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Technological aspects of an early 19th c. English and French white earthenware assemblage from Bern (Switzerland)

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Abstract

Ceramic material from the Brunneggshalde town-waste-dump of Berne, the capital of Switzerland (infilling 1787-1832) encompasses 1% white earthenwares with impressed stamps of English, French and Swiss manufactures. All stamped English (WEDGWOOD, n = 3) and French (CREIL, n = 2; NIDERVILLER n = 1) material was analyzed by XRF, XRD, SEM-BSE and SEM-EDS. The Wedgwood pottery is rich in coarse SiO₂ grains, interpreted as crushed flint fragments, with abundant signs of a high temperature treatment. They lay in a finely grained siliceous-aluminous matrix, in one specimen together with grog. The Creil material is very similar, but lacks grog. The English white earthenware differs chemically from Creil in its SiO₂, K₂O and Ba. Both bodies must be classified as siliceous-aluminous white earthenware. The CaO-rich (17 wt%) Niderviller fragment pertains to the calcareous white earthenware group. A comparison with 19 already published calcareous bodies from Lorraine shows similarities (grains of crushed sand or quartz pebbles and lead frit in a siliceous aluminous matrix), but its chemical composition differs from the published analysis of an object stylistically attributed to Niderviller. White earthenware glazes from Niderviller, Paris and the Wedgwood manufacture are transparent lead alkali glazes, and from Creil lead glazes. All samples are artificial bodies, made from a white-firing clay, to which ground flint, calcined or not, with or without grog, or ground quartz sand/quartz pebbles, calcined or not, and lead frits and chalk for the calcareous white earthenware were added. This study provides the first archaeometric results of marked Creil, Niderviller and Wedgwood tableware.

Key words: Creamware; Wedgwood; Creil; Niderviller; chemistry; technique.

Introduction

Nomenclature

White earthenware is a particular class of ceramics with a white, porous body and covered, except for the figurines, with a glaze. Such products are named “creamware” in English, “faïence fine” in French, “Steingut” in German and “terraglia” in Italian. The French nomenclature is complex and often confused, see discussion by Peiffer (2003) and Maggetti et al. (2011), but there is another problem. Earthenware, coated with a white glaze which is opacified by tin oxide (SnO_2) crystals, is commonly called “faïence” in France. According to Rosen (2009, p. 83) this term appeared for the first time in May 25, 1601 in archival sources of Nevers as “vessele de fayance” (crockery in fayance). In 1604, the ceramist Jean-Baptiste Conrade was labelled “sculpteur en terre de fayance” (sculptor of fayance earth) (Rosen, 2000). The article “Fayence” in the famous “Encyclopédie” is the oldest ever printed technical article on this subject (Diderot, 1756), illustrated by Anonymus (1763). However, since Bosc d’Antic (1775), the abundant 18th to 20th century French literature on this pottery type use the slightly modified term “faïence”. Unfortunately and confusingly, the rather similar term “faience” designs in English literature Ancient Mediterranean and Near Eastern ceramic bodies made up of crushed quartz. Spencer and Schofield (1997) deplore: “Objects from ancient Egypt and the Near East with quartz bodies and a transparent glaze were initially confused with European earthenwares which had an opaque white tin glaze, so both were called faience”. Although it has been known for many years that the two materials are very different in composition and manufacture, the name has continued to be used. Clearly, the French designations “fayance, fayence, faïence” are much older than the English “faience”, but the latter is so firmly established in Anglosaxon

literature that we suggest to follow Solon (1903) and Lane (1948) which used the French terms “FAÏENCE, faïence” for the French white tin-glazed pottery.

A short history of white earthenware

Recent research demonstrates that the invention of 18th century English creamware was roughly contemporaneous with the creation of French faïence fine (Maire, 2008). In the first decades of the 18th century, English potters preferred non-calcareous clays, abundant in England, to create new ceramic types. In contrast, French potters used non-calcareous as well as calcareous white firing clays and called the resulting wares “terre de pipe” or later faïence fine. What follows is a short summary of chapter 12 in Heimann and Maggetti (2014).

In Staffordshire’s 18th century thriving pottery district (Figure 1) local competition on how to whiten the pastes to emulate the whiteness of porcelain led around 1720 to the discovery of the immensely successful “white salt-glazed stoneware” or “common ware” (Dawson, 1997). Continuous experiments with many other raw materials such as the aluminium-rich and highly plastic Devon or Dorset “ball clays” gave birth between 1720 and 1740 to another new body called “creamware” or “cream-coloured ware” (Towner, 1978; Massey, 2007), bisque fired at 1100-1200 °C. The lead oxide used to glaze the body was contaminated with iron that imparted a creamy tint to the glaze thus giving it its descriptive name. The development of this new body is attributed to the Staffordshire potter Enoch Booth. Addition of calcined and milled flint, an invention of John Astbury of Shelton, or John Heath, or John Dwight of Fulham, improved the solidity and whiteness of the creamware. In England, the recipes for bodies and glazes were no secret, as it would have been in French manufactures, and thus were known by everybody. This explains why most 18th century English fabricants (Astbury, Enoch

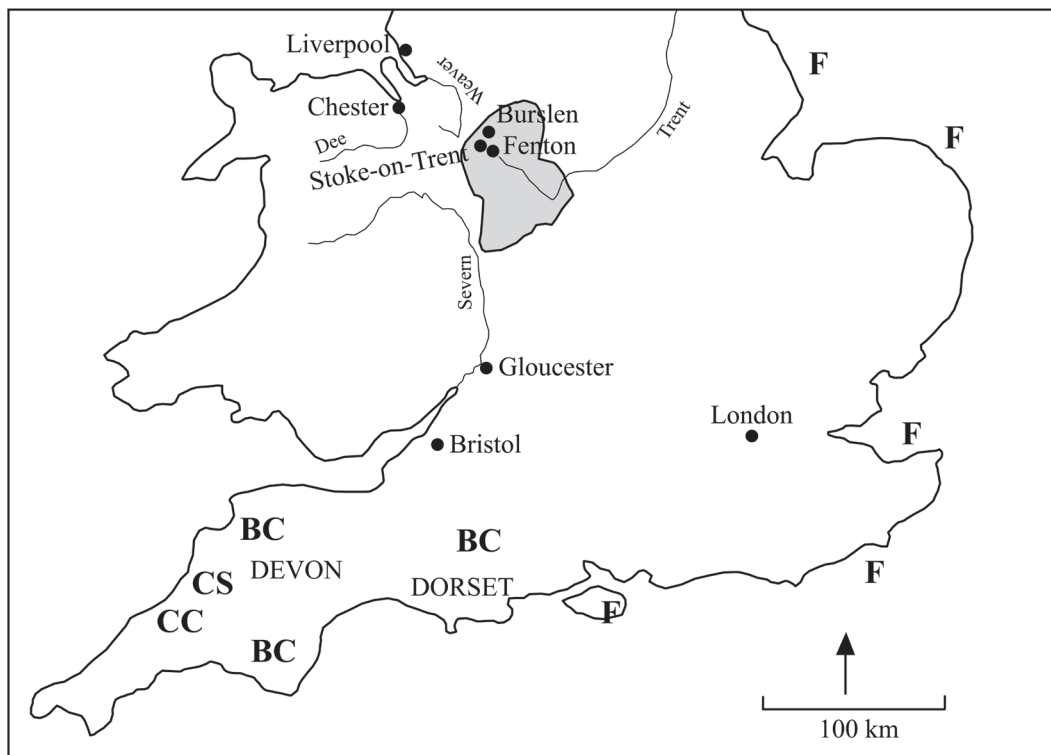


Figure 1. Map showing Southern England, the 18th century Staffordshire pottery district (grey area) and the sources of ceramic raw materials. BC = Ball clay, CC = China clay, CS = Cornish stone, F = Flint. From Heimann and Maggetti (2014).

Booth, Thomas Whieldon, Josiah Wedgwood I) produced almost identical pastes and glazes. Josiah Wedgwood I (1730-1795) created by 1761 in his own manufacture in Burslem an improved creamware body (Figure 2) by adding kaolin and feldspar to the paste, giving a much whiter and harder body as the usual creamware, called “Queen’s ware” since 1765 (Roberts, 2007). Around 1775 cobalt oxide was added to the glaze mix to optically mask the yellow iron tone. This earthenware, called “pearlware” or “china glaze ware”, had a distinct grey-blue finish and looked more like true porcelain.

Maire (2008, p. 13-17) distinguishes three periods in the historical evolution of French faïence fine: (1) 1743-1790: Faïence fine called

terre de pipe; (2) 1790-1830: Faïence fine called “cailloutage” (in the English tradition), and (3) After 1830: Faïence fine called “porcelaine opaque” (opaque porcelain) or “demi porcelaine” (half porcelain). French white earthenware originated during the years 1730-1750 in both Central (Rue de Charenton/Pont-aux-Choux manufactory in Paris; Hosotte-Reynaud, 1967; Le Duc, 1993; De la Hubaudière and Soudée-Lacombe, 2003) and Eastern (Lunéville, Lorraine) France (Guillemé-Brulon, 1995; Garric, 2006; Dawson, 2007; Smith, 2007; Maire, 2008), see Figure 3. The new paste of the Paris manufacture, created probably as early as 1740, was made of 66% unfired and 33% calcined non-calcareous Moret clay (reported



Figure 2. Tureen with plate. Wedgwood Queen's ware, Etruria manufactory, c. 1770. Tureen H: 20.5 cm, L: 36 cm. Plate L: 43 cm. Photo: Jacques Pugin. © Musée Ariana, Geneva, Switzerland.

by Hellot, quoted by De Plinval de Guillebon, 1995, p. 60) and its tableware is famous for its typical "rice-grain" or "barley corn" moulded motif (Figure 4a), probably derived from English salt-glazed wares, copied 1750-1756 at Pont-aux-Choux and in use until the closing of the factory in 1788 (Maire, 2003; Dawson 2007). The Lorraine faïence merchant Jacques Chambrette II (c. 1705-1758), established in Lunéville c. 1730 a faïence and "porcelain" manufacture (Maire, 2008, p. 95). Experiments to produce white earthenware started in 1745 or perhaps around 1731 (Peiffer, 2007, p. 124) resulting in 1748-1749 in a calcareous terre de pipe body (Maire, 2008, p. 94-95). The terre de pipe manufacture, founded 1749 (Grandjean, 1983, p. 12), became rapidly very successful, supplanting in a short time Dutch and English white earthenware imports to Lorraine and exporting its products to Germany, Italy and even Poland (Figure 4b). White earthenware

was produced at about 23 sites in 18th century Lorraine (Peiffer, 2007), see Figure 3. According to 18th century CE manuscript sources, Lorraine white earthenware bodies were generally made up of four main constituents (Maggetti et al., 2011): (1) Al-rich refractory clay, (2) chalk, (3) frit, and (4) flint. Grog, or ceramoclast (Ionescu and Ghergari, 2002), can be a supplementary addition. The absence of marks and the almost identical decorations and paintings makes it difficult to distinguish 18th c. white earthenware from these sites. Calcareous white earthenware was fired twice (Table 1).

The term cailloutage derives from the admixing of calcined and crushed flint ("cailloux") to a non calcareous paste in the typical English technical tradition. This procedure was propagated by several French technical treatises (O*** [Oppenheim], 1807; Boyer, 1827; Société d'Encouragement, 1829; Bastenaire Daudenart, 1830; Brongniart, 1844)

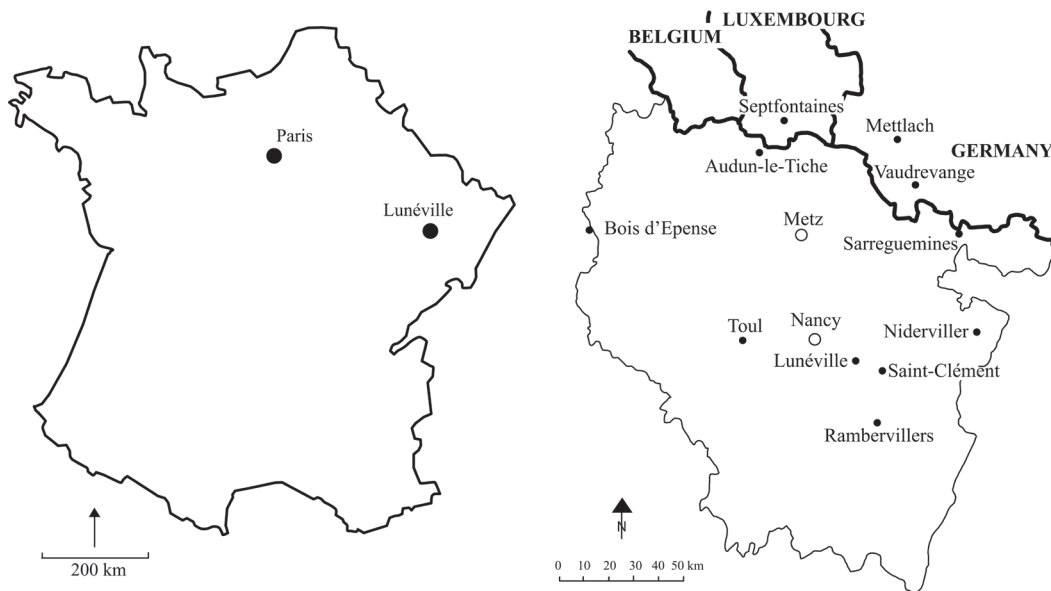


Figure 3. Left: Map of France with major 18th century white earthenware centres indicated. Right: Map of Lorraine (open circles: major towns, solid dots: manufactures). From Heimann and Maggetti (2014).



Figure 4. Representative 18th century French white earthenwares. (a) Gravy (meat juice) pot with cover, white earthenware. Moulded decoration with “rice grain” or “barley corn” patterns. Probably Pont-aux-Choux pottery factory, c. 1760-1780. Reg. no. C.127&A-1945. © Victoria and Albert Museum, London. (b) Teapot attributed to Lunéville (Sample TBL 1, Maggetti et al., 2011). Lead-glazed calcareous white earthenware (“terre de pipe”). Late 18th century CE. H: 12 cm. Private collection. Photo: Marino Maggetti.

and used by many French manufactures in the first three decades of the 19th century. The first firing is at higher temperatures as for terre de pipe pastes (Table 1), giving improved solidity to the body.

Following 70 years older English technical developments, French potters improved their bodies after 1820-30 by adding feldspar or kaolin to the cailloutage paste. This opaque porcelain or half porcelain was first fired even higher (Table 1) as the cailloutage mass and gave a much whiter body. Borax replaced some of the lead in the glaze compositions. As example, Creil presented this new body type (opaque porcelain) 1834 at the “Exposition de l’Industrie française” in Paris (Ariès, 1994).

Scientific analyses of white earthenwares

Bastenaire Daudenart (1830) published the chemical composition of a Staffordshire (Wedgwood?) paste and Salvétat (1857) reported a single Wedgwood pottery analysis. Only two recent archaeometric studies of English creamwares were published so far by Tite (1996, 5 chemical analyses) and Duffy

et al. (2002, no list of the chemical analyses). Unfortunately, the type of material analyzed is not specified (Creamware, Queen’s ware, Pearlware?).

Maggetti et al. (2011) analyzed 19 samples from Lorraine, manufactured 1755-1800 (Rosen and Maggetti, 2012). Their porous, calcareous bodies (9-16 % water adsorption) show a wide range of chemical compositions. Multivariate statistical analyses allow distinguishing among various Lorraine factories. Microstructural analyses corroborate the archival recipes as almost all Ca-rich bodies are composed of angular quartz + lead frit, both embedded in a calcareous matrix. The latter shows beside CaO-rich microareas (= chalk) also high-aluminous patches, corresponding to admixed ball type clays from the Rhine (Westerwald) region. Lorraine transparent glazes are similarly composed as the English one, but with higher alkali content (2-5 wt%). However, the specificity of Lorraine white earthenware, especially of Saint-Clément, is their tin-opacified glaze.

White, unglazed figurines of the sculptor Paul-Louis Cyfflé were studied by Maggetti

Table 1. Firing temperatures of the main white earthenware types. Typology according to Maire (2008).

Type	Bisque firing		Glaze firing	
	Pyrometer	°C	Pyrometer	°C
Creamware	1844: 90-100		1844: 27-30	
Terre de pipe	1844: 25-30, 1857: < 25-30	ca. 980	1857: < 25-30	ca. 980
Cailloutage	1844 + 1857: ca. 60	1200-1250	1844: ca. 12, 1857: 20-25	900
Opaque porcelain	1857: 89-100	1140-1300	1857: 27-30	1000-1140

Pyrometer = Wedgwood pyrometer. 1844 = Brongniart (1844, I). 1857 = Salvétat (1857). Degrees centigrade according to Munier (1957).

et al. (2010), Maggetti (2011) and Maggetti and Calame (2012). These analyses show that the artist made the pastes from a wide range of compositions, including calcareous terre de pipe, soft paste (frit) and hard paste porcelain. A Creil body analysis (opaque porcelain) was published by Salvétat (1854, 1857). Maggetti et al. (2011) discussed the archaeometric aspects of six CaO-poor tablewares of unknown provenance. Five samples (TBL 9, 18, 30, 31, 32) possess a grog rich body without quartz or flint admixture. Their origin was left open, with the exception of TBL 18 (“unknown provenance, but from Lorraine”). Meantime, their manufacturing place has been constrained by Maire (2012), who attributed these pieces to the Pont-aux-Choux manufacture in Paris, based on their typical rice-grain moulded decoration (Rosen and Maggetti, 2012, Annex). The microstructural analyses support this identification, as they are in good agreement with the paste recipe of this manufacture (a mix of local Moret clay with his calcined counterparts, see above).

Samples

Archaeology

Nearly 30,000 pottery fragments have been found during archaeological excavations at the Brunngasshalde in Bern, the capital of Switzerland (Heege, 2010). Archival sources testify that the assemblage is a backfill, made up of street construction rubble and urban waste, the whole deposited between 1787 and 1832. The urban waste consists mainly of material from the first third of the 19th century as evidenced from salt-glazed stoneware, earthenware and Delftware finds, coin dates, dated mineral water bottles, and marked white earthenware from Western Switzerland. At this time, there was a large and quite varied range of ceramic types on offer on the Bernese pottery market. Ranging from costly first-class ware (European and Asian porcelain), to gradually more affordable

imitations (French and Swiss faïence, creamware and lead-glazed earthenware) and to salt-glazed stoneware (from the German Westerwald), the requirements of the Bernese urban population of differing social levels were met. The pottery was either imported, albeit on an unknown scale (Asia, England, France, Germany), or produced locally and in the wider region around the capital. Only 33 out of 2753 white earthenware fragments could be pinpointed to their origins thanks to their marks related to Creil and Niderviller (France), Wedgwood (England), Carouge, Nyon and Matzendorf (Switzerland). All six marked white English and French pieces were selected for the present study (Figure 5, Table 2). Nider-1 is an important piece, as its impressed mark NIDERVILLER has not been reported before for white earthenware from this manufacture (e.g. Maire, 2008, p. 502).

Production dates

All samples must have been produced before 1832, the last year of the Brunngasshalde infilling. The “terminus post quem” can be constrained based on the history of the manufactures and the impressed trademarks. Creil was founded in 1797 by the Englishman Robert Bray O’Reilly, who came to France 1790 as an enthusiastic supporter of the French Revolution (Ariès, 1994; Guillemé-Brulon, 1995). He produced “poteries dites terres anglaises...” (potteries called English earths). Since 1827, director Saint-Criq-Casaux improved the paste by adding kaolin and feldspar. This new paste was named opaque porcelain after 1834 (Bontillot, 1998). Creil-1 and Creil-2 correspond most probably to the activities of the early 19th century and can be dated 1797-1832 (Ariès, 1994). The manufacture was very successful, as shown by the year 1819, when 300 craftsmen created about 1,5 million pieces (Garric, 2006). Niderviller produced white calcareous earthenware since 1772 or 1778, and English-type white earthenware (cailloutage)

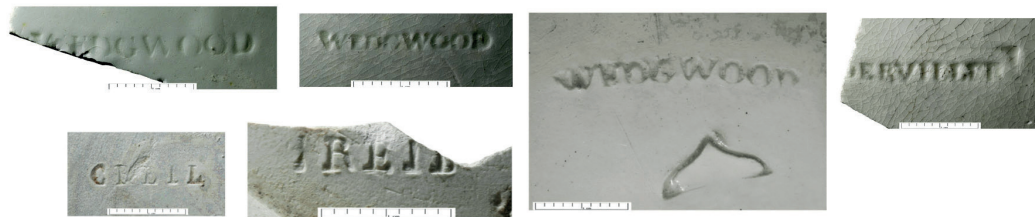


Figure 5. Marks of the analyzed samples (Heege 2010). From left to right, upper row: Wed-1, Wed-2, Wed-3, Nider-1; lower row: Creil-1, Creil-2. White bars: 1 cm total width.

Table 2. List of the specimens analyzed.

Sample No.	Inv. No.	Impressed trademark	Production date
Wed-1	102201	Wedgwood	1769-1832
Wed-2	101716	Wedgwood	1769-1832
Wed-3	101717	Wedgwood	1769-1832
Nider-1	101716	Niderviller	1793-1832
Creil-1	101716	Creil	1797-1832
Creil-2	101716	Creil	1797-1832

from 1788 on by François Lanfrey, director of the manufacture since 1778 (Soudée Lacombe, 1984). Actually, two white earthenwares are known bearing the typical late 18th century mark in the form of two interlaced “C” (Maire, 2008, p. 495). They are those of count de Custine, who owned the manufacture in 1770 and was guillotined 1793. This mark was also applied onto Niderviller’s tin glazed faïences. The new mark NIDERVILLER was therefore most probably impressed after de Custine’s death, what hypothesizes a creation of Nider-1 in the years 1793-1832. Wedgwood’s Wed-1, Wed-2 and Wed-3 were made 1769-1832, as this kind of mark was used since 1769 (Reilly, 1989, Appendix B).

Methods and Objectives

Sample preparation

From the six fragments, a small sample was obtained by cutting with a saw. Representative portions of these samples (3.0-5.5 g) were ground in a tungsten carbide mill after careful removal of the glaze. Small subsamples were used for scanning electron microscopic analyses.

Mineralogical analyses by X-ray diffractometry (XRD)

The mineralogical composition was determined through powder X-ray diffraction (Philips® PW 1800 diffractometer, CuK α , 40 kV, 40 mA, 2 θ 2-65°, measuring time 1 sec./step).

Chemical analyses by X-ray fluorescence (XRF)

2 g of powdered sample were calcined at 1,000 °C for one hour to obtain the loss on ignition (LOI). 0.700 g of calcined powder was carefully mixed with 6.650 g of MERCK spectromelt A10 (Li₂B₄O₇) and 0.350 g of MERCK lithium fluoride (LiF). This mixture was put into a platinum crucible and melted at 1,150 °C for 10 minutes (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.

Scanning electron microscopy (SEM)

Backscattered electron images (BSE) were collected with a scintillator type detector out of polished samples, using a Philips® FEI XL30 Sirion FEG electron scanning microscope. 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. Chemical compositions were determined by energy-dispersive X-ray spectrometry (EDS), operated at a beam acceleration voltage at 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 areas. The detection limits for most elements were about 0.2 wt%. Reliability of the results was proven measuring well-known glass and mineral standards (DLH2, Corning A-D and Plagioclase). 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%. Glazes were measured in

the central parts to avoid as best contamination effects due to burial and chemical body/glaze exchanges during firing.

Objectives

As outlined before, little or nothing is known about the chemical and mineralogical composition of English and French white earthenwares of the 18th and 19th centuries. The products of the most important factories such as Wedgwood's Etruria or those originated in the works around Paris (Creil, Montereau etc.) have not been addressed yet. A first study focused on early 18th c., unstamped and only stylistically dated French white earthenwares from Pont-aux-Choux (Paris) and six Lorraine factories, pertaining mostly to private and museum collections (Maggetti et al., 2011). The present paper follows a second approach in analysing marked English and French white earthenwares, unearthed during archaeological excavations of a Swiss consuming site. These sherds are dated to the Late 18th/Early 19th c. (see above). The aims of the present study are: (a) to characterize the products of Creil, Niderviller and Wedgwood by determining the mineralogical and chemical compositions of their bodies; (b) to characterize the chemical compositions of their glazes; and (3) to determine the manufacturing technique through these analyses.

Results

Ceramic bodies

Chemical contamination. There are no evidences for contamination processes during burial, as classical mobile elements (e.g. P₂O₅, MnO) show no significant enrichments (Table 3). However, lead concentrations of Wed-1, Nider-1, Creil-1 and Creil-2 bodies are significantly higher than maximum values normally found in clays (110 ppm Pb, Turekian and Wedepohl, 1961; 240 ppm Pb, Ericson et al., 1961).

Table 3. Bulk body composition for the specimens analyzed by XRF. Oxides and LOI in wt. %, elements in ppm.

Sample No.	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	Ba	Cr	Cu	Nb	Ni	Pb	Rb	Sr	Y	Zn	Zr	Sum	LOI	
Wed-1	73.70	0.75	21.74	0.68	0.00	0.14	0.90	0.31	1.06	0.05	226	85	34	12	25	643	61	90	19	32	159	99.47	0.64	
Wed-2	77.29	1.08	18.45	0.54	0.00	0.11	0.50	0.26	1.01	0.06	203	76	67	20	17	260	67	106	22	24	193	99.42	0.72	
Wed-3	75.52	0.77	20.43	0.63	0.00	0.14	0.77	0.33	0.92	0.06	219	80	27	14	24	98	49	89	22	29	184	99.66	0.65	
Nider-1	64.59	0.65	12.94	0.93	0.02	0.60	16.81	1.06	0.91	0.15	302	69	32	12	26	7424	58	389	36	27	162	99.53	7.98	
Creil-1	79.37	0.59	17.02	0.65	0.00	0.08	0.40	0.29	0.34	0.13	128	87	10	17	18	1744	17	211	73	16	101	99.17	0.40	
Creil-2	77.02	0.62	19.18	0.71	0.00	0.10	0.40	0.19	0.37	0.12	132	90	10	17	19	3764	11	227	53	16	110	99.15	0.67	
<i>Staffordshire, white earthenware (Bastenaire Daudenart, 1830, Salvétat, 1857, Tite, 1996)</i>																								
1830	70.00		24.70	1.00			4.00																	
1857a	76.10		20.45	1.00		0.14	0.75		1.6*															
1996b	78.60	1.00	17.30	0.80		<0.20	0.5	<0.2	1.6															
1996c	78.60	0.40	17.40	0.80		0.30	0.5	0.4	1.5															
1996d	76.20	0.80	19.60	0.80		<0.20	0.4	0.2	1.8															
1996e	77.00	1.00	17.20	0.90		0.40	0.5	0.4	1.8															
1996f	77.60	0.80	17.60	1.00		<0.20	0.4	0.5	1.8															
<i>Creil, opaque porcelain (Salvétat, 1854, 1857)</i>																								
1854.1857b	66.1		32.2	0.55		0.00	0.14		1.10*															
<i>Niderviller, white earthenware (Maggetti et al., 2011)</i>																								
TBL 3	66.87	0.45	16.44	0.90	0.01	0.57	10.49	2.13	1.58	0.14	420	123	27	11	47	3657	74	294	18	29	126	100.06	0.34	

Fe₂O₃ = total Fe as Fe₂O₃. The table reports also previous analyses. 1857a is a Wedgwood pottery. 1996a-d: Fe as FeO. * = Total Alc. The literature analyses were recalculated LOI-free, if necessary.

Elemental compositions. A distinguishing feature of sample Nider-1 is its high CaO content (16.8 wt%), compared to the < 1 wt% CaO of the other pieces. The Wedgwood samples show considerably higher amounts of TiO₂, K₂O, Ba, Cu, Rb, Zn and Zr, and lower contents of Sr and Y with respect to the Creil samples (Table 3, Figure 6). Both are very distinctive from the Sarreguemines cailloutage and the Paris Pont-aux-Choux ware (e.g. they have much higher silica). The Wedgwood samples are generally very similar to the compositions published by Salvétat (1857) and Tite (1996), but the potassium values are higher (Table 3). Both Creil and the Niderviller bodies do not match the analysis by Salvétat (1857) respectively Maggetti et al. (2011), see Table 3.

BSE microstructures and EDS data. Creil and Wedgwood specimens have similar microstructures, consisting of: (1) angular SiO₂ fragments with maximum diameters of 40-50 µm for Wedgwood and significantly coarser grains (100 µm max. length) for Creil; and (2) a serial size distribution of (1) within a fine-grained, porous and felt-like matrix (Figure 7). These particles are characterized by a multitude of internal cracks and sub-domains in the range of ca. 2 µm (Figure 8a). Additionally three types of inclusions were observed: (1) type A; angular inclusions with a glassy matrix and needles of mullite. This kind is present only as few grains in Wed-2 (Figure 8b); (2) type B; rounded or subangular inclusions with a phyllosilicate textural aspect and with conspicuous cracks towards the surrounding matrix (Figure 8c). Such inclusions occur only in Wedgwood samples; and (3) type C; rounded pores of former carbonatic inclusions with characteristic Ca-rich rims (up to 12.7 wt% CaO, Table 4), see Figure 8c. This inclusion type was observed in both Wedgwood and Creil samples. Types A and B have typical features of grog or ceramoclast, such as different chemical composition and

microstructure compared to the surrounding body, angular shapes and drying cracks around the inclusion (Whitbread, 1986; Cuomo di Caprio and Vaughan, 1993). Table 4 reports area compositions of both. The latter are much richer in alumina and have less silica as the type A inclusions, indicating their derivation from a kaolinite rich (high Al) clay. A single inclusion differs from the other by its higher potassia and lead contents. Microstructural features of type A are compatible with highly fired porcelain bodies. Small zircon and rutile (no anatase according to XRD) grains are scattered throughout the whole bodies of the Wedgwood and Creil samples. The matrices, that is, the former clay, of all CaO-poor samples are, as evidenced by Table 4, chemically similar and are made up of dominantly two oxides, SiO₂ and Al₂O₃. Their overall chemical composition matches those of kaolinitic-illitic clays. However, spot analyses of single grains of former phyllosilicates (Table 4) are far away from the ideal composition of calcined kaolinite (46 wt% Al₂O₃, 54 wt% SiO₂). This could be explained by a “contamination” of the analyses from the surrounding material or it may indicate the use of impure kaolinitic minerals.

The CaO-rich body of Nider-1 is composed of (Figure 9a): (1) angular SiO₂ fragments with diameters not exceeding 80 µm. As no internal cracks and sub-domains typical for calcined flint grains (Figures 7, 8) can be observed, one must assume that they correspond most probably to calcined sand or quartz pebbles; (2) angular potassium feldspar grains with max. lengths of 70 µm; (3) particles (Figure 9c) with an overall composition of c. 100 wt% CaO (with some sulphur) and a maximum length of 120 µm, probably portlandite Ca(OH)₂ as they are not stable under the electron beam; (4) roundish to angular Pb-Si frits with max. sizes of 100 µm; and (5) a subordinate, fine-grained CaO-rich matrix with phosphorous and sulphur according to many spot analyses, consisting most probably of portlandite considering the instability under

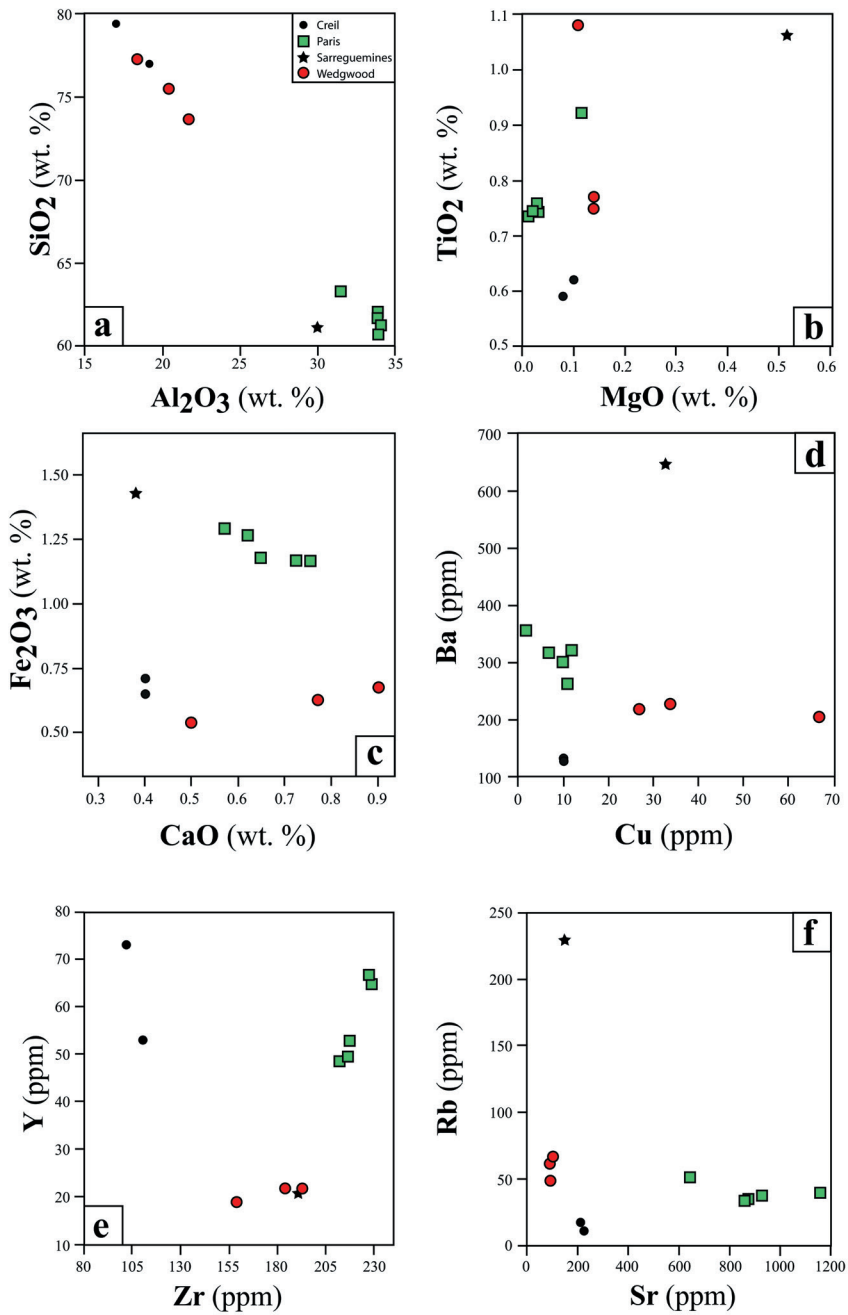


Figure 6. Body (bulk) compositions for the CaO-poor samples displayed on bivariate plots of selected oxides and elements. For Creil and Wedgwood cf. Table 3, for Paris (TBL 9, 18, 30, 31, 32) and Sarreguemines (TBL 2) cf. Maggetti et al. (2011, Table 4).

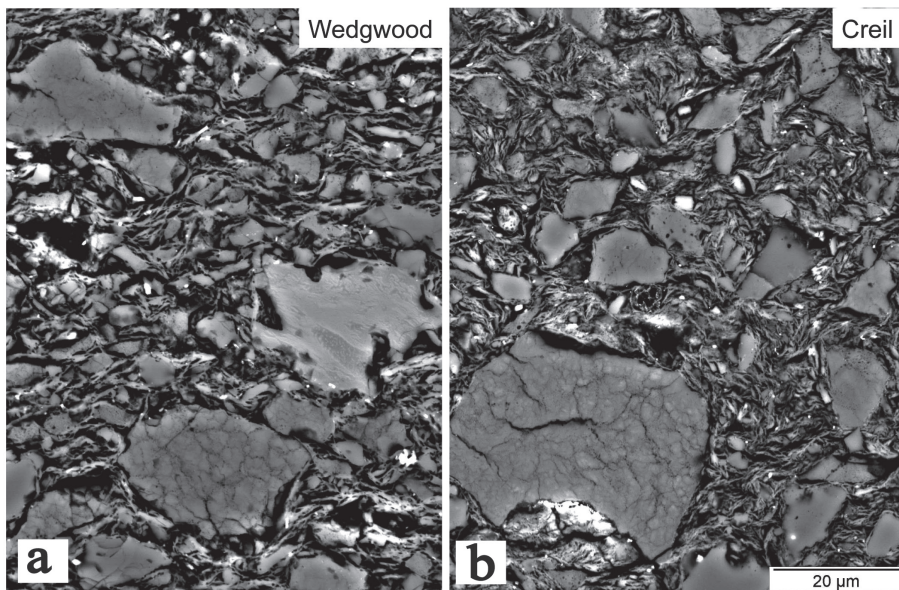


Figure 7. SEM backscattered images of Wed-2 (a) and Creil-2 (b). Visible are angular, calcined flint grains of various sizes, one inclusion type B (a, light grey), all embedded in a porous and feltry matrix. Same scale for both.

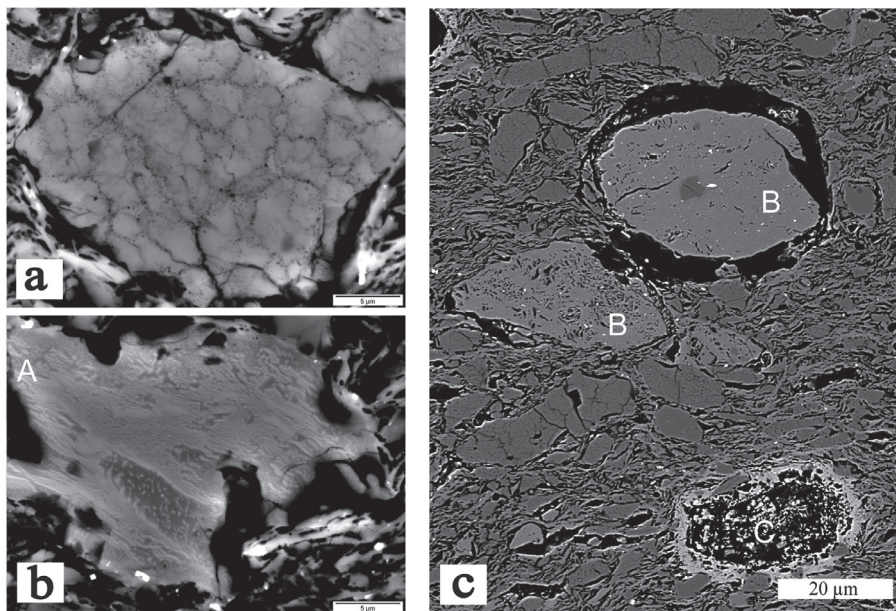


Figure 8. SEM backscattered images of calcined flint grains with characteristic internal cracks and subdomains (a, Wed-2), inclusion type A (b, Wed-2) and inclusion types B and C (c, Wed-1).

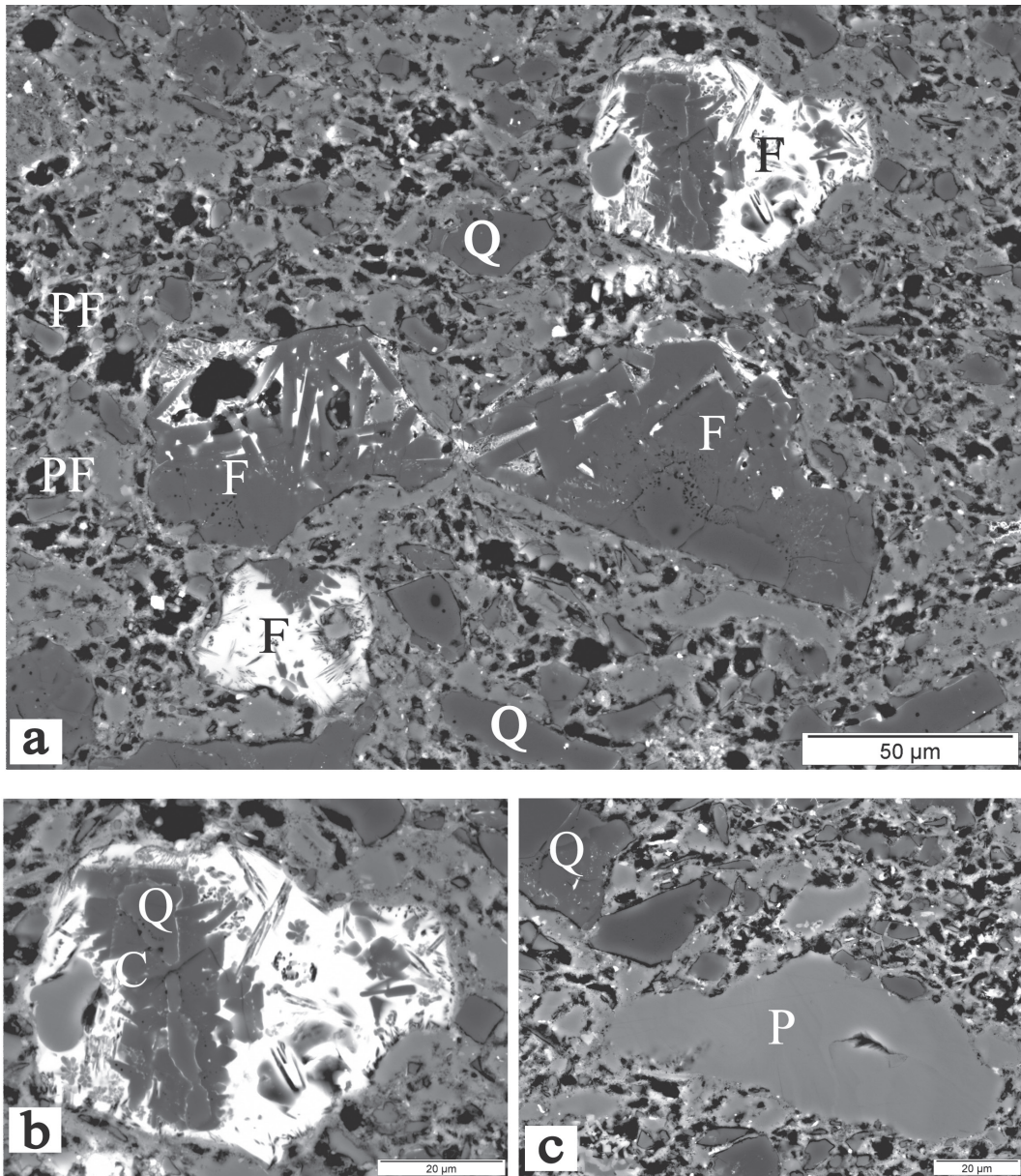


Figure 9. SEM backscattered image of CaO-rich sample Nider-1: (a) angular fragments of quartz (Q) and potassium feldspar (PF) with four angular to subangular or roundish PbO-SiO₂-frit grains (F) in a CaO-rich porous matrix. White areas of the frits = lead-rich glass; (b) Lead frit with relict quartz (Q) core, surrounded by cristobalite (C) laths in a lead rich glass (analysis Nider-1-27, Table 4). Acicular crystals were too small for analysis; (c) Crushed angular quartz and coarse portlandite (P) grains in a CaO-rich, mostly portlandite matrix.

Table 4. SEM-EDS single analyses and mean values (in wt%). All totals = 100 wt%.

Sample No.	Area (μm)	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	P ₂ O ₅	Cl ₂ O	SO ₃	K ₂ O	CaO	TiO ₂	Fe ₂ O ₃	PbO
<i>Inclusion type A</i>													
Wed-2 (n=5)	4x2 - 10x10	0.9	0.3	20.8	70.4			0.12	2.5	4.6	0.1	0.3	
<i>Inclusion type B</i>													
Wed-1 (n=7)	5x8 - 15x20	0.3	0.4	39.7	54.0				2.5	1.1	0.8	1.2	
Wed-2 (n=4)	7x10 - 15x15	0.1	1.3	39.1	52.2				2.4	0.9	0.8	3.2	
Wed-3 (n=6)	3x10 - 25x30	0.2	0.8	39.4	54.2				2.3	1.0	0.8	1.3	
<i>Rim around inclusion type C</i>													
BER 1-13	2x15		0.2	26.0	59.5				0.3	12.7	0.4	0.9	
<i>Matrix (without inclusions)</i>													
Wed-1 (n=5)	15x20	0.2	0.5	27.3	67.5				1.5	1.2	0.9	0.9	
Wed-2 (n=6)	30x50		0.3	22.9	72.7				1.5	0.6	1.3	0.7	
Wed-3 (n=10)	20x20	0.1		26.2	69.6				1.4	0.8	0.9	0.9	
Creil-1 (n=10)	20x20			26.5	67.4				1.6	0.8	1.2	1.5	1.0
Creil-2 (n=10)	20x20			27.8	67.9				0.8	0.7	1.2	1.6	
<i>Potassium feldspar in the body</i>													
Nider-1	10x25	0.3		16.8	64.0				18.5	0.4			
<i>Phyllosilicate in the body</i>													
Wed-2 (n=6)	Spot		0.4	36.8	58.7				1.7	0.5	0.6	1.3	
Wed-3 (n=5)	Spot	0.4	0.7	32.9	62.0				1.4	0.9	0.7	1.0	
Creil-1 (n=7)	Spot			30.4	65.8				0.9	0.7	0.9	1.3	
Creil-2 (n=10)	Spot			29.5	66.9				0.8	0.6	0.8	1.4	
<i>Pb-Si frit in the body</i>													
Nider-1-18	10x20		0.6	5.0	67.9		0.4		7.5	1.4	0.2	2.2	14.8
Nider-1-19	10x10	0.6		8.9	30.6	18.0	1.3		4.6	23.3	0.2	8.1	4.4
Nider-1-20	40x50		0.3	1.7	72.5		0.1		1.6	10.8		1.1	11.9
Nider-1-21	40x40		0.7	2.9	72.8				3.5	6.6	0.1	2.1	11.3
Nider-1-32	10x15	0.6		5.0	51.0		1.2		5.7	1.6	0.2	0.7	34.0
<i>Glassy areas in the frits</i>													
Nider-1-26	Spot			5.4	62.3		0.7		6.2	1.7	0.2	1.8	21.7
Nider-1-27	Spot	0.2		3.9	56.2		1.0		5.3	1.5	0.2	3.4	28.3
<i>Glaze</i>													
Wed-1 (n=6)	25x55	0.1	0.2	7.4	41.7				0.8			0.5	48.6
Wed-2 (n=5)	20x100	0.7	1.2	5.8	39.2				0.0	0.7	0.2	0.3	52.4
Wed-3 (n=5)	20x100	0.6	1.2	4.5	40.4					0.1	0.2	0.4	52.6
Nider-1 (n=3)	50x400	0.5	0.9	5.9	40.4		0.0		0.3	0.3	0.1	0.4	51.2
Creil-2 (n=2)	40x150				25.9		0.5		0.3	0.4		0.3	72.6
<i>Reaction zone body/glaze</i>													
Wed-1-7	3x2	0.6	0.2	28.3	37.4				2.7	0.8	0.3	0.8	28.9
Wed-2-22	Spot	0.4	0.3	25.3	37.6				2.7	0.4	0.1	0.7	32.5
Wed-2-23	Spot	0.5	0.3	18.7	39.4				2.6	0.3	0.5	0.5	37.2
Wed-3-6	Spot	0.9	1.0	24.8	44.3				1.3	0.6	0.4	0.7	26.0
<i>Potassium feldspar in the glaze</i>													
Nider-1	5x5	0.2		16.9	60.9				16.8			0.4	4.8

the electron beam. All frits contain two SiO₂ polymorphs: (1) as rounded individual quartzes or cores of SiO₂-clusters; and (2) idiomorphic laths, probably cristobalite in view of its crystal habitus, either as clustered individuals or surrounding quartz cores (Figure 9b). The relative amounts of glassy and SiO₂-phases in the frit particles are highly variable, ranging from few volume percent of glass to 100 vol.%. These frits show consequently a wide range of compositions (Table 4). With few exceptions, no Pb diffusion from the frits into the surrounding ceramic matrix could be measured, as expected from the sharp boundaries of the frit grains in SEM-BSE observations. In the few cases where such a contamination occurred, it didn't reach further than c. 20 μm.

Mineral associations. The studied samples pertain, as shown by their X-ray diffractograms, to two different mineral associations:

- a) α-Quartz + cristobalite + mullite + spinel + rutile: Wed-1, Wed-2, Wed-3, Creil-1, Creil-2
- b) α-Quartz + plagioclase + calcite + gehlenite (?): Nider-1.

The presence of conspicuous amounts of secondary portlandite Ca(OH)₂ was inferred from BSE observations (Figure 9c), but this could not be confirmed by XRD, probably because the crystallinity of this phase is too low. It is puzzling and not yet understood why this phase, which has formed after firing, appears as homogeneous and not as polycrystalline grains. The combined presence of gehlenite and calcite is an evidence that the latter must also be considered a secondary, post-firing phase (Maggetti, 1994).

Glazes

Burial degradation. Creil samples show severe burial leaching effects, visible as zones with typical laminar structures of weathered glass layers (Pantano and Hamilton, 2000; Bouquillon and Bonnet, 2004; Verità, 2006) affecting the whole glaze in Creil-1, or only the

external parts or the outer borders of gas bubbles in Creil-2 (Figure 10c). Obviously, these glazes were not stable under burial conditions, as they lack network stabilizer (alumina).

BSE microstructures and EDS data. Wedgwood glazes are typically 50-80, Creil glazes 5-150 and the Niderviller glaze 80 μm thick (Figure 10 a,b). Average EDS compositions are reported in Table 4. Main components are PbO, SiO₂ and Al₂O₃ with minor amounts of Na₂O, MgO, K₂O, CaO, TiO₂, Fe₂O₃ and Cl₂O. No significant differences were detected between the Wedgwood and the Niderviller glazes. Contrasting, Creil's glaze Creil-2 sets apart with very high silica and low lead. The glazes are rather homogeneous with rare gas bubbles. Crystalline phases of: (1) subangular and rounded SiO₂ grains, interpreted as relict quartz; (2) acicular SiO₂ crystals, often in clusters or surrounding quartz cores, interpreted to be cristobalite; and (3) aggregates of small, euhedral Pb-bearing potassium feldspar laths, often as clusters (pseudomorphing ancient feldspars?) were observed. (1) and (2) occur in all glazes, (3) only in Nider-1. These phases are more abundant and of greater size in the latter. It contains also an angular, relictic "ghost" frit inclusion (Figure 10d), most probably indicative of cullet additions. The glaze-ceramic interface is sharp for all specimens (Figure 10 a,b). Wedgwood samples show additional irregular and undulated intermediate zones with a thickness of ca. 5- 20 μm, consisting of small (less than 2 μm) euhedral, rectangular and zoned crystals rich in alumina, silica and lead (Table 4). These compositions are only rough estimations as the embedding glaze did surely also interfere during the SEM-EDS measurements. Creil and Wedgwood specimens show a lead infiltration from the glaze/body interface inwards, affecting the outmost 750 μm of the bodies for the former (1.7 wt% PbO close to the contact), and 80 μm (5.9 wt% PbO close to the contact) for the latter.

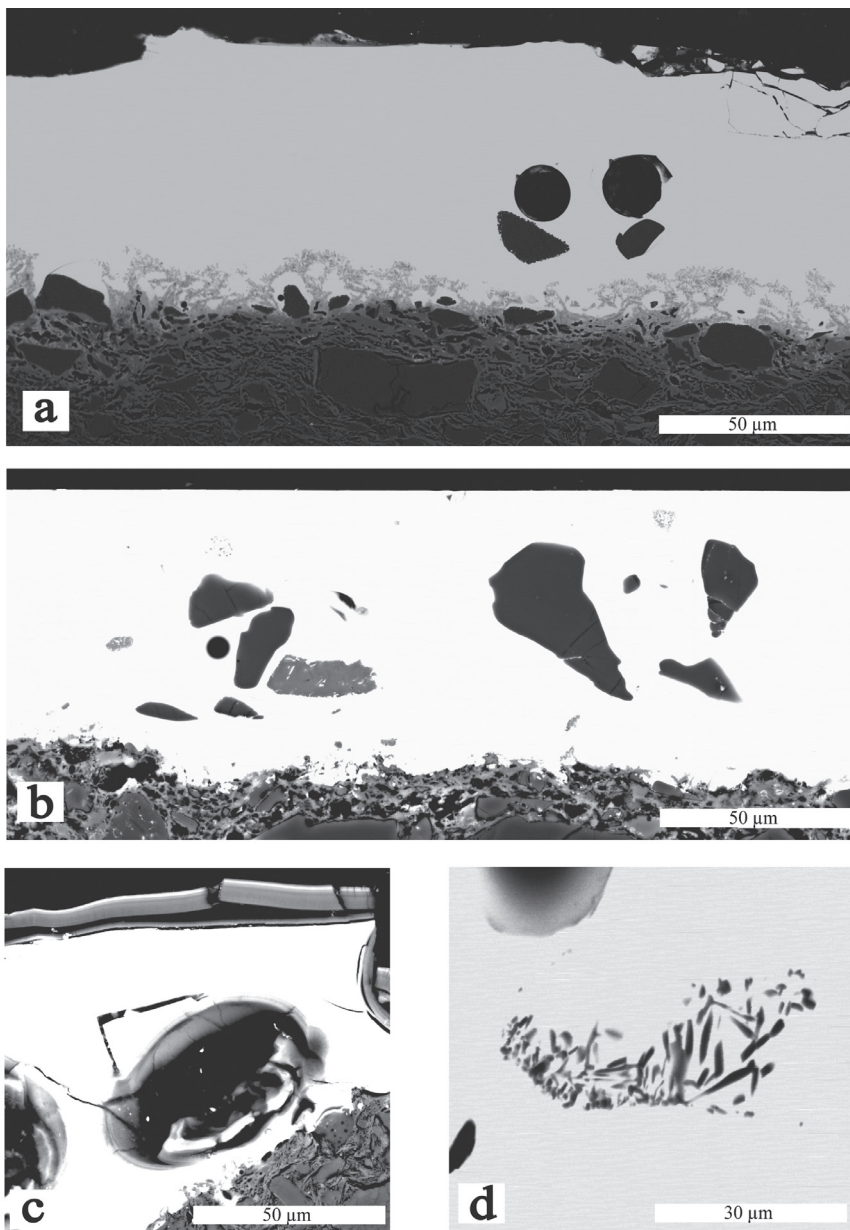


Figure 10. SEM backscattered images of the glazes (upper bright layer) applied to the body (lower dark area). (a) Wed-1 showing a wavy interface between glaze and body as well as two bubbles and two quartz relicts; (b) Nider-1 with no interface and more inclusions (black: quartz, grey: feldspar); (c) Creil-2 with no interface and incipient deterioration of the glaze starting from the outside and from bubbles; (d) Angular “ghost” inclusion of a former glassy frit (Nider-1).

Discussion

Chemical Classification

White earthenwares can be classified either according to their recipe or to their chemistry. We prefer to use a non genetic approach based on the chemical composition. A first dividing factor is CaO, attributing Nider-1 to the group of calcareous white earthenwares, typical of the 18th c. products from Eastern France (Lorraine). Creil and Wedgwood samples pertain to the siliceous-aluminous white earthenware group.

Raw Materials

In England. Staffordshire white earthenware potters used ball clays, flint, china clays and Cornish stone (Table 5). Ball clays are highly plastic sedimentary clays, with high green strength and white-firing properties (Booth and Linley, 2011). The ball clays of SW England have been sedimented in Tertiary basins (Harvey and Murray, 1997; Mitchell and Vincent, 1997; Bristow et al., 2002). Principal minerals are disordered kaolinite (20-95 wt%), mica (5-45 wt%) and quartz (1-70 wt%), see Holdridge (1956) and Wilson (1998). Subordinate phases are montmorillonite and lignite.

Chemical analyses of “Hampshire” and “Wedgwood” clays were published at the beginning of the 19th century (O*** [Oppenheim], 1807). China clay (primary kaolinite) is extracted from kaolinitised granites of Cornwall (Figure 1). It consists of kaolinite, mica, quartz, potassium feldspar and smectite (Scott et al., 1996; Bristow et al., 2002). Cornish stone is a kaolinitized, feldspar-rich, peraluminous granite of Cornwall, chemically similar to the Chinese “petuntse” (Nikulina and Taraeva, 1959; Maslennikova et al., 1993). Flint was collected on the beaches of Eastern and Southern England (Figure 1).

In France. French white earthenware potters from Lorraine used kaolinitic clays (from the Rhine region), chalk, flint or sand and frits

(Maggetti et al., 2011). Potters from other places preferred a blend of Montereau or Moret clay, either with grog (Pont-aux-Choux factory) or calcined flint or sand (= cailloutage), and later with kaolinite and feldspar (= opaque porcelain). Montereau or Moret clays are highly plastic clays (Brongniart, 1807, I p. 519-520; Cuvier and Brongniart, 1822, p. 40-59) belonging to deposits quarried around Paris in Cenozoic sediments (Paleogene, Lower Eocene, Ypresian, 56-47.8 Ma). They are made up of quartz, anatase, rutile, calcite, chlorite, and the clay fraction (< 2 μ) contains smectite, kaolinite and Fe-montmorillonite (Delfaut, 1990). The smectite content can even reach 100% (Donsimoni et al., 2004). Chemical analyses show a wide range of compositions, with e.g. Al₂O₃ values from 12 to 31 wt% (Table 6).

Body recipes

Microstructural analyses showed clearly that the studied white earthenwares are artificial bodies, made by mixing one or more white-firing clay(s) with calcined and ground flint or sand, and additional ingredients such as frits and/or a Ca-rich phase. The angular edges of the non-plastic inclusions, as well as the serial distribution (Maggetti, 1994) is an evident proof that these grains were added to the clay after grinding.

Wedgwood. As outlined above, Josiah Wedgwood I creamware is a mix of two ingredients (ball clay and calcined, ground flint), and Josiah Wedgwood I Queen’s ware a blend of ball clay with china clay and Cornish stone. Table 6 lists eight English white earthenware recipes. Clearly, the terminology wasn’t fixed in those days. Recipe A corresponds to the actual definition of creamware, the others to what today would be called Queen’s ware. The table shows the high variability of the blends. Some recipes mix two or three clays, others do not require kaolin or Cornish stone and some use paste shavings as an additional ingredient.

Table 5. Chemical analyses of English and French white firing clays, in wt%.

Provenance	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	CaO	Na ₂ O	K ₂ O	Loss	Total	Reference
<i>English Ball clays</i>											
S Devon, Group I	48.00	0.90	34.00	1.00	0.30	0.20	0.20	1.60	11.90	98.10	Clayheritage, 2013
S Devon, Group II	50.00	1.00	33.00	1.10	0.30	0.20	0.30	2.20	8.40	96.50	Clayheritage, 2013
S Devon, Group III	55.00	1.30	31.00	1.00	0.30	0.20	0.30	2.50	5.50	97.10	Clayheritage, 2013
S Devon, Group IV	67.00	1.40	22.00	0.90	0.30	0.10	0.30	2.20	7.60	101.80	Clayheritage, 2013
N Devon, Type 1	59.5	1.40	27.00	1.00	0.50	0.20	0.40	2.40	8.20	100.60	Clayheritage, 2013
N Devon, Type 2	58.00	1.30	28.00	1.00	0.40	0.20	0.40	2.50	4.50	96.30	Clayheritage, 2013
N Devon, Siliceous	75.00	1.40	16.00	0.80	0.30	0.10	0.30	1.60		95.50	Clayheritage, 2013
Ball clay, highly plastic	59.00	1.00	25.00	1.00	0.30	0.30	0.40	0.90	12.00	99.90	Digitalfire, 2013
Hycast VC	53.0	1.0	30.0	1.2	0.3	0.2	0.20	2.0	12.20	100.10	Bristow et al., 2002
Prestige Blu	54.4	1.3	30.8	1.0	nd	nd		3.1	9.00	99.60	Bristow et al., 2002
Sanblend 90	57.6	1.3	26.8	1.0	nd	nd		2.6	10.20	99.50	Bristow et al., 2002
Prestige TA	60.7	1.5	25.4	1.0	nd	nd		2.9	8.00	99.50	Bristow et al., 2002
Hyplas 71	69.0	1.7	20.0	0.9	0.4	0.1	0.4	1.9	5.40	99.80	Bristow et al., 2002
Hymod Excelsior	49.0	1.3	35.0	1.6	0.3	0.3	0.2	1.2	12.00	100.90	Bristow et al., 2002
Hymod Blue	53.0	1.0	31.0	1.4	0.5	0.3	0.4	3.2	9.20	100.00	Bristow et al., 2002
<i>English China clays</i>											
Super Std	48.00	0.01	37.00	0.41	0.25	0.10	0.15	1.20	12.80	99.92	Bristow et al., 2002
Remblend	48.00	0.05	36.50	0.96	0.30	0.07	0.10	2.00	12.00	99.98	Bristow et al., 2002
Kaolin 31	48.80	< 0.1	35.40	0.8	nd	nd		3.00	11.60	99.60	Bristow et al., 2002
A	46.70	0.03	36.22	1.23	0.25	0.06	0.07	2.11	12.11	98.78	Scott et al., 1996
B	47.78	0.01	35.95	1.37	0.20	0.04	0.07	2.64	11.60	99.66	Scott et al., 1996
C	47.88	0.02	35.95	0.74	0.21	0.08	0.08	2.30	12.61	99.87	Scott et al., 1996
D	49.29	nd	34.60	0.84	0.33	0.12	0.09	3.03	11.55	99.85	Scott et al., 1996
E	49.69	nd	33.90	0.43	0.42	0.16	0.08	2.94	12.16	99.78	Scott et al., 1996
F	51.74	0.04	30.29	0.54	0.54	0.28	0.17	4.69	10.44	99.73	Scott et al., 1996
<i>English Cornish stone</i>											
Dig 2	73.76	0.15	16.33	0.20	0.14	1.81	3.30	4.30		99.99	Digitalfire, 2013
Dig 3	74.22	0.06	15.49	0.12	0.13	1.48	3.48	4.51		99.49	Digitalfire, 2013
<i>French Ball clay</i>											
Montereau	86		14							100	O***, Oppenheim, 1807
Montereau*	78.04		12.04	1.50		2.04			6.46	100.08	O***, Oppenheim, 1807
Montereau	64.4		24.6		0.00	0.00			11.60	100.60	Brongniart, 1877
Montereau	60.26	1.50	26.53	0.79	0.14	0.51	0.25	0.73	9.29	100.00	Pellet, 1993
Montereau	59.21	1.30	27.65	1.04	0.26	0.45	0.35	0.86	8.88	100.00	Pellet, 1993
Montereau	75.10	1.40	21.44	0.80	0.16	0.68	0.07	0.36		100.01	Ravoire et al. 2004
Montereau	64.39	1.33	31.10	1.56	0.25	0.22	0.07	0.68		99.60	Ravoire et al. 2004
Montereau	80.12	1.13	16.04	1.07	0.32	0.15	0.10	1.08		100.01	Ravoire et al. 2004

* Analysis made by Oppenheim, from a terrain belonging to M. Desparda de Cuberton.

Table 6. Eight recipes of English white earthenwares compiled by Brongniart (1844, II, p. 114 + 115). A is classified as “Faïence fine cailloutée” and the other as “Faïence fine feldspathique”. D and H were named “cream colour”, and F “Queen’s ware or cream colour”.

Recipe	Ball clay 1	Ball clay 2	Clay 3	Calcined flint	Kaolin	Altered feldspar	Altered pegmatite	Shavings
A	83.0			17.0				
B	40.0	13.4		16.6	26.6	3.4		
C	43.0	5.0	5.0	15.0	14.0			8.0
D	83.0			16.0			1.0	
E	64.0			16.0	16.0	4.0		
F	54.0		6.0	16.0	16.0			8.0
G	62.0			19.0	16.0	3.0		
H	82.0			16.0		2.0		

Kaolin = China clay, Altered feldspar = Cornish stone. Probably in wt. %. All totals = 100 %.

A $\text{SiO}_2\text{-Al}_2\text{O}_3$ plot (Figure 11a) illustrates the conspicuous range of 17 English ball clays (Table 5). In this diagram, the matrices of Wed-1, Wed-2 and Wed-3 fall on the ball clays correlation line, excluding an admixing of Cornish stone in the paste’s preparation. However, this must be considered with caution as only two chemical analyses for Cornish stones could be found in literature. According to the position of the three matrices in this binary diagram and their overall chemical composition, they may represent: (1) a single, SiO_2 -rich ball clay; (2) or a batch of one or more ball clays; (3) or a batch of one or more ball clays with one or more china clays. A hint may be given considering that a mix of a Si-ball clay (TiO_2 min.-max. for 2 clays: 1.5-1.8 wt%) with a china clay (TiO_2 min.-max. for 9 clays: 0.01 wt%) would result in TiO_2 values of 0.9-1.3 wt% as shown by three Wedgwood matrices.

The amount of flint admixing can be roughly calculated as the difference in SiO_2 between body and matrix compositions (Table 3 and 4), resulting in 4-7 wt% of calcined flint (see also Figure 11a). These values are far below the 15-19 wt% according to Table 6.

Non plastic inclusion types A and B are

chemically and microstructurally very different compared to the Wedgwood’s bodies. It can therefore be excluded that they may represent former biscuits or paste shavings. Their chemical compositions were compared with chemical analyses of Si- or Al-rich ball clays ($n = 6$, Bristow et al., 2002; Clayheritage, 2013), china clay ($n = 9$, Scott et al., 1996, Bristow et al., 2002) and Cornish stone ($n = 2$, Digitalfire, 2013) in order to constrain their origin. Inclusions type A may represent, according to Table 7 and Figure 11b, former Si-rich ball clays or a mix of Si-rich ball clays with Cornish stone, and inclusions type B most probably Al-rich ball clays. Both types were fired and crushed before admixing to the matrix clays.

The Al_2O_3 contents are too low for a kaolinite (china clay) admixing. However, K_2O values >1 wt% could indicate a (low) feldspar contribution. The analyzed Wedgwood white earthenware is therefore probably not typical for his early creamware, but corresponds to a younger paste of the Queen’s ware type.

Creil. French cailloutage factories around Paris (Chantilly, Choisy, Creil, Montereau etc.)

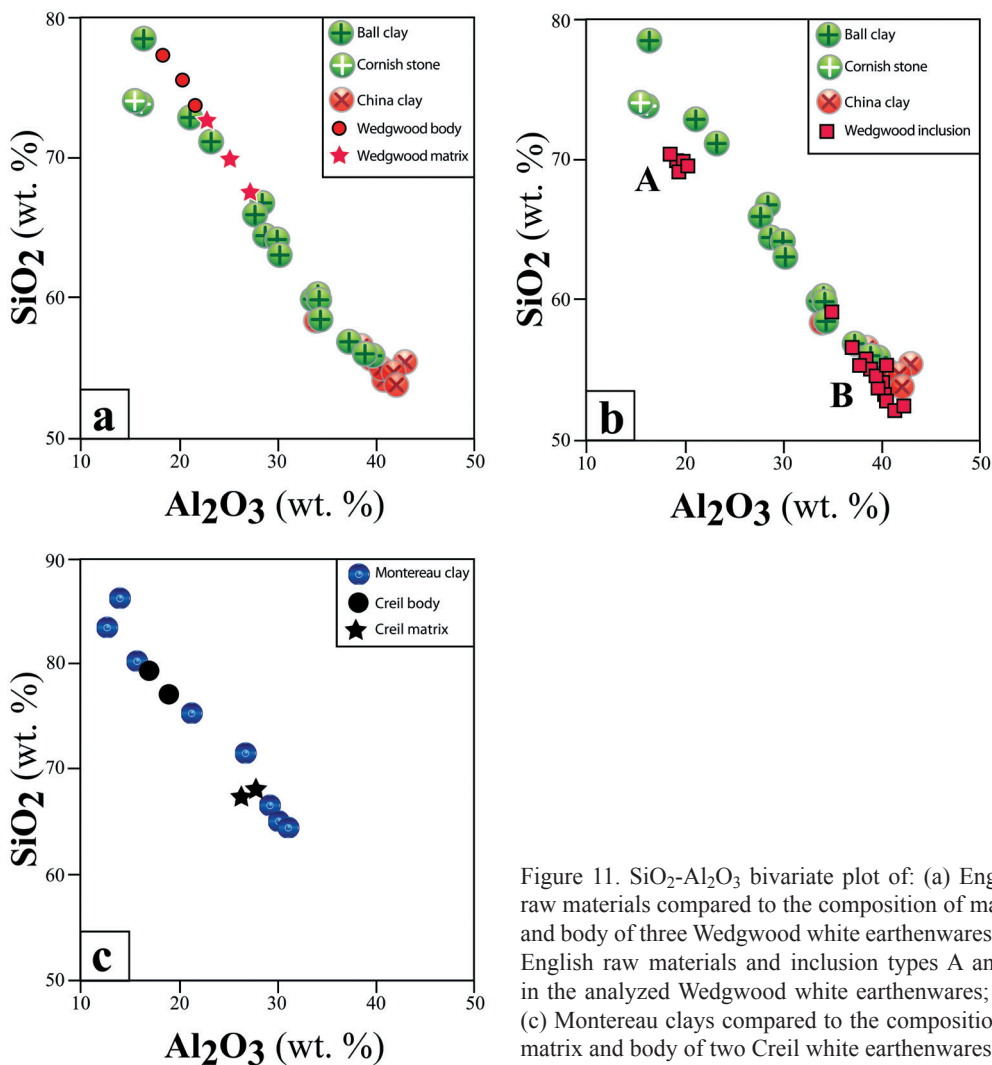


Figure 11. SiO₂-Al₂O₃ bivariate plot of: (a) English raw materials compared to the composition of matrix and body of three Wedgwood white earthenwares; (b) English raw materials and inclusion types A and B in the analyzed Wedgwood white earthenwares; and (c) Montereau clays compared to the composition of matrix and body of two Creil white earthenwares.

used the same raw materials, the same kiln types, and the same recipes (Brongniart, 1844, II). Robert Bray O'Reilly, Englishman and founder of the Creil factory in 1797, specifies (Ariès, 1994, p. 44): "Le silex broyé très fin est mis avec la masse dans la proportion de quatre baquets de silex délayé dans l'eau sur dix-huit de terre également délayée et passée au tamis (The finely ground flint is given to the

batch in the proportion of four buckets of water delayed flint to eighteen sieved of water delayed earth). Unfortunately, this original recipe, used at least during the very first months at Creil as O'Reilly left the direction on February 8, 1799, is impossible to transform into wt% dry ingredients. Other authors claim that the ratio of Montereau plastic clay to calcined flint was c. 88-87: 12-13 (O*** [Oppenheim], 1807;

Table 7. Minimum and maximum values of English raw materials compared to inclusion types A and B. Non matching elements are highlighted in bold. Si-rich ball clays (71-73 wt. % SiO₂), Al-rich ball clays (35-42 wt% Al₂O₃).

Oxide	Cornish stone (2)	Inclusion A (5)	Si-Ball clay (2)	China clay (9)	Inclusion B (17)	Al- Ball clay (4)
Na ₂ O	3.3 - 3.5	0.6 - 1.2	0.3 - 0.4	0.1 - 0.2	0.1 - 0.4	0.2 - 0.3
MgO	0.1	0.3 - 0.4	0.3 - 0.4	0.3 - 0.6	0.5 - 0.8	0.3
Al ₂ O ₃	15.5 - 16.3	19 - 22	21 - 23	34 - 42	35 - 42	34 - 40
SiO ₂	73 - 74	70 - 72	71 - 73	54 - 58	52 - 59	56 - 60
K ₂ O	4.3 - 4.5	2.2 - 2.9	2.0 - 2.3	1.4 - 5.3	2.0 - 2.7	2.0 - 2.7
CaO	1.5 - 1.8	2.7 - 7.3	0.1	0.1 - 0.3	0.8 - 1.2	0.2 - 0.3
TiO ₂	0.1	0.3	1.5 - 1.8	0.01	0.4 - 1.6	1.0 - 1.5
Fe ₂ O ₃	0.1 - 0.2	0.2 - 0.5	1	0.5 - 1.5	1.2 - 1.8	1.1 - 1.8

Bastenaire-Daudenart, 1830; Brongniart, 1844 II). In 1834, Creil presented an improved (since 1827) white earthenware body, called opaque porcelain, as a result of admixing English kaolin, which was cheaper as the French Limoges kaolin (Brongniart, 1844, II, p. 133; Ariès, 1994), and feldspar to the cailloutage paste. The blend was later improved as shown by this recipe (Salvétat, 1857, p. 359): 20 (wt%?) Montereau clay + 20 Alberstone clay + 30 English Kaolin + 18 Limoges feldspar + 12 milled flint.

Creil-1 and Creil-2 are not of the opaque porcelain type, but pertain to the cailloutage white earthenware type, as no feldspar nor kaolinite grains were found in the SEM study. This is supported by their much lower alumina and potassia compared to Creil's opaque porcelain (Table 3). Apparently, their recipe was based on alumina-rich Montereau clays if one considers the Al-richness of the matrices (Figure 11c). The amount of flint admixing can be roughly calculated as difference in SiO₂ between body and matrix (Table 3 and 4), resulting in 9-12 wt% (see also Figure 11c), a value close to the ratio of the 19th century technical treatises (O*** [Oppenheim], 1807; Brongniart, 1844).

Niderviller. François Lanfrey's son Claude-Henri Lanfrey, chemist at the manufacture from 1802 until 1832, specified body and glaze recipes in a manuscript (Lanfrey, 1832), see Table 8. Refractory clays were imported from the Rhine region - Cologne was the exporting place of this raw material -, and mixed with a high amount of chalk. Recipes A and C have no flint, but a lead-frit addition, and recipe B has no frit, but a flint supplement. Although the high CaO of Nider-1 fits well with the calcareous nature of these recipes, the grains of crushed frit and sand or quartz pebbles (also found in TBL 3, Maggetti et al., 2011) doesn't match Lanfrey's recipes. Sulphur and phosphorous indicate gypsum and bone ash as two other additions, not specified too by Lanfrey. The rounded shapes of the frit quartzes as observed in the SEM study are interpreted as having originated in a prograde fusion of primary quartz grains during the fritting process. The idiomorphic laths of the secondary SiO₂ phase, most probably cristobalite in view of its crystal habitus, indicates that this phase crystallized as liquidus phase during cooling of the frit, and not during a sub solidus reaction such as devitrification. Nider-1 differs in its microstructure and in its

Table 8. Three recipes (in pounds) according to Lanfrey (1832), cited in Heckenbrenner (2002). Recipe C is dated 1805.

Recipe	Cologne clay	Flint	Chalk	Frit	Shavings
A	36		16	8*	6
B	300	200	100		
C	200		100	100**	

* calcined mix of flint and lead.

** calcined mix of 100 flint + 6 minium + 6 NaCl + 6 grey minium.

chemical composition from TBL 3 (Table 3), the latter having for example significantly higher Al₂O₃ (16.44 wt%) and lower CaO (10.49 wt%). Both bodies are therefore a clear evidence of a continuous recipe evolution at the Niderviller manufacture, if a Niderviller origin of TBL 3 is accepted (see discussion in Maggetti et al., 2011).

Glazes

Glaze-Body interactions. The observed glaze-ceramic boundary is sharp for all samples. This observation and the very small interface (mostly ca. 5-10 µm) indicate double-firing processes, first a bisque firing followed by a second glaze firing (Molera et al., 1997), a traditional technique for white earthenware. During firing, glaze and ceramic interact with complicated digestion/diffusion processes (Molera et al., 2001; Vendrell-Saz et al., 2006). Such processes must have taken place for the analyzed samples too, as revealed by the important lead diffusion from the glaze into the body. Alongside with this glaze-body contamination, the reverse occurs, i.e. elements diffuse from the ceramic body towards the glaze. Alumina, for instance, diffuses in significant concentrations (over 1 wt%) into an alumina-free lead glaze applied on kaolinitic bodies as far as 150-200 µm (Molera et al., 2001). This finds support by a glaze profile of Wed-1 and Creil-2 revealing a body derived Al₂O₃ contamination over a distance of 35 respectively 110 µm. For the studied samples, contamination could theoretically

have affected the whole section if one considers the thickness of the analyzed glazes compared to the experimental diffusions. A given chemical composition of a thin lead glaze does consequently not correspond 'eo ipso' to its initial composition, but must be interpreted with much caution in recipe calculation. It should not be forgotten that contamination could have occurred not only during the glaze firing, but much earlier, i. e. during the fritting/melting of the glaze ingredients in the refractory, Al-rich crucible (see below). Low alumina content (ca. 1 wt%), is therefore easily explained by diffusion processes. Higher values (Wed-1, Wed-2, Wed-3: 4.5-7.4 wt% Al₂O₃, Nider-1: 5.9 wt% Al₂O₃), however, must result from the addition of clay or feldspar to the glaze mixture (see below).

Recipes. No recipes are known for Creil's cailloutage glazes. However, O*** ([Oppenheim], 1807) published a general recipe consisting of white sand (8 parts) + minium (10 parts) + potash (5 parts) + 1/1,000 of cobalt for the early 19th c. cailloutage manufactures around Paris. This mix was put in a crucible, placed in the bisque kiln and calcined. In two other recipes glass cullet are added to such a minium + potash + silica frit. Similar ingredients - with soda, saltpetre, glass cullets and some borax - are listed by Bastenaire-Daudenart (1830) for unspecified French cailloutage manufactures, and by Brongniart (1844, p. 131) for cailloutage producers in Chantilly, Creil, Choisy, Montereau etc. At Creil, younger opaque porcelain glaze

recipes were more complex, made of a frit (borax + feldspar + calcium carbonate + minium + chalk + PbO), fired in a glaze kiln (Salvétat, 1857, p. 360). This frit was mixed with additional feldspar and milled flint, with a final chemical composition of (in wt%): 56.00 silica, 10.58 lead oxide, 4.80 alumina, traces of cobalt oxide, 7.48 chalk, traces of magnesia, 9.29 Na₂O + K₂O, 7.25 boric acid and 3.60 humidity + carbonic acid. Creil-2 does not show such amounts of Al₂O₃, CaO, Na₂O, K₂O etc., but reflects by its distinct high PbO and moderate SiO₂ a typical cailloutage glaze recipe as published by O*** ([Oppenheim], 1807).

For Niderviller, Seeger (1769, quoted in Heckenbrenner, 2002) and Lanfrey (1832) mention at least three recipes (in pounds):

(a) Sand (75) + soda (25) + salt (25) + calcine (75: 1/4 tin to 3/4 lead)

(b) Sand (100) + soda (11) + salt (13) + calcine (66: 29 Sn to 100 Pb)

(c) Sand (34) + calcined lead (36) + red lead (36) + white salin (31).

Bosc d'Antic (2003, p. 171) defines "salin" as: "Red potash, also known as *salin* or *glass ash*, is the yellowish and greasy fixed alkali obtained by leaching and evaporation from the ashes of all woods and plants except maritime ones." The observed glass cullet (Figure 10d) is not mentioned in one of these recipes. The first two would give a tin opacified glassy layer, as effectively found on the previously analyzed sample TBL 3 attributed to Niderviller (Maggetti et al., 2011). With recipe 3, however, a transparent glaze is obtained. Evidently, the alumina concentration of Nider-1 is related to the presence of potassium feldspar in the glaze, as observed by SEM (Figure 10b, Table 4). This phase could derive from an impure sand or from a specific ingredient, not mentioned in the recipes. The coarse quartz grains of Nider-1 survived the glaze firing and testify a lower degree of milling compared to the quartzes of the Creil and Wedgwood glazes.

Literature doesn't mention recipes for Wedgwood's creamware glazes. But it can be assumed that they must have been close to those of the cailloutage ware, with additional clay or feldspar admixture as revealed by their important alumina content.

Melting temperatures. The melting behaviour of glazes can be discussed using phase diagrams, such as the binary system PbO-SiO₂ studied by several authors. The analyzed glazes begin to melt at the binary eutectic of 739 °C according to one of the latest publications (Smart and Glasser, 1974). Glaze Creil-2 will be completely molten at slightly higher temperatures, as its composition is very close to this binary invariant point. Under equilibrium conditions, however, much higher temperatures of 1000-1100 °C should be reached for a complete melting of the other glazes, due to their silica rich composition. In practice, these glazes contain significant amounts of other oxides such as alumina and potassia, what lowers somewhat the melting temperatures of the binary system, as reported by Geller and Bunting (1936) for the K₂O-PbO-SiO₂ and by Geller and Bunting (1943) and Chen et al. (2001) for the PbO-Al₂O₃-SiO₂ system.

Bisque firing temperatures

Wedgwood and Creil. Their XRD phase association is characterized by high temperature crystals such as cristobalite and mullite, not detected in the SEM analyses. Consequently, these phases are interpreted to occur as minute (sub- μ m) crystallites. According to dilatometric studies of Munier (1957, p. 45-46), flint's chalcedony transforms to quartz and not to cristobalite during the calcination of the flint pebbles. Further, cristobalite cannot be a high temperature reaction product of the flint's α -quartz since in this one component system temperatures of 1450 °C must be reached (Kracek, 1930). Experimental firings

of refractory, Fe-poor clays reported mullite formation at temperatures above 950 °C and cristobalite crystallization at temperatures starting at 1050 °C (Maggetti and Rossmannith, 1981; Maggetti, 1982). Such high temperatures are in good agreement with the upper limit of c. 1200-1250 °C for the first firing of creamware or cailloutage bodies (Munier, 1957) and were also inferred for the French Pont-aux-Choux tableware (Maggetti et al., 2011). Collectively, SiO₂, Al₂O₃ and K₂O constitute 96-97 wt% of the Creil and Wedgwood bodies. Consequently, phase diagrams such as the ternary SiO₂-K₂O-Al₂O₃ system can be used to further constrain the phase associations and firing temperatures of these ceramics. CaO, Fe₂O₃, MgO and Na₂O

contents were assumed to be negligible. It can be seen from Figure 12 that the five bodies fall within the mullite primary field of the phase diagram, very close to the SiO₂-Al₂O₃ joining line, forming a cluster around 20 wt% Al₂O₃ (or 80 wt% SiO₂). Under equilibrium conditions and if other fluxes such as Na₂O are not taken into account, the original paste begins to melt at 985 °C, i. e. at the ternary eutectic point. After dissolution of all the K-feldspars - but was there any K-feldspar in the original clay? -, this melt phase evolves along the silica + mullite cotectic until reaching the assumed upper firing temperature at the isotherm of 1200 °C. Not all quartz is molten at this temperature, as 1400-1500 °C would be needed for such a situation.

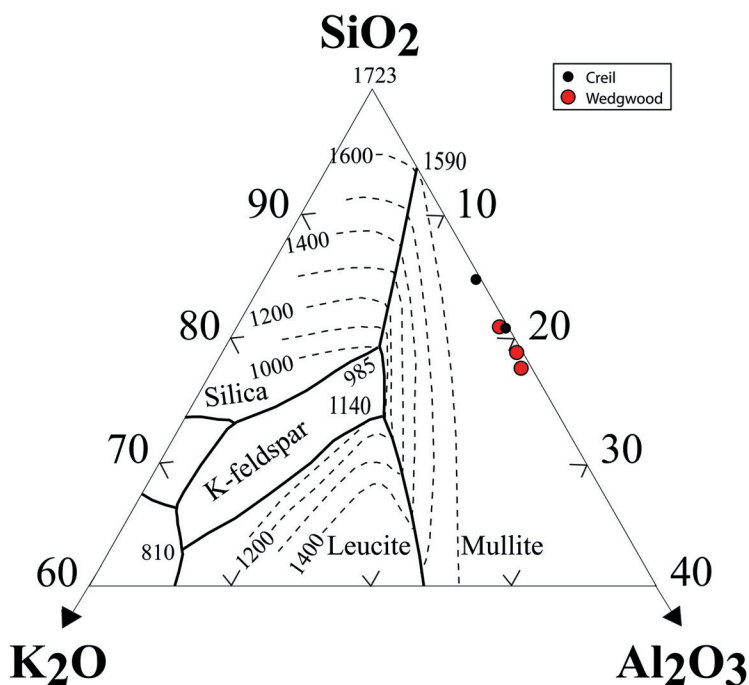


Figure 12. Compositions (wt%) of two Creil and three Wedgwood white earthenwares plotted on the high-silica part of the SiO₂-K₂O-Al₂O₃ phase diagram (simplified after Levin et al., 1964, Figure 407, p. 156). Temperatures in degrees centigrade. Isotherms are shown every hundred degrees in the silica, leucite and mullite primary fields.

However, it must be stressed that only the tiny quartz grains from the kaolinitic clay were involved in this melting process, as no reaction zones are visible at the borders of the calcined flint grains (Figures 7, 8). The amount of equilibrium 1200 °C liquid phase is, according to the lever rule, max. 6-8% for the Creil, and 8-16% for the Wedgwood samples. The higher melt amount of the latter is due to their slightly higher potassia. Such low liquid quantities explain the high porosities of the bodies, despite the high firing temperature.

However, these calculations are only rough estimations, as (1) the small amounts of CaO, Fe₂O₃, MgO and Na₂O will lower the melting temperature leading to higher melt percentages, and (2) the coarse calcined flint particles didn't react with the clay matrix. Further, if the assumed firing temperature was as high as 1200 °C, one wonders why the individual laths of phyllosilicates didn't fuse and are still visible. A lower firing temperature could therefore be more realistic.

Niderviller. The microstructure of sample Nider-1 is very special as it shows a groundmass of large patches of X-ray amorphous secondary (post firing) portlandite Ca(OH)₂. The ancient firing temperature can be estimated by comparison of the phase association (b) with the phase evolution in experimentally fired raw materials with a similar calcareous composition (Maggetti, 1982; Cultrone et al., 2001). The inferred temperature was most probably in the range 900-950 °C, a temperature close to the firing temperatures of calcareous white earthenware from Lorraine (Maggetti et al., 2011).

Conclusion

This study is the first modern chemical, mineralogical and technological characterization of early 19th c. white earthenwares from three manufactures: Creil and Niderviller in France,

and Wedgwood in England. The samples were excavated in a Swiss consumption site. The number of studied sherds is low, as only trademarked and therefore surely attributed specimens were chosen. Notwithstanding, a number of points may be stressed. Creil and Wedgwood bodies are chemically distinct, but microstructurally similar. They classify as siliceous-aluminous white earthenware, made by mixing one or more high-Al clays with calcined and milled flint. In addition, one Wedgwood sample contains two clay-based ingredients (probably grog). The calcareous Niderviller body differs in its chemical composition from a previously published analysis. Its recipe involves the mixing of one or more H-Al clays with calcined and crushed sand/quartz pebbles, chalk and gypsum. The morphological and chemical characterization of the glazes revealed severe burial degradations of the Creil samples. The absence of a marked glaze-ceramic body interface suggests a double-firing process (bisque and glaze firing), in accordance to Early 19th c. technical treatises. In addition to this similar firing technique, chemical contamination/diffusion occurred during the high temperature processes, as evidenced by lead migration from the glaze into the body and alumina diffusion from the body into the glaze.

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