Purple Reign

How ancient Chinese chemists added color to the Emperor's army

by Samir S. Patel

Purple is special. Throughout antiquity, the color was a mark of wealth, aristocracy, and royalty, in large part because it was so rare. Prior to the nineteenth century, when modern production methods made synthetic pigments common, there were only hugely expensive purple dyes, a couple of uncommon purplish minerals, and mixtures of red and blue, but no true purple pigment—except during a few hundred years in ancient China. The Chinese of the Qin and Han dynasties (221 B.C.–A.D. 220) used a mysterious lavender shade to decorate pottery and some of the famous terracotta warriors in the tomb of Emperor Qin Shihuangdi in Xi'an. This pigment, known as Han or Chinese purple, was a technological wonder, a complex synthetic compound made before the invention of paper or any codified understanding of elemental chemistry. How the ancient Chinese created this color, and the chemically related Han or Chinese blue, has puzzled scientists since the pigment was rediscovered in the 1990s. Did the Chinese stumble across the intricate formula, or did they have a little help from the other side of the world? And why did the pigment disappear entirely at the end of the Han Dynasty?

Chinese purple dates back as far as 800 B.C., and was first used to decorate objects around 220 B.C., when the terracotta army was created. Elisabeth FitzHugh identified the compound, a barium copper silicate, in 1992 while she was a conservator at the Smithsonian's Freer and Sackler Galleries. There were only two other man-made blue or purple pigments in the ancient world—Maya blue, a cooked mix of indigo and white clay, and Egyptian blue, which was used throughout the Mediterranean and the Near and Middle East from 3600 B.C. to the end of the Roman Empire. The similarity in chemical composition between Chinese purple and blue and Egyptian blue is striking—they are essentially the same, except the Egyptian formula used calcium instead of barium.

Heinz Berke, a chemist at the University of Zurich, analyzed some of the pigment from one of the terracotta warriors. Its unusual similarity to Egyptian blue led him to theorize in 2000 that there might have been some kind of technological exchange across Asia

The purple on this terracotta warrior from the tomb of Emperor Qin Shihuangdi in Xi'an is one of only three known synthetic blue or purple pigments in the ancient world.

Researchers subjected these flecks of Chinese purple to a series of high-tech tests for clues about how the ancient Chinese created such a complex compound.

hundreds of years before the Silk Road. But while Egypt and China had some contact, no Egyptian blue has been found farther east than Persia, and it would have taken extensive interaction between cultures to pass on the complicated synthesis process, which involves grinding up several raw materials in precise proportions and heating them to between 900 and 1,100 degrees Celsius. There is also no clear reason why the Chinese, if they had learned the Egyptian formula, would have replaced calcium with barium, which necessitates increasing the firing temperature by 100 degrees or more. "The two cultures were certainly in contact, but certainly not to exchange recipes for making blue stuff," writes Berke, who has moved away from his initial speculation, in an email from China, where he is a visiting scholar at Fudan University in Shanghai and the Academy of Sciences in Beijing. "These were well-kept secrets." But the similarity is curious, and questions remain about the invention of Chinese purple and blue, and the mystery of their disappearance.

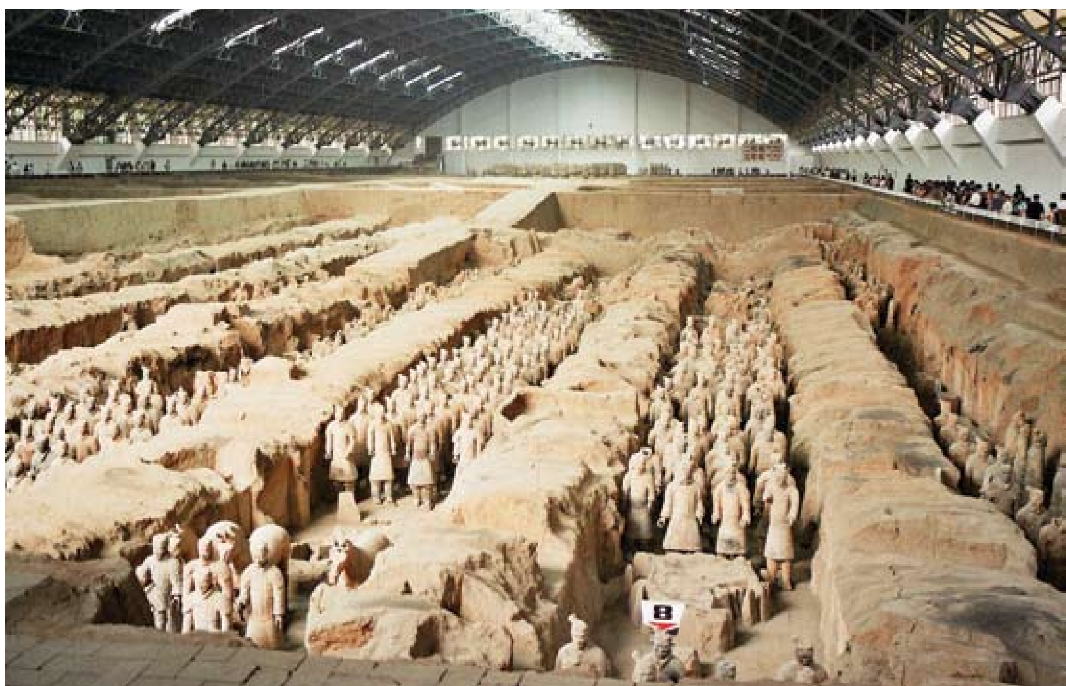
A significant clue might come from Chinese glass, according to Bob Brill, a scientist at the Corning Museum of Glass. Chinese glass from the period, unlike that from other periods or anywhere else in the world, also contains barium—as well as the copper and silica seen in Chinese purple.

"Both [Brill] and I are pretty sure that somehow the creation of these pigments, perhaps accidentally, happened while they were making glass, but we have no way of proving that at this point," says FitzHugh. "We can't really explain what the Chinese were doing."

Zhi Liu is not a chemist, conservator, or expert in ancient glass or pigments—he develops electron beam sources for the Stanford Linear Accelerator Center. But in 2003 he visited the Museum of the Terracotta Warriors in Xi'an. There, around 1,000 of the 8,000 terracotta warriors in the tomb have been excavated, and one of them restored by conservators is wearing pants that were painted purple. All of the statues once had color—green, black, white, red, and, yes, purple—but the paint quickly peels off when they are exposed to air, which is why thousands remain unexcavated.

"Initially, I thought, there was no natural purple pigment—this has *got* to be synthesized," Liu says. "How did they do that?"

Liu spoke with researchers at the museum about how he could help. After obtaining a sample from the same group of paint flecks that Berke had previously analyzed, Liu submitted the pigment to a battery of high-tech, high-sensitivity studies, including energy dispersive X-ray microanalysis



The 8,000 terracotta soldiers were all painted, but the pigment peels off when exposed to air. Some 7,000 warriors remain unexcavated until scientists devise a solution.

Crystal Method

The ancient alchemists who invented Chinese purple continue to have an impact—today on the study of physics. Suchitra Sebastian of Stanford University is a specialist in condensed matter physics, the study of how atoms and molecules interact with each other. She took microscopic crystals of Chinese purple, known to physicists as barium copper silicate, and subjected them to extremely powerful magnetic fields and temperatures close to absolute zero. Sebastian's team discovered two strange effects that could someday lead to superconductive electrical wires and super-efficient computers. First, as she lowered the temperature

Researchers may use high-tech equipment, but Chinese purple is still made almost exactly as it was during the Han Dynasty.

below two degrees Kelvin and raised the intensity of the magnetic field to 900 times the strength of the earth's, the molecules of Chinese purple crystals linked together magnetically and began behaving as a single wave of magnetic energy. As she continued to lower the temperature to within a fraction of a degree of absolute zero, the magnetic couplings between the molecules began disappearing until they became, in terms of magnetism, separate two-dimensional planes—something no material had ever done before. While this work is unrelated to archaeology, the researchers still owe a debt to the ancient Chinese. "I actually went to the archaeology journals to get ideas," says Sebastian. "Essentially the way we grow barium copper silicate crystals is very similar to the way the ancient Chinese grew them."

—Zach Zorich

and micro X-ray diffraction and fluorescence, at the Linear Accelerator Center and Lawrence-Berkley National Lab.

"We studied the microstructure of the pigment, which I think is important because you can destroy a sculpture or artifact, but the microstructure will contain information from when you first synthesize it," says Liu, who published his findings in the *Journal of Archaeological Science*.

With the results; the prior work of FitzHugh, Berke, Brill, and others; and his own research into the history of the period, Liu developed a new theory about the rise and fall of Chinese purple. He posits that it was created by ancient alchemists who stumbled across the formula while trying to create imitation jade, and that the color's disappearance is the result of the decline of the philosophy of Taoism, and its reverence for nature, after the Han Dynasty.

Barium, when added to glass, increases its refractive index, making it appear more sparkly and turbid or cloudy—more like white jade, which was highly prized by Taoist adherents, including Emperor Qin Shihuangdi, for its supposed ability to preserve the body. Taoist alchemists would have played a significant role in the creation of jadelike substances. Barium-containing Chinese glass and Chinese purple have very similar elemental compositions, and producers of both used lead as a flux to decrease melting temperature (compared with the sodium and potassium minerals used by the Egyptians). Furthermore, according to Brill, lead isotope analysis shows that the glass and the pigments were made in places close together—perhaps even the same workshops.

"Immediately you can see the similarity between those two techniques," says Liu. "Once we learned the Chinese glass information, we started putting things together."

"I suspect people will be arguing back and forth for a couple of decades," says Brill, "but I think it is unmistakable that the manufacture and the technology of Chinese blue and purple were intimately connected with the glassmaking of the times."

There is certainly circumstantial evidence for Liu's theory linking Chinese glass, the pigment, and Taoism. The end of the Han Dynasty saw Taoism decline in favor of Confucianism, which reveres human logic over the laws of nature. Around the same time, Chinese purple stops appearing on pottery and Chinese glass drops barium.

"You can make connections between philosophical change in the culture with the production of this pigment," says Liu. "Cultural change will be reflected in the material-making process."

Though intriguing, Liu's evidence is not definitive. "I personally think his hypothesis is not valid," Berke writes in an email. In a 2006 article in *Chemical Society Reviews*, Berke posits that the pigments and glasses developed independently, and came from ceramic glaze technology. Chinese purple would have been associated with nobility, he says, not philosophy or religion, so the decline of Chinese purple had nothing to do with Taoism, but was a result of political upheaval and the fact that Chinese alchemists and glass-makers left no written records. Regardless, Liu's research adds another dimension to the long-running discussion, and another layer of mystery to the massive buried army.

"It was a very interesting idea that he was relating it to something completely untechnological on the surface," says Brill. "That's an intriguing notion." ■

Samir S. Patel *is an associate editor at* Archaeology.