

Characteristic Features of Lapis Lazuli from Different Provenances, Revised by μ XRF, ESEM, PGAA and PIXE

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Abstract: The objective of this study is to find out, to what extent the geochemical characteristics of lapis lazuli can be utilized in respect to its provenance. A wide range of variables is taken into consideration depending on the quantity of samples analysed from a specific geological region and the methods applied. In order to provide evidence, a multi-technique analytical approach using μ XRF, ESEM, PGAA and PIXE is applied to samples from the most famous deposits of lapis lazuli. Special elements determined as fingerprints are compared in relation to the forming conditions obvious in textural features. The results and statistical output allow a differentiation that enables an optimized local classification of the blue stone. An absolute requirement for all geo-tracing performed on blue colored cultural objects of unknown provenance is awareness of the limits of analysis. The possible sources of lapis lazuli are tested by analysing the blue pigment used as paint on murals and ink on manuscripts from the Silk Road.

Key words: Lapis lazuli, micro-XRF, ESEM, PGAA, PIXE, pigment analyses, provenance studies.

1. Introduction

The most interesting question concerning culturally used lapis lazuli is becoming familiar with where it was mined [1]. It has been analysed in many ways to trace the blue pigment. Possible distinguishing marks are determined to characterize the original sources of the blue color applied on archaeological objects.

The chemical structure, composition of elements and mineral phases of lapis lazuli, blue paint and lazurite extracted from purified blue stone or synthetic ultramarine are investigated.

Research is performed with the characteristic features of luminescence spectra obtained by Raman-, IR-, UV- or VIS-spectroscopy [2]. Raman-spectroscopy is combined with Fourier

transform infrared (FTIR)-, nuclear magnetic resonance (NMR)- [3] or Laser induced plasma spectroscopy (LIPS) and principle elemental analysis (PCA) [4]. The natural pigment is identified herewith due to associated minerals like calcite, diopside, wollastonite and pyrite in contrast to artificial ultramarine. The distinction of natural from synthetic lapis lazuli is completed by X-ray diffraction or polarized light microscopy including grain size determination of Ca-compounds, or in combination with energy dispersive X-ray spectroscopy (EDX) and environmental scanning electron microscopy (ESEM) applied to samples of paint [5].

Characterization of both, the deposits of lapis lazuli due to minerals and elemental fingerprints and special elements in an associated phase, is done with, μ -X-ray fluorescence analysis (μ -XRF) [6] or ion-luminescence (IL), cathode-luminescence (CL) and particle induced X-ray emission (PIXE) [7]. The bulk composition of

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few cm³ sample can be done by Prompt Gamma Activation Analysis (PGAA) [8].

Lapis lazuli from Afghanistan and Tajikistan is distinguished from that of Siberia, which contains the minerals diopside and wollastonite but hardly any pyrite. Determination of the trace elements Cu, Ni and Se in the pyrite associated with the lapis lazuli of Afghanistan, Tajikistan/Pamir and Chile but not that of Siberia has been discovered as a possibility for geosourcing [9]. Chilean lapis lazuli is distinguished by the presence of wollastonite as the main mineral phase [10-12]. Trace elements in the diopside almost always associated, identified with FTIR- and Raman-spectroscopy combined with scanning electron microscopy (SEM-EDX) and other methods, show differences [13].

Based on S, Cl and Fe content of the bulk lapis lazuli, samples of different geological origins can be discriminated [8]. So far, around 100 lapis lazuli samples from Afghanistan, Ural, Chile and the Baikal region have been analysed by PGAA.

On the other hand, Ti, V and Cr especially are claimed to be significant in diopside from Afghanistan, whereas Ba is present in inclusions of lapis lazuli from Siberia [14].

In regard to the elements Ba, As and Sr, a differentiation of the blue stone is determined and confirmed with atomic absorption spectroscopy (AAS). A different composition of the associated mineral phases in paint prepared with Afghan lapis lazuli in comparison to Siberian and Chilean samples has been identified by energy dispersive X-ray spectroscopy (EDS) or Fourier transform infrared spectroscopy (FTIR) and statistical principal component analysis (PCA) [15, 16].

Mineralogical identification by polarization microscopy or X-ray diffraction and chemical identification by spectroscopic methods such as VIS-, Raman-, FTIR-, NMR-spectroscopy [17], etc. demonstrate special features for the characterization of

different natural and artificial sources. During the course of investigation, results were revised and new approaches turned out to be essentially important. More samples of the most important blue mineral pigment are analysed and compared in this study to check the factors applied in distinguishing deposits and verifying special chemical compositions.

2. Materials and Methods

Lapis Lazuli characteristic for a regional mine is chosen from geological collections of the following institutions: Federal Institute for Geosciences and Resources, Berlin; Museum of Natural History, Berlin; TU Berlin; TU Freiberg; TU München; Mineralogical Museum University Hamburg; TU Dresden; Senckenberg collections of Natural History Dresden; Museum National d'Histoire Naturelle Paris and Natural History Museum London. The samples (18) from different sources include blue sodalite (Table 1). They vary in coloration from light to dark blue and contain different whitish or brownish mineral phases. The exact locality of the provided samples cannot always be stated such as a mine in Tibet? and assignment sometimes has to be estimated, such as Buchara/Uzbekistan being identical to the label Bokhara/Turkestan due to political changes. The exploitation of mines in this region has a long tradition covering an extended area reaching the Hindu Kush Himalayan province Badakhshan that now belongs to Afghanistan and Tajikistan. Some blue stones labelled without specification of a certain provenance and even without label are also tested for fitting.

Only one sample of lapis lazuli from the Americas is added to confirm the difference from the other blue stones used for tracing Asian artefacts. The pigment is common along the Silk Road in wall paint and blue ink for decorative writing. Samples for case studies including fragments of manuscripts written in Manichaean and Sogdian and of a mural from a cave in Kizil were obtained from the Berlin Turfan collection.

Table 1 Lapis lazuli samples of different natural provenances.

Lapis lazuli	L_01	Uzbekistan	Buchara?
Lapis lazuli	L_02	Siberia	Lake Baikal
Lapis lazuli	L_03		Lake Baikal
Lapis lazuli	L_04	Afghanistan	
Lapis lazuli	L_05	Tibet?	
Lapis lazuli?	L_06	unknown?	
Lapis lazuli	L_07		Lake Baikal
Lapis lazuli	L_08	Uzbekistan	Boukharie = Bukhara
Lapis lazuli	L_09	Turkistan	Bokha'ra
Lapis lazuli	L_10	Russia	Lake Baikal
Lapis lazuli	L_11	Russia	Lake Baikal
Lapis lazuli	L_12	Russia	Lake Baikal area, Irkutskaya Oblast', Prebaikalia (Pribaikal'e), East-Siberia
Lapis lazuli	L_13	Russia	Lake Baikal area, Irkutskaya Oblast', Prebaikalia (Pribaikal'e), East-Siberia, Slyudyanka (Sludyanka)
Lapis lazuli	L_14	Afghanistan	Robat Haut Koktcha Badakhshan
Lapis lazuli	L_15	Afghanistan	Sar-e-Sang District, Koksha Valley (Kokscha; Kokcha), Badakhshan (Badakhshan; Badahsan) Province
Lapis lazuli	L_16	Afghanistan	Sar-e-Sang mine, Badakhshan
Lapis lazuli	L_17	Afghanistan	Sar-e-Sang mine, Badakhshan
Sodalite	L_18	Bolivia	

2.1 Experimental Setup

Lapis lazuli is analysed as it came from the collections and not as purified stone or extracted as lazurite or hauyne, the phases responsible for the blue color. Energy dispersive X-ray-analysis (EDX of EDAX/XL 30 ESEM of FEI) is applied to determine both the composition of the blue stone, minerals and elements of associated phases as well as the grain size, texture and crystallinity, which depend on the regional conditions of their formation in nature. Different surface morphologies indicate distinct stone typologies.

X-ray fluorescence analysis (XRF) is performed with the mobile ARTAX (Bruker Nano GmbH), which is especially suited for the application of pigment analysis to artefacts [18], and determination of characteristic elemental compositions of the color blue. The μ -XRF spectrometer is equipped with a molybdenum X-ray tube and polycapillary X-ray optics. The X-ray tube is set at 45 kV and 600 μ A. The X-ray beam is 70 μ m in diameter. Spectra are collected in a line scan of 2.25 mm for 90 s live time with 15 measurement points. The integrated CCD camera with

a laser diode allows the exact positioning of the distance of the primary radiation and the area to be measured in a magnification of 20 \times (Table 2).

Prompt Gamma Activation Analysis has been performed at the PGAA and NIPS-NORMA facilities of the Budapest Neutron Centre. The Budapest PGAA and NIPS-NORMA facilities are described by Szentmiklósi and Kis [19, 20]. The quantitative analysis with PGAA is based on the k_0 -method, described by Révay [21].

The external beam milli-PIXE measurements were performed at the 5 MV van de Graaff accelerator of the Institute of Particle and Nuclear Physics, Wigner Research Centre of the Hungarian Academy of Sciences [22]. The proton beam of 2.5 MeV energy was collimated and extracted from the evacuated beam pipe to air through a 7.5 μ m thick Kapton foil. External beam currents within the range of 1-10 nA were generally used, depending on the target objects. The objects for analysis were fixed on a computer-controlled 3D positioning stage allowing accurate sample positioning. A target-window distance of 10 mm was chosen at which distance the beam diameter was found to be about 1 mm. X-ray spectra were

collected by using a computer controlled Amptek X-123 spectrometer with an SDD type detector of $25 \text{ mm}^2 \times 500 \text{ }\mu\text{m}$ active volume and $8 \text{ }\mu\text{m}$ thick Be window. The detector with an energy resolution of 130 eV for the Mn K α line was positioned at 135° with respect to the beam direction. The target-detector distance was 25 mm. Two absorbers, $100 \text{ }\mu\text{m}$ thick aluminum, or $60 \text{ }\mu\text{m}$ thick polycarbonate, were applied to attenuate the X-rays at the energy of the major matrix elements resulting higher sensitivity and lower detection limit for the trace elements. The net X-ray peak intensities and concentrations were calculated subsequently with the GUPIX program package [23].

The results provided by the various complementary methods allow a comparison with samples of unknown assignment that are expected to match with a geological source or artificial preparation.

3. Experimental Results

3.1 Lapis Lazuli

To check elements in the samples of lapis lazuli relevant for tracing, results detected by XRF and EDX are compiled (Table 2). For this purpose Na-Ca-Si-Al-S (Cl, K, Fe) corresponding to the blue mineral phase lazurite of the sodalite group with the idealized chemical composition $[(\text{Na}_3\text{Ca}(\text{Si}_3\text{Al}_3)\text{O}_{12}\text{S}) + \text{NaCl} + \text{K}_2\text{O} + \text{FeS}_2]$ is excluded.

Listed are additional elements, common but not necessarily present in lapis lazuli. Contributed from host rocks, they may be incorporated in the metasomatically formed heterogenic solid solution series of sodalities or in associated mineral phases. Those indicated by bold characters are discussed as possible markers to distinguish lapis lazuli from different sources.

Common for the metamorphic formation of lapis lazuli in tectonically disturbed regions is a porphyritic texture with larger fragmented crystals in a fine-grained matrix. The textures of our samples of the blue stone from one region change from clastic with

different grain size to metasomatically solved (Afghan and Baikal samples with uranium L_12, L_16, Baikal samples L_3, L_7, L_10). Larger sized crystallites (Baikal L_11) or a more compact (Afghan samples L_4, L_15, Lake Baikal L_13) and homogeneous grain size (Afghan L_14, Uzbekistan L_1, L_8) indicate, furthermore, different forming conditions with inconstant rates of cooling.


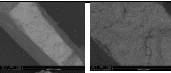





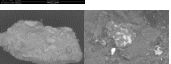





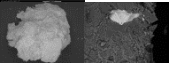

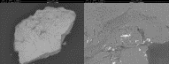

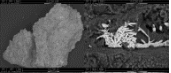

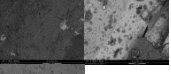



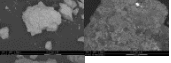



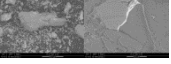

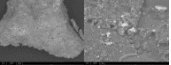

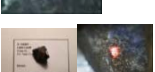


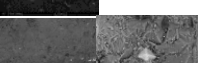
Some elements are observed within a special texture. Bound in a more compact structure is the high amount of Pb (L_4) in Afghanistan indicating constant forming conditions. Most of the samples show a metasomatic structure due to secondary forming at a low temperature ($100\text{-}200 \text{ }^\circ\text{C}$) and pressure, for example with solved Hg- or As-compounds in a clastic texture (L_3, L_7, L_10, L_12, L_16). Compounds of Se and Cr clearly show crystals grown as new mineralization on the surface (Baikal L_2 with Se and unknown? L_6 with Cr) (Table 2).

It is obvious that samples of a regional assignment show more than one metasomatic stage with primary or secondary mineralization under different conditions. Therefore, this criterion alone turns out to be not truly suited for a local characterization.

The elemental composition, especially metal ions of metamorphic skarn deposits, is considerable [24] and not always the same, so it may be regarded as significant for the lapis lazuli of a special locality.

In Afghan lapis lazuli Ti, Cr, Ni, Cu, Zn, As, Pb are mostly identified, with exception of elements as U (L_16) or Ba (L_4). There is no suggestion in the literature of U in lapis lazuli, which is detected in our samples with EDX. A similar presence of elements is detected in the samples from the Baikal region with exception of Se (L_2 as a new crystallization, L_10), and U, which here occurs together with Th (L_12). The presence of Th (the decay product of U) in Baikal lapis lazuli may indicate that the blue stone is geologically older here [25] and formed between lower Cambrian and Precambrian shields of the region. U is detected furthermore in sample L_1 from Uzbekistan. In the

Table 2 Texture and chemical composition of the blue stones.

	Labelled provenance	Blue stone XRF	Texture SEM EDX	Elements EDX and XRF [except Na-Ca-Si-Al-S(Cl,K,Fe)]
L_4	Afghanistan			Na-Mg- Ba-Ti -Mn-Ni-Cu- Pb -Zn-Rb-Sr
L_14	Afghanistan, Robat Haut Koktcha valley, Badakhshan			Na-Mg-Cr-Mn-Ni-Cu-As-Sr
L_15	Afghanistan, Sar-e-Sang District, Koksha valley, Badakhshan			Na-Mg-Cr-Mn-Ni-Cu-Zn-As-Sr
L_16	Afghanistan, Sar-e-Sang mine Badakhshan			F-Na-Mg- P-Ti -Cr-Mn- Cu-Zn-As-U -Br-Rb-Sr
L_17	Afghanistan Sar-e-Sang mine Badakhshan			Ti-Cr-Mn-Ni-Cu-Zn-As-Rb-Sr
L_1	Uzbekistan (Buchara?)			Mg-Ti-Cr-Mn- Zn-As-U -Sr
L_8	Uzbekistan (Buchara?)			Cr-Mn-Ni-Cu-As-Rb-Sr
L_9	Turkistan (Bok'hara)			Cl -Cr-Mn-Co- Br -Sr
L_2	Siberia Lake Baikal			Mg-Ti- Cr -Mn-Ni-Cu-Zn- As-Se -Rb-Sr
L_3	Lake Baikal			Mg-Ti-Cr-Mn- Ni-Cu-Zn-Pb-As -Sr
L_7	Lake Baikal			Mg-Ti-Cr-Mn- Cu-Zn-Hg -As-Rb-Sr
L_10	Lake Baikal			Ti-Cr-Mn-Cu- As-Se -Sr
L_11	Lake Baikal			Ti-Cr-Mn-Cu-Zn-As-Br-Rb-Sr
L_12	Eastern-Siberia Lake Baikal, Irkutskaya Oblast', Prebaikalia			Ti-Cr-Mn- Ni-Cu-As-Th-U -Br-Sr
L_13	Eastern-Siberia, Lake Baikal, Irkutskaya Oblast', Prebaikalia, Slyudyanka			Ti-Cr-Mn- Ni-Cu-Zn-As-Pb -Rb-Sr
L_18 sodalite	Bolivia			Na- Cl-Ba -Cr-Mn- Br -Rb-Sr
L_5	Tibet?			Na-Mg-Ti-Cr-Mn- Cu-Zn-Hg-Pb -Rb-Sr
L_6	unknown?			Na-Mg- P-Ti -Cr-Mn-Zn-Sr

variety of samples thus special elements and associations of elements such as U-Ti-Cr-As are incorporated in the blue stone during metasomatic formation [27] detected in Afghan lapis lazuli together with Cu-Zn (L-16), in the Baikal area with Ni-Cu-Th (L_12), or in Uzbekistan with Zn (L_1).

Elements typical for low temperatures such as Ba

and Sr have been observed in lapis lazuli from Siberia [26] or as As in lapis lazuli from Pamir [9, 11, 12]. The combination of the elements Ba-Ti-As-Ni is regarded as typical for Afghan lapis lazuli when analysed with PIXE on artefacts [28]. The composition of Ba-Ti is detected in sample L_4 from Afghanistan by XRF analysis, so that it may be stated as typical. The only

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other samples with Ba (L_14, L_15) identified by PIXE analysis (Table 3) come also from Afghanistan and from Bolivia (L_18). In this table no concentration

figures but the detected elements are indicated by a “+” character, only. Question marks indicate uncertain detection.

Table 3 Tabulation of the detected elements in PIXE analysis. Rows having the same sample name refer to the results obtained at different points of that particular sample.

	Cl	K	Ca	Ti	Cr	Mn	Fe	Co	Ni	Cu	Zn	Br	Sr	Ba	Pb
L_3	+	+	+	+	+	+	+	?	+	+	+	?	+	?	+
L_3	+	+	+	+	+	+	+	?	+	+	+		+	?	+
L_4	+	+	+	+		+	+		?	+	+	?			?
L_4	+	+	+	+	+	+	+		?	?	+	?			+
L_4	+	+	+	+		+	+		?		+		?		?
L_6		+	+	+	?	+	+		?		+		?		?
L_6	+	+	+	+	?	+	+	?	?	?	+		+		?
L_6	+	+	+	+	?	+	+		?	+	+				?
L_7	+	+	+	+	?	+	+		?	?	+	?	+		+
L_7	+	+	+	+	?	+	+	?	?	+	?	?	?		?
L_7	+	+	+	+		+	+	?	?	+	+	?	+		?
L_7	+	+	+	+	+	+	+		?	?	+	?			?
L_8	+	+	+	?	?	+	+	?	?	+	+		?		?
L_8	+	+	+			+	+			+	+		+	?	?
L_9	+	+	+		?	+	+	?			?	+	+		?
L_9	+	+	+			+	+	?			?		?	?	
L_9	+	+	+	?		+	+		?		?	+	?		?
L_10		+	+	+		+	+		?	?			?		?
L_10			+	+	?	+	+		?	?	?	?	?		?
L_10	+	+	+	?		+	+		?	+	+		+	?	?
L_11		+	+	+	+	+	+		?	+	+		?		?
L_11		?	?		+	+	+			+	+	+	+	?	?
L_11	+	+	+	+	+	+	+	?	?	?	+	?	?		?
L_11	?	+	+	+	+	+	+	?	?	+	+	?	?		+
L_12	+	?	+	+		+	+		?	?	?		?		?
L_12		+	+	+	?	+	+		?	?			?		?
L_12	+		+	?		+	+	?	?	+	+	+	?	?	?
L_12	+	+	+	?	+	+	+	?	?	+	+		+	?	?
L_12	+	+	+	?	?	+	+	?	?	+	+		+	?	?
L_13	+	+	+	+	+	?	+		?	+	+		?		?
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L_14	+	+	+	?	?	+	+	?	?	?			+	+	?
L_15	+	+	+	?	?	+	+	?	?	+	+		+	+	?
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L_18	+	+	+	?	?	+	+	?	?	+	+	+	+	+	?
L_18	+	+	+	+		+	+	?	?	?	+	+	+	+	?
L_18	+	+	+	?	?	+	+	?	?	?	+	+	+	+	?

In addition, Se together with As-Ti is detected only in samples L_2 and L_10 from Lake Baikal, Siberia, whereas As and Sr are present in most of the samples of lapis lazuli and thus are not significant for provenance studies. According to the literature, Se is also present in pyrite of Afghan and Chilean lapis lazuli [14]. Provided that this special element is incorporated in pyrite of the Baikal samples, it probably cannot serve as an indicator of a local occurrence.

Another element typical for low temperature formation is Hg. Never mentioned in literature relevant to lapis lazuli, it appears together with As in samples L_7 from Lake Baikal and in L_5 from Tibet?.

The mines differ chemically with association of elements such as Cr, Hg, Cu, Pb or U analysed in some of the lapis lazuli samples of each region. As regards all the samples analysed, those from Siberia/Baikal may clearly be distinguished by the compositions Se-Ti-As (L_2 and L_10) or Pb-Cu together with Cr-Ni (L_3, L_13). L_5 from Tibet? is the only additional sample containing Hg and Pb-Cu, so we suggest, that its origin may also be Siberia.

Altogether 14 lapis lazuli and 1 sodalite sample have also been analysed by PGAA. The bulk major components (Si, Ti, Al, Fe, Mn, Mg, Ca, Na, H, S and Cl) as well as some trace elements (B, V, Nd and Sm) are determined. The oxide forms of the major components are expressed in weight% (Table 4). Based on the PGAA results and on those obtained by EDX the samples can be identified as lazurite

(Ca,Na)₈[(SO₄,S,Cl)₁₋₂(AlSiO₄)₆] (Table 2, Table 4), a mineral phase in the sodalite mixed crystal row. Na, the main component of sodalites, that may substitute Ca in the crystal structure, is difficult to detect. Furthermore, K and Cl with exception of sample L_10 are always incorporated, though K is described in the literature as more typical for Afghan than Siberian and Chilean lapis lazuli [15]. The samples with Cl may contain more sodalite, verified for L_18 from Bolivia. L_9 from Turkestan/Bokhara has also much more Cl, Al and Na and no Ca and thus is completely different from the other blue stones. Very special is also Br, detected only in the two samples. The bivariate plot of Cl/Si mass ratio vs. S/Si mass ratio confirms different characteristics compared to the others. They are identified with PGGA (Table 4) to be sodalite, as labelled in the geological collection concerning L_18. Because of the very high content of Cl measured with XRF, the identification as sodalite can be stated. Thus, L_9 should get the same label.

A high content of Fe indicates pyrite (FeS₂). This associated mineral phase is mostly present in all deposits, including alteration products. Lapis lazuli with P is detected only in samples L_6 from Afghanistan and ? (L_16) of an unknown source, possibly indicating apatite, a mineral confirmed as a special phase in lapis lazuli from Afghanistan with ionoluminescence and PIXE [7].

In the next section, we demonstrate how useful the analytical results in various Cultural Heritage objects are.

Table 4 PGAA analysis of the blue stones (Zöldföldi and Kasztovszky 2013).

		SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	MgO	CaO	NaO	K ₂ O	H ₂ O	SO ₃
L03	Russia	46.9	0.451	7.77	2.50	0.118	12.4	16.9	3.91	0.92	0.27	7.26
L04	Afghanistan	32.8	0.443	8.99	8.49	0.004	5.3	6.5	4.12	3.15	0.51	18.30
L06	?	33.9	0.190	9.28	0.27	0.010	6.6	11.6	5.98	0.53	0.52	3.38
L07	Baikal	45.5	0.368	12.39	0.38	0.017	14.4	13.5	5.41	2.68	1.37	3.63
L09	Bokhaia, Turkistan	39.0	<D.L.	27.22	<D.L.	<D.L.	<D.L.	<D.L.	26.32	<D.L.	<D.L.	<D.L.
L16	Badakhshan, Afghanistan	40.0	0.215	10.73	0.08	0.006	13.2	14.5	4.52	2.10	0.95	2.94
L17	Badakhshan, Afghanistan	45.8	0.369	11.54	0.08	0.016	13.5	15.6	6.12	2.20	1.04	3.36
L18	Sodalite, Bolivia	38.8	<D.L.	26.26	<D.L.	<D.L.	<D.L.	<D.L.	26.79	<D.L.	0.64	<D.L.

3.2 Lapis Lazuli on Manuscripts

Manichaean and Sogdian manuscript fragments from the oasis Turfan/Xinjiang show decoration of flowers and headlines painted with blue ink made of lapis lazuli. In the Sogdian fragment So 18211 (Fig. 1) the color blue contains Ca-Fe-K-Si-Ti-As-Cl-S-Cu-Pb-Al and is analysed with XRF in a line scan (Figs. 2 and 3).

All elements, especially As-Cu-Pb-Zn, may correspond more to the kind of raw material from

Eastern Siberia, Lake Baikal analysed by XRF (samples L_3 and L_13). Cu-Ti and Fe are not detected in L_13 with EDX, whereas these elements are clearly identified with PIXE. In the literature lapis lazuli from a Turkish wall painting of the 14th to 16th century is assumed to be of Siberian origin and identified with PCA [15], so this source may also be considered for the manuscript.

The blue ink of the Manichaean manuscript M 233 (Fig. 4) has a totally different chemical composition (Figs. 5 and 6). Pb-Hg-Zn-Cr corresponds best to the



Fig. 1 Sogdian manuscript So18211 © BBAW-SBB SPK.

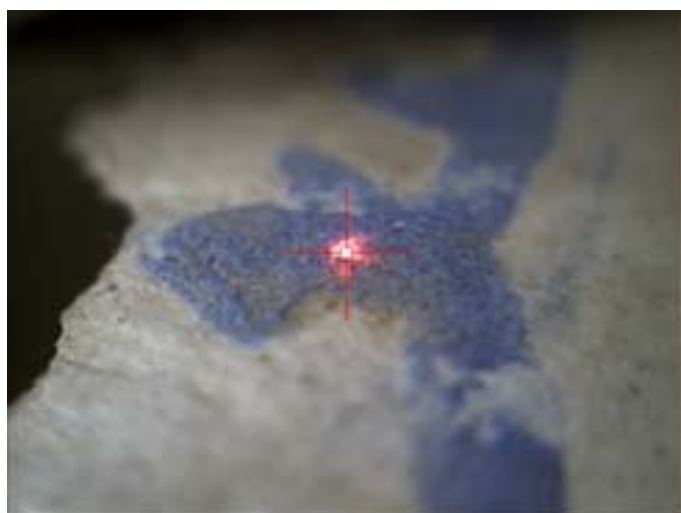


Fig. 2 XRF analysis of the blue ink of So 18211.

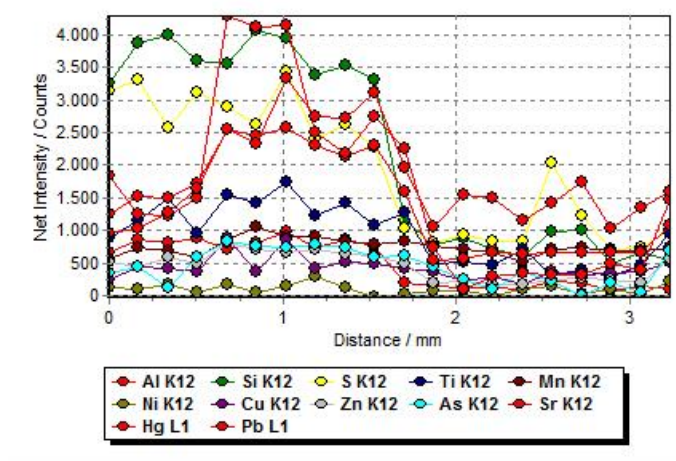


Fig. 3 Line scan of So18211 with Ca-Fe-K-Al-Si-S-As-Cl-Cu-Zn-Pb.



Fig. 4 Manichaean manuscript M 233 © BBAW-SBB SPK.



Fig. 5 XRF analysis of the blue ink of M 233.

Characteristic Features of Lapis Lazuli from Different Provenances, Revised by μ XRF, ESEM, PGAA and PIXE

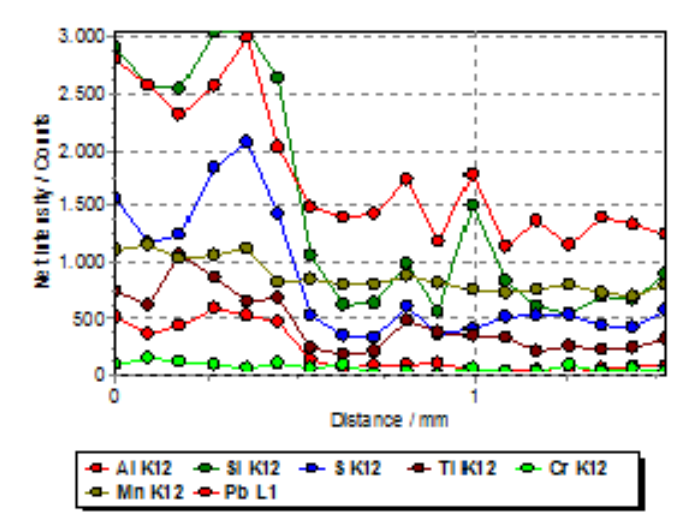


Fig. 6 Line scan of M 233 with Ca-Fe-Cl-K-Si-Pb-S-Ti-Cu-Mn-Hg-Zn-Al-Cr.

Table 5 Manichaean and Sogdian manuscripts with blue ink consisting of different elemental compositions.

	M233	M470	M7984	M2200-2202	M2204	M2206-2208	M7984	So10237-10239	So14255-6	So18151	So18211
Ca	+		+				+	+	+		+
K	+			+			+	+	+		+
Fe			+	+			+		+	+	+
Pb	+		+	+	+	+	+	+	+	+	+
Si	+	+	+	+			+	+	+	+	+
As		+								+	+
S	+	+	+	+			+	+	+	+	
Zn	+	+	+	+			+		+		
Hg	+	+			+	+			+	+	
Cu	+		+	+			+		+	+	+
Al	+	+	+	+				+		+	+
Cr	+		+				+	+			



Fig. 7 Fragment of wall with blue paint from Kizil.

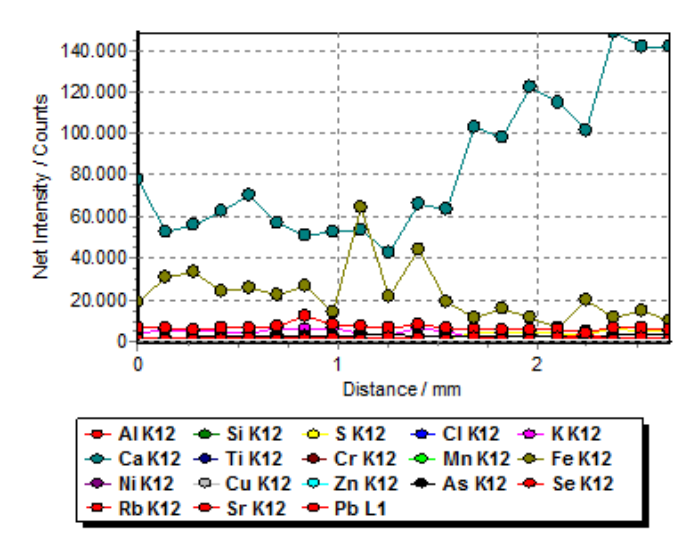


Fig. 8 XRF analysis of the blue paint from Kizil with Ca-Fe-K-Mn-Ti-Cl-Si-Al.

blue stone L_5 from Tibet ?, identified by XRF, although only Pb (no Cu-Hg-Zn-Cr-Ti) is detected with EDAX.

Unlike further Manichaean and Sogdian manuscript fragments (Table 5), the chemical fingerprint is not consistent throughout the cultural assignment. Thus, it cannot strictly separate the writings in the same way as does language or script. Exchange of artists and painting material, also mixture of pigments in culturally overlapping communication systems is assumed to be the reason for this since using lapis lazuli for writing has a very long tradition common, for example, on old Turkish manuscripts too [29].

3.3 Lapis Lazuli on Wall Paintings

The blue color applied on a wall painting in Kizil/Xinjiang from the 6th to 8th centuries (Fig. 7) is identified with VIS-spectroscopy as lapis lazuli. Ca-Fe-K-Mn-Ti-Cl-Si-Al are analysed with XRF (Fig. 8). As there is no natural lapis lazuli consisting of these elements alone, artificially produced ultramarine is assumed. Purified Afghan lapis lazuli is also applied, for example, on an Italian wall painting [15].

4. Conclusions

Samples of lapis lazuli derived from collections and characterized by various provenances are analysed and

compared to results mentioned in the literature. Groups determined by elemental and textural differentiation are created to improve separation. It turns out that more samples do not necessarily confirm former results concerning the famous mines, and textural features alone are not necessarily suited for a local differentiation. As identification of a regional fingerprint is due to the geological survey, general statements have to be critically regarded and put into relation to the quantity of samples for relevant statistics. Due to the different nature (sensitivities, penetration depth, etc.) of the various analytical methods, they usually do not detect identical elemental composition, changing even within one sample due to zoning or formation of mixed crystals in mineral analogies. Therefore, for example, it was observed that with XRF-analysis Hg is not detected in Afghan lapis lazuli, whereas with EDX it was possible to be detected - probably within a section of the sample with a different composition. Furthermore, it is sometimes difficult to detect and separate As beside Pb due to similar spectral lines. As and Ba are better identified with XRF, whereas Na, U and Th have been analysed only with EDX.

Remaining overlapping items confirmed by the different methods as special markers for the original sources of the raw material are related to the pigment

used as ink on paper and wall paint. The blue color on manuscripts is made of natural lapis lazuli attributed to different sources due to the metal ions of host minerals, provided the metal ions are not added during the preparation process of the ink used for writing and painting. Afghan lapis lazuli is hardly to be distinguished from Baikal as the source of the pigment used on the Manichaean and Sogdian manuscripts, and the ink is not the same within one cultural assignment. In contrast to this, the cave painting of Kizil is completed with well prepared, purified or artificial lapis lazuli that shows no similarity with that of natural sources.

It is a promising way to analyse even more samples with more complementary methods to confirm the special regional features postulated to clarify the origin of the blue pigment. To be sure of the results, it is absolutely necessary to consider critically the range of variation characteristics for one region, which can be optimized only by prospecting the deposits or with samples derived from field work. Finally, when a Cultural Heritage object is studied, non-destructive methods are highly preferred.

Acknowledgments

The samples of lapis lazuli are provided by A. Ehling, Federal Institute for Geosciences and Resources, Berlin; R.T. Schmitt, Museum of Natural History, Berlin; S. Herting-Agthe, Mineralogical Collections TU Berlin; S. Ungar, TU Freiberg; G. Grundmann, G. Lehrberger, TU München; J. Schlüter, Mineralogical Museum University Hamburg; W. Lange, TU Dresden; K. Thalheim, Senckenberg collections of natural history Dresden; C. Ferrais, Museum National d'Histoire Naturelle Paris and P. Tandy, Natural History Museum London.

O. Hahn, Federal Institute for Materials Research and Testing BAM, is thanked for the implementation of the Turfan project financed by the German Research Foundation DFG (Grant number HA 2728/8-1); D. Durkin-Meisterernst, Berlin Brandenburg Academy of

Sciences and Humanities BBAW; S. Raschmann, Göttingen Academy of Sciences and Humanities and J. Bispinck, State Library Berlin Prussian Cultural Heritage Foundation SBB SPK for providing the manuscripts and L. Russell-Smith, T. Gabsch, Berlin State Museums, Museum of Asian Art, Prussian Cultural Heritage Foundation SMB SPK, for providing the fragments of mural painting.

The PGAA and PIXE analyses of lapis lazuli have been done at the Budapest Neutron Centre, within the EC, supported Charisma FP7 project (Grant agreement no. 228330), the principal proposer of the PGAA experiments was Judit Zöldföldi.

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