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Article in Journal of Archaeological Science · July 2014

DOI: 10.1016/j.jas.2014.04.005

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Focus

Archaeometric investigation of the relationship between ancient eggwhite glazed porcelain (*Luanbai*) and bluish white glazed porcelain (*Qingbai*) from Hutian Kiln, Jingdezhen, China



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ARTICLE INFO

Article history: Received 13 September 2013 Received in revised form 21 March 2014 Accepted 5 April 2014 Available online xxx

Keywords: Luanbai Egg-white glazed porcelain Qingbai, bluish white glazed porcelain Reflectance spectrum Micro-structure Chemical composition Firing temperature

ABSTRACT

Hutian Kiln, located in Jingdezhen City of Jiangxi Province of China, is well-known for the productions of bluish white glazed porcelain (Qingbai) from Song Dynasties (AD 960 - AD 1279) and egg-white glazed porcelain (Luanbai) of Yuan Dynasty (AD 1271 - AD 1368). Luanbai with an opaque glaze is thought to have evolved from *Qingbai*, which has a transparent glaze; however, the precise technological details for this process have not been adequately studied. This paper presents the analyses of samples of Luanbai and Qingbai porcelains from Hutian Kiln using various microscopic studies, including visible light spectrometry and Energy-dispersive X-ray fluorescence. Some distinct technical changes have been identified that help to explain the evolution from transparent Qingbai to opaque Luanbai glaze. First, there is an increase in the proportion of potassium-rich ingredients in sherds dating to Late Song Dynasty, which suggests a change in the glaze recipe. Second, during Yuan Dynasty, both types of porcelain share the same chemical composition, but Luanbai products display distinct micro-structures and opacity in contrast to the Qingbai ware. Third, the overall firing temperature of Luanbai is around 1270 °C which is generally around 100 °C higher than that of Qingbai. The opacity of Luanbai ware may be the result of different firing techniques, including the higher firing temperature and a correspondingly longer time to heat and to cool the glazed porcelain. The results reveal new insights on the coloring mechanism of the two kinds of glaze and the transition from Qingbai of Song Dynasty to Luanbai of Yuan Dynasty.

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1. Introduction

Jingdezhen district in Jiangxi Province is the most famous region of porcelain-making in southern China. Since the period of the Five Dynasties (AD 907 – AD 960), the porcelain craftsmen in Jingdezhen district developed manufacturing techniques that eventually made this district the predominant porcelain production center in China. It has also been referred to as "the porcelain capital" of both

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China and the world in Ming (AD 1368 – AD 1644) and Qing (AD 1644 – AD 1911) Dynasties. In Jingdezhen district, more than 300 ancient kilns have been found, and 136 kilns are dated from the Song (AD 960 – AD 1279) and Yuan Dynasties (AD 1271 – AD 1368) (JPICRA and JMCK, 2007). Among these kilns, the Hutian Kiln is the most significant one, because it has the largest scale and longest history of porcelain production from the Five Dynasties to Ming Dynasty. The products of this kiln were exported to Japan and the Southeast Asian countries (Feng, 1979). The porcelain-making technology of Jingdezhen and particularly the products of this kiln over the period of seven centuries provide an excellent source of data for understanding developmental history of Chinese porcelains.

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In the Hutian Kiln, some kinds of porcelain are well-known, including Qingbai ware, Luanbai ware, and famous blue and white porcelain. These products were popular from the Song (AD 960 -AD 1279) to Qing Dynasties (AD 1644 – AD 1911), and completely changed the profile of Chinese porcelain production. Qingbai in Chinese literally means "clear blue-white" and its name derives from its transparent or translucent icv-bluish glaze. This type of glaze is also called *ving-chhing* porcelain, or bluish white glaze. Once established these Qingbai wares remained in fashion at Jingdezhen from the late 10th century until well into the Yuan dynasty (AD 1271 – AD 1368). The first major departure from the transparent Qingbai ware of glaze in the Hutian Kiln occurred in the early 14th century, when the Luanbai ware was developed, with an opaque glaze. Luanbai in Chinese literally means "egg-white", and this ware is one of the special wares ordered by the imperial court. Although it is generally eggshell white in color, some examples appear to have a light greenish hue that results from variable thicknesses of glaze covering above the porcelain body. Because of the fact that a large number of Luanbai wares were stamped with the Chinese characters for Shufu meaning 'Privy Council', it is also sometimes referred to as Shufu porcelain (Wood, 2011).

Many scholars who argue that Luanbai ware evolved from Qingbai provide the following observations: 1) some products in both wares share similar shapes and decorative styles in the early stages of Luanbai ware production, and 2) some glazes of Qingbai ware appear to be intermediate between the translucent *Oingbai* and the opaque Luanbai ware (Xiao et al., 2001; IPICRA and IMCK, 2007). However, there have been relatively few scientific analyses about this evolutionary relationship (Xiong and Chi, 2001; Chen, 2006). In addition, little information is known about the results of the alteration of raw material and firing techniques between Song and Yuan Dynasties. In this paper, colorimetric, microstructure, chemical analyses and thermal analysis are employed to clarify the color-generating mechanisms and the change of production technology between Qingbai and Luanbai wares. The results of this study help to clarify the technological changes between the Qingbai and Luanbai wares, and increase our understanding of the development of porcelain in the southern China.

2. Materials and methods

2.1. Materials

Fourteen porcelain sherds excavated from stratified deposits at the Hutian Kiln site (JPICRA and JMCK, 2007) were studied for this project; six sherds of *Qingbai* from the Southern Song Dynasty strata (ID: HT6, HT7, HT8, HT9, HT10 and HT12), three sherds of *Qingbai* from the Yuan Dynasty strata (ID: HT13, HT18 and HT19), and five sherds of *Luanbai* from the Yuan Dynasty strata (ID: HT16, HT17, HT20, HT21 and HT22). The archaeological information and appearance description of some typical samples are shown in Table 1.

2.2. Methods

After cleaning the sherds using water and then drying them thoroughly, the specimens were placed in a spectrophotometer specimen holder and the reflectance spectra was measured by a reflectance spectrophotometer (X-Rite VS450 spectrophotometer, USA). Each sample was examined at 10 nm intervals, over every wavelength (λ) from 400 to 700 nm. In addition the color of each sample was measured using color measurement software (X-Rite Color Master, USA). The optical geometry is D65 illumination and diffused viewing with aperture size of 6.0 mm diameter. The reflectance curves of a typical sample's glaze are shown in Fig. 1.

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Number	Product type	Chronology ^a	Shape	Decoration
HT6	Qingbai	Early stage of S	Bowl	With incised peony inner body
HT7	Qingbai	Late stage of S	Bowl	With incised two fish inner body
HT8	Qingbai	Early stage of S	Bowl	With incised billows inner body
HT9	Qingbai	Early stage of S	Bowl	With incised flower inner body
HT10	Qingbai	Late stage of S	Bowl	With incised flower inner body
HT12	Qingbai	Early stage of S	Bowl	With moulded peony and phoenix inner body
HT13	Qingbai	Y	Bowl	With incised chrysanthemum inner body
HT18	Qingbai	Y	Bowl	With incised chrysanthemum inner body
HT19	Qingbai	Y	Bowl	With incised chrysanthemum inner body
HT16	Luanbai	Y	Cup	_b
HT17	Luanbai	Y	Bowl	With moulded flower inner body
HT20	Luanbai	Y	Bowl	With moulded flower inner body
HT21	Luanbai	Y	Cup	-
HT22	Luanbai	Y	Bowl	With moulded flower inner body

^a S: Southern Song Dynasty (AD 1127 – AD 1279), Y: Yuan Dynasty (AD 1271 – AD 1368).

^b -: without pattern.

Table 2	
Coefficients A and B, correlation	coefficient <i>R</i> of calibration equation.

Component	Coefficient								
	Ā	В	R						
Al ₂ O ₃	0.0199	0.5666	0.9273						
SiO ₂	16.371	0.29	0.9665						
K ₂ O	-0.1505	0.1258	0.9822						
CaO	0.0424	0.0966	0.9946						
TiO ₂	0.0865	0.05	0.9795						
Fe ₂ O ₃	-0.1765	0.0264	0.9871						
Р	133.73	845.46	0.9408						
Mn	60.444	126.13	0.9463						
Sr	-35.211	76.559	0.9296						

Each sample was also cut and polished separately to make a cross section and thin section for microscopic analysis. All sections were cut perpendicular to the surface in order to determine the structural characteristics. The cross-sections of sherds were examined under a KEYENCE VHX-600 digital microscope and the thin-sections of sherds were observed under a Nikon LV100 polarizing microscope.

Chemical compositions were determined by using micro energy-dispersive X-ray fluorescence (EDAX Eagle-III μ -probe, USA). The analytical instrument was operated at 40 kV and 600 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 20%. The excited sample emits X-ray fluorescence with exit angle of 60° and is recorded by Si (Li) detector when it crosses the solar slit. The scale of energy is demarcated by Al K α and Cu K α peak energy value of Al—Cu alloy. The software employed for spectrum refraction and

Table 3
The comparative results of the certified values and EDXRF analytical results on two
ceramic reference samples (major elements: wt%; minor and trace elements: $\mu g/g).$

		Al_2O_3	SiO ₂	K ₂ O	CaO	TiO ₂	Fe ₂ O ₃	P_2O_5	Mn ₂ O	SrO
S1	С	13.4	72.9	5.0	1.6	0.3	3.3	405	463	106
	Μ	13.3	72.2	4.6	1.5	0.3	3.1	409	417	101
S7	С	19.7	55.6	2.0	3.2	1.3	13.8	1661	1477	413
	Μ	18.5	54.2	2.0	3.3	1.3	12.9	1867	1432	385

M = Measurement value; C = Certified value.



Fig. 1. Reflectance spectra of samples. a: Qingbai wares' reflectance spectra. b: Luanbai wares' reflectance spectra. (S-Q: Qingbai ware from Southern Song Dynasty; Y-Q: Qingbai ware from Yuan Dynasty; Y-L: Luanbai ware from Yuan Dynasty). *Since the shape of HT19 is not suitable for experimental device, the data is absent.

analysis was the program VISION32, which is programmed for this instrument. Results for 14 samples are listed in Table 4 along with some previously published data from the literature.

A set of reference standard samples (13 pieces) with known chemical compositions, provide by the Shanghai Institute of Ceramics of the Chinese Academy of Sciences, were individually measured by the same conditions of the ancient specimen. These thirteen reference standard samples were use to make the calibration curve and remaining two of them as unknown samples for verifying the quantification results. According to the element concentration of standard samples (C_i) and the intensity of the analytical curve (I_i) , calibration curves were calculated by the method of least squares fitting, and the equation of calibration curves is: $C_i = A_i + B_i^* I_i$ (Zhang et al., 2004). These resulted in the calculation of the coefficients A and B, and of the correlation coefficient R are presented in Table 2. From Table 2, it showed that most of the correlation coefficients were over 0.9, which suggested that the calibration line is reliable in the experimental. The reference samples (S1 and S7) with literature concentrations, used here to check the accuracy of the methods, as well as all the samples, were analyzed in five different areas for calculating the average, in order to overcome the potential problems resulting from the in homogeneity of the samples (Zhu et al., 2011). The results obtained for the major (Al, Si, K, Ca, Ti, and Fe) and minor and minor elements (P, Mn, and Sr) of the reference and porcelain samples are listed in Tables 2–3 As can be seen from Table 3, the accuracy of the results for the major elements (except the lighter elements Na and Mg) is in the range of 1–9%, and that of the trace elements is in the range of 1-12%.

For firing temperature measurement, a dilatometer device (model: DIL 402C) made by Netzsch Company was used for this experiment. The condition of measurement is: Purge gas is nitrogen, sample holder of Al_2O_3 , the heating rates is 5 °C/min, natural cooling, and the sampling rate is 60 pts/min (16pts/k). The sample was sliced into cuboids block ($1.5 \times 1.5 \times 0.5$ cm³) and polish the surface to remove the any external contamination. Then test sample in dilatometer equipment at a heating rate of 5 °C/min from room temperature with nitrogen chosen as the purge gas. The Netzsch Proteus-Thermal Analysis Software was exploited to carry out the measurements and evaluate the resulting data. Due to the size of samples, the experiment was carried on only two samples. The result is shown in Fig. 4.

3. Results and discussion

3.1. Color-generating mechanism

The reflectance spectrum curves of samples are shown on Fig. 1. These reflectance spectra show that the *Oingbai* and *Luanbai* wares have distinct color ranges. Qingbai wares (Fig. 1a) have reflection spectrum curves that vary gradually in the middle and run steeply at both ends with a narrow range of dominant wavelengths (peaked between 530 - 560 nm). They have a higher reflectance close to 60%, indicating the high reflective rates in yellow and green hues wavelength range. In contrast, the reflection spectrum curves of Luanbai wares (Fig. 1b) rise and drop gently. The dominant wavelength is around 570 nm in the yellow wavelength range, and the reflectance is relatively lower, between 40% and 50%. Those result showed that the lightness (height of reflectance) and saturation (width of reflectance) of Luanbai ware, whose hue is grayish yellow mixed with green, is obviously lower than that of Qingbai, indicating a clear distinction of glaze color between Qingbai and Luanbai wares (Liu et al., 2010).

The microstructure of typical samples is shown in Fig. 2. HT12 is the typical sample of Qingbai ware from the Song dynasty, and its glaze is transparent. HT13 is the typical sample of Qingbai ware from the Yuan dynasty, and its glaze is similar to that of HT12. HT17 is the typical sample of Luanbai ware from Yuan dynasty, and its glaze is opaque with a large number of dendritic crystal clusters. The main microstructural difference between Qingbai and Luanbai glazes is the presence of crystal clusters in the latter. A previous study has concluded that when Fe content is lower than 2%, Fe has no significant influence on the glaze color of white porcelain with transparent glaze (Yang et al., 2005). Therefore, the physical scattering effects made by crystals play a vital role for the colorgenerating of an opaque glaze. Generally, when the diameter of heterophase particle is smaller than the incident light, Rayleigh scattering phenomenon will happen (Nassau, 1991). When the particle diameter is similar or larger than the wavelength of incident light, the scattering mainly consists of Mie scattering, which displays white-like color due to the overlap of scattered light from particles with different sizes (Nassau, 1991). A large amount of precipitated crystallites (about 29.97 µm in length and 12.65 µm in width) in the glaze of HT17 is larger than the wavelength of incident light, which will cause Mie scattering and produce the opacified



Fig. 2. Microstructure of typical samples. a: HT12 under digital microscope. b: HT12 under polarized-microscope. c: HT12 under cross polarized-microscope. d: HT13 under stereomicroscope. e: HT13 under polarized-microscope. f: HT13 under cross polarized-microscope. g: HT17 under stereo-microscope. h: HT17 under polarized-microscope. i: HT17 under cross polarized-microscope.



Fig. 3. Scatter plot of CaO and K₂O contents of the samples in glaze. (S-Q: *Qingbai* ware from Song Dynasty; Y-Q: *Qingbai* ware from Yuan Dynasty; Y-L: *Luanbai* ware from Yuan Dynasty).

appearance and jade-like glaze with a less dramatic reflective curve, as shown in Fig. 2, compared to *Qingbai* transparent glaze.

3.2. Evolution process

The chemical compositions of the samples body and glaze are listed in Table 4. The body composition result shows that the

alumina levels of early Song Dynasty (with average value 18.3%) were slightly lower than late Song and Yuan Dynasties (with average value 21.1%) and the iron levels in porcelain body (with average value from 0.8% to 1.4%) shows the similar tendency. Previous scholar (Wood, 2011) believed that *Qingbai* ware's bodies in the late Song and Yuan Dynasties were based on mixture of albitic porcelain stone, plus a clay-rich material (either a true kaolin or pale stoneware clay) which is different from kaolinized micaeous porcelain stone alone in earlier Song Dynasty, and the current composition change coincides with former research.

A scatter plot of K₂O and CaO in glaze is presented in Fig. 3, indicating that most of Qingbai wares from Southern Song Dynasty (area 1) and Luanbai wares from Yuan Dynasty (area 2) separate clearly. Furthermore, two samples of Qingbai ware from Song Dynasty (HT7 and HT010(5) (Feng et al., 2007)) and three Qingbai wares from Yuan Dynasty bridge area 1 and area 2. In particular, HT7, from the late Southern Song Dynasty, is different from other Song Dynasty ones, but similar to Yuan Dynasty, implying that the recipe change began in late Southern Song Dynasty, and became popular in Yuan Dynasty. Hence, the CaO content decreased and the K₂O increased from Southern Song Dynasty (AD 1129 - AD 1279) to Yuan Dynasty (AD 1271 - AD 1368) for Qingbai glaze. Previous study showed that ancient craftsmen in Jingdezhen used to mix a certain number of plant ash in the glaze (Guo, 1993). Relatively, phosphate and manganese oxide are typical minor components of ashes but occur rarely in significantly elevated levels in geological limestone (Yin et al., 2011). The concentrations of P2O5 and MnO2, listed in

Table 4

Chemical compositions of analyzed samples (major elements: wt%; minor and trace elements: µg/g).

Number	Product type	Chronology ^a	Part	Al_2O_3	SiO ₂	K ₂ O	CaO	TiO ₂	Fe ₂ O ₃	P_2O_5	Mn ₂ O	SrO
HT6	Qingbai	S	Body	17.0	73.7	3.1	0.7	0.1	0.7	359	676	200
			Glaze	12.7	65.3	1.8	13.5	0.1	1.4	387	912	357
HT7	Qingbai	S	Body	22.2	69.5	2.3	0.7	0.2	1.2	717	504	147
			Glaze	14.0	66.9	2.6	9.6	0.2	0.9	803	546	288
HT8	Qingbai	S	Body	18.5	69.2	2.7	0.8	0.2	0.9	438	499	172
			Glaze	12.5	64.6	1.8	14.8	0.2	1.5	571	587	357
HT9	Qingbai	S	Body	16.8	65.8	2.6	0.4	0.2	0.8	796	246	171
			Glaze	13.8	64.1	1.9	13.1	0.1	0.9	491	451	267
HT10	Qingbai	S	Body	16.5	72.0	2.8	0.7	0.1	1.0	387	735	214
			Glaze	14.3	66.9	1.7	13.2	0.1	1.5	625	1049	307
HT12	Qingbai	S	Body	21.2	70.2	3.4	0.6	0.2	0.9	669	528	168
			Glaze	11.3	60.7	1.7	18.9	0.2	0.7	1449	748	1069
HT13	Qingbai	Y	Body	25.3	76.2	3.1	0.9	0.2	1.6	380	611	134
			Glaze	12.3	69.7	2.7	6.1	0.1	1.2	430	524	162
HT18	Qingbai	Y	Body	24.2	62.7	2.5	1.0	0.2	1.5	666	648	108
			Glaze	14.7	71.8	2.5	9.3	0.2	2.4	450	644	269
HT19	Qingbai	Y	Body	16.9	59.2	3.3	0.9	0.2	1.5	778	1000	84
			Glaze	15.5	73.7	2.9	7.5	0.2	1.6	282	310	207
HT16	Luanbai	Y	Body	20.9	74.1	2.4	0.4	0.1	1.7	197	497	145
			Glaze	17.3	78.1	3.5	6.2	0.1	1.3	430	612	165
HT17	Luanbai	Y	Body	22.2	69.0	2.3	0.3	0.2	1.4	324	485	147
			Glaze	14.7	73.1	3.5	6.2	0.2	1.3	482	498	195
HT20	Luanbai	Y	Body	22.9	73.7	2.6	0.4	0.2	1.6	354	559	176
			Glaze	20.1	73.3	4.6	6.4	0.3	1.2	334	556	189
HT21	Luanbai	Y	Body	21.3	64.4	2.3	0.3	0.2	1.5	377	529	144
			Glaze	15.9	70.3	4.7	4.1	0.1	1.3	430	685	154
HT22	Luanbai	Y	Body	19.0	61.2	2.0	0.1	0.1	1.0	352	406	144
			Glaze	16.4	67.3	2.7	4.4	0.2	1.4	313	644	242
HT15 ^b	Qingbai	S	Glaze	13.7	68.2	1.9	11.7	0.0	1.5		120	
HT30 ^b	Qingbai	S	Glaze	13.6	67.9	2.2	12.5	0.0	1.3		40	
HT40 ^b	Qingbai	Y	Glaze	13.9	65.7	2.9	11.3	0.1	2.0		60	
HT42 ^b	Qingbai	Y	Glaze	13.4	70.5	2.6	6.5	0.0	1.5		90	
HT50 ^b	Qingbai	Y	Glaze	14.2	68.2	2.6	9.4	0.0	1.9		90	
HT60 ^b	Qingbai	Y	Glaze	14.0	70.7	3.6	6.1	0.1	2.1		70	
HT009(5) ^c	Qingbai	S	Glaze	14.6	67.0	1.9	13.2	0.0	1.6		80	
HT010(5) ^c	Qingbai	S	Glaze	14.2	69.0	2.8	11.2	0.0	1.1		60	

^a S: Southern Song Dynasty (AD 1127 - AD 1279), Y: Yuan Dynasty (AD 1271 - AD 1368).

^b Cited from Wu et al. (2007).

^c Cited from Feng et al. (2007).



Fig. 4. The thermal curve of typical sherds by dilatomete.

Table 4, are showing usage variance in different kind of glaze and the changing correspondingly indicate the raw materials/recipe improvement in late period.

Because of the high calcium concentration the main glaze-flux for *Qingbai* ware from the Song Dynasty appears to have been made from limestone and plant ash (Zhou and Li, 1960), which is coincided with the relatively higher levels of phosphate oxide in the glazes (<u>Yin et al., 2011</u>). At least by the end of the Song Dynasty (around AD 13 Century), the recipe of the glaze included potassium feldspar mixture and evolved to a "lime-alkali" type glaze (Wood, 2011). Potassium component is preferred a high-fire glaze and will highly improve the glaze's durability and stability (Ma, 2012).

In the Yuan Dynasty, chemical compositions of *Luanbai* glaze resembles that of *Qingbai* glaze in Yuan Dynasty with high potassium and low calcium content, but the *Luanbai* glaze shows opacifying optical effects with low saturation and lightness of color. These phenomena suggest that the glaze recipe change has indirect influence on the porcelain appearance and the technology of firing has been significantly modified in the production of *Luanbai* ware such that the glaze developed opacifying inclusions.

The formation of crystalline structures in the glaze, which is basically a kind of glassy state material, is generally affected by several factors, such as the chemical composition, glass network structure, phase separation and firing process (Ma, 2012). According to thermodynamics, the cooling process of molten glass will give rise to crystallization since glass has higher free energy than crystal. The fast cooling of kiln is not advantageous for the formation of glaze crystallization (NILI, 2007). Thus, it is inferred that the slower cooling rate in the production of *Luanbai* ware is the major factor for the precipitation of crystalline structures in the *Luanbai* glaze.

Previous study (Li, 1998) and experimental result (Fig. 4) claimed that the firing temperature of *Qingbai* wares (lower than 1200 °C) in Song Dynasty is almost 100 °C–150 °C lower than *Luanbai* wares (more than 1250 °C) in Yuan Dynasty, which suggests that the firing techniques of *Luanbai* wares had been significantly improved at Hutian Kiln in Yuan Dynasty (Wang, 2007; Song, 2013).

Based on the above results, two technological processes can be identified to explain the process through which the *Qingbai* ware of the Song Dynasty evolved into *Luanbai* ware in the later Yuan Dynasty. On the one hand, the glaze recipe changed towards the end of Song Dynasty and continued into the Yuan Dynasty. The other major factor appears to be the firing technology that became established for *Luanbai* ware during the Yuan dynasty.

4. Summary and conclusion

In summary, an extended study has been carried out on *Qingbai* and *Luanbai* porcelain sherds from the 12th to 14th century, Hutian kiln, Jingdezhen, China. *Qingbai* and *Luanbai* wares have different appearance due to their glazes which are transparent and opaque respectively. Consequently, their reflectance spectra curves also have different character, which are caused by their microscopic structure. In the glaze of *Luanbai* ware, there are plenty of small-sized inclusions, such as glaze bubbles, crystalline structures and un-melted quartz, which met the requirement of Mie scattering and strengthened the effect of opaque appearance. And the crystallization can possibly be attributed to the higher temperature and the slower cooling rate in the firing process.

According to our analysis, the appearance of *Qingbai* from the Yuan Dynasty is similar to *Qingbai* ware from the Song Dynasty although its chemical composition and micro-structure resembles that of *Luanbai*. It appears that the *Qingbai* ware during the Yuan Dynasty is actually a transition product and then eventually evolves into the *Luanbai* ware.

Our results suggest that the evolution process from *Qingbai* to *Luanbai* wares had experienced changes of the chemical composition of glazes, and then micro-structure that can be attributed to higher firing temperatures and slower cooling processes. These technological innovations had a significant impact on later porcelain technology in Jingdezhen. By demonstrating the technological differences between Hutian kiln *Qingbai* and *Luanbai* glazes, this study provides a solid foundation for developing new studies of Southern white porcelain technology.

Acknowledgements

The research presented in this paper has been supported by the National Natural Science Foundation of China (NSFC, Grant no. 11275265) and CAS Strategic Priority Research Program grant no. XDA05130303. Also, the Project Sponsored by the Scientific Research Foundation for the Returned Overseas Chinese Scholars, State Education Ministry and in part by the President Fund of the UCAS.

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