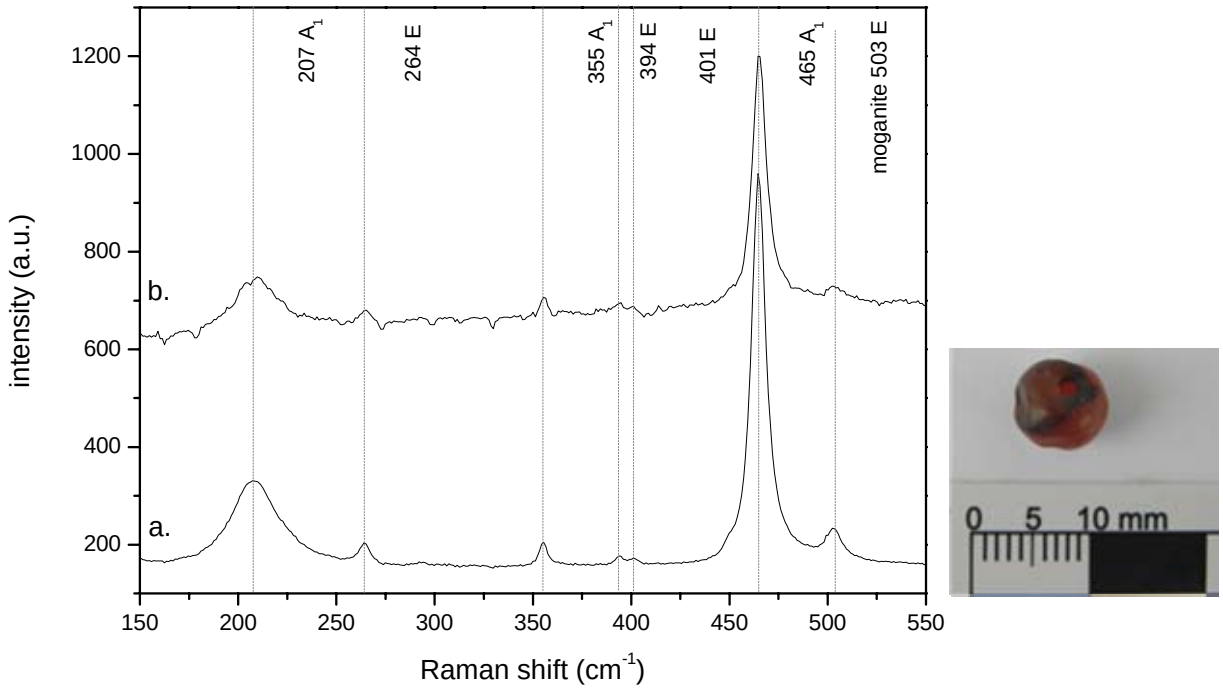

Fig. 4: *Raman spectra of bead* No. 4 *of the necklace from grave* 145/1985*, recorded from an area with inclusion of unknown brown mineral* (a) *and from the typical sample surface* (b). *The better signal-to-noise ratio in spectrum* (a) *is probably due to stronger absorption of incident radiation. Irreducible representations are denoted by Mulliken symbols. For band assignment see* [5]. *The major phase is identical with* α*-quartz* (*trigonal* SiO_2) – *carnelian, and the band at* 503 cm^{-1} *is the visible band of moganite* (*monoclinic* SiO_2) *and corresponds to* Si-O-Si *vibration.*

4. Conclusion

X-ray diffraction and Raman spectroscopy were used to analyze the beads from the the 11^{th} and 12^{th} centuries from the archaeological research of the cemetery at the Castle of Devín.

The violet beads that were taken from the necklaces were believed to be amethyst [6]. Our more precise investigations reveal that the composition is different from what used to be thought. The beads have a facetted shape with rounded edges. Their colour varies from dark violet to light violet. Some of the beads are also colourless or have a very weak violet or green tint. The light violet beads are transparent and some of them are zoned (the so-called growth zones). These beads show dull lustre. Some of the damaged beads are characterized by the presence of perfect cleavage. The growth zones, perfect cleavage and dull lustre of the beads do not correspond to the violet variety of quartz – amethyst. Based on the macroscopic features and the data provided by X-ray diffraction and Raman spectroscopy it has been found unambiguously that the violet beads had been made of fluorite.

Raman spectroscopy confirmed uniquely that the reddish orange beads had been made of quartz. The material was identified as carnelian, a fibrous modification of quartz related to chalcedony. Some of the beads also show the typical agate texture (altering lighter and darker stripes). In bead No. 4 from grave 145/1985, in addition to α-quartz (trigonal SiO_2, carnelian) also moganite (monoclinic SiO_2) was detected. This intergrowth of the mentioned polymorphs of SiO_2 is typical for agate structures [7].

Both types of beads (fluorite and carnelian) represent imports, since the raw materials used for their production do not occur in sufficient quality in Slovakia. Fluorite can possibly come from the silver deposits in the Czech Republic or from Germany. The provenance of carnelian is much more unclear as it can come from various deposits or localities scattered through Western and Northern Europe, Northern Africa or Middle East.

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