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Coteau's jewelled porcelain, a summit of ceramic art: An on-site Raman and pXRF study



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Background and Scope of the Study

The gilt-decorated porcelains of Joseph Coteau (1740–1801) and Philippe Parpette (1738–1806) unifying metal and ceramic enamel techniques have been produced from ~ 1770 to 1800 but this type of production is rare and poorly documented. Enamelled decorations of these objects display gold foils (“*paillons*”) coated with lead-based transparent and opaque enamels fired on the porcelain glaze. Rare items were produced at different factories (Sèvres Royal Factory, Comte d’Artois Factory) and it is reported that some copies were made during the 19th century [1-2].

We present here the first non-invasive Raman study of four cups and two pairs of vases (also analysed by pXRF) belonging to the productions of these factories, made by Coteau or Parpette. The decors made of enamel on gold foil (“*paillon*”) were applied both on soft-paste and hard-paste porcelain body.

The characterization of the enamels and glazes of gilt-enamelled porcelains is significant in terms of addressing the question of the link between metal and porcelain enamelling techniques during the 18th century and may potentially offer criteria of identification for distinguishing artefacts produced at different time periods [3].

[1] R. De Pinval de Guillebon, Un phénomène périodique: la mode du décor d’or appliqué et d’email sur la porcelaine française (XVIIe-XIXe siècles), *Rev. Soc. Amis Sèvres* 1, 7-22, 1992

[2] T. Preaud, Sèvres enameled porcelain: Eight dies (and a quarrel) rediscovered, *The Burlington magazine* 128[999], 390-39, 1986

[3] P. Colomban, B. Kirmizi, J-B. Clais, M. Gironda, An on-site Raman and pXRF study of Joseph Coteau and Philippe Parpette's jewelled porcelain: a summit of ceramic art, *Journal of Cultural Heritage*, 46, 82-94, 2020

Analytical Techniques

- Mobile Raman set-up (HORIBA Jobin-Yvon Longjumeau France)
 - 532 nm Ventus 300 mW laser (Laser Quantum, Fremont, CA, USA) and x50 long wd objective (NIKON France SAS, Champigny-sur-Marne, France), x200 long wd objective (Mitutoyo)

Advantages:

- high spatial resolution (in μ scale)
- contactless usage
- the structural information obtained for crystalline matter/ glassy phases.

- Portable Elio XRF instrument (XGLab Bruker, Italy)

- 40 kV tube voltage, 100 μ A current, 40 s acquisition time

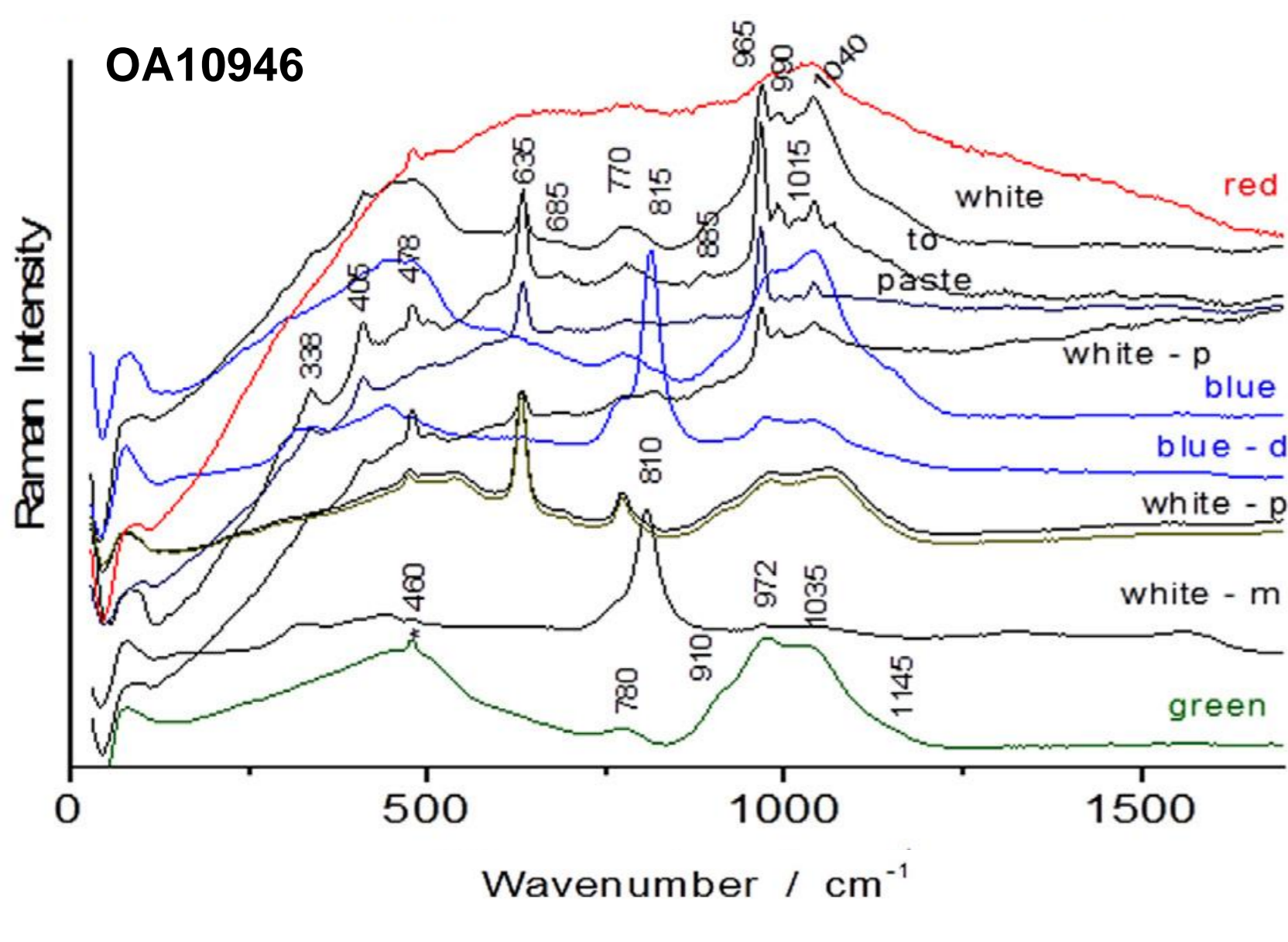
Advantages:

- non-invasive elemental analysis
- fast data collection

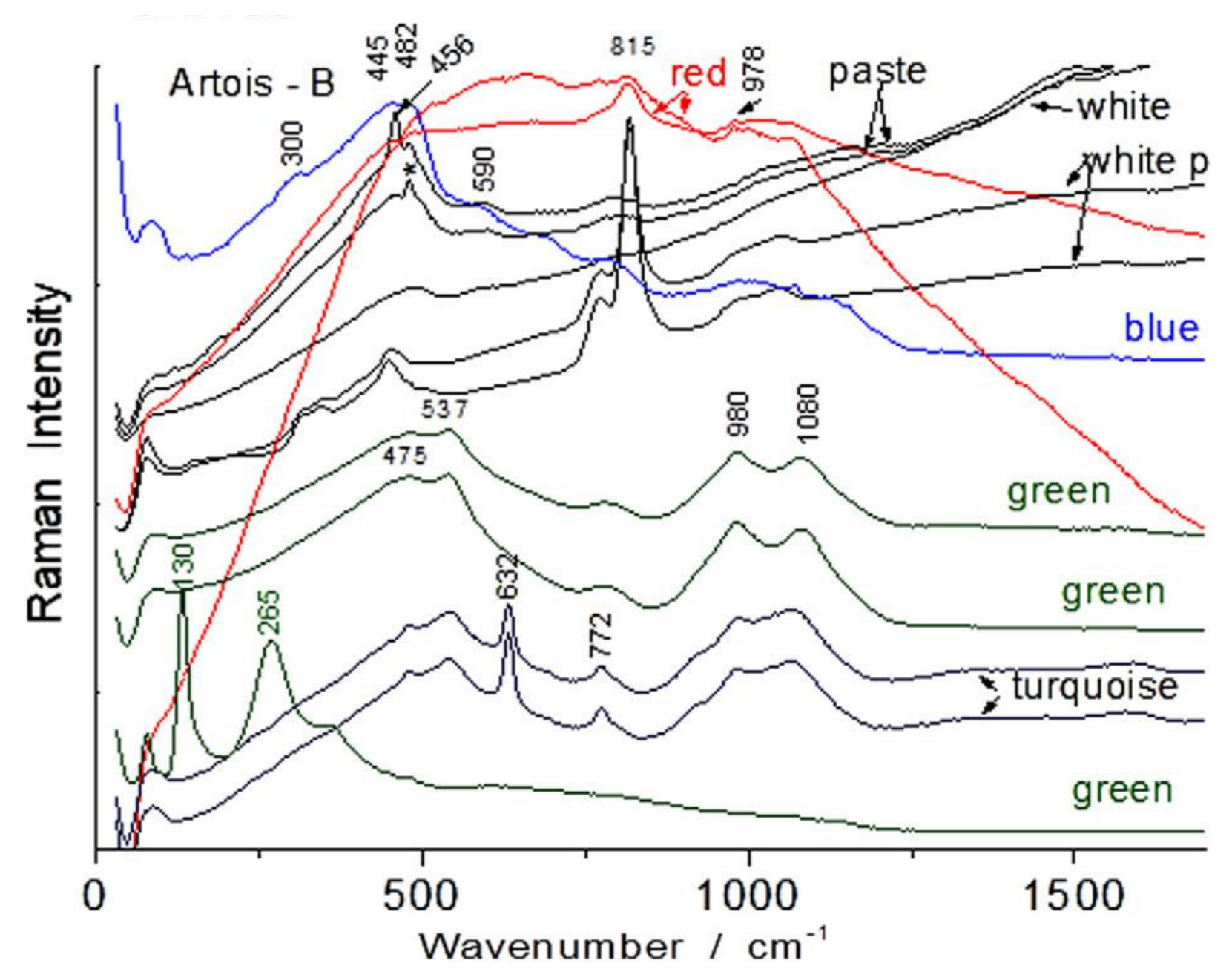


Sèvres Factory vase (OA10946) with CC mark (1780)
H:40 / D:16 cm

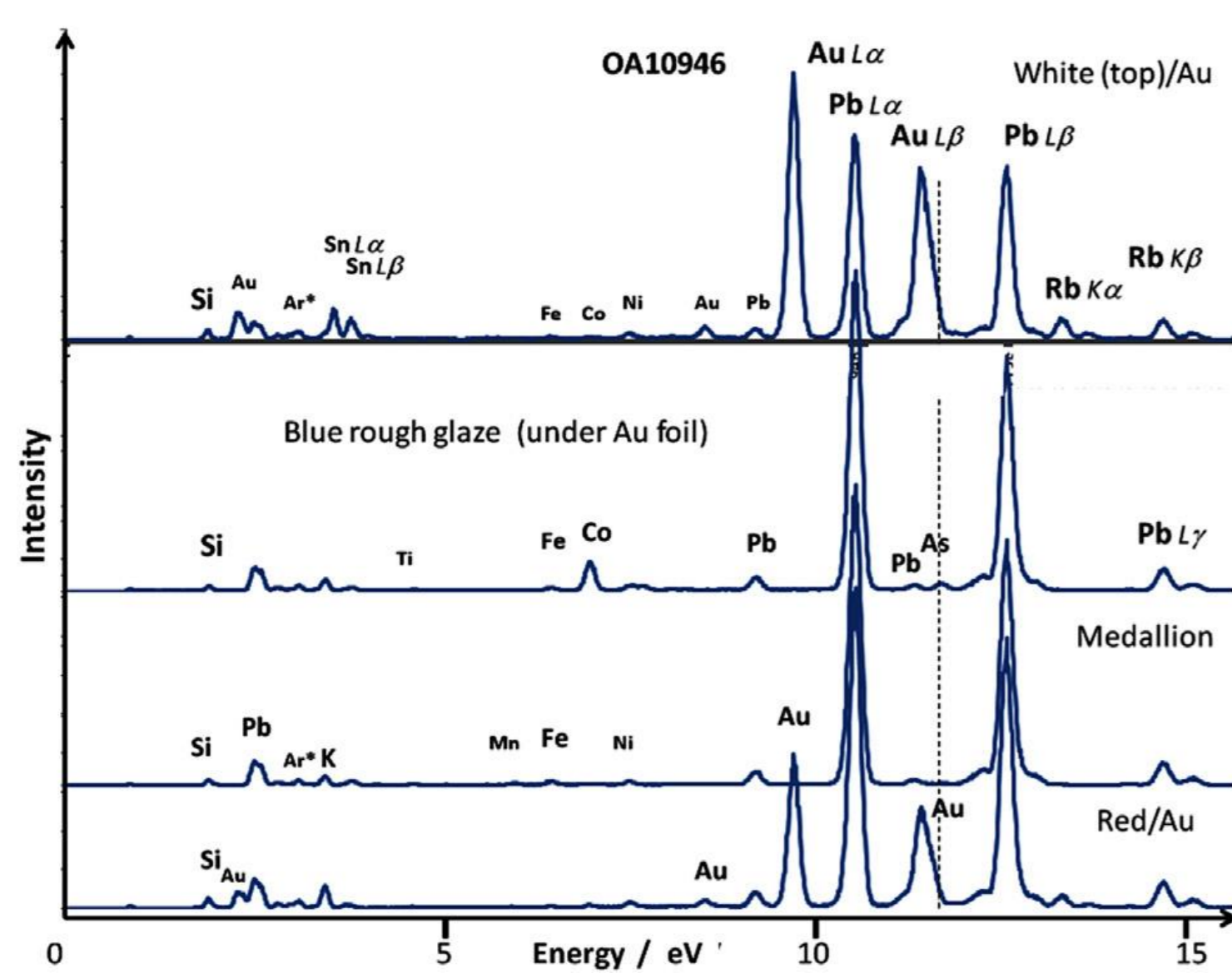
Comte d’Artois Factory vase (OA7739) with “coteau” in red and “Cuit au charbon de terre” in black marks
H:34.5 cm / L: 22 cm



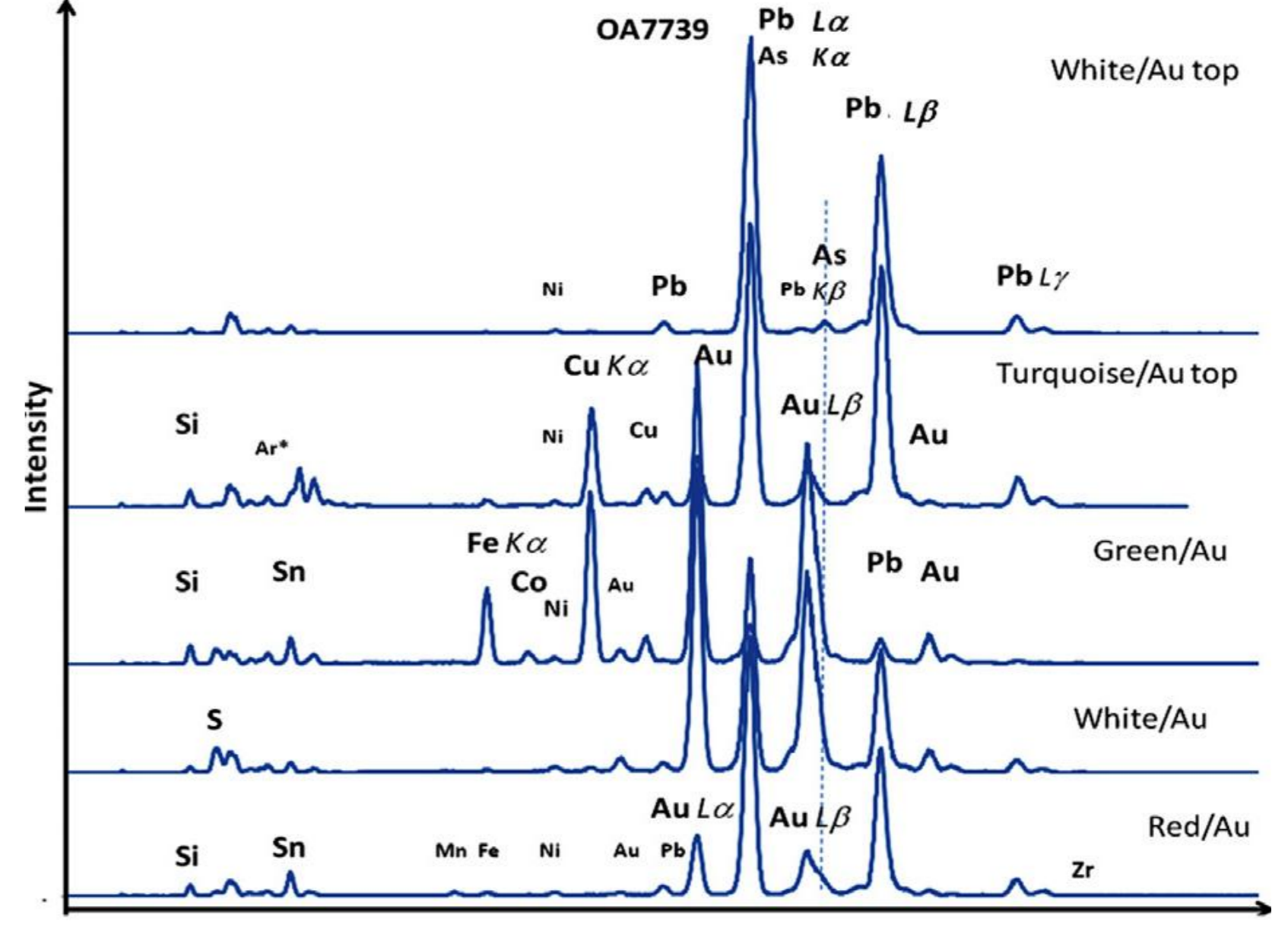
Representative Raman spectra recorded on the Sèvres vase (OA10946) (p: bead on gold foil; d: area under (lost) gold foil; m: medallion)



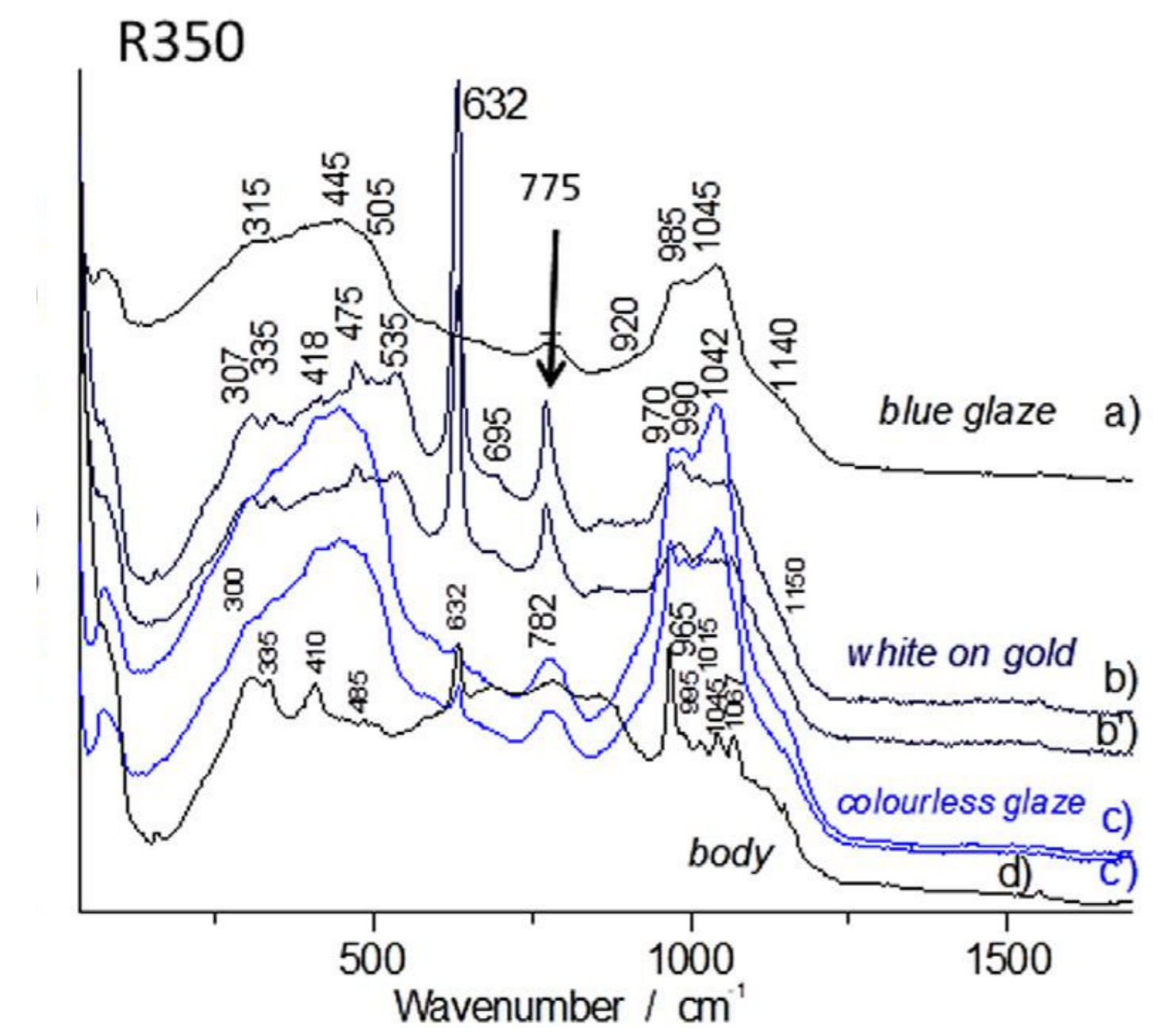
Representative Raman spectra recorded on the Comte d’Artois vase (OA7739) (p: bead on gold foil décor)



Representative XRF spectra recorded on the glaze and enamels of the Sèvres vase



Representative XRF spectra recorded on the glaze and enamels of the Comte d’Artois vase



Representative Raman spectra recorded on the glazes and white enamels of the R350 cup

Results-Discussion

- Glassy Si-O Matrix**
 - All the cups and the vase-OA10946 (Sèvres Royal F. mark): variations of lead-alkali type of glaze with ~ 970-1000 / ~ 1040-1080 cm^{-1} doublet
 - A-type: the strongest component at ~1065 to 1080 cm^{-1}
 - B-type: the strongest component at ~1040 to 1050 cm^{-1}
 - The vase-OA7739 (Comte d’Artois F.): broad band peaking at 450–500 cm^{-1} → hard-paste aluminosilicate glaze
- Enamels**
 - OA10946: Cassiterite (635-770 cm^{-1}) @ white enamel beads
Lead arsenate (810 cm^{-1}) @ white surface of the medallion
 - OA7739: Lead arsenate (815 cm^{-1}) @ white and red enamel beads
Cassiterite (632-772 cm^{-1}) @ turquoise enamel beads on the top
 Au^0 nanoparticles (fluorescence + 815 cm^{-1}) @ red enamel prepared by Perrot’ method.
- R350 cup was made using a technique different from the other cups, with its glaze and enamels having similar glass compositions. A regular 18th century production at Sèvres Factory is doubtful since the factory mark at the back side is not usual. Cassiterite was used as opacifier in the white and red enamels of this cup, indicating a possible Coteau production but with a mark applied after or a 19th century copy.
 - OA7739 vase shows the use of two opacifiers, cassiterite for turquoise enamel beads and lead arsenate for white enamels close to the foot and top of the vase. The latter decor should have been added after to adapt the decor with the addition of bronze handle pair.

Perrot’ technique

Bernard Perrot was a renowned glassmaker in the 17th century France. His particular method of producing red (ruby) glass includes the precipitation of gold nanoparticles from the acid solution with the use of As-salt which remains with colloidal Au^0 particles dispersed in the glassy matrix. The use of As-salt is confirmed by the presence of the specific As-O mode at ~ 810 cm^{-1} in the Raman spectrum of red glass/enamel [4].

This method differs from the more common technique of using tin salt for the precipitation of colloidal gold, as practiced by the German chemist J. Kunckel (the so-called Cassius purple).

[4] P. Colomban, B. Kirmizi, Non-invasive on-site Raman study of polychrome and white enamelled glass artefacts in imitation of porcelain assigned to Bernard Perrot and his followers, *Journal of Raman Spectroscopy*, 51(1), 133-146, 2020

Conclusion

The on-site Raman and pXRF study of J. Coteau and/or P. Parpette possible productions was able to characterize the different materials and enamelling techniques used, despite the limited number of studied artefacts. Assignments to possible Coteau/Parpette productions were discussed based on historical information, factory marks and the results of spectroscopical analysis, regarding the glass compositions used and the opacifiers.

❖ C. Gougeon from Musée du Louvre, is kindly acknowledged for her help in the managing of measurements.



Jewelled cup (R350) with CC mark (1780)
H: 40 / D:16 cm