

Lawrence Berkeley National Laboratory

LBL Publications

Title

Influence of Taoism on the invention of the purple pigment used on the Qin terracotta warriors

Permalink

<https://escholarship.org/uc/item/3cb9w90d>

Journal

Journal of Archaeological Science, 34(11)

ISSN

0305-4403

Authors

Liu, Z.
Mehta, A.
Tamura, N.
[et al.](#)

Publication Date

2007-11-30

Influence of Taoism on the invention of the purple pigment used on the Qin terracotta warriors

Z. Liu ^{a,c,*}, A. Mehta ^a, N. Tamura ^b, D. Pickard ^c, B. Rong ^d, T. Zhou ^d, P. Pianetta ^{a,c}

^a Stanford Synchrotron Radiation Lab, Stanford University, Stanford, CA 94305, USA

^b Ernest Orlando Lawrence Berkeley National Laboratory, 1 Cyclotron Road, Berkeley, CA 94720, USA

^c Department of Electrical Engineering, Stanford University, Stanford, CA 94305, USA

^d The Museum of Terracotta Warriors and Horses of Emperor Qin Shihunag, Lintong 710600, Xi'an, China

Abstract

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.

1. 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 to 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, 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 et al., 2006).

* Corresponding author. Stanford Synchrotron Radiation Lab, Stanford University, Stanford, CA 94305, USA.

E-mail address: zhiliu@stanford.edu (Z. Liu).

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 (BaSO_4 or BaCO_3), 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 (BaSO_4) into barium oxide (BaO). At 900e1100C: $\text{BaO} \text{ p } \text{CuO} \text{ p } 2\text{SiO}_2 \text{ } \frac{1}{4} \text{BaCuSi}_2\text{O}_6$; since BaSO_4 decomposes at a much higher temperature (1560 C), PbO catalyze a dismutase reaction leading to the in situ decomposition of BaSO_4 ($\text{PbO} \text{ p } \text{BaSiO}_4 \text{ } 4 \text{BaO} \text{ p } \text{PbSO}_4$). Berke discussed the striking similarities of the Chinese Purple and Chinese Blue ($\text{BaCuSi}_4\text{O}_{10}$) with the Egyptian Blue pigment ($\text{CaCuSi}_4\text{O}_{10}$) (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 (479e221 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 w800 ¹Ce900 ¹C (Berke, 2002; Riederer, 1997), whereas Chinese Purple starts to form between 900e1100 ¹C and Chinese Blue at temperatures in excess of 1100 ¹C (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.

2. 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 (mXRD), micro X-ray fluorescence (mXRF) 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 8e12 orders of magnitude more brilliant than the high performance rotating anode X-ray tubes



Fig. 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.

(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/mm²) 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 mXRD 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 Å 1.2 mm spot with an X-ray spectrum of 5e14 keV was incident on the sample (Tamura et al., 2002). A fragment of the as-received chip containing a large clump of pigment was scanned with 4 mm 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 et al., 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 h. Electron energy of 15 keV 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 mm at this electron energy.

To complement the EDX study, we performed mXRF experiment (Janssens et al., 1999) at beam line 6-2 of the Stanford Synchrotron Radiation Laboratory. The sample was placed on a high-precision XYZ-F 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 mm in both horizontal and vertical dimensions. We took fluorescence spectra at 14 KeV with 1.5 mm spot size in this experiment and the individual pigment clump was scanned with a 2 mm step size. Compared with EDX, synchrotron radiation based mXRF 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 14 keV X-ray in BaCuSi₂O₆ is about 60 mm. Thus, mXRF provides a more bulk sensitive information of the pigment clumps than EDX.

3. Results

Fig. 2 shows the powder XRD pattern of the purple pigments, alongside a diffraction spectrum of BaCuSi₂O₆ 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 BaCuSi₂O₆. Some peak intensities of the sample do not follow the intensities of BaCuSi₂O₆ 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 BaCuSi₄O₁₀ (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 PbSO₄ and BaSO₄, 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 mXRF and found them to be the most significant minority phases associated with the pigment. Trace amounts of iron, nickel and

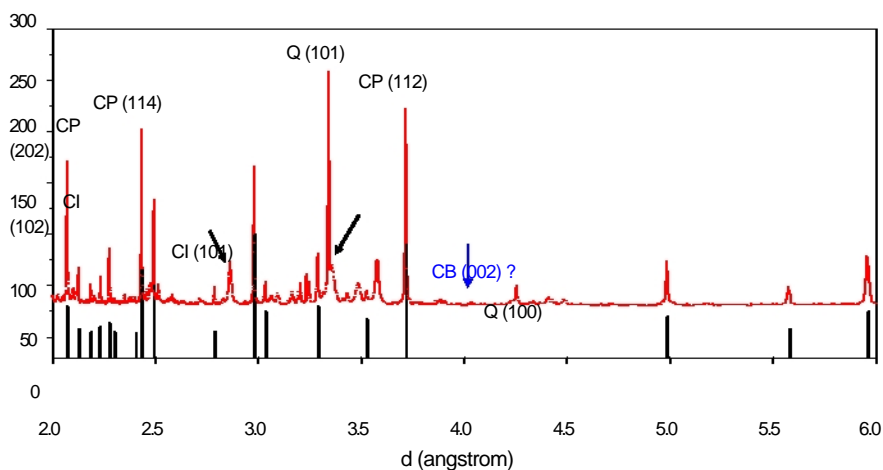


Fig. 2. X-ray powder diffraction spectrum of the purple pigment (red solid line) overlaid with data from ICDD of the BaCuSi₂O₆ crystal (black solid peaks). We label the principal peaks of Chinese Purple (CP), Chinese Blue (CB), Cinnabar (Cl) and quartz (Q) in this region.

calcium were also detected. We show the SEM image and the EDX and mXRF 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. 3b and the light green and yellow areas in Fig. 3c). A phase and crystal orientation map (Fig. 3d) was created from white beam (6 keV-12 keV) mXRD patterns on the same clump using 4 mm 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. 3d) derived from the mXRD 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 mXRF 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 T_c 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 mm-50 mm), 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.

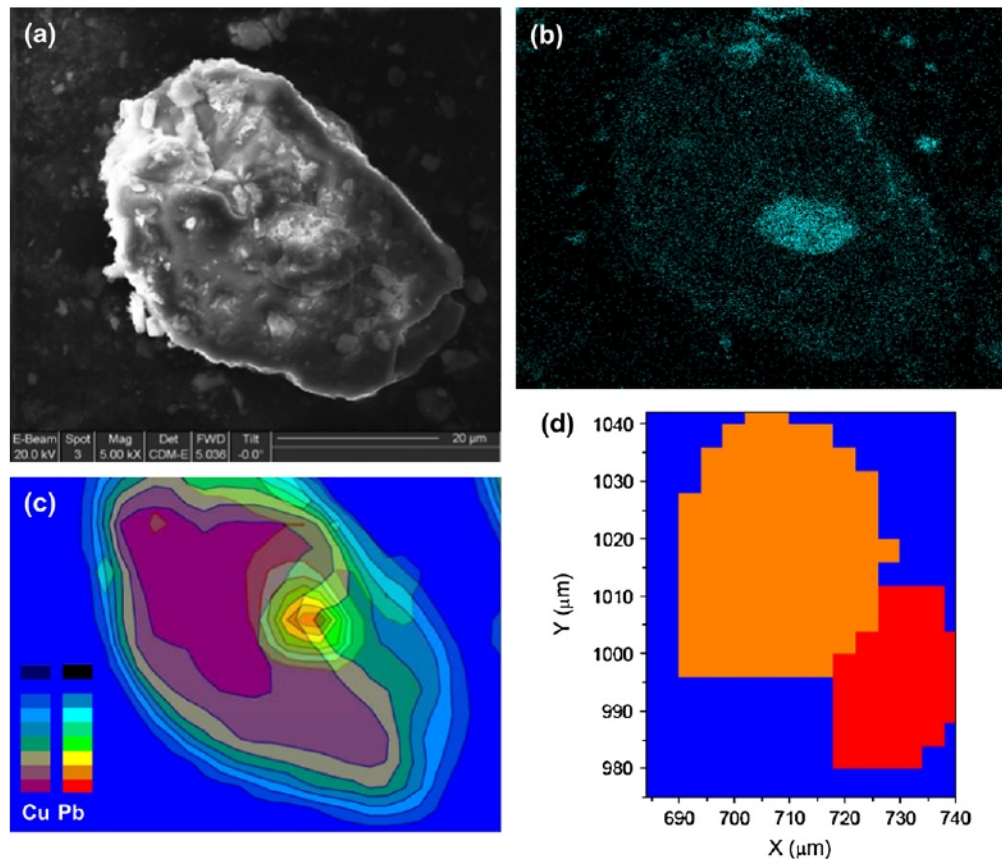


Fig. 3. (a) SEM image of the pigment clump taken at 20 KeV. (b) Lead (Pb La) concentration EDX map of the same clump is taken at 15 keV. (c) We show an overlapping mXRF (1.5 mm spot size) concentration map of Pb (light green, yellow, and orange regions) and Cu (dark green and purple regions) taken at 14 KeV. mXRF provides more bulk sensitive information than the EDX microanalysis. (d) The detailed crystallographic map derived from the mXRD (1.2 mm 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.

4. 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 (500 BCE-700 AD) 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 (500 BCE-220 AD). 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, 1966). 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, 1907), "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 et al., 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 BCE-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.

5. 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.

Acknowledgement

The research was partially funded by the France-Stanford Centre for Interdisciplinary Studies. Portions of this research were carried out at the Stanford Synchrotron Radiation Laboratory, a national user facility operated by Stanford University on behalf of the U.S. Department of Energy, Office of Basic Energy Sciences; and the Advance Light Source which is supported by the Director, Office of Science, Office of Basic Energy Sciences, of the U.S. Dept of Energy.

Appendix A. Supplementary material

Supplementary material associated with this article can be found, in the online version, at [10.1016/j.jas.2007.01.005](https://doi.org/10.1016/j.jas.2007.01.005).

Reference

Bayer, G., Wiedemann, H.G., 1976. Agyptisch Blau, ein synthetisches Farbpigment des Altertums, wissenschaftlich betrachtet. *Sandoz Bulletin* 40, 20e39.

Beck, H.C., Seligman, C.G., 1934. Barium in Ancient Glass. *Nature* 133, 982.

Berke, H., 2002. Chemistry in ancient times: the development of blue and purple pigments. *Angewandte Chemie International Editions* 41 (14), 2483.

Berke, H., Wiedemann, H.G., 2000. The chemistry and fabrication of anthropogenic pigments Chinese Blue and Purple in ancient China. *East Asia Science Technology and Medicine* 17, 94e120.

Bernard, N., Tamotsu, S., 1975. *Metallurgical Remains of Ancient China*. Nichiosha, Tokyo.

Brill, R.H., Tong, S.C., Dohrenwend, D., 1991. In: Brill, R.H., Matrin, J.H. (Eds.), *Scientific Research in Early Chinese Glass*. The Corning Museum of Glass, Corning, pp. 31e64.

Chase, W.T., 1971. *Science and Archeology*. In: Brill, R.H. (Ed.). MIT Press, Cambridge, MA, p. 80.

Eisenberger, P., 1986. 6-GeV storage ring: an advanced photon research facility. *Science* 231, 687.

FitzHugh, E.W., Zycherman, L.A., 1983. An early man-made blue pigment from China e barium copper silicate. *Studies in Conservation* 28, 15e23.

FitzHugh, E.W., Zycherman, L.A., 1992. A purple barium copper silicate pigment from early China. *Studies in Conservation* 37, 145e154.

Gan, F.X., 1991. In: Brill, R.H., Matrin, J.H. (Eds.), *Scientific Research in Early Chinese Glass*. The Corning Museum of Glass, Corning, pp. 1e3.

Gordon, B., Jones, K.W., 1993. X-ray emission imaging, Chapter 9. In: Morris, M.D. (Ed.), *Microscopic and Spectroscopic Imaging of the Chemical State*. M.Dekker, New York.

Jaime, M., et al., 2004. Magnetic-field-induced condensation of triplons in Han Purple pigment BaCuSi2O6. *Physical Review Letters* 93, 087203.

Janssens, K., Adams, F., Rindby, A., 1999. In: Janssens, K., Adams, F., Rindby, A. (Eds.), *Microscopic X-ray Fluorescence Analysis*. John Wiley & Sons, Chichester, pp. 1e10.

Jose-Yacaman, M., Rendon, L., Arenas, J., Serra Puche, M.C., 1996. Maya Blue paint: an ancient nanostructured material. *Science* 273, 223e225.

Kerr, R., Wood, N., 2004. *Science and Civilization in China* 5 (12), 609e614.

Ko, H., 1966. Pao Phu Tzu (Nei Phien) (Book of the preservation of solidarity Master; Inner chapter. In Chinese). In: Ware, J.R. (Ed.), *Alchemy, Medicine and Religion in the China of AD 320 (the 'Nei Phien' of Ko Hung 'Pao Pu Tzu')*. MIT Press, Cambridge, Mass. and London. 62.

Li, Y.D., 1983. The pigment used on the painted pottery figurines of the Qin dynasty and historic criticism on it. *KAOGU YU WENWU (Archaeology and Cultural Relics)* 3, 62e65.

Needham, J., Lu, G.D., 1974. *Science and Civilization in China* 5 (2), 282e 285.

Needham, J., Ho, P.Y., Lu, G.D., 1976. *Science and Civilization in China* 5 (3), 14e15. "Ji Ni Zi" is also known as "Chi Ni Tzu" or "Fan Tzu Chi Jan", a book attributed to Fan Li of the -5th century.

Qu, H.J., Zhang Z.H., Wu, X.J., 1999. Research on the Techniques of Making Pottery Figurines of the Qin Army. *Materials Issues in Art and Archaeology II MRS Symposium Proceedings* 185, MRS, Pittsburgh PA, pp. 459e 477.

Riederer, J., 1997. In: FitzHugh, E.W. (Ed.), *Artists Pigments. A Handbook of their History and Characteristics*, 3. Oxford University Press, Oxford, p. 23.

Sebastian, S.E., et al., 2006. Dimensional reduction at a quantum critical point. *Nature* 441, 616e620.

Seligman, C.G., Ritchie, P.D., Beck, H.C., 1936. Early Chinese glass from pre-Han to Tang times. *Nature* 138, 721.

Tamura, N., Spolenak, R., et al., 2002. Submicron X-ray diffraction and its applications to problems in materials and environmental science. *Review of Scientific Instruments* 73, 1369.

Tamura, N., MacDowell, A.A., et al., 2003. Scanning X-ray microdiffraction with submicron white beam for strain/stress and orientation mapping in thin films. *Journal of Synchrotron Radiation* 10, 137.

Wang, C., 1907. *Lun Heng (An ancient Chinese Text attribute to Wang Chong of Han dynasty); An English translation*. In: Forke, A. (Ed.), *Lun-Heng. Two Volumes. Part One: Philosophical Essays of Wang Ch'ung; Part Two: Miscellaneous Essays of Wang Ch'ung*. Luzac, London.

Yang, G., Zhang, X.Q., Shao, W.G., 1985. *The Ceramics of China. The Yangsho Culture e The Song Dynasty*. Science Press, Peking & Methues, London.