

Influence of Taoism on the Invention of the Purple Pigment Used on the Qin Terracotta Warriors

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Until the 19th century, most pigments were based on naturally occurring colored minerals and dyes, with three significant exceptions: Egyptian Blue, Chinese Blue/Purple and Maya Blue. The former two are alkaline-earth copper silicates, and because of this similarity it has been proposed that the Chinese pigments were derived from Egyptian Blue. Herein, we analyzed clumps of pigment from the Qin warriors and discovered that in spite of the structural similarity to Egyptian Blue, the micro-structural morphology of Chinese Purple is very different. Therefore, we believe that the synthesis technology for the Chinese pigments was a by-product of high-refractive index glasses (artificial jades) produced by Taoist monks. Further, the disappearance of these pigments from Chinese art and monuments concurrently with the decline of Taoism not only substantiates the link between the two, but also gives a striking example of how cultural changes in the society affected the scientific developments in ancient China.

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Introduction:

In March 1974, Chinese farmers made a remarkable archaeological find: during the sinking of wells for farmland irrigation construction near Xi'an (Shaanxi province, China) they discovered an army consisting of more than 8000 life-size terracotta figures of warriors and horses dating from the First Emperor of the Qin dynasty, Shi Huang Di (reigned ca 221 BC – ca 210 BC). The figures, facing east and ready for battle, were individually modelled with their own personal characteristics, and were accompanied by their weapons, real chariots, and objects of jade and bone. How, more than 2000 years ago, the ancient Chinese constructed these large and heavy statues and what technologies they used to finish such a large project are questions which are still only partially answered by modern archaeologists.

The discovery that $\text{BaCuSi}_2\text{O}_6$ (FitzHugh and Zycherman 1983, FitzHugh and Zycherman 1992), also known as “Chinese Purple”, was the main constituent of the purple pigment used in the paint covering the warriors constitutes an enigma in itself. This pigment was also used later in the Han dynasty in pottery (hence its other common name of “Han Purple”) and for trading. $\text{BaCuSi}_2\text{O}_6$ is a mineral that has never been found in nature, which implies that the makers of the warriors must have been able to synthesize it. The process to synthesize $\text{BaCuSi}_2\text{O}_6$ is now known to be highly complex (Berke and Wiedemann 2000, Berke 2002) and how the early Chinese chemists managed to synthesize barium copper silicates in an almost pure form, even preceding the invention of paper and the compass, is a mystery. Interestingly, these same materials are now being studied to gain insights into the mechanisms of high temperature superconductivity (Jaime et al 2004, Sebastian 2006).

In a detailed study, Berke (Berke and Wiedemann 2000, Berke 2002) showed that the manufacture of Chinese Purple was a very complicated process and that barium

(BaSO₄ or BaCO₃), copper and lead compounds as well as quartz were used in the preparation. He pointed out that lead oxide played a very important role as a catalyst in transforming barite (BaSO₄) into barium oxide (BaO). At 900-1100°C: BaO + CuO + 2SiO₂ = BaCuSi₂O₆; since BaSO₄ decomposes at a much higher temperature (1560 °C), PbO catalyze a dismutase reaction leading to the in situ decomposition of BaSO₄ (PbO + BaSiO₄ ↔ BaO + PbSO₄). Berke discussed the striking similarities of the Chinese Purple and Chinese Blue (BaCuSi₄O₁₀) with the Egyptian Blue pigment (CaCuSi₄O₁₀) (Riederer 1997). He conjectured a connection between the manufacture of the two pigments in the form of technology transfer from the makers of Egyptian Blue to the makers of Chinese Purple, and proposed that the Chinese Purple was in fact derived from the Egyptian Blue (Berke and Wiedemann 2000, Berke 2002). This would have been the earliest technology transfer between these two ancient civilizations. This supposition, however, leaves many unanswered questions. First, it is unlikely that the Chinese chemists could have acquired the technology (not just the pigment) from Egypt well before the official “silk road” (125 BC). Some earliest Chinese Purple samples date back to the “Warring States” period (479-221 BC). Considering the time needed to develop Barium based pigments, this technology transfer, if there was one, must have happened well before the “Warring States” period. But even if there existed a connection between China and Egypt, it doesn’t explain why the Chinese decided to substitute Ba for Ca (Kerr and Wood 2004) and face the challenges related to the consequent elevation of the synthesis temperature. Egyptian Blue forms at ~ 800°C-900°C (Berke 2002, Riederer 1997), whereas Chinese Purple starts to form between 900-1100°C and Chinese Blue at temperatures in excess of 1100°C (Berke and Wiedemann 2000, Berke 2002). An additional problem with the Egyptian-Chinese connection theory is that, to our knowledge, no Ca-bearing Egyptian Blue has been found in China.

In order to address these questions, we re-examined the chemistry and the morphology of purple pigments found on one of the Qin Terracotta warriors (fig. 1). By combining our findings of the technology used in the synthesis of Chinese Purple with existing archaeological evidence, we conclude that Taoist alchemists invented this pigment as well as the related pigment Chinese Blue independently from any Egyptian influence.

Experimental Methods:

Our investigation was based on a two pronged approach. We used a small fraction of our specimen, ground it into fine powder and used synchrotron radiation high-resolution powder x-ray diffraction (XRD) analysis to identify the crystallographic phases present. Then based on this inventory, we used spatially resolved x-ray and electron micro-beam techniques, such as micro X-ray diffraction (μ XRD), micro X-ray fluorescence (μ XRF) and Scanning Electron Microscopy (SEM) based Energy Dispersive X-ray (EDX) microanalysis, to study the chemistry of individual pigment clumps and map the distribution of these and other minority phases in the pigment. These chemical and phase maps gave us an insight into how the pigment was synthesized.

Synchrotron radiation is 8-12 orders of magnitude more brilliant than the high performance rotating anode x-ray tubes (Eisenberger 1986). The X-ray beams at current third generation synchrotron radiation sources can be focused to a one micrometer size spot and still maintain high photon fluxes ($>10^{10}$ ph/s/ μm^2) to obtain diffraction patterns with exposure times of only a few seconds. At a micro-focus beamline, we are, therefore, able to investigate a single object's microstructure rapidly at multiple locations.

For μ XRD experiment, the sample was placed on a high-precision XYZ stage on the micro-diffractometer at the Advance Light Source (beam line 7.3.3, Lawrence Berkeley National Laboratory) at an angle of 45° to the incident beam in the vertical plane. A x-ray CCD was placed at 90° to the incident beam, with beam line optics adjusted so that a $1.2 \times 1.2 \mu\text{m}$ spot with an x-ray spectrum of 5-14 keV was incident on the sample (Tamura 2002). A fragment of the as-received chip containing a large clump of pigment was scanned with $4 \mu\text{m}$ step increment by moving the sample carrier with respect to the x-ray beam. A white-beam Laue pattern was collected at each point of the grid and was subsequently analyzed using the program XMAS (Tamura 2003).

An FEI Strata 235DB dual-beam FIB/SEM was used in the EDX study. The collection time for a high resolution map was about 6 hours. Electron energy of 15keV was selected to avoid the damage to the sample over such a long exposure to the energetic electron beam. The probing depth of Pb L line (13.04 keV) is about $0.4 \mu\text{m}$ at this electron energy.

To complement the EDX study, we performed μ XRF experiment (Janessens 1999) at beam line 6-2 of the Stanford Synchrotron Radiation Laboratory. The sample was placed on a high-precision XYZ- Φ stage at an angle of 45° to the incident beam. A Si (Li) fluorescence detector was placed at 90° to the incident beam. The SSRL beamline 6-2 scanning fluorescence microprobe uses a Kirkpatrick-Baez mirror pair to focus a monochromatic x-ray beam up to less than $1 \mu\text{m}$ in both horizontal and vertical dimensions. We took fluorescence spectra at 14KeV with $1.5 \mu\text{m}$ spot size in this experiment and the individual pigment clump was scanned with a $2 \mu\text{m}$ step size. Compared with EDX, synchrotron radiation based μ XRF offers a much lower detection limits; and radiation damage induced in the specimen is considerably less (Gordon and Jones 1993), which is very important for biological applications and precious archaeological samples. The penetration depth of 14keV x-ray in $\text{BaCuSi}_2\text{O}_6$ is about

60 μ m. Thus, μ XRF provides a more bulk sensitive information of the pigment clumps than EDX.

Results:

Figure 2 shows the powder XRD pattern of the purple pigments, alongside a diffraction spectrum of $\text{BaCuSi}_2\text{O}_6$ obtained from the International Centre for Diffraction Data (ICDD, No. 00-043-0300). The majority of the diffraction peaks found in the purple pigments belong to $\text{BaCuSi}_2\text{O}_6$. Some peak intensities of the sample do not follow the intensities of $\text{BaCuSi}_2\text{O}_6$ standard exactly. It is known that the silicate minerals are very prone to preferred orientation. For such a textured material, the intensities of the individual lines dominated by the degree and the type of texture. No other phases of barium copper silicate, except a possible trace amount of $\text{BaCuSi}_4\text{O}_{10}$ (see the supplementary data), were found in the purple pigment samples. The powder XRD pattern shows that these samples also contain quartz and cinnabar as impurities. Cinnabar, HgS , is used as a red pigment on the terracotta warriors. We believe that most of the quartz in the powdered sample is from the soil or from terracotta substrates. These findings are consistent with the Berke's study on the similar sample using Raman spectroscopy (Berke and Wiedemann 2000, Berke 2002). However, no Chinese Blue phase is found in their samples. Furthermore, no crystalline phases of the lead or barium compounds, such as PbSO_4 and BaSO_4 , can be identified conclusively with XRD in samples studied here. This may be due to the fact that these lead compounds are in the amorphous form or that the stoichiometry of the reactants was carefully controlled so that only trace amounts of these materials remained after the initial synthesis.

We did find a pool of the lead compounds at the centre of the pigment clump using EDX microanalysis and μ XRF and found them to be the most significant minority phases associated with the pigment. Trace amounts of iron, nickel and calcium were

also detected. We show the SEM image and the EDX and μ XRF lead maps of one of the pigment clumps in Fig. 3a-c, respectively. The lead compounds are concentrated in the centre and along the right edge of the pigment clump (bright area in fig.3-b and the light green and yellow areas in fig. 3-c). A phase and crystal orientation map (fig.3-d) was created from white beam (6keV-12keV) μ XRD patterns on the same clump using 4 μ m steps. The majority of the resulting Laue patterns were found to be from the $\text{BaCuSi}_2\text{O}_6$ (Chinese Purple) phase. The sharp diffraction spots observed in this measurement are an indication of good crystallinity of the crystalline grains within the pigment. The detailed crystal orientation map of the Chinese Purple crystallites (fig.3-d) derived from the μ XRD map shows that the big pigment grains in the clump all have very similar crystallographic orientations (within 5 degrees of each other). Comparing this result to the chemical maps from the μ XRF and EDX, we found that all of the grains appear to originate from the centre of the clump which corresponds to the very high Pb concentration region. The grains, especially the orange grain, are also surrounded by lead compounds.

These chemical maps and maps of the crystallographic orientation suggest that Chinese Purple was synthesized using lead flux melting, a process very similar to that for glass making. Diffusion of heavy elements such as Ba, and even Cu, is very sluggish even at 1000 C and limits the grain sizes in a solid state synthesis to a few microns, as is frequently seen for solid state synthesis of high Tc superconductors which have similar heavy ion composition. However, if the pigment crystallites grew from a melt, as Pb elemental map and the grain growth morphology suggest, then the grain growth kinetics are not governed by diffusivity of individual ions, but by the flow due to thermal convection, which is significantly higher than solid state diffusion. Therefore, the presence of large pigment crystallites (20 μ m-50 μ m), in conjunction with the growth morphology suggest that pigment crystals grew in presence of liquid and probably even precipitated from a melt. On the other hand, Egyptian Blue was

synthesized either through a routine solid-state calcination process or often from a more efficient process using sodium and potassium based fluxes (Chase 1971, Bayer and Wiedemann 1976, Riederer 1997). However, no finding of significant sodium and potassium based flux additives was ever reported in the Chinese Purple or Chinese Blue pigments and no lead based fluxes or compounds found in Egyptian Blue.

Discussion:

Our results show that the process and the technology for making Chinese Purple are quite different than that used for Egyptian Blue. Use of lead fluxes plays a crucial role in lowering the synthesis temperature and stabilizing Chinese Purple over Chinese Blue and forms the foundation of this pigment synthesis technology. Furthermore, the combination of lead and barium compounds in the synthesis of the pigment suggests a plausible identity of the inventors of this technology as will be discussed below.

Most of the raw materials used to synthesize Chinese Purple, such as quartz, barium and lead compounds, were also used in early Chinese glass making (Beck and Seligman 1934, Seligman et. al. 1936). In 1986, Brill found that many Chinese glasses made during an early period (500BC - 700AD) have a high content of PbO and BaO (Brill et. al. 1991). Such glasses were unquestionably made in China because glasses with compositions of this sort were completely unknown elsewhere until the 19th century. In addition, there is a striking similarity between the rise and fall of barium-containing Chinese glasses and that of the Chinese purple and blue pigments. Most of the Chinese Purple and Chinese Blue samples discovered so far were made during the Han dynasty and before (500BC - 220AD). Interestingly, the composition of Chinese glasses varied over time; most barium-containing Chinese glasses found were made before and during the Han dynasty as well (Seligman et. al. 1936, Brill et. al. 1991, Gan 1991). Reasons behind the disappearance of both the early barium-containing glasses

and the Chinese Blue/Purple pigments are still debated; however, the similarities between the two materials substantiate a strong connection between the two manufacturing techniques. Understanding the origin of this early Chinese glass is a crucial step in solving the puzzle surrounding the origin of the Chinese Purple.

Historical records suggest that Taoist alchemists are responsible for the making of these barium-lead-containing glasses. It is known that jade holds a special status in Taoism. Taoist believed that jade, which they considered to be a magical material, not only held the power to preserve a human body and spirit (Needham and Lu 1974) but also was an elixir for achieving physical immortality (Ko 320). In the pursuit to understand and obtain such a precious material, the Taoist monks started to synthesize it themselves. Several records in ancient Chinese texts mentioned Taoist monks making jade (glass) by fusing stones. As recorded in “Lun Heng” (Wang 27-97), “*the Taoist monks used to make five-colored jade with five stones....*” More importantly, it also mentioned that glass could achieve a certain appearance when different raw materials were added during the process, “*Suihou (the duke of Sui) made beads out of several ‘medicines’ which were more shiny and appealing.*” As we know today, the barium glass has a larger refractive index than that of a normal glass. This would give barium glass a certain turbidity and a jade-like appearance. Glass (Jade) makers would have found this by trial and error. Barium minerals, such as Barite (BaSO_4) or Witherite (BaCO_3), are reasonably common in central China. This mineral is unusually heavy and forms “appealing” crystals, so the Chinese, as careful observers and curious chemists, would no doubt have found and experimented with it. In this process of imitating jade, they discovered the recipe of the barium containing glass. Then, the copper minerals, Malachite ($\text{Cu}_2(\text{CO}_3)(\text{OH})_2$) or Azurite ($\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$), could be added later to obtain different jade colours. We believe that this experimentation led to the eventual discovery of Chinese Purple.

As for the lead compounds, the Chinese alchemists learned how to produce the red Pb_3O_4 and white $2\text{PbCO}_3\cdot\text{Pb}(\text{OH})_2$ lead oxides at a very early stage. The earliest record of the recipe was in “Ji Ni Zi”, a book attributed to Fan Li of the -5th century (Needham 1976). Both red Pb_3O_4 and white $2\text{PbCO}_3\cdot\text{Pb}(\text{OH})_2$ lead oxides were used in the red pigment and white pigment respectively on the terracotta warriors (Li 1983). Most importantly, the lead compounds were also used routinely in Chinese Bronze making. Metallurgists from the Shang dynasty (ca 1600 BC – 1027 BC) discovered that a small percentage of lead reduced the melting temperature of copper, lowered its viscosity at the casting temperature and thus made casting easier (Bernard and Tamotsu 1975). This invention, along with the advanced molding techniques, enabled Chinese metallurgists to cast very large sized Bronze items with fine details. The use of Pb to lower the melting and casting temperatures was very well known during the Qin dynasty. Therefore, Taoist alchemists would have added lead compounds intentionally in Chinese glass and Chinese Purple to reduce the melting temperature (as a flux).

Furthermore, the availability of high temperature pottery kilns before the Han dynasty made such an operation possible. The pottery kilns at that time were fired to temperatures between 950 °C and 1050 °C (Yang et.al. 1985). A previous study (Qu et. al. 1999) found that the Qin terracotta warriors were dried and then fired to temperatures in the range of 800–1000 °C, which is the exact temperature needed to form the Chinese Purple phase. As the temperature at which the kiln could be operated for a prolonged duration increased in the later time, more of the high temperature phase, i.e. Chinese Blue, was found in the pigments made in the late Han dynasty (Berke and Wiedemann 2000). This leads us to believe that it was unlikely that the ancient Chinese craftsman knowingly controlled the temperature during the manufacturing process to obtain a certain color. The color was determined by the temperature of the kilns during the different periods.

The evolution of early Chinese glass as well as that of the Chinese Purple and Chinese Blue pigments was affected by the philosophical changes in ancient Chinese society. The influence of Taoism started to diminish during the Han dynasty. Confucianism started to become the dominant philosophy after that time. Instead of following the Tao of nature as in Taoism, Confucianism asserted that the only laws that matter were the laws of human society. The Confucians loved reason and logic, but they had practically no interest in nature. We believe that this is why few (if any) Chinese Purple or Chinese Blue pigments were used in the later dynasties. Without the support of the government and rich individuals, such a complicated “high-tech” operation was not feasible. Similarly, as the influence of Taoism diminished, so did the motivation to pursue jade, and hence the disappearance of barium content in the Chinese glasses. The disappearance of Chinese Purple and Chinese Blue and barium-lead glasses after the Han dynasty and the almost simultaneous decline of Taoism not only further enforces the link between these technologies and Taoist alchemists but also is an intriguing example of the influence of government patronage on the state of advanced technology.

Conclusion:

In summary, we argue that Chinese Purple was invented by Taoist alchemists as a by-product of the technology originally developed for synthesizing barium-containing Chinese glasses, which, in turn, were originally developed for the purpose of imitating jade. The barium compounds were added to increase the refractive index of the glass, thus giving the glass a similar appearance as jade. The development of this process also benefited from two well-developed technologies in ancient china: the earlier Bronze making (adding lead compounds to reduce the melting temperature) and pottery making (advanced pottery kilns) technologies.

As shown in this study, the evolution of the Chinese Purple was influenced by its Taoist background. The disappearance of the Chinese Purple and Chinese Blue pigment was a perfect example of how cultural changes in the society affected the development of science and technology in ancient China. Finally, it is remarkable that three ancient civilizations, Egypt, China and Maya (Jose-Yacaman et. al. 1996), invented their own blue pigments independently.

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Captions:

Figure 1: (a) Warrior # T18G21-08, a kneeling archer. The pigment samples in this study have been taken from this terracotta warrior. (b) Close-up picture of the purple paint on the terracotta warrior. (c) Images of the purple paint samples used in this study.

Figure 2: X-ray powder diffraction spectrum of the purple pigment (red solid line) overlaid with data from ICDD of the $\text{BaCuSi}_2\text{O}_6$ crystal (black solid peaks). We label the principal peaks of Chinese purple (CP), Chinese blue (CB), Cinnabar (CI) and quartz (Q) in this region.

Fig. 3: (a) SEM image of the pigment clump taken at 20KeV. (b) Lead ($\text{Pb L}\alpha$) concentration EDX map of the same clump is taken at 15keV. (c) We show an overlapping μXRF ($1.5\mu\text{m}$ spot size) concentration map of Pb (light green, yellow, and orange regions) and Cu (dark green and purple regions) taken at 14KeV. μXRF provides more bulk sensitive information than the EDX microanalysis. (d) The detailed crystallographic map derived from the μXRD ($1.2\mu\text{m}$ spot size) scan. It shows that there are two pigment grains (in orange and red) in the clump which have slightly different crystallographic orientations. The Pb compounds are found either in between the two grains or on the boundary of the grains.

Figure 1:



Figure 2:

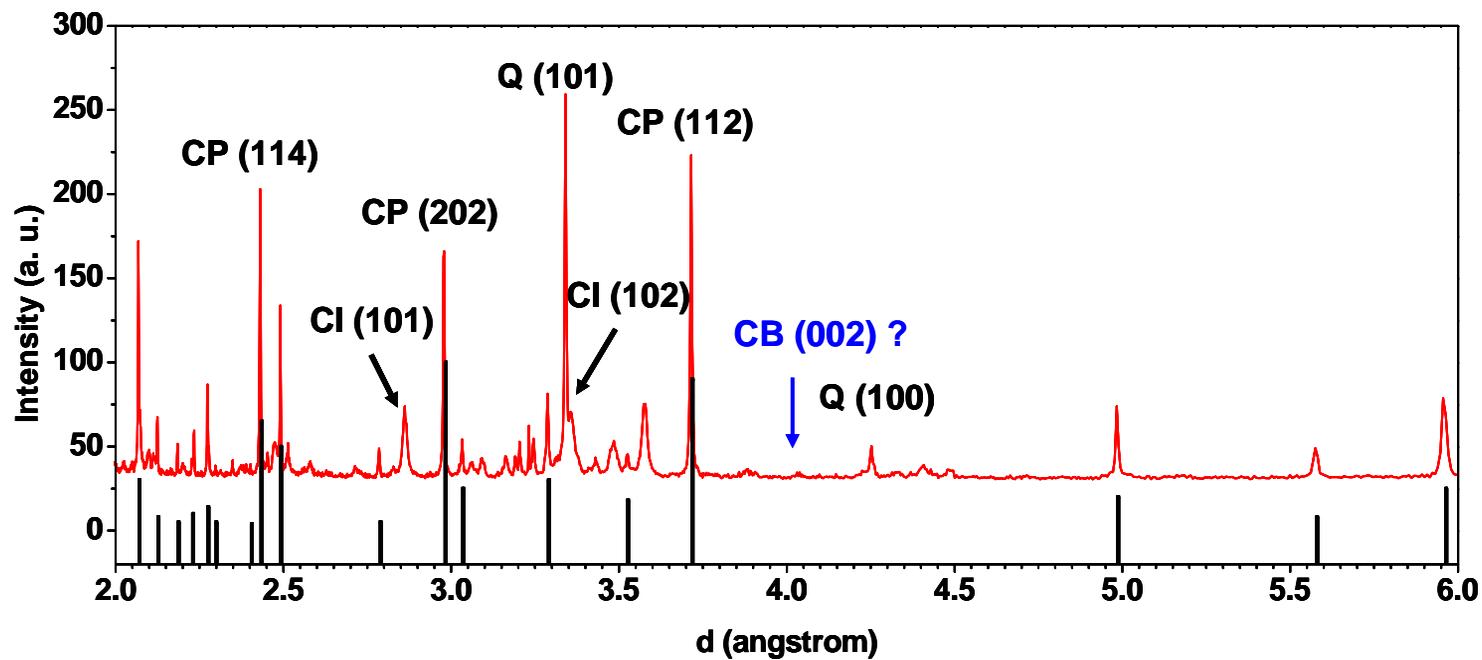
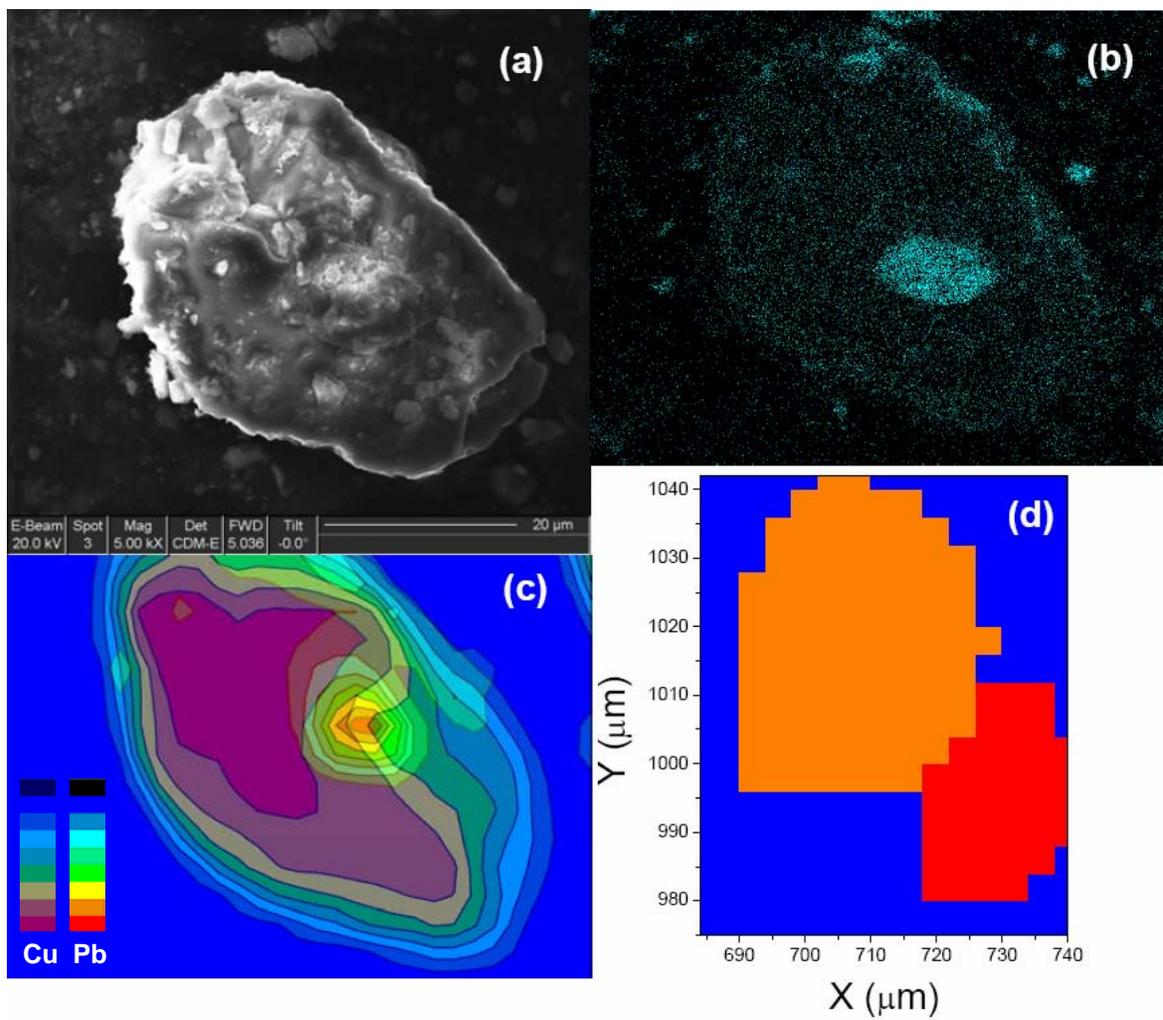


Figure 3:



1. Possible peaks of $\text{BaCuSi}_4\text{O}_{10}$

In a XRD spectrum taken from one of the three purple pigment samples, we find evidence of the possible existence of a small amount of Chinese Blue ($\text{BaCuSi}_4\text{O}_{10}$) in the purple pigments. See Figure SUP-1.

2. The change in burial custom after Han dynasty:

This philosophical change was also affected other social customs around the same time, such as the burial custom. Many jade items, including the synthesized jade/glass, were found in the tombs of the Han dynasty or before. Some of them were for decoration; some of them were definitely for the purpose of preserving the body and the spirit of the owners, as believed by Taoism, such as the jade mouth and nose plugs. The most spectacular example was the discovery of “*Jin Lu Yu Yi*” (1). The exalted and privileged dead were attired in suits of jade plaques sewn together with gold, silver or silk threads. But none was found in the tombs after the Han dynasty (2).

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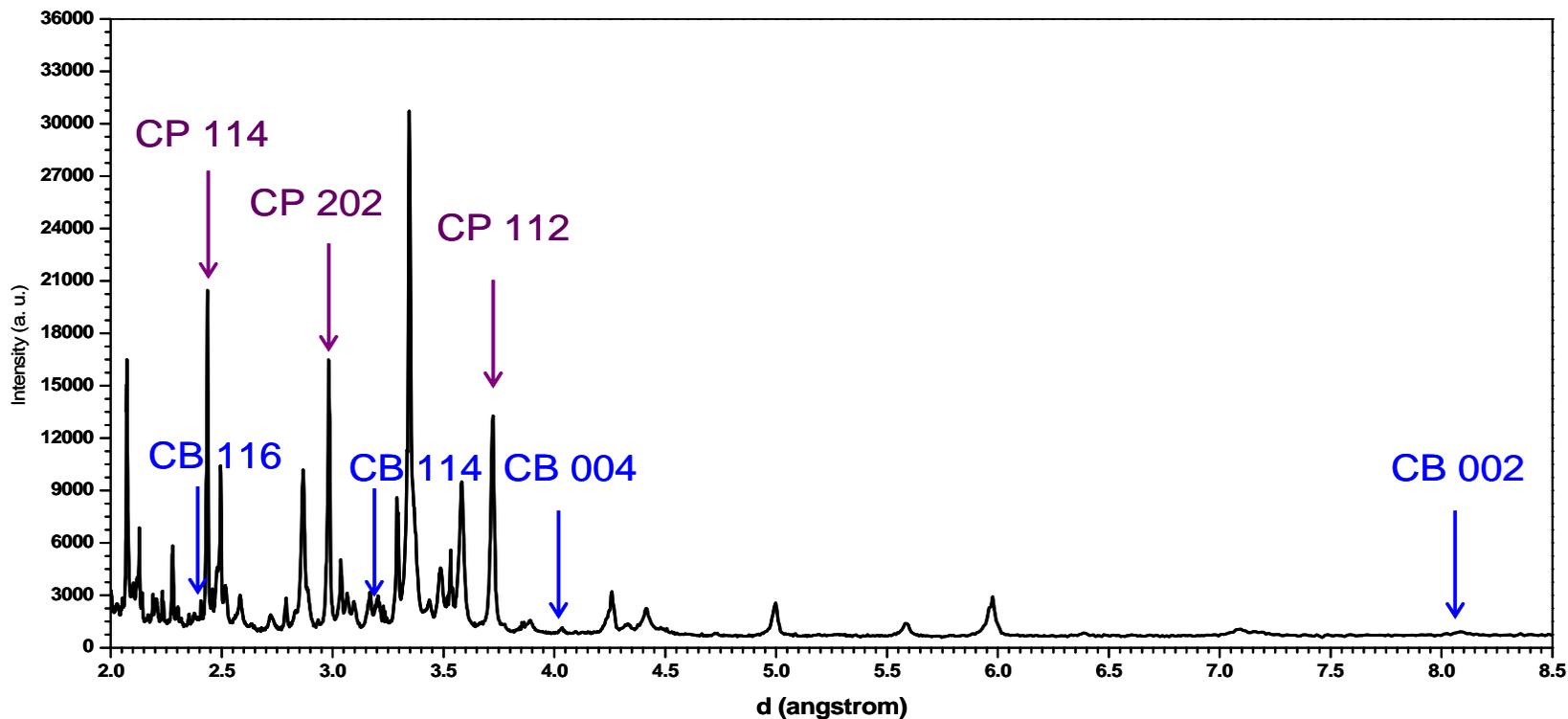


Figure SUP-1: X-ray powder diffraction spectrum of the purple pigment (black solid line). We label the positions of the principal peaks belong to the $\text{BaCuSi}_2\text{O}_6$ crystal (CP) and $\text{BaCuSi}_4\text{O}_{10}$ (CB) (ICDD data). There are two small peaks in the region of $\text{BaCuSi}_4\text{O}_{10}$ 002 (intensity 100) and 004 (intensity 39). However, there are other peaks in the 114 peak and 116 peak regions. It is difficult to identify them conclusively. If there is $\text{BaCuSi}_4\text{O}_{10}$ in our sample, it will be in a very small quantity.