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Non-invasive Raman analyses of Chinese *huafalang* and related porcelain wares. Searching for evidence for innovative pigment technologies

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Abstract

Eighteen Chinese painted enamelled porcelains and three Chinese enamelled Yixing stonewares dated to the 16th to 19th centuries and kept at the Musée national des arts asiatiques-Guimet (MNAAG), have been analysed with a mobile Raman set-up to identify their enamelling technology. Different *Grand Feu* (leadless or lead-poor colourless and blue enamel) and *Petit Feu* (lead-rich red (hematite), yellow and green (Pb-Sn/Sb/X pyrochlore) and black enamels) glazes were respectively identified on wares from the *wucai* group*, the Famille verte* group, and the *huafalang* group. Calcium phosphate was detected in a 17th century vase as a rare opacifier. Cassiterite was identified in the light green glaze of an imperial *huafalang* bowl dated to the final period of the Kangxi reign (1662-1722), *ca*. the 1st quarter of the 18th century. Lead arsenate was identified in the blue glaze of two artefacts, a *huafalang* bowl and a painted enamel water dropper, and in the blue enamel of a 19th century Yixing teapot. Lead arsenate found in some of the blue enamels appears to arise from the arsenic content in Erzgebirge cobalt ores and not due to voluntary addition. This may prove the use of raw materials or enamel powder imported from Europe in developing these opaque colours. The use of lead arsenate as white opacifier is clear for a water dropper bearing the Yongzheng emperor's mark (r. 1723-1735). The technological palette appears different for the artefacts expected to originate from the same period and provenance (imperial workshop) which is consistent with a period of intense innovation, open to technological skill from abroad - i.e. from French/European painted enamel technology - as revealed by ancient French (Jesuits) and Chinese historical reports.

Graphical abstract

Keywords: B: impurities; B: spectroscopy; C: colour; D: glass arsenic

1. Introduction

For a long-time, Chinese porcelain had been essentially monochrome (e.g. celadons) or blue-and-white (*Qinghua*) [1,2]. The pinnacle of this technology is the blue-and-white porcelain produced at Jingdezhen since 1320 at high firing temperature. From the 8th century onwards, enamelled stoneware follows a parallel but discontinuous development in China [1-4]. The joint venture of the underglaze and the overglaze technologies appeared to merge at Jingdezhen during the *Chenghua* reign (1465-1487) of the Ming Dynasty. This new technique is named in Chinese as *doucai* (colours filled within underglaze blue outlines). Multi-colour enamelled porcelains thus produced through the Ming Dynasty are denominated in Chinese with the term *wucai* (five colours). Both *doucai* and *wucai* colorations are a combination of under- and over-glaze décors. The culmination of these techniques was succeeded during the Qing Dynasty (1664-1912) with the vivid colour palette *of Famille verte* group and *Famille rose* group [5,6]. Despite the great interest of many scholars on Chinese ceramics from the stylistic approach, the number of analytical studies devoted to Chinese enamelled wares is rather limited and concerns mainly on monochrome [1,7-12] and blue-and-white porcelains [13-19]. Furthermore most of the studies are recent except the pioneer works of Zhang [5], Kingery and Vandiver [6] and then of Wood [1].

Regarding porcelain technology, the underglazed décor is drawn on a porous (generally unfired or incompletely sintered) body with an aqueous mixture containing the colouring agents/precursors that allows the depictions made of rather sharp border lines with pre-assigned coloured areas. On the contrary, the overglaze painting within the areas should be made on an already glazed (i.e. non-porous) substrate using a viscous oil-based mixture that makes the drawings less sharp. Furthermore it is difficult to make sharp applications since temperature will diffuse and oxidize small colouring ions and degrade large pigments. The achievement of a sharp delimitation between coloured glazed areas is thus a difficult task (Fig. 1) where, the low viscosity of the glaze at the top firing temperature and the fast diffusion of colouring ions tend to spread out the colours. For working out these difficulties, there exist several possibilities: the first solution is to use pigments in the place of ions as colouring agents (the later so-called *'couleurs transparentes'* technique) [20]; the second one is the application of a physical wall, such as a spinel- or chromite-based refractory line delimiting the coloured areas and hindering the diffusion of ions, as first made by Samarkand and Iznik potters (ca. 1500 [21]), or the use of a thin metal foil as inlay (*cloisonné*) when the substrate is a metal body [22-24]. The use of very viscous rue oil to mix with the colour components for painting and firing with lower temperature minimizes some of the above mentioned issues. Thus, enamelled décors with well-defined border lines between coloured areas is called '*cloisonné painted*' or '*painted*' enamel. The overglazing of an already glazed item requires the use of a glaze composition with a melting temperature about fifty/hundred, or more, °C less than that of the glaze substrate temperature, which obviously means many firing cycles for complex décors. The type of the glaze fired with the porcelain body is a potash-lime aluminosilicate that melts at about 1300°C or more [1,25,26]. The overglaze should thus melt below ~1150°C, or less. Lead-based glazes usually liquefy at temperatures below 1000°C and were commonly used in China since the Han Dynasty (ca > 221) [1]. Overglaze polychrome wares coloured with copper green, iron red, antimony-iron yellow, and iron-manganese lead-glazes were produced subsequently from the 8th century onwards [1,5,6,27-29].

New productions appeared during the Kangxi reign of the Qing Dynasty, the so-called *Famille verte* (belonging to *wucai* group) and *Famille rose* (called *fencai* ('powder colours') or *ruan cai* ('soft colours') in Chinese) and the *falangcai* or *enamel colour* ware [4,30-34]). *Falang* might be the homonym of the Chinese character meaning France at that time. For some scholars, this technique can be described as being used to imitate the European painted enamels and ascribed as being introduced by French and Italian Jesuits established since in the later 17th century at the Manchu Court [2,35-40]. Fathers J.F. Gerbillon (1654-1707, Chinese name *Zhang Chen*) and J. Bouvet (1656-1730, *Bai Jin*) developed a chemistry workshop for the Kangxi emperor in the Palace, while J. Gravereau (1690-1762, *Chen Zhongxing*), F.J. Castiglione (1688-1766, Italian, *Lang Shining*) and P.M. Grimaldi (1618-1686, Italian, *Min Mingwo*) were requested to work on painted enamel décor. It was also reported that a learned representative of Louis XIV King, F. de Fontaney (1643-1710, *Hong Ruohan*) came to the Manchu Court in 1687 with presents of enamelled wares, which led to the importation of pigments and colouring agents from France. A German expert (K. Stumpf) also contributed to establish the Imperial Glass Workshop.

A major characteristic of this 'new' enamelled artefacts was the use of opaque lead-based overglazes (Table 1), especially for the blue, yellow, and white colours [1,2,4-6,30-34]. The opaque white enamel is called *bo li bai (glassy white)* in Chinese. Green- and rose-colored enamels were named as *yangcai*, i.e. 'foreign colour' [4,32,33], where the green was obtained by copper ions and the rose by colloidal gold ("purple of Cassius"). One important characteristic of these new colours was their opacity, and their capacity to mix, alone or together, with white to form a large variety of shades [2,6]. The white pigment was described as tin oxide [33] but also as an arsenic-based compound (see Table S2 Supplementary Materials) [5], and yellow was based on lead antimonate [5,31,34]. A description of the pigments and enamel preparation methods was reported by Père d'Entrecolles in his 1712 and

1722 letters [36] and then tested in 1900 by G. Vogt, the famous technical director of the French Sèvres Manufacture [41]. The objective of Chinese potters was to achieve objects decorated with a palette rather like the one achieved with oil painting, while the use of '*couleurs transparentes*' in the previous *wucai* productions which produced décors more similar to water colours. The origin of the *cloisonné colour* technique was questioned by N. Wood [1] who claimed that the new opaque colours could well have been borrowed from the current Chinese *cloisonné* on metal technology and not imported from Europe. However, it should be noted that the technique of colour achievement regarding *cloisonné* enamel on metal is different from that of the painted enamel on porcelain where the glaze ranges typically between 20 µm (thin overglaze) to 300 µm (glaze), much lower values that those of metal enamels (up to a few mm). As noted by Kingery and Vandiver in 1986, '*the descriptions of the enamel technology are completely speculative*' [6].

Painted *falang* porcelain (*huafalang* in Chinese) wares were produced in limited quantity from the end of the Kangxi reign, both in the Palace workshops located inside the Palace and in the Imperial Manufacture of Jingdezhen. Consequently, the relevant artefacts are very rare and kept in the secure areas of the museums (Fig. 1), making reliable data concerning the glaze, colouring agents, and body characteristics even rarer and inaccessible [1,5,6,30,31].

The effectiveness of Raman spectroscopy as a non-invasive technique, especially by the mean of mobile set-up, for the identification of pigments, opacifiers, and glaze composition is now well established [13,18,20-23,25,26,31,42-48]. We report here the analysis of 21 Chinese artefacts belonging to the Paris Musée national des arts asiatiques – Guimet (MNAAG) Collection, from the end of the 16th to the 19th century. Some of these artefacts can be attributed to the imperial productions, whiles others to the private workshops (Table 1). One item of the *Famille verte* appears fairly to be a porcelain copy (G 4551) of a Limoges enamelled metal cup, assigned to be made in a private workshop [49,50]. Our first objective is the identification of the enamelling technology used in the production of *wucai, doucai* and *huafalang* wares to understand about the technological transition between the two productions. The search of lead arsenate (as opacifiers), lead stannate/antimonate pyrochlore solid solutions, also called Naples Yellow (as yellow pigments) and Au° nanoparticles (Cassius purple, as the pink colouring agent) appear as the most efficient way to identify artefacts made with unconventional technologies, in particularly those developed with possible imported *huafalang* materials. In these regards, Raman scattering has proven its efficiency to identify these colouring agents in many similar types of artefacts [20-23,31,43-46]. The following up study will be to perform precise in-depth Raman analysis from the glazed up- surface to the glaze-body interface and XRF analysis with portable instruments on identified objects in order to identify the impurities, which are characteristic of the origin of different colouring agents and the glaze stratigraphy.

2. Experimental

Technique: Raman spectra were recorded with the HE532 Horiba Jobin-Yvon mobile spectrometer equipped with a 532 nm 300 mW Ventus Quantum laser, an x200 Mitutoyo and an x50 Nikon microscope long working distance objectives, as previously described [20-22]. The laser and the spectrometer are fibre optically connected to the remote Superhead® put on a heavy and very stable stage with XYZ micrometric displacements (Fig. 1b). The x50 objective that probes a ~4x4x12 μm^3 volume is first used. A much small laser spot obtained with the x200 objective (about 0.5x0.5x2 μm^3) requires a very precise focus (a lengthy process) but guaranties the single glaze layer analysis and generally gives a much better spectrum with less background. The height position of the artefact is adjusted with the use of reams of copy paper as support. Finally, an opaque black fabric is put on the object and the remote head to prevent the ambient light and protect the scientist's eyes from the laser scattering. The focus is controlled by first maximising the intensity of the collected fluorescence/background signal and then of the pigment/glaze one. The laser power at the sample ranges between a few mW for dark coloured areas (black, red) to about 10 mW for light coloured areas (white, yellow). Recording times range between a few seconds and a few minutes. More than 250 spots were analyzed and about 230 of them were successfully recorded (see Supplementary Materials).

Artefacts: Figure 2 and Table 1 show the different groups of the analyzed artefacts among the selected objects**.** The best characteristic ones are given in Fig. 1. The photography of each studied artefact with the position of the analyzed spots is given in the Supplementary Materials. At first, three *rare* bowls attributed to the Imperial productions and made during the first quarter of the 18th century or between 1723 and 1735 were analysed. A w*ucai* plate, a water dropper, and a tea cup from the same period, exhibiting the highest quality of imperial production were selected for comparison. Six other *wucai* artefacts from earlier periods (end of 17th to beginning of 18th century) and four 18th century artefacts assigned to private kiln productions were also analysed as well as three *zisha Yixing* enamelled red stoneware artefacts (2 teapots and 1 bowl). Finally, a cup with European shape and design (18th c., Fig. 1) and a "*Kangxi"* emperor sealed artefact were analysed.

3. Results and discussion

3.1 Raman signatures

Figs 3 to 6 show the representative Raman spectra recorded during the measurements. Additional spectra are presented in Figs S1 & S2. Main peak wave numbers and assignments are given in Table S1. We will first present and discuss the Raman signature of the glaze and then those of the pigments/opacifiers. Artefacts will be considered chronologically.

Glazes: According to previous studies on hard paste [20,25,26,46,51,52] and soft paste porcelain [45,46,51], the differentiation of *Grand Feu* (i.e. a glaze fired at high temperature with the body) and *Petit Feu* (i.e. an overglaze deposited on the already fired porcelain/stoneware and hence heated at a lower temperature in a second or third thermal treatment) is obtainable by Raman scattering. The Raman signature of silicate glass presents two main broad bands: the contribution of the SiO_4 tetrahedron bending and stretching modes at ~550 cm^{-1} and ~1000 cm^{-1} respectively [42-44,52]. The centre of gravity of the later mode shifts with the flux content in the glass composition [42]. The area ratio of the bending to stretching mode decreases with the polymerisation and melting temperature [52-55]. For instance, in Fig. 3, the spectrum of the colourless glaze of G 5687 vase exhibits a rather strong band at 495 cm^{-1} and a weaker one at 1060 cm^{-1}, a signature characteristic of a *Grand Feu* K-Ca silicate glass ((in agreement with literature, Table S2), which is used for hard-paste porcelain [25,26,51]. On the contrary, the spectra collected for yellow and green glazes (G 4374, G 5687 and MG 5806) show a stronger bump at ca. 980 cm^{-1} and a much weaker one at 480 cm^{-1}, characteristic of a lead-rich glaze [42], which is very similar to that used for soft-paste porcelain [45,46,51]. Band shape and centre of gravity display a slight shift depending on the exact composition of the glaze due to the possible reaction with the pigments and the partial dissolution of the (glaze or body) substrate (Note, due to the reaction between the lead-rich overglaze and the potash-base glaze, the composition shift from surface to the body. Due to the high volatility of PbO, the composition of the overglaze is different from that of the precursor !). This could also be due to the different position of the focus of the objective in between the glaze surface and the glaze/body interface. Thus, a detailed in-depth Raman profile is usually needed to draw precisely the stratigraphy. Hence, the centre of gravity of SiO_4 stretching band lowers for the yellow and green glazes because of the use of lead-rich pigments (see further) that increase the lead content, locally. On the contrary, those of the blue spots are very similar to that of the *Grand Feu* glaze since the blue décor of *wucai* ware was drawn under the glaze (e.g. Fig. 4, G 5250 & Fig. 5, G 3361). The relative intensity of the different components of the SiO_4 stretching envelope changes with the relative proportion of the more or less connected tetrahedron (isolated, connected with 1, 2 or 3 shared oxygen of fully connected [42,53-55]), i.e. with the respective composition. For instance, the spectrum of the blue glaze (5806) shows three main components at ca. 905, 970 and 1030 cm^{-1}, indicating a more connected silicate network with a higher melting temperature than those of yellow and green glazes, which only have two main components at ca. 905 and 990 cm^{-1}.

Four types of glazes can be identified: a high temperature '*Grand Feu*' porcelain glaze with characteristic ca. 505-510 and 1040-1050 cm^{-1} features, two '*Petit Feu*' glazes with ca. 900-1005 cm^{-1} or 900-980 cm^{-1} doublets, and a glaze displaying an intermediate signature with c.a. 905, 970 and 1030 cm^{-1} triplet.

It is noteworthy that that the narrow and strong 463 cm^{-1} peak which is characteristic of $\alpha-$ quartz unreacted grains [20,45,51] is commonly observed both in the paste and glaze signatures in our artefacts, as usual for porcelain.

Pigments: Specific pigment signatures have been obtained for red, yellow, green, blue, black and some of the white or lightened shades. Alternatively, Raman spectra lack any specific signatures in the studied spectral range when the colouring agents used are ions dissolved or metal nanoparticles dispersed in the silicate network. In the first case, the Raman spectrum is that of the colourless glaze (e.g. for blue glass coloured with Co^{2+} ions); in the second case, no spectrum is generally obtained due to the huge absorption of metal nanoparticles. In rare cases, only the Raman spectrum of the second minor phases can be observed, e.g. for rose/purple glaze.

Red: The red glaze pigment is identified as hematite, having characteristic resonance component at ca 1310-1315 cm^{-1} and 223-290-405 cm^{-1} triplet [20,56], (Fig. 3 (G 4374, G 5687 & 5806), Fig. 4 (G 913 & G 4806), Fig. 5 (G 822, G 5615, MG 7368 & G 5068) and Figs S1 (G 421) and S2 (G 5696, G 1351 & G 5609, Supplementary Materials). Furthermore, small differences can be noted as the variable intensity of the 245 cm^{-1} band or slight broadening of the bands. The latter case is characteristic of the partial substitution of Fe atoms by Ti or other element, as observed when raw materials are used, such as the *bengara* earth, from Bengal, used in ancient Japanese wares [56]. These variations indicate that different raw materials had been used. On the other hand, the variable intensity of the 660 cm^{-1} component, characteristic of a hematite (Fe_2O_3)-magnetite (Fe_3O_4) mixture depends on the reducing firing conditions that promote the magnetite phase. Partial substitution with elements such as chromium could also promote the formation of the spinel structure. Precise XRF measurements are needed to better characterize these different metal features.

Yellow and green: Yellow and green colours are discussed together since these colours are often obtained by dispersion of yellow pigment in a glass matrix coloured with Co^{2+} ions [20,43,44,46,57]). The yellow pigment of the porcelain glazes was found to be a lead-based pyrochlore solid solution, an old pigment often used since the Byzantine period in Europe and appeared three millennia ago in

Egypt [58]. The end members are Pb_2SnO_4 (Lead tin yellow Type I) and $PbSb_2O_7$ but Sn and Sb ions can be partially substituted by many other elements such as Si (Naples Yellow Type II), Fe and Zn [57-63]. Furthermore, colour changes with oxygen deficiency under the reducing atmosphere. The stronger mode ranging between ca. 125 and 145 cm^{-1} is easily detected because it corresponds to the collective motion of Pb^{2+} ions (its huge intensity arise from the high ion polarisability due to the high number of electrons involved in the Pb-O bond). Because of the high mass contrast between Pb and other elements, this mode is not directly related to the Sb, Sn, Fe or Si substitution and highly depends on the synthesis parameters (i.e., firing temperature and oxygen stoichiometry). On the contrary, the internal modes between ca. 300 and 510 cm^{-1} are more sensitive to the other elements, for instance the 455 cm^{-1} one to Sn, the ca. 325-330 to Sb and the 508 cm^{-1} one characteristic of the mixed compositions. Pure Pb_2SnO_4 compound exhibits the ~195-200 cm^{-1} peak. Pyrochlore yellow pigments were detected in the 17th century *wucai* glaze (Fig. 3) but the low intensity of the signature makes it difficult to suggest how these elements were incorporated in the lead-based composition. This may indicate that the pigment quantity used is small, likely due to the novelty/rareness of this pigment. On the contrary, the very good spectrum recorded on G 5250 *falangcai* bowl (Fig. 4) indicates the use of a high-quality Sb/Sn mixed pigment, which could have been imported. A rather intense spectrum has also been collected on G 5068, the 18th century vase. The signature is consistent with a Sn-rich pyrochlore composition (Fig. 5). On the contrary, the spectra collected on the Yixing teapots, MG 3668 and MG 9604, are consistent with Sb-based Naples yellow pyrochlore composition (Fig. 6). The variety of pyrochlore signatures is indicative of different origins (workshop) and/or times of production.

Black: A homogeneous black colour is difficult to achieve in a complex décor [64] since the production of pieces such as the G 1710 vase (Fig. 2) had not been possible before the Qing Dynasty. Two types of signatures were recorded:

-i) a mixture of amorphous carbon (1355-1575 cm^{-1} doublet) [65]; this indicates that the firing was conducted under reducing conditions, as required to keep a white body [66] and/or that an organic medium or carbon powder was added, and

- ii) spinel(s) (645 to 685 cm^{-1} peak [67], e.g. in G 5687, MG 5806 (17th century, Fig. 3), MG 9604 (Yixing, 18th century, Fig. 6) and G 5609 objects (19th-20th centuries, Fig. S2). Also, there is manganese oxide(s) with a 550-595 cm^{-1} doublet, e.g. in G 4374 (16th-17th century, Fig. 3), G 913 (*huafalang* ware, 18th century, Fig. 4), G 822, G 3361 (18th century ware, Fig. 5), MG 3668 (Yixing ware, 18th century, Fig. 6) and G 5609 (19th-20th century, Fig. S2). It is difficult to determine the phase type since the huge sensitivity of manganese oxides to laser illumination may artificially induce phase transition or transformation when high power illumination was required in the on-site measurements.

Blue: Blue colour is usually obtained by the dissolution of Co^{2+} ions in the amorphous silicate network [3]. When the ion concentration exceeds a few wt% (locally), olivine silicate (Co_2SiO_4) or cobalt aluminate spinel ($CoAl_2O_4$) precipitates out [45,46], in both lead-based (soft paste) or silica-rich (hard paste) glazes respectively. The olivine Raman signature has doublet at about 825 cm^{-1} [68].

Opacifiers: Three types of white pigments were identified. Cassiterite (tin oxide-SnO_2), with a characteristic doublet at 635 and 775 cm^{-1} [69-71], was detected in light green areas of the *huafalang* G5250 ware (Fig. 4). Cassiterite, an innovative opacifier of the Late Roman period (5th Century [69]), largely was used by Islamic potters to produce *terra cotta* and faience with a complex decoration [46, 70-72], as well as by European porcelain arcanists [45,46]. A peak at 955 cm^{-1}, consistent with the calcium phosphate ($Ca_3(PO_4)_2$) signature, was noted in the yellow area of the G 5687 17th century vase (Fig. 3). It is considered that calcium phosphate (955 cm^{-1} peak) is a rather rare glaze opacifier. First used in late antique glass mosaic *tessarae* [73], it was used in rare Islamic glass [57] as the alternative opacifier of *lattimo* glass at the end of the 16th century [57,74,75] as well as that of Medici porcelain glaze [74]. Bone ash was added to the glaze mixture to obtain the precipitation of calcium phosphate. Since some potassium rich glass may also exhibit a component at ~960 cm^{-1} [42], additional Raman and XRF measurements are needed for a definitive assignment. *Lattimo* Venetian glass was found to be opacified with lead arsenate [57]. The Raman signature of lead arsenate is very strong because the high number of electrons involved in the As-O bond. This peak is observed between 810 and 830 cm^{-1} [67,76] in many coloured areas, in blue *huafalang* G 5250 (Fig. 4) and G 3361 (Fig. 5) among the 18th century wares. In the later paint brush pot, lead arsenate was also detected in the white and purple areas. Intense signatures were also obtained on enamelled Yixing wares (Fig. 6). Recently, elemental composition analysis suggested the association of (European) cobalt and arsenic in the blue décor of some *Famille rose* porcelains [78]. The different wave numbers could indicate different compositions of Pb-Ca solid solution [79]. For vivid blue-coloured enamels, the superimposition of the olivine Co_2SiO_4 contribution (ca. 825 cm^{-1} doublet) could also shift the maximum. But, when peak intensity is maximal in the white area, the assignment to lead arsenate is certain. The highest signal recorded on *Yixing* wares is consistent with the use of higher amount of pigment or of a more advanced preparation technology. It should also be noted that very similar arsenate Raman signatures were observed on the blue décor of some Medici, Saint-Cloud, Chantilly, Mennecy, Sceaux and Vincennes soft paste porcelains [45,46], in an English soft-paste ("Bone China") porcelain blue plaque made ca 1730 [80] as well as in Capo di Monte production [81], in agreement with the use of European cobalt ores.

4. Conclusions

This preliminary non-invasive on-site Raman investigation of selected *wucai* , doucai and *huafalang* artefacts confirms that lead arsenate was used for some *huafalang* objects attributed to the Imperial productions as reported by F. Zhang [5]. However, lead arsenate was not detected in all artefacts attributed to the same imperial workshop, although arsenates are very strong Raman scatterers. It is important to note that in these later artefacts (Table 1), the blue glaze composition contains less PbO than in other colours. It could be due to a reaction between the lead-based overglaze and the porcelain glaze or even the body or due to the use of an intermediate special composition. The more reasonable assumption may be that arsenic arises from the cobalt ores [45,46,80,81]. Eighteen century European porcelains made with European cobalt ores exhibit the same Raman signature as shown in refs [45,46,77,80,81], but also in some Limoges enamels [82] and glass beads [83-85] produced during the 17th and 18th century. The cobalt ores come from Erzgebirge mountains between Saxony and Bohemia and contain a high level of arsenic (As/Co ~ 0.1-0.2) [83-86], which may explain the formation of lead arsenate in the blue enamel. The ratio As/Co had reached ~0.4 during the 17th century [85]. On the contrary, Asian cobalt ores used during Ming dynasty in China and Vietnam do not contain arsenic but instead a high level of manganese, and iron [25,26,86-89]. This is a significant proof of the use of either imported cobalt ore or prepared blue enamel imported from Europe. White opacifier, namely calcium phosphate seems to be present in a 17th century vase and cassiterite, as reported by Garner [33], was also detected in the light green enamel of the Kangxi *huafalang* G 5250 bowl in association with the pyrochlore yellow colour. This could also indicate the use of imported materials (CaF_2 is used to opacify white cloisonné enamels [22]). Note that arsenic-poor and arsenic-poor cobalt was simultaneously used in France, as demonstrated for Limoges enamels produced at the end of 17th and beginning of the 18th century [82]. Consequently, the non-detection of arsenate signature in blue décor cannot exclude to the use of European arsenate-free cobalt (as in some Limoges enamels [82]) and measurement of associated traces is needed to discuss its provenance [90].

Voluntary use of lead arsenate white opacifier was identified in white areas of the G 3361 water dropper as well in the later Yixing productions (MG 3668, MG 9604 and MG 8062). The very strong arsenate Raman signature is consistent with a great mastery of the manufacture of the arsenic-based enamel. Lead pyrochlore Sb-Sn (Naples Yellow type) was also detected but was already observed in the 16th and 17th centuries wares (Fig. 3) and appears not very characteristic of the innovation here. Therefore, the study of more artefacts is required to obtain a more definitive conclusion. Recently, arsenate was detected in *Famille Rose* porcelain shards [77,78] in agreement with previous work of Zhang [5]. Identification of the minor and trace elements associated to the above mentioned colouring phases are needed to better discuss the provenance of the raw materials. Alternatively, a precise in-depth (non-invasive) Raman micro-spectrometry of the above mentioned artefacts, or the availability of shards, is required to provide a 3D view of the stratigraphy of the glassy layers forming the glaze décor. The Raman technique failed to identify the colouring ions that don't form complexes or crystallites. Diffuse reflectance spectroscopy [89,91], portable XRF [91,92] or Synchrotron µXRF/diffraction [93] should be also very useful.

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Références

1. N. Wood, *Chinese Glazes: their origins, chemistry and recreation*, A & C Black, 1999, London.
2. F. Lili, *La céramique chinoise*, China Intercontinental Press, Beijing, 2011.
3. Shenzhen bowuguan, Shenzhen Wangye bowuguan, Shenzhen shi wenwu guanli bangongshi, Shenzhen shi wenwu jiandingsuo, The Deities and Secular World in Polychrome Overglaze Decoration Ceramics of Kin and Yuan Dynasties, Beijing, Wenwu Chubanshe, 2009.
4. C. Shih, Y. Peng, On the Origin and Development of Three Terms for Qing Dynasty Overglazed Enamels: *Falangcai* (珐琅彩), *Yangcai* (洋彩) and *Fencai* (粉彩), National Palace Museum Research Quarterly, 29[4] (2012) 1-47.
5. F. Zhang, The origin and development of traditional Chinese glazes and decorative ceramic colors, in Ancient Technology to Modern Science, vol. 1, Ceramics and Civilizations Serie, W.D. Kingery, vol. 1, The American Ceramic Society, Colombus, 1985, p. 163-179.
6. W.D. Kingery , P.B. Vandiver, The eighteenth-century change in technology and style from the Famille-Verte palette to the Famille-Rose Palette, in Technology and Style, Vol. 2, Ceramics and Civilization Serie, W.D. Kingery Ed., The American Ceramic Society, Colombus, 1986, p. 363-381.
7. S.L. Feng, X.Q Feng, J.H. Zhu, G.X. Xie, L.T. Yan, L. Li, G. Li, Q.H. Shen, Nondestructive analysis on ancient porcelain of Longquan Kiln in Zhejiang Province by WDXRF, Chinese Physics C 32 (2008) 284-288.
8. L. Li, S.L. Feng, X.Q. Feng, Q. Xu, L.T. Yan, B. Ma, H. Huo, Study on the chemical composition features of Longquan celadon excavated from the Chuzhou site of Huai'an City in Jiangsu province by EDXRF, Chinese Physics C 35[7] (2011) 689-694.
9. T.Q. Zhu, H. Huang, H.M. Wong, L.M. Hu, X.B. Yi, Comparison of celadon from the Yaozhou and Xicun kilns in the Northern Song Dynasty of China by X-ray fluorescence and microscopy, J. Archaeological Sci. 38[11] (2011) 3134-3140.
10. J. Wu, M.L. Zhang, T.J. Hou, Q.J. Li, J.M. Wu, Analysis of the celadon of the Tang and the Five Dynasties unearthed from Nan Kiln and Lantian Kiln site of Jingdezhen, China, Ceramics Int. 41[5] (2015) 6851-6857.
11. M.H. He, Y.F. Xiao, S.D. Zhang, R. Liu, W. Hong, B.L. Huang, Composition analysis of ancient celadon via femtosecond laser ionization time-of-flight mass spectrometry, Appl. Surf. Sci. 351 (2015) 624-634.
12. E.T. Hall, A.M. Pollard, Analysis of Chinese monochrome glazes by X-ray Fluorescence spectroscopy, Proc. Intern. Conference Chinese Pottery & Porcelain, 1985.

13. L.D. Kock, D. de Waal, Raman studies of the underglaze blue pigment on ceramic artefacts of the Ming dynasty and of unknown origins, J. Raman Spectrosc. 38[11] (2007) 1480-1487.
14. M.S. Tite, I.C. Freestone, N. Wood, An investigation into the relationship between the raw materials used in the production of Chinese porcelain and stoneware bodies and the resulting microstructures, Archaeometry 54[1] (2012) 37-55.
15. Y.A. Qu, J. Xie, X.Q. Xi, C.J. Huang, J.L. Yang, Microstructure characteristics of blue-and-white porcelain from the folk kiln of Ming and Qing Dynasties, Ceramics Int. 40[6] (2014) 8783-8790.
16. H.S. Cheng, B. Zhang, D. Zhu, F.J. Yang, X.M. Sun, M.S. Guo, Some new results of PIXE study on Chinese ancient porcelain, Nucl. Instr. & Meth. Phys. Res. Sect. B – Beam Inter. Mater. Atoms 240[1-2] (2005) 527-531.
17. F. Du, B.R. Su, Further study of sources of the imported cobalt-blue pigment used on Jingdezhen porcelain from late 13 to early 15 centuries, Sci. China Series E – Techn. Sci. 51[3] (2008) 249-259.
18. G. Simsek, Ph. Colomban, S. Wong, B. Zhao, A. Rougeulle, N.Q. Liem, Toward a fast non-destructive identification of pottery: The sourcing of 14th-16th century Vietnamese and Chinese ceramic shards, J. Cult. Her. 16[2] (2015) 159-172.
19. T.Q. Zhu, X. Ding, C.M. Kusimba, Z.Y. Feng, Using laser ablation inductively coupled plasma mass spectroscopy (LA-ICP-MS) to determine the provenance of the cobalt pigment of Qinghua porcelain from Jingdezhen in Yuan Dynasty of China (1271-1368AD), Ceramics Int. 41[8] (2015) 9878-9884.
20. Ph. Colomban, G. Sagon, X. Faurel, *Differentiation of antique ceramics from the Raman spectra of their coloured glazes and paintings*, J. Raman Spectrosc. 32[5] (2001) 351-360.
21. Ph. Colomban, V. Milande, L. Le Bihan, On-site Raman Analysis of Iznik pottery glazes and pigments, J. Raman Spectrosc. 35 (2004) 527-535.
22. B. Kirmizi, Ph. Colomban, B. Quette, On-site Analysis of Chinese Cloisonné enamels from 15th to 19th century, J. Raman Spectrosc. 41[7] (2010) 780-790.
23. Y. Su, L. Qu, H. Duan, N. Tarcea, A. Shen, J. Popp, J. Hu, Elemental analysis-aided Raman spectroscopic studies on Chinese cloisonné wares and Painted enamels from the Imperial Palace, Spectrochimica Acta Part A – Mol. Biomol. Spectrosc. 153 (2015) 165-170.
24. J. Henderson, M. Tregear, N. Wood, The technology of sixteenth- and seventeenth century Chinese cloisonné enamels, Archaeometry 31[2] (1989] 133-146.
25. N.Q. Liem, Ph. Colomban, G. Sagon, H.X. Tinh, T.B. Hoanh, Microstructure, Composition and Processing of the 15th century Vietnamese Porcelains and Celadons, J. Cultural Heritage 4[3] (2003) 187-197.

26. Ph. Colomban, G. Sagon, L.Q. Huy, N.Q. Liem, L. Mazerolles, Vietnamese (15th century) blue-and-white, tam thai and “luster” porcelains/stoneware: glaze composition and decoration techniques, Archaeometry 46[1] (2004) 125-136.
27. J.F. Cui, Y. Lei, Y., Z.B. Jin, B.L. Huang, X.H. Wu, Lead isotope analysis of Tang sancai pottery glazes from Gongiyi kiln, Henan province and Huangbao kiln, Shaanxi province, Archaeometry 52[4] (2010) 597-604.
28. W.D. Li, J.Z. Li, J. Wu, J.K. Guo, Study on the phase-separated opaque glaze in ancient China from Qionglai kiln, Ceramics Int. 29|8] (2003) 933-937.
29. W.D. Li, J. Wu, J.Z. Li, J.K. Guo , Study on the green glaze from Qionglai kiln site in Sichuan: One of the earliest phase-separated opaque glazes in China, Materials Issues in Art and Archaeology VI, Mater. Res. Soc. Symp. Proc. 712 (2002) 365-373.
30. C. Wang, Nomenclature for Painted Enamel on Porcelain in Qing Dynasty: A Scientific Viewpoint”, *The National Palace Museum Research Quarterly* 29:3 (2012), 115-166.
31. J. Miao, B. Yang, D. Mu, Identification and differentiation of opaque Chinese overglaze yellow enamels by Raman spectroscopy and supporting techniques, Archaeometry 52[1] (2010) 146-155.
32. H.A. Crosby Forbes, Yang-ts’ai: The Foreign Colors, China Trade Museum, Milton, 1982.
33. H. Garner, The origins of Famille Rose, Trans. Oriental Ceram. Soc. 37 (1969) 1-16.
34. G.C. Williamson, The book of Famille Rose, Kegan P., Trench, Trubner & Co., London, 1937.
35. G. Loehr, Missionary-artist at the Manchu Court, Trans. Oriental Ceram. Soc. 34 (1962-1963) 51-67.
36. Père d’Entrecolle’s letters from Ching-te-chen in 1712 and 1722, translated in R. Tichane, Ching-te-Chen, New York State Institute for Glaze Research, Painted Post, New York, 1983.
37. I. Landry-Deron, Les mathématiciens envoyés en Chine par Louis XIV en 1685, Arch. Hist. Exact. Sci. 55 (2001) 423-463.
38. C.F. Shih, Evidence of East-West Exchange in the Eighteenth Century: the Establishment of Painted Enamel Art at the Qing Court in the Reign of Emperor Kangxi, *National Palace Museum Research Quarterly*, 24[3], (2007**)** 45-94.
39. C.F. Shih, *Riyue guanghua :Qinggong hua falang* 日月光華：清宮畫琺瑯 (Radiant Luminance: The Painted Enamelware of the Qing Imperial Court). Taipei: The National Palace Museum of Taipei2012.
40. X.D. Xu, Europe-China-Europe: The Transmission of the Craft of Painted Enamel in the Seventeenth and Eighteenth Centuries, *Goods from the East, 1600-1800 Trading Eurasia*, Maxine Berg ed. , Houndmills, Basingstoke, Hampshire: Palgrave Macmillan, 2015, pp. 92-106.

41. G. Vogt, La porcelaine Chinoise, Bull. Soc. D'Encouragement pour l'Industrie Nationale, 99 (1900) 530-612.
42. Ph. Colomban, A. Tournié, L. Bellot-Gurlet, Raman Identification of glassy silicates used in ceramic, glass and jewellry: a tentative differentiation guide, J. Raman Spectrosc. 37 [8] (2006) 841-852.
43. Ph. Colomban, A. Tournié, M.-C. Caggiani, C. Paris Pigments and enamelling/gilding technology of Mamluk mosque lamps and bottle, J. Raman Spectrosc. 43[12] (2012) 1975-1984.
44. M.C. Caggiani, C. Valloteau, Ph. Colomban, Inside the glassmaker technology: Search of Raman criteria to discriminate between Emile Gallé and Philippe-Joseph Brocard Enamels and Pigment Signatures, J. Raman Spectrosc. 45[6] (2014) 456-464.
45. Ph. Colomban, I. Robert, C. Roche, G. Sagon, V. Milande, Identification des porcelaines "tendres" du 18ème siècle par spectroscopie Raman: Saint-Cloud, Chantilly, Mennecy et Vincennes/Sèvres, Revue d'Archéométrie 28 (2004) 153-167.
46. D. Mancini, C. Dupont-Logié, Ph. Colomban, On-site identification of Sceaux porcelain and faience using a portable Raman instrument, Ceramics International 42[13] (2016) 14918-14927.
47. Ph. Colomban, The on-site/remote Raman analysis with portable instruments - A review of drawbacks and success in Cultural Heritage studies and other associated fields, J. Raman Spectrosc. 43 (2012) 1529-1535.
48. L. Prinsloo, N. Wood, M. Loubser, S.M.C. Verryn, S. Tiley, Re-dating of Chinese celadon shards excavated on Mapungubwe Hill, a 13(th) century iron age site in South Africa, using Raman spectroscopy, XRF and XRD, J. Raman Spectrosc. 36[8] (2005) 806-816.
49. V. Notin, L'émail peint: de Limoges à Pékin, Bull. Soc. Archéolog. & Histor. Limousin, CXL (2012) 85-107.
50. B. Zhao, G. Wang, I. Biron, Ph. Colomban, L. Hilaire-Pérez, La circulation des techniques de l'émail entre la France et la Chine du XVIIème au XIXème siècle, Le Cnrs en Chine Bulletin 21 (2016) 21-25. http://www.cnrs.fr/derci/IMG/pdf/cnrsenchine_21_fr_final_pour_le_site_cnrs.pdf
51. Ph. Colomban, F. Treppoz, Identification and Differentiation of Ancient and Modern European Porcelains by Raman Macro- and Microspectroscopy, J. Raman Spectr. 32 (2001) 93-102.
52. Ph. Colomban, O. Paulsen, Raman Determination of the Structure and Composition of Glazes, J. Amer. Ceram. Soc. 88[2] (2005) 390-395.

53. P. Ricciardi, Ph. Colomban, Raman spectroscopy of ceramic and glass, In IR & Raman spectroscopy in Forensic Sciences, J.M. Chalmers, H.G.M. Edwards, M. Hargreaves Eds, Wiley & Sons Ltd, 2012, PP. 469-479,
54. Ph. Colomban, Non-destructive Raman analysis of ancient glasses and glazes, ch. 4.2, in Modern Methods for Analysing Archaeological and Historical Glass, First Edition, K. Janssens Ed, J. Wiley & Sons Ltd 2012, pp. 275-300.
55. Ph. Colomban, Pottery, Glass and Enamelled Artefacts: How to Extract Information on their Manufacture Technology, Origin and Age? Ch. 8, In Analytical Archaeometry H. Howell & P. Vandenabeele Eds, Royal Society of Chemistry, Cambridge, 2012, pp 245-267.
56. F. Froment, A. Tournié, Ph. Colomban, Raman identification of natural red to yellow pigments: ochre and iron-containing ores, J. Raman Spectrosc. 39[5] (2008) 560-568.
57. P. Ricciardi, Ph. Colomban, A. Tournié, V. Milande, Non-destructive on-site identification of ancient glasses: genuine artefacts, embellished pieces or forgeries?, J. Raman Spectrosc. 40 (2009) 604-617.
58. B. Kirmizi, H. Gokturk, Ph. Colomban, Colouring Agents in the Pottery Glazes of Western Anatolia: A New Evidence for the Use of Naples Yellow Pigment Variations during the Late Byzantine Period, Archaeometry 57 [3] (2015) 476-496.
59. M. Pereira, T. de Lacerda-Aroso, M.J.M. Gomes, A. Mata, L.C. Alves, Ph. Colomban, Ancient Portuguese Ceramic Wall Tiles (« Ajulejos »): Characterization of the Glaze and Ceramic Pigments, J. Nano Research 8 (2009) 79-88.
60. C. Sandalinas, S. Ruiz-Moreno, Lead-tin-antimony yellow. Historical manufacture molecular characterization and identification in seventeenth-century Italian paintings, Stud. Conserv. 40 (2004) 41-53.
61. C. Sandalinas, S. Ruiz-Moreno, A. Lopez-Gil, J. Miralles, Experimental confirmation by Raman spectroscopy of a Pb-Sn-Sb triple oxide yellow pigment in sixteenth-century Italian pottery, J. Raman Spectrosc. 37 (2006) 1146-1153.
62. F. Rosi, V. Manualli, C. Milliani, B.G. Brunetti, A. Sgamellotti, T. Grygar, D. Hradil, Raman scattering features of lead pyroantimonate compounds. Part I: XRD and Raman characterization of Pb2Sb2O7 doped with tin and zinc, J. Raman Spectrosc. 40 (2009) 107-111.
63. C. Pelosi, G. Agresti, U. Santamaria, E. Mattei, Artifical yellow pigments: Production and characterization through spectroscopic methods of analysis, ePreservationScience 7 (2010) 108-115.
64. M.-C. Caggiani, Ph. Colomban, Raman identification of strongly absorbing phases: the ceramic black pigments, J. Raman Spectrosc. 42[4] (2011) 839-843.

65. S. Karlin, Ph. Colomban, Raman Study of the Chemical and Thermal Degradation of As-Received and Sol–Gel Embedded Nicalon and Hi-Nicalon SiC Fibres Used in Ceramic Matrix Composites, J. Raman Spectrosc. 28 (1997) 219-228.
66. Ph. Sciau, L. Noé, Ph. Colomban, Metal nanoparticles in contemporary potters' master pieces: Lustre and red "*pigeon blood*" pottery: Models to understand the ancient technology, Ceramics Int. 42[14] (2016) 15349-15357.
67. F. Koleini, L. C. Prinsloo, W. Biemond, Ph. Colomban, A.-T. Ngo, J.C.A. Boeyens, M.M. Van der Ryst, K. van Brakel, Unravelling the glass trade bead sequence from Magoro hill, South Africa: separating pre-seventeenth-century Asian imports from later European counterparts, Heritage Science 4 (2016) 43
68. T. Mouri, M. Enami, Raman spectroscopic study of olivine-group mineral, J. Mineralog. & Petrolog. Sci., 103 (2008) 100-104.
69. E. Neri, C. Morvan, Ph. Colomban, M. P. Guerra, V. Prigent, Late Roman and Byzantine Mosaic opaque "Glass-ceramics" *Tesserae* (5th-9th century), Ceramics Int. 42[16] (2016) 18859–18869.
70. Ph. Colomban, C. Truong, A Non-destructive Raman Study of the Glazing Technique in Lustre Potteries and Faiences (9th-14th centuries): Silver ions, Nanoclusters, Microstructure and Processing, J. Raman Spectrosc. 35[3] (2004) 195-207.
71. L.F. Vieira Ferreira, I.F. Ferreira Machado, A.M. Ferraria, T.M. Casimiro, P. Portuguese tin-glazed earthenware from the 16th century: A spectroscopic characterization of pigments, glazes and pastes, Appl. Surf. Sci. B 285 (2013) 144-152.
72. M. Tite, O. Watson, T. Pradell, M. Matin, G. Molina, K. Domoney, A. Bouquillon, Revisiting the beginnings of tin-opacified Islamic glazes, J. Archaeolog. Sci. 57 (2015) 80-91.
73. A. Silvestri, F. Nestola, L. Peruzzo, Multi-methodological characterisation of calcium phosphate in late-antique glass mosaic tesserae, Microchemical J. 124 (2016) 811-818.
74. Ph. Colomban, V. Milande, H. Lucas, On-site Raman Analysis of Medici Porcelain, J. Raman Spectrosc. 35[1] (2004) 68-72.
75. Ph. Colomban, Recent Case studies in the Raman Analysis of Ancient Ceramics: Glaze Opacification in Abbasid Pottery, Medici and 18th century French Porcelains, Iznik and Kütahya Ottoman Fritwares and Unexpected Lapis Lazuli Pigment in Lajvardina Wares, Mater. Res. Soc. Proc. Symposium OO, vol 852, P. Vandiver, J. Mass & A. Murray Eds, pp. 153-160.
76. B. Kirmizi, Ph. Colomban, M. Blanc, On-site Analysis of Limoges enamels from 16th to 19th century, J. Raman Spectrosc. 41[10] (2010) 1240-1247.

77. J. Van Pevenage, D. Lauwers, D. Herremans, E. Verhaeven,B. Vekemans, W. De Clercq, L. Vincze, L. Moens, P. Vandenabeele, A Combined Spectroscopic Study on Chinese Porcelain Containing Ruan-Cai Colours, Anal. Methods 6 (2014) 387-394.
78. R. Giannini, I.C. Freestone, A.J. Shortland, European cobalt sources identification in the production of Chinese *famille rose* porcelain, J. Archaeolog. Sci. 80 (2016) 27-36.
79. B. Manoun, M. Azdouz, M. Azrour, R. Essehli, S. Benmokhtar, L. El Ammari, A. Ezzahi, A.Ider, P. Lazor, Synthesis, Rietveld Refinements and Raman Spectroscopic Studies of Tricationic Lacunar Apatites Na_{1-x} $K_xPb_4(AsO_4)_3$ (0<x<1), J. Mol. Struct. 986 (2011) 1-9.
80. H.G.M. Edwards, Ph. Colomban, B. Bowden, Raman spectroscopic analysis of an English soft-paste porcelain plaque-mounted table, J. Raman Spectrosc. 35 (2004) 656-661.
81. P. Ricciardi, Ph. Colomban, V. Milande, Non-destructive raman characterization of Capo di Monte and Buen Retiro porcelain, J. Raman Spectrosc. 39 (2008) 1113-1119.
82. Ph. Colomban, L. Arberet, B. Kirmizi, On-site Raman analysis of 17th and 18th century Limoges enamels: Implications on the European cobalt sources and the technological relationship between Limoges and Chinese enamels, Ceramics Int. http://dx.doi.org/10.1016/j.ceramint.2017.05.040
83. R.G.V. Hancock, J. McKechnie, S. Aufreiter, K. Karklins, M. Kapches, M. Sempowski, J.F. Moreau, I. Kenyon, Non-destructive analysis of European cobalt blue glass trade beads, J. Radioanal. & Nucl. Chem. 244[3] (2000) 567-573.
84. F. Koleini F. Koleini, L. C. Prinsloo, W. Biemond, Ph. Colomban, A.-T. ngo, J.C.A. Boeyens, M.M. Van der Ryst, K. van Brakel, Unravelling the glass trade bead sequence from Magoro hill, South Africa: separating pre-seventeenth-century Asian imports from later European counterparts, Heritage Science 4 (2016) 43 http://dx.doi.org/10.1186/s40494-016-0113-2
85. R.G.V. Hancock, J. McKechnie, S. Aufreiter, K. Karklins, M. Kapches, M. Sempowski, J.F. Moreau, I. Kenyon, Non-destructive analysis of European cobalt blue glass trade beads, J. Radioanal. & Nucl. Chem. 244[3] (2000) 567-573.
86. Ph. Colomban, Rocks as blue (green and black) pigments/dyes of glazed pottery and enamelled glass artefacts – The potential of Raman microscopy, European Mineralogy Journal 25[5] (2013) 863-879.
87. M.O. Figueiredo, T.P. Silva, J.P. Veiga, A XANES study of cabalt speciation state in blue-and-white glazes from 16th to 17th century Chinese porcelains, J. Electr. Spectrosc. & Rel. Phenom. 185 (2012) 97-102.

88. M.I. Dias, M.I. Prudêncio, M.A. Pinto de Matos, A.L. Rodrigues, Tracing the origin of blue and white Chinese Porcelain ordered for the Portugese market during the Ming dynasty using INAA, J. Arcaeolog. Sci; 40 (2013) 3046-3057.
89. C. Fischer, E. Hsieh, Export Chinese Blue-and-white porcelain: compositional analysis and sourcing using non-invasive portable XRF and reflectance spectroscopy, J. Archaeolog. Sci. 80 (2016) 14-26.
90. B. Gratuze, I. Soulier, M. Blet, L. Vallauri, De l'origine du cobalt: du verre a` la céramique'', Revue d'archéométrie 20 (1996) 77-104.
91. L.F. Vieira Ferreira, A. Gonzalez, M.F.C. Pereira, L.F. Santos, T.M. Casimiro, D.P. Ferreira, D.S. Conceicao, I.F. Machado, Spectroscopy of 16th century Portuguese tin-glazed earthenware produced in the region of Lisbon , Ceramics Int. 41 (2015) 13433-13446.
92. G. Simsek, Ph. Colomban, F. Casadio,' L. Bellot-Gurlet, K. Faber, G. Zelleke, V. Milande, L. Tilliard, On-site identification of early Böttger red stonewares using portable XRF/Raman instruments: 2, glaze and gilding analysis, J. Am. Ceramic Society 98[10] (2015) 3006-3013.
93. P. Sciau Reverse engineering the ancient ceramic technology based on X-ray fluorescence spectromicroscopy, *J. Anal. At. Spectrom.* 26 (**2011)** 969-979. doi:10.1039/C0JA00212G.

Table 1: Studied artefacts

MNAAG inventory number	Type	Date (expected)	Production	Marks
G 1351	*doucai* bowl	Wanli reign (1572-1620) Ming Dynasty	Imperial manufacture of Jingdezhen	"Da Ming Wanli nian zhi" mark
G 5250	*huafalang* bowl	Final period of the Kangxi reign (*c.* 1715-1722)	Painted enamels made in the Palace workshop (The Palace Board of Works)	"Kangxi yu zhi" mark
G 4806	*huafalang/yangcai* bowl	Yongzheng reign (1723-1735)	Painted enamels made in the Imperial manufacture of Jingdezhen	"Yongzheng yu zhi" mark
G 913	*huafalang/yangcai* bowl	Yongzheng reign (1723-1735)	Painted enamels made in the Imperial manufacture of Jingdezhen	"Yongzheng yu zhi" mark
G 822	*Famille verte* dish	*c.* 1721	Imperial manufacture of Jingdezhen	"Da Qing Kangxi nian zhi" mark on the base/"wanshou wujiang" inscriptions in reserve on the inter rim (made in *c.* 1713 for the 60th birthday of the emperor)
G 5615	*Famille verte* bowl	19th c.	Private kiln (Jingdezhen)	
G 3361	*Famille rose* Water dropper	early 18th c.	Imperial manufacture of Jingdezhen	"Da Qing Kangxi nian zhi" mark
G 4551	*Famille verte* cup	1st half 18th c.	Private kiln (Jingdezhen)	"JL" mark = J. Landin (1627-1695) mark
MG 7368	*doucai* bowl	18th c.	Private kiln (Jingdezhen)	"Da Qing Yongzheng nian zhi" mark
G 4611	*doucai* cup	18th c.	Imperial manufacture of Jingdezhen /Private kiln (Jingdezhen)	"Da Ming Chenghua (1464-1487) nian zhi" apocryphal mark
G 5068	*doucai* pot	18th c.	Imperial manufacture of Jingdezhen /Private kiln (Jingdezhen)	"Da Ming Chenghua nian zhi" apocryphal mark
G 5696	*doucai* bowl	2nd half 17th – early 18th c.	Imperial manufacture of Jingdezhen	"Da Qing Kangxi nian zhi" mark
G 5609	*Famille verte* seal	17th ? 19th ?	Imperial manufacture of Jingdezhen ? Private kiln (Jingdezhen) ?	"Kangxi yulan zhi bao" inscriptions
G 4374	*wucai* vase	end 16th – mid. 17th c.	Private kiln (Jingdezhen)	
MG 5806	*wucai* vase	mid-later half 17th c.	Private kiln (Jingdezhen)	
G 5687	*wucai* vase	mid 17th c.	Private kiln (Jingdezhen)	
G 1710	*Famille noire/Famille verte* Vase	Later half 17th – early 18th c.	Private kiln (Jingdezhen)	"Biyu tang zhi"mark
G 421	*Famille verte* Vase	end 17th – early 18th c.	Private kiln (Jingdezhen)	
MG 3668	teapot	2nd half 18th c.	Private kiln (Yixing)	
MG 9604	teapot	2nd half 18th c.	Private kiln (Yixing)	
MG 8062	bowl	19th c.	Private kiln (Yixing)	

FIGURE CAPTIONS

Fig. 1: a) Representative Qing Dynasty porcelains made respectively with '*Couleurs transparentes*' (G 5696) and opaque/hua*falang* (G 5250, G 4551 and G 3361) enamels.(see Table 1 and Supplementary Materials for details; b) mobile Raman set-up.

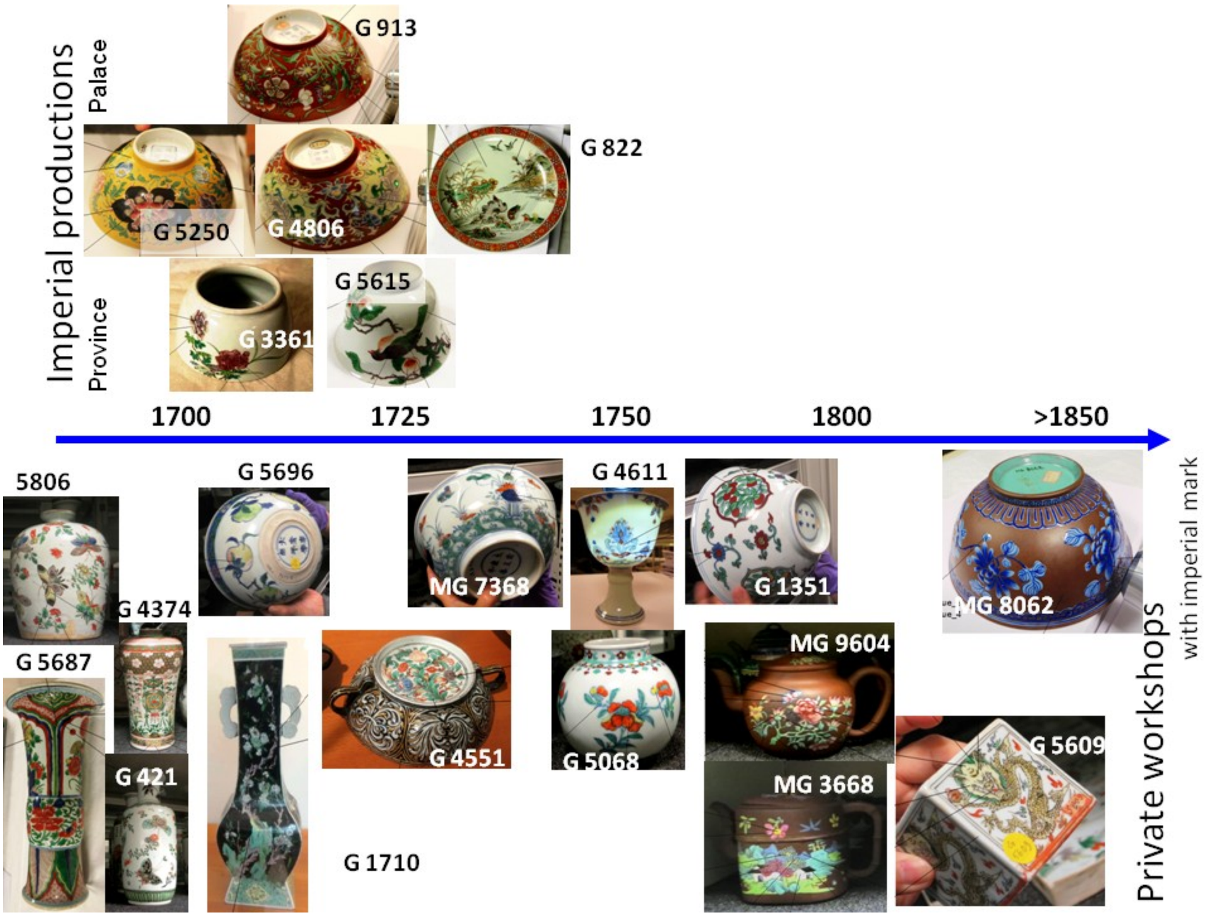

Fig. 2: Studied corpus (see Table 1).

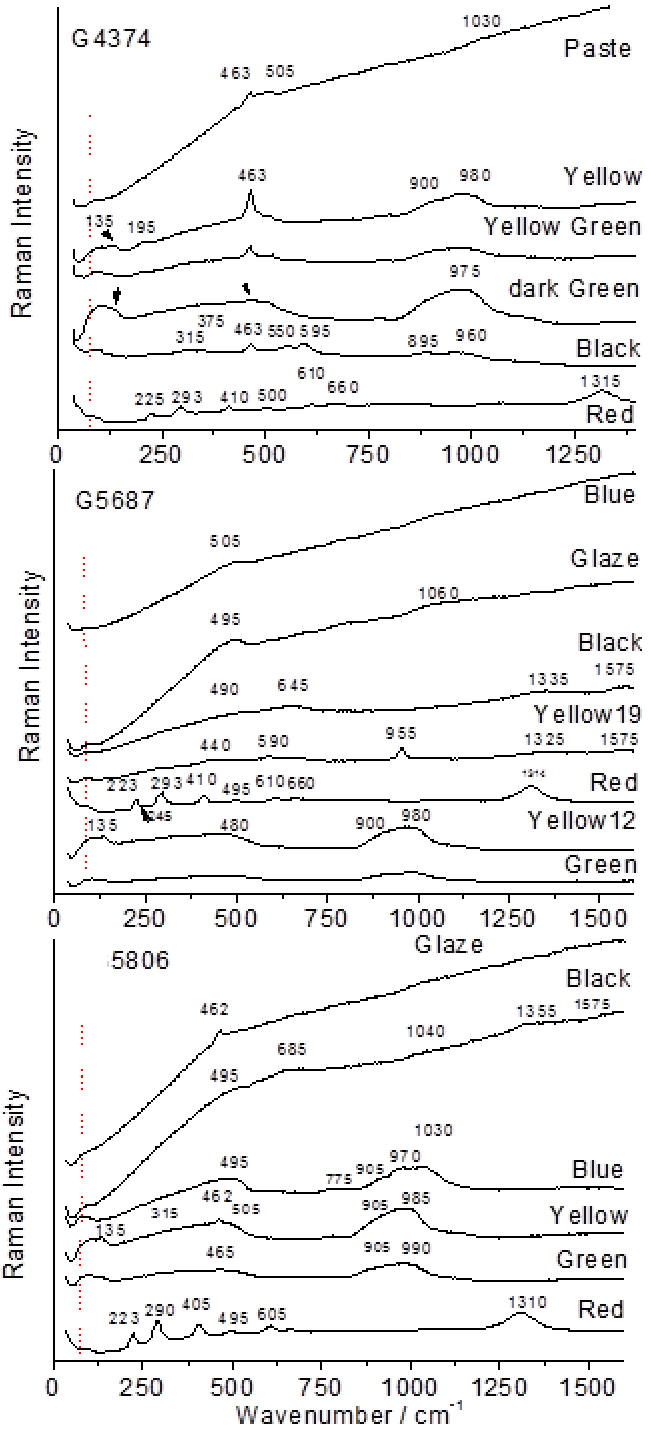

Fig. 3: Representative Raman spectra recorded on 17th (or earlier) century artefacts (see Table 1 for details).

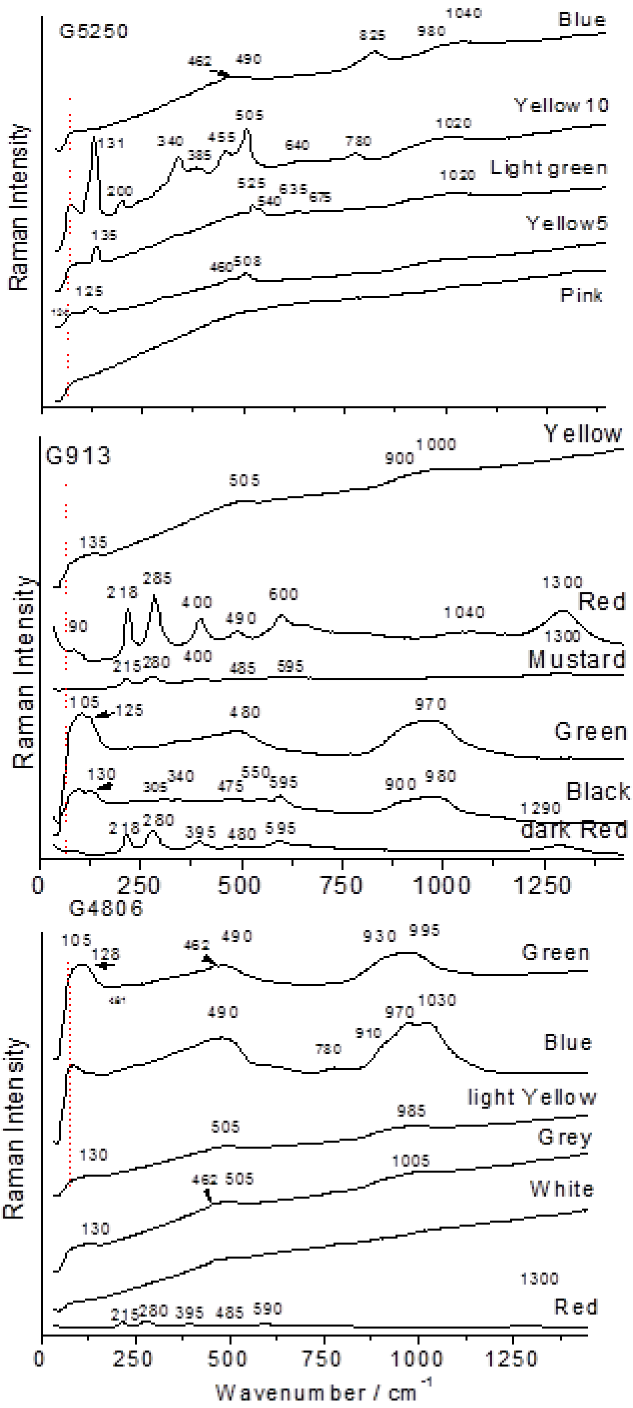

Fig. 4: Representative Raman spectra recorded on hua*falang* porcelains (imperial productions, before 1736, see Table 1).

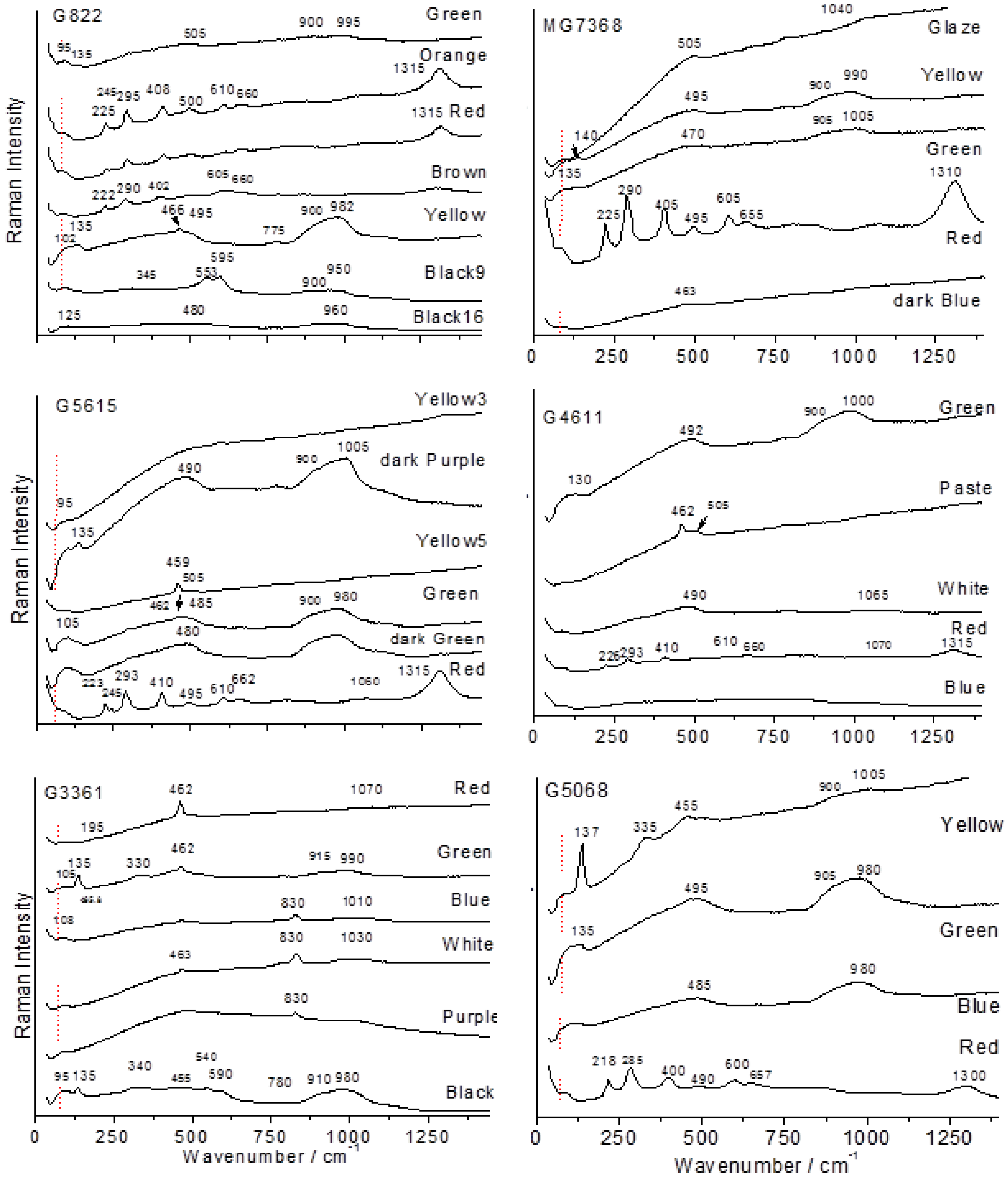

Fig. 5: Representative Raman spectra recorded on 18th century imperial productions (left column) or with imperial mark (right column).

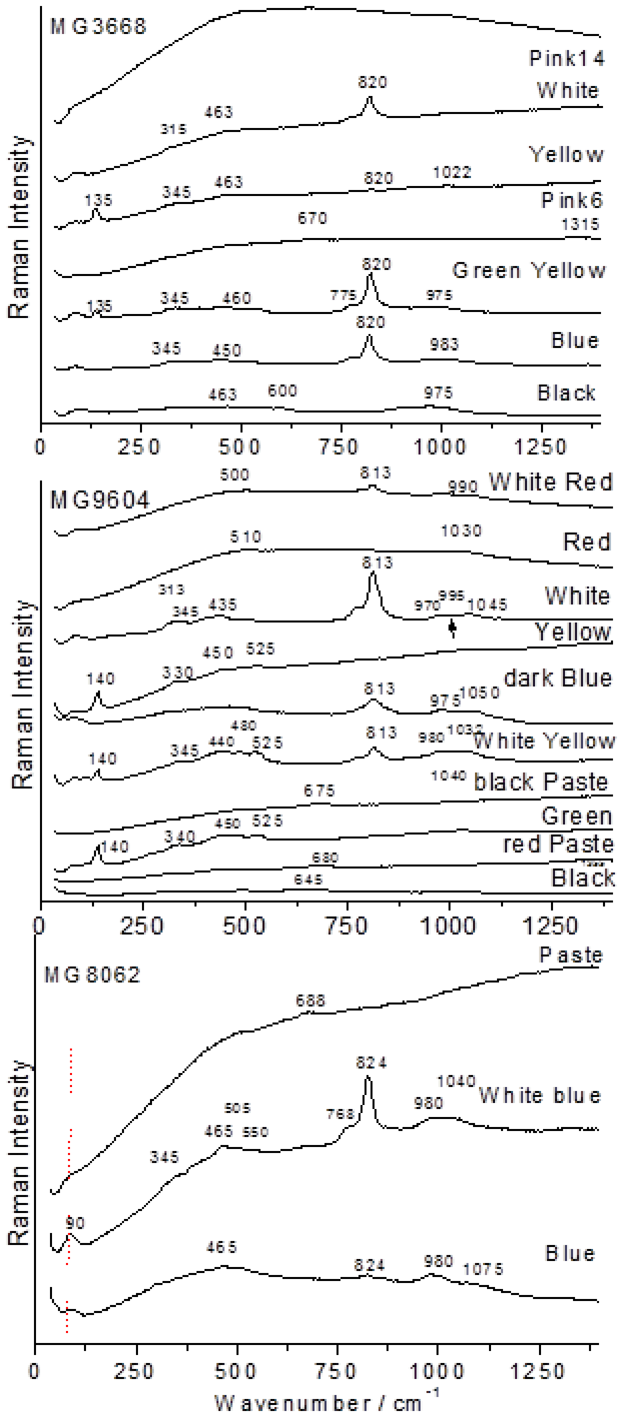

Fig. 6: Representative Raman spectra recorded on 2nd half 18th (MG 3668 & MG 9604) and 19th centuries painted Yixing stonewares.

Supplementary Materials

Non-invasive Raman analyses of *falangcai* and related porcelain wares. Searching for evidence for innovative pigment technologies

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All photos

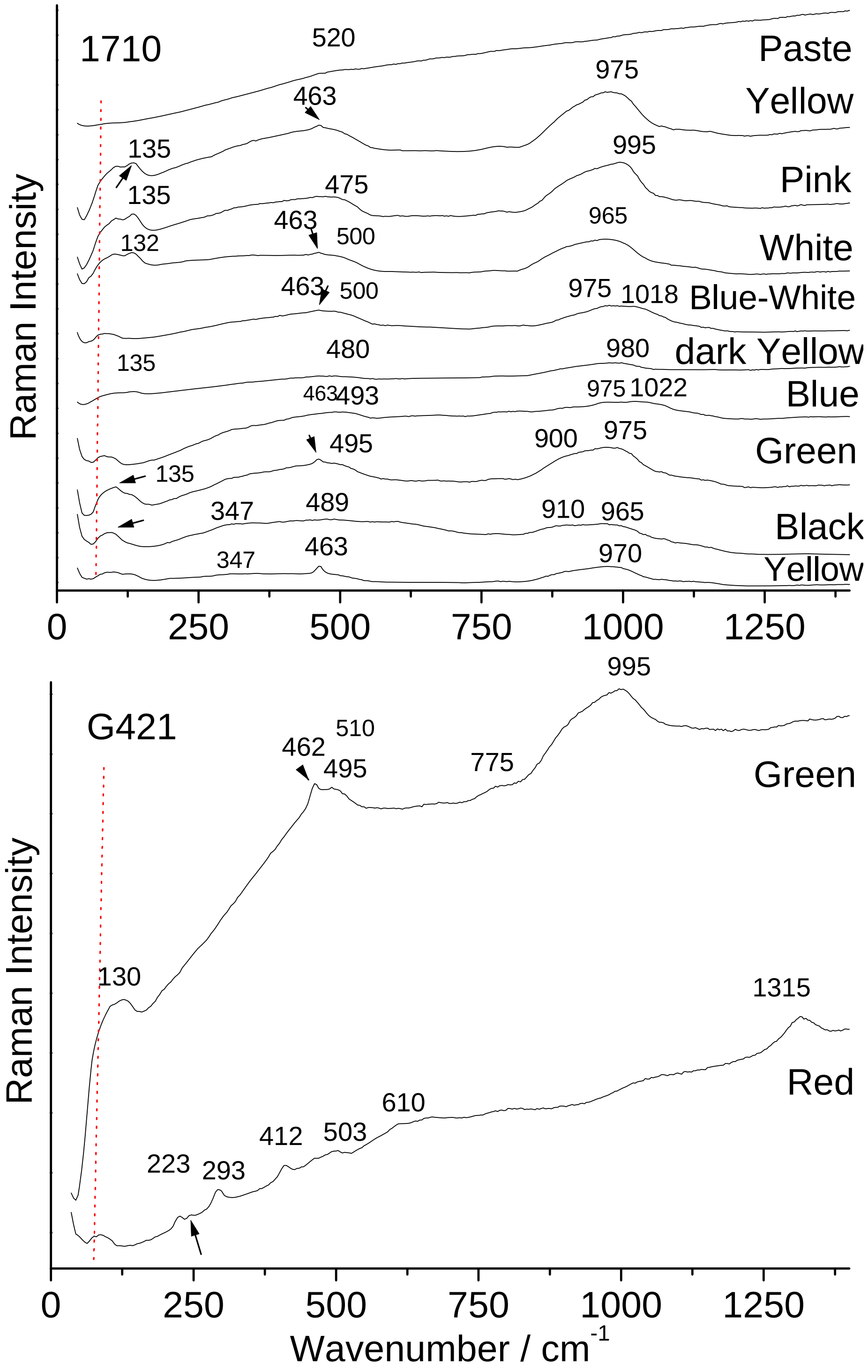

Fig. S1: Representative Raman spectra recorded in different coloured area of the 1710 and G421 artefacts, see Table 1.

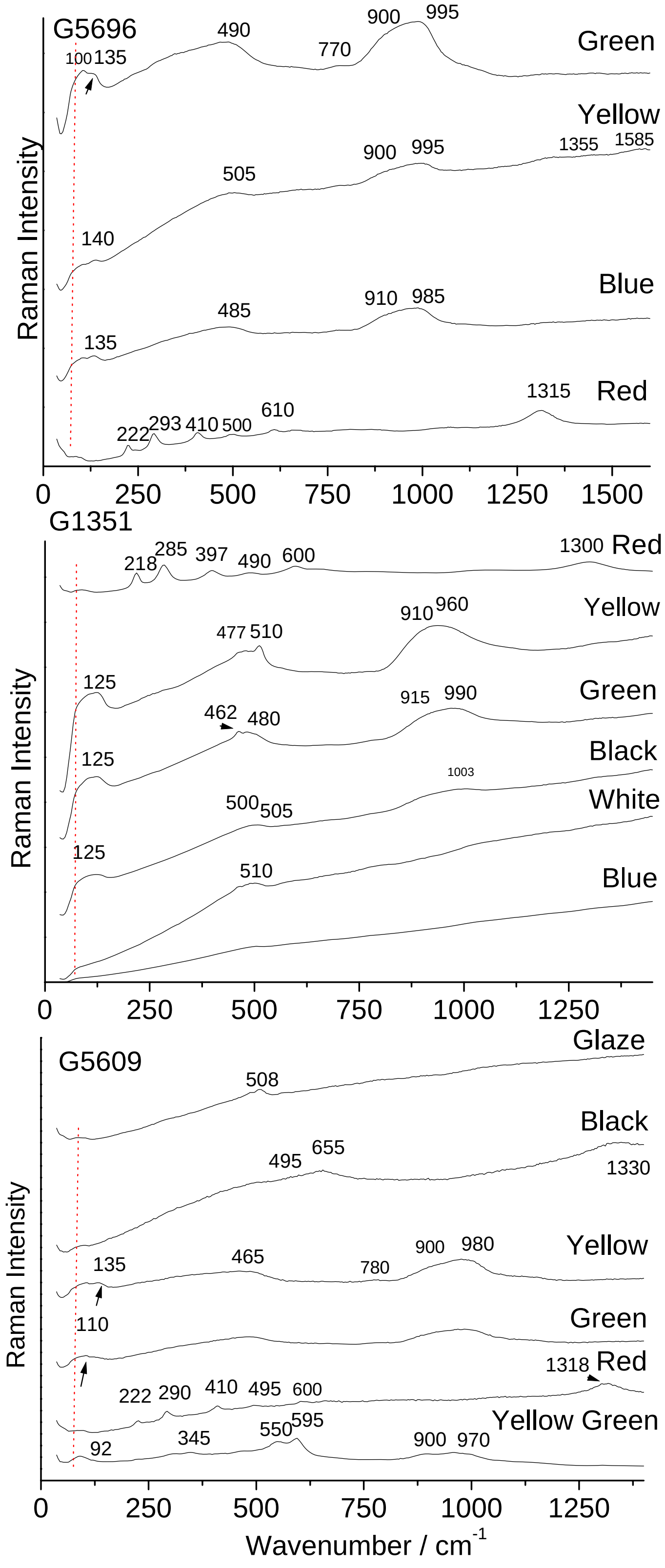

Fig. S2 : Representative Raman spectra recorded in different coloured area of the G5696, G1351 and G5609 artefacts, see Table 1.

Table S1: Main Raman peak wavenumber and assignments

		Chromophore		Matrix	
Reference Number	Color	Composition	Characteristic Peak Wavenumber (cm^{-1})	δ (cm^{-1})	γ (cm^{-1})
G1351	Yellow	Naples Yellow	511	477	939
	Red	Hematite	218/285/1300	-	-
	Green	-	-	462	481
	Black	-	-	504	1003
	White	-	-	500	-
	Blue	Naples Yellow	511	-	-
G822	Black	-	-	553/594	900/950
	Yellow	Naples Yellow	131	466	982
	Brown	Hematite	222/289/1303	-	-
		Carbon	1582		
	Red	Hematite	226/293/1314	-	-
	Orange	Hematite	226/293/1314	-	-
	Green	Naples Yellow	135	504	896/996
G4551	Green	-	-	492	960
	Yellow	-	-	485/504	1018
	Black	-	-	473	971/1021
	Yellow Black	Carbon	1562	549/583	953
	Purple	-	-	504	993
	Red	Hematite	222/293/1314	-	-
G4806	Green	-	-	462/489	979
	Blue	-	-	481	971/1028
	Yellow	Naples Yellow	131	504	989
	Grey	Naples Yellow	131	504	1003
	White	-	-	504	-
	Red	Hematite	214/281/1286	-	-
G5696	Green	Naples Yellow	131	489	989
	Yellow	Naples Yellow	139	504	996
		Carbon	1585		
	Blue	-	-	485	989
	Red	Hematite	222/293/1314	-	-
1710	Pink	Naples Yellow	136	474	993
	Yellow	Naples Yellow	136	463	968
	White	-	-	463	965
	Blue White	-	-	463	975/1018
	Black Yellow	Naples Yellow	136	482	975
	Blue	-	-	493	975/1022
	Green	-	-	463	965
	Black	-	-	489	911/961
MG9604	Yellow	Naples Yellow	140/347/523	459	1039
	White Red	Arsenate	813	501	990
	Red	-	-	508	1029
	White	Arsenate	813	436	997/1047

	White Yellow	Naples Yellow	140/341/523	440/481	979/1032
		Arsenate	817		
	Green	Naples Yellow	140/340/523	451	1039
	Black	MnO_2	647	482	975
	Blue	Arsenate	813	459	975/1050
G4611	Green	Naples Yellow	131	492	1003
	White	Arsenate	805	489	1067
	Red	Hematite	226/293/1314	-	-
	Blue	-	-	508	1071
G5687	Blue	-	-	504	-
	Black	Carbon	1334/1576	-	-
		MnO_2	647		
	Yellow 19	Naples Yellow	140	-	-
		Carbon	1324/1576		
		MnO_2	587		
	Yellow 12	Naples Yellow	140	478	972
	Red	Hematite	223/293/1314	-	-
	Green	-	-	482	972
MG5806	Black	Carbon	1355/1576	-	-
		MnO_2	655		
	Blue	-	-	493	979/1029
	Yellow	Naples Yellow	136	463	979
	Green	-	-	466	990
	Red	Hematite	223/289/1304	-	-
G5615	Yellow	Carbon	1586	-	-
		MnO_2	595		
	Purple Black	Naples Yellow	136	489	1004
	Green	-	-	463	972
	Black Green	-	-	482	972
	Red	Hematite	223/293/1314	-	-
G4374	Yellow	Naples Yellow	132	463	972
	Yellow Green	Naples Yellow	355/520	463	965
	Black	MnO_2	595	463	893/958
		Fe3O4-Cr_2MnO_4	550		
	Dark Green	-	-	463	975
	Red	Hematite	227/293/1314	-	-
MG7368	Yellow	Naples Yellow	140	497	990
	Green	Naples Yellow	140	470	1004
	Red	Hematite	228/289/1307	-	-
	Dark Blue	-	-	463	-
MG8062	White Blue	Arsenate	824	466	990/1022
	Blue	Arsenate	824	465	979/1071
G820	Green	-	-	462	971
	Red	Hematite	226/296/1314	-	-
	Yellow	Naples Yellow	135	462	971
	Purple	Naples Yellow	135	481	989
MG3668	White	Arsenate	820	466	-
	Yellow	Naples Yellow	136	463	1022
	Pink	Hematite	1314	-	-
	Green Yellow	Naples Yellow	136	459	975
		Co_2SiO_4	824		

	Blue	Co_2SiO_4	820	447	983
	Black	-	-	463	972
G5609	Black	Carbon	1331/1563	-	-
		MnO_2	655		
	Yellow	Naples Yellow	136	466	975
	Green	-	-	478	986
	Red	Hematite	227/293/1318	-	-
	Yellow Green	Chromate	344	-	900/958
		Cr_2O_3	550		
G5250	Blue	Co_2SiO_4	823	462/489	1039
	Yellow	$PbSnO_4$	131/199/454	-	1018
	Green	Naples Yellow	135	-	1018
		Cr_2O_3	523		
	Pink	Hematite	1585	-	-
G913	Yellow	Naples Yellow	135	504	1000
	Red	Hematite	218/285/1300	-	-
	Mustard	Hematite	214/277/1303	-	-
	Green	-	-	481	968
	Black	Fe3O4-Cr_2MnO_4	549	-	979
		CoO	473		
	Red Black	Hematite	218/281/1290	-	-
G5068	Yellow	Naples Yellow	140	454	1041
	Green	-	-	496	979
	Blue	-	-	485	982
	Red	Hematite	218/285/1300	-	-
G421	Green	-	-	462/492	996
	Red	Hematite	226/293/1314	-	-
G3361	Red	Quartz	462	-	-
	Green	-	-	462	989
	Blue	Co_2SiO_4	827	466	1018
	White	Arsenate	831	466	1028
	Purple	Co_2SiO_4	827	477	968
	Black	Fe3O4-Cr_2MnO_4	542	454	979

Table S2: Representative mean glaze compositions (after F. Zhang [5] and Kingery & Vandiver [6])

Oxide	*Famille verte* over	*Famille verte* over	*Famille rose* over	*Famille rose* over	*Famille rose* over	*Famille rose* over	*Famille rose* over
colour	blue	green	blue	rose	white	yellow	black
SiO_2	42.1	29.0	45.2	45.1	43.3	35.2	29.6
Al_2O_3	**0.4**	**0.6**	**0.7**	**0.6**	**1**	**0.3**	**1.5**
CaO	**0.9**	**0.15**	**0.35**	**0.3**	**0.15**	**0.8**	**0.1**
MgO	0.05	0.02	0.1	0.1	0.1	0.1	0
K_2O	**6.2**	**0.2**	**5.8**	**2.1**	**5.7**	2.75	**0.14**
Na_2O	0.4	0.1	2.7	2.75	2	1.4	0.25
FeO/Fe_2O_3	0.3	1.15	0.5	0.15	0.2	0.4	0.2
TiO_2	~0	0.02	-	-	-	-	
P_2O_5	0.02	~0	-	-	-	-	
PbO	**47.8**	**66.2**	**38.4**	**47.3**	**43.2**	**57.5**	**67.1**
CoO	0.2		0.30.1				0.25
CuO		6					0.05
SnO_2	0.3		-	0.2	0.1	2	-
As_2O_5			**1.4**	**0**	**4.3**		**0**
Au				0.1			-
MnO_2					0.03		0.5

Actually, pottery glaze composition varies from the body glaze interface to the glaze surface; -: not determined.

G4551

PurpleG4551_14
PurpleG4551_15

_bl_G4551_01
BlaG45551_02

YellowG4551_03

GreenG4551_16
GreenG4551_17

RedG4551_08

YellowG4551_09
YellowG4551_10
YellowG4551_11

YellowBlackG4551_12
YellowBlackG4551_13

BlueBlackG4551_05
BlueBlackG4551_06

BlackG45551_07

G5250

yellowG5250_10

blueG5250_12

blackG5250_01

blueG5250_02
blueG5250_03

pinkG5250_06
pinkG5250_07

yellowG5250_04
yellowG5250_05

greenG5250_09

lightgreenG5250_08

G4806

lightyellowG4806_06

blueG4806_09
blueG4806_10

greenG4806_01
greenG4806_02
greenG4806_03

greyG4806_04

redG4806_06
redG4806_07

whiteG4806_05

G913

greenG913_13

mustardG913_09
mustardG913_10
mustardG913_11
mustardG913_12

yellowG913_03

blackG913_04
blackG913_05

RedG913_01
RedG913_02

greenG913_07
greenG913_08

redblackG913_15

yellowG913_06

redflowG913_14

G1351

green1351_03
green1351_04
green1351_05

greenG1351_01

blackG1351_02

whiteG1351_12

blueG1351_11

redG1351_09
redG1351_10

yellowG1351_06
yellowG1351_07
yellowG1351_08

G421

redG421_02
redG421_03

greenG421_01

G5696

blueG5696_05

yellowG5696_06

yellowG5696_04

greenG5696_01

blueG5696_02

redG5696_03

G3361

purpleG3361_10
purpleG3361_11

whiteG3361_08

greenG3361_09

blueG3361_06
blueG3361_07

greenG3361_01

blackG3361_02

redG3361_03
redG3361_04
redG3361_05

G822

redG822_05

orangeG822_04

redG822_01

yellowG822_10
yellowG822_11
yellowG822_12
yellowG822_13

blackG822_16
blackG822_17

brownG822_14
brownG822_15

blackG822_06
blackG822_07
blackG822_08
blackG822_09

G5068

G5068blue_05
G5068blue_06

G5068green_07
G5068green_08
G5068green_09

G5068rouge_01
G5068rouge_02

G5068yellow_03
G5068yellow_04

G4611

blueG4611_03

greenG4611_05

redG4611_04

whiteG4611_01
whiteG4611_02

pateG4611_06
pateG4611_07
pateG4611_08

1710

Va1710yelflower_01
Va1710yelflower_02
Va1710yelflower_03
Va1710yelflower_04

Va1710black_01
Va1710black_02
Va1710black_03

G5615green_01
G5615green_02

G5615

G5615yellow
G5615yellow_2
G5615yellow_3
G5615yellow_4
G5615yellow_5

G5615green
G5615green_2
G5615green_3

G5615maubla

G5615blackgreen
G5615blackgreen_2

G5615RED
G5615RED_2

G5609

G5609green_13
G5609green_14

G5609black_10
G5609black_11
G5609black_12

G5609yellowgreen_5
G5609yellowgreen_6
G5609yellowgreen_7
G5609yellowgreen_8
G5609yellowgreen_9

G5609yellow_3
G5609yellow_4

G5609red_1
G5609red_2

G5609glaze
G5609glaze_15

MG3668

MG3668yellow_12
MG3668yellow_13

MG3668pink_14

MG3668yellow_11

MG3668pink_6
MG3668pink_7

MG3668greenyellow_3
MG3668greenyellow_4
MG3668greenyellow_5

MG3668white_1
MG3668white_2

MG3668black_7
MG3668black_8
MG3668black_9

MG3668bue_10
MG3668bue_11

MG9604

YxMG9604darkblue_11
YxMG9604darkblue_12

YxMG9604white_10

YxMG9604blue_9

YxMG9604yellow_3

YxMG9604white-yellow_4
YxMG9604white-yellow_5

YxMG9604black_13
YxMG9604black_14
YxMG9604black_15

YxMG9604green_1
YxMG9604green_2

YxMG9604green_6

YxMG9604white-red_8

YxMG9604red_7

MG8062

MG8062blue_1

MG8062blue_2

MG8062whiteblue_3
MG8062whiteblue_4

MG8062paste_5
MG8062paste_6

MG7368

MG7368green_4
MG7368green_5

MG7368darred_1
MG7368red_2

MG7368darkblue_1

MG7368yellow_6
MG7368yellow_7
MG7368yellow_8

G5687

G5687jaune_15
G5687jaune_16
G5687jaune_17
G5687jaune_18
G5687jaune_19

G5687jaune_12
G5687jaune_13
G5687jaune_14

G5687blue_4

G5687black_15

G5687red_1
G5687red_2
G5687red_3

G5687green_9
G5687green_10
G5687green_11

G4374

G4574red_10

G4574yellowgreen_9

G4574yellow_1
G4574yellow_2
G4574yellow_3

G4574black_4
G4574black_5
G4574black_6

G4574darkgreen_7
G4574darkgreen_8

MG5806

MG5806_1
MG5806blue_2

MG5806green_3
MG5806green_4

MG5806yellow_7
MG5806yellow_8

MG5806red_9

MG5806black_5
MG5806black_6