PETROGRAPHIC AND MINERO-CHEMICAL CHARACTERISATION OF LAPIS LAZULI: A PROVENANCE STUDY OF ROCKS AND ARTEFACTS FROM CULTURAL HERITAGE

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INTRODUCTION

Lapis lazuli is a blue semi-precious stone widely used since the ancient times; the first traces of its use date back to 7000 years ago for different purposes: beads, gems, seals and small decorative artworks were widely distributed in the Ancient East (Casanova, 2013). The remarkable value taken on during the history is proved by the large and continuous use of this rock in the ancient civilisations, although its rarity and the related difficulty to source it, due to the existence of very few quarries in which it can be found.

The Afghan mines in the Badakhshan region have been considered for long time as the only source of lapis lazuli already exploited to provide the raw material to ancient civilisation of Mesopotamia, Indus Valley and Egypt. In more recent times also other sources have been taken in consideration, mainly Tajikistan (Pamir Mountains, Lyadzhuar Dara) and Siberia (near Lake Baikal) could have possibly been exploited since antiquity, as well as other mines, at present exhausted or unknown (Hermann, 1968; Nibbi, 1981; Jarrige, 1988). Despite several scholars, in the last decades, worked on lapis lazuli, both from the historical, geological and archaeometric points of view (Delmas & Casanova, 1990; Zöldföldi *et al.*, 2006; Ballirano & Maras, 2006; Calligaro *et al*., 2011, 2014), an exhaustive provenance study is still missing.

Lapis lazuli may be either metamorphic or magmatic rock whose mineral content is characterised by widespread or localised occurrence of a blue feldspathoid, mostly lazurite, a sulphur-bearing member of the sodalite group (Hogarth & Griffin, 1976; Hassan *et al.*, 1985). Paragenesis of lapis lazuli is further composed by a wide variety of mineral phases, the most common being diopside, wollastonite, calcite, pyrite, K-feldspar, and phlogopite (Hogarth & Griffin, 1978).

This study, besides to increase the knowledge about this blue rock, could shed light on many unresolved questions, especially regarding the trade routes exploited in the ancient times. It firstly aimed at performing a systematic characterisation of rock samples of known provenance by means of a multi-technique approach, in order to create a database with the identified minero-chemical markers useful to discriminate different quarry districts. The second aim was the application of the protocol tested with the rock samples, analysing precious artefacts in non-invasive way to obtain information about the provenance of the raw material used for their realisation. The present work is part of a wide study started in 2008 (Lo Giudice *et al.,* 2009; Re *et al.*, 2011, 2013), thanks to the collaborations among different institutions: University of Torino and Firenze, and the Italian National Institute of Nuclear Physics (INFN) of Torino and Firenze. Moreover, the work obtained the support and the interest of different museums in studying their collections, in particular: the Museum of Natural History of the University of Firenze, the Regional Museum of Natural Sciences of Torino, and the two most important Egyptian museums in Italy, specifically the museums of Torino and Firenze. It is worth stressing that the multidisciplinary collaboration among the different competences involved (geologists, physicists, conservation scientists, and museum curators) has been fundamental to carry out this study and this mutual collaboration is integral part of the present work.

MATERIALS AND METHODS

To achieve the aims previously summarised, a multi-technique approach was adopted, using both invasive and non-invasive techniques, including bench-top instruments and large scale facilities: optical microscopy (OM), cold-cathodoluminescence (cold-CL), Scanning Electron Microscopy combined with Energy-dispersive X-ray spectrometry (SEM-EDX), micro X-ray Fluorescence (μ-XRF), Particle Induced X-ray Emission (μ-PIXE) and Ionoluminescence (IL). The choice of this multi-technique approach was taken, in order to perform a complete characterisation of the rock samples: the main petrographic features (texture and paragenesis), major and trace elements of specific mineral phases and their luminescence features (when present). Due to the heterogeneity and the fine grain size of this rock, as well as the need to analyse the single mineral phases to identify minero-chemical markers, μ-XRF and μ-PIXE/IL techniques have been chosen for the following reasons: the use of micro-beams (X-ray/proton) in the range 10-30 μm, the high sensitivity for trace element analysis and the possibility to carry out non-invasive analysis. Indeed, the use of non-invasive techniques is fundamental to achieve the final aim of this study, *i.e.*, the analysis of precious artefacts made in lapis lazuli, with the application of the minero-chemical markers previously identified on rock samples of known provenances.

In particular, 45 rock samples from different provenances were analysed (Table 1): Afghanistan (Badakhshan), Tajikistan (Pamir Mountains), Siberia (Lake Baikal), and Chile (Ovalle). All the samples were prepared as petrographic thin sections (ca. 100 μm thickness) and mounted on plexiglass slides to avoid possible interference of the glass holder with the excited volume of the sample. The thickness for the petrographic sections was chosen taking into account the attenuation length of X-rays according to the Henke website (http://henke.lbl.gov/optical_constants/atten2.html), and the penetration depth of the proton beam in the lapis lazuli-forming minerals.

Table 1 - Rock samples of known provenance analysed.
Each provenance is represented by a different colour that is kept to identified them in the present work

	PROVENANCE				
COLLECTION/ACQUISITION	Afghanistan (Badakhshan)	Tajikistan (Pamir Mountains)	Siberia (Lake Baikal)	Chile (Ovalle)	**TOTAL**
Museum of Natural History of Firenze	3	4	11	4	
University of Torino	18	-	-	5	
TOTAL	**21**	**4**	**11**	**9**	**45**

After an overall characterisation that allowed to obtain an overview about the microtexture and the mineralogical assemblage in the four provenances, the analyses were focused on a few single mineral phases. Systematic SEM-EDX measurements on major elements were performed on lazurite, diopside, feldspars, and phlogopite; a SEM Stereoscan 360 (Cambridge Instru-ments Ltd) equipped with a EDX Inca Energy 200 with X-Act3 SDD detector (Oxford Instruments, Tubney Woods, Abingdon, Oxfordshire OX13 5QX) was used. To integrate the compositional SEM-EDX data and, at the same time, to evaluate the presence of trace elements inside the mineral phases that could reveal markers for the provenance, μ-PIXE and μ-XRF measurements were performed. In particular, the analyses were systematically focused on diopside and pyrite crystals, providing the more useful minero-chemical markers for the provenance purposes. In addition, for diopside, also the characteristic luminescence signal was considered, thanks to μ-IL measurements performed simultaneously to μ-PIXE analyses, in order to correlate possible differences in the IL spectra to the provenance.

μ-XRF analyses of trace elements were performed with the μ-XRF Eagle III-XPL (Roentgenanalytik System GmbH & Co. KG, Taunusstein, Germany) equipped with a Rh anode (50 kV, 1 mA), polycapillary lens (variable spot size in the range 30-300 μm), a set of primary filters and an ultra-pure silicon detector.

μ-PIXE and μ-IL measurements were performed by means of different national and international facilities, depending on the general limited availability of such laboratories and based on the particular needs of the work (analysis of rock samples rather than precious artefacts). In particular: the two Italian INFN laboratories, *i.e.*, the in-vacuum microbeam line at the AN2000 accelerator of the LNL in Legnaro, Padova (Bollini *et al.*, 1993) and the external scanning microbeam facility of the Tandetron accelerator of the LABEC

Laboratory in Firenze (Giuntini *et al.*, 2007), and finally the external micro-beam line of AGLAE installed in the conservation and scientific laboratories under the Louvre museum (Pichon *et al.*, 2014).

In the second phase of the work, some archaeological artefacts and artworks have been analysed by means of the non-invasive techniques. The total number of the analysed artefacts (36) is summarised in Table 2.

Table 2. Number of artefacts analysed for each museum collection

MUSEUM COLLECTION	NUMBER OF ARTEFACTS
Museum of Natural History of Firenze	6
Regional Museum of Natural Science of Torino	5
Egyptian Museum of Firenze	10
Egyptian Museum of Torino	15

RESULTS AND DISCUSSION

Results on rocks

The main results obtained from the multi-technique characterisation of rock samples of known provenances, in order to create a database for the provenance recognition, are consecutively summarised.

The Afghan samples can be divided in two groups: one characterised by the abundant presence of K-feldspar and the other one with abundant presence of phlogopite. About trace elements, pyrite presents higher content of Ni (> 500 ppm) and diopside shows higher contents of Ti (> 3000 ppm), V (> 200 ppm), Cr (> 200 ppm) and Mn (> 900 ppm). Finally, a relatively strong band around 770 nm in the IL spectra of diopside can be present.

The samples from Tajikistan are characterised by zoned diopside with higher Na content and low amount of trace elements, allowing to suggest a metamorphic origin for lapis lazuli from this quarry district. A broad band at 690 nm in the IL spectra of diopside can be present and higher content of Cu (> 200 ppm) in pyrite was detected.

The Siberian samples are more complex, with several differences in the paragenesis, compared to the others provenances. They are characterised by the presence of iron oxyhydroxide as probable alteration products of pyrite (that is absent or relict), Ba- and Sr-feldspars, and very small crystals of barite (widespread in the groundmass of the rock). About minor and trace elements in diopside, it presents, respectively, higher amount of Fe (> 5000 ppm) and higher Sr content (> 160 ppm). Finally, the IL spectra of diopside are almost flat at wavelength above 700 nm, and most of the analysed diopside crystals are characterised by a very low or completely absent IL signal.

The Chilean samples are characterised by the widespread presence of wollastonite (absent in all the other provenances), that represents the strongest marker for the identification of this provenance, in addition to the absence of phlogopite. As regards to trace elements in pyrite, relatively high contents of Se (> 30 ppm) are observed.

The main results obtained on trace elements in diopside and pyrite are shown in Fig. 1 and Fig. 2.

To evaluate advantages and limitations of the two non-invasive techniques employed in this work, μ-XRF analyses on pyrite were compared with μ-PIXE results (Fig. 3). This study also permitted to confirm the reliability of the two databases created with the different techniques, in order to employ them in the analysis of precious or archaeological artefacts, according to the availability of the instrument and to the artefacts size (Angelici *et al.*, 2015).

The adopted multi-technique approach allowed to suggest a protocol to analyse lapis lazuli by means of both invasive and non-invasive techniques. For each provenance, at least three strong markers discriminating the different quarry districts were identified. Part of them, achievable by means of the non-invasive techniques employed in the method, has been used for the analysis of the artefacts. The choice to use non-invasive techniques was taken in order to analyse also precious artworks or archaeological findings made in lapis lazuli, since the sampling of these objects is normally not allowed. In these cases, even though the petrographic characterisation is not applicable, the use of non-invasive techniques permits to identify the stronger provenance markers, demonstrating the validity of the method also for the analysis of precious artefacts. For their study, the suggested protocol can be schematised through the flow chart shown in Fig. 4, which was applied in the present work for the analysis of different museum collections.

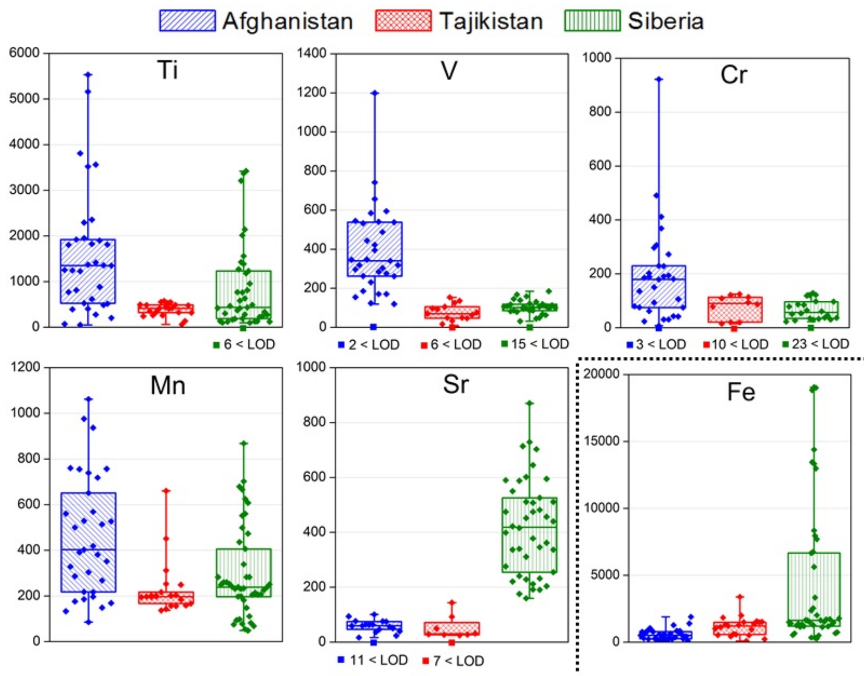

Fig. 1 - Trace and minor (Fe) elements content in diopside (expressed in ppm). Each point is an individual μ-PIXE measurement and the box charts represent the dispersion of the experimental points: the median and the two percentile values 0.25 and 0.75. The bars join the minimum and maximum values and the symbols in correspondence to zero value represent the number of measurements below the LOD (as specified at the bottom of each graph).

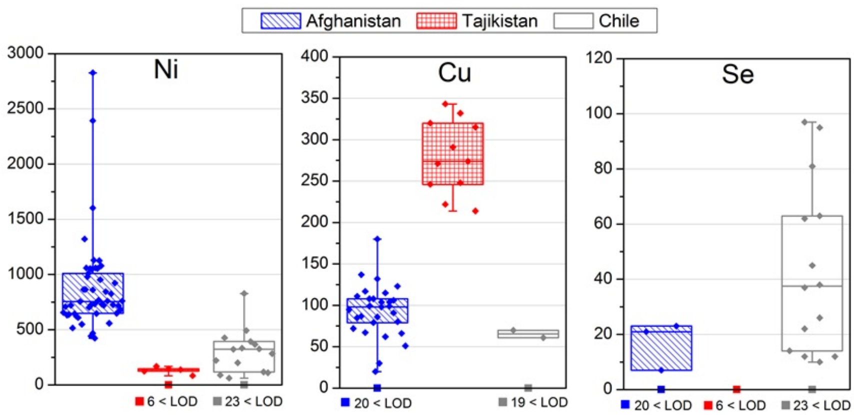

Fig. 2 - Trace elements content in pyrite (expressed in ppm). Each point is an individual μ-PIXE measurement and the box charts represent the dispersion of the experimental points: the median and the two percentile values 0.25 and 0.75. The bars join the minimum and maximum values and the symbols in correspondence to zero value represent the number of measurements below the LOD (as specified at the bottom of each graph).

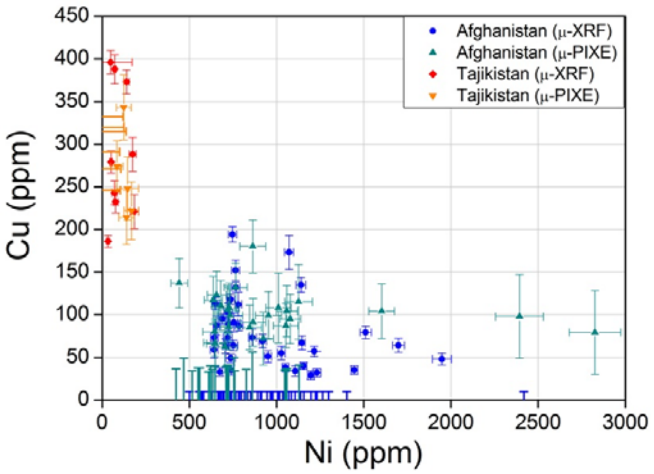

Fig. 3 - Binary graph Cu *vs.* Ni, the individual errors associated to each measurement carried out by means of both techniques are represented: the statistical error and the GUPIXWIN output (fit error) were respectively considered for μ-XRF and μ-PIXE measurements.

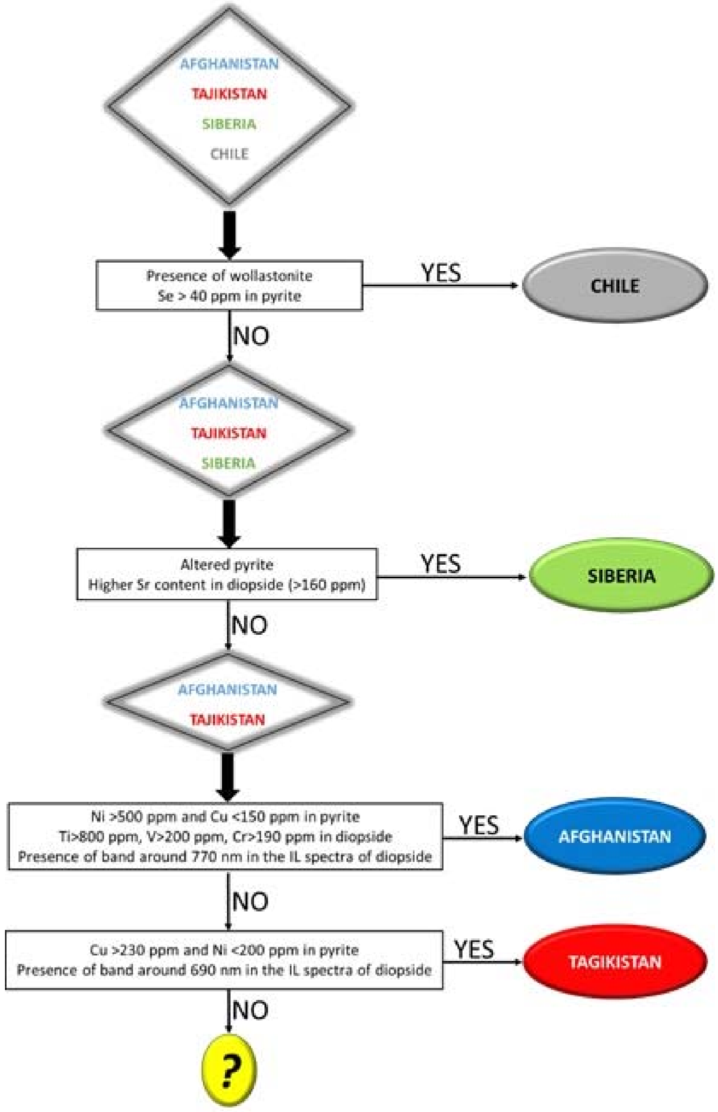

Fig. 4 - Flow chart representing the protocol adopted for the study of the artefacts.

Results on artefacts

The suggested method was initially tested on the precious artworks of the "Collezione Medicea" (XVI century) belonging to the Museum of Natural History of Firenze (Fig. 5). Since the database was not still completed (trace elements analyses on pyrite were just began), the study was exclusively focused on luminescence and trace elements content related to diopside (Re *et al.*, 2015). Nevertheless, the obtained μ-PIXE and μ-IL results were rather encouraging: in many cases, when the provenances indicated in the historical labels of the museum catalogues were vague and imprecise (very common situation in the museum collections), the analyses performed contributed to give useful indications about the possible provenance.

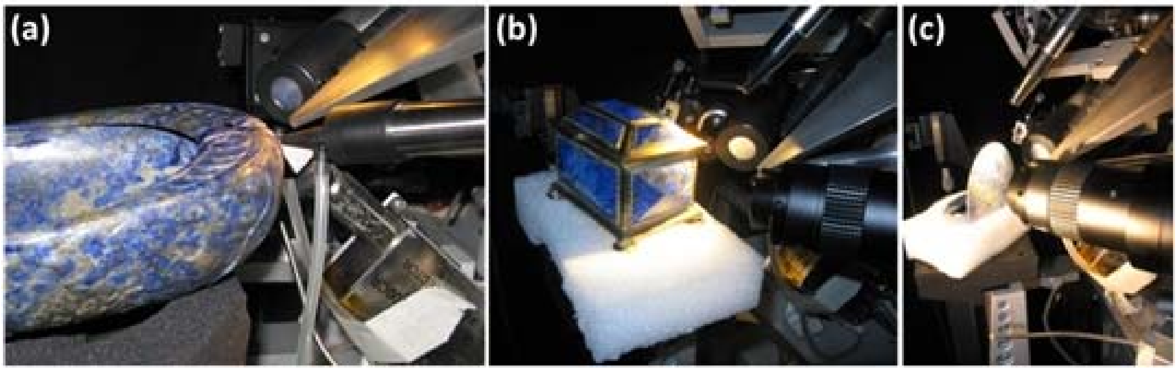

Fig. 5 - a) Oval Bowl, b) Small case, and c) Oval panel of the "Collezione Medicea" positioned for the measurements at the external micro-beam of LABEC.

Consecutively, when the complete database was available, five artefacts from the "Savoy Collection" (XIX century) of the Regional Museum of Natural Science (Torino) were studied. Since any information about the provenance of these objects were present, the integration of the data related to diopside and pyrite provided clear indication, allowing to suggest an Afghan provenance for four artefacts (Fig. 6).

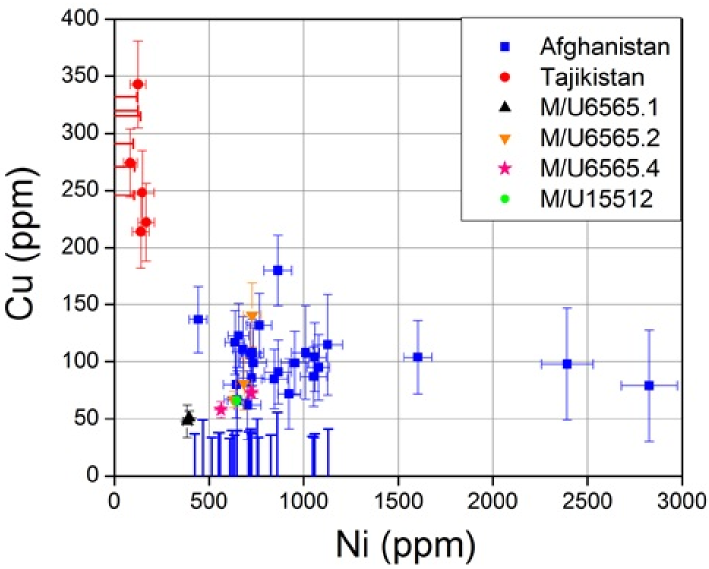

Fig. 6 - Cu *vs*. Ni contents in pyrite from μ-PIXE measurements. The individual errors associated to each measurement are plotted, whereas the values below the LOD are represented by a bar indicating the LOD value for each measurement. In different colours, the experimental data related to the "Savoy Collection" artefacts overlying to the data cluster of the Afghan samples.

For the fifth one, characterised by a relevant surface alteration, further analyses are necessary to confirm its attribution. Overall, when the identified markers are not enough to provide provenance indication, besides the variability characterising some quarry districts, also the possibility of an exploitation in the past of lapis lazuli mines now exhausted or unknown might be considered.

Finally, the same protocol was applied to the study of archaeological findings ascribable to the 1s millennium BC from the two most important Egyptian museums in Italy (Torino and Firenze). The obtained data on the Egyptian artefacts show a really good accordance with the markers identified for the Afghan provenance. In particular, trace elements in diopside (mainly Ti, V, Mn and Sr) and especially Ni and Cu contents in pyrite, are comparable to the typical concentrations detected for these elements in the rock samples from Afghanistan. It follows that, although limited to archaeological findings dated to the 1st millennium BC, first scientific evidences about the existence of a trade route connecting Mesopotamia and Egypt from ancient times, have been achieved.

CONCLUSIONS

The results obtained from this first phase of the work, characterising lapis lazuli samples of known provenance, were gathered in a database, allowing to suggest a protocol to analyse this complex rock by means of both invasive and non-invasive techniques.

For each provenance, at least three strong markers discriminating the different quarry districts were identified. Nevertheless, it is worth highlighting that to achieve better and clearer indication about the lapis lazuli provenance, the integration of analytical data related to different mineral phases is necessary.

The use of non-invasive techniques was fundamental to achieve the final aim of this study: by means of the suggested protocol, the application of the identified minero-chemical markers on the analysis of precious artworks and archaeological findings was possible. Therefore, four different museum collections (for a total of 36 artefacts) were studied: artworks ("Collezione Medicea") and specimens ("Savoy Collection") belonging to relatively recent historical periods (XVI and XIX centuries, respectively) and two collections of archaeological findings belonging to the Egyptian museums of Firenze and Torino, ascribable to the 1st millennium BC.

It is worth stressing that this work represents the first scientific study of a considerable number of Egyptian lapis lazuli artefacts, in order to support the common hypothesis of an Afghan provenance, exclusively based on archaeological evidences and ancient written sources.

The obtained data on the Egyptian artefacts show a really good accordance with the markers identified in the rock samples from Afghanistan (mainly for trace elements in pyrite). The extension of this study also on Egyptian lapis lazuli findings dated back to the 3rd millennium BC would be certainly interesting, in order to definitely confirm the long distance network of trade, as well as the wide diffusion of this rock starting from the Dynastic Period.

Similarly to the Ancient Egypt, the study might be also extended on other archaeological contexts, mainly located in the Near East, where the first evidences of the use of lapis lazuli were present and the ancient trades were developed, becoming increasingly active starting from the 3rd millennium BC. For example, the study of archaeological findings from the most ancient settlement of Mehrghar (Balochistan, Pakistan) or from the site of Shahr-i-Sokhta (Iran), in which one of the most relevant lapis lazuli findings were discovered, would help to clarify some open issues.

Primarily, the possibility to verify the provenance of the raw material, since the proximity of these settlements to the Chaghai Hills (Pakistan), *i.e.*, the geological source indicated in a few studies as a possible alternative to the Afghan one in ancient times. Moreover, the possibility to achieve the confirmation about the trade routes dynamics and diffusion of lapis lazuli in the Iranian plateau (mainly starting from the 3rd millennium BC). Specifically, the addition of such significant elements would be very helpful to reconstruct these ancient trade routes crossing a wide territory, from Mesopotamia to the Indus Valley, in order to verify the possible alternatives proposed to the most known Northern route.

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