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The birth of copper-red glaze: Optical property and firing technology of the glaze from Changsha Kiln (8th–9th century)

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ABSTRACT

Changsha Kiln rose and flourished alongside the development of China's Maritime Silk Road (8th–9th century). The kiln occupies an important place in the development of China's ceramic science and technology, notably as the source of high-temperature copper-red glaze. A variety of lime-colored glaze was one product of Changsha Kiln. Its surface was decorated with both copper-green and copper-red, and is the earliest known example of the successful firing of a copper-red glaze. This ware is representative of the birth of high-temperature copper-red glaze, but there has been a lack of research on its optical properties and the technology's origin. In this paper, OM, SEM, TEM, optical coherence tomography (OCT), XRF, fiber optic spectrometry, and other analytical techniques were used to investigate the red and green glazes of Changsha Kiln. The key result of this paper is to reveal the optical properties of copper-green and copper-red in combination with colloidal absorption, ion absorption, and scattering, and to study the key factors for the origin of the high-temperature copper red glaze.

1. Introduction

Red is the color of blood, sun, and fire. Human respect for life and nature has created the worship of the color red. A 40,000 year old mural found in El Castillo cave, Spain, consists of a pattern painted in red with ochre [1]. Lacquerware dating back 7000 years has been discovered at the Hemudu site in China and is decorated with red cinnabar [2]. Clearly, the red on such murals and lacquerware is due to the color of ochre and cinnabar themselves. Around 1500 BCE, during ancient Egypt's 18th dynasty, red glass with copper color was invented [3]. Particularly special about this kind of glass is that its color is produced by colloidal particles [4]. The application of this colloidal copper-red technology to ceramic glazes fired at a high temperature above 1000 °C can be traced back to the stoneware of Changsha Kiln in the Tang Dynasty (618–907).

Changsha Kiln was located near Shizhu Lake, Changsha City, Hunan Province, China, and was famous for its exports during the Tang Dynasty. Although statistics are incomplete, nearly 20 countries around the world have unearthed examples of Changsha Kiln stoneware. According to archaeological research, Changsha Kiln's initially fired lime monochrome-glazed stonewares and later developed the firing of polychrome-glazed stonewares [5]. The beauty and style of its porcelain were rare in the kilns of the Tang Dynasty and represented a new development in this period, away from focusing on the beauty of glaze color and concentrating instead on the attractiveness of painting and decoration [6].

The important position of the Changsha Kiln in the history of Chinese ceramics cannot be understated. One reason for this is the production of high-temperature copper-containing glaze. Copper glaze involved a different process from iron-glaze. While the iron in early Chinese glazes entered the glaze layer unintentionally along with the raw materials, the copper in the glaze was added deliberately as a coloring agent. The earliest use of copper as a glaze colorant in China began with low temperature lead green glaze during the northern Han Dynasty (25–220), but Changsha Kiln was one of the first in China to use copper as a high temperature colorant. The resulting transparent high-temperature copper-green glaze was unique in the history of Chinese ceramic production [7]. An even more important contribution by Changsha Kiln to ceramic technology was the firing of high-temperature copper-red glaze. In 1983, Chinese archaeologists excavating the

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Changsha Kiln site found sherds with red glaze [8]. The appearance of a product of this kind elevated estimations of Changsha Kiln's sophistication. To date, no earlier copper-red glaze ware has been found anywhere else in the world [9].

In recent years, many scientists have studied the technology behind the coloring of ancient copper-red silicate materials, but research has tended to focus on copper-red glass products [10–14] rather than on copper-red glaze [15–17]. Research on the copper-red glaze of Changsha Kiln has been particularly limited [18]. A kind of transparent green-and-red glazed ware was produced in Changsha Kiln, with Cu-green and Cu-red appearing on the same object, which is very rare in Chinese high-temperature glazes. The color of high-temperature copper glaze depends mainly on the firing atmosphere: green when fired in a partial oxidation atmosphere and red when fired in a partial reduction atmosphere [19]. It is thus very difficult to understand the production of such green-and-red glazed pieces [20]. Moreover, such samples seem to imply that the birth of copper-red glaze was closely related to the firing of copper-green glaze. However, there has been no scientific research on products of this type and no scientific discussion of the origin of copper-red glaze. In this paper, EDXRF, optical coherence tomography (OCT), spectrometry, SEM, and TEM were used to analyze the transparent green-and-red glaze of the middle-and-late Tang Dynasty (8th–9th century), to reveal the optical properties and causes of the red and green colors, and to discuss their firing technology and the origin of copper-red glaze.

2. Experimental porcedures

2.1. Sample

The lime glazed sherd of the mid-to-late Tang Dynasty (8th–9th century) with green and red painting unearthed from the site of Changsha Kiln is typical (Fig. 1). The painted pattern seems to depict a cloud or a bird and flower [21]. One of the patterns is red surrounded by brown, while the other is green surrounded by red. The area containing green-and-red glaze was cut into cross-sections, as shown in blue line.

2.2. Methods

A Leica MZ16A optical microscope was used to observe the cross-section of the glaze, and a ring light source was used for illumination.

A Thorlabs TELESTO-II OCT imaging system was used to analyze the transmittance of the glaze in different color zones. The wavelength was 1310 nm, the imaging speed was 91 kHz, and the axial resolution was 6.5 μm.

An EDAX Eagle III XXL X-ray fluorescence spectrometer was used to analyze the glaze. The analysis was run at a voltage of 25 kV, with a 300 s counting time, 600 μA current and a 0.3 mm diameter collimator. For the major and minor elements, quantitative measurements were achieved by correction and calibration with a set of 13 standard samples. Semi-quantitative data are available for the trace elements by using the EDAX Company's software. For the repeatability and precision check, a porcelain piece was periodically measured over the past two years. The relative standard deviation of major elements is less than 3%, and that of trace elements is less than 30 %. In order to improve representivity and precision, three spots were measured for each sample.

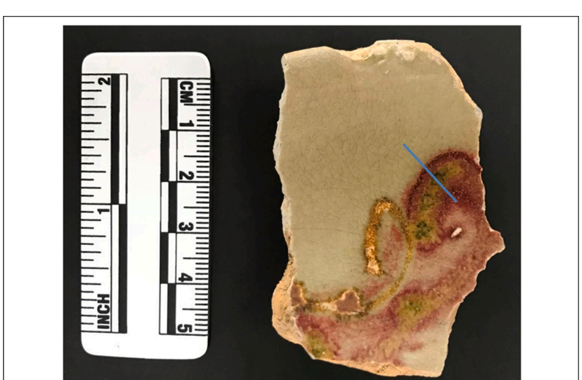


Fig. 1. The celadon brown-green-red sherd unearthed from Changsha Kiln. (For interpretation of the references to colour in the Figure, the reader is referred to the web version of this article).

A TESCAN-MIRA3 field emission scanning electron microscope was used to observe the microstructure of the glaze. A carbon coating was sprayed on the surface of the sample before the experiment. A Zeiss Auriga FIB was used to obtain polished areas and prepare samples of the micro- and nanostructure of the red glaze. A JEM-2010 F transmission electron microscope was used to take photos of nanostructures and carry out selected-area electron diffraction. The operating voltage was 200 kV and the electron beam spot was 1 nm.

Because the color zone is small, an Avantes AvaSpecHero/NIR256-2.5-HSC fiber spectrometer was used to analyze the reflectance spectrum. This instrument has the characteristics of nondestructive testing and is built using light source, spectrometer, optical microscope and support facilities. Reference [22] shows the detail information. The range of reflection spectrum collected in this test is 400−800 nm. The optical fiber probe is perpendicular to the test area, and the spot diameter is about 2 mm.

3. Results

3.1. Cross-sectional structure

Fig. 2a and b show the structure of red and green cross-sections respectively. The red glaze is measurably thicker, about 180 μm, while the green glaze is thinner, about 90 μm. In all cross-section samples, a white slip with a thickness of about 250 μm can be observed between glaze and body.

3.2. OCT results

Fig. 3 is an OCT photo. As can be seen, the dark red area, the adjacent red diffusion area, and the green area each exhibit different light transmission effects. In the dark red zone at left, a transparent layer of about 50 μm on the surface of the glaze layer can be observed, and there is a small amount of opaque material in the glaze layer below. The transparent layer on the surface of the lighter red glaze layer in the middle is similar to the dark red transparent layer, but the opacity of the glaze layer here is higher. In the green zone at right, the glaze is transparent from top to bottom.

3.3. Glaze composition

The surface composition of the different color zones is listed in Table 1. Notably, glazes from Changsha Kiln in the Tang Dynasty are high-calcium, and CaO comprises about 14–15 % of the glaze. In addition, it is apparent from the table that the main color elements of the red and green glazes are copper and iron. The iron content in the glaze layers of all colors is similar; the copper content of the red glaze is less, only 0.36 %, while the copper content of the green color is higher, reaching 2.53 %.

3.4. Microstructure

A scanning electron microscope was used to observe the microstructure of the lime glaze and color glazes; the images are shown in Fig. 4. At lower magnification (5000x), sintered pores and suspected raw material residues can be observed in the lime and green glazes without phase separation and granular substances. Pores and raw material

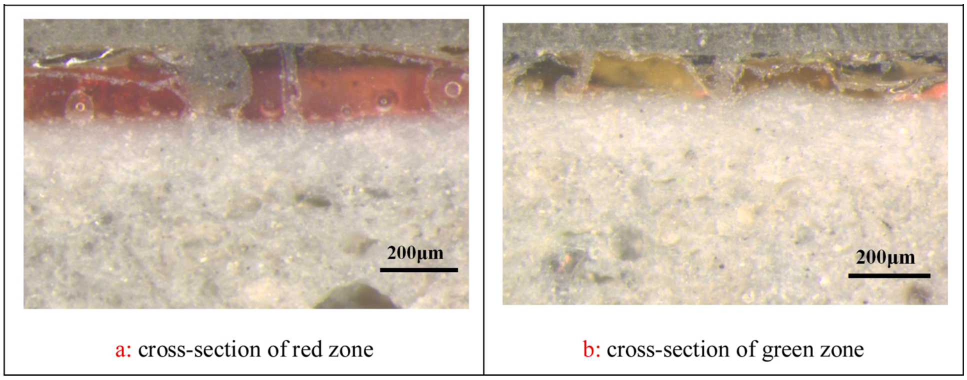


Fig. 2. The corss-section structure (by optical microscope).

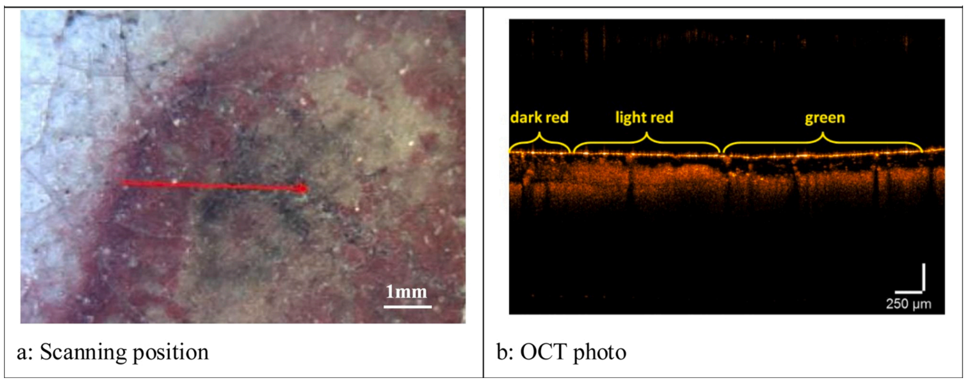


Fig. 3. OCT images of different color zones.

Table 1
Composition of red zone, green zone, and celadon glaze (wt%).

	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	K_2O	CaO	TiO_2	MnO	Fe_2O_3
red glaze	0.73	2.21	12.88	63.18	1.72	0.12	1.81	15.13	0.62	0.34	1.43
green glaze	0.81	2.31	13.59	62.69	1.24	0.09	2.06	14.49	1.01	0.40	1.64
lime glaze	0.78	2.07	12.59	63.65	1.42	0.02	1.63	14.85	0.67	0.36	1.45
	CuO	SnO_2	PbO_2								
red glaze	0.3638	0.0461	0.0277								
green glaze	2.5257	0.1148	0.1044								
lime glaze	0.0050	0.0375	0.0096								

residues can also be observed in the red glaze, along with a large number of copper-containing particles in the red zone glass matrix. The red color area was divided into two zones, dark red and light red zone, and the observation was performed at a higher magnification (50,000x). In the dark red zone, the average diameter of the bright particles was found to be 41 nm, while the average diameter of the particles in the light red zone was 88 nm.

The morphology and phase of copper particles were analyzed by transmission electron microscopy. The particles were found to have two morphologies, one a round crystal as shown in Fig. 4e and the other a polygonal crystal as shown in Fig. 4f. The diameters of both types of particle are about 80–90 nm. The SAED pattern in Fig. 4g shows symmetrical 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 confirms the existence of Cu°. While twin copper crystals were observed (Fig. 4h), Cu_2O and CuO crystals were not found in the observation area.

3.5. Glaze reflectance spectrum

Since the diameters of the red and green areas are only 1–2 mm, their color cannot be tested with an ordinary colorimeter (the minimum diameter of the measurement area is 4 mm). The reflection spectrum of the different glazes was thus collected with a fiber spectrometer. The results are shown in Fig. 5. The reflectivity of the lime glaze gradually increases after 400 nm, and gradually decreases after reaching the peak at 600 nm. The dark and light red zones show obvious absorption at 560 nm and high reflectivity at 600–700 nm. The reflectivity of the green area gradually increases from 500 nm, and the overall peak of the reflection spectrum is relatively flat.

4. Discussion

4.1. Optical properties of red and green glazes

Generally speaking, the diffuse surface reflection result of the glass glaze layer indicates scattering by second phase particles in the glaze layer, absorption by colloidal particles and colored metal ions in the glaze layer, and absorption by the body. Although the body color of this particular sample, there is a white slip between glaze and body. It is thus assumed that all incident light arriving at the slip returns, and that the absorption effect of the body can be ignored, as shown in Fig. 6. For this

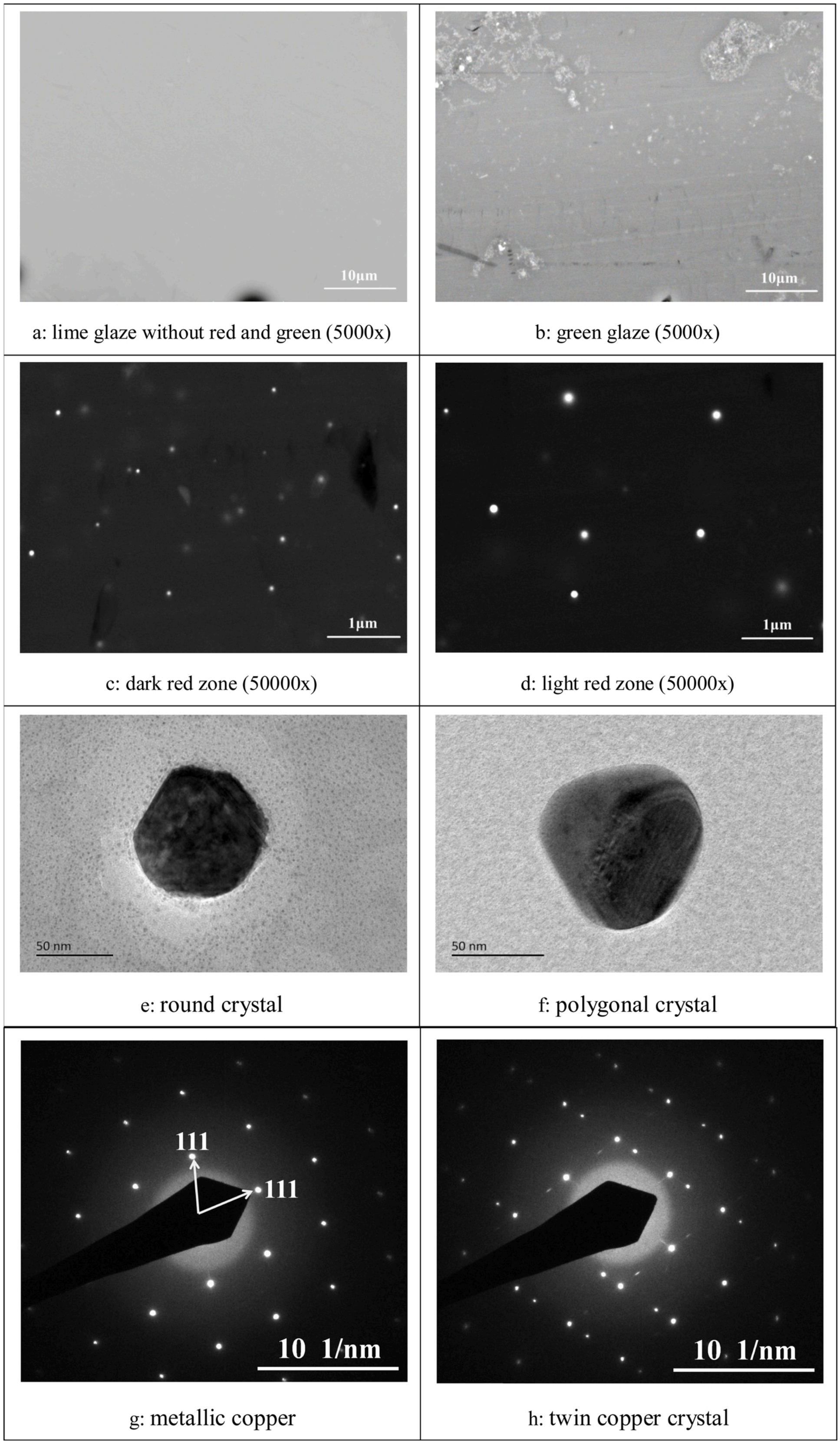


Fig. 4. Microstructure images and electron diffraction pattern of red glaze. (For interpretation of the references to colour in the Figure, the reader is referred to the web version of this article).

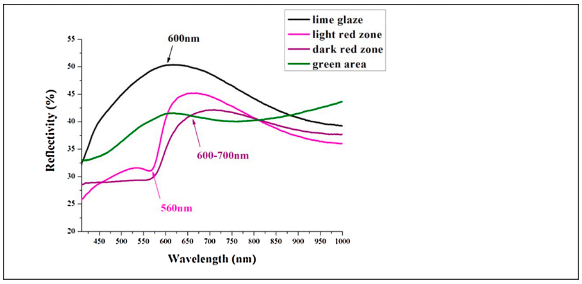


Fig. 5. Reflection spectrum of different color areas.

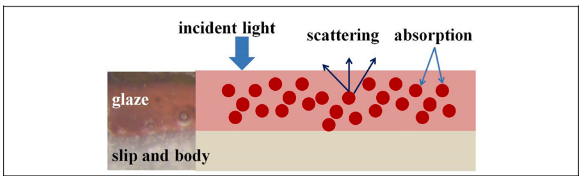


Fig. 6. Absorption and scattering of the glaze.

sample, given the chemical composition shown in Table 1 and the microstructure shown in Fig. 4, it may be inferred that the second phase particles that produce a scattering effect in the glaze layer are mainly metallic copper. The colloidal particles that produce absorption are also metallic copper, while the colored metal ions that may produce absorption are Fe^{2+}, Fe^{3+}, and Cu^{2+}.

4.1.1. Scattering and absorption by copper particles

In the study of copper red glaze, there has been a debate on whether red is produced by metal copper particles or cuprous oxide particles. Among the red glass in the West, F. Drunert et al. discovered two types of red glass with the color of metallic copper and the color of cuprous oxide [10]. In Chinese high-temperature glazes, Ian C. Freestone et al. found that the copper particles in the sacrificial red glaze samples of the Qing Dynasty were metallic copper particles [23]. Moriyoshi Yusuke found both metallic copper particles and cuprous oxide particles in one piece of modern red glaze samples [24]. According to the SAED results in Fig. 4 and the results of Yuanqiu Li et al. [18], no cuprous oxide particles were found in the copper red glaze of Changsha kiln. This also means that the copper red glaze of Changsha kiln is colored by metallic copper particles.

When metal nanoparticles are irradiated by incident light, their extranuclear electron clouds oscillate under the excitation of the electromagnetic field, thereby exciting the electromagnetic field and generating local surface plasmon resonance (LSPR) [25,26]. The LSPR frequency of gold, silver, and copper nanoparticles in the glaze layer is generally in the visible light region and results in strong absorption—-that is colloidal absorption, which can present a color different from the metal itself. Luster porcelain from the 9th–12th centuries in the Islamic world [27] and the enamel famille rose of Qing Dynasty China [28] are both based on this principle. Furthermore, when nanoparticles are present with a refractive index different from that of the glaze, the glaze

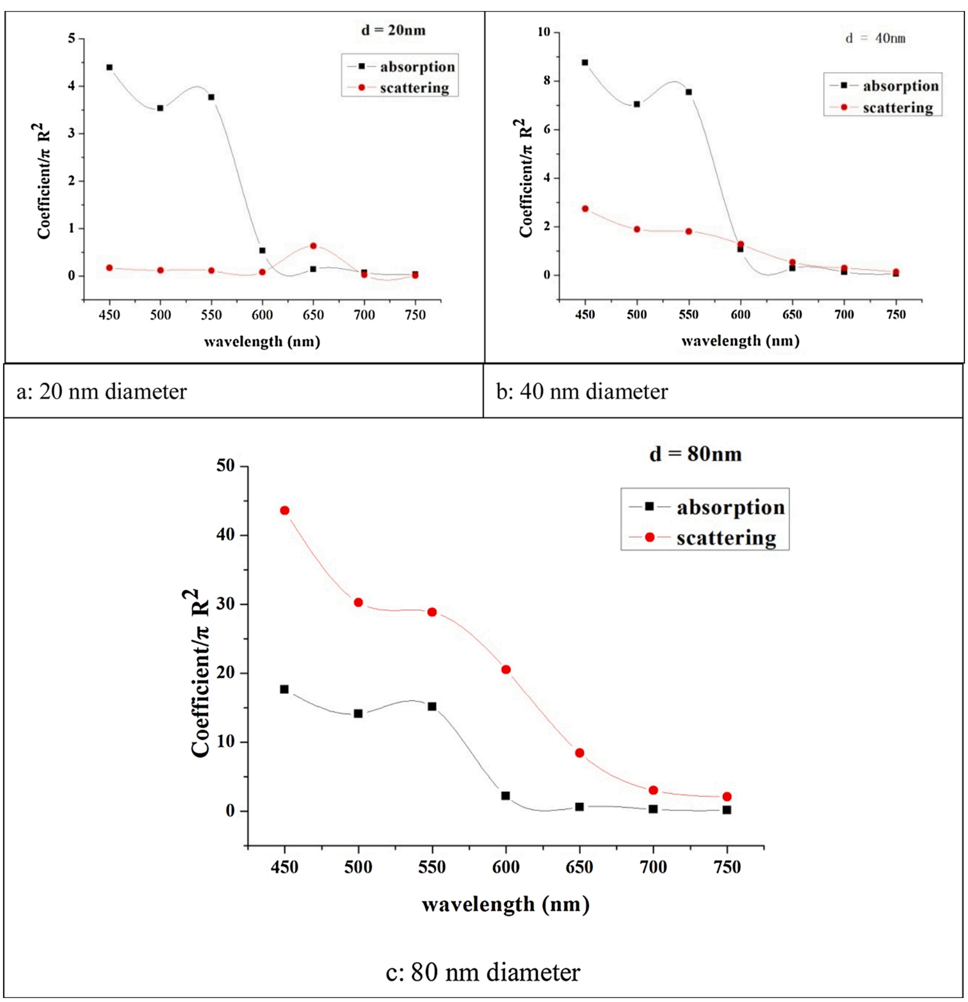


Fig. 7. Absorption and scattering coefficients of copper particles of different sizes.

also produces scattering of incident light, resulting in a blue or milky-white effect [29].

The nanometer and submicron copper particles in the glaze produce colloidal absorption and scattering simultaneously. Copper particles of different sizes have different effects. Fig. 7 are the absorption and scattering diagrams based on the data listed in '*Colour Generation and Control in Glass*' [30]. When the size of the copper particles is small (Fig. 7a), their colloidal absorption affects mainly the wavelength band below 560 nm, while scattering is mainly in the vicinity of 650 nm, and absorption is strong but scattering is weak. However, due to the low absorption coefficient (consistently less than 5), the overall effect is to absorb shorter wavelength light and to weakly reflect longer wavelength light, resulting in a faint red. When the diameter of copper particles is 40–60 nm (Fig. 7b), their colloidal absorption also affects mainly the wavelength band below 560 nm, while the coefficient of scattering in the short-wave region is slightly higher, so the overall effect is absorption of short wavelengths and reflection of long wavelengths. Because of the high absorption coefficient, the color effect is a vivid red. When the copper particles are larger (Fig. 7c), although the absorption coefficient of the copper particles in the short-wave region increases, the intensity of the short-wave light scattered by the copper particles is greater. The resulting visual effect is a faint blue or white opalescence instead of red.

4.1.2. Absorption by iron and copper ions

Iron and copper, in the first transition metal series, are the two main coloring elements in Chinese glaze. Iron ions exist mainly in the forms of Fe^{2+} and Fe^{3+} in the glass body of the glaze layer, while copper ions exist there mainly in the form of Cu^{2+} [31]. Fig. 8 are the linear absorption coefficients diagrams of Fe^{2+}, Fe^{3+}, and Cu^{2+} in the glass based on the data listed in the reference [30]. Fe^{2+} produces strong absorption in the long-wave region above 600 nm, resulting in blue-green. Fe^{3+} has weak absorption in the short-wave region below 400 nm, resulting in light yellow. Cu^{2+} produces strong absorption in the long-wave region above 650 nm, resulting in green.

4.1.3. The optical characteristics of red and green glazes

The diffuse reflectance spectrum measured from the surface of the glaze layer results from the absorption and scattering of incident light by the glaze and the body [32]. The following observations can be made from the diffuse reflectance spectrum shown in Fig. 5. (1) Dark and light red zones have low reflectivity in the short-wave region below 560 nm due to colloidal absorption by copper particles, and the light red zone also has a 500–550 nm scattering peak. The SEM results of dark red and light red areas are analyzed by image J, and the distribution of copper particles are shown in Fig. 9. The particle diameter in the dark red zone is distributed between 20 and 70 nm, and 60 % of particles have a diameter between 30 and 50 nm. The light red zone has a wider particle diameter distribution, between 20 and 160 nm, with diameters of 20–40 nm and 80–130 nm being more common. Therefore, the red color produced by colloidal copper exists in both areas (smaller copper particle size results in a stronger absorption peak; the peak disappears for copper particles smaller than 20 nm or larger than 80 nm). The light red zone also has opacities formed by scattering (the larger the copper particle size and the greater the proportion of large particles, the stronger the scattering and opacification effect, so the stronger the scattering peak).

(2) The reflectivity at 750 nm in the green glaze's reflectance spectrum is low, which should be a result of ion absorption by Cu^{2+}. (3) The composition results show that iron is present in both the red and green glazes, but only the red zone has low reflectivity near 1000 nm, which corresponds to absorption by Fe^{2+}. (4) There should be more or less Fe^{3+} in both the red and green glazes, but its absorption peak is in the ultraviolet region of 200 nm (outside the test wavelength range) so it is not reflected.

The components in the red and green glazes that have a coloring

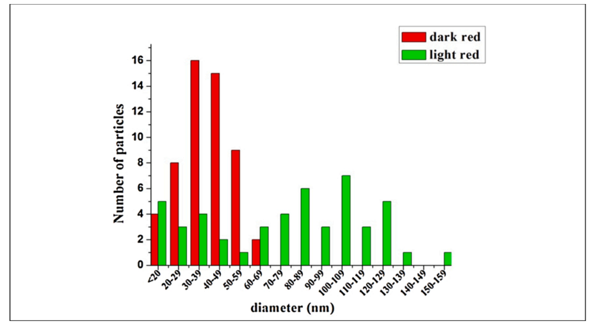
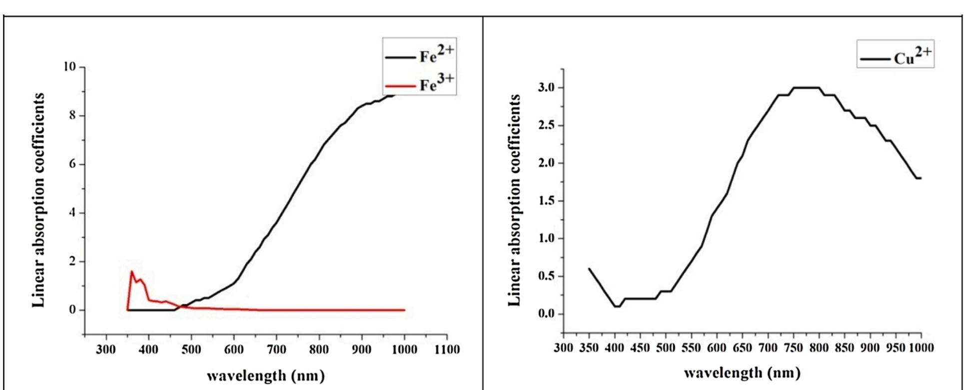


Fig. 9. Particle diameter distribution of red glaze based on the SEM results. (For interpretation of the references to colour in the Figure, the reader is referred to the web version of this article).

Table 2
Components in the red and green glazes with a coloring effect on optical properties.

	Scattering effect	Absorption effect	
	Second phase particles	Colloidal particles	d-d transitions
green glaze	none	none	Cu^{2+} Fe^{3+}
red glaze	copper particle	copper particle	Fe^{2+} Fe^{3+}



a: Linear absorption coefficients of Fe^{2+} and Fe^{3+}.

b: Linear absorption coefficients of Cu^{2+}.

Fig. 8. Linear absorption coefficients of iron and copper ions in the glass (optical density per cm pathlength per percentage by weight oxide).

effect on optical properties are summarized in Table 2. On the whole, nano-sized copper particles and Fe^{2+} metal ions have a greater effect on the color of the red glaze, while Cu^{2+} ions have a greater effect on the color of the green glaze.

From Fig. 4c and d, the average diameter of copper particles in dark red is 45 nm, and the average diameter of copper particles in light red is 78 nm. Therefore, whether viewed from the surface or in cross-section, the color of the dark red is relatively pure and transparent. The color of the light red is not only lighter but also shows a weak opalescence effect.

4.2. *The key factors for the origin of high-temperature copper red glaze*

4.2.1. *Copper content*

Table 1 is the chemical composition of red and green areas. It can be found that the content of the main components of the two color areas are similar, the only difference is that the content of Cu is quite different. According to the previous composition analysis of ancient Chinese glazes, it is found that the content of copper in copper-red glaze is within 0.2−0.5%, while the content of copper in copper-green glaze is within 2–4 % [7]. Xiong et al. analyzed the Bean Red glaze of the Qing Dynasty (1636–1912) and found that the copper content in the red area was 0.4 %, while the copper content in the green area on the same glaze was 1.48 % [33].

From known Changsha wares and archaeological excavations, it is clear that the copper-green glaze technology of the Changsha Kiln was very mature and highly productive. Given ancient Chinese painting methods, we may speculate that the potters used green raw materials with a high copper content when painting the artifact. After painting, the color material diffused to the surrounding glaze area and thus produced a gradient in copper composition on the surface. That is, the copper content in the central area was higher, while that in the surrounding area was lower. Fig. 10 is the chemical composition scan results. It can be found that the copper content gradually decreases from green to light red to dark red. Therefore, it is speculated that copper content needs to be controlled within a certain range, which is one of the key factors in the origin of high-temperature copper red glaze.

4.2.2. *Reducing atmosphere*

The conversion of high-valent copper ions in the glaze layer to Cu^0 requires the presence of a reducing agent. In the ancient West, when making copper red glass, the heat-treatment reduction method is generally used, that is, Sn^{2+}, Fe^{2+}, etc. are added to the glass in advance, and then heat-treating is performed to reduce the high-valent copper ions to Cu^0. The following reactions occur in the glaze:

$$Sn^{2+} \rightarrow Sn^{4+} + 2e^-$$

$$Fe^{2+} \rightarrow Fe^{3+} + e^-$$

For example, in the study of Goldfinger et al. [12], copper in the glass interacted with the Fe^{2+} and reduced to Cu^+ and/or Cu^0.

However, there has been no evidence of intentional addition of reducing agent to the glaze since the creation of porcelain in China. For traditional glaze, including China's famous celadon glaze, Chinese kiln workers have been reducing the high-valence elements in the glaze through CO produced by insufficient combustion fuel in the kiln, that is, a reducing atmosphere is applied to the glaze. In addition, Dou et al. found that the green glazed tiles in Yuanmingyuan turned red because of the reducing effect of CO on Cu^{2+} in the great fire [34]. The glaze in the kiln and in the fire reacted as follows:

$$CO + O^{2-} \rightarrow CO_2 + 2e\text{-}$$

According to archaeological excavations, the Dragon Kiln was used to fire Changsha wares in the Tang Dynasty [8]. Dragon Kiln is a kiln built on a mountain slope, with a length of 20−100 m and a width of 1.5–2 m [35]. It is shaped like a long dragon, hence the name Dragon Kiln. At the beginning of firing, due to the good ventilation conditions, the combustion chamber had sufficient oxygen and the fuel burns violently. Because the slope of the Dragon Kiln was large, the suction force was significant [36], which allowed oxygen to enter the kiln and the temperature to increase. When the temperature rose to a suitable range, the kiln workers used methods such as watering the fuel and closing the door of the combustion chamber to make the combustion products contain a certain amount of CO. This caused the copper in the glaze to react as follows:

$$Cu^{2+} + O^2 + CO \rightarrow Cu^0 + CO_2$$

However, the CO concentration caused by insufficient combustion was limited, that is, the reduction ability was limited. Therefore, the high-valent copper ions in the area with lower copper content (red glaze) can be partially reduced to Cu^0, while the copper ion still maintains a high-valent state in the area with higher copper content (green glaze). It can be seen that the application of reducing atmosphere in the Dragon Kiln is one of the key factors in the origin of high-temperature copper red glaze.

4.2.3. *Cooling rate*

The cooling rate must be controlled within a certain range. If it is cooled quickly, the temperature will drop rapidly and cross the temperature range with large nucleation and crystal growth rate. At this time, the viscosity of the glass will decrease, making it more difficult for copper atoms to move to each other to form new crystals. Therefore, if the cooling rate is too fast, there may be no copper particles, or the size of the copper particles is less than 20 nm, and the red color cannot be formed. If it is cooled slowly, and the residence time in the glass crystallization temperature range is too long, it may cause the crystal growth size to be larger. When the diameter of copper particles is greater than 80 nm, it will make glaze opacification and can not form red colour.

After excavating several kilns at the Changsha Kiln site, archaeologists discovered that the workers in the Tang Dynasty took a variety of reasonable measures to control the rise and fall of the temperature at the fire control site [8]. After the cooling process was completed, the outer area appeared red due to the presence of nano-sized copper particles in the glaze layer, and the central area appeared green due to divalent copper ions. Therefore, the reasonable control of the cooling rate is one

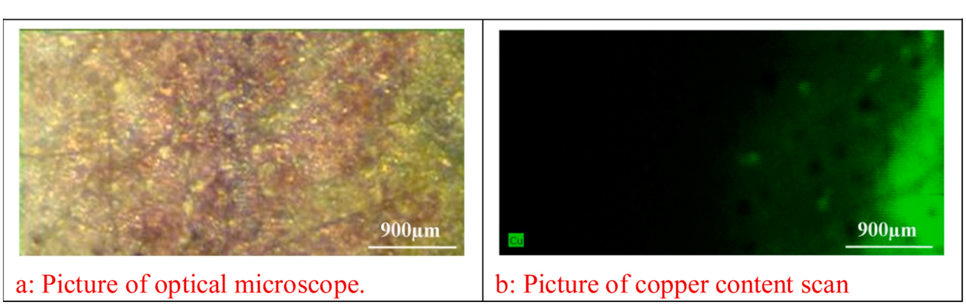


Fig. 10. Area scan of green and red glazes. (For interpretation of the references to colour in the Figure, the reader is referred to the web version of this article).

of the key factors in the origin of high-temperature copper red glaze.

It should be noted that, more than a thousand years ago, the kiln workers of Changsha Kiln in the middle-and-late Tang Dynasty were not yet mature enough to master the production process of high-temperature copper-red glaze. The occasional appearance of copper-red glaze was based more on the nature of the raw materials used for high-temperature copper-green glazes in Changsha Kiln and the use of the Dragon Kiln, which could easily produce a reducing atmosphere. However, the industriousness and creativity of workers in that era prompted them to experiment consciously with high-temperature copper-red glaze, which laid the foundation for the brilliance of Chinese copper-red glaze in future generations.

5. Conclusions

In this paper, a piece of Changsha lime glazed ware with red and green painting was analyzed using a variety of instruments and techniques. The results show:

(1) The optical characteristics of red and green glazes are determined by both scattering and absorption. Absorption consists of both colloidal particle absorption and metal ion absorption. The color of the red glaze is produced mainly from colloidal absorption by Cu° particles with a diameter of 40–80 nm and ion absorption by Fe^{2+}, while the color of the green glaze is produced mainly from absorption by Cu^{2+}.

(2) Copper content, reducing atmosphere and cooling rate are the key factors for the origin of high-temperature copper red glaze. The copper content needs to be controlled within a certain range. The diffusion of copper green pigment made the glaze had areas with low copper content. The Dragon Kiln used was easy to produce reducing atmosphere. The cooling rate was reasonably controlled. These conditions made the world's earliest high-temperature copper red glaze produced in the Changsha kiln of the Tang Dynasty in China.

Declaration of Competing Interest

We declare that we have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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