FROM ORE TO PIGMENT:

A DESCRIPTION OF THE MINERALS AND AN EXPERIMENTAL STUDY OF COBALT ORE PROCESSING FROM THE KĀSHĀN MINE, IRAN

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Abstract

Ore samples collected from the cobalt mine of Qamsar, Kāshān, were studied using optical microscopy (OM), qualitative X-ray diffraction analysis (XRD), semi-quantitative X-ray fluorescence spectrometry (XRF), and quantitative electron micro-probe with wavelength-dispersive spectrometry (EMP-WDS). These analytical data provide the characteristics of the Kāshān cobalt ore, which can be compared with the composition of the blue pigments and colourants applied to glass and glazes, not least those of Islamic and Chinese blue-and-white wares. Preliminary replication studies of the pigment were also conducted according to the descriptions given in the Persian and European historical texts reviewed in a previous paper. The resulting phases were examined under an optical microscope and a semi-quantitative energy-dispersive spectrometer (EDS) attached to a scanning electron microscope (SEM). The ore was shown to contain high Fe and As concentrations and negligible Zn and Ni concentrations. Cobaltite (CoAsS) and erythrite ($Co_3(AsO_4)_2.8H_2O$) made up the two main cobalt-bearing minerals in the ore. The washing processes that were conducted based on a historical text rendered the ore more enriched with erythrite. In light of the new data on the Kāshān cobalt ore, the origins of the blue pigments used in some of the Islamic and Chinese ceramics are reconsidered.

INTRODUCTION

There have been various Persian, Chinese and European accounts that refer to the cobalt mine of Qamsar in Iran as a main source of the cobalt used for pigments in Islamic and Chinese glazes. Reviews of the Chinese texts are given by Watt (1979), Wang (1982), Ma (1997) and Wen (2012, 70-130), and of the Persian and European texts by Matin and Pollard (2015). Whereas analyses of blue pigments applied to archaeological glasses and glazes have become prevalent over the last few decades (for a review, see Matin and Pollard 2015, 171-3), the study of the deposit itself and the associated ores have never been fully provided. A short report by Stöllner (2004) has been the sole research focusing on the historical cobalt mine of Kāshān. It identifies three separate mines on the main lode, and on the basis of the use of fire-setting and evidence of iron picks and sledgehammers found at the site suggests the date of the exploitation to be medieval or even the more recent Islamic period.

The present research examines the geological and mineralogical features of the Kāshān cobalt deposit and provides the characteristics of the ore, against which the analytical data from cobalt blue pigments applied to ceramics are comparable. Furthermore, it uses the historical accounts discussed in Matin and Pollard (2015) as a framework to investigate the ore processing technologies involved in the production of the cobalt blue pigment.

GEOLOGICAL SETTING

Kāshān cobalt mine is situated at approximately 33° 48' N, 51° 24' E, 35 km southwest of Kāshān and 7 km northwest of Qamsar. It is located in the Karkas Mountains, part of the central mountain ranges, stretching in a NW-SE direction (Ghorbani 2013, 22-23). The deposit composes one of the major outcrops of the Ūrūmieh-Dokhtar magmatic arc in west-central Iran, where several NW-SE fault-hosted vein systems, parallel to the magmatic arc, have occurred. A brief description of the regional and local geology of this deposit is given based on the geological studies of Borna (1989), Radfar *et al.* (1993), Mohammaddoost *et al.* (2010) and Mohammaddoost (2010).

The oldest outcropped units in the area surrounding the Kāshān cobalt deposit are Upper Eocene volcanics, mostly pyroclastics, lavas, tuffs, sandstones, siltstones and nommulitic limestones (Borna 1989, 11; Radfar *et al.* 1993; Mohammaddoost 2010, 36-43). The volcanic eruptions in this area have been of a strongly sodic and calc-alkaline type and submarine. These deposits are directly overlain by Oligocene-Miocene Qom formation limestones. The Qom formation deposits of this area begin with dark grey coral limestones, which are thinly laminated and dip approximately 10 degrees to the north. On top of these are white reefal limestones, showing the same dip as the grey limestones but of a greater thickness (Borna 1989, 11-13; Mohammaddoost *et al*., 2010, 61; Mohammaddoost 2010, 43-54).

The formation of the Kāshān cobalt deposit is associated with an intrusive microdioritic body intruding Qom formation limestones which create garnet and pyroxene skarn zones as well as vein-type ore mineralisation (Mohammaddoost *et al.* 2010). The intrusive body

is a dome shaped sub-volcanic mass, approximately 400×600 m^2 in size, extending across the north of the region (Fig. 1). It primarily contains magnetite, plagioclase, pyroxene, hornblende, quartz, alkali-feldspar, biotite and tourmaline (Mohammaddoost 2010, 63). The hand specimens show a porphyry texture and, due to the extensive epidote-chlorite alteration, exhibit a dark green colour. Ore mineralisation has mainly occurred in the contact zone between the microdioritic body and the Qom formation. Along this contact zone, limestones with recrystallized sugar-grained structures are observed. The mineralised vein is approximately 210 metres long and 2.5 - 3 metres wide on average. It strikes approximately north-south, along a main fault in the region, and dips 82° west (Borna 1989, 18).

<<Figure 1>>

MINERALOGY

Identification of the Kāshān ore minerals is crucial for fully understanding the processes involved in the extraction of cobalt, as well as the manufacture of the ceramic pigment and its ultimate chemical composition. Based on the descriptions given in Persian and European historical accounts (Matin and Pollard 2015), the minerals cobaltite (CoAsS), asbolite ((Ni, Co)$_{2-x}$Mn^{4+}(O,OH)$_4$.nH$_2$O; also known as cobaltian wad or earthy cobalt) and erythrite (Co$_3$(AsO$_4$)$_2$.8H$_2$O) have been suggested to be the potential cobalt-bearing minerals present in the lode.

In order to verify the information given in the texts, the first author collected ore samples from the mining site in October 2011. Samples were collected from a talus slope, in

particular, where piles of ore, excavated from old mining activities, were dumped next to the lode (Fig. OS[Online Supplement].2). Approximately 30 kg of samples were collected from the site, 5 kg of which was transferred to the Research Laboratory for Archaeology and the History of Art, Oxford, for further experiments. Rock hand specimens collected from the mining site were divided into two groups based on their physical properties, namely Groups A and B. Group A represents a massive, black, dense and fine-grained texture with occasional specular structure (Fig. OS.3; Group A). Group B exhibits an earthy, brown-grey coloured, fine-grained texture with more gangue material, primarily hornblende, epidote and calcite (Fig. OS.3; Group B). On the basis of their textures, samples of Group A appear to have been exploited from the vein core, whereas those of Group B seem to be related to the vein margins, where the vein intruded the country rock. Both groups contain secondary oxidised minerals. Among them a thin, light pink mineral is extensively observed forming crusts and filling cracks (Fig. OS.3).

<< Figures OS.2 and OS.3>>

Sample Preparation

Two types of samples were prepared depending on the analytical techniques used: polished blocks for optical microscopy (OM), quantitative electron microprobe with wavelength-dispersive spectroscopy (EMP-WDS) and semi-quantitative scanning electron microscope with energy-dispersive spectroscopy (SEM-EDS), and powders for semi-quantitative X-ray fluorescence (XRF) and qualitative X-ray diffraction (XRD) analysis.

Small samples of the collected ore, typically of a few centimetres, were taken for EMP-WDS and SEM-EDS, and samples of the replicated pigment (described below) for OM and SEM-EDS analysis. The fragments were embedded in epoxy resin, ground and polished in cross-section on successive grades down to 0.25 μm. The polished blocks were vacuum carbon-coated to ensure electrical conductivity during EMP-WDS and SEM-EDS examinations. Samples of the ore, washing concentrate, tailing and the būreh-i Yezd (discussed below) were powdered down to c. 200 mesh for XRF and XRD analysis.

Analytical Methodology

Microstructure and chemical composition of phases present were studied using a reflective light microscope and a JEOL JSM-5910 SEM-EDS at the Research Laboratory for Archaeology and the History of Art (RLAHA), University of Oxford. For analysis of each phase, an area of approximately 0.5 mm × 0.5 mm was chosen. The SEM was operated in backscattered electron (BSE) imaging mode. Accelerating voltages of 15 kV and 20 kV were used respectively for samples of ore and replicated pigments. Spot sizes of 36-38 μm, working distance of 10 mm and count time of 100 s were used for all samples. For identification of zonings or variation of minor element concentrations in minerals, polished sections were observed under a CAMECA SX-100 EMP-WDS, at the Iranian Mineral Processing Research Centre (IMPRC), Karaj. The instrument was run at 20 kV, with a spot size of approximately 35 μm, working distance of 10 mm and a count time of 20 s per element.

Mineralogical Results

According to Mohammaddoost (2010, 97-8), two phases of mineralisation occurred in the region. In the first, only oxidised minerals were produced, with levels of cobalt and copper being too low for mineralisation. The second phase generated oxidised and sulphide mineralisation, producing magnetite (Fe_3O_4), cobaltite (CoAsS), chalcopyrite ($CuFeS_2$) and pyrite (FeS_2). The Kāshān cobalt deposit was produced by the second phase of mineralisation. Table 1 shows the WDS analysis of the minerals collected from the deposit.

Magnetite

Magnetite is the major constituent of the lode. It is observed mostly as euhedral crystals, in massive and veinlet textures, typically filling voids between grains. It usually exhibits strong zonation, a common phenomenon in contact metamorphism deposits. On the basis of EMP-WDS examination, this zoning is primarily due to variations in the levels of Si and Al. Moreover, alteration of magnetite to hematite (known as martitisation) is commonly noted, particularly along the veinlets.

Cobaltite

Cobaltite is the most important mineral of economic value in the vein. It primarily presents a dispersed texture within magnetite veinlets or cement under the microscope. The strong resemblance of this mineral to pyrite and arsenopyrite under the optical microscope (colour, shape and weak anisotropy) may have been the reason for some earlier misinterpretations, suggesting cobalt-bearing pyrite and arsenopyrite as the sources of cobalt in the lode. Further studies by Mohammaddoost (2010), confirmed by

WDS analysis presented here, revealed the mineral cobaltite as the main source of cobalt in the ore. As shown in Table 1, two different generations of cobaltite were observed in the ore samples. *Group I* is usually between 400 and 800 μm in size, presents a cubic shape and contains approximately 1.5-2% Fe (Fig. OS.4(a)). *Group II*, on the other hand, is smaller in size, varying between 200-500 μm, and shows an elongated shape, containing approximately 6% Fe (Fig. OS.4(b)). The approximate composition of the cobaltite at Kāshān is ~30% Co, ~44% As and ~20% S, with little or no detectable Mn, Ni and Cu.

<<Figures OS.4 (a)&(b)>>

<<Table 1>>

In the samples collected here, cobaltite, seen as silver colour, fine-grained and euhedral crystals, was extensively replaced by the mineral erythrite ($Co_3(AsO_4)_2.8H_2O$). This rare secondary mineral, usually associated with calcite, is formed as a product of oxidation of cobaltite and is especially enriched near the surface, in the oxidised zone of the ore body. It appears as extensive pink coatings, known as 'cobalt bloom', typically filling the fractures. Under the microscope, erythrite shows a replacing texture, with cobaltite crystals representing concave edges as a result (Fig. 5).

<<Figure 5>>

Chalcopyrite

Chalcopyrite is less abundant than cobaltite in the samples. It shows a disseminated

texture under the microscope. Based on WDS analysis, chalcopyrite crystals may contain up to 3% cobalt, which substitutes for Fe. This mineral might be observed as partly altered to malachite ($Cu_2CO_3(OH)_2$) or covellite (CuS) within the hand specimens.

Pyrite

Pyrite is mostly observed in subhedral forms, accompanied by chalcopyrite, and, in some cases, is replaced by goethite (FeO(OH)). Hajalilou (1989) reported zonation in pyrite crystals due to substitution of Co for Fe. However, such zonings were not observed in the samples examined in the present work.

PHYSICAL ORE PROCESSING

Mentions of physical separation processes and the preparation of the concentrated ore, either for chemical processing or direct use in the glaze, were given in four of the accounts reviewed by Matin and Pollard (2015). Of these, only Zarrābī (1956; the original manuscript written in 1878) detailed the crushing, grinding and washing process of the rock, with Schindler (1896) referring to the washing process as *sar i āb va bun i āb*, meaning 'top water and bottom water'. On the basis of these two accounts, it appears that a density separation in water was applied on the crushed and ground rock in order to separate the ore mineral(s). Following these descriptions, an experimental investigation of the physical processing of the ore has been undertaken. The resulting materials were analysed for their chemical composition to assess the effect of the processes.

Experimental Procedure

Ore samples of Groups A and B (vein core and vein margin, as described above) were crushed by hammer into approximately 3 cm lumps. Each group was then ground separately using a 1 litre basalt mortar and pestle and passed through a 100 mesh sieve (BSS 150 μm). Before grinding the rocks, powdered limestone was pounded in the mortar to provide a parting layer and remove possible contaminations.

250 g of homogenised powdered ore from Groups A and B was weighed. The powders were divided into five 50 g batches, each going through a separate washing process. For each batch, a 500 ml graduated cylinder was filled to the volume with distilled water. The ore powder was then added to the cylinder. A period of 150 s was given for immediate precipitation of the heavy material. After this time, 250 ml of the top suspension was poured in a 2000 ml beaker. The cylinder was again filled with 250 ml distilled water, thoroughly stirred, and the above process repeated. This procedure was carried out five times for each batch to ensure a better separation of the concentrate. The precipitated fraction in the cylinder (hereinafter cited as PF1) was held aside for XRF analysis. The beaker, containing 1250 ml suspension after five washings, was given 36 h for gradual precipitation of the ore. The top clear water was then removed and the precipitated fraction (hereinafter cited as PF2) was allowed to dry in an oven at 100 °C for 2 to 4 hours. For each 50 g of the powdered ore, the amount of concentrate (PF2) obtained was approximately 2 g for Group A, and 5 g for Group B.

Bulk analysis of the powdered samples was conducted using a Phillips PW1400 XRF Spectrometer, as well as a portable XRF Niton XL3T GOLDD, and mineral identification

using a Siemens D5000 XRD at the School of Archaeology, Geography and Environmental Science (SAGES), University of Reading.

Physical Processing Results

The XRF analyses of the ore and precipitated samples (PF1 and PF2) for both Groups A and B are presented in Table 2. According to Table 2, after the washing process, the CoO concentration increased significantly in Group A. Moreover, considering the average densities for the minerals cobaltite and erythrite (6.3 and 3.1, respectively), the washing process seems to have enriched the precipitate in erythrite (the lighter cobalt mineral), while cobaltite precipitated in the first stage of the process with other heavy minerals, such as magnetite (with density of 5.1, close to that of cobaltite).

<<Table 2>>

CHEMICAL ORE PROCESSING

In an attempt to investigate the chemical processes involved in the production of ceramic blue pigment from Kāshān cobalt ore, preliminary replication experiments were undertaken based on the recipes given in the historical accounts. After firing, the phases produced were examined for their microstructure and chemical composition under the OM and SEM-EDS.

Pigment Recipe

Descriptions of the production of ceramic blue pigment from Kāshān ore are given in the accounts by Rochechouart (1867), Ali Mohammad (1888, 7), Schindler (1896, 115-6) and Olmer (1908, 57-8). These recipes were outlined in Matin and Pollard (2015, 179). In the investigation presented here, the mixtures were prepared according to Ali Mohammad's recipe as this is likely to be the more accurate version of the recipe given by the potter himself:

Lapis lazuli bud	10 parts
Yezd borax (būreh-i Yezd)	5 parts
Tangār	5 parts

Samples of Ali Mohammad's raw materials, held at the Victoria and Albert Museum, have been analysed by Reiche and Voigt (2012, 524-6), which provide a valuable basis for comparison. Among this collection, four boxes have been labelled in relation to cobalt (or *lājvard*, as it was commonly referred to in Persian): lājvard colour (*reng-e lājvard,* from the neighbourhood of Kāshān; box no. 10); fired red lājvard (*lājvard-e sorkh ātash dādeh*; box no. 11); essence of lājvard (*jowhar-e lājvard*; box no. 12) and black lājvard (*lājvard-e siāh*; box no. 13). According to Reiche and Voigt's (2012, 511) analysis, the composition of box no. 12 (essence of lājvard) was unrelated to any type of cobalt ore, showing high lead but no cobalt content. The three other boxes, on the other hand, had compositions very similar to the cobalt ore of Kāshān. Further comparison of the samples with the ore, concentrate and the gangue cannot be performed due to the semi-

quantitative nature of the analyses of Ali Mohammad's samples.

Identification of the Raw Materials

Lapis lazuli bud

Washing concentrates of ores from Groups A and B, namely PF2-A and PF2-B, were used respectively as sources of cobalt in the pigment mixtures CA and CB (Table 3).

Būreh-i Yezd and Tangār

The nature of the būreh-i Yezd and tangār was discussed in Matin and Pollard (2015, 179-180). On the basis of the chemical analyses of Ali Mohammad's samples (Reiche and Voigt 2012, 524-6), the būreh-i Yezd and tangār were effectively borax ($Na_2B_4O_7 \cdot 10H_2O$), with tangār being a more homogenous and purified form of būreh-i Yezd. The deposit situated in Khatūn-Ābād (formerly Deh Shotorān), 31 km south east of Shahr-e Bābek, today in Kermān province but previously in Yezd province, was suspected to be the source for the būreh-i Yezd and tangār used by Ali Mohammad. This was primarily based on the accounts contemporary with that of Ali Mohammad, attesting the exploitation of būreh from this deposit. In October 2012, samples of būreh-i Yezd were obtained from the local mining corporation in Shahr-e Bābek (29° 55'-30°N, 55° 20'-55° 25'E). The results of XRD analysis of the samples showed ulexite ($NaCaB_5O_9.8(H_2O)$) and gypsum ($CaSO_4.2H_2O$) as the two major minerals present, confirming the results previously given by Sabzeie and Roshan-Ravan (1985). The results did not confirm the minerals present in the samples obtained from the Khātūn-Ābād deposit to be the same as those identified in the samples of the būreh-i Yezd and tangār

used by Ali Mohammad. However, it is worthwhile noting that, as in any evaporite deposit, the minerals produced in the Khātūn-Ābād deposit may be highly variable, depending on factors such as the season of sampling and rainfall pattern. It remains to be further studied as to what are the exact factors affecting these variations and what is the range of minerals produced in the deposit. For these reasons, the samples collected from the Khātūn-Ābād deposit were used in the present study as a source of būreh-i Yezd, and pure laboratory-made borax as a source of tangār.

Grape treacle

Unlike the accounts by Schindler 1896 (115-6) and Olmer 1908 (57-8), the addition of grape treacle or mulberry juice was not mentioned by Ali Mohammad (nor by Rochechouart 1867). In order to assess its role, grape treacle was added to the recipe used in the present investigation.

<<Table 3>>

Experimental Procedure

PF2-A, PF2-B, būreh-i Yezd and tangār were weighed according to Table 3 and mixed using an agate mortar and pestle. To these was added grape treacle (with specific gravity of approximately 1.5 g/ml), thoroughly mixed, and the resulting pastes were put in 50 ml porcelain crucibles and covered by lids. The crucibles were then placed in an electric furnace. The furnace was equipped with a hood to carry away the fumes that could have resulted from volatalisation of arsenic in the ore. Firing was carried out according to the firing schedule shown in Figure 6 (950 °C maximum temperature, 15 min soaking time). The slow firing rate for the first cycle was to prevent spilling the mixture out of the

crucible during dehydration of borax. After firing, all the mixtures exhibited a spongy structure with vesicular voids. The polished sections of the samples were studied both by OM and SEM-EDS.

<<Figure 6>>

Results

CA

After firing, two major phases were observed in the polished section. A continuous uniform glass, approximately 1 mm in thickness, was formed on top of the crucible. The EDS data obtained for this glass phase are given in Table 4. The rest was a glass phase with a highly vesicular structure, although showing a very similar chemical composition to the top glass (Table 4; row 2). Attached to this, glass droplets were occasionally formed, possibly as a result of surface tension. In the top glass, particularly on the boundary with the vesicular glass, dendrites of cobalt and arsenic oxide were observed (Fig. 7(a)). In the vesicular glass phase, cobalt and arsenic (and iron) sulphides, in the form of semi-rounded phases (Fig. 7(b); Table 4; row 4), together with euhedral cobaltite crystals and tiny dendrites were observed, in particular along the edges.

<<Figures 7a & b >>

CB

Overall, the two major phases observed in the CB section were similar to that of the CA. However, in the top glass phase (Table 4), secondary diopside ($MgCaSi_2O_6$) crystals were formed. The cluster pattern observed in the vesicular glass phase in CA was formed more

extensively in CB and the cobalt phases, particularly the dendrite structures, were significantly less abundant (Table 4; row 5).

<<Table 4>>

DISCUSSION

Cobaltite vs. Erythrite

On the basis of mineralogical examinations, cobaltite (CoAsS) and erythrite $(Co_3(AsO_4)_2.8H_2O)$ are the two main cobalt-bearing minerals in the ore. Therefore, the mentions of the minerals "like white silver shining in a sheath of hard black stone" and "a red kind found in the mine which is a deposit on the outside of the stones and is like the red shells of pistachios" by Abū'l Qāsim Kāshānī (Afshar 2006, 339 and Allan 1973, 112) most probably refer to cobaltite and erythtite, respectively. In a later account by Ali Mohammad Isfahānī (1888, 7), however, only erythrite is cited; referred to as the one which "breaks out of the hill like blossoms". Among the European accounts, erythrite is only mentioned (as cobalt bloom) by Schindler (1896) and Ladame (1945). This might relate to the fact that in hand specimens, erythrite is more easily distinguishable to the eye than cobaltite. Hence only erythrite was mentioned in the reports, whilst cobaltite was also present in the ore. On the other hand, one could argue that the primary cobaltite minerals were exploited in the earlier stages of mining at this site and were not considered as the main cobalt mineral in the later periods of working. This assumption is supported by the fact that in the field investigation of the deposit, cobaltite was extensively replaced by erythrite and was rarely observed in hand specimens. This can

also be inferred from the physical processing procedure of the ore, aiming to enrich the ore in the light minerals (particularly erythrite). The notion of asbolite (mineral containing hydrated oxides of manganese and cobalt) being a major cobalt mineral in the Kāshān deposit was cited by Olmer (1908, 57), Launay (1911, 661), Ladame (1945, 196), and Wulff (1966, 163; as cobalt wads). The mineralogical and XRD examinations reported here found no evidence for the presence of this mineral in the ore.

Pigment Preparation Procedure

According to the historical accounts and experimental studies conducted, it appears that two different phases were involved in the pre-treatment of the ore. First, a density separation was carried out to concentrate erythrite. In this process, heavy minerals, particularly magnetite (together with cobaltite), would immediately precipitate, while erythrite, along with other light minerals, such as silicates, would still float in the top suspension and precipitate later in the second jar. Density separation acted more effectively on Group A ore type to separate low density cobalt-bearing minerals (e.g. erythrite) from high density minerals (e.g. magnetite). Moreover, higher concentrations of Co and As in Group A, compared to Group B, render it a more efficient ore type.

The second phase involved a chemical process to separate the cobalt compounds from the gangue. To obtain the resulting pigment after firing, Ali Mohammad (1888, 7) stated that: "let the kiln cool, remove the vessel, and break it; break open also the contents, which will be found to enclose a white substance like silver. Keep this and throw away the rest". Furthermore, Olmer (1908, 58) mentioned that: "after cooling off you get a cobalt-oxide,

which is free from earth and impurities that forms a crust all around. The inferior part is pounded, and yields a clearer grey powder". The experiments conducted here showed that phase separation takes place, with dispersed silver-like cobalt compounds standing out from the borosilicate glass matrix formed after firing. In this glass phase, the iron still present in the PF2 (precipitated fraction of the second stage of the washing process) dissolves as a flux.

Replication of the chemical pre-treatment of the ore has not been successful in forming a consistent cobalt phase that could be observed in the sample by the naked eye. The results obtained represent a pilot study and further work is required in order to assess the effects of various factors on the production of the final pigment, including the batch volume in the crucible, the firing schedule and the soaking time required.

The role of grape treacle was not completely identified in the course of the experiments. Although its purpose as the reducing agent was confirmed in some of the historical accounts, the preliminary experiments conducted were not sufficient to verify this. It might be that the compound was used as an adhesive to stick the material together to ease the handling. This remains to be elucidated by further experiments.

Kāshān as a Source of Islamic and Chinese Cobalt Pigment?

The analytical data presented here suggest that Kāshān cobalt ore is high in As and Fe but contains neither Ni, Cu, nor Zn. Hence, previous attributions of Chinese and Islamic blue pigments to Kāshān can be re-evaluated in the light of these new data. An obvious

conclusion is that any cobalt pigment containing significant traces of Zn, Cu or Ni did not originate in Kāshān, unless pigment processing such as grinding in a brass mortar might have subsequently introduced such traces. Therefore, reference to Kāshān in such cases needs to be considered with caution (e.g., Kleinmann 1991).

The XRF analyses of Abbasid blue glazes (c. 750 - 1258 AD) previously undertaken by Tamari (1995), Cowell and Zhang Fukang (2001), Wood *et al.* (2007) and Wen (2012) confirm that the cobalt blue pigment used is characterised by measureable Zn contents, but with no As. As shown here, XRF analyses of the ore (Table 2) report high As with negligible Zn content. Nor has any previous analysis of Kāshān cobalt ever revealed evidence for Zn. Although it is possible that pigment processing might remove As through volatalisation, the presence of Zn suggests that the Kāshān cobalt deposit is unlikely to have been the source of the Abbasid cobalt ore, as noted by the above-mentioned authors.

In an analytical study of the blue pigments applied to Islamic ceramics using XRF, Wen (2012, 249-251) classified the wares into seven different categories based on the varying ratios of Co, Fe, Zn, As, Ni, etc., in their blue pigments (Table OS.5). Among these, the possible source of the cobalt blue pigment applied to ceramics of Type D (characterised by the presence of Fe and As) was suggested to be Kāshān, which also corresponds closely to the analysis of the ore presented here. This group includes analysed sherds from the blue ceramics of Samarqand and Syria (11th – 16th centuries), Persian minaī wares (12th – 13th centuries), Persian lustre wares (12th – 13th centuries) and Persian,

Egyptian and Syrian under-glaze blue ceramics (14th – 15th centuries). Therefore, this leads to the suggestion that the Kāshān deposit became renowned as a source of cobalt blue pigment only after the early medieval Islamic period. This corroborates the suggestion of medieval exploitation of the mine made by Stöllner (2004), and the observation that earliest textual documents referring to the mine are medieval Islamic treatises. Furthermore, analytical study of Chinese Yuan and Ming blue and white porcelain by Wen and Pollard (2009) shows that the Chinese blue pigment prior to 1425 AD was characterised by Fe-As and low Mn, and did not contain Zn. This suggests that, like the Type D Islamic pigments, it may have originated in Kāshān itself.

<<Table OS.5>>

CONCLUSIONS

The process of attributing cobalt pigments to specific ore sources on the basis of particular ratios of elements such as As, Mn and Fe, and the presence or absence of elements such as Zn, Ni and Cu might seem somewhat unsatisfactory. It is necessitated in general because most analyses are semi-quantitative, often taken non-destructively through the glaze by XRF or SEM. Absolute concentrations are virtually unobtainable under these conditions, and are essentially meaningless because the concentration of dissolved pigment in the glaze is very variable. Where possible (i.e., when sherds can be cut and mounted), the opportunity should be taken to get better quality data. The issue of the effect of pigment processing on the trace element composition also needs further consideration.

The analyses presented here show that pigments made from Kāshān cobaltite should be characterised by high values of As and Fe, but without Ni, Zn and Cu, providing the ore processing is sufficient to eliminate chalcopyrite. Subsequent preparation of the manufactured blue pigment could, for example, introduce traces of Cu and Zn if the pigment was further ground in a brass mortar. Quantitative data might allow the correlation between Cu and Zn to be determined, to test such a hypothesis.

Finally, our study of Ali Mohammad's recipe (1888) used to manufacture blue pigment from the Kāshān ore suggests that the pigment should contain boron from the evaporites used as fluxes. Boron is difficult to measure with conventional XRF or SEM, and is therefore rarely reported in the analysis of ceramic glazes and pigments. This indicates another interesting direction for future research, especially given the recent measurement of boron isotopes as an indicator of the source of the evaporite minerals in Roman glass (Devulder *et al*. 2015).

FIGURE CAPTIONS

Figure 1. *Satellite photograph of the area surrounding the Kāshān vein deposit, showing the microdioritic dome-shaped body, Qom limestones, Eocene volcanics and the approximate trend of the vein.*

Figure OS.2. *Ore sampling location.*

Figure OS.3. *Samples of hand specimens: Group A, showing a massive, specular texture, with secondary pink crusts filling the fractures; Group B, showing an earthy texture, with an extensive pink coating.*

Figure OS.4. (*a): Polished section photomicrograph of cobaltite Group I in a magnetite veinlet, reflective plane polarised light; (b): polished section photomicrograph of cobaltite Group II embedded in magnetite, reflective plane polarised light.*

Figure 5. *Backscattered SEM images of cobaltite crystals replaced by erythrite.*

Figure 6. *Firing schedule.*

Figure 7. *Backscattered SEM photomicrographs of a section through the CA sample; a) dendrites of cobalt and arsenic oxide in the top glass matrix; b) semi rounded sulphides of cobalt and arsenic (and iron), together with tiny dendrites of cobalt and arsenic oxides.*

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