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Phase and compositional analysis of a Sèvres soft paste porcelain plate from 1781, with a review of early porcelain techniques

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Abstract: Optical microscopy, X-ray diffraction, X-ray fluorescence and scanning electron microscopy analyses were carried out on a typical Sèvres soft (frit) porcelain plate from 1781 in order to determine the chemical and mineralogical composition as well as the microstructure of its ceramic body, glaze, overglaze decoration and gilding. The body is rich in SiO_2 (73 mass%), CaO (16) and alkali oxide (8) and shows acicular wollastonite and tridymite crystals embedded in a glassy matrix consisting of SiO_2 (75), K_2O (12) and CaO (9). The 50–90 μm thick, transparent lead glaze (40.9 PbO) contains 47.6 SiO_2, 6.5 K_2O and 3.5 CaO and shows a 35–75 μm thick reaction zone (50 SiO_2, 30 PbO, 14 CaO) towards the body. The maximum thickness of the different paints is 50 μm, with 15 μm as mean thickness of the individual paint stroke. Two blue colours, for the dentil comb and the flower painting, are chemically distinct (colouring CoO in the dental rim 7, in the flower's blue 2 mass%) and contain many As- and Pb-rich globules and dendrites. Pseudohexagonal shaped platelets of Pb–Sb–Sn triple oxide crystals, embedded in a colourless glassy matrix, generate the opacity and the colour of the yellow paints. Opaque olive green colours are created by the combination of such yellow crystals with a bluish, Cu and Co bearing glassy matrix. The opaque red overglaze enamel is a mechanical mix of yellow Pb–Sb oxide crystals with an iron-rich (16 Fe_2O_3) Pb–silica glass. Purple is very homogeneous and shows tiny drops of pure gold (max. diam. 0.5 μm) in a glassy matrix (47 PbO, 46 SiO_2, 5 K_2O). Violet is a mechanical blend of flower's blue and purple. The pure (99.5 Au, 0.5 Fe_2O_3) gilt consists of several folded gold particles. The results of this study are only broadly consistent with the archival documented 18th century technologies. The compositional dissimilarities of the studied enamels suggest that each colour was independently fritted. Consequently, the original colour recipes written down by Hellot in 1753 must have been modified in the 30 years since then.

Key-words: archaeometry; Sèvres; soft paste (frit) porcelain; overglaze enamels; gilding.

1. Introduction

Hard and soft paste porcelains have similar characteristics, such as translucency and whiteness, but different body compositions. The distinction between soft or hard paste porcelain concerns the glaze, which can (soft) or cannot (hard) be scratched with a knife. Hard paste porcelain has a Pb-free glaze, which is fired together with the paste between *ca*. 1280 and *ca*. 1400 °C. The body is rich in alumina due to the high amount (40–60 mass%) of kaolin or china clay in the raw paste. In the fired paste, mullite crystals are to be found. Soft paste porcelain has a lead glaze, which is fired at temperatures around 800–900 °C, much lower than the body (*ca.* 950–1100 °C). The raw paste of the French soft paste porcelain is a blend of a silica (SiO_2) and alkali-rich frit with a white firing marl, without kaolin or China clay. The resulting products are therefore also called frit porcelains. This peculiar technique has its roots in similar technologies of the Near East (Fritwares from Egypt, Mesopotamia and Turkey, *e.g.* Iznik) and the Renaissance "Medici" porcelain (Kingery & Smith, 1985).

1.1. Short history of French soft paste porcelain

Porcelain was first produced in some quantity in France at Saint Cloud near Paris, circa 1690 (Le Duc & de Plinval de Guillebon, 1991). Some rare examples of the same type of porcelain were created in Rouen a few years before, *ca.* 1673 (Soudée Lacombe, 2006). The chemical composition of the first variety porcelain was so well balanced that it permitted a reasonably consistent production without the fear of under or overfired pieces, even in the unpredictable kilns of the period, which had no means of accurately gauging temperature (Rondot, 1999). The production sites of Rouen and Saint-Cloud closed in 1696 and 1766, respectively.

The composition of this porcelain was given, or perhaps smuggled, to a chemist called Sicaire Siroux who established a manufacture at Chantilly north of Paris. Beginning around 1731, tableware cups, vases, and decorative items were produced (Chapu, 1964). The whiteness and the translucent quality of the paste were rather poor compared to *Blancs de Chine* or German

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porcelains of the period, thus initially a white tin glaze was applied to the porcelain. The sources of inspiration were mostly oriental. Only a limited number of overglaze colours were available, including opaque red, yellow and black, and translucent green, blue and brown (Le Duc, 1996). The production at Chantilly closed in 1792. There were many other short-lived soft (frit) porcelain manufactures around and in Paris, such as Mennecy (1737–1773) (see De Plinval de Guillebon, 1994, 1995).

Misreading two letters written in 1712 and 1722 by François Xavier d'Entrecolles (Burton, 1906), a Jesuit missionary who had visited the celebrated porcelain city of Ching-Te-Tcheng, a worker from Chantilly, Claude Humbert Gérin, believed that alum ($KAl(SO_4)_2 \cdot 12H_2O$) described in one of the letters was in fact the famous and mysterious kaolin mentioned elsewhere in Entrecolles's writings. Entrecolles, having no clue whatsoever of the nature of the white material shown by the Chinese, wrote in his letter ka-o-lin. This led to endless discussions in the scientific world of Europe. By introducing this very white material, along with plaster of Paris into the ordinary frit of Chantilly, Gérin managed to produce very white and translucent porcelain in France for the first time (D'Albis, 1984, 1985, 1988). He left Chantilly in 1740 with two companions and created a small workshop in the royal castle of Vincennes, which was taken over in 1741 by the Marquis Orry de Fulvy, who, through wise investments and exacting standards, managed to equal the artistic quality of the Meissen manufacture in Saxony within only 10 years (D'Albis, 1984; Préaud & d'Albis, 1991). The Marquis died in 1751 and, through the discreet influence of the Marquise de Pompadour (Martinet, 1954), the manufacture was nationalized and belonged thereafter to the Kingdom of France. A new and handsome factory on the road to Versailles, called *Manufacture Royale de porcelaine de France*, was constructed in Sèvres in 1756 (Brunet & Préaud, 1978; Préaud & d'Albis, 1991; D'Albis, 2001). Hard porcelain was produced from 1772 onwards, after the discovery of a kaolin deposit near Limoges. Sèvres's frit porcelain production ceased 1804. With unlimited funds and the enlistment and participation of the best scientists and artists, the manufacture was ready to enter into the popular and nationalistic conception of the history of France. A summary of the history of the factory can be found in Dauterman (1986).

2. Production technique of French soft (frit) porcelain colours

2.1. Recipes of the body, glaze and overglaze enamels

The production steps and recipes of Vincennes/Sèvres soft paste porcelain (frit porcelain or *pâte tendre*) were written down in many manuscripts conserved in the archives of the *Manufacture Nationale de Sèvres*, such as the so-called books of Hellot (Bourgeois, 1905; Y 49: “First register of Hellot, compiled in 1753 by Royal order, to keep the recipes and procedures for the biscuit, the cover, the colours and the gilding, according to previous manuscripts, for the Crown”). Jean Hellot (1685–1766) made seminal contributions to the development of the ceramic, chemical, metallurgical and textile industry in France and beyond (Grandjean de Fouchy, 1769; Doru, 1975–1977; Wisniak, 2009). He was appointed in June 1751 to get hold of the secrets of the production which were, until then, scattered in different hands. This appropriation was the condition of the nationalization that took effect shortly after. Summaries of these manuscripts have been published (Brongniart, 1844; Salvétat, 1857; D'Albis, 1984, 1985, 1999; Préaud & d'Albis, 1991).

2.2. Production steps

2.2.1. Historical aspects

“Produire des porcelaines façon Saxe, c'est a dire peintes et dorées à figures humaine”. With this rather ambiguous phrasing, a Royal privilege was granted in 1745 to the manufacture of Vincennes. Translated literally, it means: “The factory of Vincennes is permitted [excluding all others in the Kingdom of France!] to produce porcelain in the manner of Saxony, which is to say, decorated and gilded with human figures”. It has been generally accepted that *Manner of Saxony* and *Human figures* may be understood as: painted and decorated with a rich palette of 30 to 50 opaque, semi-opaque, and translucent colours, as well as gilding, to produce landscapes, miniatures and scenes of all sorts. This is how porcelain had been decorated at Meissen since 1725–30, and the style was highly praised across Europe. However, in 1745, the manufacture of Vincennes was far from achieving the aim of imitating the Meissen decorative style. The secret, for instance, of gilding would not be discovered before autumn 1748. Nevertheless, since 1741, thanks to the Marquis Orry de Fulvy, who was willing to pay significant sums to reach his goals, *i.e.*, to equalize the quality of the Meissen porcelain, Vincennes made considerable progress towards catching up with the German manufacture. In 1745, he bought the secret of the production of three rare and precious colours of remarkable quality – pink, purple and violet, from Pierre Henri Antoine Taunay, a painter and enameller. These Vincennes colours were made with ruby-red glass rather than the purple of Cassius used in Germany, but the results were comparable (Brongniart, 1802; D'Albis, 1994).

Another gifted painter of Vincennes, Jean Mathias Caillat, had been successful in creating other colours similar to those used in Germany. By 1749–1750, Orry de Fulvy could claim that he had reached his goal. In 1752 Vincennes's colour palette had a hundred of different hues. Thus, the privilege of 1745 had finally been deservedly accorded and Meissen pieces could now be copied in the soft paste porcelain at Vincennes. Some rare pieces were marked with the two crossed swords of the Saxon manufacture, probably to convince investors to financially participate and support his company (Gwilt, 2014). Following the death of Orry de Fulvy in April 1751, progress continued, this time, with ground colours.

In 1753, a service with a turquoise ground colour called *bleu céleste* was produced for Louis XV. In the same year, the manufacture developed a rare and vivid cobalt blue underglaze called *bleu lapis,* which proved a great success. These rare ground colours could not be used on hard porcelain because their rate of thermal expansion was too low to accept them. They contributed greatly to the reputation of Vincennes/Sèvres, who, from then on inspired other porcelain factories, rather than imitating them.

2.2.2. *Technical aspects*

The following is taken from D'Albis' (1982) detailed account of the technology of Vincennes soft-paste porcelain. The body and the glaze contain a fair amount of alkaline oxide conferring high expansion coefficients. Very rare colours, called *alkaline colours*, such as luminous translucent turquoise and brilliant greens or blues could, henceforth, be used as ground colours. These have a strong tendency to devitrify during the firing process, especially at the high temperatures required for firing the decoration. However, these qualities were also a distinct advantage because they permitted the use of rare colours that other manufactures could only dream of. The introduction of a remarkable kiln constructed by Claude Humbert Gérin in 1748, gave the ceramists the rare ability to avoid devitrification during the firing process (Préaud & d'Albis, 1991; D'Albis, 2015b). It was a tunnel-shaped kiln, in which the pieces were suspended from metal hooks so that each piece of porcelain could achieve a perfect thermal exchange according to its size and weight. This method resulted in a faster firing time (only 1 h), which thus avoided firing cracks caused by thermal stress.

Enamels are Pb-based glassy powders, coloured or colourless, painted over the fired glaze. They melt during the subsequent firing and adhere to the underlying glaze. The overglaze enamels were made at the Vincennes/Sévres factory with the same flux, the so-called fondant universel, of Mathias Caillat's invention, with two exceptions: purple and iron red. This flux, compatible with the complete palette of colours he created, is a glass with a low melting temperature, contained 2 ounces 2 gros sand from Etampes (fired at high temperatures, washed and dried) + 1 ounce of tartrate (transformed into potassium cabonate when fired, probably very impure) + 4 ounces minimum (Préaud & d'Albis, 1991). The weight is 30.5941 g for one French ancient ounce, and 3.824 g for one French ancient gros (Lescan, 1803). The flux was melted in refractory crucibles, cooled and the glassy product crushed and ground into a fine powder. Basic colours were made blending this flux with different pigments. Many of these colours were calcined so that the crude powder had approximately the same tinge as the fired colour.

Enamel colours were less watersoluble than the ground colours. Consequently, they were mixed with gum arabic dissolved in water. Turpentine oil could not be used on hard porcelain because it contained too much carbon which could result in black spots, if it had not been fully burnt off before the glaze reached its semi-liquid state during firing. The decoration commenced by way of a first rough sketch, drawn with painted purple colours, which was then carefully dried and fired. The result was a very pale outline. The painter then added a second layer, which was again fired. This process was repeated until all the colours had reached the right intensity. The last firing was intended for the iron red colours. But this was not the case for the studied plate where red was laid down (and fired) first (Trittschack *et al.*, 2015).

The mainly alkaline ground colours were, as a fine powder, partially soluble in water. Consequently, they were difficult if not impossible to paint. In the porcelain manufacture of Vincennes, a process was invented around 1751–53 to apply an even layer of glue, called “mordant” onto the ready-fired glaze. This mordant was made with turpentine spirit mixed with mummia (a type of resin from Persia, later made from Egyptian mummies). Thereafter, the dry powdered colour was applied evenly onto the adhesive layer with the help of a silk or horsehair sieve. The piece was then fired. A second layer of mordant was applied followed by a second layer of colour and then fired again. This process was repeated until the colour reached the correct tone.

Gilding hard porcelain was much easier than soft (frit) porcelain (D'Albis, 2003). Gold precipitate could be used on hard porcelain, though it was not suitable for the glaze used on soft (frit) porcelain which contained a high amount of Pb and K oxide and tended to dissolve the tiny particles of gold. Gold precipitate used on soft (frit) porcelain is absorbed into the glaze during firing, and disappears. By the 18th century, European chemists had already discovered how to turn soft and malleable gold into powder by dissolving the metal with a mixture of hydrochloric and nitric acid. The yellow liquid obtained was then treated with an Fe-sulphate solution to become a very fine powder. The grain size was small and mixing this gold with flux powder produced an oily medium, which was easy to manipulate, even when painting delicate motifs. The Meissen factory had mastered this technique by 1719–1720 (Hunt, 1979). It took the manufacture of Vincennes nearly eight years of desperate research to achieve the same result with soft (frit) gilding. Finally, in 1748 a monk called Hippolyte sold his technique to the Marquis de Fulvy for the extraordinary sum of 3000 livres (£) and an annual pension of six hundred £ during 10 years (Préaud & d'Albis, 1991). With a “Livre”, one could buy at that time 3 kg of bread, 1 kg of sea salt, a tin or a simple faïence or porcelain plate made in China. A porcelain plate made in Meissen decorated with simple flowers would cost 14 £, the salary of a fair painter in Sèvres would reach 80–90 £ a month, and renting a furnished house in Paris 600 £ a year. Instead of precipitating gold, he crushed gold leaves with a pestle on a glass plate, using a solution of gum arabic as a binding medium. After 9 or 10 h of work he could obtain 60 g of small, spherical grains whose size was larger than that of precipitated gold. These grains proved far more

Table 1. Recipe compositions (in mass%) of frit, paste and glaze from frit porcelain of Vincennes-Sèvres (*ca*. 1742–1803) according to d'Albis (1985, 1999).

Frit		Paste		Glaze	
Sand	60.0	Frit	75.0	Litharge	38.5
Alicante soda	3.7	Chalk	16.7	Sand	28.8
Alum calcined	3.7	Marl	8.3	Flint calcined	9.6
Gypsum, calcined	3.7			Potash	12.8
Saltpetre	21.7			Soda	10.3
Sea salt	7.2				
Total	100.0	Total	100.0	Total	100.0

resistant to the aggressive glaze of the soft (frit) porcelain, and this method was used until the discontinuation of this porcelain type at Sèvres in 1804. Gilding was the final process of decoration. Again, the adhesive used was a “mordant”. This time it was made with boiling garlic, onion and vinegar, and collecting the vapours in a glass vessel. This sticky and oily liquid was mixed with a solution of gum Arabic and the gold powder in a mussel-shell (Salvétat, 1857). The gilder could paint freely with this mixture. He sometimes had to add a second layer of gold after firing in order to completely cover the ground colour. After firing, which was the last one and at the lowest temperature, the gold was polished with agate or hematite tools. In many cases, the gold was enhanced with engraved motifs, to provide liveliness, especially by candlelight.

2.2.3. The “Chaîne opératoire” at Vincennes/Sèvres

Following traditional French faïence techniques, a frit was made with the recipe's ingredients as shown in Table 1. These finely milled and mixed materials were laid out on a sand-bed at the hottest part, *i.e*., in the firebox under the hearth of the kiln, and kept there for 30–35 h. A modern description of this kiln is given by Pinto (2014, 2015). After cooling, the frit was reduced to a fine powder and milled together with “Argenteuil white marl” and “Spanish white chalk (Blanc d'Espagne)”. To improve the workability of the paste for figurines and moulded pieces such as dishes and plates, about 6 mass% of an organic binder, the so-called chymie, was added. The finished and dried piece was then stacked in saggars and fired under oxidizing conditions at temperatures of 950–1100 °C. The resulting object is indeed a true *biscuit* (twice fired – first the frit, then the object). Its rough surface had to be polished with abrasive sandstone in order to avoid glaze flaws. The raw Pb-alkali glaze, a mix of finely powdered and blended ingredients (Table 1), fritted in crucibles beneath the kiln and milled again, was dispersed in a mixture of water and vinegar, and applied to the biscuit. The latter was then fired at temperatures around 800–900 °C. It may be recalled that the second (glaze) firing of European hard porcelain occurs at higher temperatures (*ca*. 1350–1400 °C) compared to those of the first firing of their dried green bodies (*ca*. 900–950 °C).

3. Previous archaeometric analyses and goals of this study

An overview of the frit porcelain archaeometrical analyses is given in chapter 14 of Heimann & Maggetti (2014). Chemical compositions of Chantilly, Mennecy, Saint-Amand, Saint-Cloud, Sèvres and Vincennes frit porcelains were published by Brongniart (1844), Salvétat (1857), d'Albis (1985), Kingery & Smith (1985), Kingery & Vandiver (1986), and Treppoz & d'Albis (1987). As shown in Table 2, Vincennes/Sèvres bodies have high silica (73–79 mass%), low alumina (Al_2O_3, 2–3 mass%), as well as, high lime (CaO, 13–16 mass%) and alkali oxide (5–8 mass%). The Sèvres analysis given by Kingery & Smith (1985) has a low total of only 95.98 mass%. X-ray studies showed tridymite and wollastonite in the Chantilly, Saint-Cloud and Vincennes/Sèvres bodies (Treppoz & d'Albis, 1987). Raman spectroscopy identified β-wollastonite and α-quartz, but no tridymite, a phase difficult to detect as its Raman spectrum is very low in intensity (Colomban *et al.*, 2004). For Chantilly's frit porcelain, β-wollastonite, α-quartz and cristobalite were recorded (Colomban & Treppoz, 2001). Bodies from Vincennes contain β-wollastonite with traces of α-quartz and cristobalite, and bodies from Sèvres contain β-wollastonite with traces of feldspar (Colomban *et al.*, 2004). Frit porcelains from Sceaux show β-wollastonite too (Mancini *et al.,* 2016). Microstructural images of Sèvres and Vincennes bodies were interpreted by Kingery & Smith (1985) as consisting of “ . . . quartz, which has largely transformed into cristobalite/tridymite together with fine wollastonite crystals and a liquid glass phase.” The microstructure of an unglazed figurine from Vincennes consists of *ca.* 15% cristobalite + 30% wollastonite + 55% glass (Kingery & Vandiver, 1986; unfortunately, these authors did not specify the percentage type). Electron microprobe analyses of glazes from Chantilly, Mennecy, Saint-Cloud and Vincennes/Sèvres were published by Kingery & Smith (1985) and by d'Albis (1985), see Table 2. Colomban *et al.* (2004) studied the pigments of the black, blue, brown, green, rose and yellow enamel colours of Chantilly and Mennecy, and Mancini *et al.* (2016) the blue and yellow pigments of Sceaux with Raman (micro) spectroscopy.

Table 2. Chemical analyses of Vincennes and Sèvres bodies. Oxides and LOI in mass%, elements in ppm. (1a–1e) = Sèvres (Salvétat, 1857), (*) = Total Alc.; (2) = Sèvres (D'Albis, 1985; Treppoz & d'Albis, 1987); (3) Vincennes and (4) Sèvres (Kingery & Smith, 1985; Kingery, 1986. Electron microprobe analyses, Fe as FeO).

Oxide/Element	(1a)	(1b)	(1c)	(1d)	(1e)	(2) Min.–Max.	(3) c. 1750	(4) >1750	This work XRF
SiO_2	73.39	74.44	74.90	79.51	77.03	73.0–75.0	72.84	74.25	72.68
TiO_2						0–0.14	0.10	0.07	0.04
Al_2O_3	3.06	2.15	2.01	1.01	1.20	2.5–2.6	2.11	2.23	1.34
Fe_2O_3/FeO		0.97	1.00			0.5–0.6	0.30	0.29	0.24
MnO								0.78	0.01
MgO						0–0.7	0.83		0.89
CaO	15.29	15.44	15.87	12.92	16.37	14.7–16.3	15.69	15.68	15.82
Na_2O	8.26*	7.00*	6.22*	6.56*	5.40*	1.7–1.7	2.66	2.15	3.25
K_2O						3.7–4.0	4.32	0.30	5.17
P_2O_5									0.06
SnO_2						0–0.04	0.06	0.05	
PbO						0–0.09	0.20	0.18	
SO_3									
Ba									117
Cr									5
Cu									26
Nb									<2
Ni									7
Pb									4476
Rb									80
Sr									239
Y									<1
Zn									10
Zr									31
Total	100.00	100.00	100.00	100.00	100.00		99.11	95.98	99.99
LOI	2.00	0.50	0.54	0.54	0.54				0.44

In a previous paper, optical microscopy was employed to study the succession of the overglaze paints on a Sèvres frit porcelain plate (Trittschack *et al.*, 2015). The present study characterizes the body, the glaze, the opaque and transparent overglaze enamels and the gold decoration by polarizing microscopy, scanning electron microscopy (SEM), X-ray diffractometry (XRD) and X-ray fluorescence (XRF).

4. Experimental procedure

4.1. Study object

As no archaeological excavations have been undertaken on the site of the Sèvres manufacture, one must rely on pieces from private or public collections. Curators are understandably very reluctant to permit sampling of intact (or even broken) objects of highly valued 18th century frit porcelains. A poorly restored plate from the private collection of one of us (A. d'A.) was available for Trittschack *et al.* (2015) and the present study (Fig. 1). From 1753 until 1793, the two crossed letters *L* (Fig. 1a) bear single letters or combinations of letters dating the decoration (Brunet, 1953; Brunet & Préaud, 1978). The enclosed letters *dd* stand for the decoration year 1781, P 7 or P J below the crossed *L*s (Fig. 1a) is the mark of the painter Pierre le Jeune (active 1763/1768–1798/1800; Dauterman, 1986; Eriksen & de Bellaigue, 1987; Préaud & d'Albis, 1991; Sassoon, 1991) or his wife Anne Victoire Pierre (1777–1782/1794), and the Greek letter ∂ between two dots is the signature of an unidentified artist who painted the dark blue dentil pattern during the years 1779–1781. The plate is decorated with sprays of coloured flowers (Fig. 1b and c). Such overglaze (onglaze) floral decorations are known in France as *décor en bouquets détachés* (D'Albis, 2015a). The rim is painted with a dentil circular comb in overglaze deep enamel blue. A burnished small band of gilding highlights the rim further. The flowers were painted using six main enamel colours: blue, olive green, purple, red, violet and yellow. We studied the body, the enamels and the gilt. This plate is obviously not one of the finest Sèvres porcelains, because it was most probably decorated during the long hours when unsufficient light was available, the painters beginning their work at 5 or 6 am and ending at 8 pm (D'Albis, 2015a; Trittschack *et al.*, 2015).

4.2. Sample preparation and analytical methods

A thick slice was obtained by cutting the plate with a saw (Fig. 1a). A sample of 5 g was ground in a tungsten carbide mill after careful removal of the glaze. This powder was used for XRF and XRD body analysis. Subsamples from gilt and enamels were further taken from broken parts of the plate and studied by SEM.

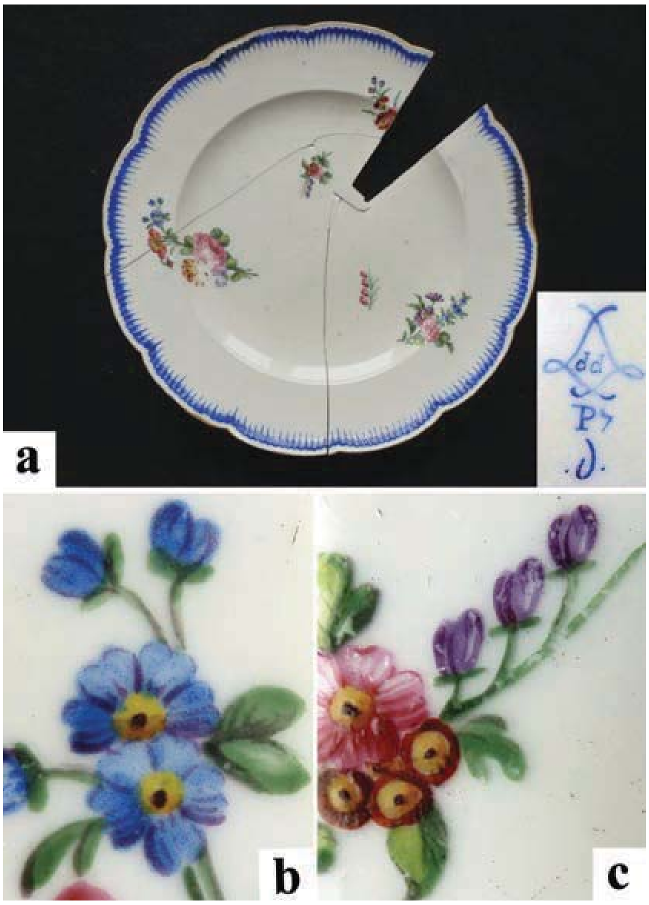

Fig. 1. (a) Studied Sèvres soft (frit) porcelain plate with overglaze floral decoration and burnished gilded rim. Height 3.0 cm, Diametre 23.8 cm, 12 lobes. Inlay: Sèvres's mark painted in blue under the base with the factory's crossed L's (an abbreviation of Louis, the King), forming by their crossing a rectangular cartouche. Private collection; (b) Closer view of a *Myosotis* sp. flower (*Boraginaceae* family); (c) Closer view of a fanciful flower. (Online version in colour.)

Chemical analysis by XRF: 2 g of powdered sample were calcined at 1000 °C for 1 h to obtain the loss on ignition (LOI). 0.700 g of calcined powder was carefully mixed with 6.650 g of MERCK spectromelt A10 ($Li_2B_4O_7$) and 0.350 g of MERCK lithium fluoride (LiF). This mixture was put into a platinum crucible and melted at 1150 °C for 10 min (Philips® PERL X-2) in order to obtain a glassy tablet. These tablets were analysed for major, minor and trace elements using a Philips® PW 2400 wavelength-dispersive spectrometer (Rhodium tube, 60 kV and 30 mA). Calibration was made on 40 international standards. Accuracy and precision were checked using laboratory reference samples. Error has been evaluated to be less than 5% for all elements analysed.

The mineralogical composition was determined by XRD, using the powder left over after the confection of the XRF tablet (Philips® PW 1800 diffractometer, Cu$K\alpha$, 40 kV, 40 mA, 2θ 2–65°, measuring time 1 s/step).

Chemical and morphological analyses by SEM: The samples were mounted in an epoxy block, flatly polished with a 0.5 µm diamond paste and then coated with a thin carbon layer. Backscattered electron images (BSE) were collected with a scintillator-type detector from the polished samples, using a Philips® FEI XL30 Sirion FEG SEM. Chemical compositions were determined by energy-dispersive X-ray spectrometry (EDS), operated at a beam acceleration voltage of 20 kV and a beam current of 6.5 nA. Standardless quantification was performed using an EDAX-ZAF correction procedure of the intensities, using spot analyses (2 µm diameter) as well as larger-area analyses of homogeneous regions. The detection limits for most elements were about 0.2 wt.%. The reliability of the results was proven by measuring well-known glass and mineral standards (DLH2, Corning A-D, plagioclase). The relative mean deviation for major and minor oxide components was 2% for concentrations in the range of 20–100 mass%, 4% for 5–20 mass%,10–20% for 1–5 mass %, and >50 mass% for <1 mass%. Boron could not be determined in the SEM-EDS, which is not a major problem as (1) no borax was used in the Sèvres frit paste technology (Brongniart, 1802) and (2) only minor amounts of borax are testified in some colour recipes (Préaud & d'Albis, 1991).

5. Results

5.1. Body

The SiO_2 concentration is high (72.68 mass%), followed by 15.82 mass% CaO, 5.17 mass% K_2O, 3.25 mass% Na_2O and 1.34 mass% Al_2O_3 (Table 2). The XRD analysis reveals a phase association dominated by wollastonite and tridymite, with subordinate quartz. The microstructure (Fig. 2) is similar to the one reported by Kingery & Smith (1985), and consists of: (1) few large closed pores (20–40 µm across), normally roundish; (2) sparse, irregularly shaped quartz grains, mostly surrounded by laths of a SiO_2-polymorph (tridymite according to XRD) and circular microcracks; (3) mostly angular patches of crystal-free, homogeneous and amorphous (according to electron backscatter diffraction) matrix, not stable under the electron beam; (4) angular patches of this glassy matrix with subidiomorphic laths of recrystallized silica, tridymite according to XRD (Fig. 4b); and (5) abundant wollastonite-rich patches with interstitial glass. These crystals have acicular shapes, are typically up to 2–3 µm long and set in the glassy matrix. The crystal-free matrix contains 72–77 mass% SiO_2, 11–13 mass% K_2O, 6–12 mass% CaO and 1.5–5 mass% Al_2O_3. The interstitial glass of the wollastonite patches is richer in Na_2O (1.0–1.3 mass%) and CaO (18.1–23.6 mass%), but lower in Al_2O_3 (0.8–1.4 mass%), SiO_2 (67.8–69.9 mass%) and K_2O (5.5–8.4 mass%; see Table 3). At the contact to the glaze, a 50–60 µm thick reaction zone is visible with no or few wollastonite patches (1 in Fig. 3). The boundary to the body is wavy and diffuse. A chemical profile across this reaction zone reveals a progressive depletion of Al_2O_3

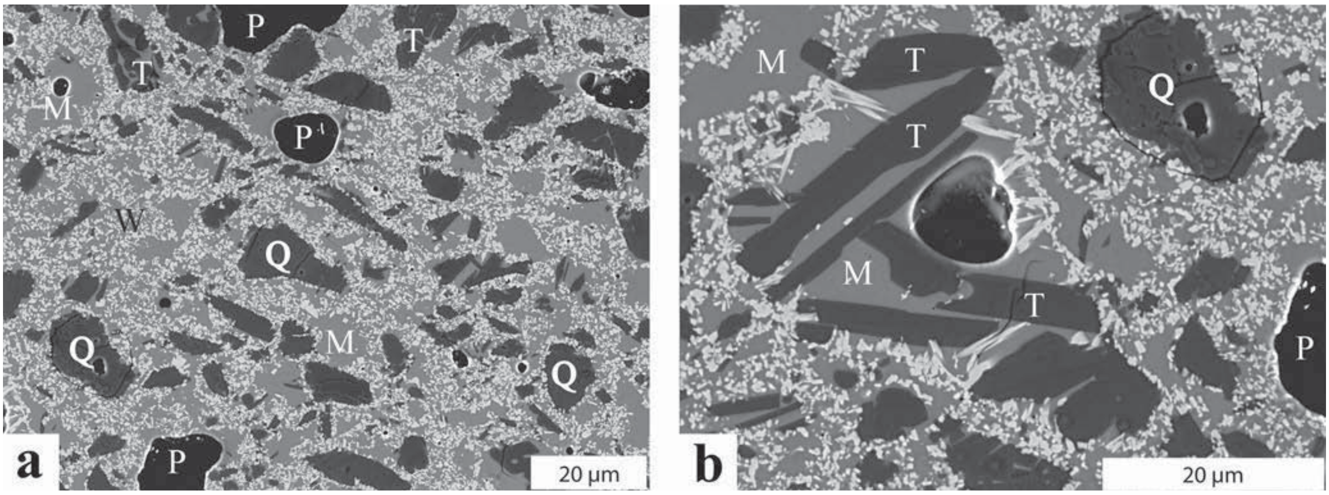

Fig. 2. Scanning-electron-microscope backscattered-electron (SEM-BSE) picture of the body. (a) General view; (b) enlarged view. Visible are some large closed pores (P, black), relictic quartz grains surrounded by circular cracks (Q, dark grey), subidiomorphic tridymite laths (T, dark grey), many small subidiomorphic crystals of wollastonite (W, white) and a glassy matrix (M, grey).

Table 3. Compositions (SEM-EDS) of some body areas (mass%). Totals normalized to 100 mass%.

An. no.	Area	Na_2O	MgO	Al_2O_3	SiO_2	SO_3	K_2O	CaO	Fe_2O_3
Homogeneous matrix glass patches without crystals									
SEV1-1	Spot	0.3	0.5	2.1	76.6		11.9	8.0	0.6
SEV1-2	Spot	0.5	0.5	2.9	77.2	0.5	12.1	5.8	0.5
SEV1-4	Spot	0.3	0.5	2.1	74.1	0.4	11.7	10.1	0.8
SEV1-5	Spot	0.2	0.5	1.5	74.1	0.6	10.1	12.1	0.9
SEV1-6	Spot	0.3	0.4	1.8	77.4	0.5	11.5	7.4	0.7
SEV1-7	Spot	0.3	0.5	2.2	77.1	0.4	11.2	7.7	0.6
SEV1-10	Spot	0.4	0.5	2.0	74.8	0.4	11.2	10.0	0.7
SEV1-11	Spot	0.3	0.4	2.1	74.0	0.5	12.5	9.4	0.8
SEV1-12	Spot	0.3	0.4	1.7	77.4	0.3	12.5	6.8	0.6
SEV1-13	Spot	0.2	0.4	5.0	71.6	0.2	11.0	10.9	0.7
SEV1-14	Spot	0.3	0.4	2.1	75.9	0.4	12.9	7.3	0.7
Mean		0.3	0.5	2.3	75.4	0.4	11.7	8.7	0.7
Wollastonite-rich patches									
EDS1	5 × 5	1.0	0.4	1.0	69.8	0.5	6.8	20.5	
EDS2	5 × 5	1.1	0.4	1.1	68.6	0.4	6.8	21.3	0.3
EDS3	5 × 5	1.2	0.3	0.8	67.8	0.3	7.1	21.9	0.6
EDS4	5 × 5	1.0	0.3	1.0	69.9	0.3	6.3	21.2	
EDS5	5 × 5	1.1	0.2	1.0	68.2	0.3	6.7	22.1	0.4
EDS6	5 × 5	1.1	0.4	0.8	67.8	0.3	6.0	23.6	
EDS7	5 × 5	1.0	0.3	0.9	69.8	0.3	5.5	22.2	
EDS8	5 × 5	1.0	0.3	0.9	69.9	0.4	6.5	21.0	
EDS9	5 × 5	1.3	0.4	1.4	69.7	0.2	8.4	18.1	0.5
EDS10	5 × 5	1.0	0.3	0.9	69.8	0.4	6.5	21.1	
EDS35	3 × 3	1.0	0.4	1.1	69.0	0.3	6.7	21.5	
Mean		**1.1**	**0.3**	**1.0**	**69.1**	**0.3**	**6.7**	**21.3**	**0.2**

(1.2 mass% at the contact) and SiO_2 (65 mass%), and an enrichment of PbO (from nil to mass%) towards the body-glaze boundary.

5.2. Glaze

The glaze shows two parts (Fig. 3): (i) a clear, homogeneous main outer zone (50–90 µm across), and (ii) a 35–75 µm thick crystal-rich inner zone, full of tiny crystals (reaction zone). These crystals do not exceed 0.3 µm and are therefore impossible to analyse precisely by SEM-EDS. Notwithstanding their Ca-richness points to a Ca-silicate (wollastonite?). The contact between both is irregular and wavy. The outer zone belongs chemically to a medium-Pb glaze type (40–42 mass% PbO) containing some 6–7 mass% K_2O, 3–4 mass% CaO and concentrations <1 mass% of Na_2O, alumina and iron (Table 4). The tiny crystals of the inner zone are

1–2.5 µm long, prismatic shaped and CaO-rich. Few large gas bubbles (max. 25 µm across) are visible in the lower part of the inner zone.

5.3. Overglaze colours and gold decoration

The maximum thickness of the different paints is 50 µm, but normally around *ca*. 15 µm. Zinc is absent in all enamels.

5.3.1. Blue (dentil comb)

The BSE images reveal a sharp, but irregular contact to the underlying glaze, few pores (max. diameter 7.5 µm), many globules (diameter up to 3.2–3.5 µm) and acicular dendrites radiating from these globules (max. length 4.3 µm), all embedded in a glassy matrix (Fig. 4). The globules have a mesentery-like internal structure and some of them are broken (Fig. 4b). These globules are the origin for the opacity of the blue paint. The chemical analyses

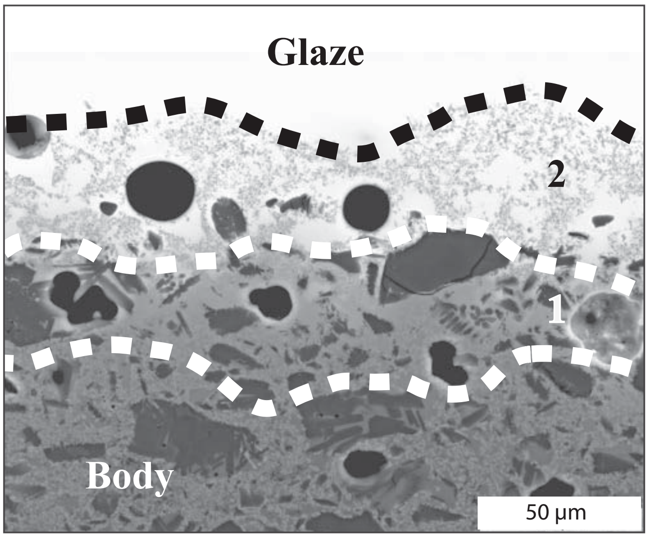

Fig. 3. SEM-BSE picture of the contact between body and glaze. (1) Reaction zone in the body; (2) reaction zone in the glaze.

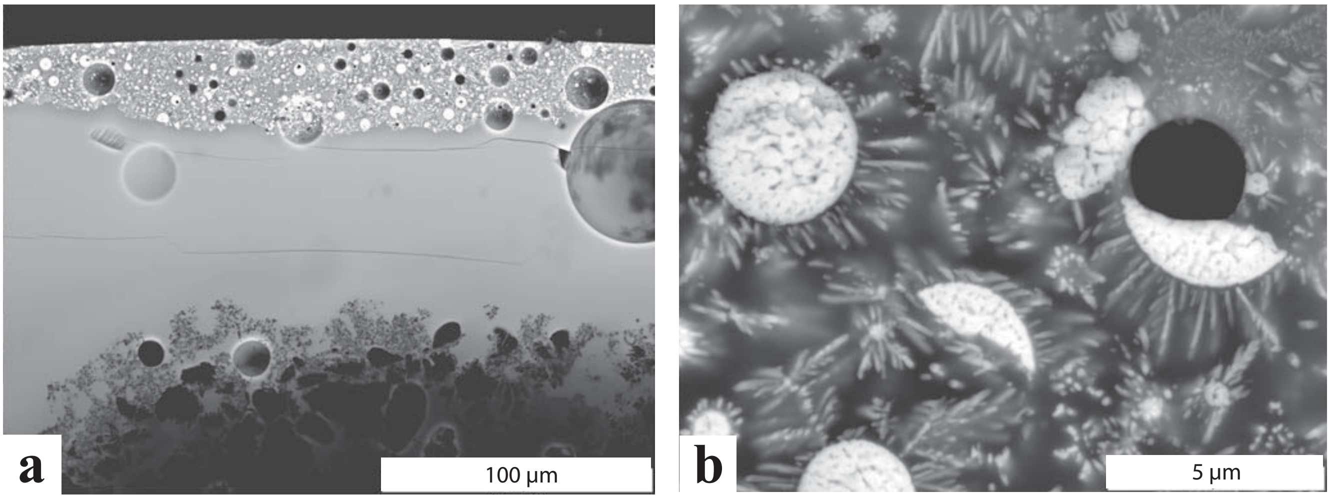

Fig. 4. SEM-BSE picture of a cross-section of the blue indented rim. (a) Aspect of the sharp contact to the underlying glaze; (b) Closeup of the dendritic aggregates and broken globules.

Table 4. Comparison of glaze compositions (SEM-EDS) with previous glaze analyses, calculated glaze compositions and reaction zone composition (mass%). Totals normalized to 100 mass%. A = Vincennes (D'Albis, 1985); B = Sèvres (Kingery & Smith, 1985), Object>1750 AD; C = Recipe for the Vincennes glaze (D'Albis, 1985); D = Recipe for the Sèvres glaze (Brongniart, 1844, II).

An. no.	Area (µm)	Na_2O	Al_2O_3	SiO_2	K_2O	CaO	Fe_2O_3	PbO	Total
Homogeneous glaze									
SEV2-32	40 × 20	0.8	0.2	47.4	5.6	3.5	0.3	42.2	100.0
SEV2-33	120 × 50	0.6	0.3	47.8	6.6	4.0	0.4	40.3	100.0
SEV2-34	200 × 30	0.7	0.3	47.5	6.9	4.0	0.3	40.3	100.0
Mean		**0.7**	**0.3**	**47.6**	**6.4**	**3.8**	**0.3**	**40.9**	100.0
Previous glaze analyses									
A		2.0		61.0	3.0	4.0		30.0	100.0
B		3.0	0.9	48.1	3.8	2.4	0.2	40.4	98.8
Calculated glaze compositions									
C		6.6		41.9	9.5			42.0	100.0
D		6.5		41.2	11.1			41.2	100.0
Reaction zone									
SEV2-31	40 × 20	0.4	0.2	49.9	5.0	14.4	0.2	29.9	100.0

Table 5. Average analyses of overglaze enamels and gilt by SEM-EDS, in mass%, normalized to 100%. *n* = number of individual analyses in the average results.

Colour	*n*	Na_2O	As_2O_3	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	Cl	K_2O	SnO_2	Sb_2O_3	CaO	MnO	Fe_2O_3	CoO	NiO	CuO	Au	PbO
Blue (indented rim)																				
Paint	4	0.4	4.8			35.0				6.5			1.0		0.4	7.0	0.5			44.4
Matrix	5		1.9			34.2			0.4	6.3			0.5		0.5	8.6	0.6			47.0
Globules	7	0.9	9.1			12.7	1.7	0.4	1.5	3.0			1.7		0.4	2.6	0.3			65.7
Blue (flowers)																				
Paint	9	0.8	2.1			34.2				3.9			1.6		0.4	1.9	0.2			54.9
Globule	1	2.6	17.1			8.0			0.8	0.9			2.9		0.3	0.4				67.0
Yellow																				
Paint	3	1.0			0.2	33.6				3.8	1.6	3.4	0.4		1.2					54.8
Matrix	4	1.0			0.1	45.0				4.3			0.3		0.9					48.4
Pigment	3										13.3	23.5			0.8					62.4
Green																				
Paint	10	1.8				31.1				3.0	2.0	4.4	1.4		1.5	0.6		2.0		52.2
Matrix	17	1.3	0.1			38.1				3.5	0.7	0.3	1.5	0.1	1.8	0.9		2.5		49.2
Pigment	12										11.6	23.9			1.1					63.4
Red																				
Paint	3	0.9				29.0			0.1	3.8		2.2	1.3		17.1					45.6
Matrix	3	0.7		0.2	0.4	34.6			0.1	3.8			1.9		16.4					41.9
Pigment												25.7			6.8					67.5
Purple																				
Paint	3	1.6			0.3	53.3				5.2			0.7		0.3				0.7	37.9
Violet																				
Paint	14	1.2	0.6		0.4	39.6			0.1	4.5			1.1		0.5	1.6	0.1		0.5	49.8
Gild																				
Paint	3														0.5				99.5	

reveal (Table 5): (1) an overall blue paint with high Pb, silica, Co and potash (K_2O) contents, moderate As-oxide and very low concentrations of Ca, Fe and Ni oxides; (2) a glassy matrix of comparable chemical composition, but with higher Co-oxide concentrations; and (3) globules, *i.e.*, spherical forms with mesentery-like association of tiny crystals, very rich in As_2O_3 and PbO, with minor amounts of other oxides as well as traces of La and Ce. Similar Pb-rich arsenates were reported by Pradell *et al.* (2013) for Catalan tin-glazed Renaissance ceramics. Dendrites did not have sufficient size to permit a quantitative chemical analysis by SEM-EDS, but qualitative measurements are broadly consistent with the same type of Pb arsenates as in the globules.

5.3.2. *Blue (flower)*

The microscopic analysis shows the heterogeneous nature of the blue strokes with deep blue, medium blue and light blue glassy grains (Fig. 5a). A cross-section reveals the patchy nature of the paints (Fig. 5b) and a thin diffusion zone in the glaze below them (Fig. 5b). The microstructure (Fig. 5c) resembles those of the blue comb (Fig. 4b), but the chemical composition is quite different. Evidently, the painter Pierre le Jeune used a colour with more Pb, but less K, Co and silica (Table 5).

5.3.3. *Yellow*

These paints have an overall homogeneous thickness of ~25 μm and a sharp, even border to the underlying glaze (Fig. 6a). Bulk analyses of the paint layer show predominantly PbO and SiO_2 with minor amounts of K_2O, SnO_2, Sb_2O_3 and CaO (Table 5). The glassy matrix does not contain tin and antimony oxide. The SEM-BSE images show densely packed thin platelets, often with pseudo-hexagonal shapes (max. diameter 7.5 μm, 0.1–0.2 μm thick; Fig. 6b), similar to those reported by Pereira *et al.* (2009) for Pb–Sn–Sb-mixed crystals. Sèvres Pb–Sn–Sb triple oxide crystals (Table 5) exhibit a core rich in glassy inclusions and a chemical zoning, both impossible to analyse with the SEM-EDS due to their small size.

5.3.4. *Green (olive green)*

It is microscopically quite similar to the opaque yellow (Fig. 7), with a maximum thickness of 50 μm, but differs markedly showing Pb–Sn–Sb crystals embedded in a SiO_2 and PbO-rich glassy matrix, the latter with CoO and CuO concentrations close to 1 and 2.5 mass%, respectively (Table 5). The crystals are smaller in the green colour compared to those of the yellow paint (Fig. 7c and d). The green colour contains rare, irregularly shaped tin oxide crystals, commonly surrounded by Pb–Sn–Sb pigments (Fig. 7c). Former colour pigment glass particles can be recognized by their sharp and cornered outlines (Fig. 7d).

5.3.5. *Red*

This maximum 10 μm thick, inclusion-rich paint has a wavy, but sharp contact to the underlying glaze (Fig. 8a–c). The red overglaze enamel is, as shown by optical and SEM-BSE images, a mechanical mix of yellow coloured

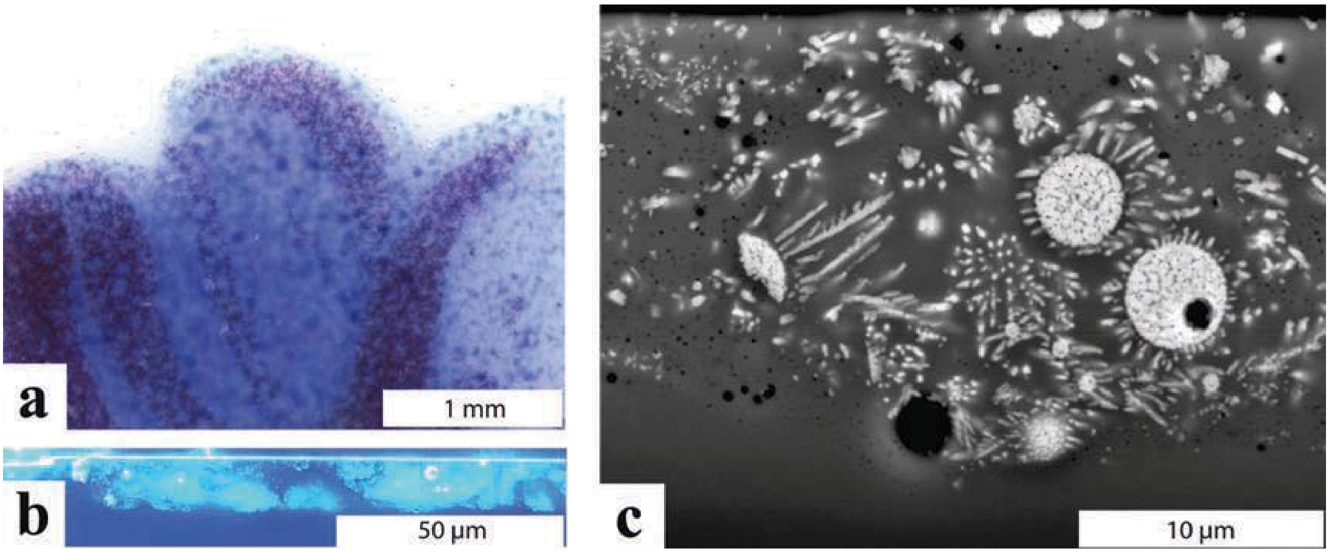

Fig. 5. Flower blue. (a) Closeup of the blue *Myosotis* petals (Fig. 1b) with grains of different blue intensities and several violet strokes. Bar 0.5 mm; (b-c) Cross-sections of the blue paint. (b) Aspect under reflected light microscopy (dark field); (c) SEM-BSE aspect of the microstructure. (Online version in colour.)

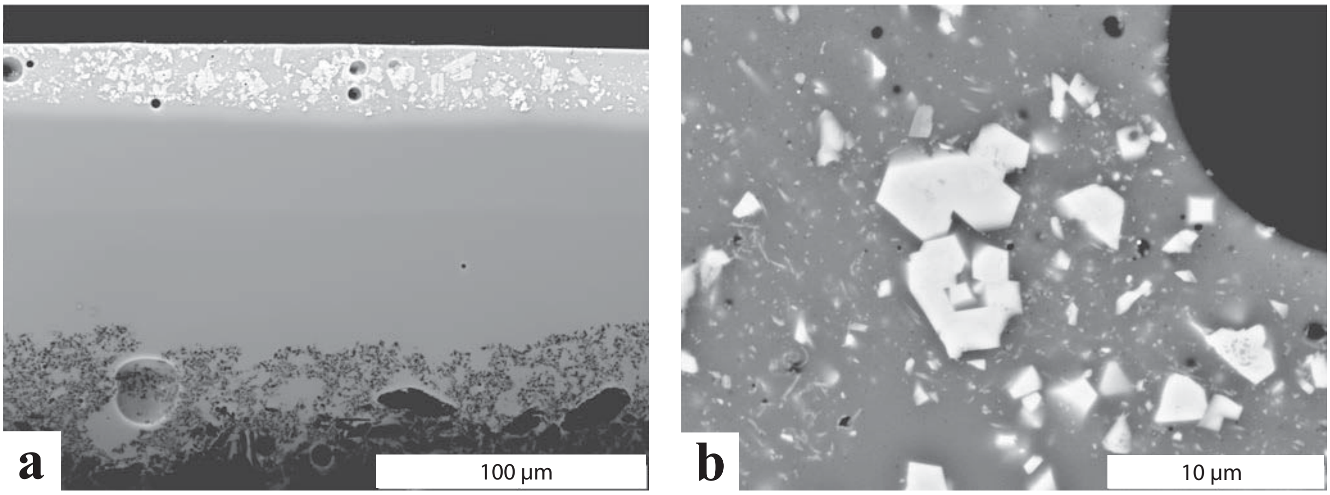

Fig. 6. Cross-sections of the yellow paint. SEM-BSE picture showing (a) the sharp contact to the underlying glaze and the richness of opacifying crystals (white) in the yellow paint; (b) the pseudohexagonal to irregular shapes and the variable dimensions of the thin lead-tin-antimonate platelets (white to grey).

glassy grains ($\leq 10\,\mu$m across; Fig. 8a and d) with powdered, red Fe-rich Pb–SiO_2 glass (Fig. 8b and c). In the former, 3–3.5 μm thick pseudo-hexagonal Pb-antimonate crystals can be observed (Fig. 8d, Table 5). In the latter, no colouring agents, such as cuprite, hematite or hercynite sub-micrometre particles, were detected.

5.3.6. *Purple*

This colour was applied as a very thin layer (7–10.5 μm thick) and has a wavy and sharp contact to the underlying glaze (Fig. 9a and b). It contains few bubbles, some tridymite or cristobalite crystals and tiny drops of pure gold with maximum diameters of 0.5 μm (Fig. 9c). This colour is of the high-Pb type, averaging 47 mass% PbO with about 46 mass% SiO_2 and 5 mass% K_2O, with no SnO_2 (Table 5).

5.3.7. *Violet*

The paint layer has a maximum thickness of *ca*. 20 μm and a wavy border to the underlying glaze (Fig. 10a–c). This enamel colour is in fact, as revealed microscopically, a curly mix of two colours, *i.e.* the flowers' blue and the purple (Fig. 10c–e). Therefore, many hues can be observed, from a deep bluish violet to a reddish violet, depending on the local concentration of blue-rich and purple-rich parts. Consequently, the chemical analyses of

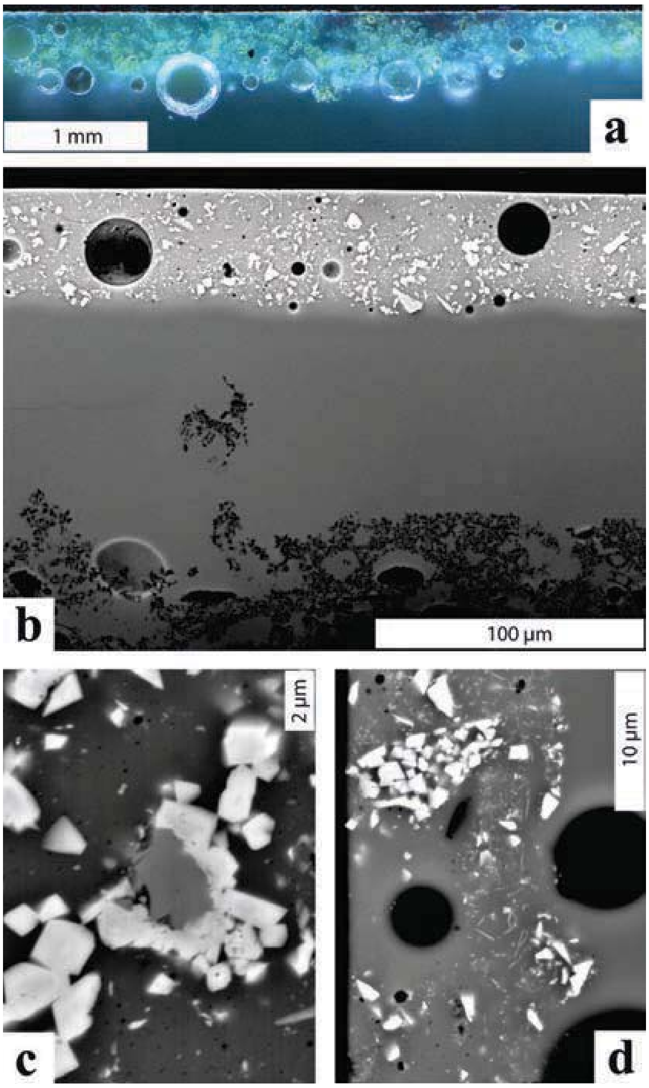

Fig. 7. Cross-sections of the green paint. (a) Aspect under reflected light microscopy showing yellow glassy grains in a bluish glassy matrix (dark field). Scale as in (b); SEM-BSE picture with the bright paint, rich in opacifying crystals (white), with a sharp contact to the underlying grey glaze, and the upper part of the glaze reaction zone; (c) a cassiterite crystal (grey) rimmed by subidiomorphic lead-tin-antimonate crystals; and (d) the heterogeneous aspect of the green paint with a marked triangular shaped yellow glass-crystal fragment with a length of 12 µm. (Online version in colour.)

these hues are a mix between both genuine blue and purple, with varying As and Au concentrations, typical for the blue and for the purple enamel, respectively (Table 5).

5.3.8. Gilt

The gold decoration has a maximum thickness of *ca.* 6.6 µm (Fig. 11a) and consists of several folded, *ca.* 0.6 µm thick Au particles (Fig. 11b). At the contact to the glaze, conspicuous gas bubbles, with a maximum diameter of 22.5 µm are present. Analyses of the gilt areas showed a very pure Au with some Fe (Table 5).

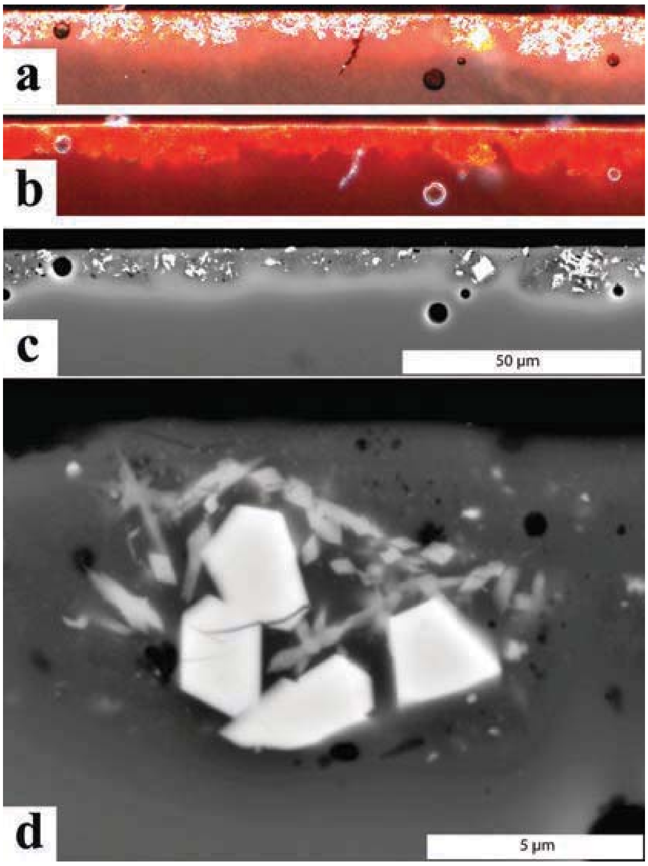

Fig. 8. Cross-section of the red paint. (a) Aspect under reflected-light microscopy (bright field). Scale as in (c); (b) The same region under reflected-light microscopy (dark field) with wavy, but sharp contacts to the underlying glaze. Scale as in (c); (c) SEM-BSE picture of the same region with few black pores and the opacifying Pb–Sb-crystals (white); (d) Close-up of the pseudohexagonal Pb–Sb-platelets in a yellow colour glassy grain (length 11 µm). (Online version in colour.)

6. Discussion

6.1. Body

The bulk chemical composition is well within the range of known analyses (Table 2), and not much different from the Sèvres “normal” body composition (mass%): 76.0 silica + 2.0 alumina + 0.75 iron oxide + 16.0 lime + 5.25 alkali oxide (Salvétat, 1857). According to this author, the paste was a mix of (mass%) 75 frit + 17–8 marl + 8–17 chalk. The marl came from gypsiferous layers near Argenteuil, and had to be diluted and levigated in order to obtain 45–46% pure marl (Brongniart, 1844, II). The mean chemical composition of the frits during the 1760s was (mass%): 89.60 silica + 1.50 alumina and Fe-oxide + 3.00 lime + 0.12 magnesia (MgO) + 6.00 alkali oxides (Salvétat, 1857). The fired frits were a mix of (mass%): 60.0 Fontainebleau sand + 22.0 saltpetre (KNO_3) + 7.2 sea salt + 3.6 alum + 3.6 soda + 3.6 gypsum. Salt was added in order to transform the Fe oxide into volatile Fe-chloride (Table 1).

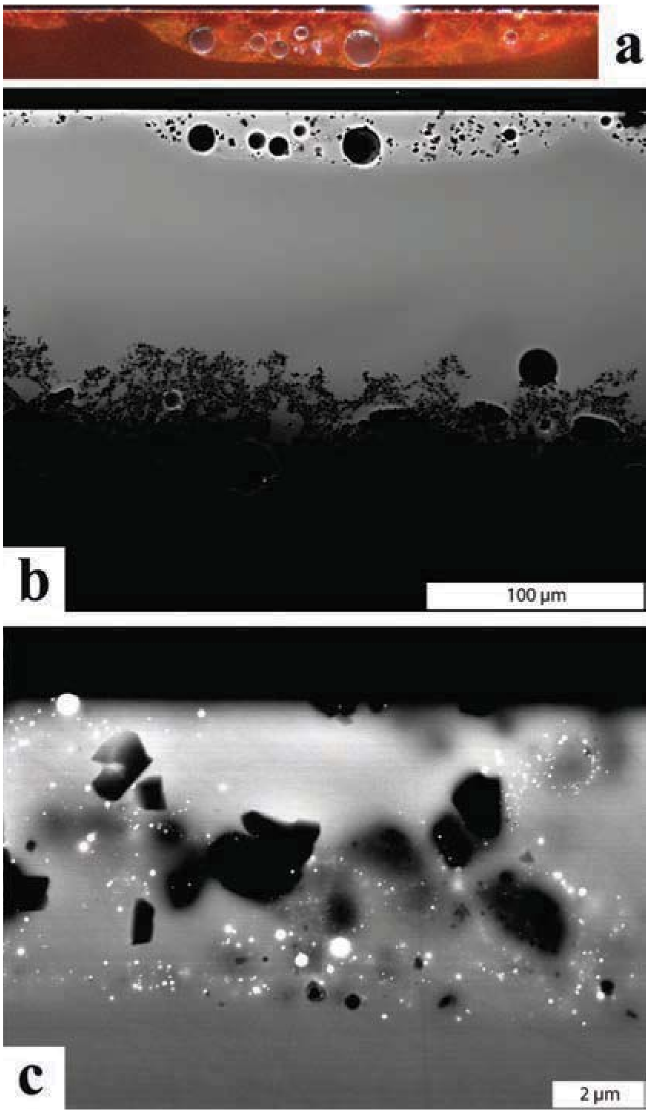

Fig. 9. Cross-section of the purple. (a) Aspect under reflected light microscopy (bright field). Scale as in (b); SEM-BSE picture of the same region with, from top to bottom: the purple paint (light grey), rich in pores (black) and tiny crystals (black; tridymite), the glaze (dark grey), the glaze reaction zone with dispersed tiny black crystals and the body reaction zone (black); (c) Close-up with tridymites (black) and small globulets of pure gold (white). (Online version in colour.)

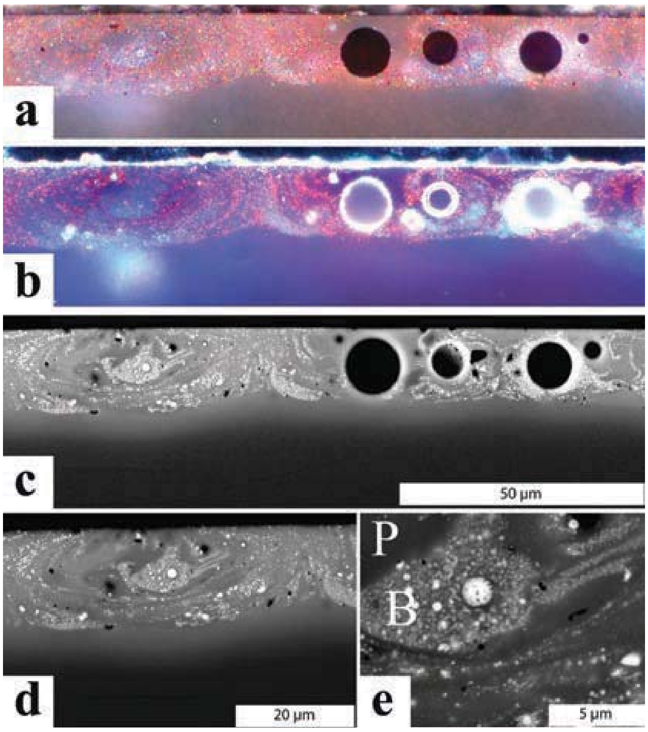

Fig. 10. Cross-section of the violet. (a) Aspect under reflected-light microscopy (bright field). Scale as in (c); (b) The same region under reflected-light microscopy (dark field) with wavy, but sharp contacts to the underlying glaze. The paint is a mingling of blue and purple streaks. Scale as in (c); (c) SEM-BSE picture of the same region with conspicuous black pores and the blue streaks (white); (d) Close-up of the heterogeneous mingling. White As-rich globulets of all kinds are visible in the bright (blue) parts and Au-drops in the dark (purple) parts; (e) Close-up of a blue (B) and purple (P) mingling. (Online version in colour.)

The high Pb content is probably a contamination effect due to incomplete removal of the Pb-rich body reaction zone when preparing the sample. The chemical composition of the matrix glass bears the signature of the frit recipe ingredients. Its high silica content can be referred to the sand, the potash to saltpetre and alum (calcined = KAl $(SO_4)_{12}$), lime to gypsum, alumina to alum, and S to alum + gypsum. Contrasting, Na_2O concentrations are very low and are due to large losses of Na during the bisque firing (Salvétat, 1857) and partially also to the well-known evaporation during the SEM-EDS measurements.

The XRD analysis shows a phase association of wollastonite and tridymite, as already reported by Treppoz & d'Albis (1987). There is no cristobalite as postulated by Kingery & Smith (1985) and Kingery & Vandiver (1986), who did not specify how they identified this phase. Are these differences due to changes in technology or raw materials with time or are they specific for the type of artefacts (figurines/tableware)? Kingery & Smith (1985) pointed out that the ternary phase diagram Na_2O–CaO–SiO_2 (Morey & Bowen, 1925; Roth *et al.*, 1961) is very well suited to study French soft (frit) porcelain equilibrium phase relationships, as the total of these three oxides is > 90 mass%. In Fig. 12, the analysed plate plots in the compatibility (cotectic) triangle of three phases, *i.e.*, β-wollastonite ($CaO.SiO_2$) + devitrite ($Na_2O\ \cdot 3CaO\ 6SiO_2$) + tridymite ($SiO_2$), which corresponds to β-CS + NC_3S_6 + SiO_2 in the technical nomenclature. This is also the equilibrium phase association for the 17 analysed French soft (frit) porcelain bodies (Heimann & Maggetti, 2014, chapter 14). However, it should not be forgotten that, this simplified system does not consider K_2O and other oxides, which have a small but measurable impact on phase relationships as well as on the invariant and divariant equilibria. Nonetheless, the Na_2O–SiO_2–CaO phase diagram can be used as a first approach. The interesting portion of this system shows two invariant points: (1) a ternary peritectic point

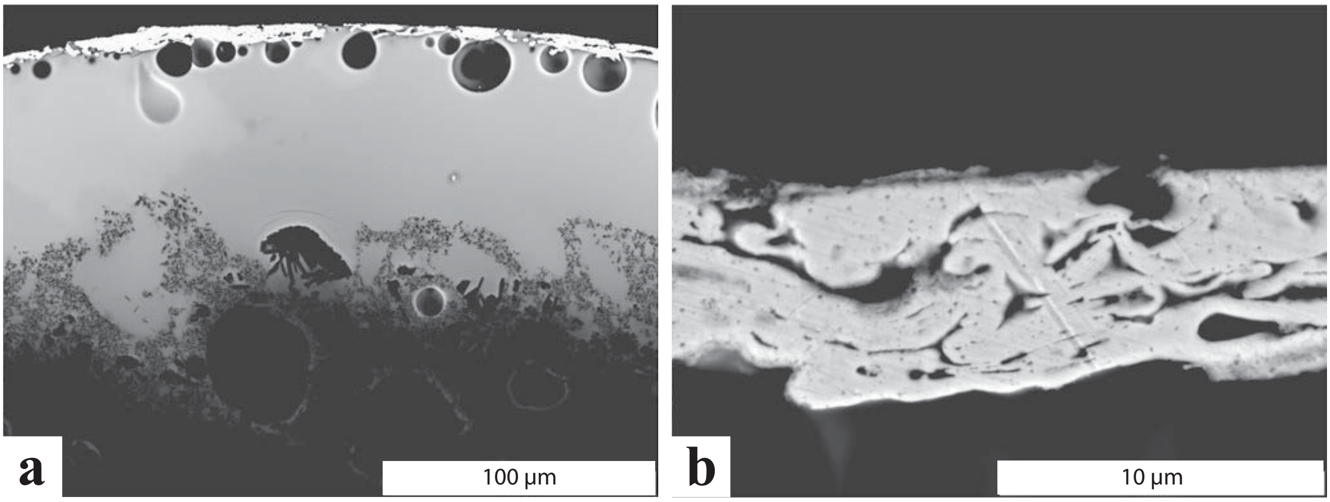

Fig. 11. SEM-BSE picture of the gold gilding showing (a) many black pores of different size at the contact to the underlying glaze (grey) and (b) the internal structure of the folded gold layers.

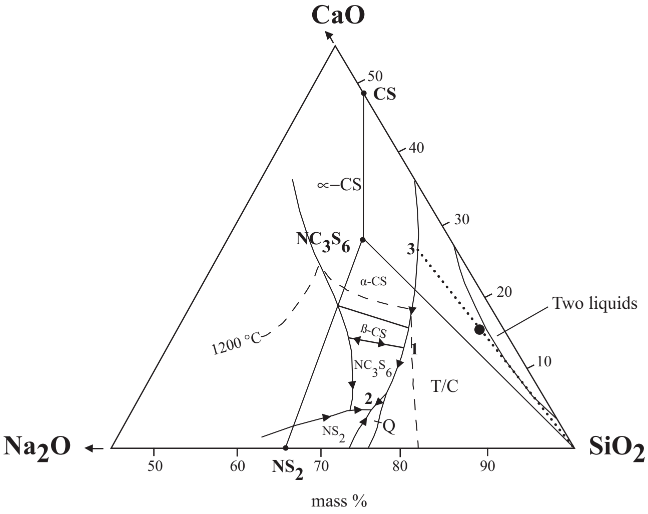

Fig. 12. Phase boundaries and coexisting phases in the high-SiO_2 corner of the ternary system Na_2O–SiO_2–CaO (redrawn after Morey & Bowen, 1925). C cristobalite SiO_2, CS wollastonite CaO.SiO_2, NS_2 water glass $Na_2O.2SiO_2$, NC_3S_6 devitrite $Na_2O.3CaO.6SiO_2$, Q quartz SiO_2, T tridymite SiO_2. **1** ternary peritectic point (1035 °C), **2** ternary eutectic point (725 °C). Black dot = body of Table 2 (this work, XRF), **3** intersection of the projection from the SiO_2 apex through the bulk composition (dotted line) with the wollastonite–silica cotectic line.

at a temperature of 1035 °C with the equilibrium [liquid L]−[β-CS]−[NC_3S_6]−[SiO_2] and (2) a ternary eutectic point at a temperature of 725 °C with the equilibrium [L]−[NS_2]−[NC_3S_6]−[SiO_2]. Under equilibrium conditions, no liquid is formed in the studied body (black dot in Fig. 12) when heating up during the bisque firing, until the peritectic temperature of 1035 °C is reached. At this temperature, a liquid phase of composition (in mass%) 13.7 Na_2O + 73.4 SiO_2 + 12.9 CaO, is generated. At the end of the peritectic reaction, the body shows (in mass%) 22.6 liquid + 26.8 β-CS + 50.6 tridymite. If heating continues, the melt follows the cotectic curve wollastonite–tridymite/cristobalite to higher temperatures, while constantly resorbing wollastonite, until the critical temperature of *ca*. 1380 °C is reached, where the melt migrates into the primary field of cristobalite. However, the bisque firing temperatures were significantly lower and did not exceed 1100 °C. At this temperature, the liquid was still on the cotectic curve. When the kiln cools down, the composition of the liquid evolves along this cotectic curve β-CS/tridymite to the peritectic point 1 (1035 °C). At this stage, the peritectic reaction (liquid + β-CS = NC_3S_6 + tridymite) consumes all liquid, leading to the final equilibrium phase association of (in mass%) 18 β-wollastonite + 26.8 devitrite + 55.2 tridymite. Wollastonite and tridymite were detected by XRD analysis, but no devitrite, a clear sign of non-equilibrium conditions. The surviving high amount of glassy phases is not surprising, considering the extreme difficulty to crystallize highly viscous melts of the pure ternary system when they reach the peritectic point (Morey, 1964). Actually, the system has more than three components, other oxides such as alumina contribute further to inhibit devitrification (D'Albis, 1985).

Microstructural observations confirm the non-equilibrium phase assemblage of the analysed soft (frit) porcelain body. The images are similar to those published by Kingery & Smith (1985), but with tridymite laths in some glassy patches, instead of cristobalite as assumed by these authors (Fig. 2b). The body consists of three main domains: (1) roundish quartz grains, partially replaced by tridymite and glass, surrounded by typical cracks due to the α/β transition during the heating and cooling of the plate, (2) patches of glass (M in Fig. 2), with or without SiO_2 laths (tridymite according to XRD), and (3) patches of glass, full of tiny subidiomorphic wollastonite crystals. The quartz grains are interpreted as incompletely melted, relictic sand grains of the frit blend. Domain (2) corresponds to the milled frits, visible as glassy patches, *i.e.*, former angular, irregularly shaped flakes of frit glass, some with tridymite crystals, which most probably crystallized during the cooling of the frit in the first firing stage. Domain (3) corresponds to the chalk or marl additions, melted during the second high-temperature (bisque) firing and crystallizing wollastonite. One would expect higher alumina in the wollastonite-rich patches compared to the frit patches, if marl was added (Table 1). As this is not the case, chalk must have been admixed. At $T_{\max}$ of the second (bisque) firing, at least four chemically distinct amorphous domain types must have coexisted in the body: a Si-rich one around the relictic quartz grains, a second, frit-derived Si-rich one (with moderate CaO), a third frit-derived Si-richer one (containing already crystallized tridymite), and a fourth chalk-derived Ca-rich amorphous phase. The microstructure indicates no complete mixing/homogenization of these amorphous phases, even after firing at ~1000 °C, a fact that is possibly due to the high viscosities of such Si- and Ca-rich phases (Kingery & Smith, 1985). Alternatively, the former glassy frit patches would only be mollified, if the bisque's firing temperature were below 1000 °C. However, slightly higher temperatures would soften the paste too much as many of these patches would become more fluid liquids, resulting in the feared collapses of figurines and crockery.

6.2. Glaze

Louis Gravant's recipe for the transparent Pb glaze is well known (Brongniart, 1844; Salvétat, 1857; D'Albis, 1985; Préaud & d'Albis, 1991). A mix of (in parts): 38 litharge + 27 Fontainebleau sand + 11 calcined flint + 15 potash + 9 soda (Brongniart, 1844, II), or (in kg): 41 minimum + 38 Fontainebleau sand + 18 potash (Salvétat, 1857), was fused in a “German” crucible (Martinón-Torres & Rehren, 2009) at the hottest spot of the kiln for 34–35 h (Hellot 7.10.1751, cited by Préaud & d'Albis, 1991). Salvétat indicates the admixture of 70 g As and 20 g Mn peroxide. A slightly different recipe with calcined flint is given in Table 1 (D'Albis, 1985, 1999). The glassy frit was extracted from the shattered crucible, and remelted one or two times. Its composition was not changed between 1745 and 1801 (Préaud & d'Albis, 1991). Table 4 reveals major differences in the bulk compositional data between calculated and analysed glazes. Very significant are the higher Na_2O and K_2O contents, the lower silica concentration, and the absence of alumina and CaO in the former. It is well known that, the firing processes of the soft paste porcelain can volatilize important amounts of Na_2O and K_2O in the Pb glaze. The depletion of both oxides in the analysed glaze is therefore not surprising. On the other hand, the lower amounts of Na and K in the analysed glazes could also be explained by a departure from the historical recipes. The alumina in the analysed glaze is most probably derived from the high alumina crucibles in which the glaze ingredients were fritted. The substantial CaO content (*ca.* 4 mass%) in the analysed glaze is suggestive, either of a different recipe using some chalk, or of a contamination process during the glaze firing, as evidenced by the conspicuous reaction zones in both body and glaze, where Ca migrated from the body into the glaze, whereas Pb migrated from the glaze into the body.

6.3. Overglaze colours and gilt

The overglaze enamels are all rich in PbO and SiO_2, as are those from China (*e.g.* Vandiver *et al.*, 1997) or from Meissen (Domoney *et al.*, 2012). As expected, the overall chemical compositions of the Sèvres and Meissen enamels are profoundly different, the former showing much higher levels of alkalis than the latter. The Meissen enamel Q4 colours differ further by their increased levels of alumina, contributed by potassium feldspar, clay or other alumosilicates (Kingery & Vandiver, 1986), which is virtually lacking in Sèvres enamels, and their lower PbO contents. By removing mathematically the chromophorous oxides in each colour, the composition of the flux used was calculated in order to compare it to the theoretical composition of the Caillat recipe (Table 6). For the enamels, this table confirms the use of quite a pure blend of dominantly potash with minor soda, because of their richness in K_2O and the very low amounts of Na_2O, CaO and Fe_2O_3. However, the concentrations in SiO_2, K_2O and PbO differ far too much from the Caillat flux. This can be explained by a conspicuous K_2O evaporation in the fritting process, if Caillat flux was used. Such high K losses, however, are not to be expected during a fritting process. It is therefore more probable that the flux recipe changed over the years. This hypothesis is corroborated if the composition of the matrix glass enveloping the colour pigments is taken into account. In those times, however, opacifiers were typically made with the “anime” process, with excess Pb (Moretti & Hreglich, 1984a,b,c). Therefore, it cannot be ruled out that the PbO/SiO_2 ratios do not reflect the flux, but rather a modified ratio due to the addition of colourants and opacifiers. Neglecting the feeble possibility that the point analyses of this amorphous matrix could not be representative of the vitrous phase of the different enamels, three conclusions can be drawn from Table 6, considering primarily the calculated ternary compositions SiO_2, K_2O and PbO of the glassy matrices: (1) no colour matches the composition of Caillat's flux; (2) the purple differs significantly from the other colours by its high silica and low PbO; (3) the blue, yellow and (olive) green colours have distinct concentrations and PbO/SiO_2 ratios, but seem to form a more homogeneous group. However, no firm conclusion can be drawn as to the use of the same or different fluxes for these three colours.

According to the phase diagram $K_2O–PbO–SiO_2$ (Geller & Bunting, 1936), the melting temperature for the vitrous phase of the first three colours is between 730 and 779 °C, and much higher for the purple.

6.3.1. Blue (dentil comb and flower)

The deep dark blue overglaze dentil comb paint is macroscopically very similar to the “Beau bleu” or “Bleu No 3”, invented in 1751 by Jean Hellot (Préaud & d'Albis, 1991; D'Albis, 2015a). The surprising extremely high CoO concentrations (up to 10 mass% in individual analyses) accounts for the deep blue colour of the indented circular comb paint. The microstructure clearly shows the

Table 6. Theoretical composition of Caillat's flux, calculated from his recipe, and recalculated colour compositions without chromophores and in components of the ternary diagram K_2O–PbO–SiO_2 (Geller & Bunting, 1936). Mass%. G = glassy matrix, P = total paint.

An. no.	Type	Na_2O	MgO	Al_2O_3	SiO_2	K_2O	CaO	Fe_2O_3	PbO	PbO/SiO_2
Caillat's flux					52.8	16.0			31.2	1.7
Composition without chromophores										
Blue	P				30.4	6.9	0.9	0.5	61.3	
Yellow	P	1.1			35.5	4.0	0.4	1.2	57.8	
Green	P	0.8	0.1		31.4	3.7	1.4	1.6	61.0	
Blue	G				38.7	7.1	0.6	0.5	53.1	
Yellow	G	1.0			45.0	4.3	0.3	0.9	48.5	
Green	G	0.8	0.4		33.1	4.0	1.5	1.7	58.5	
Purple	P	1.6		0.3	53.7	5.2	0.7	0.3	38.2	
Ternary composition										
Blue	P				30.8	7.0			62.2	2.0
Yellow	P				36.3	4.2			59.5	1.6
Green	P				32.6	3.9			63.5	2.0
Blue	G				39.2	7.2			53.6	1.4
Yellow	G				46.1	4.4			49.5	1.1
Green	G				34.6	4.2			61.2	1.8
Purple	P				55.3	5.4			39.3	0.7

heterogeneity of this blue glass, which is composed of tiny angular fragments, welded together during the firing of the blue decoration. The shapes of such fragments are clearly visible in Fig. 4b. The globules and the dendrites of these vitrous fragments were already present before the last step in the preparation of the blue colour, *i.e.*, the crushing of the blue glass, because they are obviously broken (Figs. 4b and 5c). The spherical shape of the globules points to a liquid in equilibrium with another liquid, whereas the typical morphology of the dendrites can be explained by a fast crystallization in a quenched liquid. Therefore, two liquids must have coexisted during the synthesis of this colour, one rich in Co and Pb (which solidified as vitrous matrix) and another rich in Pb, As and silica (from which the globules and dendrites crystallized).

The association of Co with As and Ni gives some hints on the composition of the original raw materials of the blue paint, most probably Co arsenides (*e.g.*, smaltite, $CoAs_2$) or Co-As suphides (*e.g.*, cobaltite, CoAsS). The As–Co–Ni association is typical for primary ores from the Erzgebirge mines in Saxony (Gratuze *et al.*, 1996; Porter, 1997; Zucchiatti *et al.*, 2006). However, according to Hellot (Bourgeois, 1905), Sèvres used Co from a Spanish mine at Saint-Juan le Plan in the Pyrenees (Préaud & d'Albis, 1991). It would be interesting to know the chemical composition of this Co source in order to find out if the factory changed the supply for the blue enamel with evolving time. In any case, the analysed blue does not correspond exactly to the recipes for Hellot's blues no. 2 and 3 (Bourgeois, 1905). For these blues, cobalt ore is first oxidized to *zaffer* during 5 h at a moderate firing temperature until no As vapours are visible. In a second step, the *smalt*, *i.e.*, the blue glass, is obtained by melting a finely milled mix of 200 grains [One French or Paris grain = 53.11 mg; Anonymous, 1816] of this zaffer + 400 grains of Estampe sand [for blue no. 2, or 400 grains of quartz for blue no. 3] + 400 grains of potash + 20 grains of borax. This alkaline, Pb-free smalt is pounded in a glass mortar, milled to an extremely fine-grained powder on a glass slab. Other recipes mention different ratios as well as soda instead of potash (Préaud & d'Albis, 1991). Evidently, the richness in As_2O_3 and PbO of the analysed comb and flower blue, and their microstructure, exclude a synthesis following the abovementioned Hellot's blue no. 2 and no. 3 recipes. According to Table 6, no Caillat flux was used. Instead, the blue colour glass could have been produced by: (1) a milled blend of As-rich zaffer, sand or quartz, potash, soda and a Pb oxide, subsequently fused; or (2) a milled blend of As-rich zaffer with a transparent Si–K–Pb glass, thereafter molten. However, if one considers that Pb arsenate was deliberately added to enamels from Limoges (Röhrs, 2004), not all As in Sèvres' blue colour must necessarily be associated with the Co in zaffre, but some could be derived from a separate additive.

6.3.2. *Yellow and green*

The chromophorous pigment of the two colours is identical. It is not a simple Pb antimonate (calcined *Naples Yellow*) with the theoretical formula $Pb_2Sb_2O_7$, as assumed for similar enamels of Meissen (Domoney *et al.*, 2012) and of Du Paquier (Bezur & Casadio, 2009), but a more complex Pb–Sn–antimonate mixed crystal (Table 5). Its theoretical formula is controversial, either $Pb_2SbSnO_{6.5}$ (Turner & Rooksby, 1959; Cascales *et al.*, 1986), or $Pb_2Fe_{0.5}Sb_{1.5}O_{6.5}$ (Cascales *et al.*, 1985), or $Pb_2Sb_{2-x}Sn_xO_{7-x/2}$ (Hradil *et al.*, 2007). This yellow Pb–Sn–Sb pigment is stable up to 1100 °C (Dik *et al.*, 2005) and has been identified in opaque yellow coloured glasses (*e.g.*, Turner & Rooksby, 1959; Moretti & Hreglich, 1984a,b,c) or as a ceramic glaze pigment (Lazzarini & Hreglich, 1977; Sandalinas *et al.*, 2006; Duran & Castaing, 2008; Maggetti *et al.*, 2009; Miao *et al.*, 2010; Duran *et al.*, 2011; Rosi *et al.*, 2011). It was also found in enamels of the 11th c. CE (Turner & Rooksby, 1959). The Pb–Sb–Zn triple oxide darkens the yellow and gives an orange overtone (Rosi *et al.*, 2011).

Table 7. Origin of olive green ceramic colours and enamels as interactions of a coloured matrix glass with yellow pigments.

Glassy matrix		Yellow pigment			Literature
Co	Cu	Pb–Sb	Pb–Sn–Sb	Pb–Zn–Sb	
x		x			Colomban *et al.* (2001), Pappalardo *et al.* (2004), Dell'Aquila *et al.* (2006), Sendova *et al.* (2007)
x			x		Maggetti *et al.* (2009)
x				x	Coentro *et al.* (2012)
	x	x			Agosti *et al.* (1997), Alloin *et al.* (1997), Tite (2009), Beillard *et al.* (2001), Padeletti *et al.* (2006), Zucchiatti & Bouquillon (2011), Domoney *et al.* (2012), Holakooei (2014)
x	x		x		This work

These yellow coloured cristalline phases act on the one hand as opacifiers of the enamel and, on the other hand, as colouring agents. As for the yellow enamel, the analysis did not show any chemical colouring element in the matrix glass. The combination of such a colourless matrix glass with yellow crystals, results in an opaque yellow colour. But when a Pb-glass coloured either blue by Co or green by Cu, is blended with yellow crystals, an opaque, green colour is obtained. Such a combination of a cobalt blue or a copper green vitrous matrix with $Pb_2Sb_2O_7$ crystals, is common in ceramic colours and enamels, but the combination with other yellow pigments, such as Pb–Sb–Zn or the triple oxide Pb–Sb–Sn, can also be found (Table 7). Nevertheless, our study shows the first case in which the green opaque colour is the result of the combination of a vitrous Co + Cu matrix with yellow Pb–Sn–Sb pigments.

The microstructures of both colours show an excellent melting of their matrices. The Pb–Sn–Sb crystals have regular contours with sharp edges, indicating that they were in equilibrium with the surrounding liquid (Figs. 6 and 7). The monocrystals of cassiterite with irregular contours, which are found in the form of isolated particles or surrounded by Pb–Sn–Sb (Fig. 7c), are remains of the synthesis of these yellow pigments (*cf.* discussion in Maggetti *et al.*, 2009). The gas bubbles visible in these colours are most probably remains of the gum arabic and water “glue”, destroyed during the firing.

The “Books of Hellot” (Bourgeois, 1905) contain many recipes for yellow and green, some of them are a combination of Hellot's “Beau Bleu 2” with yellow $Pb_2Sb_2O_7$ crystals, but no recipe refers to the synthesis of mixed Pb–Sb–Sn crystals or the use of a Cu and Co-bearing glassy matrix. Evidently, the original formula evolved since 1751–1753.

6.3.3. Red

The high levels of Fe oxide (with no alumina) are indicative that this enamel was manufactured using Fe-rich compounds, mixing and crushing together ferrous oxide with four times its weight in flux (Préaud & d'Albis, 1991). These authors, in order to obtain Fe oxides of different shades, dried Fe sulphate, called “Vitriol de Mars”, at a temperature of 110°C and then oxidized it in a refractory recipient, at different temperatures, to obtain orange (*ca.* 650 °C), orange-red (650–700 °C) or violet (750–900 °C) colours. The sulphates were obtained by attacking metallic Fe, *e.g.*, needles and leaf springs, with sulphuric acid. The hue of the analysed plate was obtained by mixing powdered red glassy particles with milled yellow coloured frit grains, rich in Pb-antimonate crystals. The idiomorphic shapes of the latter suggest that they were in equilibrium with the surrounding liquid during their synthesis. However, it is puzzling and not well understood why the Sèvres factory used a Sb–Sn–Pb opacifier for the green and yellow enamels and a Sb–Pb opacifier for the red enamels. Such Pb antimonate crystals were also reported for red enamels in the Meissen and Du Paquier factories (Bezur & Casadio, 2009; Domoney *et al.*, 2012). The question what causes the red colour of the glassy matrix remains open; the absence of Cu and the richness in Fe could be indicative of the presence of nanoparticles of hematite (Fe_2O_3), not detectable by SEM-EDS.

6.3.4. Purple

This colour, the so-called Purple of Cassius is caused by colloidal Au nanoparticles. It can be prepared following different procedures (Krünitz, 1785). Normally, such particles are precipitated by separately dissolving Au and Sn in *aqua regia* (nitro-hydrochloric acid) and mixing both solutions, where Sn will reduce Au (Hunt, 1976, 1981; Carbert, 1980; D'Albis, 2003; Lowengard, 2006; Bishop & Sutton, 2010; Louis, 2012). Kunckel von Löwenstern (1716) claimed that it was not Andreas Cassius of Leyden who discovered this powerful colour for ruby glass and for pink to maroon overglaze enamels (Cassius, 1685), but Johann Rudolph Glauber (Glauber, 1659), see also Hunt (1976, 1981) and Bishop & Sutton (2010). However, the process of reducing Au by Sn was described much earlier in a 15th-century Bolognese manuscript of painter's recipes (Merrifield, 1849). Some of the 18th century treatises of preparing purple of Cassius are cited in Lowengard (2006). Purple of Cassius was used in the hard paste porcelain manufacture in Meissen and in the Du Paquier manufacture in Vienna. Accordingly, analyses of Meissen purple/pink overglaze enamels showed 2–11 mass% SnO_2 and 2–7 mass% Au_2O_3 (Domoney *et al.*, 2012), and the purple enamels on pieces from the Du

Paquier hard porcelain manufacture in Vienna contain significant amount of Au and Sn too (Bezur & Casadio, 2009). A similar technique was used for the so-called Kunckel's red glass (Kunckel, 1679; Kunckel von Löwenstern, 1716).

In contrast, the purple of the analysed plate contains neither Sn (nor does it contain Ag). This specific Sèvres purple is therefore not the “Purple of Cassius” of the hard paste porcelain enamels, but another variety, obtained with fulminating gold (Krünitz, 1785; Brongniart, 1802). It was invented in 1740 by Antoine Henri Taunay who sold this colour, a colloidal Au sol, to the Vincennes porcelain factory at an exorbitantly high price, until Sèvres bought Taunay's secret on June 11, 1754 for the incredible sum of 6,000 livres and an annual pension of 600 livres (D'Albis, 1994). Brongniart (1802) describes the preparation of the purple enamel as follows: *The soft paste porcelain carmine is made with slowly decomposed fulminating gold, and muriate of silver; it does not contain tin; which proves that the combination of the oxide of this metal with that of gold is not essential for the existence of the purple colour*. However, no Ag compound is necessary as described by Préaud & d'Albis (1991): *The Taunay process is similar to the procedure for ruby glass, made by mixing fulminating gold with different fluxes, then heated until the gold, finely divided and well spread throughout the mixture, gives its colour to the enamels. The fulminating gold was obtained by precipitating a yellow metal salt from the gold chloride into which ammonia had been poured. This mixture had to be handled with the greatest care as it could, on the spur of the moment, under a sudden heat burst, cause a detonation*. Taunay's technique consisted in adding Au chloride to an appropriate flux and in melting the blend in a crucible. At the end of the first melting, the resulting liquid is colourless. It is poured out onto a sheet of metal and, when heated once more, the melt will be coloured. Different shades were obtained according to different Au contents or by modifying the composition of the flux. For instance, pinks called “carmines” were produced by adding Ag salts to the mixture. In the French factories, the solution was mixed with the powdered flux, dried and ground to a fine enamel powder, which the painters used in a gum arabic watery suspension. The purple flux of Sèvres varies significantly from the fluxes of other enamels because of its lower content in PbO and its higher content in SiO_2 (Table 6). A modern synthesis of this colour was experimented with by Dargaud *et al.* (2007).

6.3.5. Violet

According to Préaud & d'Albis (1991), this colour was obtained by mixing two fluxes in equal parts with fulminating Au. But this was not the case for the analysed violet enamel, which was created, as revealed by the microtextural analysis, by a mechanical combination of two colours: the Co-coloured blue and the Au purple. Such a colour blend created a wide palette of bluish purple nuances, depending on the relative abundances of both primary colours. Similar mixtures of Cu and Co with purple of Cassius were reported for different hues of Du Paquier purple (Bezur & Casadio, 2009).

6.3.6. Gilt

If Au powder precipitates from an Au solution in *aqua regia* by ferrous sulphate, as Meissen did in the early years, the resulting tiny particles have spherical shapes, contrasting with the flat Au particles produced in Sèvres by the grinding of gold leaves in a viscous medium such as honey or gum arabic during 9–12 h (Hunt, 1979). Tiny particles are well suited for hard paste porcelain, but not for soft paste porcelain gilding, because they will dissolve quickly in the Pb and alkali-rich glaze. The grinding method supplied greater and more resistant particles. The results of the studied plate are quite in agreement with the traditional gilding method of the soft (frit) porcelain of Sèvres (*cf.* supra), because we can see in Fig. 13b the layering of thin Au sparkles, severely misshaped, either during the laying of the gold, or during the burnishing. The large gas bubbles under the gilding (Fig. 11a) show that the vapours produced during the firing of the gilding by the thermal decomposition of the *mordant* were unable to escape, as the layer of Au blocked their way, and they remained trapped as gas bubbles in the softened underlying enamel. The Au is much purer than the 80–94 mass% Au_2O_3 in Meissen (Domoney *et al.*, 2012). The presence of Fe is most probably purely accidental, as the Au on Vincennes-Sèvres soft paste porcelain was not obtained by precipitation with Fe sulphate from Au chloride. Obviously, the hematite burnishers used to polish the gold layer left behind some amounts of Fe_2O_3 (Préaud & d'Albis 1991).

7. Conclusions

This analysis of a Sèvres soft (frit) porcelain plate provides a glimpse into the manufacture of body, glaze, enamels and gilt produced in the Royal factory around 1781. Pure enamels, as well as mixed colours were in use at the painting department. The compositions and the microstructures are broadly consistent with 18th-century technologies described by contemporary documents to be found in the archives of the manufacture (Bourgeois, 1905; Y 49). The individual overglaze enamels are compositionally dissimilar. Obviously, synthesis of the colours occurred using individual frits and not only one base frit formulation (Caillat's flux) as usually assumed. Modifications of the original colour recipes must therefore have occurred in the 30 years since Hellot's reports (1751–1753), as recorded in the manuscripts of Pierre-Joseph Macquer (Bourgeois, 1905). Though the analysis of a single object allows to draw only limited conclusions, future technical studies of additional dated pieces as well as meticulous searches in the archives of Sèvres are needed to explore whether the paste, glaze and overglaze enamel colour recipes evolved between 1740 and 1804, that is, the time span when soft (frit) porcelain was produced in Vincennes/Sèvres (1740–1804).

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