



Colour-generating mechanism of copper-red porcelain from Changsha Kiln (A.D. 7th–10th century), China



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ABSTRACT

Changsha Kiln, located at Changsha in Hunan Province, south of China, is famous for exported and coloured porcelain during the Tang Dynasty (A.D. 7th–10th century) period. Although the opinion that copper-red porcelain originates from Changsha Kiln is widely accepted in academic circles, chemical characters of glaze and colour mechanism of its copper-red porcelain have not been fully investigated and studied. Therefore, a shard of opaque glaze porcelain with red pigments which excavated at Changsha Kiln (A.D. 7th–10th century) was analyzed by Energy dispersive X-ray fluorescence (EDXRF), Synchrotron X-ray absorption near-edge spectroscopy (XANES), micro X-ray diffraction (μ -XRD), microscopy and scanning electron microscopy (SEM) methods. Combining with XANES and μ -XRD results, it indicates that metal copper is the major colouring-generation element status of the red hue. On the other hand, for the first time the study demonstrates that glaze of the sample from Changsha kiln is a typical phase separated-crystalline glaze with large particles surrounding acicular crystals which lead the opaque appearances. Because the sample from Changsha Kiln is Chinese ancient early stage copper-red porcelain relic, it will help to understand the origin of copper-red porcelain in China and enrich the knowledge of Chinese ancient ceramic culture.

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1. Introduction

Copper in different oxidation states will show different colours in glassy matrix. Due to this characteristic, in China, copper had been used as a colourant to make faience wares dating back to the Western Zhou Dynasty (11th–8th century B.C.) [1]. And the use of copper as colourant in glass works began at Warring States period (5th–3rd century B.C.). Until the Han Dynasty (3rd century B.C.–A.D. 3rd century), copper was applied to pottery decoration as colourant material [2]. During these early stages of manufacture, copper made artifacts mainly show blue or green because of divalent copper ion effects. Copper-red appeared much later than copper-green. And it was appeared firstly in glass in the Six Dynasties period (A.D. 3rd–6th century) and then was applied to

high-fired porcelain [3,4].

Copper-red has always been one of the hot issues in ancient ceramic academic circles for a long time. Changsha Kiln (A.D. 7th–10th century) is the original kiln which succeeded to produce high temperature copper-red porcelain with both red decoration porcelain and true copper-red monochrome porcelain firstly, even in the whole world [4–6]. Changsha Kiln site is located at Tongguan County in Changsha City of China, and it mainly fired in the Tang Dynasty (A.D. 7th–10th century) period. Changsha Kiln made two recognized significant contributions to Chinese ancient ceramics: multi-colour painted technique and invention of copper-red porcelain [7].

Scientific researches on Changsha Kiln began in the 1950s. Feng first discovered Changsha wares and stated that the products of Changsha Kiln were underglaze due to their condition of preservation [8]. Some scholars considered that Changsha Kiln also fired overglaze porcelain as well as underglaze porcelain [9–11]. Preliminary experiments prove that copper is the major colourant in red and green pigments of Changsha wares, while iron is the

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major colourant in brown pigments of Changsha wares [2,12,13]. Wood considered that Changsha copper-red porcelain contained tin oxide and that dissolved stannous oxide (SnO) made cuprous oxide deoxidize to colloidal copper metal to get copper-red effect [14]. In addition, Chen confirmed that the monochrome opaque glaze from Changsha Kiln was a kind of phase separation glaze by TEM and EDAX methods [15].

Because only a little amount of copper-red porcelain was successfully produced in Changsha kiln, although scholars admitted that the first successful use of copper-red in Chinese ceramics occurred at the Changsha Kiln, only a few shards of copper-red porcelain relics from the Tang Dynasty have been unearthed and absent fully scientific analysis as well [4,5,14,16]. Currently, scientific researches on colouration mechanism and production processes of its copper-red porcelain, especially copper-red pigments with opaque glaze situation, have not been noticed and studied yet.

So, in this paper, we analyzed a significant sample which excavated from Changsha Kiln by various scientific methods to give comprehensive studies on the glaze and its colour mechanism. Firstly, chemical composition was determined by Energy dispersive X-ray fluorescence (EDXRF). Then, to identify the copper species contained in red pigments, we applied X-ray absorption near-edge spectroscopy (XANES) and micro X-ray diffraction (μ -XRD). Meanwhile, stereomicroscopy was used on the sample to clarify the position of the pigments. Finally, the micro-morphological structure of glaze was analyzed by scanning electron microscopy (SEM) to reveal the formation of opacified glaze.

2. Materials and methods

2.1. Sample

The piece of copper-red pigments with opaque glaze porcelain, named as CS2, was supplied by the Institute of Cultural Relic and Archaeology of Hunan Province (see Fig. 1). Hunan Provincial Institute of Cultural Relics and Archaeology excavated Changsha Kiln site during 2010, and discovered this sample at wicket of the Y40 kiln of the site. The sample belongs to the initial stage copper-red porcelain product in China.

2.2. Experimental details

Chemical composition analysis is performed on an Eagle-III μ -probe energy-dispersive X-ray fluorescence (EDAX International Inc., USA). The spectrometer was equipped with a Rh X-ray target. The analytical instrument was operated at 40 kV and 60 μ A voltage-current of the X-ray tube, with a vacuum optical route and a beam spot of 40 μ m, and dead-time was around 30%. The excited sample emitted X-ray fluorescence with exit angle 65° and was recorded by Si (Li) detector when it crossed the solar slit. Red pigments, glaze and body were tested for 3 times respectively. And the final measurement results were the average of these three group's testing values. The mean is shown in Table 1.

Copper *K*-edge XANES spectra were collected at the beam line 4W1B, Beijing Synchrotron Radiation Facility (BSRF), China. The electron energy of the storage ring was 2.5 GeV, and during the measurements, the electron current dropped from 250 to 150 mA. XANES spectra were collected in fluorescence yield mode using Silicon Drift Detectors detector. The Si (111) double crystal monochromator was employed to scan over the *K*-edge of copper at 8979 eV. Result of the sample is illustrated in Fig. 2 along with standard references.

The micro X-ray diffraction (μ -XRD) patterns were collected on beam line 15U of the Shanghai Synchrotron Radiation Facility (SSRF, Shanghai, China) by angle-resolved measurements with a wavelength of 0.6888 Å. The monochromatic X-ray beam was produced by using double crystals (silicon 111) and was focused to a beam size of 3 (vertical) \times 4 (horizontal) μ m² full width at half-maximum by a pair of Kirkpatrick–Baez mirrors. The diffraction patterns were recorded by using a rayonix SX165 CCD detector. CeO₂ powder was used to calibrate the distance and orientation of the detector. The collected images were integrated into one-dimensional diffractions patterns by the software of FIT2D [17]. Red pigments on the sample were beaten to powder to achieve better results. We tested on different parts of red pigments for 3 times and got the same results. The result is shown in Fig. 3.

The sample was finely cut and polished separately to cross section and thin section for observation. The cross-section was examined and photographed with a Nikon SMZ1000 stereomicroscopy and the thin-section was observed and photographed with an Olympus BX51 polarizing microscopy.

The cross section had been cut flatly and polished, and then eroded through 2% HF acid for about 2 min. After the sample dried naturally, it was coated in vacuum with gold for about 2 min. After



Fig. 1. Photographs of CS2. (a) top view of CS2, scale bar: 1 cm; (b) micro-view of CS2, scale bar: 500 μ m.

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