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Chemical and Physical Investigations of Egyptian and Chinese Blue and Purple

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Introduction

The production of Egyptian Blue can be traced back from earlier than 3000 B. C. up until approximately 300 A. D. One of the earliest documentation of Egyptian Blue is found on the Tablets of an olive oil container, which certifies the quality of the oil blessed by the Godess Iset (pre-dynastic). Another proof for the early use of Egyptian Blue is the Mastaba of the vesir of Mereruka (2300 B. C., Saqquara). This and other samples are shown in Table 1 and represent a selection of identified Egyptian Blue up to the Greek-Roman period.

A contemporary artist, E. Arpagaus, has studied mineral colours and pigments of Egypt and surrounding areas (Arpagaus, 1996) showing the variety of different colours, which were prevalent in nature. The presented blue pigment has however been artificially produced in the manner of the Egyptians.

In ancient times continents and countries were connected by famous trade routes; the link between the Western World and ancient China was established via the Silk Road. Aside from its economic function this adventurous and risky route played an outstanding role in the distribution and exchange of ideas and technologies between East and West. The relatively constant composition of Egyptian Blue over the period of the Old Kingdom up to the Ptolemaic and Greek-Roman time (Table 2) indicates that the information about the production of coloured pigments never got lost. For blue pigments this is attributed to the fact that they had a prominent role in religious rites and everyday life. States adjoining the Silk Road were challenged by the tradition of blue production and its use in manufactured Egyptian goods to either obtain it by trade or to produce it themselves. This background was apparently a major driving force for the expansion of artificial blue and even other pigments.

The change in location and the need for further improvements of artificial pigments induced new technological developments, which generated similar advanced materials such as strontium and barium copper silicates as in the Iraqi and Iranian samples of Brick Nimrud (British Museum London) the Sistrum Hasanlu and the Goblet Hasanlu, Iran (both Metropolitan Museum New York) and barium in Chinese artefacts represented by the blue and purple octahedral sticks and samples of the Terracotta Army, all compiled in Table 1.

The Chinese samples are attributed to the Warring States, Quin and Han period 600 B. C. till approximately 200 A. D.. As we will see in the later context they contain man-made blue and purple pigments called Chinese Blue and Purple, sometimes also denoted as Han Blue and Purple (Fitzhugh, 1992). They were used in colouring applications and they refer to destinct, but very related chemical compounds. Only Egyptian and Chinese Blue are found as minerals in nature (Cuprorivaite, Effenbergerite (Giester, 1994)). They are, however, so rare that any utilization of these minerals by ancient civilizations can be excluded. It should be mentioned at this point that the only mineral pigment used by earlier civilizations, which naturally appeared blue and did not demand chemical transformation or processing, was lapis lazuli (Reinen, 1999). Its scarcity in nature caused it to become highly esteemed, at least in the western hemisphere. Presumably as a consequence of the general scarceness, the blue has been attributed divine character in some civilizations, such as the Egyptian.

In general colour has played a major role in the development of civilizations and has acquired important cultural functions as one of the essential ways of human self-expression and affectation. Colours produce aesthetic stimulation, which is reflected in art forms. All this emphasizes the outstanding role of colour in human development, and colouring substances in the form of pigments have thus always been used by mankind as they became available.

Apparently motivated by the lack of natural blue minerals and mankind's intrinsic desire for colours, people were driven to invent blue pigments. It is may be worth mentioning that among those invented Blues there is also the Indigo based Maya Blue, which had wide-spread application within Indian cultures (José-Yacaman, 1996). Any of the mentioned man-made blue pigments but also Chinese Purple required sophisticated chemical and technological developments, which could only be mastered in a sound cultural and technological environment. In the following article we will see that the chemistry behind these man-made pigments is quite complicated. Ancient chemical achievements could not be based on atomic or molecular grounds. Therefore any progress was established by long and tedious processes of empirical probing.

Investigated Original Samples of Egyptian Blue, Chinese Blue and Purple

The investigated ancient samples of Egyptian Blue and Chinese Blue and Purple are summarized in Table 1. The Egyptian samples cover a span of almost 3000 years starting with Blue from the 6th Dynasty of the Old Kingdom to the Roman time.

The oldest sample stems from the Mastaba of Mereruka in Saqqara, Egypt. Mereruka was vesir to King Teti, reaching the Mastaba from his tomb through a fictive door to receive the daily sacrifice from his relatives, who prepared the altar (Wiedemann, 1997b). The second sample originates from the tomb of General Antef, Middle Kingdom, 11th Dynasty. General Intef reported to Mentuhotep II as the commander of the troops. He belonged to the most important courtiers, which is also expressed by the location of his tomb in close vicinity to the funeral temple of his King in Thebes. The next three samples studied came from the New Kingdom period. Blue from the crown of the famous bust of Nefertete (Ägyptisches Museum der Staatlichen Museen Berlin, Germany) and Blue of the Talatat Stones of the Temple of her husband Echnaton (Amarna, Egypt). The cylindrical seal, which is also dated to the New Kingdom and whose orgin falls into a very productive period for artisans,

Time	Name	Colour	PL	RS	X-Ray	EDX
2345-2181 B.C.	Mastaba of Mereruka	EB	+	+	+	+
2133-1991 B.C.	Tomb Intef	EB	-	+	+	-
1340 B.C.	Bust of Nofretete, blue of crown	EB	-	+	-	+
1353 B.C.	Echnaton temple, blue of Talatat	EB	-	+	-	+
1300 B.C.	HGW, Cylinder Seal, Thebes	EB		+	-	+
13th – 7th Century B.C.	Brick Nimrud, Iraq	EB	+	+	+	-
712-332 B.C.	HB, Amulet Bes	EB	+	+	-	+
500 B.C.	Ba-bird, Soul	EB	-	+	+	+
3rd Century B.C.	Mummy cartonage	EB	+	+	+	+
1st Century B.C.	Ptah Sokaris Osiris Fig., Munich	EB	-	+	+	+
Roman time	Mummy coffin, Cairo	EB	-	+	+	+
Han Dynasty	Stick Freer Gallery, Washington	CP	+	+	+	+
Han Dynasty	Stick Royal Ontario Museum	CP	-	+	-	-
Han Dynasty	Stick 4069 Oestas. Mus.,Sweden	CB/CP	+	+	+	+
Han Dynasty	Stick 4070 Oestas. Mus.,Sweden	CP	+	+	+	+
Qin Dynasty	Sample I, Terracotta Army	CP	-	+	-	+
Qin Dynasty	Sample II, Terracotta Army	CP	-	+	-	+

Appendix (substances not investigated by us)

Time	Name	Colour	PL	RS	X-Ray	EDX
9th Century B.C.	Sistrum Hasanlu, Iran*	EB ?	-	-	+	+
9th Century B.C.	Goblet Hasanlu, Iran*	EB ?	-	-	+	+

EB = Egyptian blue, CP = Chinese purple, EB? contains probably $SrCuSi_4O_{10}$
PL = Photoluminescence, RS = Raman Spectroscopy, *Metropolitan Museum of Arts, New York

Table 1. Egyptian, Mesopotamian and Chinese samples investigated by different physical methods.
表 1. 利用不同物理方法对埃及、美索不达米亚和中国的试样的研究。

is the property of one of the authors (fig. 1). It has been described in detail elsewhere (Wiedemann, 1997a). The sample of Brick Nimrud comes from Mesopotamia and is dated to the 13th – 7th century B. C. Today it is the property of the British Museum, London.

The Late Egyptian Period is documented by several other samples. Amulet Bes was protecting those who wore it by the powers of the dwarfish God Bes. It is dated to the 24th Dynasty and is the property of one of the authors (colour plate XV, fig. 1). The wooden falcon figure Ba-bird (Kestner Museum, Hannover, Germany) contains blue areas, from which a sample was studied. Ba-bird from approximately 500 B. C. symbolized a protection god at burial ceremonies (Wiedemann, 1997b). The figure Ptah-Sokaris-Osiris from the 1st century B. C. stems originally from Memphis, Egypt. It is now property of the Staatliche Sammlung Ägyptischer Kunst, Munich, Germany (ÄS 19). It served as a container for corpses. A sample of the Blue was taken (Wiedemann, 1997b). The samples of the mummy cartonage and the mummy coffin represent Egyptian Blue from Ptolemaic and Roman times. Their present locations are unknown.

Four of the six originally investigated samples of Chinese Blue and Purple (Table 1) were taken from original Blue or Purple sticks of octagonal shapes. It is thought that these sticks were trade items. They were used as pigment bases in paints and applied by grinding. The general phenomenology of the Freer Gallery sample has been described earlier by FitzHugh (FitzHugh, 1983; FitzHugh, 1992). The photograph of a slice of the Freer Gallery sample (colour plate XV, fig. 2) shows its purplish blue colour and the representative size of such sticks.

The Royal Ontario Museum Sample stick came from a blue octagonal stick said to have come from Jincun near Luoyang, China (FitzHugh, 1992). 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 (FitzHugh, 1992), from which powdery material was taken for investigation. The stick samples were recently discussed (Berke, 2000).

Distinct samples from different parts of the Terracotta Army (sample I and II), were investigated as cross sections of the pigment layer. Earlier investigation showed the presence of Chinese Purple and other pigment materials (Herm, 1995; Thieme, 1995). Application of Raman spectroscopy and electron microscopy with EDX were expected to confirm these results, but also to deliver further information on the nature of the pigment content. Colour plate XV, fig. 3 shows the microscopic photograph of one of the studied cross sections (sample I) containing a crystallite of Chinese Purple.

All the samples were compared to pure Egyptian Blue and Chinese Blue and Purple or their mixtures, obtained by contemporary independent synthesis (among others Bayer, 1991).

Chemistry of Egyptian and Chinese Blue and Chinese Purple

Compositions and Structures

Egyptian and Chinese Blue are calcium and barium copper silicates with the compositions $CaCuSi_4O_{10}$ and $BaCuSi_4O_{10}$, (Finger, 1989; Fitzhugh, 1983; Fitzhugh, 1992) respectively. They thus differ in the replacement of calcium with barium. Their chemical relationship is so close that crystals of both compounds adopt exactly the same habitus (Pabst, 1959; Chase, 1971; Bayer, 1976) and on the microscopic scale they are isostructural. Their structures consist of puckered infinite silicate layers composed of $(SiO)_4$ silicate squares, which are condensed together via oxygen bridges and thus form a two-dimensional network of connected $(SiO)_4$ and $(SiO)_8$ rings. Each silicon atom bears a terminal oxygen group, which can either contribute to binding of Cu^{2+} or Ca^{2+}/Ba^{2+}. As sketched in fig. 4 four oxygen atoms from a silicon atom of four adjacent $(SiO)_4$ rings accommodate a copper ion in square planar arrangement. The calcium or barium ions are employed in a similar fashion, however in an alternating way, with the coppers they twice pick four oxygens from two adjacent layers for binding and in this manner, they 'glue' the layers together.
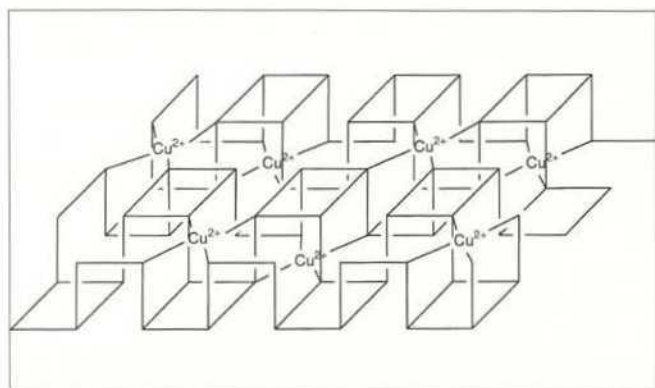

Fig. 1. Schematic representation of the puckering of a $Si_4O_{10}^{4-}$ layer in Ca, $BaCuSi_4O_{10}$ induced by Cu^{2+} coordination. Every other open square is filled by Cu^{2+}. The non-filled squares are occupied by Ca^{2+} or Ba^{2+} connecting the layers. The structure of Egyptian Blue was determined by Pabst (Pabst, 1959) and redetermined by Bensch (Bensch, 1995). The structure of Chinese Blue was studied by Finger (Finger, 1989).

图 1. 由 Cu^{2+}配位引起的 Ca, $BaCuSi_4O_{10}^{4-}$层皱褶的示意图。每隔一个敞口的方格由 Cu^{2+} 填充，非填充的方格由连接层间的 Ca^{2+}或 Ba^{2+}占据。埃及蓝的结构由帕布斯特(Pabst, 1959)测定，本施(Bensch, 1995)重新测定。中国蓝的结构由芬格研究(Finger, 1989)。

In $CaCuSi_4O_{10}$ and $BaCuSi_4O_{10}$ the copper ions are thus in a very similar oxygen atom environment. Since the pigment properties, e. g. the blue colour, are merely related to the copper ions (chromophore), both compounds have almost the same colour properties. The structure of Egyptian Blue was first unraveled quite some time ago (Pabst, 1959; Bensch, 1995), while that of

Chinese Blue has been elucidated more recently (Finger, 1989). It is a frequent observation, that layered structural frameworks with preferred spatial orientations of the chromophores give rise to pleo- or dichroism. Two or more different colours (dichroism or pleochroism) can be seen in different orientations of the crystal faces when irradiated with (white) light. Egyptian Blue does show pleochroism (Bayer, 1976) and due to the close structural resemblance of Egyptian and Chinese Blue, we can assume that Chinese Blue is also pleochroic. When grinding is applied to solid matter, particle size, crystal shape and crystal face distributions are changed and subsequently the overall colour appearance may concomitantly be altered. While large platelets of Egyptian or Chinese Blue appear light blue (colour plate XV, fig. 3), when grinding is applied, both pigments becomes more bluish. This is illustrated in photographs of powders of the Chinese pigments (colour plate XV, fig. 5).

Chinese Purple's composition is $BaCuSi_2O_6$. It formally contains two equivalents of quartz (SiO_2) less than Chinese Blue. It should be mentioned at this point that an analogous 'Egyptian Purple' with the formula $CaCuSi_2O_6$ could to date not be prepared. Chinese Purple may be viewed as a reaction intermediate (so-called kinetic product) while producing Chinese Blue. Even though Chinese Purple also consists of layers in its microscopic structure (fig. 7a and 7b), these layers differ signifantly in their basic structural motifs from that of Egyptian and Chinese Blue.

There is no other extended silicate framework like that of the Blues. The silicate condensation process is stopped at the $(SiO)_4$ four ring stage generating a patchwork of isolated $Si_4O_{12}^{8-}$ four-ring units infinitely connected by Cu-Cu bonded moieties to build-up a $Cu_2Si_4O_{12}$ layered structure (Janczak, 1992). Like in Chinese Blue the barium ions are located between the layers and hold these together by coordinative contacts. Figure 7b also shows a piece of a $[Cu_2Si_4O_{12}^{4-}]\sim$ layer as taken from a single-crystal X-ray structure of Chinese purple.

The extraordinary and very unique feature of this structure is tighed up to the copper-copper bond, which was overlooked in the earliest structural determination of Finger et al (Finger, 1989). This inner core of the structure of Chinese Purple is thus related to the dimer of prototypical copper acetate, $Cu_2(acetate)_4$, which also contains a bridged Cu-Cu unit, where the bridging functions are provided by the acetate ions. Early Chi-

Fig. 2a. Schematic representation of the structure of Chinese Purple with the principle arrangement in layers of Ba^{2+} and $Cu_2Si_4O_{12}^{4-}$.
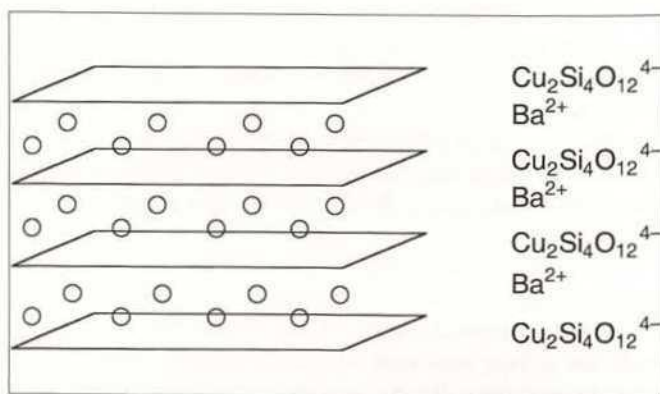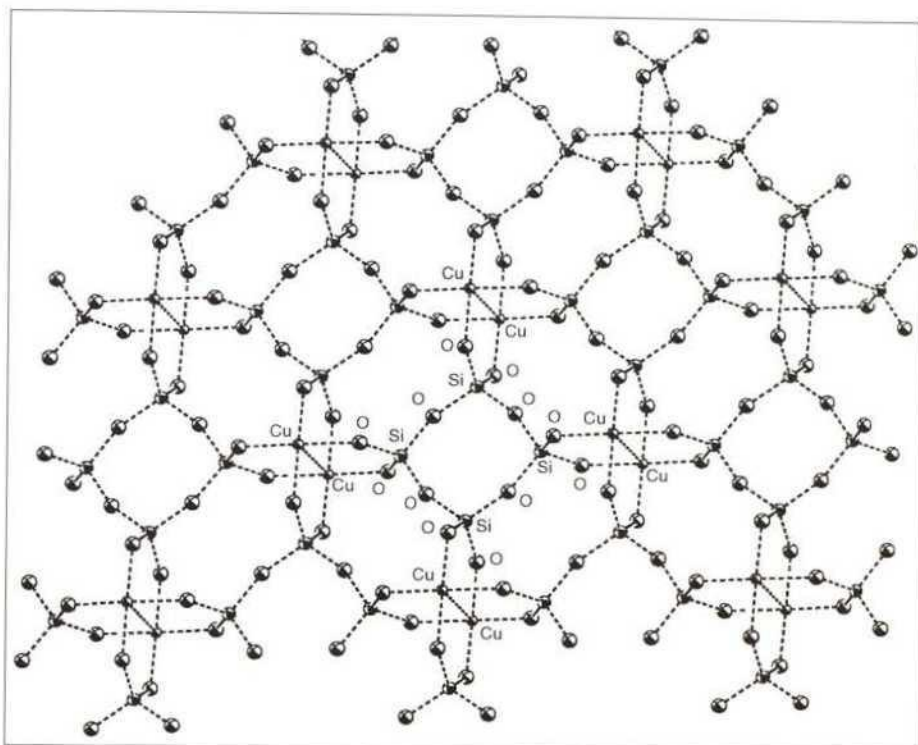
图 2a. $Ba^{2+}Cu_2Si_4O_{12}^{4-}$层状规则排列的中国紫结构的示意图。

Fig. 2b. Sketch of the structure of Chinese Purple, $BaCuSi_2O_6$, as obtained from a single crystal X-ray diffraction study. Only the $[Cu_2Si_4O_{12}]^{4-}$ layer is presented. The Cu-Cu distance is 2.73 Å.

图 2b. 由单晶 X-射线衍射研究得到的中国紫 $BaCuSi_2O_6$ 结构简图。只显示 $[Cu_2Si_4O_{12}]^{4-}$ 层的结构。 Cu-Cu 距离为 2.73Å。

nese chemists were thus, to our knowledge, the first humans to prepared a chemical compound containing a metal-metal bond. This peculiar finding is even more important in view of the chemical fact, that in compounds other than in metals, metal-metal bonds still have nowadays the flair of curiosities.

It is important to note that in Chinese Blue and Purple the copper ions are rigidly fixed in the structural framework. As a consequence of that, they can effectively absorb and emit light: the latter is effective, when excited by light with short wavelengths inducing fluorescence (Ajo, 2000). Layered structures such as Chinese Purple are also expected to display pleochroic features similar to those of Egyptian and Chinese Blue. On grinding, Chinese Purple changes it's colour tone from more bluish to more purplish (colour plate XV, fig. 5).

Stability Properties of Egyptian and Chinese Blue and Chinese Purple

The thermal and chemical stabilities of Egyptian and Chinese Blue on the one hand and Chinese Purple on the other are strikingly different. This can be related to two structural factors:

(a) contrary to Egyptian and Chinese Blue the silicate framework of Chinese Purple consists of relatively small $Si_4O_{12}^{8-}$ units connected by only weak coordinative bonds to copper and barium

(b) Chinese Purple contains a chemically labile Cu–Cu bond

The more silica-rich Egyptian and Chinese Blue are more SiO_2-like with a higher degree of condensation in the silicate framework. Melting, which requires breakage of the silicate layers into smaller molecular units, is thus only possible at elevated temperatures. This was confirmed by an isothermal heat treatment of corresponding Chinese samples at 1200 °C for four hours. Pure Chinese Purple melted to a viscous, black green glass,

whereas Chinese Blue only showed increased sintering. X-ray investigation of these samples quenched from 1200 °C proved that the former was amorphous and vitreous, while the latter was unchanged $BaCuSi_4O_{10}$. $BaCuSi_4O_{10}$ actually starts to decompose at 1170 °C under loss of O_2. It can however be reoxidized completely at 1060 °C. (Wiedemann, 1997b; Bayer 1976). The thermal decomposition of Chinese Purple is expected to take place according to the following equation

$$3\ BaCuSi_2O_6 \rightarrow BaCuSi_4O_{10} + 2\ BaSiO_3 + 2\ CuO$$

Barium and copper meta-silicates are formed first, the former has even been detected in experiments under melt conditions (Bayer, 1991). At temperatures above approximately 1000 °C the potential decomposition product $CuSiO_3$ (dehydrated dioptase) is known not to be stable and to liberate tenorite and quartz (Kiseleva, 1993), the latter may subsequently be consumed by Chinese Purple to generate Chinese Blue. Under conditions of above 1050 °C the copper(II) oxide content of these compounds could furthermore turn into copper(I) oxide and oxygen:

$$2\ CuO \rightarrow Cu_2O + 1/2\ O_2$$
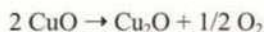
Prolonged firing of Chinese Purple thus results in additional formation of Chinese Blue, colourless barium meta silicate and red cuprite (Cu_2O). Powdered mixtures of these constituents would actually generate a more reddish appearance of the Chinese Purple, the more the higher the cuprite content is. All of these components have been identified in samples of Chinese Purple made by independent synthesis, and which underwent prolonged thermal treatment.

What both, the Egyptians and the Chinese could not know, was the reactivity of their pigments in the presence in chemical or biological agents. In acids a striking difference in the chemical stability of Chinese Purple and Chinese Blue was observed (Pabst 1959; FitzHugh 1983) and could be confirmed by our

157

own experiments. Egyptian and Chinese Blue are stable in dilute acids, whereas Chinese purple, $BaCuSi_2O_6$, rapidly fades and decomposes. The same effect is observed when these pigments are exposed to an aqueous solution of oxalic acid. As products Ba- and Ca-oxalates could be identified by EDX, X-ray diffraction and simultaneous thermogravimetry / mass spectrometry investigations (Lamprecht, 1997). This is an important finding with respect to conservation procedures, since it demonstrates that in the deterioration of works of art, lichens, which excrete oxalates or even oxalic acid, may play a relevant role (Seaward, 1989).

In turn, it has been shown in previous investigations on coloured Egyptian papyri, that spores and fungi did not exist in areas where Egyptian Blue was used as a pigment. These findings were confirmed by further studies of different papyri. This can be explained by the fact that copper is a strong fungicide, which was proven by experiments with limestone covered by lichens. No further growth occurred in areas where the lichens were removed and which was subsequently painted with Egyptian Blue (Wiedemann, 1996; Lamprecht, 1997) (colour plate XV, fig. 7, 8)).

It is interesting to note that the production of blue bread is mentioned in documents of the 18th dynasty (1500 B.C.) in ancient Egypt (Sethe, 1961). Since the Egyptians produced air-dried bread for emergency situations, it may be that they had some knowledge about the conservation effect of Egyptian Blue. As shown in figure 8 Chinese Blue has similar fungicidal properties. Chinese Purple, however, deteriorates under the influence of oxalate producing lichens and leaves light blue residues behind. Chemical reactions of Chinese Purple with oxalic acid produced a double salt $BaCu(C_2O_4)_2$ of light blue colour (colour plate XV, fig. 7,8). It is therefore probable that the light blue colour of the trousers of some Terracotta Warriors (Ledderose, 1992) may not be the original colour, but rather the transformed Chinese Purple, which occured under the influence of oxalate excreting lichens.

Synthesis of Egyptian Blue

Preparation of Egyptian Blue has been carried out by our group and others. In our search for optimal conditions for the preparation, various techniques have been reported. The synthesis of Egyptian Blue was mostly in powdery form as a pigment, but also as a compact body. The effect of the firing temperature and of the atmosphere on its formation and stability has been demonstrated elsewhere (Bayer, 1976). The effect of various fluxes on the development of the tone of blue colour has been confirmed by microscopical light studies. Compact bodies were produced either directly from mixtures of the raw material or from presynthesized Egyptian Blue by heating the dry-pressed powders at 900 °C in air. This proved that, in the raw material samples, the flux (Na_2CO_3) migrates and is concentrated in the surface, whereas the flux-free interior remains greenish and practically does not react. On the other hand the compact bodies made from presynthesized Egyptian Blue powder are less intensively coloured, but blue throughout. The morphology of the surface of the compact bodies reveal $CaCuSi_4O_{10}$ crystals embedded in the flux materials. Single crystals of Egyptian blue could be prepared by long-time annealing (100 h, 880 °C) of a borax-flux containing mixtures of the raw materials. Based on the results of synthetic experiments, it seems probable that the fine-textured

Egyptian blue objects, e.g. cylinder seals, were made by a two-stage firing cycle in oxidizing atmosphere. A single firing at 900 °C of bodies formed directly from the raw material mixture leads to fragile structures. This is due to the migration of alkali flux to the surface, forming a coarser-textured surface layer of Egyptian Blue, but leaving the bulk unreacted and greenish coloured. Therefore, the preferred method would be first to synthesize the Egyptian blue pigment, then the finely ground material can be used for forming the objects with addition of an organic binder (e.g. gelatine or wax) in order to get sufficient strength. For improved sintering at 900 – 950 °C it is of advantage to add some flux or even better to add glass powder. These additions form a grain boundary melt, which enhances the liquid phase sintering. The objects should not be heated higher than 1000 °C, since above this temperature Egyptian Blue decomposes irreversibly to tridymite and glass.

Synthesis of Chinese Blue and Purple

Detailed studies on the chemical composition, as well as of the phase diagram of this Ba-Cu silicate-system revealed that there exist – in contrary to the mentioned Egyptian Blue, $CaCuSi_4O_{10}$ – at least four stoichiometric ternary phases (Finger, 1989; Malinovskij, 1984; Tsukada, 1999):

$BaCuSi_4O_{10}$ (blue), $BaCuSi_2O_6$, (purple), $BaCu_2Si_2O_7$ (blue), $Ba_2CuSi_2O_7$ (lightblue).

This seems to be of considerable advantage for the Egyptian manufacturer, but certainly caused difficulties to those Chinese manufacturers trying to synthesize pure tones. On the other hand it was an advantage for those Chinese painters, who wished to vary their tone of colour from blue to purple in mixtures (colour plate XV, fig. 5).

The Chinese applied the Egyptian Blue analogue $BaCuSi_4O_{10}$ and the purple phase $BaCuSi_2O_6$. These phases differ in colour strength and tone, e. g. the Chinese painter was able to enlarge the spectrum of his blue colour palette by using or admixing one or the other purplish or bluish phase. Of course the choice was limited with respect to the skills in fabricating pure phases.

The synthesis of the pure phases is not direct: depending on the raw materials used, their ratio, the addition of fluxes and of course the temperature, atmosphere and reaction time different products, but usually a mixture of compounds is obtained. Since the Chinese civilization was very adept at functionalizing natural minerals, it seems of special interest, which resources for barium were used: Barite, $BaSO_4$, is found in a variety of deposits all over China, or Witherite, $BaCO_3$, which is much rarer and sometimes associated with barite. As will be shown the choice between these minerals can be quite relevant for the products obtained by the available techniques. It is very likely that copper-sulfides were used together with barite and silica sand or quartzite. Thus, one can assume that the copper minerals for the fabrication of the blue and purple BaCu-silicate pigments e.g. used in the Mogao Grottoes were collected in deposits of the Gansu province, e.g. near Lanzhou, Gulang or Jiayuguan (Gloria, 1985). Our experimental studies focused on the effect of the barium mineral used. As copper source tenorite, CuO, was used, since any copper sulfide is oxidized to CuO well below the temperature where the reaction starts (Bayer, 1992). The parent materials $BaSO_4$, $BaCO_3$, CuO, Cu_2S, SiO_2 were homogeneously

mixed and slightly compacted. Heating times at the various temperatures were usually 20 hours. The identification of the crystalline reaction products was done by X-ray diffraction. The influence of fluxes such as NaCl, Na_2CO_3 and PbO (found in various pigments) were studied. Additional investigations were concerned with the thermochemical reactivity of the various pigment samples. Previous studies on $BaCuSi_4O_{10}$ blue confirmed that there is a distinct effect not only of the temperature used but also of the Ba-compound and of the fluxes added on the colour tone of this pigment (Bayer, 1976).

Mixtures of $BaCO_3$, CuO and quartz powder were prepared with different, stoichiometric ratios (1/1/2, 1/1/4, 1/2/2 and 2/1/2). The mixtures were filled in porcelain crucibles, slightly compacted and heated at 900, 1000 and 1100 °C in air. To some of these mixtures 3 % Na_2CO_3 or 5 % PbO or 10 % NaCl were added as a flux. TG/DTA runs of 1/1/2 and 1/1/4 mixtures showed that, owing to the presence of SiO_2, the decomposition of $BaCO_3$ already starts below its phase transition at around 800 °C (Wiedemann, 1986; Wiedemann, 1992). The decomposition to $BaO+CO_2$ proceeds faster above this temperature and is complete at about 950 °C. The solid state reaction to Ba-Cu-silicates probably starts around 900 °C. Depending on the $BaO/CuO/SiO_2$-ratio partial melting and reduction of Cu^{2+} to Cu^{1+} occurs at temperatures above 1050 °C. The purple compound $BaCuSi_2O_6$ is formed as the primary Ba-Cu-silicate, also in mixtures with the stoichiometry 1/1/4. It is thermally less stable than $BaCuSi_4O_{10}$ and melts with decomposition around 1100 °C.

As mentioned above, the addition of fluxes have a definite effect on the formation and the colour of the pigment. Pure $BaCuSi_4O_{10}$ can be synthesized by adding fluxes such as Na_2CO_3 or borax. The addition of more than 5 % Na_2CO_3 and heating above 1000 °C resulted in the melting of the purple $BaCuSi_2O_6$ compound to a glass. However, the fluxes may also cause side reactions. Addition of NaCl causes volatilisation of some copper as $CuCl_2$ and disproportionation to CuO in the cooler zone of the furnace. In starting mixtures where $BaCO_3$ is present as the barium source, the addition of Na_2SO_4 causes the intermediate formation of $BaSO_4$ due to the displacement reaction $BaCO_3 + Na_2SO_4 \rightarrow BaSO_4 + Na_2CO_3$ in the temperature range of 600 to 800 °C, (Bayer, 1987). Fluxes such as Na_2CO_3, PbO or borax did not cause problems. Since many original Chinese Purple pigments contained a high proportion of lead oxide, this oxide was also tried as a flux. It was found to be very effective in the formation of both Chinese Purple and Chinese Blue already at 900 °C. However, additions of more than 5% PbO led to partial melting and glass formation above 1000 °C (Wiedemann, 1997a and b).

In addition to their function as flux, lead additives can activate $BaSO_4$. In the presence of lead oxide (or carbonate) a dismutation reaction with barite can be envisaged, which leads to equilibrium formation of lead sulfate

$$PbO + BaSO_4 \lessgtr BaO + PbSO_4$$

Since pure lead sulfate decomposes at around 1000 °C to $PbSO_4 \cdot 2$ PbO (Malinowski, 1996), much lower than $BaSO_4$, which decomposes at 1560 °C, it can be anticipated that the BaO will be withdrawn from the equilibrium by the Chinese Blue or Purple formation, while the PbO part will be reintroduced into the barite decomposition process. Thus, lead additives can also take over the function as a catalyst for the decomposition of $BaSO_4$ at comparatively low temperatures, which is a decisive circum-

stance especially for the preparation of the thermally less stable Chinese Purple.

When copper sulphide minerals are used as starting material, their oxidation leads to the evolution of SO_2, which reacts with $BaCO_3$ to $BaSO_4$. Compared to a parent mixture of identical stoichiometry where CuO is used instead of e.g. Cu_2S distinct changes of the colour tone of the product are observed. In both cases, however, Chinese Purple (1/1/2) and Chinese Blue (1/1/4), as well as mixtures of both can be identified by X-ray diffraction. Obviously the presence of $BaSO_4$ changes the synthesis pathway of the different phases: $BaSO_4$ has a higher thermal stability and starts to decompose under the reaction conditions only slowly above 950 °C. As thermogravimetric measurements proved a large amount of $BaSO_4$ dues not react even after heating for 20 hours at 1100 °C. Therefore the ratio between the reaction products $BaCuSi_2O_6$ and $BaCuSi_4O_{10}$ and hence also the colour tone differs from that of corresponding mixtures using $BaCO_3$ as barium source (Wiedemann, 1997b). The slower decomposition rate of $BaSO_4$ mobilising only small amounts of BaO obviously favours the primary formation of the silica-rich Chinese Blue, $BaCuSi_4O_{10}$. Even for 1/1/2 starting mixtures and at 1100 °C, $BaCuSi_4O_{10}$ continues to persist besides Chinese Purple, $BaCuSi_2O_6$. This is in contrast to the corresponding starting mixtures containing $BaCO_3$, where the formation of Chinese Purple is strongly favoured and where reactions generally start at lower temperatures.

The fact that we have the possibility to investigate blue copper pigments as testimonial on the technological skills of ancient Egyptian and Chinese manufacturers also accounts for the chemical stability of these synthetic and simultaneously aesthetic products. It could be shown that the silica-rich phases Egyptian Blue, $CaCuSi_4O_{10}$ and Chinese Blue, $BaCuSi_4O_{10}$ adopt analogous structural frameworks. As the X-ray diffraction confirms, there is also a $SrCuSi_4O_{10}$ analogue, which seems to be present in certain archeological samples (Sistrum and Goblet Hasanlu, Iran of Table 1).

Physical Investigations of Ancient Egyptian Blue, Chinese Blue and Purple Samples

Methods of Characterization for Ancient Pigments

Ancient pigment samples often appear as heterogeneous mixtures and due to this varying contents of the pigment are present in coloured materials. Apart from this, the pigments themselves may have differing compositions based on the fact that they might consist of more than one similar, but distinguishable chemical species. Quite often the origins of this are complicated phase diagrams of such materials, which make it difficult to define appropriate conditions in the synthesis of a peculiar species. Accurate analyses of multicomponent heterogeneous mixtures constitute challenging problems in chemistry, especially in view of the fact that the analyses are expected to be carried out in a nondestructive fashion applying samples in the milli- or microgram range.

In recent years however, physicists and chemists have developed an arsenal of very powerful, sophisticated methods for the detailed investigation of ancient materials. In particular miniaturization, utilization of new physical effects and advanced computerization have contributed to an enormously improved situation, which allows us to obtain satisfying information on the na-

ture of such mixtures. Important applicable methods typical of the analysis of compact and powdery samples are:

A) Thermal analysis

Most widely used in this area are thermogravimetry (TG) and differential thermal analysis (DTA) with its frequently used branches of differential thermal gravimetry (DTG) or differential scaning calorimetry (DSC), which allow characterization of materials through thier physical and chemical behaviour under the influence of temperature.

B) Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray analysis (EDX)

Applied to ancient samples SEM is superior for their surface characterization and studies of their macroscopic fine structure (e. g. texture, surface appearence and composition etc.). EDX is used in combination with electron microscopy and provides reasonable estimates of elemental compositions in the surface regime of materials.

C) Powder X-ray diffraction

A useful method to determine and identify single components in heterogeneous mixtures by their characteristic powder X-ray diffraction patterns.

D) IR and Raman spectroscopy

Raman and IR spectroscopy are (sometimes complementary) vibrational spectroscopy methods. Dealing with solid samples Raman spectroscopy is superior to IR spectroscopy. Usually it is applied in combination with a microscope and allows easy identification of mixtures of phases according to the vibrational patterns of the atoms in the microscopic structures of unique components.

E) UV/Vis spectroscopy and laser induced photoluminescence (PL)

Both methods support the characterization of chromophores of pigments or dyes.

In the following section the described methods are applied to a selection of samples of Table 1.

A) Thermal analysis of Egyptian and Chinese Blue and Purple

In conjunction with Egyptian Blue and Chinese Blue and Purple preparations TG or DTA methods have been used for the pursuit of the solid state reaction courses. Figure 9 shows in an exemplary way the TG curve for the formation of Egyptian Blue from Malachite (Wiedemann, 1986).

First we see the decomposition of Malachite between 300 and 400 °C to produce CuO. At approximately 550 – 740 °C CaO and CuO react with SiO_2 in the presence of the flux to generate $CaCuSi_4O_{10}$, Egyptian Blue. Similarly, the solid state reaction between azurite, calcium carbonate and sand also leads to Egyptian Blue.

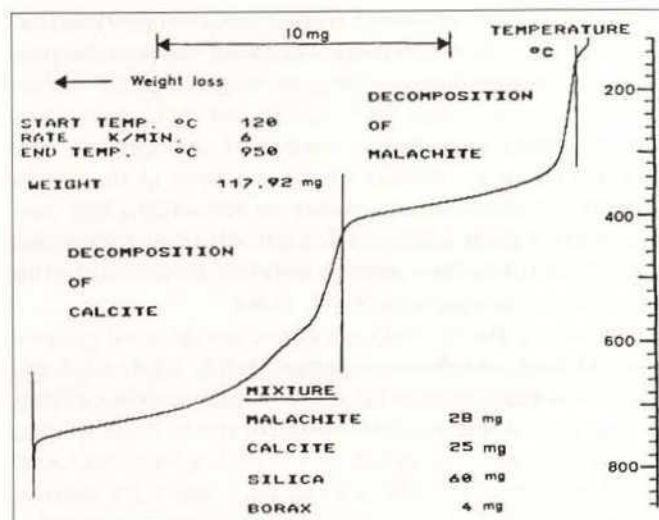The synthesis of Chinese Blue was similarly studied by TG and DTG in fig. 10 starting from $BaCO_3$, quartz and CuO.

Fig. 3. TG curve for the reaction of Malachite, $CaCO_3$ and SiO_2 to form Egyptian Blue, $CaCuSi_4O_{10}$. The reaction starts with the decomposition of Malachite. With beginning decomposition of $CaCO_3$, the formation of $CaCuSi_4O_{10}$ sets on. This process is finished somewhat above 700 °C.

图 3. 孔雀石, $CaCO_3$ 和 SiO_2 生成埃及蓝 $CaCuSi_4O_{10}$ 的反应的热重曲线。反应从孔雀石分解开始。随着 $CaCO_3$ 开始分解, $CaCuSi_4O_{10}$ 开始形成, 这个过程在超过 700°C 后结束。
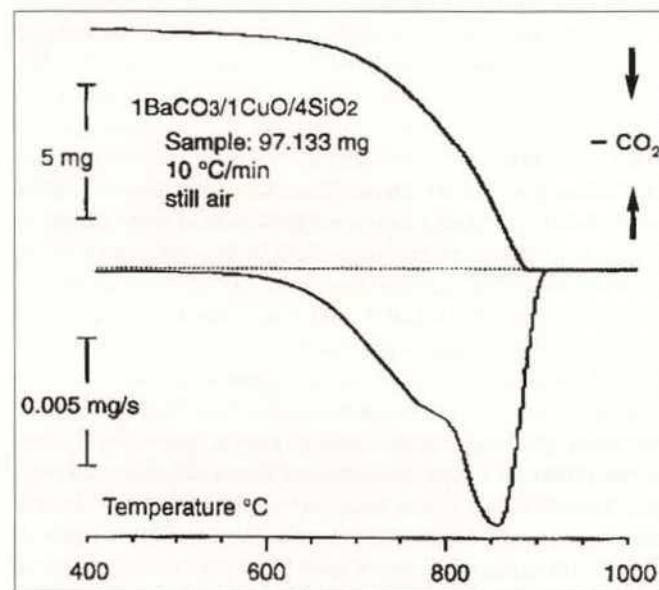

Fig. 4. TG (above) and DTG Curves (below) of the reaction of $BaCO_3$, CuO and 4 SiO_2 to afford $BaCuSi_4O_{10}$. The reaction starts at approximately 650 °C to form BaO. At around 800 °C the formation of $BaCuSi_4O_{10}$ sets in and is over at around 900 °C.

图 4. $BaCO_3$, CuO 和 $4SiO_2$ 生成 $BaCuSi_4O_{10}$ 的反应的热重(上图)和差示热重(下图)曲线。大约在 650°C 反应开始, BaO 形成。$BaCuSi_4O_{10}$ 的形成在 800°C 左右开始, 900°C 左右结束。

DSC reveals that quartz ist the least reactive component in mixtures of starting materials. Therefore, the decrease of the quartz peak at 572 °C (phase transition α-quartz → β-quartz) may be used as a criterion for the completeness of such reactions.

Actually, very few of the ancient Egyptian Blue materials were completely free of residual quartz. Most of them contained varying amounts of unreacted quartz, in spite of their bright

colour appearance. For example, in figure 11 DSC curves of a contemporary Egyptian Blue and ancient Egyptian Blues of Table 1 are shown, which demonstrate by their quartz peak (and partly by their calcium carbonate peak), residual contents of these starting materials, which would even allow quantification (Wiedemann, 2001).
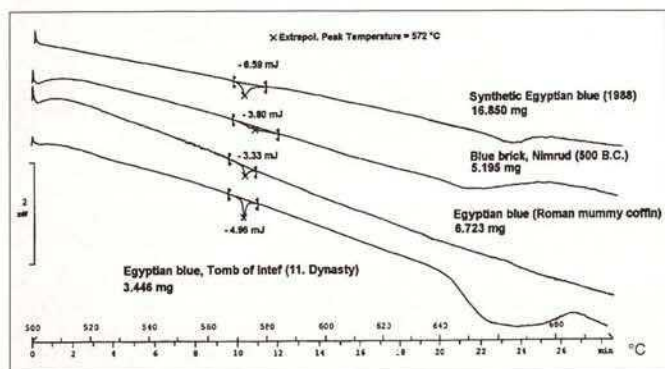

Fig. 5. DTA curves for selected Egyptian Blue samples as designated. The left peaks correspond to the quartz transitions (see text) and the right ones to the decompositions of $CaCO_3$.

图 5. 选定的埃及蓝样品的差热分析曲线。左边的峰对应于石英转变(见文章内容)，右边的峰对应于 $CaCO_3$ 分解。

Thermal analysis investigations of contemporary synthesized Chinese Blue lead to very similar conclusions as for Egyptian Blue (Wiedemann 1997 a and b), e. g. that residual quartz contents are expected to be traceable even in ancient samples. Whether this conclusion is valid for Chinese Purple, as well, is unclear. A respective study was attempted on the ancient Chinese Purple Freer Gallery stick which by Raman spectroscopy was claimed to contain some SiO_2. However, the assignment of the Raman band of quartz is ambiguous, since in the range of $460\ cm^{-1}$ it may be obscured by the presence of a weak band of Chinese Purple appearing at approximately the same wave-number. DSC measurements did not reveal a quartz peak. This may be attributed to the possibility that there is indeed no quartz present. An alternative interpretation could be based on the relatively high reactivity of $BaCuSi_2O_6$: At the given temperature the excess quartz reacts further with Chinese Purple to give Chinese Blue in an almost thermoneutral fashion according to the equation:

$$BaCuSi_2O_6 + 2\ SiO_2 \rightarrow BaCuSi_4O_{10}$$

Thus, Egyptian and Chinese Blue samples may be analyzed by DSC for residual quartz contents (also for $CaCO_3$ and perhaps even for $BaCO_3$). However, when applying DSC for excess quartz studies of Chinese Purple, it is not clear yet, whether reliable conclusions can be drawn.

B) Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray analysis (EDX) of samples of Egyptian Blue and Chinese Blue and Purple

In this section it will be demonstrated that the combined techniques of SEM and EDX applied to the Egyptian and Chinese

samples such as indicated in Table 1 are very benificial for the elucidation of surface structures of pigments and their elemental compositions. Figure 12 clearly shows two electron micrographs of two samples of the crown of Nefertete and of stick 4070, which reveal a platelet-like microcrystalline structure of the Egyptian Blue and the Chinese Purple content.

Table 2 and 3 contain valuable EDX microsonde type applications for the determination of the elemental composition of ancient pigment surfaces. A statistical approach was used with measurements at different surface locations in order to average local deviations. Interpretation of these values lead to the following conclusions:

The investigated Egyptian Blue samples show grossly constant composition over time, which is surprising, especially in view of the great period of time which their origins span. Regarding the average values of all samples, in comparison with the theoretical composition of Egyptian Blue $CaCuSi_4O_{10}$, the ideal values for calcium and copper were usually underscored by the Egyptian producers, while the amounts of silicon were always too high. This is confirmed by the results of the thermoanalytical studies (vide supra) and of the Raman investigations

Fig. 6. SEM photographs of sample crown of Nefertete (above) and Stick 4070 (below) revealing crystallinity and the platelet-like structure of both samples.

图 6. Crown of Nefertete 样(上图)和 Stick4070 样(下图)的扫描电镜图。该图显示了两个样品的结晶性及其类片状结构。
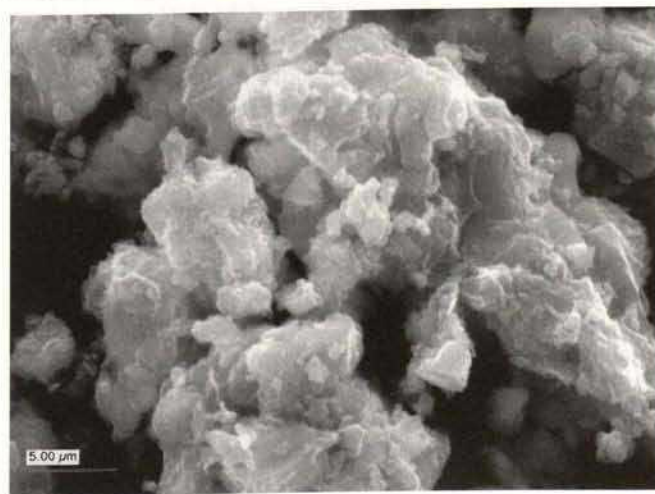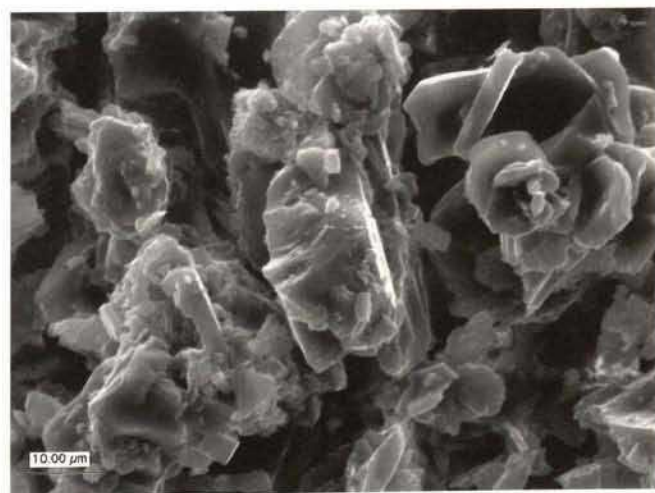
Time	Period	Composition, [%] weight			Objects
		Ca	Cu	Si	
2575-2134 B.C.	Old Kingdom	15.2	21.3	63.0	Mereruka, Saqq. Egypt
2040-1640 B.C.	Middle Kingdom	14.9	21.5	63.8	Tomb Intef, Egypt
1340 B.C.	New Kingdom	17.4	30.2	52.3	Nefertete, Berlin, Germany
1353 B.C.	New Kingdom	24.0	22.5	53.5	Echnaton Temple, Blue of Talatat
712-332 B.C.	Late Period	13.6	28.1	58.3	Bes Amulet, Egypt
332 B.C. – 395 A.D.	Greek-Roman	18.4	22.5	59.2	Mummy Coffin
13th-7th Cent. B.C.	Mesopotamia	8.2	13.0	73.0	Brick Nimrud, Iraq
		16.0	22.7	60.4	Average of all samples
		18.6	29.4	52.0	Egyptian Blue, theoretical

Table 2. Composition of Egyptian Blue samples from different periods.

表 2. 不同时期埃及蓝试样的成分。

Sample	Ca	Ba	Cu	Si	Pb	S
Freer Gallery	2.5 (3.5)	35.3 (13.0)	5.6 (4.7)	37.7 (64.8)	11.4 (3.4)	2.0 (2.3)
Stick 4069	3.1 (6.2)	31.6 (18.2)	13.2 (16.6)	15.8 (44.5)	35.4 (13.7)	–[a]
Stick 4070	1.0 (1.7)	36.5 (17.0)	15.6 (15.7)	25.9 (58.9)	20.7 (6.4)	–
a Not analyzed due to a too high amount of lead						

Table 3. Compositions of chinese stick samples with respect to major constituents [weight or atom % (in brackets)] from EDX. Other elements of minor amounts add up to 100 %.

表 3. 能量分散 X 光射线荧光下的中国颜料棒试样的成分，涉及主要组分[重量比或原子百分比(括号内)]。加其余的微量元素，合计为 100 %。

(vide infra), which in several samples show the presence of residual quartz. The "cleanest" Egyptian Blue is contained in the sample of the Nefertete bust, which is in all constituents quite close to the theoretical values. The greatest deflection is given by the Mesopotamian Brick Nimrud, which deviates by more than 10 % in calcium and more than 16 % in copper. Intrestingly it shows a high amount of quartz. An interpretation of this observation would be that the brick presumably was designed as a sophisticated construction material, which required specialized material properties and consequently a different chemical composition.

Deviations from the ideal compositions of Egyptian Blue may in general arise from inclusions of the flux material, starting materials or furthermore from influences of the matrix, in which the pigments were embedded. Quite often this is seen by the appearance of additional elements in the compositional analysis. For instance the samples of the Nefertete bust contains the metal ions of Na, K, Mg, Al, Fe and Ti and the non-metal elements S and Cl as minor constituents. Similarly, the Talatat and the Bes samples have traces of K, Mg, Al, Fe and S, Cl and Al, Fe and S, Cl. The Ptah Sokaris sample consists additionally of zinc, besides traces of K, Ti, Fe and Cl. The zinc content is also found in certain Raman bands not identified in other Egyptian Blue samples. Zinc is therefore a unique companion of ancient Egyptian Blue samples. Its origin and possible function is yet unclear. It should be noted in this context that tin has been frequently found in original samples of Egyptian Blue (Jaksch, 1983).

The ancient Chinese samples analysed by EDX do not show clear-cut atomic ratios with respect to $BaCuSi_4O_{10}$ or $BaCuSi_2O_6$ (Table 3). The Ba/Cu atomic ratios are however approximately 1:1. Quite counterintuitively, stick 4069, which consists of an approximate 1:1 mixture of Chinese Blue and Purple with silica-rich Chinese Blue (see also powder X-ray studies) possesses less Si atomic content than stick 4070. This contradiction can only be reconciled with the assumption that stick 4070 additionally contains quartz or other quartz-rich compounds.

The sticks also contain non-Purple or Blue constituents in greater quantities. As already noted in earlier research (FitzHugh, 1992), they are often mixtures of compounds and also consist of calcium in quantities > 1 % and great amounts of lead. While calcium with its relatively low content can safely be identified as an unintended ingredient accompanying starting materials from sand, Barytes or Witherite, the lead content is of chemical relevance and was added as an essential ingredient to all the ancient Chinese pigment preparations (vide supra). The amount of lead in stick 4069 is especially high, even exceeding 30 % in weight (Table 3).

Minor constituents of the sticks are: Freer Gallery stick: Na, K, Al, Fe, Cd and S, Cl; stick 4069: Al, Fe, Cd; stick 4070: Al, Fe. It should be noted that stick 4069 presumably also contains sulphur, which could not be analyzed by EDX due to overlap with a too intense lead X-ray emission. Quite remarkable are the cadmium contents of the Freer Gallery stick and of stick 4069. Because of the uniqueness of this element in the blue and purple pigment content, its presence may point to a common mineral or even synthetic origin. The nature and function of the chloride content of the Freer Gallery stick is still puzzling. It was supposedly introduced as NaCl or KCl. The accompanying amounts
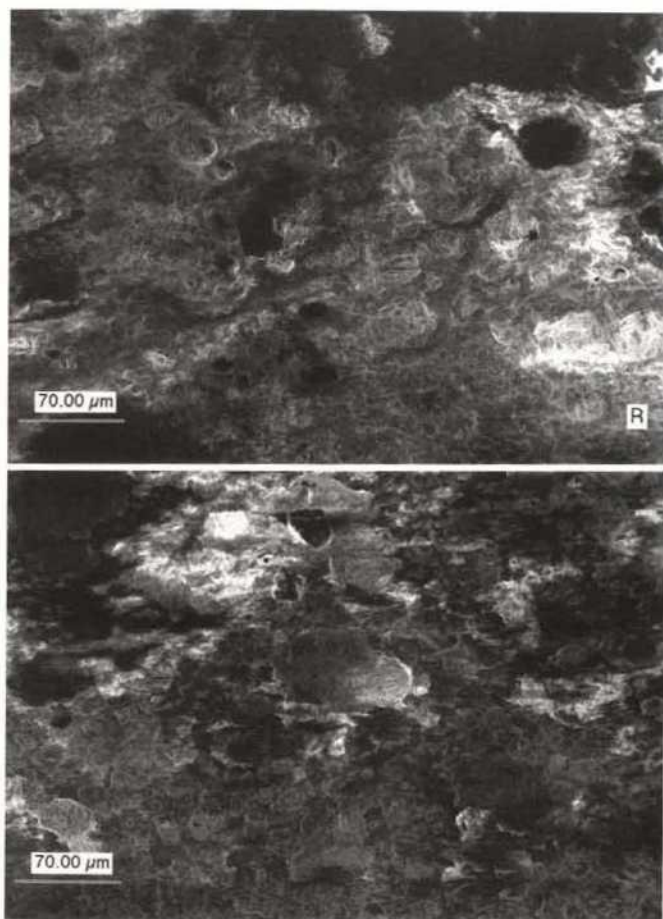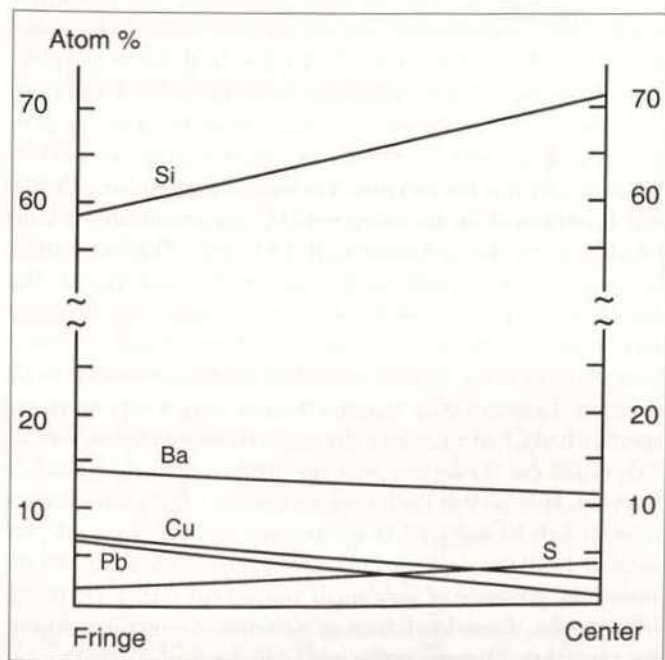
Fig. 7. SEM of the Freer Gallery stick comparing the surface morphologies of the fringe (above) and the centre area (below).

图 7. 弗里尔画廊样品边缘(上图)和中心区域(下图)表面形态的扫描电镜图。

Fig. 8. Schematic plot of the profile of the atomic content of Ba, Cu, Pb, S and Si in the slice of the Freer Gallery stick.

图 8. 弗里尔画廊样品切片中 Ba, Cu, Pb, S 和 Si 原子含量分布示意图。

of aluminium are presumably in all samples of impure quartz as a starting material, which was very likely used in the synthesis as crude sand.

From the Freer Gallery stick the octagonal plate, shown in colour plate XV, fig. 2, was investigated in greater detail. It reveals a porous but otherwise hard and compact surface. It can be divided into a darker central core and a lighter fringe section. Magnifications of these areas by SEM show qualitatively no difference in the heterogeneous microcrystalline surface morphology of the core and the fringe areas. Both sections have obviously darker pigment areas and lighter inclusions (fig. 13).

Based on the areal dependent EDX analysis a schematic profile of the major elemental constituents can be established (fig. 14).

In absolute measures the silicon content is very high, it even increases drastically from the outside to the inside of the sample. Similarly, but to a much lower extent the amount of sulphur increases, while the other elements of significance like Ba, Cu and Pb conversely decrease in this direction. Lead even reaches almost zero atomic content in the center. From the DSC measurements (vide supra) it seemed likely that there is no free SiO_2 in this sample. The high silicon value can thus only be interpreted in terms of the presence of silicates (presumably mainly glassy Ba-silicates). Furthermore, it can safely be anticipated that sulphur appears as sulphates. Lead and barium sulfate should thus meet to a noticable extent on the transition of the outer to the inner part ($PbSO_4$) and in the center area ($BaSO_4$). The "outside" lead is assumed to appear primarily as PbO (as confirmed by Raman spectroscopy). Finally it should be noted that the atomic copper content of this sample is quite low. In ideal Chinese Purple it is expected to be 25 % considering the cationic ingredients alone. Thus, in total copper not even half of the Ba content is reached. Nevertheless, as we will later see, only Chinese Purple was definitely identified by Raman spectroscopy, so that the "excess" barium is not expected to be engaged in the formation of other barium-copper-silicate phases, such as $Ba_2CuSi_2O_7$.

The amount of lead decreasing from outside to inside may be interpreted in terms of a specific preparation process for this stick. It may be assumed that, before reaction, the lead (as PbO or $PbCO_3$) covered the reactants as a crust. (See also FitzHugh, 1992). At higher reaction temperatures the lead starts to penetrate the inner parts of the stick by diffusion. However, the lead did not apparently fully reach the center to the extent required for completion of the chemical processes. In the presence of lead, the described catalytic decomposition (vide supra) of the presumed major starting constituent $BaSO_4$ is expected to be promoted producing Chinese Purple and volatile sulphur compounds. With this in mind the lead gradient would then also explain the sulfur profile increasing from outside to inside (see fig. 14). Not shown in the diagram is the minor constituent chloride, which appears only in the central area to a detectable extent. All the given observations make it reasonable to assume that the inner section consists more of non-purple compounds, while the fringe area shows more of Chinese Purple. Contrary to the generally lighter appearance of the fringe section, Chinese Purple is apparently to a greater extent associated with the lead.

Judging from EDX studies, the Terracotta Army, samples I and II, indeed consists of the Chinese Blue and Purple constituents Ba, Cu and Si. As in the earlier investigations (Herm, 1995; Thieme, 1995) a relatively high Pb content was noticed (fig. 15). This could be related to its function as a synthetic additive, but could also point to its role as a pigment component in

form of PbO or PbCO$_3$ in mixture with Chinese Purple. Sample II contains, besides Chinese Purple, cinnabar, phosphorite or apatite and ilmenite, FeTiO$_3$, representing red, white and brown colouring tones. The ilmenite and the phosphorus compounds were found as isolated pieces on the mm scale and could therefore be studied separately by EDX without a disturbing background. The EDX analysis revealed almost exactly the atomic ratios expected for FeTiO$_3$ and Ca$_3$(PO$_4$)$_2$.

In particular, it is worth mentioning that the EDX analysis of
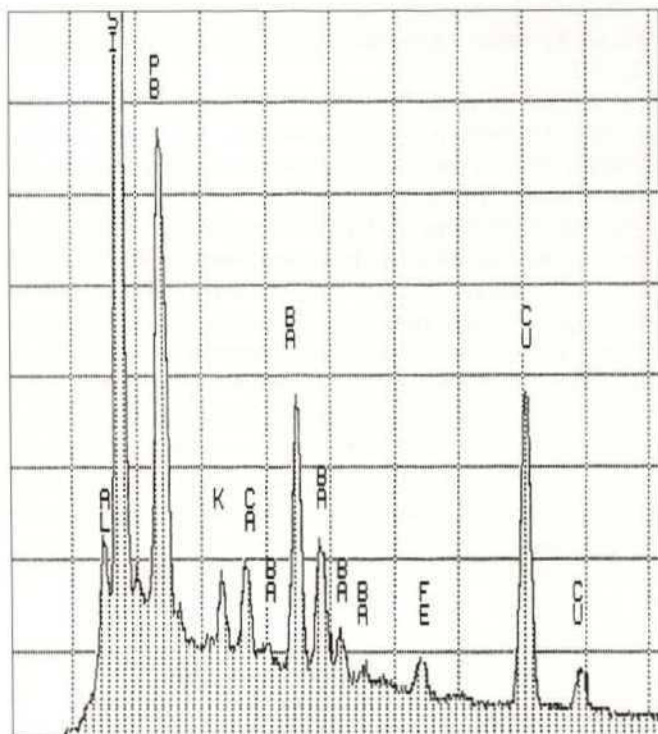
Fig. 9. EDX of sample I of the Terracotta Army displaying the major constituents Ba, Cu, Si and Pb and minor quantities of other elements as impurities.

图 9. 兵马俑样品 I 的能量色散 X-射线分析。结果显示样品主要成份为 Ba, Cu, Si 和 Pb 并含微量的其它元素杂质。

sample II demonstrated that it apparently not only possesses a 'spread out' lead content, but also consists in significant amounts of lead in areas where Chinese Purple is located. This may allow us to conclude that lead compounds were also added in the preparations of Chinese Purple samples.

C) X-ray powder diffraction studies on original samples containing Egyptian and Chinese Blue and Chinese Purple

X-ray powder diffraction studies have been commonly used to identify major microcrystalline components in heterogenous mixtures. In original pigment samples this normally holds for the pigment content. Figure 16 shows powder diffraction patterns of Egyptian Blue (Cuprorivaite), Chinese Blue (Effenbergerite) and synthetic Chinese Purple drawn out of the Blues schematically as stick diagrammes. To some extent the patterns of the Blues resemble each other because of their structural relationships.

Several Egyptian Blue samples in Table 1 have been analysed and consist of prevailingly CaCuSi$_4$O$_{10}$ according to the presence of the respective major Egyptian Blue reflections of Figure 16. Impurities could only be identified properly when they were contained as major constituents. This was the case for the strong quartz content of Brick Nimrud.

The Chinese samples, the Freer Gallery stick, stick 4069 and stick 4070 were analyzed by X-ray powder diffraction, as well. The pigment component of the Freer Gallery stick and of stick 4070 was Chinese Purple. Chinese Blue was not found to be present within detection limit. However, from the powder diffraction analysis of stick 4069, it could be derived that it consists of an approximately 1:1 mixture of Chinese Blue and Purple. The Freer Gallery stick shows the greatest amounts of impurities. They were identified as BaSO$_4$, PbSO$_4$ and BaCO$_3$. Several remaining reflections of this quite heterogeneous mixture could not be assigned, but are assumed to belong to certain crystalline areas of silicates.

The powder diffractogramme of stick 4069 contained minor reflections for BaSO$_4$ and PbSO$_4$, while that of stick 4070 displayed additional reflections for PbCO$_3$ (see fig. 17). A few reflections in each of the samples could not be designated.

D) Micro-Raman spectroscopy of original samples containing Egyptian and Chinese Blue and Chinese Purple

Micro-Raman spectroscopy can advantageously be used for the identification of pigments in heterogeneous mixtures like paints and paint applications. Concerning Barium-copper-silicates it previously has been applied only in the case of Chinese Purple (Finger 1989, see also McKeown, 1997). Our Raman studies on various ancient samples (indicated in Table 1) and reference samples brought about well-defined conclusions. In the spectral range of 1200 – 100 cm^{-1} Egyptian Blue and Chinese Blue samples show two very strong Raman emissions between 1080 and 1090 cm^{-1} and 1100 cm^{-1}, respectively, and around 430 cm^{-1} for both types of species. In an exemplary way the Raman spectra of the Crown of Nefertete and the Amulet Bes are shown in figure 18.

The Chinese Blue bands at around 1100 cm^{-1} are thus of little higher energy than the corresponding ones of Egyptian Blue, a fact which could be used for their distinction. The two major bands of the corresponding strontium blue SrCuSi$_4$O$_{10}$ would appear at 1090 and 425 cm^{-1} very close to those of Egyptian Blue. In all the Egyptian Blue samples indicated in Table 1, we were thus able to identify Egyptian Blue by Raman spectroscopy. Major and dominant contents of impurities could be detected only in a few samples. For sample Ptah-Sokaris-Osiris, which consists of Zn according to EDX, this presumably is indicated by a very strong Raman band at 745 cm^{-1}. This band could, however, not yet be attributed to a certain chemical species. The Raman band of quartz (460 to 470 cm^{-1}) is especially strong in certain spots of the spectrum of Brick Nimrud and otherwise seen in the samples Ba-bird indicating medium amounts. In all the other Egyptian Blue samples there is only a very weak respective band. Unfortunately, the major Raman emission for CaCO$_3$ (1088 cm^{-1}) overlaps with the 1080 – 1090 cm^{-1} band of Egyptian Blue so that the limestone content of original samples cannot easily be analysed. In agreement with the EDX results for sulphur, the Raman spectra of several Egyptian Blue samples revealed the presence of very small amounts of CaSO$_4$ (Mastaba of Mereruka, Tomb Intef, Bust of Nefertete, Amulet Bes, Mummy cartonage, Mummy coffin and Cylinder Seal, Thebes).

Fig. 10. Stick representations of the Powder X-ray Diffractogrammes of Egyptian Blue, CaCuSi₄O₁₀ (Cuprorivaite), Chinese Blue, BaCuSi₄O₁₀ (Effenbergerite) and Chinese Purple, BaCuSi₂O₆. Only the more intense reflections are given.

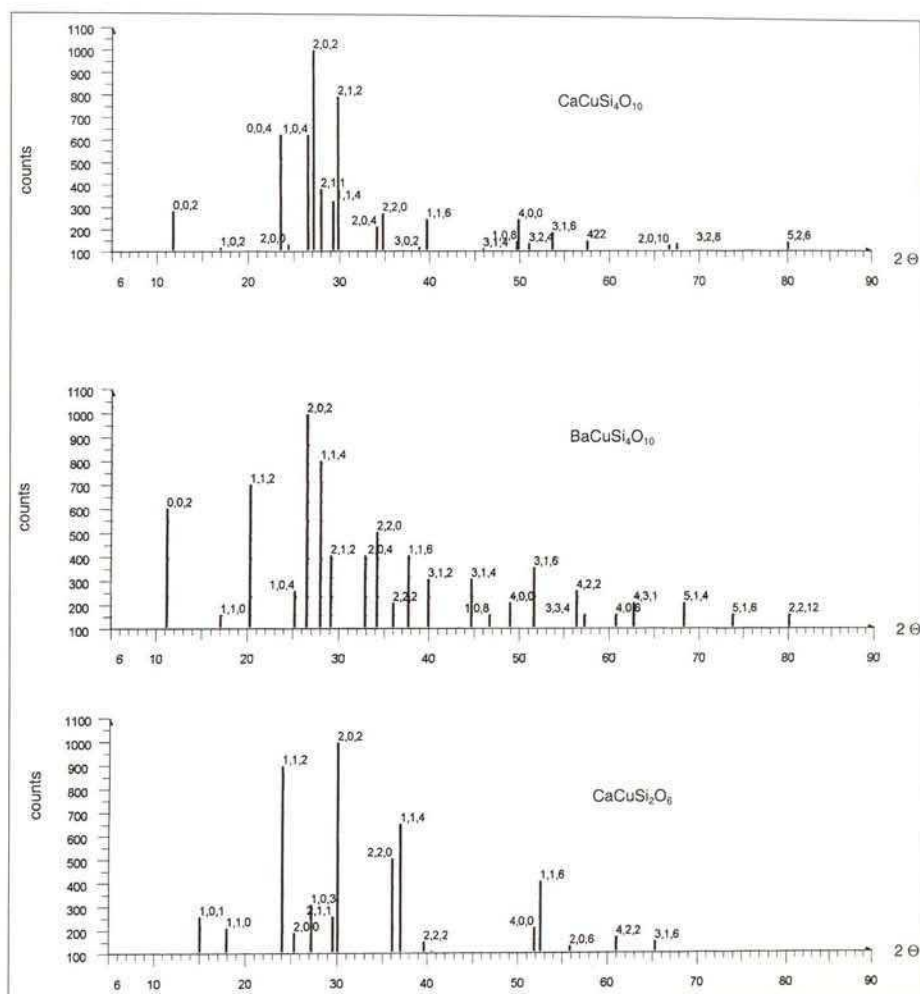图 10. 埃及蓝 $CaCuSi_4O_{10}$ (Cuprorivaite), 中国蓝 $BaCuSi_4O_{10}$ (Effenbergerite) 和中国紫 $BaCuSi_2O_6$ 的粉末 X-射线衍射图。图中只给出较强的反射峰。

Fig. 11. Stick representation of the Powder X-ray Diffractogramme of Stick 4070. Lines not designated belong to Chinese Purple. o refers to major lines of PbCO₃. *Not assigned.

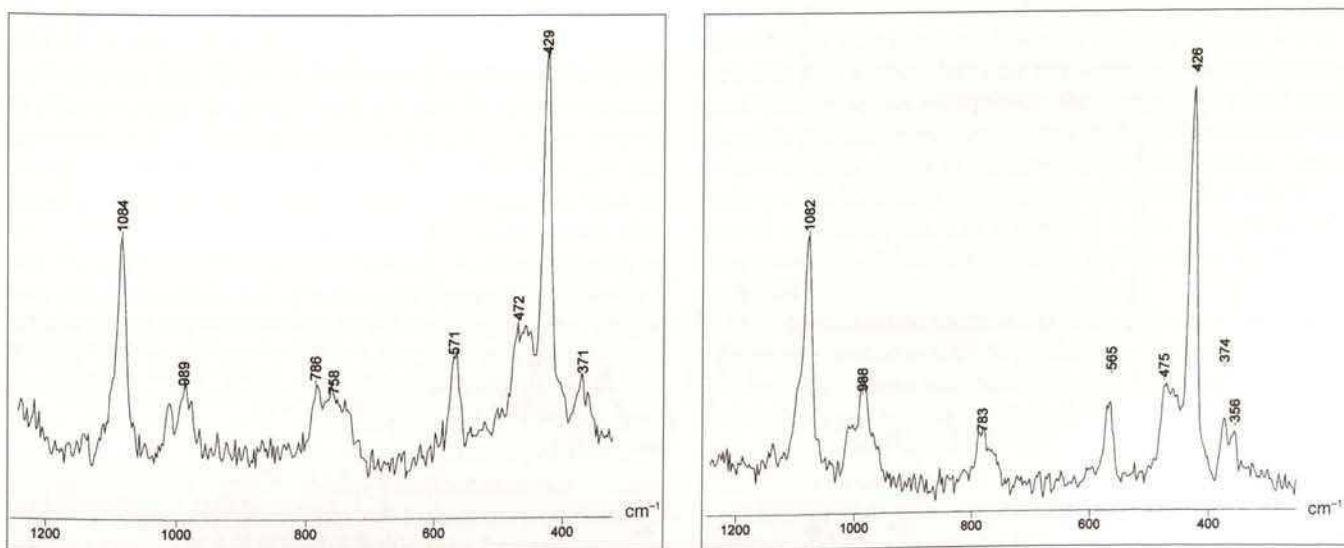图 11. Stick4070 样品的粉末 X-射线衍射图。未标识的峰属于中国紫。°表示 PbCO3 的主要峰。*未归属。
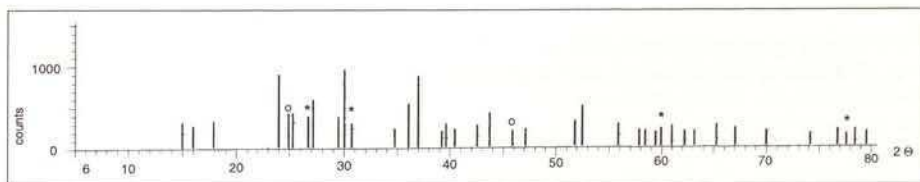
Fig. 12. Raman spectra of original samples of Egyptian Blue (Excitation Laser 514 nm). Left the spectrum of the blue from the crown of Nefertete. Right the spectrum of the Amulet Bes. Both samples display primarily Egyptian Blue.

图 12. 埃及蓝原样的拉曼光谱(激发光 514nm)。左图为 Crown of Nefertete 样的光谱，右图为 Amulet Bes 样的光谱。两个样品都

From the Chinese samples, stick 4069 contains Chinese Blue, which however is is mixed with Chinese Purple (see fig. 19). This confirms the result of the powder X-ray studies.

Spectra of Chinese Purple samples revealed, as finger-print patterns, two strong bands at around 590 cm^{-1} and 514 cm^{-1}. A band at 990 cm^{-1} could also be identified, but in contrast to the
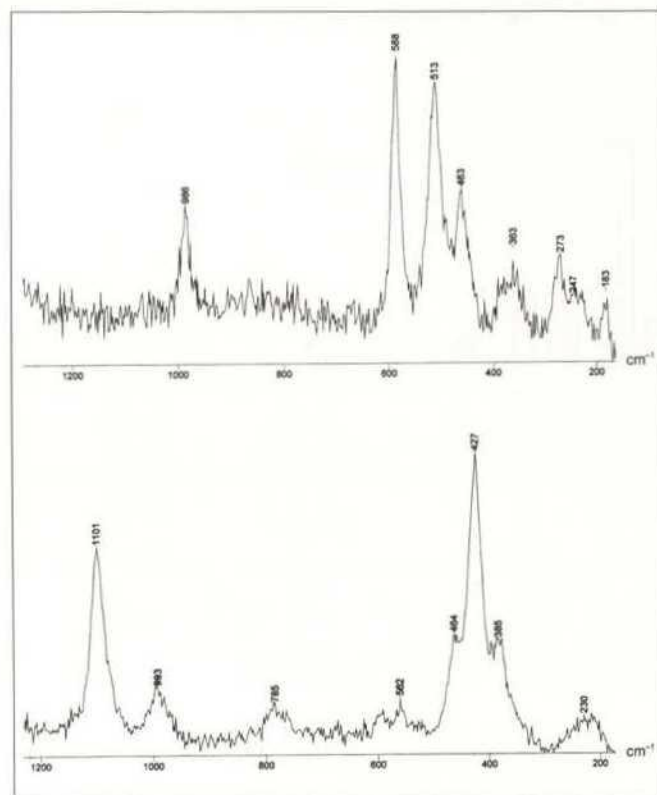
blue pigments this band at higher wave-numbers is only of medium intensity. Chinese Blue and Chinese Purple are thus easily distinguishable by Raman spectroscopy.

In all Chinese samples the following potential impurities were checked, which might originate from the minerals used, the added flux or chemical transformations occuring during synthesis: CuO, Cu$_2$O, azurite, BaCO$_3$, BaSO$_4$, PbCO$_3$, PbCO$_3 \cdot$ 2 PbO, PbSO$_4$, CdO and SiO$_2$. Several Chinese samples presumably show a Raman emission for quartz, which varies in relative intensity from sample to sample. However, identification of the Raman band of minor amounts of quartz 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. In the Raman spectrum of the Chinese sample, the Royal Ontario Museum stick, no definite conclusions on impurities could be drawn due to the low quality of the spectrum caused by an insufficient amount of sample. Stick 4069 showed quartz, however no spectrum of isolated spots showing BaSO$_4$ and BaCO$_3$ expected from the powder X-ray results could be found. Stick 4070 unambigously showed the presence of PbCO$_3$.

As in the case of the EDX analysis, the slice of the Freer Gallery stick was investigated in greater detail by Raman spectroscopy. Table 4 shows the results of the Raman study at 12 different spots following an approximate order from outside to inside. In general the given collection of spectra makes clear that this stick is a very heterogeneous mixture, since several other components have been detected besides Chinese Purple.

Several bands were assigned to crystalline or glassy silicate phases. Other attributable phases were CaCO$_3$, BaCO$_3$, BaSO$_4$, PbSO$_4$, PbO and perhaps SiO$_2$. They are in full agreement with the elemental contents analyzed by EDX. Apparently due to some arbitrariness in the choice of the measured spots and the heterogeneity of the sample, an accurate areal dependence like that of the EDX analysis could not be established.

It is however clear that, due to the various residual constituents, it can be concluded that the stoichiometry of the starting materials did not match that of Chinese Purple. An insufficient copper content leads to production of several non purple constituents. Presumably the bands around 940 and 421 cm^{-1} account for glassy phases with polysilicate (SiO$_3^{2-}$) units and the bands at 914 cm^{-1} for disilicate (Si$_2$O$_7^{6-}$) (Frantz, 1995). Due to

Fig. 13. Raman spectra of stick K 4069 at two different spots (Excitation Laser 514 nm). The spectrum above corresponds to Chinese Purple, the spectrum below to Chinese Blue with some impurity of quartz (464 cm^{-1}).

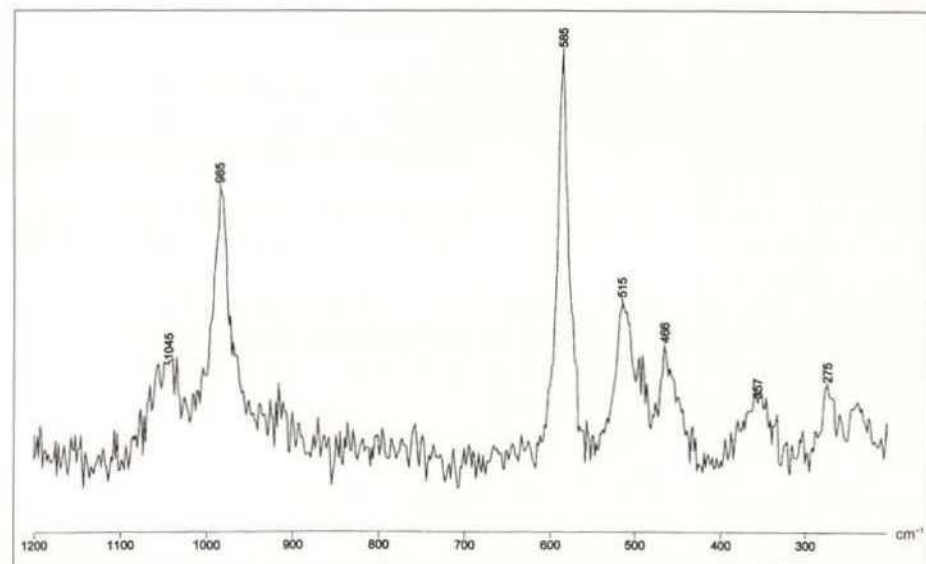图 13. K4069 样品两个不同位置的拉曼光谱(激发光514nm)。上图对应于中国紫，下图对应于混有石英杂质(464cm-1)的中国蓝。

Fig. 14. Raman spectrum of sample I of the Terracotta Army (Excitation Laser 514 nm) displaying the spectrum of Chinese Purple with some impurity of PbCO$_3$.

图 14. 兵马俑样品I的拉曼光谱(激发光 514 nm)。谱图显示了带有 PbCO$_3$ 杂质的中国紫的光谱。

	1085											$CaCO_3$
			1059	(1059)	1057	1060	1060	1060	1057	1056		$BaCO_3$
986	988	984			985			985				CP/$BaSO_4$
965	966	965			967	966	966	967	966	966		$PbSO_4$
			939	945			941	939			941	SiO_3^{2-} (glass)
			915	(915)			914	914				$Si_2O_7^{6-}$
757	754	754	754	757	753	754	750				752	$PbSO_4$
	637											$CaCO_3$
588	587	588	586	586	587	588	587	587		588	586	CP
516	514	518	515	514	516	516	516	518		516	516	CP
469	466	466	(466)	(466)	466	468	465			464	466	CP/SiO_2
			418	421			419	421			421	SiO_3^{2-} (glass)
	391											$CaCO_3$
356		356	351	352	353	353	354	351	356	351		CP
276	278	280			274		274	274		275		CP/PbO
									243			?
185		185	184	198		187	191				186	CP
148	142	148										PbO

Table 4. Raman data of various spots (column) of sample Freer Gallery stick with assignments. CP = Chinese Purple. Weak bands in brackets; ? = not assigned.

表 4. 确定了的弗里尔画廊颜料棒试样的不同点的拉曼数据。 CP = 中国紫。括号中为弱谱带; ? = 没有确定。

the great stoichiometric excess of SiO_2 (see also EDX analysis) glass formation seems to be very plausible and indeed the relatively hard general nature 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 use as pigments (Le Chatelier, 1900). This historic discovery was certainly made without knowledge of the existence of Chinese Blue and Purple and may simply reflect need for artificial colouring matter.

The Terracotta Army samples I and II consist of Chinese Purple as indicated by the appearences of the major Raman bands for this compound (fig. 20).

A relatively high $PbCO_3$ or PbO 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 cinnabar could be traced as indicated also by EDX. I and II also showed substantial quantities of matrix constituents, such as quartz. This is assumed to be a natural circumstance associated with their use in paints. It should, however, be noted that none of both samples showed the presence of Chinese Blue. Sample I possessed considerable amounts azurite crystallites (major Raman band at 402 cm^{-1}), which apparently stood for the blue colouring tone in the pigment layer. 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 is to be attributed to a mineral or chemical origin or whether it was related to a colouring function.

E) UV/Vis and Photoluminescence spectroscopy (PL) of Egyptian Blue and Chinese Blue and Purple

As mentioned before, Chinese Blue and Purple contain copper(+II) ions as effective chromophores. The electronic structures of chromophore models of Chinese Blue and Purple have been calculated by us in order to trace any difference in the absorption spectra expected for Chinese Blue and Purple (Density Functional Calculations). In an ideal square planar silicate ligand environment as in Chinese Blue, the copper ion should give rise to only one visible absorption in the orange, which is seen as the complementary blue colour (compare with the UV/vis spectrum of Egyptian Blue (Ford, 1979)). For Chinese Purple, however, two visible electronic transitions are expected to appear. One causes an absorption in the orange with a blue complementary colour very much as predicted for Chinese Blue. The other transition occurs in the green, which then appears purple with its complementary counterpart. Both electronic transitions indeed arise from the Cu-Cu bonding in this compound. The experimental verifications of these predictions are yet to be established.

Photoluminescence spectroscopy is to a certain extent a complementary method to UV/Vis spectroscopy. For instance, when irradiated by a green laser beam Chinese Blue and Purple very effectively transform this light into fluorescent infrared light between 800 – 1100 nm (Ajo, 2000). This means that when sun light shines on Chinese Blue and Purple, they not only give rise to a blue or purple colour perception, but additionally emit heat radiation. Whether or not this latter circumstance may have an

effect on human perception is not clear, and has to our knowledge not yet been investigated. The luminescence spectra of synthetic samples of Chinese Blue and Purple reveal that the fluorescent light of both is emitted as a characteristic double band pattern, where the shorter wavelength band appears as a less intense shoulder for Chinese Purple, while for Chinese Blue they have about the same intensity. The emission maxima of both compounds appear at somewhat different wavelength: 945 and 995 nm for Chinese Purple and 930 and 970 nm for Chinese Blue. The similarity of these emission bands with respect to their positions, and, to a certain degree, also to their intensities indicate that it is the copper(+II) ions that gives rise to luminescence. Unfortunately, this observation makes it impossible to use luminescence to identify and distinguish Chinese Blue and Purple in complex mixtures of both components.

Conclusions Drawn from the Chemical and Physical Investigations of Egyptian Blue and Chinese Blue and Purple

Our investigations gave clear evidence that the ancient Egyptian samples of Table 1 are all based on the chemical compound $CaCuSi_4O_{10}$, which is commonly denoted as Egyptian Blue. The samples of Table 2, investigated for their compositions, normally deviate from the theoretical values. They show mixtures originating from their production process or from the fact that they were paint applications. A gross trend of constant compositions of the blue pigments can be recognized over a period of approximately 3000 years. This naturally required a stable route of transmission, that is, a reliable mechanism for the handing-down of the manufacturing recipe, which apparently could only be provided in the environment of a highly developed civilization.

Egyptian Blue was produced from quite abundant minerals. Only the copper component needed to be made available from mining sites. Copper mining was quite common at the time. It played a major role in the Egyptian civilization and also in previous human developments. The general situation of the resources did not impose restrictions on the spread of the use of Egyptian Blue. However, because of difficulties connected to the sintering-type solid state synthesis and the fact that Egyptian Blue cannot be processed by casting, technological restrictions emerged. Besides the general requirement that the minerals used for Egyptian Blue preparation required pretreatments like grinding and compacting, the production of compact blue bodies demanded specific sophisticated developments involving multistage processes. The physical and chemical conditions for successful production of Egyptian Blue were not too difficult and could usually be established with ease, such as the optimal temperature for the reaction, the temperature control and the maintainance of the reaction temperature over a longer period of time. Based on these circumstances the Egyptian pigment could be produced with satisfying quality over a great span of time.

For the Chinese pigments the general situation seems somewhat different. First of all it seems quite plausible that the production of Chinese Blue and Purple was based on the knowledge of the production of Egyptian Blue. Chemically the blue compounds resemble each other quite closely, and differ in the chemically minor variation of the replacement of calcium with barium. Such a variation is be anticipated for ancient craftsmen, who were involved in purely empirical testing and did not have knowledge of atomic views and the Periodic Table of Elements.

Nevertheless, it cannot be ruled out that the chemical developments for Chinese Blue and Purple occured independently without any relationship to those of Egyptian Blue. This has to be stressed especially in view of the fact that there is no historical documentation concerning the ancient production methods of Chinese Blue and Purple in China. However, there are the two ancient artefacts, the Goblet and the Sistrum Hasanlu from Iran, which prove the spreading of the man-made Blue into regions considerably east of Egypt. Secondly, it is indicated by these artefacts that chemical variations of Egyptian Blue occured by modifying $CaCuSi_4O_{10}$ into at least partly the strontium derivative $SrCuSi_4O_{10}$. Both these facts provide further support for the hypothesis that the preparation of Egyptian Blue may have also become the basis for the development of ancient Chinese blue and purple pigments. The transmission of knowledge along the Silk Road, which also passed through Iran and which is anticipated to have been used as a trade route as early as least 1000 B. C. To the present date we have to assume that Chinese Blue and Purple appeared no earlier than the Warring States period and that for this reason, these Chinese pigments are 'younger' than Egyptian Blue. They emereged in historic times when the Silk Road was in full operation as a trade path and concomitant with this as a potential path for the exchange of ideas.

Even if they were based on the knowledge of Egyptian Blue, development of Chinese Blue and Purple faced several difficulties. Firstly there was the mineral problem, that barium minerals are much rarer than those of calcium. Barite ($BaSO_4$) or Witherite ($BaCO_3$) display the prominent property of being heavy, which makes them recognizable in nature and perhaps because of this characteristic they caught the interest of eager human beings. In China barium minerals are not rare and thus it seems plausible that they were utilized. The other necessary ingredients for Chinese Blue and Purple production were abundant; SiO_2 used as quartzite or sand and copper as copper sulphide, malachite or azurite. Therefore, we can hypothesize about the actual synthetic procedure. The use of barite demanded the addition of lead salts, such as lead carbonate or lead oxides. As we have seen, lead salts promote the decomposition of the quite stable barite and can also act as a flux additive. With the given combination of ingredients Chinese Blue and Purple could then have been obtained by a sintering-type process at temperatures between 900 and 1000 °C. It should be noted that this temperature is about 150 – 200 °C higher than that required for the production of Egyptian Blue. In the technically highly developed China of the Qin and Han time the achievement of such temperatures seemed to be no principal problem (Wagner; 1996). However, the severer synthetic conditions with respect to Egyptian Blue required more intense provisions concerning the construction of firing devices etc. Applying appropriate temperature conditions would have permitted a typical batch of Chinese Purple to have been finished within 10 – 24 hours, while the production of Chinese Blue presumably must have taken twice as long. It seems to be somewhat of a technological problem how these relatively high temperatures could have been maintained for a longer period of time within narrow limits. In order to obtain acceptable product results, the temperature control had to be quite accurate, presumably + −50 °C for Chinese Purple. Efficient temperature controlling devices were to our knowledge not known in the Qin and Han period or earlier. Therefore, the accomplishment of a steady temperature level had to be a matter of empirical testing and the production had to be supervised by experienced personnel. Manufacturing of the thermally less sensi-

tive Chinese Blue would not have required such strict control. This compound could even have been brought to melt at least for a short period of time.

For Chinese Purple it was not possible to obtain a homogeneous melt and it therefore had to be produced by a sintering or pseudo-sintering process. By doing so, relatively dense compact bodies like the described sticks were efficiently obtainable, since the sintering temperature is only about 100 – 150 °C from the potential melting point of the pure compound.

As previously indicated, Chinese Blue and Chinese Purple could have been produced as unique components or as mixtures controlled by the addition of appropriate amounts of SiO_2 and by applying appropriate temperatures and reaction times. If mixtures of both were the desired product, this could however have been achieved easiest by grinding the pure components together. In this way it was possible for Chinese painters to have all tones from blue to purple available. It is evident that the sticks of Purple and Blue were essential components of coloration mixtures of paintings and sculptures, as the Purple was used in the case of the analysed samples of the Terracotta Army. As mentioned before it is probable that the sticks were trade items. Their use thus required that pigment particles were ground from the sticks and added to the paint or colouring mixtures.

Relating back to the physical studies of the original Chinese samples, these made clear that, except for stick 4070, all of them contained considerable amounts of impurities. Highly contaminated is the Freer Gallery stick which witnesses incomplete chemical reaction and by a Cu:Ba ratio even considerably below 1, the additional formation of presumably glassy silicate components. These observations point out that the sticks were not of optimum pigment quality. Nevertheless, the overall appearance of the sticks seemed to be satisfactory with regard to their colouration properties.

In view of the fact that the preparation of Chinese Blue and Purple are still nowadays sometimes not easy to tackle, the invention of Chinese Blue and Purple may be considered a fine chemical and technological achievement. It is indeed an outstanding example of how the level of science and technology, which is well-described for ancient China by Joseph Needham and his collaborators (Needham, 1976) may positively influence civilizations. For early Chinese Culture we thus may recognize a steady unbiased impetus for improvements accompanied by high civilization standards.

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埃及与中国的蓝色及紫色的化学和物理研究

本文叙述11个古代埃及蓝($CaCuSi_4O_{10}$)颜料样品和6个含中国蓝($BaCuSi_2O_6$)的中国颜料原样品的物理-化学研究。所有这些古代颜料都对应于固定的化学物质并通过化学合成方法得到。文章对这些化合物的化学进行了广泛的综述，尤其是对它们的化学结构进行了讨论。其结构表现为无限连接的$Si_4O_{12}^{4-}$单位的层状结构或含有孤立硅酸根环的$[Cu2Si_4O_{12}^{4-}]$∞层的层状结构。异构的埃及紫和中国紫含有作为发色体的正方平面的Cu^{2+}离子。中国紫表现很特别的 Cu-Cu 键合的现象。这些化合物的稳定性依赖于它们的化学结构。埃及蓝和中国蓝很稳定，而中国紫化学和物理性质都易变。这一点归因于孤立硅酸盐环和 Cu-Cu 键的存在。

文章详细叙述了这些化合物的现代及古代的制备方法，包括合成的物理及化学条件。着重阐述了在制备中国蓝和中国紫中铅化合物添加剂的作用。

用热分析、扫描电镜、粉末 X-射线衍射、拉曼光谱、光致发光光谱对原样进行了表征，明确了样品的元素及物相组成，从而确定了制备这些颜料的原料、添加剂及制备条件。

跨越 3000 多年的不同源地的埃及蓝具有相对稳定的路线。中国颜料的合成需要更严格的物理和化学条件，这些条件更加难以满足。在这种情况下，中国蓝和中国紫的制备方法被假设为是建立在更古老的化学相关的埃及蓝的制备方法的基础上。不管怎样，中国颜料的精细化学品的成就需要进一步发展。