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Philippe Colomban, Lucie Arberet, Burcu Kirmizi

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Philippe Colomban,[1] Lucie Arberet,[1] Burcu Kırmızı[1,2]

[1] Sorbonne Universités, UPMC Univ. Paris 06, MONARIS UMR8233, 4 Place Jussieu, 75005 Paris, France
[2] Mimar Sinan Fine Arts University, School of Conservation and Restoration of Movable Cultural Property, Cumhuriyet Mahallesi Silahşör Caddesi No 71, Bomonti/Şişli, 34380 İstanbul, Turkey

Corresponding author: philippe.colomban@upmc.fr

Abstract

Limoges enamels on metal from the 17th to 18th centuries were analysed by non-invasive Raman microspectrometry with a mobile set-up in storage at the Musée des Arts Décoratifs (Paris) in order to identify the types of glazes and pigments used and to compare them with those found in Chinese *cloisonné* and *falangcai* enamels painted on metal and porcelain from the Kangxi and Yongzheng reigns (Qing dynasty). Certain French Jesuit and Chinese historical records report exchanges of technical know-how and artefacts during this period from France to China. Particular attention is paid to the detection of lead arsenate in blue and white enamels as well as in the whitened ones. Lead arsenate appears to be formed in blue enamels due to the high arsenic content of European cobalt ores exploited during the period in question.

<mark>+ Graphical abstract</mark>
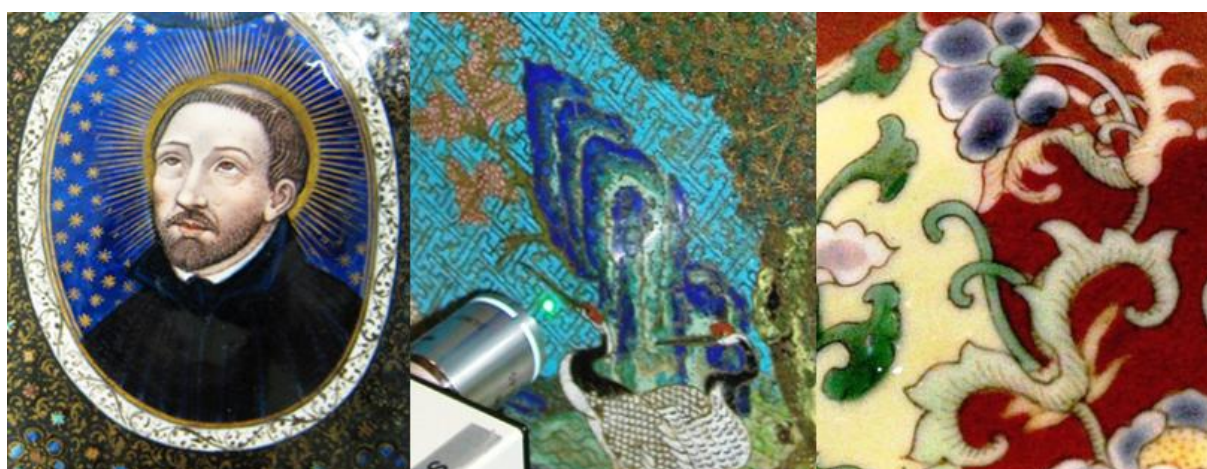
1. Introduction

The term "enamelling" refers to the application of a coloured glaze to a metal, ceramic or glass substrate. The earliest examples of enamelling on metal are observed in the golden rings from the Mycenaean tombs dating to the second millennium B.C. in Cyprus [1, 2], and Celtic jewellers brought this art to a high level of quality with various enamelling techniques such as *champlevé* and *cloisonné* as early as the 3rd century B.C. [3, 4]. The Byzantines then particularly achieved the mastery of enamelling, mainly the *cloisonné* technique, from the 8th century onwards [5]. At the same time, Western Europe showed a continuous development in enamel making during the Middle Ages, when Limoges became a centre of the production of enamels on copper alloys during the 12th century in France. So-called painted enamels emerged in the 15th century at Limoges [2, 6-9], where craftsmen mastered the painting of elaborate, multi-coloured scenes and figures on the entire metal substrate with a sophisticated know-how of the use of different glaze compositions and numerous firing cycles. Artefacts made during the Middle Ages and the Renaissance are highly prized by scholars and collectors [6, 8]. However, the enamels produced after the Renaissance are considered less worthwhile in Europe at the present time and rarely studied [6, 9]. In China, these artefacts were highly appreciated at the time of their production and served as models for *cloisonné* and painted enamels on porcelain and metal respectively [10] during the Qing dynasty, namely the Kangxi (1662-1722) and Yongzheng (1723-1735) reigns [11-13]. The painted enamel porcelains are also called *falangcai* ware, *falang* being the homonym of the name given to France at that time. It is generally suggested that the art of *cloisonné* enamelling on metal had arrived China from the west by way of Byzantine craftsmen in the 14th century, and the technique was developed and became widespread during the Ming dynasty (1368-1643) [9, 10]. Multi-coloured *cloisonné* objects were being produced to adorn temples, since they had a flamboyant nature with elaborate decorations.

Painting on a non-porous body, such as a metal substrate or an already glazed pottery, requires a viscosity-controlled mixture, generally oil-based, that allows the painting of complex decorations made up of different coloured areas. The sharp delimitation between coloured glazed areas is a difficult task to overcome due to the low viscosity of the glaze at the top firing temperature (low viscosity and good wetting being required to obtain a glossy and regular coating) as well as the fast diffusion of colouring ions from one area to the adjacent one. Thus, a first method to tackle this difficulty is the use of pigments, i.e., coloured

powders made of a special crystalline phase, stable in the molten glaze, in the place of ions as colouring agents [14]. The second method is the application of a refractory phase to border the coloured areas, such as those made by Iznik potters with chromite/spinel type of pigments [15]. The last method, which is specific to metal substrates, is the addition of thin strips of metal called *cloisons* to delimit the coloured areas. These strips are pasted or welded to the metal substrate. The different coloured areas are obtained by fusing coloured and/or opacified glass powders in between the strips. The artefact is then polished to achieve a glossy surface. Regarding the overglazing of an already glazed artefact, the use of a glaze composition with a melting temperature about a hundred or more degrees centigrade lower than that of the glaze substrate is required. Many firing cycles are thus necessary for artefacts presenting complex painted decorations.

According to French and Chinese historical records, the new technique of enamel painting was made in order to obtain more sophisticated decorations and assumed to be executed by the French and Italian Jesuits who served at the Chinese court during the 17th and 18th centuries [11-13, 16, 17]. During the Qing dynasty, France and China became culturally and scientifically engaged with the arrival of the French Jesuit mission to China in 1685 according to the order of the Kangxi emperor (r. 1661-1722) for the recruitment of skilled scientists and artisans for the Chinese court [11, 17-19]. The Jesuits were led by J. de Fontaney (1643-1710, Chinese name: *Hong Ruo*), who brought a selection of enamelled wares (clocks and watches) from France as a gift to the Chinese court. The gifts of enamel works raised a greater interest in enamel production in the court, which also led to the importation of the pigments and colouring agents from the west. The French Jesuits J.F. Gerbillon (1654-1707, Chinese name *Zhang Cheng*) and J. Bouvet (1656-1730, *Bai Jin*) established a chemistry workshop, and J.B. Gravereau (1690-1762, *Ni Tianjie*) with the Italians G. Castiglione (1688-1766, *Lang Shining*) and P.M. Grimaldi (1618-1686, *Min Mingwo*) developed the technique of enamelling [11]. Chinese craftsmen also tried to imitate the visual aspect of European decorations and paintings in the invention of *Famille Rose* and *Famille Verte* porcelains, also called *yangcai* (foreign colours), *fencai* (powder colours) or *ruancai* wares (soft colours) [20-24]. Major characteristics of these "new" enamelled objects were the use of opaque overglazes, especially for the blue, yellow and white colours [11, 20-25]. Copper-coloured green enamels and rose ones that were based on colloidal gold (Cassius' purple), were usually named as *yangcai*, i.e., foreign colours.

Some technical information regarding painted enamels on porcelain was first obtained by G. Vogt, head of the Sèvres Factory laboratory in the late 19th century, as reported by

Garner [22] and Williamson [23]. The important characteristics of these new colours were their opacity and their capability of mixing with white, alone or together, to form a large variety of shades [24, 25]. The white pigment (opacifier) has been described as made of tin oxide [22] but also as an arsenic-based compound [25]. Tin oxide had been in use as an opacifier since the 5th century [26] and arsenic was first used in the making of *lattimo* glass in Murano during the 16th century [27]. However, its common use as a glass opacifier was developed during the second half of the 19th century [28].

Regarding the colour yellow, lead-based pyrochlore pigment [9, 23, 25, 29, 30] had already been used in the form of antimonate in ancient Egypt and Mesopotamia and is usually known as Naples yellow, a very common yellow pigment after the 16th century [29]. However, this type of pigment was most of the time used in the form of solid solutions ranging from stannates to antimonates with partial substitution by many other ions (Fe, Zn, Si, etc.) [30-35]. The compositional analyses of *Famille Rose, Famille Verte* and *cloisonné* wares as well as *cloisonné* enamels on metal have been reported by a few authors [21, 24, 25, 35-38], but as noted by Kingery and Vandiver in 1986, "the descriptions of the enamel technology are completely speculative" [24] due to the very small number of artefacts studied.

We report here on the on-site Raman analyses of six ca. 18th century Limoges enamelled artefacts which are representative of the potential models viewed by early Chinese craftsmen. For instance, recently a painted porcelain from Kangxi reign belonging to the collection of the French Musée National des Arts Asiatiques–Guimet has been identified as having the shape and decorations typical of Limoges enamelled metal works [12]. Since the artefacts are rare ones, Raman spectrometry as a non-invasive analytical technique was used. One of the artefacts (GR21) has already been partially analysed on-site by Raman spectrometry [9]. In other previous work covering Limoges production from the 16th to 19th centuries, technological changes were evidenced according to the modifications in the enamel compositions over time, which were determined either by XRF [39-41] or PIXE [6]. However, these elemental analyses cannot exactly identify the colouring phases, while Raman scattering can. The present work focuses on the identification of the colouring phases, in particular those containing an arsenate phase.

2. Materials and Methods

2.1 Technique

Raman spectra were recorded with the HE532 Horiba Jobin-Yvon mobile spectrometer equipped with a 532 nm 300 mW Ventus Quantum laser and a x200 Mitutoyo and a x50

Nikon microscope long working distance objectives, as previously described [9, 10]. The laser and the spectrometer are fibre optically connected to the remote Superhead® put on a heavy stage with XYZ micrometric displacement. The x50 objective probes a volume of ~4x4x12 μm^3 while the x200 objective probes a much smaller volume of about 0.5x0.5x2 μm^3. The very small laser spot obtained with the x200 objective required a precise focus that took much time to be obtained, but this guaranteed the analysis of the single glaze layer and a higher intensity of the pigment phase. The height position of the artefact was controlled with the use of a ream of copy paper as a support. Finally, an opaque black fabric was put over the artefact and the remote head to prevent the ambient light and protect the scientist's eyes from the laser scattering. The focus was controlled by maximising the collected fluorescence/background signal intensity and then the pigment/glaze one. More than 250 spots were analysed and about 230 of them were found to be successful. On-site collected spectra with a portable Raman instrument show a rather large background due to the contribution of the filter and the fluorescence arising from the surface deposits. However, cleaning of the artefacts is not authorized. Consequently, the rather large background and the medium spectral resolution led to a certain inaccuracy in the measurement of the peak positions (ca. $\pm$ 2 cm^{-1}).

2.2 Artefacts

All artefacts belong to the collection of Musée des Arts Décoratifs (Union Centrale des Arts Décoratifs) in Paris (Figs. 1 to 5). Their full descriptions and historical contexts have been published before [6].

- 20434 A&B (9.8 x 7.2 cm each), *Saint Ignatius (Ignace)* and *Saint Xavirius (Xavier)*, assigned to the second quarter of the 17th century, attributed to Léonard II Limosin (1560/65-1635) or more likely to his brother Léonard III (1590/1600-1666), see details in ref. [6] cat. 48.
- GR21 (10 x 7.7 cm), *Virgin and child*, assigned to first half 17th century and attributed to Jean Limosin (1580-1645), grandson of the famous Léonard Limosin; see details in ref. [6] cat. 47, and some spectra have been given in [31].
- 20435 (17 x 14 cm), *Saint Nicolas*, signed on the reverse side "*Bapt[te] Nouailher émaillieur à Limoges*," 18th century, see details in ref. [6] cat. 51.
- 2001.34.1.1-2 (7.8 x 7.9 cm) cup, believed to have been made at the Laudin family workshop, beginning of the 18th century, see details in ref. [6] cat. 54.

- 12160 A & B (9 x 6.5 cm each), *Ascension* and *Assumption*, potentially attributed to Baptiste Nouailher, 18th century, see details in ref. [6] cat. 52.
- 41873 (9 x 6.5 cm), Wedding purse covered with an enamelled metal plate of the *Marquis de Dune Seigneur de la Chaban*e, stylistically attributed to the Nouailher family workshop, 18th century, see details in ref. [6] cat. 53.

3. Results and Discussion

3.1 On-site Raman Analyses

Figs. 1-5 show the representative spectra recorded during the measurements with the portable Raman set-up in storage at the Musée des Arts Décoratifs. We will first present and discuss the Raman signatures of the glazes and then those of the pigments/opacifiers. Artefacts will be considered chronologically and in relation to their assignment to different workshops [6].

3.1.1. Glazes

The Raman signature of a silicate type glass presents two main broad features, the contribution of the SiO_4 tetrahedron bending (at ~550 cm^{-1}) and stretching modes (at ~1000 cm^{-1}) respectively [42-45]. The centre of gravity of the latter mode downshifts with the flux content (i.e., as a function of the polymerisation degree and of the melting temperature). The area ratio of the bending to stretching mode decreases when the polymerisation degree and the melting temperature fall as well [42-45]. Since the symmetric stretching Raman modes of SiO_4 are much stronger than the asymmetric ones, the different components of the ca. 1000 cm^{-1} band can be considered as representative of the different types of SiO_4 tetrahedron of the glaze network: isolated tetrahedron, tetrahedra connected by 1, 2 or 3 shared oxygen atoms or fully connected. For instance, addition of PbO increases the number of poorly connected tetrahedra, and the component(s) at a wavenumber below 980 cm^{-1} becomes dominant [42,43]. In a previous study covering Limoges production from the 16th to 19th centuries [9], two main types of glazes with subgroups were identified: i) A-type PbO-reach glass (with addition of K_2O and CaO) with a stretching band peaking at ~980 cm^{-1} or less, ii) B-type soda glass with maximum up to ~1075 cm^{-1}; where B'-type soda-lime glass can be distinguished from soda glass on the basis of the maximum of the bending band, shifting from ca. 480 to ca. 560 cm^{-1} [42].

The results of this study match well with those of the previous study. In general, two types/variants of glass were observed for each artefact, and sometimes three types were identified. This indicates that many firing cycles were executed, as commonly made in the

glazing technology of enamelled metals. According to the previous study [9], 17th century artefacts (assigned to the Limosin workshop) have generally been made with B (and variant B') type, i.e. without PbO-rich glaze, with the exception of the black enamel of sample GR21 (A-type). According to the results of this study, 18th century artefacts were found to be A-type glass for different colours such as blue (20435), yellow (20435, 41873 & 2001.34.1), and white (41873).

3.1.2. Pigments

Raman spectroscopy will detect pigments and some chromophores (Fe-S amber complex) of glass but is not able to identify the presence of colouring ions. For instance, the lack of specific signature for green enamel is consistent with the use of Cu^{2+} ions.

Raman analyses showed that the opacification of the Limoges enamels studied was carried out with tin oxide (cassiterite, 635-775 cm^{-1} doublet [26, 27]) for the white areas of all artefacts, as previously observed for similar and older items [9].The peaks are narrow and rather strong, indicating the use of a highly crystalline cassiterite. According to the previous study, another opacifying agent, namely lead arsenate, was also observed only in the 19th century Limoges artefacts [9].

The red colour was found to be always achieved with the same pigment as hematite ($\Box$-Fe_2O_3), easily detected with its strong resonance feature at ~1310 cm^{-1} and a series of peaks at 223, 290, 405, 493 and 605 cm^{-1} [46]. This pigment is also used for the flesh tones (carnation, Fig. 1).

The Raman signature of the blue coloured areas exhibits a more or less strong peak at ~830 cm^{-1}, with a shoulder at ~790 cm^{-1} (20434A, GR21 and 2001.34.1), suggesting the use of lead arsenate. The same signature is also observed in "black" area (Fig. 1: actually the black area appears dark blue under high-power illumination). The Raman spectrum of olivine (Co_2SiO_4) also exhibits its stretching doublet in the same wavenumber range [47], but the peak bandwidth is much narrower. The intensity of Si-O stretching tends to be much lower than that of As-O because of the smaller polarizability and the lower number of electrons involved in the bond. Thus, the stretching band of arsenate-based compounds is always very strong and peak between 800 and 830 cm^{-1} [48,49]. The change in the peak positions might possibly be due to the formation of different solid solutions of lead arsenate where Pb may partially be substituted by K, Na and Ca ions due to the glaze composition [49]. Consequently, the strong peak observed at ca. 830 cm^{-1} in some enamels/glazes can be assigned to arsenic-based compounds, as proposed by Van Pevenage et al. [50] for similar *Famille Rose* wares of China. The large bandwidth is consistent with the orientational

disorder of arsenate ions. At the same time, it is also noteworthy that blue enamels of many Limoges artefacts from the middle of the 16th century display a significant arsenic content [6]. For instance, in sample 40185 (*La Mise au Tombeau*, ca. 1560-1570), the presence of a considerable amount of arsenic was confirmed by previous PIXE analysis [6] and Raman signature was observed as such [9]. In fact, arsenic is a minor element commonly found in European cobalt ores: the Co/As ratio reaches 0.4 for the 16th to 17th century European glass and decreases to ~0.1 during the 18th century [28, 51-55]. On the contrary, Asian cobalt ores are rich in manganese and iron [55-58] and require a firing under strong reducing atmosphere [59] to develop only the blue colour of Co^{2+} ions [15]. Similar Raman signatures have been recorded on some Chinese *cloisonné* enamels (e.g., Fig. 5) and on many blue glazes of French, Italian, and English 18th century soft-paste porcelains [60-62] where distinguishing the cobalt silicate and lead arsenate contributions was not discussed or the Raman features were wrongly assigned to cobalt silicate. The characteristic lead arsenate peak at ca. 830 cm^{-1} is clearly observed in the blue enamels of the Limosin and Laudin Family workshops (Figs 1 and 2, Table 1) but not in the Nouailher workshop (or as possible traces), indicating the use of different cobalt sources at that time.

Yellow and green colours were obtained with the $Pb_2[Sb/Sn/Fe/Zn]_2O_{7-\delta}$ pyrochlore pigment, recognizable with its strong low wavenumber peak (135-140 cm^{-1}). The position of this peak assigned to the motion of Pb^{2+} ions depends on many factors (composition, oxygen non-stoichiometry, firing temperature, etc.). The observation of the stretching modes characteristic of Sn-O (~450 cm^{-1}) or Sb-O (~508 cm^{-1}) is much more pertinent [9, 30, 31] to be able to discriminate between the different pyrochlore solid solutions. Raman peak at ca. 128 cm^{-1} is observed for sample 20435 (St. Nicolas, Nouailher Family workshop) while peaks at 136 cm^{-1} were measured for samples 12160A (*Ascension* and *Assumption*), 41873 (Marquis *de Dune*) (both from the Nouailher family workshop) and 2001.34.1 (Laudin family cup). The intense ca. 510 cm^{-1} peak indicates Sb-rich compositions for samples 2001.34.1.1, 20435 and 12160, as also confirmed by previous PIXE analysis [6].

Some dark or black shades (20434A, 20435, 12160A, 41873 and 2001.34.1) are obtained by the addition of black (amorphous) carbon (sp^3-sp^2-C-C stretching doublet at 1350-1600 cm^{-1}) [63]. The observation of a peak at ~955 cm^{-1} characteristic of phosphate in the 2001.31.1 cup indicates the use of "black ivory", which is a carbon powder prepared by burning ivory or more usually bones [29]. No specific signature is recorded for the brown area (Fig. 1). This is consistent with the use of Fe^{2+}/Fe^{3+} ion mixture as colouring agent.

Chromate and chromite phases often found in black pigments give a strong peak at ca. 845 cm^{-1} [15, 64, 65]. Thus, the peak at 849 cm^{-1} observed in the black area of the cup from the Laudin workshop (2001.34.1.1-2, Fig. 2) can be assigned to a similar phase. Before the development of the chromate industry, green enamels and glazes were obtained by dissolving Cu^{2+} ions in lead-based glass (i.e., turquoise colour is obtained in alkaline glass) [66] or by dispersing yellow pigment grains in a blue coloured glass matrix [15]. The later method was probably used in the *Ascension* and *Assumption* plaques (12160A & B, Fig. 4, Nouailher workshop). On the contrary, the absence of a specific Raman signature, except that of the carbon doublet, in the green areas of the samples from the Laudin (2001.34.1.1-2, Fig. 2) and Limosin (GR21, 20434, Fig. 1) workshops is in agreement with the use of Cu^{2+} ions dispersed in the glassy matrix. The spectrum recorded on the green spots of the *St. Ignatius* shows the carbon doublet (1321-1566 cm^{-1}) and a well defined peak at 983 cm^{-1}, tentatively assigned to wollastonite (CaSiO$_3$), which is a common phase in calcium-rich glazes [60]. Here, the carbon doublet arises from the black layer bellow the green spot. When the focus is changed, the carbon contribution disappears and the spectrum corresponds to that of the green enamel.

3.2. Comparison with Chinese Enamels and European Blue Porcelains

Chinese *cloisonné* and Limoges painted enamels have previously been studied by various techniques such as Raman [10, 37], PIXE [6], XRF [36, 40, 41] and EPM and XRD [38]. In Fig. 6, the glaze types of Chinese *cloisonné* enamels are compared with those of Limoges enamels. Arsenate signature is clearly recorded for whitened yellow area of the 23778-2 artefact and the dark blue area of the 23661 one (Fig. 5). A very strong peak is measured on pink areas (e.g., the clouds). It is possible that the achievement of the pink colour with gold nanoparticles promotes the intensity of the Raman scattering. The common features correspond to the period when both Chinese and French historical records report exchanges of know-how and materials through the Jesuits. The on-going study on *falangcai* imperial porcelains produced at the Qing Court workshop [13] also identified the Raman signature of lead arsenate in many blue coloured areas. Similar Raman signatures have been reported in the blue decorations of many European 18th century porcelains as well [60-62]. Thus, the hypothesis of the use of cobalt-containing raw materials imported from Europe under the guidance of the Jesuits present at the Manchu Court seems to be reasonable. Supporting this hypothesis, the Raman spectra previously recorded on Chinese Ming and contemporary Vietnamese blue-and-white porcelains [56-58] which were well characterized by XRF or EDS [56-59], do not display such signatures. The elemental compositions of these artefacts clearly

show the use of manganese-rich cobalt, typical of Asian sources [55-58, 67, 68]. In some artefacts produced at the imperial workshop, the Raman signature of lead arsenate is observed in the white areas, indicating the particular and innovative use of this opacifier in China at the beginning of the 18th century.

4. Conclusions

This study demonstrates the potential of on-site Raman analysis as a non-invasive technique to characterize the types of glazes and pigments/opacifiers used in enamelled artefacts which are rare and valuable pieces. The results of this study are in good correlation with the previous Raman study of Limoges enamels from the 16th to 19th centuries [9]. At least two types of glass were identified regarding the same artefact, mostly based on soda and soda-lime compositions as well as a lead-based type of glass in some of the 18th century Limoges artefacts. These results indicate different firing cycles for the same artefact, thus a sophisticated production technology. Cassiterite was found as the opacifying agent for the white areas of the Limoges enamels analysed. The red colour was always obtained with hematite, while Sb-rich lead-based pyrochlore type of pigment was detected in the yellow areas. The black was achieved by the use of amorphous carbon, accompanied with phosphate or more rarely chromate/chromite phases. The green areas were either made by the dissolution of Cu^{2+} ions in the glaze or the dispersion of a lead-based pyrochlore pigment in a blue glassy matrix. The characteristic ~830 cm^{-1} peak that was observed in the blue coloured areas of the artefacts from the Limosin and Laudin family workshops (Table 1) is assigned to lead arsenate, which was most probably formed due to the high level of arsenic in the cobalt ores used, originating from European sources. It is known that European cobalt sources include arsenic as a major element, and a considerable amount of arsenic was detected in the previous PIXE analyses of Limoges enamels [6]. Thus, the presence of the arsenate phase is attributed to the use of European cobalt sources, rather than the deliberate use of lead arsenate as an opacifying agent. Similar conclusions were reported very recently for some *Famille Rose* porcelains [70]. The results of the studies on 16th-19th century Limoges enamels also enable us to make comparisons with those of the Chinese *cloisonné* enamels and *falangcai* imperial porcelains produced during the same period, shedding light on the cultural interactions between France and China on the basis of technical know-how and the trade in raw materials in enamel production. The Raman technique failed to identify the colouring ions. Diffuse reflectance spectroscopy could be useful [71] but was not allowed by the Curators.

Acknowledgments

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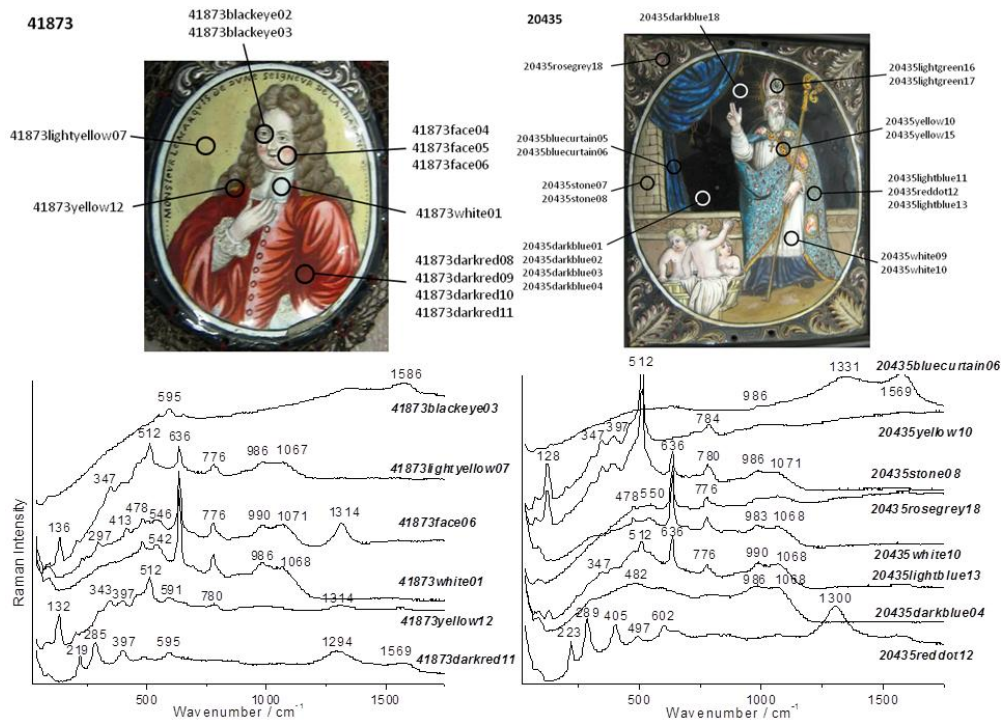
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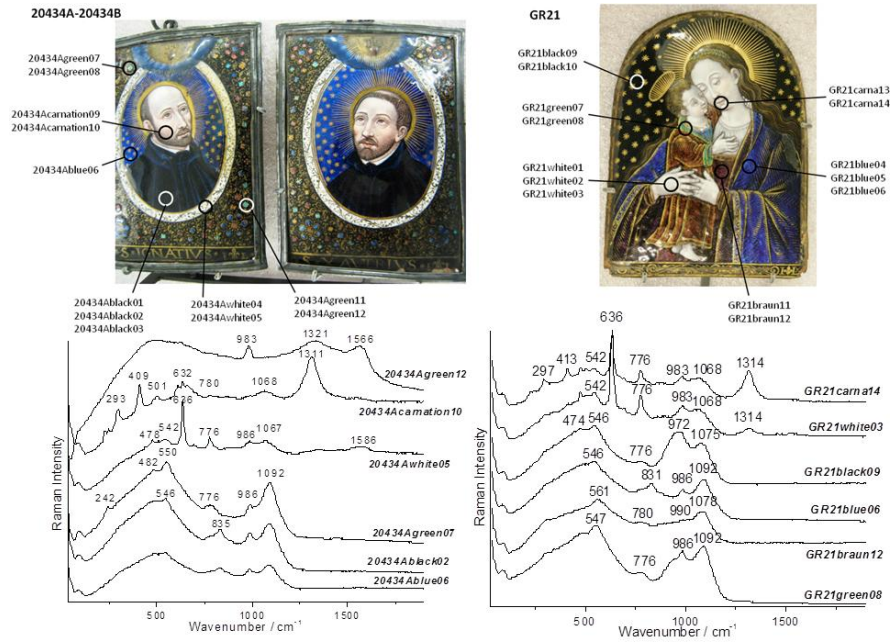
Fig. 1: Limoges enamels from the Limosin family workshop: 20434 A (*St. Ignatius*) & B (*St. Xavirius*) assigned to Léonard II Limosin (ca. 1630), and GR21 (*Virgin and Child*) assigned to J. Limosin (before 1650). Analysed spots are shown.
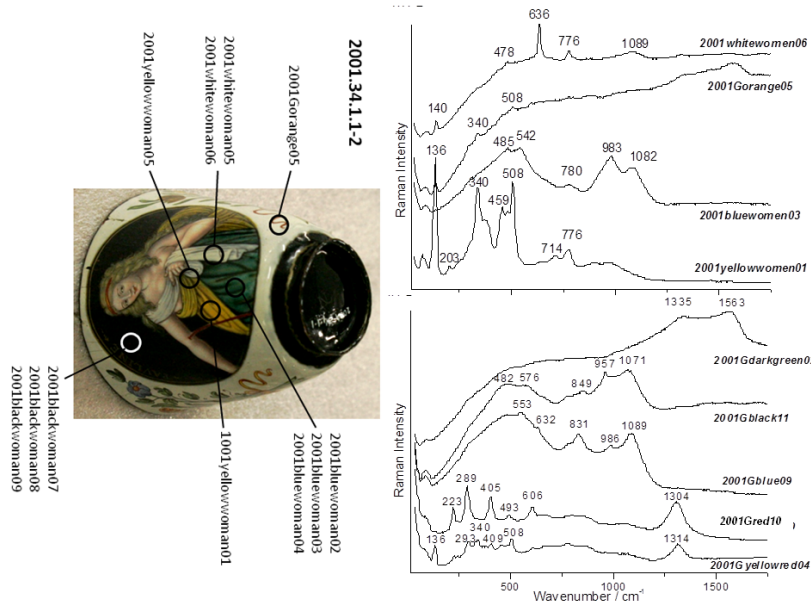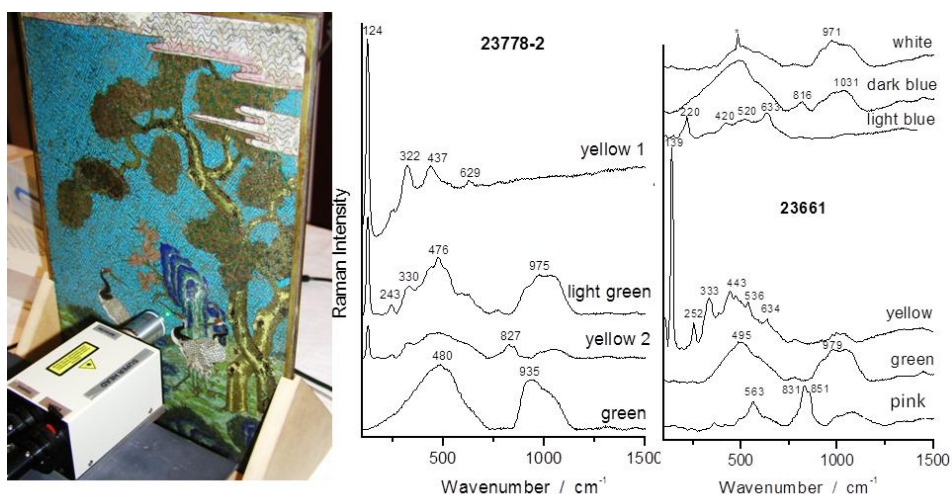

Fig. 2: Limoges enamels from the Laudin family workshop attributed to Noel II or Nicolas II Laudin.
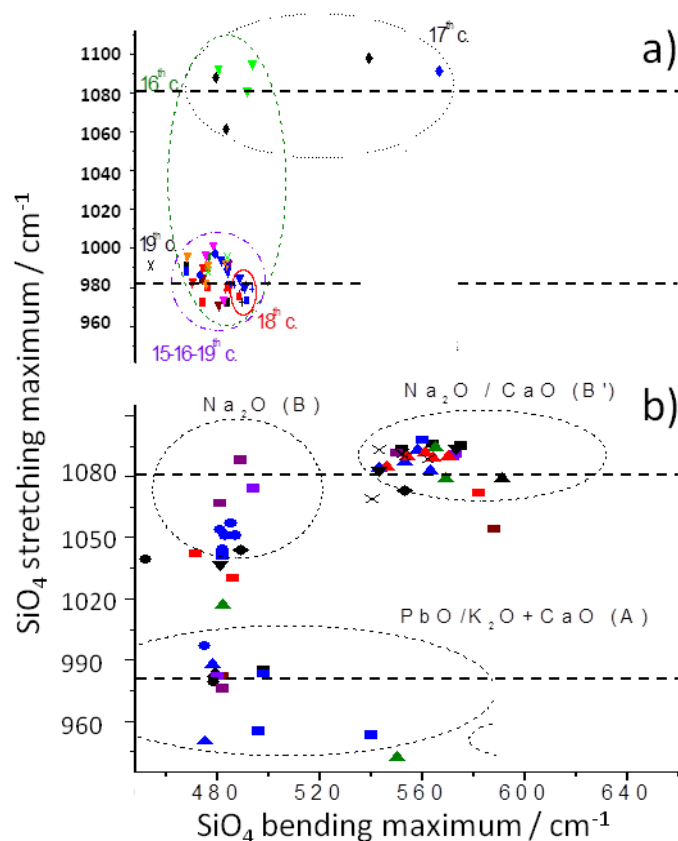
Fig. 3: Limoges enamels assigned to the Nouailher family workshop (18th century): *Marquis de Dune, Seigneur de la Chabane* (41873) and *St. Nicolas* (20435).
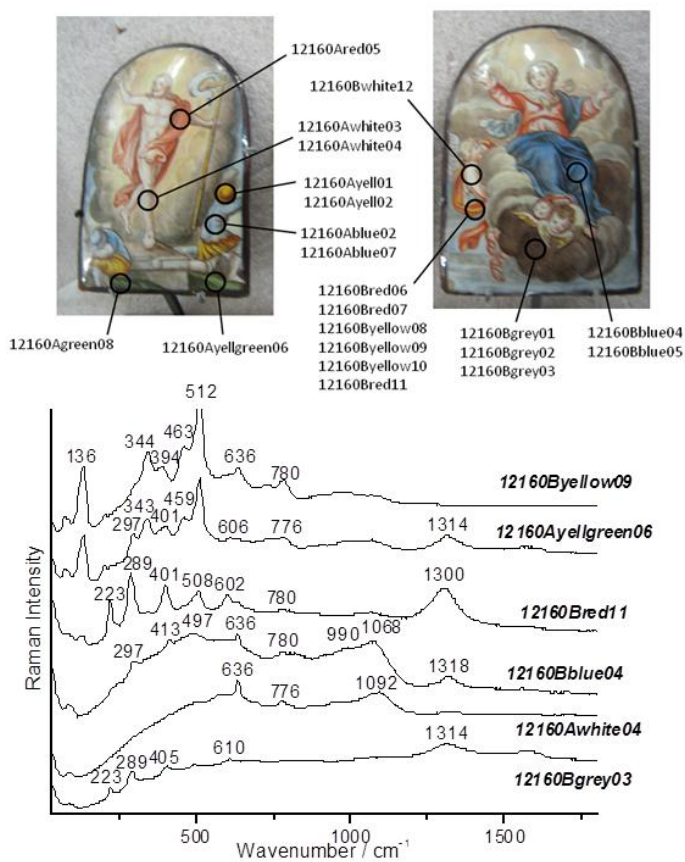
Fig. 4: Limoges enamels from Nouailher family workshop (18th century): *Ascension* and *Assumption*.

Fig. 5: Example of 18th Chinese *cloisonné* enamel spectra (23778-2, panel shown here, and 23661, vase). See ref. [6] for details.

Fig. 6: Comparison of the stretching and bending maximum of the SiO$_4$ Raman signature for Chinese *cloisonné* enamels: a), after [10], and Limoges enamels b), after [9]. Three types of enamel composition (A, B and B') are observed for Limoges enamels, the A lead-richer compositions (stretching peak < 1000 cm^{-1}) being mainly observed for 19th century Limoges artefacts. Most of the Chinese *cloisonné* enamels show similar compositions except for some of artefacts assigned to production from the end of the 16th and 17th century.