

Validation with Raman spectroscopy of lapis lazuli provenance study

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Summary. — Lapis lazuli is a stone appreciated in the art world since ancient times; its use dates back to more than 6500 years ago. There are few mineral sources of this stone in the world and the provenance characterization is an open question. However, the rarity of the sources certainly represents a positive aspect for the indication of the origin of artefacts. Lapis lazuli is a rock consisting mainly of lazurite, diopside, calcite and pyrite; other constituents may be present, linked to the different mines. In this work, we present the development of a method for the recognition of the sources of lapis lazuli. The results obtained on stones from five samples of known origin and on three sets of unknown polished stones were obtained with Raman analysis. We thus verified the results achieved by our previous assignment based on the use of the synergy between the characteristic fluorescence of X-rays and the luminescence stimulated by X-rays. The choice of using Raman spectroscopy as a fast, non-invasive and portable method to determine the geological provenance of lapis lazuli pigments will then be discussed. Finally, we were able to obtain a clearer distinction for the different classified provenances.

1. – Introduction

Lapis lazuli is a semi-precious stone. It has been treasured and prized since the dawn of the ancient civilizations of Mesopotamia, Egypt, China, Greece, and Rome. In fact, artefact like lapis lazuli's beetles have been found in pharaohs' tombs and in other prehistoric contexts of Asia, Africa, and Europe [1, 2]. Despite it is widely used the knowledge on its mineral source is still partial.

Lapis lazuli is composed of different minerals, the one which gives the blue colour is lazurite, the principal one, a tectosilicate mineral with sulfate, sulfur and chloride. Other accessory minerals in order of importance and presence may be diopside, calcite, pyrite,

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feldspars, and wollastonite. Their proportion may vary and may be a clue for provenance study.

Only a few sources of lapis lazuli exist in the world, due to the peculiar geological condition required for its forming [3]; historical sources were often in impervious sites, among them the principal has been Sar-e-Sang in Badakshan district of present-day Afghanistan: the lapis lazuli from here seem to have travelled through and supplied the entire Middle East, Egypt, and the Indus valley. Other sources have to be considered: a Siberian deposit is located for sure in the southern end of Lake Baikal; two quarries are located in central Asia (Pakistan and Tajikistan); another important site, and the most exploited in recent times, is in the Ovalle Cordillera in the Chilean Andes. Quarries of minor importance include Myanmar, Baffin Island of Canada, and the centre of the USA (Colorado, Wyoming, Utah) [4-6]. Old manuscripts from XIII and XIV century, report local mines in Persia, but they might be only a single small quarry exhausted in the XIV century.

As is widely known, the distinction of origin is due to the percentage of accessory minerals present. Their investigation is therefore at the centre of the instrumental analyses applied for this purpose so far. Actually, elemental analysis such as PIXE (Particle-Induced X-ray Emission) [7,8], or the more affordable XRF (X-Ray Fluorescence) [9] can be useful to detect typical trace elements and recognize mineral phases. In addition, it has been noticed that luminescence methods like Ion Luminescence (IL), Radio Luminescence (RL) allow exploiting luminescence proprieties of different minerals, thus they can be used for provenance discrimination as well [10,11]. With the purpose to examine the distribution of mineral phases microscopic analyses were performed too [12-14]. The latest studies have shown the good advantages of XRL (X-Ray Luminescence) and the possibility to go towards a portable instrument for application in Cultural Heritage field. XRL is able to detect luminescent bands that characterize each source and to identify the luminescent centres, and consequently the minerals, responsible for a given emission [15,16].

In order to achieve a complete knowledge of lapis lazuli provenance, in a previous work we applied a non-destructive, portable and low-cost method safe for the precious objects in our custody. Our previous method was based on the joint use of XRF and XRL and, in order to get the synerfic responce of these two techniques, we developed a statistical data treatment. Radioluminescence was used to give further confirmation to the assumptions made in the first part of the research work [16].

Recently, we applied Raman analysis on the same samples of the first part of the research with the aim of giving another validation of our method using an independent and likewise portable technique. Moreover, confirming and re-evaluating the provenances assigned was a further purpose. Raman spectroscopy is a spectral analysis of light inelastically scattered from a sample irradiated by a laser. The spectral intensity is reported as a function of the Raman frequency shift, which is the difference between the frequencies of the incident and scattered light. This yields direct informations on the molecular vibrational frequencies of the sample. Raman spectroscopy as a fast, non-invasive method for discovering that lapis lazuli is widely used in the field of cultural heritage. This method is mostly used to distinguish ultramarine blue, the pigment produced by lapis lazuli, from other blue pigments, *e.g.*, azurite, Egyptian blue. In addition, it is applicable to almost all the artefacts like glass, paintings, plasterworks, manuscripts, raw materials and more [17-21]. Few authors indicate this spectroscopic analysis as a good method to speculate about the provenance [17,18,22] probably thanks to the indirect information (age, period, geographical area) they already had. Raman emission bands of lapis lazuli

are well known; besides, the bands characteristic for the provenance are reported in several databases [23,24]. Lazurite is well identified by Raman spectroscopy by the presence of a strong band centred near 549 cm^{-1} and weaker bands centred between 582 cm^{-1} and 586 cm^{-1} . These emissions are due to the symmetric stretching mode of S_3^- and S_2^- , respectively [23]. It is worth to note that a relationship between the colour hue and the intensity ratio of the S_3^- and S_2^- peaks at 547 cm^{-1} and 584 cm^{-1} has been reported in the literature [20,24]. In addition, the bending vibration of S_3^- at 258 cm^{-1} and the first overtone of the stretching vibration at 1093 cm^{-1} are visible in almost all the Raman spectra of lapis lazuli [19]. From the work of Schimidt *et al.* [17] we learn that many lapis lazuli's Raman spectra contain multiple strong bands in addition to those characteristic of lazurite and furthermore only a laser set at 785 nm shows other features of the spectrum. Besides, they observed that the relative intensity of these bands remains constant between spectra taken from a different area of their samples, but the total intensity varies with respect to the well-known lazurite band. These features could come from a mineral different from lazurite.

2. – Samples and methods

Samples considered in this work are the same as those analysed in our previous part of the research [16] except for the egg (sample 36). For clarity, the same reference number will be indicated as reported in table I.

2.1. Samples. – Nine samples, already analysed in our research [16], have a known origin and belong to the Museum of the mineralogical, gemological, and petrographic collection in the Department of Earth Science Ardito Desio of the University of Milan. The samples labelled as Afghanistan(12), Chile 1 (4/11) and Siberia (17/18) were acquired in 1937 by the Department. Two more samples labelled as Canada (1/3) and Chile 2 (13/16) were acquired in the 1960s for educational purposes from the same Department. Moreover, we analysed four more Afghan polished stones (samples 19-22) from the Kremer set of raw materials for painting (40th anniversary, 2017) property of the Department of Material Science, University of Milano Bicocca.

Some unknown stones have also been tested. The analysis of jewellery of unknown origin was useful to better verify the classification capacity of the proposed methods. The stones are set on pieces of jewellery from three different private collections. The hypotheses of provenance assigned in [16] to each piece of jewellery analysed are shown in table I.

2.2. Methods. – Raman spectra were acquired using i-Raman Plus, (B&WT TEK Inc. USA), in both portable and bench-top micro-Raman mode. The excitation source was a laser operating at 785 nm at 418 mW (tunable) of incident power. Integration time and laser level were set for each sample to optimize the signal. The best measurement time was chosen on a case-by-case basis, as well as the laser power, as not to exceed 10%. Furthermore, not all samples could be measured with micro-Raman. Samples like the rings and bracelet pearls were analysed in portable mode. The magnification of the microscope in micro-Raman mode was chosen based on the sample shape and the best image quality given by the camera. The instrument has only 785 nm laser excitation but in the literature this wavelength is reported as the best to see useful characteristics of the Raman spectrum for provenance attribution. In fact, using 633 , 514 , or 488 nm excitation, spectra show only the characteristic lazurite bands [17,18,25].

TABLE I. – *Known and unknown provenance samples list; in the first column, the numbers refer to the code of our previous work [16]. * For private collections, the provenance assumed at the conclusion of the previous work has been reported.*

Code	Provenance	Features	Property
1/3	Canada	Rough, bright and opaque blue area.	Department of Earth Science, UniMI
4/11	Chile	One side rough, one side polished. Blue area with white inclusions.	Department of Earth Science, UniMI
12	Afghanistan	Rough, small intense blue areas	Department of Earth Science, UniMI
13/16	Chile	Rough, blue part quite homogeneous with small light blue inclusions.	Department of Earth Science, UniMI
17/18	Siberia	Rough. Light blue area with grey inclusions.	Department of Earth Science, UniMI
19	Afghanistan	Polished, rounded, white inclusions.	Department of Material Science, UniMIB
20	Afghanistan	Polished, rounded and flat.	Department of Material Science, UniMIB
21	Afghanistan	Polished, rounded and flat.	Department of Material Science, UniMIB
22	Afghanistan	Polished rounded and flat.	Department of Material Science, UniMIB
23	Siberia*	Earring, cabochon	Collection 1
24	Siberia*	Earring, cabochon	Collection 1
25/28	Chile (25-26-28) + Siberia (27)	Bracelet, 4 cabochon	Collection 1
29	Chile*	Ring, Cabochon	Collection 1
30	Afghanistan*	Brooch, cabochon	Collection 1
31	Chile*	Ring, cabochon	Collection 2
32	Chile*	Earring, cabochon	Collection 3
33	Chile*	Earring, cabochon	Collection 3
34/35	Chile*	Necklace, cabochon	Collection 3

3. – Results

3.1. Known provenance Raman results. – We applied Raman spectroscopy on our nine samples of known origin, the results are summarized in figs. 1, 2.

All the spectra show a low characteristic peak at 549 cm^{-1} and a narrow band for the other assigned vibration in lazurite lattice at 1093 cm^{-1} [23] does not always show up. The lack of a shaped 549 cm^{-1} band in Afghan rock fragment reference samples is reported in Dominguez-Vidal *et al.* work [26] as in our result. Moreover, the spectra

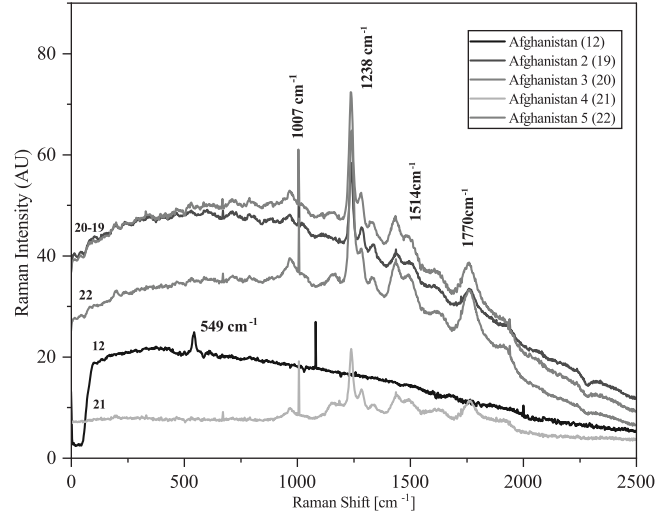


Fig. 1. – Raman spectra acquired from Afghan samples. These spectra are characterized by an accentuated curvature before 1100 cm^{-1} and a narrow band at 1007 cm^{-1} . Above 1100 cm^{-1} , bands at 1238 , 1514 , 1770 cm^{-1} are indicated [17]. Furthermore, the characteristic peak of lazurite at 549 cm^{-1} on rough sample 12 is reported.

collected exhibit several and strong bands above 1100 cm^{-1} , in addition to bands attributable to lazurite. As well as Schmidt *et al.* [17], we can identify spectra patterns for every provenance.

Namely, we could observe in Afghan spectra, shown in fig. 1, bands centred at 1021 , 1238 , 1289 , 1331 , 1430 , 1514 , 1624 , 1770 cm^{-1} in samples 19, 20, 21, 22. These bands are

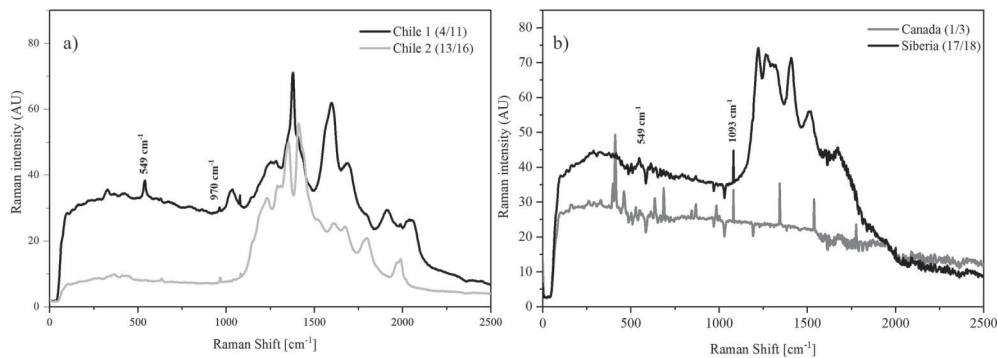


Fig. 2. – (a) Raman spectra acquired from Chilean samples. These spectra are characterized by a low Raman intensity before 1100 cm^{-1} and a band at 970 cm^{-1} . Above 1100 cm^{-1} , there are several bands between 1200 and 1400 cm^{-1} . The two samples probably differ because they were mined from two different Chilean lapis deposits. (b) Raman spectra acquired from Canadian and Siberian samples. These spectra are characterized by a low Raman intensity before 1100 cm^{-1} and a narrow band at 1093 cm^{-1} . Above 1100 cm^{-1} , there are broadbands between 1200 and 1400 cm^{-1} , in the Siberian sample. The Canadian sample spectrum is very noisy and shows several spikes.

in agreement with those observed by Schmidt [17] in their samples: a medieval manuscript whose lapis lazuli used should be from Afghanistan and an Afghan sample certified by Kremer. All the polished samples 19, 20, 21, 22 from Kremer collection (see table I) do not present a well-defined characterizing peak at 549 cm^{-1} which instead occurs in the rough sample number 12. Nevertheless, they are denoted by an accentuated curvature before 1100 cm^{-1} and a broadband at 1238 cm^{-1} . This curvilinear trend is present only in these four reference stones (samples 19, 20, 21, 22) and, as we will see later, in all the stones set in jewellery. We can therefore suppose that it is a characteristic due to the polishing of the sample.

The second spectral pattern shown in fig. 2(a) could be associated to the Chilean sample number 4/11 and 13/16. In addition to the lazurite band features at 339, 629, 1033, 1240, 1298, 1370, 1417, 1620, 1689, 1800, 1908, 1990, 2084 cm^{-1} were identified. This pattern is in agreement with the second spectral pattern proposed by Schmidt [17], with a not-so-strong intensity before 1100 cm^{-1} and several bands between 1200 and 1400 cm^{-1} . The Chile spectrum also shows an emission band centred at 970 cm^{-1} that can be referred to wollastonite, a mineral peculiar to Chilean samples [14]. The difference between the two spectra is perhaps due to the provenance from different mines in the Chilean lapis lazuli deposit but it is still a confirmation of the hypotheses of provenance advanced in our previous work for sample number 13/16 which was supposed to be a Persian lapis [16].

In fig. 2(b) spectra of Canadian (1/3) and the Siberian (17/18) samples are shown. There are some differences: Canadian spectra are characterized by a broadband at 411 cm^{-1} and narrow bands, but in general these spectra are very noisy. To the best of our knowledge, we do not have any literature source to compare to our Canadian spectral pattern. Siberian spectra present strong bands in the same region of Chilean ones but in this case, there are no isolated bands. Oustromov *et al.* [22] report that Siberian samples are generally characterized by the presence of the S_3^- and S_2^- centres which raise $549\text{--}582\text{ cm}^{-1}$ bands, but no more information about different bands are provided. In conclusion, we could appreciate a different spectral pattern for these two provenances but we do not have bibliographic sources to make a comparison.

The shown spectral features above 1100 cm^{-1} could be explained as fluorescence bands. It is proposed that they are due to an electronic mechanism that arises from the exposure to 785 nm radiation of one of the accessory mineral phases in lapis lazuli samples [17]. By analysing the data obtained with SEM-EDS, Schmidt *et al.* suggest that diopside ($\text{CaMgSi}_2\text{O}_6$) is the source of the non-lazurite features in the 785 nm Raman spectra of natural lapis lazuli. However, the observed features above 1100 cm^{-1} do not correspond to the known Raman spectrum of diopside, which typically consists of sharp bands at 323, 356, 386, 559, 666, and 1013 cm^{-1} [27]. These fluorescence bands in the 785 nm are due both to lazurite and diopside and their intensity masks the presence of diopside bands [17].

From our previous elemental analyses with XRF, carried out to observe the accessory minerals, we have observed that the samples Chile 1 (4/11), Chile 2 (13/16), Siberia (17/18) those with the bands of greatest intensity after 1100 cm^{-1} have a large amount of Ca, an element that could confirm the presence of diopside in association with Mg, which in any case was below the minimum detectable level by XRF. We also know that the Siberian (17/18) sample shows a considerable content of Fe and Sr, about an order of magnitude higher than all the other origins. Other authors [4, 7, 14] show that the high contents of Fe and Sr in the diopside are typical of Siberian lapis lazuli. This would explain the intense fluorescence after 1100 cm^{-1} of the Siberian sample. Interestingly,

not all diopside produce these strong fluorescence bands. In fact, representative Raman spectra collected from a sample of standard diopside from Canada and reported in the paper by Schmidt *et al.* [17] do not show these fluorescence bands. This suggests that the diopside found in association with lapis lazuli is not pure and contains accessory mineral phases. The absence of bands above 1100 cm^{-1} can therefore be explained by the measurement in a point without diopside. For example, the absence of the bands above 1100 cm^{-1} of the rough Afghan sample (12) could be justified by a low diopside content. Moreover, the presence of low quantities of transition metals as manganese (Mn), iron (Fe), titanium (Ti) through the excitation of their d-orbitals, may create accessible states in the lapis lazuli with no pure lazurite [17, 28]. We confirmed the presence of these transition metals in our sample with XRF analysis [16].

3.2. Classification of unknown provenance samples. – To validate our method, in the first part of our research we also analysed unknown provenance samples [16] that, thanks to the statistical analysis, were found to confirm our first provenance assumption presented in table I.

The results of collection 1 are shown in fig. 3. In fig. 3(a) we observe the Raman spectra of samples 23–24, two earrings and one of the four bracelet stones (27) that were assumed to be Siberian lapis lazuli. However, the Raman spectra obtained do not match the pattern of Siberian samples. Indeed, these spectra seem to have all the characteristics of the Afghan spectral pattern: we report three out of many characteristic bands at 1238 , 1514 , 1770 cm^{-1} . In this case, the first hypothesis seems contradicted.

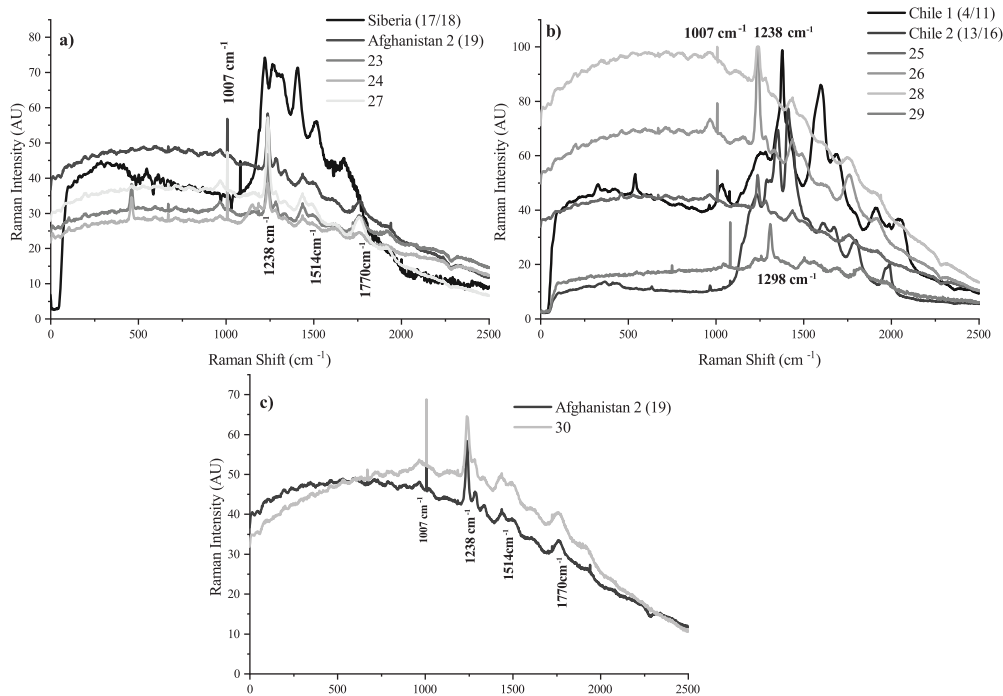


Fig. 3. – Raman spectra acquired from (a) sample 23, 24, 27 and Siberian and Afghan samples to make comparison. (b) Samples 25, 26, 28, 29 and Chilean samples to make a comparison. (c) Sample 30 and Afghan sample to make a comparison.

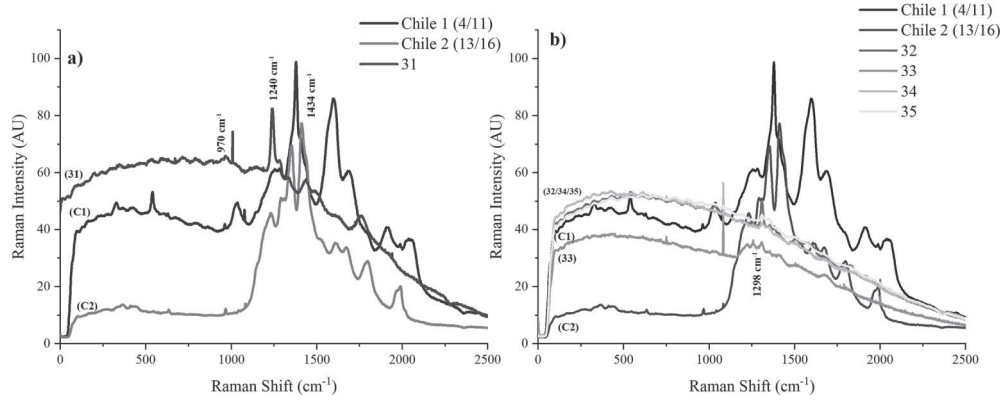


Fig. 4. – Raman spectra acquired from (a) sample 31 and Chilean samples to make a comparison, (b) samples 32, 33, 34, 35 and Chilean samples to make a comparison.

In [16] we speculated on the Chilean provenance for sample 29 and on the other stones of the bracelet (25-26-28) (fig. 3(b)). Using Raman spectroscopy only sample 29 looks like a modern Chilean lapis lazuli, indeed it shows: low intensity before 1100 cm^{-1} , and different bands between 1200 and 1400 cm^{-1} ; it also shows a peak at 1093 cm^{-1} which also occurs in the spectra of Chile 1 and a band between 1298 and 1308 cm^{-1} . The ring has a different mounting both in the geometric decoration and in the alloy, this conclusion was already discussed in our previous work [16], the results presented here reinforce the hypothesis that sample 29 was added later to complete the set. Samples 25-26-28 show an Afghan Raman spectral pattern with all the characteristics explained in sect. 3.1. The presence of the 970 cm^{-1} band is suspect, but unlike the Chilean samples, it is less narrow. The last sample of collection 1 that we describe is the brooch (30) (fig. 3(c)) which is the only one with a spectrum that confirms our previous hypothesis resulting in an Afghan lapis lazuli. Consequently, this result would assign, with the exception of the ring (sample 29), an Afghan provenance, adding value to the jewels.

Collection 2 consists of a single sample (31), a ring. Raman spectra acquired from sample 31 are shown in fig. 4(a). Through the XRF/XRL data analysis this stone reflects the characteristics of Chilean lapis lazuli, in this case, the comparison does not hold up. In more detail: sample 31 Raman spectra show a broadband at 970 cm^{-1} , a narrow band at 1007 cm^{-1} and also a band at 1240 cm^{-1} this makes us lean towards a different assignment from the Chilean one.

The provenance of the jewellery of the collection 3 seems to be confirmed by the Raman analysis. Namely, samples 32, 33, 34, 35 show a broadband at 1035 cm^{-1} and the typical Chilean lapis lazuli band at 1093 cm^{-1} . In addition, several bands arise between 1200 and 1400 cm^{-1} .

We want to point out that the curvilinear trend is present in all polished sample (19–35). Moreover, they are distinguished by the absence of a broad lazurite diagnostic band at 549 cm^{-1} .

4. – Conclusions

Raman proved to be a suitable method for the classification of provenance of lapis lazuli. Based on the Raman spectra obtained, we were able to verify the spectral pattern

for each provenance. Furthermore, Raman spectroscopy could validate our previous results, and the advantage it brings adds to those already presented and researched. It was thus possible to confirm the assignments for the samples of known provenance and to put forward hypotheses of different provenance for the stones set in the jewellery. Our method that uses the synergy between XRL, XRF, and Raman spectroscopy is therefore applicable to artefacts of interest in the field of cultural heritage as it is portable and non-invasive. However, it remains essential to analyse a greater number of reference samples, covering all possible historical and modern origins, for the creation of a useful database.

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