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Inscribed Gems: Material Profiling beyond Visible Examination

Abstract: A series of thirty-five engraved gems from the collection of the Museum für Kunst und Gewerbe, Hamburg, were re-examined using non-destructive material-science methods in order to verify the previously determined rock type. The results of four selected, engraved gems containing pictorial elements as well as inscribed letters are presented in detail as a showcase of opaque gems. These intaglios originate from different epochs and places in the Mediterranean. They were analysed using both classical gemmological approaches and the more advanced Raman and infrared-reflectance spectroscopic methods, which can fingerprint the solid material on the basis of its atomic structure and chemical composition. The results demonstrate the potential of these spectroscopic methods for unambiguous identification of engraved gems and, more importantly, the necessity of applying them along with traditional gemmological methods for a correct material identification, which may furthermore help in tracing the origin of the inscribed gem.

1 Introduction

The appearance of writing and creation of written artefacts was a key factor for the development and survival of ancient cultures. To better understand the role of written artefacts in this evolution, researchers ought to examine not only the message left by former generations, but also the process of creating the message: choice of writing support, development of suitable tools, and the establishment of production processes.

The diversity of written artefacts in terms of material support is huge and includes clay tablets, stones, metal, ivory, parchment, palm leaves, paper, etc. Among these, gems were chosen as both portable and durable, seemingly everlasting messengers, i.e. they were intended to deliver the text message to different places within the same time period as well as into the future. Gems are generally characterized by appealing visual appearance (to catch the eye)¹ as

¹ See e.g. Rapp 2009.

well as by having mechanical and chemical resistance to intensive everyday use. However, gemstones with a high level of hardness, such as ruby or sapphire (Al_2O_3 -based, Mohs hardness² 9) and diamond (built up of four-coordinated carbon, Mohs hardness 10) are very difficult to carve and hence are rarely used as writing supports. Thus, most of the ancient engraved gems are varieties of quartz (SiO_2 , framework silicates, Mohs hardness ~7), jade (composed of chain silicates, Mohs hardness ~6–7), and rocks containing predominantly layered silicates which have Mohs hardness ranging between 2 and 4. Typical examples of silica varieties are carnelian, jasper, agate, chalcedony, and opal, whereas the latter group includes soapstone, serpentinite, and mica rocks. Carnelian can be clearly distinguished from the other rocks mentioned above because it is translucent and appears optically homogenous and reddish in colour. Agate, chalcedony, and opal can also be identified by their common visual appearance. However, these mineral varieties may appear opaque, like jade, soapstone, serpentinite, and mica rocks, and sometimes the identification of opaque rocks via classical gemmological methods can be very challenging or almost impossible, even for experienced researchers, especially if the samples do not exhibit polished surfaces suitable for the determination of optical constants.

This reality calls for the application of more sophisticated analytical methods, which are sensitive to both the atomic structure and chemical composition and thus can provide the information necessary to unambiguously identify the mineral phases composing the gem. Since such methods should be non-destructive, one has to use techniques in which the reflection signal from the sample is analysed. Therefore, Raman spectroscopy and infrared (IR) reflectance spectroscopy are very suitable for this purpose. Both methods are based on the interaction between the incident electromagnetic radiation and the so-called normal vibrational modes of the solid sample, i.e. the set of atomic vibrations around the equilibrium positions of atoms that are allowed to exist in the material without destroying it. Hence, the resulting measured spectra carry unique information about the atomic-scale configuration and can truly fingerprint crystalline as well as amorphous phases.

Over the last decade, Raman spectroscopy has become popular for fast, easy-to-handle, non-destructive mineral identification.³ This is partially due to

² The Mohs hardness scale represents the scratch resistance of solids relative to ten reference minerals, with diamond having the maximum value of 10. The absolute hardness plotted against the Mohs hardness resembles an exponential growth function. See e.g. Rapp 2009.

³ See e.g. Giarola et al. 2012; Centeno 2015.

the continuously growing databases available online, free of charge,⁴ but also because of the establishment of strategies and protocols for quantitative determination of the chemical formulas of complex silicate minerals.⁵ A thorough quantitative analysis of the phase and chemical compositions is also of great significance for analysing portable, mineral-base written artefacts because it may considerably advance provenance studies. However, Raman spectroscopy has one drawback that may hamper its application to natural samples: the existence of strong photoluminescence background (due to substitution or structural defects) combined with weak Raman signals may result in unfeasibility to detect any usable spectral profile. Infrared reflectance spectroscopy is rarely used for mineral identification because the assessable spectral range for probing the atomic vibrations is restricted due to instrument limitations. Besides, the collected spectral profiles are quite different from the IR spectra measured in the common transmittance regime due to the combined effect of multiple light-matter interaction processes. Nevertheless in the case of poor-quality Raman spectra, IR reflectance spectroscopy becomes the technique of choice as a non-destructive method that is also applicable to samples exhibiting strong photoluminescence.

In order to explore the potential of Raman and IR reflectance spectroscopy for identifying the rock type of engraved gems, we have analysed thirty-five samples from the collection of the Museum für Kunst und Gewerbe (MKG), Hamburg. Here we report our results for four selected samples, which contain symbols and written text along with engraved figures; these samples appear opaque and are thus representative for our study. We show that the original material assignment of these gems needs to be revised, and also demonstrate that if the writing support is atypical, then the material profile can be a marker for provenance.

2 Materials and methods

2.1 Samples and classical examination

The catalogue numbers, locality, and inscription age of the intaglios studied here are given in Table 1. The table also summarizes the previous rock-type

⁴ See e.g. Lafuente et al. 2015.

⁵ Bendel and Schmidt 2008, 1055; Bersani et al. 2009, 484; Bersani et al. 2018, 684; Huang et al. 2000, 473; Kuebler et al. 2006, 6201; Leissner et al. 2015, 2682; Watenphul et al. 2016, 970.

identification.⁶ Gem #1964.294 has been so far described as soapstone, gems #1964.324 and #1965.130 as jasper, and gem #1965.122 as moss agate. The intaglios were first re-examined using classical non-destructive gemmological approaches, namely: (i) observation of general appearance (e.g. colour, transparency, texture, occurrence of luminescence upon UV irradiation); (ii) determination of specific gravity and refractive index; and (iii) further physical properties (e.g. magnetic activity).

Table 1: Gem catalogue number, locality and age of inscription (after Zazoff 1975), material identification according to classical gemmological methods, and material identification via Raman or IR reflectance spectroscopy.

Gem	Locality / inscription age	Classical gemmological methods		Raman / IR spectroscopy
		previously	this study	
1964.294	Melos, Greece (?); second half of the 7 th c. BCE	soapstone	serpentinite	muscovite variety
1964.324	Phoenicia – Carthage; 6 th c. BCE	green jasper	green jasper	opal A + glauconite as a colouring agent
1965.122	locality unknown; 3 rd –4 th c. CE; inscription: Greek	black jasper	serpentinite + magnetite	Fe-containing antigorite + magnetite
1965.130	Persia; 6 th –7 th c. CE	moss agate	serpentinite with magnetite grains	antigorite + magnetite

2.2 Raman spectroscopy

The Raman spectra were collected in back-scattering geometry with a Horiba Jobin-Yvon T6400 triple-monochromator system equipped with an Olympus BX41 confocal microscope and an LN₂-cooled Symphony CCD Detector. The spectra were excited with the green line ($\lambda=514.532$ nm) of the Coherent Innova 90C FreD Ar⁺ laser. The spectrometer was calibrated to the position of the Raman peak of Si wafer at 520.5 cm⁻¹, the spectral resolution was ~2 cm⁻¹, while the precision in determining the peak positions was ~0.35 cm⁻¹. All spectra were

⁶ Zazoff 1975 provides a catalogue with commentary of the collection of engraved gems at the MKG.

collected with 50× long-working distance objective, using a confocal hole of 400 μm , which helped to reduce the undesired photoluminescence background. The laser power delivered on the sample surface was ~ 7.9 mW, while the diameter of the laser spot was approximately 2 μm . Several points from the same sample were probed in order to check for reproducibility of the spectra from the areas with the same appearance under a microscope. The Raman spectra presented below are baseline corrected for the continuum photoluminescence background, using spline interpolation, and temperature reduced to account for the Bose-Einstein phonon population. It is worth noting that none of these data-evaluation steps influences the peak positions, and the aforementioned evaluation procedure is not required for a simple phase identification based on qualitative comparison with reference spectra.

2.3 IR reflectance spectroscopy

The IR reflectance spectra were collected with a Bruker Vertex 70 FTIR spectrometer equipped with a Hyperion 2000 IR microscope with a 15× IR objective, using a Globar as IR white source, a wide-range MIR-FIR beam splitter, and an LN-MCT-D316-025 detector. The instrumental resolution was 2 cm^{-1} and the mirror scanner velocity was 20.0 kHz. The spectra were collected from an area of the size $80 \times 80\text{ }\mu\text{m}$.

The spectra of the engraved gems were compared with the spectra of reference mineral samples from the collection of the Mineralogical Museum, CeNak, Universität Hamburg, which were measured under the same experimental conditions as the gem spectra.

3 Results and Discussion

3.1 Engraved gem #1964.294

Among the intaglios in the collection of the MKG, two stones – due to their characteristic material and style – are referred to as island gems, that is, archaic intaglios, probably from Melos. The Cycladic island was a centre of art at the end of the seventh as well as at the beginning of the sixth century BCE.⁷ Boardman points out that ‘serpentine’ is the most common gem used in Melos and is

⁷ Boardman 1963, 106–107, refers to the exquisite pieces of jewelry from the Melian school.

represented in almost every shade of green. Furtwängler called the material steatite, thus trying to qualify the colour or translucency, and he has been followed by most subsequent archaeologists who have considered the matter (including Zazoff 1975).⁸ Interestingly, Boardman also touches on the subject of the disagreement between scientists and archaeologists over terminology. Although he admits that the description will be ‘wholly unacceptable to the petrologist’, he deems its use justified in this case, since ‘no archaeologist will be misled by another’s use of it’.⁹ This approach might have been acceptable in times when natural sciences and humanities had less contact, and collaborative work was seen as unnecessary. One of the aims of the cooperation between scientists and humanities scholars in Hamburg is to correct these obvious mistakes and prevent them from occurring again.

Gem #1964.294 is a lentoid intaglio (2.00 – 1.95 – 0.63 cm), drilled horizontally and obviously engraved with a manual graver. It shows the upper body of a winged horse antipodically connected to a winged Capricorn, which is a typical Melian pictorial element. Zazoff emphasizes the special quality of the work which distinguishes the stone from other specimens and dates it to the second half of the seventh century BCE.¹⁰ Gem #1964.290, on the other hand, is amygdaloid and has been dated to the beginning of the seventh century BCE.¹¹ The decoration is a lizard in top view, although there are several alterations to the natural form of the animal.

Using gemmological approaches, this sample has been identified as soapstone (Zazoff) or serpentinite (this study). It is commonly accepted that soapstone consists largely of talc (end-member formula $\text{Mg}_3[\text{Si}_4\text{O}_{10}](\text{OH})_2$), which is a layered silicate mineral exhibiting a sandwich structure of two SiO_4 -tetrahedral layers and one MgO_6 -octahedral layer. Serpentinite is a rock composed predominantly of serpentine minerals: another group of layered silicates characterized with an end-member formula $\text{Mg}_3[\text{Si}_2\text{O}_5](\text{OH})_4$ and a sandwich structure of one SiO_4 -tetrahedral and one MgO_6 -octahedral layer. The three main structural polymorphs of serpentine are antigorite, lizardite, and chrysotile, which differ from each other in the undulation of the sandwich slabs. The spectral differences among the three serpentine minerals (if they have exactly the same composi-

⁸ Boardman 1963, 15. Furtwängler 1900, 22.

⁹ Boardman 1963, 16.

¹⁰ Zazoff 1975, 355, n. 9 and t. 247, Boardman 1963, 63, n. 247. On the technique, cf. Boardman 1963, 19–20, who shows similar intaglios from Melos now to be found in London, Paris, and Munich amongst other places.

¹¹ Zazoff 1975, 355–356, n. 10 and t. 247.

tion) are only subtle, but serpentines can be clearly distinguished from the other layered silicates and in particular from talc via their Raman scattering.¹²

Raman spectroscopy revealed that gem #1964.294 is neither soapstone, nor serpentine (see Fig. 1).

Fig. 1: Raman spectra of gems #1964.294 and #1964.290 compared to reference spectra of serpentine (Fe-containing antigorite), soapstone, muscovite, and Cr-bearing muscovite (fuchsite) as well as photographs of the engraved side of the samples. In the graph, the dashed vertical line traces the position of the strongest OH-stretching peak in near-end-member muscovite; the vertical arrow points to the higher-wavenumber shoulder, which is more pronounced in gems #1964.294 and #1964.290 than in the reference muscovite samples. Spectra in the plot are vertically offset for clarity.

The Raman spectrum profile of this sample clearly indicates that it is muscovite (another layered silicate with the chemical formula $\text{KAl}_2[\text{AlSi}_3\text{O}_{10}](\text{OH})_2$), as the positions of all observed peaks generated by framework vibrations (in the range 15–1200 cm^{-1}) match those of reference near-end-member muscovite as well as of Cr-bearing muscovite. Muscovite is commonly transparent and colourless to pale yellow, whereas Cr-bearing muscovite, having a tiny amount of Cr replacing Al in the octahedral layer, can be light greenish, which is a bit closer to the appearance of gem #1964.294. However, colour and translucency can be influenced by the presence of other chemical elements substituting for Al or by the small average size of the mineral grains. If only the latter occurs, the Raman

¹² Wang et al. 2015, 829.

spectra would not be affected, whereas compositional changes larger than 2–3 % should reflect onto the Raman spectra. Variations in the crystal chemistry of hydrous silicates can be best detected via changes in the positions and relative intensities of the Raman or infrared peaks generated by the OH stretching modes, which appear in the range 3400–3750 cm^{-1} .¹³ A close examination of this spectral range indicates that the strongest OH-stretching peak of gem #1964.294 is slightly shifted to higher wavenumbers in comparison with the reference muscovite and that the higher-wavenumber shoulder near 3650 cm^{-1} is more pronounced for the studied gem than for the reference muscovite. This result indicates that the engraved gem is built of muscovite with specific (atypical) crystal chemistry. Further studies involving complementary analytical methods on series of reference samples are necessary in order to establish a correlation between Raman spectra and the crystal chemistry of muscovite, which will make possible the non-destructive determination of the chemical composition of engraved artefacts with muscovite rocks as a writing support. Nevertheless, Raman spectroscopy clearly shows that this sample consists of muscovite with substitution disorder, and its appearance additionally suggests that it is an aggregate of fine-grained muscovite.

It should also be noted that according to Raman spectroscopy, among all thirty-five engraved gems from the MKG collections that were part of this investigation, only the two samples from Melos, #1964.290 and #1964.294, exhibit the same atomic structure and chemistry. Thus, a scientific analysis of similar island gems ascribed to this area, which macroscopically appear as soapstone or serpentinite, may prove useful in establishing whether in fact they are muscovite with the same crystal chemistry as that of #1964.294 and consequently, the same provenance.

3.2 Engraved gem #1965.122

The dark and polished intaglio (2.00 – 2.52 – 0.54 cm), with a pictorial element and inscription, probably dates to the third or fourth century CE (Zazoff). The gem features a female lion-griffon, combining elements of a griffon, a lioness, as well as other animals, and resembles in its presentation the griffon of Nemesis as depicted in Roman art, although the right fork here is supported on a branch and not on a wheel as usual.¹⁴ Above the figure, the Greek letters KAKAXE can

¹³ Leissner et al. 2015, Watenphul et al. 2016.

¹⁴ Zazoff 1975, 390 n. 82; Simon 1962, 770–771.

be read.¹⁵ These seem to be an abbreviated form of κακόν and ἀλακεῖν, ‘to ward off evil’. This combination of words is found in Hesiod’s *Theogonia*, when the poet describes the suffering of Prometheus. Heracles is credited with relieving the sinner (*Theog.* 527): κακὴν δ’ ἀπὸ νοῦσον ἀλάκεν, ‘relieved from pernicious disease’. The verb is mainly found in the Homeric epics, and Pindar uses it once, praising Chiron as a protector.¹⁶ These mythological references to gods and heroes are well in line with the depiction of the griffon, which was originally used at the Persian royal court as a symbol of power.

This intaglio has been previously ascribed as jasper (Zazoff), which is an opaque rock containing predominantly quartz and other minor minerals that determine the colour of the stone (usually reddish, brownish, yellowish, green, or black). Our re-examination using classical approaches, however, suggests this gem is serpentinite, although serpentine is usually greenish rather than blackish in colour. Additional mineral grains embedded into the serpentine matrix could hardly be seen when examining with a classical gemmological lens. However, this gem displays strong magnetic activity, indicating a large fraction of magnetite (Fe_3O_4), which should be responsible for the overall black colour of the intaglio.

One could speculate that the magnetic behaviour of this stone was recognised by the ancient users and consequently added to the magic qualities of the intaglio, which are defined by the inscribed text; we would then have an ancient ‘spiritual’ variant of a modern concept from our technology-oriented society: ‘material properties determine the material functionality’.

The Raman spectroscopic analysis (see Fig. 2) confirmed the conclusion of our macroscopic re-examination: under high magnification, plenty of submicrometre-size mineral grains with high reflectivity can be observed, whose Raman scattering indicates they are magnetite, while the matrix shows a typical spectrum of serpentine, more specifically Fe-containing antigorite¹⁷. As can be seen in Fig. 2, the Raman spectrum collected from the matrix of #1965.122 is almost identical with that of the reference greenish antigorite, indicating nearly the same crystal chemistry. The main compositional variation in serpentines is

¹⁵ Zazoff 1975, 390, interprets them as a combination of κακος [sic] and ἀπαλλάσσω, ‘Vom Bösen befreien’. He is right on the general meaning, but the derivation he posits is not entirely correct.

¹⁶ E.g. Homer, *Iliad*, 23, 185: ἀλλὰ κύνας μὲν ἀλακε Διὸς θυγάτηρ Ἀφροδίτη ‘The daughter of Zeus, Aphrodite, warded off the dogs’, referring to her protection of Hector’s corpse; Hector had been slain by Achilles, who had threatened that Hector’s corpse would be consumed by dogs. Similarly: Homer, *Iliad*, 19,30; 21,138 and Pindar, *Nemean Odes*, 4,60.

¹⁷ Wang et al. 2015, 829.

the ratio Fe^{2+}/Mg in the octahedral layer. Our ongoing study on series of reference antigorite samples with different amounts of iron aims to establish a method for non-destructive determination of Fe^{2+}/Mg , which is another material parameter that can quantitatively characterise written artefacts on a serpentine base.

Fig. 2: Raman spectra of gem #1965.122 collected from the matrix and from blackish inclusions, compared to reference spectra of Fe-containing antigorite (serpentine mineral group) and magnetite, respectively, as well as a photograph of the engraved side of the intaglio. Spectra in the plot are vertically offset for clarity.

3.3 Engraved gem #1965.130

Most interesting is a large (3.4 – 3.4 – 1.44 cm) and unique intaglio classified by Zazoff as a Sassanian seal and dated to the sixth or seventh century CE. Zazoff based his dating on the form of the crown of the bust on the reverse.¹⁸ On the obverse he sees Gaymoarth, the Iranian *Urmensch* depicted within a circle of creatures present at his birth.¹⁹ A long inscription in Pahlavi surrounds the pictorial elements on both sides as well as on the vertical rim of the disc. It seems that the artist tried to copy a template but did not understand it. The

¹⁸ Zazoff 1975, 395 n. 93.

¹⁹ Zazoff refers to Ackerman 1936, 126-127, who presents an illustration of a similar seal now in the Museum of Fine Arts in Boston (see n. 21).

remnants do not allow for a complete textual context and meaning.²⁰ The decipherable parts contain conjurations and thus point to the use of the disc in magical contexts. In a comprehensive study on magic seals from Sassanian Iran, R. Gyselen shows two close parallels from Berlin and Boston but is unaware of the piece in Hamburg.²¹ She is cautious in identifying the figure on the back of the disc and does not attempt a mythological match.²² Another seal of the same kind was described by E.W. West in 1882. He saw ink impressions of a stone amulet enclosed in a letter written by A.D. Mordtmann from Constantinople in 1875 to Prof. Haug in Munich. The disc seems to have been offered to Dr. Mordtmann for the sum of £ 45.²³ West considers the inscription legible and understandable, dates it, due to linguistic criteria, to the late seventh century CE and even provides a translation. In the text, which he interprets as part of a private letter – although from an insulting correspondence between two men – he sees no indication of the later use of the disc as an amulet. Whether the stone described by him is in fact one of the three discs now kept in Hamburg, Berlin, and Boston or yet another example of this specific kind of object remains to be seen.²⁴

Based on its macroscopic appearance, this sample has previously been identified as moss agate. The dominant mineral phase of agate is quartz (crystalline SiO₂ polymorph), and moss agate refers to greenish agate, which contains moss-like mineral inclusions, usually green amphibole or chlorite. Re-examination using classical approaches, however, suggests that the matrix is also serpentine (see Table 1) and contains blackish grains with metallic lustre that may be magnetite. The latter assumption is supported by the fact that whole gem exhibits subtle magnetic activity.

20 Zazoff 1975, 395 n. 93, indicating that the information on the inscription was provided by R.N. Frye, a historian and orientalist, who held a visiting professorship at the University of Hamburg in 1968–69.

21 Gyselen 1995, 25–28 with Figs 2a and 2b. On the Boston seal, see Pope and Ackerman 1964, 803 and pl. 256 W AA. The disc is presented as a ‘Gnostic amulet’ in the online collection of the Museum of Fine Arts, <<https://collections.mfa.org/objects/134006/gnostic-amulet;sessionId=16F89FDFC20A15060E8911DAD7CCE9A9>> (accessed on 1 Dec. 2020). On the Berlin seal, see Enderlein 1986, 28, n. 24.

22 Gyselen 1995, 28: ‘personnage à pieds fourchus’. It seems to her that the engraver wanted to depict a person dressed in a characteristic fashion, which is still hard to define.

23 West 1882, 223.

24 C.G. Cereti will closely scrutinize the example from Hamburg and prepare a publication.

The Raman scattering collected from this sample (see Fig. 3) verifies that the dominant phase is a serpentine polymorph, most probably antigorite²⁵. However, the positions of the OH-stretching peaks indicate that this serpentine mineral contains a smaller amount of Fe²⁺ in comparison to the reference green antigorite as well as to the matrix of gem #1965.122. For now, only qualitative statements can be made, but as mentioned above we are currently working on developing a strategy for non-destructive quantitative determination of the crystal chemistry of this subgroup of layered silicates. The Raman analysis also confirms that the grains with metallic lustre are magnetite.

Fig. 3: Raman spectrum of gem #1965.130 compared to a reference spectrum of Fe-containing antigorite (serpentine mineral group) and photographs of the top and bottom side of the intaglio. Spectra in the plot are vertically offset for clarity.

3.4 Engraved gem #1964.324

This Phoenician pendant (1.45 – 1.08 – 0.77 cm) has the typical form of a scarab, held by a golden band and is dated to the sixth century BCE. Isis-Hathor is carved within a field framed by a ribbon. She sits on a throne wearing the head-dress of Hathor: the sun within the horns of a cow. Whereas the ankh symbol on the side of her throne is probably a deliberate reference to eternal life, the other hieroglyphs are arranged in a nonsensical way and do not form a readable text. The inscription is thus to be seen as an imitation of an Egyptian artefact inspired by the Egyptianising models circulating at the time. To the untrained eye

²⁵ Wang et al. 2015, 829.

of the ancient beholder, the hieroglyphs may have presented a protective ‘text’ with magical functions.²⁶

Macroscopic examination, previously by Zazoff and now undertaken as part of this study, identifies this gem as green jasper. It should be recalled that jasper is a rock with quartz (crystalline SiO_2) as the chief mineral. Our efforts to detect Raman signals on the topic of the photoluminescence background failed, although Raman peaks from quartz were easily detected from other jasper samples exhibiting a similar level of photoluminescence background. Hence, we suppose that gem #1964.324 might be non-crystalline, since amorphous solids in general have much weaker Raman cross section than crystalline solids. We have tried to use red laser (632.8 nm) or blue laser (488.0), but the undesired photoluminescence background remained too high. Neither did prolonged irradiation of the sample help to reduce the background. Thus, we applied IR reflectance spectroscopy to check the mineral phases composing this sample (see Fig. 4).

Fig. 4: Infrared reflectance spectrum of gem #1964.324 compared to reference spectra of quartz, opal A, and glauconite as well as photographs of the top and bottom side of the sample. The arrows in the plot mark the contribution of glauconite to the IR spectrum of gem #1964.324; spectra are vertically offset for clarity.

The comparison with reference IR reflectance spectra collected from quartz and opal A (amorphous $\text{SiO}_2 \cdot n\text{H}_2\text{O}$) reveals that the matrix is amorphous opal, i.e. this

²⁶ Zazoff 1975, 357, n. 11. We would like to thank L. Mascia, Hamburg, for valuable insights from her ongoing PhD project.

gem cannot be classified as jasper. Moreover, examination of a few green earth pigments via IR reflectance spectroscopy shows that the gem contains glauconite, having characteristic peaks at 960 and 668 cm^{-1} (marked by arrow in Fig. 4). It is worth noting that both opal A and glauconite are commonly formed as a result of marine sedimentary diagenesis, i.e. they may indeed appear together in a mineral assembly, which is fully consistent with the mineral phase identification via IR reflectance spectroscopy.

4 Conclusion

We demonstrate that:

- Classical gemmological approaches alone can be insufficient to properly identify the material of opaque engraved gems.
- Raman spectroscopy is a very efficient non-destructive method for immediate mineral-phase identification of opaque gems, based on literature data and existing spectral databases. Moreover, this analytical method has great potential in developing strategies for non-invasively determining the content of minor elements in the structure of layered silicates, e.g. serpentines and muscovite; such a determination would help to better characterize the writing support and, in turn, to verify the provenance of portable rock-based written artefacts.
- Infrared reflectance spectroscopy can be also useful for non-destructive material profiling of engraved gems, especially when the utilization of Raman spectroscopy is impeded due to the presence of pronounced and undesired photoluminescence background. In this case, however, it is advisable for researchers to select and measure suitable reference minerals or rocks by themselves, because the quality of the sample surface and the experimental conditions can considerably affect the total reflectivity, which interferes with the peaks generated by atomic vibrations.

For the study of written artefacts in general, close mineralogical analysis of gems is both necessary and highly advantageous. Apart from information about provenance – for which a large and internationally available database will have to be established – information about the quality of the stones as well as about their appearance adds to the description of the writing and the pictorial elements. Only a holistic approach of this sort renders it possible to understand not merely the gem and its engravings separately, but the written artefact as an undivided entity.

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References

- Ackerman, Phyllis (1936), 'The Iranian Serpentarius and Gemini', *Bulletin of the American Institute for Persian Art and Archaeology*, 4.3: 126–129.
- Bendel, Verena and Burkhardt C. Schmidt (2008), 'Raman spectroscopic characterisation of disordered alkali feldspars along the join $\text{KAlSi}_3\text{O}_8\text{--NaAlSi}_3\text{O}_8$: application to natural sanidine and anorthoclase', *European Journal of Mineralogy*, 20: 1055–1065.
- Bersani, Danilo, Irene Aliatis, Mario Tribaudino, Luciana Mantovani, Artur Benisek, Michael A. Carpenter, Giacomo Diego Gatta and Pier Paolo Lottici (2018), 'Plagioclase composition by Raman spectroscopy', *Journal of Raman Spectroscopy*, 49: 684–698.
- Bersani, Danilo, Sergio Andò, Pietro Vignola, Gaia Moltifiori, Iari-Gabriel Marino, Pier Paolo Lottici and Valeria Diella (2009), 'Micro-Raman spectroscopy as a routine tool for garnet analysis', *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 73: 484–491.
- Boardman, John (1963), *Island Gems. A Study of Greek Seals in the Geometric and Early Archaic Periods*, London: Society for the Promotion of Hellenic Studies.
- Centeno, Silvia A. (2015), 'Identification of artistic materials in paintings and drawings by Raman spectroscopy: some challenges and future outlook', *Journal of Raman Spectroscopy*, 47: 9–15.
- Enderlein, Volkmar (1986), *Das Siegel im Altertum. Gebrauchsgegenstand und Kunstwerk*, Berlin: Staatliche Museen zu Berlin.
- Furtwängler, Adolf (1900), *Die antiken Gemmen: Geschichte der Steinschneidekunst im Klassischen Altertum*, Band 2: *Beschreibung und Erklärung der Tafeln*, Leipzig: Giesecke & Devrient.
- Giarola, Marco, Gino Mariotto, Marriana Barberio and David Ajo (2012), 'Raman spectroscopy in gemmology as seen from a "jeweller's" point of view', *Journal of Raman Spectroscopy*, 43, 1828–1832.
- Gyselen, Rika (1995), *Sceaux Magiques en Iran Sassanide* (Studia Iranica. Cahiers, 17), Paris : Association pour l'Avancement des Études Iraniques.
- Huang, E., C.H. Chen, T. Huang, E.H. Lin and Ji-An Xu (2000), 'Raman spectroscopic characteristics of Mg-Fe-Ca pyroxenes', *American Mineralogist*, 85: 473–479.
- Kuebler, Karla E., Bradley L. Jolliff, Alian Wang and Larry A. Haskin (2006), 'Extracting olivine (Fo-Fa) compositions from Raman spectral peak positions', *Geochimica et Cosmochimica Acta*, 70: 6201–6222.

- Lafuente, B., R. T. Downs, H. Yang, N. Stone (2015), 'The power of databases: The RRUFF project', in T. Armbruster and R. M. Danisi (eds) *Highlights in Mineralogical Crystallography*, Berlin: De Gruyter, 1–30.
- Leissner, Lisa, Jochen Schlüter, Ingo Horn, Boriana Mihailova (2015), 'Exploring the potential of Raman spectroscopy for crystallochemical analysis of complex hydrous silicates: I. Amphiboles', *American Mineralogist*, 100: 2682–2694.
- Pope, Arthur Upham and Phyllis Ackerman (1964), *A Survey of Persian Art from Prehistoric Times to the Present*, vol. 2: *Sasanian Periods*, Tehran: Soroush Press.
- Rapp, George (2009), *Archaeomineralogy*, 2nd edn, Berlin: Springer.
- Simon, E. (1962), 'Zur Bedeutung des Greifen in der Kunst der Kaiserzeit', *Latomus*, 21: 749–780.
- Wang, Alian, John J. Freeman and Bradley L. Jolliff (2015), 'Understanding the Raman spectral features of phyllosilicates', *Journal of Raman Spectroscopy*, 46: 829–845.
- Watenphul, A., Martina Burgdorf, Ingo Horn, Jochen Schlüter and Boriana Mihailova (2016), 'Exploring the potential of Raman spectroscopy for crystallochemical analysis of complex hydrous silicates: II. Tourmalines', *American Mineralogist*, 101: 970–985.
- West, E. W. (1882), 'An Engraved Stone with Pahlavi Inscription from Baghdad', *The Indian Antiquary. A Journal of Oriental Research*, 11: 223–226.
- Zazoff, Peter (1975), *Antike Gemmen in Deutschen Sammlungen*, vol. 4, Wiesbaden: Franz Steiner.