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An on-site Raman and pXRF study of Joseph Coteau and Philippe Parpette's jewelled porcelain: a summit of ceramic art

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Abstract: Gilt-decorated porcelains of the French enamellists Joseph Coteau and Philippe Parpette, unifying metal and ceramic enamel techniques had been produced for a short time period, between ~ 1770 to 1800 AD. However, this type of production was limited and poorly documented. Their enamelled decorations consist of lead-based transparent and opaque enamels coating gold foils fired on the porcelain glaze. Rare items had been produced at different factories (Sèvres Royal Factory, Comte d'Artois Factory) and it is reported that some copies had been made during the 19th century. We present here the first (non-invasive) Raman study of four cups and two pairs of vases (also analyzed by pXRF) belonging to the productions from these factories. The decors made of enamel on gold foil (*paillon* in French) were applied both on soft-paste and hard-paste porcelain body. The bonding between the gold foil and the glaze was found to be obtained by addition of arsenic and perhaps some other fluxes (boron, bismuth?). Differences were identified in the glazing/enamelling technology. The use of cassiterite opacifier seems to be characteristic of Coteau's technique.



Keywords: porcelain; enamel; glaze; on-site Raman; pigments; gold.

Highlights

This is the first study of Coteau/Parpette's jewelled (hard-/soft-paste) porcelains by Raman spectroscopy.

Use of arsenic as a flux to bind gold foils to glaze is revealed.

Cassiterite in some enamels is linked to Coteau's production.

1. Research Aim

The configurational development of non-invasive analytical techniques such as Raman microspectroscopy [1-4] allows studying rare masterpieces for which technical information regarding the materials used and production technology is limited. Important advantages of Raman microspectroscopy are high spatial resolution (in microns scale), contactless usage and the structural information obtained not only for crystalline matter but also for amorphous, glassy phases. Mobile X-ray fluorescence spectroscopy (pXRF) is also a technique of choice for non-invasive elemental analysis of valuable cultural objects. However, light elements (e.g. boron, carbon, oxygen, and sodium) are not measured by this technique and standard handheld instruments require contact with the studied object limiting the type of objects to be studied [5-10]. Last generation of portable XRF spectrometers allows a ~10 mm gap between the instrument and the studied artefact and the identification of elements complement the Raman analysis very well. Mobile motorised XYZ stages are however required.

The present study deals with the on-site Raman characterization of outstanding late 18th century French porcelains with complex décor made of enamelled areas covering a thin gold foil (so-called *paillon* in French, obtained by forming and cutting with a steel die) placed on the glazed porcelain, the later called "*jewelled porcelain*". Vases, plates, cups, saucers and other pieces thus decorated with enamels, presented the appearance of being inlaid with precious stones, *en cabochon*, set in gold on rich coloured grounds, in close imitation of ruby, turquoise, sapphire, pearl and other gems. These items can be regarded as analogous of the Chinese porcelains and jades decorated with inlaid-gems by the Ottoman goldsmiths [11-13]. The jewellery of Chinese porcelains, as a well-organized Ottoman craft in service of the sultans, had been carried out by a specialized group of craftsmen mainly from the mid-16th century to the mid-17th century. Objects with inlaid-gems were then made by Mogul goldsmiths [14]. An aesthetic relationship can also be drawn with some French snuffboxes also decorated with enamels and gold foils from the 17th and 18th centuries [15,16]. The technique on porcelain had been used by the enamellist Joseph (or Jean-Joseph) Coteau (1740-1801), in collaboration (see further) with the painter Philippe Parpette (1738-1806). Information on Joseph Coteau and Philippe Parpette and their productions is limited and available mainly in the description of outstanding clocks in auction and exhibition catalogues [17-22] and in the books of Atlee Barber [23] and Sassoon [24] as well as in two short papers [25,26]. There is no real study on the material composition of their productions and the technical procedure used.

Coteau was born in Geneva and accepted as a master of enamel painting in 1766 by St-Luc Academy in Paris. He is well known for the decoration of exceptional clocks and a complete soft-paste porcelain service offered by the King of France, Louis XVI and the Queen Marie-Antoinette to Sophie-Dorothea Augusta Luisa von Württemberg, *Comtesse du Nord*, spouse of Pavel Petrovich, future Paul

I, the Emperor of Russia [27]. Coteau worked as a freelance enamellist in different factories, particularly at the Sèvres Royal Factory where Parpette was also appointed, and at Comte d'Artois Factory. The competition between the two craftsmen was very strong, for instance the administration of the factory asking Parpette to control and give arguments to discuss the lowering of the invoices sent by Coteau for his work at Sèvres [25,26]. It seems that Coteau was the only one to have the expertise to make enamel-on-gold foil decoration on hard-paste porcelain although Parpette is also known to make such decorations, but only on soft-paste porcelain [25]. However, he claims to be the first to make such decors on hard-paste porcelain. The production of Coteau is limited and remains highly appreciated, as the auction prices demonstrate. Philippe Parpette was born in Chantilly in 1738 and worked as a painter/enamellist at the royal manufacture of Sèvres from 1755 up to his death in 1806 and at the manufacture of Chantilly from 1770 to 1773. He is well known as a painter of flower decors. It is reported that Edmé Samson (1810-1891), a factory master who produced many 'replicas' of pottery masterpieces, later succeeded to make similar jewelled porcelains. Then, Camille Naudot (1862-1938) and André Fernand Thesmar (1843-1912) are also reputed to have produced gilt-enamelled artefacts [25,26].

Enamelling and glazing metal wares and porcelains are different technologies due to the large difference of thermal expansion of the substrate, with the thermal expansion of metals being about twice that of porcelain [28-31]. Consequently, firing temperatures of the enamels applied on metal wares and porcelains (overglazes) are also different. However, there are similarities between metal enamels and pottery overglazes, both in relation to firing temperature and composition as well as the pigments used. In this context, links between renowned examples of enamels on metal such as Limoges and Chinese *cloisonné* enamels and porcelain overglazes such as Chinese Qing porcelains (*fangcai* ware) have been established in historical reports and partially demonstrated by analytical studies [32-37]. The earliest gilded pottery had probably been made by the Abbasids but the oldest preserved ones belong to Persian (Ilkhanid period) *minai* (or *hafrang*) pottery from the 13th century [38]. First gilded Asian porcelains were made by Yuan potters at the end of the 13th and 14th centuries (The *Pax Mongolica* facilitated the exchanges between Iran and the Far-East), then the technique spread from China to Vietnam and Japan (*kirande* decor) during the 15th and 16th centuries [39,40]. Similar (fired) gilding on porcelain was made in France, at Saint-Cloud Factory, at the end of the 17th century—very beginning of the 18th century and gold foils then started to be enamelled for the first time [25]. In all these gilded artefacts, thickness of the gold coating is very thin, being a few microns or less [39]. In Germany, Meissen Factory, particularly the Dinglinger Brothers, also produced porcelains with enamelled gold decoration [25].



Fig. 1. The analyzed cups and their marks. Details of their decors are shown (see also Table 1).

Enamelling on gold and other metal objects is an old technique which reached a high level by the Byzantine craftsmen from the 8th century AD. The technique then developed during the second part of the Middle-Ages in Western countries, at e.g. Silos, Burgos (Spain) and Limoges (France) [32-34] and flourished during the 17th century with the miniaturisation of enamels such as in enamelled watches and snuff boxes [15,16,41]. The identification of the phases and elements forming the

enamels and glaze of gilt-enamelled porcelains is significant in terms of addressing the question of the link between metal and porcelain enamelling techniques during the 18th century and may potentially offer criteria of identification for distinguishing artefacts produced at different time periods.

2. EXPERIMENTAL

2.1 Artefacts

The eight artefacts analysed including four cups and two pairs of vases, are listed in Table 1 and shown in Figures 1 and 2. The spots to be analyzed were only selected on the vertical face of the cups for technical reasons: Raman analysis with long working distance microscope objectives must be made perpendicular to the surface of the artefact to collect efficiently the small part of light inelastically scattered (the Raman signal) and setting of the mobile XRF instrument is difficult for high concave and convex surfaces of objects.

Studied artefacts belong to the collections of Musée du Louvre in Paris (see Table 1). Marks of Sèvres Royal Factory with characteristic inter-crossed double \mathcal{L} character (\mathcal{L} for Louis XIV, The Sun King) [23,24] are present on the bases of the cups (three marks written with gold ink, one with blue, Fig. 1) and on one pair of vases (gilded mark, Fig. 2). The letter (double letter after 1778) in between inter-crossed double \mathcal{L} indicates the year of production (Table 1). Two marks are special such as the gilded mark of R350 cup without letter(s) in between the inter-crossed double \mathcal{L} but with LG indication below (Fig. 1). The gilded mark of R348 cup shows a graph interpreted as *II* or better *LI* which would correspond to the year 1786 (according to some authors, *LI* was never used or not used for 1786 at least). Similar LG characters are also observed in R350 cup but with HP characters written. Usually, these additional letters represent the gilder's/painter's signature and LG should correspond to Pierre-Antoine Le Guay (1743-1819) [42].

The two pairs of vases show additional bronze decors. The vases with CC mark (corresponding to 1780) which have bronze handles, plated on both sides, are productions of the Sèvres Factory. It is possible that this pair of vases was the one described as "*vases beau bleu*" in the 1780 Le Guay Registre mentioned by Préaud [26,42] and was assigned to Parpette. The vases produced at Comte d'Artois Factory (Limoges, also called Duc d'Artois Factory) [43] show bronze handles in scrolls and a bronze stopper. The mention "*cuit au charbon de terre in 11 aoust 1783*" which means fired with earth coal in 11 august 1783 in black and the name "*coteau*" in red (Figure 2) were marked on the back side of the foot. It is known that use of coal as fuel was a novelty in France in those years. It is worthy to mention here that Chinese Ming and Vietnamese potters had already used earth coal as fuel for centuries before to produce the high temperature required for sintering porcelain and the

method implies the use of ceramic boxes (“cazettes”) to protect each artefact from the atmospheric pollution during the firing process (some colouring elements are volatile and may contaminate neighbouring artefacts; ashes from coal give rise to punctual defects).



Fig. 2. The analyzed vases and their marks: left, Sevres Factory vase (OA10946) with CC mark (1780); analyzed area is located around the medallion; right, Comte d’Artois Factory vase (OA7739) with “coteau” in red and “CUIT AU CHARBON DE TERRE” in black marks; analyzed areas are below the top, the central bandeau and the decor close to the bottom.

Table 1: The historical information about the studied artefacts and their physical characteristics (H: height ; L: width ; D: diameter)

Artefact	Inventory number	Size (cm)	Factory	Physical description	Mark/year
cup	TH1291	H:6 D:5.5	Sèvres	Body; colourless and blue glaze; blue mark; blue under gold foil; black, white, red, green enamels	Blue, <i>LL</i> +DD/1781
cup	OA10655	H:4.5 D:5	Sèvres	Body; colourless glaze; turquoise-blue, blue, white, red, green enamels	Gilt, <i>LL</i> +EE/1782
cup	R348	H:7 D:6.7	Sèvres	Body; colourless glaze; white, green, turquoise, red enamels	Gilt, <i>LL</i> + <i>ff</i> /1786 (?)
cup	R350	H:6.7 D:6.5	Sèvres	Body; colourless and blue glaze; blue, white, pink, red, green enamels	Gilt, <i>LL</i> /?
Vase (pair)	OA10946	H: 40 D: 16	Sèvres	Body, colourless and blue glaze; blue under gold foil, white, grey, red, light orange, green enamels	Gilt, <i>LL</i> +CC/1780
Vase (pair)	OA7739	H:34.5 L:22	Comte d'Artois	Body; colourless and blue glaze; blue, white, red, green, turquoise enamels	coteau <i>Cuit au charbon de terre le 11 aoust 1783</i>

2.2 Raman microspectroscopy

Due to the rareness and high value of the artefacts, Raman analyses were carried out at the museum storage room with a mobile HE532 Raman set-up (HORIBA Scientific Jobin-Yvon). The different coloured areas of the porcelain artefacts were analysed non-invasively. In order to obtain a better statistical view of the representativeness of the collected data, at least three Raman spectra were recorded for each colour. The Raman set-up includes a remote SuperHead[®], the HE532 spectrometer (920 lines/mm; resolution $\sim 4 \text{ cm}^{-1}$) and a 532 nm 300 mW laser (Ventus Quantum). The use of green laser is advantageous in the analysis of glassy artefacts. The SuperHead[®] which is an optical remote device equipped with microscope objectives for the micro analysis of the artefacts and connected by optic fibres to the spectrometer and the laser source, was placed on a heavy and very stable stage with XYZ micrometric displacements for the precise adjustment of the laser beam focus as well as precise recording of the spectra [4]. The set-up includes a Horiba Scientific CCD detector which is cooled at 200 K by Peltier Effect. The reliability of the Raman spectrum starts above 80 cm^{-1} due to the edge filter but a flat spectral background is only obtained over 500 cm^{-1} . During the measurements, height position of the artefact was adjusted with the support of reams of copy paper. A x200 Mitutoyo microscope objective ($\sim 13 \text{ mm}$ long working distance) was used for the analysis of the cups while a x50 Nikon (17 mm long working distance) was used for the study of the vases. These objectives provide small focused beams (waist $\sim 0.5 \mu\text{m}$ and $2 \mu\text{m}$; in-depth $\sim 2 \mu\text{m}$ and $5\text{-}10 \mu\text{m}$, respectively), perpendicular to the sample surface, which allow the recording of spectra not/poorly contaminated by the sub-layers. The power of laser illumination was roughly controlled at the SuperHead[®] with a variable shutter at the arrival of the optic fibre connected to the laser. The focus quality of the laser beam was also first checked by visual examination at very low laser power in the dark. The SuperHead[®] and the artefact analysed were covered with a black textile piece in order to

prevent the ambient light causing false peaks and protect the scientist's eyes from the laser scattering. Then, the laser power was increased according to the colour of the analysed spot during the analysis, to about 1 mW for the black/dark coloured areas and 10 mW for the colourless areas and body. The focus was first adjusted by moving the 3-direction micrometre stage to obtain the maximum level of counts on the laptop screen which corresponds to a focus at the sample surface. In the first instance, the carbon signal is usually observed very rapidly due to elimination of the dust at the surface of the artefact together with some decrease of the background level. Modification of the focus allows recording of good spectra from the very surface to the substrate. The spots to be analyzed were selected on the vertical face of the cups for technical reasons. The microscope objective axis must be perfectly perpendicular to the analysed surface due to the rather low numerical aperture (~ 0.5 and 0.8) of super long working distance objectives. Thus, the Raman signal (small part of light inelastically scattered) is collected efficiently. The very small laser spot (about $0.5 \times 0.5 \times 2 \mu\text{m}^3$) obtained with x200 objective requires a very precise focus which takes longer times to adjust but it is more efficient for the analysis of the single enamelled layer without any contribution of the substrate, eliminating the commonly observed fluorescence from the sub-layers. Thus, it provides a spectrum with less background than those obtained with less sophisticated common objectives. In fact, the shape of the spectral background gives information about the colour of the analysed spot: flat for a blue area, decreasing for a red area and increasing for yellow or green areas (see further). Obviously, the signal level is lower for a black or heavy coloured area due to the absorption of light. Thus, a lower power of illumination is required for these areas. Recording times of the spectra vary between a few seconds and a few minutes as a function of the number of accumulations required (3 to 100), and also in relation to the microscope objectives used.

2.3 X-ray fluorescence analysis

XRF analysis was performed non-invasively using a portable Elio XRF instrument (ELIO, XGLab Bruker, Italy). The set-up includes a miniature X-ray tube system with a Rh anode (max voltage of 50 kV, max current of 0.2 mA, and a 1 mm collimator), and a large area Silicon Drift Detector (SDD) (50 mm^2 active area) with energy resolution of $< 140 \text{ eV}$ for Mn $K\alpha$, an energy range of detection from 1 keV to 40 keV, and a maximum count rate of $5.6 \times 10^5 \text{ cps}$. Measurements were carried out in the point mode using a motorised XYZ stage, with the following operating conditions: an acquisition time of 40 s, a tube voltage of 40 kV and current of $100 \mu\text{A}$. No filter was used between the X-ray tube and the artefact. Three measurements were made for each coloured area analysed in order to achieve a better statistical view. The working distance (distance between the sample and detector) during analysis was around 15 mm, the distance between the instrument front and the artefact being about 10 mm. In the case of high objects with concave and convex surfaces, adjustment of the mobile XRF

instrument is difficult thus the measurements must be carried out perpendicularly to the surface of the artefact. High intensity spectral signals were obtained with the optimization of the signal-to-noise ratio (SNR) by selecting the set-up parameters chosen. Information thickness during analysis of the enamel is estimated to be close to 4 μm at Si K_{α} , 130 μm at Cu K_{α} , 220 μm at Au L_{α} , and 2.5 mm at Sn K_{α} . The data obtained were processed using the data reduction software provided by the factory, which enables automatic peak recognition supported by manual peak selection and checking. The software also enables curve fitting based on chosen elements to provide match between the measured spectra and theoretically predicted spectra calculated from fundamental parameters (FP). Semi-quantitative elemental compositions were also calculated for the elements of interest using FP by the instrument software when the sample thickness fulfils the infinite thickness criteria.

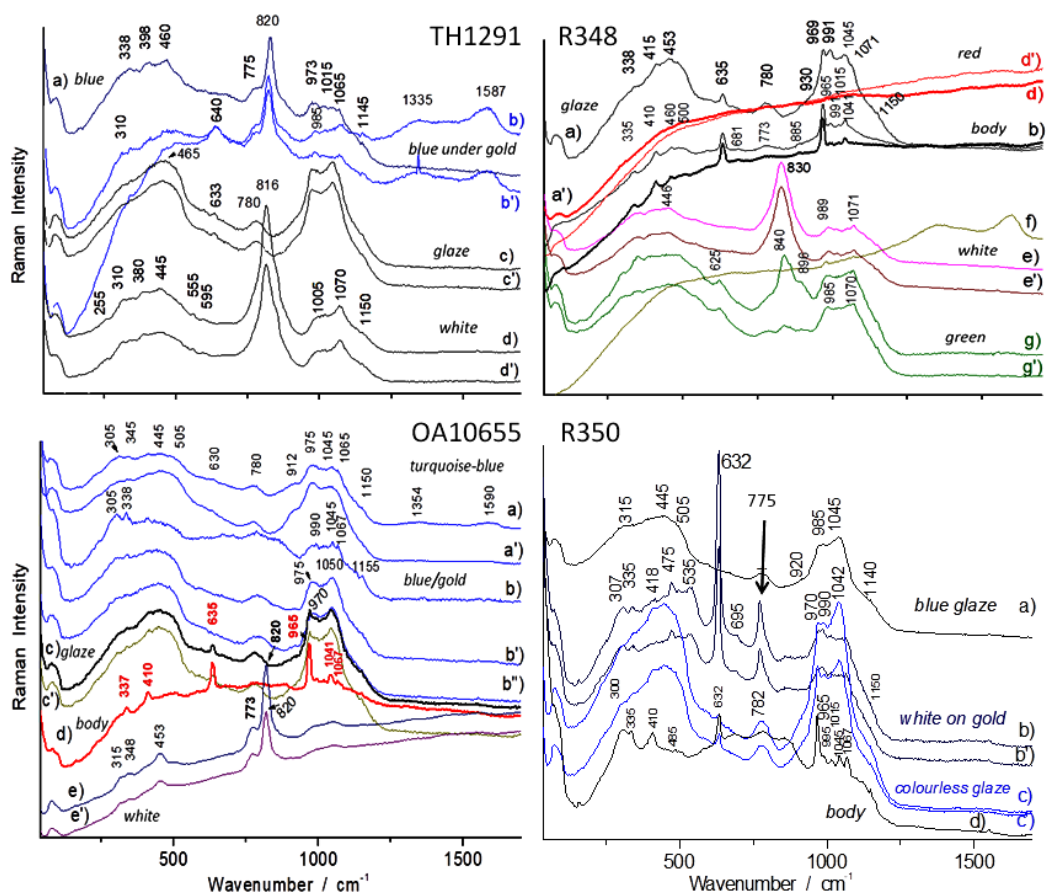


Fig. 3. Representative Raman spectra recorded on different spots of the cups: porcelain body (R348: b; OA10655: d; R350: d), colourless glaze (TH1291:c,c'; R348: a,a'; OA10655: c,c'), blue glaze (TH1291: a; R350: a) and blue (OA10655: a,a',b,b',b''), white (TH1291: d,d'; R348: e,e'; OA10655: e,e'; R350: b,b'), green (R348: g,g') and red (R348: d,d') enamels on gold foil (see text); R348 f: green enamel on gold restoration.

3. RESULTS AND DISCUSSION

3.1. Raman analysis

Figs 3 to 6 show representative Raman spectra recorded for the different parts of the porcelain artefacts such as body, glaze and enamel on gold foil. Results are summarized in Table 2 and will be discussed as follows.

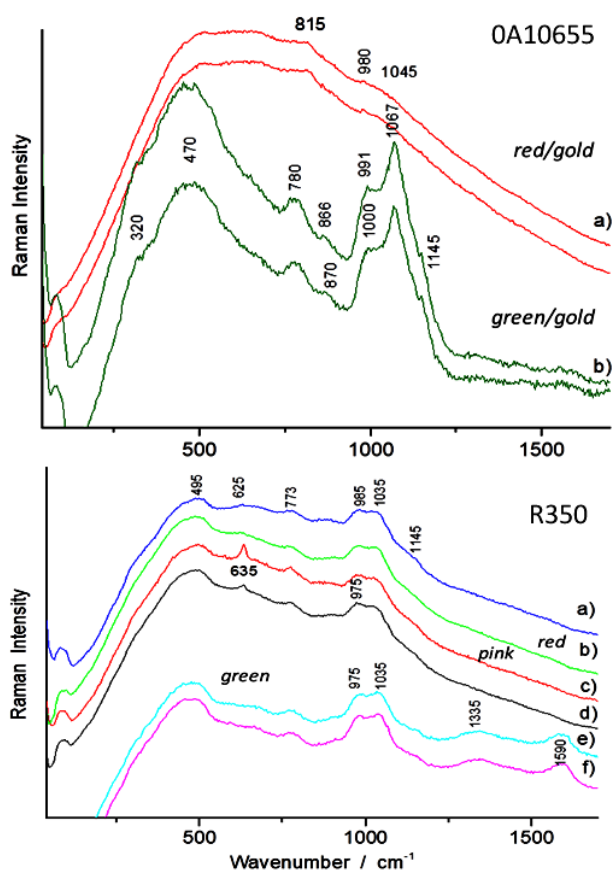


Fig. 4. Representative Raman spectra of OA10655 (top) and R350 (bottom) recorded on different spots of green and red/pink enamels on gold foil (see text).

Body

Four artefacts (OA10655, R348, R350 and OA10946), all bearing the mark of Sèvres Royal Factory, show the characteristic peaks of β -wollastonite (CaSiO_3) as the narrow 635-965 cm^{-1} doublet which is the signature of soft-paste porcelain [44-46]. For one artefact (TH1291 cup), the signature of β -wollastonite could not be obtained as well as any signal to be associated with hard-paste (quartz, mullite, aluminosilicate glass), indicating a paste with a low amount of wollastonite or a hard-paste porcelain [44,47]. This may be related to the fact that the Raman spectrum of hard-paste porcelain is always very weak and broad, difficult to extract from the background, especially when a mobile Raman set-up is used. In the latter case, the spectrum displays only in some points a weak ca. 460 cm^{-1} peak, that of the Si-O bending mode of quartz. The signatures of other phases

(glassy matrix and mullite) are usually too weak due to the high ionicity of the alumina-rich network to be clearly detected with a mobile Raman set-up [35,47]. On the contrary, quartz signal (~ 460) and the very tiny bands characteristic of mullite (broad ~ 460 , 500 , 590 and 1150 cm^{-1} bands [44,47,48]) (Fig. 6), characteristic of the hard-paste porcelain were detected in some spots for the vases from Comte d'Artois Factory (OA7739).

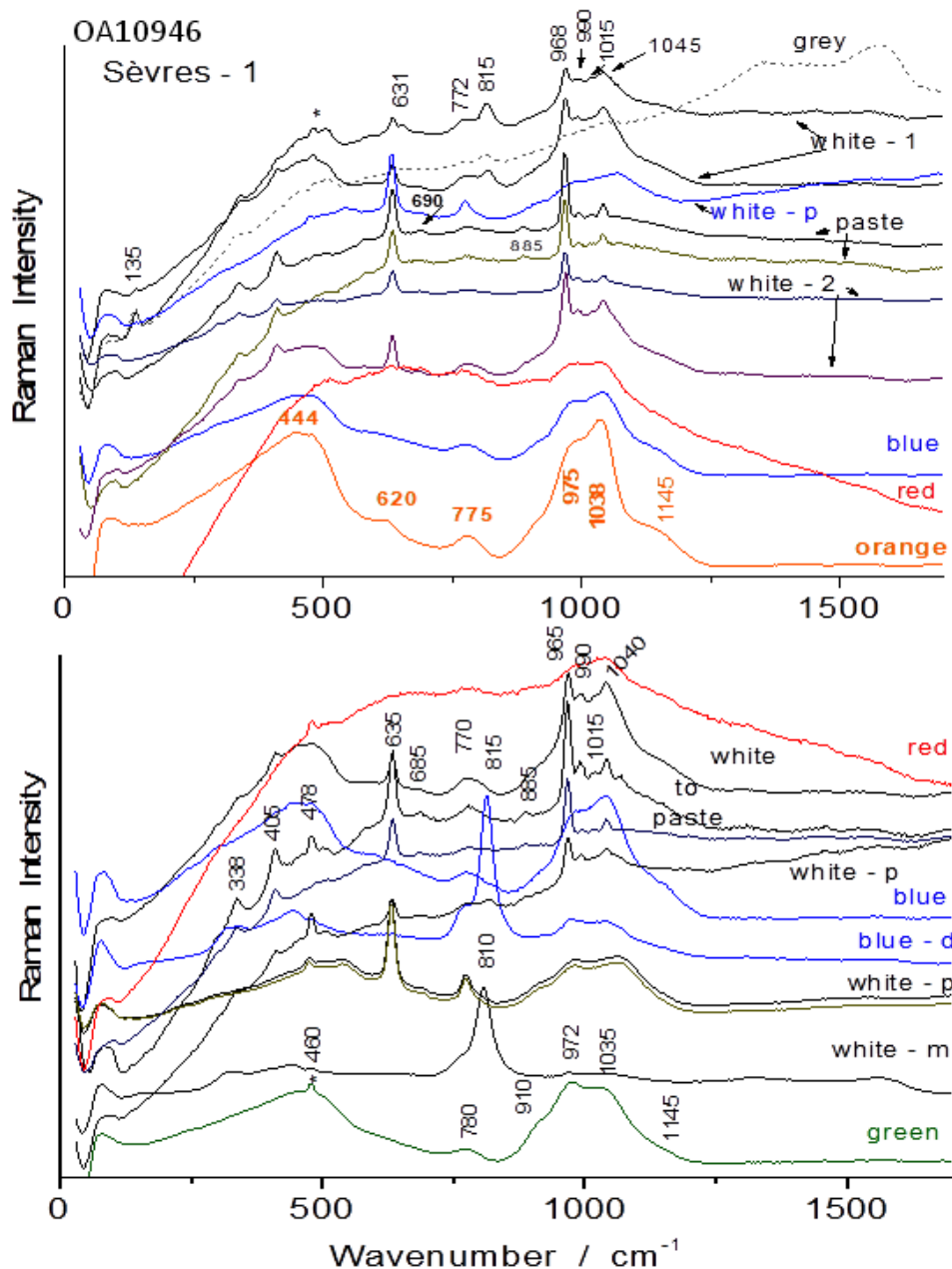


Fig. 5. Representative Raman spectra recorded on the paste, glaze (white-1 & -2, top) and enamels (grey, white-p, white-m, red, orange, green) of two Sèvres Factory vases (top and bottom, OA10946); p: spectra recorded on bead on gold foil decor; d: area under (lost) gold foil; m: medallion.

Glaze and enamels

Cups: We will first consider the cups presented in Fig. 1. Three different types of white opacifiers are observed. Cassiterite (SnO_2) with its characteristic $632\text{-}775\text{ cm}^{-1}$ doublet [45] was detected in the white 'beads' of R350 cup (soft-paste porcelain) (Figure 3-bottom right). For the other ones, opacification was achieved with two different arsenic-based compounds. Lead arsenate apatite (composition close to $\text{Na}_{0.4}\text{K}_{0.1}\text{Ca}_{0.5}\text{Pb}_4(\text{AsO}_4)_3$), with the characteristic well-defined $773\text{-}820\text{ cm}^{-1}$ doublet, already identified in the comprehensive study of a soft-paste porcelain plate produced at Sèvres Royal Factory in 1781 [48,49], is clearly observed in OA10655 cup (Fig. 3-bottom left). A similar signature is also observed in TH1291 cup for (dark) blue glaze, where the gold foil was lost (Fig. 1- top left and right), but a different type of signature was measured in the white enamel with a broader band at $\sim 816\text{ cm}^{-1}$ (Fig. 3-top left). This is also the case for the white enamel of R348 cup (Fig. 3- top right). Arsenic-based phases exhibit a very strong spectrum [35,48-51] due to the high number of electrons involved in As-O covalent bonds, even in very small amounts (less than a few % wt). These phases may result from deliberate addition of arsenic or from the use of European cobalt ores, particularly 17th century cobalt ores being rich in arsenic which lead to precipitation of lead arsenate apatite by reaction with lead-based glazes/enamels [34-36, 48-52]. The bandwidth at half height of the As-O stretching band varies from about 10 cm^{-1} for lead arsenate apatite doublet to about 40 cm^{-1} for the broader feature, with the peak maximum shifting from ~ 815 to 830 cm^{-1} . The presence of arsenic-based phases has already been observed for 17th and 18th century enamelled wares (porcelains, glass and metal wares [34,35,48,50-52]) and are also reported for majolica glazes, as detected by other techniques [53,54]. The band broadening may be due to the presence of variant arsenic phases with different amounts of incorporating elements. The superimposition of the As-O peaks with other possible phases or the poor crystallinity of these arsenic phases may also give rise to band broadening.

A small carbon doublet ($\sim 1335\text{-}1585\text{ cm}^{-1}$ [55]) is also observed in some cases (Figures 3 and 4). Due to the resonance character of its Raman spectrum, traces of carbon (<1 % wt) display significant intensity [45,46]. Carbon doublet was well detected in the blue area of TH1291 cup where the gold foil has been lost (photo: Fig. 1- top right, spectrum: Figure 3, '*blue under gold*'). This observation is consistent with the firing process under reducing conditions (the reducing atmosphere being required to obtain a white porcelain body) and the use of an organic mixture to stick the foil on the glaze (the standard procedure for gilding [39,56]). The covering of the glaze with the metal foil may have preserved this organic material from complete burning and oxidation during the firing process. This finding is also consistent with the observation of many bubbles in the glaze (Fig. 1-top right, TH1291) indicating a fusion and a reaction. A significant carbon doublet is observed in some places e.g. of the white enamel of R348 cup (Fig. 3-top right) and in the green enamel of R350 cup (Fig. 4-bottom).

In the red enamel of OA10655, a small As-O band at 815 cm^{-1} was detected (Fig. 4-top), which overlaps on the spectral background peaking at $\sim 550\text{ cm}^{-1}$ (actually 500 nm in the absolute scale) and decreasing on the red shift side, according to light absorption by red colour of the enamel. This specific signature is attributed to the use of colloidal gold, following Bernard Perrot's technique which involves precipitation of gold nanoparticles from the acid stock solution with arsenic salt, which remains with colloidal gold particles dispersed in the glassy enamel matrix. The use of arsenic salt is confirmed by the presence of the specific As-O stretching band, as also discussed previously in the Raman studies of Perrot glass [51], Chinese and Limoges *cloisonné* enamels [34] and French enamelled watches [41]. As a renowned glassmaker in the 17th century France, Perrot is the precursor of this technique for producing red coloured (ruby) glass several years before the German chemist Johann Kunckel who followed another route for the same process using tin salt (the so-called "Cassius purple") [41,50,56,57].

Vases: Representative Raman spectra of the Sèvres vases (OA10946) are given in Figure 5. The characteristic signature of β -wollastonite (ca. $635\text{-}965\text{ cm}^{-1}$ doublet) was detected in the glazeless body (from the back of the foot) of these Sèvres artefacts (OA10946) as well in their colourless glazes (Fig. 5: top and bottom; labelled white). As shown in the figure, focus of the laser spot from the colourless glaze surface through the body resulted in the disappearance of the glaze signature (Si-O stretching mode components at ~ 910 (shoulder), ~ 980 and 1040 (strong) and 1145 (shoulder) cm^{-1} ; Si-O bending mode at $\sim 450\text{ cm}^{-1}$) [58-61]. Raman spectrum of the blue glaze shows an almost pure signature of the glassy Si-O matrix, not very different from that recorded on the orange enamel (Fig. 5-top; 'orange' spectrum). Detection of the sole glass signature indicates that colouring of the glazes/enamels was achieved with the dispersion of transition metal ions in the glassy silicate matrix, such as Co^{2+} ions for the blue, Fe^{3+} for the orange, Cu^{2+} for the green (see further). On the other hand, detection of the ca. $635\text{-}770\text{ cm}^{-1}$ doublet shows that white enamelled beads on gold were opacified with cassiterite. In contrast, the strong 810 cm^{-1} peak of the As-O bond indicates that opacification was made with an As-based compound in the white surface of the medallion. It is also important to note the strong 815 cm^{-1} peak detected in the blue rough area, which could be analyzed due to the loss of gold foil (Fig. 1-top). The presence of bubbles indicates a strong reaction due to addition of a specific material rich in arsenic to promote the sticking between the glaze and the gold foil.

Figure 6 shows the representative Raman spectra of the pair of vases as productions of Comte d'Artois Factory (OA7739). As mentioned before, the characteristic signature of hard-paste porcelain with the narrow quartz peak at 456 cm^{-1} and several broad bands at ca. 460 , 590 , 800 and $1000\text{-}1200\text{ cm}^{-1}$ [44,48] was recorded on the back side of the glaze-free foot on both of these vases. The blue glaze shows the typical glaze spectrum fired with the hard-paste porcelain body [44], with strong ca.

480 band, weak bands at ca. 590, 800 and 900-1150 cm^{-1} along with a narrow very weak 445 cm^{-1} peak of stressed quartz grains (Fig. 6-bottom) [48].

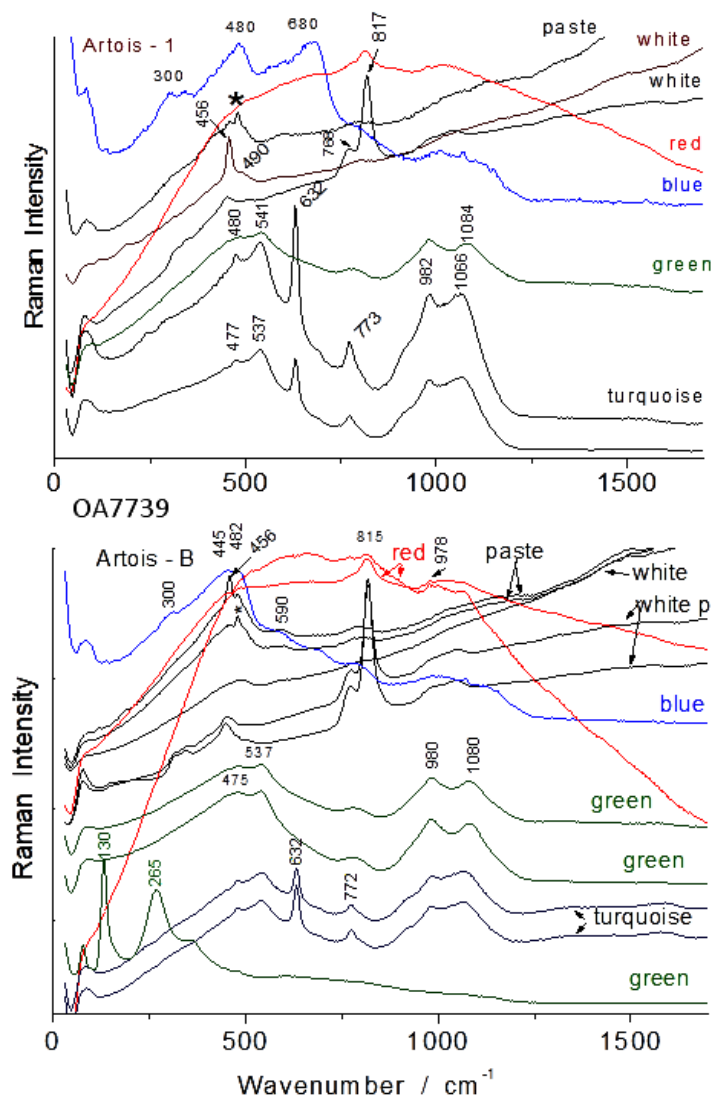


Fig. 6. Representative Raman spectra recorded on the paste, glaze (white, blue) and enamels (white, green, turquoise) of two Comte d'Artois Factory vases (top and bottom, OA7739); p: spectra recorded on bead on gold foil; * plasma line from the bulbs.

Arsenic-based phases as an opacifier (very strong $\sim 815 \text{ cm}^{-1}$ peaks) are observed for white and red enamel beads on gold foil while cassiterite was found close to the top of the vases in opaque turquoise enamel beads. Furthermore, the signature of lead oxide (PbO) with the 80 cm^{-1} peak and $130\text{-}265 \text{ cm}^{-1}$ doublet was detected on the green enamel, due to the saturation of the glassy matrix by an excess of lead (see further) [48]. Red enamel on gold foil also shows the 815 cm^{-1} peak characteristic of an arsenic-rich phase and the background profile characteristic of a red optically clear glass coloured with Au° nanoparticles [36,41]. The As-O signature indicates that Perrot's procedure was also used here to prepare the red coloured enamel.

Table 2: Crystalline phases identified by Raman microspectroscopy and related elements detected by pXRF (Major, minor, traces).

Artefact	Paste (Body)	Glaze		Enamel on gold				Remarks (made by)
		colourless	coloured	Under gold foil	white	Blue/turquoise	green	
TH1291 (1781)	(hard- or soft-paste?)	Traces of β -wollastonite?	As-apatite (blue)	As-apatite, carbon	As-based opacifier	As-based phase		Coteau or Parpette?
OA10655 (1782)	β -wollastonite	β -wollastonite			As-apatite		Au ⁰ (+As-based phase)	Soft-paste Lead-rich glaze (Coteau)
R348 (1786?)	β -wollastonite	β -wollastonite, phosphate ?			As-based opacifier		As-based opacifier	Au ⁰
R350	β -wollastonite	β -wollastonite			<u>cassiterite</u>		carbon	Au ⁰ , cassiterite
Vase Sèvres OA10946 (1780)	β -wollastonite	β -wollastonite		As-apatite	<u>Cassiterite</u> Medallion: As-based opacifier apatite			Au ⁰
Elements	Si,Ca,K, Pb,Fe, Ni,Sr,Rb		Si,Pb Co Ni (blue)	Pb,Si K,As,Co Fe,Ti	Si,Pb,(Au) Sn Fe,Co,Ni,Rb Medallion : Si, Pb K,Mn,Fe,Ni		Si,Pb Cu (Au),Fe Co,Ni	Si,Pb Au,K Fe,Co,Ni
Vase Comte d'Artois OA7739 (1783)	Quartz (\Leftrightarrow hard paste)	Mullite-like glass	cobalt aluminate (blue)		As-apatite (top and centre)	Cassiterite	lead oxide	Au⁰ As-based phase
Elements	Si,Ca Pb,Fe (Au) S,Ti,Ni,Sr,Zr		Si Co,Ca,Ti,Fe,Ni,As Sr,Zr	Si,Pb Sn/As Fe,Ni,Cu	Si,Pb (Au) Sn,Cu Fe,Ni		Si,Pb (Au) Sn,S,Cu,Fe Co,Ni	Si,Pb Sn,Au,As Mn,Fe,Ni,Zr

Glassy matrix

Raman spectra of the glazes and enamels on the gold foil display the characteristic signature of glassy silicates which are mainly composed of SiO₄ polymeric units connected to each other by their oxygen atoms [58- 61]. The connectivity of the glass network is directly related to the presence of other elements in the glass composition such as alkali/earth-alkali elements (sodium, calcium, potassium etc.) and lead which are added in order to modify the physical properties of glass, resulting in the depolymerization of the network. The Raman signature of glassy silicates typically includes Si-O bending and stretching bands in the range ~500 and ~ 1000 cm⁻¹, respectively. The compositional changes of glass are reflected in the area ratios of these bands and the band components in the stretching range, allowing for the classification of different glass types [58-61]. Table 3 lists the different components the Si-O bending/stretching bands obtained for the different types of glassy coatings (glazes/enamels) used in the artefacts. Raman signatures correspond to a typical hard-paste glaze (broad band peaking at 450-500 cm⁻¹) [40,44,47,58,60] only for Comte d'Artois Factory vases. The glaze spectra recorded on the other artefacts correspond to those expected for soft-paste

porcelains [44-46,48], with $\sim 970-985\text{ cm}^{-1}$ to $\sim 1040-1065\text{ cm}^{-1}$ doublet indicating lead-alkali glass composition. The higher the lead oxide (PbO) content, higher the depolymerisation degree will be – and lower the melting temperature - and hence the intensity of $\sim 980\text{ cm}^{-1}$ component [60]. However, due to the very low intensity of asymmetric stretching modes of SiO_4 vibrational unit, the signature of glassy silicates in the stretching mode range (ca. $800-1200\text{ cm}^{-1}$) reflects the distribution of SiO_4 tetrahedron, isolated or with sharing 1, 2, 3 or 4 oxygen atoms to form the polymerized glassy network. Addition of fluxes, in particular PbO, lead to disappearance of some of the Si-O bonds and the amount of low polymerized tetrahedra (components below $\sim 1050\text{ cm}^{-1}$) increases at the place of (nearly)full polymerized ones (components above $\sim 1050\text{ cm}^{-1}$)[58]. It is important to note that spectra recorded for TH1291 cup, where β -wollastonite was not detected in the paste, show that its glaze and enamel compositions are similar with those of soft-paste porcelain.

Overall, the presence of three types of glazes/enamels in the artefacts are suggested: i) the hard-paste aluminosilicate glaze with strong broad $\sim 450\text{ cm}^{-1}$ band (OA7739), ii) the A-type glaze/enamel of lead-alkali composition with the strongest component at ca. $1065-1080\text{ cm}^{-1}$ and iii) the B-Type glaze/enamel of lead-alkali composition with the strongest component at ca. $1040-1050\text{ cm}^{-1}$ (Table 3). Raman signatures measured on the enamels on gold appear to be similar for TH1291, OA10655 and R348 cups and belong to A-type. In general, it can be concluded that the “ $\sim 980\text{ cm}^{-1}$ ” component may shift to $1000-1005\text{ cm}^{-1}$ while the “ $1040-1065\text{ cm}^{-1}$ ” component to $1070-1080\text{ cm}^{-1}$.

Furthermore, the intensity of the 780 cm^{-1} component may decrease. The composition of the enamels and accompanying glazes is rather similar for R350 cup and OA10946 vase belonging to Sèvres productions. Comparison of the Si-O bending mode area vs. stretching mode area ratio, which is representative of the polymerization degree [58,59] and hence directly a function of the melting temperature, shows marked differences. For A-type glass, the ratio is close to 4.5 according to a high firing temperature ($\sim 1000-1050^\circ\text{C}$) [59,61]; for B-type glass, the ratio is close to 1-1.1 according to a firing temperature less than 900°C , i.e. lower than the melting temperature of pure gold at 1064°C .

The differences in the Raman signatures of B-type glazes with their accompanying enamels for OA10655 and R348 cups are likely due to more complex compositions used, more than a “simple” addition of lead oxide to decrease the firing temperature of enamels (addition of boron or bismuth cannot be detected by mobile Raman and XRF analyses). This may also be consistent with different productions although the mark dates are rather close to each other. Thus, the questions arise: Were all the cups made by Parpette and/or Coteau or were they fired at different temperatures by the same enamellist?

Table 3: Representative glaze/enamel signatures of the artefacts analysed (S: strong; m: medium; w: weak; sh: shoulder; v: very).

Artefact (Date)	Glaze	Remarks	Enamel	Remarks
Cup TH1291 (1781)	465S, 780w, 960-973S, 1065S, 1150sh	A-type	445S, 973-1005S, 1070S, 1150sh	Rather similar (A-type) Coteau or Parpette production?
Cup OA10655 (1782)	445S, 780w, 970S, 1050S, 1150sh	B-type (rather similar to A-type)	470S, 780w, 1000S, 1067S, 1145sh (top technical quality)	In cooperation with Coteau?
Cup R348 (1786?)	450S, 780w, 980S, 1045S, 1150sh		445S, 985S, 1070S, 1150sh	
Cup R350 (?)	445S, 785w, 985S, 1045S, 1140sh		445S, 985S, 1045S, 1150sh	Glaze and enamel similar: B-Type Coteau production or copy?
Sèvres vases OA10946 (1780)	445vS, 775w, 900sh, 975S, 1040S, 1145sh		445S, 620sh, 775w, 900sh, 975S, 1040S, 1145sh	B-Type Coteau production?
Comte d'Artois vases OA7739 (1783)	300w, 450vS, 590sh, 700sh, 800sh, 990-1100m	Hard-paste	475-537S, 780w, 910sh, 980S, 1080S	A-type Coteau production

3.3 XRF Analysis

Figs 7 and 8 show representative XRF spectra recorded on the Sevres (OA10946) and Comte d'Artois (OA7739) vases and the data obtained are summarized in Table 2. It was not possible to obtain a spectrum on the glaze-free back side of the foot of OA7739 vase due to the shape of the bronze foot (Fig. 2). The XRF spectrum of the paste (body) of OA10946 vase is fully consistent with that of soft-paste porcelain with strong calcium and (weak) silicon signals. The intensity of silicon as the major element appears much lower than that of lead, due to the lower efficiency of detection in the low energy range. The high silicon and calcium contents found are responsible for the formation of β -wollastonite (β -CaSiO₃) which was well detected by Raman microspectroscopy. Potassium was also well detected, which is also a significant element in these soft-paste compositions. The rather limited intensity of lead L_α and L_β peaks is consistent with the addition of a few % wt of lead oxide (PbO) before the firing process to promote the liquid phase required to weld the quartz grains (common for all fritwares) [10]. Surface pollution during the firing of enamels is also possible. Analysis on a fracture or cross-section of the artefact towards the body is required for a final decision. Comparison with spectrum recorded on the blue glaze shows the much higher PbO content which was used to allow melting at lower temperatures than that of the body mixture in order to preserve its shape. Cobalt is the main colouring element in the glaze, as also previously deduced from the Raman data. XRF analysis shows that the foil is made of gold along with a small amount of silver element. The addition of silver is usually observed in the gilding process since it is supposed to be promoting the adhesion with the glassy coating [39]. Rubidium and lead elements were also detected to some extent with calcium in trace amounts.

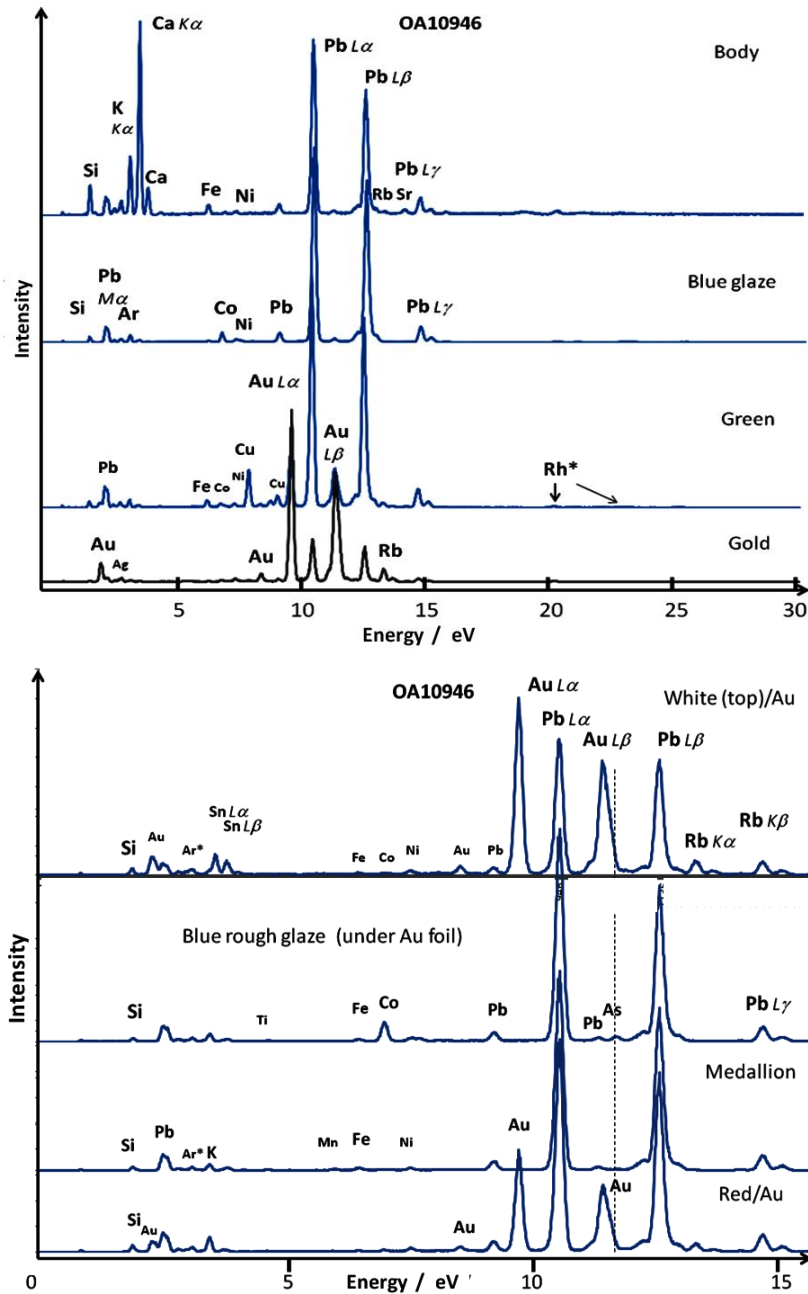


Fig. 7. Representative XRF spectra of OA10946 soft-paste porcelain vase (*: elements coming from the X-ray tube).

Rubidium can be a marker of the calcium-rich mixture used to seal the gold foil (rubidium is an impurity of the calcium compound). The presence of lead traces could not be intrinsic due to alloying with gold but may more likely be due to the contamination by volatilization of lead oxide during firing, which covers all the surface of the artefact with a lead-oxide-rich thin film. XRF spectra show that all the enamels and most of the glazes analysed contain significant amount of lead, confirming the Raman data (*Glassy Matrix*). Presence of lead is identified in the spectra by its intense characteristic peaks in the K and L region.

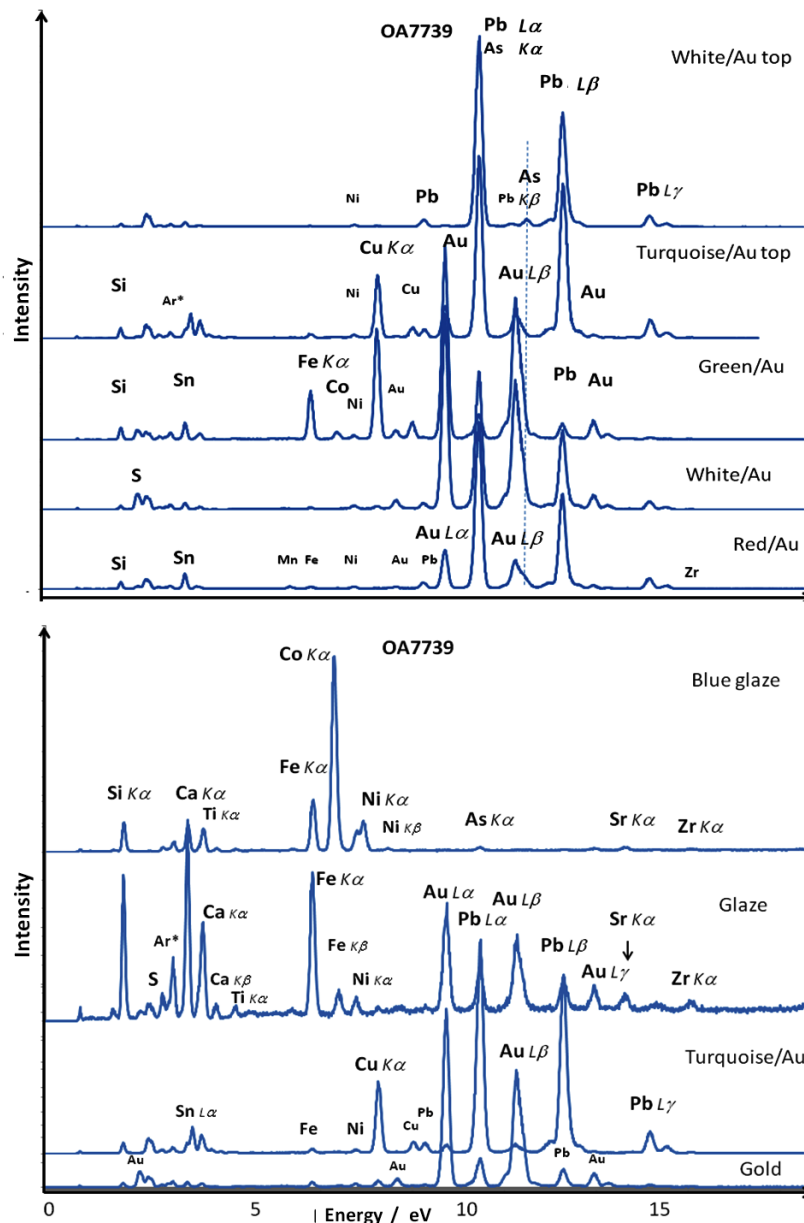


Fig. 8. Representative XRF spectra of OA7739 hard-paste porcelain vase (*: elements coming from the X-ray tube).

It is important to note that the L_{α} peak of lead overlaps with K_{α} peak of arsenic in the case of their mutual presence and arsenic can only be detected visually by its K_{β} peak. However, $As K_{\beta}$ can be disturbed by one of the Au peaks (in relevant presence of gold). In this case, it becomes quite difficult to identify arsenic when it is present in traces. Raman signature is thus needed to confirm/detect arsenic-based phases and support the inclusion of arsenic in the data reduction made by the XRF software. Observation of gold peaks in the enamels is possibly related to the small thickness of the

enamel which permits a significant contribution of the gold foil substrate: the in-depth probed for gold signal is about 100-150 μm .

The green enamel of OA10946 vase also includes a high level of lead together with silicon, as discussed before (see *Glassy matrix*). Copper was found to be the main colouring element together with traces of cobalt. These findings are also consistent with the Raman spectrum obtained (Fig. 5-bottom). Small amounts of iron and traces of nickel are also observed, as in the case of the body. The analysis of the rough blue glaze area of OA10946 vase, with bubbles and voids at the place where the gold foil was lost [as also observed in TH1291 cup (Fig. 1, top)] shows the additional presence of arsenic, which was not detected in the glossy blue glaze. Arsenic was well detected with its K_{β} peak in this area. This finding matches up very well with the Raman spectrum obtained on the same area, displaying the signal of the arsenate apatite As-O bond (Fig. 5-bottom) [35,48]. Detection of the arsenic element confirms the use of an arsenic-based compound to stick the gold foil. A note in the Pr aud paper [26] and a sentence in the de Plinval de Guillebon one [25] mention some prior analyses which also identified the use of arsenic, but without references. Presence of bubbles is consistent with the addition of organic medium to stick the gold foil before firing but also indicates an efficient flux including not only arsenic. The textbook of Bertran et al., already cited in [39] also reports the use of bismuth [56]. Specific analysis of the white enamel "bead" close to the top of the vase shows the presence of tin (L_{α} and L_{β} weak peaks are visible at low energy) besides lead and silicon (Fig. 7-bottom), but the more intense K_{α} and K_{β} peaks are also observed at high energy (but not shown). This is also in correlation with the Raman spectrum, showing the presence of cassiterite as opacifier (Fig. 5-bottom). Traces of arsenic were also detected in the white enamel of the medallion with its K_{β} peak (Fig. 7-bottom), in accordance with the arsenate apatite signature in the Raman spectrum (Fig. 5-bottom). Presence of an iron-based compound may be suggested together with the detection of manganese and nickel traces which might be impurities, for achieving a brownish tint inside the medallion. In the red enamel, the rather strong intensity of gold peaks obtained is consistent with the possible presence of colloidal gold in the glassy matrix but this could also be due to the small thickness of the enamel covering the gold foil.

The XRF spectrum recorded on the blue glaze of Comte d'Artois OA7739 vase (Fig. 8-bottom) is completely different than the glaze/enamels of the S vres vase. It is a lime-based hard-paste glaze fired at high temperature without any lead and coloured in blue by a significant addition of cobalt. This is consistent with the precipitation of nanosized cobalt aluminate (CoAl_2O_4) and supports the Raman spectrum recorded on this vase, with a combination of the signature characteristic of hard-paste porcelain glaze (main broad components at ~ 300 , 480 and 590 and 980-1100 cm^{-1}) [40,44, 58] and that of CoAl_2O_4 nanoparticles (480 and 680 cm^{-1} bands [62]) (Fig. 6-top). The formation of

CoAl₂O₄ nanoparticles by precipitation was also previously reported for blue Sèvres porcelain [63]. It is also important to note that aluminium due to its low atomic number is hardly detected by the portable XRF instrument in these conditions. The presence of arsenic in the blue glaze may be related to the use of European cobalt sources rich in arsenic or its deliberate addition to adjust the hue. However, the achieved ultramarine colour is more consistent with the first assumption. Analysis of the colourless glaze shows a composition containing high amounts of calcium, as in the case of Sèvres soft-paste body (OA10946) but with only minor lead content, which prevents precipitation of β -wollastonite. It is possible that the lead content detected arises from the contamination by lead volatilization during the firing of enamel-on-gold decor. Unexpectedly, a small amount of gold was also detected, likely due to contamination from the foil (gold is volatile at high temperatures). This finding may indicate a high firing temperature, not far away from the melting temperature of gold alloy, ca. 1000°C (pure gold: 1064°C), also proving that the enamel-on-gold decoration is more risky on hard-paste porcelain than the soft-paste one. Iron, titanium and zirconium elements were also detected in the glaze which may be reflected from the paste.

Small amounts of copper, nickel, and iron were detected in the gold foil of OA7739 vase together with lead. Iron can be related to the punching out of the gold foil with a steel die. The composition of the gold alloy is thus different from that of the Sèvres vase. This may offer a tool for the classification of these artefacts. Lead is again possibly related to lead oxide volatilization during the firing process.

The enamels contain significant amount of lead, as in the case of the Sèvres vase. White enamel beads on gold foil, measured on the top of the vase or in the centre, show arsenic peaks with a well-defined K β peak, characteristic of the arsenic-based opacifier, as also observed in the Raman spectra (Fig. 6-bottom). XRF spectra recorded in the centre also present strong peaks of gold, likely due to the contribution of the gold foil below the enamel layer. Turquoise and green enamels on gold foil were apparently made with the use of copper ions in lead-rich matrix. This is well correlated to their Raman spectra showing the signature of lead-alkali glass (Figure 6). Cobalt and iron were also used, especially in the green enamel possibly to adjust the hue. Tin was also detected in the turquoise enamel in accordance with the Raman detection of cassiterite (Table 2, Figure 6). It was also detected in the red and white enamels as well. In the red enamel, presence of the gold peaks is also due to the use of colloidal gold in the glassy matrix, as also evidenced by the specific signature with the As-O band in the Raman spectra obtained (Fig. 6), pointing to the utilisation of Bernard Perrot's technique.

3.4. Discussion

The results of this study allowed us to characterize the body compositions, colorants/opacifiers and glass compositions used in the glazes/enamels of the porcelain artefacts considered as possible productions of Joseph Coteau or Philippe Parpette. Obviously, R350 cup had been made using a technique different from the other cups, with its glaze and enamels having similar glass compositions. It is important to note that cassiterite was used as opacifier in the white and red enamels of this cup while it was also detected along with an arsenic-based opacifier in the case of the Comte d'Artois vases produced by Coteau. These outcomes may possibly indicate different productions. Our experience in the Raman study of porcelains have pointed out that 19th century Samson's porcelain body exhibits a very strong fluorescence under green laser excitation, not observed for this R350 cup. Consequently, it is suggested to rule out a later Samson Factory copy. A regular 18th century production at Sèvres Factory also seems to be doubtful since the \mathcal{L} mark at the back side is not usual. Production by Comte d'Artois Factory can also be excluded since there is no reason to add a Sèvres mark on Comte d'Artois porcelain. A later production, by Camille Naudot (1862-1938) and Fernand Thesmar (1843-1912) are possible. De Plinval de Guillebon reported [25] that the use of cassiterite was characteristic of Coteau's recipes. If we use this criterion, it can be proposed that the artefacts including cassiterite had been made by Coteau and the others with soft-paste body, at least those with valuable Sèvres mark, had been decorated by Parpette. R350 cup will thus correspond to a Sèvres production by Coteau but with a mark applied after or to a 19th century copy.

Mark DD indicates that TH1291 cup should have been made in 1781, as possible productions of Coteau or Parpette (Table 2). Marks contribute to the dating but cannot be a definite proof, due to fakes or posterior additions. The loss of some of the gilt decor indicates that the craftsman could not succeed in mastering all the process. This is consistent with a date related to the beginning of this type of production. According to Préaud [26], soft-paste porcelains were decorated by Parpette, not by Coteau. But, historical records report that artefacts made by Coteau were considered to have a better quality than the other contemporary porcelains [26]. Thus, a possible Parpette production can be assigned for this cup.

The EE mark of OA10655 cup corresponds to 1782 and detection of a strong lead arsenate apatite signature for white enamel beads is consistent with a better mastering of the use of arsenic-based opacifier. We can consider this artefact as an example of the top quality from the technical point of view and thus, an assignment to Coteau seems coherent.

The mark of R348 cup is questionable (\mathcal{Y} = 1786 or fake mark). However, the arsenic-based opacifier in the white enamels shows a broad band as in the case of TH1291 cup. Thus, it seems to be more similar with TH1291 cup rather than OA10655 cup as the "reference".

Cassiterite opacification was identified in white enamel beads (on gold) for Sèvres vases (CC 1780 mark), as in the case of R350 cup. These artefacts are most probably attributed to the productions of Coteau. Comte d'Artois vases show the use of two opacification techniques such as cassiterite for turquoise enamel beads and lead arsenate apatite for white enamels located close to the foot and the top of the vase. It is obvious that the latter decor was added after in order to adapt the decor with the addition of bronze handle pair.

4. CONCLUSION

This preliminary on-site Raman and pXRF study about the productions of Joseph Coteau and/or Philippe Parpette was able to identify the different materials (colouring agents, opacifiers, glass types etc.) and enamelling techniques used, despite the limited number of studied artefacts. The use of mobile Raman instrument coupled to a micrometric stage, with long working distance microscope objectives which were adjusted perpendicular to the surface of the artefacts for the analysis, allowed us to obtain high quality Raman spectra of the body, glaze and enamel parts. The very high magnification x200 objective particularly made it possible to analyse the very surface of the artefacts (glazes/enamels) without any contribution from the sub-layers. Coteau's enamel-on-gold decoration was applied both on soft-paste and hard-paste porcelains. Assignments of the productions to Coteau and Parpette are proposed by considering both Raman and pXRF measurements and historical information. Raman analysis appears to be more efficient than pXRF to detect the arsenic-based crystalline phases. Similarly, the light element carbon, which cannot be detected by pXRF, was efficiently detected by Raman analysis. Potential XRF fingerprints such as rubidium, nickel, iron have been detected in the gold foils used, which can be used as a criterion to identify different productions.

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