ANTIMONATE OPAQUE GLAZE COLOURS FROM THE FAIENCE MANUFACTURE OF LE BOIS D'ÉPENSE (19TH CENTURY, NORTHEASTERN FRANCE)*

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Three types of antimony-based, opaque ceramic colours were used in the faience workshop of Le Bois d'Épense during the first decades of the 19th century; that is, yellow, tawny and green. Yellow is generated by lead antimonate crystals (Naples Yellow), which are incorporated into an uncoloured glass matrix. According to SEM–EDS measurements, these pigments contain iron. The tawny colour is the optical result of the combined presence of similar yellow, iron-bearing lead antimonate particles in a Fe-rich, brownish glass matrix. The green opaque colour is produced by the combination of a blue cobalt glass and yellow $Pb–Sn–Fe$-antimonate crystals. Cores of zoned pigments lighten the recipes, according to which the pigments were produced. First, they were synthesized by calcination, ground and then mixed with a colourless, brown or blue glass powder. The resulting powder mixture was added to a liquid agent and used as high-temperature ceramic colour.

KEYWORDS: FRANCE, LE BOIS D'ÉPENSE, FAIENCE, GLAZE, TIN OXIDE, LEAD ANTIMONATE, LEAD–TIN ANTIMONATE, OPAQUE CERAMIC COLOUR

THE FRENCH FAIENCE TECHNOLOGY OF THE 18TH AND 19TH CENTURIES

The manufacturing techniques of tin-opacified potteries—for example, faiences—are well known thanks to contemporary documents published by Diderot and d'Alembert (1751–80), Bastenaire-Daudenart (1828) and Brongniart (1877). More recent publications by Deck (1903), Munier (1957), Rosen (1995), Peiffer (2000), Maggetti (2007) and the edition of the *Caussy* manuscript by de la Hubaudière and Soudée Lacombe (2007) complete the information.

In the 18th and 19th centuries, the CaO-rich faience body was fired at least twice. The first firing, named the biscuit firing, was followed by a second, high-temperature firing, during which the tin-opacified glaze was vitrified and the high-temperature colours were fixed on the decorated pieces. When a biscuit fired body, coated with a watery SnO_2-rich glaze powder, is fired in the second firing, the dilatation coefficients of the biscuit ware and the resulting glassy coating need to be as close as possible (Munier 1957; Tite *et al.* 1998). If this is not the case, the glaze may craze or flake off.

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Styles of faience decoration in the 18th and 19th centuries

High-temperature decoration (grand feu decoration) In this technique, painters used to work directly on the powdery, very fragile surface of the unfired glaze. Therefore, they needed to have a steady hand and be well prepared for the task, because a wrong brushstroke was difficult to repair. Considering the high temperature and the extended period of time required for firing, these colours fuse very strongly with the glaze. Not many colours are able to resist such high temperatures, and the so-called high temperature palette is therefore limited to only a few colours: blue, green, brown to purple, yellow, black, red, white and pink. The first three examples are transparent and their coloration is due to the dissolved presence of ions of cobalt in the case of blue, of copper in the case of green and of manganese in the case of brown to purple. Yellow, a lead antimonate also known as *Naples Yellow* (Clark *et al.* 1995), is an ancient opaque pigment, which was already used in the Near East in the early second millennium BC (Wainwright *et al.* 1986). Black is often generated by manganese and iron oxide crystals, occurring either alone or mixed. Red is a delicate colour, because its stability in high firing temperatures is low: therefore it is little used in faience making. Potters had access to calcined iron rich sands as the *Armenian bolus* and later to the *Rouge de Thiviers* (Rosen 1995; Rosen *et al.* 2006). White is a tin-opacified lead glaze, very rich in tin oxide—used, for example, in the *bianco sopra bianco* technique. Pink is produced after 1835 from a combination of chromium and tin oxides (Brongniart 1877; Caiger-Smith 1973; Blondel 2001; D'Albis 2003; Hamer and Hamer 2004).

Glaze painting (on-glaze decoration) This muffle fire decoration technique was introduced into the French faience technologies around 1740 by Paul Hannong of Strasbourg (Blondel 2001). It consists in applying the paints on the fired glaze, previously decorated or not, before firing it for a third time, a process that will fix this kind of decoration.

Application The powdered ceramic colours were mixed with water in small bowls. It was possible to use powder of a pure tone or mixtures thereof—for instance, blue and green—which lead to different colorations. During firing, the powder melted and combined with the fused glaze.

Technology of glaze colours

The ceramic colours consist of coloured glass, which has been finely ground, so that even very fine strokes can be executed. The colour results from the addition of metal oxide colorants to an uncoloured flux (ionic coloration) or from the incorporation of natural or synthetic crystals into an uncoloured or coloured flux (opaque colours). More rarely, the colour is due to the presence of a colloidal suspension of Cu, Ag and Au (lustre). The ceramic colours can therefore be divided into two major categories: transparent colours and opaque colours.

Brongniart (1877) dedicates a considerable part of his essay to the preparation technique of pigments and ceramic colouring agents, thus indicating the importance that he attaches to this technological aspect. During the 18th and the early 19th centuries, it was commonplace for each workshop to prepare their own colours and to keep their secrets jealously. Archives and publications mention countless recipes and numerous trials, some of which were more and others less successful. Archaeological excavations have unearthed the results on such test pieces; that is, in the form of small goblets or ceramic objects. The secrecy around disclosing
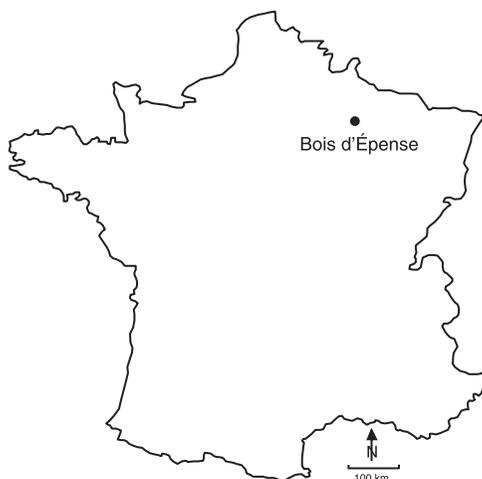
Figure 1 *The location of the manufacture at Le Bois d'Épense.*

the recipes becomes understandable, because the colours, consisting of transparent or opaque vitreous powders, had to have dilatation coefficients comparable amongst them, the glaze and the ceramic body. Objects destined for culinary purposes required colours whose chemical composition was resistant to liquids such as vinegar, tea or coffee. Besides, these colours needed to be very resistant to abrasion, in order to avoid scratching through metallic objects, such as knives and forks. It was not easy to combine all these requirements, so it is understandable that each workshop put a lot of time, effort and money into refining their recipes. Local and foreign resources were used to prepare clays, glazes and colours, continuously taking into account their physical and chemical properties.

THE FAIENCE MANUFACTURE OF LE BOIS D'ÉPENSE

The tin-glaze earthenware or faience manufacture called *Le Bois d'Épense*, situated close to the small town of *Les Islettes*, was located in the north-east of France, right on the boundary between the present Champagne–Ardenne and Lorraine regions (Fig. 1). It was the most important among a dozen similar manufactures belonging to the Argonne group. The Bois d'Épense manufacture, first established in 1735 by Henri-Louis Leclerc, soon closed down in 1742. The activity proper only started in 1764, when François Bernard, then director of another manufacture in Clermont-en-Argonne, situated just a few miles away, transferred it to the other side of the French border to Le Bois d'Épense, where the taxes were less heavy, and began to produce *grand feu* polychrome or high-fired faience as well as cooking ware. At its early stage, the manufacture employed 30 workers. With the parallel development of the equally successful creamware production, the 1780s were particularly prosperous, with 80 employees, and the manufacture expanded regularly until Bernard's death in 1800, even attracting workers away from neighbouring manufactures. After 1800, François Bernard's son left his wife Marie Parpaite to rule the manufacture, which was by far the largest in the east of France. During all this time, 200 people are said to have been employed there, producing all sorts of faience and creamware until the late 1810s. Marie Parpaite died in 1836, and her three

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children continued the production. When they sold the manufacture to the Godechal brothers in 1840, 80 people were still at work there. In 1848, what can largely be seen as a family business finally closed down for good, at the same time as a great many manufactures that had started in the middle of the 18th century. Until very recently, only five rather different marked pieces of ceramics were known to bear witness to this huge amount of production. But fortunately the present owners of the site have picked up a considerable quantity of scattered sherds, and archaeological excavations were carried out there in 1993 (Thévenard and Copret 1993), providing us with the necessary reference material and giving us the opportunity for a more complete survey (Rosen 2007).

So far, the chemical and crystallographic characterization of the high-temperature colours, applied to opacified glazes, has been subject to only few investigations (see below). Maggetti *et al.* (2007) provide information on the high-temperature colours blue, purple, black and red as used in the faience workshop of Les Bois d'Épense during the 19th century. In this study, the opaque colours yellow, tawny and green will be analysed in detail.

SAMPLING AND ANALYTICAL PROCEDURE

The 10 analysed samples are surface findings and belong to faiences produced during the first half of the 19th century. The opaque colours consist of two yellow (BEI 3Y, BEI 54Y), three tawny (BEI 3T, BEI 5T, BEI 6T) and five green (BEI 3G, BEI 5G, BEI 6G, BEI 7G, BEI 56G) samples. Identification of the pigment phases relied on semi-quantitative analyses with a scanning electron microscope (SEM). Backscattered electron images (BSE) were collected with a scintillator type detector out of polished samples, using a FEI XL30 Sirion FEG 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. The bulk chemical compositions of the opaque colours 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. EDS analyses were also run to obtain qualitative chemical information on the colouring inclusions. These data are presented in Table 1. Standardless quantification was performed for the tin-opacified glazes and the coloured glasses, using an EDAX-ZAF correction procedure of the intensities. Spot analyses (2 μm diameter) of homogeneous areas, without visible crystals, were performed for the determination of the glass matrix composition (Table 1). Larger areas (20×15 to 60×50 μm) containing the pigments and the glass matrix—that is, bulk analyses—were measured at different points and averaged to evaluate the chemical composition of the bulk opaque glazes (Table 1). The detection limits for most elements were about 0.2 wt%. The reliability of the results was proven by measuring well-known glass standards (DLH2, Corning BCD and Obsidian). The relative mean deviation for major and minor oxide components was 2% for concentrations in the range of 20–100 wt%, 4% for 5–20 wt%, 10–20% for 1–5 wt% and > 50% for > 1 wt%.

RESULTS

Antimonate-opacified colours

Opaque yellow   In the yellow paintings, *Naples Yellow* ($Pb_2Sb_2O_7$) was identified as the colouring and opacifying pigment. Qualitative measurements of these particles always exhibit iron as a minor component (Fig. 2, BEI 3Y). Therefore, these grains do not have the stoichiometric

Table 1 Average analyses by SEM–EDS of opaque glazes from the faïence factory at Le Bois d'Épense (wt%): n, number of individual analyses of different glazes in the average; analyses of the tin-opacified glaze from Maggetti et al. (2007)

|	n	Na_2O	MgO	Al_2O_3	SiO_2	K_2O	SnO_2	CaO	FeO	TiO_2	CoO	PbO	SrO	CuO	Sb_2O_3	MnO	Cl	NiO	ZnO	BaO	As_2O_3
Glass matrix																					
Opaque yellow	5	2.6	0.2	4.1	42.8	2.2	2.7	1.3	0.8			41.1			0.7		0.5				
Opaque tawny	14	2.6	0.2	2.3	43.6	2.9	1.2	0.9	3.0			41.2	0.2		0.5		0.1				0.8
Opaque green	14	2.5	0.2	3.2	45.1	3.4	1.1	0.5	1.1		0.5	38.8	1.2	0.2	0.1	0.1	0.2	0.6	0.1	0.2	0.3
Bulk																					
Opaque yellow	3	2.4		3.3	41.1	1.5	13.3	1.4	0.7			31.6			3.4		0.1				
Opaque tawny	9	1.9		2.3	31.9	2.2	1.8	1.2	3.7			42.6	0.5	0.1	10.1	0.1	0.1				1.4
Opaque green	15	2.1	0.1	2.9	42.5	2.5	5.8	0.9	0.9	0.1	0.4	36.4	0.9	0.2	1.7	0.1	0.3	0.8	0.1	0.2	0.6
Tin-opacified lead-alkali glaze																					
Glass matrix	42	2.4		5.1	49.0	4.4	2.2	0.5	0.5		0.2	34.1					0.7				
Bulk	23	2.2		4.9	46.0	4.0	9.3	0.6	0.5			31.5					0.6				

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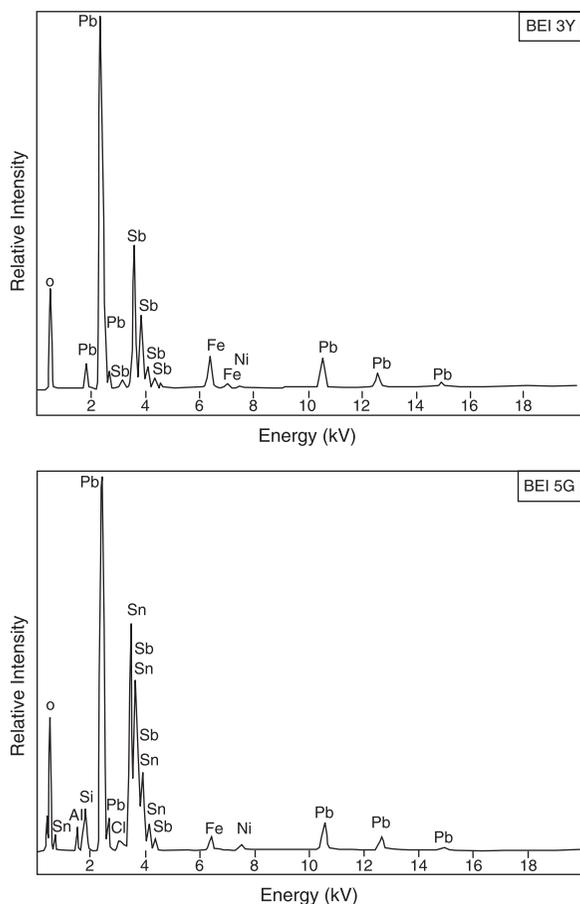
Figure 2   *SEM–EDS spot analyses of the pigments in an opaque yellow (BEI 3Y) and an opaque green painting (BEI 5G).*

composition of 58 wt% PbO and 42 wt% Sb_2O_5 with a PbO/Sb_2O_5 ratio of 1.38 (Caley 1962; Kaczmarczyk and Hedges 1983; Lilyquist and Brill 1993; Shortland 2000, 2002), but correspond to approximately 65% PbO, 30% Sb_2O_3 and 5% FeO. Figure 3 shows that pigment grains differ strongly in size, form and sphericity. Coarse particles may be zoned and show a homogenous Sb–Fe oxide core with a rim consisting of small *Naples Yellow* grains (Fig. 3(c)). Some cassiterites can be seen in the yellow painting (Fig. 3(b)). In the glass matrix, SiO_2 and PbO occur in approximately equal parts, along with a few wt% of Al_2O_3, SnO_2, Na_2O, K_2O and CaO (Table 1).

Opaque tawny   The opacity of this painting glaze is caused by small particles of lead anti-monate yellow within the glass (Fig. 4). The Fe-contents of these crystals are similar to those in the opaque yellow glaze. The particles are dispersed inhomogeneously: their grain size and grain form differ very strongly and they have angular edges. In some cases, zoned pigments with Sb–Fe oxide cores (approximately 30 wt% FeO, 70 wt% Sb_2O_3) and Pb–Fe–Sb rims (Figs 4(c) and 5) can be observed. Chemically, these rims correspond to iron-bearing lead
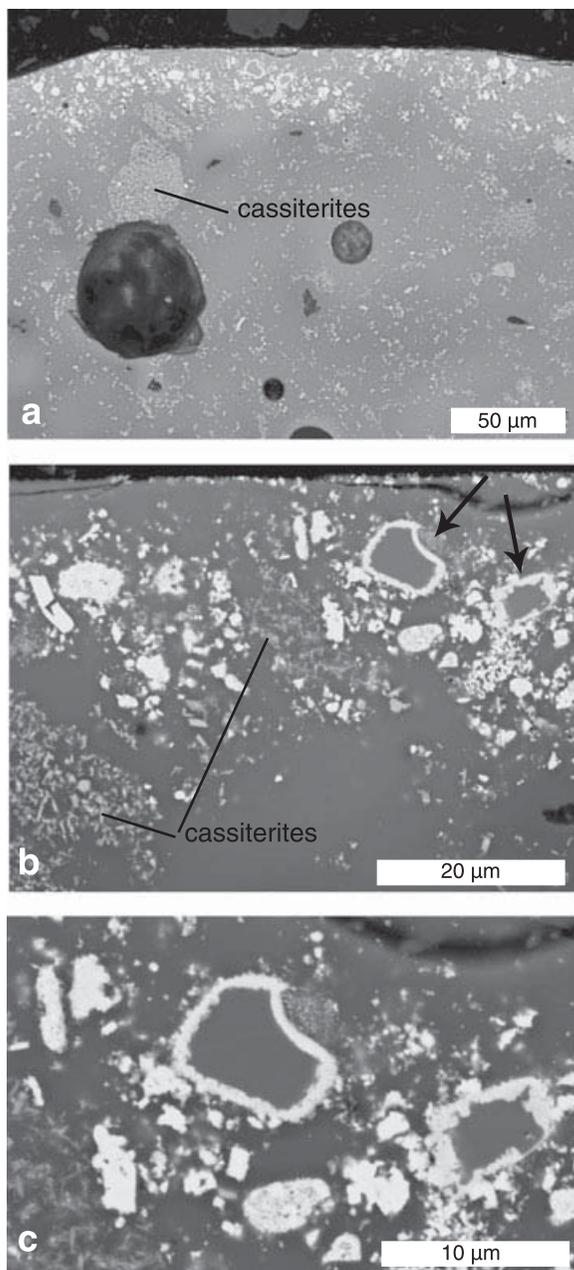
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Figure 3 *Backscattered SEM micrographs of a yellow painting (BEI 54Y). (a) The tiny lead antimonate paint layer is visible on top of the tin-opacified glaze. The glaze shows a heterogeneous distribution of the cassiterite particles. (b) In the yellow layer, two zoned particles can be seen (arrows). (c) The zoned particles show an iron-bearing antimony oxide core surrounded by a small rim of Naples Yellow crystals.*
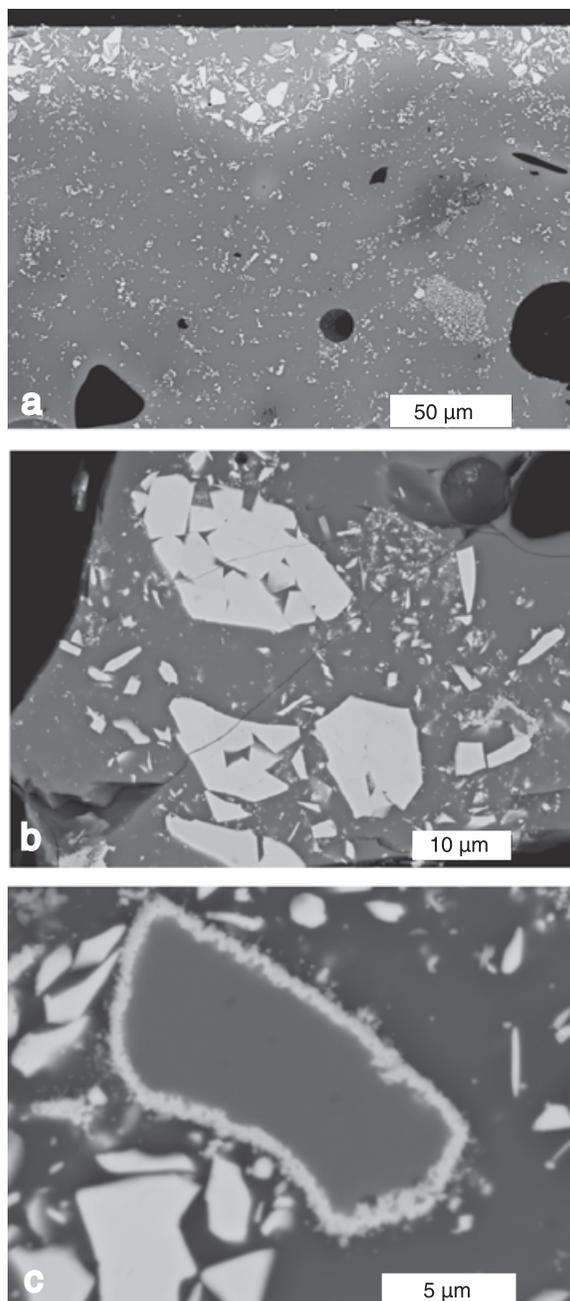
Figure 4 *Backscattered SEM micrographs of tawny paintings. (a) Tin-opacified lead-alkali glaze (below) and lead antimonate particles (above), separated by a wavy borderline (BEI 5T). (b) Chemically homogeneous lead antimonate crystals (BEI 3T). (c) A zoned particle with an Fe–Sb oxide core and a Pb–Sb–Fe oxide rim (BEI 6T).*
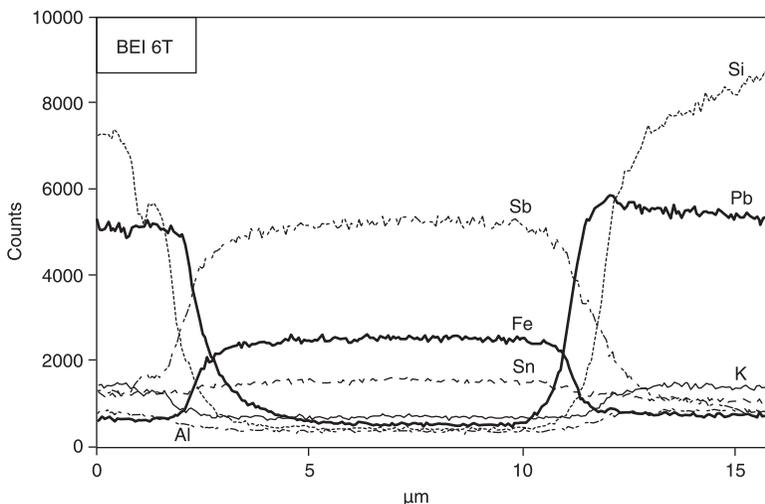
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Figure 5 *A SEM–EDS profile through the zoned pigment from Figure 4 (c).*

antimonate crystals. The glass matrix does not differ significantly from the previous one; however, it shows higher Fe and As, but lower Al and Sn contents (Table 1).

Opaque green This glass is opacified by crystals, which can be described as a solid solution of $Pb_2Sn_2O_6$–$Pb_2Sb_2O_7$ (Fig. 2, BEI 5G). No chromium was detected. Grain size and grain form differ very strongly among the specimens (Fig. 6). The edges are mainly angular. In the green strokes, a few coarse cassiterites with sharp edges can be observed, along with a lot of small, roundish SiO_2-crystals (most probably partially dissolved quartz). There are roundish cassiterite crystals, which are coated by a small-grained Pb–Sn–Fe-antimonate rim (Fig. 6 (c)), as well as mixed crystals, which appear to be homogeneous. The SiO_2–PbO ratio in the glass matrix and the amount of the other oxides vary relatively strongly among the specimens. But the glass phase always contains a considerable amount of cobalt, nickel and arsenic (Table 1). This glass is characterized by a small amount of zinc, which is lacking in the yellow and tawny opaque colours. The amount of cobalt dissolved in the glass is sufficient to turn it blue.

Tin-opacified lead-alkali glaze

The thickness of these glazes ranges from 200 to 500 μm. They contain a few rounded quartz crystals and often show a transformation to a prismatic SiO_2 phase—most probably cristobalite, according to Molera *et al.* (1999) and Fortina *et al.* (2005)—in the rim, caused by firing. Bubbles occur in some rare cases. The tin oxide particles show a heterogeneous distribution and form small clusters (Figs 3 (a), 4 (a) and 6 (a)). The glaze/body interface is sharp (Maggetti *et al.* 2007). The absence of such an interface is consistent with the application of the liquid glaze to an already fired body (Molera *et al.* 2001). Area measurements show that all tin-opacified glazes are SiO_2–PbO glazes (a total of ~80 wt% for both oxides) containing about 9 wt% SnO_2, with other oxides occurring in concentrations < 5 wt% (Table 1). Spot analyses of the pure glass matrix shows SnO_2 values of about 2 wt%.
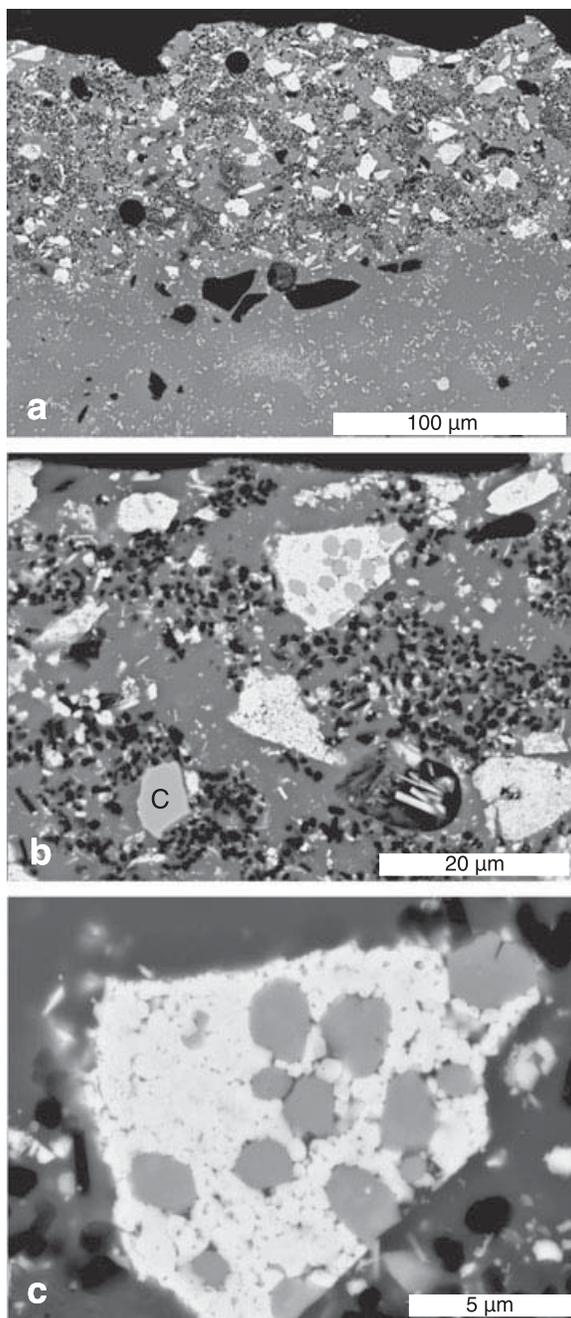
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Figure 6 *Backscattered SEM micrographs of a green painting (BEI 56G). (a) Lead–tin antimonate particles in a green opaque painting (above) with, in black, small rounded SiO₂ phases (probably quartzes). The border to the tin-opacified glaze is wavy and not very sharp. The glaze contains some former angular quartzes with rounded edges (black). (b) Fragments of agglomerated pigment particles, showing in some cases rounded cassiterite inclusions (grey). On the lower left, a large cassiterite (C) is visible. (c) A single opaque pigment particle, showing rounded grey cassiterite crystals embedded in a granular matrix of lead–tin antimonate grains.*

DISCUSSION

Yellow lead antimonate, lead stannate and lead–tin antimonate pigments

Typology Throughout the centuries, four yellow lead mixtures were used in painting and glass manufacture. These are: (1) the cubic lead antimonate yellow (= the mineral *bindheimite*), with a theoretical formula $Pb_2Sb_2O_7$ (e.g., Turner and Rooksby 1959; Rooksby 1964; Moretti and Hreglich 1984a,c; Wainwright *et al.* 1986; Clark *et al.* 1995; Mass *et al.* 2002; Shortland 2002; Dik *et al.* 2005—and literature therein); (2) the orthorhombic lead–tin yellow I, with the formula Pb_2SnO_4 (e.g., Kühn 1968, 1994; Martin and Duval 1990; Clark *et al.* 1995; Ravaud *et al.* 1998—and literature therein); (3) the cubic lead–tin yellow II, with the formula $PbSn_{1-x}Si_xO_3$ (e.g., Rooksby 1964; Kühn 1968, 1994; Martin and Duval 1990; Clark *et al.* 1995; Heck and Hoffmann 2000, 2002; Heck *et al.* 2003; Tite *et al.* 2008—and literature therein); and (4) the cubic lead–tin antimonate yellow—that is, a Pb–Sn–Sb solid solution, with the formula $Pb_2Sb_{2-x}Sn_xO_{6.5}$ (e.g., Turner and Rooksby 1959; Moretti and Hreglich 1984a–c; Ravaud *et al.* 1998; Dik *et al.* 2005; Sandalinas *et al.* 2006; Hradil *et al.* 2007—and literature therein).

Use as ceramic colours Lead antimonate has been identified as the most commonly used colouring and opacifying agent in ceramic high-temperature glazes (Lazzarini and Hreglich 1977; Wainwright *et al.* 1986; Keblow Bernsted 2003; Sakellariou *et al.* 2004; Padilla *et al.* 2005). However, of both lead–tin yellows, only lead–tin yellow II was detected (Lazzarini and Hreglich 1977, 1978; Keblow Bernsted 2003). This is hardly surprising, because lead stannate of either form is usually thermally stable only up to *c.* 900–950°C (Clark *et al.* 1995; Tite *et al.* 2008). In a second high-temperature faience firing, however, temperatures range from 950 to 1050°C. They therefore significantly exceed the upper stability temperature of both lead–tin yellows. So far, the fourth yellow pigment—that is, lead–tin antimonate—has been identified as a glaze colour only by Lazzarini and Hreglich (1977) and Sandalinas *et al.* (2006). As shown by Dik *et al.* (2005), lead antimonate and lead–tin antimonate are stable up to 1100°C. Consequently, they easily withstand the temperatures of the second firing. Therefore, the lead–tin antimonate yellow pigment used at the workshop of Bois d'Épense provides the third evidence of its use as a ceramic high-temperature colour.

Technology

Strongly coloured opaque ceramic colours can be produced in two ways (Fig. 7). The first step is common for either colour and consists of the synthesis of the pigment by calcination in a furnace. The resulting product is cooled, ground and (method A) mixed with raw glass batch materials, then fired at high temperatures for some hours, cooled and crushed to obtain a homogeneous, ceramic opaque colour, or (method B) mixed with already prepared, powdered glass to form a ceramic opaque colour. In the first case, the pigments are subjected to high temperatures for an extended period of time and important dissolution phenomena should be expected. It is therefore likely that the angular pigment grains would transform into more spherical fragments, or into one with rounded edges. In the second case, the pigments are fixed into the matrix glass only in the high-temperature ceramic firing; consequently, less time remains for the pigments to react with the matrix glass. It may therefore be expected that the angular grain forms tend to be preserved. Each of the two processes can be differentiated by means of microscopic analysis.
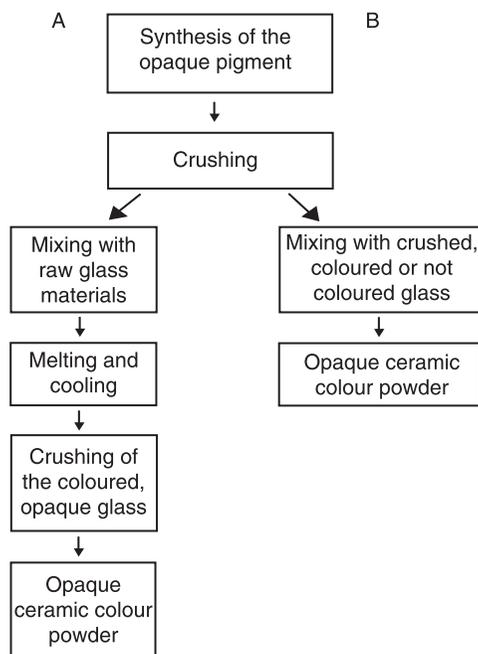
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Figure 7   *Production steps for opaque ceramic colours.*

Lead-antimonate-opacified ceramic colours When producing lead antimonate synthetically, consideration needs to be given to the question of whether the initial material is used as sulphides, oxides or metals. Shortland (2002) puts forward a theoretical point of view on the roasting of the minerals galena (PbS) and stibnite (Sb_2S_3) in the presence of excess lead, which leads to the formation of PbO and Sb_2O_5. Both finally react to the final lead antimonate following the reaction $2PbO + Sb_2O_5 = 2Pb_2Sb_2O_7$. Rooksby (1964) obtained lead antimonate by mixing Pb and Sb oxides and calcinating at 900°C. In 43 Venetian glass recipe manuscripts from the 17th and 18th centuries, Moretti and Hreglich (1984a–c) found 15 Pb–Sb-yellow pigment recipes. Interestingly, all of them account for approximately 6–7 wt% Fe_2O_3. Piccol-passo (1557–8: see also Rakham and van De Put 1934; Lightbown and Caiger-Smith 1980; L'Hôte *et al.* 2007) mentions a similar Fe addition in one of his yellow recipes. Venetian recipes describe the production of yellow glasses according to two steps. In the first, the opaque pigment is synthesized by calcination; and in the second, the opaque glass is produced. In their detailed experiments, Moretti and Hreglich (1984a–c) followed the 17th- and 18th-century recipes. First, lead antimonate was synthesized by calcination of minium + anti-mony sulphide + iron oxide at 750°C for 5 h. Next, minium (Pb_3O_4) and quartz sand were added to the product, which was subsequently heated in a crucible at 1000°C for 5 h. The resulting glass was not yellow, but an opaque brown-to-yellow colour, which is not surprising considering the high Fe content. Moretti and Hreglich have not analysed the crystals further; nor have they discussed the possible incorporation of iron into the structure of the *Naples*

Yellow crystals. They link the brown coloration to the iron contained in the glass. Furthermore, the authors investigated the question of whether, during the 17th and 18th centuries, the yellow pigment was produced from sulphides, oxides or metals. In the experiment, three theoretical mixtures of *Naples Yellow* were calcined at 900°C: (1) minium + Sb_2S_3 (stibnite); (2) minium + Sb_2O_3; and (3) Pb metallic + Sb metallic. The best outcome—that is, a rich yellow–orange colour and a homogeneous product—was obtained from the mixture containing both oxides. The sulphide experiment resulted in an inhomogeneous product of a slightly light yellow colour. In the metal experiment, part of the Sb evaporated, which led to an inhomogeneous and hard product. Test series run by Dik *et al.* (2005) confirm the superiority of the oxide mixtures in comparison to the other two. Almost pure (> 95%) lead antimonate yellow was produced by calcination of PbO with Sb_2O_3 in the presence of NaCl at temperatures starting from 750°C. It is the so-called *potter's yellow* I according to the *Mariani recipe*, an early 17th-century Italian treatise on miniature painting technique, compiled by the miniaturist Valerio Mariani da Pesaro (Dik *et al.* 2005). As described previously by Zerr and Rübencamp (1922), several shades of yellow were obtained, depending on the temperature. If NaCl is replaced with K-tartrate in the mixture, an almost pure (> 95%) lead antimonate yellow (*Mariani's potter's yellow II*) is obtained at temperatures above 900°C. Type I as well as type II remains stable up to 1100°C. Piccolpasso (1557–8) indicates several recipes for the syntheses of these pigments. Sakellariou *et al.* (2004) experimented with one of them, mixing one part massicot (PbO) to three parts Sb_2O_3 and firing the ground mixtures for 5 h at three temperatures: 800, 900 and 1100°C. The best result, a rich yellow colour, was obtained at the highest temperature. The first Northern European recipe for the production of *Naples Yellow* was presented in the 18th century by the French scientist Fougeroux de Bondaroy (1769), a few years after the publication of the Italian production process (Passeri 1758). It differs from the earlier Italian recipes as it includes potassium alum, $KAl(SO_4)_2 \cdot 12H_2O$ as an ingredient, resulting in the formation of $K_2Pb(SO_4)_2$ as an additional minor phase (Dik *et al.* 2006). The occurrence of this sulphate in paint samples will be helpful for authenticity and technological studies (Dik *et al.* 2006), but not for ceramics, due to its destruction during the faience firing. Different *Naples Yellows* from 19th-century pigment collections were examined by Dik *et al.* (2002). The chemical composition and the structure of these pigments show great variations, as indicated by the 19th-century literature, which shows a great diversity of the recipes for lead antimonate yellow. To confirm this, Brongniart (1877) presented 10 *Naples Yellow* recipes used at the porcelain manufacture of Sèvres. The major constituents are potassium antimonate and lead oxide, mixed with different additions such as zinc carbonate and iron oxide. Astonishingly, iron oxide appears in almost all of the recipes (in 8 of 10).

Lead–tin-antimonate opacified ceramic colours   In 43 Venetian glass recipe manuscripts from the 17th and 18th centuries, Moretti and Hreglich (1984a–c) found a total of 64 Pb–Sb–Sn yellow pigment recipes. In 26 recipes Fe oxide is added; eight recipes call for ZnO instead of iron oxide, and in 38 recipes both oxides are absent. In an experiment, three recipes were reproduced based on the average composition of these three types of recipe. First, the pigments were made by calcination, then opaque glass was produced. The pigment with Fe resulted in an ochre colour, the Zn-doped pigment in a golden colour and the Fe- and Zn-free pigment in a yellow colour of the opaque glass. In each of the three cases, the pigment is a cubic Pb–Sb–Sn mixed crystal. The $Pb_2Sb_2O_7$–$Pb_2Sn_2O_6$ solid solution—that is, the *Mariani's potter's yellow type III* (Dik *et al.* 2005)—was synthesized by these authors by heating a mixture of PbO + Sb_2O_3 + SnO_2 + NaCl, in the weight ratio mentioned in the Mariani recipe.

More than 90% of pure $Pb_2Sb_{2-x}Sn_xO_{6.5}$ was obtained above 750°C, with relict SnO_2 and NaCl. This pigment is stable up to 1100°C. Other recipes for the production of Pb-Sn-Sb yellows, with silica and zinc oxides, are reported in the *Ricettario Darduin* ot Murano (Zecchin 1986; Sandalinas *et al.* 2006), with successful syntheses of such pigments by Sandalinas and Ruiz-Moreno (2004) and Hradil *et al.* (2007).

The technology of the opaque ceramic colours from the faience factory at Le Bois d'Épense

Yellow and tawny ceramic colours   The opaque pigment of both colours is the yellow lead antimonate. The antimony oxide cores of the zoned pigments are the result of incomplete calcination reactions and show that synthesis occurred with oxides, not sulphides.

The yellow pigment of the workshop at Le Bois d'Épense always contains some iron, as for majolica (Bultrini *et al.* 2006). This may indicate that the pigment has been produced in analogy to Piccolpasso's recipes and the Venetian 'anime' (Moretti and Hreglich 1984a–c) or to mostly all Sèvres recipes (Brongniart 1877), which contain some iron in their initial mixture, even when the recipe does not state explicitly why iron oxide is being added. However, it is also possible that the Fe concentrations in the antimony oxide cores, which may originate from ferrous stibnites, provide sufficient evidence to explain the iron content of the end-product. Zinc was not detected by SEM–EDS. Therefore, this result does not match the *Naples Yellow* recipe of the Le Bois d'Épense chemist Gabriel Michel of the years 1800–1820, which shows zinc oxide as a minor constituent (Châtelet w.d.). The angular outline, the inhomogeneity in grain size and grain form, and the rarely rounded edges of the pigments, along with the low Sb concentrations in the glass matrix, indicate that the powdered lead antimonate grains reacted only briefly with the glass. This indicates production method B. In a first step, the lead antimonate was generated by calcination. The powdered opacifying agent was then added to an independently produced raw glass powder. This mixture was used as a ceramic colour. In the high-temperature firing, the raw glass melted, corroded the lead antimonate particles only briefly and incorporated some percentage of Sb. If the glass was colourless, opaque yellow was the result. For a slight Fe-content of the glass, the oxidizing faience firing would lead to a mixed colour, due to the combination of yellow crystals in a brown glass matrix, thus appearing tawny to the human eye. Spot analyses show some chemical similarity between the two matrix glasses, even though the brown glass differs from the uncoloured one, for example, in its arsenic, as well as in its iron content.

Green colour   The opaque pigment is a complex, lead–tin-antimonate mixed crystal and corresponds to the *potter's yellow type III* of Mariani (Dik *et al.* 2005). Large, isolated cassiterites and pigment clusters with incorporated cassiterites can be interpreted as relicts from the pigment production, according to the experimental reproduction of the Mariani recipe by Dik *et al.* (2005). For this colour as well as for others, the angular pigment outlines indicate that the opaque glass production occurred according to method B. The matrix glass into which the mixed crystals are incorporated differs very strongly, both morphologically and chemically, from the initial glass of the two other colours, because it contains a large amount of roundish quartz crystals, which were not fully melted during rough glass production. Zinc was used in minor amounts in the recipe of this colour, as shown by SEM–EDS. The green opaque colour is generated by the combination of a blue cobalt glass and yellow Pb–Sn–Fe-antimonate crystals. The possibility of such a mixed colour has been postulated by Shortland (2002) for Early Egyptian green opaque glasses and by Dell'Aquila *et al.* (2007) for Italian majolica.

CONCLUSION

Three high-temperature, opaque ceramic colours were in use at the Le Bois d'Épense faience factory during the early 19th century. These colours are a combination of yellow crystals and coloured or uncoloured glasses. The crystals contain lead and antimony, with or without tin. Lead stannate was not used, due to its instability at the high temperatures of the second faience firing. Yellow opaque colours were prepared by mixing lead antimonate particles with a colourless glass, opaque tawny by mixing lead antimonate particles with an iron-bearing, brown glass and opaque green by mixing lead–tin antimonate particles with a cobalt-bearing, blue glass. It is interesting to note that the manufacture did not use the powerful copper green in high-fire decorations, as other manufactures did. This was probably to avoid important bleeding of dissolved copper. In muffle fire decoration, however, copper green was profusely used. The feared bleeding phenomena were less important, due to the lower temperatures of this third faience firing.

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