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Jun ware glazes: chemistry, nanostructure and optical properties

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Abstract

A set of the *Classic* and *official* Jun ware shards found at various kilns at Yuzhou (Henan) are analyzed. The blue color and *milky* appearance of the glazes subject of intense debate as being due to either the glaze nanostructure or chemistry. The presence of submillimetre areas showing different color and opacity gives to the glazes a three dimensional *cloudy sky* appearance. Nanostructure and chemistry of the glazes, oxidation state of iron and nature of the copper nanoprecipitates are studied at a submillimetre level. Images of the glaze nanostructures are obtained using a Focus Ion Beam and Scanning Electron Microscope with nanometric resolution. The size and volume fraction of the nanostructures determined by image treatment are related to the chemical composition of the glazes. Differences between kiln productions are found and the origin of the color and opacity of the glazes discussed in terms of the chemistry and nanostructure.

Keywords

Glaze, color, absorption, scattering, Jun ware, nanostructure, liquid immiscibility

Introduction

Jun ware is one of the five famous wares created in the Northern Song dynasty (960–1126) in the first quarter of the 12th century (Tichane 1978; Wood 1999 and 2013) and which continued being produced during the Jin (1115–1234), Yuan (1271–1368) and early Ming (1368–1435) Dynasties. Jun ware is a high-fired grey-bodied stoneware with a subtle high temperature glaze of a pale bluish tone (Tichane 1978; Wood 1999 and 2013). It is classified as Classic Jun (including monochrome and Splashed Jun) and Official Jun (also called numbered Jun) (Tichane 1978; Wood 2013). Although there is not much debate about the continuity in the production of the Classic Jun, there is still a lot of debate about the dating of Official Jun, either placing it in the early Ming dynasty (Baoping 2006–7) or in the Jin or Yuan dynasties (Miao 2016). The Classic Jun is characterized by an opalescent light blue glaze to which purple/red splashes are applied while the Official Jun is characterized by the presence of a purple/red glaze either mixed or applied over a darker blue glaze. However, looking more closely, the blue glaze contains submillimeter areas of different blue shade and opacity which give to the glaze a three dimensional *cloudy sky*-like appearance. Contrariwise to other glazes translucency, medium gloss and depth of appearance are the most sought after characteristics of these glazes. The origin of the opalescent blue colors shown by Jun wares has been the object of many studies and much debate (Tichane 1978; Kingery and Vandiver 1983, 1986a and 1986b; Chen et al 1983 and 1989; Wood 2013; Wang et al 2012; Vandiver 2016). Scattering due mainly to the presence of a glass nanostructure but also of small microcrystallites of wollastonite and cristobalite, of undissolved quartz grains and submillimeter bubbles are considered responsible for the opalescence. The formation of a glass nanostructure has been proved to be a consequence of the specific composition of the Jun glaze, that is, a lime glass with a high $\text{SiO}_2:\text{Al}_2\text{O}_3$ ratio (above 7:1) which, when fired at temperatures of about 1200°C, undergoes a liquid-liquid separation (Kingery et al 1983; Chiang and Kingery 1983). Although it is known that the liquid-liquid phase separation depends primarily on the cooling rate for each specific composition within the immiscibility gap (Kingery and Vandiver 1983, 1986a and 1986b; Chen et al 1983 and 1989; Kingery et al 1983, Chiang and Kingery 1983; Vandiver 2016), the analytical models are not able to explain properly the final glass nanostructure and consequently, the mechanism of this process is still unsolved (Yimin et al 2005; Yang et al 2007; Vandiver 2016). Finally, the presence of

phosphorus and also magnesium have also been highlighted as favouring the development of the glass nanostructure and therefore for the enhanced opacity.

The presence of metal ions (iron and titanium) is also considered responsible for the blue color. However, the high amount of iron and titanium of the glazes (1.5-3 wt% Fe_2O_3 and 0.15-0.5 wt% TiO_2) should give a darker and more greenish color than the one shown (Kim et al 2011; Wood 2013). Various studies highlighted the combined effect of iron and titanium in the glaze (Kim et al 2011; Wood 2013) and in good agreement with Chinese porcelain analysis and modern replications gave a consistent maximum content of about 0.2% TiO_2 to obtain a blue glaze (Wood 1999).

Another characteristic of Jun ware glazes is that the reaction between the glaze and the stoneware ceramic gives rise to chemical inter-diffusion, so that an Al_2O_3 richer and CaO and SiO_2 poorer dark olive-brown glaze is formed at the interface where anorthite (calcium feldspar) crystals develop (Kingery and Vandiver 1983 and 1986a; Chen et al 1983, 1989; Wood 2013; Vandiver 2016). Although this glaze color is seen in those areas showing a thinner glaze, in particular at the edges of the objects, it is present everywhere below the blue glazes affecting their color and appearance.

Finally, the red and purple colors have also been studied and are related to the presence of copper on top of the blue glazes. The color has mainly been associated with the presence of cuprite (Chen et al 1983) although the presence of copper metal nanoparticles or even copper sulfide particles in the glaze has also been described, in particular in those blue glazes which show a dark blue and purplish color.

A selection of Jun wares showing various colors and appearances (see **Figure 1**) are analyzed and the reasons for their appearance discussed. The main novelty of this study is that the nanostructure is revealed within specific polished areas of the glazes cross section by a Focus Ion Beam (FIB) attached to a Scanning Electron Microscope (SEM) with a Schottky field emission which has nanometric resolution. The main advantage of this procedure is that the size and volume fraction of the glass nanostructure may be quantified at different areas of the glaze showing different colors and optical effects, and consequently relate them to the nanostructure. This method is selected in preference to Transmission Electron Microscopy (TEM) because, although the images obtained by TEM may have a higher magnification, they

also show overlapping nanostructures over the whole sample thickness (60-70 nm) which makes image analysis difficult. Finally, the chemical composition of the different areas of color glazes is also determined by means of an EDS attached to the SEM. Nevertheless, in order to measure the composition of the nanostructures TEM-EDS of some selected structures was also performed. Another important factor is the oxidation state of iron in the glazes, this is determined from different color areas of the glazes by Mossbauer spectroscopy.

Following this procedure the chemistry and nanostructure of different color areas of the glazes are determined. This will unambiguously reveal the causes of the variances in opalescence and color within different areas of the glazes and also of the differences between *Classical* and *Official* Jun ware glazes.

Finally, the diffuse reflectance of the glazes surfaces is measured by UV-Vis spectroscopy and the CIE *Lab** color coordinates determined, and the data is discussed in terms of the nanostructure and chemistry of the glazes, taking into account the overlapping of glaze areas and glaze layers with different opalescence and color.

Experimental procedures

The Jun ware samples studied belong to the collection of the Palace Museum in Beijing. They were excavated at Yuzhou (Henan). Six shards from the excavation of the Juntai kiln (JS23, JS24, JS26, JS27, JS77 and JS78)¹⁹ (Zhao 1975) and two from the excavation of the Zhiyaochang kiln in 2004 are analyzed (JS76 and JS80). Both kilns are found on the same site (500 meters apart) and belong to the official kilns from the court, that is, Official Jun. Four of the Juntai kiln shards show a red/purple glaze on one side and a blue glaze on the other side (JS78, JS24, JS26, JS27), the other two show light over dark blue glazes on both sides (JS77, JS23). From the two shards from Zhiyaochang kiln, both show only darker and lighter blue glazes (JS78, JS80) respectively. Three more shards were obtained from the excavation of the Liujiamen kiln, located 20 km to the west. They belong to the Classic Jun and two of them (JS2 and JS4) show red/purplish splashes (Splashed Jun) and the other a light blue glaze (JS5). Surface and cross section images from a selection of the studied shards are shown in **Figure**

1. The Classic Jun glazes from Liujiamen are homogeneous and show intermixed transparent blue areas and white patched clouds, except for the red/purple patches related to the red splashed decorations. The Official Jun blue glaze-surfaces show a dark blue background covered by whitish filaments (hair-like), and red and purple areas in the red glazes.

A crossbeam workstation (Zeiss Neon 40) equipped with SEM (Shottky FE) and 30 kV Ga-FIB columns, was used to obtain polished areas of the different color glaze areas from which SEM images were obtained at 5 kV; before ion beam polishing the area was coated with a thin protective Pt layer (1 μm thick) by ion-beam-assisted deposition. The ion beam was also used to prepare, extract, and polish the lamellae necessary for further TEM investigation. From the area previously coated with a thin protective Pt layer a lamella was cut and transferred to a TEM grid. In a final step, the lamella was thinned down to a thickness transparent to the electron beam (<60 nm). Chemical compositions of color glaze areas and the areas from where the images were obtained were measured by SEM-EDS (INCAPentaFETx3 detector, 30mm², ATW2 window and mineral and glass standards) operated at 20kV, with 120s measuring times.

High Resolution Transmission Electron Microscopy (HRTEM) images of some selected nanostructures were obtained on a JEOL JEM-2100 Lab6 electron microscope with an operating voltage of 200 kV. The chemical composition was determined by energy dispersive x-ray spectroscopy detector attached to the microscope.

Image treatment of the SEM pictures obtained was performed using ImageJ software (Schneider et al 2012). The area fraction, size distribution and average size of the nanostructures are determined from at least two pictures of each area.

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 (spot size of 3mm x 1mm and 1nm resolution, D65 standard illumination source, barium sulfate provided a white standard).

The ⁵⁷Fe Mössbauer spectroscopy studies of the various color glazes were performed in transmission geometry at room temperature using a 25mCi ⁵⁷Co source embedded in the Rh matrix. Mössbauer transmission spectra were collected in a velocity range of 4 mms⁻¹ and

1600 channels before folding. The spectrometer was calibrated using standard sodium nitroprusside. To model the distribution of iron sites in the amorphous glass, a two-dimensional Gaussian distribution for the isomer shift and the quadrupole splitting characterized by the average and standard deviation $\langle IS \rangle$, $\sigma(IS)$, $\langle QS \rangle$, $\sigma(QS)$ - and with a single correlation parameter between them, $\rho(IS, QS)$ (Alberto et al 1996; Stoch et al 2014). This fitting method has been successfully used in CaO-SiO₂-Fe-O glasses (Alberto et al 1996).

Theoretical Mie scattering extinction and scattering cross-sections were calculated for the spherical droplets up to third order using the series of spherical multipole partial waves (van de Hulst 1981).

Results

Cross sections of the glazes from a selection of the different kiln shards showing different colors are shown in **Figure 1**. Typically, the Classic Jun glazes from Liujiamen show a thick homogeneous glaze (above 1 mm thick). Chemical line profiles obtained on the cross sections of the glazes show a more or less homogeneous composition except where the presence of some quartz (Si rich peaks) and calcium phosphate particles (Ca and P rich peaks) are identified. Consequently, transparent blue areas and white clouds appear intermixed.

The Official Jun glazes from Zhiyaochang and Juntai show a marked decrease in the Ca content across the glazes, which is directly related to the light blue over dark blue glazes. Consequently, the glaze surface has the appearance of a net of whitish filaments over a dark blue background (**Figure 1**). Zhiyaochang glazes are extremely thin (about 0.3 mm) while Juntai glazes are thicker (between 0.6 and 0.8 mm) but thinner than Liujiamen glazes.

An olive-brown transparent glaze at the ceramic-glaze interface is seen in all the samples. It is characterized by a higher Al and K, and lower Ca contents than the blue glazes and a thickness which varies between 50 and 100 μm for Liujiamen and Juntai and between 100 and 150 μm for Zhiyaochang. At the ceramic-glaze interface crystallites of Ca-rich feldspar (Ca and Al rich peaks) are identified.

Chemical analysis of different color areas of the glazes were obtained by SEM-EDS on the polished cross sections of the glazes. **Figure 2A** shows, in good agreement with the literature, that the blue color of the glazes is related to a $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio which is above 7; while the brown glazes show a higher Al_2O_3 content resulting from the interaction with the ceramic. We can also see that a lighter blue color is obtained in those glazes showing a higher CaO content (between 7% and 10% for the dark blue and between 9% and 14% for the light blue), **Figure 2B**. Finally, the TiO_2/FeO ratio of color glazes is kept low, below 0.25 while the olive-brown glazes show larger values (between 0.2 and 0.8), **Figure 2C**.

Figure 3, 4 and 5 show the typical glass nanostructures corresponding to different color areas of the glazes from the three kiln samples studied, Juntai, Zhiyaochang and Liujiamen. All the color areas show the presence of a glass nanostructure which is a consequence of the formation of two immiscible liquids at high temperature. Contrariwise, the nanostructure is not observed in the olive-brown glaze. The glaze nanostructure shows light glass nano-droplets on a dark glass matrix, which is a consequence of the different chemical composition of the both glasses (droplets and matrix). Our data is in good agreement with the literature (Kingery and Vandiver 1983, 1986a and 1986b) in which it is reported that the $\text{K}_2\text{O}-\text{Al}_2\text{O}_3-\text{CaO}-\text{SiO}_2$ quaternary system with 70.5 and 76.5 mol% SiO_2 and a $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio above 7 showed the formation of calcium rich droplets in a silica rich matrix, at maximum temperatures between 1200°C and 1300°C. SEM-BSE images of calcium rich glass droplets are expected to show a lighter color than those glass matrix areas which are silica rich.

Two different types of nanostructures are observed, spherical glass nano-droplets over a darker glass matrix which are smaller in the dark blue areas than in the light blue areas; and worm-like nano-droplets in the darker blue areas which are thicker and form large interconnected structures in the lighter blue areas. Spherical droplets are the main nanostructure found in the Classic Jun while small worms and worms forming interconnected areas in the light blue areas predominate in the Official Jun glazes. The volume fraction which is equal to the area fraction (Underwood 1970) of the light droplets structure, the size distribution and average size of the droplets in terms of area and also of diameter for the spherical droplets are calculated from the images, and the chemical composition determined by SEM-EDS. **Figure 6** shows some relevant correlations between the nanostructure observed and the chemical composition.

Figure 6A shows how spherical droplets are the main nanostructure in the Classic Jun while worms and large interconnected areas predominate in the Official Jun glazes. **Figure 6B** shows how small spherical droplets and larger spherical droplets in the Ca richer areas predominate in Liujamen glazes, while small spherical droplets, then worms and finally interconnected structures predominate with increasing CaO contents in the Juntai and Zhiyaochang glazes. **Figure 6C** shows that the color glazes have always a low TiO_2/FeO contents independently of the nanostructures formed which is contrary to the situation for the brown glaze. **Figure 6D** show that the volume fraction of droplets increases with the CaO contents of the glaze up to a maximum of about $25\pm 2\%$. **Figure 6E** shows that the size of the nano-droplets increases more or less linearly with the CaO content of the glazes. This linearity is lost when a low amount of very large spherical droplets are formed, which often happens closer to the interface of the ceramic and the glaze in some Liujament glazes (see **Figure 5**). Those large droplets are formed in areas showing a high P_2O_5 content (**Figure 6F**).

The chemical composition of the droplets and matrix has been studied by TEM-EDS analysis. Two lamellas of $6\text{ }\mu\text{m} \times 5\text{ }\mu\text{m}$ and 60 nm thick were cut, thinned, extracted and polished by the FIB; one from a Classical Jun glaze (JS4) showing typical large spheres nanostructure (**Figure 7A**) and another from an Official Jun glaze (JS80) showing a large interconnected nanostructure (**Figure 7B**). The images are obtained in transmission and consequently, in contrast to the SEM images, the droplets appear dark in a light matrix.

TEM-EDS analysis of the droplets and the matrix was also attempted using short counting times to avoid, as far as possible, the Na and K diffusion outside the area. The area analysis was compared to those measured in a nearby area by SEM-EDS, and was used to calibrate the EDS spectrum corresponding to the droplets and matrix, a procedure which provided a semiquantitative analysis of the droplets and matrix. Consistent results were obtained for the JS4 which are given in **Table I** but not for JS80. The spherical droplets from JS4 (**Figure 7A**) are Ca rich, but they also concentrate Mg, Fe, Ti, and P, whereas the matrix is Si rich and appears also to concentrates K and Na, although the data corresponding to those two elements is less accurate and has a larger variation ($\sim 30\%$) between measurements. The index of refraction, density at room temperature (RT) and at 1400°C , and viscosity related to both glasses were estimated (Priven and Mazurin 2003; Flugel 2007). The results obtained for JS4 suggested that the spherical droplets were produced by nucleation and growth

within the metastable region of the liquidus separation curve. In this case, the droplets have already the equilibrium composition, with a sharp interface with the matrix around and equilibrium at all stages of transformation.

On the contrary, analysis of different dark and light areas in the interconnected nanostructure from JS80 (**Figure 7B**) was attempted, but large variations in the composition were always obtained. In fact the results showed a continuous change in the composition across the nanostructure-matrix interface. This result suggests that the nanostructure evolved in the unstable area of the liquidus separation curve by spinodal decomposition. In this case the concentration of diffusing species varies from point to point and has a diffuse boundary.

The differences in the chemical composition, in particular the K_2O/Na_2O ratio, between the Classical and Official Jun glazes may be responsible for this different behavior, although the use of a different soaking temperature should also be considered.

The oxidation state of iron in the glazes is also very important, and for this reason in those cases when this was possible, the different color glazes were mechanically separated and analyzed by Transmission Mossbauer Spectroscopy. **Figure 8** shows the spectra and **Table II** the fitted parameters for a dark blue (JS77), a light blue (JS80 and JS4) a dark blue over a brown glaze (JS23) and a brown glaze (JS78). The dark blue and light blue glazes contain predominantly Fe^{2+} (82% of the total iron content), but in contrast, the brown glaze shows a predominant Fe^{3+} contribution (77% of the total iron content) and the blue over brown glaze an intermediate content (47% of the total iron content). Reducing conditions are necessarily kept before the melting of the glaze to ensure the predominance of Fe^{2+} in the glaze.

Nevertheless, the presence of other metal transition ions which may have several oxidation states, such as titanium (Ti^{3+} and Ti^{4+}), manganese (Mn^{2+} , Mn^{3+} , Mn^{4+}) or arsenic (As^{3+} , As^{5+}), among others, are known to modify ratios between the oxidation states of the multivalent species contained in the molten glass (Kim et al 2011; Jeon et al 2014). Titanium, the metal transition element found in the Jun glazes, has been identified as the main color modifier in high temperature Chinese glazes, with the blue glazes containing $TiO_2 < 0.2\%$ and with the addition of higher TiO_2 turning the bluish glaze green (Wood 2013). Recently, some studies combining Mossbauer Spectroscopy and Electron Spin-Resonance Spectroscopy (Kim et al

2011; Jeon et al 2014) have demonstrated the oxidation of Fe^{2+} into Fe^{3+} and simultaneous reduction of Ti^{4+} into Ti^{3+} in high temperature celadon glazes. In fact, our data shows that the blue/green color of the glazes is not related to the absolute content of TiO_2 but rather to the TiO_2/FeO ratio. Fe^{2+} is the predominant ion in the blue glazes which contained a TiO_2/FeO ratio below 0.25 while Fe^{3+} is the predominant ion in the olive-brown glazes which have a TiO_2/FeO ratio above 0.25 (**Figure 2C** and **Figure 6C**).

With regard to the red and purple areas of the glazes, **Figure 9** shows the FIB-SEM images for Classical and Official Jun wares, in both of which copper rich nanoparticles, larger in the red areas (~30-70 nm) and smaller in the purple areas (~10-30 nm), are seen. The particles appear mainly present inside the Ca-rich droplets.

A representative selection of the UV-Vis reflectance spectra of the glazes is shown in **Figure 10A**. A large reflectance between 400 nm and 600 nm for the lighter blue glazes is observed. The curve appears asymmetrically peaked at 400 nm (blue) for those which are dark blue. An important absorption peak between 550 nm and 600 nm, related to the presence of copper metal nanoparticles (Kreibig and Vollmer 1995), is observed in the red and purple glazes. Finally, dark violet and olive-brown glazes show a low reflectance at all wavelengths.

Generally speaking the color seen is the combination of intermixed dark blue transparent and white opaque regions for the Classic Jun glazes. For the Official Jun, a light blue glaze, in which the white opaque areas dominate, covers a dark blue glaze where the dark blue transparent areas dominate. Consequently the surface color of the glazes depends on which areas dominate over the other, and the overlapping of translucent layers with different color. A red color is observed in the opaque white areas containing copper metal nanoparticles while the purple/violet colors are obtained in those dark blue transparent areas where copper metal nanoparticles are present. A selection of the different cases is shown in **Figure 10A**: mixed light blue/dark blue (LB&DB), light blue (LB), dark blue (DB), light blue over dark blue (LB over DB), brown (Bwn) red (E) and purple (P) glazes.

The color coordinates (Cie *Lab**) were also calculated for all the glazes and are shown in **Table III** and in the hue wheel shown in **Figure 10B**. The hues of light blue glazes vary between blue-green and turquoise while the hues of mixed light and dark blue and of light over dark blue glazes vary between turquoise and blue. The hues of dark blue glazes

correspond to blue, and the purple and red hues vary between blue violet and magenta. Finally, the brown and some dark purple glazes show also a very low saturation. As the olive-brown glaze is present always below the blue glazes, the final color of the glazes depends not only on the relative amount and disposition of white opaque and transparent blue areas but also on their thickness.

Discussion

The results obtained demonstrate the formation of two different types of nanostructures in the historical Jun ware glazes; that is, either spherical calcium, iron, titanium and phosphorous rich droplets in a silica rich matrix, or worms and interconnected structures of variable composition. The first type predominates in the Classic Jun glazes while the second one in the Official Jun glazes. The formation of both nanostructures is consistent with the existence of an immiscibility region in the system (Kingery et al 1983; Chiang et Kingery 1983). The simultaneous addition of K_2O (or Na_2O) and Al_2O_3 to a CaO rich glass was found to reduce the maximum temperature for liquid-liquid separation, and at the same time greatly enlarged the compositional immiscibility region (Kingery et al 1983; Chiang et Kingery 1983). In agreement with our results, calcium rich droplets in a silica rich matrix occurring in the $K_2O-Al_2O_3-CaO-SiO_2$ quaternary system with 73.5 ± 3.5 mol% SiO_2 and a SiO_2/Al_2O_3 ratio above 7 at maximum temperatures between $1200^\circ C$ and $1300^\circ C$ were reported in the literature (Kingery and Vandiver 1983, 1986a and 1986b; Chen et al 1983 and 1989). Moreover, a fine interconnected nanostructure (some tens of nanometers in size) was obtained for SiO_2/K_2O contents of about 11 while decreasing the ratio to 7 produced a structure with larger lime rich droplets (about $2 \mu m$ in diameter) with wollastonite precipitates inside. The equivalent $Na_2O-Al_2O_3-CaO-SiO_2$ quaternary system showed also immiscibility with typical maximum temperatures about $1250^\circ C$. Consequently, a high SiO_2/Al_2O_3 ratio (above 7) is necessary to generate the immiscibility region, while a high SiO_2/K_2O ratio (~ 11 , above 13 in our case) is responsible for the fine nanostructure obtained. Our data suggests also that a low K_2O/Na_2O ratio (below 5) is also favoring the formation of spherical droplets (nucleation and growth) while a higher K_2O/Na_2O ratio favors the formation of worms and interconnected structures (spinodal decomposition). However, the firing temperature which may be different between samples is also an important parameter responsible for the nanostructure formed.

Nevertheless, this is not relevant when comparing the nanostructures formed in different areas of the same glaze, where only the differences in the chemical composition (mainly the CaO content but also to some extent the P content) are responsible for the nanostructure developed.

On the other hand, the existence of liquid immiscibility (Si rich and Fe rich) in multicomponent basaltic systems has long been recognized (Roedder 1977 and 1992; Philipotts 1982). Recently the existence of a super-liquidus with silicate liquid immiscibility at temperatures of 1200°C at 1 atm and reducing conditions (Hou and Veksler 2015) has been reported. In those cases two liquids, a silica rich (incorporating also Al, K and Na) and an iron rich (incorporating also Ca, Mg, P and Ti) were reported, in agreement with our glazes nanostructures.

The double-glass nanostructure with different refraction indices is responsible for the scattering of the light, the so called Mie scattering. The light travels thorough the glaze until it is scattered in the nanostructure (after either single or multiple scattering processes) or absorbed by the metal ions present in the glaze.

The light back-scattered in the nanostructure (after either single or multiple scattering processes) reaches the surface of the glaze; consequently, a larger volume fraction of droplets will produce a higher total diffuse reflectance (producing more luminosity and also more opacity). Contrariwise, the light reaching the glaze-ceramic interface will be essentially absorbed in the nanostructure-free olive-brown glaze. The color observed is therefore a combination of both scattering and absorption in the glaze.

Figure 10C shows the iron and titanium absorption bands for a silicate glass (Bamford 1977; Ehrt et al 2001). Apart from a large UV absorption band, Fe^{3+} shows weak absorption bands in the blue while Fe^{2+} has an intense broad absorption band in the red and infrared giving yellow and blue hues respectively; Ti^{3+} shows weak broad absorption band in the green-yellow giving a pinkish color to the glass.

With regard to the light scattered, the range of wavelengths depends of the size of the droplets (van de Hulst 1981). For an equivalent volume fraction of spherical droplets the wavelength dependent scattering coefficient may be calculated, **Figure 10D**. For those

droplets with $d \ll \lambda$, the light scattered follows the so-called Rayleigh approximation, $I_s \sim 1/\lambda^4$; this means that the light is predominantly scattered in the UV-violet-blue. However, the light scattered by large droplets (≥ 400 nm) is shifted to longer wavelengths, that is, from blue to yellow. Moreover, multiscattering will also take place; it will be responsible for scattering at larger wavelengths. Similarly, the presence of worms or interconnected structures will also produce scattering at larger wavelengths (van de Hulst 1981). Finally, the presence of a higher volume fraction of the droplets is responsible for greater scattering, and consequently for a higher luminance and opacity of the glaze. Nevertheless, the characteristic Ultraviolet light absorption counteracts the large scattering at short wavelength of the glazes, with the so-called glass cut-off occurring between 300 nm and 400 nm depending on the glass composition, **Figure 10A**.

Consequently, those areas of the glazes containing small droplets have blue-biased scattering which combined with a dominant Fe^{2+} absorption will make them appear dark blue. In contrast those areas containing larger nanostructures have a broad yellow-shifted scattering which combined with the dominant Fe^{2+} absorption make them appear light blue. As the areas containing smaller droplets also contain a lower volume fraction, they tend to show lower luminance and appear more transparent than those having larger nanostructures which show a high reflectance (luminance) and appear more opaque.

Finally, the presence of sub-millimeter areas or glaze layers containing small droplets (dark blue and transparent) with others containing larger nanostructures (light blue and more opaque) will give the final color (dark or light blue) and the pearly translucency to the glazes.

Although the presence of bubbles has been considered also responsible for the opacity shown by the glazes, the micrometric size of the bubbles cannot account for the scattering observed. On the contrary, the glaze nanostructure resulting from a high temperature liquid-liquid immiscibility is responsible for the light scattering and, consequently, the increase in the luminosity and opacity of the glaze.

The Surface Plasmon Resonance (SPR) extinction peak between 550-600 nm (**Figure 10A**) demonstrates the presence of copper metal nanoparticles in both the red and purple glazes (Kreibig and Vollmer 1995). The exact intensity, position and width of the SPR peak depends

mainly on the size of the nanoparticles, **Figure 10C**. The color obtained is a combination of red on a white glaze (ie red) and red on a blue glaze (ie purple).

Finally, the presence of Ca-rich areas (submillimeter structures) is not only responsible for the enhanced opacity but also for a greater density and lower viscosity (at the firing temperature) of the liquid as compared to the Ca-poor areas (Priven and Mazurin 2003; Flugel 2007). This together with the different nanostructures formed (small and large spheres, or worms and large interconnected areas) may also be accountable for the different flow patterns (white filaments and clouds) observed.

Conclusions

Chemical and nano- and micro-structural differences between Jun wares from Juntai and Zhiyaochang and Liujiamen kilns showing various colors and appearances have been identified. The different nanostructures observed (worms and largely interconnected areas predominant in the Official Jun glazes, and spherical droplets predominant in the Classic Jun glazes) have been related to the different K_2O/Na_2O content of the glazes. Higher CaO is responsible for a greater volume fraction of droplets and higher P_2O_5 in the calcium rich areas to larger spherical droplets.

The different color and appearance of the glazes is related to the glass nanostructure, through the combination of scattering at the interfaces between the two glass phases, and large absorption of the metal ions present in the glazes (predominantly Fe^{2+} in the blue areas and Fe^{3+} in the brown glazes). A small size/low volume fraction and a large size/high volume fraction of droplets are responsible for the dark blue-transparent areas and light blue-opaque regions respectively. The overall color of the glazes is enhanced by the presence of a dark brownish glaze between the dark or light blue glaze and the ceramic interface. The red and purple colors are the result of the presence of small copper metal nanoparticles in the light blue opaque and dark blue transparent areas. The small copper metal nanoparticles appear to be incorporated into the Ca-rich droplets.

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Figure captions

Figure 1. (left) Surface, (middle) cross section image and (right) Si, Al, Ca, Fe and K cross section line scans corresponding to different color shards from the three kilns studied.

Figure 2. (A) $\text{SiO}_2/\text{Al}_2\text{O}_3$ versus $\text{K}_2\text{O}/\text{Na}_2\text{O}$, (B) $\text{SiO}_2/\text{Al}_2\text{O}_3$ versus CaO and $\text{SiO}_2/\text{Al}_2\text{O}_3$ versus TiO_2/FeO of the shards analyzed. Dots for Liujiamen, stars for Zhiyaochang, and diamonds for Juntai kiln shards. The colors account for dark blue (blue), light blue (cyan), red (red), purple (purple) and olive-brown (olive) glazes.

Figure 3. SEM images of FIB polished images corresponding to (A) blue and (B) olive-brown color areas for from a typical Official Jun from Juntai kiln showing the characteristic worm and worm with large interconnected nanostructures.

Figure 4. SEM images of FIB polished images corresponding to blue (JS78) and olive-brown (JS80) color areas for typical Official Jun from Zhiyaochang kiln showing the characteristic worm and worm with large interconnected nanostructures

Figure 5. SEM images of FIB polished images corresponding to the color areas indicated from a typical Classic Jun from Liujiamen kiln shards showing the characteristic spherical droplet nanostructures. The size distributions are also shown.

Figure 6. Relationship between chemical composition and nanostructure. Dots: Liujiamen; stars: Zhiyaochang and diamonds: Juntai kiln shards.

Blue: small spheres; cyan: large spheres; red: worms and magenta: large interconnected areas. (A) $\text{SiO}_2/\text{Al}_2\text{O}_3$ versus $\text{K}_2\text{O}/\text{Na}_2\text{O}$. (B) $\text{SiO}_2/\text{Al}_2\text{O}_3$ versus CaO. (C) $\text{SiO}_2/\text{Al}_2\text{O}_3$ versus TiO_2/FeO of the areas analyzed. (D) Volume fraction of droplets versus CaO contents. (E) Droplets area versus CaO and (F) P_2O_5 content respectively. The line in (D) and the band in (E) are drawn as a guide to the eye.

Figure 7. TEM images of (A) JS4 showing black spherical nanodroplets over a light matrix and (B) JS80 showing largely interconnected nanostructure.

Figure 8. Transmission Mossbauer spectroscopy for different color glazes. From bottom to top: JS77F dark blue glaze, JS4F light blue glaze, JS23 brown and blue glaze and JS78 brown glaze.

Black line: fitted spectra; red line: Fe^{2+} doublet; blue line: Fe^{3+} doublet; green line: Fe^{3+} doublet.

Figure 9. FIB-SEM images of the nanostructures from (A) *Classic Jun* (JS4) red (top) and purple (bottom) areas and (B) *Official Jun* (JS27) red (top) and purple (bottom) areas. Large copper metal nanoparticles are observed in the red areas while smaller copper metal nanoparticles in the purple areas.

Figure 10. UV-Vis diffuse reflectance spectra. (A) Characteristic spectra of the different glaze color combinations: Mixed light blue/dark blue (LB&DB), light blue (LB), dark blue (DB), light blue over dark blue (LB over DB), brown (Bwn), red (R) and purple (P) glazes.

(B) *Cie Lab** color coordinates from the different color glazes.

(C) Absorbance by unit thickness of a lime silicate glass with the same concentration of Fe^{2+} , Fe^{3+} , Ti^{3+} and Ti^{4+} . Extinction cross section spectra for 30 nm and 60 nm Cu^0 nanoparticles.

(D) Scattering coefficient calculated using Mie theory for the same volume fraction of spherical droplets of varying sizes.

Table I. Chemical composition of the spherical droplets and of the matrix for JS4 determined by TEM-EDS. The index of refraction (n) and density (ρ) calculated from the chemical composition after [Priven and Mazurin, 2003, and viscosity (η) after Flugel 2007.

JS4	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	P ₂ O ₅	K ₂ O	CaO	TiO ₂	FeO	n	ρ (g/cm ³) RT	ρ (g/cm ³) 1400°C	Log(η (Pa·s)) 1250°C
Matrix	1.4	0.9	9.3	74.4	0.2	3.9	8.9	0.2	0.8	1.503	2.729	2.322	3.1
Droplets	0.2	3.7	8.2	59.7	1.1	1.0	23.1	0.5	2.4	1.545	2.443	2.538	1.9

Table II. Mössbauer fitted parameters. (o) octahedral and (t) tetrahedral coordination. <IS> and <QS> Average values and σ (IS) and σ (QS) Gaussian widths of the distributions of the Isomer Shift and Quadrupolar Splitting and ρ (IS,QS) correlation parameter between IS and QS.

sample	glaze		<IS>	<QS>	σ (IS)	σ (QS)	ρ (IS,QS)	%
JS77	dark blue	Fe ²⁺ (o)	1.07	2.02	0.09	0.49	0.28	82
		Fe ³⁺ /Fe ²⁺	0.52	1.08	0.18	0.62	0.27	18
JS4	light blue	Fe ²⁺ (o)	1.07	1.94	0.11	0.47	0.65	82
		Fe ³⁺ (t)	0.20	1.29	0.10	0.37	0.54	18
JS23	brown & blue	Fe ²⁺ (o)	1.02	1.84	0.22	0.50	0.00	51
		Fe ³⁺ (t)	0.31	1.30	0.14	0.17		30
		Fe ³⁺ (t)	0.20	0.38	0.07	0.12		19
JS78	brown	Fe ²⁺ (o)	1.00	1.92	0.20	0.54	0.00	23
		Fe ³⁺ (t)	0.25	1.32	0.18	0.24		47
		Fe ³⁺ (t)	0.21	0.34	0.07	0.13		30

Table III. Cie Lab^* color coordinates obtained from the Reflectance UV-Vis spectra measured directly on the surface of the glazes. Rear (R) and front (F) sides. L^* lightness, a^* and b^* color coordinates, chroma, $c^* = \sqrt{a^{*2} + b^{*2}}$, hue, color measured in terms of the angular position in the CIE Lab^* chromaticity diagram,

$$h^* = \tan^{-1}(b^*/a^*) \text{ and saturation, } s^* = c^* / \sqrt{c^{*2} + L^{*2}}.$$

kiln	glaze	color	L^*	a^*	b^*	c^*	$h^*(^\circ)$	$s(\%)$
<i>Zhiyaochang</i>	JS76R	dark blue	43.3	-0.3	-7.2	7.2	268.0	16.4
		light ov. dark blue	31.0	-2.1	-1.5	2.6	214.1	8.4
	JS76F	dark blue	34.4	0.1	-11.9	11.9	270.7	32.7
		light ov. dark blue	50.4	-6.6	-10.4	12.3	237.6	23.7
	JS80F	light blue	60.7	-5.9	1.0	6.0	170.7	9.9
	JS78F	brown	29.4	0.1	-0.2	0.3	146.6	1.0
<i>Juntai</i>	JS26R	light & dark blue	37.2	-3.0	-4.8	5.7	238.3	15.1
	JS26F	Purple	28.9	6.3	-5.8	8.5	317.2	28.3
	JS24R	light & dark blue	44.5	-2.5	-4.8	5.4	242.2	12.0
	JS24F	purple	38.9	5.3	-5.8	7.9	311.1	19.9
	JS27F	purple	43.6	8.6	-6.0	10.5	325.1	23.4
	JS27R	light blue	51.0	-8.1	-3.0	8.6	200.6	16.6
	JS77R	dark blue	43.3	-0.3	-7.2	7.2	268.0	16.5
		light ov. dark blue	53.2	-7.2	-7.8	10.6	227.2	19.5
	JS77F	dark purple	28.3	1.0	-1.0	1.4	315.4	5.0
		dark blue	29.5	0.4	-4.2	4.5	291.8	15.0
	JS23R	dark blue	44.4	-0.4	-6.1	6.2	265.8	13.7
		brown	29.5	1.0	2.9	3.1	71.9	10.3
	JS23F	light blue	44.0	-3.8	-2.8	4.8	216.3	10.8
		dark purple	33.3	1.3	-1.3	1.8	314.4	5.5
<i>Liujiamen</i>	JS2R	light & dark blue	43.3	-4.8	-3.5	5.9	216.1	13.5
	JS2F	red	38.0	4.5	0.0	4.5	121.2	11.8
	JS4R	light & dark blue	43.0	-5.3	-3.0	6.1	209.5	14.0
	JS4F	light blue & dark blue	40.9	-3.6	-5.0	6.2	234.3	15.0
	JS5R	light blue	67.8	-8.0	-2.4	8.3	196.9	12.2
	JS5F	light blue	58.3	-7.3	-4.0	8.3	208.6	14.0