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A short but glorious porcelain glaze of Early Ming Dynasty: New finding of raw material and colorants in the copper red glaze

Cui Jia [a], Gen Li [a], Ming Guan [a], Jin Zhao [a], Yi Zheng [b], Guangyao Wang [a], Xiangjun Wei [b,*], Yong Lei [a,*]

[a] The Palace Museum, Beijing, China
[b] Shanghai Synchrotron Radiation Facility, Shanghai Advanced Research Institute, Chinese Academy of Sciences, Shanghai, China

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ABSTRACT

Copper red glaze is considered to be Chinese unique high-temperature copper colored glaze. The sample of Hongwu underglaze red of the Ming Dynasty was analyzed by scanning electron microscopy (SEM), synchrotron radiation micro-X-ray fluorescence spectroscopy (SR-μ-XRF), synchrotron radiation micro-X-ray diffraction (SR-μ-XRD) and transmission electron microscopy (TEM), the results show that there are nano-scale metal copper particles in the diffusion layer of the glaze, and irregular copper sulfide particles at the bottom layer. The presence of metal copper nanoparticles shows the glaze red, but under the influence of black copper sulfide, the appearance of underglaze red is relatively dull and dark. It is assumed that the pigments in Hongwu underglaze red are natural copper ores due to the existence of irregular particles. Referring to the record of "Bright red clay" in ancient literatures, a mixture of cuprite and chalcopyrite are probably the raw materials, the exhaustion of which may be the main reason for the interruption of copper red glaze after the mid-Ming Dynasty.

1. Introduction

Copper red glaze is a famous high-temperature colored glaze type in ancient China. Copper as the main coloring agent was added to the porcelain glaze to show bright red after firing. Although copper was used to provide bright red colors in silicate melts in the Middle East and probably in Mesopotamia at least 3000 years ago [1], the copper-red effects in Chinese porcelain seem to be an independent ceramic development in terms of ceramic technology, including different chemical compositions and firing temperatures, and the most important evidence for this is that the glaze from China is from an earlier period than that from the Middle East [2,3].

The use of copper coloring in ceramic glaze has a long history in China. Although copper-colored porcelains had already been fired in Changsha kilns [4,5] in the Tang Dynasty, and in Jun kilns [2,6] in the Song Dynasty, it is generally believed that genuine copper-red glaze emerged in the late Yuan Dynasty (AD 1271–1368) [7], and reached the peak during the Ming Dynasty (AD 1368–1644).However, it was lost after the late Ming Dynasty until it was re-fired in the early Qing Dynasty (AD 1644–1912).

Copper red glaze, as the official kiln porcelain, was an important type of porcelain of sacrifice, furnishings and decoration in the court since it was made. The reason is that the emperor attached great importance to red. The rulers of Yuan and Ming dynasty graded colors and made red a noble color. The first emperor of the Ming Dynasty Zhu Yuanzhang also highly respected red, and officially proclaimed "Red is the most distinguished color"(以红色为贵) [8]. It was recorded in the book *Kui Tian Wai Cheng* [9] of the Ming Dynasty: "(The porcelain) fired in Yongle, Xuande (of the Ming dynasty), …. Bright red glazes were the most precious ones."In addition, it is very difficult to fire copper red glaze with a uniform color for the technical limitations at that time. Therefore, copper-red glaze was always precious during its development history.

The copper red glaze of the Hongwu period in the early Ming Dynasty was at the beginning stage of copper-red glaze firing, which was an important stage of succession.

In the Hongwu period, the copper red glaze was basically all underglaze red, and the color was dark red and sometimes grey. The glaze surface of a considerable part of the porcelains had the appearance of halo, black, and uneven color, which formed its unique characteristics. This indicates that the underglaze red in the Hongwu period may be in an unstable firing stage, many factors such as raw base glaze, raw copper materials, and firing process may cause changes in the

* Corresponding author.
E-mail addresses: weixiangjun@sinap.ac.cn (X. Wei), leiyong@dpm.org.cn (Y. Lei).

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appearance of copper red.

For the coloration of copper-red glazes in ancient China, the general view is that the copper-red color comes from metal copper particles and/or the monovalent copper crystals. Nigel Wood believed that there were at least five forms of copper in Chinese glaze, namely the CuO(copper oxide)crystals, Cu^{2+} ions, Cu_2O (cuprite) crystals, Cu^{+} ions, metal copper, and it is the Cu_2O crystals and copper colloidal that make the glaze appear red [2]. The analysis of a copper red glaze in the Ming Dynasty showed that there were metal copper particles and Cu_2Oin the glaze [10]. A study on a sacrificial red glaze plate of the Qing Dynasty believed that the copper particles in the red were all metal copper instead of Cu_2O [11]. In addition, the structure and copper content of the glaze layer are also considered to have an influence on the color of the glaze [12,13]. In the study of ancient Egyptian copper-red glass, it was believed that copper and cuprite colored the glass [14,15]. In view of the above controversy, the survey of the coloring mechanism in the copper red glaze of the Ming Dynasty will affect the research of Chinese traditional copper coloring technology.

In addition, the development of copper red glaze in Ming and Qing Dynasties was discontinuous. After the mid-Ming Dynasty, the production of copper-red glaze was almost extinct. Fukang Zhang et al. analyzed the copper-red glaze of the Ming and Qing dynasties and thought that the chemical compositions of the glaze in Ming and Qing dynasties were completely different, and the copper-red glaze of the Ming Dynasty may be lost due to depletion of raw materials or kiln technology [7,16]. Research on the source of the raw materials of copper-red glaze in the Ming Dynasty will help to solve the mystery of the lost copper red glaze in the Ming Dynasty.

In 2014, a large number of porcelain specimens were unearthed from the Nandaku Site in the Forbidden City. Their ages range from the Hongwu period of the Ming Dynasty to the Guangxu period of the Qing Dynasty, and are presumed to be court supplies. It provides samples for us to study the color mechanism and microstructure of copper red glaze. In this paper, the copper coloration mechanism and the raw materials of Hongwu underglaze red in the Ming Dynasty is discussed based on modern scientific analysis, and combined with the study of ancient literature, geology information and reaction kinetic mechanisms.

2. Experimental procedures

The underglaze red porcelain sample (Fig. 1) studied here belongs to the Palace Museum in Beijing. It was excavated from a pit site of ceramic shards unearthed in the south western corner of the Forbidden City in August, 2014 [17].The sample has dense patterns with distinct intervals of red and white. It is considered to be fired during the Hongwu period of the Ming Dynasty(AD 1368-1398) and belongs to the official kiln samples. The color of the sample is dark red with grey, and the edges of the pattern are hazy.

Prior to the SEM, a small piece of the sample was cut off and then to polish. The cutting and mechanical polishing work was carried out consecutively on the Leica EM TXP. To obtain an advanced smooth surface, the mechanically polished plane was then milled by broad Ar-ion beam in Leica EM TIC 3X. This preparation is essential to reveal the shape of the particles in glaze. After Ar-ion milling, the sample was attached to a pin-type stub and sheathed in a silver conductive adhesive. Note that the sample surface was coated with a thin layer of carbon to create a conductive surface. The sample was then observed by field emission scanning electron microscope Zeiss Merlin FE-SEM. Mechanical polishing, Ar-ion milling and SEM observation were carried out at Core Labs, Institute of Geology and Geophysics, Chinese Academy of Sciences.

UV–vis diffuse reflectance measurements were obtained from the surface of the glazes using a double beam UV–vis spectrophotometer (Shimadzu 2700) equipped with ISR 3100 Ulbricht integrating sphere.

Element mapping on the cross section by SR-μ-XRF and SR-μ-XRD were performed at beamline BL15U1 of the Shanghai Synchrotron Radiation Facility (SSRF) [18]. A double-crystal Si (111) monochromator was used to set the energy of the excitation radiation delivered by undulators, to 18 keV (λ =0.0688 nm). The full width half maximum spot size, focused by a pair of Kirkpatrick-Baez mirrors, was approximately $3 \times 3\ \mu m^2$. A Vortex-90EX silicon drift detector (SDD; SII, USA) was used to collect the X-ray fluorescence signals during elemental mapping experiments. The step sizes were 2 μm and the dwell time at each pixel was 3 s. The μ-XRF images of elements with discernible peaks (K or L lines) in the spectra were collected, including Ca-Kα, K-Kα, Mn-Kα, Fe-Kα, Cu-Kα, S-Kα, Al-Kα, and Si-Kα.

For TEM analysis, the region of interest on the polished sample was selected to *in-situ* cut with a Zeiss Auriga Compact, focused ion beam (FIB) system equipped with an Omni probe Auto Probe 200 micromanipulator at the Institute of geology and geophysics, Chinese Academy of Sciences. FIB experiments were carried out at 5–30 kV high voltage with beam currents from 2 nA to 50 pA to obtain FIB foils (two foils).The TEM bright-field (BF)/dark-field(DF) imaging, selected area electron diffraction (SAED) and high-resolution transmission electron microscopy (HRTEM) imaging were carried out using a JEOL-2100 TEM operated at 200 kV, with a LaB_6 electron gun at the Institute of Geology and Geophysics, Chinese academy of sciences [19].

3. Results

3.1. Optical image of glaze surface and cross section

We began our study by employing apparent morphology of the ancient sample. On the surface of the glaze layer (Fig. 2A), there are large and dense bubbles distributed throughout the glaze, and the boundary of the red pattern in the glaze is not very clear. The thickness of the glaze layer is approximately 400 microns. The cross-section image (Fig. 2B) shows that the glaze layer can be divided into three parts: the black pigment layer at the bottom, the red diffusion layer in the middle and the top transparent layer.

In the underglaze red process, the pigment is first painted on the pre-fired body, and then a layer of transparent glaze is covered on the upper

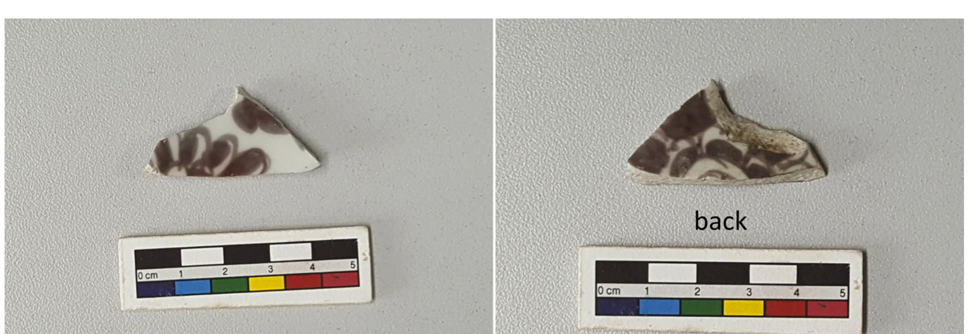

Fig. 1. Photographs of the sample of Hongwu underglaze red (YLHM), which was excavated from the Nandaku Site of the Forbidden City.

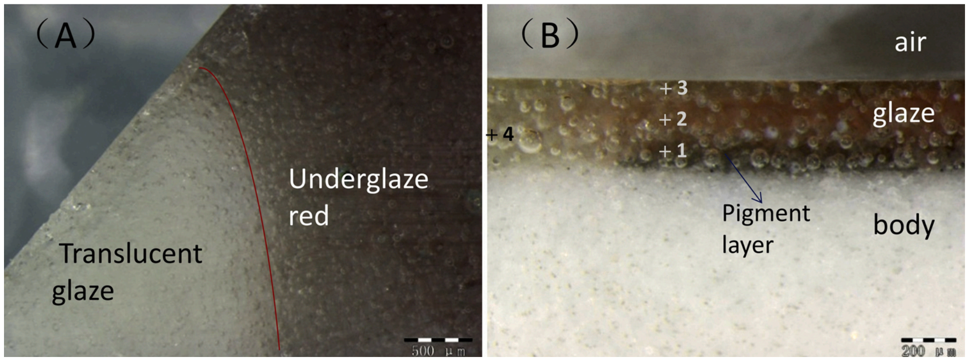

Fig. 2. Surface(A) and cross-section images (B) of the underglaze red sample YLHM.

layer for firing, so an obvious pigment layer will be formed near the body. The results of the elemental composition of different positions show that the colors of the glaze layers are different with the change of copper content, as presented in Table 1. The copper content of the pigment layer is the highest, and the copper content of the transparent glaze is the lowest.

3.2. The color of the "red" patterns on the glaze surface of the underglaze red

The UV–vis diffuse reflectance curves of two underglaze red samples are shown in Fig. 3. For YLHM, a large reflectance between 600 nm and 700 nm is observed, and there is an important absorption peak between 550 nm and 600 nm, which is related to the presence of metal copper nanoparticles [20]. The absorption peak is not sharp and has a wide range probably because of the wide particle size distribution instead of a uniform particle size range.

Previous studies have indicated that the color seen is related to the combination the upper translucent glaze, red opaque and black pigment regions. Therefore, the surface color of the glazes depends on which areas dominate over the others [21]. In our study, the red color observed maybe come from metal copper nanoparticles of the pigment base.

3.3. Morphology of crystals in the cross-section glaze sample

The size and distribution of copper particles can be judged intuitively by SEM back-scattered electron images. As shown in Fig. 5, copper particles are extremely unevenly distributed in the glaze, and the particle sizes also varied greatly. Large particles are mainly concentrated near the body, and some smaller copper particles are distributed in the middle and upper layer of the glaze layer. The copper particles in the three areas of A,B and C in the glaze were observed. It was found that the copper particles near the upper layer of the glaze are smaller: the copper particles at A are about several tens of nanometers, the B is about several hundred nanometers to 1μ, and the irregular large particles at C are about 5–10 microns. The statistical histogram of the particle size shows that the size range of most particles is from a few nanometers to tens of microns.

In addition, according to the shape and element analysis of the particles, they can be classified into three main types. The first type is spherical nanoparticle, which mainly distributed in the upper and middle layers of the glaze layer, as shown in A, and contain copper and trace arsenic; the second type is micron-scale spherical copper particle, which mainly distributed near the body, and the composition is also copper and trace arsenic; the third one is irregular large particle, which has an elemental composition of two parts: one part contains Cu and As, and the other contains Cu and S (Fig. 4). Therefore, these particles with two parts show different brightness in the back-scattered electron image, and it may be related to the raw materials that were not completely melted.

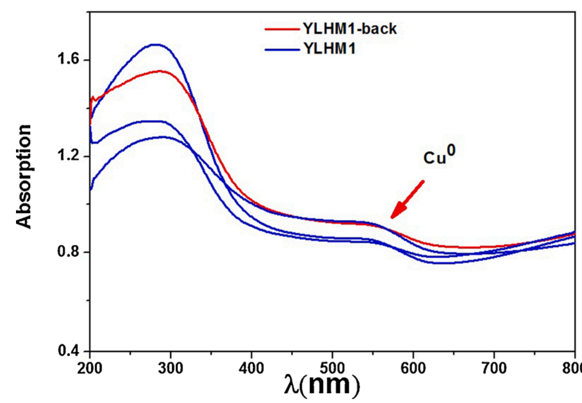

Fig. 3. UV–vis diffuse absorption spectra of the red color of the sample YLHM: red in three different areas(YLHM) and one area on the back(YLHM-back). (For interpretation of the references to colour in the text, the reader is referred to the web version of this article).

3.4. SR-μ-XRF mappings and SR-μ-XRD on the cross-section

Elemental mapping can be performed by μ-XRF with a spatial resolution 2 μm of BL15U1 Hard X-ray Micro-Focusing Beamline in SSRF. The results of the copper, arsenic, sulfur, calcium and iron mappings are shown in Fig. 6. Obviously, the distribution of copper elements shows that much larger particles are in the bottom layer, and the tiny particles are in the upper layer. In the same copper particle, sulfur and arsenic occupy different positions respectively, which is consistent with SEM observations. Iron is mainly distributed in the lower part of the glaze, and it is likely to be introduced together with copper as the pigment. In

Table 1
Element composition at different positions on the cross section (wt%).

	Al_2O_3	SiO_2	K_2O	CuO	TiO_2	CaO	Na_2O	MgO	MnO	Fe_2O_3
1	19.87	66.46	5.55	0.98	0.07	3.53	2.02	0.11	0.14	1.11
2	16.26	69.04	7.00	0.40	0.07	3.59	1.85	0.22	0.17	1.29
3	16.72	67.45	6.22	0.21	0.06	5.54	2.15	0.25	0.17	1.16
4	13.77	72.76	6.28	0.17	0.04	2.91	2.45	0.28	0.12	1.15

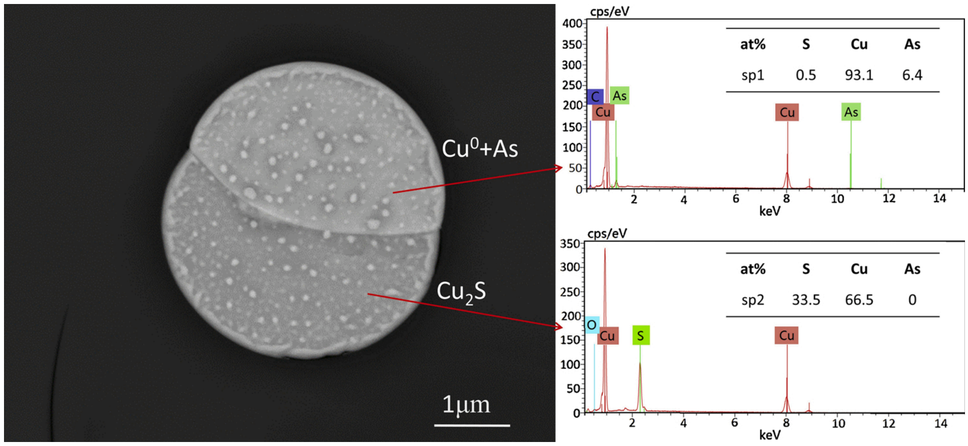

Fig. 4. A copper particle with two parts. One part contains Cu and As, and the other part contains Cu and S element.

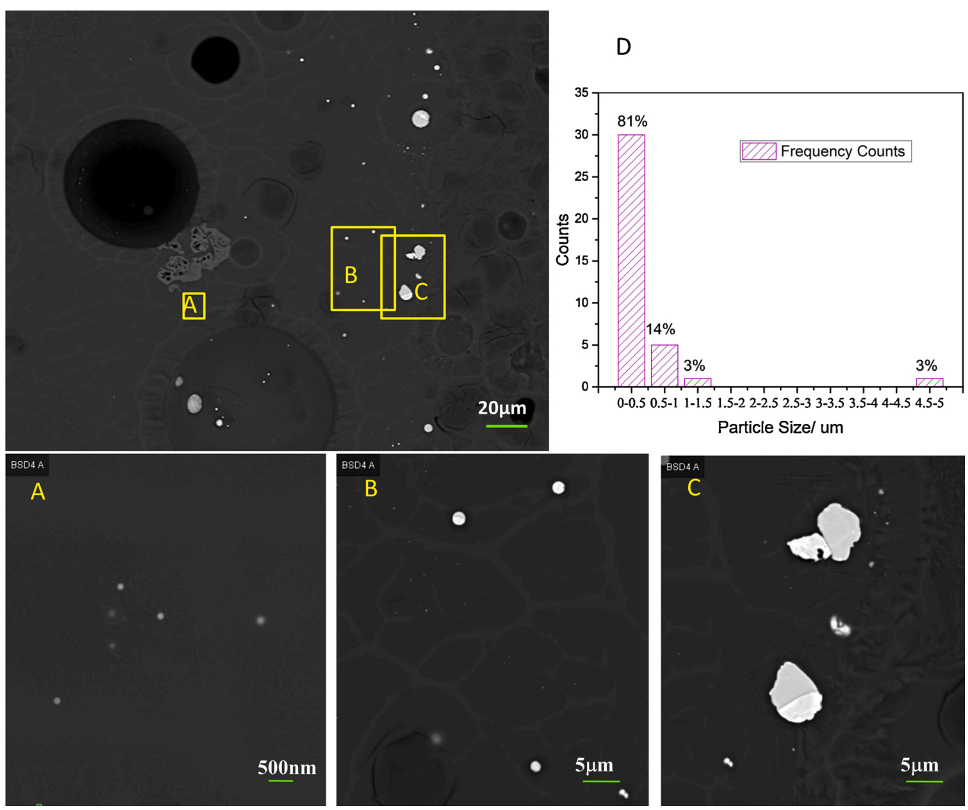

Fig. 5. (A), (B), (C) Back-scattered electron images of crystals with spherical or irregular shapes in the glaze. (D)Statistical histogram of the size of the particles containing Cu.

order to further determine the phase of the copper particles, SR-μ-XRD was performed on the two areas A and B on the Cu mapping, and it was inferred that A was copper and B was Cu_2S.

3.5. Phase identification of Cu particles by TEM-SAED

Bright-field TEM and SAED analyses were performed to further investigate the crystal shape, phase and distribution across the cross-section of the surface glaze layer. As shown in Fig. 7, the FIB technology was used to prepare the particle samples on the cross section of glaze. The SEM images show that the particles at B are spherical with diameters about 100 nm, and the particle at A are ellipsoidal and consists of two parts with a length of about 10 microns.

The SAED patterns in Fig. 8 show symmetric spots, indicating the highly crystalline nature of the particles. The metallic copper has a face-centered cubic structure, and the SAED image of the particles at B confirms the existence of Cu^0. The large particle at A contains not only copper, but also copper sulfide. Based on the measurement of the d-spacing and the angle, the pattern is indexed using the Cu_7S_4 phase, which is different from the previous SR-μ-XRD results. The difference in Cu: S atomic ratio may be caused by the degree of copper sulfurization.

4. Discussion

In general, the appearance of the underglaze red fired during the Hongwu period of the Ming Dynasty opened the history of the high-temperature copper red glaze of the Ming Dynasty. However, there are few studies on the microstructures and the color of the Hongwu

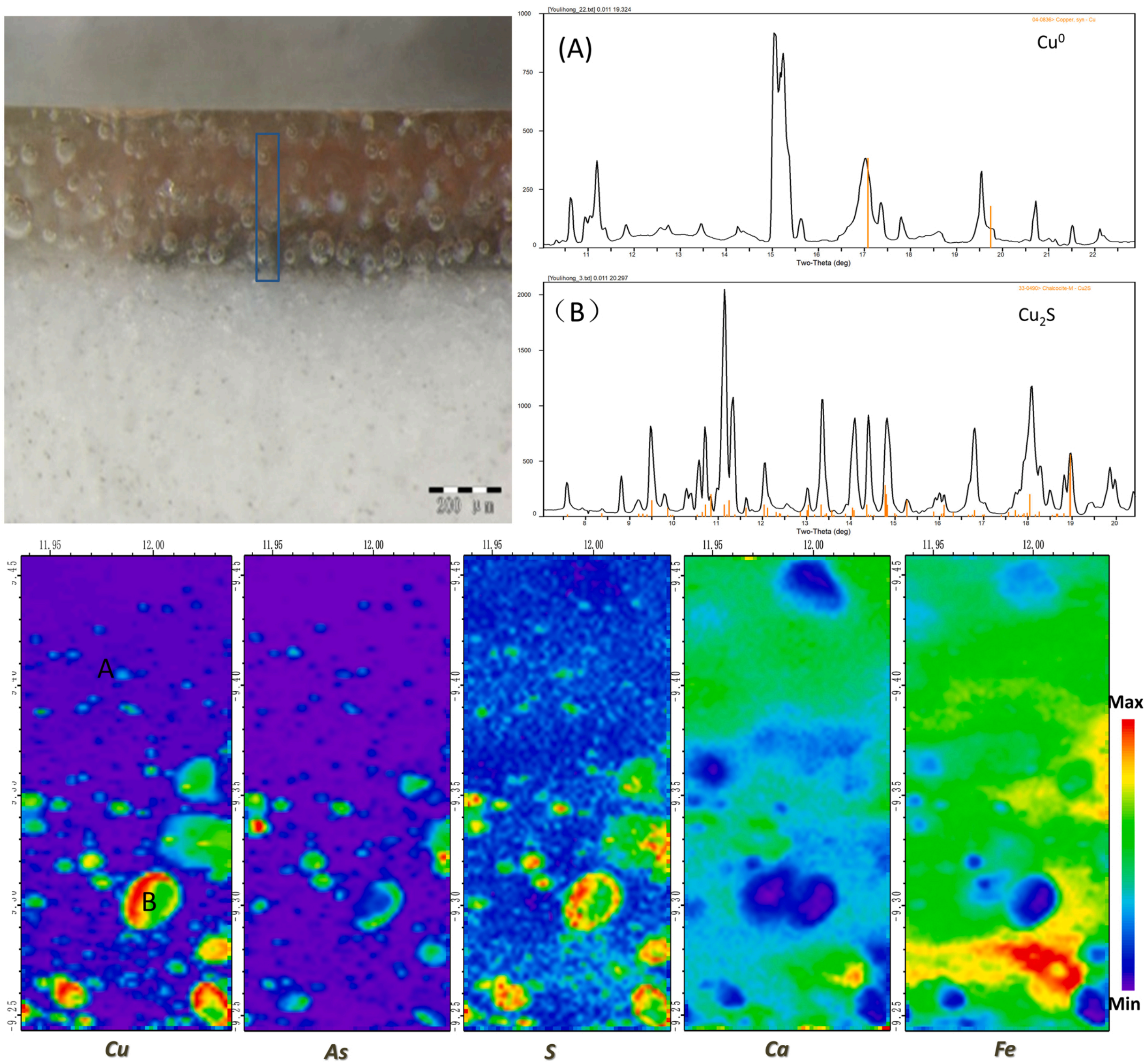

Fig. 6. An optical image of underglaze red cross-section and element mapping of Cu, As, S, Ca and Fe. (A) and (B) SR-μ-XRD of the points selected based on the results of Cu fluorescence mapping.

underglaze red due to the short firing time and the scarce quantity.

For the process of underglaze red, the pigment is applied to the pre-fired body first, and then a transparent glaze is applied to that, followed by firing. Finally, a red pattern is formed that can be seen on the surface. Generally speaking, the red color we see should be the color of the bottom layer, just like blue and white glaze. In fact, the color is actually a mixture of the upper translucent glaze, the red layer, and the dark pigment layer on the bottom due to the diffusion of copper elements into the glaze after firing(shown in the cross-sectional image of Fig. 2), so the underglaze red of Hongwu is still darker than the copper red glaze of the Qing Dynasty.

Many Chinese and foreign experts have also discussed whether the color of the ancient Chinese copper red glaze is caused by metal copper (Cu^0) or cuprite (Cu_2O). In view of our precious Ming Dynasty samples, through cross-validation by SEM-EDS, SR-μ-XRD and TEM-SAED, it is believed that copper nanoparticles play an important role in coloring of Hongwu underglaze red, and the particles are distributed throughout the entire glaze layer and their size is several nanometers to several hundreds of nanometers. However, due to the presence of larger Cu_2S in the bottom layer, which is black or gray-black, the color of the appearance in Hongwu underglaze red is the superimposed color of copper nanoparticles and Cu_2S, resulting in a dull red color. This also is a unique and recognizable feature of Hongwu underglaze red.

Because there are few records of the raw materials of the copper red glaze of the Ming Dynasty in ancient China, it is always be a concern about which kind of material and how is used to Hongwu underglaze red. The existence of some large irregular particles (5–30 μm) in the pigment layer of the glaze provides us with the possibility to solve the above problems.

Those irregular particles (shown in Fig. 5C) have no sharp edges and corners, indicating that they are not secondary products, and are likely to originate from the residue of raw materials. In addition, the large particles have a complex composition. They usually contain Cu_2S and copper, and the copper part also contains a small amount of As. Since sulfur and arsenic are volatile elements and cannot be added directly, they should be introduced with the raw materials [13]. In summary, the raw material of glaze red should be natural ore raw material, which may contain chalcopyrite (Cu_2S). The primary mineral of copper ore is sulfide, and then weathered to form various secondary minerals. Copper ores such as arsenite copper and toxic sand often contain sulfur and arsenic [22].

However, there are some problems if the raw material of copper red

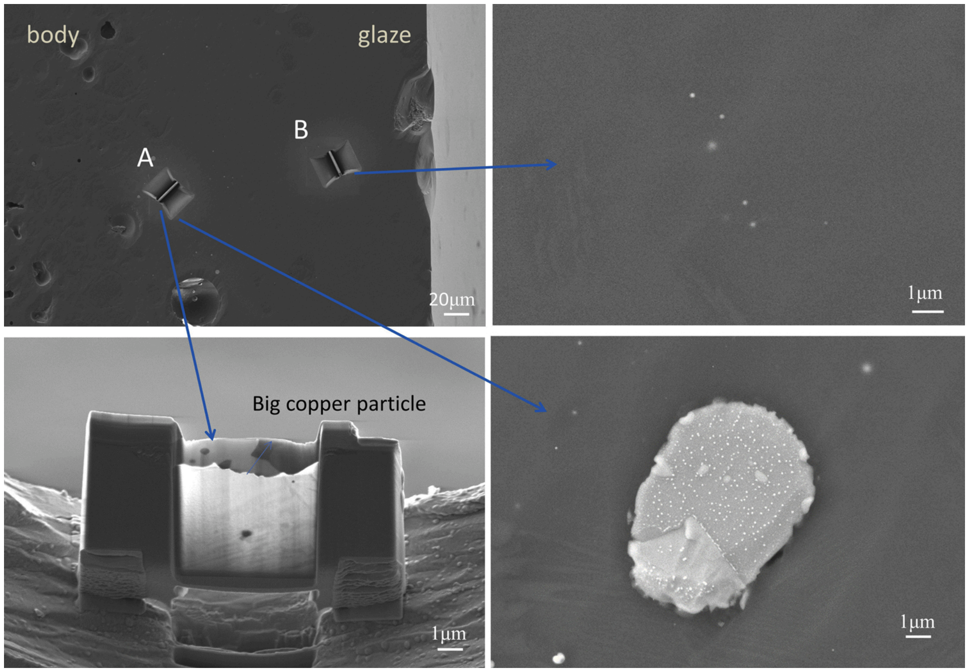

Fig. 7. SEM images of A and B corresponding to different color areas show the particles with large difference in size and shape. The particle of A by FIB is shown.

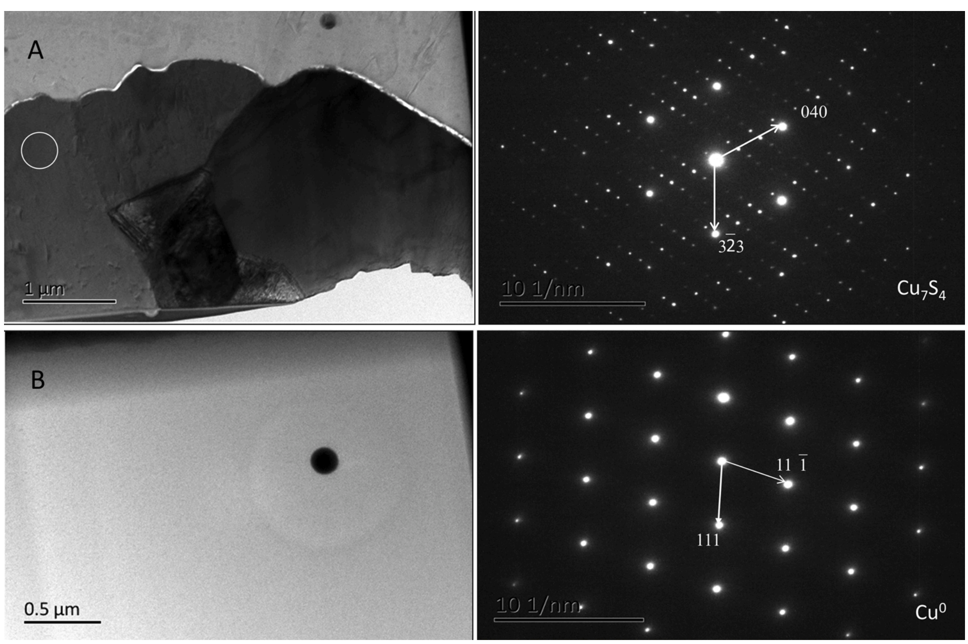

Fig. 8. Bright-field TEM images and selected-area electron-diffraction patterns of particles of A and B.

glaze is chalcopyrite. Due to the strong binding of copper and sulfur, under high temperature chalcocite needs to react under an oxidizing atmosphere to produce Cu_2O, and then Cu_2S reacts with Cu_2O to produce metal copper and sulfur dioxide, as shown in formula (1) and (2) [23]. However, most of the porcelains were fired in a reducing atmosphere in the Ming dynasty, which was unfavorable for reaction of formula (1). It is unlikely that only chalcocite is used as a raw material of the underglaze red.

$$2Cu_2S_{(l)} + 3O_2 = 2Cu_2O_{(l)} + 2SO_2 \tag{1}$$

$$Cu_2S_{(l)} + 2Cu_2O_{(l)} = 6Cu_{(l)} + SO_2 \tag{2}$$

$$\Delta G_2^0 = (8600 - 14.07T) \times 4.1868\ (J)$$

$$Cu_2O_{(l)} + CO = 2Cu_{(l)} + CO_2 \tag{3}$$

$$\Delta G_3^0 = (-31600 + 5.78T) \times 4.1868\ (J)$$

According to the record of Chinese ancient literature *Kui Tian Wai Cheng*in the Ming Dynasty: “During the period of Jiajing of Ming Dynasty, although the blue and white glaze made by Huiqing was famous, the bright red soil was cut off, the firing process was very different from before… After Muzong claimed the emperor, he ordered to fire the Xuande’s bright red glaze. Minister Xu Shi claimed that the bright red soil was extinct and only alum red could be fired." It shows that the recorded raw materials of red glaze in the Ming Dynasty had two characteristics, one is red soil, and the other is relatively rare. Fukang Zhang [16] also believed that the loss of copper-red glaze technology in the late Ming Dynasty is related to the severance of raw materials. The only copper-bearing mineral in nature relatively close to the characteristics of "bright red clay" in ancient literature is cuprite. The natural mineral cuprite is a red oxide mineral, formed by weathering copper sulfide, in the form of granules or soil, usually formed in the secondary weathering zone near the surface of the copper mine. At the beginning of the Ming Dynasty, the only two copper mines in the country were Dexing and Yanshan in Jiangxi [24], and the former is much larger and closer to Jingdezhen; what's more, the Dexing copper mines were mainly chalcopyrite ($CuFeS_2$) and chalcocite (Cu_2S) distributed near the earth surface [25], so it is likely to form a small amount of red cuprite. It was very possible to be noticed and used as a raw material for firing copper-red glaze for its bright color. The cuprite is usually distributed near the chalcopyrite, so it is inevitable that chalcopyrite is mixed in the raw materials.

Cuprite is easily reduced to metal copper by carbon monoxide in a reducing atmosphere, as shown in formula (3). At the same temperature within the firing range of porcelain, $\Delta G_3 < \Delta G_2$, which causes reaction in formula (3) takes priority over reaction in formula (2), so that the final products in copper red glaze are metal copper and residual Cu_2S.

5. Conclusions

It is founded that the red glaze layer of the Hongwu underglaze red unearthed in the Forbidden City is divided into the bottom pigment layer, the copper red diffusion layer and the transparent layer. Nanometer-scale spherical metal copper particles are observed in the diffusion layer, and micron-scale irregular cuprous sulfide particles are present in the underlying pigment layer. Because the red copper crystals are colored with the black cuprous sulfide, the Hongwu underglaze red appears dark red instead of the bright copper-red. Due to the record of " The bright red soil was extinct " in ancient literature, we inferred that the pigments used in the underglaze red of the Ming Dynasty may come from the cuprite mine mixed with a small amount of chalcopyrite. The depletion of raw materials led to the interruption of copper red glaze in the late Ming Dynasty.

Declaration of Competing Interest

We declare that we have no financial and personal relationships with other people or organizations that can inappropriately influence our work, there is no professional or other personal interest of any nature or kind in any product, service and/or company that could be construed as influencing the position presented in, or the review of, the manuscript entitled. All authors have seen the manuscript and approve the revision.

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