

AN ANALYSIS OF THE GEM-BLUE GLAZE OF YE WANG'S KOJI POTTERY*

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Koji pottery is a glazed ceramic art used widely for figurines. In early Taiwan, it was employed in temple construction for decorative purposes. Ye Wang (1826–87) is the first historically documented Koji artist of Taiwan and also the most prominent Koji pottery artist, noted for his modelling and glazing skills. Unfortunately, his unique technique was lost following his death in 1887. In order to provide vital information for ongoing conservation work on Koji pottery, this study analysed the physical and chemical characteristics of Ye Wang's gem-blue glaze, to discover the glaze formula. DSC combined with the two-thirds rule revealed that the firing temperature of Ye Wang's works of art was most probably around 878–923°C. EPMA revealed that the gem-blue glaze has high alkali levels, and belongs to the $\text{PbO-K}_2\text{O-B}_2\text{O}_3\text{-Na}_2\text{O-SiO}_2$ system, deriving its unique colour from copper, iron, manganese and cobalt. This study found high potassium levels in the gem-blue glaze, which are generally a characteristic of traditional Chinese glazes. In addition, a unique discovery of boron, commonly used in famille rose, was also identified in the glaze. By comparing spectra of historical and reconstructed glazes and adjusting the proportion of chromophoric elements, this study found a glazing formula with colours close to those of Ye Wang's gem-blue glaze.

KEYWORDS: KOJI POTTERY, GLAZE, ELECTRON MICROPROBE ANALYSIS, DIFFERENTIAL SCANNING CALORIMETRY, VISIBLE SPECTROSCOPY ANALYSIS, FAMILLE ROSE, SANCAI

INTRODUCTION

The traditional art of Koji pottery is an artistic treasure of Taiwan. Early Koji pottery was used primarily as an architectural decoration in temples and domestic houses, through the application of artistic technologies such as shaping, glazing and firing. Koji pottery is characterized by its vivid shapes, clear glazes and themes with historical allusions, allegorical subjects or auspicious symbols. These works reflect the everyday lives and religious faith of ordinary Taiwanese people in the Qing Dynasty. They can also be used as historical sources to study the artistic and cultural development of Taiwan (Zuo 1997). In particular, Koji pottery is characterized by its use of bright and transparent glazes. These transparent glazes are usually named after natural substances or gems, such as gem-blue, emerald-green, rouge-red and amber-yellow colour (Wang 1999; Li 2007).

In the developmental history of Koji pottery in Taiwan, Ye Wang was the first and most prominent Koji pottery artist in the region. He was unique in his choice of themes, shaping, decorations, colouring and his exquisite glazing techniques, earning him the honourable nickname, 'King of Taiwanese Koji Pottery' (Chiang 1997). Ye Wang's works can still be found in both the Xuejia Tzu-chi Temple and the Jiali Zhen-xing Temple in Tainan City, Taiwan (Figs 1 and 2).

*Received 9 March 2011; accepted 8 September 2011

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Figure 1 *Ye Wang's Koji pottery artwork, Zhou Dun-yi appreciates the lotus: a story scene panel on the wall of Zhen-xing Temple, Tainan City, Taiwan.*



Figure 2 *Ye Wang's Koji pottery artwork, Jiang Zi-ya rides atop a four-non-likes: collection of the Ye Wang Koji pottery museum of Tzu-chi Temple, Tainan City, Taiwan (height 11.8 in/30 cm).*

There are inherent difficulties in the preservation and continuation of Koji pottery. Koji pottery was created at low temperatures in temporary kilns (Chiang 2004), causing the body to have a low degree of sintering and the glaze to be more fragile, which in turn causes the pottery to deteriorate and thus to present preservation problems. On the other hand, the glazing formulae have always been shrouded in secrecy, and as such, Ye Wang's glazing formula has also remained a mystery. Even though craftsmen today are able to formulate similar hues, they still cannot replicate the gem-like crystal characteristics created by Ye Wang. We therefore conducted this study to uncover the secrets behind Ye Wang's glazing formulae and to help in the preservation of his remaining works of art. Ye Wang's preferred colour, gem-blue glaze, is not only deep blue in colour but also has a crystal clear hue like a sapphire. The focus of this study is on this gem-blue glaze (Figs 3 and 4).

In this study, we reviewed the relevant literature on the traditional production techniques of Koji pottery, and then incorporated various aspects of materials analysis to identify the physical and chemical characteristics of Ye Wang's glazes. On the basis of these results, attempts were made to reproduce the gem-blue glaze through simulation experiments. However, because of inevitable inhomogeneity in the ancient glaze texture, matrix effects and volatilization of light elements during the firing process and subsequent analysis, one might anticipate differences between the results derived from instrumental analysis and the original glaze recipes used by Ye Wang. Therefore, this study compared the spectral characterization of the glazes when attempting to recreate the original formula. The results of these analyses pointed to the key elements in Ye Wang's glaze formula and permitted a successful reconstruction of the original recipe. These findings also revealed the factors contributing to the



Figure 3 An image of a gem-blue glaze, Ye Wang's Koji pottery artwork, Emperor Wu of Liang and maid: collection of the Ye Wang Koji pottery museum of Tzu-chi Temple (height 12.6 in/32 cm).



Figure 4 An image of a dark-blue glaze, Ye Wang's Koji pottery artwork, Lei Zhen-zi: collection of the Ye Wang Koji pottery museum of Tzu-chi Temple (height 11.8 in/30 cm).

characteristically beautiful appearances of the gem-blue glazes. The results of the study can be used by contemporary artists to serve in the continuation of this traditional art of glazing, as well as contributing knowledge that may prove invaluable to the conservation community.

RESEARCH METHODS

The aim of this research was to discover Ye Wang's technique for gem-blue glaze production and elucidate the mechanism of its colour production. An initial literature review was undertaken to uncover any documentary evidence relating to the methods used by Ye Wang and his contemporaries. These formed the basis for the experimental firings undertaken later in the study. The experimental work was divided into three stages. The first stage of the experimental study involved electron microprobe analysis (EPMA) and colorimetric analysis of surviving sherds of Ye Wang's glazes, to identify the physical and chemical characteristics of these traditional glazes. These were combined with high-temperature differential scanning calorimetry (HT-DSC) to determine the firing temperatures. The second stage focused on actual glaze mixing and sintering experiments, on the basis of data derived from an initial analysis of the original objects. The third stage compared the spectra of the glazes made with different chromophoric elements to those of Ye Wang's, to identify the most similar glaze formula. Finally, spectral characterization and microscopic examination were employed to check the similarities in hue and appearance between the reconstructed glaze and Ye Wang's glaze.

Characterization of the original glazed sherds

Evaluation of the firing temperature There are various documentary sources relevant to the firing temperature of Ye Wang's works of art. Chien (2001) indicated that traditional Koji pottery in Taiwan was made in temporary kilns assembled in temples and residences. Shih (2000) further stated that traditional Koji pottery was fired in brick kilns at approximately 600°C, using charcoal and rice hulls as fuel. Chiang (1997) suggested that the figures used to decorate buildings in Taiwan were mostly made of low-fired clay, produced within a temperature range of 750–900°C. Due to the variety of opinions found in the literature, this study conducted thermal analysis to infer the probable temperature of Ye Wang's kilns. The objects of this study were Koji pottery glaze fragments from Ye Wang's works of art as provided by the Xuejia Tzu-chi Temple (Fig. 5). The glaze fragments were preserved when the temple underwent renovation.

Glaze is formed by an indefinite chemical proportion of non-crystalline solids and thus does not have a specific melting point but, instead, a wide melting temperature range (Hsueh 2003). While the glaze does not have a specific melting point, it does have a glass transition temperature (T_g). The glass transition point refers to the temperature at which glassy substances convert from a vitreous state to a metastable melt (Mazurin 2007). To identify the T_g of Ye Wang's glaze, this study used a high-temperature differential scanning calorimeter (HT-DSC; model HT-DSC 404, Netzsch Instruments, Inc.) to analyse three glaze samples of different colours; namely, amber-yellow glaze, emerald-green glaze and rouge-red glaze. The operating temperature range in the



Figure 5 Koji pottery fragments of Ye Wang's works of art.

study was between 30 and 800°C with an incremental ramp of 10°C min⁻¹ increment and used air as the purge gas.

After identifying the T_g through differential scanning analysis, we applied Sakka and Mackenzie's (1971) two-thirds rule relating the glass transition temperature (T_g) and the liquidus temperature (T_{liq}); namely, $T_g/T_{liq} = 2/3$. In this way, it was possible to predict the liquidus temperature of the glazes so as to infer the glazing temperature of Ye Wang's Koji pottery.

Electron microprobe analysis Sample fragments of Ye Wang's glaze were first cleaned and cold-mounted vertically in epoxy resin. When cured to hardness, the resin block was ground and polished to give cross-sections through the glaze. These were subsequently carbon coated for EPMA analysis. Qualitative and quantitative analysis on the glazes was conducted using a field emission electron probe micro-analyser (FE-EPMA, JXA-8500F, JEOL Ltd), equipped with four wavelength-dispersive X-ray spectrometers (WDS). The crystals used were TAP, LDEB, LIF, LIFH, PETJ, PETH, LDE1H and LDE2H.

Due to the diversity of the elemental components of Ye Wang's glaze, the influence of matrix effects derived from its complicated composition inevitably introduced inaccuracies in the X-ray analysis. Moreover, the use of high-energy electron beams in the analysis will have volatilized the lighter elements, which in turn led to quantitative inaccuracies. Additionally, Ye Wang's glazes are unstable low-fired glazes and the samples themselves had undergone hundreds of years of weathering and aging. This may well have led to changes in their structure and composition. Therefore, the selection of samples and criteria for analysis were crucial to quantitative investigation of the chemical structure of Ye Wang's glaze. Due to long-term weathering effects, the surface of the glaze had been visibly damaged and thus would not accurately represent the actual composition of the glaze. Therefore, backscattered electron (BSE) images were used to evaluate the texture and the weathering conditions of the sample, so that it was possible to select five relatively homogeneous points for analysis while avoiding the weathered regions. The average of these points was then taken as representative quantitative data.

For the reasons outlined above, this study incorporated Hartmann's (1997), Verità *et al.*'s (2002), Angelini *et al.*'s (2004) and Tite *et al.*'s (2007) suggestions for conducting elemental analysis on vitreous substances. Because high-energy electron beams trigger the evaporation of B, Na and K, quantitative elemental analysis was first conducted on light elements and alkalis. The accelerating voltage in the analysis was set at 12 kV, the beam current was 15 nA, and the defocused beam had a diameter of 20 µm. To minimize any matrix effects in the glaze, glass specimens of known composition (soda–lime glass, potassium–lime glass, cs glass, soda–zinc glass and barium–zinc glass; JEOL Ltd) were used as quantitative comparison standards. The output signal was corrected using the ZAF correction program.

Simulated sintering experiments

Traditional Chinese glazing comprises two types: raw glazing and fritted glazing. Raw glazing pertains to the mixture of various materials with water, according to a given ratio. The mix is applied directly to the surface of the bisque prior to glaze firing. Fritted glazing requires that glaze materials be fired into vitreous form and then ground into powder before being distributed on the bisque. In terms of Ye Wang's methods of production, past studies have shown that Ye Wang's glazes were 'gem glazes' characterized by colour, brightness and clarity, derived from the 'fritting method' (Chiang 1997; Wang 1999). The simulations in this study were therefore also conducted through the fritting method based on Chen's (2004) findings. First, the formulae used for glazing

were selected on the basis of the elemental analysis of Ye Wang's original glazes. All substances used in the glaze simulation were reagent grade, including: SiO₂ (STREM), Al₂O₃ (Sigma-Aldrich), B₂O₃ (Sigma-Aldrich), Na₂CO₃ (J. T. Baker), K₂CO₃ (J. T. Baker), CaCO₃ (Sigma-Aldrich), MgO (Fluka), PbO (J. T. Baker), CuO (STREM), Fe₂O₃ (STREM), MnO₂ (ACROS), TiO₂ (ACROS) and CoO (Aldrich). The glaze ingredients were ground and mixed in a ceramic crucible and placed into a furnace at 920°C to render them into vitreous form. The vitreous mass was then quenched in water to form a vitreous frit. The resulting mass was then placed in an oven to dry and subsequently ground to powder using a planetary ball mill (model PM100, Retsch GmbH) at 400 rpm for 6 min.

To simulate the glazing process, the frit powder was then applied to a ceramic base that simulated Ye Wang's clay in colour and chemical composition. A measured amount of frit powder was mixed with water and evenly applied on the bisques and placed into the oven to dry before being returned to the tube furnace (model HTF55322C, Lindberg/Blue M). The heating rate, the retention time at 920°C and the cooling rate were 5°C min⁻¹, 20 min and 5°C min⁻¹, respectively.

Glaze colorimetric analysis

The colorimetric analysis adopted spectral colour measurements based on the Commission International de L'Eclairage (CIE) 130-1998 standard method of colour measurement (CIE 1998). In this method, the light source was introduced into the integrating sphere to generate uniform diffused illumination on the specimen. The angle between the viewing line and the normal line on the specimen was 8° (di: 8°), and the reflective lights of the specimens were analysed by the spectrometer (2048 elements linear silicon CCD array, B&W Tek, Inc.). The range of the spectrum record was from 380 to 780 nm.

Colorimetric analysis is divided into absorption spectra and reflection spectra. In this study, we employed absorption spectra to observe the absorption bands of specific chromophoric elements. The reflection spectra of objects correspond to colour, as judged by the human eye; therefore, reflection spectra were employed to observe the colour resulting from mixes of chromophoric elements.

For analysis of differences between the colour of the ancient glaze and that of the reconstructed glaze, we converted the spectra to the CIE colorimetric system. The spectral distribution data (CIE standard illuminant D65 spectral power distribution, $P(\lambda)$) of D65 and the spectral reflectance ($\rho(\lambda)$) of the glaze as well as the colour matching function ($V(\lambda)$) of CIE 1931 were processed using computer software to obtain the CIE tristimulus values. The same software was used to convert the tristimulus into the CIE 1931 standard colorimetric system and the CIE 1976 $L^*a^*b^*$ colour space standard colorimetric system.

RESULTS AND DISCUSSION

Thermal analysis

Figure 6 shows the HT-DSC analysis of Ye Wang's amber-yellow, rouge-red and emerald-green glazes. The glass transition temperature (T_g) was determined from the intersection of two tangents to the straight portions of the curve, which corresponds the temperature of the transition from the vitreous state to the metastable liquid state of the glaze (Mazurin 2007). The T_g values of the amber-yellow glaze, rouge-red glaze and emerald-green glaze were about 585°C, 610°C and 615°C, respectively. After obtaining the glass transition temperatures, the equation $T_g/T_{liq} = 2/3$

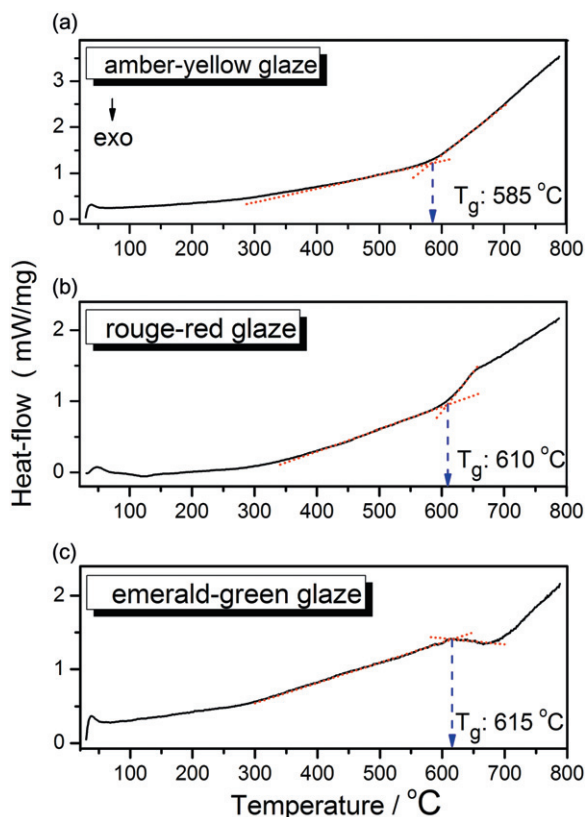


Figure 6 HT-DSC analysis of Ye Wang's glaze: (a) amber-yellow glaze; (b) rouge-red glaze; (c) emerald-green glaze.

was employed to derive the liquidus temperatures (T_{liq}), which were 878°C, 915°C and 923°C for the amber-yellow, rouge-red and emerald-green glazes, respectively.

The results of the thermal analysis showed that the T_{liq} of the amber-yellow glaze was relatively low compared to that of the rouge-red and emerald-green glazes. Furthermore, microscopic observation of the glazes on Ye Wang's Koji pottery sherds-47 (Fig. 7) showed that the emerald-green glaze (Fig. 8) and the rouge-red glaze (Fig. 9) were not completely fused but, instead, had become translucent glazes. In contrast, the amber-yellow glaze (Fig. 10) was completely matured. The fact that three different colours of glaze showed different levels of fusion for the same firing temperature confirms that the results of the thermal analysis were correct, and that the T_{liq} of amber-yellow glaze is lower than that of emerald-green and rouge-red glazes. The results also suggest that the glazing temperature of Ye Wang's kilns may sometimes have been lower than the fusion temperatures of rouge-red and emerald-green glaze.

Elemental analysis

Table 1 shows the quantitative EPMA results. The results confirm that in Ye Wang's Koji pottery glaze, SiO_2 is the network former; Na_2O , K_2O are network modifiers or fluxes, and CaO and MgO act as stabilizers. PbO plays a dual role as both glass network former and network modifier



Figure 7 There are different colour glazes on Ye Wang's Koji pottery sherds-47.

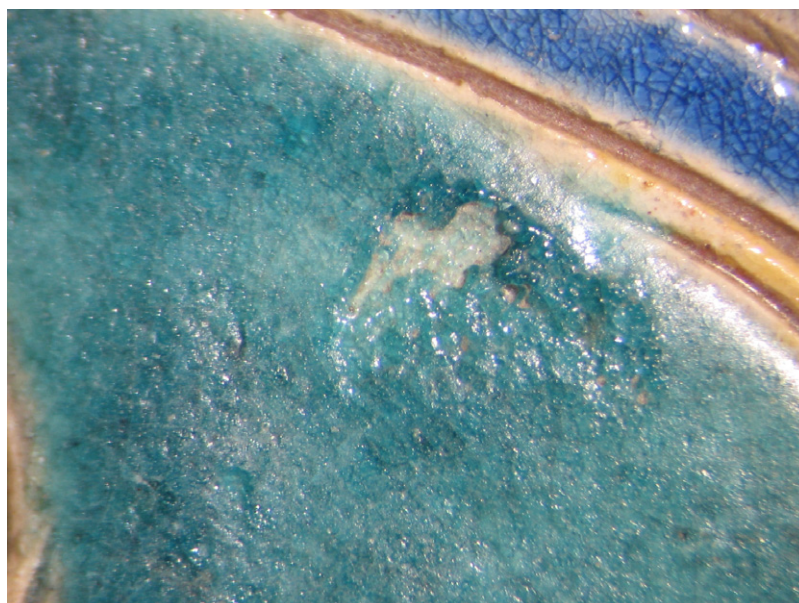


Figure 8 A detail of the immature emerald-green glaze of sherds-47 (Leica MZ 7.5 stereomicroscope: magnification, 25 \times ; light source, 3000K).

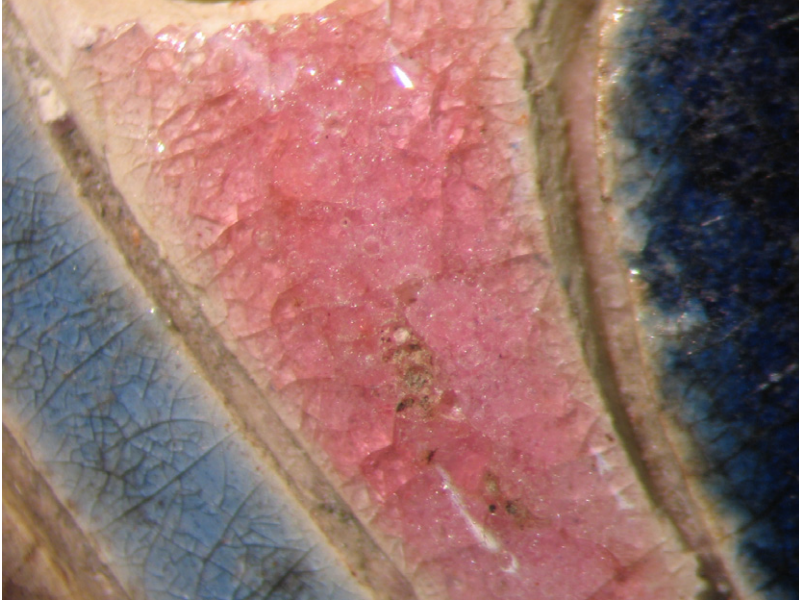


Figure 9 A detail of the immature rouge-red glaze of sherds-47 (Leica MZ 7.5 stereomicroscope: magnification, 25 \times ; light source, 3000K).

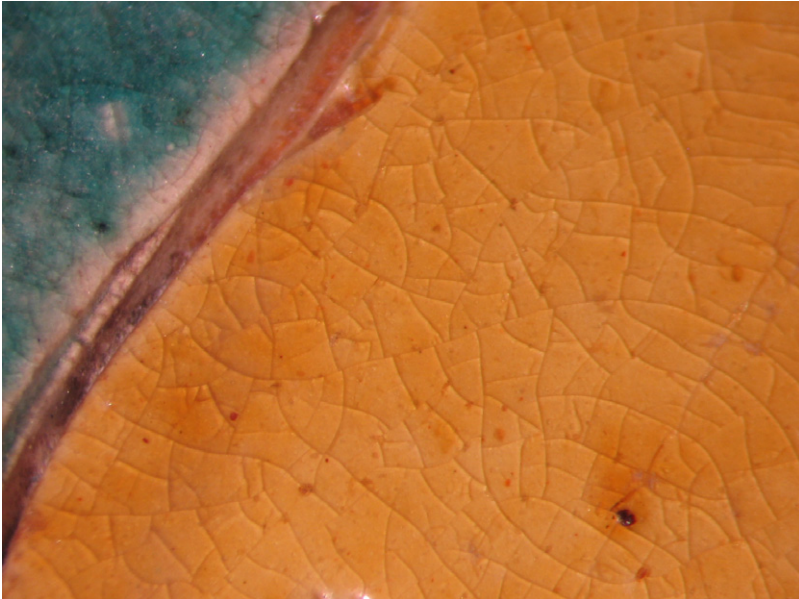


Figure 10 A detail of the fused amber-yellow glaze of sherds-47 (Leica MZ 7.5 stereomicroscope: magnification, 25 \times ; light source, 3000K).

Table 1 The mean EPMA chemical analysis of glazes sampled from Ye Wang's artwork fragments, expressed as weight percentages of element oxides

Glaze colour/sample number	SiO ₂	Al ₂ O ₃	B ₂ O ₃	Na ₂ O	K ₂ O	CaO	MgO	PbO	CuO	Fe ₂ O ₃	MnO ₂	TiO ₂	CoO	P ₂ O ₅	SnO ₂	As ₂ O ₅	BaO	Cl	Total
Gem-blue/18	43.74	0.35	5.93	3.55	12.42	0.63	0.17	30.52	0.58	0.43	0.23	0.06	0.30	0.02	0.02	0.71	0.08	0.16	99.90
Dark-blue/yb16	42.83	0.57	10.90	3.71	12.81	0.04	0.07	26.03	0.13	2.14	0.10	0.13	1.00	0.02	0.03	0.49	0.12	0.12	101.24
Dark-blue/yb9	41.85	0.42	9.67	4.35	9.89	0.24	0.12	29.04	0.09	1.87	0.06	0.03	1.01	0.01	n.d.	0.86	0.24	0.10	99.85
Amber-yellow/yb4	19.41	3.35	0.26	0.10	0.33	0.07	0.12	73.41	0.15	2.39	0.08	0.24	n.d.	0.03	n.d.	0.04	0.05	0.18	100.21
Amber-yellow/yb7	20.98	3.83	0.24	0.16	0.51	0.06	0.12	69.03	0.24	2.58	n.d.	0.29	n.d.	0.06	n.d.	n.d.	n.d.	0.12	98.22
Amber-yellow/yb6	30.15	5.31	0.40	0.22	0.94	0.35	0.18	56.62	0.14	2.09	0.01	0.29	n.d.	n.d.	n.d.	n.d.	0.38	0.05	97.13
Emerald-green/yb1	42.12	0.30	11.11	7.80	0.48	2.19	0.28	25.05	2.80	0.05	0.31	n.d.	n.d.	0.02	n.d.	0.04	0.22	0.79	93.56
Emerald-green/yb2	40.42	0.39	11.56	8.23	0.50	2.28	0.28	24.65	2.58	0.03	0.22	0.02	n.d.	0.09	n.d.	0.12	0.21	0.82	92.40
Emerald-green/yb8	36.17	0.73	9.70	6.76	0.67	1.63	0.25	35.81	3.07	0.06	0.23	0.10	n.d.	0.11	n.d.	0.06	0.11	0.14	95.60
Emerald-green/yb10	38.54	1.80	7.48	6.74	0.79	1.37	0.21	34.01	3.19	0.06	0.24	0.19	n.d.	0.07	n.d.	0.08	n.d.	0.15	94.92
Emerald-green/20	46.28	0.60	9.35	7.55	0.57	1.21	0.25	19.54	2.97	0.21	0.32	0.02	n.d.	0.01	n.d.	0.06	0.14	0.30	89.38
Rouge-red/47	39.28	0.64	0.03	0.23	4.25	0.16	0.08	52.97	n.d.	0.30	0.09	n.d.	n.d.	0.05	0.02	0.05	0.04	0.18	98.37
Ceramic body*	68.45	18.63	n.d.	0.5	1.64	2.76	1.36	n.d.	n.d.	1.27	n.d.	0.72	n.d.	0.1	n.d.	n.d.	0.03	n.d.	95.46

* The ceramic body was analysed by inductively coupled plasma atomic emission spectrometry (ICP-AES).
n.d., Not detected.

(Lakshminarayana and Buddhu 2006; Delfa *et al.* 2008). Emerald-green glaze, gem-blue glaze, and dark-blue glaze also contain B_2O_3 . If categorized by their main components, emerald-green glaze would lie in the $PbO-B_2O_3-Na_2O-SiO_2$ system and is Cu green; amber-yellow glaze would be a $PbO-Al_2O_3-SiO_2$ system and is Fe yellow; and rouge-red would be a $PbO-K_2O-SiO_2$ system and would have derived its colour from colloidal gold (Li 2007; Tseng *et al.* 2009b).

The gem-blue glaze would lie in the $PbO-K_2O-B_2O_3-Na_2O-SiO_2$ system and the main chromophoric element is cobalt (Co): the hue mainly depends on the coordination of the ions. The coordination structures of cobalt ions include tetrahedral $[Co^{II}O_4]$ and octahedral $[Co^{II}O_6]$ coordination (Bamford 1977; Paul 1990). The form $[Co^{II}O_4]$ produces a dark blue colour, while $[Co^{II}O_6]$ produces a light red colour (Wilk and Schreiber 1997). The coordination structure of cobalt ions changes with the basicity of the glaze. Studies have shown that increasing the basicity of the glaze converts octahedral coordination $[Co^{II}O_6]$ into tetrahedral $[Co^{II}O_4]$ (Llusar *et al.* 2001). In borosilicate glasses, the cobalt ion turns blue in a high-basicity glaze and amethyst in a low-basicity glaze (Vogel 1994). To summarize, the hue of cobalt (II) is decided by the relative proportion of $[Co^{II}O_4]$ and $[Co^{II}O_6]$, which in turn is dependent upon the basicity of the glaze. The results of EPMA showed that the alkali ($Na_2O + K_2O$) content of the gem-blue glaze at 15.97 wt%, is relatively high compared to that of amber-yellow, emerald-green and rouge-red glazes. Basicity boosts the proportion of $[Co^{II}O_4]$ and converts the glaze from amethyst to blue. Analysis also revealed that the dark blue was coloured by cobalt, and in comparison, the dark-blue glaze contains higher amounts of cobalt, iron and boron, with less copper and manganese than the gem-blue glaze.

Ye Wang's gem-blue glaze contains high levels of potassium and lead; the colouring is jointly formed by cobalt, copper, iron and manganese. These characteristics are similar to those of the Chinese *fahua* formulae. *Fahua* ware was prevalent in the mid-late Ming Dynasty around the Shanxi area, and consisted of everyday utensils with unique decorations. The glaze decoration was often bordered to provide a three-dimensional look (Feng *et al.* 1982). In composition, the majority of *fahua* glazes exhibit high potassium and lead content (Wood 1999); therefore, in terms of chemical composition, the gem-blue glaze is related to Chinese *fahua* glaze.

In addition to potassium and lead as fluxes, elemental analysis also confirmed the existence of boron in Ye Wang's glaze. This result supports the statements of previous studies, in which borax was identified as the flux in Koji pottery during the Qing Dynasty (Fang 2001; Chen 2004). The application of boron in glaze materials is rare; the only known examples are the Liao Dynasty green-glazed tile found in Longquanwucun and the Qing Dynasty *famille rose* (Chang 2000). The green-glazed tile of Longquanwucun is the earliest known glaze to contain boron, and no other boric oxide glazes seem to have been developed following the Liao Dynasty (Wood 1999). For this reason, the possibility of identifying boron in Ye Wang's glaze originating from Longquanwucun during the Liao Dynasty is remote. As for *famille rose*, it is a type of painted porcelain specifically for imperial wares in the 18th-century Qing Dynasty, referred to as *falancai* in the Forbidden City. The literature indicates that the *famille rose* palette used in the palace before 1728 originated from Europe (Chang 2000). In addition to employing boron as a supplementary flux, another novel attribute was gold-rose glaze, made using colloidal gold on lead-oxide-potassia-silica bases (Kingery and Vandiver 1985). Analysis of Ye Wang's rouge-red glaze revealed that it was also a type of gold-rose glaze (Li 2007; Tseng *et al.* 2009a). From the boron and gold characteristics, it can be inferred that Ye Wang's glaze is related to *famille rose*. Another characteristic element in the gem-blue and dark-blue glazes is arsenic. As natural cobalt ores generally come in asbolite or smaltite forms (Chang 2000), it is likely that the arsenic in the cobalt-blue glaze originates from cobalt ore.

In a comprehensive view of Ye Wang's glazes, previous analysis has shown that the primary colouring of amber-yellow glaze originates from Fe. The amber-yellow glaze lies in the PbO–Al₂O₃–SiO₂ system, similar to Tang *sancai* and Liao *sancai*, and is a typical low-fired *sancai* style (Xu 2009). The gem-blue glaze has characteristics similar to Chinese *fahua*; therefore, Ye Wang's glazing technique is possibly the last version of Chinese *sancai* incorporated with *fahua* architectural traditions. Furthermore, B was extensively used as a supplementary flux, and colloidal gold was employed to create the rouge-red glaze. The use of gold-rose chromophore and boron may be the result of European influence; however, whether this influence was conveyed through China or directly from Europe requires further verification.

Glaze spectroscopic analysis and the colouration mechanism

As can be seen from the gem-blue glaze elemental analysis in Table 1, Ye Wang's unique hue of gem-blue glaze was not derived only from the cobalt ion. Copper, iron and manganese ions also have colouring effects. The EPMA results for these elements are as follows: CoO, 0.30 wt%; CuO, 0.58 wt%; Fe₂O₃, 0.43 wt%; MnO₂, 0.23 wt%. Although cobalt is not the largest component, the glaze is still coloured blue from the relatively stronger colouring effects of cobalt. Nevertheless, copper, iron and manganese ions also influence the spectral properties of gem-blue glaze jointly. Therefore, by comparing the spectral characteristics of the glazes when only adding one or two chromophoric elements, this study investigated the influence of copper, iron and manganese specific absorption bands in visible light on the hue of gem-blue glaze. Figure 11 shows the glaze samples and Table 2 lists the sample composition.

Through this comparison, we discovered the influence of copper ions on the spectral characterization of Ye Wang's gem-blue glaze. Sample 1 in Figure 11 refers to the unglazed ceramic body, Sample 2 refers to a transparent base glaze without chromophoric elements; Sample 3 is a base glaze with 0.30 wt% CoO; Sample 4 is a base glaze with 0.58 wt% CuO; and Sample 5 is a base glaze with 0.58 wt% CuO and 0.30 wt% CoO. A comparison of the absorption spectra of Samples 2 and 4 in Figure 12 (a) reveals that copper ions absorb wave bands beyond 500 nm. As can be seen in the reflection spectra in Figure 13 (a), compared to Sample 3, which only derived its colour from cobalt, Sample 5 derives its colour from both cobalt and copper and has a weaker reflection energy distribution in the 675–780 nm range. Therefore, the red-coloured wavelength has significantly weakened in the copper–cobalt glaze. Thus we confirm that copper ions absorb the red light emitted by the cobalt ion.

Regarding the effect of the spectral characterization of iron ions on gem-blue glaze, Sample 6 in Figure 11 is a base glaze with 0.43 wt% Fe₂O₃; and Sample 7 is a base glaze with 0.43 wt% Fe₂O₃ and 0.30 wt% CoO. Figure 12 (b) compares iron ion glaze and base glaze absorption spectra. The electron orbit of Fe³⁺ ([Ar] 3d⁵) is in a half-filled state and thus has a lower probability of electronic transition. In other words, the colouring ability of Fe³⁺ is very weak. Furthermore, the Fe₂O₃ concentration is low and thus has weak colouring effects. Therefore, the difference between the glaze with the addition of 0.43 wt% Fe₂O₃ absorption spectra and base glaze absorption spectra is not very evident. As can be seen in the comparison of reflection spectra in Figure 13 (b), trace amounts of iron ions do not influence the hue of Ye Wang's gem-blue glaze significantly.

Regarding the effect of the spectral characterization of manganese ions on gem-blue glaze, Sample 8 in Figure 11 is a base glaze with 0.23 wt% MnO₂; and Sample 9 is a base glaze with 0.23 wt% MnO₂ and 0.30 wt% CoO. The comparison of the absorption spectra of Samples 2 and 8 in Figure 12 (c) shows that the manganese ions displayed maximum absorption at approxi-



Figure 11 A colour comparison of bare substrate, the base glaze and glazing samples doped with individual and mixed chromophoric elements.

mately 480 nm. As can be seen from the reflection spectra in Figure 13 (c), the addition of MnO₂ would change the reflection energy distribution of gem-blue glaze.

Based on the spectroscopic analysis, the four transition-metal ions—cobalt, copper, iron and manganese—have their own absorption bands. As can be seen in the reflection spectra in Figure 14, Sample 3 derives its colour from cobalt alone and Sample 10, which was made according to the formula derived from the EPMA results, derives its colour from cobalt, copper, iron and manganese ions. Samples 3 and 10 were comparable with the reflection spectra of Ye Wang's gem-blue specimens. The reflection energy distribution of Sample 3 is strong in both blue and red bands, and Sample 10 is close to Ye Wang's glaze, but there are still differences. These differences can be attributed to the ignition loss of components, the inhomogeneity of the ancient glaze texture and matrix effects during analysis. Therefore, this study was based on comparing the spectra to adjust the proportion of chromophoric elements, trying to modify the formula of the simulated glaze to approach Ye Wang's gem-blue glaze.

A comparison of the reconstructed glaze and Ye Wang's glaze

According to Figure 14, Sample 10 was more intense than Ye Wang's gem-blue glaze in the 380–500 nm range. Figure 12 (b) shows that iron ions will absorb light in the 380–500 nm band, so an increase in the concentration of iron ions could decrease the reflection energy of the glaze at 380–500 nm. After adjusting the composition, the hue of Sample 11 was very close to Ye Wang's gem-blue. The recipes for the reconstructed glaze are listed in Table 3.

Table 2 The composition of glaze samples used in colorimetric analysis (in wt%)

Sample number	Base glaze							Chromophoric elements				
	SiO ₂	Al ₂ O ₃	B ₂ O ₃	Na ₂ O	K ₂ O	CaO	MgO	PbO	CuO	Fe ₂ O ₃	MnO ₂	CoO
2	43.74	0.35	5.93	3.55	12.42	0.63	0.17	30.52	n.a.	n.a.	n.a.	n.a.
3									n.a.	n.a.	n.a.	0.30
4									0.58	n.a.	n.a.	n.a.
5									0.58	n.a.	n.a.	0.30
6									n.a.	0.43	n.a.	n.a.
7									n.a.	0.43	n.a.	0.30
8									n.a.	n.a.	0.23	n.a.
9									n.a.	n.a.	0.23	0.30
10									0.58	0.43	0.23	0.30
11									0.58	1.00	0.23	0.25

n.a., Non-additive.

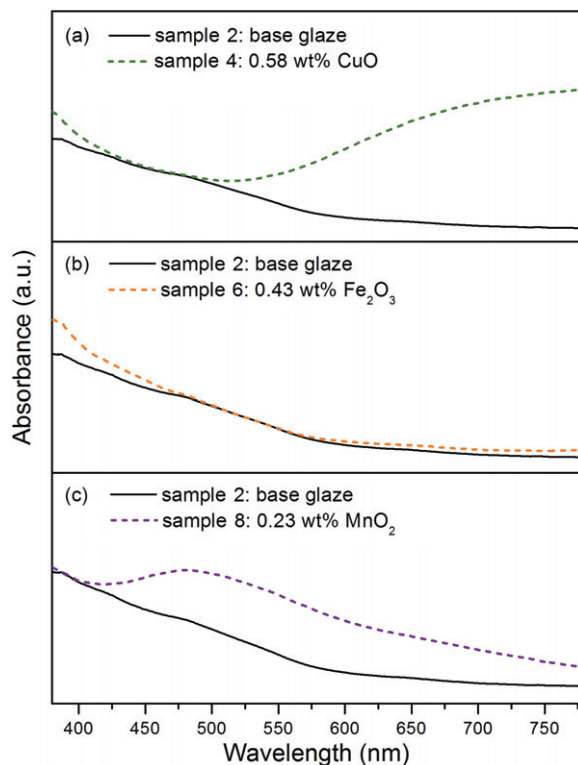


Figure 12 Absorption spectra of: (a) copper glaze and base glaze; (b) iron glaze and base glaze; and (c) manganese glaze and base glaze.

The surface reflection of the reconstructed glaze (Sample 11; see Fig. 15) was brighter and not softer than that of Ye Wang's, most probably because the reconstructed glaze was new and had not experienced weathering, having a more even surface than the old glaze. Optical micrographs of the reconstructed glaze and Ye Wang's glaze (Figs 16 and 17) showed that both glazes were transparent and cracked. The surface of Ye Wang's glaze had many scratches, signs of deterioration and small bubbles. The bubbles on the reconstructed glaze, conversely, were not as evident. This issue can be further investigated in future studies.

The results of colorimetric analysis are presented in Table 4. The following equation was used to derive the colour differences between the samples:

$$\Delta E^*_{ab} = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2} \quad (1)$$

Sample 11 has a colour difference (ΔE^*_{ab}) of 1.69 in relation to Ye Wang's glaze.

CONCLUSIONS

The purpose of this study was to discover Ye Wang's lost glazing formula by conducting thermal analysis, elemental analysis and spectroscopic analysis. HT-DSC was combined with the

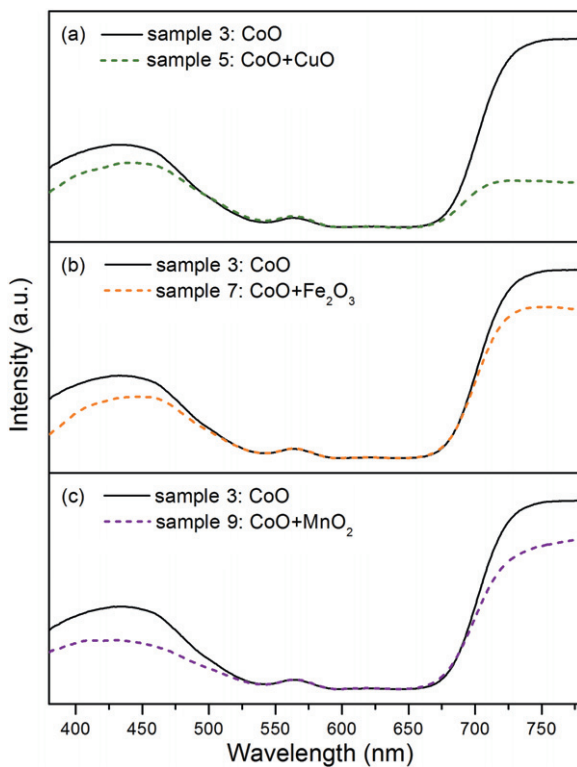


Figure 13 Reflection spectra of: (a) cobalt glaze and cobalt–copper glaze; (b) cobalt glaze and cobalt–iron glaze; (c) cobalt glaze and cobalt–manganese glaze.

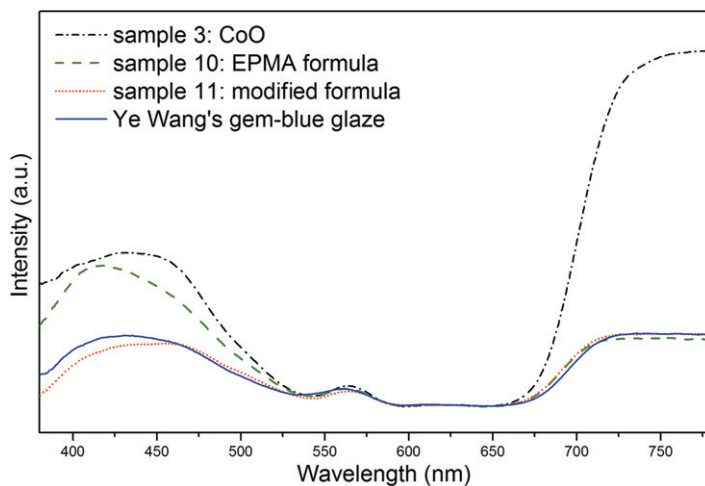


Figure 14 Reflection spectra of Ye Wang's gem-blue glaze and Samples 3, 10 and 11.

Table 3 Recipes for reconstructed gem-blue glaze

Reagent recipe (wt%)				Raw materials recipe (wt%)			
Base glaze		Colouring agent		Base glaze		Colouring agent	
SiO ₂	41.14	CoO	0.22	Quartz (SiO ₂)	37.40	Cobaltous oxide (CoO)	0.22
Al ₂ O ₃	0.33	CuO	0.52	Borax (Na ₂ B ₄ O ₇ ·10H ₂ O)	13.89	Cupric oxide (CuO)	0.52
B ₂ O ₃	5.58	Fe ₂ O ₃	0.89	Soda (Na ₂ CO ₃)	1.33	Ferric oxide (Fe ₂ O ₃)	0.89
Na ₂ CO ₃	5.71	MnO ₂	0.21	Potash (K ₂ CO ₃)	15.58	Manganese dioxide (MnO ₂)	0.21
K ₂ CO ₃	17.14			Limestone (CaCO ₃)	0.96		
CaCO ₃	1.06			White lead (2PbCO ₃ ·Pb(OH) ₂)	30.23		
MgCO ₃	0.33						
PbO	28.71						



Figure 15 A colour difference analysis of the reconstructed glaze (Sample 11) and Ye Wang's gem-blue glaze.

two-thirds rule to infer the liquidus temperature of Ye Wang's glaze. The results showed that the firing temperature of Ye Wang's works of art was most probably around 878–923°C.

The results of EPMA showed that Ye Wang's gem-blue glaze took the form of a PbO–K₂O–B₂O₃–Na₂O–SiO₂ system. Gem-blue glaze has a high basicity among Ye Wang's colour glazes. High basicity can increase the proportion of [Co^{II}O₄], making the glaze turn from amethyst to blue. Elemental analysis combined with spectroscopic analysis further showed that Ye Wang's gem-blue glaze derives its colour from the combination of copper, iron, manganese and cobalt, and it is this combination that makes Ye Wang's glaze unique.

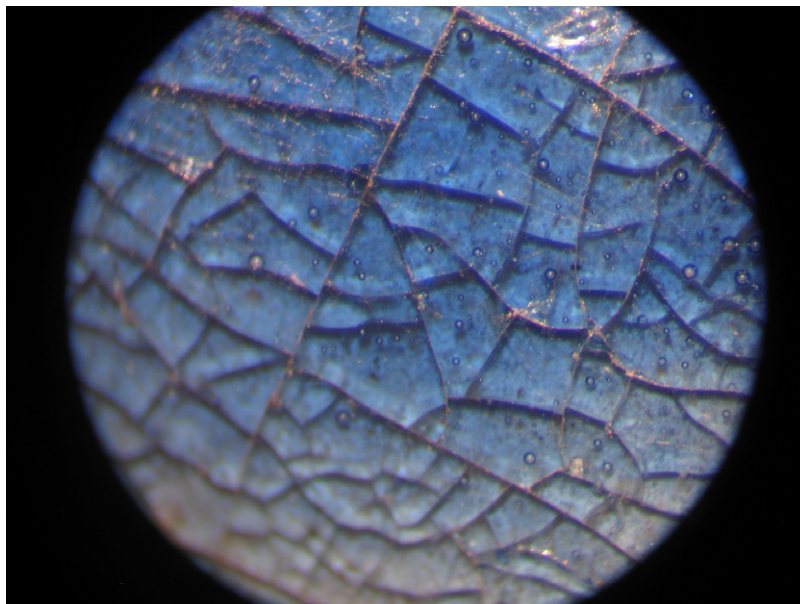


Figure 16 A microscopic image of Ye Wang's gem-blue glaze (Leica MZ 7.5 stereomicroscope: magnification, 32 \times ; light source, 3000K).

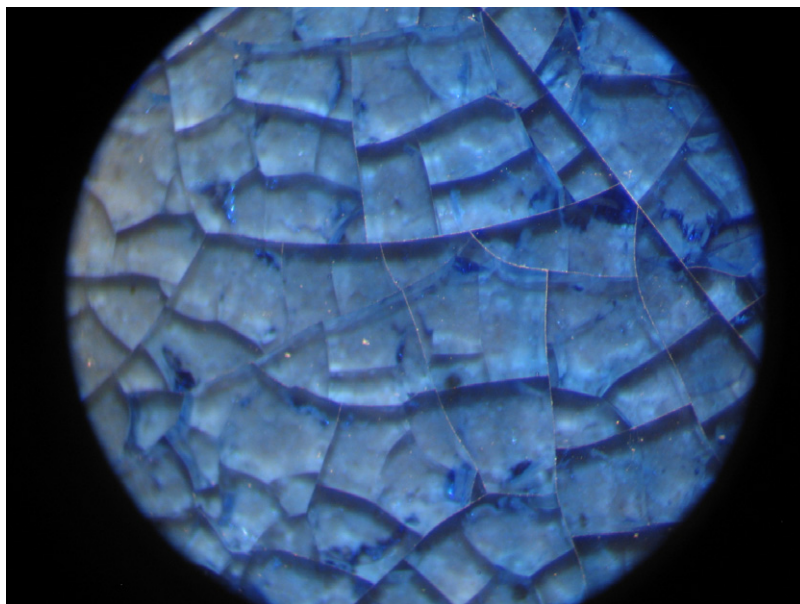


Figure 17 A microscopic image of reconstructed glaze (Sample 11) (Leica MZ 7.5 stereomicroscope: magnification, 32 \times ; light source, 3000K).

Table 4 Colour difference analysis of the recreated glazes and Ye Wang's gem-blue glaze

Sample	Tristimulus values			CIE 1976 L*a*b*			Colour difference
	X	Y	Z	L*	a*	b*	ΔE^*_{ab}
Ye Wang's gem-blue glaze	7.86	7.67	18.00	33.29	5.45	-24.78	–
Sample 10	8.46	7.61	23.22	33.16	11.38	-34.74	11.59
Sample 11	8.33	8.27	19.01	34.53	4.30	-24.67	1.69

By adjusting the proportion of chromophoric elements in a new glaze formula based on comparing its spectra to those of Ye Wang's works of art, this study made the hue of the reconstructed glaze very close to Ye Wang's gem-blue. The colour difference between the original and reconstructed glaze is only 1.69 ΔE^*_{ab} units.

The elemental analysis of Ye Wang's glaze revealed another fact, that the gem-blue contains high potassium levels, characteristic of traditional Chinese glazes. Moreover, Ye Wang employed boron, which was commonly used in *famille rose*. Therefore, Koji pottery inherits traditional Chinese glazing techniques and is influenced by *famille rose*.

ACKNOWLEDGEMENTS

The authors are indebted to Dr Gordon Turner-Walker for his valuable suggestions and for improving the language of this paper. They also thank the staff of the Ye Wang Koji pottery museum of Tzu-chi Temple for providing the fragments of Ye Wang's works. Financial support from the National Science Council, Taiwan (NSC 97-2113-M-224-001) is acknowledged.

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