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Lo Giudice, Alessandro; Angelici, Debora; Re, Alessandro; Gariani, Gianluca; Borghi, Alessandro; Calusi, Silvia; Giuntini, Lorenzo; Massi, Mirko; Castelli, Lisa; Taccetti, Francesco; Calligaro, Thomas; Pacheco, Claire; Lemasson, Quentin; Pichon, Laurent; Moignard, Brice; Pratesi, Giovanni; Guidotti, Maria Cristina. Protocol for lapis lazuli provenance determination: evidence for an Afghan origin of the stones used for ancient carved artefacts kept at the Egyptian Museum of Florence (Italy). ARCHAEOLOGICAL AND ANTHROPOLOGICAL SCIENCES. 9 (4) pp: 637-651.
DOI: 10.1007/s12520-016-0430-0

Protocol for lapis lazuli provenance determination: evidence for an Afghan origin of the stones used for ancient carved artefacts kept at the Egyptian Museum of Florence (Italy)

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Abstract

Despite the Badakhshan Province (Afghanistan) remains the most plausible hypothesis for the lapis lazuli used in antiquity, alternatives proposed in literature are worth to study to confirm or disprove their historical reliability. In this work a protocol for determining the provenance of lapis lazuli rocks used for carved artefacts is described. Markers for the univocal attribution of the raw material to a source were identified analysing 45 rocks of known provenance (among which 15 georeferenced) from 4 quarry districts. To the best of our knowledge, this reference database is the widest in provenance studies on lapis lazuli. All the markers are recognisable by means of Ion Beam Analysis (IBA) techniques, in particular micro-PIXE (Proton Induced X-ray Emission) and micro-IL (IonoLuminescence). These techniques are non-invasive and applicable in air, allowing to analyse artworks and rocks of practically any shape and dimension without sample preparation.

The protocol was applied to determine the provenance of raw material used for carved lapis lazuli artefacts kept at the Egyptian Museum of Florence, the second most important Egyptian museum in Italy, second only to the museum of Turin. The collection in Florence has a great historical value and includes several lapis lazuli pendants, scarabs, small statuettes and amulets ascribable mainly to the 1st millennium BC. Following the protocol, 11 of these artefacts were analysed by means of IBA techniques. Results ascribe the raw material to the Afghan quarry district.

Keywords

Lapis lazuli, Provenance, Ancient Egypt, Archaeometry, μ-PIXE, Ionoluminescence

INTRODUCTION AND BACKGROUND

Historical context

Lapis Lazuli is a very attractive semi-precious stone. Due to its peculiar blue colour and its rareness, lapis lazuli has been used since Neolithic Era for the manufacturing of precious objects and jewels (beads, gems, seals, small decorative artworks, etc). The earliest evidence of the use of lapis lazuli comes from archaeological finds in Mehrgarh (Pakistan) where ornaments in lapis lazuli have been discovered in VII millennium BC burials (Jarrige 1991). During the Chalcolithic period the number of objects made in lapis lazuli increased as confirmed by their dissemination through the Iranian plateau and the Indus Valley. The greatest success of this stone occurred in the 3rd millennium with a diffusion all over the Middle East and in part of Central and Southern Asia (current Turkmenistan, Afghanistan and Pakistan) (Casanova 2013). Lapis lazuli played a key role as precious material particularly in the Syro-Mesopotamian area, where the majority of archaeological findings of handworks made of this rock are concentrated. Moreover lapis lazuli was also cited many times along with gold, in the first-written poem, the Epic of Gilgamesh. Afterwards lapis lazuli has been continuously used until the first millennium BC, when it was gradually replaced by other synthetic materials. Nevertheless its use in glyptic, and also as pigment from VII century AD, has continued onward.

In Ancient Egypt, lapis lazuli has been used for scarabs, pendants, beads and inlaid jewels since IV millennium BC (Sofianides and Harlow, 1990), in particular many artefacts were found in Hierakonpolis and Abydos necropolis. As well as carnelian, turquoise and malachite, lapis lazuli was considered a sacred stone; in particular it was associated with the colour of the night sky. This is why many amulets and scarabs were manufactured with this and other sacred stones, although, they were often replaced by the less expensive faïence and coloured glass paste. The use of lapis lazuli did not reach in ancient Egypt a diffusion comparable with the one achieved in the Mesopotamian area, but nonetheless remains remarkable. In fact, the Tôd treasure, discovered in 1936 in Egypt (Pierrat-Bonnefois 1995), contains a huge set of ancient lapis lazuli, second only to the corpus of objects in the royal tombs of Ur. Ascribed to Amenemhat II (around 1929-1898 BC), the treasure was found in the basement of a temple dedicated to the worship of Monthu, 30 km South of Luxor. The finding includes thousands of blocks of raw lapis lazuli, minute fragments, beads and carvings. This discovery was very important because most of the objects are not of Egyptian origin, but they come from Anatolia, Mesopotamia and Iran. According to their typology, the objects are in fact distributed on a time frame of about 700 years, from the latter half of the 3rd millennium BC to the early 2nd millennium BC. Among the jewels, mostly ascribable to the second half of the 3rd millennium in Mesopotamia, there are numerous lapis lazuli amulets similar to those found in Susa and Mari (Shafer 1963). For these reasons the treasure represents a unique evidence of lapis lazuli trade among Ancient Egypt, Eastern Mediterranean and Near East civilisations.

Sources of lapis lazuli

Where do the lapis lazuli rocks used by Ancient Egyptians, and generically in antiquity, came from? Due to the low probability of geological conditions in which it can be formed only few sources of lapis lazuli exist in the world (Von Rosen 1988). For this reason, the possibility to associate the raw material to man-made objects is feasible and could help historians and archaeologists to reconstruct ancient trade routes, especially for the ancient time when written testimonies are scanty or absent at all (Tosi, 1974). Although the distance is not the only factor to be taken into account, it is logical to assume that the sources of lapis lazuli should be where the material was used in antiquity or in the neighbour regions. In the diffusion area of lapis lazuli in ancient time (VII – I millennium BC), shown in Fig. 1, the most important source of lapis lazuli, still currently exploited, is in Badakhshan Province (Afghanistan), in particular the quarry district of Sar-e-Sang. According to the archaeological evidences, the majority of the authors agree in

considering the Badakhshan Province as the only source of lapis lazuli in antiquity. This hypothesis would imply a continuous use of these quarries for nearly nine thousand years, making this area one of the oldest mining sites in the world, and a trade up to almost 4000 km already in the 4th millennium BC.

However, in addition to the Afghan quarries, other potential Asian extraction sites are known (Mindat) or hypothesised (Fig. 1). In particular Liadjura-Dara (Tajikistan), at about 200 km north-east of Sar-e-Sang, is currently the only other well documented geological source in the diffusion area of lapis lazuli in ancient time. Moreover also in the Swat Valley, in the north of Pakistan near the Afghan border and less than 200 km from Sar-e-Sang, veins of lapis lazuli are reported (Khaliq 2006). Other two well-known Asian sources of lapis lazuli are near Irkutsk, in the south region of Lake Baikal area (Siberia), and near Mogok in the Mandalay Region (Myanmar). In both cases the distance from Mesopotamia is more than 6000 km and up to almost 7000 km respectively from Egypt, nevertheless few authors did not exclude Lake Baikal area as an occasional source of lapis lazuli in antiquity (Hermann 1968).

Also the Chagai Hills district in Pakistan has been suggested as a potential lapis lazuli source in many works (Jarrige 1988; references in Law 2014); rock samples purported to be from this district have even been used in provenance studies (Delmas 1990; Casanova 1992; Ballirano 2006). The interest in this area arises from the fact that the Chagai Hills lie just 300 km west to the Mehrgarh site, about 400 km closer than Badakhshan Province. However, doubts have been expressed on the real existence of this source, that is neither documented nor supported by geological data, and it has been speculated that the lapis lazuli rock samples associated with Chagai Hills actually came from the Badakhshan quarries (Law 2008; Law 2014).

In the few previous provenance studies are also mentioned analysis on rocks from not well specified sources in “Persia” and “Levant” (Borelli 1986; Cipriani 1988), in Ural Mountains (Casanova 1992; Zöldföldi 2006), in Iran and in Pakistan (Ballirano 2006), in Russia and in Siberia (Gambardella 2016) that are not, however, well documented. This is also an issue common to many museum stone collections in which there is a lack of information about the exact provenance of the stones and only a general indication is available. In these cases it is not possible to know whether there are actually other sources of lapis lazuli or instead these rocks could be attributed to known sources. For instance Russia and Siberia rocks could be essentially attributed to the same source, i.e. the Lake Baikal area.

Finally, some lapis lazuli sources have been proposed on the basis of ancient written testimonies, but their existence has not yet been proven, in particular the Dizmar district on the border between Armenia and Iran, the Mazandaran and Kerman regions in Iran (Hermann 1968) and the Sinai Peninsula (Nibbi 1981). These sources could be related to small local quarries now depleted, or to extraction sites exploited in some historical periods and later forgotten. Some of these hypotheses are not simple to verify, taking into account that the suggested areas are often in regions of difficult access. It should also be noted that in ancient testimonies some confusion might have been done both between lapis lazuli and other blue rocks, such as azurite or turquoise, and also between extraction sites of lapis lazuli and transit/trade zones, often object of misinterpretations. This is probably the case of the Sinai source, supposed to be exploited by Ancient Egyptians, but not supported by geological data (Herrmann & Moorey 1983; Aston 2000).

As a matter of fact, a systematic and exhaustive provenance study of the raw material utilized in works of art is nowadays still lacking. Despite the origin from Badakhshan of the lapis lazuli used in antiquity remains the most plausible hypothesis, the variety of the proposed possible alternatives is worth to be studied by means of an analytical technique approach to confirm or disprove their historical reliability.

MATERIALS AND METHODS

Lapis lazuli rock and previous provenance studies

Lapis lazuli is generically classified as a metamorphic rock, even if this definition could not be considered exhaustive, due to the complexity of mechanism involved in its genesis. It is characterised by the presence of the mineral lazurite (giving the blue colour to the rock), combined with other types of minerals which presence and relative amount varies from and within quarries. Among these there are: hauyne, sodalite, nosean, K-feldspars, Na-feldspars, anortite, mica group minerals like phlogopite, monoclinic pyroxenes like diopside, wollastonite, nepheline, titanite, apatite group minerals, calcite, dolomite and pyrite. Considering all the existent quarries, more than 30 mineral phases in lapis lazuli rocks have been reported so far in literature.

The question about the provenance of lapis lazuli used in ancient time was investigated by means of different kinds of analysis techniques, comparing physico-chemical properties of rocks of known provenance with archaeological finds. An example are the studies carried out on the collection of the Museum of Mineralogy of Florence (Borelli 1986; Cipriani 1988) including both 22 rocks from 4 provenances (Badakhshan, Lake Baikal, Chile and Italy) and objects of the Medici Family (XV century AD). Moreover, another work was made by Delmas and Casanova (Delmas 1990; Casanova 1992). Using analytical techniques, they compared 21 rocks from 4 sources (Badakhshan, Pamir Mountains, Chagai Hills and Urals Mountains) with lapis lazuli waste products mainly found in the archaeological site of Shahr-i-Sokhta (III millennium BC) in the southeastern part of Iran. Another investigation by means of micro-destructive techniques was made by Ballirano (Ballirano 2006) who analysed pigments used in the Sistina Chapel by Michelangelo comparing the results with those obtained on 10 rocks from 4 provenances (Badakhshan, Chagai Hills, Pakistan and Iran). Moreover (Favaro 2012) analysed 9 rocks from 3 provenances (Afghanistan, Siberia and Chile) comparing results with ultramarine blue pigments. Finally a very interesting work was recently made by Law (Law 2014) that compared 18 rocks (Afghanistan, Chagai Hills, Myanmar and Lake Baikal) with 7 artefacts from 6 different archaeological sites in the Indo-Iranian area.

About the use of non-invasive techniques it has to be cited the studies of (Zöldföldi 2006) carried out on 37 rocks from 4 provenances (Badakhshan, Lake Baikal, Chile, Ural Mountains) and (Gambardella 2016) on 34 rock samples from 7 sources (Afghanistan, Chile, Siberia, USA, Tajikistan, Iran and Myanmar). Finally, Calligaro (Calligaro 2011; Calligaro 2014) is the only one that studied artefacts from Ancient Egypt, comparing 11 objects from Tôd treasure with 8 rocks from 4 provenances (the Badakhshan province of Afghanistan, the Pamir Mountains in Tajikistan, the borders of Lake Baïkal in Russia and the Coquimbo region in Chile).

In many of these works, when comparisons between ancient artefacts and rocks were carried out, it was found a match not only with Afghanistan, but also with Chagai Hills, Pamir and Ural Mountains. Although the results of these studies are innovative and interesting, it should be noted that in many cases either the number of analysed rocks and/or objects is not enough to be representative. In these cases the proposed markers and the provenance results should be confirmed extending the measurements over a larger number of samples, both rocks and artefacts. Moreover the used techniques are sometimes invasive and not applicable to precious objects. Finally it is to remember the difficulty in the availability of rocks of referenced provenance, also in museums collections. Consequently the results showing a similarity amongst lapis lazuli from different sources, for example Chagai Hills and Afghanistan (Law 2014), could be attributed not to an effective exploitation of various quarries, but instead to a wrong attribution of the provenance of the reference lapis lazuli rocks. For all these reasons, until now the studies in this field are not-conclusive and the question of the determination of lapis lazuli origin by means of an analytical approach still presents some unresolved issues.

Protocol for lapis lazuli provenance determination

To solve the issue we started in 2008 a long-term research, involving an interdisciplinary team. Until now, 45 lapis lazuli rocks of known provenance from 4 quarry districts have been analysed, creating a database that, to the best of our knowledge, is probably the widest in provenance studies on this material. Our database is composed by: 21 samples from Badakhshan in Afghanistan, 4 samples from Liadjura-Dara, Pamir Mountains in Tajikistan, 11 samples from Lake Baikal area in Siberia (4 from Malaya Bistraya quarries and 7 from Sludyanka River quarries) and 9 samples from Coquimbo region in Chile. Samples from Tajikistan and Siberia are georeferenced, i.e. GPS coordinates are known. In the case of Lake Baikal a geological expedition was organised by the authors to collect samples from two quarries in the area (Malaya Bistraya and Sludyanka River) considering that the mines are no longer exploited and it is difficult to find rocks of recorded provenance. More details about the analysed samples can be found in our previous studies (Lo Giudice 2009; Re 2011; Re 2013; Angelici 2015; Re 2015).

Although obviously not suitable as a source of lapis lazuli for Ancient Egypt, the Chilean provenance was considered because the quarries are currently exploited and lapis lazuli samples from this provenance area are easy to find. Moreover results could be useful in future studies because there are hypotheses about a utilization of this rock by pre-Columbian civilisations (Da Cunha 1989).

It is interesting to observe that the study of lapis lazuli from all the known quarry districts and the identification of univocal markers can be useful to help in the identification of fakes and forgeries (Craddock 2009).

Due to the heterogeneity of lapis lazuli, instead of searching markers in the whole stone, we mostly focused our attention in searching minero-chemical markers inside single mineral phases. Since the crystals dimensions can vary from fraction of a micron to hundreds of microns, we decided to use mainly microscopic techniques (optical microscopy, scanning electron microscopy coupled with microanalysis, ion beam analyses and others, as explained in the section: experimental set-up and measurements), which allow us to observe and to analyse one specific crystal, avoiding the contribution from the neighbouring ones. We looked for the presence or the absence of a mineral phase, minor/trace elements inside a peculiar mineral, and the different luminescence of the same mineral. In particular for a high number of crystals, chemical analyses were carried out on two mineral phases that demonstrated to be suitable as markers: diopside ($CaMgSi_2O_6$) and pyrite (FeS_2). The significant statistics (more than 94 diopside crystals and 80 pyrite crystals were analysed) for these mineral phases, contributed to take in account the variability in trace elements also within the same sample. Even if other techniques have been used for these studies (i.e. Optical and Raman Microscopy, X-ray Fluorescence, Scanning Electron Microscopy with Microanalysis, Cathodoluminescence) it was verified that all the markers found are simultaneously detectable by means of ion beam techniques, in particular μ-PIXE (Proton Induce X-ray Emission) and μ-IL (IonoLuminescence) (Calusi 2008; Re 2011; Lo Giudice 2012). Besides, these techniques are non-invasive and applicable in air, allowing to analyse artworks and rocks of practically any shape and dimension without sample preparation (Re 2015). We also demonstrated the possibility to use μ-XRF (X-Ray Fluorescence) analysis to found markers based on trace elements with outcomes similar to those obtained by μ-PIXE (Angelici 2015).

In Fig. 2 the protocol used to associate a lapis lazuli rock to one of the four provenances we studied until now is summarised. In the main block diagram, only “strong markers” were taken into account, which means physical-chemical features that are systematically present or absent in all the 45 analysed samples. Moreover, for Chilean and Afghan samples also other “weaker marker” are shown, that are features very frequent for these lapis lazuli quarry districts but not observed in all the samples.

The Chilean lapis lazuli are the easiest to distinguish due to the widespread presence of wollastonite ($CaSiO_3$), which was observed in all the analysed rock samples. Wollastonite can be recognised acquiring in a few seconds the ionoluminescence spectrum (Calusi 2008; Lo Giudice 2009; Re 2015; Czelusniak 2016). In fact lapis lazuli from all provenances have a strong prevalent white-yellowish ionoluminescence, visible to the naked eyes, that is due to wollastonite in Chilean samples (IL spectra have a double broad bands at 560 nm and 620 nm) and to diopside in Asian samples (IL spectra centred at 580 nm). In addition Chile is the only provenance in which selenium is present in amount higher than 40 ppm in pyrite crystals (Re 2013). However, this quantity is not always reached and this marker is to be considered weaker than the presence of wollastonite. Samples from Siberia are the only ones characterised by iron oxide-hydroxide minerals pseudomorphosed after pyrite, only sometimes occurring as relict, and a strontium content higher than about 180 ppm in diopside crystals (Re 2013; Re 2015). Instead, idiomorphic pyrite crystals are well preserved in lapis lazuli from Tajikistan and from Afghanistan. The trace elements analysis on pyrite crystals seems to be the best way to distinguish Tajikistan from Afghanistan provenance (Re 2013). In fact in samples from Afghanistan, pyrite crystals contain sensible contents of nickel (more than about 330 ppm) and low quantity of copper (below 240 ppm). Moreover only diopside crystals of the Afghan samples show higher quantity of titanium (> 710 ppm) or vanadium (>210 ppm) or chromium (>220 ppm) than Tajik samples (Re 2015) or a strong ionoluminescence band at about 770 nm. It is to be stressed that although all the rock samples analysed until now have been successfully associated to one of the four sources of lapis lazuli by means of this protocol, increasing the number of analysed samples all the quantities in ppm proposed as lower or upper limits for a provenance may have to be modified (due to the natural heterogeneity of each quarry district).

Recently the first part of the protocol was successfully applied on precious artefacts from the Medici Collection kept in the Museum of Natural History of Florence (Re 2015).

Analysed objects from Egyptian Museum of Florence

The 11 lapis lazuli carved objects analysed in this work belong to the collection of the Egyptian Museum of Florence. It is the second most important Egyptian museum in Italy, second only to the museum of Turin. The very first nucleus of antiquities was already settled in Florence during the 18th century. During the 19th century, this original core of pieces was implemented by others acquisitions; the promoter was Leopold II, Grand Duke of Tuscany in the period from 1824 to 1859. He bought some new collections of artworks and artefacts and together with Charles X of France he funded an archaeological expedition in Egypt, the so called Franco-Tuscan expedition (1828-1829). The expedition was directed by the French Jean François Champollion and the Italian Ippolito Rosellini, considered pioneers of Egyptology. In 1882, the Egyptian Museum was officially established in the present seat and Ernesto Schiaparelli was appointed to direct the museum. Under his direction the museum implemented the collections thanks to two excavation campaigns and numerous acquisitions until 1894, when the Egyptologist became the director of the Egyptian Museum of Turin. The collection in Florence has a great historical value and includes also several precious carved amulets made in lapis lazuli (pendants, small statues, scarabs and amulets), which are ascribable mainly to the 1st millennium BC, considering stylistic features and iconography.

The artefacts analysed in this work belong to different acquisitions (Tab. 1): two amulets are part of the finding of the Franco-Tuscan expedition (1828-1829), a scarab was acquired in the Theban Necropolis during the first Schiaparelli expedition (1884-1885) and other two objects come from the original Grand-Ducal Collections. A group of four objects results from acquisition and private collector donations to the museum: Valle de Paz (1868, donation), Nardi (1885, purchase) and the more recent Wilson-Barker (1948, donation). The djed amulet does not belong to a definite

acquisition, but certainly it is part of the finding of the Franco-Tuscan expedition or of the Gran-Ducal Collections. Finally one of the wdjat eyes is of unknown acquisition.

In addition to the different acquisition modalities, the analysed objects were selected also on the basis of their iconography and archaeological significance (Guidotti 2015). Among the selected artefacts there are two precious scarabs (cat. 1275 and cat. 6524). In Ancient Egypt scarabs were used as seals or for funerary purposes on the mummies; this is the case of the Florence Museum objects. In particular the first scarab (cat. 1275) has a small hole in the backside probably used for hanging or to sew it on the mummy, whereas the second scarab (cat. 6524) is a hearth scarab that was placed on the mummy in correspondence of the heart of the departed to make it lighter in the judgment of Osiris that every soul had to face in order to enter the afterlife. The second scarab presents a fragmented backside, probably because it was originally part of a pectoral. Another analysed funerary object is a djed pillar (cat. 1361); it represented solidity and durability and it was placed in many parts of the mummy, mainly on the throat. Moreover, three objects are a representation of gods. The first (cat. 179) is an amulet representing the Maat Goddess (Schiaparelli 1887), the personification of truth and justice and embodying the cosmic order. Maat amulets, almost always made in lapis lazuli, were placed mainly on the mummy chest. Also in this case there is a small hole on the back. The second (cat. 64) is a head of the Goddess Hathor that was originally part of a fairly rare small statue, both in terms of iconography and for the material quality. In fact, the lapis lazuli used appears different in term of colour from that used for other artefacts. The third artefact (cat. 10316) is a stylized representation of Bes, God protector of households, pregnant women and infants. Also in this case lapis lazuli appears to be different because it is poor in lazurite and considerable of lower quality. Finally five wdjat eye amulets (cat. 1644, cat. 3914, cat. 7298, cat. 10284 and cat. 1600) were analysed. This kind of amulets was very common and widespread in Ancient Egypt and represents the eye of the God Horus, symbol of protection and integrity (Guidotti 2013).

Experimental set-up and measurements

As previously observed, all the markers are detectable by means of Ion Beam Analysis, in particular μ-PIXE (Proton Induce X-ray Emission) and μ-IL (IonoLuminescence), non-invasive techniques applicable in air without sample preparation and that allow analysing artworks and rocks of almost any shape and dimension.

Ion Beam Analyses were performed at two external scanning micro-beam facilities: the INFN LABEC Laboratory in Florence (Giuntini 2015-1; Giuntini 2015-2; Giuntini 2007; Calusi 2011) and the AGLAE facility at the C2RMF in Paris (Calligaro 2000; Pichon 2014). In both cases, μ-PIXE and μ-IL analysis on Ancient Egyptian objects were performed in air, without any preparation and using 3 MeV proton beam (Fig. 3). At INFN LABEC laboratory the beam was about 20 μm wide and a 150 pA current was used on selected areas of 1×1 mm^2. At AGLAE the beam was about 30 μm wide and a current of about 500 pA was used on selected areas of 1.5×1.5 mm^2.

As required by the described protocol for lapis lazuli attribution, elemental quantitative analyses by means of μ-PIXE were carried out on pyrite and diopside crystals. To find these minerals and considering the impossibility to perform preliminary invasive analysis on artefacts, the first step was a survey of all the samples by means of optical imaging and microscopy. This approach was sufficient to identify candidate pyrite crystals and white areas characteristic of diopside. Concerning pyrite crystals, μ-PIXE mapping were performed to verify the presence of iron and sulphur as main elements and to select the more homogeneous part of the crystals for quantitative analysis, as shown in Fig. 4. Instead, diopside crystals were found not only by means of μ-PIXE mapping, but also exploiting the strong luminescence properties of this mineral that exhibit a strong emission at about 580 nm. In particular the broad beam IL microscopy

apparatus was used at INFN LABEC (Lo Giudice 2012; Re 2015) and μ-IL mapping at AGLAE (Pichon 2015-1). Also in this case μ-PIXE maps were used to select the more homogeneous part of the crystals for quantitative analysis. Moreover, to avoid possible systematic errors and to ensure the reliability of the results, during all measurement sessions a number of previously analysed pyrite and diopside crystals in lapis lazuli from Afghanistan and Tajikistan rocks were measured and used as references.

The micro-PIXE spectra obtained at INFN LABEC were quantitatively analysed by means of GUPIXWIN (version 2.2.3) (Campbell 2010) using a set of reference standards: a soda-lime container from NIST and thick pure elements from Goodfellow Cambridge Ltd. Instead, at AGLAE, the elemental quantification was subsequently obtained using the TRAUPIXE program (Pichon 2015-2) with the pivot procedure normalisation between major and trace concentrations. This program is based upon the same GUPIXWIN version with processing parameters adjusted using the Dr-N (Diorite) geostandard.

RESULTS AND DISCUSSION

In accordance with the protocol summarised in Fig. 2 the first step for all the samples was the identification of wollastonite or diopside as one of the main mineral phases. As expected all Egyptian objects show a prevalent ionoluminescence centred at 580 nm, a feature characteristic of diopside that is present in all the studied rocks of Asian provenance (Calusi 2008, Lo Giudice 2009, Re 2015). Fig. 5 shows some of the IL spectra collected in correspondence of strong luminescent crystals, which were confirmed to be diopside by means of μ-PIXE elemental analysis. The absence of wollastonite excludes the Chilean provenance for all samples, a result that was expected (due to the objects typology and their historical period), but nonetheless important, as it is a further proof of the reliability of the method to recognise Chilean samples.

The second step of the protocol was the measurement of strontium contents in the diopside crystals and the composition of iron-based inclusions. In fact for all of the Siberian samples, i.e. from the Lake Baikal region both from Sludyanka River and Malaya Bistraya River districts, pyrite crystals present an altered form. In particular they are characterised by the presence of iron oxide-hydroxide minerals (probable alteration products of pyrite), presenting an intensive compositional zoning in which sulphur-free zones prevail (Re 2013, Angelici 2015). Only in rare cases, very small pyrite crystals (below about 30 μm) show unaltered aspect with neither oxidised margins nor core zones. For the Egyptian objects studied in this work the majority of the mapped pyrite crystals (more than 20) are well preserved and stoichiometrically corresponding to FeS_2, a feature characteristic of Tajikistan and Afghanistan rocks; in many cases, as in Fig. 4, crystals are very large, up to 0.5 mm^2, and are easily visible to the naked eyes. In Siberian rocks such features were never observed. It is interesting to observe that various pyrite crystals in Egyptian artefacts have a certain degree of chemical weathering: this is an oxidation process of pyrite where the first reaction products going in solution are ferrous iron and sulphate (Blowes 2003). The process is a superficial one, in accordance with the analysed objects, probably subject to burial, percolating waters and humidity. In Fig. 4 are visible small areas and veins inside the pyrite crystal that show a loss of sulphur due to this kind of degradation. The level of degradation is heterogeneous: in fact in the same object are present both unaltered pyrite crystals and others almost completely altered. A microscopy image of a strong chemical weathered pyrite crystal in an Egyptian artefact (sample Cat.10284) is shown in Fig. 6. It is very similar to what observed in a previous work on Tôd treasure (Calligaro 2014), where oxidation turned pyrite in brown/red stained grains, involving adjacent areas in the process. In the case of Tôd treasure, this phenomenon was mainly observed on the surface of the artefacts. A limited or absent chemical weathering was instead observed in the inner part of the cut samples. On the contrary finding altered pyrite crystals is a feature of all the Siberian rocks,

observed even in fresh cut samples, and it is related to hydrothermal processes during the petrogenesis (Re 2013; Angelici 2015).

Also the second strong marker excluding the Siberian provenance confirms the initial attribution. Actually, the strontium content in diopside crystals of all Siberian rocks in the database were always higher than 160±40 ppm, with a maximum of 870±30 ppm and a median of the distribution at about 420 ppm (Re 2015), while, the maximum strontium content measured in diopside crystals was 90±40 and 140±20 ppm in Afghan and Tajik rocks respectively. Diopside crystals in Egyptian objects suitable for trace elements analysis were identified by means of ionoluminescence maps and on the basis of stoichiometry in order to avoid spurious signal from other phases, as we limited the analyses only to the crystals for which the stoichiometry was coincident within experimental errors to what expected for this mineral phase. In particular 18 points of interest were selected on 8 out of 11 Egyptian objects; the measured strontium and other trace elements concentrations useful for provenances study are reported in Tab. 2. When possible, for every object more than one diopside crystal was analysed to take in account the variability in trace elements within the same sample. In Fig. 7 are also shown the box charts of the same values of Tab. 2 in comparison with rocks from our database (Re 2015). The box charts represent the dispersion of the experimental points: each point is an individual μ-PIXE measurement, the boxes include 50% of analysed points (from 25 to 75%) and are separated in two parts by the median line, while the bars join the maximum and the minimum detected value. In this representation (called box and whisker plot), error bars are not reported to make the graphics more readable. The square symbols in correspondence to the 0 value represent the numbers of measurements below the limit of detection (LOD). As shown in Tab. 2 and Fig. 7, 5 out of the 8 analysed Egyptian objects show a Sr content in diopside in the same range of Afghan and Tajikistan rocks, all other objects being also compatible within 2σ. Such results seem to exclude a Siberian provenance of the Egyptian artefacts, although it should be observed that the data distribution is slightly different from that expected for Afghan and Tajik samples. In particular there are 4 analysed diopside crystals (i.e. 20% of analysed points) that have a Sr contents between 160 ppm and 200 ppm, slightly higher than observed for these two provenances. Discrepancies could be due to the limited number of Afghan reference rocks in our database. Although 21 samples are a sufficient starting point to attribute raw materials to a provenance, in the future the analysis of further rocks could broad the boundary values found so far because of the natural heterogeneity of the extraction sites. Moreover it should be noted that all the samples used for our database were collected in the last century and although the proposed markers are characteristic for all the rocks of a district, small differences for quarries in the same area were observed. These differences are not discussed here, but could be useful in future studies to distinguish among extraction sites in the same district and perhaps to identify the location of ancient quarries. About the other trace elements interesting for provenance study in diopside crystals (Re 2015), it must be observed that almost all the 90 values in Tab. 2 are in the range expected for Afghan and Tajik rocks and only 2 data related to manganese are outside (which means about 2.2% of the total). Moreover, it is interesting to observe that although the head of the Hathor Goddess (cat. 64) and the Bes God amulet (cat. 10316) are compatible with an Afghan or Tajik provenance, they seem to be slightly different from other objects due to the very low contents of all trace elements in diopside crystals. As in the case of strontium, this could be explained with a difference in the extraction site inside the same district. As already stated, the lapis lazuli used for these artefacts appears different in term of colour from those used for the other artefacts, in particular the Bes God amulet (cat. 10316) is poor in lazurite and with a considerable low quality.

The third step of the protocol was the analysis of trace elements in pyrite crystals, in particular nickel and copper, which appear the most effective fingerprint to distinguish Afghan samples from Tajik samples. In Tab. 3 a summary of the results on 13 pyrite crystals selected on 6 Egyptian objects is reported. When possible, for each object more than one

pyrite crystal was analysed to take into account the variability of trace elements within the same sample. In the other 5 objects, the analysed pyrite crystals were not stoichiometric, due to chemical weathering, therefore they were not suitable for a reliable quantitative analysis. In Fig. 8 the box charts of Cu and Ni show a good match of Egyptian artefacts and Afghan rocks from our database (Re 2013; Angelici 2015). To better observe the differences between Afghan and Tajik rocks and the results on Egyptian artefacts, Cu versus Ni contents in pyrite crystals are shown in Fig. 9 (values below the LOD, which is around 100 ppm for Ni and 50 ppm for Cu, are represented on the axes). Moreover, as expected, in all the pyrite crystals selenium was below LOD, which is a further proof of the validity of the method to recognise Chilean samples.

Finally in six Egyptian artefacts also the marker related to titanium contents in diopside is compatible with an Afghan provenance of the lapis lazuli, i.e. greater than 710 ppm. It must be observed that almost all the 90 values in Tab. 2 are in the range expected for Afghan rocks and only 4 data related to manganese an iron are outside (which means about <5% of the total).

Summarising, on the basis of the results, the raw material used to carve 9 of the 11 lapis lazuli artefacts analysed in this work can be ascribed to an Afghan provenance. For the other 2 objects (cat. 10316 and cat. 64) a Siberian provenance is excluded. They are compatible with an Afghan or Tajik provenance but it is not possible to distinguish among them because the analysis on the pyrite crystals were not carried out and the measurements of trace element contents in diopside crystals was not sufficient alone.

CONCLUSIONS

In this work a protocol for determining the provenance of raw material used to carve lapis lazuli artefacts is described. Markers were obtained analysing 45 rocks of known provenance from 4 quarry districts: Badakhshan in Afghanistan, Liadjura-Dara in Tajikistan, Lake Baikal area in Siberia and Coquimbo region in Chile. To the best of our knowledge, for every provenance, the number of studied rocks is equal or higher than in any previous provenance study on lapis lazuli. The created database constitutes a sufficient starting point to attribute raw materials to a provenance, although in future its representativeness must be further augmented to increase the markers reliability or to revise them. Moreover the database must be extended to rocks from other quarry districts. An important point is that all the markers are recognisable by means of Ion Beam Analysis. These techniques are non-invasive and applicable in air, allowing to analyse precious artworks and rocks of almost any shape and dimension without sample preparation.

The protocol was applied to determine the provenance of raw material used for 11 carved lapis lazuli artefacts kept at the Egyptian Museum of Florence. Analysed objects are scarabs, amulets and small statues, mainly ascribable to the 1st millennium BC, considering stylistic features and iconography. For 9 objects an Afghan provenance was deduced. The other 2 artefacts are compatible both with Afghan and Tajik provenances and it is not possible to distinguish between them, because the analysis on pyrite crystals was not yet carried out. It is interesting to observe some differences in distribution of trace element contents in diopside crystals in comparison to referenced rocks. This information could be related to the natural heterogeneity of the extraction sites and it could be useful in future studies to distinguish amongst different quarries in the same district.

Although the results of this work must be strengthened by increasing the number and the archaeological representativeness of the analysed artefacts, the scientific prove of the presence of Afghan lapis lazuli in Ancient Egypt is a further confirmation of trading of this stone up to 4000 km from its extraction site in the first millennium BC, excluding the possibility of other local sources exploited in ancient time, as it has long been supposed by the majority of archaeologists.

ACKNOWLEDGEMENTS

Financial support by the Transnational Access to Research Infrastructures activity in the 7th Framework Program of the EU (CHARISMA Grant Agreement n. 228330) is gratefully acknowledged. The authors warmly thank all the people participating and contributing to this provenance study during the last years.

The authors wish to warmly thank CHNet, the INFN network of laboratories working in the Cultural Heritage field, for supporting this research, both in terms of instrumentation, competencies and grants. Moreover, the INFN experiment CHNet-imaging is acknowledged with gratitude.

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TABLE CAPTIONS

Table 1. Objects from the Egyptian Museum of Florence analysed in this work. For each object catalogue number, short description, dimensions, historical period and acquisition are indicated.

Table 2. Trace elements (expressed in ppm) in diopside crystals in lapis lazuli Egyptian artefacts; each line is one point of analysis (i.e. one diopside crystal) and when an element is under the limit of detection (LOD) it is indicated with < LOD.

Table 3. Trace elements (expressed in ppm) in pyrite crystals in lapis lazuli Egyptian artefacts; each line is one point of analysis (i.e. one pyrite crystal) and when an element is under the limit of detection (LOD) it is indicated with < LOD.

FIGURE CAPTIONS

Fig. 1. Map of the approximately diffusion area of lapis lazuli in ancient time (IV-I millennium BC). The blue squares are documented quarries, the orange circle are hypothetical sources whose existence has not been proven, the yellow triangle is the first documented site where lapis lazuli was used (Mehrgarh, VII millennium BC).

Fig. 2. Schematic diagram of the protocol we propose to identify the provenance of lapis lazuli by means of non-invasive techniques (in our case μ-PIXE and Ionoluminescence).

Fig. 3. Measurement set-up at the AGLAE (C2RMF in Paris) and the LABEC (INFN in Florence) laboratories during analysis of the hearth scarab Cat. 6524 and the wdjat eye Cat. 1600 respectively.

Fig. 4. Procedure for μ-PIXE analysis of pyrite crystals (hearth scarab Cat. 6524): (a) and (b) identification of a candidate pyrite crystal by means of optical imaging and microscopy, (c) μ-PIXE maps of some elements in the selected area (about 1mm × 1mm). μ-PIXE spectra for quantitative analysis were collected in the more homogeneous part of the pyrite (white box).

Fig. 5. Some of the IL spectra of diopside crystals acquired from the analysed samples. A representative spectrum is shown for each object. The main feature is the characteristic peak centred at 580 nm, common to all the spectra.

Fig. 6. Optical image of a strong chemical weathered pyrite crystal in an Ancient Egyptian artefact (Cat. 10284)

Fig. 7. Trace element contents in diopside crystals (in ppm): comparison between Egyptian artefacts and rocks from our database (Re 2015). The square symbols in correspondence to 0 value represent the numbers of measurements below the limit of detection (LOD).

Fig. 8. Ni and Cu contents in pyrite crystals (in ppm): comparison between Egyptian artefacts and rocks from our database (Re 2013, Angelici 2015). The square symbols in correspondence to 0 value represent the numbers of measurements below the limit of detection (LOD), that is around 100 ppm for Ni and 50 ppm for Cu.

Fig. 9. Cu versus Ni contents in pyrite crystals from μ-PIXE measurements. The individual errors associated with each measurement are plotted, whereas the values below the limit of detection (LOD around 100 ppm for Ni and 50 ppm for Cu) are represented on the axes.

	**Catalogue Number: 64** Statue head: Hathor Goddess Dimension: ~ 3 cm x 2,3 cm Period: Late (VII-IV century BC) Acquisition: Grand-Ducal Collections
	**Catalogue Number: 179** Amulet: Maat Goddess Dimension: ~ 2,5 cm x 1,1 cm Period: Late (VII-IV century BC) Acquisition: Egypt, Franco-Tuscan Expedition 1828-1829
	**Catalogue Number: 1275** Amulet: scarab Dimension: ~ 2,1 cm x 1,5 cm Period: Late (VII-IV century BC) Acquisition: Grand-Ducal Collections
	**Catalogue Number: 1361** Amulet: djed pillar Dimension: ~ 2,6 cm x 1 cm Period: unknown Acquisition: Franco-Tuscan Expedition 1828-1829 or Grand-Ducal Collections
	**Catalogue Number: 1600** Amulet: wdjat Eye Dimension: ~ 4,7 cm x 5,6 cm Period: 3th Intermediate - Late (X-IV century BC) Acquisition: Egypt, unknown
	**Catalogue Number: 1644** Amulet: wdjat eye Dimension: ~ 1,5 cm x 1,8 cm Period: 3th Intermediate - Late (X-IV century BC) Acquisition: Egypt, Franco-Tuscan Expedition 1828-1829
	**Catalogue Number: 3914** Rectangular plate, wdjat eye Dimension: ~ 1,4 cm x 1.,7 cm Period: Late (VII-IV century BC) Acquisition: donation, Valle de Paz 1868
	**Catalogue Number: 6524** Hearth Scarab Dimension: ~ 5,3 cm x 3,4 cm Period: Late (VII-IV century BC) Acquisition: Egypt, Thebes (necropolis), first Schiaparelli Expedition 1884-1885
	**Catalogue Number: 7298** Amulet: wdjat eye Dimension: ~ 1,5 cm x 1,7 cm Period: New Kingdom – Late Period (XVI-IV century BC) Acquisition: purchase, Nardi 1885
	**Catalogue Number: 10284** Rectangular plate, wdjat eye Dimension: ~ 2,3 cm x 2,4 cm Period: Late (VII-IV century BC) Acquisition: donation Wilson-Barker 1948
	**Catalogue Number: 10316** Amulet: Bes God Dimension: ~ 2,4 cm x 1,2 cm Period: New Kingdom – Late Period (XVI-IV century BC) Acquisition: donation Wilson-Barker 1948

Table 1

Cat.	Object	Ti	V	Cr	Mn	Sr	Fe
64	Statue head: Hathor Goddess	60 ± 20 60 ± 20 30 ± 10	90 ± 10 110 ± 10 90 ± 10	< 15 < 13 < 12	280 ± 10 320 ± 10 290 ± 10	40 ± 20 18 ± 10 30 ± 10	380 ± 10 410 ± 20 180 ± 10
179	Amulet: Maat Goddess	1200 ± 60	330 ± 40	140 ± 20	1140 ± 40	80 ± 50	540 ± 30
1275	Amulet: scarab	2290 ± 60 2430 ± 80	190 ± 30 210 ± 30	100 ± 20 70 ± 10	920 ± 30 960 ± 40	200 ± 50 90 ± 30	870 ± 30 380 ± 20
1644	Amulet: wdjat Eye	2680 ± 130 2600 ± 80 2580 ± 80 1360 ± 40	220 ± 40 210 ± 30 210 ± 30 180 ± 20	110 ± 20 90 ± 10 110 ± 20 120 ± 10	840 ± 50 810 ± 30 750 ± 30 960 ± 30	190 ± 70 60 ± 20 110 ± 40 190 ± 30	320 ± 30 340 ± 20 3210 ± 80 470 ± 20
3914	Amulet: wdjat Eye	2900 ± 70 2340 ± 50	170 ± 30 250 ± 30	110 ± 20 120 ± 10	780 ± 30 780 ± 20	160 ± 40 100 ± 30	2670 ± 40 780 ± 20
7298	Amulet: wdjat Eye	2350 ± 70 1900 ± 60	200 ± 20 200 ± 20	80 ± 10 80 ± 10	610 ± 20 640 ± 20	110 ± 20 70 ± 20	270 ± 10 330 ± 20
10284	Amulet: wdjat Eye	1090 ± 40 1000 ± 40	200 ± 20 240 ± 20	50 ± 10 90 ± 10	1790 ± 50 1810 ± 40	70 ± 20 90 ± 20	810 ± 30 1440 ± 40
10316	Amulet: Bes God	300 ± 20 340 ± 20	120 ± 10 90 ± 10	< 13 < 11	230 ± 10 290 ± 10	120 ± 20 40 ± 10	610 ± 10 820 ± 20

Table 2

Cat.	Object	Ni	Cu
1275	Amulet: scarab	790 ± 50 740 ± 50	110 ± 30 130 ± 30
1361	Amulet: djed pillar	600 ± 30	120 ± 20
1600	Amulet: wdjat Eye	1000 ± 200 970 ± 110	< 35 80 ± 20
1644	Amulet: wdjat Eye	660 ± 50 600 ± 160	140 ± 30 100 ± 30
3914	Amulet: wdjat Eye	690 ± 40 650 ± 60	100 ± 20 150 ± 40
6524	Hearth Scarab	620 ± 20 680 ± 30 590 ± 120 560 ± 110	100 ± 10 150 ± 10 150 ± 20 < 30

Table 3


LAKE BAIKAL (SIBERIA)
MOGOK (MYANMAR)
DIZMAR
MAZANDARAN
MESOPOTAMIA
IRANIAN PLATEAU
LIADJURA-DARA (TAJIKISTAN)
BADAKHSHAN (AFGHANISTAN)
SWAT VALLEY (PAKISTAN)
SINAI
EGYPT
KERMAN
MEHRGARH
CHAGAI HILLS
INDUS VALLEY
200 km

FIG. 1

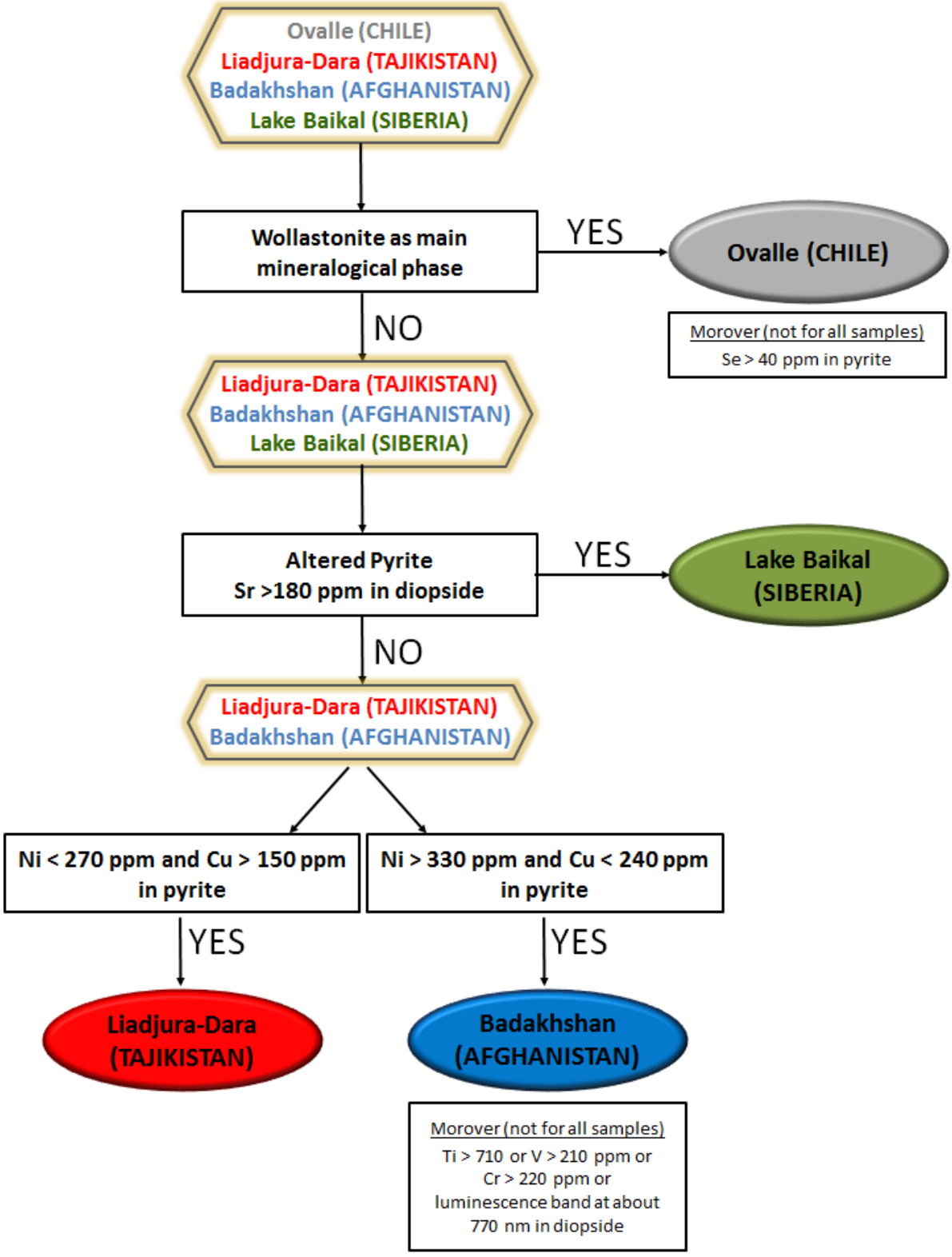
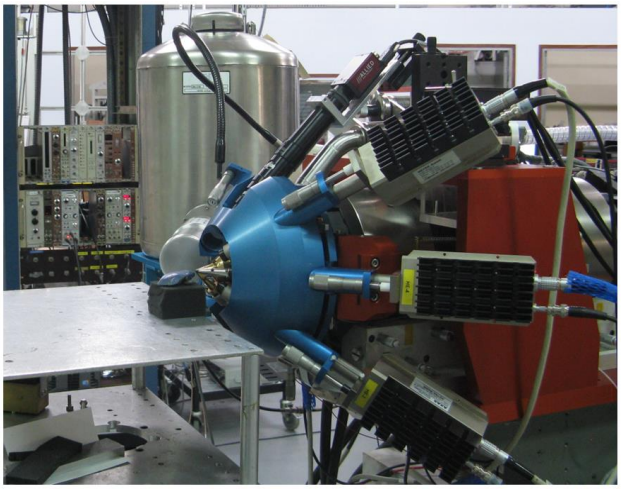

Ovalle (CHILE)
Liadjura-Dara (TAJIKISTAN)
Badakhshan (AFGHANISTAN)
Lake Baikal (SIBERIA)
Wollastonite as main mineralogical phase
YES
Ovalle (CHILE)
Morover (not for all samples)
Se > 40 ppm in pyrite
NO
Liadjura-Dara (TAJIKISTAN)
Badakhshan (AFGHANISTAN)
Lake Baikal (SIBERIA)
Altered Pyrite
Sr >180 ppm in diopside
YES
Lake Baikal (SIBERIA)
NO
Liadjura-Dara (TAJIKISTAN)
Badakhshan (AFGHANISTAN)
Ni < 270 ppm and Cu > 150 ppm in pyrite
Ni > 330 ppm and Cu < 240 ppm in pyrite
YES
YES
Liadjura-Dara (TAJIKISTAN)
Badakhshan (AFGHANISTAN)
Morover (not for all samples)
Ti > 710 or V > 210 ppm or
Cr > 220 ppm or
luminescence band at about
770 nm in diopside

FIG. 2



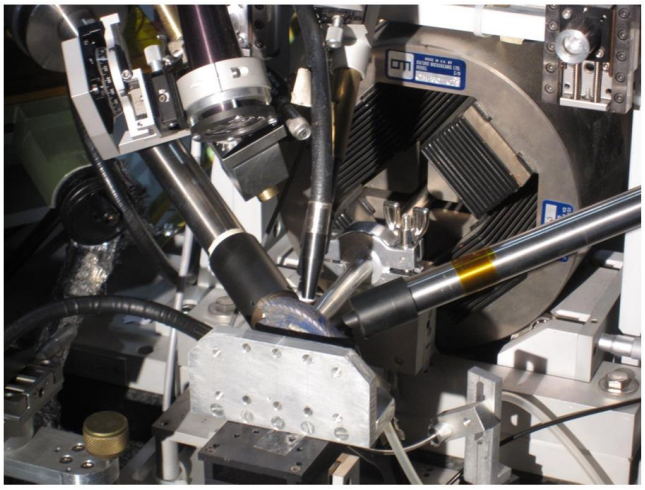


FIG. 3

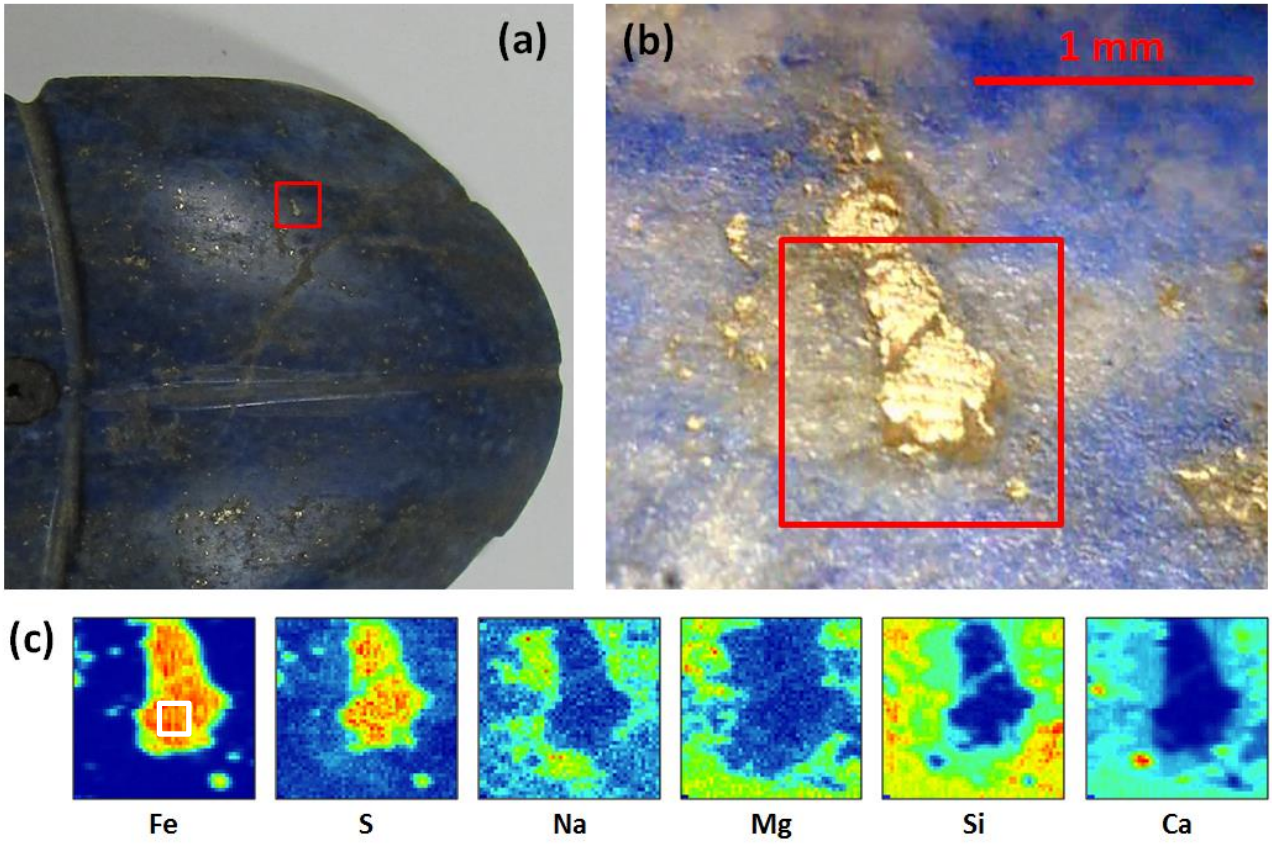


FIG. 4

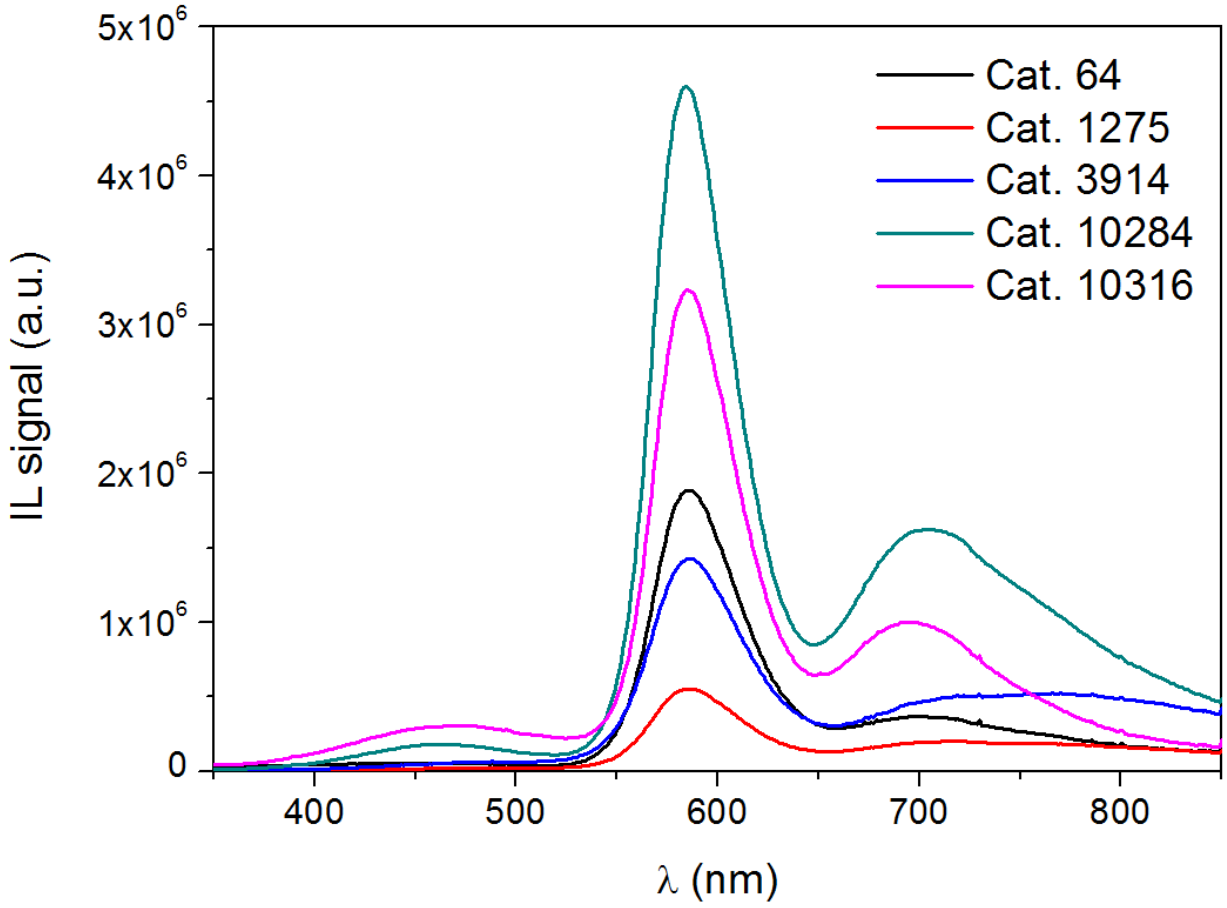

5x10^6
4x10^6
3x10^6
2x10^6
1x10^6
0
IL signal (a.u.)
400
500
600
700
800
λ (nm)
Cat. 64
Cat. 1275
Cat. 3914
Cat. 10284
Cat. 10316

FIG. 5

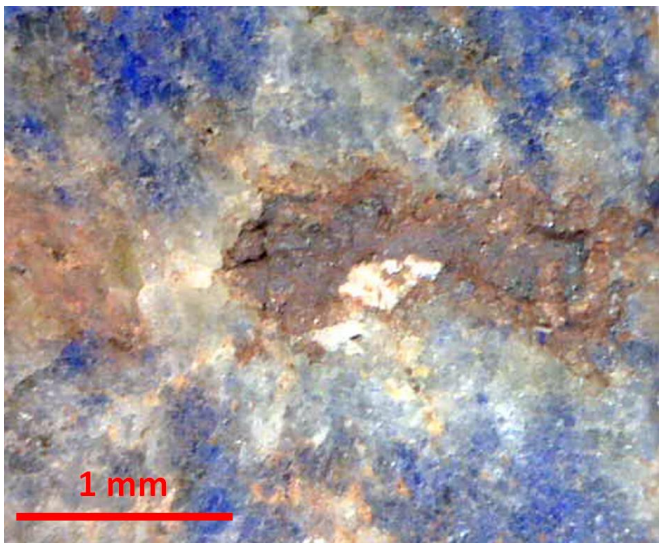


FIG. 6

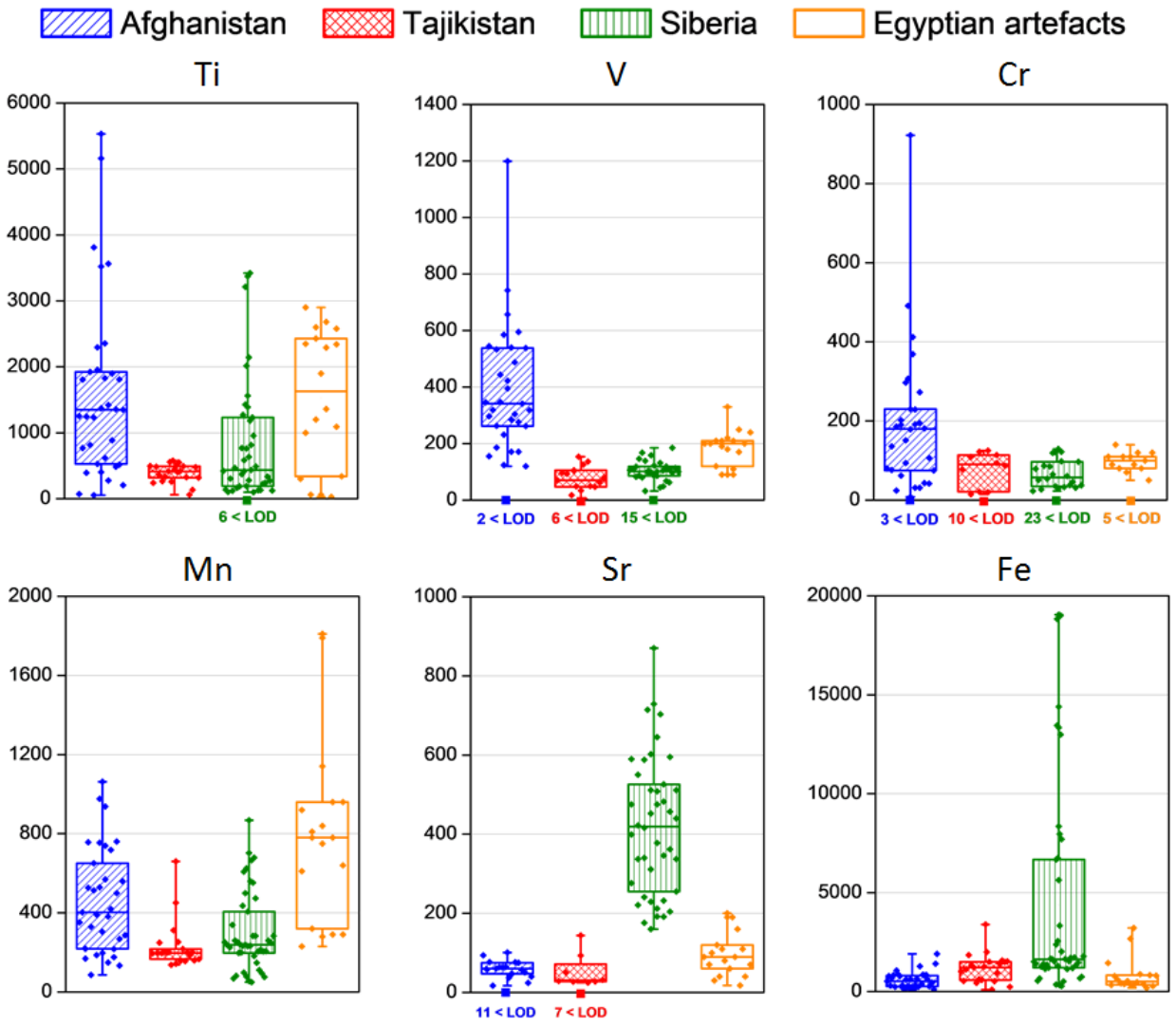

Afghanistan
Tajikistan
Siberia
Egyptian artefacts
Ti
6000
5000
4000
3000
2000
1000
0
6 < LOD
V
1400
1200
1000
800
600
400
200
0
2 < LOD
6 < LOD
15 < LOD
Cr
1000
800
600
400
200
0
3 < LOD
10 < LOD
23 < LOD
5 < LOD
Mn
2000
1600
1200
800
400
0
Sr
1000
800
600
400
200
0
11 < LOD
7 < LOD
Fe
20000
15000
10000
5000
0

FIG. 7

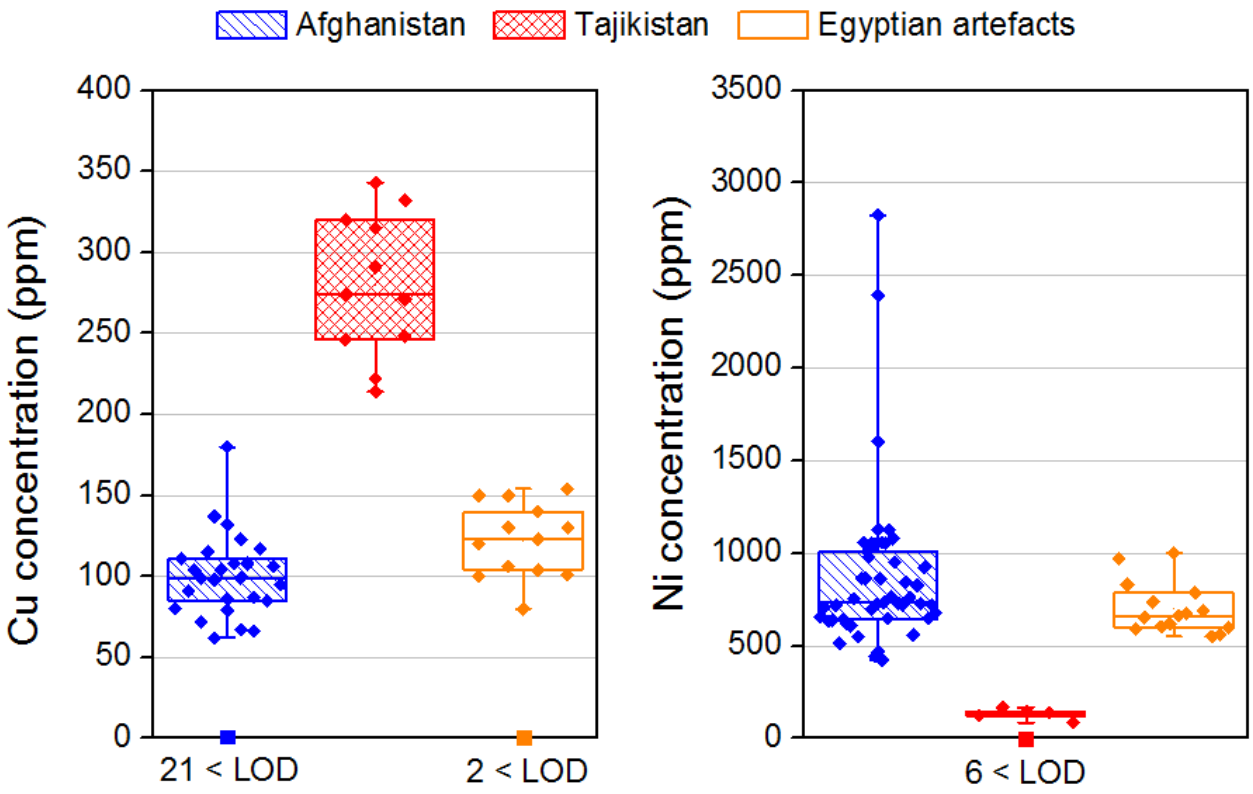

Afghanistan
Tajikistan
Egyptian artefacts
Cu concentration (ppm)
400
350
300
250
200
150
100
50
0
21 < LOD
2 < LOD
Ni concentration (ppm)
3500
3000
2500
2000
1500
1000
500
0
6 < LOD

FIG. 8

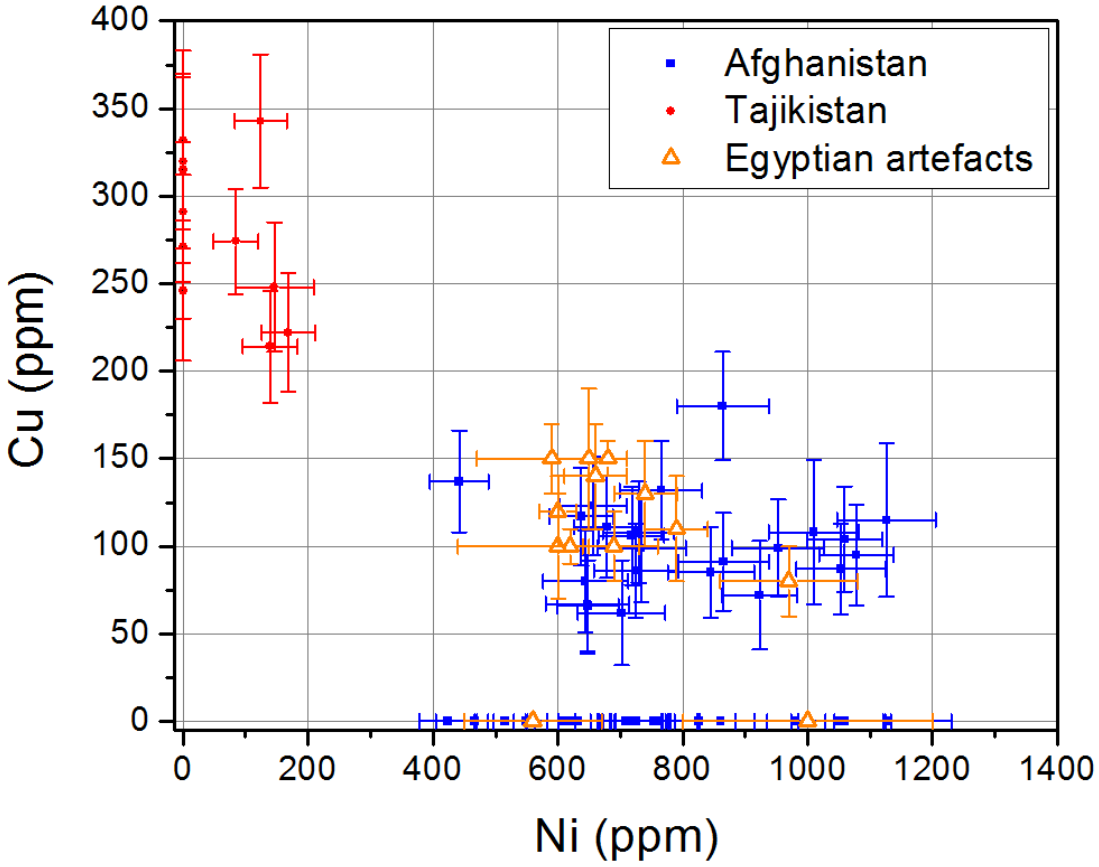

Afghanistan
Tajikistan
Egyptian artefacts
Cu (ppm)
Ni (ppm)
0
50
100
150
200
250
300
350
400
0
200
400
600
800
1000
1200
1400

FIG. 9