

## Effect of Iron Oxide and Phase Separation on the Color of Blue Jun Ware Glaze

Fen Wang\*, Changan Yang, Jianfeng Zhu, and Ying Lin

*Shaanxi University of Science and Technology, Xi'an 710021, China*

Based on the traditional Jun ware glaze, the imitated Jun ware glazes were prepared by adding iron oxide and introducing phase separation agent apatite through four-angle-method. The effect of iron oxide contents, phase separation and the firing temperature on the color of Jun ware glazes were investigated by a neutral atmosphere experiment, optical microscope and scanning electronic microscope. The results showed that the colorant, mainly  $\text{Fe}_2\text{O}_3$ , contributed to the Jun ware glaze blue and cyan colors of Jun ware glaze. The light scatter caused by the small droplets in phase separation structure only influenced the shade of the glaze color, intensify or weaken the color, and thus made the glaze perfect and elegant opal visual effects, but was not the origin of general blue or cyan colors of Jun ware glaze. In addition, the firing temperature and the basic glaze composition affected the glaze colors to some extent.

**Keywords:** Blue Jun Ware Glazes, Phase Separation Structure, Iron Oxide, Coloring Mechanism.

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### 1. INTRODUCTION

Most of unearthed Jun ware glazes are blue with different hues and known as opalescence blue glazes.<sup>1,2</sup> According to the hue of color, the glazes can be divided into azure glaze, celeste blue glaze and moon white glaze, respectively. There are many viewpoints about the origins of blue colors and the role of iron oxide in the Jun ware glaze. Most of researchers believe that opalescence blue was caused by phosphate crystals,<sup>3</sup> especially ferrous phosphate<sup>4</sup> in the glaze. Kingery believes that the reflection and scattering of the glaze might occur due to the inhomogeneous structure of Jun ware glaze and its color was caused by the combination of opalescence, arisen from light scatter by small droplets of phase separation, and iron oxide.<sup>5</sup> However, most of the researchers, such as Tichane, Chen, Liu and so on, argue that blue colors of Jun glaze was only caused by the scattering of phase separation droplets, so the Jun ware blue was often called as “opalescence blue.”<sup>6–8</sup> With regard to the role of iron oxide in the glaze, there are also many different viewpoints. Guo believes that besides the effect of phase separation the blue of Jun ware glaze was not only caused by iron oxide but also associated with the content and proportion of cobalt

and copper.<sup>9</sup> Li believes that beside the effect of the concentration and size of phase separation droplets, another important factor is the effect of iron oxide, which made the opalescence blue glaze turn green or even yellow. That is to say, iron oxide did not make the glaze blue. On the contrary, it made the glaze turn green or yellow.<sup>10</sup> Zhang believes that blue colors of Jun ware glaze was a visual effect caused by the dispersed phase separation droplets in the glaze layer, which had a scattering effect on the visible light with short wavelength.<sup>11</sup> Ferrous oxide also played an auxiliary role on the appearance of Jun ware glaze. Based on the above analysis, it can be summarized that most of the researchers support the viewpoint that the blue was merely opalescence blue, arisen from the scattering of small droplets in phase separation glaze. The role of iron oxide in the glaze is still debatable. There are some viewpoints on the role of iron oxide: (1) Iron oxide was one of the blue colorants. (2) Iron oxide could make the opalescence blue hue shift to green or yellow color, that is to say, it was an adverse factor. (3) Iron oxide played an auxiliary role on the blue color of glaze. Therefore, it is necessary to further investigate the coloring mechanism of blue Jun ware glaze and the relationship between iron oxide contents and the glaze colors. In the current work, effect of iron oxide and phase separation on the color of Jun ware glazes was investigated through experimental

\*Author to whom correspondence should be addressed.

analysis. The color mechanism of blue Jun ware glaze was also discussed.

## 2. EXPERIMENTAL DETAILS

According to the chemical analysis of some ancient Jun ware glazes,<sup>7,9,10</sup> the preliminary basic glazes composition was 40~60% feldspar, 10~25% quartz, 5~15% calcite, 0~5% kaolin, 8~17% talc and 1~5% ZnO. Based on the above recipe, four-angle-method was adopted and the sample numbers are shown in Figure 1. Then different amounts of iron oxide (0, 2% and 5%) were added into all the basic glaze recipes to obtain the blue Jun ware glaze samples.

The raw material mixture was mixed with 60% water and milled by rapid milling machine for 20 min. The glaze slip was sieved and 0.3 wt% of commercial-grade dispersive agent  $\text{Na}_2\text{SiO}_3$  was added. The density of the slip was adjusted to 1.6–1.7  $\text{g}/\text{cm}^3$ . The glaze slip was applied to the biscuit testing pieces (stoneware body,  $\varphi$  4.5–5 cm) by dipping. The pieces were fired to different temperatures ranged from 1180 °C to 1230 °C with a heating rate of 2 °C/min, followed by soaking for 20 min at the maximum temperatures. The glaze samples were obtained after cooling down to room temperature. After cutting, grinding, polishing, the samples were corroded with 10% HF acid for 10 s and dried after being washed by distilled water. The microstructure of the as-prepared samples was examined by scanning electron microscopy (SEM, Hitachi S-3400N).

## 3. RESULTS AND DISCUSSION

### 3.1. Effect of Iron Oxide Content and the Basic Glaze Composition on the Glaze Colors

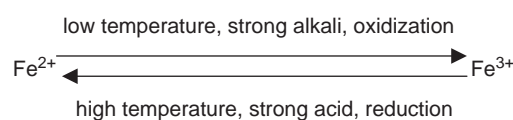
The as-prepared glazes with different amounts of iron oxide fired at reduction atmosphere always showed cyan

with different shades. However, the glazes showed different kinds of color when fired at neutral atmosphere. Figure 1 showed the relationship of the glaze color and its composition. In the case that the amount of iron oxide was below 3% the glazes located in the area of ABC triangle almost showed milky white. And the glazes in the vicinity of Corner D was colorless and transparent. On the contrary, the glazes with the color of blue, green, brownish yellow, etc. could be easily obtained when the amount of iron oxide was more than 5%, as shown in Figure 1.

The reason accounting for the versatile colors of the glazes was the role of iron oxide. When iron ions absorbed the visible lights selectively the valence electrons of iron ions in the glaze could hop between different energy levels and thus the glazes were colored. The electron configuration of Fe is  $[\text{Ar}]3d^64s^2$ . When being ionized Fe atoms lost two electrons of the outmost shell and transformed into  $\text{Fe}^{2+}$  ions.  $\text{Fe}^{2+}$  ion could be further ionized and transformed into  $\text{Fe}^{3+}$ . The electron configuration of  $\text{Fe}^{3+}$  is  $[\text{Ar}]3d^54s^0$ .  $\text{Fe}^{3+}$  is very stable and cannot be further ionized because it has five electrons on its *d* orbital. Consequently, iron ions includes  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$ , which have different absorption peaks in visible light spectrum and made the glazes different colors.  $\text{Fe}^{2+}$  could be easily oxidized into  $\text{Fe}^{3+}$  and  $\text{Fe}_2\text{O}_3$  would also decompose into FeO and  $\text{O}_2$  at high temperatures.

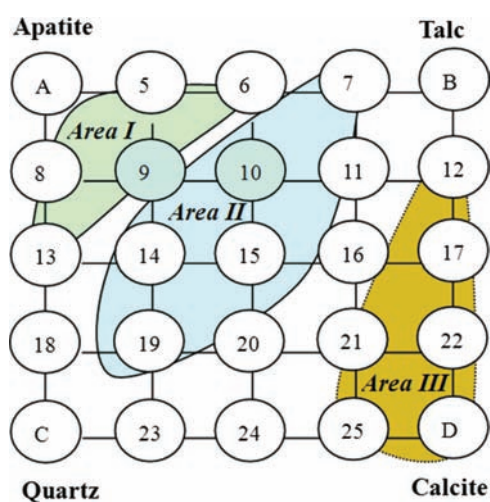
$\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  can coexist commonly.<sup>12</sup> In silicate glass,  $\text{Fe}^{3+}$  could form octahedron  $[\text{FeO}_6]$  with six coordinate oxygen ions and also form tetrahedron  $[\text{FeO}_4]$  with four coordinate oxygen ions.  $[\text{FeO}_4]$  could greatly absorb ultraviolet and visible light and made the glaze yellow and green while  $[\text{FeO}_6]$  hardly absorbed the visible light and made the glaze colorless or light pink.<sup>13</sup>

Professor Weyl<sup>14</sup> had done systematically study on the form of iron in glass. He argued that the relationship of  $\text{Fe}^{3+}$  and  $\text{Fe}^{2+}$  was as following:



Consequently,  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  could also coexist in the glaze and their relative amount might be influenced by many factors such as the amount of iron oxide, firing temperature, firing atmosphere, impurity element, basic glaze composition, and so on. That is why the as-prepared glazes showed many kinds of color. However, in the case of firing at a reduction atmosphere most of the iron ions were  $\text{Fe}^{2+}$ , which was the main reason for the green of celadon.

Among all the samples in Figure 1 Sample 14 were selected to investigate the firing temperature on the color of glaze. As shown in Figure 2 all the samples showed color feature of fancy glaze due to the segregation of iron oxide. When the firing temperature was 1180 °C the color feature of the glaze was milky blue background dotted



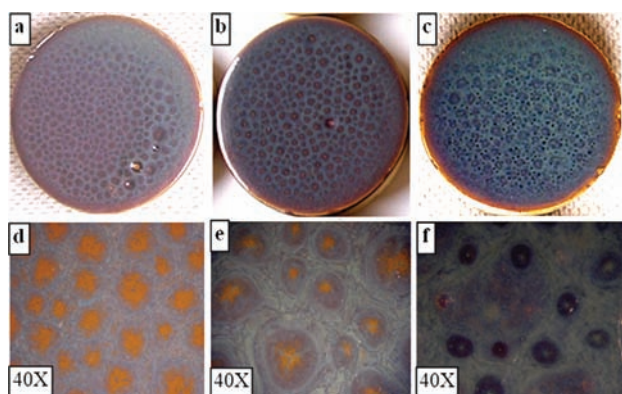
**Figure 1.** Schematic diagram of four-angle-method and the relationship of glaze color and its composition. Area I: Light green area; Area II: Blue area; Area III: Brownish yellow area.

with red spots due to the precipitation of red  $\text{Fe}_2\text{O}_3$  crystals from the glass phase. With increasing the firing temperature the precipitated  $\alpha\text{-Fe}_2\text{O}_3$  crystals would dissolve in the glass gradually. The amount of  $\alpha\text{-Fe}_2\text{O}_3$  crystals decreased and the blue glass rings formed which surrounded the red  $\text{Fe}_2\text{O}_3$  crystals due to the segregation of iron ions. With further increasing the firing temperature to  $1230\text{ }^\circ\text{C}$  all the red  $\text{Fe}_2\text{O}_3$  crystals re-dissolved in the glass and the glaze became light blue background dotted with dark blue spots.

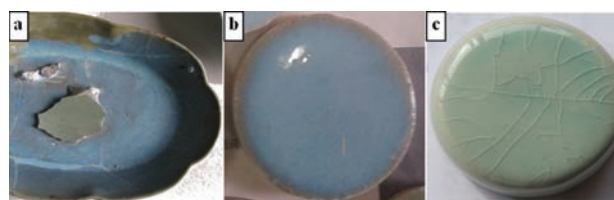
### 3.2. Effect of Phosphorus Oxide on the Glaze Color

Figure 3(a) showed an ancient Jun ware sample attached with a fragment of celadon. It can be seen that the ancient Jun ware sample was opalescence blue while the fragment of celadon was green. Figures 3(b) and (c) show the imitated Jun ware sample with P element and without P element, respectively. The sample with P element was opalescence blue while the sample without P element was green. Based on the above phenomena it can be concluded that it is P element that made Jun ware opalescence blue.

P element would facilitate the occurrence of phase separation of the glaze. The unit of silicate glass is  $[\text{SiO}_4]$  and the unit of phosphate glass is  $[\text{PO}_4]$  with a double-bond oxygen. When some  $\text{Ca}_3(\text{PO}_4)_2$  was introduced into the glaze composition  $\text{P}^{5+}$  would accelerate the phase separation of the silicate glass due its high valence and field strength. The ion potential of  $\text{P}^{5+}$  ( $Z/r = 14.7$ ) is higher than that of  $\text{Si}^{4+}$  ( $Z/r = 9.52$ ). The introduction of  $\text{P}^{5+}$  would increase the Gibbs free energy of the silicate glass. In order to decrease the Gibbs free energy  $\text{P}^{5+}$  would capture the bridge oxygen of silicate network and break the bond between  $\text{Si}^{4+}$  and  $\text{O}^{2-}$ .  $\text{P}^{5+}$  and the captured bridge oxygen would separate from the silicate network, along with alkali metal ions and alkaline-earth metal ions, and form a large amount of droplets rich in  $\text{P}^{5+}$ , alkali metal ions and alkaline-earth metal ions. The droplets would not re-dissolve in the matrix (silicate molten) due to the difference of composition and density, and thus the phase



**Figure 2.** Appearance (a)–(c) and optical micrographs (d)–(f) of Sample 14 fired at different temperatures: (a), (d)  $1180\text{ }^\circ\text{C}$ ; (b), (e)  $1200\text{ }^\circ\text{C}$ ; (d), (f)  $1230\text{ }^\circ\text{C}$ .

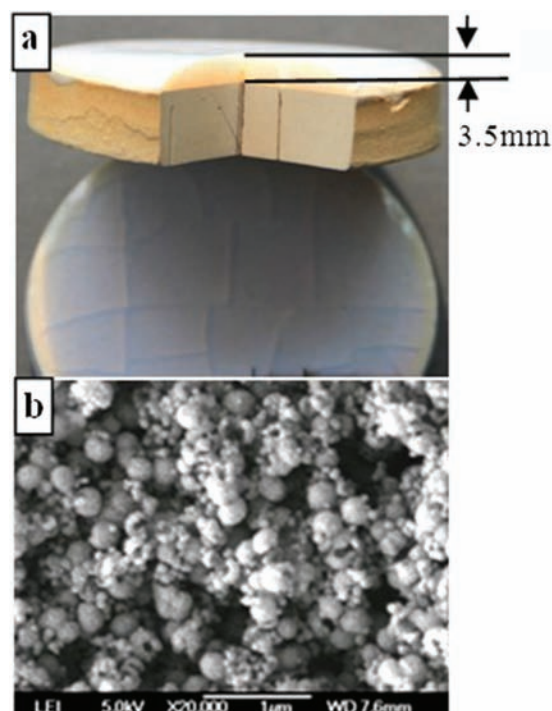


**Figure 3.** (a) Appearance of the ancient Jun ware sample attached with a fragment of celadon; (b) Appearance of the imitated Jun ware glaze sample; (c) Appearance of the imitated celadon sample.

separation structure formed. Additionally, the introduction of  $\text{P}^{5+}$  would also decrease the viscosity of silicate molten and thus the droplets could grow up very quickly. The decreased viscosity would also facilitate the aggregation of impurity ions. Hence, for the imitated Jun ware glaze with P element,  $\text{Fe}^{2+}$  was liable to precipitate around the droplets and bubbles, and was protected from being oxidized by the viscous silicate molten, which accounted for the blue color of the imitated Jun ware sample with P element.

### 3.3. Effect of Phase Separation on the Color of Glaze

According to the results of Kingery<sup>5</sup> the glaze composition of Jun ware glaze include P element and locates in the phase separation region of  $\text{K}_2\text{O-CaO-Al}_2\text{O}_3\text{-SiO}_2$  system. Therefore phase separation is common for Jun ware glaze. Many researchers believe that the blue of Jun ware glaze was opalescence blue caused by Rayleigh scattering. However, not all the phase separation structure



**Figure 4.** (a) Appearance of the opalescence blue sample without iron oxide; (b) SEM image of the opalescence blue sample without iron oxide.

could cause opalescence blue. The conditions for Rayleigh scattering are as following: (1) the size of the droplets is approximate to one tenth of the wavelength of visible light; (2) the distance between adjacent droplets is about three times of the diameter of droplets. If the phase separation droplets of Jun ware glaze meet the condition of Rayleigh scattering it can present beautiful cyan blue color. Whereas for many Jun ware glazes the phase separation structure was worm-like, which would diffusely reflected visible light, opacification would occurred and weakened the blue color of the glaze. This accounted for the light blue of the Jun ware glaze with a relative large amount of iron oxide. However, the glaze with an idea phase separation structure but without iron oxide in the composition could not present cyan blue color but present weak opalescence blue (Fig. 4). It can be concluded that iron oxide is also necessary for the coloring of Jun ware glaze.

#### 4. CONCLUSIONS

- (1) Iron oxide acted as the colorants in Jun ware glaze, which had the close relation with the phase separation structure. Colorant and the phase separation structure were both inevitable for blue Jun glaze colors.
- (2) It is iron oxide contents that made the Jun ware glaze appear different kinds of color. Besides, phase separation droplets made the glaze blue or cyan colors with different shades depending on the size, concentration and structure of the droplets.
- (3) The colorants of iron oxide caused the basic color of Jun ware glaze merely, but the phase separation structure not only influenced the coloring hue, but

also endowed the glaze with a beautiful and opal-like appearance.

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