



Technological connections in the development of 18th and 19th century Chinese painted enamels

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ARTICLE INFO

Keywords:

Chinese Painted Enamel
Canton Enamel
Enamelled Metal
Overglaze
Cloisonné

ABSTRACT

Chinese painted enamel is an artistic tradition of enamelled copperwares developed during the Kangxi period (1662–1722), commonly referred to as Canton enamel after the Wade-Giles spelling of Guangzhou. In this study, enamel fragments from areas of damage in the decorated surface of ten Chinese painted enamel objects dating to the 18th and early 19th century in the collections of the Ashmolean and Fitzwilliam Museums were non-destructively analysed with ESEM-EDX (Environmental Scanning Electron Microscopy - Energy Dispersive X-Ray Spectroscopy). After analysis, the enamel fragments were reattached to the objects using a conservation grade adhesive. Quantitative EDX elemental analysis is presented for the white enamel, underdrawings, eight painted enamel colours, outlines, and gilding. The enamel-glass composition, opacifier and colourants are discussed and compared to ceramic, glass, and enamelled metal technologies in use during the Ming Dynasty (1368–1644).

The results show that Chinese painted enamels combine Chinese and European technology to create a new and distinct art form.

1. Introduction

Chinese painted enamel is an artistic tradition developed at the turn of the 18th century. These works are almost exclusively enamelled copperwares, although examples on gold exist in imperial collections (Shih, 2012, p. 59). The details surrounding the early stages of development are unclear, however it is believed that the technique began in China between 1684 and 1714 in Guangzhou (Yang, 1987a, p. 54). Chinese painted enamels were also made in the Zaobanchu (Office of Manufacture) (Zaobanchu, 2005) workshops within the Forbidden City in Beijing. The imperial workshops opened in 1693 under the direction of emperor Kangxi (1662–1722) (Chang, 1991) and reportedly manufactured cloisonné, although it is unlikely that Chinese painted enamels were made there until the glass workshop opened in 1696 (Chang, 1987, p. 88). The Zaobanchu had a dedicated enamelling workshop from 1716 to 1789 (Arapova, 2017; Kerr, 1986, p. 114), and production slowed dramatically or ceased entirely after the workshop closed. The two production centres had a close relationship and skilled Chinese enamellers moved between them (Yang, 1987a, p. 62–63). They were also connected because enamels were commissioned from the Guangzhou workshops as tribute (Curtis, 2009, p. 59). For example, Emperor

Qianlong (1736–1795) received at least 980 Chinese painted enamel pieces from Guangzhou in 1756 (Hsia-Sheng, 1999, p. 51).

Production of Chinese painted enamels in Guangzhou continued throughout the 19th century, many examples from this period can be seen in public collections (Arapova, 1988; Palace Museum Beijing, 2020; Philadelphia Museum of Art, 2020; Victoria and Albert Museum, 2020). As it is today, Guangzhou was an important port and centre of international trade throughout the Qing dynasty (1644–1911). The scale of the porcelain trade passing through Guangzhou was immense, for instance the British H.E.I.C. (Honourable East India Company) acquired at least 1 million pieces of Chinese export porcelain in the 1719–21 season (Crosby-Forbes, 1982, p. 7), representing only a fraction of wares exported to Europe that year. Therefore, it is unsurprising that Guangzhou painted enamel designs are heavily influenced by export porcelain patterns and motifs. The stylistic relationship between the two media has been explored in depth throughout the last century (Garner, 1969; Hobson, 1912; Kerr, 2000; Welsh, 2015, p. 31). Enamelled copperwares were exported on a much smaller scale than porcelain and were not included in inventories, in part due to the scarcity of copper and subsequent ban on export of this metal, even in finished pieces (Jörg, 2015, p. 39).

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<https://doi.org/10.1016/j.jasrep.2022.103406>

Received 10 June 2021; Received in revised form 16 February 2022; Accepted 25 February 2022

Available online 4 March 2022

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Technological connections between Chinese painted enamel and porcelain have also been a subject of academic interest due to the development of the technique coinciding with advances in overglaze enamelling on porcelain (Garner, 1969). The overglaze palette expanded significantly in the second half of Kangxi's reign, perhaps most importantly with the introduction of opacification across all colours (Kingery and Vandiver, 1985). Several colours were introduced including pink and brighter hues of blue and yellow. The earlier restricted palette has been historically referred to as *Famille Verte* for the dominate transparent dark greens, the broader opacified palette was called *Famille Rose* after the new pink overglaze. From 1684 emperor Kangxi actively recruited Jesuit missionaries educated in science and art, installing glass blowers and enamellers in the Zaobanchu workshops. Jesuits worked as craftsmen in Beijing for over fifty years, creating an open avenue for technological exchange in these media (Curtis, 2009). Painted enamelling on copper was initially developed in the Netherlands, Italy and France in the 16th century (Speel, 2008, p. 21–30) leading to the hypothesis that Jesuits introduced the technique to China. The development of Chinese painted enamel was undoubtedly more complex, given how advanced ceramic technology was in China at that time, and that the first formally trained enameller, French Jesuit Jean-Baptiste Gravereau, arrived in 1719 (Curtis, 2004, p. 56; Welsh,

2015, p. 19). German Jesuit Kilian Stumpf, a scientist and skilled glassblower who headed the Zaobanchu glass workshop from 1697 to 1720, is a more likely candidate to introduce innovations (Curtis, 1993).

Theories on the technology of Chinese painted enamels remained purely hypothetical until the first scientific analysis was carried out with XRF (X-Ray Fluorescence) by researchers at the Victoria and Albert Museum in 1999 (Kerr, 2000; Mills and Kerr, 1999). The study compared the elemental composition of pinks on Chinese and European objects in different media, finding that pinks on Chinese painted enamels and overglazes on Chinese porcelain had the closest compositions. Röhrs (2004, p. 236) included EMPA (Electron Probe Micro Analysis) of two colours, turquoise and white, on a Chinese painted enamel dated to 1880 in his PhD thesis on Limoges painted enamels. In 2016, five colours from an example in the Beijing palace museum were analysed with XRF for comparison to a cloisonne ornament (Su et al., 2016). The object is a double gourd shaped vase with bats, clouds and auspicious characters on a pink ground, a typical Guangzhou motif. ESEM-EDX analyses of Armorial Ewer EA1957.36 were presented in a conference paper (Norris and Shortland, 2018), the results are included in Table 2. μ -XRF analysis of two objects, a Chinese porcelain and a Chinese painted enamel, was recently published by Norris et al. (2020). Another recent study employed Raman Microspectrometry and XRF to



Fig. 1. A) OC.74B-1938 Ruby Backed Plate circa 1730–1770, B) EA1978.1812 Square Dish with Deer c. 1740–1750, C) EA1978.1866 Dish with Landscape c. 1760, D) EA1978.1847 Vase with Landscape c. 1750, E) EA1978.1857 Teapot with Black Dragons c. 1736–1820, F) EA1978.1858 Teapot with Dragons on Blue Ground c. 1736–1820, G) EA1957.36 Armorial Ewer c. 1736–1820, H) MAR.O.48-1912 Brazier c. 1800, I) EA1964.56 Square Plate c. 1736–1912, and J) MAR.O.177A-1912 Stacked Box c. 1796–1912. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

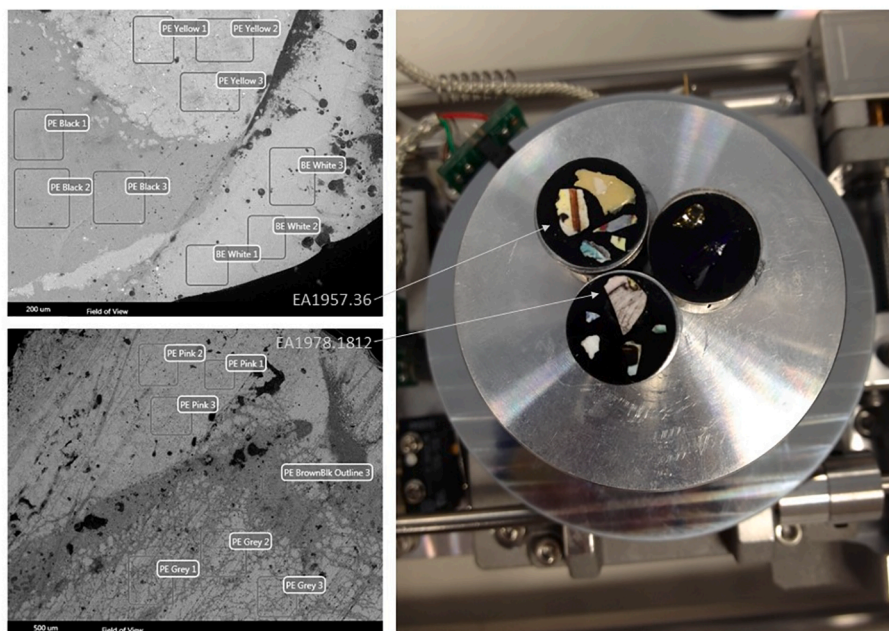


Fig. 2. Left, BSE images with bulk analysis areas annotated. Right, fragments mounted on stubs for ESEM-EDX analysis.

analyse twelve Chinese painted enamels in the Musée du Louvre and Musée Chinois collections (Colomban et al., 2020a).

Further in-depth research is required to fully understand the technology of Chinese painted enamels. The aim of this paper is to characterize the elemental composition of Chinese painted enamels from the 18th and early 19th centuries, in particular objects attributed to the Guangzhou production centre. The sample set in this study includes three objects from the Fitzwilliam Museum, University of Cambridge: OC.74B-1938, MAR.O.48-1912 and MAR.O.177A-1912, and seven objects from the Ashmolean Museum, University of Oxford: EA1978.1812, EA1978.1847, EA1978.1866, EA1957.36, EA1978.1857, EA1978.1858 and EA1964.56, see Fig. 1 for images of each object in this study.

2. Methodology

The objects in this study were selected because they had delaminated enamel fragments on the surface which could be detached without causing damage to the artwork. A fragment from each object was removed and the location documented. The samples were examined and cleaned with acetone on cotton swabs under a binocular microscope, they were then mounted on stubs with double sided self-adhesive carbon disks. After analysis, the undamaged fragments were cleaned again and reattached to the objects with a common conservation grade adhesive (Paraloid B72, ethyl methacrylate copolymer in acetone). Stub mounted fragments and Backscattered Electron (BSE) images taken during ESEM-

EDX analysis are illustrated in Fig. 2. Low magnification was used to identify features in the decoration and distinguish between different colours on the surface.

Samples from each object were non-destructively analysed with a Hitachi SU3500N environmental scanning electron microscope (ESEM) fitted with an energy-dispersive X-Ray detector (EDX). The data is processed and normalised through propriety TEAM software (Texture and Elemental Analytical Microscopy) using stoichiometry, the results are an average of three bulk analysis. The analytical conditions were: 30-50x magnification, 20Kv accelerating voltage and 50 s acquisition time. ESEM-EDX analysis was initially controlled for this study using a block mounted polished section of high lead glass standards DLH1 (65% PbO) (Walton and Tite, 2010) and Corning C (36.7 % PbO) (Adlington, 2017). Calculations of relative standard deviation and error utilized as metrics for precision and accuracy for evaluation are given in Table 1 (Abzalov, 2008; Stanley and Lawie, 2007). The output was calculated as oxides using stoichiometry and normalised to 100% (except halogens and noble metals).

An important benefit of ESEM-EDX is that the samples do not need to be coated for analysis, therefore the material taken from the artwork is undamaged and can be reattached, rendering the analysis non-destructive. However, there are disadvantages to this approach which are important to consider when interpreting the results. In environmental (ESEM) versus traditional scanning electron microscopy (SEM), lower pressure is used at the cost of a minor reduction in resolution and

Table 1

Certified values vs normalised ESEM-EDX results for polished block mounted standards DLH1 and Corning C presented as wt.% oxide. σ = standard deviation, RSD = relative standard deviation, δ = relative error.

	DLH1					Corning C				
	Certified	Mean (n=10)	σ	RSD %	δ	Certified	Mean (n=6)	σ	RSD %	δ
Na ₂ O	1.0	1.5	0.1	9.2	0.5	1.1	1.2	0.2	15.3	0.1
MgO	0.3	0.3	0.1	22.5	0.0	2.8	2.9	0.2	6.2	0.1
Al ₂ O ₃	4.0	5.0	0.1	2.5	0.3	0.9	1.0	0.1	12.8	0.1
SiO ₂	26.0	28.3	0.5	1.6	0.1	34.9	35.9	0.5	1.5	0.0
K ₂ O	1.0	1.0	0.1	5.3	0.0	2.8	2.9	0.1	3.7	0.0
CaO	1.0	1.3	0.0	3.1	0.3	5.1	5.7	0.1	1.6	0.1
Fe ₂ O ₃	1.0	1.7	0.1	6.9	0.7	0.3	0.9	0.1	13.9	1.7
PbO ₂	65.0	61.0	0.6	0.9	-0.1	36.7	31.1	0.2	0.8	-0.2

Table 2
Normalised ESEM-EDX results for stub mounted fragments from 18th and early 19th century Chinese painted enamels presented as wt.% oxide, except for Cl, Ag, and Au as w% element. “-” indicates that the element was not detected, O* = Opaque, Turq = Turquoise.

Object	Date	Layer	Colour	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	P ₂ O ₅	K ₂ O	CaO	TiO ₂	MnO	Fe ₂ O ₃	CoO	NiO	CuO	ZnO	As ₂ O ₃	SnO ₂	BaO	PbO	Cl	Ag	Au
OC.74B-1938	1730–1770	Enamel	White	0.3	–	0.6	41.9	–	6.1	0.3	–	–	0.6	–	–	–	–	5.7	–	–	43.0	1.70	–	–
OC.74B-1938		Painted	Green	0.4	–	0.9	46.0	–	7.5	0.1	–	–	0.6	–	–	3.8	1.9	2.6	3.1	–	29.8	3.2	–	–
OC.74B-1938		Outline	Black	1.0	–	3.2	44.7	1.7	6.2	0.9	–	1.6	1.3	0.4	–	0.6	0.7	2.5	1.4	–	29.9	3.9	–	–
EA1978.1812	1740–1750	Counter	White	0.1	–	0.3	35.2	–	8.2	0.6	–	–	0.6	–	–	3.1	–	8.4	–	–	43.4	–	–	–
EA1978.1812		Underdrawing	Brown	0.3	–	3.1	46.9	0.2	10.8	0.9	0.2	2.6	2.9	0.2	–	1.7	1.3	2.6	–	–	26.2	–	–	–
EA1978.1812		Painted	Grey	–	–	1.4	44.0	–	6.9	0.4	–	1.0	1.4	–	–	0.6	0.6	6.0	–	–	38.0	–	–	–
EA1978.1812		Painted	Pink	–	–	1.2	41.0	0.3	6.3	0.4	–	–	0.7	–	–	–	0.7	6.5	–	–	42.1	0.9	–	–
EA1978.1812		Painted	Yellow	0.3	–	1.4	43.1	0.1	5.5	0.4	–	0.4	0.9	–	–	–	1.3	3.9	3.7	–	37.2	1.9	–	–
EA1978.1847	circa 1750	Enamel	White	–	–	0.3	35.9	–	9.3	0.2	–	–	0.8	–	–	–	1.5	7.6	–	–	44.4	–	–	–
EA1978.1847		Painted	Turq. Blue O*	–	–	0.9	34.9	–	8.7	1.5	–	–	1.2	–	–	2.3	3.8	6.2	–	–	40.6	–	–	–
EA1978.1866	circa 1760	Counter	White	0.7	–	0.0	36.6	0.8	8.0	–	–	–	0.6	–	–	–	–	7.3	–	–	45.9	–	–	–
EA1978.1866		Painted	Black	1.3	–	3.0	39.4	–	8.9	1.8	–	3.4	7.7	0.8	–	1.0	0.7	3.8	–	–	27.9	–	–	–
EA1978.1866		Painted	Turq. Green	–	–	0.6	40.4	–	7.6	0.2	–	–	0.6	–	–	1.0	0.6	7.3	0.3	–	40.4	1.2	–	–
EA1978.1866		Gilding	Gilding	0.2	–	0.7	9.0	–	2.2	0.4	–	0.9	2.4	–	–	0.4	0.2	1.1	–	–	7.1	–	6.3	69.0
EA1957.36	1736–1820	Enamel	White	0.4	–	0.5	37.9	–	6.8	0.7	–	–	0.8	–	–	–	–	7.7	–	–	43.7	1.6	–	–
EA1957.36		Underdrawing	Brown	1.8	–	4.8	26.6	1.3	4.6	3.0	–	4.3	17.4	1.1	–	0.7	1.3	4.6	–	–	27.4	1.2	–	–
EA1957.36		Painted	Black	0.5	–	2.8	38.5	–	9.8	1.9	–	3.6	8.1	0.4	–	0.9	0.8	3.1	–	–	29.6	–	–	–
EA1957.36		Painted	Yellow	0.3	–	0.8	37.6	0.7	6.2	0.9	–	–	0.8	–	–	–	0.9	6.2	1.6	–	42.6	1.5	–	–
EA1978.1857	1736–1820	Enamel	White	0.8	0.9	0.3	45.2	–	2.9	1.6	–	–	0.9	–	–	–	–	5.8	–	–	38.2	3.5	–	–
EA1978.1857		Underdrawing	Brown	0.4	–	1.4	34.6	–	5.2	1.4	–	0.5	12.6	0.4	–	0.3	–	4.1	–	–	38.8	–	–	–
EA1978.1857		Painted	Blue	0.5	–	0.7	47.1	–	4.9	0.9	–	–	1.2	0.8	–	0.4	0.3	4.1	–	0.9	37.9	–	–	–
EA1978.1857		Painted	Pink	0.3	–	0.9	50.0	–	5.5	0.4	–	–	0.6	–	–	–	0.7	2.8	–	–	35.8	3.0	–	–
EA1978.1857		Painted	Turq. Green	0.2	–	0.8	48.4	–	9.8	0.5	–	–	0.9	–	–	5.6	3.8	2.6	–	–	27.4	–	–	–
EA1978.1858	1736–1820	Enamel	White	0.5	–	0.6	40.9	–	7.7	0.4	–	–	0.7	–	–	–	–	5.5	–	–	43.7	–	–	–
EA1978.1858		Painted	Blue	0.4	–	1.3	43.4	–	7.2	0.7	–	–	1.5	1.0	0.3	0.8	1.0	4.6	–	1.1	36.3	–	–	–
MAR.O.48-1912	circa 1800	Counter	Turq. Blue O*	2.1	–	0.6	42.4	–	12.0	1.9	–	–	0.6	–	–	1.0	0.1	6.8	–	–	32.6	–	–	–
MAR.O.48-1912		Enamel	White	1.4	–	1.2	39.6	0.2	8.4	1.0	–	–	0.8	–	–	1.4	0.8	8.6	–	–	36.6	–	–	–
MAR.O.48-1912		Painted	Turq. Blue	1.7	–	1.7	39.5	0.1	9.0	4.2	–	–	1.2	–	–	10.8	1.3	7.3	–	–	23.0	0.3	–	–
MAR.O.48-1912		Outline	Black	2.4	–	5.2	29.6	0.3	6.6	5.6	–	7.5	2.0	1.3	–	4.7	1.3	5.0	–	0.4	27.1	0.6	–	–
EA1964.56	1736–1912	Counter	White	0.3	–	0.3	39.2	–	8.7	0.4	–	–	0.7	–	–	–	–	7.2	–	–	43.3	–	–	–
MAR.O.177A-1912	1796–1912	Counter	White	0.6	–	0.4	32.7	–	6.5	0.5	–	–	0.7	–	–	3.4	0.7	7.8	–	–	46.9	–	–	–

EDX accuracy caused by scattering of X-rays when they interact with atmospheric gasses (Newbury, 2002). The same phenomena can alter the trajectory of electrons in the beam causing them to interact with a small area around the focal point described as a skirt. Both problems can be mitigated by making the beam gas path length as short as possible. The interaction volume should also be considered (Goodhew et al., 2000, p. 127) because the samples are mounted on stubs rather than in cross section. The depth of analysis has been calculated theoretically for this material (Norris, 2021, p. 102-105) demonstrating that X-rays can penetrate the thin painted layers and result in detectable fluorescence from the substrate for many elements in the composition. Although the samples were cleaned under a binocular microscope it is possible that deposits or corrosion products are present on the surface of some samples.

Relevant to this study is the detection of fluorine because fluorite (CaF₂) is a common opacifier in Chinese enamels and glass (Quette, 2011, p. 311; Yang, 1987b, p. 74). Fluorine is a low-Z element which cannot be detected with XRF techniques in air. It has been shown that it is possible to detect fluorine with the ESEM-EDX instrument using block mounted samples of locally sourced fluorite purchased from Hunan Province (Norris, 2021, p. 112).

3. Results

The ESEM-EDX results are presented in Table 2, some samples have surface decoration with more than one colour. The body and surface decoration of Chinese painted enamels are layered. The body is made of thin copper sheet with a layer of fired enamel on both sides, the enamel on the underside or interior is called the counter enamel (Speel, 1998, p. 33). Decorated surfaces are also fired, they are set out in an underdrawing followed by polychrome painted enamels, outlines, and painted gilding, see Fig. 3.

4. Discussion

The ESEM-EDX results have shown that Chinese painted enamels are high lead silicates with up to 47% PbO. Potassium was detected in every sample at 2–12% K₂O, this element acts as a flux (Moretti and Hreglich, 2013, p. 30) and could possibly influence the hue of enamels and glass coloured with copper (Kerr and Wood, 2004, p. 630). Sodium and calcium are also important to the glass composition, working as a flux and stabiliser respectively. The levels of these elements are similar in the enamels, counter enamels, and painted enamel decoration regardless of colour.

The proportion of lead and silica in Chinese painted enamels are plotted alongside overglazes on Chinese porcelain (Giannini, 2015) and Chinese cloisonné enamels (Henderson et al., 1989; Quette, 2011, p. 317–319) in Fig. 4. The overglazes in Giannini's study are from 22 Chinese porcelains in the collection of the Victoria and Albert Museum dating to the late 17th and 18th century. The study by Quette included ten objects dating from 1350 to 1500, and the study by Henderson analysed five objects attributed to 1500–1650. The graph illustrates that the amount of lead in Chinese painted enamels (23–47% PbO) is more consistent than the wide range detected in overglazes on porcelain (up to 77% PbO). High lead overglazes tend to be yellow and green, whereas

low lead overglazes are predominantly red and black. This suggests that overglazes required multiple firings at high and low temperatures, whereas Chinese painted enamels were formulated to mature at a midrange.

The composition differs from Limoges painted enamels which have more variation in the proportion of glass formers and a different balance of fluxes. Early Limoges production, in the 15th to mid-16th centuries, was low or lead free (<10% PbO) (Biron, 2004; 2015, p. 367; Perez y Jorba et al., 1993; Röhrs, 2004, p. 235–237). Analysis of examples dated to the 18th century are limited, but 17th century objects produced just before the development of the technique in China are relevant, some of these were made with 20–30% PbO (Röhrs et al., 2006). Lead oxide increases in Limoges painted enamels to levels similar to Chinese painted enamels in the 19th century. Limoges painted enamels are high in sodium rather than potassium, except for the period between 1480 and 1530, where chemically unstable compositions were produced by combining high levels of both fluxes (11–15% of Na₂O and K₂O). In contrast, the glass composition of Chinese cloisonné enamels from the Ming Dynasty (1368–1644) is very similar at 8.2–52% PbO accompanied by high potassium. The relationship is more obvious when looking at the average and standard deviation of lead to silica in Chinese painted enamels (avg. 40% SiO₂ with stdv. 5.5, 37% PbO with stdv. 6.8) and Chinese cloisonné enamels (avg. 42% SiO₂ with stdv. 6.3, 36% PbO with stdv. 9.3).

4.1. Opacification

White enamels in this study are opacified with arsenic at an average of 7.2% As₂O₃, and in the polychrome painted enamel decoration at 2.5–7.3% As₂O₃, this is consistent with previous studies on Chinese painted enamels. Identification of arsenic with ESEM-EDX in a high lead matrix relies on the As Kβ peak at 11.72 keV because the Kα peak is masked by the Pb Lα peak at 10.55 keV. As described in the methodology section, arsenic peaks in the polychrome painted layers could be a result of the white layer beneath (Thomsen et al., 2005) due to the layered nature of the material and mounting system used in this study.

Arsenic opacification is consistent with 18th century overglazes on Chinese porcelain (Giannini, 2015, p. 414-419; Kingery and Vandiver, 1985). Ceramic overglazes are not the source of this technology because white overglaze enamel, and control over overglaze opacification across the polychrome colour palette, was an important innovation developed in both media simultaneously during the Kangxi period (1662–1722). Analysis of Ming (1368–1644) and Qing (1644–1911) glass is very limited (Henderson et al., 2018), existing studies have identified both fluorite and a combination of fluorite and lead arsenate opacification in Qing period glass objects (Curtis, 2004, p. 18; Hykin et al., 2010, p. 170). Before the turn of the 18th century, opacification was achieved with fluorite in Chinese glass (Yang, 1991, p. 138, 1987a, p. 76) and metal enamels (Colomban et al., 2020a; Henderson et al., 1989; Kirmizi et al., 2009; Quette, 2011, p. 311; Su et al., 2016; Twilley, 1995, p. 165). In the cloisonné studies, high arsenic was only detected in white enamels on the Qianlong period (1736–1795) Ornament from the Fuwang chamber by Su et al. (2016) and Mei-ping Vase EAX.3894 dated to the mid-17th century (Henderson et al., 1989). The Mei-ping Vase appears to be an early and possibly rare example of the transition from fluorite to lead

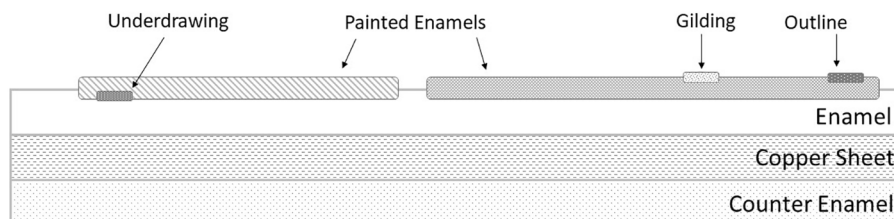


Fig. 3. Diagram showing the layers of a Chinese painted enamel object in cross section.

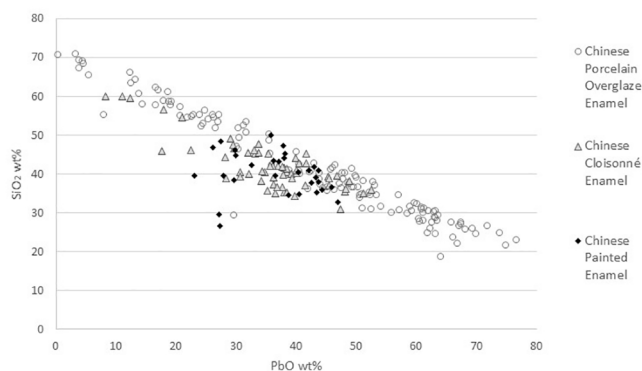


Fig. 4. Scatterplot of SiO₂ to PbO (wt%) of Chinese painted enamels given in Table 2, overglazes on late 17th and 18th century Chinese porcelain (Giannini, 2015, p. 414–419), and Chinese cloisonné enamels from 14th–17th centuries (Henderson, Tregear and Wood, 1989; Quette, 2011, p. 317–319).

arsenate opacification. Notably, fluorine was not detected in the Chinese painted enamel samples from the Ashmolean and Fitzwilliam collections. The objects in this study form part of a wider sample set of 58 examples dated to the 18th century (Norris, 2021, p. 19–130). Fluorine was not detected in the art works included in the larger study, except for a late 18th century stylistic subgroup emulating Chinese cloisonné (Norris et al., 2022). A more sensitive technique would be required to completely exclude the presence of fluorine because trace amounts could be masked by iron (F K α 0.68 and Fe L α 0.71 keV).

Arsenic is inconsistent with European painted enamels which employ tin opacification (Biron, 2004; Colombari et al., 2020b); the objects in these studies are French, English, and Swiss. Tin was also identified as the opacifier in a German painted enamel dated to 1670 (Manners, 2021; Norris, 2021, p. 205 and 475). Colombari et al. (2020a) identifies cassiterite (SnO₂) as an opacifier in the yellow and green decoration on three Chinese painted enamel objects (Ewers F1467.1–2 and Bottle R975). If this mineral is present, it is likely a result of recrystallization of cassiterite (SnO₂) from lead stannite (PbSnO₃) used as a yellow colourant, which can occur from 600 °C (Tite et al., 2008).

Venetian glass making has been referenced as a technological source for arsenate opacification (Curtis, 1993; Kingery and Vandiver, 1985), and is given as the opacifier in a Giovanni Darduin recipe for opalised

Venetian girasole glass dated to 1683 (Moretti and Hreglich, 2013, p. 31). Lead arsenate was also identified as the opacifier in a Venetian glass saucer attributed to the 18th century by Ricciardi et al. (2009). Knowledge of this technique could possibly have reached China through Joachim Bouvet who arrived in Guangzhou in 1699 to set up a plate glass factory (Curtis, 2009, p. 42). In his previous role as director of the French imperial glass works, Bouvet worked alongside Murano glass makers who may have been familiar with arsenic opacification. Presumably, a different technology was sought out because fluorite could not opacify the enamel enough to obscure the copper body of the vessel. It is interesting that Chinese painted enamels are not opacified with tin, given that was the dominant technology in Europe at that time. It may be that arsenic was more cost effective if the raw materials were abundant, or less time consuming because the enamel could be made without fritting. White enamel was required in large quantities because it is used to coat the entire surface of the object. It was likely made in a process similar to the method for white overglaze enamels described by Jesuit Père d'Entrecolles in his 1712 and 1722 letters (Burton, 1906, p. 95 and 177). “This white is made from the powder of a transparent rock which is calcined in an oven...to half an ounce of this powder they put an ounce of white lead.”

4.2. Painted decoration

In the initial stage of manufacture, the copper body is coated in enamel and fired to create a monochrome enamelled surface. Four types of painted decoration are used to embellish the Chinese painted enamel artworks in this study: underdrawings, painted enamels, outlines, and gilding. The first step in painting is to layout important parts of the design in an underdrawing, see Fig. 5. Analyses of three underdrawings are given in Table 2, they are based on high iron up to 17% Fe₂O₃ accompanied by high aluminium up to 4.8% Al₂O₃, manganese up to 4.3% MnO, cobalt up to 1.1% CoO, and copper up to 1.7% CuO. Underdrawings are matt and painted in thin layers with a fine line weight, see Fig. 5. As in red overglazes on Chinese porcelain, aluminium may have been added to increase the vibrance of the colour and lower the melting temperature (Vandiver et al., 1997). There is no pattern in the amount of iron and aluminium oxides in Chinese painted enamel underdrawings, excluding a consistent mineral or clay source (Norris, 2021, p. 278). This is supported by the historic account from Père d'Entrecolles in 1712, who describes the red colourant for overglaze enamel on porcelain as being made from calcined copperas (pyrite FeS₂) (Tichane, 1983, p. 81 and 119). Alum was mentioned by d'Entrecolles as an ingredient in copper red glaze (sang-de-boeuf) demonstrating that mineral sources of aluminium oxide were used in ceramic production in the 18th century.

Polychrome painted enamels are applied to the surface in a second stage, they are vitrified and glassy in appearance. Pieces have been embellished with as many as 15 distinct painted enamel colours, OC.74B-1938 for example has a palette of eleven. The two yellow enamels in this study are coloured with an average of 2.6% SnO₂ and 1.1% ZnO. Tin was also detected in the light green on OC.74B-1938 at 3.1% SnO₂ in combination with 3.8% CuO and 1.9% ZnO, the thin wash of turquoise green on the reverse of EA1978.1866 is coloured with 0.25% SnO₂ in combination with 0.96% CuO and 0.58% ZnO. Lead stannate yellow (PbSnO₃) was an established colourant in Ming dynasty cloisonné enamels (Henderson et al., 1989; Quette, 2011, p. 317–319) and European glass (Tite et al., 2008).

Tin is absent in the turquoise green on EA1978.1857, and the three turquoise blues which are coloured with up to 11% CuO and 3.6 ZnO. The bluer turquoises are heavily opacified with arsenic at an average of 6.7% As₂O₃. Translucent green overglazes coloured with copper and iron were well established in the Ming Dynasty (Vandiver et al., 1997), translucent Chinese painted enamel turquoises are a continuation of that tradition. Opacified turquoises are generally counter enamels on Chinese painted enamel objects, opaque turquoise painted enamels such as

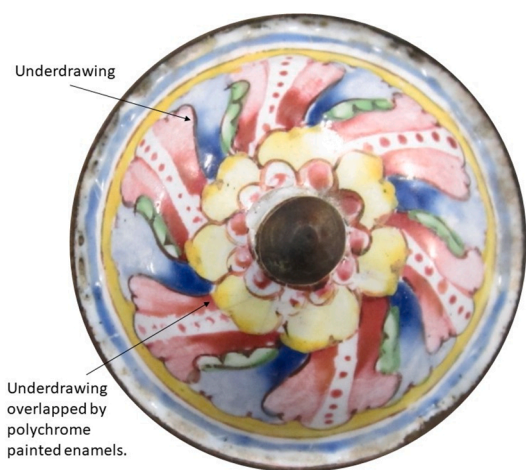


Fig. 5. Detail of the lid from EA1978.1858 highlighting the underdrawing which is painted in a fine line weight. Underdrawings are typically warm brown in colour leaning toward red or orange. In this example, polychrome painted enamel decoration clearly overlaps the underdrawing. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

the shoulder of EA1978.1847 are rare. The colour shift toward blue appears to be influenced by the addition of arsenic rather than colourants.

Blue enamels on EA1978.1857 and EA1978.1858 are coloured with an average of 0.88% CoO, 1.4% Fe₂O₃, 0.56% CuO and 0.66 ZnO; 0.3% NiO was detected in EA1978.1858. Both examples are manganese free and include barium, which is only detected in the blue enamels and the high cobalt (1.3% CoO) black outline on MAR.O.48–1912. Arsenic was detected in both blues in this study, but if there is an association with cobalt, it is masked by the high arsenate composition of the white enamel substrate. The absence of manganese differs from Chinese painted enamel blues on copper analysed in previous studies (Colomban et al., 2020a, Vase R975; Norris et al., 2020, Ruby Backed Plate C.107–1931; Su et al., 2016, Double Gourd HFL-1). These blues are coloured with a cobalt associated with manganese and nickel derived in part from imported smalt (Colomban et al., 2020a; Giannini et al., 2017). Manganese rich blues in these studies appear to be a mixture of imported and domestic cobalt (Wen et al., 2007) which would have reduced costs and produced a warmer hue (Wen, 2012, p. 274–280). Whereas the manganese free blues used to decorate EA1978.1857 and EA1978.1858 are coloured exclusively with imported cobalt. Although the results of this study cannot conclusively distinguish between Iranian (Fe-Co-Ni-As) and European ores (Fe-Co-Zn-In-Pb or Fe-Co-Ni-As-Mo-Bi-U) (Gratuze, 2013, p. 323), it is most likely to be the Saxon cobalt identified in blue Qing porcelain overglazes of the same period (Giannini et al., 2017).

Previous studies on Chinese painted enamels using XRF have shown that colloidal gold is the colourant in pink (Mills and Kerr, 1999; Norris et al., 2020). The amount of gold required to create this colour is below the limit of detection with ESEM-EDX due to the high lead composition which masks the element in the spectra. Zinc oxide was detected in both pinks at an average of 0.73% ZnO and is absent in the white enamel substrates. Pink was not used in Chinese porcelain, glass or cloisonné enamels before the development of the Chinese painted enamel technique. At this time, colloidal gold was firmly established in Europe as the colourant for ruby red glass, this is the most obvious source of technology for the colour (Kerr, 2000). By the 17th century there were more than a dozen recipes for colloidal gold ruby glass and enamels (Hainbach, 1924, p. 170-175; Kerr and Wood, 2004, p. 636). The most common being the Purple of Cassius method which uses tin oxide to initiate precipitation (Von Kerssenbrock-Krosigk, 2008, p. 123–137). The exact formula used to produce pink Chinese painted enamel is unclear; tin oxide was not detected in these samples, excluding most of the recipes. Arsenic, rather than tin, was used as the reducing agent in a method employed by French glass maker Bernard Perrot in the 17th century (Colomban and Burcu, 2020). It is not possible to confirm or rule out the Perrot technique in this study because of the high amount of lead arsenate in the white enamel. Other possibilities include Cohn's Gold Ruby Glass and Alumina Purple (Hainbach, 1924, p. 173-174). Aluminium oxide is elevated in both examples compared to the white enamel substrate, making Alumina Purple (potassium alum, gold trichloride, and ammonia) a good candidate. The two black painted enamels analysed are areas of scroll work near the rims of EA1957.36 and EA1978.1866. On average they are coloured with 3.5% MnO, 7.9% Fe₂O₃, 0.6% CoO, 0.9% CuO and 0.7% ZnO. The composition is consistent with the addition of iron and copper, perhaps in the form of brass corrosion products, added to the domestic cobalt ore (high Mn-Fe) used in blue underglaze on Chinese porcelain (Giannini et al., 2017).

Outlines are a third type of painted decoration; they are similar to underdrawings in line weight but tend to be black rather than brown and are applied over the polychrome painted enamels. The composition of the outlines differs from black painted enamels, MAR.O.48-1912 is much higher in manganese and copper with barium, in contrast all of the colourants are low in OC.74B-1938 and 1.4% SnO₂ was detected. Outlines are typically black, but other colours are used especially in diaper patterns, these often include reds and turquoises.

The fourth and final type of painted decoration is gilding fired on to the enamelled surface. Before gilt highlights can be applied, the object is fired to 650–800 °C to fix the painted enamels (Mengoni, 2013, p. 108; Wood, 2011, p. 229). Painted gilding on Chinese porcelain uses a lead flux and requires a separate lower firing at 600–800 °C (Burton, 1906, p. 118; Kerr and Wood, 2004, p. 698). The maturation temperature of the enamels and painted gilding are likely at the high and low ends of these estimates respectively. Objects with gilt rims and feet would have had a further firing to attach amalgam gilding by burning off the mercury at 250–350 °C (Kerr and Wood, 2004, p. 694). Applying amalgam gilding to unenamelled metal components is common in Chinese Cloisonné. The example of painted gilding analysed in this study was applied in a fine line weight over the black scrollwork on EA1978.1866, it is 6.3% silver and 69% gold, the remaining oxides are associated with the enamel and painted enamel layers below.

5. Conclusion

The results of this study show that the Chinese painted enamel technique was developed by drawing on Chinese and European ceramics, glass, and enamelled metal technologies, and imported materials. A striking innovation in Chinese painted enamel is the development of an enamel-glass composition with a midrange maturation temperature that can be used as a medium for controlled gradations in opacification and colour. The glass composition is an amelioration of Chinese cloisonné enamel evidenced by similarities in the proportion of glass formers, fluxes, and stabilisers. Chinese cloisonné is also a direct technological predecessor of lead stannite yellow, which was not used in Chinese ceramics before the development of Chinese painted enamels, and amalgam gilding applied to unenamelled metal components. The technology for underdrawings, turquoise green and black painted enamels, black outlines and painted gilding are derived from Chinese ceramics.

New colours were developed using European techniques and imported materials. Of great importance was the development of lead arsenate opacification used to obscure the metal body and create the white enamel ground onto which polychrome painted enamels are delicately painted. Arsenic opacification was not the dominant technology in China or Europe until the Chinese painted enamel technique was developed. An example of lead arsenate opacification in Chinese Cloisonné in the 17th century exists, but most Ming examples are opacified with fluorite. Historic accounts and recent analysis of Venetian glass are strong evidence that the technology is European. This closely guarded Venetian glass making technique was likely transferred to China through French glass makers working in Guangzhou and Jesuit missionaries working in Beijing alongside knowledge of how to make a pink colourant from colloidal gold. Cobalt imported from Europe also contributed to the development and ongoing manufacture of Chinese painted enamels as shown by the manganese free blue painted enamel compositions. Green and turquoise blue are also innovative colours. The new green, which is yellower, combines tin and copper oxides used in Chinese cloisonné and ceramics. Whereas turquoise blue combines copper established in Chinese ceramics with arsenic opacification associated with Venetian glass.

At least five different media are predecessors of the technology and materials used to manufacture Chinese painted enamels: Chinese cloisonné, Chinese ceramics, Venetian glass, continental European glass, and European smalt. These artistic traditions were brought together due to mandate and financial backing of the court. Emperor Kangxi (1662–1722) was known for his interest in science and the arts, but undoubtedly, he also recognised the importance of the export market including the extraordinary demand for porcelain. Investment in technology which could improve the export trade was sensible, and this paper demonstrates the close compositional links between the development of Chinese painted enamels and advances in Qing porcelain overglazes. It is interesting to note that there are also clear differences

between the two media. For example, most Chinese painted enamels are mainly translucent or lightly opacified, whereas porcelain overglazes feature a translucent and opaque version of every colour. The proportion of silica to lead shows that overglazes were applied through multiple firings with high, medium, and low firing colours. In contrast, Chinese painted enamels have a consistent mid-range balance between these elements regardless of colour, linking them to Chinese cloisonné enamels.

The results of this study highlight that Chinese painted enamels are derived from rich and established artistic traditions in China and Europe. Local and imported materials, technologies, and skills were brought together to create a full palette of innovative colours and a completely new art form.

CRedit authorship contribution statement

Dana Norris: Methodology, Investigation, Visualization, Writing – original draft. **Dennis Braekmans:** Formal analysis, Writing – review & editing, Supervision. **Andrew Shortland:** Conceptualization, Resources, Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

We would like to thank the Ashmolean and Fitzwilliam Museums for facilitating this research by lending samples for analysis. Specifically, to Shelagh Vainker, Mark Norman, Daniel Bone, Alessandra Cereda, James Lin and Jo Dillon. Acknowledgement also goes to Roger Keverne whose keen interest was a driving force behind this project, and to Errol Manners who lent the armorial German painted enamel bowl for comparison to Chinese painted enamels. Special thanks must be given to Jonathan Painter for his support and advice on the analysis.

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