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## **On-site identification of early Böttger red stoneware using portable XRF/Raman instruments: 2, glaze & gilding analysis**

*Running title: Glaze & gilding analysis of early Böttger red stoneware*

G. Simsek<sup>1,2,3</sup>, Ph. Colomban<sup>4\*</sup>, F. Casadio<sup>3</sup>, L. Bellot-Gurlet<sup>4</sup>, G. Zelleke<sup>3</sup>, K.T. Faber<sup>1</sup>, V. Milande<sup>5</sup>, and L. Tilliard<sup>5</sup>

<sup>1</sup> *Department of Materials Science and Engineering, Northwestern University, Evanston, IL, USA*

<sup>2</sup> *Labex MiChem, Ladir, UPMC, 4 Place Jussieu, c49, 75252 Paris Cedex 05, France*

<sup>3</sup> *Art Institute of Chicago, Chicago, IL, USA*

<sup>4</sup> *Sorbonne Universités, MONARIS, umr 8233 CNRS, UPMC Univ. Paris 06, 4 Place Jussieu, c49, 75252 Paris Cedex 05, France*

<sup>5</sup> *Cité de la Céramique – Sèvres & Limoges, Place de la Manufacture, 92310 Sèvres, France*

\* corresponding author : Ph. Colomban philippe.colomban@upmc.fr

### Abstract

Twenty-one glazed red stoneware objects, with gilded or gold-painted decor from different collections (Cité de la Céramique, Sèvres, France; Art Institute of Chicago, USA; a private collection) attributed to 18<sup>th</sup> century Böttger, Meissen (Saxony) have been analyzed with a portable X-ray fluorescence spectrometer (XRF) and portable or fixed Raman micro-spectrometer in laboratory/museum/collector rooms. Analysis was aimed at gaining a deeper understanding of the technology of production of the gilding and black glaze, to augment what is known from the limited literature. Three different techniques to obtain a golden décor emerged as a result of this study: i) a true gilding with gold, ii) gold with mercury, and iii) an alloy of copper and zinc.

## 1. Introduction

The black-glazed red stoneware (sometimes called *Boccaro* ware) developed by Ehrenfried Walther von Tschirnhaus and Johann Friedrich Böttger at the Court of Augustus the Strong, Prince-Elector of Saxony was celebrated as a “completely new kind of porcelain”<sup>1</sup> by their contemporaries and represents the first step in porcelain production in Saxony.

Notwithstanding the historical importance of this highly technological and artistic achievement, in-depth technical studies of Böttger stoneware and its decoration are limited.<sup>2-18</sup>

Böttger started the manufacture of red stoneware composed of iron-rich clays firstly in 1706 in Meissen and two years later in Dresden. Production continued serially until the introduction of white porcelain in 1714 and took place occasionally after 1717.<sup>2,6</sup> Böttger stoneware was produced with two main types of surface finishes; unglazed and glazed wares. An intaglio carving technique was also used to further enhance the decoration, exploiting the interplay between the polished and unpolished, glazed and unglazed areas creating a harmonious work of contrasting texture and visual properties.<sup>1</sup>

The brown- or black-glazed stoneware was often decorated with gold and might have included depictions of East Asian or western motifs painted with unfired (cold) colors.

Böttger was one of the earliest recorded pioneers of gold decoration, which might be a result of the fact that he was a young alchemist before his attempts to produce porcelain. According to Bishop and Sutton<sup>12</sup>, he experimented both with the Chinese/Vietnamese ancient technology of using gold leaf physically bound to the ceramic surface<sup>19,20</sup> and also with the 18<sup>th</sup> century technique of application of liquid gold (i.e. finely divided gold powder applied in a medium, and successively fired).<sup>20</sup> They report that he started by adhering the gold leaf first and heating the artifact over hot coals to make it more durable. Later, in order to prevent stripping and lumping problems caused by gilding, he tried to prepare a mixture of gold

powder with ferrous sulfate in *aqua regia* to produce “a quite beautiful and very fine precipitate”, according to the new technique introduced by Kunkel.<sup>12,21</sup> After the death of Böttger, the new director of the Meissen Factory, Johannes Gregorius Höroldt<sup>22</sup> continued to develop the gilding technique of his predecessor with the aim of achieving a reliable, durable gold layer and he also set about producing a range of fired colors for the painted decorations, some of whose recipes have been used up to this day.

Importantly, when analyzing the material composition of the applied decoration one should always keep in mind the possibility of later embellishment, long after the object’s production, as has been also documented for white hard paste porcelain at Meissen.<sup>14</sup>

Most of the previous studies on Böttger stoneware are primarily focused on the measurements of the composition of the red stoneware paste in order to determine its main characteristics and trying to distinguish it from other stoneware of different origins such as those produced in Europe in the 17<sup>th</sup> and 18<sup>th</sup> centuries at Delft (Holland), Staffordshire (England), Plauen on Havel and Bayreuth (Germany) and various production centers in China.<sup>17</sup>

The present study focuses on the investigation of the decoration of 21 objects from different collections (Département du Patrimoine et des Collections de la Cité de la Céramique, Sèvres, France, here after noted SB; Art Institute of Chicago, USA (A); private collection (PC)) ornate with dark glazes varying in color from chocolate brown to deep black, with gilding and a limited amount of cold-color decoration (Fig. 1). The 16 artifacts from Sèvres represent a key benchmark group of securely attributed objects. This is an ideal group to derive objects-based inferences on Böttger’s 18<sup>th</sup> century workshop practices due to their excellent provenance as gifts from Meissen to Sèvres (1837 and 1875), as well as purchases made in Dresden by the director of the Sèvres porcelain manufactory Alexandre Brongniart (1836). The high value and significance of the objects studied, all of museum quality, prevented any sampling for the study, thus directing the research to an exclusively non-invasive analytical

approach. The sample set chosen for this investigation makes this one of the largest published studies focusing on the decoration of the red stoneware,<sup>9,13-16,18</sup> as most of the few existing publications focus on the body composition<sup>4,6,7,11</sup>. In most of these previous works the darkly glazed examples were only barely studied. The aim of this paper is thus to contribute to a better knowledge of the first Meissen production and to advance our understanding of the different methods used to produce dark glazes and gold decoration.

## **2. Experimental Set-up**

### **2.1 X-ray fluorescence spectroscopy (XRF)**

XRF analysis was performed using a Brüker Tracer III-V (Brüker AXS, Karlsruhe, Germany) portable system equipped with a rhodium (Rh) target X-ray tube that was operated at 33kV, 2 $\mu$ A to identify the network modifiers and coloring/gilding agents found on the glaze as previously described.<sup>17</sup> A vacuum pump was used during testing to enhance the detection of low Z elements (from aluminum to titanium). The beam size at the surface is roughly 0.15 cm<sup>2</sup>. Due to the heterogeneity in composition and variation of the glaze thickness, the measurements were carried out on at least three different areas of the enamel. The results are reported as the mean values of all the individual point analyses done on each object. For qualitative evaluation purposes the K $\alpha$  lines of Al, Si, K, Ca, the transition metal elements (Ti, Cr, Mn, Fe, Cu, Zn) and trace elements (Rb, Sr, Y, Zr) as well as the L spectral lines of lead were taken into consideration. The L spectral lines of gold and mercury were also considered in cases of glaze ornamentation and gilding. As silicon is the major element of both glaze and body, Si counts are measured between 10.000 (min.) and 40.000 (max). In order to compare measurements where the instrument tip-surface artifact distance varies, most of the element mean area counts are normalized by those of Si. Complementary XRF analysis of gold decors was also performed using a NITON XL3t GOLDD+ (ThermoFisher,

Tewksbury, USA) portable system equipped with a silver anode X-ray tube and an SDDGOLDD detector that was operated at 50 kV 200 $\mu$ A in order to corroborate and strengthen the previous results. The beam size of the instrument was  $\sim 0.5 \text{ cm}^2$  and a camera visualized the analyzed spot. Typically gold leaf thickness larger than 0.2  $\mu\text{m}$  are sufficient to avoid contribution of the gold substrate.

## **2.2 Raman spectroscopy (RS)**

Raman analyses were performed *in-situ* using a laboratory system for analyzing the coffee pot of the Art Institute of Chicago and a portable unit for the private and Sèvres Museum's collections. A confocal Labram 300 Horiba-Jobin Yvon Raman spectrometer (Lille, France) with a 532 nm green laser was used at the Art Institute (Fig. S1, Supplementary Materials).

Raman measurements were carried out with a 50x long working distance (LWD) objective (NA = 0.55, Olympus) to avoid any contact with the surface of the object. The recording time of a spectrum varied between 30 and 120 seconds. Because the stoneware paste is rich in iron oxide, a low laser power was used on the objects in order to prevent any phase transformation of iron oxide (e.g. from magnetite to hematite). Most of the analyses were performed interposing neutral density filters between the incoming excitation and the 50x LWD objective, the laser power being equal or less than 1 mW at the sample surface.

The mobile analyses were performed using a portable HE532 (Horiba Jobin Yvon, Lille, France), equipped with a Peltier-cooled (200K) matrix charge coupled device (CCD) detector associated with a Laser Quantum Ventus (Stockport, UK) YAG laser, which has a nominal maximum power of 80 mW. The spectrum collecting time was less than 10 seconds with a resolution of  $\sim 4 \text{ cm}^{-1}$ . A 50x LWD objective (NA= 0.45, Nikon) was used during measurements. The illumination power was controlled with the laser power control and a variable size hole at the entrance of the remote optical head fiber connected to the laser and

the spectrometer (SuperHead<sup>TM</sup>, Horiba Jobin Yvon, Lille, France) so as to further reduce the laser power to about 5-8 mW at the sample with 532 nm laser excitation. Baseline subtraction was performed during post-processing of the spectra to assist with the interpretation and to derive the polymerization index for the glassy phases as extensively explained in the literature.<sup>23-27</sup>

### 2.3 Colorimetry

Color measurements were performed on the glazes by an X-Rite GRETAG MACBETH SpectroEye portable spectrophotometer equipped with a gas-filled tungsten light source. The internal spectral resolution is 3.3 nm and the reflectance spectrum is between 380 and 730 nm. Color coordinates were expressed in the CIE (*Commission Internationale pour l'éclairage*) L\*a\*b\* color system, using the illuminant C and the 2° viewing angle.

### 3. Objects

This paper concerns the characterization of 21 glazed Böttger stoneware objects examined at the Cité de la Céramique of Sèvres, the Art Institute of Chicago and an important private collection (See Fig. 1). Specifically one object was analyzed at the Art Institute, 16 objects at Sèvres, and four objects in a private collection. Detailed information about the analyzed objects that are part of publicly held collections is provided as supplementary material (See Table S1). This study also includes a brief overview of the results of Raman measurements on the body of mostly unglazed stoneware, whose characterization with XRF is extensively discussed in a previous paper<sup>17</sup>. The glazes of the objects examined vary in color from black to dark brown through gradations of reddish and chocolate brown, and for the most part also include golden decorations (Fig. 1).

## 4. Results and Discussion

### *(1) Body*

Collecting useful XRF data in the often very thin and sometimes faceted unglazed rims and bases of glazed objects is difficult, given the relatively large aperture of the XRF instrument used. In fact, the unglazed rim often only partially covers the aperture of the XRF instruments, a factor that can significantly affect count rates. When this is compounded by geometry and orientation effects it can significantly affect the relative count fractions for important elements such as Al and Ti, as demonstrated by Bezur and Casadio<sup>15</sup>. Often such exposed thin rims are also smeared with residual Pb-rich glaze material, which further affects the reliability of relative count rates. Therefore, reliable XRF measurements of the body composition were obtained only for three of the studied glazed objects, which had large flat unglazed bases (SB 2244-12, coffee pot; SB 2244-14, cup; SB 2272-10, bottle). Analysis revealed a composition of major elements (Si, Al, Ti, Fe) and trace elements (Zr, Rb, Sr, Ni, Cu, Zn, Cr) representative of the raw materials used, as well as fluxes (K, Ca and Pb) representative of the production technology. These agreed well with the fairly large compositional range measured for Böttger stoneware production, as previously discussed (Fig. S2).<sup>17</sup> Representative as-recorded Raman spectra for unglazed Böttger red stoneware previously studied with XRF<sup>17</sup> are presented in Fig 2, the most frequent spectra correspond to hematite, rutile, and anatase. Actually, two different hematite signatures are observed, that of pure hematite (H) and broader signature typical of hematite solid solution (H\*, Al or Ti replacing some Fe atoms). These compounds were already identified in previous works on Meissen porcelain and stoneware.<sup>8,9</sup> These phases have very high Raman scattering cross-section and are therefore more easily detected. While hematite is definitely a predominant phase, the same cannot be said of Ti-rich inclusions. The carbon 1350-1600  $\text{cm}^{-1}$  doublet is commonly observed, indicating a final firing under strong reducing atmosphere. The signature



of quartz at  $465\text{ cm}^{-1}$  is also detected, as well as the  $\sim 510\text{ cm}^{-1}$  peak indicating unreacted feldspar grains, as commonly observed for porcelain and stoneware.<sup>8,9,19,28</sup> The number of phases identified in-situ depends on the analyzed spot and in order to obtain a truly representative description of the phase distribution extensive Raman area mapping should be performed on samples removed and prepared as cross-sections, which were not available for this study.

## ***(2) The black and brown glazes***

Glazed Böttger stoneware is divided in groups in this study according to two broad classes of colors for their glazes: black or brown. Some of the objects are decorated with gilding or painting (Table 1 and Supplementary Materials, Table S1): six objects out of 21 have a brown glaze (Fig. 1). The color measurements of the glazes presented in the Table 1 show the differentiation between black and brown colors in terms of the higher level of  $a^*$  (red) and  $b^*$  (yellow) factors. As-recorded and baseline-subtracted Raman spectra are presented in Figs S3 and 3 a & b, respectively. The  $\text{SiO}_4$  tetrahedron has a characteristic vibrational spectrum signature, which is slightly modified as a function of the geometric arrangement of each  $\text{SiO}_4$  tetrahedron vs. its neighbors and because of the electric perturbations due to neighboring cations. Because strong covalently bonded structures have Raman spectroscopic signatures orders of magnitude larger than those of ionic ones, the Raman spectrum of a silicate consists, as a first approximation, solely of the signature of the Si-O network. The Raman spectrum of silicate glass consists of two broad bands, one around  $500\text{ cm}^{-1}$  ( $\text{SiO}_4$  bending vibrations) and one around  $1000\text{ cm}^{-1}$  ( $\text{SiO}_4$  stretching vibrations); librational/collective modes, i.e. the so-called Boson peak are observed below  $300\text{ cm}^{-1}$ .<sup>23</sup> Thus the Raman spectroscopic signature of amorphous (and crystalline) silicates, i.e. their peak wavenumbers and relative intensities, depend on the silicate nanostructure, in particular on the different tetrahedron types (isolated

or sharing 1, 2, 3 or 4 oxygen atoms), and can be directly correlated to the glass degree of polymerization, null for isolated tetrahedral, maximal for tetrahedra sharing all their oxygen atoms with neighboring ones. Previous studies on glass, glaze and enamel<sup>9,23,24-27</sup> developed a useful method for the classification of glass spectra that is based on the plot of Si-O bending peak area vs. that of the Si-O stretching peak area, the so-called polymerization index,  $I_p$ . All the Meissen' glaze spectra show a strong Si-O stretching band peaking at  $\sim 950\text{ cm}^{-1}$ , characteristic of a lead-based glaze (Fig. 3a).<sup>21,25,29</sup> The specific position of the Si-O bending convolution of bands (in the range of about  $400\text{ to }600\text{ cm}^{-1}$ ) depends on the O-Si-O angle, and hence, on the glass nanostructure, i.e. on the composition and processing.<sup>23-25</sup> The boson peak ( $30\text{-}300\text{ cm}^{-1}$ ) is generally very strong, but has been suppressed by the baseline subtraction procedure.<sup>23-25</sup> This procedure is necessary to enable the comparison of spectra recorded with fixed and portable instruments, i.e. with different baseline backgrounds.<sup>24,30</sup> The strongest band of hematite, centered at  $1330\text{ cm}^{-1}$  (resonance combination band)<sup>31</sup>, is detected in some glazes as is the carbon doublet. On the glaze decoration the carbon identified may actually be due to dust and/or the transformation of traces of organic materials on the surface into carbon black under the laser beam, especially when metal particles (gilding) are present in the illuminated spot. The metallic phases are very efficient conductors of the focused thermal energy of the laser, promoting transformation of residual organic matter into carbon.

It has been pointed out that the ratio of the area of the Si-O bending band vs. that of the stretching band is directly related to the degree of polymerization of the  $\text{SiO}_4$  network of the glass<sup>23-27</sup> (called the index of polymerization,  $I_p$ ), and hence, to the fluxes used and the processing temperature of the glaze. Low  $I_p$  values (0.5-1.5) are measured for highly depolymerized glass such as lead-rich glazes; high  $I_p$  values (2.5-5) are measured for hard paste porcelain glazes, fired at high temperature with the body.<sup>23,26</sup> Comparing the  $I_p$  values

of the objects analyzed (Fig 3) two groups are visible, one with  $I_p < 2$ , the other with  $I_p$  comprised between 2.5 and  $\sim 4$ . The first group is consistent with *Petit Feu* glazing. In this technique the PbO-rich glaze is applied on an already fired object, which is subsequently fired at temperature  $< 900\text{-}1000^\circ\text{C}$ .<sup>25-27</sup> The glazes with higher  $I_p$  values have likely been sintered at higher temperature. Additionally, it is interesting to note that the brown-glazed objects have lower  $I_p$  values than the black ones, which can be correlated to the chemical composition of the glaze. Attempts at comparing the  $I_p$  values calculated from the Raman spectra with the Si-normalized net area counts for Pb as measured by XRF (Fig. S4 Supplementary Materials) proved unsatisfactory. The Pb signals measured with XRF are significantly affected by the glaze thickness and contributions from the body due to the fact that the X-ray interaction volume is much larger than a single layer of glaze. Raman spectroscopy is thus better adapted to the glaze study as it is strictly a surface technique.

It is noteworthy to consider the XRF scatterplot of the normalized Pb vs. Ca net area counts (Fig. 4a). As described in a previous work<sup>17</sup> the area counts for those elements have been normalized by those of silicon, in order to minimize the error due to the variable distance between the artifact and the XRF instrument tip. All of the brown glazes with the exception of SB 8405 tend to be clustered at net area counts for Pb and Ca fluxing agents. Figure 4b, revealing the index of polymerization vs. the position of the Si-O bending vibration shows two clearly divided groups that are largely correlated with glaze color. Moreover, from the scatterplot showing the normalized Cu vs. Ni and Mn XRF net area counts in Fig. 5, similar differentiation is seen. The group with higher Si-O bending wavenumber fit with the group with higher Cu and Mn normalized net area counts. This may indicate the use of different firing conditions. By observing these graphs it appears that the black and brown glazes are reasonably well differentiated, with the black glaze showing relatively higher normalized net

area counts for Mn and Cu, leading to the conclusion that the black colour is obtained by addition of manganese and copper (Fig. 5b).

### ***(3) Colored Décor and Gilding***

Four objects exhibit a colored décor executed with cold (unfired) colors over the black glaze: a coffee pot (A1995-96), a tankard (SB2244-7), a sake bottle (SB2244-8) and a bottle (SB2272-10). Since the colored decoration was not the primary focus of this study it was not analyzed systematically. Only a few areas of green, rose, white and blue colors were analyzed with the portable Raman instrument, but not all areas tested rendered useful spectra.<sup>8</sup> A weak increase of the laser power led to the appearance of the carbon doublet, visible also in some of the spectra presented in Fig. 3b and assigned to the thermal degradation of the organic medium of the cold color decoration. This confirms that colored décor is a cold painting and not due to a coloring agent dispersed in a glaze and successively fired.

Fig. 3b shows representative spectra recorded on the coloured/gilded decorations. The spectrum recorded on the white decor of the sake bottle SB2244-8 shows a strong peak at  $\sim 815\text{ cm}^{-1}$ , characteristic of arsenate white.<sup>21,32</sup> Due to the time limitations of access to the item, XRF analysis of this décor was not carried out. Additionally, the peak at  $980\text{ cm}^{-1}$  can be assigned to calcium phosphate, a white pigment also documented in the glaze decoration of Medici porcelain.<sup>21,29,33</sup> Arsenate white was first used in Venice at the end of 16<sup>th</sup> century to produce *lattimo* glass objects but it was not used as porcelain enamel pigment before the 19<sup>th</sup> century.<sup>21</sup> Therefore this finding brings into question whether Böttger's workshop demonstrated an innovative use of the material or if a later (19<sup>th</sup> c.) decoration was applied to an otherwise black glazed 18<sup>th</sup> century piece. Although this practice was not unusual at the time<sup>14</sup>, both by dealers or at the factory, given the provenance of this object, it is unlikely that a Meissen or a Dresden dealer would have restored the white areas before Brongniart gave

the sake bottle to Sevres in 1836. A 2009 study by Miliani et al.<sup>18</sup> conducted on 21 objects in the Dresden collection (Staatliche Kunstsammlungen) demonstrated the use of the following pigments: lead white (cerussite and hydrocerussite), vermilion, copper greens, azurite, and Prussian blue. However the present study also shows a mixture of gypsum ( $1010\text{ cm}^{-1}$ ), chalk ( $1080\text{ cm}^{-1}$ ) and hematite for the cup SB224- 9, so clearly more studies on even higher numbers of glazed artefacts are required to establish the full range of Böttger's cold color palette for stoneware and confirm or disprove his innovative use of arsenate white. Certainly the finding of very early uses of Prussian blue, as documented by Miliani et al.<sup>18</sup> testifies to a high degree of experimentation and innovation in the early days of the production.

Primary XRF analyses of the golden decorations (Figs 1 and 6) have revealed the presence of different techniques to obtain a gilded look: i) a true gilding with gold, ii) an application of gold associated with mercury as amalgam gilding or as vermilion-containing paint underlayer<sup>32</sup>, and ii) an alloy of copper and zinc. The use of pure gold on all gilded decors was clearly observed on the brown dish (SB 8405, Fig. 1) and black saucer (SB 2244-9). Gilding associated with mercury was applied on the surface of the brown teapot (SB 2244-10) and brown saucer (SB 7115-2). For the latter object the Raman spectrum collected on the 'gilded' area shows also peaks characteristics of reddish-yellow PbO, indicating a glaze saturated with PbO or a PbO painting layer, or an oily medium of application that contained a PbO drier. An alloy of copper and zinc was encountered on the coffee pot (A 1995.96) and tea caddy (PC 18).

In their study on the glaze and decors of Böttger stoneware, Miliani et al.<sup>18</sup> mentioned that the gilding decoration most widely used was made of brass for general purposes and gold for finer decorations. The gilded decoration on the lobed dish with German L & C heraldic symbol, SB 8405, is almost pure gold (the minor Cu content arising from the contribution of the Cu-rich glaze (Fig. 5)). It is applied with particular skill as is apparent in the disposition of

the scrolling tendrils along the undulating border and in the entwined monogram topped by a ducal coronet. This contrasts with the more generic kinds of gilded patterns such as the leaves on the cup and saucer (SB 2244\_9).

The objects SB2244-9 cup, SB 2244-10 teapot, SB 7115-2 saucer and SB 8405 dish were chosen for further XRF analysis with the aim of confirming the composition of gold decors analyzed previously. The ability to visualize the analyzed area with the Niton instrument helped to identify different spots, with good or poor adhesion of the gilded decoration (Fig. 7). The analyses showed that small amounts of mercury was partly present on the gilding of all objects. Visual examinations of the gilding decor in different places under tangential lighting show that the mercury-rich area generally correspond to areas of discontinuous gilding. Large amounts of sulphur were detected in all objects analyzed. This is both consistent with the use of amalgam to stick a gold leaf on an area where the adhesion of gold was poor after the firing and/or with the use of a ferrous sulfate procedure. However the spot size and related spatial resolution of the instruments used do not allow differentiation of mercury-based compounds promoting the gold adhesion with incompletely gilded area or vermillion lines applied to demarcate the area to be gilded.<sup>16</sup>

## **5. Conclusion**

The synergistic use of XRF and Raman instruments to investigate the glazes and decoration of Böttger stoneware offers a powerful combination for the complete characterization of these technologically advanced and aesthetically refined precious objects. While XRF analysis gives semi-quantitative information about the elements present in the body and gilded decoration, its use is limited to the characterization of black and brown glazes, as the interaction volume of the XRF beam is invariably larger than the glaze layer alone except for a gilded surface (a 0.2 $\mu$ m gold film is sufficient to stop the X-Ray beam). On the other hand,

Raman analysis, which is a surface analysis, with penetration of the order of approximately 5-50 microns in the conditions used, allows classification of the glaze composition type and provides access to information about the firing parameters (reducing atmosphere, low or high firing temperature) through the detection of specific phases and the calculation of the polymerization index.

Of the 21 objects studied, the analysis revealed two groups of dark glazes fired at higher or lower temperatures, with the black glazes showing higher Mn and Cu content, as measured with XRF. The colored décor of many objects was confirmed to be applied by cold painting over the brown or black lead-rich enamel and included some materials, such as gypsum, calcium phosphate and arsenate whites that have not been documented for Böttger stoneware previously and would warrant further investigation on other collections of these objects. The evidence of different types of gilding with pure gold (physically or chemically bound to the substrate), gold associated with mercury (by restoration or complementing the original technique because the poor quality of the fired gilding) and brass gilding confirms the great variability of procedures and high degree of experimentation during the years in which Böttger invented and presided over the production of red stoneware, making it material for high artistic expression.

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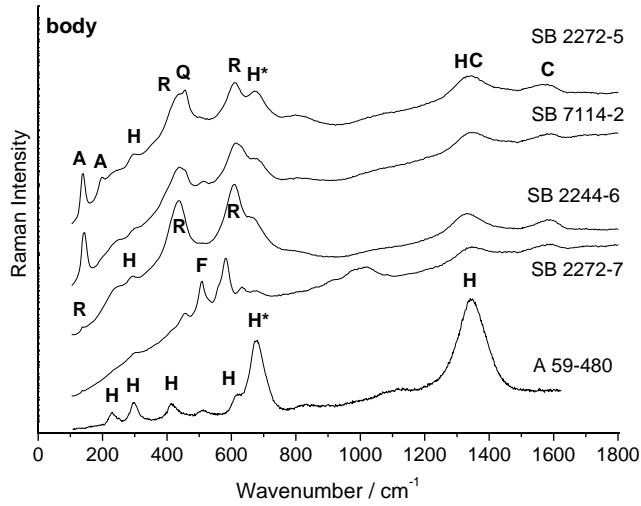


**Figure 1:** Representative views of glazed Böttger red stoneware (SB\*, Sèvres Collection, A\*, Art Institute of Chicago Collection and PC, Private Collection; details in Table S1, Supplementary Materials). Codes in bold represent the artefacts whose body composition has been previously studied with XRF<sup>17</sup>.

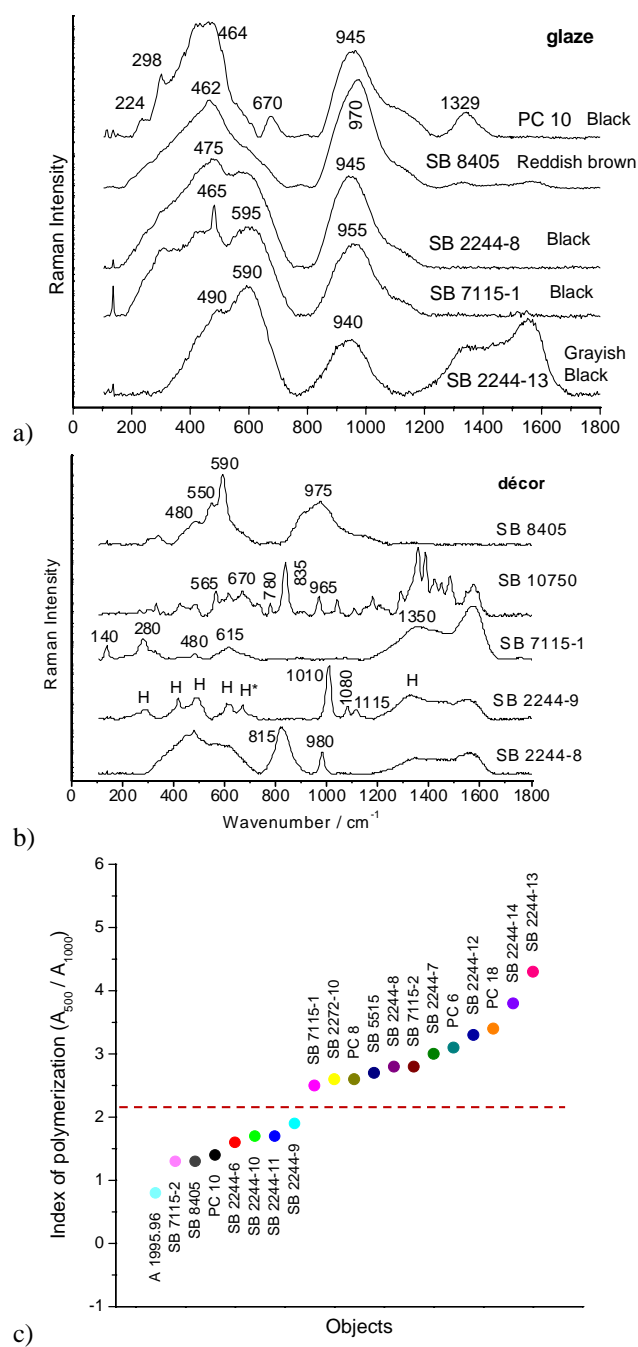
Suggestion for images:

SB 7115\_2 Now shows cup on inverted saucer. Would you consider cropping the saucer out so that the cup is better featured?

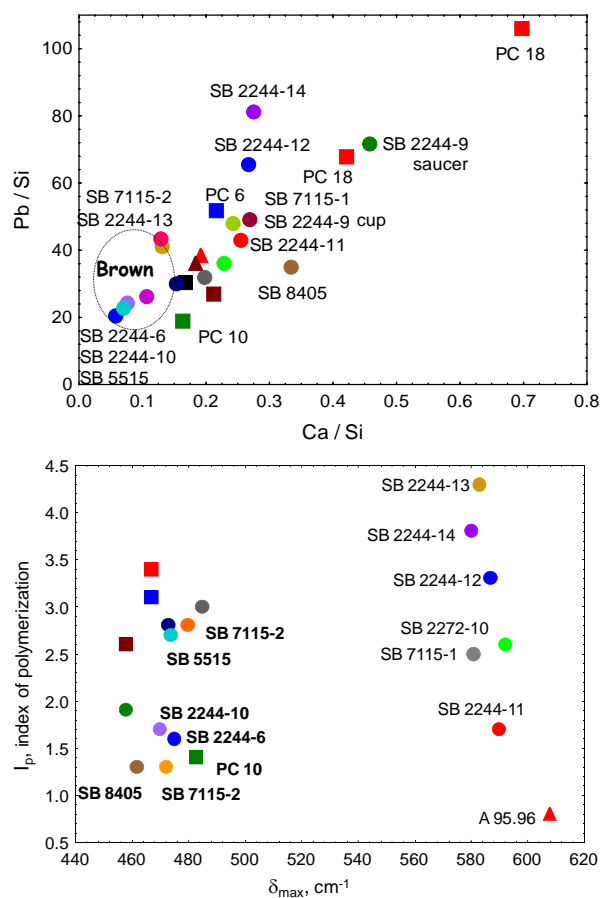




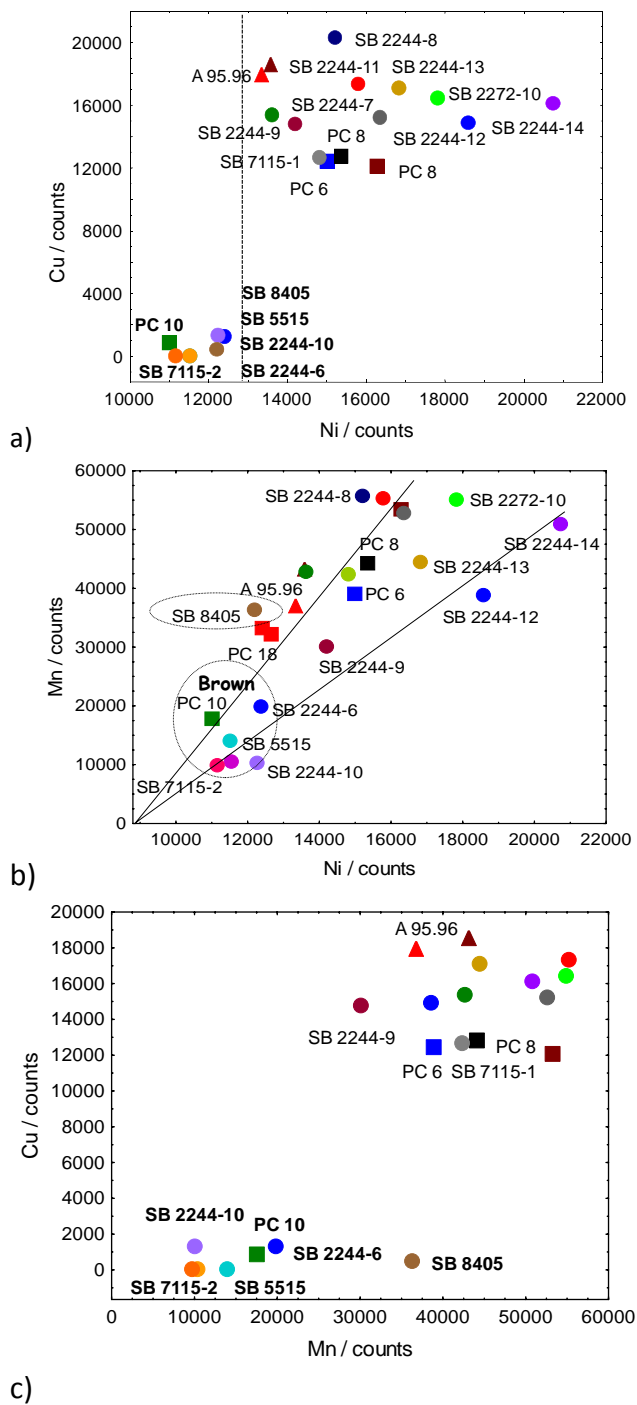
**Figure 2:** Representative as recorded Raman spectra showing the phases found in the bodies of unglazed red Böttger red stoneware as described in ref.17. The peaks characteristic of the different phases are labeled: H, hematite; H\*, hematite and magnetite mixture; Q, quartz; R, rutile; A, anatase; F, feldspar; C, carbon.



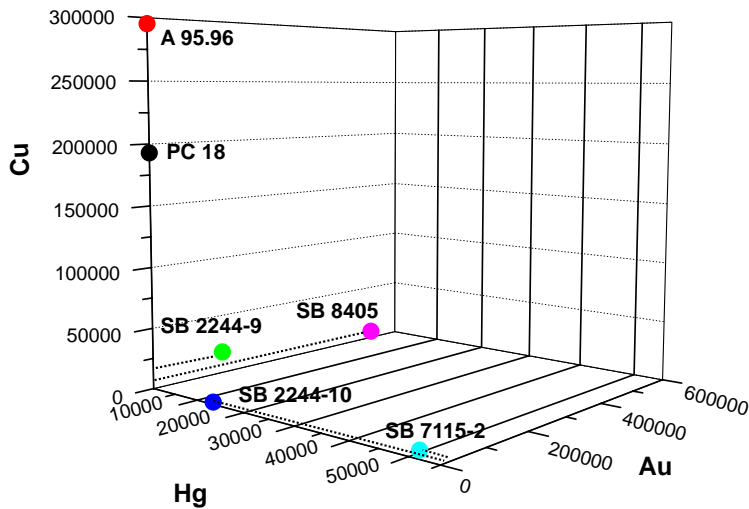
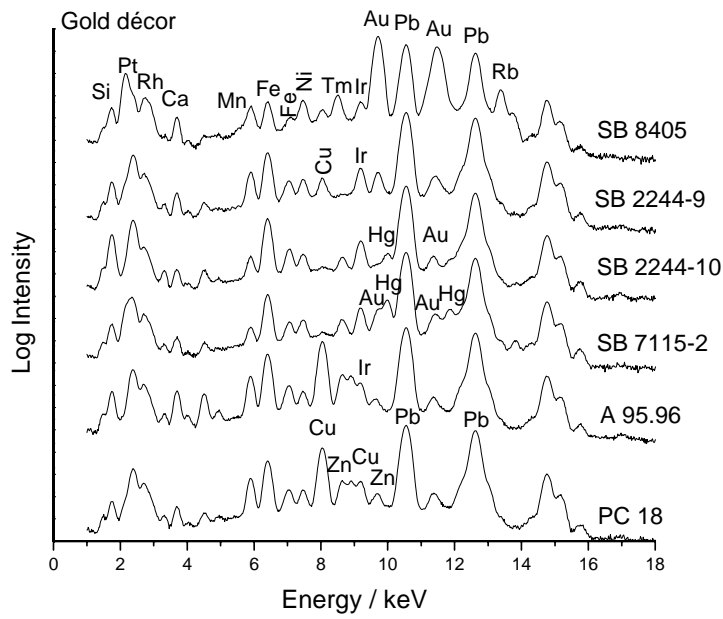
**Figure 3:** Representative baseline-subtracted Raman spectra recorded on the glaze (a) and décor (b) of the objects examined for this study; the Index of polymerization is given in (c).



**Figure 4:** Scatterplot of Pb/Si versus Ca/Si XRF mean net area counts (33 kV excitation energy) showing the variation of the composition measured on the glaze. Data obtained from the Art Institute of Chicago, USA, (solid triangle), Cité de Céramique, Sèvres, France (solid circle), private collection (solid square, see Table 1 for labels). b) Calculated index of polymerization ( $I_p$ ) vs position of the maxima of the Raman Si-O bending band ( $\delta_{max}$ ,  $cm^{-1}$ ) for brown and black glaze.



**Figure 5:** Scatterplot of Cu vs Ni (a), Mn vs. Ni (b) and Cu vs. Mn XRF number of counts for the glazed objects.



**Figure 6:** Representative XRF spectra of gold décors of different composition (Au, Au+Hg and Cu+Zn) and scatterplot of Hg, Au and Cu XRF count number recorded on the golden color.



**Figure 7** : Detail of the gilded area for SB 8405 dish (a) and SB 2244-9 bowl.

**Table 1.** Description of glazed Böttger red stoneware including measured CIE Lab factors, L: lightness, a (red) and b (yellow): color-opponent dimensions.

Code	Object	a*	b*	L*	Glaze color	Surface
A 1995.96	Coffeepot				Black	Unfired colors and gilded
SB 2244_6	Tankard				Brown	Gilded
SB 2244_7	Tankard	2.34	0.13	4.18	Black	Unfired colors and gilded CHECK
SB 2244_8	Sake bottle	1.21	-0.16	6.27	Black	Unfired colors and gilded
SB 2244_9	Saucer	2.29	-0.93	19.14	Black	Gilded
SB 2244_9	Cup	9.60	5.11	13.32	Black	Gilded
SB 2244_10	Teapot	9.29	10.34	14.76	Brown	Gilded
SB 2244_11	Teapot	0.53	-0.81	9.01	Black	No décor
SB 2244_12	Coffeepot	1.92	-1.32	7.88	Black	Partially glazed
SB 2244_13	Vase				Black	No décor
SB 2244_14	Cup	0.64	-1.37	5.41	Black	No décor
SB 2272_10	Vase	2.83	0.09	4.16	Black	Unfired colors and gilded
SB 5515	Teapot	4.92	5.93	14.25	Brown	Décor
SB 7115_1	Tea caddy	1.26	-0.61	6.20	Black	Gilded
SB 7115_2	Saucer	12.93	15.27	13.18	Brown	Gilded
SB 7115_2	Cup	8.28	6.37	14.21	Brown	Gilded
SB 8405	Plate	13.28	12.83	19.41	Brown	Gilded
PC 6	Teapot				Black	Gilded
PC 8	Cup & Saucer				Black	Gilded
PC 10	Figure				Black	Gilded base
PC 18	Tea caddy				Black	Gilded

**On-site identification of early Meissen Böttger red stoneware made  
at Meissen using portable XRF/Raman instruments: 2, glaze and gilding analyses**

G. Simsek<sup>1,2,3</sup>, Ph. Colomban<sup>4\*</sup>, F. Casadio<sup>3</sup>, L. Bellot-Gurlet<sup>4</sup>, K.T. Faber<sup>1</sup>, G. Zelleke<sup>3</sup>, V. Milande<sup>5</sup>, and L. Tilliard<sup>5</sup>

<sup>1</sup> *Department of Materials Science and Engineering, Northwestern University, Evanston, IL, USA*

<sup>2</sup> *Labex MiChem, Ladir, UPMC, 4 Place Jussieu, c49, 75252 Paris Cedex 05, France*

<sup>3</sup> *Art Institute of Chicago, Chicago, IL, USA*

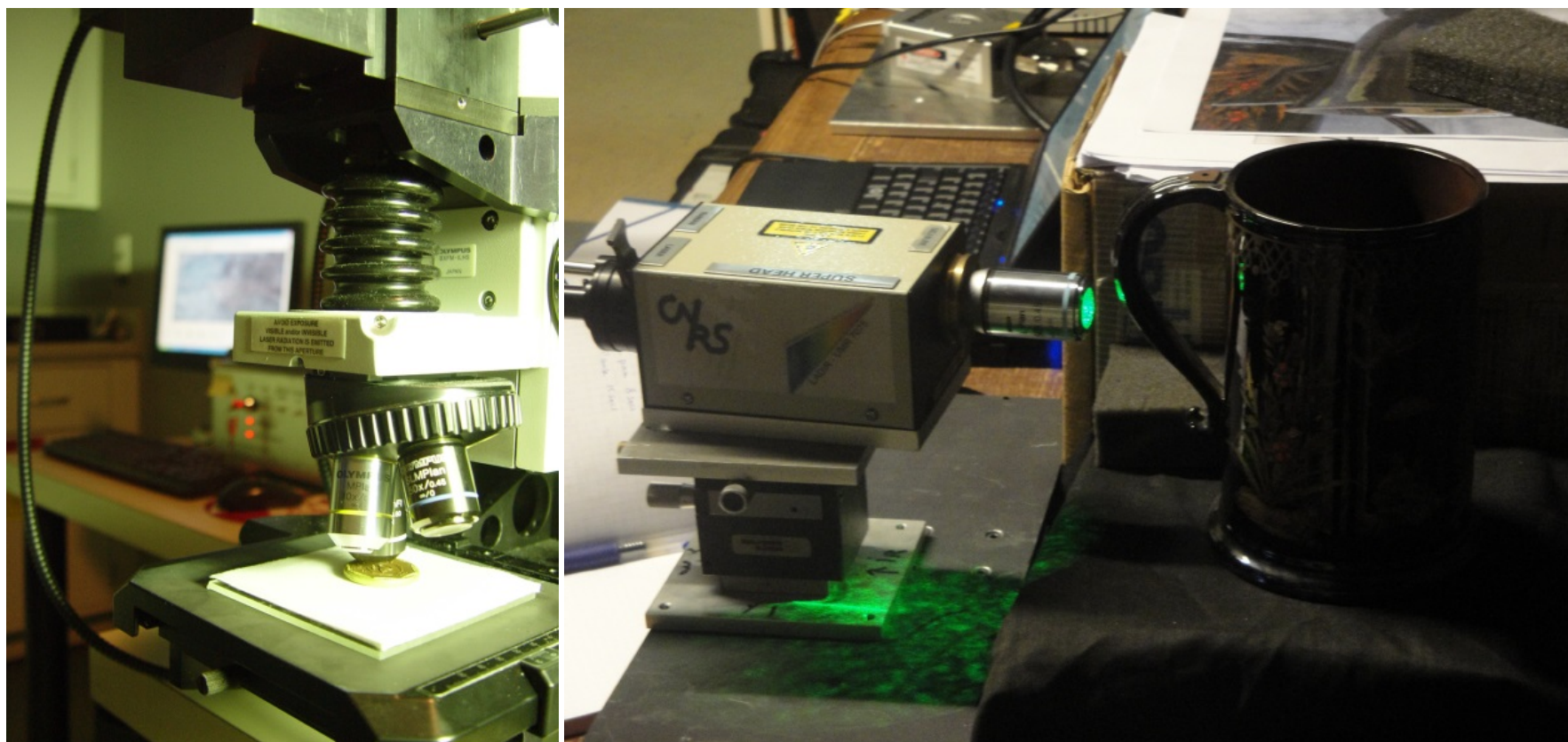
<sup>4</sup> *Sorbonne Universités, MONARIS, umr 8233 CNRS, UPMC Univ. Paris 06, 4 Place Jussieu, c49, 75252 Paris Cedex 05, France*

<sup>5</sup> *Cité de la Céramique – Sèvres & Limoges, Place de la Manufacture, 92310 Sèvres, France*

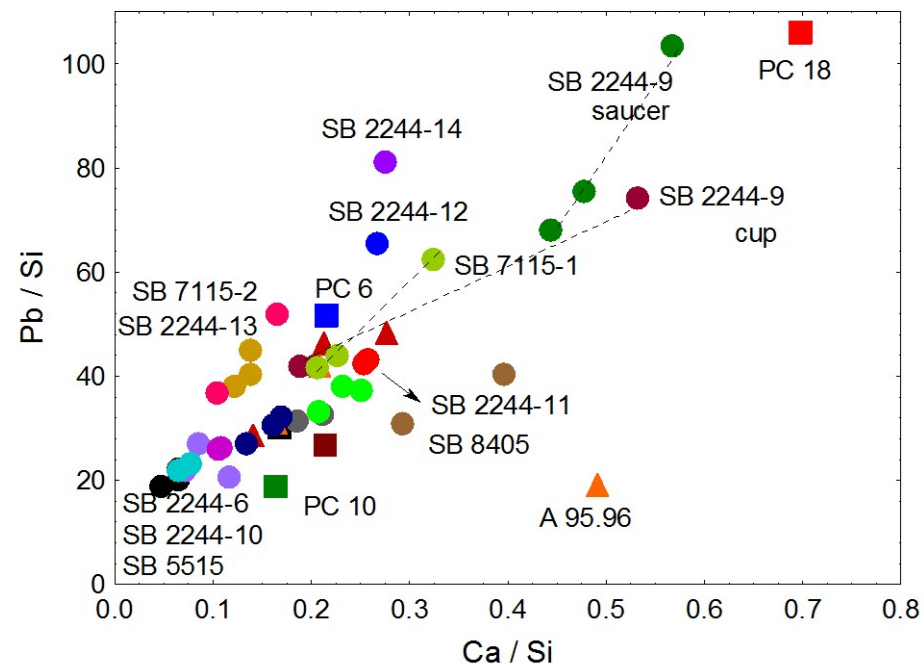
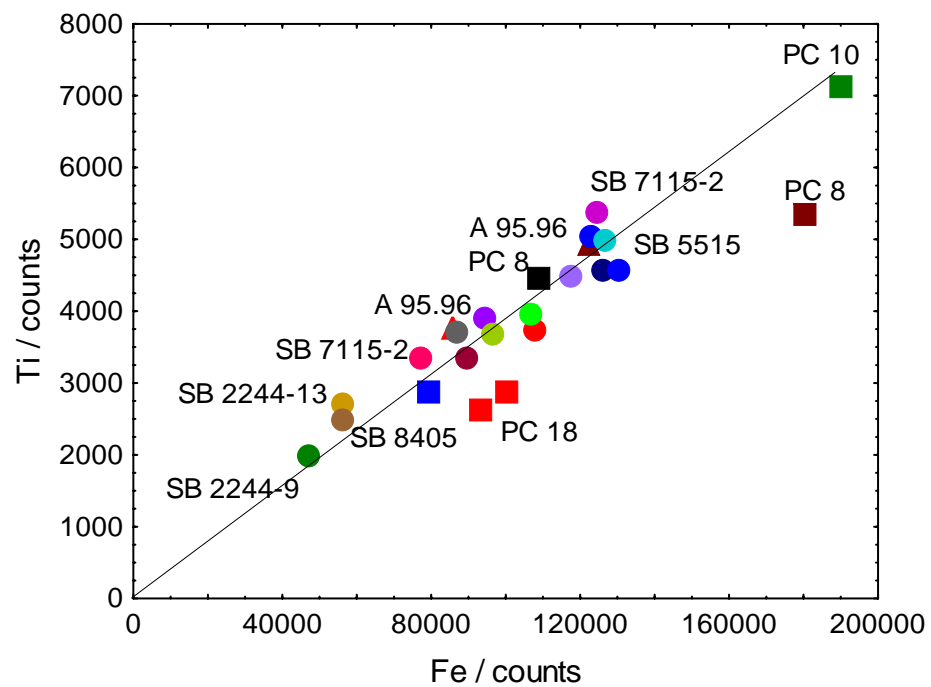
\* corresponding author : Ph. Colomban philippe.colomban@upmc.fr

Supplemental Figures

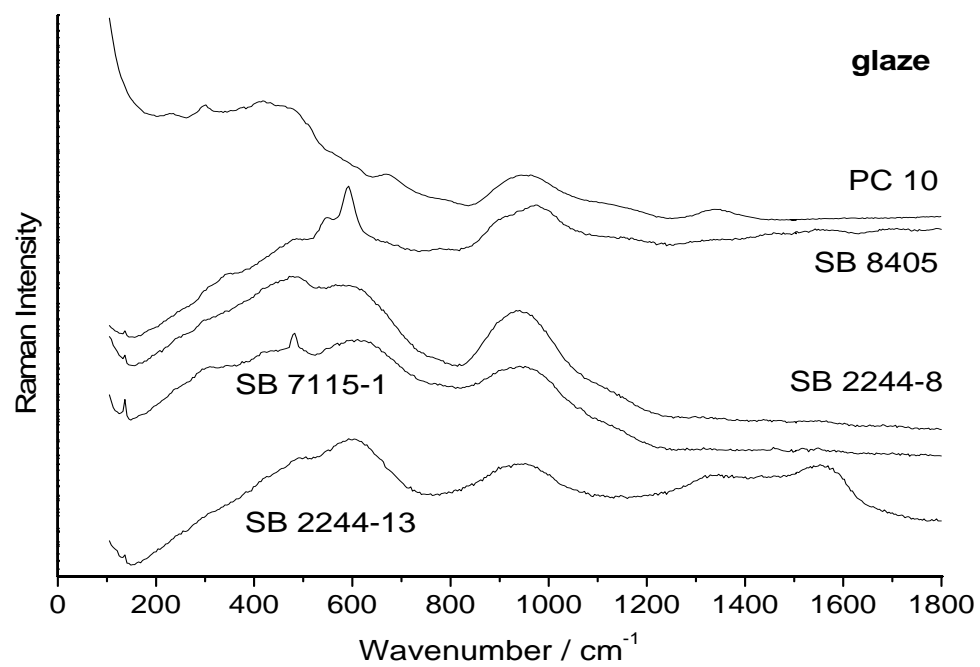




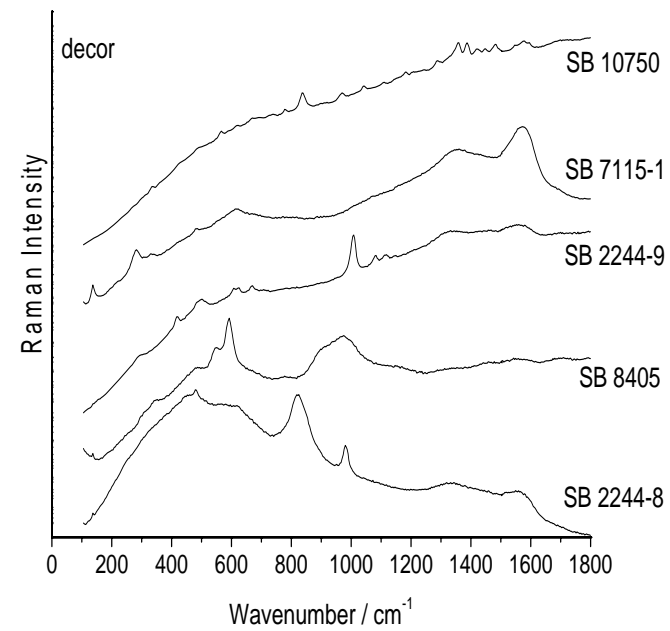
**Figure S1:** A laboratory (left) and portable (right) Raman set up. The distance between object and portable instrument is 15 mm. A black textile is put on both the remote head and artifact before increasing the laser power at the required level to screen off unwanted ambient light.



**Figure S2:** Scatterplot of Ti vs Fe XRF net area counts and Pb vs. Ca (normalized by Si).

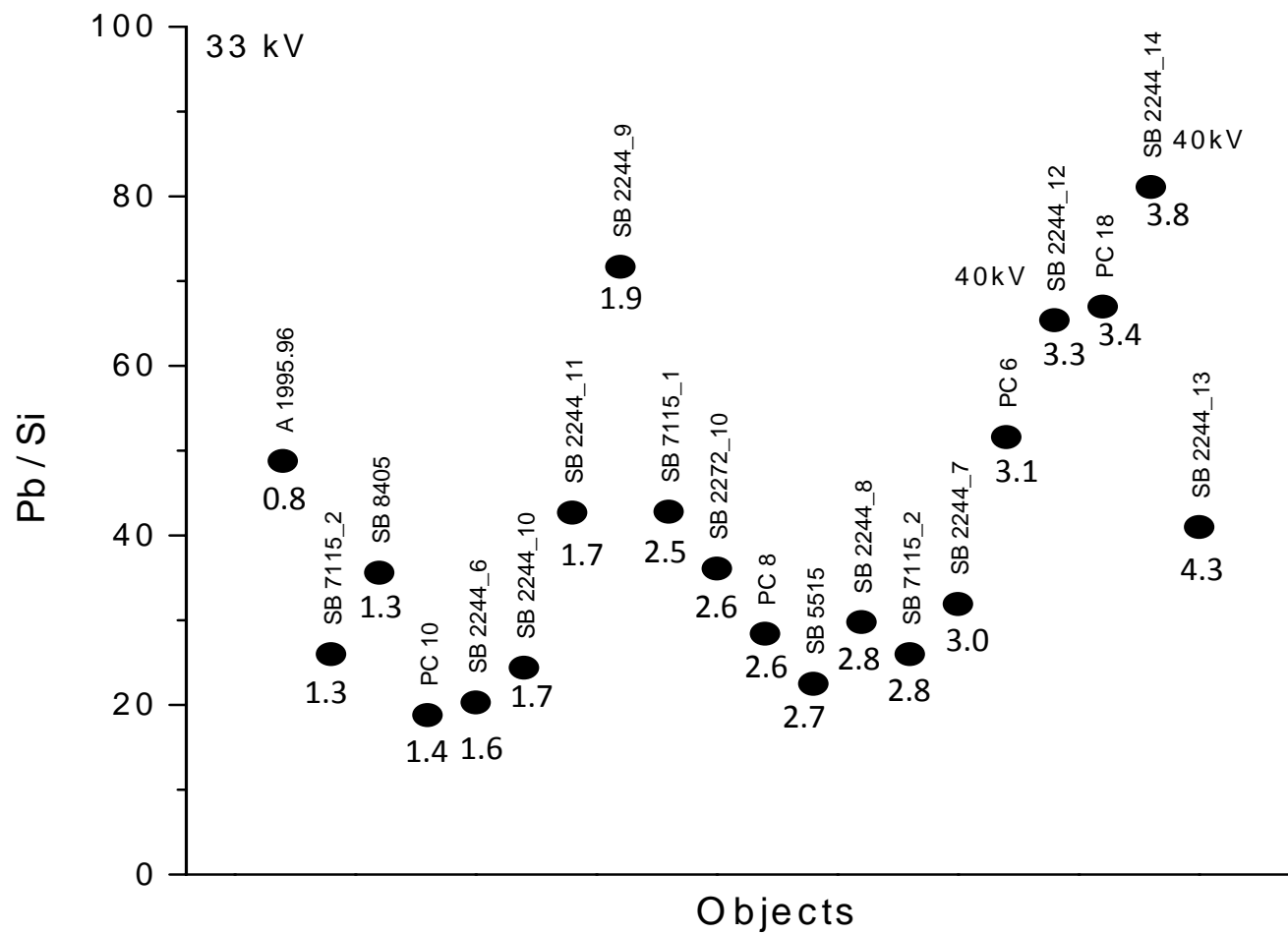


a)















b)

**Figure S3:** Representative as recorded Raman spectra on glaze (a) and overglaze decoration (b).



**Figure S4.** XRF Pb net area counts normalized by Si. The objects are listed according to their increasing  $I_p$  value (see below the labels) (see Fig. 3c).

<b>Inventory number</b>	<b>Object's identifier (this article)</b>	<b>Object</b>	<b>Artisan (if known)</b>	<b>Production Year (estimated)</b>	<b>Production place</b>	<b>Dimensions (cm)</b>	<b>Acquisition date</b>	<b>Motive of acquisition</b>	<b>Picture</b>
1995.96	A 1995.96	Coffee pot		1715	Meissen Factory	20.5x13.5x9.1	1995	Restricted gift of Mrs. Marilyn Alsdorf in memory of her husband	
MNC 2244-6	SB 2244-6	Tankard	Böttger	1715	Meissen Factory	14x13x9.1	1836	Purchased in Dresden by Brongniart	
MNC 2244-7	SB 2244-7	Tankard		1713-1720	Meissen Factory	16.7x11.7x5.5	1836	Purchased in Dresden by Brongniart	
MNC 2244-8	SB 2244-8	Sake Bottle		18th century	Meissen Factory	17x11	1836	Purchased in Dresden by Brongniart	
MNC 2244-9	SB 2244-9	Cup & Saucer	Böttger	1710	Meissen Factory	2.8x13.4	1836	Purchased in Dresden by Brongniart	

						9.3x4.5			
MNC 2244-10	SB 2244-10	Teapot	Böttger	1710	Meissen Factory	7.5x13.2x8	1836	Purchased in Dresden by Brongniart	
MNC 2244-11	SB 2244-11	Teapot		1713-1720	Meissen Factory	17x9.50x12	1836	Purchased in Dresden by Brongniart	
MNC 2244-12	SB 2244-12	Coffee pot	Jacob- Johann Irminger	1715	Meissen Factory	13x17.70x7	1836	Purchased in Dresden by Brongniart	
MNC 2244-13	SB 2244-13	Vase		1713-1720	Meissen Factory	13.1x8	1836	Purchased in Dresden by Brongniart	
MNC 2244-14	SB 2244-14	Cup		1710-1719	Meissen Factory	13x10.1x8.8	1836	Purchased in Dresden by Brongniart	
MNC 2272-10	SB 2272-10	Bottle		1715-1720	Meissen Factory	36.7x17.2	1837	Sent by Dresden Museum	

MNC 5515	SB 5515	Teapot	Böttger	1710	Meissen Factory	10.3x16.5x10.2	1860	Gift of Charles de Férol	
MNC 7115-1	SB 7115-1	Tea caddy		1713-1720	Meissen Factory	12x11	1875	Gift of Dresden Museum	
MNC 7115-2	SB 7115-2	Cup & Saucer	Böttger	1710	Meissen Factory	Saucer: 2.5x12.3  Cup: 3.4x7.4	1875	Gift of Dresden Museum	 
MNC 8405	SB 8405	Dish	Factory	1710	Meissen	Plate 32,8 x 28,5 x 5,8 cm	1885	Bequest of Baron Charles Davillier	

**Table S1:** A selection of the studied objects that are part of publicly accessible collections

Code	$\nu$ , $\text{cm}^{-1}$	$\delta$ , $\text{cm}^{-1}$	$I_p$	Estimated firing T ( $^{\circ}\text{C}$ )
A 1995.96	970	608	0.8	<900
SB 2244_6	955	475	1.6	<1000
SB 2244_7	961	485	3	<1200
SB 2244_8	955	473	2.8	<1200
SB 2244_9	943	458	1.9	<1000
SB 2244_9				
SB 2244_10	952	470	1.7	<1000
SB 2244_11	958	470/590	1.7	<1000
SB 2244_12	951	475/587	3.3	<1400
SB 2244_13	953	583	4.3	<1400
SB 2244_14	966	580	3.8	<1400
SB 2272_10	964	592	2.6	<1200
SB 5515	940	474	2.7	<1200
SB 7115_1	964	581	2.5	<1200
SB 7115_2	952	472	1.3	<1000
SB 7115_2	934	480	2.8	<1200
SB 8405	969	462	1.3	<1000
PC 6	947	467	3.1	<1400
PC 8	944	458	2.6	<1200
PC 10	945	483	1.4	<1000
PC 18	940	467	3.4	<1400

**Table S2.** Raman parameters of the glaze structure, representing  $\nu\text{Si-O}$ , stretching peak;  $\delta$  Si-O bending peak;  $I_p$ , polymerization index and estimated firing temperature.<sup>23-26</sup>