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ORIGINAL ARTICLE

Emulation and technological adaptation in late 18th-century cloisonné-style Chinese painted enamels

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Abstract

Cloisonné-style motifs are rare and enigmatic in Chinese painted enamels because of their distinct technological development at the end of the 18th century. Five late Qianlong to Jiaqing period (1736–1820) Chinese painted enamels with cloisonné-style motifs are investigated using environmental scanning electron microscopy–energy dispersive X-ray spectroscopy. Back-scattered electron images and elemental analysis are combined to study the decorative enamelled surface. The compositions of the layers within the enamel, that of the counter enamel and the polychrome decoration on the surface are determined and identified. Fluorine and elevated amounts of calcium were detected, indicating that fluorite was likely used as a raw material. The presence of this mineral, which is typical of Chinese cloisonné, confirms that these objects share both aesthetic and technological relationships.

KEYWORDS

Canton enamel, cloisonné, enamelled metal, ESEM-EDX, glass, overglaze, porcelain

INTRODUCTION

Painted enamel technology was developed in Europe during the 16th century with early productions in the Netherlands, Italy and France (Speel, 2008, pp. 21–30). The technique came into use in China during the Kangxi period (1662–1722) in Guangzhou (Yang, 1987a, p. 54). Chinese painted enamels are metal objects that have been enamelled and then decorated with polychrome patterns and motifs. Most painted enamel objects are copper, although gold has also been used as a substrate (Bryant, 2002, p. 28; Shih, 2012, p. 59). The metallic body is coated with enamel and fired, creating a monochrome vitrified surface. The enamelled surface is

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decorated by hand with polychrome painted enamel colours. These enamels are ground into a fine powder and mixed with a medium such as doemendina oil, and applied to the surface with fine brushes (Curtis, 2009, pp. 119–120). The object is fired again to fix the painted decoration, and subsequent firings are used to fix painted and amalgam gilding on the enamelled and unenamelled metal components, respectively.

Cloisonné is also a type of enamelling on copper. This artistic technique was developed in the Mediterranean region c. 1450 BCE (Speel, 1998, p. 107). The technique continued to be used throughout the Byzantine Empire (395–1453 CE) and was established in China by the 15th century (Brinker & Lutz, 1989, pp. 46–51; Garner, 1971, pp. 50–59; Quette, 2011, pp. 7–9). In this technique, flat metal wires are attached perpendicular to the surface of the object to create a raised pattern of cells (Brinker & Lutz, 1989, pp. 65–73). The cloison cells are filled with enamel, fired, and the surface ground flat and polished with a sequence of abrasives. One of the most common Chinese cloisonné patterns is a stylised motif of lotus flowers and scrollwork on a turquoise blue ground. The pattern is associated with Buddhism, as a symbol of purity, and is a frequent motif on ritual objects (Bartholomew, 2012, p. 36; Brinker & Lutz, 1989, pp. 56–59).

Stylistic links between Chinese painted enamels and Chinese porcelain have been made in the past (Crosby-Forbes, 1982, pp. 29–30; Garner, 1969; Hobson, 1912; Kerr, 1986, pp. 110–114; Welsh, 2015, pp. 30–36). Decoration of Chinese painted enamel has also been influenced by cloisonné, albeit to a lesser extent. A few of the earliest examples from the Kangxi period (1662–1772) have stylistic connections to cloisonné; see the works highlighted by Shih (2012, p. 39). The objects in this study belong to a small group of late 18th-century Chinese painted enamels decorated with cloisonné-style motifs evoking the lotus pattern on turquoise. Artworks with this motif can also be found in the Beijing Palace Museum (2020, 故00117924, 故00119488 and 故00118119), the Hermitage (Arapova, 1988, pp. 228, 246–247) and the British Museum (British Museum, 2020, OA + 0.6938 and OA + 0.7143). The Covered Bowl in Beijing and the Cosmetics Box at the British Museum are marked Jiaqing (1796–1820). Chinese painted enamels with other cloisonné-style motifs are extremely rare, but a distinct correlation can be seen in the chrysanthemum on yellow ground patterns of painted enamel vase 列-253 in Taiwan NPM (Shih, 2012, p. 94) and the cloisonné vase 故00119555 in Beijing Palace Museum (2020).

Cloisonné-style Chinese painted enamels are copper vessels decorated to look like lotus pattern Chinese cloisonné but made using the painted enamel technique without cloison cells. They emulate Chinese cloisonné stylistically, meaning they were made to 'closely imitate the spirit of the admired period' (Kerr, 1986, p. 44). The decoration on these objects is more intricate than cloisonné because it is painted rather than made from a network of cloison cells in hammered wire. The painted gilding emulating the wires is particularly striking due to the fine line weight and brilliant metallic sheen achieved through firing on a smooth glassy surface. The objects in this study are attributed to the late Qianlong to Jiaqing period (1750–1820). In all probability they were produced in Guangdong, possibly commissioned as tribute to the court (Hsia-Sheng, 1999, p. 51). Some of these shapes are common in cloisonné harking back to ancient bronzes. In particular the censer, or Fangding, in the Altar Set is an archaic form (Ashmolean Museum of Art and Archaeology, 2013; Brinker & Lutz, 1989, p. 54; Palace Museum Beijing, 2020, 故00118770). The group in Figure 1 was investigated as part of a PhD research project on Chinese painted enamels. In the wider study, elemental analysis of 128 objects dating from the early 18th to 21st centuries was carried out (Norris, 2021, pp. 119–130). It was demonstrated in the thesis that adaptation, or the transfer of technology and the amelioration needed to apply it to a new media, was central to the development of the Chinese painted enamel technique during the Kangxi period (1662–1722) (Norris, 2021, pp. 304–311). The existence of this late 18th-century stylistic subgroup shows that the craftspeople who produced these artworks were familiar with cloisonné forms and patterns. However, it was unclear if the relationship was purely aesthetic, or if there are technological connections between the two media. To answer this question, it was necessary to analyse the elemental composition of the enamel



FIGURE 1 Chinese painted enamel objects with cloisonné-style motifs dated to the late Qianlong to Jiaqing period (1736–1820). (a) Altar set consisting of a pair of vases, a pair of candlesticks and a censer in the Fangding form CPEAS1. (b) A pair of candlesticks CPE347.A-b. (c) A double gourd vase CPE329. (d) A covered box CPECB1. (e) Ewer CPESU1 [Color figure can be viewed at wileyonlinelibrary.com]

surface and painted decoration. A technique sensitive enough to detect the range of elements used as colourants, opacifies and the glass components was necessary for this investigation.

It is useful to define some of the enamelling terms in this paper. Speel (1998, p. 46) begins her definition of *enamel* as 'a glass capable of being fused to certain metals, to ceramic surfaces and to some other quantities of glass to form resistant, durable and decorative glazes. Although often used in a wider sense … the term enamel in its historic and usual application refers to glass fused to a metal surface.' The Chinese term *falang* (or *falan*) (Brinker & Lutz, 1989, p. 47) can also be used to describe enamels on metal, ceramics and glass. When the term *enamel* is used in this paper it refers to the fired coating on the front or exterior of the object. The *counter enamel* is the coating applied to the interior, reverse or inside the footring (Speel, 1998, p. 33). The candlesticks in examples A and B in Figure 1 are unusually complex because they have *interior counter enamels* inside the stems which differ in colour and opacity from the *exterior counter enamels* inside the drip trays. *Painted enamel* is used to describe the polychrome decoration on the enamelled exterior of these copper objects. *Overglaze enamel* (Fournier, 2000, p. 230) is used to distinguish polychrome enamel decoration on porcelain. *Painted gilding* is used to differentiate between gilding on the enamelled surface and amalgam gilding on the metal components such as the rims and feet. The diagram in Figure 2 shows the layers that make up the vessel wall.

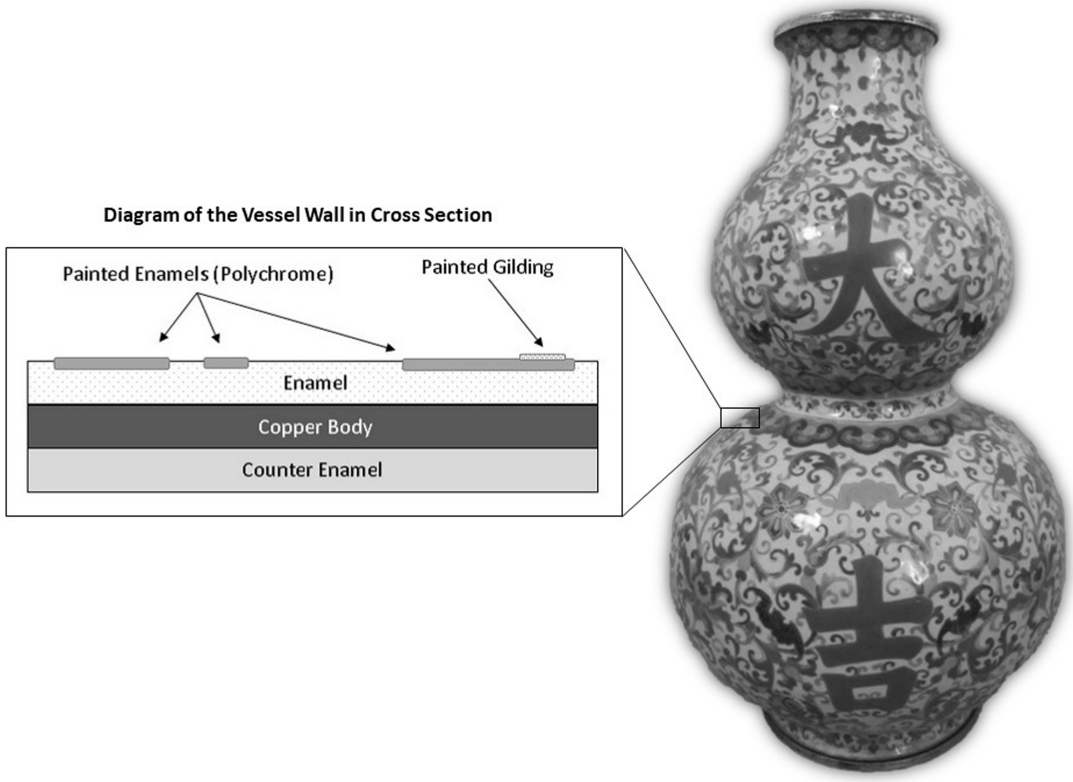


FIGURE 2 Diagram of the layers which make up the vessel wall in cross-section on double gourd vase CPE329

The compositional relationship between overglazes on Chinese porcelain, Chinese cloisonné and Chinese painted enamel on copper has been explored through scientific analysis in previous studies (Colomban et al., 2020; Henderson, Wood, & Tregear, 1989; Kerr, 2000; Norris et al., 2020). The results of PhD research on Chinese painted enamel (Norris, 2021, p. 304–311) demonstrated that Qing dynasty (1644–1911) Chinese painted enamels on copper and overglazes on porcelain share technology but are not identical. Both are opacified with arsenates, which were used infrequently in Chinese cloisonné (Henderson, Tregear, & Wood, 1989) and Venetian glass (Curtis, 1993; Janssens, 2013, p. 30; Kingery & Vandiver, 1985, p. 317) before the development of the Chinese painted enamel tradition. Colourants were found to be similar across the Chinese painted enamel and porcelain overglaze palettes (Giannini, 2015, pp. 414–425; Norris, 2021, pp. 304–311). They are both innovative compared to earlier artistic traditions, combining Chinese and European ceramic, glass and metal enamelling technologies. However, the glass composition differs between these two media because lead and silica vary significantly in overglazes, but not in Chinese painted enamels. The consistent proportion of these glass formers and the level of potassium in Chinese painted enamel are very similar to Chinese cloisonné (Norris, 2021, p. 211).

MATERIAL AND METHODOLOGY

Most 18th-century Chinese painted enamel objects have white enamel and white or turquoise counter enamel. It was clear from visual examination that artworks with cloisonné-style motifs

were made with a different manufacturing technique from other Chinese painted enamels in the PhD sample set. Each of the objects in this subgroup had small areas of damage where surface fragments 3 mm or less in diameter had come away from the copper substrate. The surface fragments look different to other Chinese painted enamels because they have distinct white and turquoise layers, whereas fragments from objects with more typical white enamel grounds have a single enamel layer.

Small fragments that had delaminated from the surface were taken from existing areas of damage for analysis. The samples were surface cleaned and mounted on stubs before being analysed by environmental scanning electron microscopy (ESEM; Hitachi SU3500N) located at Cranfield University. The microscope is coupled with an energy-dispersive X- ray spectroscopy (EDX) detector and the data are processed through proprietary texture and elemental analytical microscopy (TEAM) software for imaging and elemental analysis. Backscattered (BSE) images were taken of each stub-mounted fragment. Relatively low 30-50× magnification was used consistently so that the entire fragment was visible in the BSE image, which allowed individual colours and features within the decoration to be targeted for elemental analysis. Three bulk analyses were carried out for each colour at 20 kV accelerating voltage for 50 s. A lead glass standard DLH1 (65% PbO) (Walton, 2004, p.172) was analysed at the start and end of each analytical session to monitor instrumental drift and as quality control. ESEM-EDX analysis of standard DLH1 prepared as a block-mounted polished section, and as a stub mounted fragment are given in Table 1. Calculations of relative standard deviation and error are utilised as metrics for precision and accuracy for evaluation (Abzalov, 2008; Stanley & Lawie, 2007). The output was calculated as oxides using stoichiometry and normalised to 100% (except halogens and noble metals). The results presented in Table 2 are calculated averages of three bulk analysis for each colour; results in Table 3 are single analysis of the areas annotated in Figures 3 and 4.

Samples do not need to be coated when using ESEM-EDX, which is a significant advantage when studying art and archaeological objects because it is non-destructive. After elemental analysis, the undamaged fragments in the main study were cleaned and reattached with a conservation-grade adhesive. However, the appearance of layers in the enamel and presence of fluorine justified further investigation. Fluorine was detected in several samples from objects with cloisonné-style decoration, and only in these objects, which were part of a much larger assemblage. Detection of this element is significant because fluorite (CaF_2) is the most common opacifier in Chinese cloisonné enamels (Colomban et al., 2020; Henderson, Tregear, &

TABLE 1 Certified values versus normalised ESEM-EDX results for polished block-mounted and stub-mounted standard DLH1 presented as wt% oxide

	DLH1	DLH1 (polished)				DLH1 (stub)			
	Certified	Measured				Measured			
		Mean ($n = 3$)	σ	RSD %	δ	Mean ($n = 8$)	σ	RSD %	δ
Na_2O	1.00	1.49	0.05	2.75	−0.49	1.34	0.13	9.34	−0.34
MgO	0.33	0.30	0.01	2.72	0.09	0.27	0.07	24.71	0.18
Al_2O_3	4.00	4.97	0.04	0.58	−0.24	4.79	0.27	5.57	−0.20
SiO_2	26.00	28.50	0.06	0.16	−0.10	27.45	0.79	2.89	−0.06
K_2O	1.00	1.07	0.04	2.75	−0.07	1.00	0.06	5.63	0.00
CaO	1.00	1.28	0.03	1.61	−0.28	1.32	0.06	4.50	−0.32
Fe_2O_3	1.00	1.61	0.01	0.51	−0.61	1.99	0.18	9.22	−0.99
PbO_2	65.00	60.79	0.09	0.11	0.06	61.84	0.86	1.40	0.05

σ, standard deviation; RSD, relative standard deviation; δ, relative error.

TABLE 2 Normalised ESEM-EDX results for stub-mounted fragments from Chinese painted enamels with cloisonné-style decoration presented as wt% oxide, except for F, Cl, Ag and au as w% element

	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	K_2O	CaO	MnO	Fe_2O_3	CoO
CPEAS1										
Enamel (decorated exterior)	1.15	0.08	1.45	43.69	1.06	10.21	3.50	–	0.74	–
Turquoise blue										
Blue painted enamel	0.89	–	2.34	59.98	–	5.90	0.85	1.39	2.82	2.14
Pink painted enamel	0.63	–	0.89	41.90	–	5.75	0.53	–	0.86	–
Red painted enamel	0.73	–	0.79	44.16	–	7.61	0.34	–	5.33	–
Turquoise green painted enamel	0.37	–	1.03	42.63	–	7.03	0.37	–	0.93	–
Painted gilding	0.48	0.16	0.68	17.35	–	2.17	0.61	–	1.07	–
Counter enamel	0.33	0.33	1.27	28.70	2.46	5.91	2.47	–	1.18	–
Opaque turquoise blue										
CPE347.a-b										
Enamel (decorated exterior)	1.29	–	1.42	49.35	0.31	6.19	4.99	–	0.68	–
Turquoise blue										
Exterior counter enamel inside trays	0.55	–	1.18	40.96	0.16	4.54	1.01	–	0.90	–
Opaque turquoise blue										
Counter enamel inside stem	0.15	–	0.45	18.34	2.54	4.84	1.45	–	0.82	–
Opaque turquoise blue										
CPE329										
Enamel (decorated exterior)	1.76	–	1.40	50.50	0.14	8.27	4.76	–	0.66	–
Turquoise blue										
Counter enamel inside footring	–	–	0.51	39.15	–	7.81	1.33	–	0.90	–
Semi-opaque white										
CPECB1										
Exterior enamel	2.08	–	1.12	41.12	–	11.53	4.57	–	0.91	–
Turquoise blue										
CPESU1										
Counter enamel lid	0.25	–	0.57	31.13	0.20	5.31	0.26	–	0.71	–
Opaque turquoise green										

TABLE 2 (Continued)

	NiO	CuO	ZnO	As_2O_3	PbO	F	Cl	Ag	Au
CPEAS1									
Enamel (decorated exterior)	–	4.84	0.37	4.82	25.97	0.42	1.70	–	–
Turquoise blue									
Blue painted enamel	0.44	1.64	0.27	4.55	16.25	–	0.12	–	–
Pink painted enamel	–	0.18	–	5.21	42.07	–	1.96	–	–
Red painted enamel	–	–	–	3.22	37.74	–	0.09	–	–
Turquoise green painted enamel	–	6.24	–	3.02	38.27	–	0.11	–	–
Painted gilding	–	1.67	–	0.50	10.04	–	0.29	1.29	63.68
Counter enamel	–	2.30	–	8.43	46.41	–	0.22	–	–
Opaque turquoise blue									
CPE347.a-b									
Enamel (decorated exterior)	–	6.40	0.94	4.91	22.32	0.46	0.74	–	–
Turquoise blue									
Exterior counter enamel inside trays	–	4.23	0.40	7.77	34.70	–	3.60	–	–
Opaque turquoise blue									
Counter enamel inside stem	–	8.00	2.00	14.44	46.16	–	0.82	–	–
Opaque turquoise blue									
CPE329									
Enamel (decorated exterior)	–	4.70	0.61	4.51	21.25	0.62	0.81	–	–
Turquoise blue									
Counter enamel inside footring	–	–	1.25	6.81	42.19	–	0.06	–	–
Semi-opaque white									
CPECB1									
Exterior enamel	–	3.14	–	6.19	27.72	0.99	0.63	–	–
Turquoise blue									
CPESU1									
Counter enamel lid	–	2.61	–	8.84	48.87	–	1.37	–	–
Opaque turquoise green									

'–' indicates that the element was not detected.

TABLE 3 Normalised ESEM-EDX results for polished block-mounted fragments from Chinese painted enamels with cloisonné-style decoration presented as wt% oxide, except F and Cl

	Na_2O	MgO	Al_2O_3	SiO_2	K_2O	CaO	MnO	Fe_2O_3	CoO	CuO	ZnO	As_2O_3	PbO	F	Cl
CPEAS1															
Layer A/area 1: White base layer adjacent to copper body	–	–	1.07	33.03	8.88	2.17	–	1.22	–	5.93	0.72	6.44	40.51	0.02	–
Layer B/area 2: Dark area in heterogeneous turquoise blue	2.61	0.61	3.48	48.74	16.61	5.91	–	0.91	–	2.21	–	1.89	14.35	2.68	–
Layer B/area 3: Light area in heterogeneous turquoise blue	2.50	–	0.92	46.98	16.90	3.40	–	0.66	–	2.50	–	3.78	20.91	0.98	0.46
Layer C/area 4: Homogeneous turquoise blue layer	2.45	–	0.60	47.55	17.03	2.69	–	–	–	2.56	–	3.60	22.15	0.79	0.58
Layer D/area 6: Blue painted enamel on the surface	2.20	–	1.16	49.94	19.28	1.04	1.04	2.19	1.68	1.09	–	4.53	15.84	–	–
CPE347.a-b															
Layer E/area 5: Turquoise green painted enamel on surface	–	–	0.98	44.41	10.07	0.62	–	1.12	–	4.73	0.54	3.38	34.15	–	–
Layer A/area 2: Light area in heterogeneous white layer	0.92	–	0.40	35.72	10.68	0.86	–	0.54	–	2.35	–	7.66	40.38	0.49	–
Layer A/area 3: Dark area in heterogeneous white layer	0.86	–	1.00	48.81	11.63	6.01	–	0.56	–	1.76	–	4.03	22.89	2.46	–
Layer B/area 1: Turquoise blue layer on the surface	1.94	–	1.25	47.70	17.66	6.41	–	0.63	–	2.19	–	4.13	14.05	3.61	0.43
CPE329															
Selected area 1: Bulk analysis turquoise blue	3.00	–	1.01	45.41	14.67	2.93	–	–	–	2.25	–	4.68	25.59	0.46	–
Spot 1: Dark inclusion	1.39	–	1.90	53.71	19.44	4.72	–	–	–	1.94	–	3.31	12.45	1.12	–
Spot 2: Light inclusion	2.00	–	0.52	33.19	9.67	13.37	–	–	–	2.20	–	12.11	24.48	2.45	–
Spot 3: Long needle like crystals	2.00	–	0.51	28.50	7.24	2.89	–	1.01	–	1.65	–	12.11	42.13	0.76	1.20
Spot 4: Second dark inclusion	1.57	–	1.75	53.99	21.09	2.56	–	–	–	1.88	–	2.60	14.07	0.49	–
CPECB1															
Area 1: Lighter area in turquoise blue	1.39	–	1.33	35.83	11.54	4.48	–	1.28	–	2.65	0.97	4.08	35.64	0.82	–
Area 2: Darker area in turquoise blue	1.00	–	1.10	45.55	16.04	4.06	–	–	–	2.96	1.02	3.46	24.08	0.72	–

'–' indicates that the element was not detected.

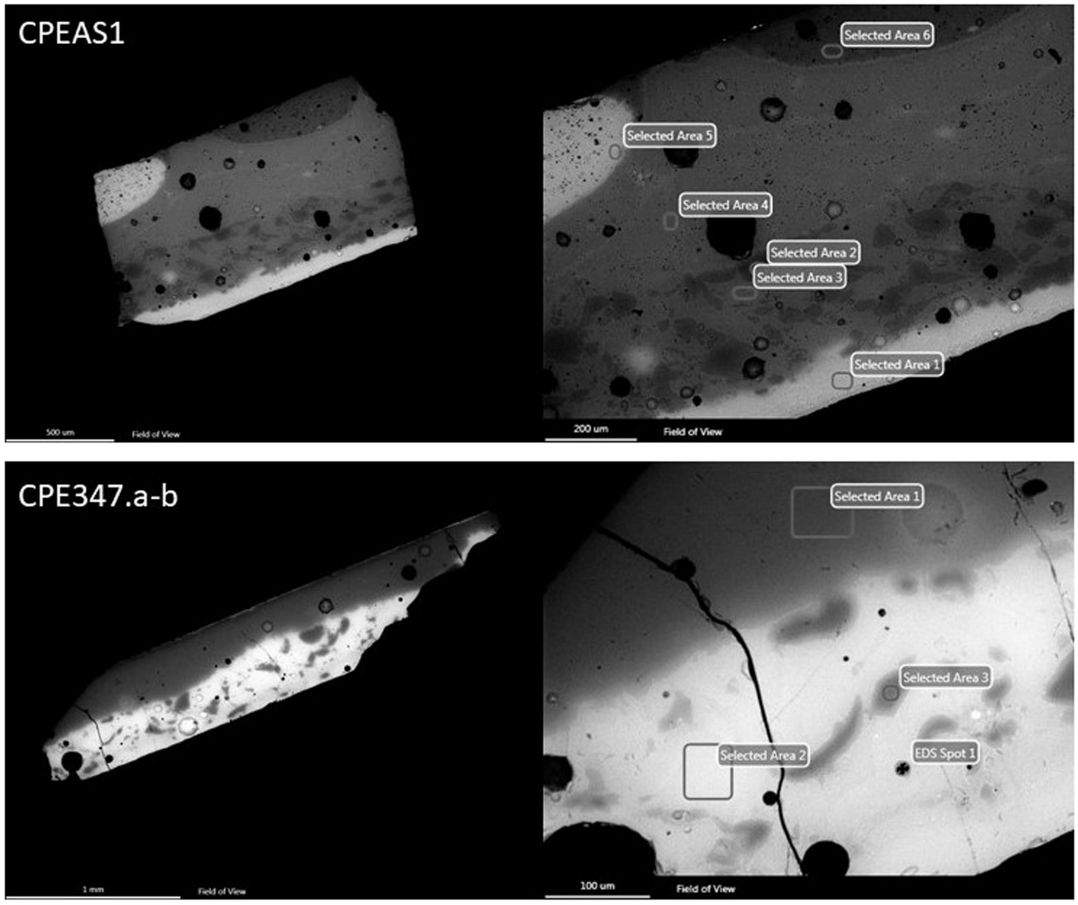


FIGURE 3 Above: BSE images of a fragment from the Fangding in altar set CPEAS1. Below: BSE images of a fragment from candlesticks CPE347.A-b. Layers are annotated on the left with letters; areas and spots on the right correspond to the analysis in Table 3

Wood, 1989; Kirmizi et al., 2009; Quette, 2011, pp. 311–319; Su et al., 2016; Twilley, 1995). Opacification was achieved in Chinese cloisonné by partially melted crushed fluorite in the glassy matrix. Since calcium is a common stabiliser in glass, it is the presence of fluorine which is most interesting as an elemental marker for the raw material fluorite. Fluorine is a low-Z element near the limit of detection with ESEM-EDX. The F Kα line at 0.68 can be masked by iron due to the Fe Lα 0.71 emission line, which can be problematic because iron is present in most enamel samples. To ensure that the instrument was able to detect this element, and that peaks were not due to an instrument artefact or misinterpretation, block-mounted samples of fluorite locally sourced from Hunan Province were analysed under the same conditions. Distinct fluorine peaks and correspondingly high calcium peaks were detected in the mineral sample (Norris, 2021, p. 112).

To investigate further, cross-sections of the four enamel fragments in which fluorine was detected were mounted in resin blocks and polished with a specific goal to study the layered structure of the enamel. For consistency with the stub-mounted fragments the ESEM analytical conditions remained identical.

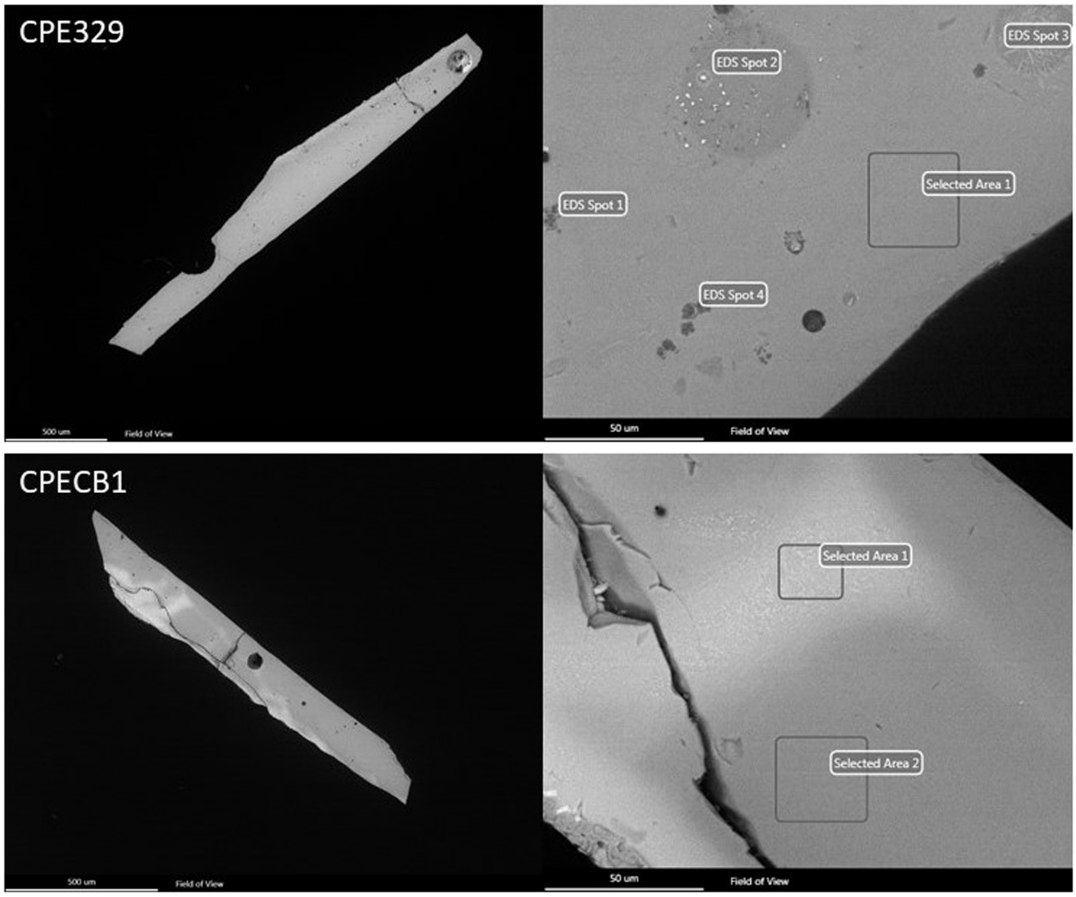


FIGURE 4 Above: BSE images of a fragment from the decorated exterior of double gourd vase CPE329. Below: BSE images of a fragment from the decorated exterior of cloisonné style box CPECB1. The annotated areas on the images to the right correspond to the analysis in Table 2

RESULTS

The results of elemental analysis of the stub-mounted samples are given in Table 2 and polished (fluorine-containing) samples are in Table 3. The first fragment is from the decorated exterior of the Fangding in Altar Set CPEAS1; this fragment has several painted colours, and the layers can be seen in cross-section in Figure 3. The second sample from this object is from the counter enamel on the interior of the Fangding vessel. Three fragments were analysed from Candlesticks CPE347.a-b. The first is from the decorated exterior enamel (BSE image Figure 3), and the other two fragments from CPE347.a-b are counter enamels. The first of these is from the interior of a drip tray, which is decorative because it is visible when the object is on display. The second is from inside the stem; this counter enamel is not visible when the object is assembled and is functional rather than decorative. Two fragments from Double Gourd Vase CPE329 were analysed: one from the decorated exterior enamel (BSE image in Figure 4) and the second a white counter enamel on the underside of the base. The fragment from Covered Box CPECB1 is from the decorated exterior (BSE image in Figure 4), and the fragment from Ewer CPESU1 is from the counter enamel on the interior of the lid.

BSE images of block-mounted fragments in cross-section are presented in Figures 3 and 4. An image of the entire fragment is on the left; the layers in the samples from the decorated surface in Figure 3 have been lettered for clarity. A second image at higher magnification is on the right; these are annotated with the analysis spots in Table 3. The fragments from CPEAS1 and CPE347.a-b are complete, including the decorated surface through to the layer adjacent to the copper body. They measure approximately 0.8 mm and 0.6 mm from the decorated surface to the body, respectively, and the painted enamel layers on the fragment from CPEAS1 are ~0.1–0.2 mm thick. The BSE images show that the decorated enamel fragment from Altar Set CPEAS1 has three distinct enamel layers (A–C), two painted enamel layers on the surface (D and E), and painted gilding (F). The uppermost enamel layer (C) has a faint line running parallel to the other layers, indicating that this material could have been applied in two coats. The fragment from Candlestick CPE347.a-b has two distinct enamel layers (A and B). In both samples, enamel layer A would have been in contact with the copper body.

The fragments from CPE329 and CPECB1 in Figure 4 are incomplete; the decorated surface is intact but the surface, which would have been in contact with the body, has been lost. The images show that the sample from Double Gourd Vase CPE329 is relatively homogeneous when compared to those in Figure 3. Distinct light and dark areas can be seen in the sample from Cloisonné Style Box CPECB1 but they are not structured layers. Elemental analysis of the areas annotated in the BSE images in Figures 3 and 4 are presented in Table 3.

DISCUSSION

The implications regarding the obtained results are discussed here and subdivided into different sections to provide a systematic overview. The results and implications of elemental analysis for the stub-mounted fragments are discussed in Section 4.1 (Table 2). The layering in BSE images presented in Figures 3 and 4 are described in Section 4.2. Compositional analysis of areas within the layers of the block-mounted samples given in Table 3 are discussed in Section 4.3.

Compositional analysis of stub-mounted fragments

Distinct translucent and opaque layers are visible with the naked eye when looking at fragments from the decorated exterior of the cloisonne-style Chinese painted enamels in this study. Examination showed that these objects were made using an application technique where an opaque layer was applied to obscure the metal body. The second translucent layer gives the jewel-like reflection and turquoise colour which emulates Chinese cloisonné with the lotus pattern. The assumption was that this upper translucent layer would be similar in composition to the turquoise green painted enamel coloured with copper (see Table 2).

Elemental analysis of the stub-mounted fragments yielded exciting and somewhat unexpected results with the presence of fluorine. Detection of this element alongside elevated calcium in all four enamel samples shows that fluorite was used as a raw material. Fluorite is determined as a direct link to Chinese cloisonné and glass technology (Henderson, Tregear, & Wood, 1989; Yang, 1987b p. 76) and was not detected in any other 18th-century objects in the PhD sample set (Norris, 2021). It is useful to compare these results to the average composition of white enamels on objects with more typical motifs in Table 4. The major glass formers in white enamel differ from the average composition in this group, which is 24% PbO, 46% SiO_2, 9.1% K_2O and 1.6% Na_2O. The reduction in lead could reflect the addition of fluorite as a raw material, but it does not explain the increases in silica, potassium and sodium. The four exterior enamels are coloured with an average of 4.8% CuO, and an average of 5.1% As_2O_3 was detected. The amount of arsenic detected, and the absence of other opacifiers such as tin and

TABLE 4 Average and standard deviation of normalised ESEM-EDX results for stub-mounted white enamel fragments from 29 18th-century Chinese painted enamel objects, presented as wt% oxide, except Cl

	Na_2O	Al_2O_3	SiO_2	P_2O_5	K_2O	CaO	TiO_2	MnO
Average	0.54	0.66	39.6	0.16	7.60	0.77	0.02	0.01
σ	0.72	0.50	4.02	0.35	1.74	0.59	0.13	0.04

TABLE 4 (Continued)

	Fe_2O_3	CuO	ZnO	As_2O_3	PbO	Cl
Average	0.79	0.37	0.28	7.26	41.10	0.84
σ	0.24	0.74	0.49	1.39	4.11	0.86

σ, standard deviation (Norris, 2021, p. 140).

antimony, demonstrates that arsenates are the main opacifier in 18th-century Chinese painted enamels. Arsenate opacification is consistent with developing technology at that time; Kerr and Wood (2004, p. 650) specify that lead arsenate opacification was used in a lead-alkali silicate in Chinese cloisonne enamels and overglaze enamels on porcelain at the turn of the 18th century.

The opaque counter enamels have a different composition from the layered enamel on the exterior; notably, fluorine is absent in all of them. The white counter enamel on the underside of CPE329 is similar in composition to white enamels on other Chinese painted enamel objects, as is the counter enamel inside the drip tray on CPE347.a-b, which is coloured with copper at 4.2% CuO. A different trend can be seen in the remaining turquoise counter enamels. These three counter enamels have an average of 47% PbO, 26% SiO_2, 5.4%K_2O, 0.2% Na_2O, 4.3% CuO and 11% As_2O_3. They are higher in lead than the average white Chinese painted enamel given in Table 4, and considerably higher than the decorated exterior enamel (24% PbO). Potassium and sodium are lower in these counter enamels, whereas arsenic has increased when compared to the average white enamel composition.

The fragment from the exterior of CPEAS1 is the only decorated sample with painted enamel colours and gilding. The results show that the blue painted enamel has comparatively high aluminium (2.3% Al_2O_3) and silica (60% SiO_2), and is coloured with cobalt accompanied by nickel (0.4% NiO), high manganese (1.4% MnO) and high iron (2.8% Fe_2O_3). The colourants in the blue on CPEAS1 are consistent with blue painted enamels analysed in previous studies (Colomban et al., 2020; Norris et al., 2020; Su et al., 2016). The artworks in these studies are all 18th-century Chinese painted enamels with polychrome decoration painted on a white enamel ground. Su et al. studied the composition of a Double Gourd Vase HFL-1 decorated with a bat and cloud pattern dated to the Qianlong period (1736–1795) from the Fuwang chamber in the Imperial Palace of China. Colomban et al. analysed objects from the Musée du Louvre in Paris and Musée Chinois in France; they are a pair of Ewers F1467.1–0.2 made in cloisonné with a central reserve panel in painted enamel marked Qianlong, and Dish R975 dated to the 18th century with a floral motif. Norris et al. investigated the composition of Ruby-backed Plate C.107–1931 dated to 1730–1770 in the Victoria and Albert Museum in London; this object is decorated with a figurative scene and the pattern is named after the dark pink or ruby colour on the reverse.

The colourant in the pink painted enamel is assumed to be colloidal gold, which cannot be detected with this instrument in a high-lead glass. Multiple recipes for pink (ruby or purple) glass colourants were established in Europe at this time (Kerr & Wood, 2004, p. 636). They are described by Hainbach (1924, pp. 170, 174) as gold dissolved in nitrohydrochloric acid (aqua regia $HNO_3 + 3HCl$). The presence of colloidal gold is supported by elevated chlorine in the pink spectra at 1.9% Cl when compared to the other painted decoration at <0.3% Cl. Gold has been confirmed as the colourant in pink painted enamels in previous studies (Kerr, 2000; Norris et al., 2020; Su et al., 2016).

The red painted enamel is the first published analysis of this colour outside of PhD research (Norris, 2021, p. 155). It is coloured with 5.3% Fe_2O_3, which is consistent with two other late 18th-century examples in the thesis (EPC1 at 8.6% Fe_2O_3 and EPC3 at 6.0% Fe_2O_3), but lower than the amount detected in red dots and fine outlines found on two additional objects of a similar date (CPE312 at 28% Fe_2O_3 and EPC11 at 24% Fe_2O_3). Red painted enamels should not be confused with underdrawings, which are the fine red-brown iron-rich lines painted to layout the motif before applying the polychrome painted enamel decoration (Norris et al,, 2020). Underdrawings differ from red painted enamels in colour, opacity, application style and composition. It is interesting to note that aluminium can influence colour and melting point (Kingery & Vandiver, 1985, p. 369; Vandiver et al., 1997, pp. 32–33). Aluminium is relatively low in Chinese painted enamel red (~1–2% Al_2O_3), whereas it is higher in Chinese painted enamel underdrawings (~2–5% Al_2O_3), and consistently higher in red overglazes (~5–15% Al_2O_3) (Kingery & Vandiver, 1986, pp. 374–375; Wood, 2011, p. 230; Giannini, 2015, p. 418; Norris, 2021, p. 278).

Turquoise green painted enamel is coloured by copper at 6.2% CuO, whereas the turquoise blue enamel substrate has an average of 2.5% CuO. Potassium is elevated in turquoise green (10% K_2O) when compared to the bluer substrate, which has an average of 7% K_2O. Turquoise green and green painted enamels are also compositionally distinct; green is yellower due to the addition of tin oxide (Norris et al., 2020). The different colours used to achieve the cloisonné-style pattern on a Chinese painted enamel vase are annotated in Figure 5.

Painted gilding is also present on this fragment; 64% gold and 1.3% silver were detected in this decoration. The ratio of gold to silver in the painted gilding on CPEAS1 is 49:1 parts Au to Aq. This ratio is much higher than the average ratio of 2.5:1 detected in painted gilding on 18th-century Chinese porcelains by Giannini (2015, p. 419). The results show that the gold is very pure due to the relatively low amount of silver detected. The difference in composition



FIGURE 5 Left: vase with a cloisonné-style lotus pattern over turquoise ground, Qianlong period (1736–1795) (Keverne, 2011, p. 63). Right: annotated detail showing the subtle difference between turquoise blue, turquoise green and green hues (Norris, 2021, p. 281) [Color figure can be viewed at wileyonlinelibrary.com]

may be explained by the fact that gold leaf is used in amalgam gilding on the rims and feet of Chinese painted enamels. Excess gold from this process could easily be gathered and mixed with a medium for painting highlights on enamelled areas. The gold used for gilding on porcelain in Jingdezhen has come from raw material with higher silver content, this could be coinage or unrefined gold ores.

BSE images of block-mounted samples

The four fragments from the decorated exteriors were block mounted to study the layers in cross-section. The fragment from CPEAS1 has several distinct layers, which cannot be seen with the naked eye or binocular microscope; the layers are annotated on the left of Figure 3. Working from the copper body towards the uppermost surface there is: a layer of opacified enamel (layer A); a compositionally heterogeneous turquoise layer (layer B); a homogeneous translucent turquoise layer (layer C); two painted enamels at the surface in blue and turquoise green (layers D and E); and a bright fleck of gilding on the surface (F). Note that the painted enamel decoration (layers D and E) has sunk into the enamel substrate, creating a flat surface. The borders between each of these layers are distinct, showing that they were fixed in separate firings. There is a faint band in the middle of the homogeneous turquoise layer (layer C), indicating that there may have been two applications of this enamel.

The second fragment in Figure 3 is from CPE347.a-b. This fragment has two distinct layers: a compositionally heterogenous layer with dark areas in a lighter matrix (layer A), which would have been applied to the copper body initially; and a compositionally homogeneous turquoise layer forming the uppermost surface (layer B). The border between them is distinct, indicating that the first layer was fired before the second layer was applied. Both the fragments in Figure 4 are incomplete because the side which would have been in contact with the copper body has been lost. The turquoise enamel sample from CPE329 is homogeneous at 30× magnification; it is possible to see dark and light inclusions and voids or bubbles at higher magnification in the image on the right. The sample from CPECB1 has distinct light and dark areas, perhaps indicating two layers; these areas are mixed in a way that suggests they did not have separate firings.

Elemental analysis of block-mounted samples

Areas within the layers that were analysed are annotated on the right of Figures 3 and 4; the results are presented in Table 3. Only the samples from CPEAS1 and CPE347.a-b are complete and have the opaque layer which would have been in contact with the copper body (layer A in both samples). This layer appears compositionally homogeneous in CPEAS1, but CPE347.a-b is heterogeneous in appearance, with large dark areas in a lighter matrix. The spots analysed in layer A on CPEAS1 and the light matrix in layer A on CPE347.a-b are consistent with the typical composition of white enamel given in Table 4. Low fluorine (0.02–0.49% F) and slightly elevated calcium (0.9–2.2% CaO versus the average white enamel at 0.8% CaO) were detected in layer A on both samples. The darker area in layer A on CPE347.a-b is much higher in fluorine (2.5% F), calcium (6.0% CaO), and silica (49% SiO_2); this area is lower in lead (23% PbO) and arsenic (4.0% As_2O_3). The results suggest that the dark areas in layer A on CPE347.a-b could be coarsely ground fluorite with associated silica.

The sample from CPEAS1 is highly complex because it includes an intermediate compositionally heterogeneous layer consisting of light and dark amorphous areas (layer B). Both the light and dark spots in this layer (areas 2 and 3) are low lead (14–21% PbO) with high silica (47–49% SiO_2), potassium (both 17% K_2O) and sodium (2.5–2.6% Na_2O). The darker area 2 is

TABLE 5 Average and standard deviation of the major elements in the composition of the uppermost transparent enamel layer in the polished block-mounted fragments presented as oxide wt% (this is the surface onto which the polychrome decoration is applied)

	F	Na_2O	Al_2O_3	SiO_2	K_2O	CaO	Fe_2O_3	CuO	ZnO	As_2O_3	PbO
Average composition of the transparent layer	1.40	2.10	0.99	46.55	16.35	4.02	0.16	2.49	0.26	3.97	21.47
Standard deviation	1.48	0.85	0.28	1.24	1.30	1.70	–	0.35	–	0.56	5.14

From Table 3: CPEAS1 layer C, CPE347.A-b layer B, CPE329 area 1 and CPECB1 area 2).

higher in fluorine (2.7% vs. 1.0% F), calcium (5.9% vs. 3.4% CaO) and aluminium (3.5% vs 0.9% Al_2O_3). The lighter area 3 is higher in arsenic (3.8% vs. 1.9% As_2O_3) and the composition is similar to the comparatively homogeneous turquoise layer on the surface (layer C). From these results, layer B appears to be made of two different coarsely ground materials, with the darker areas containing more fluorite.

The transparent turquoise enamel layer, which forms the uppermost surface, is present in all four samples. See the average composition of this layer in Table 5. These are layer C in CPEAS1, layer B in CPE347.a-b, the entire thickness of the sample from CPE329 (area 1) and the darker material in the sample from CPECB1 (area 2). The translucent turquoise layers on the uppermost surface are low in lead when compared to the average Chinese painted enamel composition (41% PbO in Table 4 vs. 22% PbO in Table 5.) fluorine and elevated calcium were detected, representing fluorite. All four examples are very high in potassium, at an average of 16% K_2O—double the level detected in an average white enamel. Iron was not detected in three out of four samples, indicating a very pure silica source such as quartz (Si_2O) rather than sand, which would have significant impurities (Janssens, 2013, pp. 28–30).

Notably, fluorine is absent in both the painted enamels on the uppermost surface of sample CPEAS1 (layers D and E). As seen in the results from the first analysis on stubs, the blue painted enamel has a high silica and low lead composition, whereas the turquoise green enamel is closer to the average composition for white enamels. Sodium is absent in the turquoise green enamel, and potassium is extremely high in the blue painted enamel, at 19% K_2O. These results differ from the stub-mounted analysis, which could be attributed to the smaller spot size and single analysis area. However, the difference is more likely due to X-rays passing through the thin painted enamel layers, allowing elements in the enamel substrate to be excited when mounted on stubs (Thomsen et al., 2005).

CONCLUSIONS

The results of this study have revealed a complex and sophisticated range of enamel compositions in the manufacturing of cloisonné-style Chinese painted enamels. The results show that cloisonné motifs were not simply emulated through the painted design, but that the technology of cloisonné was also adapted to produce this sophisticated stylistic subgroup. Fluorite was replaced by lead arsenate as the opacifier when Chinese painted enamels were developed. The reason for this change in technology is unclear, but it is likely that fluorite was not opaque enough to obscure the copper body of a vessel when ground finely and applied in a thin layer. An experimental piece in the Imperial collection could be an example of this (Shih, 2012, p. 74). This small hinged box (列-360-51) appears to have a pink ground because the copper body is visible

through the enamelled surface, evidenced by the colour change in areas of damage where the body has oxidised.

The decorative exteriors of cloisonné-style Chinese painted enamel objects are made by layering a cloisonné-type enamel made with fluorite, over a lead arsenate opacified enamel. This approach is different from cloisonné, where coarsely ground fluorite was used both to opacify and give the illusion of depth in cloison cells, which are deeper. The opaque layer obscures the copper body, so it is acceptable for the upper layers to be translucent. This study shows that the cloisonné composition was adapted for use as the topcoat by grinding it finely and applying it as a thin layer. The aim was to emulate turquoise cloisonné enamel by achieving a similar colour and perception of depth.

Using Altar Set CPEAS1 as an example, the enamelling process begins by applying lead arsenate opacified enamels to the interior and exterior of the object to obscure the copper body. The turquoise interior, or counter enamel, is coloured with copper and applied to prevent the body from distorting (Speel, 1998, p. 33). The counter enamels are fluorine free, whereas the exterior opacified layers had low fluorine (this could be contamination from the topcoat). Once the counter enamel and opaque enamel (layer A) were applied, the object was fired for the first time. The firing temperature is estimated to be between 650 and 800°C (Mengoni, 2013, p. 108; Wood, 2011, p. 229). An intermediate heterogeneous turquoise layer was applied to the exterior (layer B), and the object was fired for a second time. A third, and possibly a fourth, layer of translucent turquoise enamel was applied to the exterior as a topcoat and the object was fired again (layer C). The composition of the uppermost surface layer is atypical for Chinese painted enamels, not only because the glass composition includes fluorite, but it also has a very pure silica source and elevated potassium. The uppermost translucent enamel layer allows light to penetrate the surface before being reflected by lower opaque layers, creating a luminous jewel-like quality reminiscent of cloisonné.

From this point the piece is decorated in the same way as other Chinese painted enamels. Polychrome painted enamel colours are applied before firing the object again at least once; this can include underdrawings and outlines not studied in this group (Norris et al., 2020). The polychrome decoration sinks into the enamel layer below, producing a flat glossy surface. The object is fired two more times to fix painted gilding on the enamelled surface at approximately 600°C, and then at 250–350°C to fix the amalgam gilding to the unenamelled rims and key fret flanges (Kerr & Wood, 2004, pp. 698, 694).

The elaborate layering technique used in cloisonné-style Chinese painted enamels requires a large investment in materials, labour and firing costs. They would have been more expensive to produce than Chinese painted enamels with white grounds and porcelain style motifs, and therefore higher status objects. It is very likely these objects were produced in a cloisonné workshop where the appropriate tools, kilns and raw materials, including minerals such as fluorite, quartz and gold leaf, were available. The fact that this style emerged at the end of the 18th century may be rooted in a reduction of state support via commissions (Curtis, 2009, p. 59; Hsia-Sheng, 1999, p. 51) and wider economic instability (Lovell, 2011, pp. 32–38). Symptomatic of this decline, the imperial enamelling workshop was closed in 1789 (Kerr, 1986, p. 114). During this period of reduced resources, it is likely that Chinese painted enamels and cloisonné were increasingly made in the same workshops. The resulting environment would have been a fruitful place for stylistic experimentation and technological adaptation in both media.

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DATA AVAILABILITY STATEMENT

The data that supports the findings of this study are available in the supplementary material of this article.

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