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

Philippe Colomban,<sup>1\*</sup> Yizheng Zhang,<sup>1</sup> Bing Zhao,<sup>2</sup>

<sup>1</sup>Sorbonne Universités, UPMC Univ. Paris 06, MONARIS UMR8233 CNRS, 4 Place Jussieu, 75005 Paris, France

<sup>2</sup>CNRS, CNRS/EPHE/Collège de France/UPD07, CRCAO UMR8155, 52 rue du Cardinal Lemoine, 75005, Paris, France

\*Corresponding author

[Philippe.colomban@upmc.fr](mailto:Philippe.colomban@upmc.fr)

### Abstract

Eighteen Chinese painted enamelled porcelains and three Chinese enamelled Yixing stonewares dated to the 16<sup>th</sup> to 19<sup>th</sup> 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 17<sup>th</sup> 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 1<sup>st</sup> quarter of the 18<sup>th</sup> 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 19<sup>th</sup> 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 8<sup>th</sup> 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 17<sup>th</sup> 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  $\mu\text{m}$  (thin overglaze) to 300  $\mu\text{m}$  (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 16<sup>th</sup> to the 19<sup>th</sup> 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 Au<sup>0</sup> 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 18<sup>th</sup> century or between 1723 and 1735 were analysed. A *wucai* 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 17<sup>th</sup> to beginning of 18<sup>th</sup> century) and four 18<sup>th</sup> 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 (18<sup>th</sup> 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<sub>4</sub> tetrahedron bending and stretching modes at ~550 cm<sup>-1</sup> and ~1000 cm<sup>-1</sup> 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<sup>-1</sup> and a weaker one at 1060 cm<sup>-1</sup>, 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<sup>-1</sup> and a much weaker one at 480 cm<sup>-1</sup>, 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<sub>4</sub> 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<sub>4</sub> 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<sup>-1</sup>, 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  $\text{cm}^{-1}$ .

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

It is noteworthy that the narrow and strong 463  $\text{cm}^{-1}$  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  $\text{Co}^{2+}$  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  $\text{cm}^{-1}$  and 223-290-405  $\text{cm}^{-1}$  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  $\text{cm}^{-1}$  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  $\text{cm}^{-1}$  component, characteristic of a hematite ( $\text{Fe}_2\text{O}_3$ )-magnetite ( $\text{Fe}_3\text{O}_4$ ) 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  $\text{Co}^{2+}$  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  $\text{Pb}_2\text{SnO}_4$  (Lead tin yellow Type I) and  $\text{PbSb}_2\text{O}_7$ , 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  $\text{cm}^{-1}$  is easily detected because it corresponds to the collective motion of  $\text{Pb}^{2+}$  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  $\text{cm}^{-1}$  are more sensitive to the other elements, for instance the 455  $\text{cm}^{-1}$  one to Sn, the ca. 325-330 to Sb and the 508  $\text{cm}^{-1}$  one characteristic of the mixed compositions. Pure  $\text{Pb}_2\text{SnO}_4$  compound exhibits the  $\sim 195\text{-}200$   $\text{cm}^{-1}$  peak. Pyrochlore yellow pigments were detected in the 17<sup>th</sup> 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 18<sup>th</sup> 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  $\text{cm}^{-1}$  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  $\text{cm}^{-1}$  peak [67], e.g. in G 5687, MG 5806 (17<sup>th</sup> century, Fig. 3), MG 9604 (Yixing, 18<sup>th</sup> century, Fig. 6) and G 5609 objects (19<sup>th</sup>-20<sup>th</sup> centuries, Fig. S2). Also, there is manganese oxide(s) with a 550-595  $\text{cm}^{-1}$  doublet, e.g. in G 4374 (16<sup>th</sup>-17<sup>th</sup> century, Fig. 3), G 913 (*huafalang* ware, 18<sup>th</sup> century, Fig. 4), G 822, G 3361 (18<sup>th</sup> century ware, Fig. 5), MG 3668 (Yixing ware, 18<sup>th</sup> century, Fig. 6) and G 5609 (19<sup>th</sup>-20<sup>th</sup> 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  $\text{Co}^{2+}$  ions in the amorphous silicate network [3]. When the ion concentration exceeds a few wt% (locally), olivine silicate ( $\text{Co}_2\text{SiO}_4$ ) or cobalt aluminate spinel ( $\text{CoAl}_2\text{O}_4$ ) 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  $825\text{ cm}^{-1}$  [68].

Opacifiers: Three types of white pigments were identified. Cassiterite (tin oxide- $\text{SnO}_2$ ), with a characteristic doublet at  $635$  and  $775\text{ cm}^{-1}$  [69-71], was detected in light green areas of the *huafalang* G5250 ware (Fig. 4). Cassiterite, an innovative opacifier of the Late Roman period (5<sup>th</sup> 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  $955\text{ cm}^{-1}$ , consistent with the calcium phosphate ( $\text{Ca}_3(\text{PO}_4)_2$ ) signature, was noted in the yellow area of the G 5687 17<sup>th</sup> century vase (Fig. 3). It is considered that calcium phosphate ( $955\text{ cm}^{-1}$  peak) is a rather rare glaze opacifier. First used in late antique glass mosaic *tesserae* [73], it was used in rare Islamic glass [57] as the alternative opacifier of *lattimo* glass at the end of the 16<sup>th</sup> 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  $830\text{ cm}^{-1}$  [67,76] in many coloured areas, in blue *huafalang* G 5250 (Fig. 4) and G 3361 (Fig. 5) among the 18<sup>th</sup> 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  $\text{Co}_2\text{SiO}_4$  contribution (ca.  $825\text{ cm}^{-1}$  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, Menecy, 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 17<sup>th</sup> and 18<sup>th</sup> 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 17<sup>th</sup> 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 17<sup>th</sup> 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<sub>2</sub> 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 17<sup>th</sup> and beginning of the 18<sup>th</sup> 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 16<sup>th</sup> and 17<sup>th</sup> 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  $\mu$ XRF/diffraction [93] should be also very useful.

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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 <sup>th</sup> c.	Private kiln (Jingdezhen)	
G 3361	<i>Famille rose</i> Water dropper	early 18 <sup>th</sup> c.	Imperial manufacture of Jingdezhen	“Da Qing Kangxi nian zhi” mark
G 4551	<i>Famille verte</i> cup	1 <sup>st</sup> half 18 <sup>th</sup> c.	Private kiln (Jingdezhen)	“JL” mark = J. Landin (1627-1695) mark
MG 7368	<i>doucai</i> bowl	18 <sup>th</sup> c.	Private kiln (Jingdezhen)	“Da Qing Yongzheng nian zhi” mark
G 4611	<i>doucai</i> cup	18 <sup>th</sup> c.	Imperial manufacture of Jingdezhen /Private kiln (Jingdezhen)	“Da Ming Chenghua (1464-1487) nian zhi” apocryphal mark
G 5068	<i>doucai</i> pot	18 <sup>th</sup> c.	Imperial manufacture of Jingdezhen /Private kiln (Jingdezhen)	“Da Ming Chenghua nian zhi” apocryphal mark
G 5696	<i>doucai</i> bowl	2 <sup>nd</sup> half 17 <sup>th</sup> – early 18 <sup>th</sup> c.	Imperial manufacture of Jingdezhen	“Da Qing Kangxi nian zhi” mark
G 5609	<i>Famille verte</i> seal	17 <sup>th</sup> ? 19 <sup>th</sup> ?	Imperial manufacture of Jingdezhen ? Private kiln (Jingdezhen) ?	“Kangxi yulan zhi bao” inscriptions
G 4374	<i>wucan</i> vase	end 16 <sup>th</sup> – mid. 17 <sup>th</sup> c.	Private kiln (Jingdezhen)	
MG 5806	<i>wucan</i> vase	mid-later half 17 <sup>th</sup> c.	Private kiln (Jingdezhen)	
G 5687	<i>wucan</i> vase	mid 17 <sup>th</sup> c.	Private kiln (Jingdezhen)	
G 1710	<i>Famille noire/Famille verte</i> Vase	Later half 17 <sup>th</sup> – early 18 <sup>th</sup> c.	Private kiln (Jingdezhen)	“Biyu tang zhi” mark
G 421	<i>Famille verte</i> Vase	end 17 <sup>th</sup> – early 18 <sup>th</sup> c.	Private kiln (Jingdezhen)	
MG 3668	teapot	2 <sup>nd</sup> half 18 <sup>th</sup> c.	Private kiln (Yixing)	
MG 9604	teapot	2 <sup>nd</sup> half 18 <sup>th</sup> c.	Private kiln (Yixing)	
MG 8062	bowl	19 <sup>th</sup> c.	Private kiln (Yixing)	

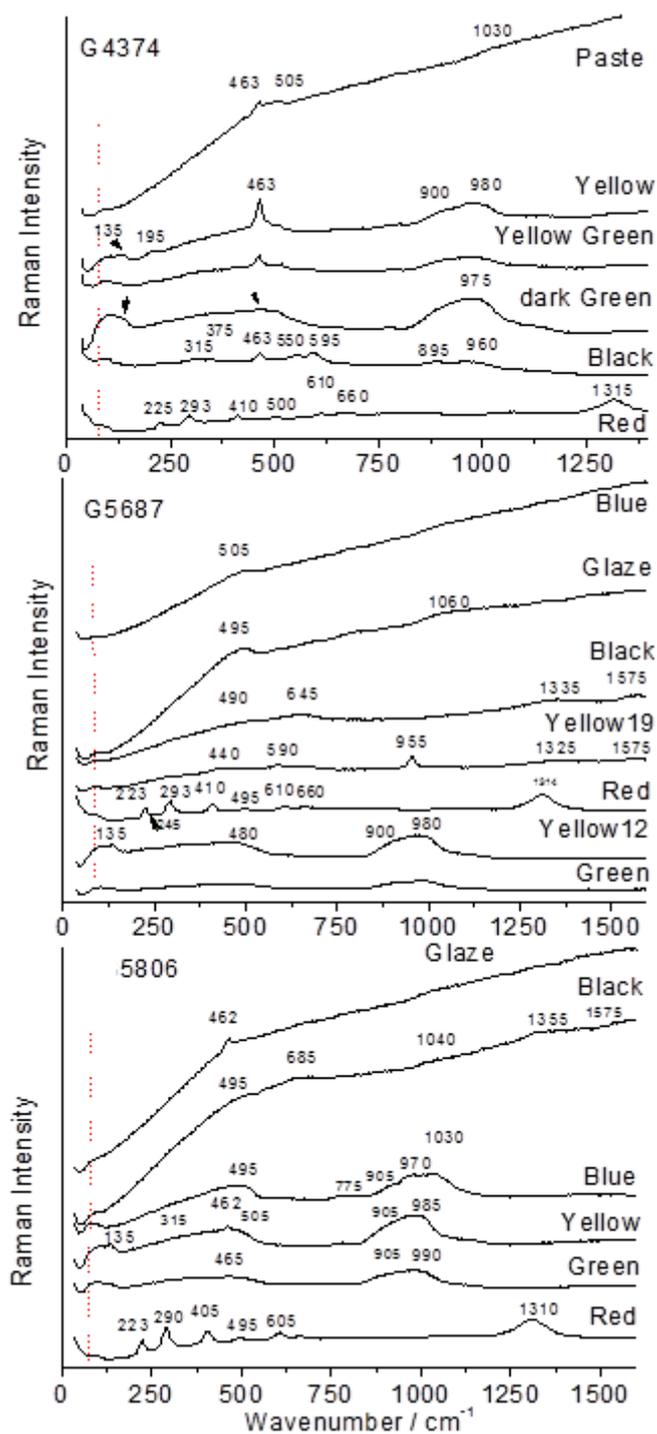
FIGURE CAPTIONS



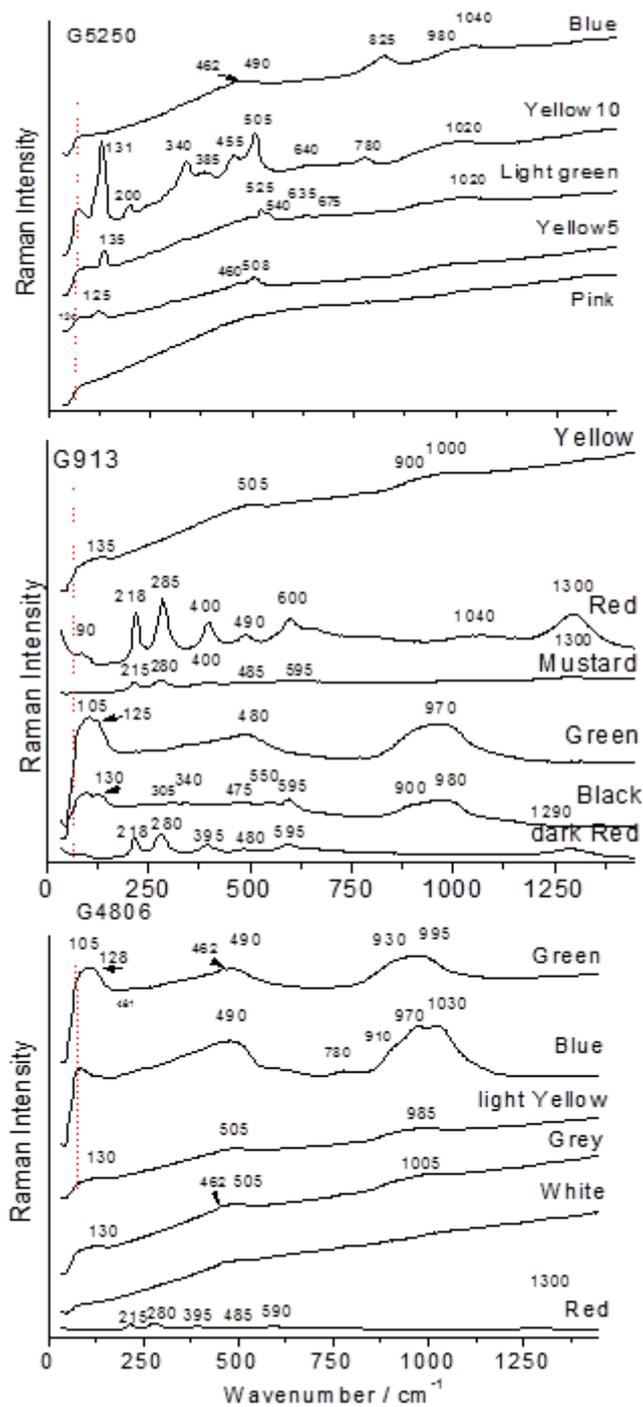
**Fig. 1:** a) Representative Qing Dynasty porcelains made respectively with '*Couleurs transparentes*' (G 5696) and opaque/*huafalang* (G 5250, G 4551 and G 3361) enamels.(see Table 1 and Supplementary Materials for details; b) mobile Raman set-up.



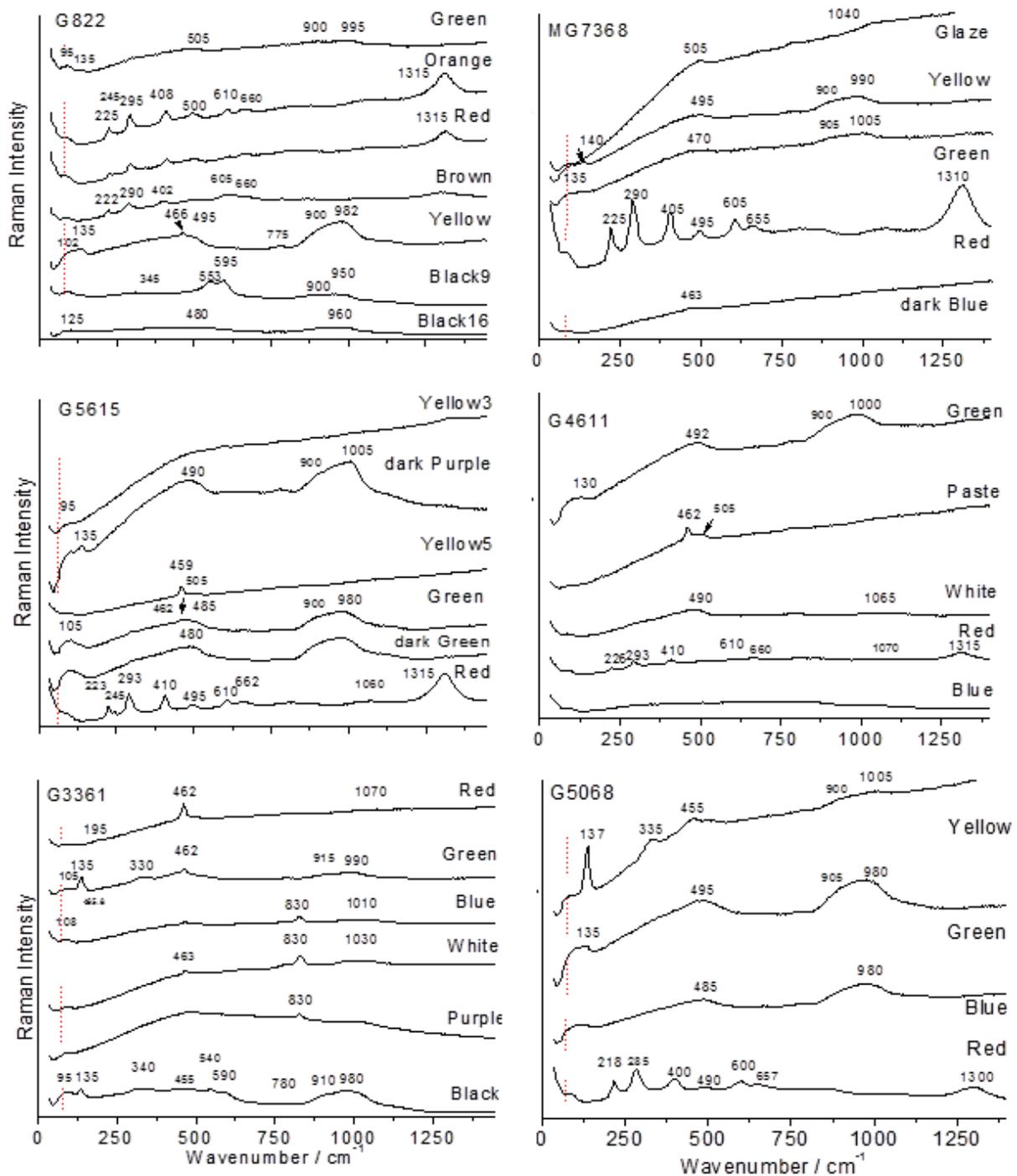
Fig. 2: Studied corpus (see Table 1).



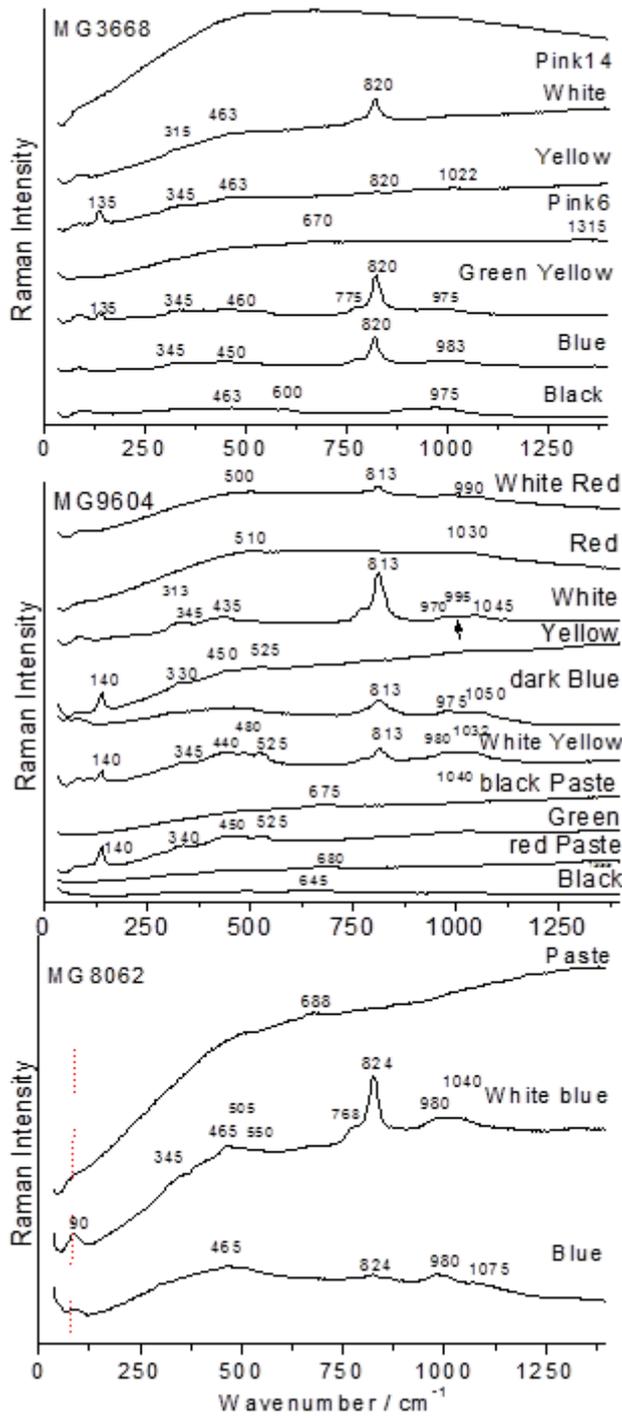
**Fig. 3:** Representative Raman spectra recorded on 17<sup>th</sup> (or earlier) century artefacts (see Table 1 for details).



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



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



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

Supplementary Materials

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

Philippe Colomban,<sup>1\*</sup> Yizheng Zhang,<sup>1</sup> Bing Zhao,<sup>2</sup>

<sup>1</sup>Sorbonne Universités, UPMC Univ. Paris 06, MONARIS UMR8233, 4 Place Jussieu, 75005 Paris, France

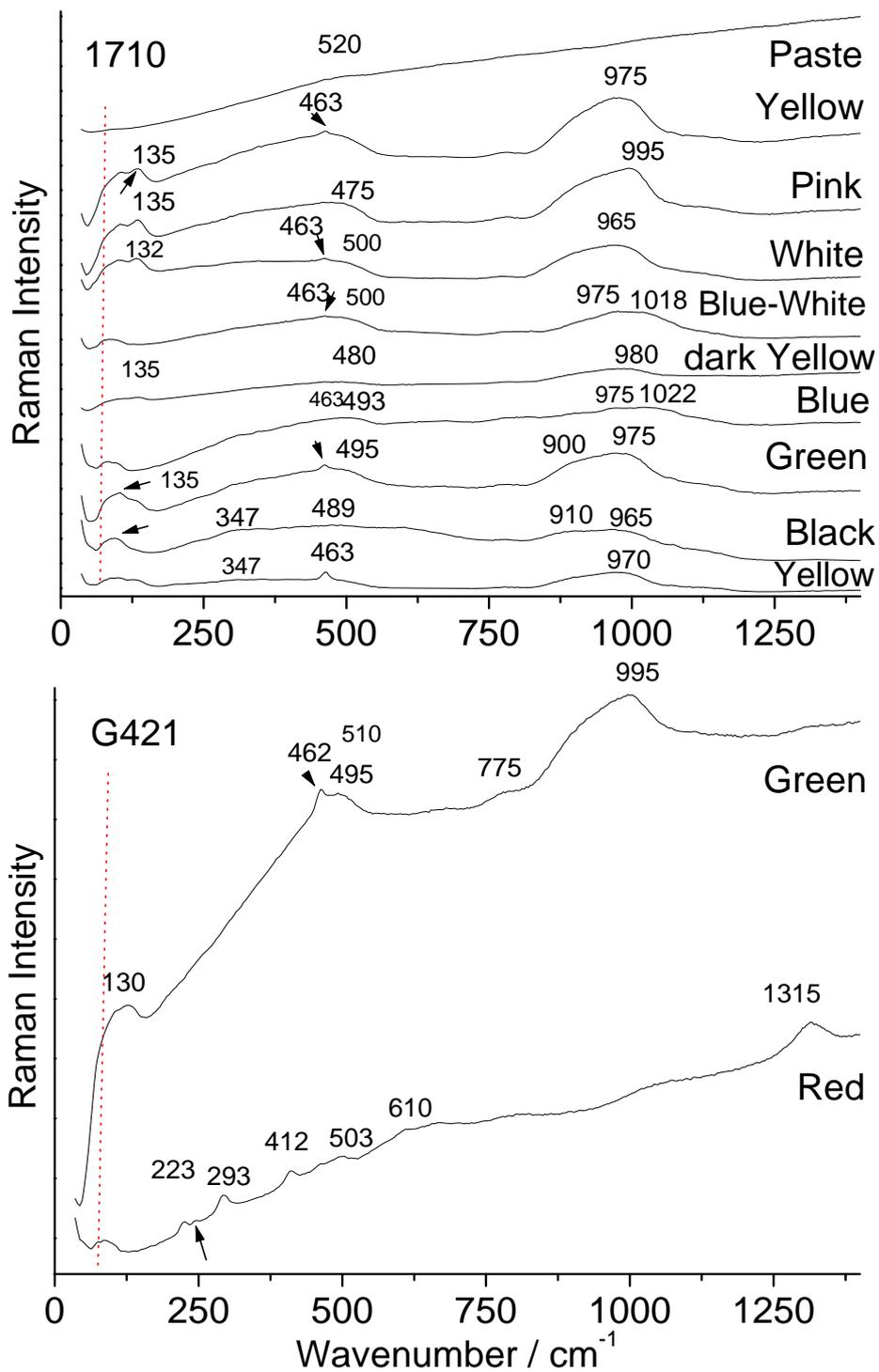
<sup>2</sup>CNRS, Collège de France, CRCAO UMR8155, 52 rue Cardinal-Lemoine, 75005, Paris, France

\*Corresponding author

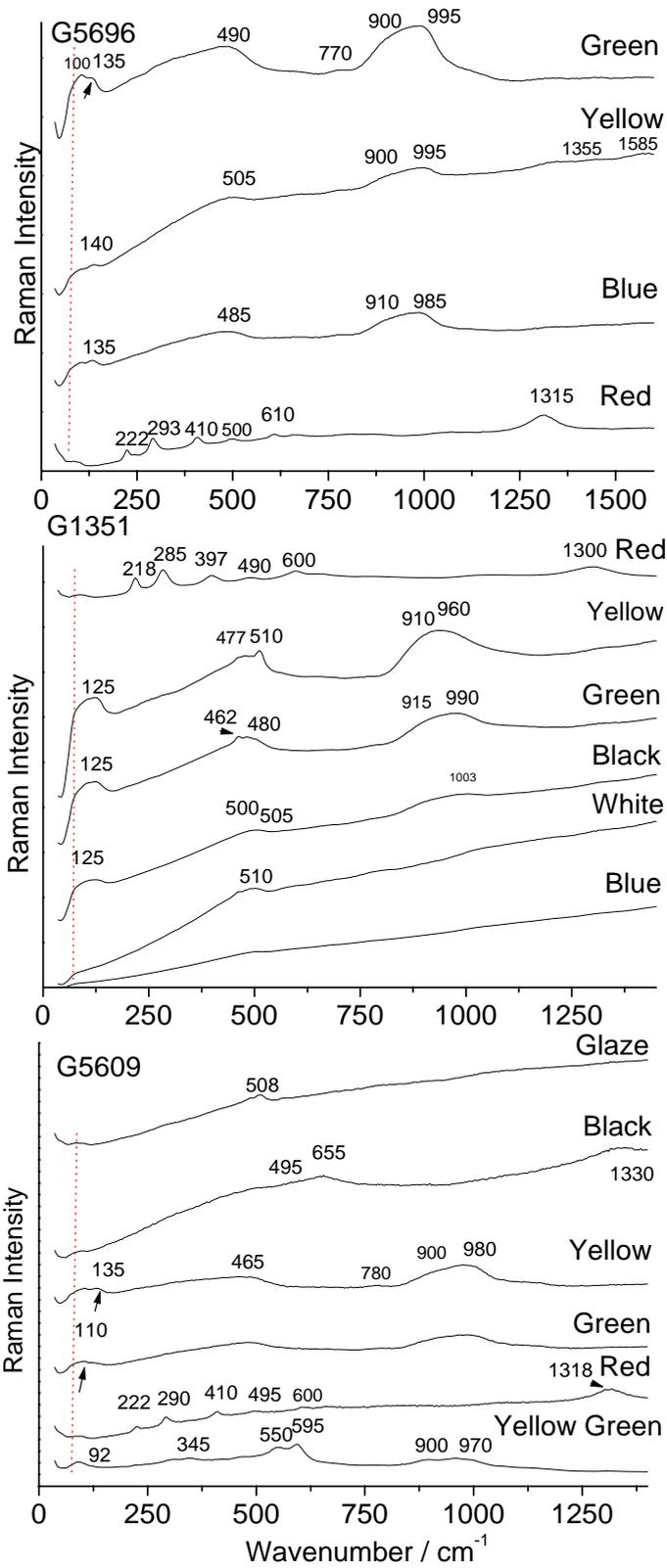
[Philippe.colomban@upmc.fr](mailto:Philippe.colomban@upmc.fr)

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		$\delta$ (cm <sup>-1</sup> )	Matrix $\gamma$ (cm <sup>-1</sup> )	
		Composition	Characteristic Peak Wavenumber (cm <sup>-1</sup> )			
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 <sub>2</sub>	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 <sub>2</sub>	647		
	Yellow 19	Naples Yellow	140	-	-
		Carbon	1324/1576		
		MnO <sub>2</sub>	587		
	Yellow 12	Naples Yellow	140	478	972
	Red	Hematite	223/293/1314	-	-
	Green	-	-	482	972
MG5806	Black	Carbon	1355/1576	-	-
		MnO <sub>2</sub>	655		
	Blue	-	-	493	979/1029
	Yellow	Naples Yellow	136	463	979
	Green	-	-	466	990
	Red	Hematite	223/289/1304	-	-
G5615	Yellow	Carbon	1586	-	-
		MnO <sub>2</sub>	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 <sub>2</sub>	595	463	893/958
		Fe <sub>3</sub> O <sub>4</sub> - Cr <sub>2</sub> MnO <sub>4</sub>	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 <sub>2</sub> SiO <sub>4</sub>	824		

	Blue	Co <sub>2</sub> SiO <sub>4</sub>	820	447	983
	Black	-	-	463	972
G5609	Black	Carbon	1331/1563	-	-
		MnO <sub>2</sub>	655		
	Yellow	Naples Yellow	136	466	975
	Green	-	-	478	986
	Red	Hematite	227/293/1318	-	-
	Yellow Green	Chromate	344	-	900/958
		Cr <sub>2</sub> O <sub>3</sub>	550		
G5250	Blue	Co <sub>2</sub> SiO <sub>4</sub>	823	462/489	1039
	Yellow	PbSnO <sub>4</sub>	131/199/454	-	1018
	Green	Naples Yellow	135	-	1018
		Cr <sub>2</sub> O <sub>3</sub>	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 <sub>3</sub> O <sub>4</sub> -	549	-	979
		Cr <sub>2</sub> MnO <sub>4</sub>			
		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 <sub>2</sub> SiO <sub>4</sub>	827	466	1018
	White	Arsenate	831	466	1028
	Purple	Co <sub>2</sub> SiO <sub>4</sub>	827	477	968
	Black	Fe <sub>3</sub> O <sub>4</sub> -	542	454	979
		Cr <sub>2</sub> MnO <sub>4</sub>			

**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 <sub>2</sub>	42.1	29.0	45.2	45.1	43.3	35.2	29.6
Al <sub>2</sub> O <sub>3</sub>	<b>0.4</b>	<b>0.6</b>	<b>0.7</b>	<b>0.6</b>	<b>1</b>	<b>0.3</b>	<b>1.5</b>
CaO	<b>0.9</b>	<b>0.15</b>	<b>0.35</b>	<b>0.3</b>	<b>0.15</b>	<b>0.8</b>	<b>0.1</b>
MgO	0.05	0.02	0.1	0.1	0.1	0.1	0
K <sub>2</sub> O	<b>6.2</b>	<b>0.2</b>	<b>5.8</b>	<b>2.1</b>	<b>5.7</b>	2.75	<b>0.14</b>
Na <sub>2</sub> O	0.4	0.1	2.7	2.75	2	1.4	0.25
FeO/Fe <sub>2</sub> O <sub>3</sub>	0.3	1.15	0.5	0.15	0.2	0.4	0.2
TiO <sub>2</sub>	~0	0.02	-	-	-	-	-
P <sub>2</sub> O <sub>5</sub>	0.02	~0	-	-	-	-	-
PbO	<b>47.8</b>	<b>66.2</b>	<b>38.4</b>	<b>47.3</b>	<b>43.2</b>	<b>57.5</b>	<b>67.1</b>
CoO	0.2		0.30.1				0.25
CuO		6					0.05
SnO <sub>2</sub>	0.3		-	0.2	0.1	2	-
As <sub>2</sub> O <sub>5</sub>			<b>1.4</b>	<b>0</b>	<b>4.3</b>		<b>0</b>
Au				0.1			-
MnO <sub>2</sub>					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



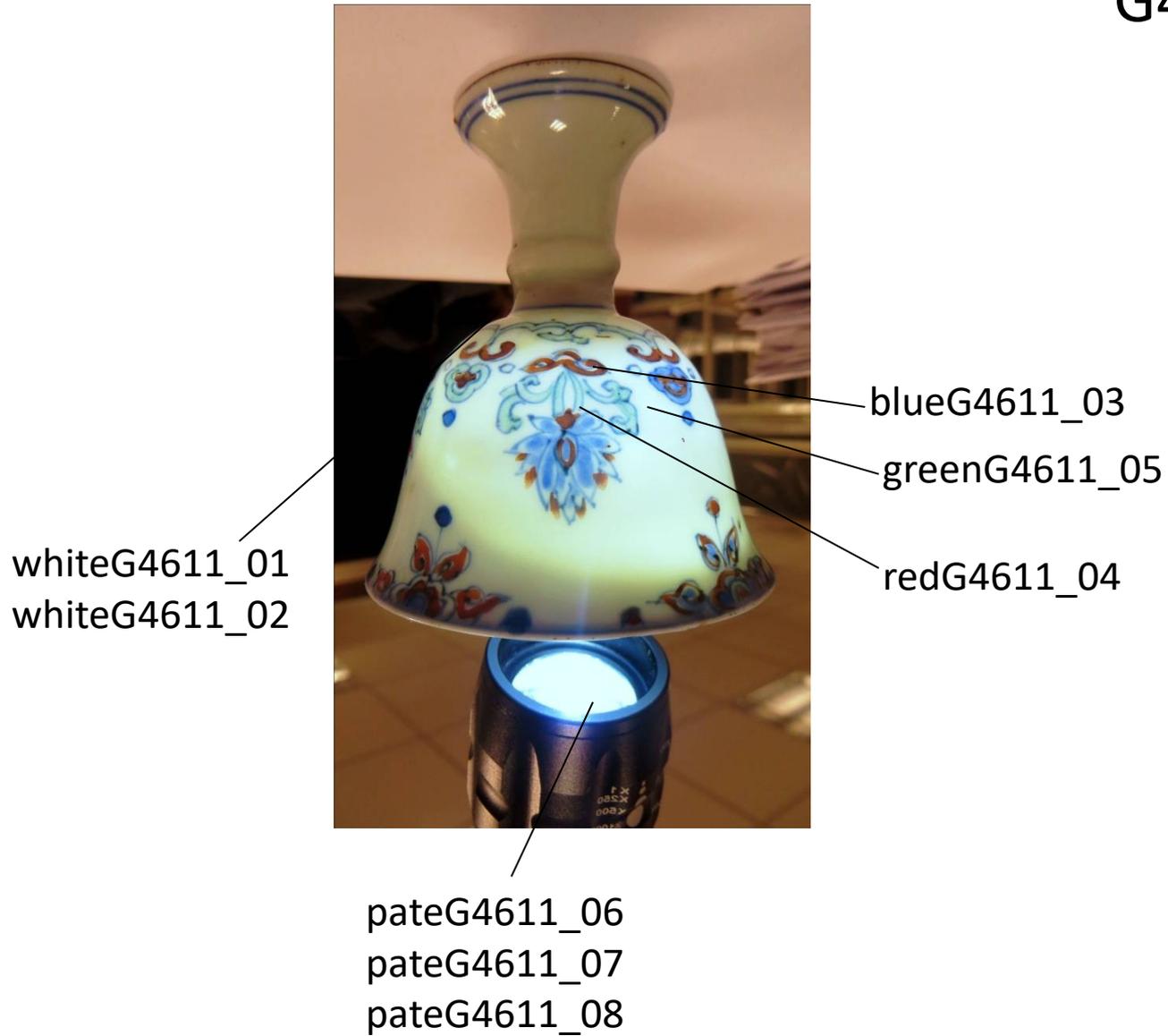
G5068blue\_05  
G5068blue\_06

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

YxMG9604green\_1

YxMG9604black\_13 YxMG9604green\_2

YxMG9604black\_14

YxMG9604black\_15

YxMG9604white-red\_8

YxMG9604red\_7

YxMG9604green\_6

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