

Ancient Man-made Copper Silicate Pigments Studied by Raman Microscopy

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Abstract: This article describes the application of Raman microscopy (micro-Raman spectroscopy) to the characterization and identification of alkaline earth copper silicates, which were used in ancient times as blue and purple pigments and were man-made. Thus, Egyptian Blue ($\text{CaCuSi}_4\text{O}_{10}$), Chinese Blue ($\text{BaCuSi}_4\text{O}_{10}$) and Chinese Purple ($\text{BaCuSi}_2\text{O}_6$) give rise to well-defined Raman spectra (excitation 514 nm), which allowed the identification of Egyptian Blue in 11 original Egyptian samples from the VIth Dynasty to Roman times and that of Chinese Purple in six ancient Chinese samples dated from the Warring States period to the Han Dynasty (479 BC to 220 AD). One greenish-blue Egyptian sample turned out not to contain Egyptian Blue but rather a mixture of cupro-wollastonite and libethenite. Some of the Egyptian Blue samples showed only minor admixtures of CaSO_4 or silica. Four of the Chinese samples were colour sticks. In one original Chinese stick sample Chinese Blue was recognized as an additional pigment component. One colour stick was revealed to be highly contaminated with Ba-silicates, BaCO_3 , CaCO_3 , PbSO_4 , BaSO_4 , PbO , and SiO_2 . The investigated two pigment layer samples of the Terracotta Army, Xi'an, China were analysed by Raman spectroscopy and were found to contain, in addition to Chinese Purple, azurite, vermilion, iron oxide red, PbCO_3 , PbO , and BaSO_4 . Chinese Blue was not found.

Keywords: Archaeometry · Chinese Blue · Chinese Purple · Egyptian Blue · Raman spectroscopy

1. Introduction

Various analytical methodologies efficiently contribute to the quantification of conclusions on materials of archaeological and cultural value [1][2]. The use of analytical tools first of all provides physical and chemical data, which may then be transformed into valuable information concerning the history and other backgrounds of such objects. In this regard pigments of artefacts play a prominent role. Several analytical techniques are well-suited for their proper characteriza-

tion. One of them is Raman spectroscopy, which has been utilized to an increasing extent in the recent years and has proved to be a very powerful tool at the arts/science interface. Selected references may witness the state of the arts [3–34].

The invention of Raman spectroscopy by Sir Ch. V. Raman was acknowledged with the Nobel Prize in 1930 and this was the onset of a long-lasting, but eventually very beneficial development toward an analytical technique that is nowadays applied in practically all matter-oriented sciences. For decades the utilization of the Raman experiment suffered from insufficient intensity of the scattered light of the Raman effect. However, instrumental developments of the past ten years have led to an enormous improvement in sensitivity, which allow that even minute amounts of sample (μm and μg range) are analysed in a non-destructive manner [4]. Thus, Raman spectroscopy, especially in conjunction with a microscope (micro-Raman spectroscopy), has advanced to a microanalytical tool appropriate for analysis of micro-scale heterogeneous mixtures such as those appearing in forensic analyses [35] and archaeological studies [3–34].

2. Instrumental Conditions for the Application of Raman Spectroscopy as an Archaeometric Method

Raman spectroscopy involves the irradiation of a sample with (laser) light (usually in the visible or near-IR range) and the analysis of the components of the inelastically scattered light [36]. The sample excited by an incident beam emits light at discrete wavelengths and with given intensities. However, the intensity ratio between the excitation beam and the emitted light is several orders of magnitude. This caused detection problems in the past, but more recently Raman instrumentation has become much more sensitive [5] mainly due to the advent of very effective holographic filters separating the incident beam light out from the scattered light and due to enormously improved sensitivity of the detectors for the scattered light, such as photodiode arrays or, even better, coupled cluster discharge (CCD) detectors.

Laser beam energies of sometimes only a few milliwatts are sufficient to illuminate microscopic sample spots of a few μm^2 , and even these conditions allow appropriate Raman spectra to be obtained. As mentioned above, a typical

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set-up for a Raman spectrometer comprises the spectrometer and a video-camera-controlled microscope (micro-Raman spectroscopy), which additionally enables the surface of a sample to be scanned in the μm range. This is of enormous advantage for archaeometric studies, since the heterogeneity of samples is quite often above this limit. The practical spectral resolution of commercial spectrometers is normally between 1 and 5 cm^{-1} , which is satisfactory with respect to the expected band widths of the Raman emissions.

In current practice, rare cases of limited applicability of micro-Raman spectroscopy still persist when the sample or a distinct chemical component of a sample mixture does not show the Raman effect or when the samples absorb most of the incident beam. Furthermore, the sample may show fluorescence. The latter two disadvantages can quite often be overcome by changing the wavelength of the incident laser, *i.e.* changing the laser that normally operates at fixed wavelength.

3. Pigment Applications of Raman Spectroscopy

As mentioned above, the use of Raman spectroscopy in arts and archaeometry for the identification of pigment and other materials, such as binders, varnishes and matrices in general, became more common in the early nineties. In particular, micro-Raman spectroscopy has contributed recently to the pace of development. Prominent applications with pigments involve manuscripts, paintings and other artefacts and support the establishment of identity, manufacturing processes, cultural and historical background, and even the nature of conservation problems [4–34]. Raman spectroscopy identifies chemical species and such in mixtures by IR emissions due to specific vibrations of the atomic framework of a component. In archaeometric and arts applications pigments are mostly solid inorganic or organic compounds and glassy phases, which in most cases give rise to characteristic Raman bands. In the recent years libraries of spectra of ancient and contemporary pigments have been [37] or are about to be established [38], which greatly assist the identification processes. This article will exclusively focus on the Raman analysis of blue and purple copper silicate pigments, which were used in the ancient Egyptian and Chinese civilizations and were produced by synthetic procedures.

4. Egyptian Blue and Chinese Blue and Purple

Egyptian Blue and Chinese Blue and Purple are defined chemical species with the compositions $\text{CaCuSi}_4\text{O}_{10}$, $\text{BaCuSi}_4\text{O}_{10}$, and $\text{BaCuSi}_2\text{O}_6$. Their (historical) preparations and structures are briefly discussed to the extent that this article needs as reference. A more detailed background is given in earlier descriptions [39–45].

4.1. Egyptian Blue

As denoted by its name Egyptian Blue was prepared by the Egyptians, and can be traced back to predynastic times. Earliest artefacts studied date back to 3600 BC. Its use was perpetuated through all periods of Egyptian civilization and penetrated into the Greek and Roman cultures. The invention of Egyptian Blue has been attributed to insufficient availability of stable blue minerals. In fact, the only natural blue mineral of stability and colour properties comparable or even superior to the man-made Egyptian Blue and which did not require chemical transformation prior to use was the rare mineral lapis lazuli [46].

The manufacturing processes of Egyptian Blue in modern times were traced back starting in early 19th century. These studies have been reviewed elsewhere [39][41] and are not the primary focus of this article, however, implicitly selected aspects of them will appear when original samples are analysed with respect to their chemical compositions. Of relevance are therefore the starting materials and remains of these and eventually side products; the latter became apparent from studies of independent synthesis. The starting materials for Egyptian Blue were normally calcite (CaCO_3), quartz (SiO_2) and copper-containing components, such as malachite, azurite or even copper metal. Normally the synthetic procedure required addition of a flux, which, however, in most cases is difficult to trace due to its presence in amounts below (Raman) detection limits.

4.2. The Chinese Pigments

Chinese Blue and Purple, sometimes also denoted Han Blue and Purple, are also copper silicates, but contain barium instead of calcium. Chinese Blue, $\text{BaCuSi}_4\text{O}_{10}$, is the heavier isostructural homologue of Egyptian Blue, and possesses very similar chemical and physical properties. Chinese Purple constitutes another unique phase of the composition $\text{BaCuSi}_2\text{O}_6$ containing less quartz than

Chinese Blue [43–45]. Chinese Blue and Purple appeared in Warring States period (479–221 BC) and can later be traced in the Qin and Han Dynasty (221 BC–220 AD). It should be mentioned that an ‘Egyptian Purple’, which would correspond to $\text{CaCuSi}_2\text{O}_6$, has yet not been detected and is probably non-existent. The preparations of the Chinese copper silicates demand more severe physical conditions than Egyptian Blue and if the pure Chinese Blue and Purple compounds are of interest they also require strict control of stoichiometry of the starting materials. The ancient synthesis started mostly from very stable barite, BaSO_4 , sometimes also from witherite, BaCO_3 , as barium-containing components, which, especially for the chemical break-down of BaSO_4 , required the addition of lead oxide or carbonate as catalyst. All these factors indicate that the development of Chinese Blue and Purple in ancient times have to be considered fine technical achievements (in modern terminology they would be called ‘High Technology’). The increased complexity of the resulting pigment mixtures complicates the pigment analysis in comparison to Egyptian Blue. However, as we will see later Raman spectroscopy can efficiently contribute to unravel the constituents of the mixtures and concomitantly contribute to elucidation of the historical role of these pigments.

4.3. Structures of Egyptian Blue, Chinese Blue and Purple

Egyptian and Chinese Blue are isostructural sheet silicates [47–50] consisting of a puckered two-dimensional network of condensed silicate tetrahedrons. These are arranged in tetragonal arrays of four-membered silicate rings to additionally generate eight-membered rings. The resulting network pattern is sketched in Fig. 1.

The puckering in the final layer is apparently to the most part induced by the coordination of the cations and here mainly by Cu^{2+} , which demands a square-planar environment. Cu^{2+} sits above or below every other silicate square and pulls four adjacent squares together to enable strong oxygen contacts. In an alternating fashion with Cu^{2+} , the Ca^{2+} or Ba^{2+} ions take the remaining positions above and below the squares, but moreover they interconnect the $\text{CuSi}_4\text{O}_{10}^{2-}$ layer by doubling their coordination sphere to establish eight-coordination. As mentioned before the whole framework attains tetragonal symmetry, however the local symmetry of an isolated planar $\text{Si}_4\text{O}_{12}^{8-}$ ring (D_{4h}) is lowered

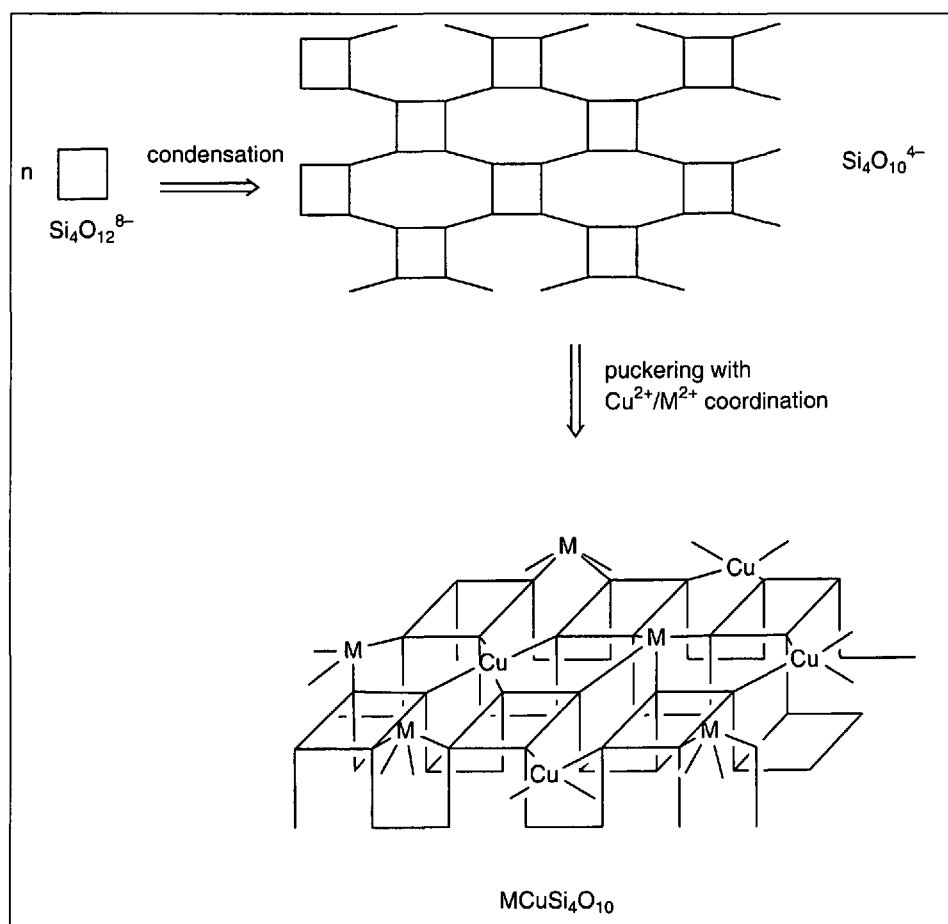


Fig. 1. Schematic sketch of the condensation process of a four-membered silicate ring ($\text{Si}_4\text{O}_{12}^{8-}$) to build up a $\text{Si}_4\text{O}_{10}^{4-}$ layer and its puckering induced by coordination of Cu^{2+} and M^{2+} ($\text{M} = \text{Ca}, \text{Ba}$).

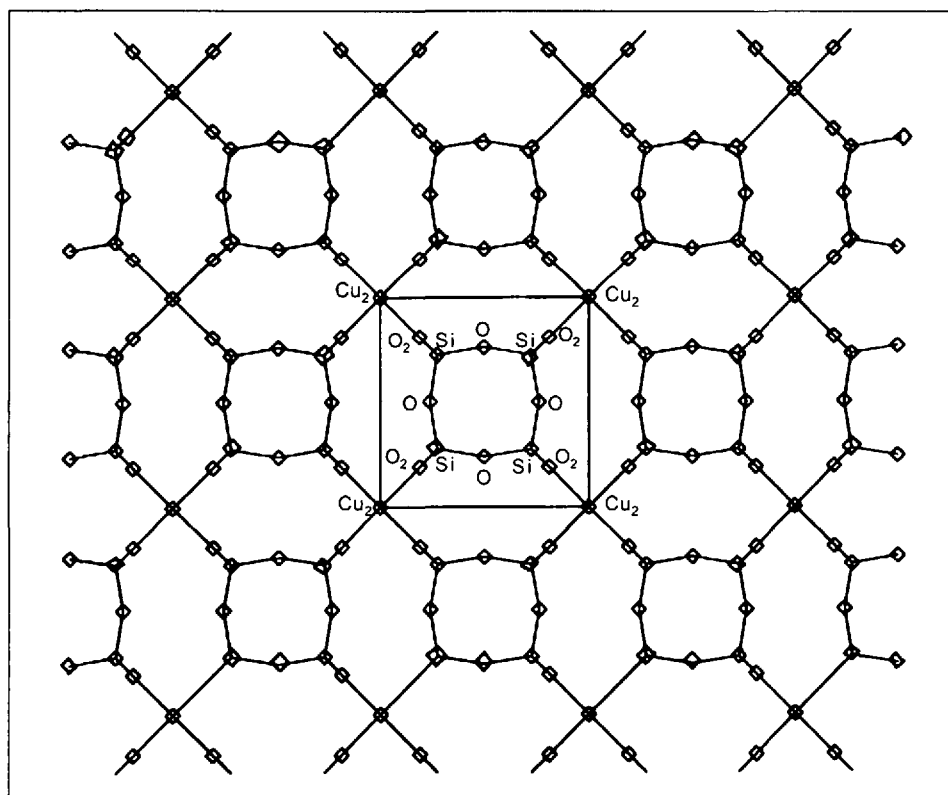


Fig. 2. Schematic top view of a $\text{Cu}_2\text{Si}_4\text{O}_{12}^{4-}$ layer of Chinese Purple ($\text{BaCuSi}_2\text{O}_6$).

to C_{2v} in the condensed arrangement of Egyptian and Chinese Blue.

The structure of Chinese Purple shows three significant features [49][51], which are partly distinct from those of Egyptian and Chinese Blue:

- There is no extended silicate framework, rather the structure is composed of planar four-membered silicate rings [51a]
- Cu-Cu bonded units [51b] hold the four-member rings together to form layers of $[\text{Cu}_2\text{Si}_4\text{O}_{12}^{4-}]_\infty$
- Similar to Egyptian or Chinese Blue, the Ba^{2+} ions are located above and below the silicate rings and thus interconnect the layers.

A top-view projection of a $[\text{Cu}_2\text{Si}_4\text{O}_{12}^{4-}]_\infty$ layer is schematically sketched in Fig. 2.

Due to the presence of isolated four-member silicate rings, Chinese Purple may be viewed an intermediate in the condensation process to Chinese Blue. From experimental studies it was recognized that Chinese Purple is indeed a kinetic product on the way to Chinese Blue [42-45]. Concerning the Raman properties of Chinese Purple, it is important to keep in mind the two above-mentioned structural features distinguishing it from the Blues, because these two properties are principally well-suited for Raman spectroscopic detection.

5. Raman spectra of Egyptian Blue, Chinese Blue and Purple

Exemplary spectra of pure $\text{CaCuSi}_4\text{O}_{10}$, $\text{BaCuSi}_4\text{O}_{10}$, and $\text{BaCuSi}_2\text{O}_6$ samples are shown in Fig. 3. Overall the spectra of the Blues are very similar emphasizing their close chemical relationship, while the spectrum of Chinese Purple shows only little resemblance with the general band pattern of the other two pigments.

In the following the main features of the Raman spectra are briefly discussed. The spectra have been analysed with respect to the principal types of structures by aid of lattice dynamics calculations for both types of compounds [52][53]. The $\text{MCuSi}_4\text{O}_{10}$ phyllo-silicates ($\text{M} = \text{Ca}, \text{Sr}, \text{Ba}$) possess $P4/ncc$ [47][48] and $\text{BaCuSi}_2\text{O}_6$ $I4/mmm$ symmetry [49][51]. Since both types of species thus belong to centrosymmetric space groups, total symmetric vibrations should give rise to intense Raman bands. For the Egyptian and Chinese Blues the bands at 1088 and 1102 cm^{-1} are respectively assigned to a_{1g} $\nu(\text{SiO})$ vibrations, while the other

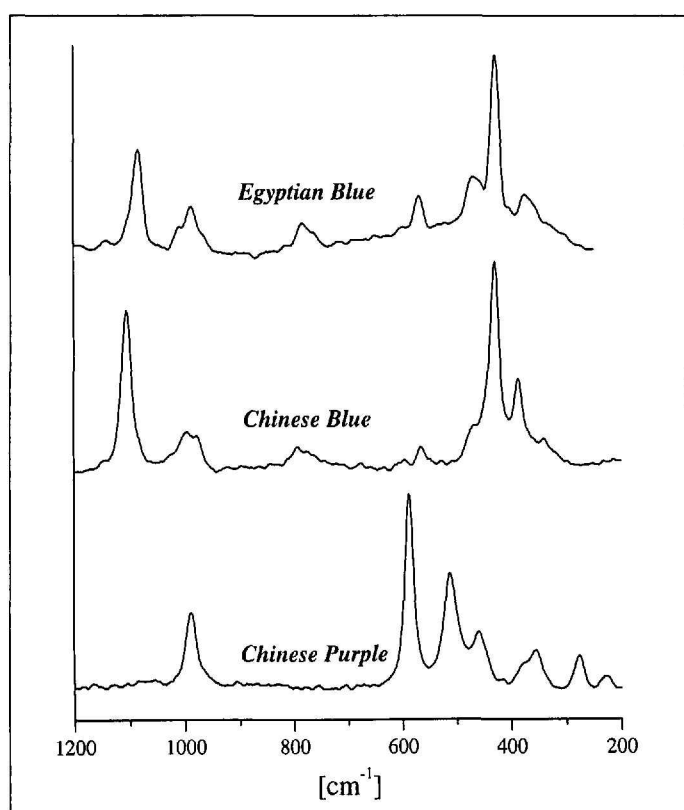


Fig. 3. Raman spectra (514 nm) of Egyptian Blue ($\text{CaCuSi}_4\text{O}_{10}$), Chinese Blue ($\text{BaCuSi}_4\text{O}_{10}$) and of Chinese Purple ($\text{BaCuSi}_2\text{O}_6$) in the range 1200–200 cm^{-1} . Major bands of Egyptian Blue: 1088(s), 992(w), 789(w), 575(w), 471(w), 435(s), 363(w), 201(w) cm^{-1} ; Chinese Blue: 1102(s), 997(w), 791(w), 562(w), 427(s), 383(w) cm^{-1} and Chinese Purple: 990(m), 588(s), 516(m), 459(w), 354(w), 276(w), 183(w) cm^{-1} .

bands at 435 (Egyptian Blue) and 427 cm^{-1} (Chinese Blue) are attributed to a_{1g} bridging oxygen breathing modes. The relative constant position of these bands points to almost exclusive motions of the closely related silicate frameworks of $\text{CaCuSi}_4\text{O}_{10}$ and $\text{BaCuSi}_4\text{O}_{10}$. From the bands of lower intensities it is worth mentioning that those at 363 ($\text{CaCuSi}_4\text{O}_{10}$) and 383 cm^{-1} ($\text{BaCuSi}_4\text{O}_{10}$) are attributable to vibrations with strong Cu–O character [54]. The band of $\text{CaCuSi}_4\text{O}_{10}$ at 201 cm^{-1} is presumably due to a Ca–O vibration, since it is missing in $\text{BaCuSi}_4\text{O}_{10}$.

a_{1g} -Type bands of $\text{BaCuSi}_2\text{O}_6$ are those at 990, 588, 516, 459 and 276 cm^{-1} . While the 990 cm^{-1} band of medium intensity belongs to a $\nu(\text{SiO})$ vibration, those at 588 and 516 cm^{-1} are attributed to a $\delta_s(\text{SiO}_2)$ mode of the silicate groups [49] and, similar to the $\text{MCuSi}_4\text{O}_{10}$ compounds, to an oxygen breathing vibration, respectively. Bands at 276 and 183 cm^{-1} are assigned to vibrations with Cu–O character, however, based on earlier analyses of complexes with Cu–Cu bonds, these vibrations are expected to bear additional Cu–Cu bond character [55][56]. The mentioned lattice dynamics calculations predict the vibration with mainly Cu–Cu character to appear at 63 cm^{-1} [52], unfortunately out of the analysis range of standard Raman spectrometers.

In several earlier cases Raman spectroscopy has been successfully applied to

identify Egyptian Blue in ancient artwork [3b][13][29][45][57]. Our group has recently introduced Raman spectroscopy to trace $\text{BaCuSi}_4\text{O}_{10}$ and $\text{BaCuSi}_2\text{O}_6$ in blue and purple colour sticks dated to the Warring States, Qin and Han Periods and also in pigment samples of the Terracotta Army of the Qin Dynasty from Lintong near Xi'an, China [44][45]. A more detailed Raman analysis including that of Egyptian Blue in ancient samples is presented in this article, which nicely demonstrates its straight-forward applicability as an archaeometric method [5].

6. Raman Investigations of Original Egyptian, Mesopotamian, and Chinese Samples

The ancient samples of Egyptian Blue and Chinese Blue and Purple investigated by Raman spectroscopy are summarized in the Table. The Egyptian samples cover a span of almost 3000 years starting with Blue from the 6th Dynasty of the Old Kingdom to a sample of the Roman time.

The oldest sample stems from the Mastaba of Mereruka in Saqqara, Egypt, which possesses wall paintings with prevailing blue colour. Mereruka was vesir to the King Teti arriving in the Mastaba from his tomb through a fictive door [41]. The second sample originates from the tomb of General Antef, Middle Kingdom, 11th Dynasty. General Antef re-

ported to Mentuhotep II (2069–2014 BC) as the commander of the troops. The next three samples studied came from the New Kingdom period. Blue from the crown of the famous bust of Nefertete (Aegyptisches Museum der Staatlichen Museen Berlin, Germany) and Blue of the Talatat Stones of the Temple of her husband Echnaton [41]. The cylindrical seal, which is dated also to the New Kingdom and falls in a very productive period for artisans, is the property of one of the authors. It has been described in detail elsewhere [42]. The sample of Brick Nimrud (Fig. 4) originates from Mesopotamia and is dated to the 13th–7th century BC. Today it is property of the British Museum, London [58a].

The Egyptian Late Period is documented by several other samples. The blue Amulet Bes protected those who wore it by the powers of dwarfish God Bes. It is dated to the 24th Dynasty and is property of one of the authors. The next sample of this period originates from a relief of the Tomb of Ibi, chief steward of the divine adoratrice under Psammetichus I (Fig. 5).



Fig. 4. Photograph of a fragment of Brick Nimrud from Mesopotamia dated to the 13th–7th century BC (British Museum, London).

Table. Egyptian, Mesopotamian, and Chinese samples investigated by Raman spectroscopy

Period	Name, origin, or present location	Blue or Purple Pigments	Other Pigments	Impurity
2345–2181 BC	Mastaba of Mereruka, Saqqara	EB		CaSO ₄
2133–1991 BC	Tomb Antef, Thebes	EB		CaSO ₄
1340 BC	Bust of Nefertete, blue of crown, Amarna	EB		CaSO ₄ **
1353 BC	Echnaton temple, blue of Talatat, Amarna	EB		CaSO ₄ **
1300 BC	Cylinder Seal, Thebes	EB		CaSO ₄
13th–7th Century BC	Brick Nimrud, Iraq	EB		SiO ₂
712–332 BC	Amulet Bes, Egypt	EB		
663–525 BC	Tomb Ibi, Thebes		W/L	
500 BC	Ba-bird, Soul, Memphis	EB		SiO ₂
3rd Century BC	Mummy cartonage	EB		
1st Century BC	Ptah Sokaris Osiris Figure	EB		
Roman time	Mummy coffin, Cairo	EB		CaSO ₄
Han Dynasty	Stick Freer Gallery, Washington	CP		SiO ₂ , CaCO ₃ , BaCO ₃ , BaSO ₄ , PbSO ₄ , Ba-silicates
Han Dynasty	Stick Royal Ontario Museum	CP		
Han Dynasty	Stick 4069, Oestas. Museum	CB/CP		SiO ₂ **
Han Dynasty	Stick 4070, Oestas. Museum	CP		BaCO ₃
Qin Dynasty	Sample I, Terracotta Army	CP	azurite, vermillion, iron oxide red, PbCO ₃	SiO ₂
Qin Dynasty	Sample II, Terracotta Army*	CP	BaSO ₄ ,	SiO ₂

EB = Egyptian blue, CP = Chinese purple; W = cupro-wollastonite, L = libethenite; * the lower lying terracotta layer also contains FeTiO₃ and Ca₃(PO₄)₂ as established by EDX [44]; ** uncertain due to low amounts.

The wooden falcon figure Ba-bird, Kestner Museum, Hanover, Germany contains blue areas, from which a sample was studied. The Ba-bird from approximately 500 BC symbolized a protection god at burial ceremonies [41]. The figure Ptah-Sokaris-Osiris from the 1st century

BC stems originally from Memphis, Egypt. It is now property of the Staatliche Sammlung Aegyptischer Kunst, Munich, Germany (ÄS 19). It served as a container for corpses. A sample of the Blue was taken [41]. The samples of the mummy cartonage and the mummy coffin contain

Egyptian Blue from Ptolemaic and Roman times. Their present locations are unknown.

Four of the investigated six original samples of Chinese Blue and Purple (Table) were taken from original Blue or Purple sticks of octagonal shapes. It is

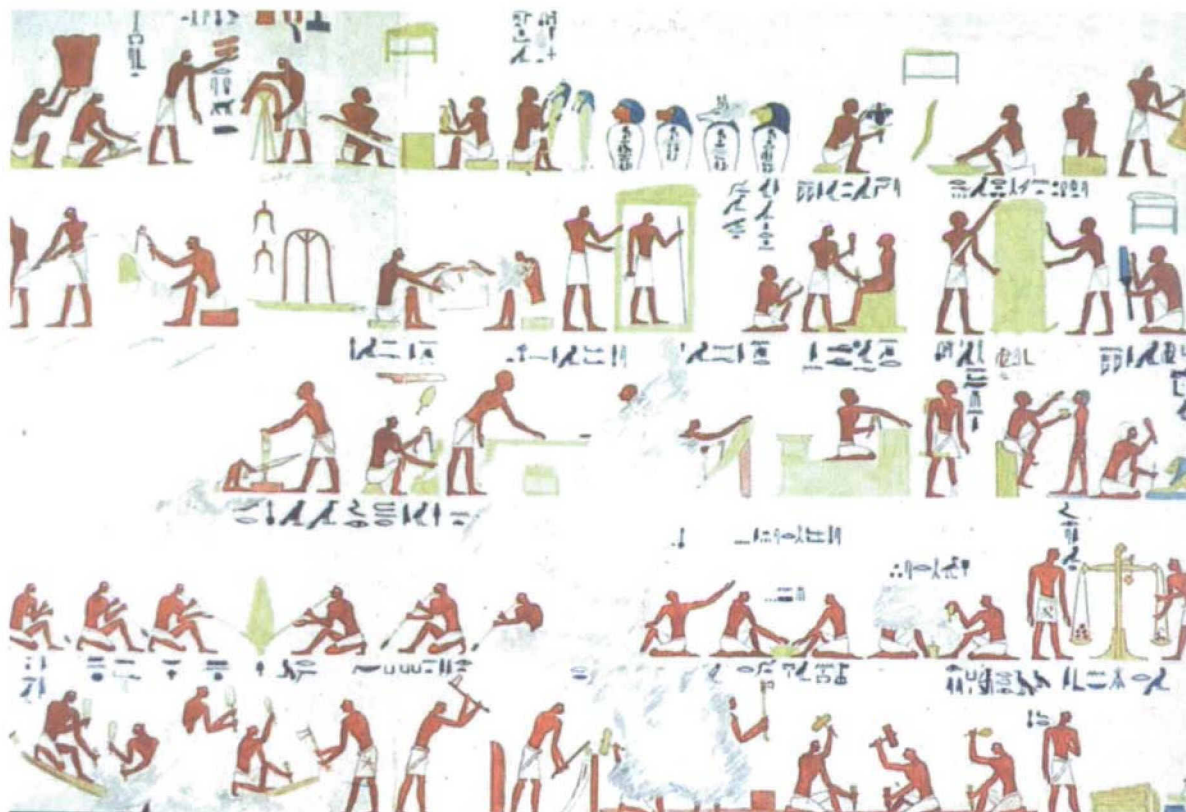


Fig. 5. The photograph of a section of the relief of Theban Tomb 36 (Tomb Ibi), which shows craftsmen at work. Several areas have a greenish-blue colour [58b].

thought that these sticks were trade items. They were used as pigment bases in paints and applied by grinding.

The general phenomenology of sample Freer Gallery has been described earlier by FitzHugh [59][60]. It is displayed in Fig. 6.

Sample stick Royal Ontario Museum came from a blue octagonal stick said to have come from Jincun near Luoyang, China [60]. It is reported to be made of mainly blue particles with scattered purple ones. The two samples of sticks from the Museum of Far Eastern Antiquities in Stockholm, K 4069 (Blue) and K 4070 (Purple) are described as worn and porous materials [60], from which powdery material was taken for investigation. In addition the stick samples were discussed recently [44].

Distinct samples from different parts of the Terracotta Army were also studied by Raman spectroscopy (Fig. 7). A group of Terracotta Soldiers is shown in Fig. 7a. From a fragment of the hat of a soldier (Fig. 7b) the pigment layer (sample I) was investigated as an embedded cross section (Fig. 7c). In Fig. 7d fragments of the trousers of a Terracotta soldier are displayed, from which the pigment layer was studied (sample II). It is presented as an embedded cross section in Fig. 7e. Earlier investigations of these samples have clearly revealed the presence of Chinese Purple and other pigment materials [61][62]. Application of Raman spectroscopy were expected to confirm these results, but perhaps also to deliver further information on the nature of the pigment content.

All the samples were compared to pure Egyptian Blue and Chinese Blue and Purple or mixtures of them, obtained by contemporary independent synthesis [63].

The Egyptian and Mesopotamian samples listed in the Table contain the chemical species $\text{CaCuSi}_4\text{O}_{10}$ (mineral name cuprorivaite) except for the blue-green sample Tomb Ibi, which will be considered separately. In most cases the Raman spectra reveal an even high content of this blue pigment. Earlier findings of El Goresy on other ancient Egyptian samples showed that these consisted of considerable amounts of wollastonite (CaSiO_3) [64], which could not be detected in our study, at least in amounts above the Raman detection limit. El Goresy even defined Egyptian Blue as a mixture of wollastonite and cuprorivaite. Wollastonite could have definitely been traced by Raman spectroscopy, as α - or β -wollastonite or in its vitreous form [29].



Fig. 6. Exemplary photograph of stick Freer Gallery demonstrating its octagonal shape and its true size (above). Microscopic view of a chip of stick Freer Gallery revealing its porous and heterogeneous nature (below). Colour sticks of this kind are anticipated to have been trade items. They were applied as pigment bases in paints by grinding.

As indicated in the Table, several of the listed Egyptian Blue samples show CaSO_4 (gypsum or anhydrite recognized by their Raman emission at 1012 cm^{-1}) [65] as a minor admixture, which presumably stems from natural CaCO_3 resources used as one of the starting components. It should be mentioned that Egyptian Blue also shows a very weak Raman band at this wavenumber, which obscures the analysis of very low CaSO_4 contents. For that reason some of the CaSO_4 assignments in the Table are uncertain as indicated.

Two samples can be shown to contain α -quartz, recognized by the strong Raman band at 468 cm^{-1} . Especially sample Brick Nimrud shows considerable amounts of quartz. Its admixture may be interpreted in terms of a tuning of the material properties with regard to construction purposes. In an exemplary way the Raman spectrum of silica 'contaminated' Brick Nimrud is displayed in Fig. 8 showing besides the bands of Egyptian Blue the strong α -quartz emission.

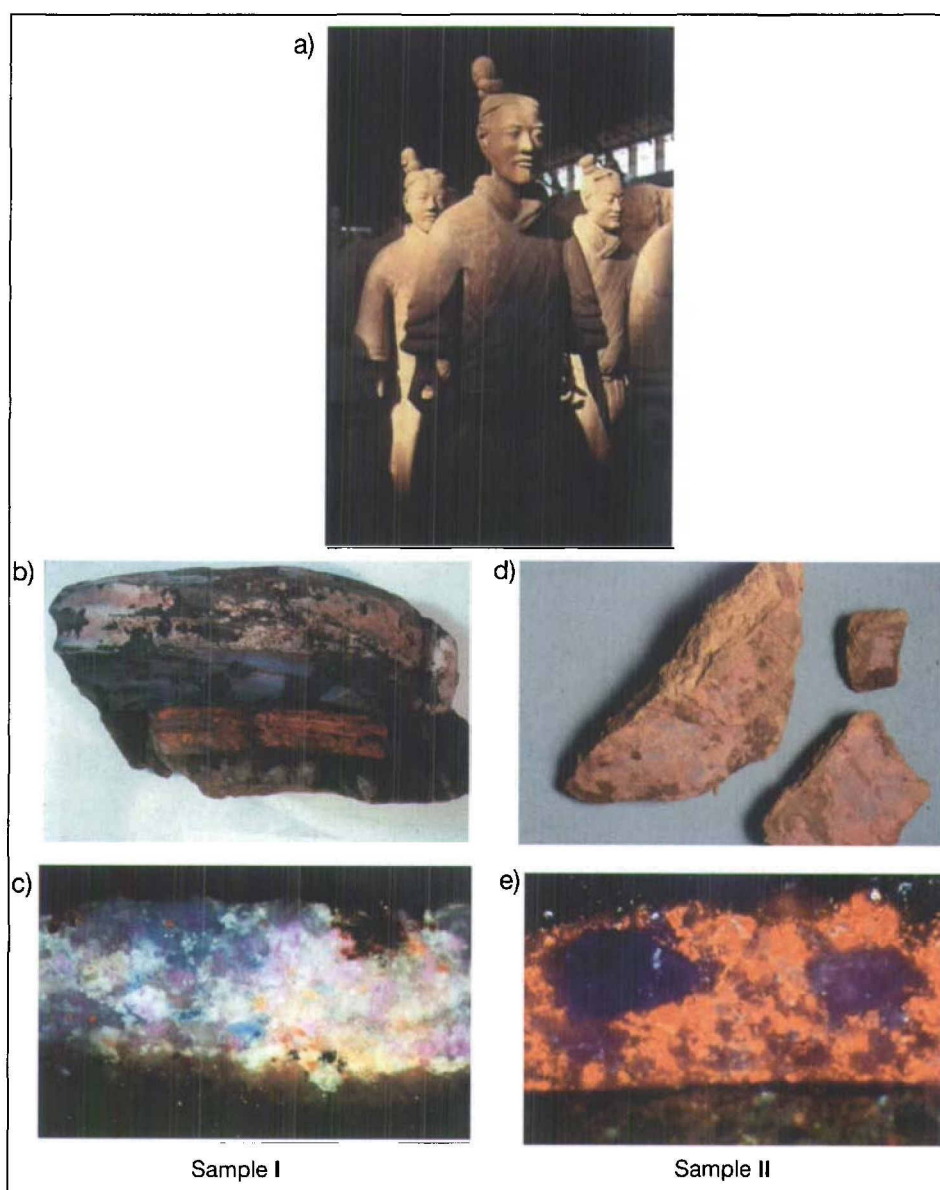
To a lesser extent α -quartz was seen in sample Ba-bird, however, no obvious function can be associated with this admixture. Other samples may also contain minute quantities of α -quartz, which cannot be analysed due to overlap with the weak band of Egyptian Blue at around 470 cm^{-1} . In this context the question arises whether other metastable phases of silica could be detectable by Raman spectroscopy [65]. Of interest are α -tridymite and α -christobalite. The former has been traced in preparations of Egyptian Blue previously [41b]. The presence of these quartz modifications could principally allow conclusions on the thermal

treatment of the samples during the preparation, since in pure state at least α -quartz can be converted to α -tridymite or α -christobalite only by heating them above $870\text{ }^\circ\text{C}$ and $1470\text{ }^\circ\text{C}$. Unfortunately the main Raman band of christobalite overlaps with that of Egyptian (or even Chinese) Blue at around 430 cm^{-1} . However, the major Raman band of tridymite at 516 cm^{-1} could be seen in the presence of Egyptian Blue. A mixture of both should therefore be Raman detectable. In none of the Raman spectra of Egyptian Blue in the Table could this band be traced. Therefore, it can be stated that these samples are tridymite-free.

CaCO_3 impurities could in principle be identified by the major Raman bands at 1084 and 280 cm^{-1} . However, since the strong 1084 band would overlap with the 1088 cm^{-1} of Egyptian Blue, the presence of CaCO_3 could only be verified by the 280 cm^{-1} band. None of the Egyptian Blue samples in the Table showed this band. Major amounts of other impurities could be detected only in the sample of Ptah-Sokaris-Osiris, which consists of Zn compounds according to EDX studies [45], this presumably is indicated by a very strong Raman band at 745 cm^{-1} . This band could however not yet be attributed to a particular chemical species.

The unique greenish-blue sample of Tomb Ibi does not contain Egyptian Blue according to the Raman analysis, rather it seems to be a mixture of cupro-wollastonite and libethenite ($\text{Cu}_2(\text{PO}_4)(\text{OH})$) [66]. With the exception of a less structured band area between 1100 and 1000 cm^{-1} , the overlay of the two compounds fits well with the spectrum of the sample Tomb Ibi, displayed in Fig. 9.

Fig. 7. Samples of the Terracotta Army Xi'an, China. a) A group of terracotta soldiers; b) shows the fragment of a painted hat of a terracotta soldier (fragment 009-98) and below this in c) a microscopic view of a cross section (horizontal extension 1 mm). Bottom left: Purple particles of this sample (sample I) correspond to Chinese Purple and scattered blue grains to azurite. Other pigment content see text. Fragments of the purple trousers of a soldier (fragments 003-92) are shown in d). A microscopic view (enlargement 500 times) of a cross section of its pigment layer corresponding to sample II is presented in e). The displayed part has a horizontal extension of 0.22 mm. The pigment layer contains grains of Chinese Purple and other pigment particles (see text). Below the pigment layer one can find a layer of lacquer and next to this terracotta.



It should be mentioned that cuprowollastonite has been detected previously in other Egyptian artefact samples [29]; it has been defined as α -wollastonite with some Ca^{2+} replacement by Cu^{2+} . By Raman spectroscopy, however, cuprowollastonite cannot be distinguished from wollastonite.

Our Raman studies on the various ancient Chinese barium-copper-silicate samples (Table) and reference samples also brought about well-defined conclusions. From the Chinese stick samples, stick 4069 contains Chinese Blue in mixture with Chinese Purple. All other stick samples show no bands for Chinese Blue and consist mainly of Chinese Purple as the colouring matter.

In all Chinese samples the following potential impurities were checked, which might originate from the minerals used, the added flux or chemical transformations occurring during synthesis: CuO , Cu_2O , BaCO_3 , BaSO_4 , PbCO_3 , PbO , PbSO_4 , CdO , and SiO_2 . The Terracotta Army samples I and II are pigment application cases. They were studied in order to reveal Chinese Blue or Purple, but also other pigments. Several Chinese samples presumably show a Raman emission for silica, which varies in relative intensity from sample to sample. However, identification of the Raman band of minor amounts of SiO_2 in mixtures with Chinese Purple is obscured by the fact that Chinese Purple also possesses an emission of medium to weak intensity in this region. The Raman spectrum of the Chinese sample, stick Royal Ontario Museum, allowed no definite conclusions on impurities due to the low quality of the spectrum caused by an insufficient amount of sample. For stick 4069 the major α -quartz band could pre-

sumably be identified, however spots containing BaSO_4 or BaCO_3 expected from the powder X-ray results [45] could not be traced. Stick 4070 unambiguously showed the presence of BaCO_3 .

A slice of Stick Freer Gallery was investigated by Raman spectroscopy in greater detail. The Raman studies at various spots made clear that this stick is a very heterogeneous mixture, since other components found in significant amounts have been detected besides Chinese Purple. Several bands were assigned to crystalline or glassy silicate phases. Other attributable phases include CaCO_3 , BaCO_3 , BaSO_4 , PbSO_4 , PbO and perhaps also SiO_2 . An exemplary Raman spectrum is displayed in Fig. 10 demonstrating the heterogeneity of the sample and some of the impurities.

From this it became clear that the stoichiometry of the starting materials did not fully match those theoretical amounts required to obtain pure Chinese Purple.

In addition it became apparent that BaSO_4 was used as a starting material which partly remained unreacted. Presumably the bands at around 940 and 420 cm^{-1} account for glassy phases with polysilicate (SiO_3^{2-}) units and the bands eventually present at 914 cm^{-1} for disilicate ($\text{Si}_2\text{O}_7^{6-}$) [67]. Due to a great stoichiometric excess of SiO_2 , glass formation seems to be very plausible and indeed the quite hard general appearance of the disc speaks for a relatively high amount of glassy phases. It is maybe quite amusing to see that an early German patent from 1900 describes the preparation of glassy highly coloured barium-copper-silicates for the use as pigments [68]. This modern times discovery was certainly made without knowledge of the existence of ancient Chinese Blue and Purple and may simply reflect man's timeless need for artificial colouring matter.

The Terracotta Army samples I and II consist of Chinese Purple as indicated by

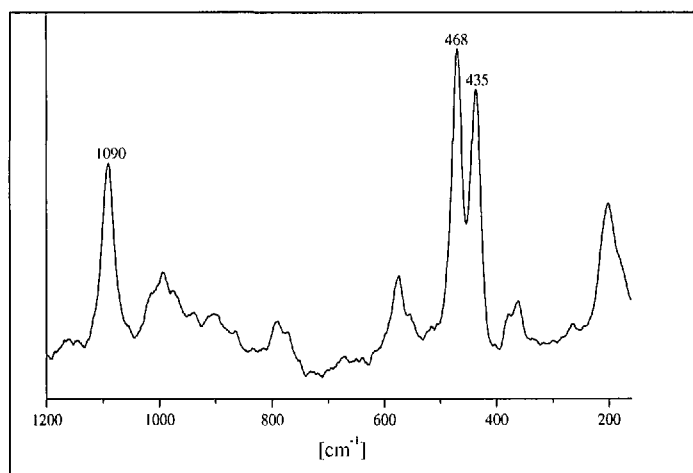


Fig. 8. Raman spectrum of sample Brick Nimrud in the range 1200–200 cm^{-1} (514 nm). The spectrum shows the presence of Egyptian Blue (see Fig. 1) and α -quartz (468 cm^{-1}).

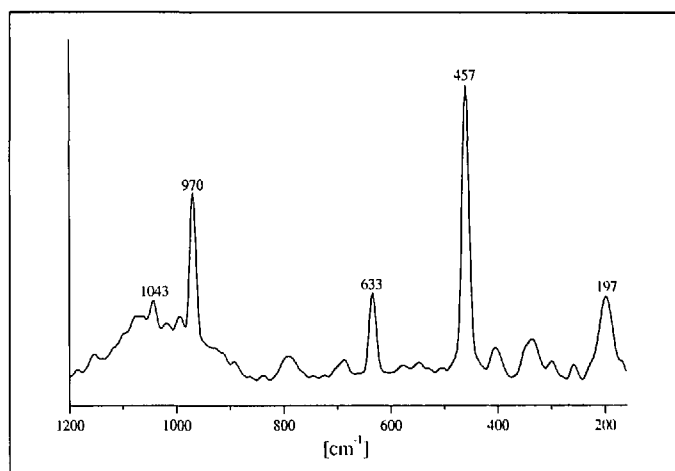


Fig. 9. Raman spectrum of sample Tomb Ibi in the range of 1200–200 cm^{-1} (514 nm). The spectrum shows the presence of cuprowollastonite (1043, 970, 633 cm^{-1}) and of libethenite (457, 197 cm^{-1}).

the appearances of the major Raman bands for this compound (Table). A typical Raman spectrum of Chinese Purple obtained from sample I is displayed in Fig. 11.

In contrast to the sticks the Terracotta Army samples represent mixtures of actual paints, which are naturally more heterogeneous. Their *a priori* heterogeneity, however, makes it sometimes difficult to decide whether a specific component has to be attributed to a mineral or to a chemical origin or whether it was related to a colouring function. A significant PbCO_3 (major Raman band at 1050 cm^{-1} see Fig. 11) or PbO (major Raman band at 143 cm^{-1}) [37] content was noted. This could be related to their function as synthetic additives, but could also point to their role as colouring components. For sample I and II vermilion (cinnabar, HgS) [37] could be traced. The other red pigment definitely detected in sample I *via* Raman analysis is iron oxide red (haematite, Fe_2O_3) [15][37]. I and II also showed substantial quantities of α -quartz. This is assumed to be a natural circumstance associated with their use in paints. It should however be noted that neither sample showed the presence of Chinese Blue. Sample I possessed considerable

amounts of crystallites of azurite (major Raman band at 402 cm^{-1}) [65], which apparently provided the blue colouring tone in the pigment layer. The Raman spectra of the additional pigments of vermilion, azurite and iron oxide red are exemplarily displayed in Fig. 12 as they were obtained from different spots of sample I. The Raman spectrum of sample II shows besides the mentioned components the presence of BaSO_4 as a whitening agent. Furthermore a Raman band at 1035 cm^{-1} is detected at several spots of the pigment layer, which however could not yet be attributed to a pigment species with certainty.

7. Conclusions Drawn from the Investigations of Original Samples of Egyptian Blue, Chinese Blue and Purple

The described investigations have demonstrated that Raman microscopy is a very powerful archaeometric tool to study samples of the ancient man-made copper silicate pigments Egyptian Blue, Chinese Blue and Purple. Even if they are embedded in matrices or are constituents of heterogeneous mixtures, like in paint applications, Raman microscopy will enable these pigments to be traced. Specific

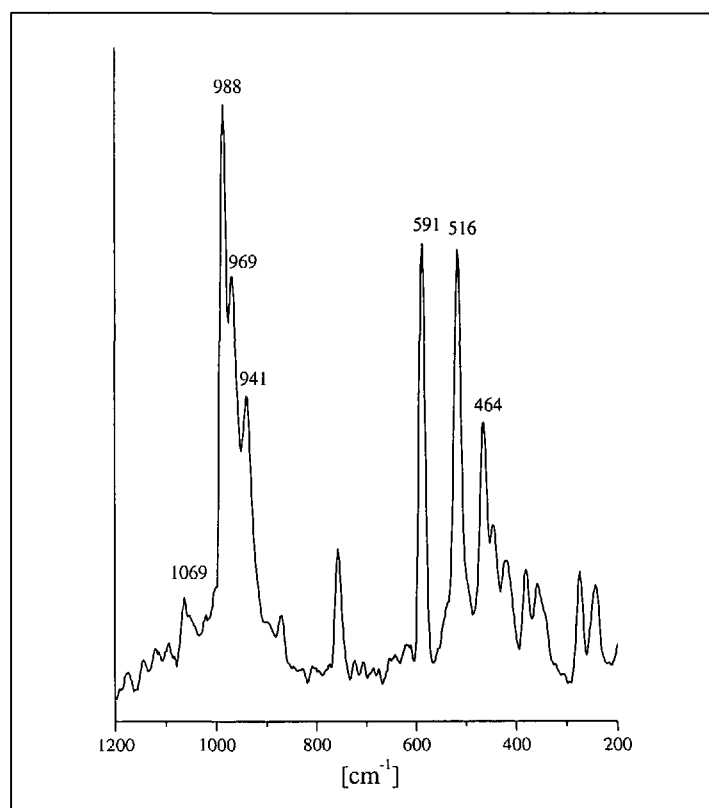


Fig. 10. Raman spectrum of sample stick Free Gallery in the range 1200–200 cm^{-1} (514 nm). The major bands are attributed to BaCO_3 (1069 cm^{-1}), BaSO_4 (988 cm^{-1}) PbSO_4 (969 cm^{-1}), Basilicates (941 cm^{-1}) and Chinese Purple (591, 516, 464 cm^{-1}).

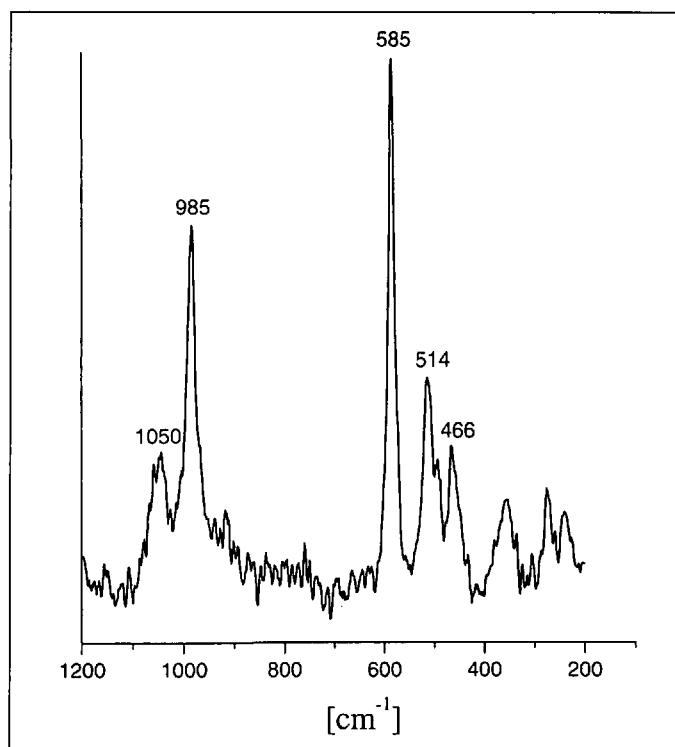


Fig. 11. Raman spectrum (range 1200–200 cm^{-1} , 514 nm) of a spot of sample I of the Terracotta Army, Xi'an, China displaying bands for Chinese Purple and a band attributed to PbCO_3 (1050 cm^{-1}).

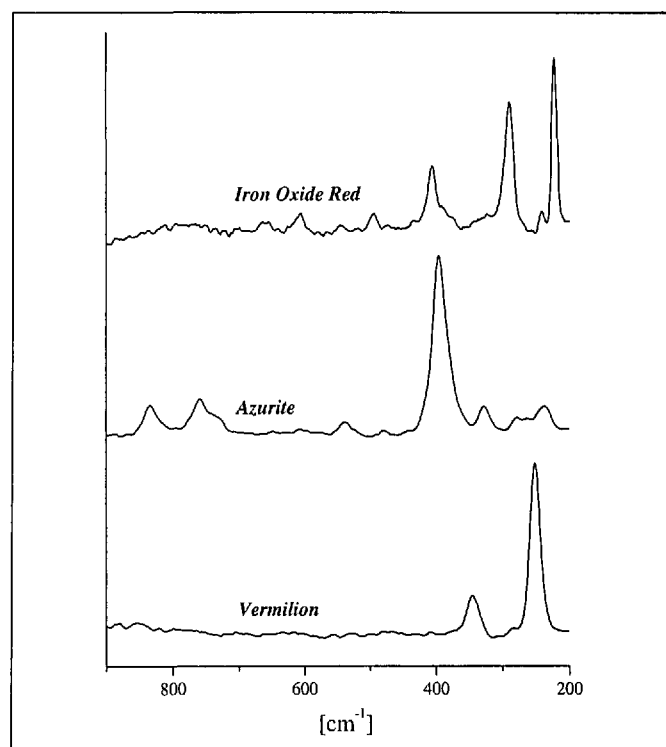


Fig. 12. Raman spectra (range 900–200 cm^{-1} , 514 nm) of selected pigment spots as obtained from sample I of the Terracotta Army.

results were obtained from 12 original Egyptian and Mesopotamian samples. 11 of them revealed the prevailing presence of Egyptian Blue ($\text{CaCuSi}_4\text{O}_{10}$). Only one sample turned out to be a mixture of wollastonite and libethenite. Traceable impurities of some samples were CaSO_4 and SiO_2 .

From the six investigated ancient Chinese samples four were colour sticks and two paint applications from the Terracotta Army. According to our Raman investigations the colour sticks consisted of Chinese Purple ($\text{BaCuSi}_2\text{O}_6$) and in one case a mixture of Chinese Purple and Chinese Blue ($\text{BaCuSi}_4\text{O}_{10}$) was found.

Obviously due to difficulties in the preparation, the sticks contained impurities, which were quite prominent for stick Freer Gallery. Major admixtures were remaining barium starting materials and lead compounds, which functioned as a synthetic additive. The Terracotta Army samples revealed besides Chinese Purple the presence of azurite, vermilion, iron oxide red, PbCO_3 , PbO , BaSO_4 as pigments. Chinese Blue was not detected.

8. Experimental

A Renishaw System 1000 Raman microscope was used for the Raman measurements. This system comprises a Leika DM LM microscope equipped with a 50x

objective, a spectrometer with a 1200 grooves/mm grating and a NIR enhanced, Peltier-cooled CCD camera. For the blue pigments an air-cooled argon ion laser served as the excitation source with a wavelength of 514 nm and an output of 10mW. When necessary, the laser power on the sample was reduced. The back-scattered laser radiation is prevented from entering the spectrograph by two holographic supernotch filters. Spectra were usually recorded in the frequency range 2000–200 cm^{-1} with the excitation at 514 nm. All spectra are baseline-corrected.

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