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Abstract

During the 18th century many European manufactures tried to imitate Chinese, Vietnamese and Japanese porcelain. To address the lack of kaolin source they had to test new processes inspired from the fritware technology. Unfortunately, the Sceaux Factory production is poor documented: it was only vaguely reported that different technologies were used to produce soft-paste and hard-paste porcelain as well as different kinds of faiences, including an undocumented "*faïence japonnée*". In order to bring new information, a selection of 25 objects from the *Département du Patrimoine et des Collections de la Cité de la Céramique*, Sèvres, France, attributed to the 18th century Sceaux Factory production, has been analyzed with a portable 532nm Raman spectrometer in museum reserves. Identification of the crystalline phases of the body and glaze as well as pigments allows differentiating the different technologies. According to previous studies on porcelains produced by other factories in Paris area (Chantilly, Saint-Cloud, Mennecy, Vincennes/Sèvres, etc.), wollastonite (β $CaSiO_4$) appears to be characteristic of soft-paste porcelain paste. Therefore, the absence of wollastonite peaks is consistent with a faience body and the concomitance with the presence of quartz peaks can correspond either to hard-paste porcelain or to faience. Cassiterite, wollastonite and quartz are identified as glaze opacifiers. Different olivine and pyrochlore compositions have been evidenced for blue and yellow pigments, respectively. This fact can be related to different pigment technologies (periods or Master).

Keywords: pottery, porcelain, soft-paste, hard-paste, Sceaux, Raman

INTRODUCTION

Chinese, Vietnamese and Japanese porcelains imported by Portuguese and then VOC traders during the 16th and 17th centuries were highly appreciated by European Courts [1]. With the exception of Medici hybrid porcelain produced during a few years in Florence (1575-1587) [2] attempts to produce similar objects in Europe did not succeed before the end of the 17th century (Rouen: >1673 and Saint-Cloud >1695)[3,4]. Actually two routes were experimented: the soft-paste technique issued from the fritware technology (rather similar to ancient Egyptian "faience" and Ottoman Iznik/Kütahya productions)[5-7] and the hard-paste technique [7] similar to that of China ware. China wares require to be prepared by sintering-reaction a mixture of kaolin (a hydroxylated aluminosilicate similar to clays), pegmatite (mainly K- and Na-based feldspars) and sand (silica) [7-9]. Firing led to the formation of a K-rich liquid phase that dissolved other phases and promoted, above 1250°C, the formation of mullite needles. Needles formed a bird nest mesh retaining the liquid phase and preventing the deformation of the object shape [10]. The final alumina-rich material (typical composition: K_2O 4 wt%, Al_2O_3 26 wt% and SiO_2 70 wt%) consists in mullite needles (~16-20% in volume) in a glassy matrix plus some relics of poor dissolved raw materials (~20 % vol. quartz and feldspar). Glazed artefact can be obtained in a single firing cycle. On the contrary, the soft-paste body is silica-rich (K_2O 4 wt%, Na_2O 1.7 wt%, CaO 16 wt%, Al_2O_3 2.5 wt% and SiO_2 75 wt%) [7]. Following the antique fritware technique, sand grains were cemented together by addition of a small amount of clay/marl, carbonates (and glue) and glass (the frit). On heating the glass melts, reacts with and welds the quartz grains. The firing temperature required to sinter soft-paste porcelain is 200 to 400°C lower than that required to prepare hard-paste porcelain (1200 to 1450°C, typically) [11,12]. The low sintering temperature of soft-paste porcelain imposed the choice of lead-based glazes, easily scratched by a knife, a characteristic at the origin of the name. Two firings are made, the first for the body and the second for the glaze and its décor. Furthermore evolution of the mixture viscosity with temperature is very different: for hard-paste porcelain the viscosity decrease is slow, what permits a large temperature window (also optimized by the temperature dwell duration); on the contrary the window is very small for fritware: a few tens of degrees are sufficient to go from an unfired object to a flake! Wollastonite β ($CaSiO_4$) forms on cooling lime-saturated silicate melt.

The lack of kaolin sources limited the attempts to produce hard-paste wares in Europe. E. W. von Tschirnhaus and J.F. Böttger were the first to search and identify kaolin in Saxony and to achieve in 1710 the production of red than white hard-paste stoneware and porcelain [13,14]. The know-how spread to Vienna (1718), Strasburg (1751) and then in many towns [7]. Production of soft-paste wares was concomitant, namely in Saint-Cloud (1695), Chantilly (1725), Vincennes/Sèvres (1740/1756) and Mennecy (1748) [7]. Actually porcelain production in France was a King Family' privilege that strongly limited the number of factories.

François Bardin, an ancient arcanist from the Saint-Cloud Manufacture founded a factory in Paris, rue de Charonne in 1720 and then moved in 1735 to Villeroy Castle, south of Paris, belonging to the Duke L F.A. de Neufville. In 1748 he displaced the factory to the neighbour village, Mennecy (objects are signed D.V.). He died in 1765 and his widow associated the factory to that of J. Julien and S. Jacques at Sceaux, then moved at Bourg-la-Reine, in 1772 under the protection of L.C. de Bourbon (objects are signed B.R.). Simultaneously, L.F. de Bey founded a porcelain factory in Sceaux (joint village of Bourg-la-Reine) in 1735 under the protection of Main Duchesse. In 1748 Jacques Chapelle, after having worked in Vincennes and Strasburg jointed him (objects are signed J.C.). Immediately, a decision from the King Council imposed to stop the production because of the Vincennes Royal Factory Porcelain Privilege. Chapelle and Bey claimed not to produce porcelain but some "*Faience japonnée*", a new and unknown type of pottery. Actually they produced different pastes, faiences and porcelains, and in 1753 finally obtained the permission to make porcelain. From 1763 to 1772 the Sceaux Factory belonged to J. Julien and S. Jacques, owners of the Mennecy Factory. In 1772 Richard Glot bought the factory (mark: SX or SP, with anchor) and continued the production up to 1794 [15-18]. The very complex history of Sceaux productions requires objective clarification tools to support assignments based on stylistic criteria, many items being free of marks.

Raman (micro)spectroscopy allows efficient identification of amorphous and crystalline phases made of covalent bonds [19-21]. Fifteen years ago [22,23] we demonstrated the potential of Raman scattering to document the technology of production of ancient ceramic objects, in particular to discriminate between alumina-rich hard-paste and silica-rich soft-paste porcelain. We demonstrated also that the glaze composition type and pigments can be recognized from the Raman spectra [24]. We were also the first to conduct on-site analysis of ancient pottery and glass [5,6, 25-29]. We present here a comprehensive on site study of artefacts from the Collection of Sèvres Cité de la Céramique assigned to the Sceaux Factory. Many of these artefacts entered in the Collection at the beginning of the 19th century [30]. Comparison will be made with previous measurements performed at the Laboratory with bench-top instruments in 2004 for well referenced objects from Saint-Cloud, Chantilly, Vincennes, Sèvres and Mennecy Factories. Additionally, faience, soft-paste porcelain and intermediate type shards excavated from the ancient Chantilly production site will be considered for comparison.

EXPERIMENTAL METHODS AND OBJECTS

Fig. 1 shows the portable set-up used to analyse the artefacts in the Cité de la Céramique Reserves. A Nd:YAG Laser (Quantum Ventus 100 or 300 mW, UK) emitting at 532 nm injects the beam in an optical fibre up to a remote SuperHead® (Jobin-Yvon Horiba, France). The optical head is equipped with a long working distance microscope objectives (50x Nikon, 50x and 200x Mititoyo, Japan). The same optics is used to focus the beam on the artefact and to collect the scattered light. The laser light is edge filtered and sent through a second optic fibre to the HE532 Spectrometer (Jobin-Yvon Horiba) equipped with a Peltier cooled CCD. The quality of the focus is optimised at very low laser power by eyes examination. A rather heavy (8 kg) micrometric XYZ stage supports the remote head and permits to move it at the micron scale. The weight of the stage guaranties the absence of vibrations during the measurement. Furthermore, the object to analyse and the XYZ stage are put on paper sheets to avoid any vibrations. We first adjust the focus point with eyes examination at very low laser power in the dark. A black textile is then put on the object and head in order to protect them from the ambiance light and the operator from the laser light. Working in dark is welcome. The laser power is increased to have between ~10-20 mW (body and white glaze analysis) and 1-4 mW (coloured glaze). The maximum of the background (fluorescence) intensity indicates that the focus is close to the best. The final focus is adjusted following the quality of the Raman signature. Micronic displacement of the focus through the glaze from the top surface to the body allows measuring the glaze thickness and analysing underglaze décor and glaze-body interphase. Spectral resolution is ~5 cm^{-1}. Baseline subtraction can be made according a procedure established previously in order to highlight the low intensity Raman peaks [31].

Figs 2 to 4 show the studied artefacts. Spots analyzed are shown in Supplementary materials (Figs S1 to S6). Information is summarized in Tables 1 and 2. A first group presented in Fig. 2 consists in three plates, a dish, a stopper and a ewer all assigned as “faience” and a clock support, marked J. Chapelle on the back, assigned as a soft-past porcelain The shape of the object copies that of similar metal artefact. Figs 3 and 4 shows artefacts assigned to be made of soft-paste porcelain. Many décors are made inspired from Meissen productions. Special attention should be paid to the high quality enamelled biscuit such as item MNC26234.

Porcelain and faience shards recovered during building works performed where the ancient Chantilly Factory was originally located, sliced with a diamond saw (Minitom Struers, Danemark) in order to get a good section were used for comparison.

RESULTS AND DISCUSSION

Figs 5 and 6 show characteristic spectra. Even in the case of low fluorescence contribution, because of the edge filter and the optic fibres, the background increases linearly from ~100 to ~ 450 cm^{-1} and then remains almost constant [31]. Small waves are observed when the Raman signal is very weak due to the multilayer structure of the dielectric notch filter. The Raman signal being proportional to the polarizability of the chemical bonds involved, a strong signal is observed only for lead-based glazes (e.g. #19184 and 25991) and for lead-based pigments (yellow (and green) pigments).

Body analysis

Phases identified in body are listed in Table 3. Artefacts are listed as a function of their expected production date listed in Sèvres Museum records considering stylistic criteria and marks. We will first consider the artefacts identified as tin oxide glazed faience and faience *fine* in Sèvres Museum catalogues (Table 1).

The impossibility to obtain a spectrum exhibiting narrow peak(s) is consistent with the fact that the object is faience. However the very porous character of the faience body (typically 15 to 25% [32]) hinders the formation and collection of the Raman scattering. Furthermore, a biologic film is generally present at the pore surface of ancient pottery, which promotes fluorescence. For instance items #5778.2, 19184, 23422 and 76486 don't exhibit spectra. We can conclude doubtless that their body is not a soft-paste. Two of them, items #23422 and 76486, were assigned as Sceaux and probably Sceaux soft-paste porcelain in Sèvres catalogue (Table 2). The assignment is wrong. Note that all the artefacts exhibiting a Raman signature consistent with that expected for faience have been produced during the first years, according the historical records above mentioned.

Peaks of β wollastonite at ~972 (νs SiO_4), 635 (δas SiO_4), 998-1022-1046 (νas SiO_4), 416 (δs SiO_4) and 347 (R' SiO_4) are characteristic of soft-paste porcelain [7]. Traces of wollastonite are observed for the items #25991 stopper and #5497 Mustard pot, what questions their assignment as *faience fine* (Table 1, see further discussion). Quartz signature is also observed for the first artefact. Quartz is commonly the only observed peak on hard-paste porcelain [7] because un-dissolved quartz grains remain present in the body. Contamination of the un-glazed part with glaze during the fabrication is also possible. The best criterion to discriminate between faience and porcelain is the clear ton obtained on porcelain (open porosity < 2%).

All items presented in Figs 3 and 4 exhibiting a strong wollastonite Raman fingerprint are doubtless soft-paste porcelain. Finally, two items # 10053 and 13713 don't exhibit wollastonite peaks and could be made of hard paste porcelain (see further). Items #9096 and 25991 where wollastonite traces are weak could be a material intermediate between faience and soft paste, in other words an incompletely fired soft-paste. Intensity of the Raman signature of quartz is absent or very small/rare for soft-paste body [3]. Cristobalite was not evidenced, contrarily to Chantilly Factory productions [3]. The two plates items #4162 and 19674 assigned as faience in Sèvres catalogue (Table 1) exhibit wollastonite spectra characteristics of a soft-paste body.

Because of the lack of Raman data regarding faience body from the 18th century, we analyzed Chantilly shards rather similar to Sceaux faience. Fig S7 compares typical sections of a soft-paste and a fine faience excavated from the Chantilly Factory. The soft-paste body is rather dense; the mean grain size is ~15µm and the mean pore diameter ~30 µm. The pore size of faience is larger (~100µm) but the grain size smaller. Collection of Raman spectra in many points of the shard section with 50x objective (analyzed surface ~25 μm^2) confirms that the phase observed for Chantilly soft-paste is wollastonite β. For faience shard we only observed in some spots the signature of quartz and in rare cases the spectrum of rutile could be detected. Note that the huge intensity of the later phase makes easy the detection of traces. This confirms that the absence of wollastonite and quartz signature is consistent with a faience body.

Glaze and colouring agents

Most of the glazes exhibit the signature of β wollastonite (Table 3). Some glazes are opacified with cassiterite. This is the case for three faience (items # 5778.2, 19184 and 20505b) as expected by Curators, five soft-pastes (items #22748, 23257, 23258, and 4162) and one hard-paste (#10053). The three faience (5778, 20505b and 19184) and three porcelains (23257, 13713 and 14156) glazes don't show wollastonite peaks.

Two different signatures are observed for blue décors: i) nothing according to the presence of Co^{2+} ions dissolved in the glaze [24,34,35] (faience 23422, soft-paste 5497 and soft-paste 4162), ii) a strong peak at around 820 cm^{-1}, as expected for the olivine $CoSiO_4$ structure [24]. Actually the shift of the peak position from 812 to 830 cm^{-1} and the different intensities indicates different compositions or structural distortions resulting from different preparation/origin of the cobalt raw material (Fig. 6). Similar variable signatures are observed for some green décor (#25991 faience, 21622 soft-paste and 23422 soft-paste), the green colour being obtained by dispersing yellow pigment and blue glass/pigment [24,34]. Two different yellow pigments are also identified. Their Raman spectra show characteristic modes of $Pb_2M_{2-x}M'_xO_{7-\delta}$ pyrochlore, the so called Naples Yellow pigment: a strong Pb-O mode peaking at 124 to 137 cm^{-1} and a Sb-O mode at ~508 cm^{-1} [35-43]. The shift of the first peak to higher values is correlated to the intensity increase of the 330 and 450 cm^{-1} modes, according to the partial substitution of Sb atom by Sn, Zn, Si etc. atoms [35-43]. No correlation is found with the nature of the body, the different glaze composition should be chosen to control the hue. The wavenumber shift and relative intensity don't only depend on the composition but also from the firing temperature and atmosphere.

Classically red and orange colours are obtained with hematite (see intense signal in #4162, 20505b, 23422 and 14156 with 217, 286, 400, 499, 600 and ~1300 cm^{-1} peaks).

Wavenumber maxima of the SiO_4 bending vs. stretching massifs allow discriminating between the different compositions of the glaze [44]. However the complex shape of the background for portable instruments makes often the determination of the bending band maximum inaccurate. However some pieces of information can be extracted from the stretching mode. Almost all glazes exhibit peaks between 1000 and 1010 cm^{-1} a lower value than observed for hard-paste glaze, because of the lower firing temperature [45]. This indicates that the glass is partially depolymerised, according to the addition of lead to allow a firing at ~1000°C or less (*Petit Feu*). Lower stretching maxima are measured for yellow glaze, up to 975 (19674) 940 (20505b) or even 910 (14156) cm^{-1} because of the lead addition associated to the yellow pigment.

CONCLUSIONS

Despite the complex background and the medium resolution of portable instruments, the on-site non-invasive analysis of artefacts led important results. Body analysis of some artefacts assigned as faience exhibits the wollastonite β spectrum, a phase typical of soft-paste porcelain according to previous studies on porcelains produced by other Factories in Paris area (Chantilly, Saint-Cloud, Mennecy, Vincennes/Sèvres, etc.). Incomplete firing of a soft paste could maintain a level of porosity sufficiently high to make the manual acoustic test close to that expected for faience and led to a wrong assignment. Analysis of the sample microstructure (i.e. sampling for thermal expansion and composition measurements) is needed to go deeper in the discussion, especially to collect arguments to establish if the incompletely firing was intentionally or not. In this way, "*faience japonnée'* would be a soft-paste porcelain, intentionally incompletely fired in order to respect the King' privilege. The absence of wollastonite peaks and the presence of a quartz peak can correspond either to hard-paste porcelain or to faience; the differentiation can be made from the sound and the mass of the object. The mullite signature, characteristic of hard-paste porcelain is hardly detected because its intensity is always very low. An advanced laboratory instrument and a rather high laser power focused on the pottery section or microfracture are needed. Glaze Raman signatures are typical of lead-glaze composition. Cassiterite, wollastonite and quartz are identified as glaze opacifiers. Different olivine and pyrochlore compositions have been evidenced for blue and yellow pigments, respectively.

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FIGURE CAPTIONS

Fig. 1: Set up used for on-site analysis. The black textile is put on the object and remote head when the laser power is increased. An example of collected spectrum is shown: the two narrow peaks are the signature of β wollastonite.

Fig. 2: Sceaux pottery assigned as Faience except the clock support marked J. Chapelle on the back (see Table 1).

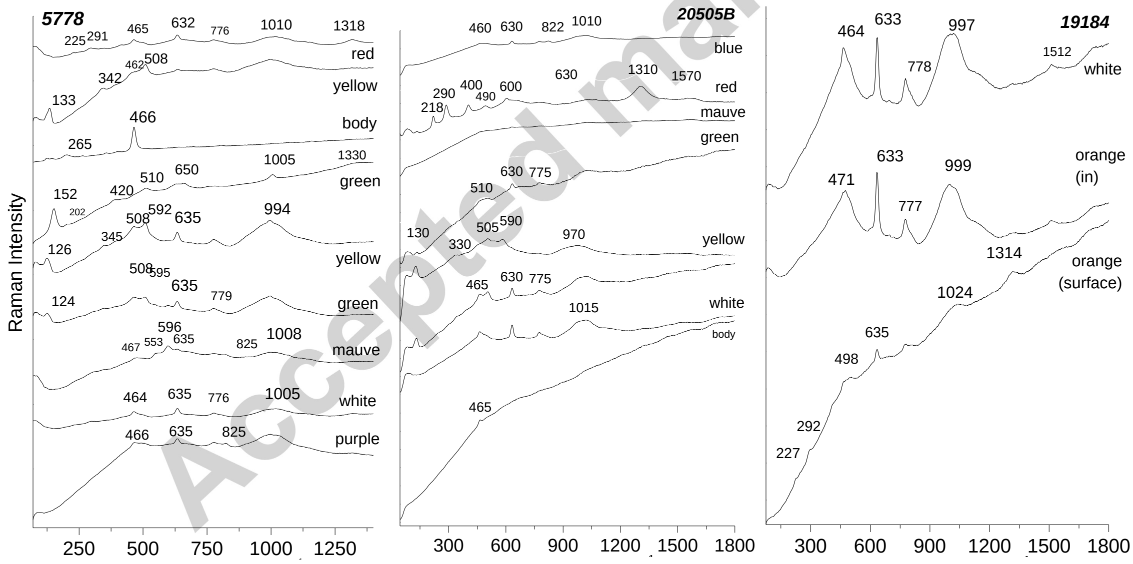
Fig. 3 : Sceaux pottery assigned as porcelain (see Table 2), except 16486 artefact assigned to Chantilly or Vincennes Factory, 8789 figurine to Mennecy, 9120 soupier potentially to Paris and 14156 to Vinovo (close to Turin, Italy) production.

Fig. 4: Sceaux pottery assigned as porcelain (see Table 2), except 10053 figurine assigned to Mennecy.

Fig. 5: Representative Raman spectra collected on body, white and coloured glaze. Top spectra are shown as collected. A baseline subtraction has been made for other spectra.

Fig. 6: Representative Raman spectra collected on body, white and coloured glaze. Top spectra are shown as collected.

Fig. 7: Representative Raman recorded for blue and yellow décor.



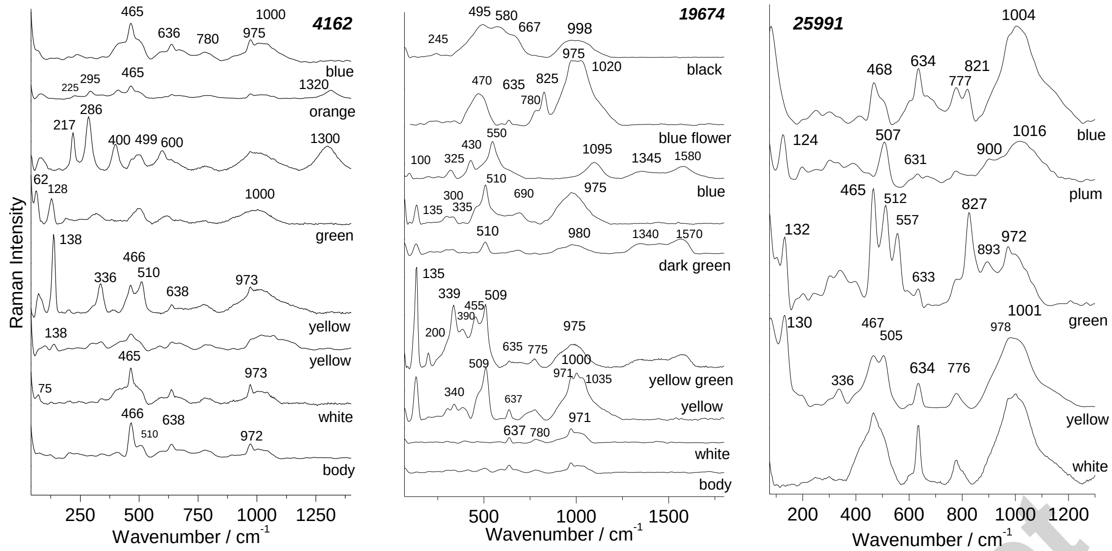
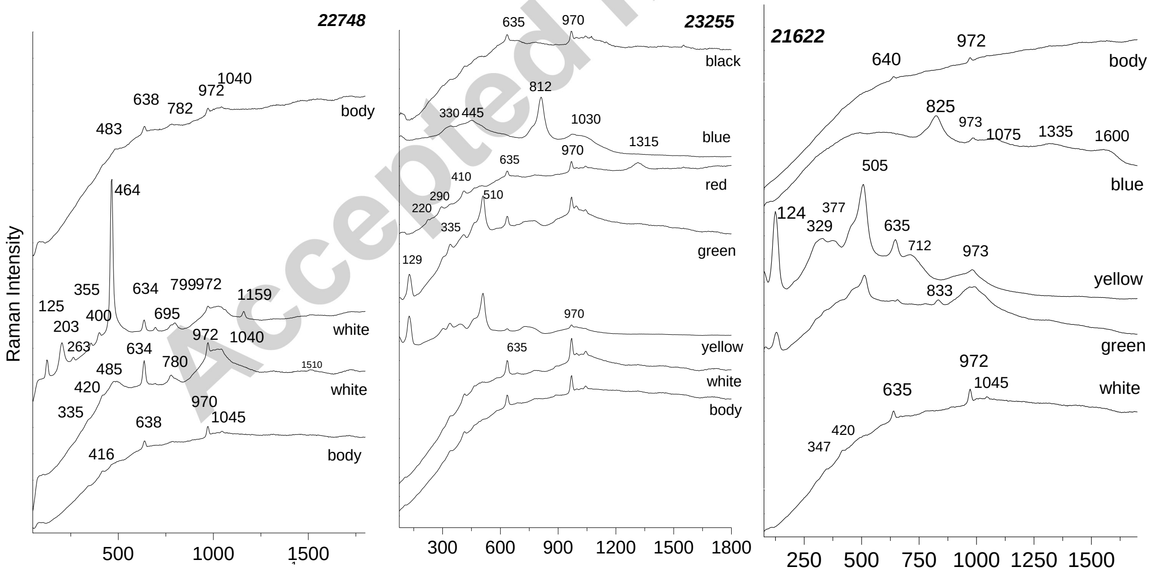


Fig. 5: Representative Raman spectra collected on body, white and coloured glaze. Top spectra are shown as collected. A baseline subtraction has been made for other spectra



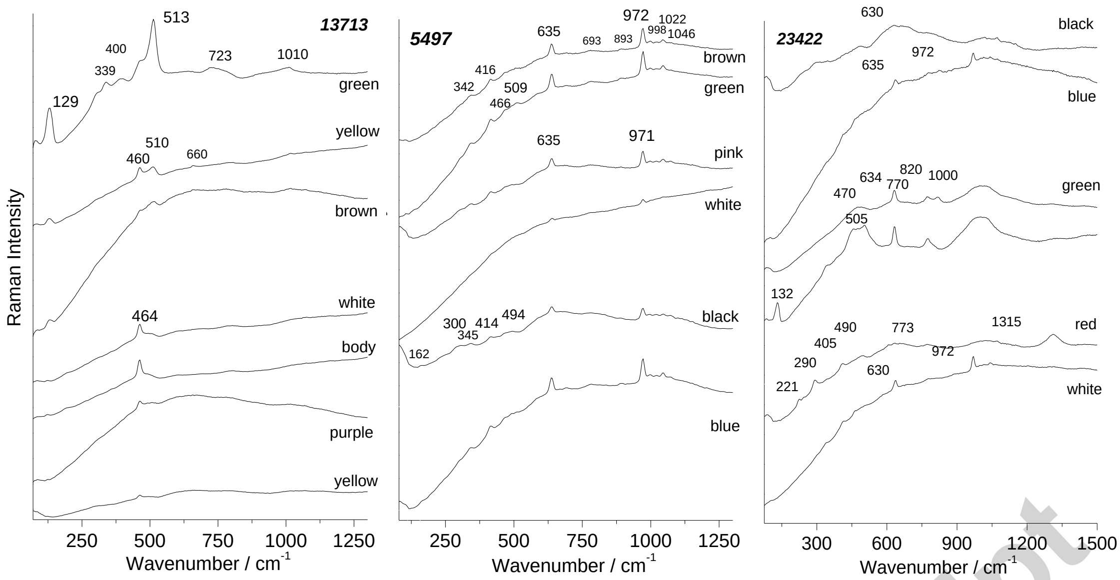


Fig. 6: Representative Raman spectra collected on body, white and coloured glaze. Top spectra are shown as collected.

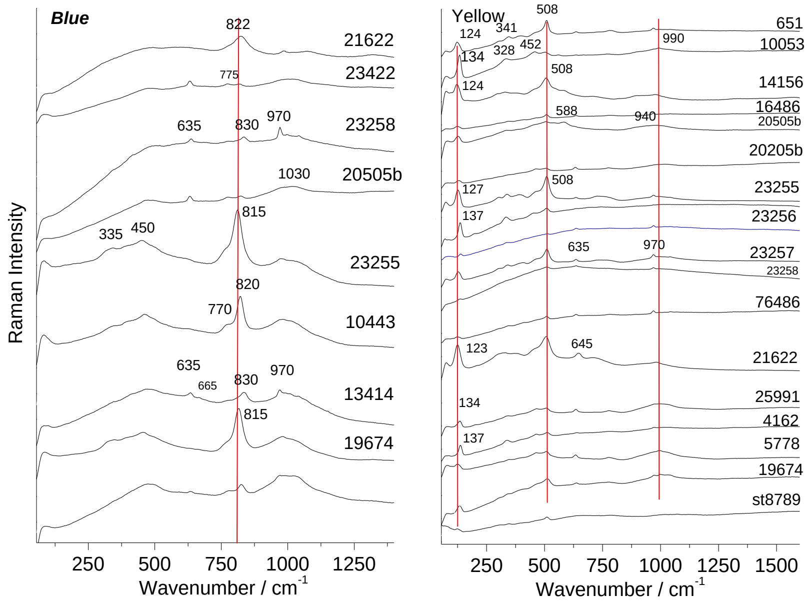


Fig. 7: Representative Raman recorded for blue and yellow décor.

TABLE CAPTIONS

Table 1: Studied objects listed as “Sceaux faience”. Date of production is expected from the stylistic analysis (MNC: Musée National de la Céramique reference number).

Date	Factory	Type (assignment)	MNC	Object
1750	Sceaux	Tin oxide glazed faience	5778.2	plate

1753-55	"	Tin oxide glazed faience	20505b	plate
1750-60	"	Tin oxide glazed faience	19184	pitcher
1770-80	"	*Faience fine*	4162	*plate*
1770-80	"	*Faience fine*	19674	*display plate*
1780-90	"	*Faience fine*	25991	*tureen stopper*

Table 2: Studied objects listed as "porcelain". Date and place of production are expected from the stylistic analysis.

Date	Factory	Type (assignment)	MNC	Object
1754	"	Soft-paste	22748	clock support

1765-70	Sceaux	“	23255	ewer
“	“	“	23256	sugar pot
“	“	“	23257	plate
“	“	“	23258	plate
~1770	“	“	21622	pot-pourri
1774	“	“	13414	pot shadow
1775	“	“	13713	pot stopper
“	“	“	10443	sugar pot

~1775	"	"	9096	ewer
1772-85	"	"	5497	mustard pot
18th c.	"	"	26234	figurine
18th c. ?	"	"	*23422*	*plate*
18th c. ?	Sceaux or Paris?	"	9120	tureen
18th c.	Mennecy	"	10053	*figurine*
18th c. ?	Mennecy?	"	St8789	figurine
18th c. ?	Chantilly or Vincennes?	"	16486	coffee pot

18^{th} c.	?	“	651	figurine
18^{th} c. ?	?	?	879-7	milk pot
18^{th} c. ?	?	?	76486	*pot stopper*
18^{th} c.?	Vinovo?	?	14156	cream pot

Table 3: Phases identified in the body and in colourless/white glazes of analyzed objects. Dates of production are expected from the stylistic analysis. Assignments in contradiction with visual curator assignment are underlined.

Code	**Object**	**Date**	**Body phases**		**Glaze**			**Assignment**
			Wollastonite	*Quartz*	*Wollastonite*	*Cassiterite*	*Quartz*	
5778.2	Plate	1750				X	x	*Faience*

20505b	Plate	1753-55		x		X	x	*F* ?
22748	Clock	1754	x		x	X	x	***Soft-paste***
19184	Pitcher	1750-60				X		Faience
4162	Plate	1770-80	x	x	x	X		**Soft-paste**
19674	Display plate	“	x		x			**Soft-paste**
25991	Stopper	1780-90	(traces)	x	x	X	x	**Soft-paste?**
23255	Ewer	1765-70	x	(traces)	x			*Soft-paste*

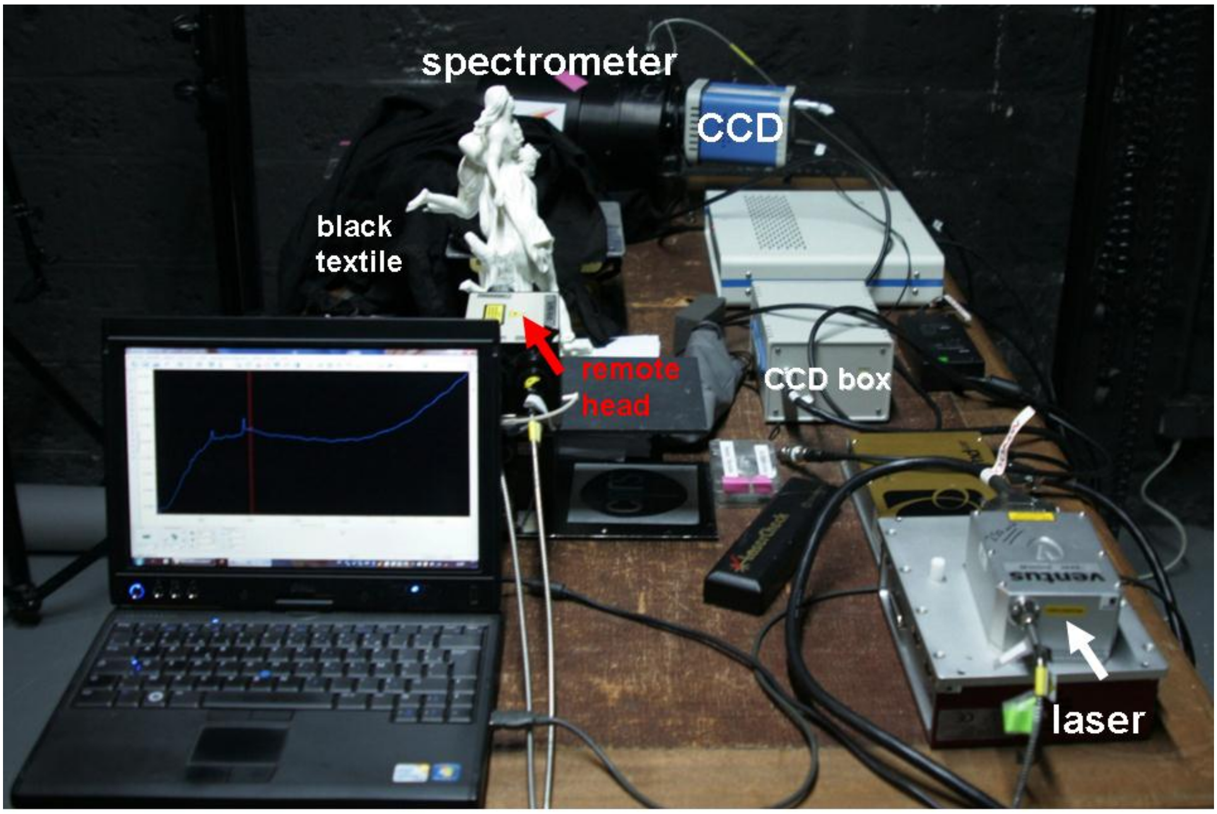
23256	Sugar pot	“	x		x		(traces)	*Soft-paste*
23257	Plate	“	x	(traces)		X		*Soft-paste*
23258	Plate	“	x	(traces?)	x	X	(traces?)	*Soft-paste*
21622	Pot-pourri	1770	x		x			*Soft-paste*
13414	Pot shadow	1774	x	x	x			*Soft-paste*
13713	Pot stopper	1775		x			x	Hard paste
10443	Sugar pot	“	x	x	x		x	*Soft-paste*

9096	Ewer	“	x		x			*Soft-paste*
5497	Mustard pot	1772-85	(traces)		x		x	*Soft-paste*
26234	Figurine	18^{th} c.	x		x		(traces?)	*Soft-paste*
23422	Plate	18^{th} c.?			x		x	**Faience?**
9120	Dish	“	x		x			*Soft-paste*
10053	Figurine	18^{th} c.		x	x	X?	x	**Hard-paste?**
St8789	Figurine	18^{th} c.?	x	x	x	(traces?)	x	*Soft-paste*
16486	Coffee	“	x	(traces)	x		x	*Soft-paste*

	pot							
651	Figurine	18th c.	x		x			*Soft-paste*
879.7	Milk pot	18th c.?	x	Traces?)	x		x	*Soft-paste*
76486	Pot stopper	"			x			Faience ?
14156	Cream pot	"	x				x	

Highlights

- First on-site Raman identification of Sceaux faience and porcelain.
- Differentiation between faience, and soft-paste/hard-paste porcelain.
- faience japponée identification

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23256
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