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Original article

The influence of Qing glass technology on Qianlong and Jiaqing painted enamel copperwares

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ABSTRACT

The white enamel surfaces of ten Chinese painted enamels dating to the Qianlong and Jiaqing periods (1736–1820) were studied with Laser Ablation Inductively Coupled Mass Spectrometry (LA-ICPMS). These enamels are opacified with lead arsenate, a dramatic change in technology from fluorite and lead stannite opacification used in Chinese and European enamels before the 18th century. The primary goal of this project was to test the hypothesis that boron is a significant component in Chinese painted enamels. Borax ($Na_2[B_4O_5(OH)_4]\cdot 8H_2O$) was used by glassmakers working in the imperial workshops in Beijing in the mid-18th century, and boron has been detected in some examples of Qing glass and enamels. Quantitative analyses of major, minor, and trace level elements were carried out with LA-ICPMS. Three compositional groups were identified by the amount of borax in the enamel: high borax (at 6.7% B_2O_3), low borax (up to 1.3% B_2O_3), and borax free. The results show that it is possible to distinguish between objects made in Beijing and Guangzhou through elemental analysis, and that there are two distinct compositional groups of Chinese painted enamel produced in Guangzhou during this period.

1. Introduction

Chinese painted enamels are decorative art objects made in enamelled copper. The earliest Chinese painted enamel pieces date to the Kangxi period (1662–1722) [1], a time of significant technological and stylistic change in ceramics, glass, and enamelled metals due to trade and the exchange of ideas between China and Europe. Artworks in this media were often produced in the form of vessels, small plaques, and ornaments. They are made by enveloping both sides of the copper body in a layer of fired enamel before applying painted decoration. In the 18th century the enamel coating on most objects was white, although it is not uncommon for the interior, or counter enamel, to be turquoise. Enamelling the surface in white created a smooth neutral ground for painting delicate patterns. This paper looks specifically at the technology of the white enamel layer on Chinese painted enamel objects.

The development of painted enamelling on copper in China coincided with the introduction of new colours and opacification in Chinese glass, porcelain overglaze enamels, and cloisonné. During the Ming dynasty (1368–1644) white was not present in porcelain overglaze enamels [2,3]. Cloisonné enamels developed independently from ceramic technology during this period, the palette included white opacified with fluorite [4,5]. Analyses of Ming dynasty glass are unsurprisingly few [6] due to the recycalbility of the material. However, a historic account by Sun Tingquan translated by Yang [7] includes two hues of white, both of which are opacified with fluorite.

Early attempts to make Chinese painted enamels were carried out between 1685 and 1717 [1] and were successful by 1692 [8]. In these three decades of technological advancement, lead arsenate white, overglaze cobalt blue, colloidal gold pink, and lead stannite yellow were added to porcelain overglaze enamels [9]. These colourants were combined with existing technology to produce a much wider colour palette in ceramics, glass, and enamelled metals. Of these new colours, white is of particular interest because effective control over the opacity of every colour was achieved. The significance of this was noted by Sir Harry Garner: “*Undoubtedly the only innovation of major importance in the porcelain of the Ch’ing dynasty* (in contrast to Ming dynasty porcelain) *was the introduction of the famille rose enamels… The introduction from Europe of rose-pink enamel, derived from gold, and even more important, the opaque white enamel derived from tin, enabled shading to be introduced in all colours and led to a type of painting much closer to that of painting in oils or watercolour*” [10].

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Garner's assumption that white overglaze enamel was opacified with tin has subsequently been proved inaccurate by elemental analysis [11], although this was a sound hypothesis given that tin opacification was the dominate technology in Europe at that time [12]. Compositional analysis has also confirmed that opacification in white Ming Dynasty cloisonné enamels was achieved with fluorite [4,5]. Analysis of Qing porcelain overglaze enamels [13–15], enamelled metals [16–18], and glass [19–21] identify a shift in technology toward lead arsenate opacification.

Only on rare occasion have white enamels opacified with tin been identified on early Qing pieces. For example, white overglaze enamels on two small porcelain plates in the Victoria and Albert Museum (B.fr.1730.8 Q_18Y and B.fr.1750.3 Q_18Q) dated to 1730 and 1750 respectively [14]. On the hands of a figure in a painted enamel reserve panel on cloisonné Ewer F1467C marked Qianlong (1736–1795) [22, (Figure 7)] and on Imperial Bowl 1931.676 marked Kangxi (1662–1722) in the Baur Foundation collection [23]. These exceptions are likely evidence of prepared enamel cakes imported from Europe. Tin opacification was one of the key technical differences in a recent study of painted enamel teapots in the Beijing Palace Museum, where one of four very similar objects was confirmed to have been made in France [24].

Venetian, Bohemian, and Bavarian glass traditions have been suggested as possible sources of technology for lead arsenate opacification [11,21,25]. Lead arsenate opacification was recorded as an ingredient in opal glass by Giovanni Darduin in his book of 297 Murano glass recipes dated between 1683 and 1711 [26,27]. This technique may have spread via Italian glassmakers including Bernard Perrot (1638–1709) who immigrated to France and established a glassworks in Orléans [28,29]. Although arsenic was not detected in recent analysis of sixteen glass objects associated with this maker [30]. Bohemian glass made at Gratzen (Nové Hrady) was heavily influenced by Perrot while under the glassworks was under the direction of Louis le Vasseur d'Ossimont [31]. Both opal and crystal glass were produced in Gratzen between 1673 and 1694, with the latter being made of "ground quartz, saltpetre, arsenic, borax, and tartar" [31]. In transparent crystal glass arsenic would act as a decolourant and fining agent [26,32]. The combination of saltpetre, arsenic and borax was also employed by Johann Christoph Fiedler in Munich for crystal glass between 1677 and 1689 and in ruby glass by Michael Müller near Winterberg between 1683 and 1709 [31].

Knowledge of opal, ruby, and crystal glass traditions in the Munich-Prague region could have been transferred to China via Jesuit Missionaries. Their first mission to China began at the end of the 16th century and was successful due to a willingness to adopt local languages and customs [33]. Apart from being adept linguists, Jesuits pursued excellence in all manner of sciences, medicine, and arts. Their approach to missionary work was conversion through "indirect evangelization" or the use of science as proof of the truth of Christianity. They had a significant presence in China by the end of the Ming dynasty, converting approximately 150,000 Chinese people including 120 members of the imperial family. German Jesuit Johann Adam Schall von Bell managed to bridge the transition from the Ming to Qing dynasty by remaining at the residence in Beijing during the final invasion of Manchu troops. Having revised the imperial calendar under emperor Chongzhen (1628–1644), Schall demonstrated his knowledge of astronomy to the new court by correctly predicting an eclipse. He was made director of the office of astronomy by emperor Shunzhi (1644–1661) shortly thereafter.

It is notable that the continuation of the Jesuit mission into the Qing dynasty was due in part to their knowledge of lenses. Emperor Kangxi (1662–1722) began to actively recruit Jesuits with "skills in the arts and sciences" to work in the Zaobanchu workshops in 1681 [34]. In 1696 he built a glass works adjacent to the Jesuit church in the Imperial City headed by German Jesuit Kilian Stumpf (1655–1720) [19]. A plate glass factory was established in Guangzhou in 1699 with close links to French Jesuit Joachim Bouvet, former director of the French royal glass works which had recruited Murano mirror-makers [34]. Jesuit glass workers were active in China until the 1750s [7,19] making decorative art objects, plate glass for windows, mirrors, and lenses for scientific and medical use including eyeglasses, magnifying glasses, and telescopes. A range of glass compositions were in use during the development of Chinese painted enamels. Ma et al. [21]identified six glass compositions, one of which is consistent with the historic account of a Jesuit recipe employing arsenic, fluorite, and borax [7,35].

Research using ESEM-EDX (environmental scanning electron microscopy with energy dispersive X-ray spectroscopy) has established that the proportion of major glass formers in Chinese painted enamels, silicon and lead, are very similar to cloisonné [16]. The composition of enamel differs from glass because enamels are used to decorate glass objects, and therefore must vitrify at a lower melting temperature. Evidence of the use of fluorite and borax in 18th century Chinese painted enamels has emerged in previous studies. Fluorite was detected in a small group of late 18th century artworks decorated with cloisonné-style motifs during this period [36]. To this point, the role of borax in Chinese painted enamels has been unclear. Boron was detected at 10.3% B_2O_3 in a late 19th century Chinese painted enamel with Microprobe (EMPA) analysis [37]. This element was also present in two out of four Chinese painted enamels dated to the Qing dynasty (1644–1911) analysed by [17] with laser induced breakdown spectroscopy (LIBS).

2. Research aim

The aim of this paper is to determine if borax is a major component of 18th century Chinese painted enamels using LA-ICPMS (Laser Ablation Inductively Coupled Plasma Mass Spectrometry). High lead compositions can be problematic for the spectroscopic study of X-rays produced by oxides at minor ($<1\%$) and trace levels ($<0.1\%$) if they are overlapped by lead emission lines. This phenomenon impacts the quantification of arsenic in Chinese painted enamel whites because the As $K\alpha$ 10.54 peak is masked by Pb $L\alpha$ 10.55, therefore analysis relies on As $K\beta$ 11.72. Accurate quantification, and in some cases detection, of low-z elements such as boron, fluorine, sodium, magnesium, and aluminium are difficult with ESEM-EDX in a high lead arsenate matrix.

3. Material and methods

3.1. Sample set

The elemental composition of the white enamel on ten Chinese painted enamel objects were analysed in this study with Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICPMS). Images of each object in the sample set are presented in Fig. 1. These artworks belong to private collections and are dated stylistically. A.) Vase CPERK2 marked Qianlong (1736–1795) is the only object in the sample set with a distinctly imperial motif, formerly in the collection of Hermann Mandl (1856–1922), it is not unlike Vases 列−360–1–1 in the Taiwan National Palace Museum collection [38]. B.). Lobed Vase CPE302, also marked Qianlong, is similar in shape and motif to a pair of Copper Vases and Covers formerly in the collection of Basil and Nellie Ionides [39] and Covered Vase 116,637 in the Beijing Palace Museum [40]. C.) Hu Vase CPE324 has an archaic bronze form [41]. Two examples marked Qianlong with the same shape and very similar decoration are in the Beijing collection, accession numbers 119,881 and 116,811 [40,42].

Fig. 1. A.) Vase CPERK2, Qianlong (1736–1795); B.) CPE302 Lobed Vase, Qianlong (1736–1795); C.) CPE324 Hu Vase, Qianlong (1736–1795); D.) Charger CPES20, Qianlong (1736–1795); E.) Frame CPE253, Qianlong (1736–1795); F.) Jardinières CPEJP1, Late Qianlong- Jiaqing (1775–1820); G.) Kettle EPC10, Qianlong (1736–1795); H.) Basket EPC4, Late Qianlong- Jiaqing (1775–1820); I.) Four Trays from a Supper Set EPC9, Late Qianlong- Jiaqing (1775–1820); J.) Teapot EPC1, Late Qianlong- Jiaqing (1775–1820).

D.) Charger CPES20 resembles Rijksmuseum Dish AK-RAK-2007–7 [43] in shape, size, and motif; the museum's Dish is dated between 1730 and 1750. E.) Frame CPE253 likely housed a mirror. A Chinese painted enamel frame with a mythical beast masque at the base is in the collection of the Philadelphia Museum of Art [44] accession number 1988–27–113. This frame houses a reverse glass painting and is attributed to the late

18th or early 19th century. F.) Pair of Jardinières CPEJP1 can be compared to five examples of "Potted Landscapes" in the Beijing collection [1]. All five are tribute objects made in Guangzhou for the Qing court during the Qianlong period. A covered bowl with the same monochrome blue floral pattern was bequeathed to the Victoria and Albert Museum by Sir Harry Garner, accession number C.59&A-1964 [45], it is marked Jiaqing (1796–1820).

G.) Kettle EPC10 is a common example found in many museum collections, AK-RAK-2003–1-E in the Rijksmuseum [46] has the same vessel shape and basketry style weaving over a cast metal handle. This shape was popular in European silver, a Kettle by British silversmith William Atkinson dated to 1727 in the Rosenburg Castle collection [47] is a good example. H.) Basket EPC4 has a similar cast handle and textile sleeve. The basket shape also emulates silver, it is remarkably like a Basket by silversmith Edward Aldridge made in 1759 [48]. Chinese painted enamel Basket 1988–27–89 in the Philadelphia Museum of Art [49] collection is dated to the 18th century. I.) Four Trays from a Supper Set EPC9, likely part of a larger set comprised of a central circular dish surrounded by eight smaller trays, see C.113–1913 in the Victoria and Albert Museum [50]. J.) Teapot EPC1 has a large body more typical of kettles, this style of handle is often seen on porcelain teapots. Simplified scrollwork in blue has also been used to decorate the handle of Lidded Wine Pot 1988–27–110a,b [51].

3.2. LA-ICPMS

Fragments of enamel from the decorated surface of each object were ablated in the chamber of an Agilent 8900 triple quadrupole ICP-MS coupled with a ESI New Wave Research NWR 193 ArF excimer laser. The ICP-MS was operated with a plasma power set at 1380 W, a plasma gas flow of 15 L min^{-1}, and an auxiliary gas flow of 0.90 L min^{-1}. Helium was used as carrier gas (800 ml min^{-1})

Table 1
LA-ICPMS results for white Chinese painted enamels presented as wt% oxides for the major components.

	CPERK2 Vase	CPE324 Hu Vase	CPEJP1 Jardinière	EPC4 Basket	CPE302 Vase	CPES20 Charger	EPC1 Teapot	EPC10 Kettle	EPC9 Trays	CPE253 Frame
B_2O_3	6.712	1.272	1.080	0.985	0.645	0.003	0.002	0.001	0.001	0.001
Na_2O	3.011	0.875	0.496	0.483	0.332	0.134	0.091	0.065	0.041	0.127
MgO	0.024	0.009	0.046	0.009	0.046	0.062	0.008	0.005	0.005	0.006
Al_2O_3	0.181	0.062	0.546	0.112	0.133	0.554	0.089	0.093	0.045	0.069
SiO_2	45.679	37.578	33.003	30.672	29.535	33.932	33.218	32.066	32.422	33.571
K_2O	8.483	10.975	8.238	8.761	6.258	9.496	8.571	8.344	8.194	8.707
CaO	0.077	0.033	0.567	0.020	1.867	1.012	0.017	0.015	0.018	0.016
TiO_2	0.008	0.002	0.022	0.004	0.005	0.019	0.003	0.002	0.001	0.002
MnO	0.001	0.000	0.016	0.003	0.003	0.001	0.000	0.001	0.000	0.000
Fe_2O_3	0.051	0.110	0.202	0.056	0.082	0.092	0.076	0.074	0.086	0.073
CuO	0.008	0.208	0.180	0.007	0.511	0.070	0.012	0.011	0.031	0.013
As_2O_3	4.023	5.967	3.927	4.753	3.200	4.803	5.530	4.759	6.214	4.711
SnO_2	0.001	0.004	0.053	0.000	0.057	0.214	0.027	0.009	0.010	0.011
Sb_2O_3	0.004	0.072	0.224	0.039	0.231	0.227	0.027	0.046	0.044	0.056
PbO	31.469	42.100	51.144	53.645	55.849	49.147	52.056	54.379	52.742	52.398

in single MS mode with no cell gas. Each spot was ablated during 60 s with a laser fluence of 6 J cm^{-1}, a repetition rate of 15 Hz and a spot diameter of 50 µm. Gas blank was recorded during the 15 s warm-up time and the 15 s washout time. Each sample was analysed in triplicates. The ICP-MS was tuned on the glass SRM NIST612 to achieve high sensitivity and stability (RSD $< 5\%$). The plasma condition was monitored with U/Th ratio (0.9–1.1) and ThO/Th ratio was used to assess a low oxide level (ThO/Th < 0.01). The ICP-MS was setup in full-quant mode for the acquisition of 44 masses. The integration times was set to 0.02 s for most of the isotopes. The integration time was increased to 0.1 s to provide a better sensitivity for 9Be and reduced to 0.0001 s for 208 Pb in order not to overload the detector. Instrumental drift was corrected by regularly measuring the SRM NIST 612. For the analysis of the enamels, the first 20 s of ablation were considered as pre-ablation and were not used in the calculation of the concentration. Quantitative data were obtained using the sum normalization approach [52] with NIST 612, NIST610, Corning B and Corning D as external standards and SiO_2 as the internal standard. The accuracy results on the SRMs DLH1, NIST610, NIST 612, Corning B and Corning D (Supplementary Materials 1) regularly measured in the batches were compared to accepted values [53–56].

4. Results

LA-ICPMS results for the major components commonly found in enamel and glass are presented Table 1 as wt% oxides. Minor and trace level elements are given in Table 2 as parts per million (ppm). The results are presented by the level of B_2O_3 to highlight the compositional groups identified in this study. It was not possible to detect fluorine with this instrument because of its high ionization potential (17.4 eV) and various interferences. Fluorine was not detected in any of these samples in a previous study using ESEM-EDX [57].

5. Discussion

The results show that all ten white enamels are high lead potassium glass opacified with arsenic at 32–56% PbO, 30–46% SiO_2, 6.3–11% K_2O, and 3.2–6.2% As_2O_3. The sample set can be divided into three groups based on the amount of boron. Half of the objects belong to a boron free group (CPES20, EPC1, EPC10, EPC9 and CPE253), four to a low boron group (CPE324, CPEJP1, EPC4, and CPE302), and one has high boron (CPERK2). There is a positive correlation between the amount of boron and sodium in the five samples where this element is present, demonstrating that borax ($Na_2[B_4O_5(OH)_4]\cdot 8H_2O$) is a component in these enamels, see Fig. 2.A. The high borax composition has 6.7% B_2O_3, the low borax composition ranges between 0.6–1.3% B_2O_3, and the borax free compositions have a maximum of 0.003% B_2O_3.

These results demonstrate that borax is a component in the enamel, rather than a flux in the painting medium used to apply the polychrome painted enamel decoration [58]. There are several benefits which may explain the addition of borax to Chinese painted enamels. Borosilicate glass is used today to make labware, cookware (Pyrex), and telescopes because they have lower thermal expansion and are therefore resistant to thermal shock [59]. Borax acts as a flux lowering melting temperature, producing a harder chemically resistant surface with fewer firing flaws [60]. Lead borosilicates were used to make prisms and spheres [27] because it changes the optical properties by increasing refractive index and light dispersion.

Looking at the results as a whole, a relationship between magnesium and aluminium can be seen in all three groups. This suggests a small amount of clay may be present, clays including kaolinite and halloysite typically have high Al_2O_3 with low to trace levels of MgO [61,62]. Small amounts of clay may have been introduced indirectly during the processing of raw materials in ceramic mortars or added intentionally as a deflocculant [58].

5.1. Source of borate minerals

Borate minerals are defined as compounds containing or supplying boric oxide (B_2O_3). Despite being one on the rarest element on earth, the ability of boron to bond with oxygen and to combine with any cation have led to the discovery of more than 230 different borate mineral species [60]. However, the few most abundant types can be divided in four chemical groups: Ca-borates, Na-borates, Na-Ca-borates, and Mg-borates. The large borate deposits are rare and typically occur in the uplifted side of rift subduction zones in Neogene to Holocene non-marine evaporitic environments. Cenozoic volcanism surrounded by hydrothermal springs, arid or semi-arid climate, and playa-lake environment seem to be essential conditions for the formation of large Na- and Ca-borate deposits [63,64]. The earliest source of borate has been located in the Tibetan plateau deposits. From the second half of the 19th century, deposits of historical or commercial importance have been identified and mined in Italy (Tuscany), Turkey (Anatolia), USA (California), and South America (Central Andes) [65,66]. In north-eastern China, another source of borate (Mg-borates) has been discovered in the Liaoning province [67].

The production period of the artefacts analysed in this study is ranging between the second quarter of the 18th and the first quarter of the 19th century. Therefore, the Tibetan deposits are

Table 2
LA-ICPMS results for white Chinese painted enamels presented ppm, minor and trace level components.

	CPERK2 Vase	CPE324 Hu Vase	CPEJP1 Jardinière	EPC4 Basket	CPE302 Vase	CPES20 Charger	EPC1 Teapot	EPC10 Kettle	EPC9 Trays	CPE253 Frame
Li	34.825	8.369	9.074	9.608	5.136	2.593	2.187	3.156	2.153	3.173
Be	0.045	0.022	0.662	0.088	0.063	0.143	0.027	0.055	0.009	0.016
P	48.469	22.594	75.006	11.336	37.730	18.457	12.358	10.020	11.832	10.003
S	246.971	233.046	361.775	56.315	725.990	123.253	109.988	76.569	137.951	144.974
Cl	741.209	2783.530	484.971	676.894	525.534	512.654	979.352	422.994	388.577	787.610
V	1.683	0.652	3.381	0.659	0.968	2.118	0.714	0.656	0.898	0.484
Cr	1.047	0.659	1.926	0.481	0.846	1.907	0.822	0.520	0.900	0.632
Co	0.176	0.333	3.343	0.445	4.768	0.142	0.231	0.125	0.141	0.115
Ni	1.901	1.316	8.741	0.711	7.408	1.592	2.726	2.745	2.664	2.417
Zn	1.553	7.109	77.910	2103.495	2888.340	26.652	9.079	1.726	6.322	1.584
Ga	0.423	0.081	0.648	0.155	0.194	0.616	0.121	0.105	0.049	0.092
Ge	0.289	0.292	0.408	0.435	0.351	0.403	0.227	0.162	0.187	0.182
Rb	5.790	24.449	18.594	21.286	16.284	38.954	24.245	17.809	37.413	27.214
Sr	5.890	1.260	20.763	1.497	13.513	6.728	0.995	0.688	0.597	0.828
Y	0.256	0.095	1.149	0.268	0.515	1.706	0.246	0.062	0.087	0.132
Zr	3.395	0.661	9.930	1.161	1.548	16.131	1.340	0.498	0.483	1.143
Nb	0.629	0.064	0.834	0.110	0.189	0.514	0.095	0.041	0.044	0.070
Mo	0.072	0.187	0.477	0.041	0.169	0.033	0.037	0.034	0.042	0.028
Ag	59.648	62.554	44.090	47.421	63.806	117.453	41.139	57.764	108.309	71.678
In	0.103	0.179	1.638	0.222	2.091	19.726	0.783	0.281	0.285	0.363
Cs	0.116	0.312	0.550	0.093	0.158	0.507	0.218	0.118	0.154	0.265
Ba	7.264	3.582	25.914	3.641	7.765	17.787	3.939	1.977	1.357	2.347
La	0.531	0.204	1.748	0.495	0.429	3.169	0.718	0.121	0.128	0.243
Ce	0.907	0.294	3.161	0.533	0.947	5.980	0.630	0.288	0.240	0.447
Au	0.242	0.018	0.266	0.007	0.064	0.243	0.013	0.022	0.015	0.008
Bi	8.944	15.708	52.240	12.351	4676.687	402.823	4.434	4.121	7.040	11.725
Th	0.200	0.072	0.640	0.122	0.202	1.075	0.114	0.067	0.054	0.092
U	0.059	0.021	0.216	0.039	0.319	0.180	0.032	0.015	0.019	0.022

likely the source of the borate used in the enamel. More than 57 lakes containing mainly Na-borate minerals (borax and tincalconite) have been identified in this area. They are located near rift zones in the Gangdise-Nyainqêntanglha and Himalaya Mountains. The carbonate-rich lakes with high salinity are recording the higher concentration in boron, which coincide with high values of B in the nearby geothermal springs. The water from the springs and the volcanic sedimentary rocks also supplies Li, as well as Cs and K in a lesser extent. [60,68]. The results of the LA-ICP-MS analysis showed a very good correlation (R^2=0.99) between Li and B_2O_3 supporting the Tibetan provenance of the borax identified in the enamels, see Fig. 2.B. However, it should be noted that high concentrations of Li are also recorded in borate deposits in South America, USA, and Turkey [60,66].

5.2. Borax free white enamels

The borax free group has the simplest composition in this study. These objects were made in Guangzhou between 1736 and 1820 and are all decorated in styles typical of contemporary export porcelain. The proportion of the two major glass formers and primary flux, $SiO-K_2O-PbO$, is derived from Chinese cloisonné technology [16]. Arsenic is clearly the opacifier at an average of 5.2% As_2O_3, and fluorite (CaF_2) can be ruled out in four of the five samples due to the very low calcium levels at 0.015–0.018% CaO.

Four out of five of the borax free examples (EPC1, EPC9, EPC10, and CPE253) have remarkably similar levels of trace elements, see Table 2. The composition of Charger CPES20 is slightly different and is often closer to the low borax group. All five borax free samples have similar proportions of iron oxide and silica demonstrating that these objects have a mutual raw material source of silicon, see Fig. 2.C. A correlation can also be seen between sulphur and lead, consistent with a sulphur rich mineral such as galena (PbS), Fig. 2.D. There appear to be two groups based on the ratio of sulphur to lead. All of the borax free samples and Basket EPC4 are a low sulphur group. CPERK2 fits in the high sulphur group with CPE324, CPEJP1, and CPE302 if both components are increased proportionately.

Low magnesium points to a mineral source of potassium which is consistent with historic glass making accounts [7]. The use of mineral nitre (saltpetre KNO_3) is supported by potassium correlating with chlorine, likely due to halite (NaCl) impurities, Fig. 2.E. Overall the sample set falls into two main groups when comparing arsenic and antimony in Fig. 2.F, most of the borax free white enamels plot together in the low antimony group.

5.3. High borax white enamel

Vase CPERK2 differs significantly from the rest of the examples in this study. The vase is marked Qianlong (1736–1796) and is decorated in the style of the imperial workshops in Beijing. It is ten percent higher in silica and twenty percent lower in lead than averages for the other nine samples. Potassium and arsenic are consistent with the other white enamels, but boron is much higher at 6.7% B_2O_3. Boron and sodium combined as borax make up approximately 10% of this enamel. Borax acts as a flux and a vitrifier [26], allowing for a composition with relatively higher silica and lower lead.

In Fig. 2.C there is a much lower proportion of iron to silica in this example, representing a different and purer silicon source with increased lithium. CPERK2 plots differently in Fig. 2.D because it is significantly lower in lead. If both components (S-PbO) are increased proportionally, the high boron sample is in line with the rest of the sample set. Chlorine is consistent with most samples indicating a mutual source of potassium, but antimony is lower indicating a different raw material source of arsenic or more effective refining processes, Fig. 2.F and 2.E.

The composition of the white enamel on Vase CPERK2 echoes Qianlong period Jesuit glass technology. Translation of the 1753 Zaobanchu record number 3438 by Yang [7] recounts the Jesuit glass recipe as: 47.5% horse-tooth stone, 28% saltpetre, 12.3% borax, 5.1% white lead, 5.1% arsenic, and 2% fluorite; the term horse-tooth stone refers to quartz [21]. This sample is roughly equivalent to the

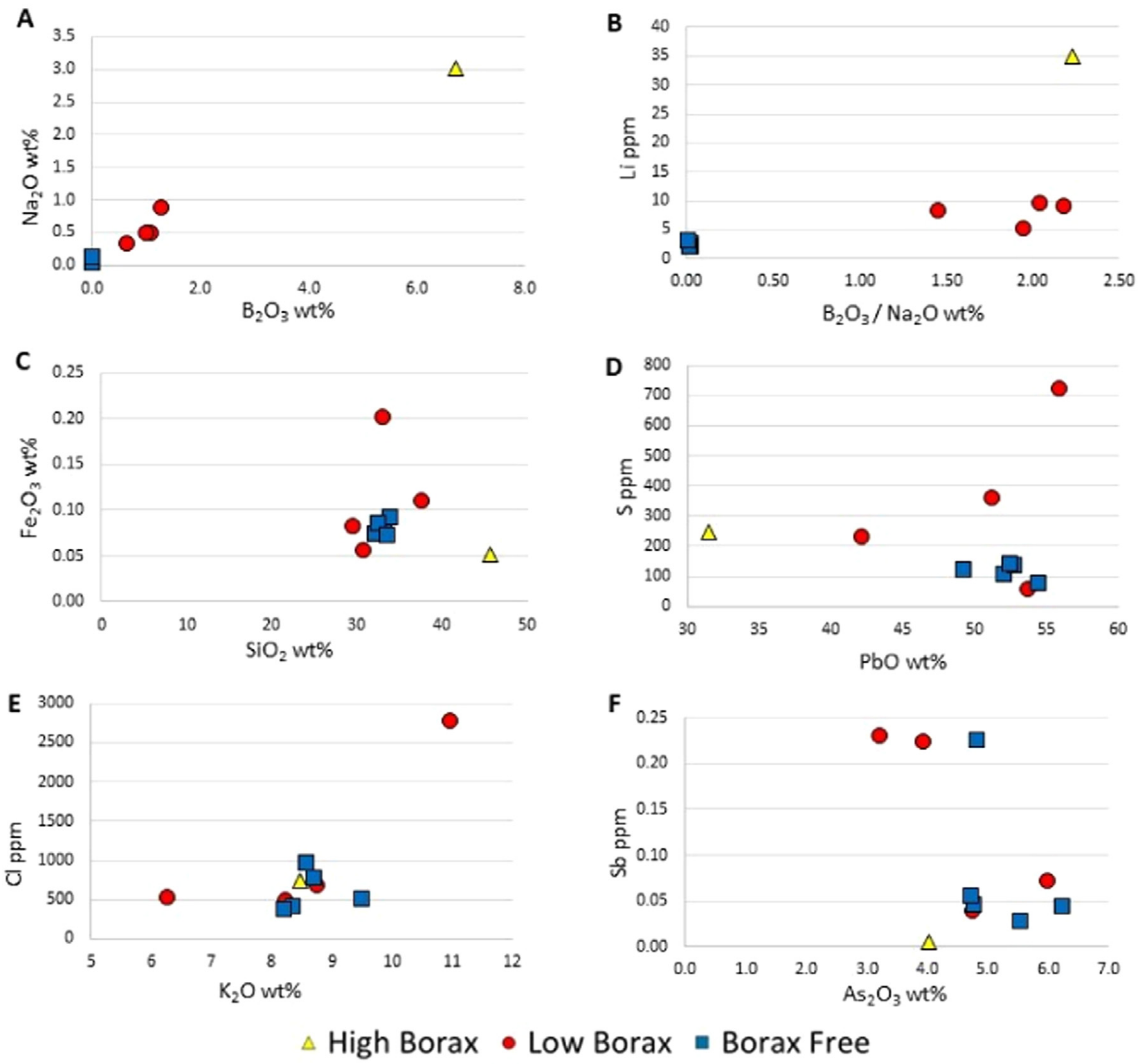

Fig. 2. Scatterplots of major elements given as weight percentage of oxides (wt%) from Table 1 and trace level elements presented as parts per million (ppm) from Table 2 of white enamel layers on Qianlong and Jiaqing (1736–1820) Chinese painted enamel objects.

Jesuit glass recipe in silica, borax, and arsenic; it was formulated to have a lower melting temperature by adjusting the amount of lead and potassium.

The amount of boron detected in this sample is similar to a Qianlong period cloisonné ornament from the Fuwang chamber in the Beijing Palace Museum [18]. Fluorine was detected in the white cloisonné using Raman spectrometry. Calcium is much higher in the ornament at 14% CaO than Vase CPERK2 at 0.077% CaO. Based on the amount of calcium detected this sample could have a maximum of 0.11% CaF_2. Fluorine was not detected in this sample with ESEM-EDX [57] but at this level it would have been below the limit of detection in that study. The presence of fluorite in CPERK2 is unlikely but cannot be entirely ruled out.

5.4. *Low borax compositions*

The low borax group has more diversity in composition than the borax free group. Boron was detected between 0.65–1.3% B_2O_3 in this group. These objects are attributed to the Guangzhou production centre between 1736 and 1820. Hu Vase CPE324, Lobed Vase CPE302, and Jardinières CPEJP1 are decorated with patterns that would have appealed to the domestic Chinese market. Basket EPC4 emulates British silver and was most likely made for the export market, but it may have appealed to the Chinese as exotica. The proportion of silica and lead are similar to the borax free group except for CPE324 which has higher silica and correspondingly lower lead. Arsenic and potassium levels are also consistent with the borax free group, although the opacifier is elevated in CPE324 at nearly 11% As_2O_3. CPE324 and EPC4 are low in calcium at 0.02 and 0.03% CaO making it very unlikely that fluorite is present. CPEJP1, CPE302 have higher calcium at 0.57 and 1.9% CaO, levels which could represent the intentional addition of fluorite at a maximum of 0.79% and 5.28% CaF_2. Fluorite was not detected in either of these samples with ESEM-EDX [57]. Spectral analysis of Fluoride Opal Glass standard #4 [69] showed that F is underreported with ESEM-EDX. Therefore, an alternative technique is required to exclude fluorine from CPEJP1 and CPE302.

Jardinière CPEJP1 has distinctly higher iron when compared to silica, likely representing a lower quality silicon source than the rest of the sample set, Fig. 2.C. CPE324 is much higher in sulphur to lead in Fig. 2.D, and higher in chlorine to potassium in Fig. 2.E. CPE302 is low in chlorine, this reflects the lower amount of potassium rather than a different level of impurity. The low borax group is split between the high and low antimony groups in Fig. 2.F. CPE324 and EPC4 are low antimony at levels similar to four objects in the borax free group, suggesting a mutual source of arsenic. CPEJP1 and CPE302 are in the high antimony group alongside CPES20 which has a borax free composition.

6. Conclusion

White enamels on the ten objects in this study are all SiO_2-K_2O-PbO glass opacified with lead arsenate ($PbAs_2O_6$). Boron was detected in five examples, where present, there is a clear correlation between boron and sodium demonstrating that borax ($Na_2[B_4O_5(OH)_4]{\cdot}8H_2O$) was a component in these enamels.

Three compositional groups were identified in this study: high borax, low borax, and borax free. The high borax composition was only identified in the vase made in the imperial workshops. This enamel is clearly influenced by Jesuit glassmakers working in the Zaobanchu who used a similar amount of borax in glass making. For the first time, artworks attributed to Guangzhou can be divided into two groups based on their elemental composition. The borax free composition used in Guangzhou is similar to late Ming Chinese cloisonne with arsenic replacing fluorite as the opacifier. The low boron Guangzhou group is more diverse in composition, potentially reflecting the movement of enamellers between Beijing and Guangzhou during a time when multiple glass compositions were produced. These results show that the use of borax was transferred from Jesuit glassmaking practices in Beijing to Guangzhou where it continued into the 19th century.

Although there is no obvious difference in the appearance of opacified borosilicate and boron free enamels, there are several practical advantages. Boron rich enamels are more resistant to thermal shock, an important attribute for teapots, brasiers, and candlesticks used in a domestic setting. Increasing hardness and reducing firing flaws such as blisters, crawling, and crazing greatly improve quality. Lowering the melting temperature could also improve working properties when firing in a muffle kiln, where the artwork is monitored visually and drawn out at the point of vitrification.

Trace elemental analysis has made it possible to identify patterns between the major components in the enamel and impurities related to their raw materials. Overall, the Beijing enamel has lower levels of impurities suggesting higher quality raw materials or better refining processes. The results also show uniformity in the borax free Guangzhou group, suggesting that four of these artworks were made in a mutual workshop.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.culher.2023.03.008.

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