European cobalt sources identified in the production of Chinese *famille rose* porcelain

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Abstract

The blue pigments on 112 fragments or small objects of Qing Dynasty Chinese, 95 of underglaze blue and white and 17 overglaze enamelled porcelains were analysed by LA-ICPMS. The underglaze blues on both blue and white and polychrome objects were created with a cobalt pigment that was rich in manganese with lesser nickel and zinc. This suite of accessory elements is generally considered to be characteristic of local, Chinese, sources of pigments. However, the blue enamels were very different. The cobalt pigment here has low levels of manganese and instead is rich in nickel, zinc, arsenic and bismuth. No Chinese source of cobalt with these characteristics is known, but they closely match the elements found in the contemporary cobalt source at Erzgebirge in Germany. Textual evidence has been interpreted to suggest that some enamel pigment technologies were transferred from Europe to China, but this is the first analytical evidence to be found that an enamel pigment itself was imported. It is possible that this pigment was imported in the form of cobalt coloured glass, or smalt, which might account for its use in enamels, but not in an underglaze, where the colour might be susceptible to running. Furthermore, the European cobalt would have given a purer shade of blue than the manganese-rich Chinese cobalt.

Keywords

CHINA, PORCELAIN, COBALT BLUE, FAMILLE ROSE, LA-ICPMS

1 Introduction

Cobalt is a strong colorant used in many areas of the world for the production of pigments and blue glass and glazes. Its earliest use is probably in Egypt in the Late Bronze Age, around 16th century BC. Its first use in China was in the Spring and Autumn period (770-475 BC) when it was used as a colouring agent in glazed beads then later in low-firing glazes on Tang sancai and blue glazed earthenwares (Garner 1957, p.1). Its first use in Chinese glass dates back to the Han Dynasty, while the earliest Chinese example of the use of cobalt as an underglaze pigment comes from the ninth century, Tang port of Yangzhou City (Wang et al. 1993, see also Wood et al. 2007). It was perfected in the blue and white porcelain of the Yuan dynasty in the early fourteenth century CE, and the technology was adopted at Jingdezhen, which went on to become the most important kiln site in China, effectively a city devoted to the production of porcelain (Tichane 1983; Harrison-Hall 1997). Chinese blue and white porcelain represents one of the most successful and influential developments in the history of ceramic technology. A convergence of the technologies of high-fired white stoneware and underglaze painting with a cobalt pigment, it became a major component of Chinese porcelain production and was particularly important as an export ware, initially to the Islamic world and later to Europe (Medley, 1989, p. 178). It has been emulated by industries across the world, and remains commercially important today (Finlay 1998). Here new data are reported which demonstrate for the first time that European cobalt sources played an important role in the development of Chinese enamelled porcelains in the eighteenth century.

Cobalt has attracted archaeometric attention because the relatively limited number of sources that were accessible to early craftsmen, along with the variable compositions of the ores, makes it possible to characterise and attribute the pigments to their region or even mine of origin (Gratuze 2013). In particular, the clear interplay of style and technology between the blue and white wares of China and the Near East from the Tang to Ming periods (7th-17th centuries; (Medley, 1989; Rawson, 1984; Vainker, 1989)) has led to increasingly sophisticated analytical studies with a view to determining the source of cobalt and contributing to an understanding of the processes of technological transfer and innovation (Kerr and Wood, 2004; Wen and Pollard, 2016; e.g. Wen et al., 2007; Zhu et al., 2015).

The application of low-firing lead-rich coloured enamels over the glaze of previously high-fired stonewares and porcelains can be traced back to the end of the 12th to the beginning of the 13th Century (Medley 1989; Wood 1999; Kerr and Wood 2004). In China they were first applied onto white slipped high-firing, glazed stonewares, known as *cizhou* wares, and in the late 14th century the enamelling techniques used in the northern *cizhou* kilns spread to Jingdezhen in the south (Wood, 1999). In the Qing dynasty (1644-1911) in the reign of the the Kangxi emperor (1672-1722) the initial palette of the *famille verte* family, known in Chinese as *wucai* or five-colour was developed, comprising copper-green, iron-yellow, iron-red and turquoise overglaze enamels on porcelain decorated with underglaze cobalt (e.g. Medley, 1989; Vainker, 1989, p. 202).

The Kangxi reign (1662-1722) was a period of great stability and support for the craft

Fig. 1 Detail of the *Famille rose* enamels painted in this case on the Daoguang-reign period porcelain (a) B.fr.1850.2 and (b)B.fr.1850.3 (b). (photo: R Giannini).

industries, including an emphasis on painted enamel work on glass and metal, as well as ceramic, which was driven by the emperor himself. Workshops were attached to the Imperial Court in Beijing and foreign craftsmen were sought to develop techniques. Late in the seventeenth century the mature *famille verte* palette, including for the first time an *overglaze* cobalt blue enamel, was developed (Vainker, 1989). Towards the very end of the Kangxi period (Sato, 1981; Vainker, 1989), extensive development work in the Palace workshops in Beijing, discussed in detail by Kerr and Wood (2004) and also by Curtis (2009) led to the development of the *famille rose* group of enamels, which included a red based upon colloidal gold and an arsenic opaque white, which in mixing could produce a wide range of red and pink shades (Fig. 1). This palette appears to have been transferred for production at the Imperial kilns in Jingdezhen at the beginning of the reign of the succeeding emperor, Yongzheng (1722-1735). In addition to the high artistic quality of some of the ceramics, several characteristics of *famille rose* or *fencai* have attracted scholarly attention. The development of a gold-based pink at this time corresponds with the development of gold ruby glass in Europe, the practical application of which is particularly associated with the German chemist Johann Kunckel (Hunt, 1976). Europeans with knowledge and skills in glass and enamel production were attached to the Chinese Imperial Court and workshops were established, for example the glass workshop headed by the Jesuit missionary Kilian Stumpf in 1697 (Curtis, 1993). Furthermore, one of the terms by which the *famille rose* palette was known to the Chinese craftsmen was "foreign colours" (*yangcai*), and the official list of porcelain produced at Jingdezhen in the Yongzheng reign refers to the use of European or foreign decoration on at least six occasions (Bushell, 1896). All of this led to the idea that the *famille rose* palette was heavily influenced by European practice and possibly that the technology itself was transferred. However, limited analytical work has so far failed to identify any unambiguously European compositions on *famille rose* pieces (Kingery and Vandiver, 1986) and furthermore has suggested a strong link with compositions of earlier Chinese cloisonné enamels on metalwork (Henderson, 1989; Kerr and Wood, 2004; Mills and Kerr, 1999; Vainker, 1989). The influences on the development of *famille rose* therefore continue to be a subject of significant interest.

Our understanding of porcelain production and technology in the Qing Dynasty has been surprisingly dependent upon the account of a single person, Père d'Entrecolles, a French Jesuit missionary. Through conversations with the craftsmen and direct observation, d'Entrecolles was able to document many aspects of industrial practice, in two famous letters dated 1712 and 1722, which attracted wide attention in the eighteenth century as Europeans attempted to discover the secret of porcelain. English translations in print are provided by Burton (1906; slightly abridged) and Tichane (1983) with an on-line version provided at www.gutenberg.com. Significantly for the present work, d'Entrecolles's last communication from Jingdezhen was more-or-less at the time when *famille rose* production was introduced at Jingdezhen, but he does make some interesting observations about earlier enamels and cobalt.

Cobalt blue was such a widespread colour in Chinese ceramic production from the fourteenth century onwards that a critical role in the development of the enamel palette has not been considered in detail. However, there are some tantalising indications that production of a cobalt blue enamel was not straightforward. Firstly, there is the fact that it was the very last of the overglaze colours to be added to the earlier *famille verte* palette (Vainker, 1989, p. 202). Secondly, the analysis of *famille verte* enamels by Kingery and Vandiver (1986) reveals the cobalt blue to be the only colour with an elevated potash content of around 6% relative to less than 0.5% for the other colours. With some hindsight, this suggests a deliberate addition of potassium to the blue and a significant difference in the technology of the base glass relative to the other colours at that time.

The present paper reports new quantitative results for the cobalt on the later blue-and-white ceramics of the Qing Dynasty (1644-1912). While most are agreed that by the end of Ming times the pigments used on Chinese underglaze blue were obtained from Chinese sources (Wen and Pollard, 2016; Wen et al., 2007; Zhu et al., 2015), our results suggest that the situation under the Qing was more complex. In particular, we focus on the pigments on the polychrome enamelled wares which were extensively exported to Europe during this period.

1.1 Cobalt pigments

The blue colour produced by cobalt-based pigments can be due to the presence of cobalt in both its crystalline and solution-ionic forms. As the Co^{3+} ion is not stable in the temperature range required for glass melting, only those cobalt compounds which are derived from the divalent cobalt ion Co^{2+} are of interest in glass technology (metallic Co assumes a significant role only in the field of enamel on metal, where it contributes to the adherence of the ground coats) (Weyl, 1951, p. 170). In particular, in alkaline glazes, Co^{2+} ions in tetrahedral coordination (i.e. present in the vitreous structure as glass formers, in the form of CoO_4 complexes) give rise to blues or blue-purples (or blue hues in lead-based matrices), while in the octahedral coordination (Co^{2+} ions are inserted in the position occupied by alkali ions, CoO_6 complexes) confer pink hues to the glass (Weyl, 1951, pp. 179–80, 182–4). Cobalt is one of the most stable and powerful colouring agents and saturated blue tints in common glassy systems occur for CoO concentrations as low as 0.25% (noticeable blues are already observed at levels of c. 0.005% CoO) (Kerr et al., 2004; Weyl, 1951, pp. 179–80). In Chinese blue underglazes CoO is usually found at levels of about 0.1-1% (Kerr et al., 2004).

Cobalt does not exist as a native metal, though there are many cobalt-bearing minerals from which it can be extracted (Henderson, 2000, p. 30). The analysis of the impurities naturally occurring in the cobalt ores (e.g. iron, copper, manganese, nickel, arsenic, sulphur, bismuth) might therefore provide a valuable support in revealing the cobalt sources employed by the ancient craftsmen. For example, the association of arsenic and sulphur (and sometimes zinc) may suggest the use of cobaltite (CoAsS) or smaltite ($CoAs_2$), while nickel and arsenic of the minerals erythrite ($Co_3(AsO_4)_2 8H_2O$) or skutterudite ($(Co,Ni)As_{3-x}$), manganese of the mineral asbolane $(Co,Ni)_{1-y}(MnO_2)_{2-x}(OH)_{2-2y+2x}\,n(H_2O)$. Several cobalt-compounds can also contain significant amount copper. Finally, blue compounds could also be obtained from cobalt, nickel, iron and copper-rich residues after separating bismuth from its ores (Frank, 1982).

2 Methodology

2.1 Sample selection

Several sets of porcelain samples were chosen for analysis. All fragments had to be small enough to fit into the sample chamber of the laser system, so less than 100x100x25mm. The first set (codes N.bw.R*) were blue and white jar lids excavated at Jingdezhen and lent by Professor Nigel Wood and Oxford University, all dated from 17th to 20th centuries AD. The next set were sherds from either the Vung Tao Cargo (B.bw.VTC.1690-*) or the Nanking Cargo (B.bw.NC.1750-*), dated by Mary Tregear (Ashmolean Museum) to 1690 and 1750 or thereabouts. Most of this was Jingdezhen export porcelain bound for the European market. The next set was from the Victoria and Albert Museum sherd collections and represent a variety of fragments from the Qing Dynasties including blue and white (V&M.bw.*), *famille rose* (V&M.fr.*) and a single *famille vert* (V&M.fv.1385-1902). The final set were acquired from private collections and represent blue and white (B.bw.[date].*), *famille rose* (B.fr.[date].*) and a single *famille verte* (B.fv.1700.1) fragment of various porcelain types dating to the 18th and 19th centuries. In total the blue areas on 92 examples of blue and white underglaze, three underglazed blue on a polychrome vessels and 17 *famille rose* blue enamels were analysed.

2.2 LA-ICPMS

Table 1: LA-ICPMS operating conditions

ICP-Q-MS - Thermo Electron Corporation XSERIES 2	Working Conditions
RF power (W)	1430-1470
Coolant gas flow rate (L min^{-1})	15 (Ar)
Auxiliary gas glow rate (L min^{-1})	0.9
Nebulizer flow rate (L min^{-1})	0.8-1.2
Extraction (V)	-720/-750
Detector mode	counting and analogue mode
Acquisition mode	peak hopping
Channel per mass	1
Channel spacing	0.02
Dwell time (ms)	20-50
Sweeps	15-20
Total acquisition time (s)	50-60
Sampling events	1-3
Replicate per sample	>3
ThO^+/Th^+	<0.02%
CeO^+/Ce^+	<0.2%
LA - New Wave Research, Q switched Nd:YAG	Working Conditions
Wavelength (nm)	213
Laser ablation chamber	Standard
Ablation mode	spot - scan (<1500 μm path, 10 μm s^{-1})
spot diameter (μm)	80
Pulse time (ns)	2
Energy (mJ)	0.42
Energy density (fluence) (J cm^{-2})	>20
Pulse repetition rate (Hz)	10
Carrier gas flow rate (ml min^{-1})	500 (He)

The sherds were ablated directly in the large sample chamber of a New Wave 213 laser attached to a Thermo Series II ICPMS. The ablation conditions and ICPMS set up were optomised using a series of experimental samples and the conditions used are shown in Table 1. The results of runs on the unknowns were interspersed with gas blank runs and calibrated against NIST SRM 610 glass reference material, doped with a nominal concentration of 500 ppm for most trace elements, and NIST 612 (50 ppm nominal concentration) using the consensus values (Jochum et al., 2011). Each batch of samples included multiple measurements from NIST 610 and 612 throughout the duration of the session to allow for correction of instrument drift. Repeat measurements of Corning A were made throughout the analytical period and the results of those analyses are reported in Table 2 and compared to accepted values (Shortland et al., 2007; Vicenzi et al., 2002; Wagner et al., 2012). The results reveal that for the majority of trace elements agreement with accepted values, as expressed by the percentage difference between the determined and accepted values (RD) is usually better than 20%. The greatest deviation from accepted or consensus values was shown by P and K, regarded as difficult elements to determine by LA-ICPMS. Phosphorus has a high ionization potential and all isotopes of potassium have high background counts because of their proximity to Ar, the plasma gas.

Table 2:Runs by LA-ICPMS against Corning A secondary standard showing deviation from accepted values.

	CMG A					
Analyte	Measured (n=33, 11 runs)	SD	Accepted value^{1,2}	Accepted value^{3}	RD^{1,2}	RD^{3}
	mg·kg^{-1}	mg·kg^{-1}	mg·kg^{-1}	mg·kg^{-1}	%	%
Li	45	*4*	46	51	-2	-12
Be	0.06	*0.03*	0.06		0.4	
B	607	*54*	537	851	15	-28
Na	102171	*4178*	106083	99407	-3	3
Mg	13332	*802*	16043	15078	-17	-12
Al	4962	*118*	5291	4339	-6	14
Si	317805	*3172*	310883	316768	2	0.3
P	655	*35*	341	371	92	77
K	24152	*1449*	22639	28714	7	-16
Ca	35626	*788*	35954	35311	-0.5	0.9
Ti	4697	*119*	4226	4428	11	6
V	37	*770*	34	39	0.6	-12
Cr	20	*0.6*	18	21	10	-4
Mn	7594	*312*	6921	8752	10	-13
Fe	7171	*442*	6537	6841	10	5
Co	1222	*27*	1188	1336	3	-9
Ni	184	*5*	160	181	15	2
Cu	9700	*408*	7842	8786	24	10
Zn	461	*42*	410	386	14	20
As	29	*3*	25		15	
Rb	80	*8*	82	82	0.02	-0.9
Sr	874	*85*	860	897	3	-1
Zr	41.7	*0.8*	40	37	4	13
Nb	0.56	*0.06*	0.6		-5	
Ag	16.3	*0.4*	14		14	
Sn	1526	*25*	1194	1357	28	12
Sb	14849	*1381*	10649	14002	39	6
Cs	0.29	*0.04*	0.2		22	
Ba	4444	*94*	3905	4122	10	8
La	0.31	*0.03*	0.3		12	
Ce	0.23	*0.03*	0.2		-3	
Au	0.11	*0.02*	0.1		11	
Pb	699	*15*	595	678	18	3
Bi	9.5	*0.3*	7.8	9.0	22	5
Th	0.31	*0.02*	0.3		3	
U	0.18	*0.02*	0.2		12	

[1] Shortland et al., 2007
[2] Vicenzi et al., 2002
[3] Wagner et al., 2012

The results were calibrated using the mathematical approach first proposed by Gratuze (Gratuze, 1999) as an alternative to the use of an internal standard. The protocol used here followed that laid out by van Elteren (van Elteren et al., 2009). This essentially works in a similar fashion to a normalised EDS system on an SEM. It assumes that all elements are measured and calculates oxygen by stoichiometry. The total is then normalised to 100% and either presented as weight percent oxide or converted back to elemental ppm.

3 Results

Table 3: Averages of undecorated glazes for blue and white and polychrome wares

	Co	Mn	Ni	Cu	Zn	As	Ba	Bi	U
Qing A									
Average *	37.7	988	31.6	46.5	54.9	2.1	79.4	0.1	11.2
SD	64.6	1177	34.1	24.7	28.6	1.5	36.5	0.1	2.5
Qing B									
Average **	72.9	461	48.4	39.5	29.4	1.7	94.6	0.0	10.1
SD	60.2	100	72.4	11.7	17.0	1.7	30.3	0.0	1.8
Qing C									
Average	8.5	873	3.5	27.6	54.2	2.3	720	0.0	3.1
SD	5.2	577	1.0	30.6	34.2	3.5	188	0.0	0.9
Polychrome	4.3	721	21.9	99.0	65.1	5.1	78.7	0.6	11.9
Average	5.3	276	12.0	118	139	14.7	28.9	2.0	3.2

The LA-ICPMS was used to provide analyses of the undecorated glazes on the blue and white and polychrome (enamelled) wares (Table 3) and the areas of dark-blue glaze in the underglazed blue and white (Table 4), the dark blue underglaze in the polychrome (Table 4) and enamels in the polychrome *famille verte* and *famille rose* (Table 5). Care was taken to target the darkest blues and of as similar a hue as possible, to minimise possible differential diffusion of colouring wlements in the glaze. The major and minor element characteristics of the glazes are well known (Wood, 1999), and have been extensively published and our detailed analyses of these and the new trace element data will be presented and discussed elsewhere (Giannini et al, in prep). However, the results are pertinent to the present study of cobalt blue. The blue and white wares can be split into three slightly differing groups, Qing A, B and C. The largest group, Qing A, is the most similar to the polychrome wares. Both Qing A and the polychrome wares are consistent with production at Jingdezhen, as would be expected, whereas Qing B and Qing C are probably from other production sites (Giannini et al, in prep). Table 3 presents the analyses of undecorated white glazes, showing those elements that are conventionally thought to be linked with cobalt colorants (as discussed above). The table shows that the white glazes themselves have low levels of these elements, typically tens of ppm or lower for most. The exceptions are manganese in all the porcelain analysed, where the average content is up to 1,000 ppm Mn and Ba in the Qing C group, which averages 720 ppm Ba. This shows that with the exception of these two elements (discussed below) the raw materials of the glazes do not significantly contribute to elevated concentrations of those elements associated with the blue colourants, which are the main interest of this paper. Even though the underglaze blue is analysed through the glaze and intimately mixed with it, the contribution of the overlying glaze in terms of these elements is minimal.

Table 4: LA-ICPMS analyses of underglaze blue areas of glazes on Qing blue and white Chinese porcelains.

Sample	Fe	Co	Mn	Ni	Cu	Zn	As	Ba	Bi	U
QING Group 'A'										
N.bw.R1	7289	1934	12084	149	35	103	4.8	352	0	12.1
N.bw.R2	6609	1226	9028	85	44	73	6.2	212	0	11.1
N.bw.R60	6618	415	2626	16	43	42	5.7	105	0	11.4
N.bw.R76	6690	3768	13420	361	18	223	3.2	321	0.1	9.5
B.VTC.bw.1690.1	9680	11418	51876	780	63	272	72.2	934	0	10.2
V&A.bw.C.459-1915	7986	3694	20520	105	59	172	113.3	229	0	9.3
V&A.bw.C.94-1952	5038	605	4058	101	74	86	1.8	57	0.2	6
N.bw.R17	7985	3814	17586	259	31	153	248.2	337	0	10.5
N.bw.R31	7657	3034	20386	62	80	95	62.1	499	0	10.9
N.bw.R49	8170	3794	14242	197	37	107	36.1	289	0	10
N.bw.R59	6100	2335	13461	51	40	102	8.8	394	0.1	11.9
B.bw.1700.1	8413	3548	16287	189	26	50	62.3	366	0	9.2
B.bw.1720.1	5855	1698	10208	62	35	119	20.7	247	0	11.1
B.bw.1720.2	4630	609	3006	16	48	58	2.5	145	0.1	10.3
N.bw.R15	6089	4749	9966	186	36	117	62.7	201	0	9.3
N.bw.R18	8688	7742	23700	375	24	159	123	269	0	10.4
N.bw.R20	13767	4605	25987	502	43	121	634.5	477	0	13
N.bw.R21	7557	3055	11436	55	39	128	298.3	524	0	13.9
N.bw.R23	11679	6722	17944	129	28	207	12.3	351	0	9.3
N.bw.R24	6195	1892	11972	80	51	58	2.8	250	0	8.1
N.bw.R26	5936	1325	6495	41	24	79	11.4	147	0	18.3
N.bw.R28	6995	3922	12952	388	42	102	604	519	0.1	7.3
N.bw.R29	9712	4142	14214	46	24	87	8.5	271	0	10.4
N.bw.R32	5986	2854	14960	102	26	64	4.7	272	0	12.9
N.bw.R33	5585	1629	14918	111	52	76	17	318	0	15.9
N.bw.R34	8050	3370	12097	54	31	118	19.9	203	0	10.2
N.bw.R38	7298	2001	8061	49	40	92	73.4	246	0	10.7
N.bw.R40	7290	1903	12179	79	51	65	7.5	192	0	14
N.bw.R41	5631	1642	12821	79	34	51	2.4	348	0	10.7
N.bw.R42	7293	2997	17957	73	31	72	16.3	275	0	9.5
N.bw.R43	12191	4614	18144	159	44	146	148.3	441	0	9
N.bw.R45	5795	3480	7345	197	23	121	54.4	194	0	8.2
N.bw.R47	6782	1729	7447	83	30	74	8.2	247	0	9.2
N.bw.R48	5670	3040	14700	27	32	100	2.8	327	0	9.4
N.bw.R50	8095	1302	6125	17	38	64	39.3	178	0	8
N.bw.R51	6262	1394	9865	43	34	58	2.3	197	0	13

N.bw.R52	6918	3155	7589	203	35	153	14.1	184	0	11.7
N.bw.R53	9447	2095	13368	81	44	93	5.4	180	0.7	52.8
N.bw.R54	9444	2094	13422	94	47	120	4	199	0.7	12.5
N.bw.R55	7863	6463	40197	326	31	177	106.6	668	0	9.5
N.bw.R57	6357	698	5919	13	13	74	5.7	261	0	7
N.bw.R61	8556	459	4597	27	38	71	2.9	94	0.2	17
N.bw.R62	7298	1683	5852	38	27	69	5.8	164	0.1	9.4
N.bw.R72	9407	2238	9358	24	23	188	2.7	118	0	11.1
B.bw.1740.1	9725	3070	18225	106	52	123	2.3	316	0	9.6
B.bw.1750.1	8139	3969	18614	204	49	187	115	559	0	12.1
B.bw.1750.2	7654	2302	10252	28	122	86	4.7	245	0	6.3
B.NC.bw.1750.1	8113	2091	12259	87	42	95	54.9	319	0	13.5
B.NC.bw.1750.2	7421	2296	11762	141	38	86	66	358	0	12
B.NC.bw.1750.3	9217	4734	26102	102	35	178	39.7	686	0	9.3
B.NC.bw.1750.4a	9653	2172	13682	59	46	78	4.2	438	0	11.4
B.NC.bw.1750.4b	7788	1767	13400	51	47	116	22.6	282	0.1	11.1
B.NC.bw.1750.5	9228	3237	18034	234	36	112	170.2	404	0	8
B.NC.bw.1750.6a	6984	1001	6394	41	38	45	3.9	221	0	12
B.NC.bw.1750.6b	7450	2067	11431	40	27	35	43.8	339	0	11.9
B.bw.1780.6	6984	2319	12131	242	75	80	119.3	545	0	8.2
N.bw.R16	4846	1158	10915	154	43	55	1.4	142	0	9.9
N.bw.R25	5233	1591	4104	23	25	74	4.7	211	0	11.6
N.bw.R56	9997	5237	31631	117	35	138	77.6	1125	0.1	11.3
N.bw.R58	8907	3696	22541	123	24	134	4.2	295	0	16
N.bw.R65	8535	1807	11246	18	16	84	4.6	166	0	12.5
N.bw.R4	7832	670	3638	10	39	35	1.6	103	0	11.6
N.bw.R39	7824	5399	12460	65	21	131	2.2	360	0	12
N.bw.R66	10213	6710	36041	331	47	192	32.8	1111	0	9.4
B.bw.1800.6	9929	2291	10674	63	100	94	3.1	188	0	12.4
B.bw.1830.1	9669	5426	19872	36	78	105	3.8	240	0	13.3
B.bw.1830.2	8954	3236	13708	16	75	72	2.2	231	0	11.1
B.bw.1830.3	7062	1572	6324	12	97	61	2	206	0	9.5
B.bw.1830.4	6559	3860	17031	28	98	49	3.1	218	0	13.2
B.bw.1850.1	9608	4799	17495	45	152	143	7.2	214	0	8.8
N.bw.R27	5620	2546	8396	170	26	123	436.8	115	0	7.2
N.bw.R36	7616	7192	24673	325	38	361	3	412	0.3	13.9
N.bw.R37	7089	3894	18134	73	50	83	2.3	277	0	10.5
N.bw.R63	6745	5123	23434	364	52	90	105.9	269	0.1	12.2
N.bw.R68	8238	8393	32481	303	29	178	6.7	679	0	8
B.bw.1890.1	4909	2062	9872	9	67	48	14.3	135	0.1	9.5

QING Group 'B'

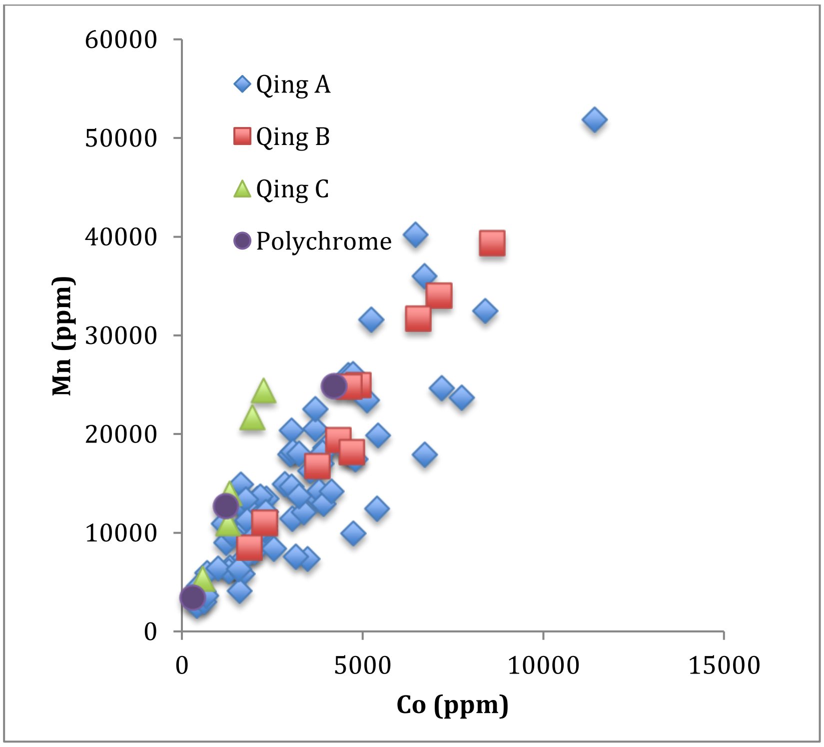
B.bw.1780.1a	6558	2294	10990	50	35	43	2.7	257	0	9
B.bw.1780.1b	4625	1872	8482	38	33	33	5.4	180	0	9.5
B.bw.1780.2a	8764	4885	24927	68	54	212	8	399	0	8.9
B.bw.1780.2b	11847	8600	39344	151	73	203	23.5	524	0	8.9
B.bw.1780.3	7502	3750	16747	147	37	37	166.2	285	0	9.4
B.bw.1780.4	9187	7114	34018	108	44	41	19.4	444	0	8.2
B.bw.1780.5	6345	4328	19388	92	55	55	7.4	366	0	8.1
N.bw.R44	9266	6544	31702	984	140	195	998.8	673	0	11.8
N.bw.R71	4920	4703	18145	210	48	54	2.3	322	0	8.5
N.bw.R70	6158	4626	24806	59	32	70	19.8	561	0	14.7
QING Group 'C'										
B.bw.1800.1	7921	1950	21738	139	34	83	30.1	1634	0	3.5
B.bw.1800.2	8001	2256	24454	184	87	95	2	1541	0	3.9
B.bw.1800.3	7645	1320	14007	13	11	83	0.8	1239	0	4.7
B.bw.1800.4	3838	1272	10961	26	10	19	1.7	1216	0	2.2
B.bw.1800.5	3803	572	5345	15	12	26	0.5	1025	0	1.9
underglaze on polychrome										
V&A.ub.C.176-1934	8184	4214	24859	180	22	45	5.8	233	0	6.5
V&A.ub.C.925-1921	5290	301	3407	15	55	42	0.9	89	0	11.2
B.ub.1720.1	10578	1220	12701	537	76	51	1.6	212	0.1	10.9

Table 5: LA-ICPMS analyses of blue enamels on *famille verte* and *famille rose* porcelains

Sample	Reign	Date	Fe	Co	Mn	Ni	Cu	Zn	As	Ba	Bi	U
B.fv.1700.1	Kangxi	1700	4614	3665	1142	537	499	88	9806	71	1258	25
V&A.fv.1385-1902	Kangxi	1662-1722	3744	2283	5895	272	683	149	1848	136	364	12.4
B.fr.1730.4	Yongzheng	1730	6996	6519	1277	2397	328	1960	19847	8390	2729	106.1
B.fr.1730.6	Yongzheng	1730	6979	4519	285	1662	429	2056	16340	3441	2012	179.6
B.fr.1730.8	Yongzheng	1730	7741	4406	2611	1448	2074	1089	16162	956	2418	113.4
B.fr.1730.9	Yongzheng	1730	4736	5275	2779	1716	1805	1714	20882	3725	2196	125.3
B.fr.1740.1	Qianlong	1740	8844	8574	553	1736	357	1450	26158	5126	3505	51.3
B.fr.1750.2	Qianlong	1750	3827	4886	405	1573	228	1208	11496	1223	3574	88.4
B.fr.1750.3	Qianlong	1750	5405	5136	2673	1985	824	855	14613	313	11182	60.6
B.fr.1770.1	Qianlong	1770	7602	4164	181	5883	529	184	12737	38	485	124.2
B.fr.1770.3	Qianlong	1770	5620	4403	337	2157	305	846	8362	10741	993	93.1
B.fr.1800.1	Jiaqing	1800	7411	5360	2329	1407	668	687	16012	829	1871	28.8
B.fr.1850.1	Daoguang	1850	4099	13396	126	644	5613	450	22802	74	2073	3.9
B.fr.1850.2	Daoguang	1850	2980	7516	271	490	293	138	18744	51	485	4.6
B.fr.1850.3	Daoguang	1850	3671	2974	85	295	14785	371	15961	27	325	1.5
B.fr.1850.4	Daoguang	1850	3792	5379	178	542	9482	1624	15713	136	1140	6.5
B.fr.1870.1	Tongzhi	1870	4849	20999	238	758	7567	583	33475	120	1533	5.1

For the underglaze blue and white (Table 4), the main colouring element was, as expected, cobalt with an average of around 3300ppm Co. The blue and white underglaze blues have relatively low levels of iron (averaging 7650ppm Fe), raised levels of manganese, averaging 15,500ppm Mn, and there is a clear correlation between the cobalt and manganese (Figure 1) and with zinc (Figure 2). These exceptionally high manganese contents render the contribution of manganese from the glaze (discussed above) as insignificant. There may also be correlations with barium (with some high barium outliers) and nickel, which is also elevated compared to the white glaze, but they are not as strong. The cobalt pigment from the Qing blue and whites looks very consistent, although it is interesting that the Co/Mn ratio in the Qing C group is distinct from the others, being relatively richer in manganese, perhaps reflecting a slightly different source (see Figure 1 where the Co/Mn correlation is much steeper).

Figure 1: Plot of manganese against cobalt for underglaze blue painted areas on Qing blue and white Chinese porcelains and underglaze blues in polychrome wares



In contrast, there are two clear groups within the polychrome wares. Three of the analyses in Table 4 are underglaze blue from polychrome vessels (and plotted on Figure 1 and Figure 2 with the other underglaze blues). They are in many ways similar in composition to the underglaze blues of the blue and white (although one is higher in nickel). However the blue overglaze enamels on the polychrome wares are very distinct (Table 5). They are low in manganese, only 1240ppm Mn on average, even though the cobalt concentrations are about twice those of the blue and white at 6300ppm. They are also higher in nickel (Figure 3) and zinc (Figure 4) and much higher in arsenic, bismuth and uranium (Figure 4 and Figure 5).. While this overglaze cobalt pigment is very variable, there is some separation between the enamels analysed according to date, with nineteenth century enamels having lower concentrations of other elements such as Ni and U relative to cobalt (Fig.6).

Figure 2: Plot of zinc against cobalt for blue glazes on Qing, blue and white Chinese porcelains and underglaze blues in polychrome wares

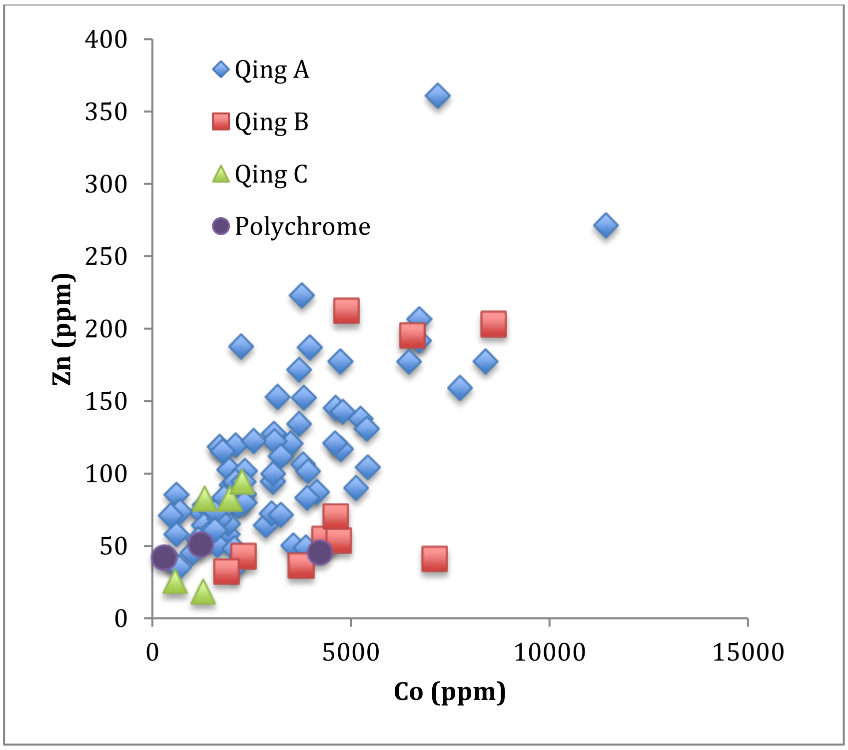


Figure 3: Plot of nickel against cobalt for blue enamels and underglazes of the polychrome wares

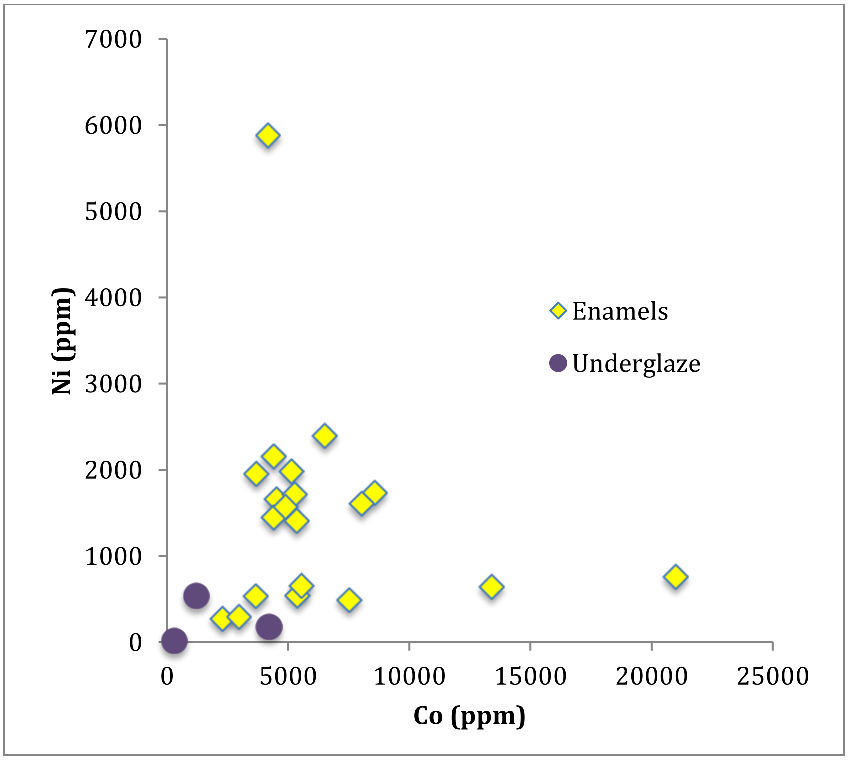


Figure 4: Plot of arsenic against zinc for blue enamels and underglazes of the polychrome wares

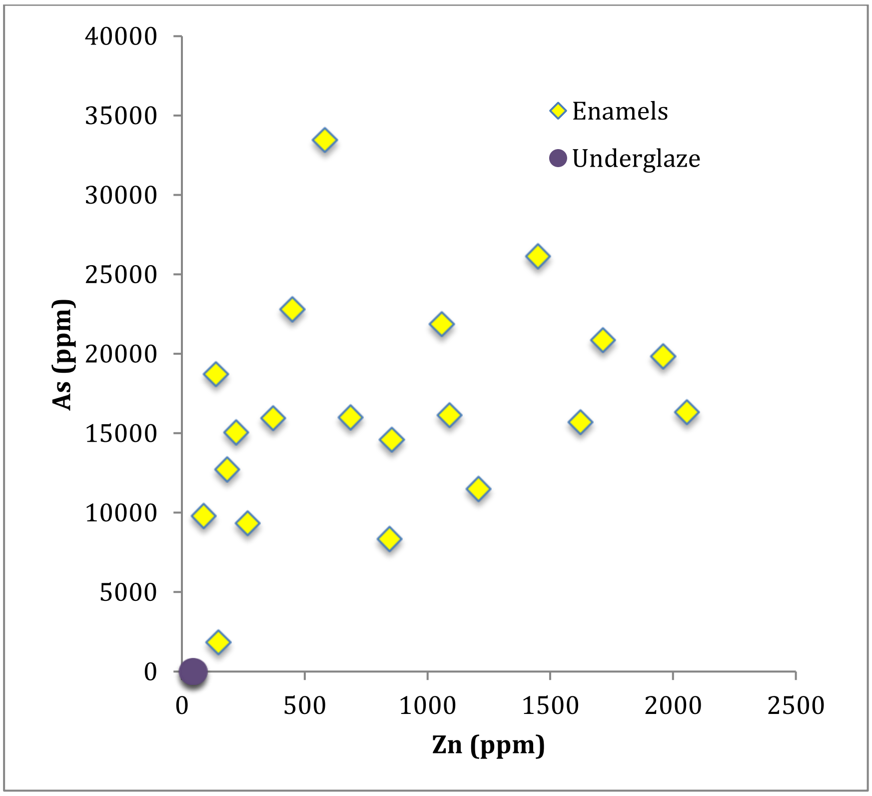


Figure 5: Plot of uranium against bismuth for blue enamels and underglazes of the polychrome wares

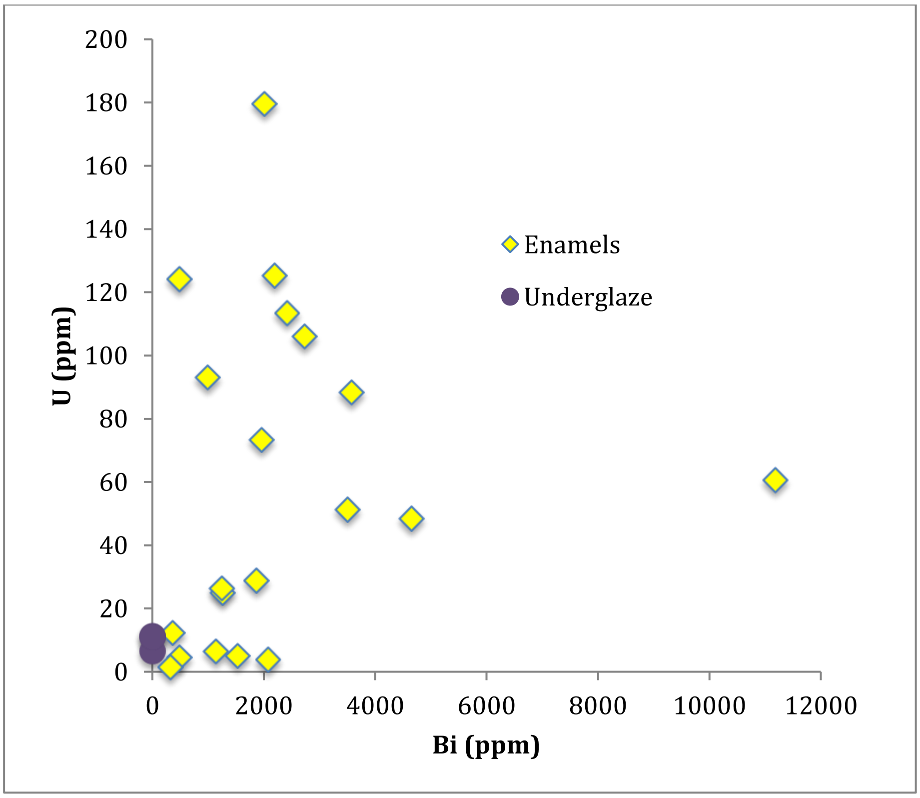
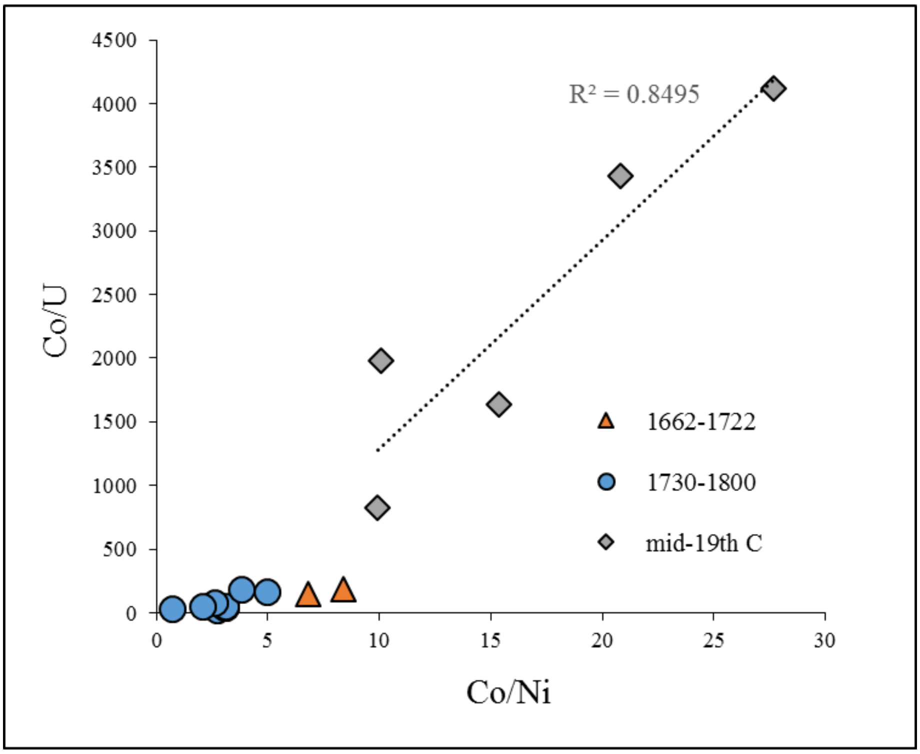


Figure 6: Ratios of cobalt to uranium and nickel in blue enamels according to date



4 Discussion

All the analysed underglaze blue decorations of the Qing dynasty samples (Qing A-C) showed Mn/Co ratios that indicated the use of high Mn-cobalt pigments of the pyrolusite or "wad" type and C. However, there are some subtle differences between them. While Qing A and B groups have similar Mn/Co ratios (average of 5.1±1.7 and 4.7±0.4 respectively, Qing C is distinctly lower in Co, with a Mn/Co ratio of 10.1±1.1. Qing C is also lower in Ni, Cu and much lower in As, but significantly higher in Ba. There is the suggestion that the Qing B group might be bimodal with respect to Zinc (see Figure 2), three analyses having a Zn content of around 200ppm, whereas the rest are only about 50 ppm. Although there are small variations, it seems reasonable to conclude that Qing A and B are perhaps from one Co source, whereas Qing C, while still of the high Mn pyrolusite type, may be from a different source. The results agree with analyses of blue glazes of both folk and imperial porcelain (recovered from the provinces of Jiangxi, Yunnan, Fujian, as well as from Hong Kong and spanning from the late Ming period until the end of the Qing dynasty), which revealed Mn/Co ratios mostly ranging between 4 and 8 (although the iron is at the lower end of those reported in previous analyses) (Yap & Tang 1984; Yu & Miao 1997; Yu & Miao 1996; Yu & Miao 1998; Cheng et al. 2004; Wen et al. 2007, Wen and Pollard 2016; Zhu et al 2016) . Nickel and zinc were the main pigment impurities. In terms of possible cobalt sources used for the underglazes, contemporaneous Chinese records stated that, at the time of the Qing dynasty, different cobalt pigments were obtained from the provinces of Zhejiang (e.g. possibly erythrite from the prefectures of Shaoxing and Jinhua, which included various subtypes, such as the *yuanzhi, zhiliao,* and *tianqing*), Yunnan, Jiangxi (Yunzhou and Fengcheng), Guangdong, and Guangxi. The ores from Zhejiang and Yunnan were considered of higher quality, while the Jiangxi cobalt pigment was superior to those of the Guangdong and Guangxi areas (Tichane, 1983, p. 201; Wang et al., 1993). In the early part of the 20th century, it seems that the best blue was the *chu-ming* or *chu-ming-liao* from the province of Yunnan (or the pigment *ti-lo*, which was rated even above the *chu-ming* blue).

The cobalt pigment used in the dark-blue enamels is completely different. While it is quite variable, it is low in manganese (all but one is <3000ppm), ten times higher on average in nickel and eight times higher in zinc. The average arsenic values are very high, in excess of 16,000ppm As. While the bismuth in the underglaze samples never exceeds 1ppm and is often not detected, in the enamels it averages 2,300ppm. The uranium is also very different being significantly lower, only 10ppm on average compared to 60ppm in the enamels. It is clear that the enamels have a very different cobalt source to the proposed local source used in the underglaze blue on both the blue and white and the polychrome wares. No other examples of cobalt with this characteristic type of composition have been recorded in Chinese ceramics, although high nickel cobalt has been reported in Chinese Qing dynasty Jingdezhen enamel-type glazes (Wood et al 2002).

Gratuze (Gratuze, 2013 see especially Table 5.1.4) has a useful table based on and extension of his previous work (Gratuze et al., 1996, e.g. 1995) which lists nine groups of cobalt pigment groups used from the Middle Bronze Age to the nineteenth century AD in the West. Group 8 is listed as Co-As-Ni-Bi-W-Mo-U-Fe and is sourced to Erzgebirge in Germany. The source appears to be used as early as 1400BC, and widely from the sixteenth century to eighteenth centuries AD and has been found in French glass (Soulier et al., 1996) and *della Robbia* glazed ceramics (Zucchiatti et al., 2006) amongst others. Of particular pertinence is its association with the production of eighteenth century English porcelain (Middleton and Cowell, 1993). It is one of the most important cobalt sources of the period and has a high arsenic, nickel and bismuth composition, with elevated uranium, very similar to that observed in the blue enamels of the *famille rose* porcelain. While it is not possible to fully exclude other possibilities on compositional grounds alone (for example Co-As-Ni ores occur in Iran and in some regions of China), the specific elemental signature observed here, notably the high Bi and U, appears to have been associated only with early modern European cobalt to date and this coupled with the chronological coincidence in its use, and the use of a different underglaze cobalt in China, strongly argue that the cobalt pigment used in the Chinese enamels was imported from Europe.

This identification of Saxon cobalt on eighteenth century Chinese porcelain is consistent with the evidence uncovered by Watney (1973:1, footnote 6), who reported documentary evidence dating to 1778 and 1795 that the East India Company was exporting “smalts” to China from London, and which indicate that this trade was on such a scale that at least in 1795 this resulted in a shortage of material of the desired quality for porcelain manufacture in England. In fact, the data of the present study suggest that the export of cobalt from Europe to China for use in porcelain production continued throughout most of the eighteenth and into the nineteenth centuries. It is not clear if London was the only point of departure for Saxon cobalt. However, prodigious quantities of cobalt from continental Europe were imported into Britain for use not only in ceramics and glass, but also as a whitener in textile production. Watney (1973) notes that 286,739 pounds weight of smalt was imported into England in 1754. Re-export of a proportion of this material by the East India Company would have been logistically straightforward.

The compositional groupings within the Ni- and As- cobalts used in the enamels may reflect changes in production method (fig. 6). The strong correlation observed in the nineteenth century enamels may reflect the introduction of new practices to refine the ore (Copeland, 1980, pp. 162–3) and/or the sale of Saxon cobalt according to grade, i.e. the impurity content (Taylor 1977). However, it is noted that ceramic producers in nineteenth century Britain, for example at the Spode factory, favoured cobalt from Sweden, rather than Saxony (Copeland 1980) and it is possible that a change to cobalt derived from Swedish cobaltite (CoAsS) ores had occurred.

The apparently exclusive use of European cobalt in Chinese overglaze enamels requires explanation, particularly given that native cobalt blue pigment was being used in great abundance in the underglaze decoration of both enamelled and plain blue-and-white wares, so presumably was not in short supply. It seems likely that this was because the cobalt used in the overglaze enamels was in solution in the glass, rather than a crystalline pigment. The properties required of cobalt pigment are very different in enamel and underglaze decoration. In order to produce detailed decoration in underglaze blue it was necessary to immobilise the pigment under the glaze, so that sharp lines did not "bleed" and this had been mastered centuries before, using either an iron-rich imported cobalt pigment or, from as early as the Hogwe Period (late 14th century) and abundantly later in the Ming Dynasty, native manganese-rich Chinese cobalt, which can also be relatively high in cobalt (Wen et al 2007, Wen and Pollard 2016). Stable underglaze painting would have been easier to achieve with cobalt applied in a crystalline form rather than as a glass. The development of a good enamel, with a pure blue colour and without discolouration would have been a very different problem. Overglaze enamels fluxed by lead, as are all of the Qing enamels (Kingery and Vandiver 1986) require firing in an oxidising kiln, otherwise the lead will tend to precipitate as metal or sulphide and blacken the glaze. Under such conditions the manganese in cobalt derived from Chinese asbolane-type ores would have tended to oxidise to give a counteracting purple colouration and a less pure blue, and the reddish tinge of Chinese cobalt blue is noted specialists such as Bushell (1896; 1981 edition p. 267). Indeed, this oxidisation of manganese is evidenced by the frequent use of manganese purple enamel in the *famille rose* palette. Saxon cobalt did not have this problem as the cobalt source was relatively low in Mn. Furthermore, the exported product was primarily in the form of "smalt" – a pre-prepared cobalt-bearing silicate glass fluxed with about 15% K_2O which was widely used in frescoes and oil painting from the fifteenth century on (for analyses, see e.g. Ciliberto et al., 1994; Spring et al., 2005). In Europe, smalt was distinguished from "zaffre", the cobalt oxide pigment typically used in underglaze painting on ceramics. It seems likely that

Chinese potters, who had mastered the production of a suitable underglaze pigment, had difficulty developing the desirable shade of blue enamel using locally available materials, so chose to use smalt from Saxony, which was the dominant cobalt in the European market. Interestingly, particles of European smalt have been identified in Qing Dynasty lacquer by Julie Chang (pers. comm.), confirming that this form of cobalt was being imported into China.

A potentially important finding is the identification of Saxon cobalt in the two examples of *famille verte* enamel with overglaze blue painting, which appear to date to the period of the Kangxi emperor (1662-1722; Table 5: B.fv.1700.1 and V&A. fv.1385-1902). This is in the period in which the *famille rose* palette was developed in Beijing, before production had been taken up at Jingdezhen. In his second letter (1722) from Jingdezhen, Pere d'Entrecolles suggested that there was an opportunity to supply a good European cobalt into China (e.g. Burton, 1906, p. 121). The present analyses indicate, however, that this was already happening. It is quite possible that the traded cobalt was not reaching Jingdezhen, as it is known that some enamelling on ceramic was carried out in Beijing, and some in Canton, where there was an established industry of cloisonné enamelling on copper. Alternatively d'Entrecolles may have been unaware of the use of imported cobalt at Jingdezhen, in spite of the detailed report on craft practices that he provides. He indicates that Jingdezhen was said to have had a million inhabitants and three thousand furnaces, and it is unlikely that the full range of practices are represented in the letters. As reported by Kingery and Vandiver (1986) and also observed here, the blue enamel on *famille verte* has higher potash than the other colours, fully consistent with the use of potash-rich smalt as the colourant. However, it should also be noted that high potassium levels were a common characteristic of Chinese cloisonné enamels since the 15th century (Biron and Quette 1997, 35-40). It is possible therefore that relatively high potassium contents represent a Qing technology for producing glazes, so a combination of this and the smalt could be the reason for the higher potassium contents.

These findings also point to a clearer understanding of the use of the term "foreign colours" to describe the *famille rose* palette. The official list of patterns produced in Jingdezhen in the Yongzhen period (1723-35) refers to "foreign colours" or "foreign decoration" six times in a total of fifty-eight entries (Bushell, 1896; Hobson, 1948, p. 97). The meaning of this term has been unclear – was it due to the use of such a palette on European enamelled wares, was the colour technology based upon European practice, or were the enamels themselves imported? Attention has focused particularly upon the introduction of the gold pink enamel, as the use of gold-based reds and pinks became common in European glass and glaze at around the end of the seventeenth century, following the discovery by the German chemist Johann Kunckel that a finely divided precipitate of gold nanoparticles could be precipitated by tin to yield "Purple of Cassius" (Hunt 1976 for a detailed discussion). The discussion of the development of the *famille rose* palette has in particular focussed upon the use of colloidal gold pink and whether or not the pigment or the technology was directly imported from Europe but the evidence has been considered ambiguous (Kerr and Wood, 2004; Kingery and Vandiver, 1986) (Mills and Kerr 1999). In fact, the present study shows that the apparently simpler cobalt blue technology provides a direct link with European materials and emphasises a literal element in the use of the term “foreign colours”.

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5 Conclusions

The results of this study indicate that some Chinese cobalt sources of the pyrolusite-rich or wad type, for example Qing C, may be distinguished using compositional analysis. Furthermore it has been shown that the Ni- and Bi-rich pigments of the overglaze enamels of the later nineteenth century (Daoguang and Tongzhi, Table 5, Fig. 6) differ from the Yongzheng and Qianlong examples, suggesting a chronological change in the ore source or pigment processing. These findings have implications for the study of cobalt sources in general, as they indicate that quantitative analysis of the blue areas of blue-and-white glazes may provide information which is not only helpful in distinguishing productions of different ore deposit types, but may also discriminate on the basis of relatively minor variations in the pigment which occur due to production changes. The spatial resolution of LA-ICPMS, its sensitivity to concentrations at the ppm level and the quantification capabilities offer clear advantages over the less sophisticated versions of X-ray fluorescence, although these are obviously valuable in determining broad compositional groups.

This study of the blue pigments used in underglaze and enamelled Chinese porcelain has shown that there are two distinct pigments being used. While both are cobalt coloured, the elements associated with the cobalt are different. The underglaze blue on the blue and white porcelain and the polychrome underglaze blues have Mn/Co ratios that show a high Mn-cobalt pigment was used, with nickel and zinc as the main impurities. This is consistent with local, Chinese sources of cobalt. However, the enamels of the *famille verte* and *famille rose* wares are very different, having low manganese and much higher nickel, arsenic, bismuth and uranium.. This is unlike any cobalt source reported from other Chinese ceramics, but is very similar to a contemporary European source – Erzgebirge in Germany. This was used in European ceramics and glass and textual sources have suggested that it was being imported into China. It is therefore very likely that the source of this pigment is Europe. While it has been suggested (but is unproven) that some of the technologies used in Qing porcelain enamels, for example colloidal pink, might be derived from Europe (Kerr and Wood 2004), this is the first evidence that a pigment itself was transported over large distances. It is possible that the pigment was in the form of smalt, a cobalt glass, which might explain why it was used for enamels, but not for underglaze blues but it is also likely to have provided a better shade of blue.

The blue enamels analysed here were exclusively made using European cobalt, and the trade in this material appears to have lasted throughout the eighteenth and nineteenth centuries. The chain of supply was extensive. Saxon cobalt was incorporated into a potassium silicate glass in Europe, then imported to European trading centres, including London, but possibly others. It was then traded on to Canton. From there it was taken up to Jingdezhen, where it was used to manufacture enamelled porcelain. The porcelain then travelled the reverse route, back to the consumers of Europe. This is an impressive early example of a globalised trading network. However, it is interesting to note that in its general form, if not its extent, it echoes the situation several centuries before, when Persian cobalt was used to decorate the blue and white wares of the Yuan Dynasty, which were then exported across the Islamic world.

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(Cheng et al., 2004; Yap and Tang, 1984; Yu and Miao, 1996, 1998, 1997)