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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 *wucui* 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 than 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, while 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 Au⁰ 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 $\sim 4 \times 4 \times 12 \mu\text{m}^3$ volume is first used. A much smaller laser spot obtained with the x200 objective (about $0.5 \times 0.5 \times 2 \mu\text{m}^3$) requires a very precise focus (a lengthy process) but guarantees 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 *wucui* 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 *wucui* 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 SiO₄ 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 SiO₄ 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 SiO₄ 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 the narrow and strong 463 cm^{-1} peak which is characteristic of α - 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 arises 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 $\sim 195\text{-}200$ 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 ($\text{Ca}_3(\text{PO}_4)_2$) 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 $\sim 960\text{ cm}^{-1}$ [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, Mennecey, 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 *wucaï*, *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]. Eighteenth 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 \sim 0.1-0.2) [83-86], which may explain the formation of lead arsenate in the blue enamel. The ratio As/Co had reached \sim 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 (CaF₂ is used to opacify white cloisonné enamels [22]). Note that arsenic-poor and arsenic-rich 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 μ XRF/diffraction [93] should be also very useful.

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Références

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Table 1: Studied artefacts

| MNAAG inventory number | Type | Date (expected) | Production | Marks |
|------------------------|---|---|---|--|
| G 1351 | <i>doucai</i> bowl | Wanli reign (1572-1620) Ming Dynasty | Imperial manufacture of Jingdezhen | “Da Ming Wanli nian zhi” mark |
| G 5250 | <i>huafalang</i> 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 | <i>huafalang/yangcai</i> bowl | Yongzheng reign (1723-1735) | Painted enamels made in the Imperial manufacture of Jingdezhen | “Yongzheng yu zhi” mark |
| G 913 | <i>huafalang/yangcai</i> bowl | Yongzheng reign (1723-1735) | Painted enamels made in the Imperial manufacture of Jingdezhen | “Yongzheng yu zhi” mark |
| G 822 | <i>Famille verte</i> 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 | <i>Famille verte</i> bowl | 19 th c. | Private kiln (Jingdezhen) | |
| G 3361 | <i>Famille rose</i> Water dropper | early 18 th c. | Imperial manufacture of Jingdezhen | “Da Qing Kangxi nian zhi” mark |
| G 4551 | <i>Famille verte</i> cup | 1 st half 18 th c. | Private kiln (Jingdezhen) | “JL” mark = J. Landin (1627-1695) mark |
| MG 7368 | <i>doucai</i> bowl | 18 th c. | Private kiln (Jingdezhen) | “Da Qing Yongzheng nian zhi” mark |
| G 4611 | <i>doucai</i> cup | 18 th c. | Imperial manufacture of Jingdezhen /Private kiln (Jingdezhen) | “Da Ming Chenghua (1464-1487) nian zhi” apocryphal mark |
| G 5068 | <i>doucai</i> pot | 18 th c. | Imperial manufacture of Jingdezhen /Private kiln (Jingdezhen) | “Da Ming Chenghua nian zhi” apocryphal mark |
| G 5696 | <i>doucai</i> bowl | 2 nd half 17 th – early 18 th c. | Imperial manufacture of Jingdezhen | “Da Qing Kangxi nian zhi” mark |
| G 5609 | <i>Famille verte</i> seal | 17 th ? 19 th ? | Imperial manufacture of Jingdezhen ? Private kiln (Jingdezhen) ? | “Kangxi yulan zhi bao” inscriptions |
| G 4374 | <i>wucan</i> vase | end 16 th – mid. 17 th c. | Private kiln (Jingdezhen) | |
| MG 5806 | <i>wucan</i> vase | mid-later half 17 th c. | Private kiln (Jingdezhen) | |
| G 5687 | <i>wucan</i> vase | mid 17 th c. | Private kiln (Jingdezhen) | |
| G 1710 | <i>Famille noire/Famille verte</i> Vase | Later half 17 th – early 18 th c. | Private kiln (Jingdezhen) | “Biyu tang zhi” mark |
| G 421 | <i>Famille verte</i> Vase | end 17 th – early 18 th c. | Private kiln (Jingdezhen) | |
| MG 3668 | teapot | 2 nd half 18 th c. | Private kiln (Yixing) | |
| MG 9604 | teapot | 2 nd half 18 th c. | Private kiln (Yixing) | |
| MG 8062 | bowl | 19 th c. | Private kiln (Yixing) | |

FIGURE CAPTIONS



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

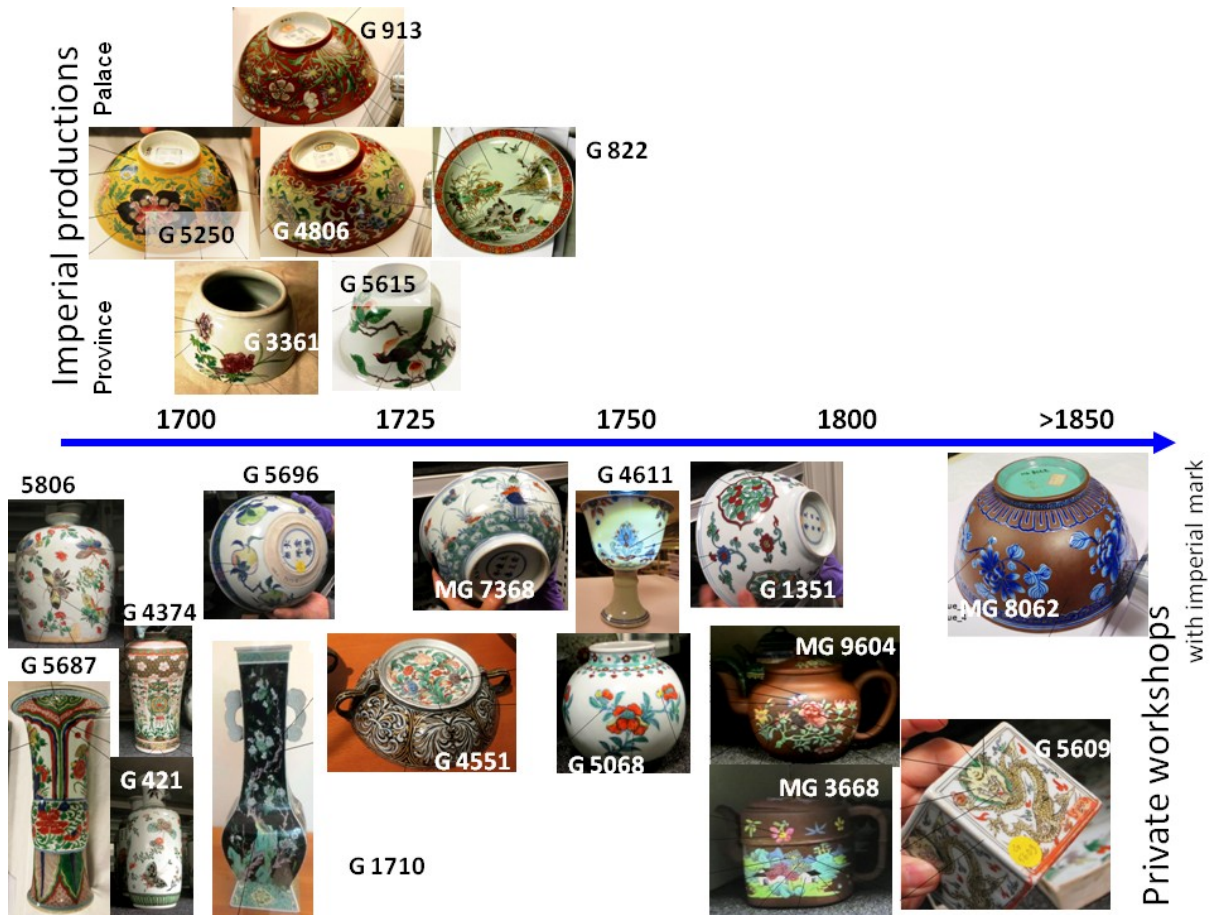


Fig. 2: Studied corpus (see Table 1).

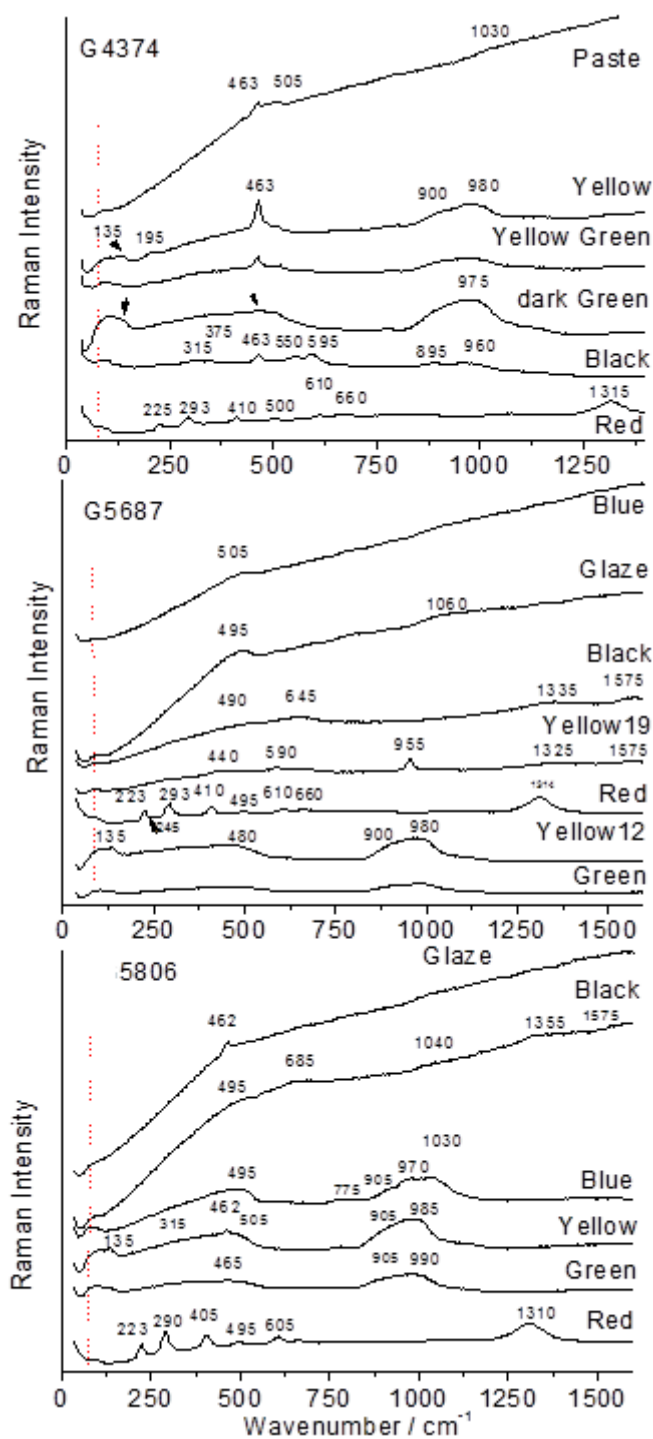


Fig. 3: Representative Raman spectra recorded on 17th (or earlier) century artefacts (see Table 1 for details).

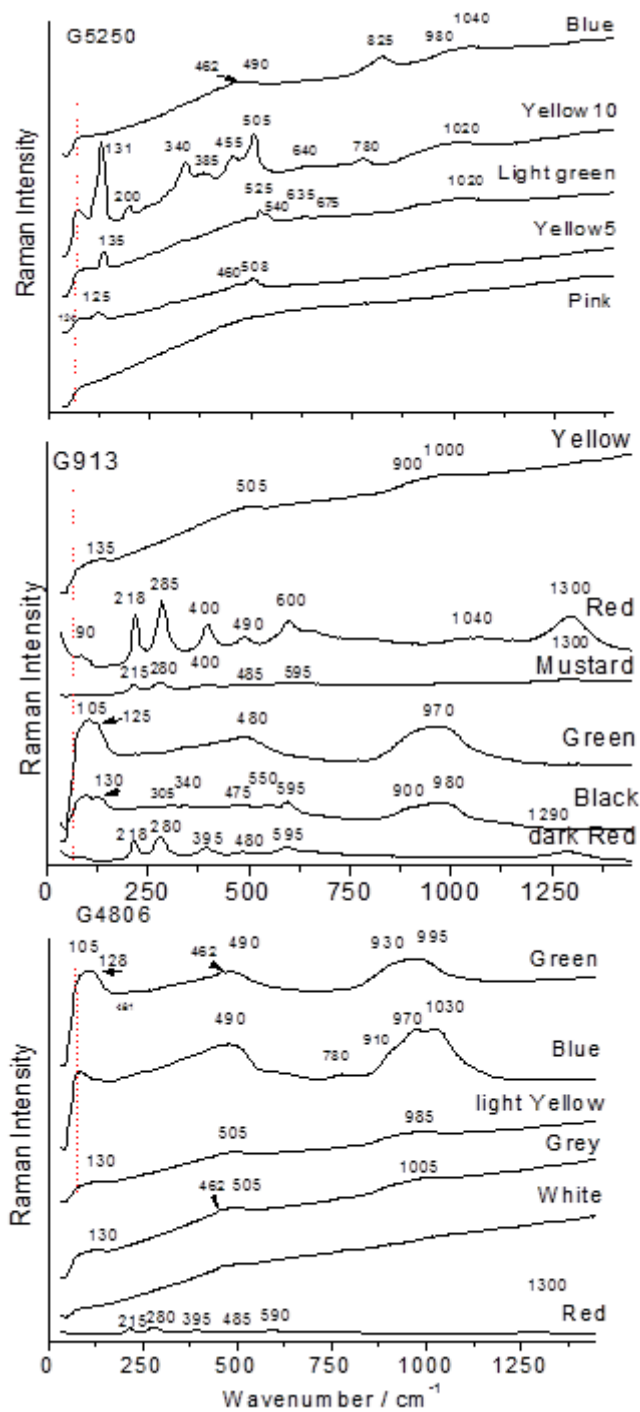


Fig. 4: Representative Raman spectra recorded on *huafalang* porcelains (imperial productions, before 1736, see Table 1).

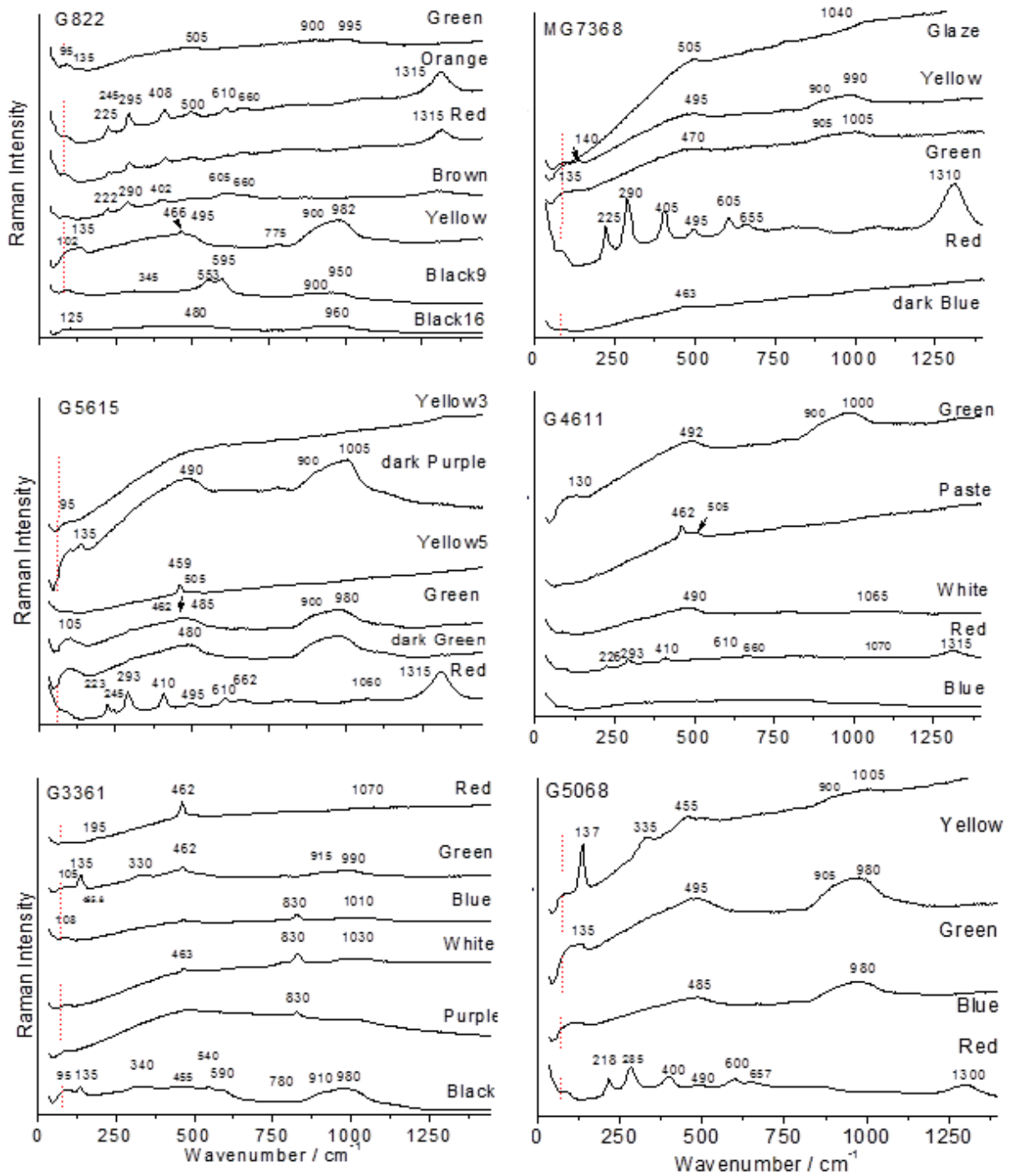


Fig. 5: Representative Raman spectra recorded on 18th century imperial productions (left column) or with imperial mark (right column).

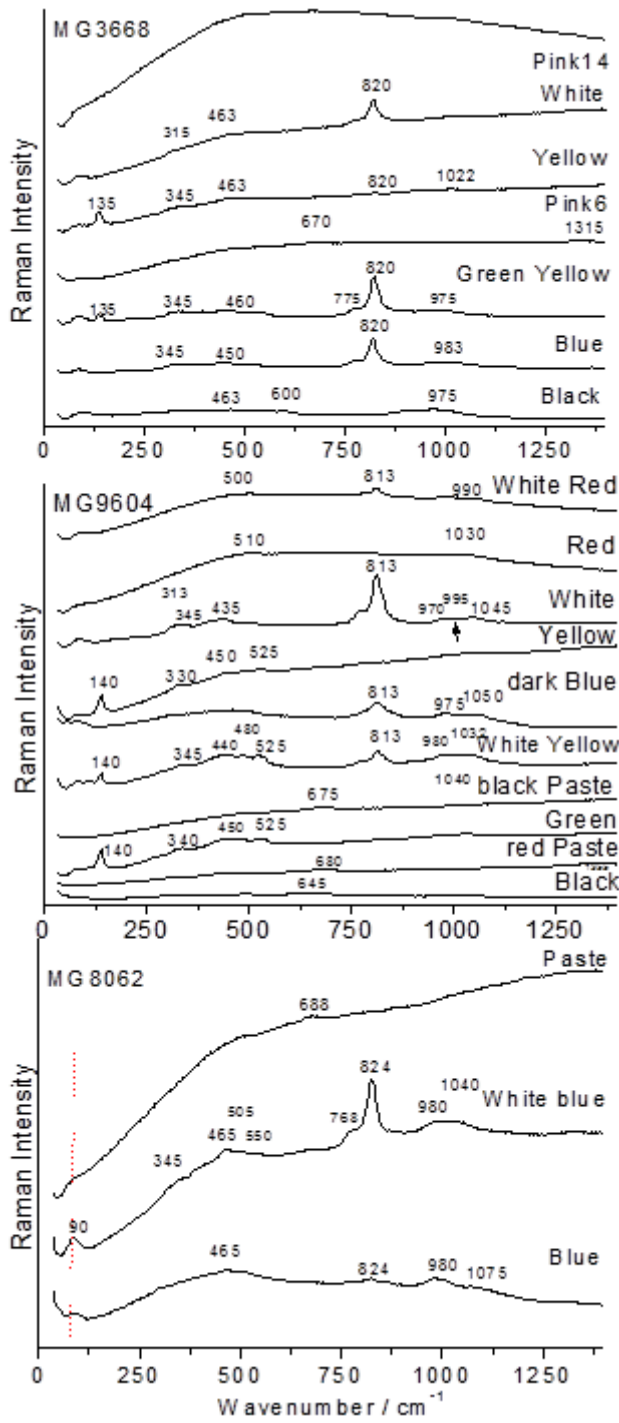


Fig. 6: Representative Raman spectra recorded on 2nd half 18th (MG 3668 & MG 9604) and 19th centuries painted Yixing stonewares.

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

Ph. Colomban – MNAAG Droits réservés

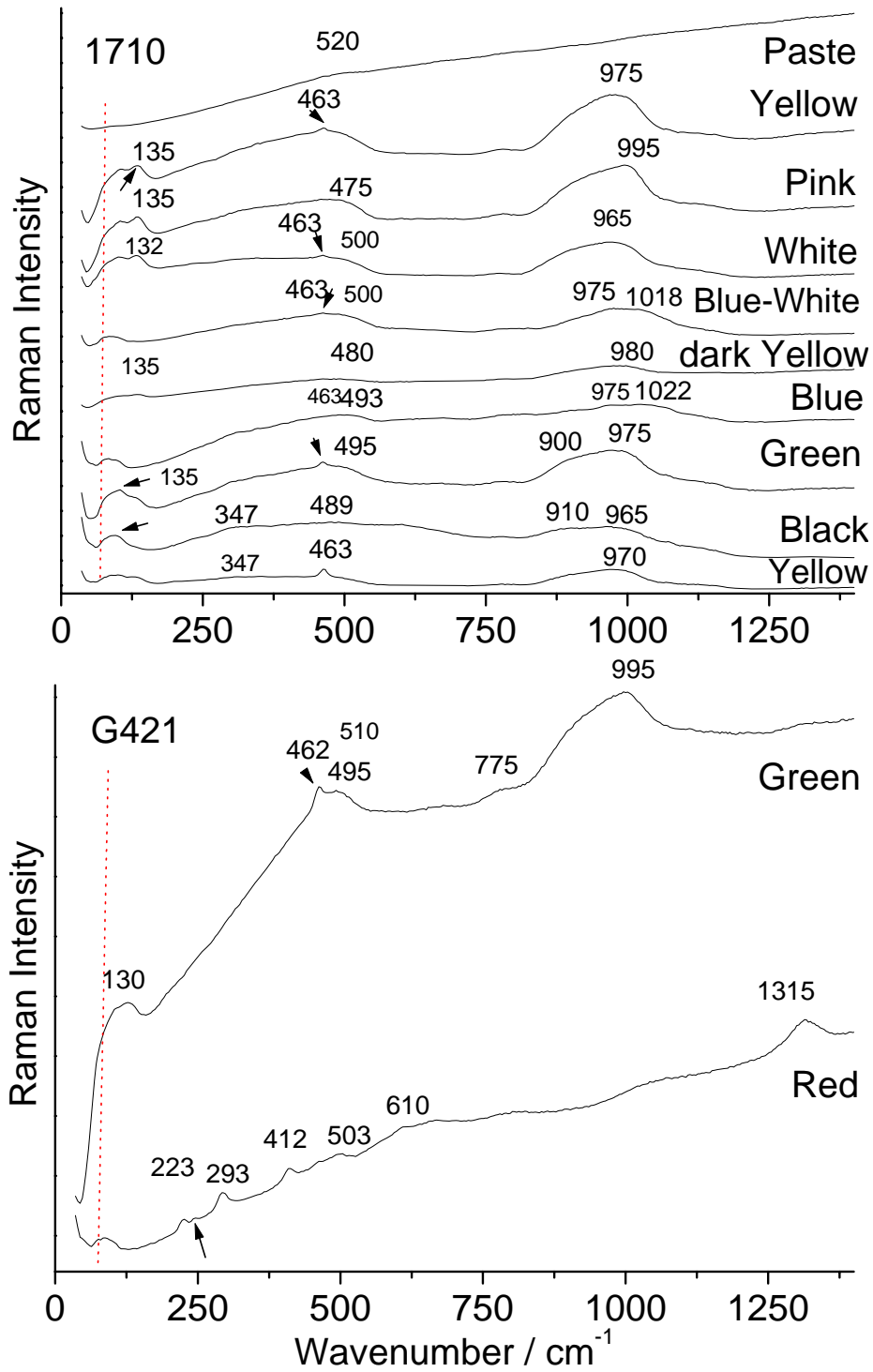


Fig. S1: Representative Raman spectra recorded in different coloured area of the 1710 and G421 artefacts, see Table 1.

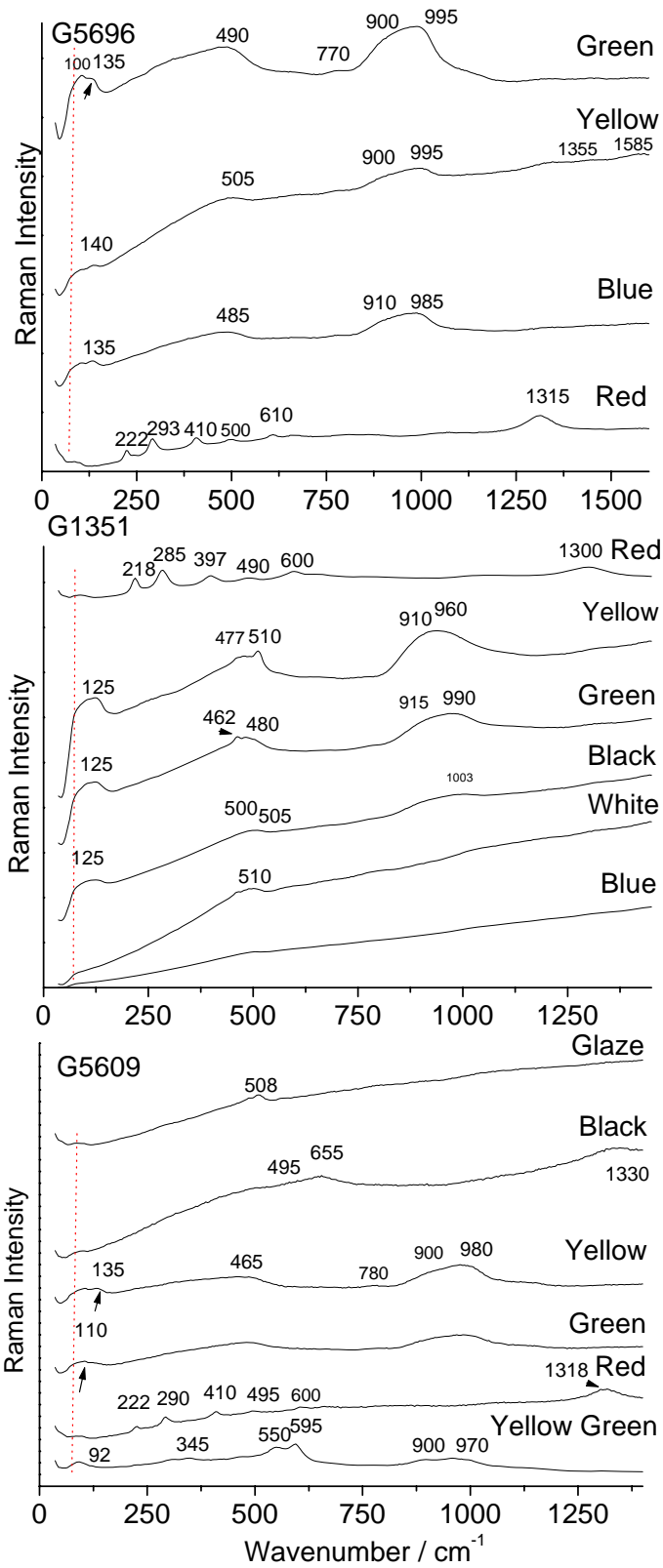


Fig. S2 : Representative Raman spectra recorded in different coloured area of the G5696, G1351 and G5609 artefacts, see Table 1.

Table S1: Main Raman peak wavenumber and assignments

| Reference Number | Color | Chromophore | | δ (cm ⁻¹) | Matrix γ (cm ⁻¹) | |
|------------------|--------------|---------------|--|------------------------------|-------------------------------------|------|
| | | Composition | Characteristic Peak Wavenumber (cm ⁻¹) | | | |
| G1351 | Yellow | Naples Yellow | 511 | 477 | 939 | |
| | Red | Hematite | 218/285/1300 | - | - | |
| | Green | - | - | 462 | 481 | |
| | Black | - | - | 504 | 1003 | |
| | White | - | - | 500 | - | |
| G822 | Blue | Naples Yellow | 511 | - | - | |
| | 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 | - | - | |
| G4551 | Green | Naples Yellow | 135 | 504 | 896/996 | |
| | 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 | |
| 1710 | Red | Hematite | 222/293/1314 | - | - | |
| | 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 Arsenate | 140/341/523 817 | 440/481 | 979/1032 |
| | 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 |
| | | Fe ₃ O ₄ - Cr ₂ MnO 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 ₂ SiO ₄ | 824 | | |

| | | | | | |
|-------|--------------|----------------------------------|--------------|---------|---------|
| | Blue | Co ₂ SiO 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 ₂ O ₃ | 550 | | |
| G5250 | Blue | Co ₂ SiO ₄ | 823 | 462/489 | 1039 |
| | Yellow | PbSnO ₄ | 131/199/454 | - | 1018 |
| | Green | Naples Yellow | 135 | - | 1018 |
| | | Cr ₂ O 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 | Fe ₃ O ₄ - | 549 | - | 979 |
| | | Cr ₂ MnO ₄ | | | |
| | | 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 ₂ SiO ₄ | 827 | 466 | 1018 |
| | White | Arsenate | 831 | 466 | 1028 |
| | Purple | Co ₂ SiO ₄ | 827 | 477 | 968 |
| | Black | Fe ₃ O ₄ - | 542 | 454 | 979 |
| | | Cr ₂ MnO ₄ | | | |

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

| Oxide | <i>Famille</i> <i>verte</i> over | <i>Famille</i> <i>verte</i> over | <i>Famille</i> <i>rose</i> over | <i>Famille</i> <i>rose</i> over | <i>Famille</i> <i>rose</i> over | <i>Famille</i> <i>rose</i> over | <i>Famille</i> <i>rose</i> 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 ₂ O 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 ₂ O | 6.2 | 0.2 | 5.8 | 2.1 | 5.7 | 2.75 | 0.14 |
| Na ₂ O | 0.4 | 0.1 | 2.7 | 2.75 | 2 | 1.4 | 0.25 |
| FeO/Fe ₂ O ₃ | 0.3 | 1.15 | 0.5 | 0.15 | 0.2 | 0.4 | 0.2 |
| TiO ₂ | ~0 | 0.02 | - | - | - | - | |
| P ₂ O 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 ₂ O 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

RedG4551_08



YellowG4551_03

GreenG4551_16
GreenG4551_17

YellowG4551_09
YellowG4551_10
YellowG4551_11

YellowBlackG4551_12
YellowBlackG4551_13

BlueBlackG4551_05
BlueBlackG4551_06
BlackG45551_07

G5250



yellowG5250_10

blueG5250_12

blackG5250_01

pinkG5250_06
pinkG5250_07

yellowG5250_04
yellowG5250_05

greenG5250_09

lightgreenG5250_08

blueG5250_02
blueG5250_03

G4806



greenG4806_01
greenG4806_02
greenG4806_03

greyG4806_04

whiteG4806_05

redG4806_06
redG4806_07

blueG4806_09
blueG4806_10

lightyellowG4806_06

G913



green1351_03
green1351_04
green1351_05

greenG1351_01 blackG1351_02

G1351

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

greenG3361_01

blackG3361_02

redG3361_03
redG3361_04
redG3361_05

blueG3361_06
blueG3361_07

G822



G5068



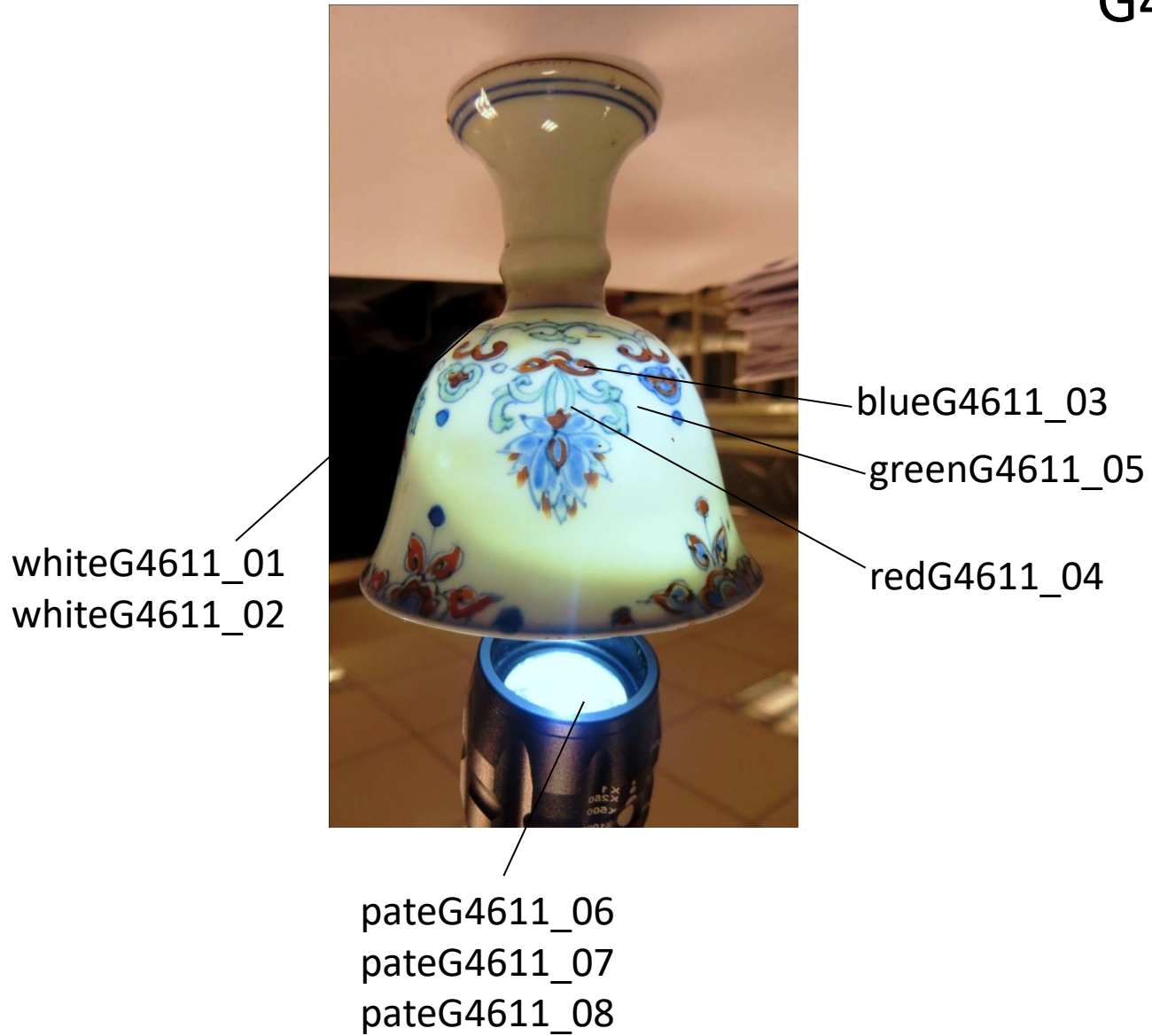
G5068blue_05
G5068blue_06

G5068green_07
G5068green_08
G5068green_09

G5068rouge_01
G5068rouge_02

G5068yellow_03
G5068yellow_04

G4611



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



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

MG7368green_4

MG7368green_5

MG7368



MG7368darred_1

MG7368red_2

MG7368darkblue_1

MG7368yellow_6

MG7368yellow_7

MG7368yellow_8

G5687jaune_15

G5687jaune_16

G5687jaune_17

G5687jaune_18

G5687jaune_19

G5687



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