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The origin of emeralds embedded in archaeological artefacts in Slovenia

Izvor smaragdov v arheoloških predmetih na Slovenskem

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Abstract

Roman gold jewellery, which was excavated in Ptuj (Poetovio) and consists of a necklace, earrings and a bracelet with embedded emeralds, is part of the Slovenian archaeological artefacts collections. Crystallographic characteristics, inclusions, luminous phenomena and geological characteristics were determined in order to establish the origin of the emeralds. Chemical composition of the emeralds was determined non-destructively using the methods of proton-induced X-rays and gamma rays (PIXE/PIGE). The results were compared with reference emeralds from Habachtal in Austria and with green beryls from the Ural Mts. Literature data for emeralds from Egypt and modern-day Afghanistan area were used to interpret the results. Specifically, these sites were known for emeralds being mined for jewellery in Roman times. It was assumed that emeralds from archaeological artefacts originated from Habachtal in Austria, given that this site was the nearest to the place where found. But the emeralds from the necklace and earrings in fact came from Egyptian deposits. The origin of emeralds from the bracelet could not have been determined absolutely reliably due to the lack of comparative materials; they may originate from a site in modern-day Afghanistan or from Egypt, but certainly not from the same site as the previously mentioned emeralds in the necklace and earrings.

Izvleček

V zbirkah arheoloških predmetov na Slovenskem hranimo zlat rimski nakit, ki je bil najden na Ptuj (Poetovio); verižico, uhana in zapestnico, ki imajo okovane smaragde. Da bi določili njihov izvor, smo poskušali ugotoviti kristalografske značilnosti ter določiti vključke, luminiscenčne pojave in geokemične značilnosti smaragdov. Kemijsko sestavo smaragdov smo izmerili nedestruktivno z metodama protonsko vzbujenih rentgenskih žarkov in žarkov gama (PIXE/PIGE). Dobljene rezultate smo primerjali z referenčnimi smaragdi iz Habachtala v Avstriji in zeleno obarvanim berilom iz Urala, medtem ko smo za interpretacijo rezultatov uporabili še literaturne podatke za smaragde iz Egipta in iz območja današnjega Afganistana. Ta nahajališča so bila namreč v času izdelave rimskega nakita znana po izkopavanju smaragdov. Domnevali smo, da so smaragdi iz arheoloških predmetov iz Habachtala v Avstriji, saj je bilo to nahajališče najbližje mestu najdbe, nazadnje pa ugotovili, da so smaragdi iz verižice in uhanov iz nahajališč v Egiptu. Kar zadeva smaragde iz zapestnice, zaradi pomanjkanja primerjalnega gradiva nismo mogli povsem zanesljivo določiti njihovega izvora; lahko so iz nahajališča v današnjem Afganistanu ali pa iz Egipta, vendar ne z istega nahajališča kot prej omenjeni smaragdi iz verižice in uhanov.

Introduction – emeralds and people through time

The human race has been associated with emeralds for more than 4,000 years. As early as in the Antiquity, they were the symbol of the magic wisdom of God Hermes. The Egyptian Queen Cleopatra was a great lover of jewels, particularly emeralds. Her legendary emerald mines remained

a mystery for ages, and it was only about a century ago that they were rediscovered in the vicinity of the Red Sea (FINLAY, 2006).

In the Ancient Greece, Pliny often wondered whether anything in this world could be at all greener than a genuine emerald. The Greeks believed that jewels had a healing power and brought luck at the same time. Nero, the dissolute

arsonists of Ancient Rome, simply loved watching gladiator fights through emerald sunglasses (HENN, 1990).

The Holy Grail, too, was made of emerald which, however, has remained a mystery till this very day. Through history, people have been attributing various properties to the emerald, such as preventing carnality, invigorating memory, and helping us, when put on the tongue, during the summoning of spirits and conversation with them. In the end it was the Blessed Hildegard from Bingen who claimed that the emerald grows in the morning, when green meadows are the freshest, which evaluates emerald green colour (JERŠEK & DOBNIKAR, 2005).

In Islamic tradition, the Muslims, too, highly esteemed emeralds and their green colour. Emerald green was allegedly the cloak and turban of the Prophet Muhammad. Green colour thus became also the colour of Islam, as can be noted on their national flags. The colour symbolises the posthumous paradise promised to people by Muhammad. Outwardly, the Muslim rulers showed, by wearing emeralds, not only that they were immensely rich but that they were protected by God Allah himself (FINLAY, 2006).

The Celts and Romans mined these gemstones at the historic site of Habachtal in the Hohe Tauern in Austria at an altitude between 2,000 and 2,200 m (HENN, 1990). Historically significant emerald sites are also located in Egypt and Afghanistan (HENN, 1990), as well as in the Ural Mts according to some data (CALLIGARO et al., 2000). Through discovery of increasingly new sites, emeralds became more and more accessible, and after their discovery in Columbia in 1545 AD, they became one of the most precious gems (BAUER, 1968). As natural emeralds are still relatively scarce, they are produced in laboratories as well (HENN, 1990).

In archaeological artefacts from the Roman period, particularly in gold jewellery, a necklace, earrings and a bracelet with embedded emeralds have been found in sites in Ptuj Slovenia (TUŠEK, 1985). The origin of these emeralds, however, has not been researched in detail as yet. Owing to the relative proximity of the emerald site at Habachtal in Austria it seemed most likely that they originated from this very upland site. This is why we studied crystallographic, physical and geochemical characteristics of emeralds embedded in archaeological artefacts in Slovenia and compared them with reference emeralds from Habachtal. A green coloured beryl from the Ural Mts was also part of our analyses, whereas reference emeralds from Egypt and Afghanistan were not available, forcing us to rely on literature sources in the interpretation of results (JENNINGS et al., 1993; CALLIGARO et al., 2000).

Historically significant emerald sites

The largest site of emerald crystals in Europe is located in Austria at Habachtal in the area of Hohe Tauern National Park. The first mention of emerald finds reaches back to the Celtic-Roman times (HENN, 1990). Emerald mining was resumed as late as in the 18th century. Under

the Legbachscharte Pass, several pits were dug. Through centuries, their owners changed and, together with them, the rules as to who and under what conditions may mine these gemstones. Entrance to the pits is prohibited mainly for safety reasons, while searchers are allowed to look for emeralds on the dump in front of the mine. Beryl crystals are located in black and green biotite-actinolite slate and, less often, in magnesite-actinolite slate (REČNIK et al., 1994).

Major rocks in the wider area of Habachtal are serpentinites. In the narrower area, where emeralds occur, a series of serpentinites and magnesite slates runs parallel to the tectonic border, which separates central gneisses from the formation composed predominantly of garnet schists and amphibole gneisses. Minerals in serpentinites are enriched with chrome, while minerals in schists and amphibolites are the carriers of beryllium and aluminium. At the contact between serpentinites and schists, magnesite, actinolite, chlorite and biotite were extracted as reaction products. About some 65 million years ago, at the beginning of alpidic regional metamorphism, chrome enriched beryl began to extract at their contacts (REČNIK et al., 1994).

All Habachtal emeralds crystallize in the form of hexagonal prism that ends with pinacoid. Their cleavage takes place perpendicularly to the longitudinal axis *c*. Emerald crystals are dark green, more often pale green and of various green-white tints. Totally transparent crystals are very rare indeed. Quite often, they are cloudy to partially transparent and untransparent. White and light coloured crystals are usually larger and more transparent than green crystals (BAUER, 1968). Crystals are often cracked on basal planes owing to the tectonic events taking place during their origin. Emeralds contain inclusions of mica, tourmaline, titanite, epidote, apatite, and rutile. Emerald excavation in the Habachtal area is very poor in comparison with other sites across the world (HENN, 1990).

Emerald deposits in Egypt are considered historic, as precious stones were dug in this area more than 1,650 years BC ago. Egypt allegedly represented one of the three sources of emerald sites for Europe and Africa in the Greek-Roman times. Well known for those times were the following sites with chronological order of the carried out excavations: Gimal Valley A and B (4th-5th centuries), Nuqrus Valley and Sikait Valley (6th-9th centuries) and Zubara (12th-16th centuries) (SHAW et al., 1999).

Today, emerald sites are known from the island of Zabargad in the Red Sea and a place some 100 km south of modern-day Cairo in the Sikait-Zubara Valley. Through the excavations carried out in the 19th century, the British establish on the basis of discovered tools that emeralds had been dug in this area more than 1,650 years BC ago. For those particular times, Egypt was an important source of emeralds that were highly appreciated both in India and Europe (FINLAY, 2006).

The emeralds from Egypt crystallized in mica slate at the contact with granite. They are pale green, full of inclusions and often very small (FINLAY, 2006). Most important among inclusions are the fluid inclusions, while growth tube are uniquely characteristic (JENNINGS et al., 1993).

Once upon a time, emeralds were also dug in the area of the Panjshir Valley on the edge of Hindukush Mts in Afghanistan. In the Antiquity, this area was called Bactrian, as reported by Theophrastus, and was known already from the time of Alexander the Great between the 3rd and 1st centuries BC (CALLIGARO et al., 2000). Digging was resumed at the beginning of 1970 (JENNINGS et al., 1993).

Some people believe that the sites in the Ural Mts, too, are a possible source of emeralds in the times of the Romans (CALLIGARO et al., 2000), while the great majority of data on emeralds originate from the period after 1830 (BAUER, 1968), when they were found near the Tokowaya River. Those from historically significant sites, on the other hand, were supposed to be dug from 1500 BC onwards, which means that emerald mines existed as early as in the Antiquity. Pliny the Elder, too, writes about Ural emeralds from Scythia site in his work *Historia Naturalis* (CALLIGARO et al., 2000). The Ural emeralds contain inclusions of brownish to almost colourless actinolite crystals, which are independent or occur in tiny clusters, as well as biotite and three-phase inclusions, while tourmaline is a rare inclusion (HENN, 1990).

Crystallographic characteristics of emeralds

One of the emeralds' characteristic feature is their prismatic habitus, which is stipulated by hexagonal prisms of the first order $a(100)$. Separate crystals end with the basic pinacoid $c(001)$, while their morphological diversity is created by additional crystal surfaces, among which hexagonal bipyramid of the first order $d(101)$, hexagonal bipyramid of the first order $e(111)$, dihexagonal prism $f(210)$ and hexagonal prism of the second order $g(110)$ are found. Separate crystal surfaces can be more or less pronounced on crystal surfaces, which means that totally short prismatic crystals can also be found, or the peaks of crystals are fairly rounded at first sight due to the mass of crystal surfaces (JERŠEK & VIDRIH, 2009).

Crystallogenic trend reveals the sequence of crystallization from the very short prismatic to short prismatic, medium prismatic and long prismatic crystals, depending on the presence of different alkaline elements (KOSTOV & KOSTOV, 1999).

Inclusions in emeralds

Owing to the manner of crystallization, emeralds contain a very high number of inclusions, which is the reason why experts decided to name them emerald garden. Frequent inclusions in emeralds are fluid inclusions, whereas solid inclusions are often chromite, spinel, picotite,

actinolite, biotite, pyrite, calcite and dolomite (GÜBELIN & KOIVULA, 1986). Inclusions in emeralds are characteristic due to the location and also very important for their identification. Characteristic inclusions in emeralds from Habachtal are biotite, talk, actinolite and tremolite (HENN, 1990), in emeralds from Ural crystals we can find phlogopite (HENN, 1990) and for emeralds and green beryl's from Egypt are typical growth tubes (JENNINGS et al., 1993). In gemological practice, the emerald is the only gemstone in which its quality regarding the purity and thus the presence and type of inclusions is evaluated by naked eye and not with a 10x magnifying loupe.

Green coloured beryl as a gemstone

Emeralds are gem quality of a beryl with a green colour caused by the presence of chromium. There are two other green beryl's used as a gem; green beryl and vanadium beryl. Green beryl is green because of a presence of iron and vanadium beryl because of a presence of vanadium.

Material

In Slovenia, only a few artefacts with embedded emeralds have been found by archaeologists (Table 1). A well known is the gold jewellery of a lady from Roman Poetovio with light emerald crystals set in it. It was found in 1982 in Mežanova ulica in Ptuj – archaeological site Hajdina (EŠD 581) – stored in a brick chest, which contained a skeleton grave with a double burial of mother and child. The gold necklace (Fig. 1) (Inv. No. A 164) is composed of 31 golden parts, three emerald crystals (V-1, V-2, V-3) and clip. The necklace is kept by the Institute for the Protection of Cultural Heritage of Slovenia, Preventive Archaeology Centre, Regional Department Ptuj (TUŠEK, 1985).

Two gold earrings (Fig. 2) (Inv. Nos. 80CP001/002 and 80CP001/003) were found in 1980 within the area of the Secondary School Centre on Volkmerjeva cesta in Ptuj. They were located in grave No. 1, where a female skeleton lay. Both earrings have an emerald crystal set in them (U-1, U-2) and are kept by the Archaeological Department of the Regional Museum Ptuj-Ormož (TUŠEK, 1985).

The third archaeological artefact is a bracelet in two fragments (Fig. 3). It was found in 2009 in the area of Ljudski vrt Primary School, grave No. 154 (Inv. No. PN 627). It contains three emerald crystals (Z-1, Z-2, Z-3) and is kept by the Archaeological Department of the Regional Museum Ptuj-Ormož.

As comparative material, ten emerald crystals from Habachtal in Austria (Fig. 4) (Inv. Nos. 623-a, 623-b, 623-c, 627, 628, 1475, 1478, 1488, M-1, M-2) and green beryl from the Ural Mts (Fig. 5) (Inv. No. 1470) were chosen; all of them, with the exception of samples M1 and M2 (private collection), are from the renowned Zois Mineral Collection (Table 1) (ČINČ JUHANT & JERŠEK, 2005).



Fig. 1. The golden necklace (A 164) with three emeralds (V1-3). Collection of Institute for the Protection of Cultural Heritage of Slovenia, Preventive Archaeology Centre, Regional Department Ptuj Photo: Miha Jeršek

Sl. 1. Zlata verižica (A 164) s tremi smaragdi (V1-3). Zbirka Zavoda za varstvo kulturne dediščine Slovenije, Center za preventivno arheologijo, Regionalni oddelek Ptuj Foto: Miha Jeršek



Fig. 2. Gold earrings (80CP001/002, 80CP001/003) with emeralds U2,3), collection of Regional Museum Ptuj-Ormož. Photo: Miha Jeršek

Sl. 2. Zlata uhana (80CP001/002, 80CP001/003) s smaragdi U2,3), zbirka Pokrajinskega muzeja Ptuj-Ormož. Foto: Miha Jeršek



Fig. 3. The golden bracelet in two fragments (PN 627) with three emeralds (Z1-3), collection of Regional Museum Ptuj-Ormož. Photo: Miha Jeršek

Sl. 3. Zlata zapestnica v dveh delih (PN 627) s tremi smaragdi (Z1-3), zbirka Pokrajinskega muzeja Ptuj-Ormož. Foto: Miha Jeršek



Fig. 4. Emerald from Habachtal, collection of Slovenian Museum of Natural History (Inv. No. 623, c). Photo: Miha Jeršek

Sl. 4. Habachtalski smaragd, zbirka Prirodoslovnega muzeja Slovenije (inv. št. 623, c). Foto: Miha Jeršek



Fig. 5. Green coloured beryl from Ural, collection of Slovenian Museum of Natural History (Inv. No. 1470). Photo: Miha Jeršek

Sl. 5. Zeleno obarvani beril iz Urala, zbirka Prirodoslovnega muzeja Slovenije (inv. št. 1470). Foto: Miha Jeršek

Methods

Macroscopic description

The emeralds were initially observed with naked eye and a 10x magnifying loupe. Crystallographic characteristics, inclusions and colour were determined. With the aid of a calliper, the emeralds' size was measured.

Gemmological microscope

The emeralds were studied with gemmological microscope (model KSW 63/11434.3), which is in fact a stereomicroscope with 10x to 80x magnification.

UV lamp

With standard ultraviolet lamp, the luminous phenomena in the samples (fluorescence and phosphorescence) were studied with shortwave and longwave UV light.

Table 1. Samples of emeralds and green beryls in this study

Tabela 1. Vzorci smaragdov in zelenih berilov v tej raziskavi

Object / Predmet	Inv. Nos. / Inv. št.	Collection / Zbirka	Mark / Oznaka
Golden necklace	A 164	Institute for the Protection of Cultural Heritage of Slovenia, Preventive Archaeology Centre, Regional Department Ptuj	V1, V2, V3
Golden earrings	80CP001/002 80CP001/003	Regional Museum Ptuj-Ormož	U1, U2
Golden bracelet	PN 627	Regional Museum Ptuj-Ormož	Z1, Z2, Z3
Emerald, Habachtal	623-a, 623-b, 623-c, 627, 628, 1475, 1478, 1488	Slovenian Museum of Natural History	623-a, 623-b, 623-c, 627, 628, 1475, 1478, 1488
Emerald, Habachtal	M-1, M-2	Private collection	M-1, M-2
Green beryl, Ural	1470	Slovenian Museum of Natural History	1470

PIXE and PIGE methods

The PIXE and PIGE methods are based on the irradiation of samples with high energy ions, which induce the characteristic X-rays and gamma rays in the matter. Protons with the energy of a few MeV penetrate up to 100 μm deep into the matter, so that the measurements show the condition not only on the surface but a few 10 μm deep as well, for it has to be considered that the protons slow down whilst passing through the matter, whereas the reaction cross sections are quickly reduced with energy. In a sample, the created X-rays are also absorbed, while for the much harder gamma rays the absorption effects are negligible. The measuring procedure is non-destructive, given that the radiation with protons does not cause visible traces, which means that the methods are suitable for the analysis of valuable objects, including precious stones.

Measurements with the PIXE – PIGE method were carried out at the Tandetron accelerator of the Jožef Stefan Institute in Ljubljana. Measuring was executed with the proton beam in the air, as this enables a simple setting of sample and selection of the place for irradiation. The protons' nominal energy was 2.5 MeV, and while passing through a 2 μm thick window made of tantalum foil and 1 cm wide air gap this energy was reduced to approximately 2.2 MeV. The beam profile was Gaussian, with 0.8 mm full-width at half maximum. To the X-ray detector, which was placed under the angle of 45° with regard to the proton beam, the induced X-rays also travelled through a 5.7 cm wide air gap. Due to the absorption in the air gap, we were able to detect with X-rays only the elements heavier than silicon. At each selected point, two measurements were made. With the first one we measured the low energy spectrum of elements between silicon and iron, while during the second measurement the proton current was increased to a few nA; at the same time, we measured the high energy X-ray spectrum of elements heavier than iron, and gamma spectra. For this purpose, the X-ray detector was equipped with additional absorber made of 0.1 mm thick aluminium foil. From the gamma spectra, the elemental concentrations of Na, Mg and Al were determined. In the spectra, lines of lithium and fluorine also appeared,

but they were not taken into account in the quantification of results, as no suitable standards were at hand. The concentrations of beryllium, too, were considered only mathematically.

The uncertainties in concentrations of the major elements are of the order $\pm 5\%$, while in elements in concentrations below 0.1% they can be greater, i.e. 10–15 %. Measuring uncertainties are greater also during measurements made on natural beryls, which have tiny mineral impurities on their surface, usually flakes of mica, owing to which higher concentrations of potassium and aluminium were determined.

Results

Macroscopic description

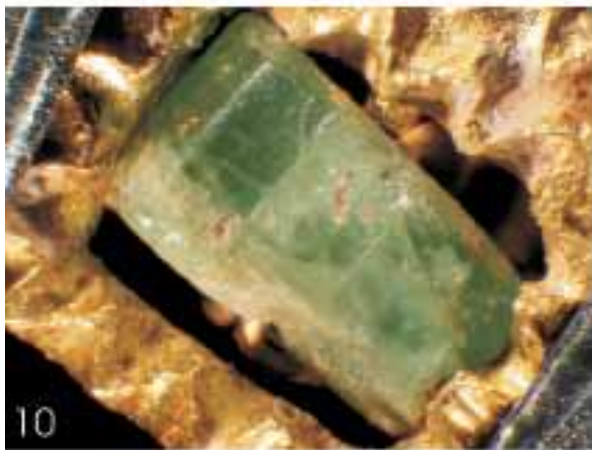
Emerald crystals from Habachtal are mostly translucent and not transparent. Their crystal surfaces seem like being etched and are seldom smooth. This “etchy” appearance is the result of their growth in parent rock or of partial dissolution. The colour of emeralds is not uniform. Some are colourless (Inv. No. 628), others of different green shades. They have several mica inclusions. General ratio between the crystals' width and length ranges from 1:3 to 1:6.

Table 2. The size of emeralds in archaeological artefacts (V-1, V-2, V-3 – emeralds from the necklace, U-2 and U-3 emeralds from the earrings, and Z-1, Z-2 and Z-3 the emeralds from the bracelet).

Tabela 2. Velikost smaragdov v arheoloških predmetih (V-1, V-2, V-3 – smaragdi iz verižice, U-2 in U-3 smaragda iz uhanov ter Z-1, Z-2 in Z-3 smaragdi v zapetnici).

Sample	Dimensions (mm)	Sample	Dimensions (mm)
V-1	V= 4.2; Š= 3.65 V= 4.2; Š= 4 V= 4.2; Š= 4.45	Z-1	V= 3.1; Š= 2.85 V= 3.1; Š= 2.9 V= 3.1 . Š= 3
V-2	V= 4.4; Š= 4.15 V= 4.4; Š= 4.15 V= 4.4; Š= 4.55	Z-2	V= 4.95; Š= 2.6 V= 4.95; Š= 2.65 V= 4.95; Š= 2.95
V-3	V= 4.2; Š= 4 V= 4.2; Š= 4.45 V= 4.2; Š= 5.7	Z-3	V= 0.9; Š= 2.35 V= 0.9; Š= 2.4 V= 0.9; Š= 2.55
U-2	V= 3.75; Š= 2.55	U-3	V= 3; Š= 4.65

PLATE 1 – TABLA 1



The emeralds embedded in archaeological artefacts apparently differ from each other. Those in the bracelet are apparently opaque and of different colour shade (bluish green), with a fairly large amount of mica. The emeralds in the necklace and earrings are translucent to transparent, of green colour with numerous fluid inclusions and relatively little amount of mica (Pl.1, figs. 6 to 13).

The size of emeralds in archaeological artefacts was ascertained by measuring the distances between two opposite surfaces of the hexagonal prism (\bar{S}) and the height of emerald between two pinacoids (V). Results of the measurements are given in Table 2.

Crystallographic characteristics of the emeralds

The crystals of Habachtal emeralds have a characteristic prismatic habitus, which is stipulated by the surfaces of the hexagonal prism of the first order $a(100)$, and end with pinacoid c surface (001) (Fig. 14). The green beryl from the Ural Mts also has a distinct prismatic habitus with developed surfaces of hexagonal prism of the first order $a(100)$ and pinacoid $c(001)$. The three crystal surfaces of the first order prism are sanded and polished.

The emeralds from the archaeological artefacts have, apart from the hexagonal prism of the first order $a(100)$ and pinacoid $c(001)$, other crystal surfaces developed as well. We determined the hexagonal bipyramid of the first order $d(101)$, hexagonal bipyramid of the second order $e(111)$

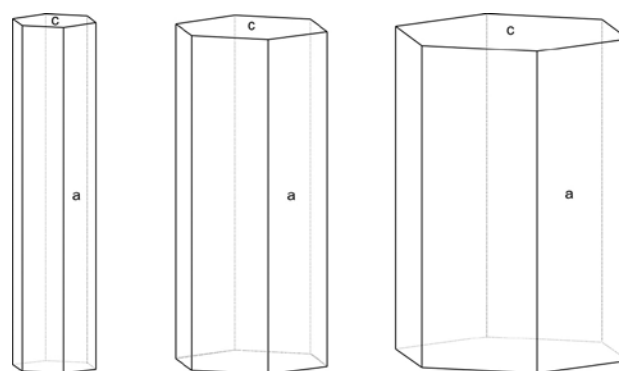


Fig. 14. Crystallographic characteristics of the emeralds from Habachtal. Only hexagonal prisms of the first order $a(100)$ and pinacoid $c(001)$ crystal surfaces are developed. Drawing: Miha Jeršek

Sl. 14. Kristalografske značilnosti smaragdov iz Habachtala. Razvite so samo kristalne ploskve heksagonalne prizme I. reda $a(100)$ in pinakoid $c(001)$. Risba: Miha Jeršek

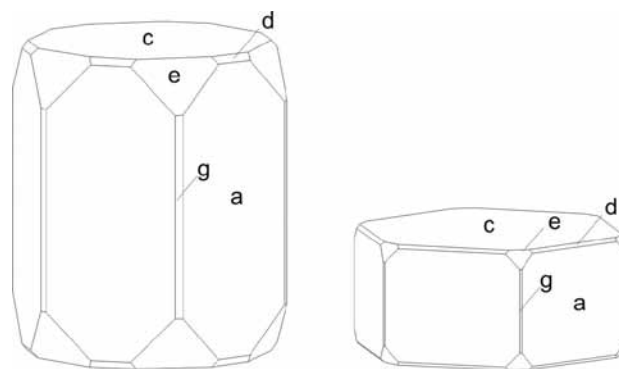


Fig. 15. Crystallographic characteristics of the emeralds from the earrings. In addition to hexagonal prisms of the first order $a(100)$ and pinacoid $c(001)$, emerald crystals have hexagonal bipyramid of the first order $d(101)$, hexagonal bipyramid of the second order $e(111)$ and hexagonal prism of the second order $g(110)$. Drawing: Miha Jeršek.

Sl. 15. Kristalografske značilnosti smaragdov v uhanih (U-2, U-3). Kristali smaragda imajo poleg heksagonalne prizme I. reda $a(100)$ in pinakoida $c(001)$ razvite še heksagonalno bipiramido I. reda $d(101)$, heksagonalno bipiramido II. reda $e(111)$ in heksagonalno prizmo II. reda $g(110)$. Risba: Miha Jeršek

PLATE 1 – TABLA 1

- | | |
|----|---|
| 6 | Emerald from the necklace (V-1)
Smaragd v verižici (V-1) |
| 7 | Emerald from the necklace (V-2)
Smaragd v verižici (V-2) |
| 8 | Emerald from the necklace (V-3)
Smaragd v verižici (V-3) |
| 9 | Emerald from the earring (U-2)
Smaragd v uhanu (U-2) |
| 10 | Emerald from the earring (U-3)
Smaragd v uhanu (U-3) |
| 11 | Emerald from the bracelet (Z-1)
Smaragd v zapestnici (Z-1) |
| 12 | Emerald from the bracelet (Z-2)
Smaragd v zapestnici (Z-2) |
| 13 | Emerald from the bracelet (Z-3)
Smaragd v zapestnici (Z-3) |

Photos (fotografije): Miha Jeršek

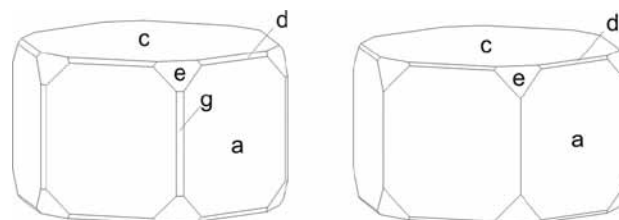


Fig. 16. Crystallographic characteristics of the emeralds from the archaeological artefacts – the necklace (V1-3). In addition to the hexagonal prism of the first order $a(100)$ and pinacoid $c(001)$, the emerald crystals have hexagonal bipyramid of the first order $d(101)$, hexagonal bipyramid of the second order $e(111)$ and hexagonal prism of the second order $g(110)$ developed as well. Drawing: Miha Jeršek

Sl. 16. Kristalografske značilnosti smaragdov v arheoloških predmetih – verižica (V1-3). Kristali smaragda imajo poleg heksagonalne prizme I. reda $a(100)$ in pinakoida $c(001)$ razvite še heksagonalno bipiramido I. reda $d(101)$, heksagonalno bipiramido II. reda $e(111)$ in heksagonalno prizmo II. reda $g(110)$. Risba: Miha Jeršek

and the hexagonal prism of the second order $g(110)$ (Figs. 15 and 16). The crystal (V-1) on the necklace has no surfaces of the hexagonal prism of the second order $g(110)$, but these are present in the other (V-2) crystal in the necklace. Although the crystals



Fig. 17. Detail from the bracelet's emerald shows that emeralds from this jewellery have, in addition to the hexagonal prism of the first order $a(100)$ and pinacoid $c(001)$, have other crystal surfaces developed as well, but owing to their unclear position or poor condition the surfaces could not have been determined in a greater detail. Photo: Miha Jeršek

Sl. 17. Detajl smaragda iz zapestnice nam razkriva, da imajo smaragdi v tem nakitu poleg heksagonalne prizme I. reda $a(100)$ in pinakoida $c(001)$ razvite še nekatere druge dodatne kristalne ploskve, ki pa jih zaradi nejasne lege oziroma slabše ohranjenosti nismo mogli natančneje določiti. Foto: Miha Jeršek

in the bracelet (Z1-3) are not so well preserved, it can still be noted that that crystal has similar crystallographic characteristics as the emeralds in the necklace (V1-3) and in the earrings (U-2, U-3). The emeralds in the bracelet are partially preserved as natural crystals, but are partly sanded, given that the surfaces that supposedly belong to the hexagonal prism are explicitly unparallel between each other. In some places, we furthermore determined additional crystal surfaces of the hexagonal bipyramid (Fig. 17).

On the basis of the crystallographic characteristics we can conclude that the crystals of the Habachtal emeralds and of the Ural beryl are characteristically prismatic and that they developed, apart from pinacoid surface, only surfaces of the hexagonal prism, while the emeralds from the archaeological artefacts have other crystal surfaces developed as well. Apart from it, the Habachtal emeralds are medium to long prismatic, whereas the crystals of the emeralds from the archaeological artefacts are short to medium prismatic and, in general, more barrel-shaped, with several developed types of crystal surfaces. This leads us to the fact that the emeralds under consideration were formed under different conditions (Kostov & Kostov, 1999), which could indicate that they originate from different sites.

Luminescent phenomena

While studying samples with UV lamp, i.e. with short- and long-wave UV light, the tested samples did neither fluoresce nor phosphoresce, which means that chromium is not the only or most significant colouring ion.

Inclusions

The Habachtal emeralds are not translucent to transparent and contain numerous fluid and mica inclusions both in crystals themselves and partly on the surface of emerald crystals. The Ural green beryl has, similarly, numerous fluid inclusions and

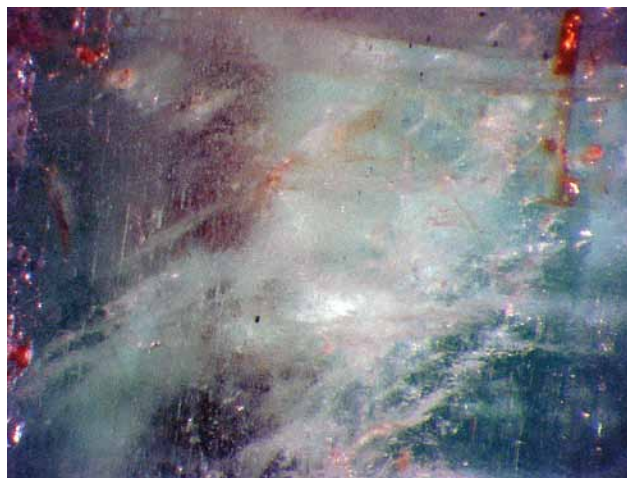


Fig. 18. Fluid inclusions in sample V-3, 40 x magnification. This type of inclusions were found in all emerald samples except in the emeralds from the bracelet, where inclusions could not be defined due to the emeralds' opacity. Photo: Miha Jeršek

Sl. 18. Tekočinski vključki v vzorcu V-3, 40-kratna povečava. Tovrstne vključke smo našli v vseh vzorcih smaragdov razen v smaragdi v zapestnici, ker so le ti neprozorni in jih zato ne moremo določiti. Foto: Miha Jeršek

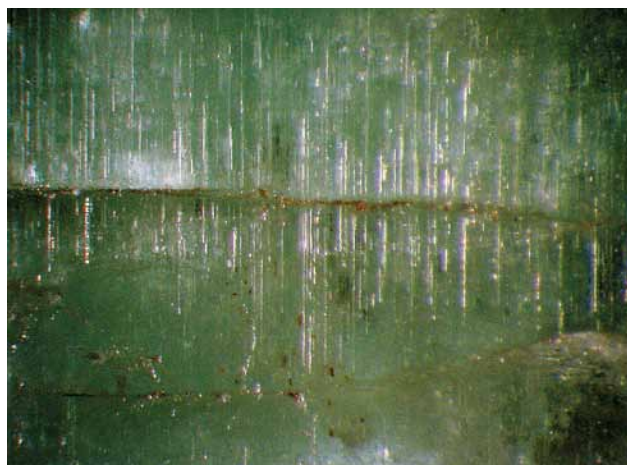


Fig. 19. Growth tube from sample V-3, 30x magnification. This type of inclusions were found in emeralds from the necklace, while those from earrings are less developed and look more like normal liquid inclusions. In emeralds from the bracelet, no such inclusions were found. Photo: Miha Jeršek

Sl. 19. Tekočinski kanali v vzorcu V-3, 30-kratna povečava. Tovrstne vključke smo našli v smaragdi v verižici, medtem ko so v uhanih manj izraziti in so bolj podobni običajnim tekočinskim vključkom. V smaragdi v zapestnici jih nismo našli. Foto: Miha Jeršek

exhibit zonal colours, which change from light to dark green, and mica inclusions.

The emeralds from the archaeological necklace and earrings contain fluid inclusions (Fig. 18). Parallel growth tube were found in all emeralds from the necklace (V1-3) (Fig. 19), while in the earrings they were not so distinct or could generally be attributed to fluid channels. The emeralds from the bracelet (Z1-3) contain a great amount of mica both on the surface and in the interior (Fig. 20). Other inclusions were not found owing to the opacity of the samples.

Emeralds are known to contain numerous inclusions, which has also been ascertained by us from the studied samples, both the emeralds embedded in the archaeological artefacts and reference emeralds. In the emeralds from the archaeological artefacts, inclusions in the form of parallel growth tube were particularly salient. We found them in the emeralds embedded in the necklace and earrings, but not in the bracelet's emeralds. Neither were they found in reference emeralds. According to the literature data (JENNINGS et al., 1993), it is the very parallel growth tube that are characteristic of the Egyptian emeralds, which has also been confirmed by other researchers (HYRŠL, 2012). We presume that differences would be visible between micas as well, considering that they occur as inclusions in all samples and that they differ among each other already when samples are examined under a gemmological microscope. This is why it would be reasonable to analyse them in greater detail in the near future.

PIXE/PIGE method

Twelve samples were analysed with the PIXE/PIGE method. As reference material, samples from Inv. Nos. 628, 1470, 1488, M-1 and M-2 were taken. Emerald samples from archaeological artefacts were V-1, V-2, V-3, U-2, U-3, Z-1 and Z-2. During data analysis, statistical error was below 5 % in Mg, while total error in Mg was about 10 %. In other elements, total error could be taken as 5 %, except for the smallest concentrations, where it was again about 10 %. Measurements are given in Table 3.

Table 3 presents results of the analyses of emeralds in the archaeological artefacts, reference emeralds and literature data (Austria, Afghanistan, Egypt, India, Roman-Gaul) as to the content of selected oxides that are significant in determining their origin (CALLIGARO et al., 2000).

Characteristic grouping of the measured data was tested by principal component analysis (PCA) using the oxides of Na, Mg, Al, K, and Ca; the concentrations were transformed according to $c = \ln(1+c)$ following the method of Duerwer et al., 1975. As shown in Figure 21, the emeralds for particular artefacts are nicely grouped, indicating that each artefact contains emeralds from an individual source. According to CALLIGARO et al., 2000, more precise locations can be determined from the $\text{Na}_2\text{O}/\text{MgO}$ and $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ bivariate plots.



Fig. 20. In emerald samples from the bracelet, mica could be found as an inclusion (on the right in brown) or as an enclosing rock on emerald crystal (left), where crystal structure is expressed. Photo: Miha Jeršek

Sl. 20. Sljuda v smaragdih je v vzorcih smaragдов iz zapestnice ohranjena kot vključek (na desni strani v rjavi barvi) ali kot prikamnina na kristalu smaragda (levo), kjer je prepoznavna še kristalna oblika. Foto: Miha Jeršek

The $\text{Na}_2\text{O}/\text{MgO}$ relationship shows certain data grouping (Fig. 22), which leads us up to the same or at least very similar environment in which green beryls were formed. The Ural green beryl's MgO and Na_2O values completely differ from others, which means that the emeralds from the archaeological artefacts do not originate from

Table 3. Comparison of oxides from emeralds in archaeological artefacts, reference emeralds and literature data (CALLIGARO et al., 2000) (Austria, Afghanistan, Egypt, India, Roman-Gaul).

Tabela 3. Primerjava oksidov v smaragdih v arheoloških predmetih, primerjalnih smaragdih in podatkih iz literature (CALLIGARO et al., 2000) (Avstrija, Afganistan, Egipt, Indija, Rimsko-Galija).

	Sample	Na_2O	MgO	Al_2O_3	K_2O	CaO
1	V-1	1.93	2.54	14.9	0.04	0.16
2	V-2	2.25	2.60	15.3	0.07	0.30
3	V-3	1.93	2.59	15.9	0.04	0.17
4	U-2	1.85	2.27	14.3	0.18	0.66
5	U-3	2.14	2.89	13.0	0.12	0.95
6	Z-2	1.54	2.70	14.5	1.42	0.17
7	Z-1	1.29	2.85	12.7	1.67	0.19
8	1488 (Habachtal)	2.00	4.10	14.6	0.39	0.31
9	628 (Habachtal)	1.85	4.56	15.2	0.33	0.21
10	M-2 (Habachtal)	1.86	7.36	12.1	0.11	2.94
11	M-1 (Habachtal)	1.77	3.07	14.6	0.05	2.00
12	1470 (Ural)	0.06	0.11	19.7	0	0
13	Habachtal	2.10	2.70	15.4	0.04	0.06
14	Afghanistan (Panshir)	1.50	1.80	16.6	0.05	0.00
15	Egypt (D. Zabara)	2.60	2.90	15.4	0.06	0.03
16	India (Adjmer)	1.80	1.80	16.8	0.04	0.03
17	Roman-Gaul (found in Paris)	2.20	2.50	15.1	0.13	0.09

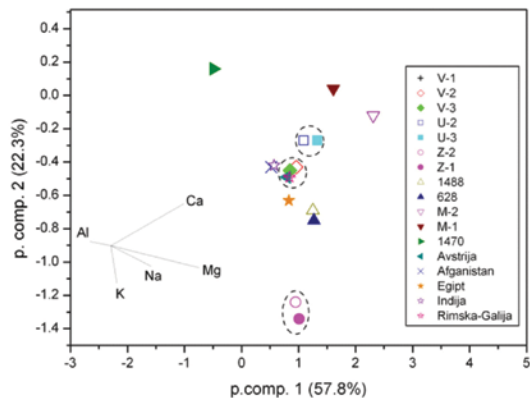


Fig. 21. Characteristic grouping of archaeological and reference emeralds according to principal component analysis (PCA).
Sl. 21. Razdelitev arheoloških in referenčnih smaragdov v skupine z metodo glavnih osi (PCA).

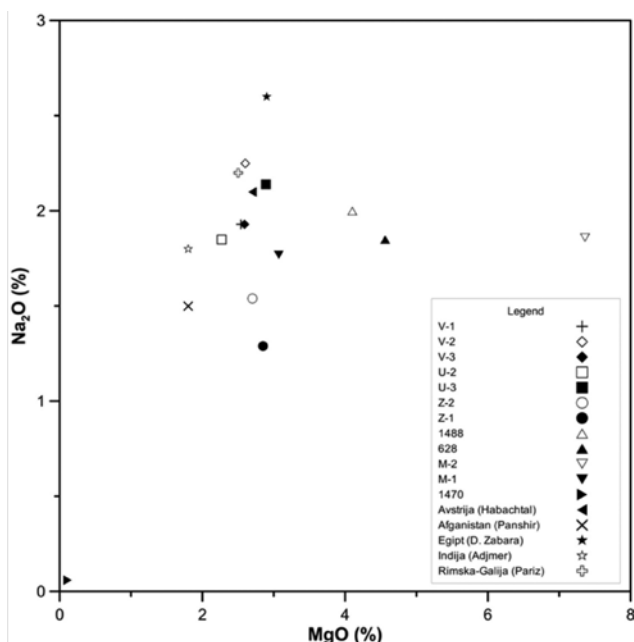
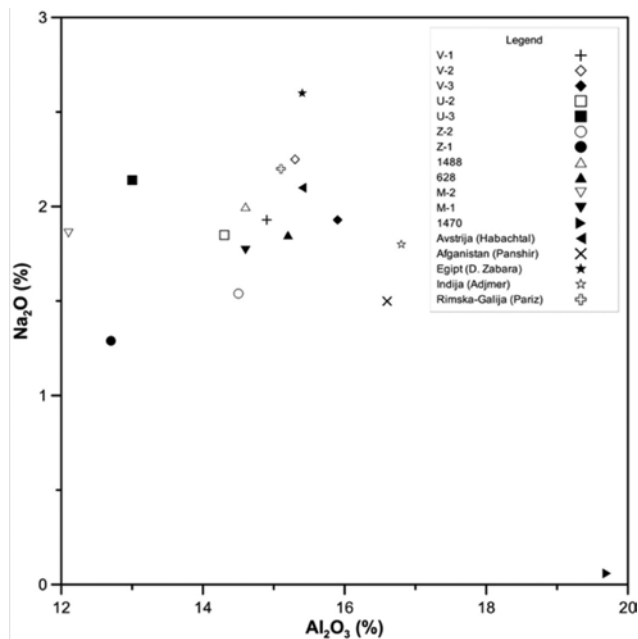


Fig. 22. Graphical representation of $\text{Na}_2\text{O}/\text{MgO}$ concentrations in emeralds from archaeological artefacts, reference emeralds and literature data (CALLIGARO et al., 2000) (Austria, Afghanistan, Egypt, India, Roman-Gaul).

Sl. 22. Koncentraciji Na_2O in MgO v smaragdih v arheoloških predmetih, primerjalnih smaragdih in podatkih iz literature (CALLIGARO et al., 2000) (Avstrija, Afganistan, Egipt, Indija, Rimska-Galija).

this historically significant site in the Ural Mts. Similarly, the data of given relationship between sodium and magnesium oxide for Habachtal emeralds are grouped. Characteristic of them is the changeable magnesium oxide content, which is also a result of the numerous mica inclusions, whereas the sodium oxide content is more or less constant. For the emeralds from the archaeological bracelet, however, we can say with certainty that they do not originate from the sites at Habachtal. Their relationship of oxides is very near the literature data (CALLIGARO et al., 2000) for emeralds from Afghanistan.

The magnesium oxide content in other emeralds from the archaeological artefacts (V1-3, U2, U3)



Sl. 23. Koncentraciji Na_2O in Al_2O_3 v smaragdih v arheoloških predmetih, primerjalnih smaragdih in podatkih iz literature (CALLIGARO et al., 2000) (Avstrija, Afganistan, Egipt, Indija, Rimska-Galija).

Fig. 23. Graphical representation of the $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ concentrations in emeralds from the archaeological artefacts, reference emeralds and literature data (CALLIGARO et al., 2000) (Austria, Afghanistan, Egypt, India, Roman-Gaul).

is fairly constant, while the sodium oxide content changes. Part of this data "cluster" is also the investigated Roman-Gaul sample, which is kept by the Carnavalet Museum (Paris) and originates from African sites (CALLIGARO et al., 2000). If compared with literature data (CALLIGARO et al., 2000), we can conclude that they have somewhat higher magnesium oxide content than Indian emeralds and lower sodium oxide content than the single emerald from Egypt. Given that the values of relationship between magnesium and sodium oxide for the samples of emeralds from the necklace and earrings is still near enough, we believe that they originate from a common site which, after all, has been confirmed by the value of the mentioned relationship for the single sample (Roman-Gaul). The differences between given samples and, above all, the difference towards other literature data for Egyptian emerald may lie in the fact that we are dealing with some other microlocation, as there were several mines in Egypt (SHAW et al., 1999).

The $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ relationship (Fig. 23) shows, similar as the $\text{Na}_2\text{O}/\text{MgO}$ relationship, certain data grouping, which leads us up to the same or at least very similar environment in which green beryls were formed. For the Ural green beryl we can reiterate that we are again dealing with a completely different story, which additionally confirms that the emeralds from the archaeological artefacts were not formed under same conditions as the Ural green beryl. For other samples we can generally establish, the same as for samples from literature data (CALLIGARO et al., 2000), that Al_2O_3 content changes to a relatively

lesser extent than Na_2O content. Regarding the Z1-2 samples, we can confirm once again that in view of Na_2O content they are the nearest to the emeralds from Afghanistan, while in connection with Al_2O_3 content this fact leads us to believe that they might be from some other site – from Egypt, perhaps – but certainly not from the same microlocation. Particularly salient is one literature datum (Egypt) (CALLIGARO et al., 2000) for the emerald from Egypt, while the other (Roman-Gaul) is from the cluster of data for emeralds from the archaeological artefacts in Slovenia. These data are grouped in the central part of the diagram, where Habachtal, Indian and studied emeralds in the archaeological artefacts belong. A certain groupation can indeed be detected, i.e. that the Habachtal emeralds have lower Na_2O and Al_2O_3 content, and that Indian emeralds have relatively more Al_2O_3 , while the emeralds from the archaeological artefacts have relatively more Na_2O and average Al_2O_3 content.

On the basis of geochemical analyses of emerald samples we may thus conclude that the emeralds from archaeological necklace and earrings (V1-3, U2, U3) most probably originate from sites in Egypt (the valleys of Gimal del A and B, Nuqrus, Sikait, Zubara), whereas the emeralds from the bracelet (Z1-2) originate from sites in the region of modern-day Afghanistan (Panjshir valley) or from Egypt, although from a different microlocation than the emeralds embedded in the bracelet and earrings.

Conclusions

So far, the origin of emeralds from the archaeological artefacts in Slovenia has not been researched from the aspect of geochemical (CALLIGARO et al., 2000) and mineralogical characteristics (BAUER, 1968; HENN, 1990), while in archaeological respect the finds have been appropriately described (TUŠEK, 1985).

As the emeralds from the archaeological artefacts have preserved their crystal surfaces, we decided to compare the forms of crystals from Habachtal with those in the archaeological jewellery. The Habachtal emeralds have a characteristic and simple prismatic habitus, which is stipulated by the surfaces of hexagonal prism of the first order $a(100)$ and pinacoid $c(001)$. The emeralds from archaeological artefacts have, apart from hexagonal prism of the first order $a(100)$ and pinacoid $c(001)$, other crystal surfaces as well, i.e. surfaces of hexagonal bipyramid of the first order $d(101)$, hexagonal bipyramid of the second order $e(111)$ and hexagonal prism of the second order $g(110)$. It was established that the crystallographic characteristics of emeralds from Habachtal (HENN, 1990) differ from the crystallographic characteristics of emeralds from the archaeological artefacts in Slovenia, which can of course be associated with different conditions during their origin and therefore other sites.

The geochemical characteristics that can reveal the origin of emeralds were studied already by Calligaro and his associates (2000). On the basis of relations between Na_2O and MgO and Na_2O and Al_2O_3 , he tried to establish the origin of emeralds, comparing them with reference emeralds from various sites. On the basis of our results and literature data (CALLIGARO et al., 2000), we concluded that the green beryl from the Ural Mts is a completely different story, that emerald samples from the bracelet originate from the region of modern-day Afghanistan, whereas emerald samples from the necklace could possibly originate either from Egypt or Habachtal. The geochemical characteristics of emeralds from Habachtal and Egypt do not differ enough to be able to stipulate the site merely on the basis of their characteristic chemical composition. If, however, the crystallographic characteristics (HENN, 1990) and the characteristic inclusions in the form of growth tube (JENNINGS, 1993) are also taken into account, then the samples of emeralds from the archaeological artefacts (necklace and earrings) originate from Egyptian sites. The differences in geochemical characteristics can be attributed to the microlocation inside Egyptian sites.

At the beginning we set up a working hypothesis that the emeralds embedded in the archaeological artefacts in Slovenia originated from the Habachtal site in Austria. On the basis of geochemical and crystallographic characteristics as well as characteristic inclusions, however, it was established that the emeralds from the necklace and earrings originated from Egypt (the valleys of Gimal A and B, Nuqrus, dolina Sikait, Zubara). As far as emeralds from the bracelet are concerned, on the other hand, their origin could not have been determined with utmost certainty owing to the lack of reference material; they may be from a site in modern-day Afghanistan or from Egypt, but certainly not from the same site as the previously mentioned emeralds from the necklace and earrings.

Acknowledgement

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Uvod - smaragd in ljudje skozi čas

Ljudje smo s smaragdi povezani že več kot 4.000 let. Že v antičnem času so predstavljali simbol magične modrosti boga Hermesa. Egipčanska vladarica Kleopatra je izredno cenila dragulje, še posebno smaragde. Njeni legendarni rudniki smaragdov so dolgo ostali skrivnost, šele pred približno sto leti so jih znova odkrili v bližini Rdečega morja (FINLAY, 2006).

V Stari Grčiji se je Plinij spraševal, ali je sploh lahko karkoli bolj zeleno od pristinega smaragda. Grki so verjeli, da imajo dragulji zdravilno moč in da prinašajo srečo. Razvratni požigalec starega Rima, Neron, je skozi smaragdna sončna očala najraje opazoval boje gladiatorjev (HENN, 1990).

Tudi sveti Gral je narejen iz smaragda, njegova vrsta pa ostaja še dandanes neznanka. Ljudje so v zgodovini smaragdu pripisovali lastnosti, da preprečuje poltenost, krepi spomin, položen na jezik pomaga pri klicanju duhov in pogovoru z njimi. Nazadnje je še blažena Hildegarda iz Bingena trdila, da smaragd raste zjutraj, ko so zelene livade najbolj sveže, kar ovrednoti njihovo smaragdno zeleno barvo (JERŠEK & DOBNIKAR, 2005).

Muslimani so prav tako v islamski tradiciji cenili smaragde in njihovo zeleno barvo. Smaragdno zelen naj bi bil plašč in turban preroka Mohameda. Tako je zelena barva postala tudi Barva Islama in jo lahko opazimo na njihovih zastavah. Barva simbolizira posmrtni paradiz, ki ga je Mohamed obljubljal vernikom. Muslimanski vladarji so z nošenjem smaragdov navzven kazali ne le, da so neizmerno bogati in politično močni, ampak da jih varuje sam bog Alah (FINLAY, 2006).

Kelti in Rimljani so kopali smaragde v zgodovinskem nahajališču Habachtal v Visokih Turah v Avstriji, na nadmorski višini med 2.000 in 2.200 m (HENN, 1990). Zgodovinsko pomembna nahajališča smaragdov so še v Egiptu in Afganistanu (HENN, 1990) po nekaterih podatkih tudi na Uralu (CALLIGARO et al., 2000). Z odkrivanjem vedno novih in novih nahajališč so smaragdi postali vse bolj dostopni. Z odkritjem nahajališč smaragdov v Kolumbiji so postali eni najbolj cenjenih draguljev (BAUER, 1968). Ker je naravnih še vedno premalo, jih izdelujejo tudi v laboratorijih (HENN, 1990).

Med arheološkimi predmeti iz rimskega obdobja, predvsem v zlatem nakitu, so na Slovenskem našli verižico, uhana in zapestnico z vgrajenimi smaragdi (TUŠEK, 1985). Izvor teh smaragdov še ni bil podrobneje raziskan. Zaradi relativne bližine nahajališča smaragdov v Habachtalu v Avstriji se je zdelo najverjetneje, da je njihov izvor prav v tem visokogorskem nahajališču. Zato smo raziskali kristalografske, fizikalne in geokemične značilnosti smaragdov v arheoloških predmetih na Slovenskem in jih primerjali z referenčnimi smaragdi iz Habachtala. V analize smo vključili še zeleno obarvan beril iz Urala, medtem ko referenčnih vzorcev smaragdov iz Egipta in Afganistana nismo imeli na razpolago in smo se pri interpretaciji rezultatov oprli na literaturne vire (JENNINGS et al., 1993; CALLIGARO et al., 2000).

Zgodovinsko pomembna nahajališča smaragdov

V Avstriji, na območju narodnega parka v Visokih Turah, je največje evropsko nahajališče kristalov smaragda, v dolini Habachtal. Prve omembe o najdbah smaragda segajo v keltsko-rimski čas (HENN, 1990). Kasneje so s kopanjem nadaljevali v 18. stoletju. Pod prelazom Legbachscharte so izkopali kar nekaj rogov. Lastniki so se skozi stoletja menjavali in z njimi tudi pravila o tem, kdo in pod kakšnimi pogoji lahko koplje smaragde. Vstop v rove je prepovedan predvsem iz varnostnih razlogov. Iskalci lahko iščejo smaragde na odvalu pred rudnikom. Kristali berila so v črno zelenem biotitno-aktinolitnem in redkeje v lojevčevu-aktinolitnem skrilavcu (REČNIK et al., 1994).

Glavne kamnine v širšem območju Habachtala so serpentiniti. Na ožjem področju, kjer se pojavljajo smaragdi, poteka serija serpentinitov in lojevčevih skrilavcev vzporedno s tektonsko mejo, ki loči centralne gnajse od formacije, ki jo v večini sestavljajo granatovi blestniki in amfibolovi gnajsi. Minerali v serpentinitih so obogateni s kromom, medtem ko so minerali v blestnikih in amfibolitih nosilci berilija in aluminija. Na stiku med serpentiniti in blestniki so se kot reakcijski produkti izločili lojavec, aktinolit, klorit in biotit, nato pa se je na njihovih stikih pred približno 65 milijoni let, z začetkom alpinske regionalne metamorfoze, začel izločati beril, ki je obogaten s kromom. (REČNIK et al., 1994).

Vsi smaragdi iz Habachtala kristalizirajo v obliki heksagonalne prizme, ki je zaključena s pinakoidom. Njihova razkolnost poteka pravokotno po vzdolžni osi c. Kristali smaragdov so temno zelene barve, pogosteje blede zelene ter vse do zeleno belih odtenkov. Popolnoma prosojni kristali so prava redkost. Pogosto so motni do delno prosojni in neprosojni. Beli in svetlo obarvani kristali so navadno večji in bolj prosojni od zelenih (Bauer, 1968). Kristali so pogosto napokani po bazalnih ravninah zaradi tektonskega dogajanja ob nastanku. Smaragdi vsebujejo vključke sljude, turmalina, titanita, epidota, apatita in rutila. Količina izkopanih smaragdov na Habachtalskem območju je zelo majhna v primerjavi s količino smaragdov, ki jo izkopljejo v drugih nahajališčih po svetu (HENN, 1990).

Nahajališča smaragdov v Egiptu veljajo za zgodovinska, saj so na tem območju kopali drage kamne že več kot 1650 let pr.n.št.. Egipt naj bi predstavljal enega od treh virov smaragdskih nahajališč za Evropo in Afriko v grško-rimskem času. Za takratni čas so bila znana naslednja nahajališča s kronološkim redom izkopavanja: Dolina Gimal del A in B (4.-5. stol.), dolina Nuqrus in dolina Sikait (6.- 9. stol.) in Zubara (12.-16. stol.) (SHAW et al., 1999)

Danes so znana nahajališča smaragdov na otoku Zabargad v Rdečem morju in 100 km južno od današnjega Kaira v dolini Sikait-Zubara. Z izkopavanji v 19. stoletju so Angleži na podlagi najdenega orodja ugotovili, da so tu smaragde kopali že več kot 1650 let pr.n.št.. Za takratni čas je bil Egipt pomemben vir smaragdov, ki so bili

cenjeni tako v Indiji kot tudi v Evropi (FINLAY, 2006).

Smaragdi iz Egipta so kristalizirali v sljudnem skrilavcu na stiku z granitom. Smaragdi so blede zeleni, polni vključkov in pogosto zelo majhni (FINLAY, 2006). Med najpomembnejšimi vključki so tekočinski vključki, posebno značilni pa so tekočinski kanali (JENNINGS et al., 1993).

Smaragde so nekoč kopali na tudi območju doline Panjšir, na robu gore Hindukuš v Afganistanu. V antičnem času se je to področje imenovalo baktrijsko, kot poroča Theophrastus in je znano še za časa Aleksandra Velikega od 3.-1. stol. p.n.št. (CALLIGARO et al., 2000). S ponovnim kopanjem so pričeli na začetku leta 1970 (JENNINGS et al., 1993).

Nekateri menijo, da so tudi nahajališča na Uralu v Sibiriji možen vir smaragdov v času Rimljanov (CALLIGARO et al., 2000), velika večina podatkov o smaragdih iz Urala pa izvira iz obdobja po letu 1830 (BAUER, 1968), ko so jih našli v bližini reke Tokowaya. Tiste iz zgodovinsko pomembnih nahajališč pa naj bi kopali že od leta 1.500 pr. n. št. Tako, da so rudniki smaragdov znani še iz antičnih časov. Tudi Plinij starejši navaja v svojem delu *Historia Naturalis* legendo o uralskih smaragdih iz nahajališča Scythia (CALLIGARO et al., 2000). Smaragdi iz Urala vsebujejo vključke rjavkastih do skoraj brezbarvnih aktinolitnih kristalov, ki so samostojni ali v drobnih skupkih, biotit in trofazne vključke, redko pa je vključek turmalin (HENN, 1990).

Kristalografske značilnosti smaragdov

Za smaragde je značilen prizmatski habitus, ki ga določajo heksagonalne prizme I. reda a (100). Posamezni kristali so zaključeni z osnovnimi pinakoidom c (001), morfološko pestrost kristalov smaragda pa ustvari dodatne kristalne ploskve, med katerimi najdemo heksagonalno bipiramido I. reda d (101), heksagonalno bipiramido I. reda e (111), diheksagonalno prizmo f (210) in heksagonalno prizmo II. reda g (110). Posamezne kristalne ploskve so lahko na kristalih bolj ali manj izrazite, tako da lahko najdemo tudi povsem kratko-prizmatske kristale, ali pa so vrhovi kristalov zaradi množice drobnih kristalnih ploskev na prvi pogled precej zaobljeni. (JERŠEK & VIDRIH, 2009).

Kristalogenetski trend razkriva zaporedje kristalizacije od zelo kratko prizmatskih, do kratko prizmatskih, srednje prizmatskih in dolgo prizmatskih kristalov v odvisnosti od prisotnosti različnih alkalnih prvin (KOSTOV & KOSTOV, 1999).

Vključki v smaragdih

Smaragdi vsebujejo zaradi načina kristalizacije zelo veliko število vključkov, zato so jim strokovnjaki nadeli ime smaragdni vrt (francosko *jardin*). Pogosti vključki v smaragdih so tekočinski vključki, med trdnimi pa so pogosti kromit, kromov spinel, picotit, aktinolit, biotit, pirit, kalcit in dolomit (GÜBELIN & KOIVULA, 1986). Vključki v smaragdih so značilni za posamezna nahajališča in zato je njihova določitev

pomembna za ugotovitev njihovega izvora. Značilni vključki za smaragde iz Habachtala so biotit, lojevec, aktinolit in tremolit (HENN, 1990), v smaragdih iz Urala najdemo flogopit (HENN, 1990), za smaragde in zelene berile iz Egipta pa so še posebej značilni tekočinski kanali (JENNINGS et al., 1993). V gemološki praksi je smaragd edini dragulj, pri katerem se njihova kakovost glede na čistost in s tem na prisotnost ter vrsto vključkov, vrednoti s prostim očesom in ne z lupo 10x povečave.

Zelena obarvani berili kot dragulji

Smaragdi so zeleno obarvani berili draguljarске kakovosti. Poznamo pa še dva zeleno obarvana berila, ki sta uporabna kot draga kamna; zeleni beril, ki je obarvan zaradi primesi železa in vanadijev beril, ki je obarvan zaradi primesi vanadija.

Material

Arheologi so na Slovenskem našli samo nekaj predmetov s smaragdi (tab. 1). Poznan je zlat nakit dame iz rimske Petovione, ki ima vdlane svetle kristale smaragda. Najden je bil leta 1982, na Mežanovi ulici na Ptuju, na arheološkem najdišču Hajdina (EŠD 581). Nahajal se je v opečnati skrinji, v kateri je bil skeletni grob, z dvojnimi pokopom matere in otroka. Zlata verižica (sl. 1) (inv. št.: A 164) je sestavljena iz 31 delov, treh smaragdskih kristalov (V-1, V-2, V-3) in sponke. Ogrlico hrani Zavod za varstvo kulturne dediščine Slovenije, Center za preventivno arheologijo, Regionalni oddelek Ptuj (TUŠEK, 1985).

Dva zlata uhana (sl. 2) (inv. št. 80CP001/002 in 80CP001/003) sta bila najdena leta 1980, iz območja Srednješolskega centra, na Volkmerjevi cesti, na Ptuju. Nahajala sta se v grobu številka 1, kjer se je v sledih nahajal ženski skelet. Uhana imata vkovana kristala smaragda (U-1, U-2). Hrani ju Arheološki oddelek Pokrajinskega muzeja Ptuj-Ormož (TUŠEK, 1985).

Kot tretji arheološki predmet je zapestnica v dveh delih (sl. 3). Najdena je bila leta 2009, na območju Osnovne šole Ljudski vrt, grob 154 (inv. št. PN 627). Vsebuje tri smaragdne kristale (Z-1, Z-2, Z-3). Hrani jo Arheološki oddelek Pokrajinskega muzeja Ptuj-Ormož.

Kot primerjalni material smo izbrali deset kristalov smaragda iz Habachtala v Avstriji (sl. 4) (inv. št. 623-a, 623-b, 623-c, 627, 628, 1475, 1478, 1488, M1, M2) in zeleno obarvan beril iz Urala (sl. 5) (inv. št. 1470), vsi, razen vzorcev M1 in M2, pa so iz znamenite Zoisove zbirke mineralov (tab. 1) (ČINČ JUHANT & JERŠEK, 2005).

Metode

Makroskopski opis

Vzorci smo najprej opazovali s prostim očesom in lupo 10x povečave. Določali smo kristalografske značilnosti, vključke in barvo. S pomočjo kljunastega merila smo izmerili velikost smaragdov.

Gemološki mikroskop

Smaragde smo pregledali z gemološkim mikroskopom, ki je pravzaprav stereolupa s povečavami od 10 do 80x. Model gemološkega mikroskopa je bil KSW 63/11434.3.

UV svetilka

S standardno ultravijolično svetilko smo preiskovali luminiscenčne pojave pri vzorcih (fluorescenca in fosforescenca) s kratko in dolgovalovno ultravijolično svetlobo.

Metodi PIXE in PIGE

Metodi PIXE in PIGE temeljita na obsevanju vzorca z visokoenergijskimi ioni, ki v snovi vzbudijo karakteristične rentgenske žarke in žarke gama. Protoni z energijo nekaj MeV prodrejo do 100 μm globoko v snov, tako da meritve ne kažejo le stanja na površini, ampak nekaj 10 μm globoko - upoštevati moramo namreč, da se protoni pri prehajanju skozi snov upočasnjujejo, reakcijski preseki pa se z energijo hitro manjšajo. Nastali rentgenski žarki se v vzorcu tudi absorbirajo, medtem ko so učinki absorpcije pri veliko trših žarkih gama zanemarljivi. Merilni postopek je nedestruktiven, saj obsevanje s protoni ne povzroča vidnih sledov, tako da sta metodi posebno primerni za analizo dragocenih predmetov, med katere spadajo tudi dragi kamni.

Meritve z metodo PIXE - PIGE smo opravili na tandemskem pospeševalniku Instituta Jožef Stefan v Ljubljani. Merili smo s protonskim žarkom v zraku, ker omogoča enostavno nameščanje vzorca in izbiro mest za obsevanje. Nominalna energija protonov je bila 2,5 MeV, pri prehodu skozi 2 μm debelo okence iz tantalove folije in 1 cm široko zračno režo se je ta energija zmanjšala na približno 2,2 MeV. Profil žarka je bil Gaussov, s širino 0,8 mm na polovični višini. Vzbujeni rentgenski žarki so do detektorja rentgenskih žarkov, ki je bil postavljen pod kotom 45° glede na protonski žarek, prepotovali še 5,7 cm široko zračno režo. Zaradi absorpcije v zračni reži smo lahko z rentgenskimi žarki zaznali le elemente, težje od silicija. V vsaki izbrani točki smo opravili dve meritvi. S prvo smo merili nizkoenergijski spekter elementov med silicijem in železom, pri drugi pa smo tok protonov povečali na nekaj nA in merili hkrati visokoenergijski rentgenski spekter elementov, težjih od železa, in spekter gama. Detektor rentgenskih žarkov smo v ta namen opremili z dodatnim absorberjem iz 0,1 mm debele aluminijeve folije. V spektrih gama smo zajeli elemente Na, Mg in Al. V spektrih se sicer pojavljajo tudi črte litija in fluorja, vendar jih pri kvantifikaciji rezultatov nismo upoštevali, ker nismo imeli ustreznih standardov. Prav tako smo koncentracije berilija upoštevali le računsko.

Negotovosti pri koncentracijah večinskih elementov so reda $\pm 5\%$, pri elementih v koncentracijah pod 0,1% pa so lahko večje, in sicer 10-15%. Merilne negotovosti so večje tudi pri meritvah na naravnih berilih, ki imajo na površini drobne mineralne nečistoče, navadno lističe sljude, zaradi katerih smo z meritvami določili večje koncentracije kalija in aluminija.

Rezultati

Makroskopski opis

Habachtalski kristali smaragdov so večinoma prosojni in ne prozorni. Kristalne ploskve imajo videz, kot da bi bile najedkane, redko so gladke. Videz je posledica rasti v kamnini ali pa je najedkanost posledica delnega raztapljanja. Smaragdi so barvno neenoviti. Nekateri so brezbarvni (inv. št. 628), drugi različnih odtenkov zelene barve. Imajo veliko vključkov sljude. Splošno razmerje med širino in dolžino kristalov je v razmerju od 1 : 3 do 1 : 6.

Smaragdi v arheoloških predmetih se navidezno med seboj ločijo. In sicer so smaragdi v zapestnici na videz neprozorni, imajo tudi drugačen barvni odtenek (modrikasto zelen) in vsebujejo veliko sljude.

Smaragdi v verižici in uhanih so prosojni do prozorni, zelene barve s številnimi tekočinskimi vključki in relativno malo sljude (tabla 1, sl. 6 do 13).

Velikost smaragdov v arheoloških predmetih smo izmerili tako, da smo izmerili razdalje med dvema nasprotnima si ploskvama heksagonalne prizme (Š) in višino smaragda med dvema pinakoidoma (V). Rezultati meritev so podani v tabeli 2.

Kristalografske značilnosti smaragdov

Kristali smaragdov iz Habachtala imajo značilen prizmatski habitus, ki ga določajo ploskve heksagonalne prizme I. reda a (100) in so zaključeni s ploskvijo pinakoida c (001) (sl. 14). Zeleno obarvan beril iz Urala ima prav tako izrazit prizmatski habitus z razvitimi ploskvami heksagonalne prizme I. reda a (100) in pinakoida c (001). Tri kristalne ploskve heksagonalne prizme I. reda so zbrušene in spolirane.

Smaragdi v arheoloških predmetih imajo poleg heksagonalne prizme I. reda a (100) in pinakoida c (001) razvite še druge kristalne ploskve. Določili smo heksagonalno bipiramido I. reda d (101), heksagonalno bipiramido II. reda e (111) in heksagonalno prizmo II. reda g (110) (sl. 15 in 16). Kristal (V-1) na verižici nima ploskev heksagonalne prizme II. reda g (110), medtem ko jih drugi (V-2) kristal v verižici ima. Kristali na zapestnici (Z1-3) so slabše ohranjeni, a se še vedno da opaziti, da ima kristal podobne kristalografske značilnosti kot jih imajo smaragdi na verižici (V1-3) in uhanih (U-2, U-3). Smaragdi v zapestnici so deloma ohranjeni kot naravni kristali, deloma pa so obrušeni, saj so ploskve, ki naj bi pripadale heksagonalni prizmi, med seboj izrazito nevporedne. Poleg tega smo na nekaterih mestih določili dodatne kristalne ploskve heksagonalne bipiramide (sl. 17).

Na osnovi kristalografskih značilnosti lahko zaključimo, da so kristali smaragdov iz Habachtala in berila iz Urala značilno prizmatski in imajo poleg ploskve pinakoida razvite samo še ploskve heksagonalne prizme, medtem ko imajo smaragdi v arheoloških predmetih razvite še druge kristalne ploskve. Poleg tega so smaragdi iz

Habachtala srednje do dolgo prizmatski, medtem ko so kristali smaragdov iz arheoloških predmetov kratko do srednje prizmatski in v splošnem bolj sodčkasti in imajo razvitih več vrst kristalnih ploskev. To nas navaja na dejstvo, da so obravnavani smaragdi nastali pri različnih razmerah (KOSTOV & KOSTOV, 1999), kar lahko pomeni, da so tudi iz različnih nahajališč.

Luminiscenčni pojavi

Pri pregledu vzorcev z ultravijolično svetilko, s kratko in dolgovalovno ultravijolično svetlobo, preiskovani vzorci niso fluorescirali in tudi niso fosforescirali.

Vključki

Smaragdi iz Habachtala niso prosojni do prozorni in vsebujejo veliko tekočinskih vključkov in vključkov sljud tako v samih kristalih kot deloma na površini kristalov smaragda. Podobno ima zeleno obarvan beril iz Urala številne tekočinske vključke, conarno obarvanost, ki se spreminja od svetlo do temno zelene ter vključke sljud.

Smaragdi iz arheoloških predmetov, iz verižice in uhanov, vsebujejo tekočinske vključke (sl. 18). Tekočinske kanale smo našli v vseh smaragdih v verižici (V1-3) (sl. 19), medtem ko le ti v uhanih niso tako izraziti oziroma jih lahko pripišemo splošno tekočinskemu vključkom. Smaragdi v zapestnici (Z1-3) imajo veliko sljude tako na površini kot v notranjosti (sl. 20) medtem ko drugih vključkov zaradi neprozornosti vzorcev nismo našli.

Za smaragde je znano, da vsebujejo veliko vključkov, kar smo ugotovili tudi v preiskovanih vzorcih in sicer tako v smaragdih iz arheoloških predmetov kot v primerjalnih smaragdih. V smaragdih iz arheoloških predmetov posebno izstopajo vključki v obliki tekočinskih kanalov. Našli smo jih v smaragdih v verižici in v uhanih medtem ko v smaragdih v zapestnici ne. Prav tako jih nismo našli v primerjalnih smaragdih. Po literaturnih podatkih (JENNINGS et al., 1993), so prav tekočinski kanali značilni za smaragde iz Egipta in so jih določili tudi drugi raziskovalci (HYRŠL, 2012). Predvidevamo tudi, da bi bile razlike vidne med sljudami, saj se le te pojavljajo kot vključki v vseh vzorcih in so že pri pregledu vzorcev z gemološkim mikroskopom med seboj drugačne. Zato jih bo smiselno v prihodnosti podrobneje analizirati.

Metoda PIXE/PIGE

Z metodo PIXE/PIGE smo analizirali 12 vzorcev. Za primerjalno gradivo smo izbrali vzorce z inv. št. 628, 1470, 1488, M-1 in M-2. Vzorci smaragdov iz arheoloških predmetov so bili V1, V2, V-3, U-2, U-3, Z-1 in Z-2. Pri analizi podatkov je bila statistična napaka pri Mg pod 5 %, celotna napaka pri Mg pa je bila okoli 10 %. Pri drugih elementih lahko vzamemo celotno napako 5 %, razen pri najmanjših koncentracijah, kjer lahko doseže 10-15 %. Rezultati meritev so podani v tabeli 3.

V tabeli 3 so zbrani rezultati analiz smaragdov v arheoloških predmetih, v primerjalnih smaragdih in po podatkih iz literature (Avstrija, Afganistan, Egipt, Indija, Rimska Galija) glede na vsebnost izbranih oksidov, ki so pomembni za določitev njihovega izvora (CALLIGARO et al., 2000).

Izmerjene podatke smo najprej poskusili razdeliti v skupine z metodo glavnih osi (PCA), tako da smo upoštevali okside Na, Mg, Al, K in Ca; pri tem smo uporabili logaritemsko transformacijo $c' = \ln(1+c)$ po Duewerju et al., 1975. Na sliki 21 smaragdi iz posameznih arheoloških predmetov jasno nastopajo skupaj, kar kaže, da so pri vsakem predmetu uporabili smaragde iz izbranega individualnega vira. Po CALLIGARU et al., 2000, lahko podrobneje določimo lokacije virov iz dvojnih diagramov $\text{Na}_2\text{O}/\text{MgO}$ in $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$.

Razmerje med Na_2O in MgO nam kaže določeno grupiranje podatkov (sl. 22), kar nas navaja na enako ali pa vsaj zelo podobno okolje, v katerem so zeleno obarvani berili nastali. Zeleno obarvani beril iz Urala ima vrednosti MgO in Na_2O povsem drugačne od ostalih, tako da so zgodba zase. To pomeni, da smaragdi iz arheoloških predmetov ne izvirajo iz tega zgodovinsko pomembnega nahajališča na Uralu. Podobno se grupirajo podatki danega razmerja med natrijevimi in magnezijevimi oksidom za smaragde iz Habachtala. Zanje je sicer značilno, da se spreminja vsebnost magnezijevega oksida, kar je tudi posledica številnih vključkov sljude, medtem ko je vsebnost natrijevega oksida bolj ali manj stalna. Zato pa lahko za smaragda iz zapestnice iz arheoloških predmetov (Z1-2) ugotovimo, da ne izvirata iz nahajališč v Habachtalu. Njuno razmerje oksidov je zelo blizu literaturnemu podatku (CALLIGARO et al., 2000) za smaragde iz Afganistana.

Preostali smaragdi iz arheoloških predmetov (V1-3, U2, U3) imajo dokaj stalno vsebnost magnezijevega oksida, medtem ko se vsebnost natrijevega oksida spreminja. V ta »oblak« podatkov sodi tudi preiskovani vzorec Rimska Galija, ki ga hranijo v muzeju Carnavalet (Pariz), ki izhaja iz severno afriških nahajališč (CALLIGARO et al., 2000). Če jih primerjamo z literaturnimi podatki (CALLIGARO et al., 2000), lahko ugotovimo, da imajo nekoliko višjo vsebnost magnezijevega oksida kot smaragdi iz Indije in nižjo vsebnost natrijevega oksida kot en smaragd iz Egipta. Ker so vrednosti razmerja med magnezijevim oksidom in natrijevimi oksidom za vzorce smaragdov iz verižice in uhanov vendarle dovolj skupaj, menimo, da izvirajo iz skupnega nahajališča, kar potrjuje tudi vrednost omenjenega razmerja za en vzorec (Rimska Galija). Razlike med danimi vzorci in predvsem različnost drugega literaturnega podatka za smaragd iz Egipta nakazujejo, da gre morda za drugo mikrolokacijo, saj je bilo rudnikov v Egiptu več (SHAW et al., 1999).

Razmerje med Na_2O in Al_2O_3 (sl. 23) nam podobno kot razmerje med Na_2O in MgO kaže določeno grupiranje podatkov, kar nas navaja na enako ali pa vsaj zelo podobno okolje, v katerem so zeleno obarvani berili nastali. Za zeleni beril

iz Urala lahko ponovno ugotovimo, da je tudi v tem primeru zgodba zase, kar nam dodatno potrjuje, da smaragdi iz arheoloških predmetov niso nastali v enakih razmerah kot zeleni beril iz Urala. Na splošno lahko za druge vzorce, kakor tudi za vzorce iz literaturnih podatkov (CALLIGARO et al., 2000) ugotovimo, da se vsebnost Al_2O_3 spreminja relativno manj kot vsebnost Na_2O . Za vzorca (Z1-2) lahko ponovno potrdimo, da sta glede na vsebnost Na_2O še najbližje smaragdov iz Afganistana, medtem ko nas v povezavi z vsebnostjo Al_2O_3 to dejstvo navaja, da so morda iz kakega drugega nahajališča; morda iz Egipta, vendar ne iz iste mikro lokacije. Posebej izstopa en literaturni podatek (Egipt) (CALLIGARO et al., 2000) za smaragd iz Egipta, medtem ko je drugi (Rimska Galija) znotraj oblaka podatkov za smaragde iz arheoloških predmetov na Slovenskem. Ti podatki se grupirajo v osrednjem delu diagrama, kamor sodijo habachtalski, indijski in preiskovani smaragdi v arheoloških predmetih. Zaznamo lahko določeno grupacijo, in sicer da imajo smaragdi iz Habachtala nižjo vsebnost tako Na_2O kot Al_2O_3 , indijski imajo relativno več Al_2O_3 , medtem ko imajo smaragdi iz arheoloških predmetov relativno več Na_2O in povprečno vsebnost Al_2O_3 .

Na osnovi geokemičnih analiz vzorcev smaragdov lahko zaključimo, da so smaragdi iz arheoloških predmetov, verižice in uhanov (V1-3, U2, U3) zelo verjetno iz nahajališč v Egiptu (dolina Gimal del A in B, dolina Nuqrus, dolina Sikait, Zubara) medtem ko so smaragdi iz zapestnice (Z1-2) iz nahajališč na območju današnjega Afganistana (dolina Panjšir) ali pa iz Egipta, vendar druge mikro lokacije kot smaragdi iz verižice in uhanov.

Zaključek

Izvor smaragdov v arheoloških predmetih na Slovenskem do sedaj ni bil raziskan s stališča geokemičnih (CALLIGARO et al., 2000) in mineraloških značilnosti (BAUER, 1968; HENN, 1990) medtem ko so v arheološkem pogledu najdobe opisane (TUŠEK, 1985).

Smaragdi v arheoloških predmetih imajo večinoma ohranjene kristalne ploskve in zato smo primerjali oblike kristalov iz Habachtala in tiste v arheološkem nakitu. Smaragdi iz Habachtala imajo značilen in preprost prizmatični habitus, ki ga določajo ploskve heksagonalne prizme I. reda a (100) in pinakoida c (001). Smaragdi v arheoloških predmetih imajo poleg heksagonalne prizme I. reda a (100) in pinakoida c (001), še druge kristalne ploskve in sicer ploskve heksagonalne bipiramide I. reda d (101), heksagonalne bipiramide II. reda e (111) in heksagonalne prizme II. reda g (110). Ugotovili smo, da se kristalografske značilnosti smaragdov iz Habachtala (HENN, 1990) razlikujejo od kristalografskih značilnosti smaragdov iz arheoloških predmetov na Slovenskem, kar lahko povežemo z drugačnimi razmerami pri njihovem nastanku in s tem na drugo nahajališče.

Geokemične značilnosti, ki nam lahko pokažejo izvor smaragdov, je raziskoval že CALLIGARO s sodelavci (2000). Na osnovi razmerij med Na_2O in MgO ter Na_2O in Al_2O_3 je ugotavljal izvor smaragdov in jih primerjal z referenčnimi smaragdi iz različnih nahajališč. Na osnovi naših rezultatov in podatkih iz literature (CALLIGARO et al., 2000) smo ugotovili, da je zeleni beril iz Urala povsem svoja zgodba, vzorci smaragdov iz zapestnice izvirajo iz območja današnjega Afganistana, medtem ko bi vzorci smaragdov iz verižice lahko izvirali iz Egipta, kot tudi iz Habachtala.

Geokemične značilnosti smaragdov iz Habachtala in Egipta se ne razlikujejo dovolj, da bi določili nahajališče samo na osnovi značilne kemijske sestave. Če pa upoštevamo še kristalografske značilnosti (HENN, 1990) in značilne vključke v obliki tekočinskih kanalov (JENNINGS, 1993), pa so vzorci smaragdov iz arheoloških predmetov (verižica in uhana) iz nahajališč v Egiptu. Razlike v geokemičnih značilnostih lahko pripišemo mikrolokaciji znotraj nahajališč v Egiptu.

Na začetku smo postavili delovno hipotezo, da so smaragdi v arheoloških predmetih na Slovenskem iz nahajališča Habachtal v Avstriji. Na osnovi geokemičnih in kristalografskih značilnosti ter značilnih vključkov, pa smo ugotovili, da so smaragdi iz verižice in uhanov iz nahajališč v Egiptu (dolina Gimal del A in B, dolina Nuqrus, dolina Sikait, Zubara). Za smaragde iz zapestnice zaradi pomanjkanja primerjalnega gradiva nismo mogli povsem zanesljivo določiti izvora; lahko so iz nahajališča v današnjem Afganistanu ali pa iz Egipta, vendar ne iz istega nahajališča, kot prej omenjeni smaragdi iz verižice in uhanov.

Zahvala

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