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Man-made blue and purple barium copper silicate pigments and the pabstite ($\text{BaSnSi}_3\text{O}_9$) mystery of ancient Chinese wall paintings from Luoyang

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Abstract

Man-made ancient Chinese barium copper silicate pigments: Chinese (Han) Purple, $\text{BaCuSi}_2\text{O}_6$; Chinese (Han) Blue, $\text{BaCuSi}_4\text{O}_{10}$; Chinese Dark Blue, $\text{BaCu}_2\text{Si}_2\text{O}_7$ (in summary called Chinese blues), and platelet-like crystals of $\text{BaSnSi}_3\text{O}_9$ were detected on mural paintings of a tomb in Luoyang City, Henan Province, China, dated to Western Han Dynasty (206 BC–8 AD). The pigments of the LY01 and LY02 samples were analyzed by archaeometrical methods: powder X-ray diffractometry (XRD), scanning electron microscopy (SEM–EDX) and micro-Raman spectroscopy. While the artificial nature of the ancient barium copper silicates was undoubted, the synthetic or mineral origin of $\text{BaSnSi}_3\text{O}_9$ of these murals had to be clarified. Involvement of the rare mineral pabstite $\text{Ba}(\text{Sn},\text{Ti},\text{Zr})\text{Si}_3\text{O}_9$ from the Tian Shan mountains could be ruled out due to absence of Ti and Zr in the elemental composition. Tin compounds as admixtures to the lead minerals—the latter required as flux additive for the preparation of the Chinese blues—or tin admixtures to pristine barium starting minerals could be excluded, as well as the use of tin containing mineral mushistonite ($\text{CuSn}(\text{OH})_6$), primarily intended to be applied as copper source. Related to the findings for the production of Egyptian Blue ($\text{CaCuSi}_4\text{O}_{10}$), bronze or bronze scrap including also corroded material was used intending copper recycling. For the synthesis of the Luoyang Chinese blues only low amounts of bronze or bronze scrap were required providing the additional advantage to form in presence of air a tin/lead oxide flux with lowered vitrification temperatures and viscosities. This marked the advent of an ‘innovative production technology’ avoiding addition of large amounts of lead minerals as an effective lead-only flux. Despite of the chemical similarity to production of Egyptian Blue, the tin/lead based developments for the Chinese blues were anticipated to be independent excluding technology transfer from ancient Egypt. For further substantiation of the appearance of pabstite in the Luoyang Chinese blues a contemporary independent synthesis was sought, carried out under conditions similar to those of the barium copper silicate syntheses (1000 °C, but absence of a flux) starting from cassiterite (SnO_2), quartz (SiO_2) and witherite (BaCO_3).

Keywords: Barium copper silicate pigments, Chinese Purple ($\text{BaCuSi}_2\text{O}_6$), Chinese Blue ($\text{BaCuSi}_4\text{O}_{10}$), Chinese Dark Blue ($\text{BaCu}_2\text{Si}_2\text{O}_7$), Pabstite ($\text{BaSnSi}_3\text{O}_9$)

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Introduction

The man-made barium copper silicate pigments Chinese (Han) Purple ($\text{BaCuSi}_2\text{O}_6$), Chinese (Han) Blue ($\text{BaCuSi}_4\text{O}_{10}$) and Chinese Dark Blue ($\text{BaCu}_2\text{Si}_2\text{O}_7$) (in summary called the Chinese blues) were widely used as blue and purple pigments in ancient China during the Warring States Period (475–221 BC) until the end of Han Dynasty (206 BC–220 AD). Chinese Blue [1] and Chinese Purple [2] were first discovered on ancient Chinese artifacts by Fitzhugh in 1983 and 1992, respectively. These Chinese pigments were also found in pigment layers of purple, green or blue faience beads [3, 4], mural paintings [5], painted bronzes [1], painted potteries, terracotta warriors and other types of figurines [6, 7] and as compact body materials of octagonal sticks [8] excavated from the Chinese provinces Gansu, Shaanxi, Inner Mongolia, Henan, Hebei, Jilin, Shandong and Jiangsu. Chinese Dark Blue ($\text{BaCu}_2\text{Si}_2\text{O}_7$), the ‘third’ out of the four BaO-CuO-SiO_2 phases, was detected in 2008 on ancient Chinese artwork [9]. The earliest barium copper silicate pigment find was a light green faience bead dated to the late Spring and Autumn period (770–476 BC) [10] marking the onset of the appearance of man-made ancient Chinese blues. In greater abundance Chinese Purple and Chinese Blue began to appear in late Warring States period [11] as pigment layers of paintings and glazed objects, and as compact body artifacts.

In recent years the archaeometry of barium copper silicate pigments was based on instrumental analyses using powder X-ray diffraction (XRD), electron probe microscopical analysis (EPMA), Raman spectroscopy and Scanning Electron Microscopy combined with energy dispersive X-ray spectrometry (SEM–EDX) [12–20].

Preliminary SEM–EDX studies searching for barium copper silicates in the pigment layers of a mural from early Western Han Dynasty (206 BC–8 AD) from a tomb of Luoyang City and bulk purplish-blue and yellow-green

pigments of a Tomb Guard Jar of late Eastern Han Dynasty (25–220 AD) from Sanmenxia City, China, revealed high tin contents. This observation was considered a conspicuous and at the same time mysterious circumstance, which caught our interest and we decided to study two samples of the mural from early Western Han Dynasty (LY01 and LY02) in greater detail by archaeometrical methods.

Experimental part

Selection of the LY01 and LY02 samples of the mural of the Luoyang tomb

The archaeological site is located in Shaogou Village of today’s Luoyang City, Henan Province. In Figs. 1, 2 cutouts of the mural of the tomb Luoyang are shown named ‘Beating the Ghost’ dated to 48–8 BC (late Western Han Dynasty) [21]. Two small pieces of purple pigments samples (LY01 and LY02) were taken from the people’s clothes. The sampling areas are circled in red, which included material from the pigment and the plaster layers.

Sample preparation

The samples LY01 and LY02 were embedded into epoxy resin cross-sectioned and polished for micro-Raman spectroscopy. For the SEM–EDX analysis the samples were coated with a thin carbon layer to improve surface conductivity and to prevent accumulation of charge.

Micro-Raman spectroscopy

For the micro-Raman measurements a Renishaw System 1000 Raman microscope was used. This system comprises a Leica DMLM microscope equipped with a 50× objective, a spectrometer with a 1200 grooves/mm or 1800 grooves/mm grating and a NIR enhanced, Peltier-cooled CCD camera. Incident laser beam

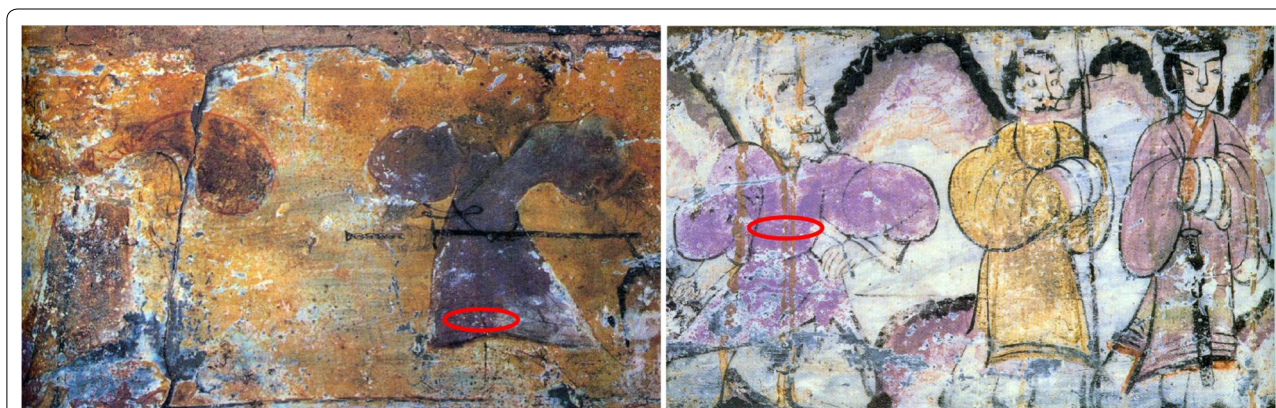
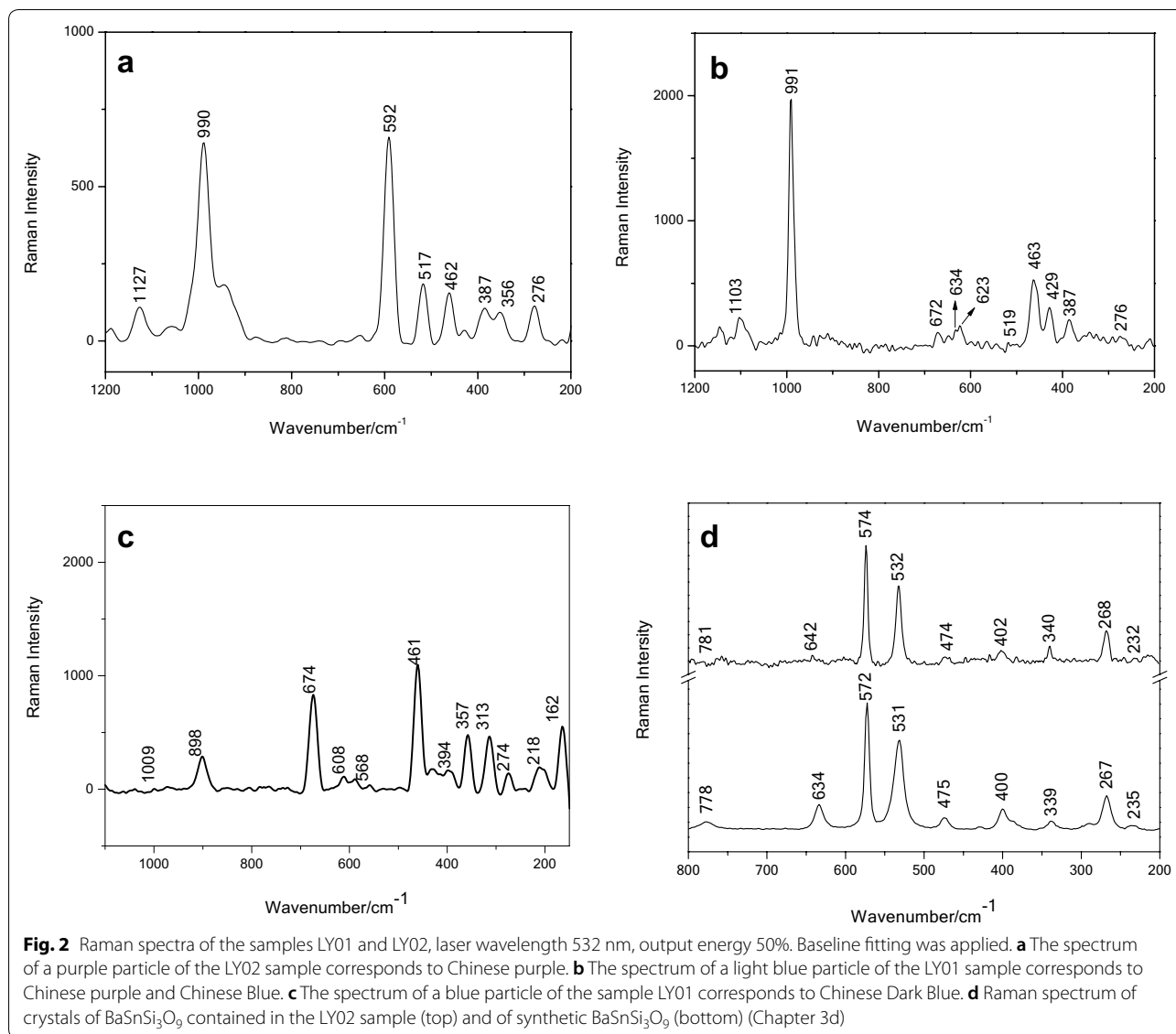


Fig. 1 Mural of ‘Beating the Ghost’ of the tomb Luoyang City. The red circles indicate the sampling areas: LY01 left and LY02 right



wavelength 532 nm, output energy at 50%. For the spectra of Fig. 2 baseline fitting was applied.

XRD

The powder X-ray diffraction RIGAKU D/MAX-TTRIII (CBO) with Cu-K α radiation ($\lambda = 0.154$ nm) was used. The θ - θ configured goniometer permitted automated collection of intensity versus scattering angle scans. A first attempt was carried out using the following parameters: 2θ angles in the range between 10° and 90° with a scan speed of $10^\circ/\text{min}$ using a locked couple measurement. The X-ray diffraction patterns were simulated using the MDI Jade 6.0 Software.

SEM-EDX

Philips SEM 515 (PW 6703) Scanning Electron Microscope, operating at 26 kV. The EDX analysis was performed at various points throughout the cross-section by measuring the emitted X-rays with a Tracor Northern 5400 EDX system equipped with a Si/Li detector.

Archaeometrical results

Raman analysis of BaCuSi₂O₆, BaCuSi₄O₁₀ and BaCu₂Si₂O₇

The powdered samples of LY01 and LY02 were studied by micro-Raman spectroscopy (Fig. 2) finding Chinese Purple (BaCuSi₂O₆), Chinese Blue (BaCuSi₄O₁₀) and Chinese Dark Blue (BaCu₂Si₂O₇) in the two samples. The pigments were identified by comparison with spectra of

earlier investigations. Raman bands at 990m, 588s, 516m, 459w, 354w, 276w and 183w cm^{-1} were used to reference Chinese Purple [14], bands at 1102s, 997w, 791w, 562w, 427s and 383w cm^{-1} to reference Chinese Blue and bands at 1014m, 891s, 673s, 607w, 558w, 458v, 355w, 311w cm^{-1} to reference Chinese Dark Blue [22].

Raman analysis of pabstite ($\text{BaSnSi}_3\text{O}_9$)

Based on their triangular shapes the crystals of Fig. 3a, b were ascribed to pabstite ($\text{BaSnSi}_3\text{O}_9$). Fortunately, one of the LY02 crystals, which EDX elemental composition was close to the $\text{BaSnSi}_3\text{O}_9$ stoichiometry (Chapter 3c), was large enough to enable detection by micro-Raman spectroscopy (Fig. 2d, top) revealing $\text{BaSnSi}_3\text{O}_9$ Raman bands at 574s, 532s, 474m, 340w and 268w cm^{-1} . Further substantiation that $\text{BaSnSi}_3\text{O}_9$ was present came from the perfect match with a Raman spectrum of material prepared by contemporary independent synthesis (Fig. 2d, bottom). Furthermore, the spectrum was in good agreement with that of mineral pabstite of the RRUFF library (RRUFF, ID R060386). The Raman spectra of the LY01 sample displayed besides the pabstite spectrum an additional small band at 634 cm^{-1} , which was ascribed to the presence of cassiterite (SnO_2) (RRUFF, ID R040017) (Fig. 2b) supposed to originate from tin containing starting materials transformed via chemical reactions of the pigment preparation (Chapter 4).

SEM–EDX analyses

SEM–EDX analyses were carried out on the samples LY01 and LY02 using a Philips SEM 515 (PW 6703) Scanning Electron Microscope. The overall composition (at.%) of the pigment layer of LY01 consisted of 36.5 Si, 8.2 Cu, 28.6 Ba, 1.2 Pb, 8.9 Sn, 10.5 Al and 1.8 K, while

that of LY02 (at.%) contained 35.8 Si, 7.8 Cu, 29.6 Ba, 2.7 Pb, 4.4 Sn, 10.1 Al and 2.5 K (at.%). The tin and lead contents varied in both samples significantly. The Al values are relatively high, which together with the presence of silicon and potassium (around 2%) are suggested to point to the use of a special potassium alumosilicate plaster. The contents of the elements Si, Cu and Ba of the LY samples were constant within the limits of $\pm 1\%$. The contents of silicon, barium and copper of the pigment samples indicate the presence of the Chinese blues. Compared to ancient tin-free samples of the Chinese blues the lead contents of the LY samples are relatively low [10, 16, 17, 23–25].

Figure 3a depicts the SEM micrograph of LY01 marking spot-like or 2-dimensional EDX locations. The major EDX elemental contents are listed in Table 1 (at.%) together with propositions for compounds fitting to the given stoichiometries. The EDX2, 3, 4, 5, 6 and 7 areas of LY01 display triangular crystals, which shapes would be consistent with the presence of pabstite ($\text{BaSnSi}_3\text{O}_9$). Also their elemental compositions pointed to pabstite, but the EDX analyses of these crystals varied in composition, thus, not giving full proof for the $\text{BaSnSi}_3\text{O}_9$ compositions. The spot-like measurements EDX8, 9 and 10 display needle-like crystals, which elemental compositions were approx. in accord with the composition of Chinese Purple ($\text{BaCuSi}_2\text{O}_6$). The crystal shapes of Chinese Purple samples obtained by contemporary synthesis are platelets. Apparently, the crystal shapes of Chinese Purple depend on the surrounding lead mixtures, from which they crystallized [10].

Related to Fig. 3a, b displays the SEM image of LY02 with EDX locations indicated. The major elemental contents of these locations are listed in Table 2. The EDX1

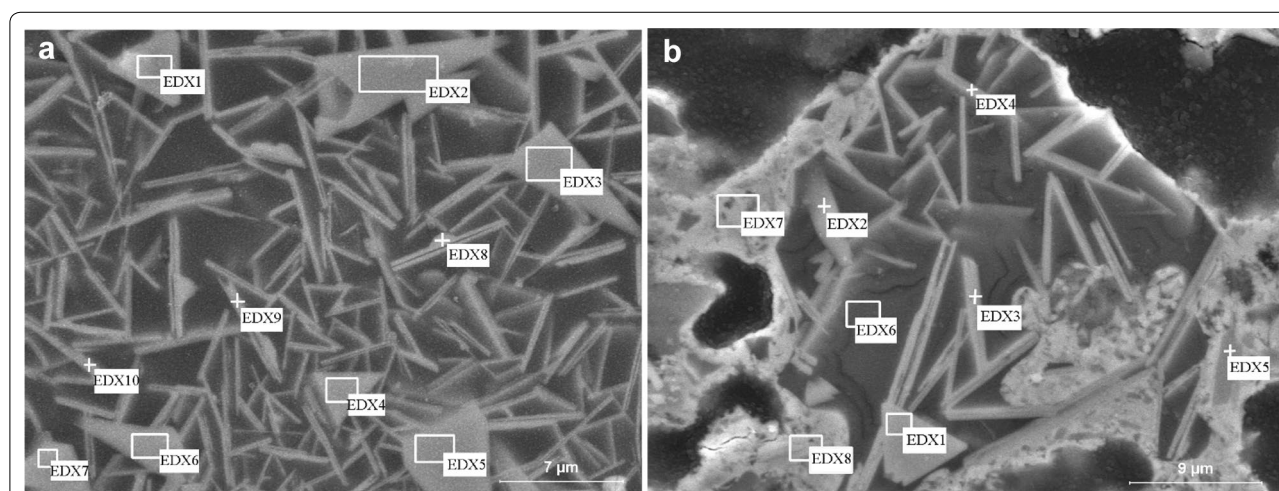


Fig. 3 SEM images for the cross-sections of LY01 (a) and LY02 (b) with indications of the EDX locations

Table 1 Elemental compositions of the SEM–EDX areas of sample LY01 shown in Fig. 3a (at.%), (CP Chinese Purple, CB Chinese Blue)

| EDX | Element | | | | | | Compound |
|-------|---------|------|------|------|-----|---|------------------------------------|
| | Si | Cu | Ba | Sn | Pb | | |
| EDX1 | 38.7 | – | 10.9 | 49.5 | – | – | – |
| EDX2 | 58.9 | 1.0 | 19.5 | 18.4 | – | – | BaSnSi ₃ O ₉ |
| EDX3 | 59.4 | 0.8 | 18.9 | 18.7 | – | – | BaSnSi ₃ O ₉ |
| EDX4 | 62.5 | 1.1 | 18.4 | 15.7 | – | – | BaSnSi ₃ O ₉ |
| EDX5 | 64.1 | – | 16.0 | 15.9 | – | – | BaSnSi ₃ O ₉ |
| EDX6 | 65.8 | 1.3 | 15.2 | 13.3 | 0.8 | – | BaSnSi ₃ O ₉ |
| EDX7 | 64.0 | – | 14.9 | 14.8 | – | – | BaSnSi ₃ O ₉ |
| EDX8 | 61.6 | 10.6 | 9.8 | – | – | – | CP |
| EDX9 | 67.3 | 4.8 | 6.7 | 2.5 | 3.8 | – | CP |
| EDX10 | 64.9 | 9.5 | 10.5 | – | 1.5 | – | CP |

The values do not add up to 100%, since minor elemental contents are not listed

Table 2 Elemental composition of the SEM–EDX areas of sample LY02 shown in Fig. 3b (at.%), (CP Chinese Purple, CB Chinese Blue)

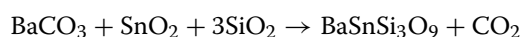
| EDX | Element | | | | | | Compound |
|------|---------|------|------|------|-----|---|------------------------------------|
| | Si | Cu | Ba | Sn | Pb | | |
| EDX1 | 60.9 | 0.3 | 14.8 | 12.5 | – | – | BaSnSi ₃ O ₉ |
| EDX2 | 65.8 | 0.7 | 11.3 | 11.9 | 1.8 | – | BaSnSi ₃ O ₉ |
| EDX3 | 63.2 | 10.9 | 11.7 | – | 1.8 | – | CP or CB |
| EDX4 | 66.4 | 10.3 | 11.2 | 3.8 | 1.0 | – | CP or CB |
| EDX5 | 62.4 | 11.0 | 10.8 | – | 6.1 | – | CP or CB |

The values do not add up to 100%, since minor elemental contents are not listed

and EDX2 areas also show crystals of triangular shapes confirming the presence of pabstite (BaSnSi₃O₉) (EDX1 and EDX2) and the EDX3, EDX4 and EDX5 areas contain needle-shaped crystals, which elemental compositions would correspond to Chinese Purple or Chinese Blue.

Independent contemporary synthesis of pabstite (BaSnSi₃O₉)

A contemporary synthesis of pabstite (BaSnSi₃O₉) was carried out according to the following equation

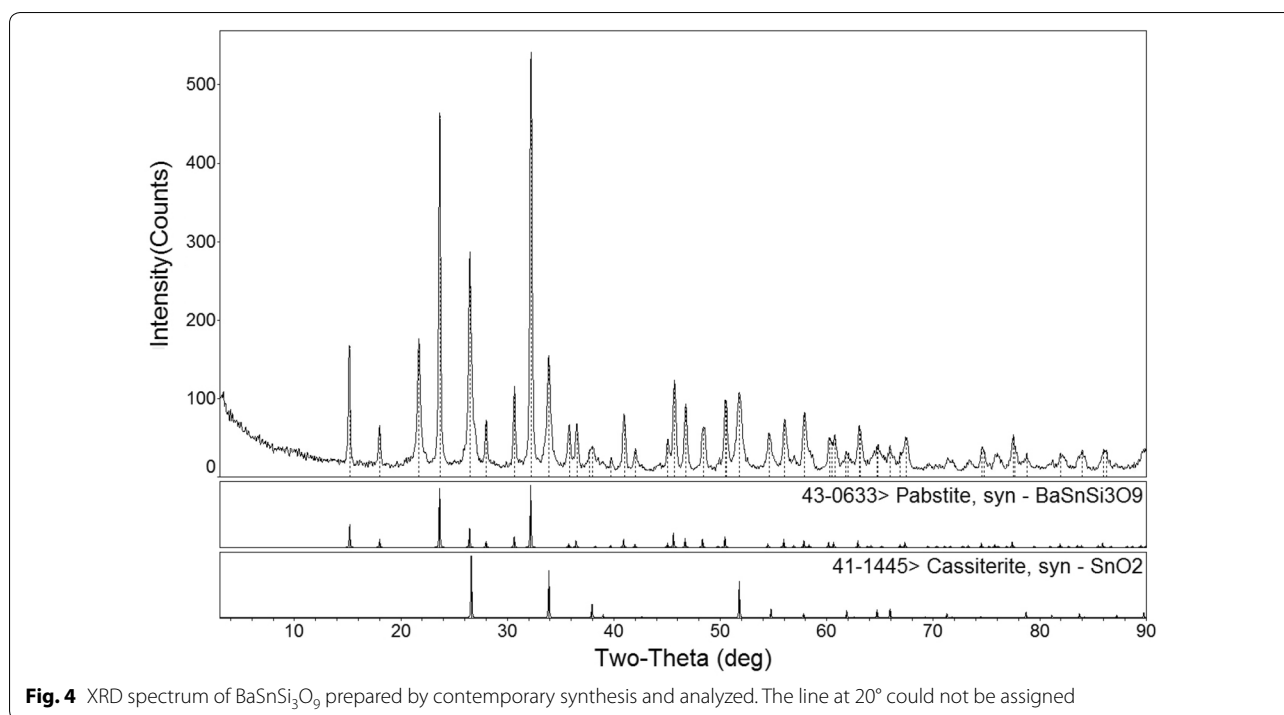


with the starting components in 1:1:3 stoichiometric ratio. BaCO₃ was used as a barium oxide source and SnO₂ (cassiterite) as a tin source. The combined solid starting materials were ground in an agate mortar and the mixture was kept for 6 h at 1000 °C, the temperature, at which the barium copper silicate flux synthesis of the ancient Chinese blues was carried out. The resulting white powder was analyzed by XRD (Fig. 4). The obtained line pattern revealed a mixture of compounds with BaSnSi₃O₉ as the main product and SiO₂ and SnO₂

as remaining starting materials. A line of low intensity at approximately 20° could not be assigned. BaSnSi₃O₉ is known to form colorless hexagonal crystals [26], often even under conditions when impure starting materials were used. The bottom Raman spectrum of Fig. 2d corresponds to BaSnSi₃O₉ prepared by contemporary synthesis. It agrees well with the spectrum of the BaSnSi₃O₉ crystal of the LY02 sample (Fig. 2d top) and with the reference spectrum from the RRUFF library [27]. Based on the result of the independent experiment and the Raman analysis we conclude that the triangle shaped crystals of the SEM images of Fig. 3 correspond to pabstite.

Discussion

Egyptian Blue was the first man-made pigment of ancient civilizations, which appeared during the fourth dynasty in the 3rd millennium BC and had wide applications in painting, preparation of faience and of compact body objects of the Old, Middle, and New Kingdoms, the Ptolemaic and Roman times [28]. Saleh reported for a sample of Egyptian Blue a content of 1.7% tin oxide (cassiterite (SnO₂)) [29] taken from a



pigment cake found in the tomb of Cheruef (reign of Amenophis III, 18th Dynasty). They attributed the presence of cassiterite to an accidental event that the used copper ore was tin contaminated. Later Jaksch [30] argued that Egyptian copper ores do not contain tin in amounts to account for the relatively high tin concentrations in Egyptian Blue samples. Their study additionally revealed that cassiterite crystals were present in many of their Egyptian Blue samples, which pointed to an intended synthetic application of tin admixtures. According to Jaksch tin oxide was found in Egyptian Blue samples of monuments and tombs erected during the reign of Thutmose III (1479–1425 BC) and in monuments of the 18th, 19th and 20th Dynasties and the Ptolemaic and Roman times. In absence of the trace elements tungsten or molybdenum the appearance of tin oxide marked the use of a reprocessed material and the advent of the introduction of a new preparation technique for Egyptian Blue throughout the periods of the 18th Dynasty till the Roman times. The tin oxide originated from bronze or bronze scrap and was utilized as an opacifier of lead glazes, particularly applied for the glazing of pottery [31]. Upon heating tin oxide dissolves in lead oxide and upon cooling finely divided cassiterite (SnO_2) or PbSnO_3 [32, 33] crystallizes from the glaze resulting in an opaque white glaze layer. Generally, lead oxide/tin oxide mixtures melt together at elevated temperatures, but two other effects become relevant: lowering of the glass vitrification temperature

with respect to a lead oxide-only melt and also lowering of the viscosity of the melt in the mixture. These two properties would be also of great advantage for the use as a flux in the syntheses of Egyptian Blue. To exploit these technological advantages further the application of tin/lead oxide mixtures were established using bronze or bronze scrap in such preparations and providing at the same time the copper source, but some amounts of a lead mineral had still to be added.

For related chemical and physical reasons the described effects of tin oxide/lead oxide mixtures of the Egyptian Blue synthesis could also be advantageous in preparations of the Chinese blues, for instance, when used as a flux. This raised several spontaneous questions: What was the function of the tin content of the starting materials, for instance, to create synthetic advantages or to improve the pigment quality? Was tin intendedly added or was it accidentally introduced as a companion of certain starting materials and why were the lead and tin contents of the LY samples relatively low?

To answer these questions, we want to first find out what were the most probable tin containing raw materials for the preparation of the LY samples. We excluded actually the direct use of mineral tin salts like cassiterite (SnO_2), since such ingredients never appeared as starting materials of pigment syntheses in ancient China. BaCO_3 and SiO_2 were frequently used starting materials.

Trying to trace the tin origin in the LY Chinese Blue pigments we established 5 plausible possibilities:

1. Use of the rare mineral pabstite ($\text{Ba}(\text{Sn},\text{Ti},\text{Zr})\text{Si}_3\text{O}_9$) from the Tian Shan mountains [34] to be applied as a barium source or added accidentally in the manufacturing process of the Chinese blues. Pabstite from Tian Shan locations can be ruled out, since it contains considerable amounts of titanium and zirconium and both of these elemental constituents were not detectable in the EDX analysis of the LY samples.
2. The common barium starting material for the syntheses of the Chinese blues was witherite (BaCO_3) or rarely barite (BaSO_4). Minerals of these compounds never appear associated with tin compounds (RRUFF), which excludes introduction of the tin content into the LY samples by this way.
3. Lead minerals were commonly applied as flux additives in the preparation of the Chinese blues, often in large amounts [8, 10, 16, 17, 23–25]. Since tin compounds can be companions of lead minerals we assumed that the tin content could have been introduced as an admixture to the lead starting mineral. But the lead contents of the LY samples are relatively low compared to the majority of original barium copper silicate samples, even lower than their tin contents. The use of a lead-only flux additive and introduction of tin as a minor companion can therefore be ruled out. Another reason, why tin could not have accompanied the lead mineral, is that minerals combining both elements do exist in nature exclusively as sulfides (RRUFF). From this fact follows that in case sulfides were used in the synthesis of the LY samples, the EDX analyses should have revealed at least small contents of sulfur, but even not traces of sulfur were detected.
4. Another possibility is that bronze or bronze scrap (bronze patina or bronze slag considered as bronze scrap) were applied as the copper starting materials for the syntheses of the Chinese blues. In this context it is interesting to note that bronze corrosion has been applied as pigment base materials [35]. Ancient Chinese bronze has relatively high lead contents [36] in contrast to bronze of the Western hemisphere. We therefore put forward the notion that in the firing process of the Chinese blues the alloyed tin contents of bronze or bronze scrap were converted to tin oxide (SnO) or cassiterite (SnO_2) by aerial oxidation and the lead contents to lead oxides (mainly PbO). Thus, cassiterite could be generated as the key chemical precursor for the formation of pabstite in the LY samples. Furthermore, it is worth mentioning in this context that bronze patina often contains mushistonite ($\text{CuSn}(\text{OH})_6$) [37] formed by weathering and that mushistonite would turn into cassiterite by dehydration upon heating.
5. Mushistonite ($\text{CuSn}(\text{OH})_6$) (RRUFF, ID R060153) is found in China as a mineral (Ping Wu, Xuebaoding, Sichuan Province) [26] and could principally be considered as the sole copper starting material for the preparation of the LY blue pigments. Visually mushistonite can be confused with the mineral malachite ($\text{Cu}_2(\text{CO}_3)(\text{OH})_2$) (RRUFF, ID 4809), which frequently served as the copper source to prepare the Chinese blues (as well as bronze). Mushistonite as the sole copper/tin starting material seems however less plausible, since its composition would lead to a copper to tin ratio of 1:1 in the LY samples, but in none of the LY samples such EDX values were found.

From the above list of possible ways that tin was introduced into the manufacturing process of the LY barium copper silicate pigments we cannot exclude points (4) and (5) as the tin source, but from these two aspects we favor point (4) even more. Chemically Egyptian Blue is related to the Chinese blues and bronze and bronze scrap was definitely involved in the developments of Egyptian Blue ($\text{CaCuSi}_4\text{O}_{10}$) and the primary intention to use bronze or bronze scrap was to substitute copper minerals as starting materials achieving copper recycling. The advantages of lowered vitrification temperatures and lowered viscosities via the use of bronze or bronze scrap would also hold for the flux synthesis of the Chinese blues avoiding in this case the presence of great amounts of lead-only fluxes [8, 10, 16, 17, 23, 25]. Ancient Chinese bronze or bronze scrap has besides tin low lead content generating a lead/tin oxide flux directly when used as a starting material of the Chinese blues. Due to the small content of lead in ancient Chinese bronze or bronze scrap the lead/tin mixture would be present in only small amounts. The annealed flux would be opaque and had to be considered as an ‘impurity’ of the pigments. The presence of only small amounts of the flux influenced the overall appearance of the pigments only marginally; rather we expect that the use of bronze or bronze scrap generated higher pigment qualities due to a higher crystallinity of the final product.

Since the Chinese production developments were chemically similar to the Egyptian ones, one could hypothesize that the Chinese invention was triggered by a technology transfer from ancient Egypt to ancient China [17]. However, to substantiate this notion more cases of tin containing samples of the Chinese blues had to be studied. Up to now tin was identified only in one more case of the Chinese blues, which are the bluish-green and purplish blue pigments of a Tomb Guard Jar excavated from Sanmenxia dated to the later period of Eastern Han Dynasty (25–220 AD) [38].

Conclusions

The three barium copper silicates Chinese Blue ($\text{BaCuSi}_4\text{O}_{10}$), Chinese Purple ($\text{BaCuSi}_2\text{O}_6$) and Chinese Dark Blue ($\text{BaCu}_2\text{Si}_2\text{O}_7$) were identified by archaeometry as the blue and purple pigments of a mural of a Western Han Dynasty tomb of ancient Luoyang City. Platelet-like triangular crystals were characterized as pabstite ($\text{BaSnSi}_3\text{O}_9$). The possibility was excluded that pabstite was added as a mineral from the Tian Shan mountains, furthermore that tin was introduced as a companion of added lead or barium starting minerals, both essential ingredients to the chemical cocktail of barium copper silicate preparations. Also, the mineral mushistonite ($\text{CuSn}(\text{OH})_6$) was ruled out as the sole copper/tin component of the starting materials. By exclusion we could thus establish plausibility that the copper starting material for the Luoyang pigments was bronze or bronze scrap providing besides copper also lead and tin. The primordial reason for the use of these materials was the substitution of copper minerals to establish a kind of copper recycling. But moreover, this change in synthesis led to a new production procedure avoiding the use of great amounts of a lead oxide flux. Due to the less viscous lead/tin oxide fluxes the preparations enabled shorter reaction times and lower temperatures, which probably led to higher product qualities in comparison to the high-lead syntheses of the Chinese blues.

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Authors' contributions

All the experiments were designed and carried out by ZZ, QM and HB. The data were analyzed by ZZ and QM. The manuscript was written by ZZ and QM, and revised by QM and HB. All authors read and approved the final manuscript.

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Availability of data and materials

The datasets analyzed during the current study are available from the corresponding author on reasonable request.

Competing interests

The authors declare that they have no competing interests.

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