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## 20 Years of on-site Raman Analysis of rare works of arts: Successes, Difficulties and Prospects

Philippe Colombar

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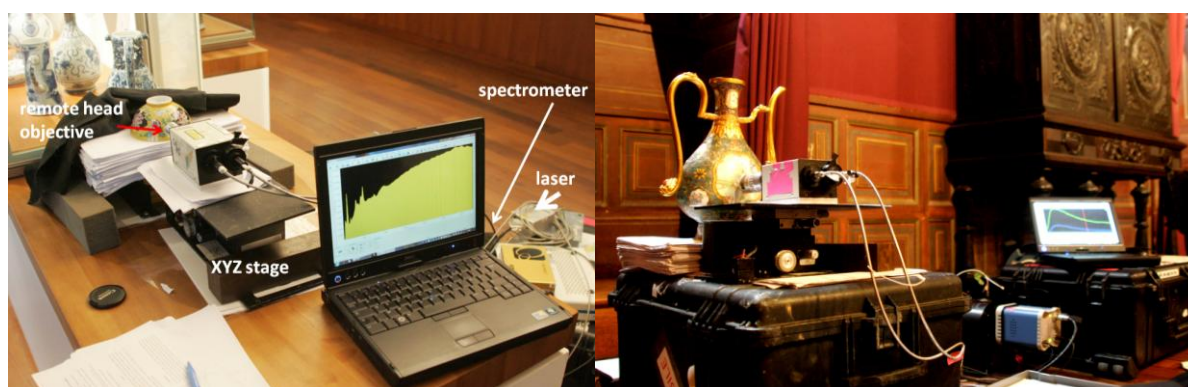
# 20 Years of on-site Raman Analysis of rare works of arts: Successes, Difficulties and Prospects

**Philippe Colomban<sup>1</sup>**

<sup>1</sup> MONARIS UMR8233, Sorbonne Université, CNRS, 4 Place Jussieu, 75005 Paris (France)  
email: [philippe.colomban@sorbonne-universite.fr](mailto:philippe.colomban@sorbonne-universite.fr)

**Keywords:** multivariate analysis; colours; on-site; mobile instruments; authentication; optics

The study, in particular of the state of conservation, and the authentication of works of art are issues in full development and Raman microspectroscopy in conjunction with X-ray fluorescence are the reference techniques due to their perfectly non-invasive character, and the availability of mobile instruments. Although mobile instruments have been available for more than 20 years, their use has only recently exploded with the tightening of formalities allowing the movement of valuable objects and changes in practices. Our team having been among the first to develop the Raman analysis of works of art, whether in the laboratory with the development of the MOLE in 1975 at LASIR [1,2] and on site from the 2000s [3, 4] at the same time of David Smith at MNHN, Paris [5], we will focus the presentation on fire arts objects, most of which are enameled (metal, glass or ceramic). These sophisticated objects were technological achievements at their time of production, made for the elite, traded very early on at long distance, and their value which can reach now several millions of € imposes on-site and non-invasive procedures. Except for the identification of gems and some minerals [6,7], their Raman analysis requires the use of high-performance due to the simultaneous presence of vitreous phases generating a signature of broad bands and crystalline phases giving narrow peaks but mainly at low wavenumbers.[4,5,8-10] With the development of particular procedures (use of sophisticated optics (very high magnification, zoom and telescope)[11-13], micrometric stages/mapping, subtraction of the continuous background, dating from proton corrosion[14], multivariate analysis [5,15]) and an understanding/modeling of the spectra [16], the parameters of processing (temperature) are deduced [5-8] and restorations/fakes/copies are identified. The combination with on-site pXRF analysis/mapping is highlighted [17-21] as well as the interest of measuring full spectral range in order to use information present in the 'fluorescence' background.[22] Difficulties (limitation in the choice of exciting wavelength, control of the ambient temperature and lighting, preservation of the artifact, limited access time for measurement, etc.) and future developments (on-site mapping, multiscale analysis, etc.) will be discussed [23].



**Figure 1** Examples of On-site Raman analysis using a mobile set-up.

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 AAA 2023  
6-9 September 2023, Athens

**20 years  
of on-site Raman analysis  
of rare works of art:  
successes, difficulties  
and prospects**



**Monaris UMR8233** Laboratory,  
**Sorbonne Université, Paris, France**



*From molecule to nano-object: Reactivity, Interactions & Spectroscopies*

# Outline

1. Why on-site analysis using mobile set-up
2. Instruments: Raman studies of Cultural Heritage masterpieces  
an historical overview (1975 –present)
3. Required Procedures, difficulties and modeling : example: understanding the Raman signature of glassy and crystalline silicates / pigments / opacifiers
  - Authentication: stained glass windows
  - Conservation : rock art
  - History of Art & Technique :Tracing the technological exchanges between Europe and Asia
    - blue colour
      - Lapis lazuli or cobalt
      - Glass type
4. Conclusions & perspectives

# 1. Why on-site analysis using mobile set-up

- **Exceptional artifacts located in secure room**

*Bibliothèque Nationale, Paris, Grandes Heures de Rohan  
ca 1430-1435, Expected value : > 5 million €*



*Musée national des Arts asiatiques - Guimet  
Imperial bowls, ca 1720-1750, > 3 million € each*



*Louvre, Arts déco, Cernuschi, etc.  
Fondation Baur (Genève),  
Galeria nazionale di Arte Moderna (Roma), etc.*

- **Unmovable Artifacts**

*Rock art, Drakensberg South Africa*

*Stained glass windows*

*Sculpture, buildings, etc.*



**Drakensberg  
South Africa**



**Ste-Chapelle  
Paris**



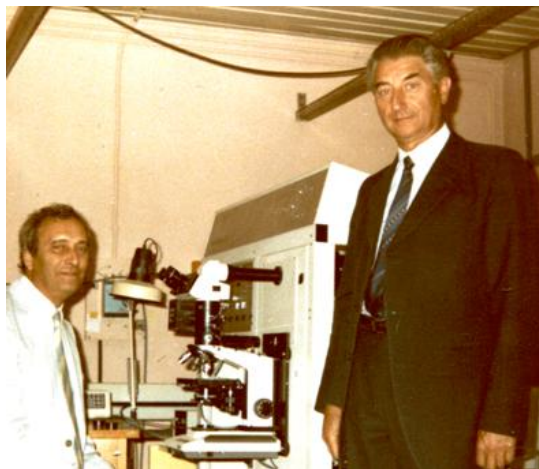
**Objectives:** authentication, documentation  
conservation

# Outline

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Broad band spectra !

## 2 Raman studies of Cultural Heritage masterpieces : an historical overview (1974 –present)



Professor Michel Delhaye (right) presenting one of the first microprobe equipped with optical microscope (MICRODIL 28, DILOR) and a RQticon512S linear diode array detector cooled at -200°C by Peltier Effect, at LADIR CNRS, Thiais (ca 1980)

Colomban Ph. (1979). Une nouvelle technique d'analyse: la microsonde Raman, *L'Industrie Céramique*, 734, 815-820.

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Michel Delhaye & Paul Dhamelin court (LASIR CNRS) were the first to build a Raman microprobe; the **MOLE (Molecular Optic Laser Examiner)** started to be commercialized in 1976 by Instrument SA Jobin-Yvon (now HORIBA Scientific)

Rapidly, replacement of the PM by a diode array detector (DILOR OMARS, MICROMARS and MICRODIL 28) and then CCD (XY DILOR, LABRAM)



Jehlicka & Culka (2022), Critical evaluation of portable Raman spectrometers: From rock outcrops and planetary analogs to cultural heritage – A review, *Anal. Chim. Acta*, 1209, 339027

**LABRAM Infinity**

YAG 532nm

He 633nm

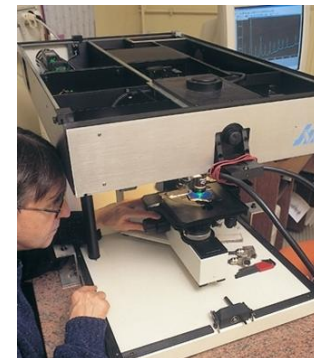
End of 1990s

Transportable

High resolution

> 80 cm<sup>-1</sup>

Flat background



>2010

Variety of compact, Palm-held instruments (green to nIR laser)

Poor to medium resolution > 200 cm<sup>-1</sup>



# The first steps

2003

## 3- Air-cooled laser



2 optic fibers => spectrometer  
<= laser 2x3 m

HE 532 JY

Microscope objective  
x500, 800 or 1000



## 2- Remote head

SuperHead®

X-Y-Z

Laser : 532nm 100mW

## 1- Spectrometer : fixed parts, Peltier-cooled CCD

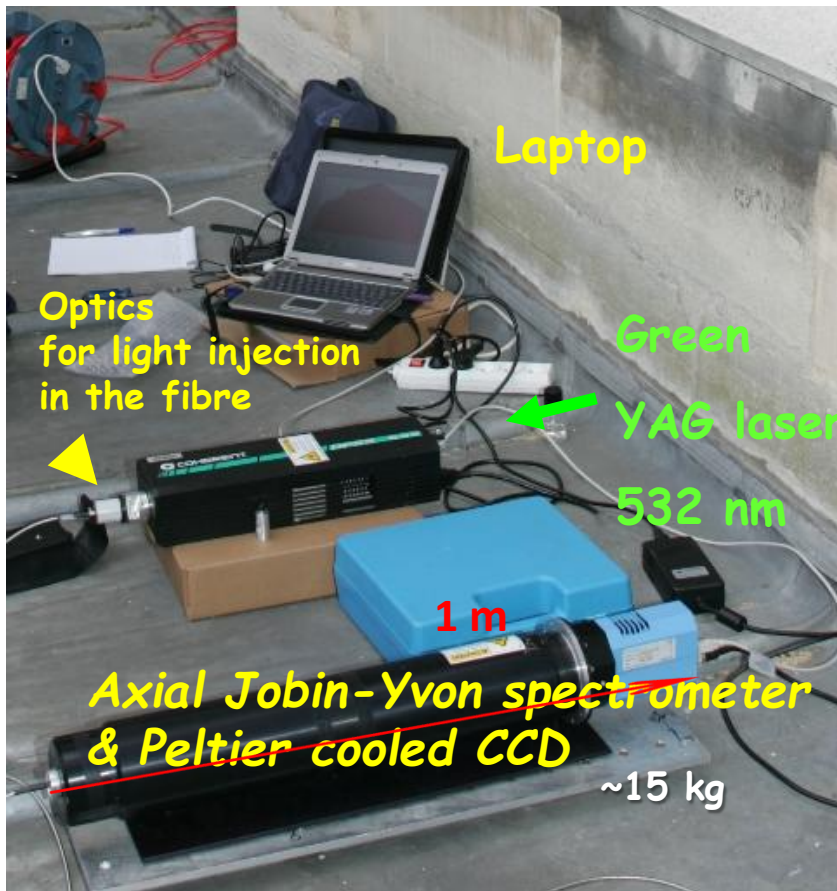
*Musée national de Céramique, Sèvres*

Broad bands, heterogeneous materials  
high magnification, thick film

Ph. COLOMBAN, V. MILANDE, L. LE BIHAN  
On-site Raman Analysis of Iznik pottery glazes and pigments  
J. Raman Spectrosc. 35 (2004) 527-535.

Horiba Jobin Yvon

2x10m long fiber optics, 25m of electric cable



2005

High resolution  
Flat background  
>250 cm<sup>-1</sup>



difficulty of  
access by  
narrow  
spiral staircase

Broad bands, sunlight, access

Outside



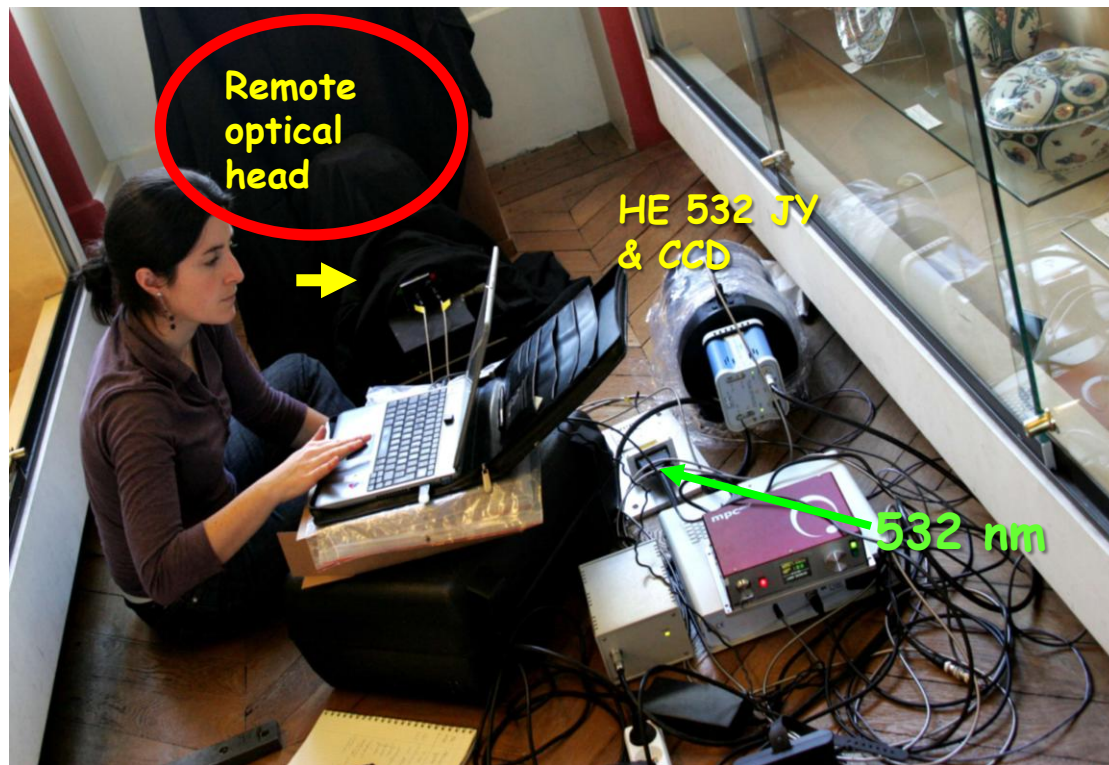
Inside



Sainte-Chapelle, île de la Cité, Paris

Ph. COLOMBAN, A. TOURNIE  
On-site Raman Identification and Dating of  
Ancient/Modern Stained Glasses  
at the Sainte-Chapelle, Paris.  
J. Cultural Heritage 8 [3] (2007) 242-256.

## > 2007 : compact set up



High resolution  
Flat background  
>80 cm<sup>-1</sup>

Laser Quantum  
Ventus 100/300 mW  
&  
CCD and shutter boxes

Main characteristics  
able to record  
broad band  
Raman signatures  
(e.g. glass)

*Musée national de Céramique, Sèvres*

P. RICCIARDI, Ph. COLOMBAN, A. TOURNIE, V. MILANDE

Non-destructive on-site identification of ancient glasses: genuine artefacts, embellished pieces or forgeries ?

J. Raman Spectrosc. 40 (2009) 604-617.

# High performance long working distance optics

No contact - measurements on concave surfaces - micron spot

NIKON  
x50 ( $\Leftrightarrow$  magnification 500)  
1000€ HT

also  
x10 (100)  
sd  $\sim 30\mu\text{m}$   
p  $\sim 50\mu\text{m}$

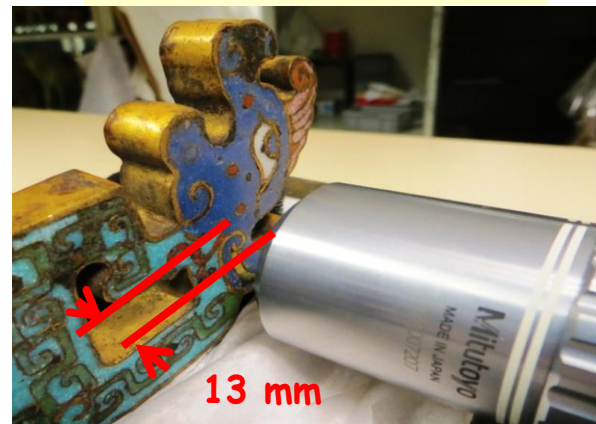


spot diameter  $\sim 4\mu\text{m}$   
Along z up to  $15\mu\text{m}$   
easy focus

A precise  
adjustment  
at  $1\mu\text{m}$  scale  
requires a  
stable  
XYZ stage



Mitutoyo x50 or  
x200 ( $\Leftrightarrow$  magnification 2000)  
8000€ HT



spot diameter  $\sim 0.5\mu\text{m}$   
(close to the limit of diffraction)  
along z  $\sim 2\mu\text{m}$   
focus adjustment  
time consuming



# Adapted laser source(s) power (and protection from solar/bulb light) (10 to 30 mW laser beam at the sample) *easier job if the peaks are narrow*

No darkness => work on evening/night  
=> high laser power: x10 to 100 times  
more than at the lab!

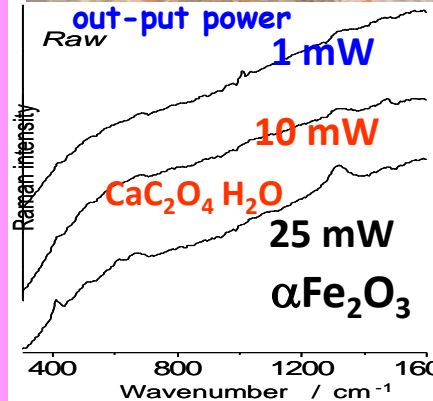


South Africa, San rock art  
RSA BU1, Eastern Cap

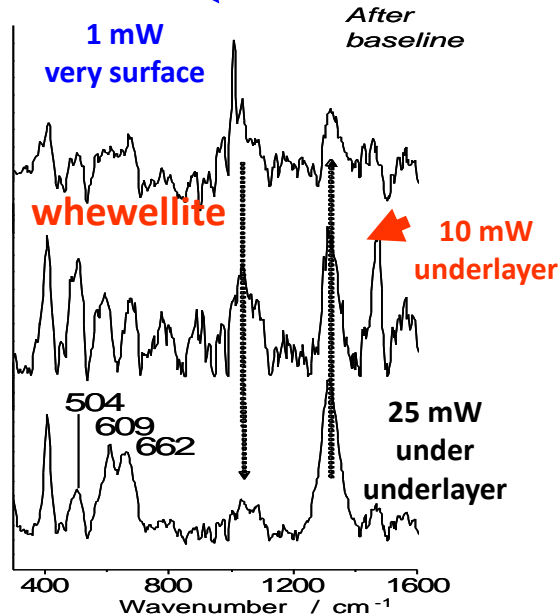
Efflorescence:

many layers cover the painted Layer

In-depth analysis requires increasing Laser power



Gypsum surface



in depth analysis : focus & power  
Pigment & surface deposits

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Authentication: stained glass windows  
Conservation  
History of Art & Technique: Tracing the technologies exchanges / blue colour
  - Lapis lazuli or cobalt
  - Glaze type. When Europe taught enamelling to China and Japan
4. Conclusions & perspectives

# Standard colorant agent of glass: $\text{Co}^{2+}$ ions and Co-rich spinel/olivine pigments

Cobalt not detected by EDS/XRF in some blue glass, but 0.05 wt% is sufficient to color a glass

## Lapis lazuli cannot be identified by elemental analysis !

green  
to  
blue  
Laser

Resonance  
Raman  
Effect

$\text{Co}^{2+}$  &  $\text{S}_n^-$

Only under UV laser  
the Raman signature  
of the host framework  
is recorded

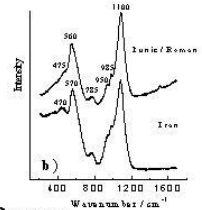
### 1<sup>st</sup> evidence:

Clark, R.J., Curri, M.L., Laganara, C., 1997. Raman microscopy: The identification of lapis lazuli on medieval pottery fragments from the south of Italy. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 53(4), 597-603.

### Ewer, 13<sup>th</sup> Lapis lazuli as unexpected blue pigment in Iranian Lâjvardina ceramics



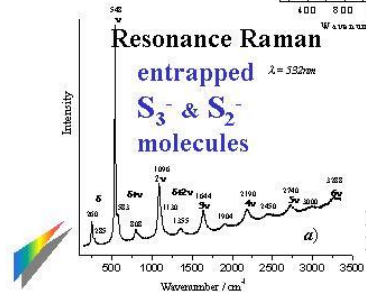
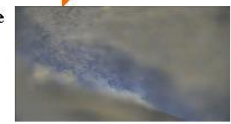
Abû'l Qâsim Kâshani alchemist's treatise 14<sup>th</sup>



Body / glaze x 100



x 1000



Calcium-rich glaze  
Si 70.5 at%  
Ca 14.7 at%  
Co 0.9 at%  
(Ni, Cr, Zn)

Lapis lazuli = lazurite + diopside  
Ph. Colomban, *J. Raman Spectrosc.* 34 (2003), 420  
Improve the blue shade

Lapis lazuli evidenced in  
Ptolemaic glass/glaze  
1<sup>st</sup> c BCE (Egypt)  
Roman glass  
1<sup>st</sup> c. BCE (Pompei)  
13<sup>th</sup> c. Normand Court  
(Sicilia, Apulia)  
14<sup>th</sup> c. Iran  
14<sup>th</sup>-15<sup>th</sup> c. Mamluks  
18<sup>th</sup> Meissen Saxony

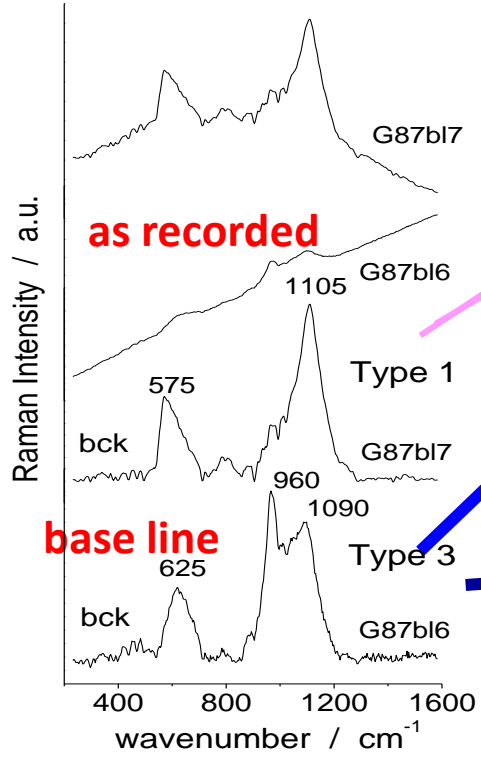
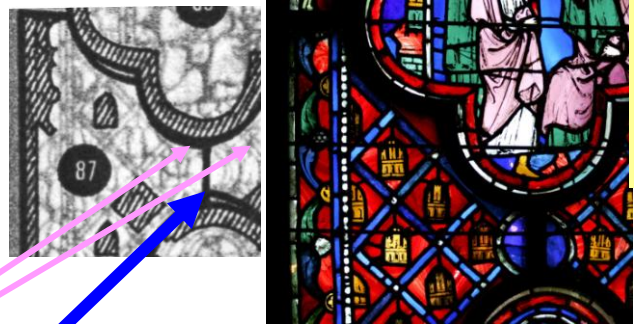
both Co & lapis lazuli



CVMA (historians)  
Corpus vitraerum Medii Aevi  
Attribution (googles)  
Dashed = 19<sup>th</sup> c. restoration

L. Grodecki et al.: white: medieval; dashed: 19<sup>th</sup> c.  
Stylistic visual examination, 1950

Built 13<sup>th</sup> century  
Destruction of the basement  
of stained glass windows  
during French Revolution (~1790)  
Restoration ~1870 by taking  
pieces everywhere +  
addition of new pieces

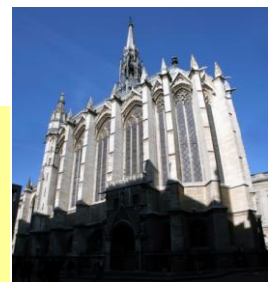


Na-glass 19<sup>th</sup> c.

K-glass 13<sup>th</sup> c.

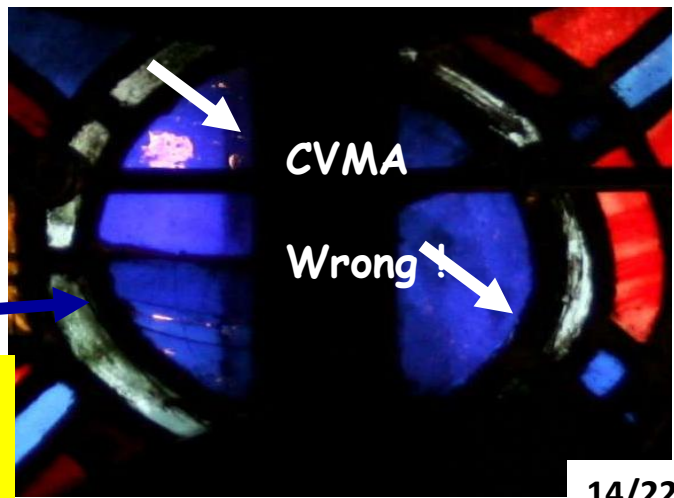
50% wrong !

St Louis  
(Louis IX)  
Christ Passion  
Relics  
reliquary

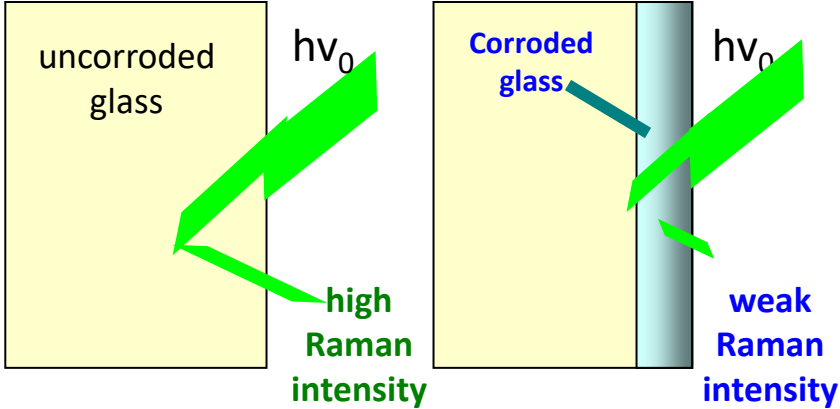
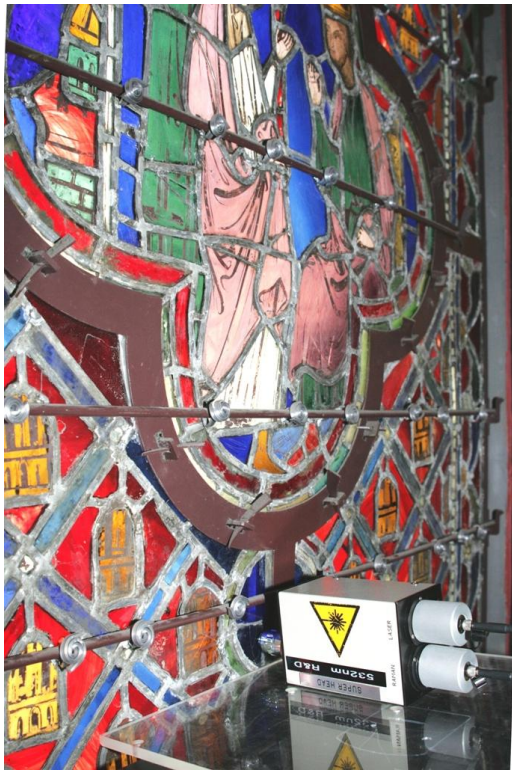


signature &  
intensity

K-glass  
original  
Middle-age

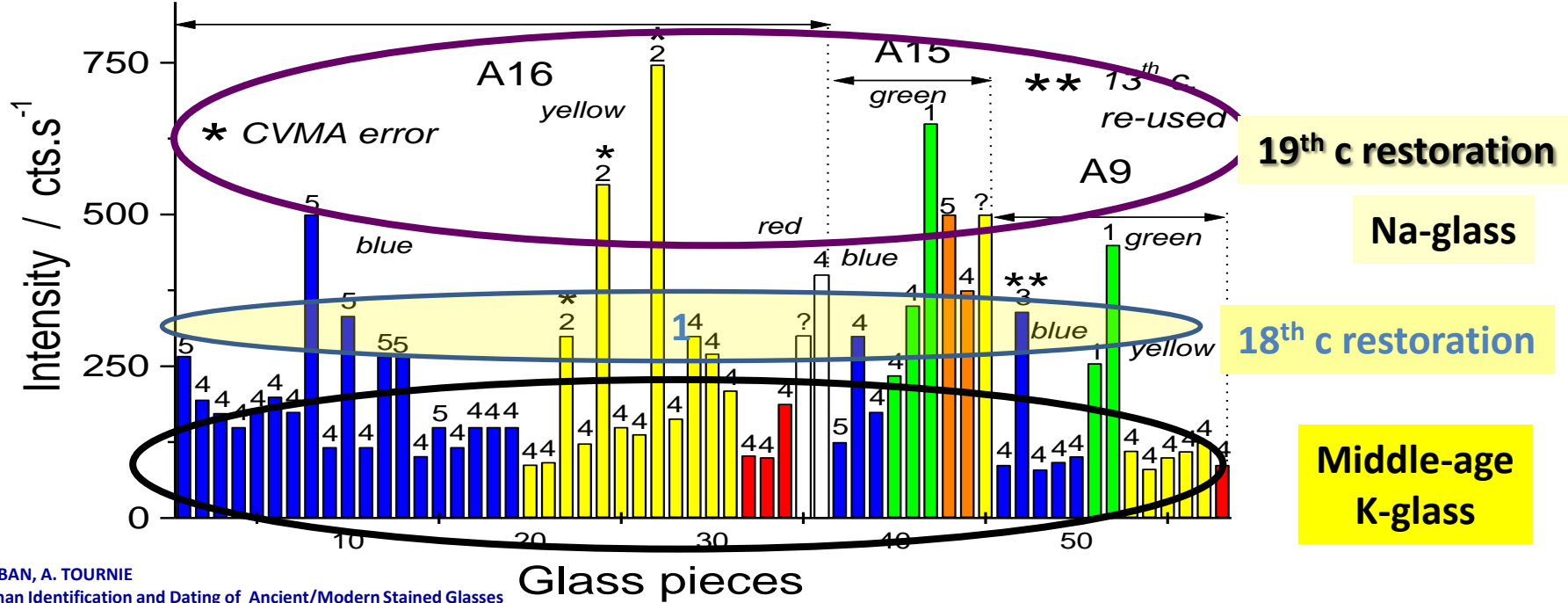


# Absolute intensity changes ⇔ dating



**Surface corrosion by meteoritic water**

**Weathering: loss of optical quality of the glass => differentiation between old corroded & restored glasses**



Ph. COLOMBAN, A. TOURNIE  
 On-site Raman Identification and Dating of Ancient/Modern Stained Glasses  
 at the Sainte-Chapelle, Paris. J. Cultural Heritage 8 [3] (2007) 242-256.

- 4: potash-glass (mediaeval)
- 1,2: soda-glass (19<sup>th</sup> c.)
- 5: soda-glass (18<sup>th</sup> c.?)

Middle ages

### Dating

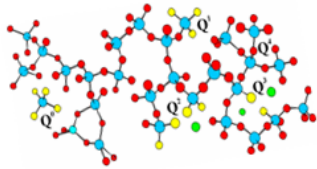
**Weathering = loss of optical quality of the glass surface**

on-site out-side measurements => differentiation

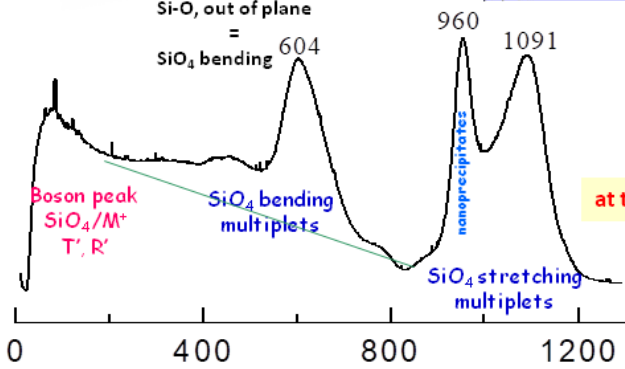
between old corroded & restored glass pieces

# Raman modelling of the Si-O network

Glassy polymeric Si-O network

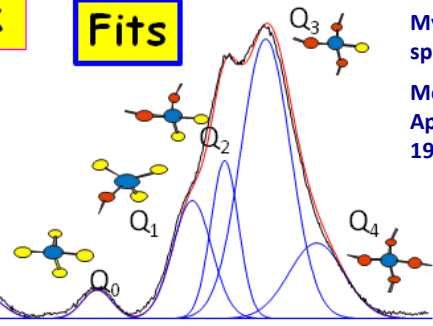


Si-O, out of plane  
= SiO<sub>4</sub> bending



SiO<sub>4</sub> bending Multiplets  
10 E δ<sub>3</sub> bands

## Fits



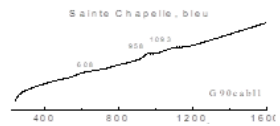
SiO<sub>4</sub> stretching Multiplets  
5 A<sub>1</sub> v<sub>3</sub> bands

Baseline subtraction

at the laboratory!

- Q<sub>0</sub> isolated tetrahedron
- Q<sub>1</sub> Si-O-Si bridge
- Q<sub>2</sub> 2 Si-O-Si bridges
- Q<sub>3</sub> 3 Si-O-Si bridges
- Q<sub>4</sub> full polymerised = SiO<sub>2</sub>

on site !  
Need to define a baseline subtraction procedure



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Spectrum



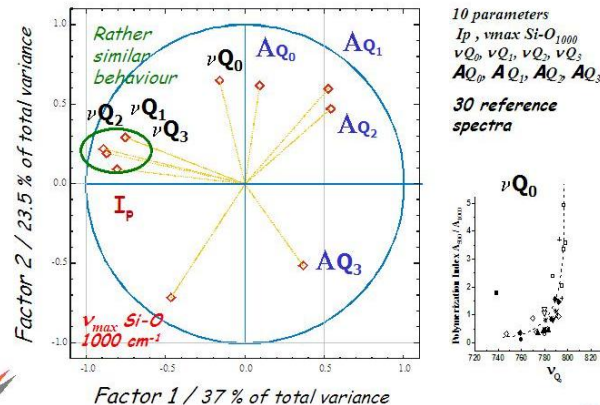
Fits



parameters

# Multivariate analysis PCA + Hierarchical classification

PCA Principal Component Analysis : selection of pertinent parameters



17

## Application to stained glass window (composition, corrosion)

P. Coloban, A. Tournié, On-site Raman Identification and Dating of Ancient/Modern Stained Glasses at the Sainte-Chapelle, Paris. J. Cultural Heritage 8 [3] (2007) 242-256.

## Application to Iznik/Kütahya pottery (provenance)

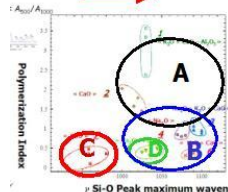
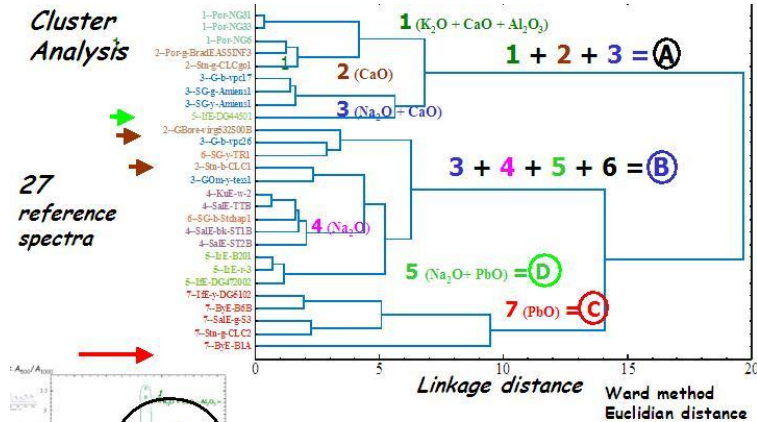
P. Coloban, Recent Case studies in the Raman Analysis of Ancient Ceramics: Glaze Opacification in Abbasid Pottery, Medici and 18<sup>th</sup> century French Porcelains, Iznik and Kütahya Ottoman Fritwares and Unexpected Lapis Lazuli Pigment in Lajvardina Wares Proc. of MRS 2004 Fall Meetings, 29<sup>th</sup> November–3 December 2004, Boston, USA, Symposium OO, vol 852, P. Vandiver, J. Mass & A. Murray Eds, 153-160.

## Application to Qing dynasty porcelain (ingredient provenance)

J. Burlot, D. Vangu, L. Bellot-Gurlet, P. Coloban, Raman identification of pigments and opacifiers: Interest and limitation of multivariate analysis by comparison with solid state spectroscopical approach J. Raman Spectrosc. 2023, submitted.

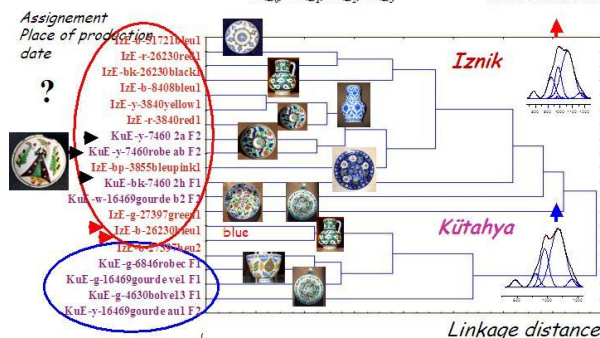
Cluster Analysis

27 reference spectra

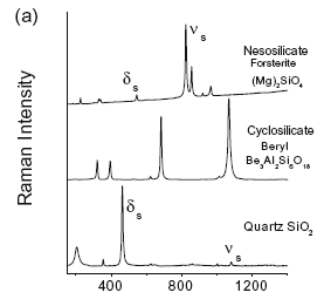


10 parameters :  $I_p$ ,  $v_{max\ Si-O_{1000}}$ ,  $\nu_{Q_0}$ ,  $\nu_{Q_1}$ ,  $\nu_{Q_2}$ ,  $\nu_{Q_3}$   
 $A_{Q_0}$ ,  $A_{Q_1}$ ,  $A_{Q_2}$ ,  $A_{Q_3}$

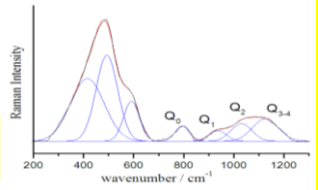
Ward method  
Euclidian distance



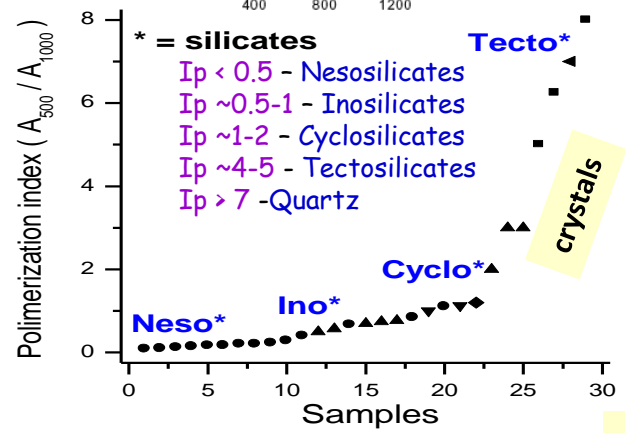
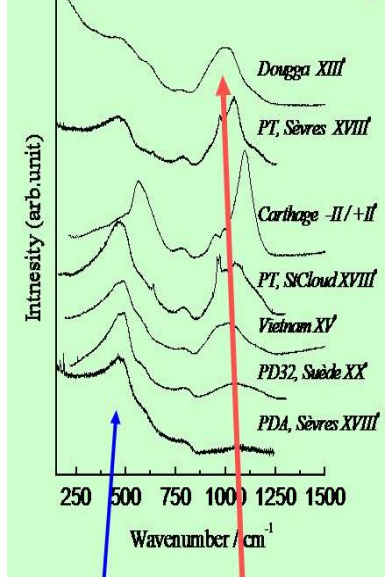
# Raman intensity ratio $A_{500} / A_{1000}$ : technology (Tf, etc.)



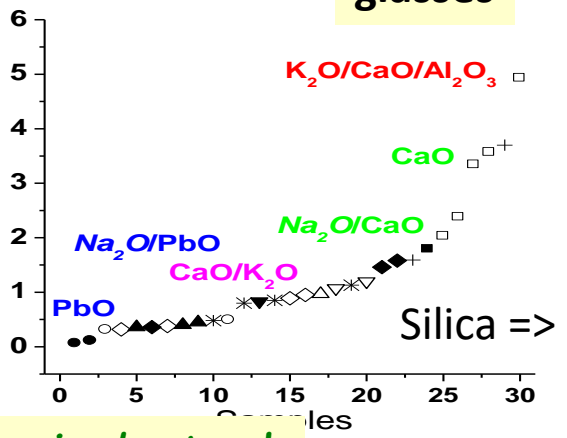
full polymerized network



Melting temperature =>



quartz  
Melting temperature =>



de-polymerized network

same for crystalline and amorphous phosphates !

- $Ip < 0.3 - 0.8$  - Pb rich silicates ~ 600°C
- $0.8 < Ip < 1.1$  - Na rich silicates ~ 1000°C
- $1.1 < Ip < 2.5$  - Ca rich silicates ~ 1200°C
- $Ip > 2.5$  - K rich silicates => +1400°C

working/melting temperature

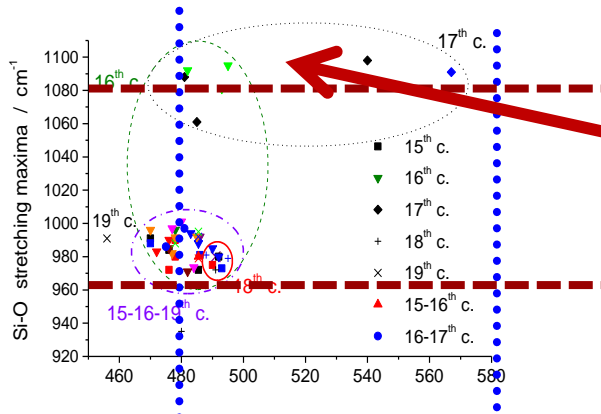
Ph. COLOMBAN  
 Polymerisation Degree and Raman Identification of Ancient Glasses  
 used for Jewellery, Ceramics Enamels and Mosaics  
 J. Non-Crystalline Solids 323 [1-3] (2003) 180-187.

# Chinese cloisonnés



Kangxi paravent

PbO



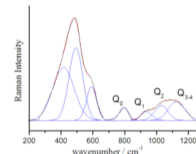
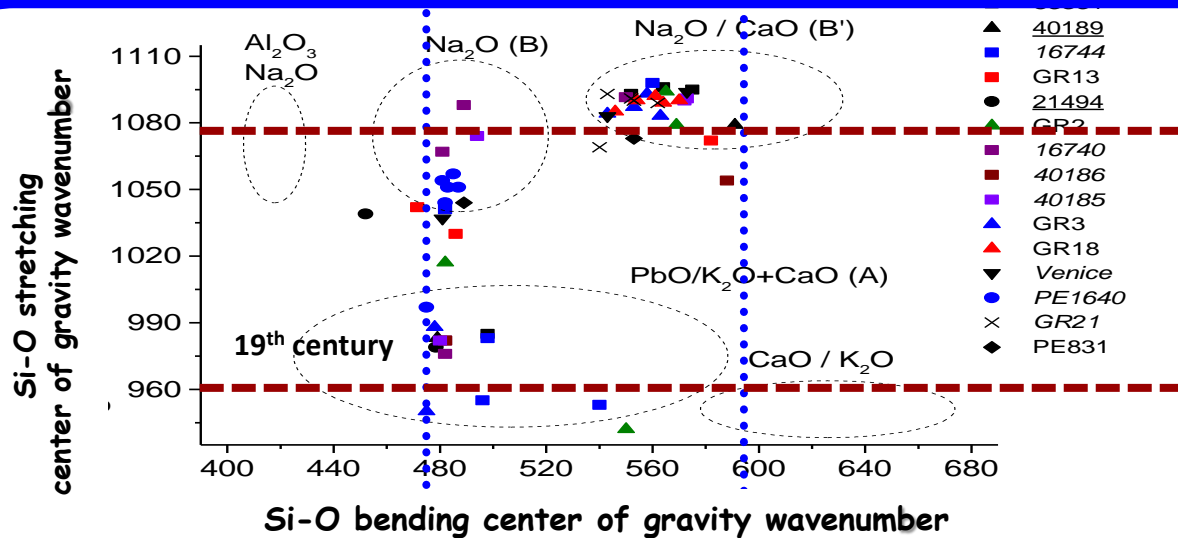
except  
for some 17<sup>th</sup> productions  
"French technology"

China Court Jesuits

Lead-based enamels  
15 to 19<sup>th</sup> century  
Very narrow distribution  
especially for 18<sup>th</sup> c. one  
→ Same workshop?



## China cloisonné - Painted Limoges enamels comparison of glassy matrices



Limoges painted enamels  
15<sup>th</sup> up to 18<sup>th</sup> century  
sodium-based enamels

# Qing Dynasty Imperial *huafalang* painted enamelled artefacts

(18<sup>th</sup> century : Kangxi to Qianlong reign)

Identification of artefacts with painted enamels prepared with Ingredients imported from Europe

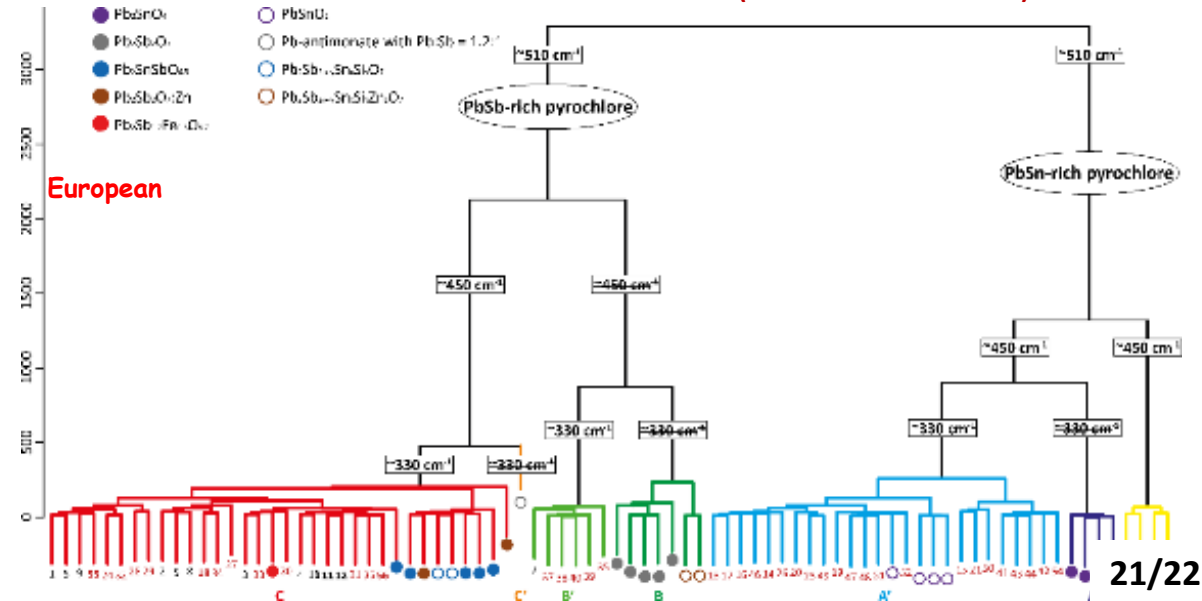
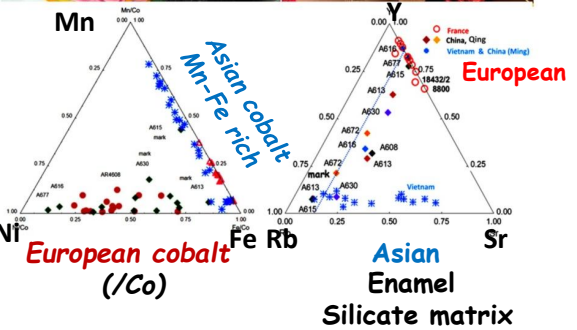
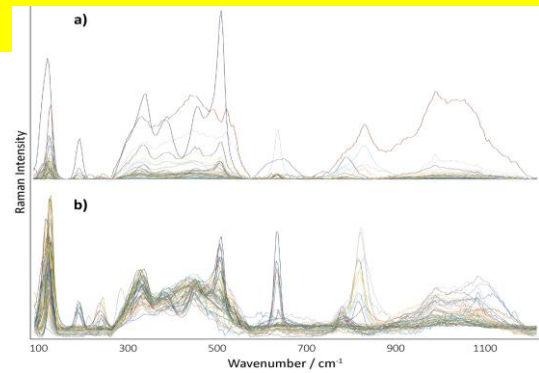
**Yellow (and green) enamels**  
3 different structures both for Sn- and Sb-based Naples yellow (pyrochlore-like) pigments

Variables:  
wavenumbers, band width & area of pigment signature (silicate matrix excluded)



pXRF

Raman



J. Burlot, D. Vangu, L. Bellot-Gurlet, P. Colombar, Raman identification of pigments and opacifiers: Interest and limitation of multivariate analysis by comparison with solid state spectroscopical approach J. Raman Spectrosc. 2023, submitted.



## 4. Conclusions & Perspectives

### On-site non-invasive identification of amorphous and crystalline phases

- ⇔ Authentication (anachronisms, characteristic phases, ...)
- ⇔ Conservation (corrosion)
- ⇔ Datation (very surface protonation increases with centuries)

### Requirements

Convenient laser source (color and power 100 to 300 mW)

High energy, good resolution spectrometers.

High magnification advanced optics

Deep understanding of the light-matter interaction and modeling  
to extract information (statistical comparison, Raman is not a standard  
analytical technique)

### Prospects

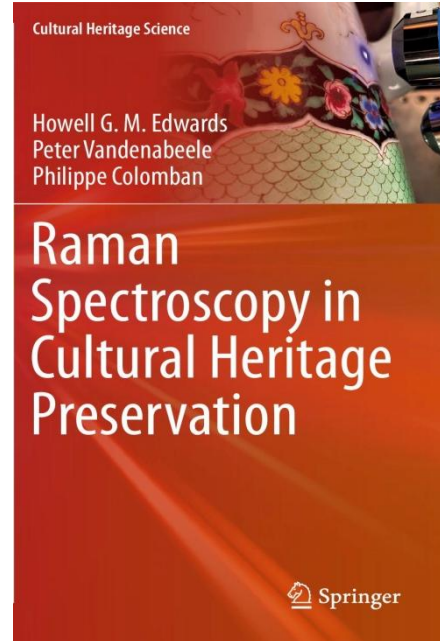
Compact spectrometer with blue laser

On-site Raman mapping

Higher performance CCD (pixel resolution)

Stand-off set-up (telescope, pulsed laser)

On-site SERS measurement, etc.



*Thanks for attention*

# $S_3^-$ chromophore Lapis lazuli already observed in



- **Ptolemaic glass, 1<sup>st</sup> c BCE**  
'Begram Hoard', Afghanistan  
Coll. Musée national des arts asiatiques - Guimet  
(Caggiani et al., Anal. Methods 2013)
- **Ptolemaic enamelled faience (Pompei)**  
(A. Mangone, G. E. De Benedetto, D. Fico, L. C. Giannossa, R. Laviano, L. Sabbatini, I. D. van der Werf, A. Traini, New J. Chem., 2011, 35, 2860-2868)
- **Roman Lübsow chalice**  
S. Greiff, J. Schuster, J. Cult. Herit. 2008, 9 Suppl., e27
- **14<sup>th</sup> c. Swabian-Normand-Islamic pottery (Sicilia, Apulia)**  
(R.J.H. Clark, C. Laganara et al., Bari University)
- **13<sup>th</sup>-14<sup>th</sup> c. Swabian-Normand-Islamic enameled glass**  
(M.C. Caggiani, A. Mangone et al., Bari University)
- **14<sup>th</sup> c. Lajvardina pottery**  
(Ph. Colomban)\*\* *in combination with ~2% Co !!*
- **14<sup>th</sup>-15<sup>th</sup> c. Mamluk glass** (some time in combination with Co)
- **18<sup>th</sup> Böttger porcelain (Saxony)** : *lapis as whitening agent of the glaze*



OA  
7352



Lamp bearing  
the name of *Sayf al-Din Tankizbughâ*  
Body : circa 1362  
Egypt or Syria (Europe for foot)  
Foot : 19<sup>th</sup> c. restoration Ph.J. Brocard

Comparison of coloring agents in Europe and China  
in the 17<sup>th</sup> - 18<sup>th</sup> centuries in  
glass/enamel (*Qing Dynasty*)

The phases detected by Raman micro-spectroscopy  
are in bold, those whose elements are detected  
by mobile XRF fluorescence are in italics.  
**In red underlined the imported recipes.**

17世纪在欧洲和中国玻璃/珐琅着色剂的比较。  
通过便携显微拉曼光谱检测的晶体粗体显示  
通过移动XRF荧光检测到的元素 以斜体书写  
红色下划线表示为进口配方

Color 颜色	Europe 欧洲 (name/ formula) (物质名称/化学式)	Date ( post quem ) century 发明使用时间 (世纪)	Chine 中国 (特征物质/化学式) (characteristics/formula)	Date d'innovation/usage (Dynastie) 发明使用时间 (王朝)
White 白色	<i>Cassiterite (SnO<sub>2</sub>)</i> 锡石	<5 <sup>th</sup> 5世纪之前	<u>Imported 进口的</u>	
			Fluorite (CaF <sub>2</sub> ) 萤石	> Song 自宋朝
	<i>K, Ca – Pb Arsenates</i> 砷酸盐 钾、铅和砷酸钙 <i>Na<sub>1-x-2y</sub>K<sub>x</sub>Ca<sub>y</sub>Pb<sub>4</sub>(AsO<sub>4</sub>)<sub>3</sub></i> <i>(Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>) phosphate</i> 磷酸钙	~16 <sup>th</sup> 16世纪之前	<u>Imported 进口的</u>	
Blue 蓝色	<i>Arsenic-rich cobalt</i> 富砷钴矿	~16 <sup>th</sup> - 19 <sup>th</sup> 从16世纪到19世纪	<i>Mn-rich cobalt</i> 富锰钴矿 (Han blue 汉蓝) <i>Arsenic-rich cobalt</i> 富砷钴矿	Yuan – Ming “元”、“明” 时期
	<i>Pb<sub>2</sub>Sn<sub>2</sub>O<sub>6</sub> - Pb<sub>2</sub>Sb<sub>2-x</sub>M<sub>x</sub>O<sub>7-d</sub></i> <i>M= Fe, Si, Zn (Naples Yellow)</i> (烧绿石固溶体) <i>pyrochlore</i>	Antiquity (Sn) 古代 (15 <sup>th</sup> ) 15世纪 文艺复兴时期 (Sb-Sn,Si,Zn,Fe)	<i>Fe<sup>2+</sup>/Fe<sup>3+</sup> ions</i> <i>Fe<sup>2+</sup> / Fe<sup>3+</sup> 离子</i>	>Han 汉代以来
Green 绿色	<i>Cu<sup>2+</sup></i>	Antiquity 古代	<i>Cu<sup>2+</sup>离子</i>	>Han 汉代以来
	<i>Blue + Yellow</i> 蓝色+黄色	Renaissance	<u>Imported 进口的</u>	
Red 红色	<i>Hematite (Fe<sub>2-x</sub>M<sub>x</sub>O<sub>3</sub>)</i> 赤铁矿	Roman 罗马帝国	<i>Hematite (Fe<sub>2-x</sub>M<sub>x</sub>O<sub>3</sub>)</i>	> Ming 自明朝
	<i>Hercynite (Fe<sub>2-x</sub>M<sub>x</sub>O<sub>3</sub>)</i> 海长岩	Roman 罗马帝国		
	<i>Cu<sup>0</sup> nanoparticles</i> 铜纳米粒子	Celtic 凯尔特人	<i>Cu<sup>0</sup>铜纳米粒子</i>	> Yuan 自元朝
	<i>Au<sup>0</sup> nanoparticles</i> 金纳米粒子	Roman (?) 罗马帝国 Renaissance (15 <sup>th</sup> )	<u>Imported 进口的</u>	

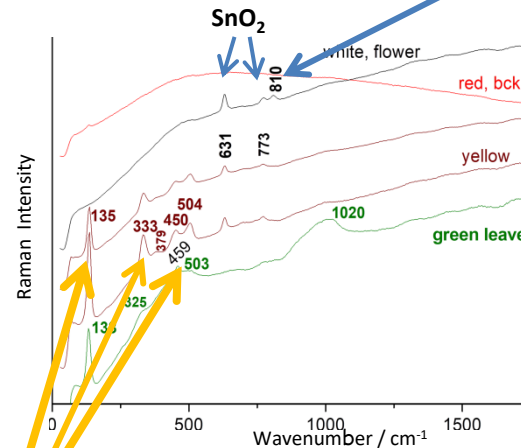
# Qing Dynasty Imperial *huafalang* bowl (18<sup>th</sup> century : Kangxi to Qianlong reign)

Pb-Ca/K-arsenate

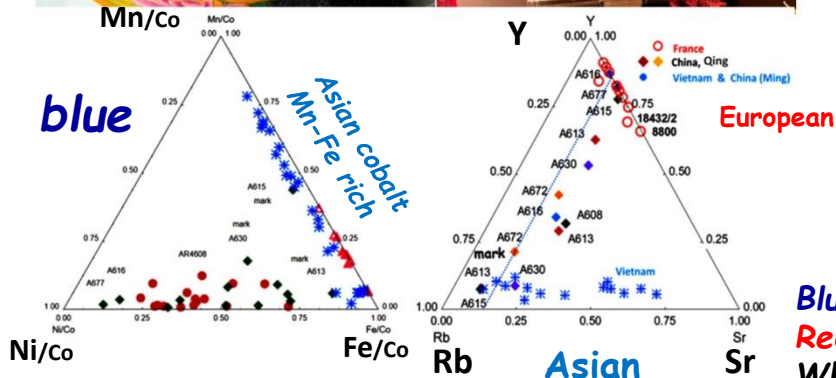


pXRF

pRaman



**Red** : metal nanoparticle fluorescence ( $\text{Cu}^{\circ}$  or  $\text{Au}^{\circ}$ )  
**White**: cassiterite  $\text{SnO}_2$  + Pb-Ca/K-arsenate  
**Yellow**: Lead stannate/antimonate + cassiterite  
**Green**: idem (+ $\text{Cu}^{2+}$ )

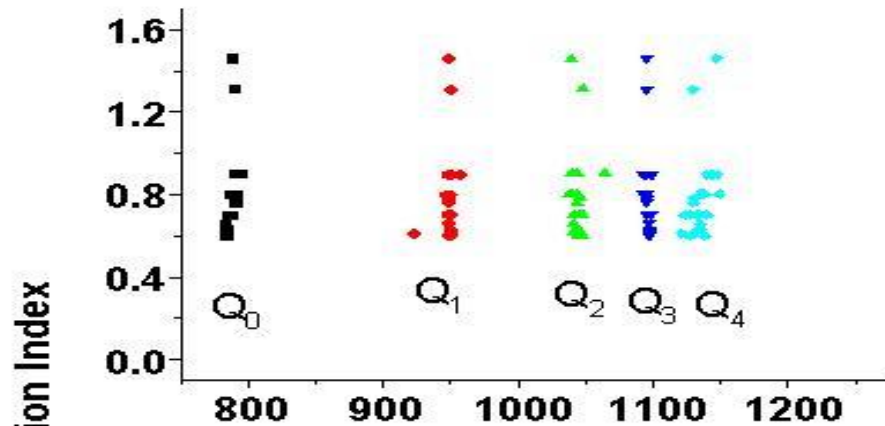


↔ **European cobalt**  
(Ni, As no Mn)

**Asian**  
Enamel  
Silicate matrix

## *huafalang* enamels

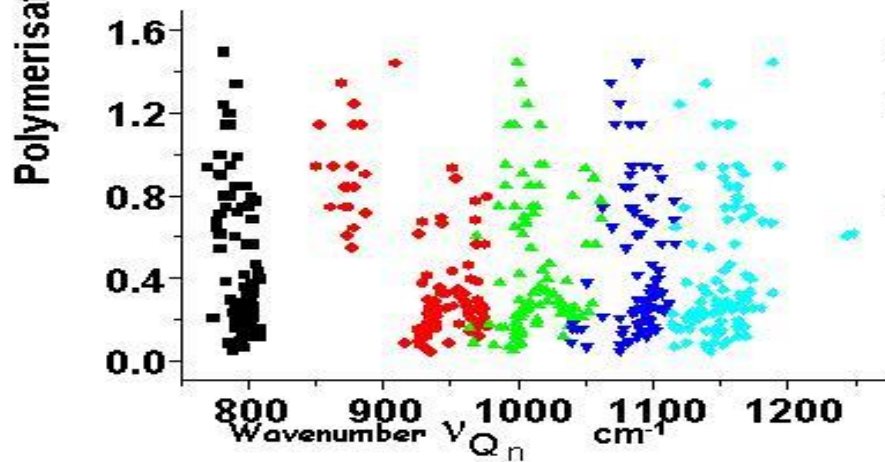
**Blue**: Imported European cobalt under Jesuits guidance  
**Red**:  $\text{Au}^{\circ}$  NPs (imported under Jesuits guidance)  
**White** : European recipes  
**Yellow & green**: Chinese recipes already imported from Europe during Previous Dynasty (Ming)



## SiO<sub>4</sub> network

Roman glasses :  
 an unique signature  
 whatever the origin :  
 Italy, France, Tunisia

single technology &  
 composition



Stained glasses :  
scattered signatures

⇒ *Churches, France*  
 many workshops &  
 many compositions

