RAMAN SPECTROSCOPY APPLIED TO GEMMOLOGY

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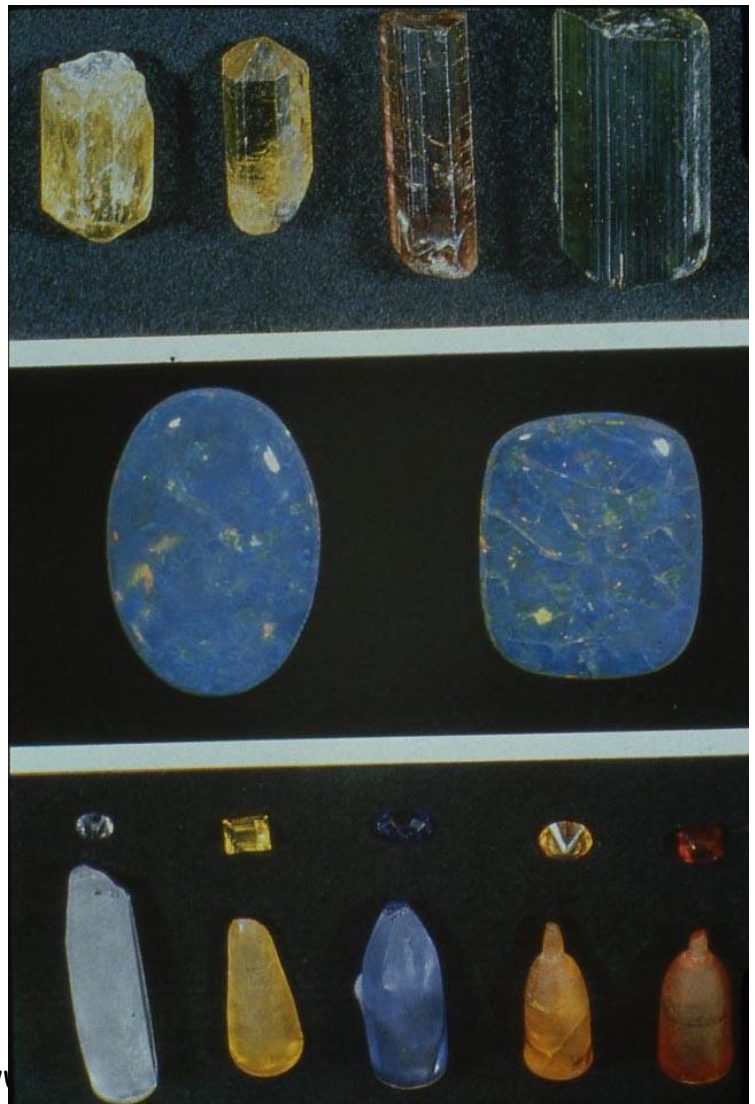
Introduction

Sir Chandrasekhara V. Raman (1888-1970)



Raman now routine in gemmological laboratory, since late 1990s with development of CCD detectors & notch filters

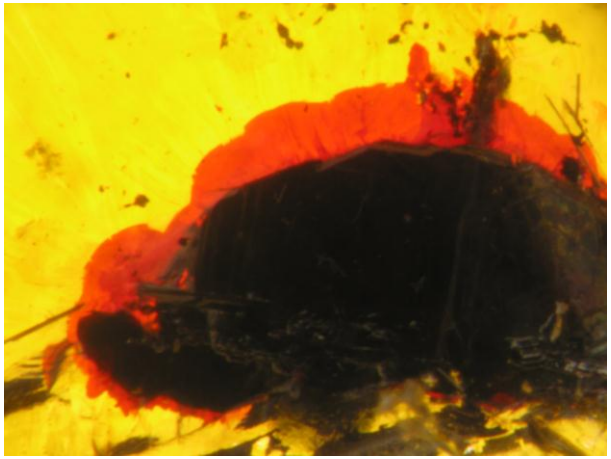
Classical vs laboratory gemmology

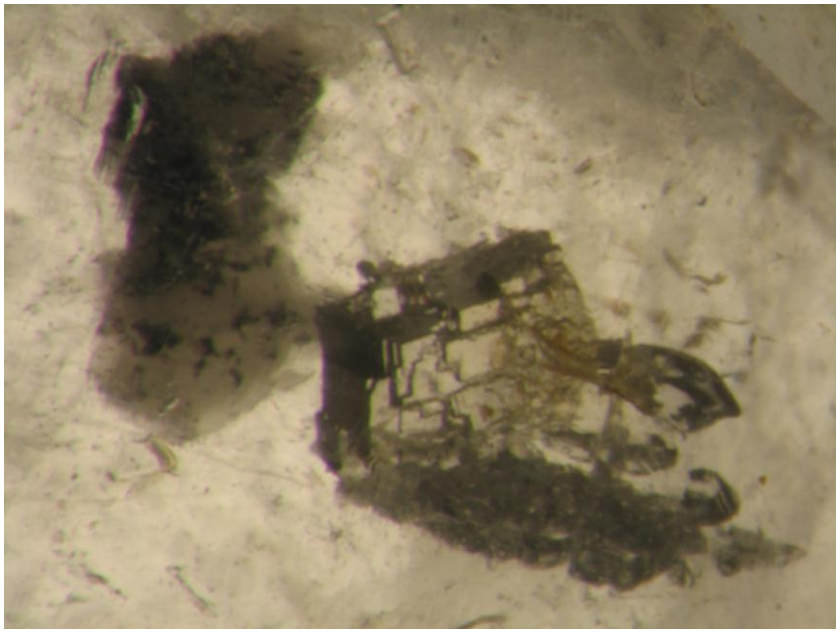
True gemmological concerns, not academics of gems

2 - Raman spectroscopy applied to gems: Strengths and limitations

Why is Raman useful to gemmologists?
Mostly **species identification**,

special mention
for **identification**
of inclusions
inside gem
matrix, without
extraction

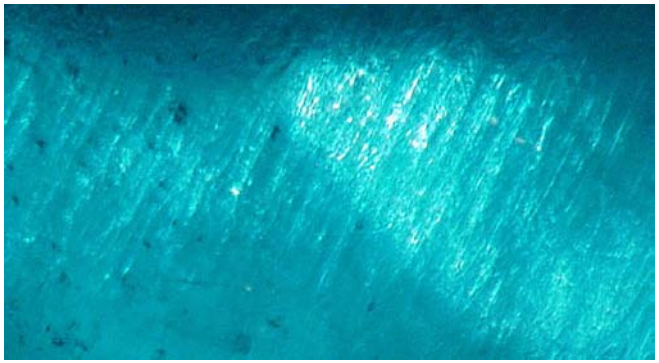


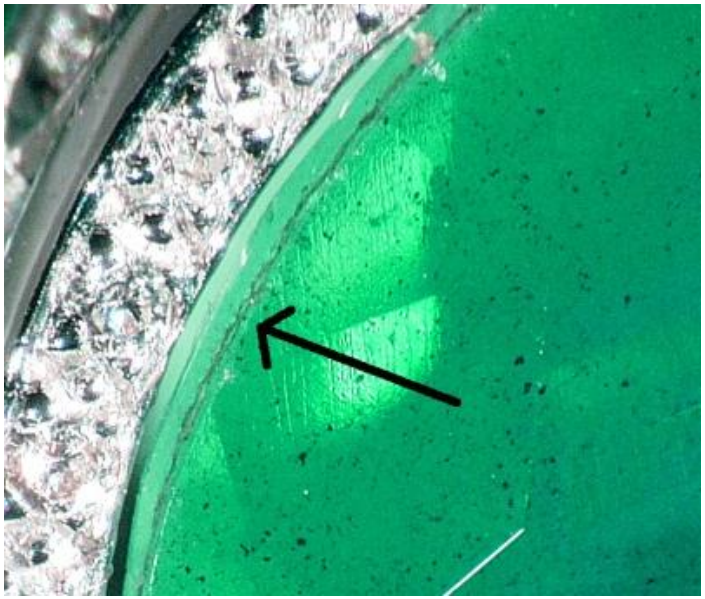


- **No sample preparation** (no polished surface for rough)
- **No optical contact** (unlike index of refraction)
- **Non destructive** (not even microdestructive)
- Well adapted to rounded or **irregular shape** objects (pearls, rough gems, carvings, jewels)
- Spectra **through a window** (museums, watches)

- Sometimes, **speed** is of the essence

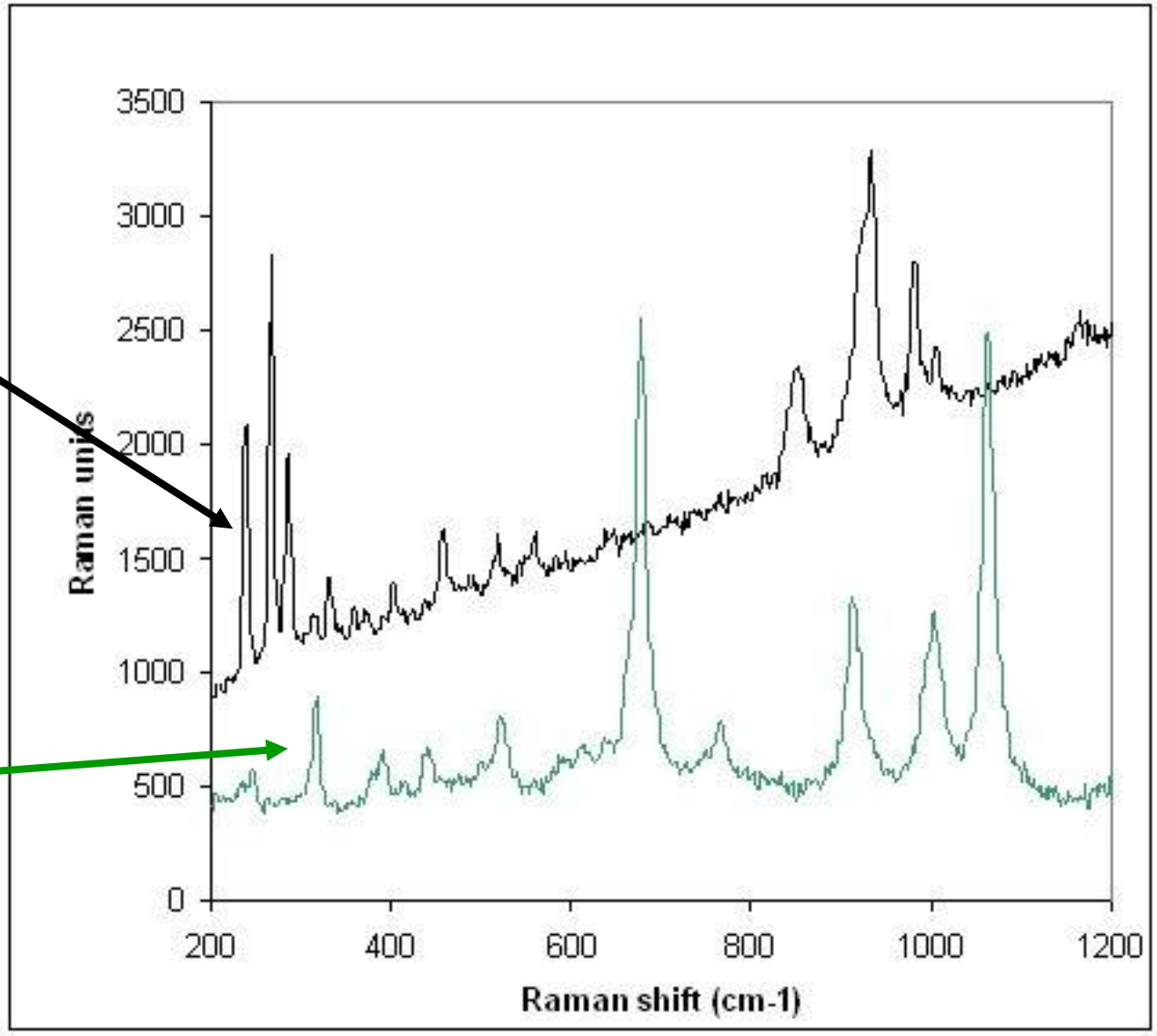
A surprising doublet



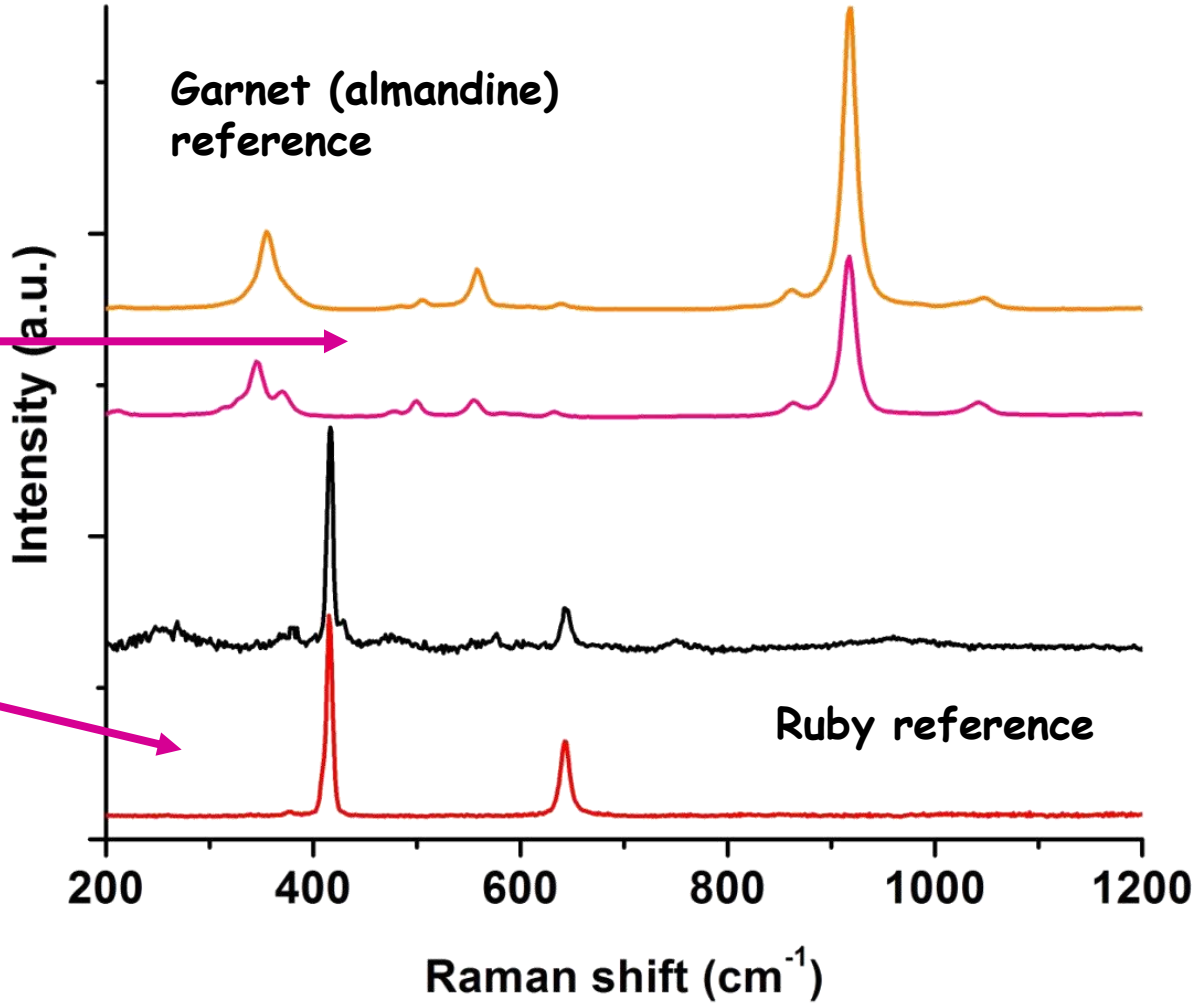


Topaz !

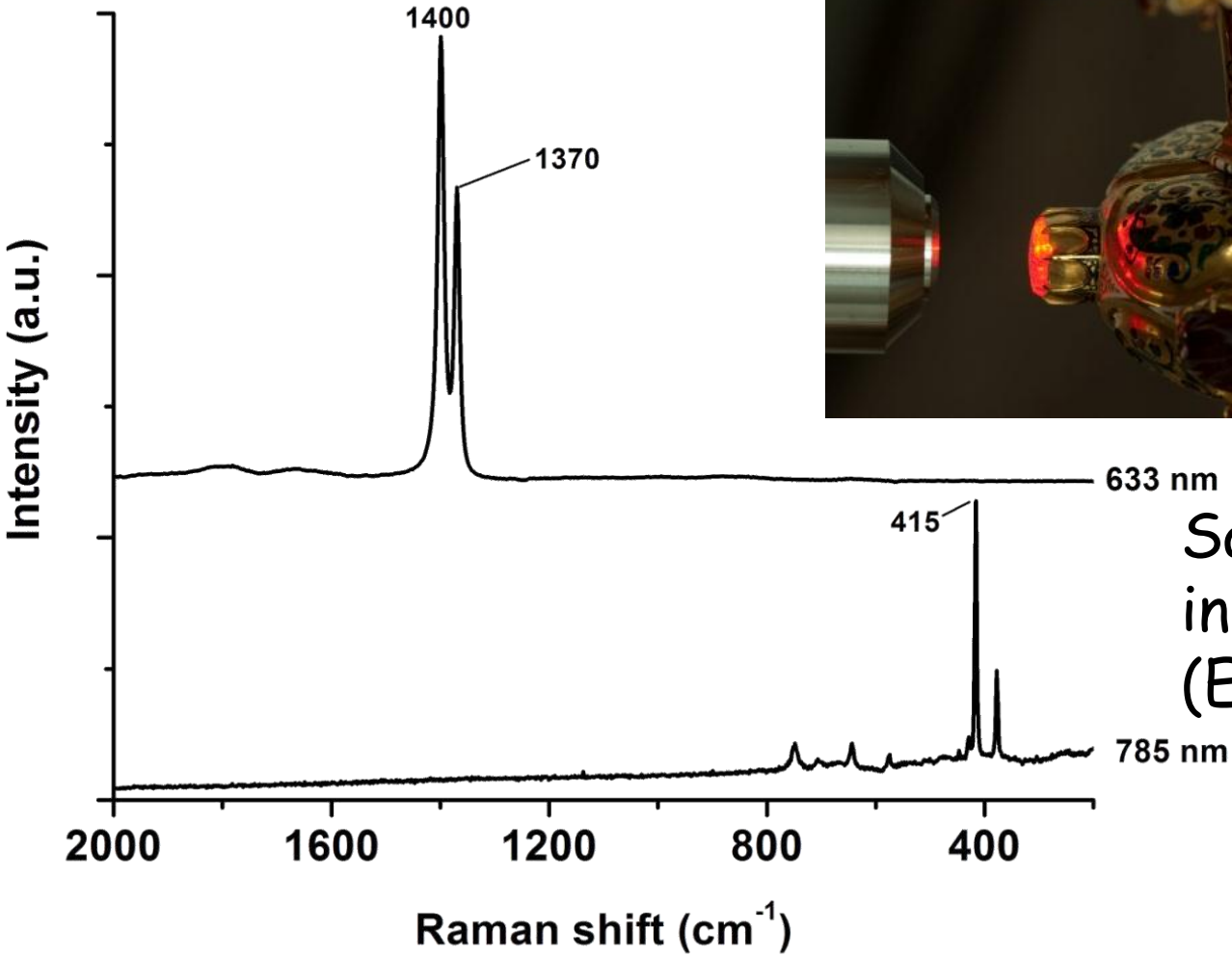
Beryl



Russian hydrothermal synthetic emerald / Topaz doublet

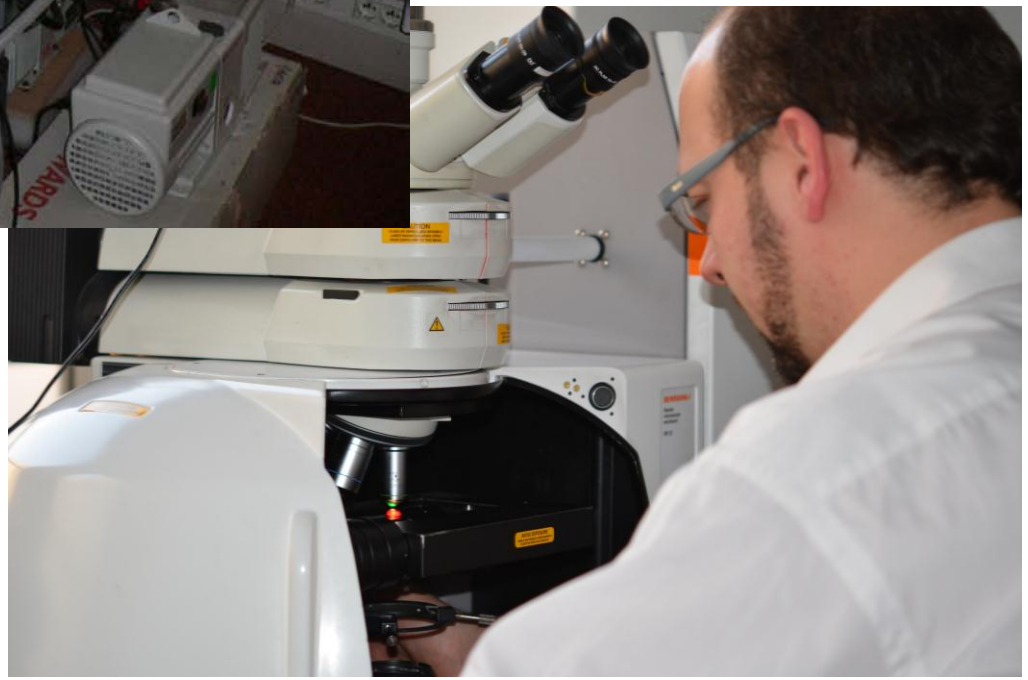

Garnet (almandine) reference
Ruby reference
Intensity (a.u.)
200
400
600
800
1000
1200
Raman shift (cm-1)

Different excitations to avoid luminescence phenomena



Sacred object
in an Swiss abbey
(Einsiedeln)

Typically dispersive Raman instruments
514 nm green line of Ar^+
Other lines rarely available



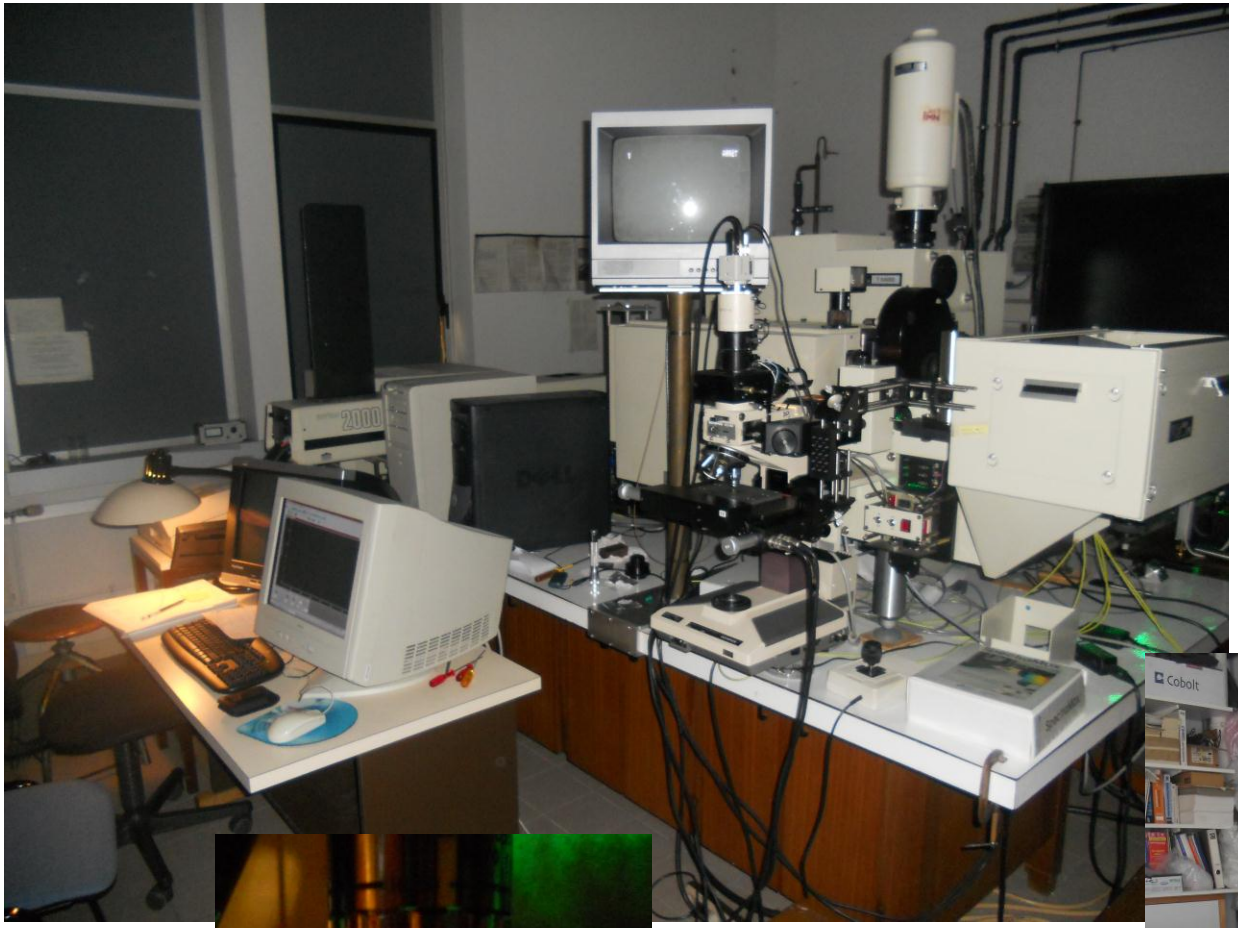
Instrumentation

Instrumentation

Evolution towards mutliple lasers
- Obtain resonance conditions (adapt to absorption):
  Ex yellow laser for pearls
-Avoid luminescence: red/NIR laser (large choice)
  in particular 1064 nm Nd3+:YAG laser (FT Raman)
- Excite desired luminescence: Ex UV HeCd 325 nm laser for diamond HPHT treatment detection

Instrumentation

Microprobe is of the essence for inclusions and microfeatures



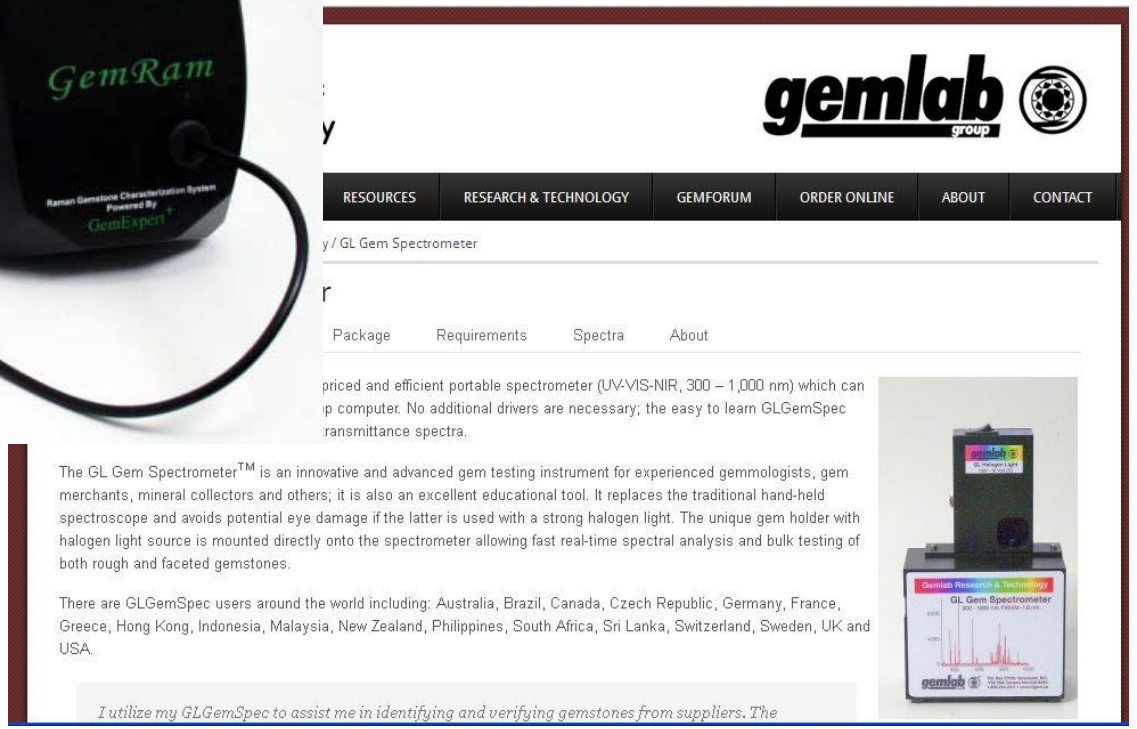
Instrumentation

FT Raman rarely used
Ideal for opal
User (student) friendly

Instrumentation

Small dedicated instruments with some database

Usually Peltier cooled CCD detectors



Instrumentation

Getting the gem to the spectrometer

Holding small gem
with home-made devices
For our FT Raman

Limitations of Raman spectroscopy for gems

Poor or weak Raman scatterers

Strong absorbers: black oxides

Disordered materials; opal, glass imitations

Many oxydes: cubic zirconia,…

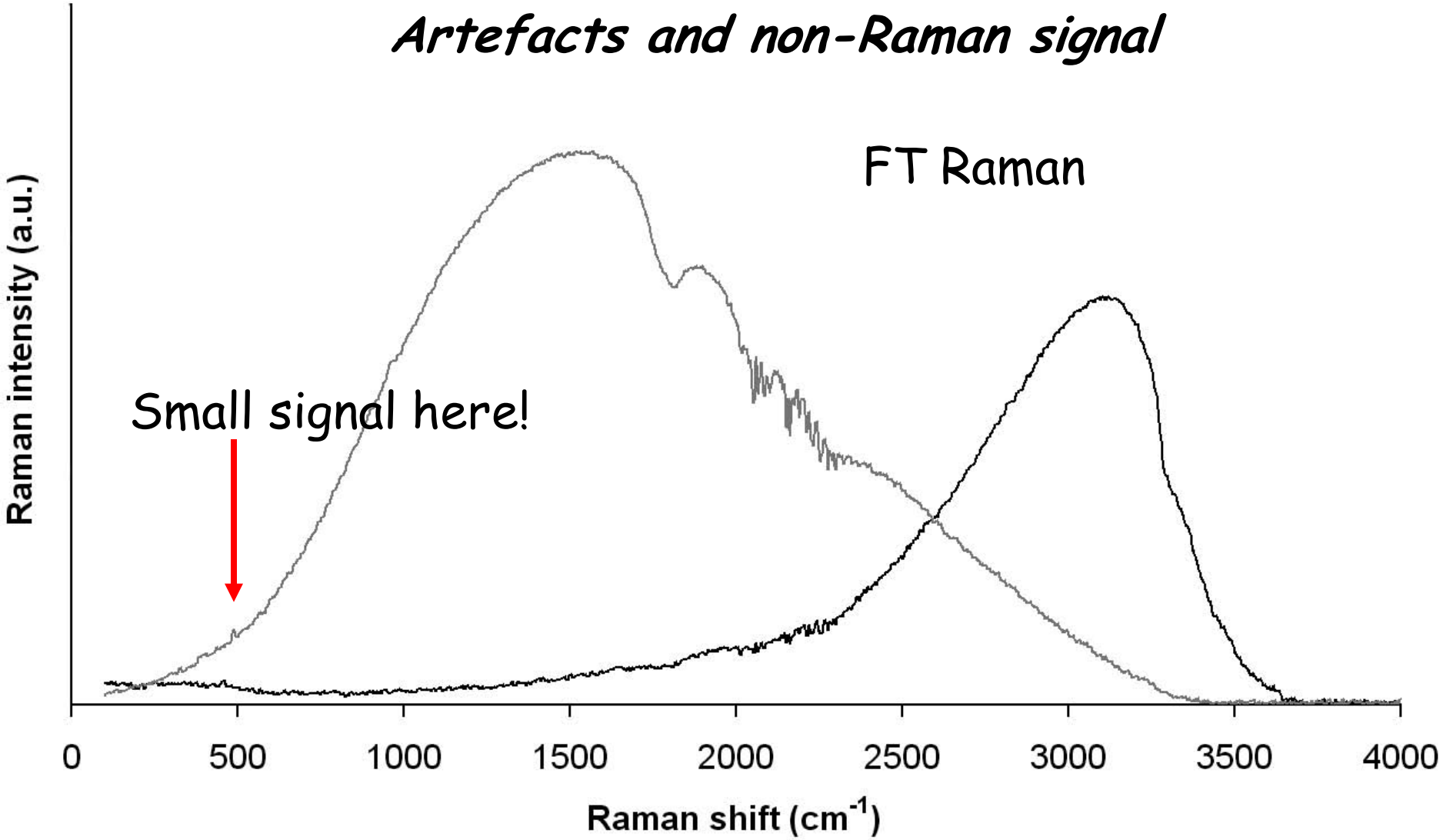
…

Long accumulations is often the only solution

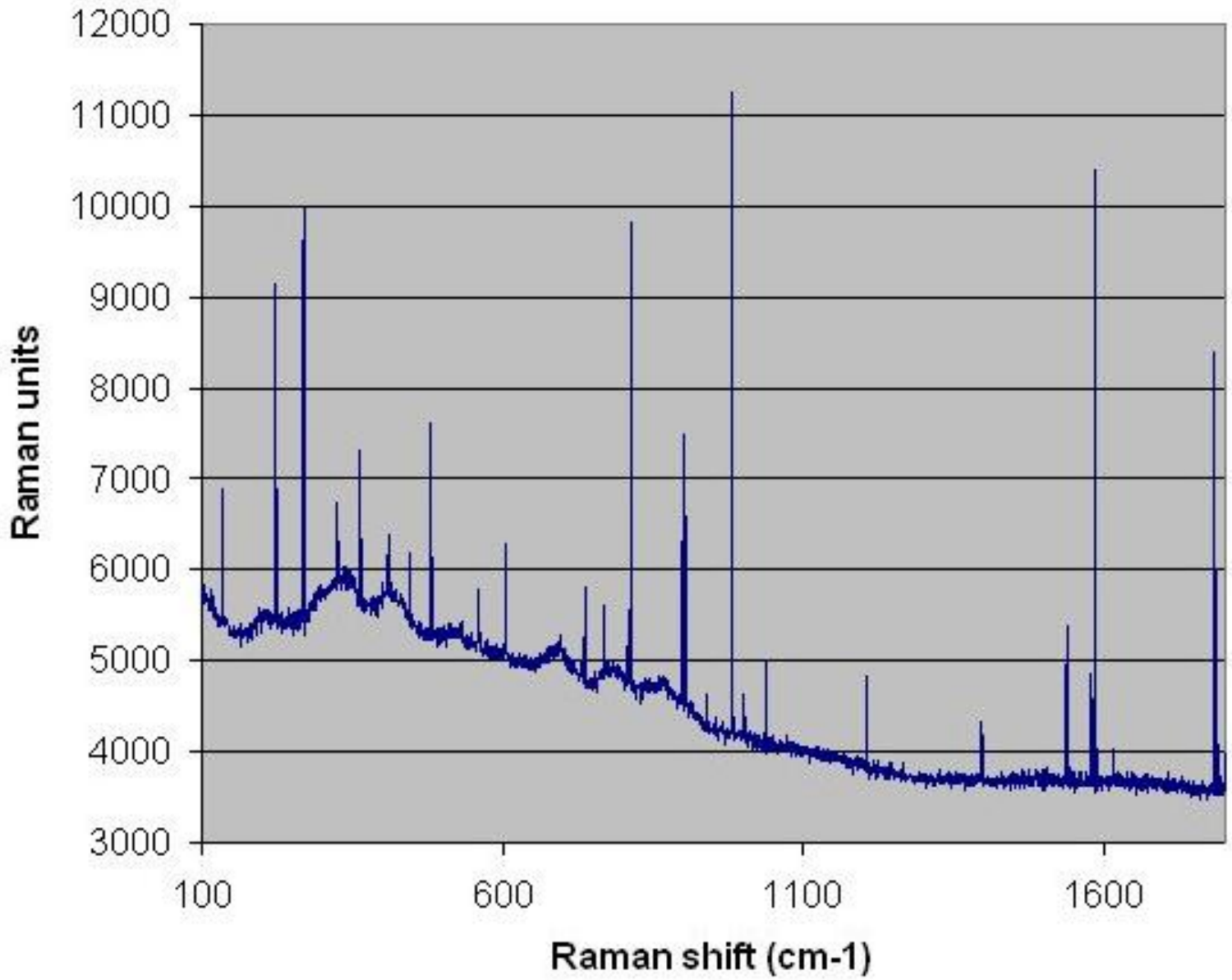
Cubic zirconia

Limitations of Raman spectroscopy for gems

Artefacts and non-Raman signal



Thermal emission?
weakens with cooling

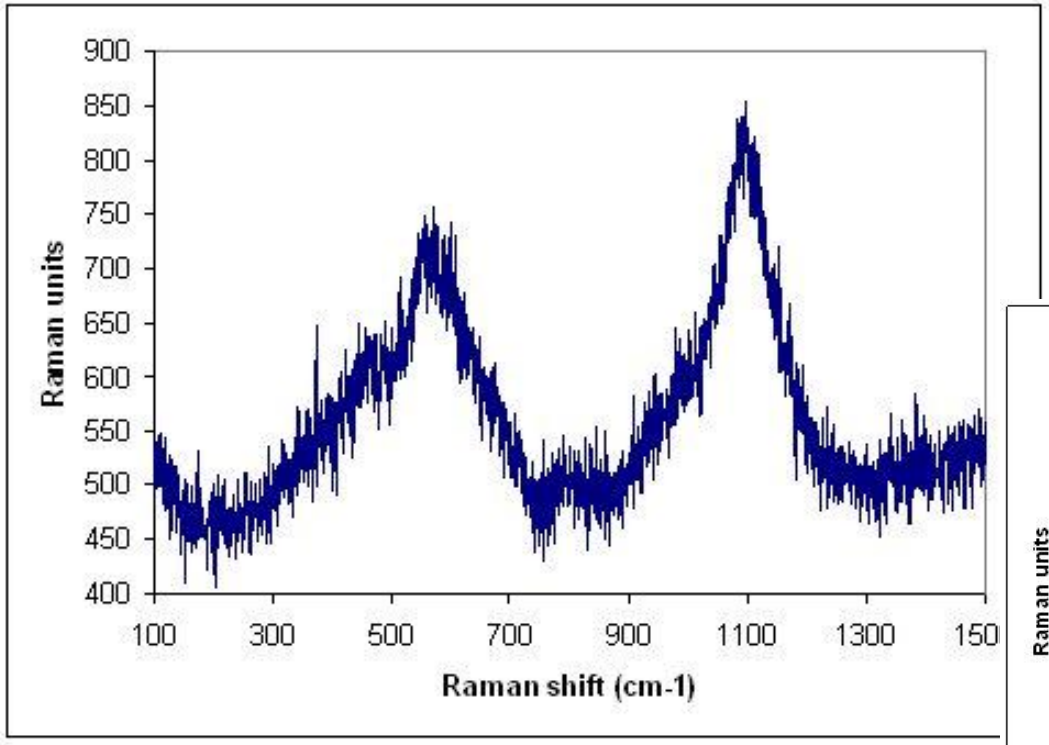


Anything causing the detector to react (including nearby instruments)

Rare on FT Raman, common on cooled CCD

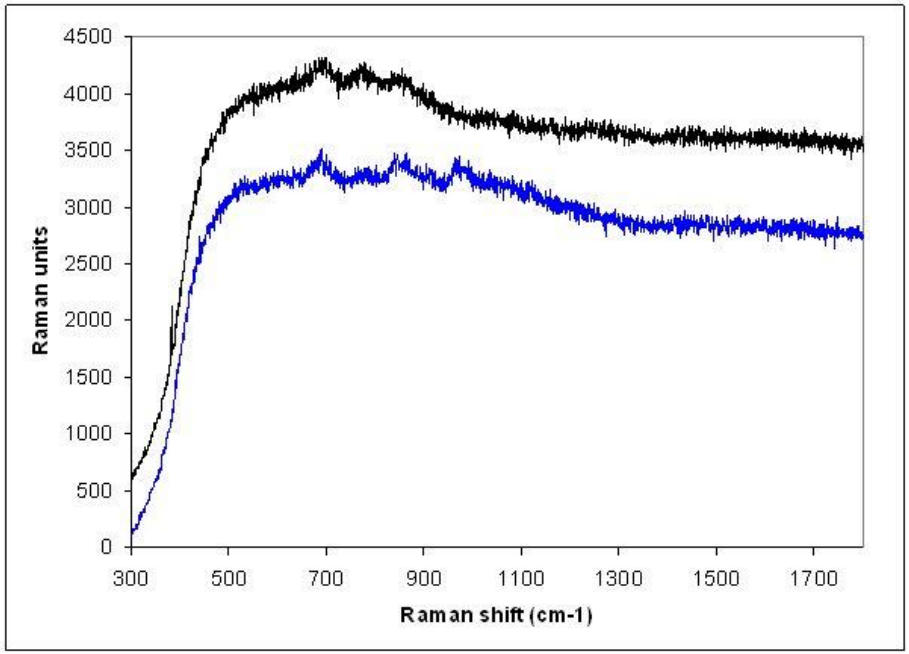
Glass or coatings of the objective

Experimental errors:
Glue, sample holding material, plas
Outside fluorescent lamp (in the green)

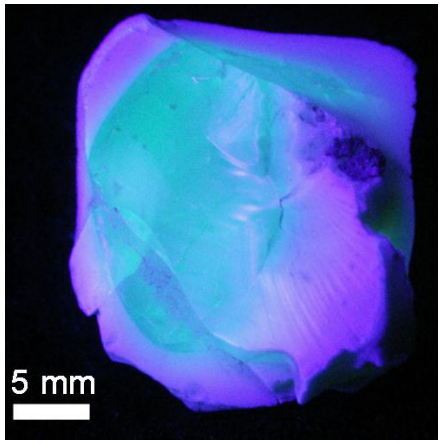


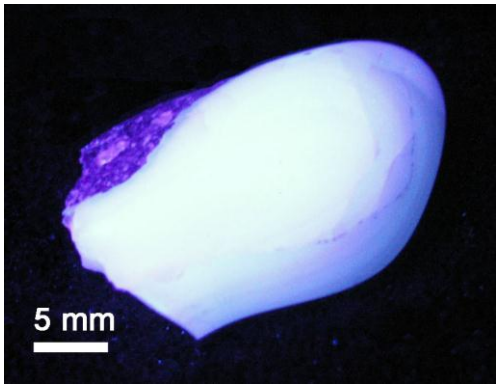
Glass holding the sample

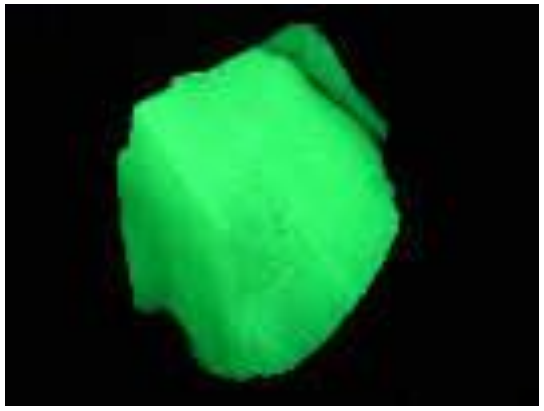
Spectrum without and with lamp



Competition with luminescence signal



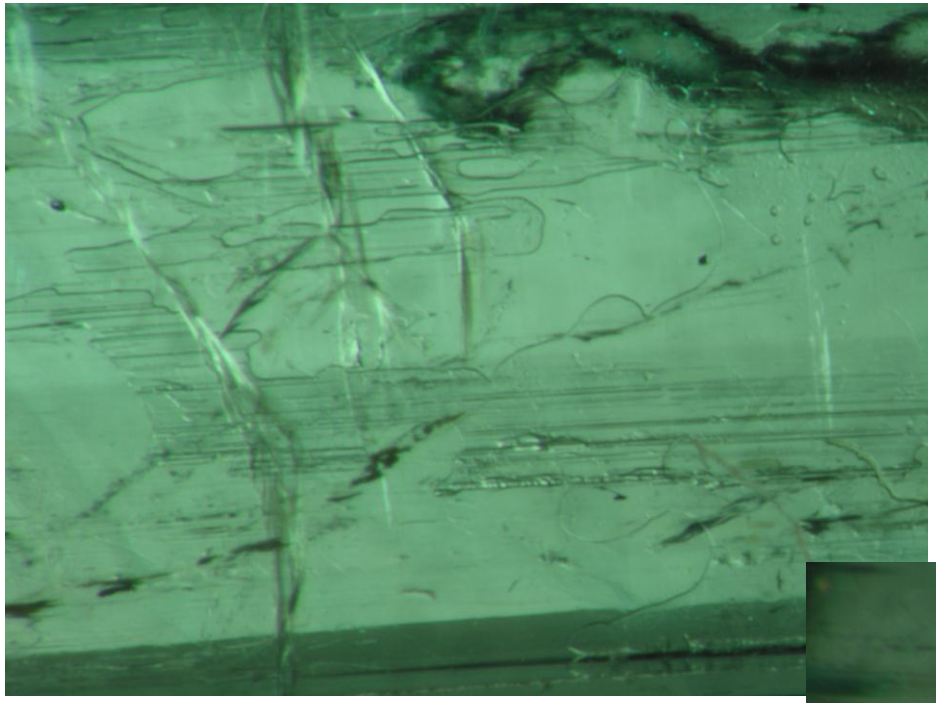


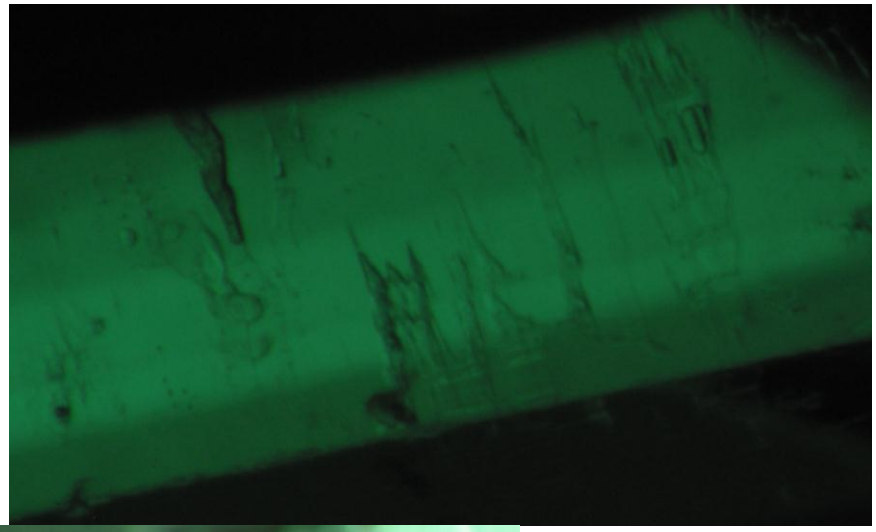


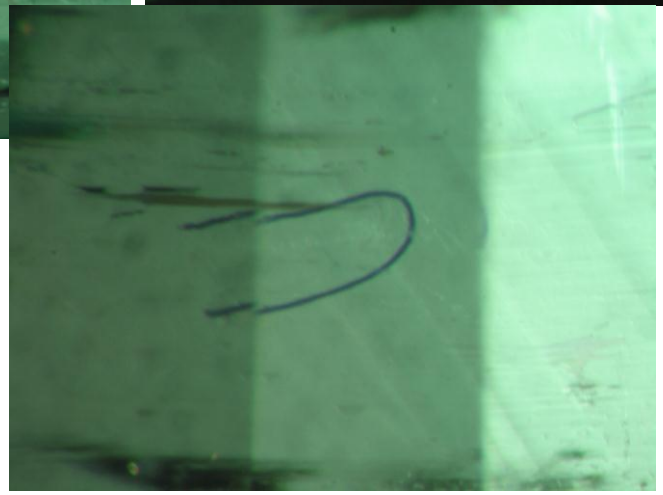
Opal with even 1 ppm uranium luminesces too strongly to obtain a Raman spectrum, especially with 514 nm line of an Ar^+ laser

Volume sampled:

The micro advantage can turn into a problem
Not an average method, usually a local probe,
even without a microprobe







Difficulty for small,
needle-like inclusions

Keeping gemology in mind when interpreting Raman signals

Gemstone Identification Using Raman Spectroscopy

Raman microspectroscopy is an ideal method for the examination of marketable gemstones because of the lack of sample preparation involved and the nondestructive nature of Raman analysis.

Amanda L. Jenkins and Richard A. Larsen

In recent years, the gemstone market has been flooded with stones of questionable origin. Frequently, even thorough analysis by a qualified jeweler cannot reveal unequivocally whether the gemstone is genuine or fake. In the worst case, sophisticated analytical methods struggle to differentiate modified diamonds, causing considerable concern to the international gemstone trade. Raman microspectroscopy is an ideal method for the examination of marketable gemstones because of the lack of sample preparation involved and the nondestructive nature of Raman analysis. The micro-Raman study of a stone also provides a unique record for identification purposes. This article discusses the variety of Raman spectra that can be obtained from different families of gemstones, comparing and contrasting spectra from genuine and

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Richard A. Larsen
is an applications chemist at Jasco.

Raman analysis of both stones provided an interesting discovery. Neither stone had the characteristic amethyst Raman bands; however both stones did display the strong bands at 4392 and 4360 cm^{-1}, characteristic of ruby. Comparison of the spectra of these stones versus that of a known ruby, proved that these two amethysts were indeed rubies despite their purple coloring (Figure 5). In this instance three

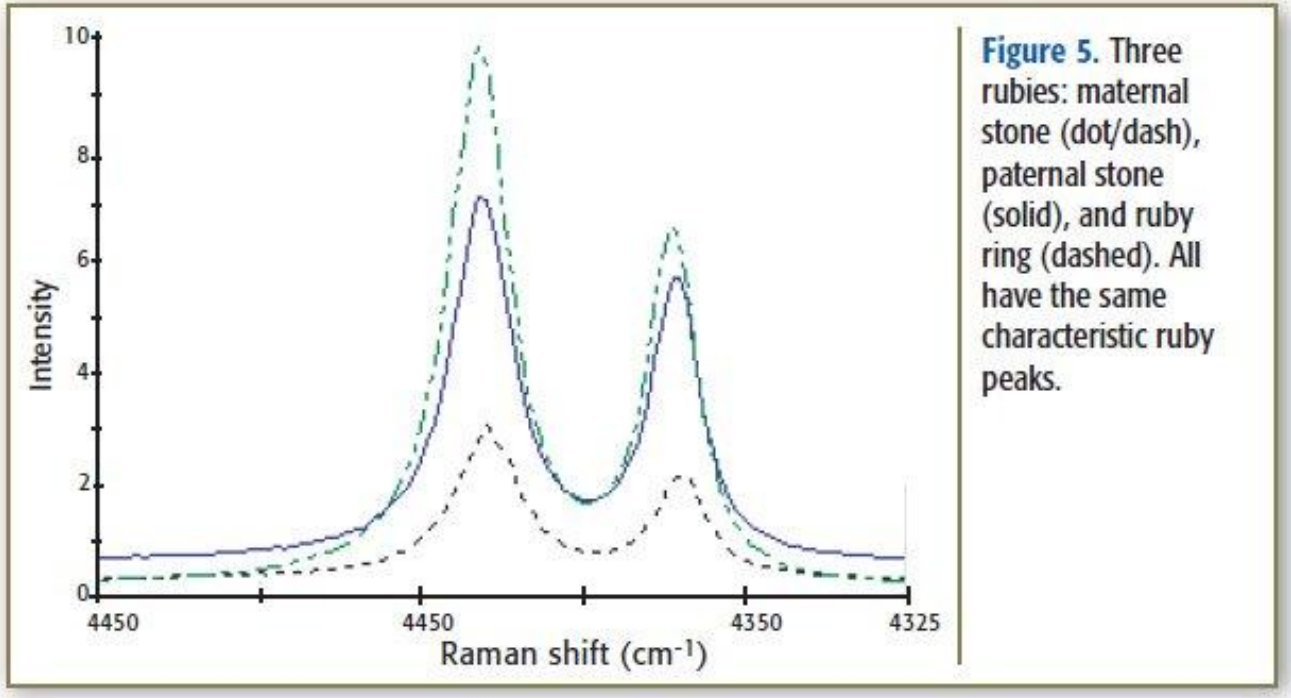
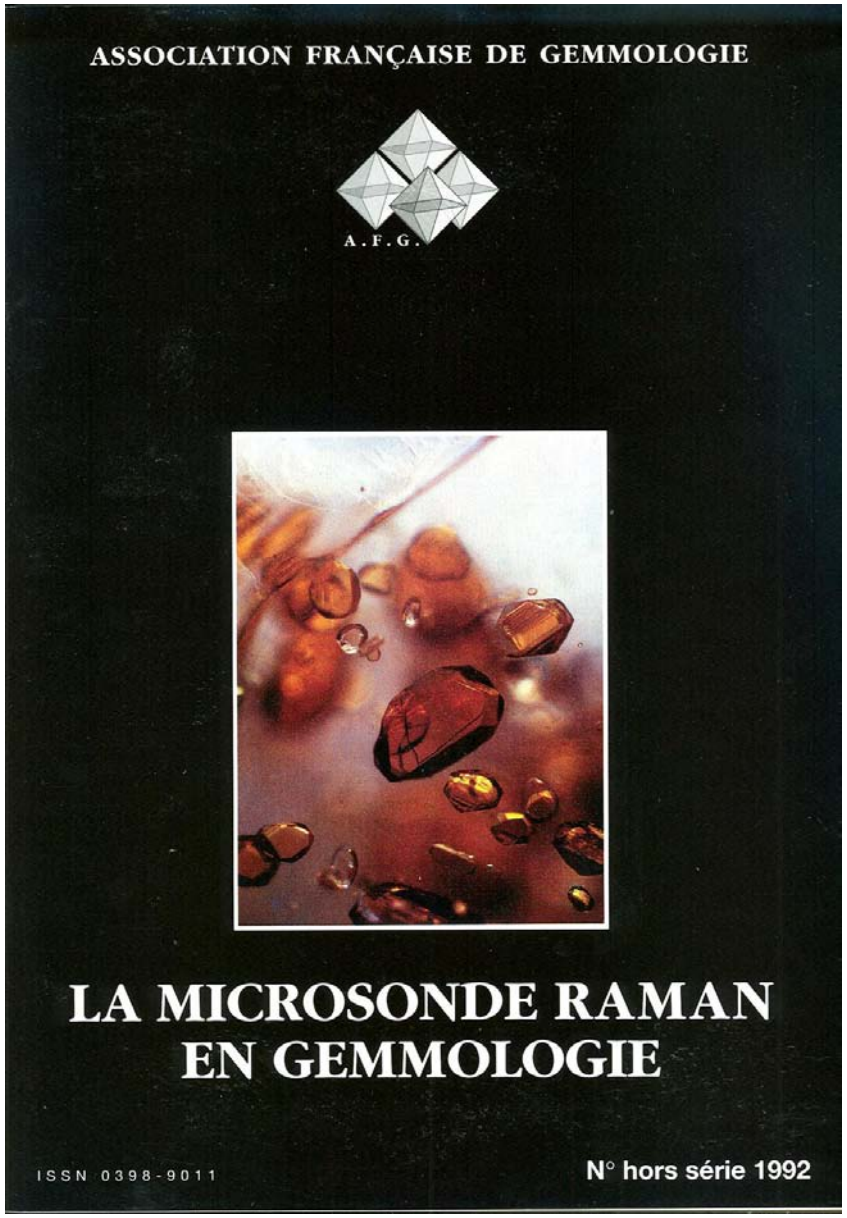


Figure 5. Three rubies: maternal stone (dot/dash), paternal stone (solid), and ruby ring (dashed). All have the same characteristic ruby peaks.

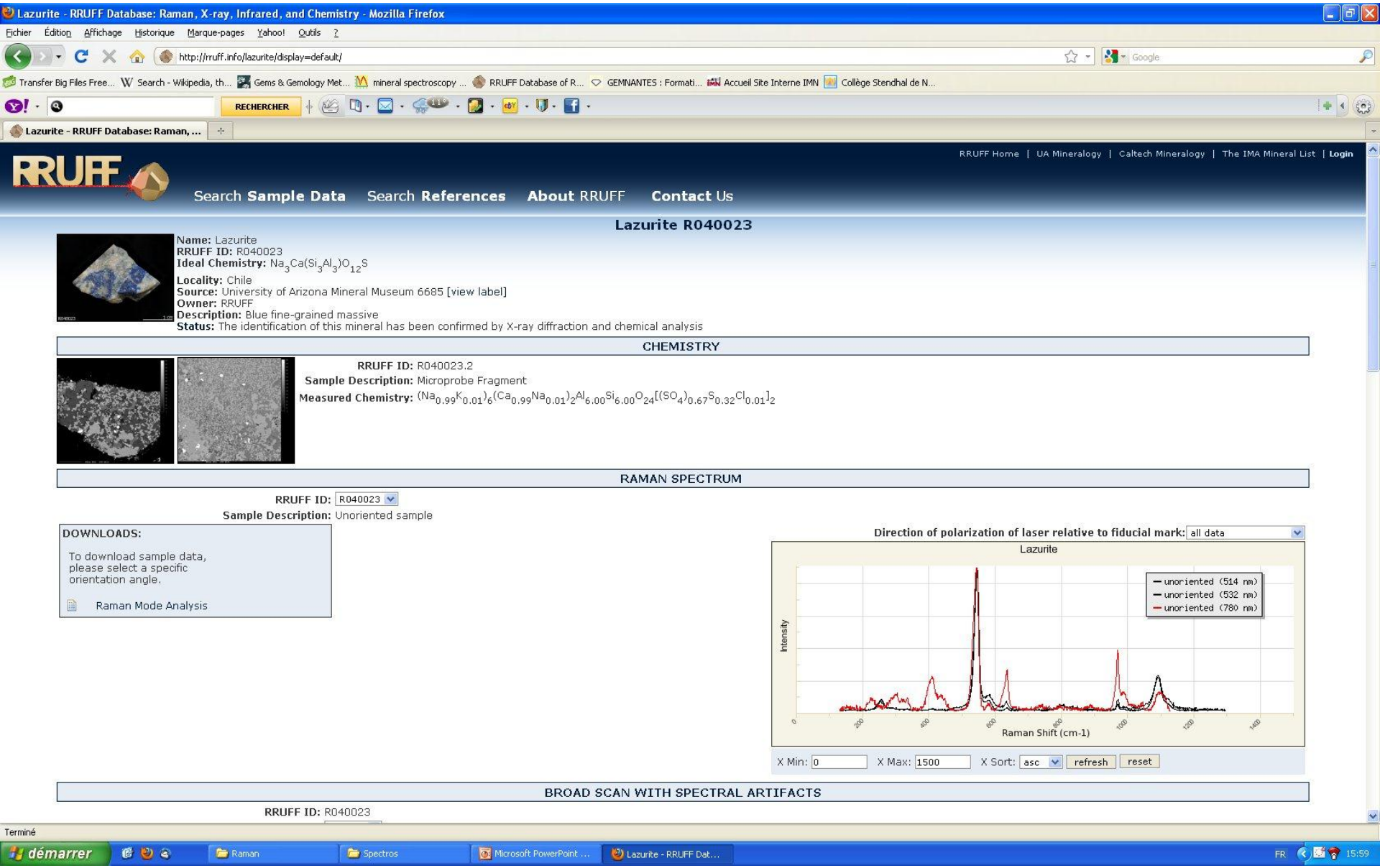
3 -Determination of the gem species



Databases

60 of the most common gems

Still useful for routine



Beware of luminescence: Ex hibonite

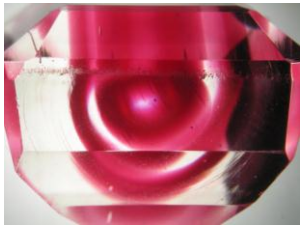
Problem with mineralogical or geological databases:

- **Some gem materials of interest are missing**

- Organics: ivory, tortoise shell, etc…

SGG

- Imitations and synthetics:
  Cubic zirconias, YAG, strontium titanante,..
  Glasses of gemological interest, « plastics »

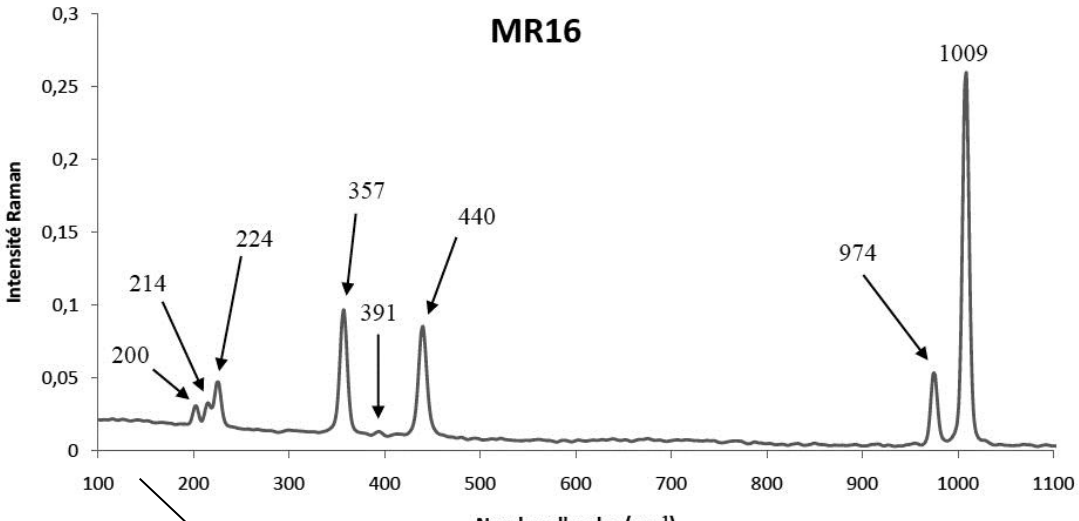


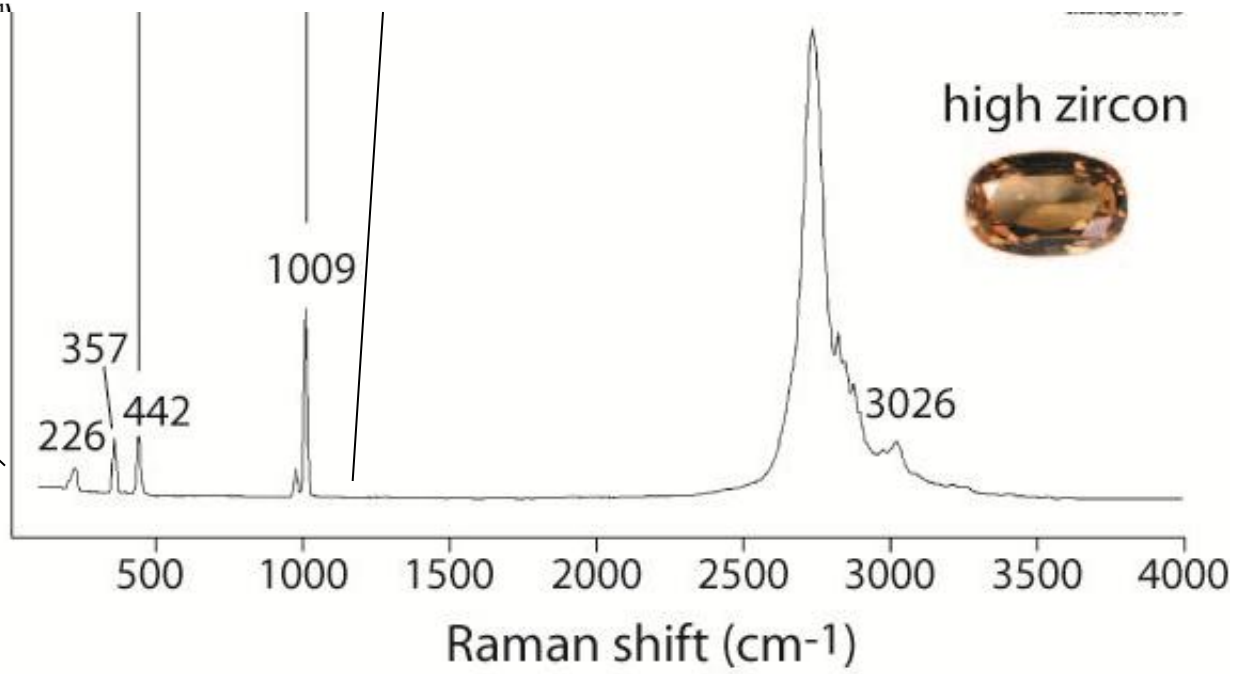
Lead glasses

BaZr Glass

Search in general literature much more time consuming

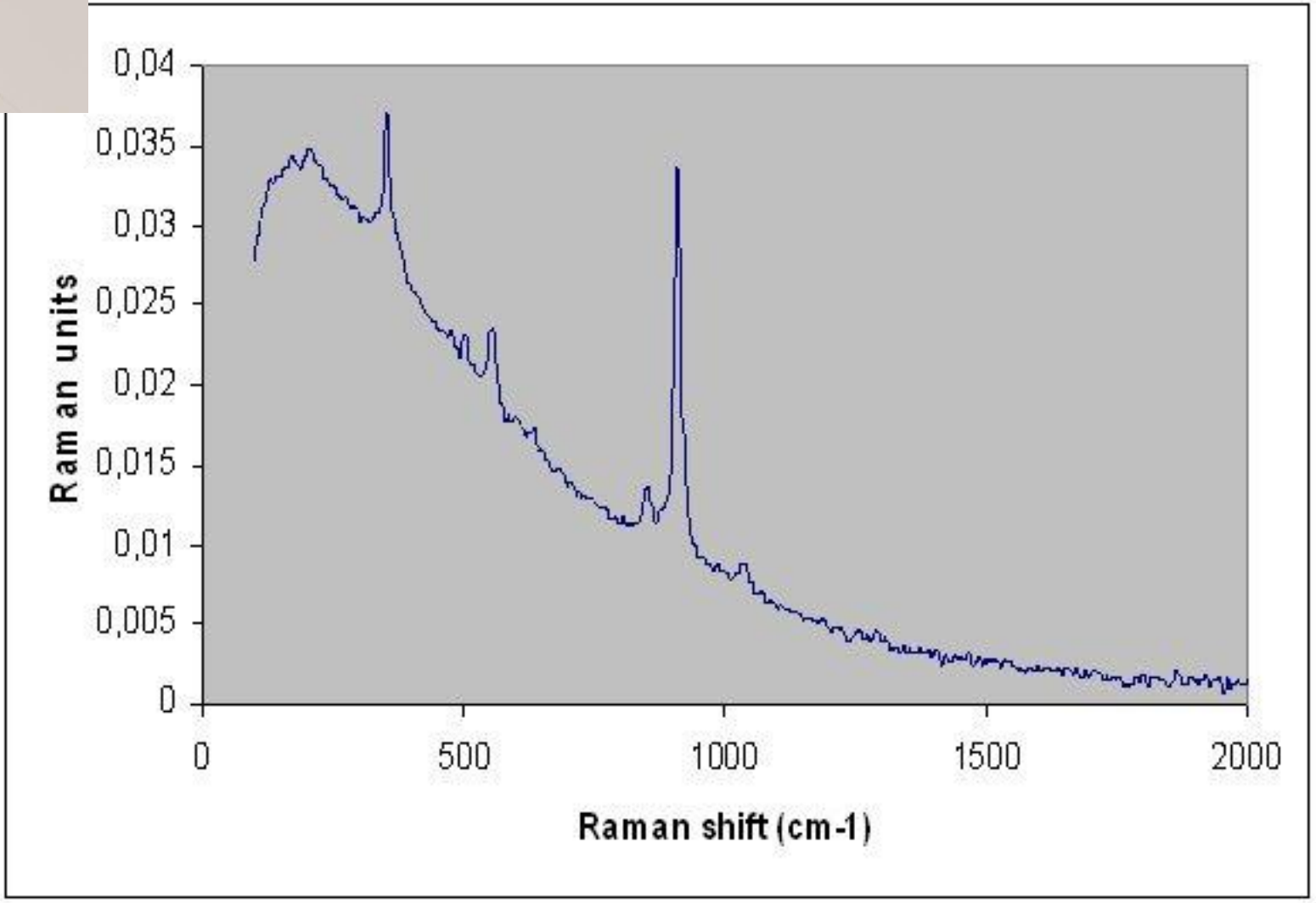
Restricted spectrum vs full spectrum





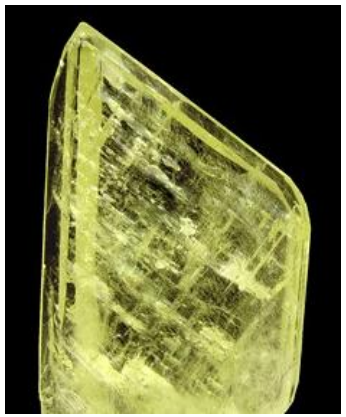
Macrosamples

Brown stone « over the limits »; no inclusion, no luminescence, no (hand-held visible) spectrum



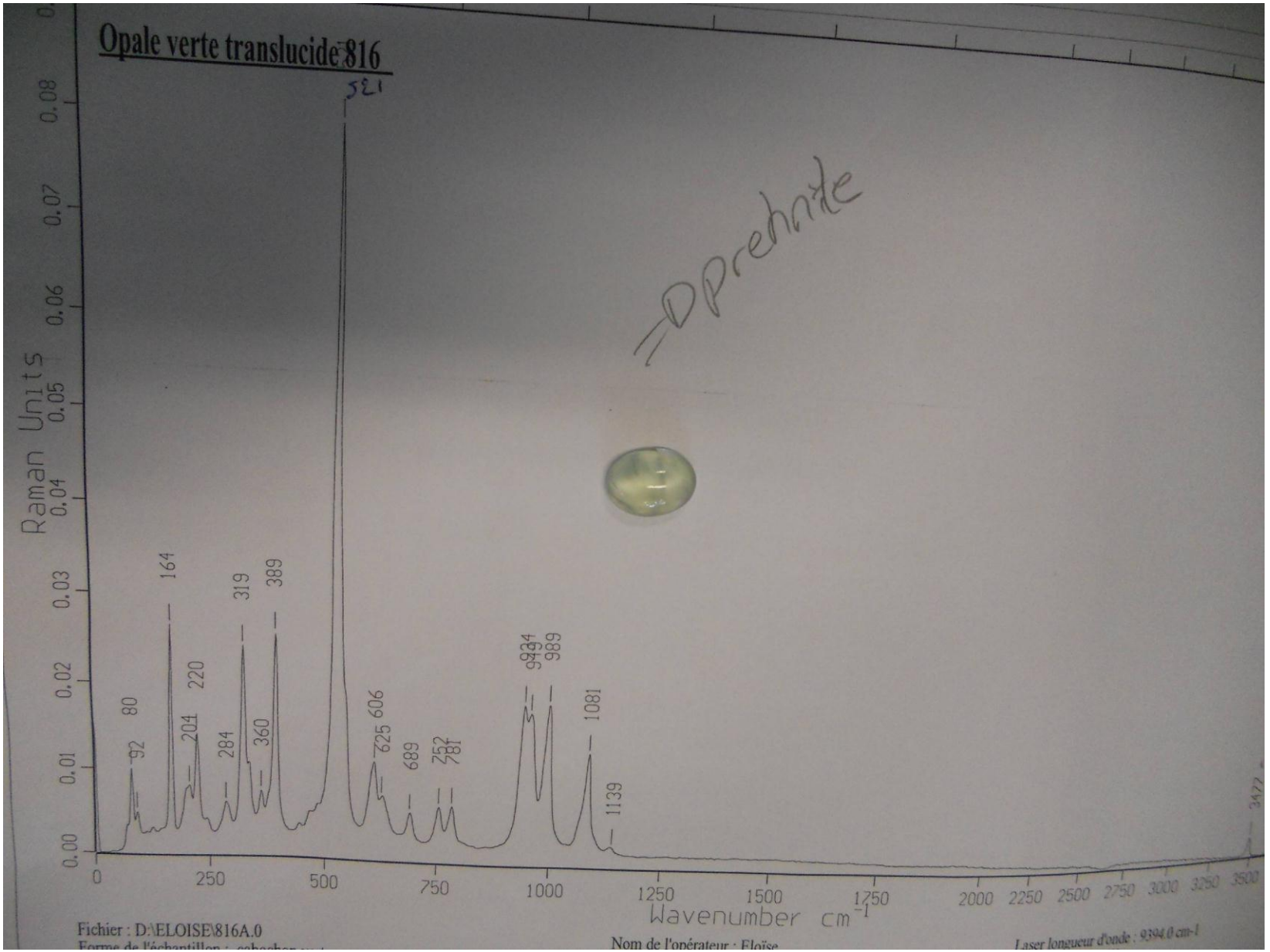
Macrosamples

All gem « amblygonite »
are actually montebrasite species



Solid solutions: approximate chemistry. Garnets, peridots, tourmalines

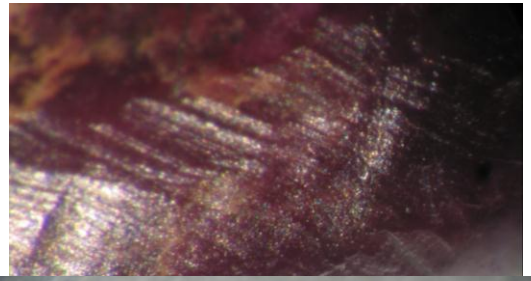
Macrosamples

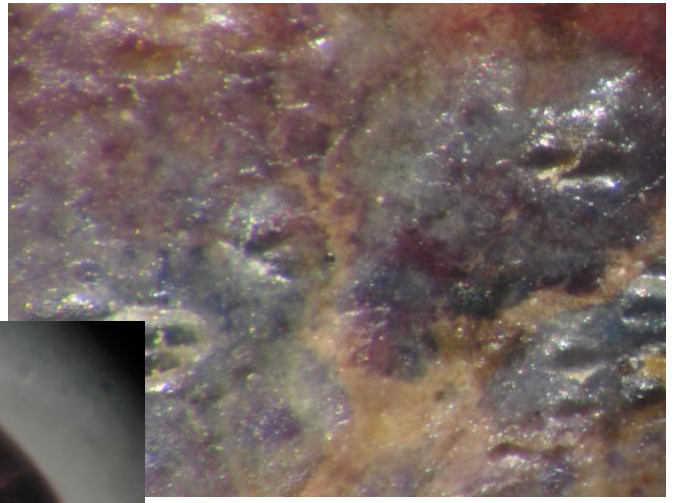


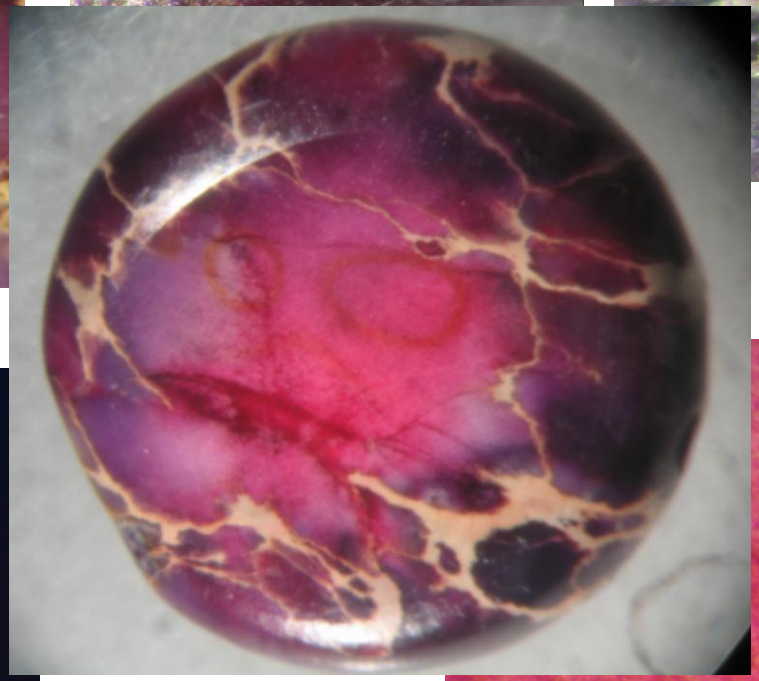
The curious case of the purple stone with spectacles

Macrosamples

soft

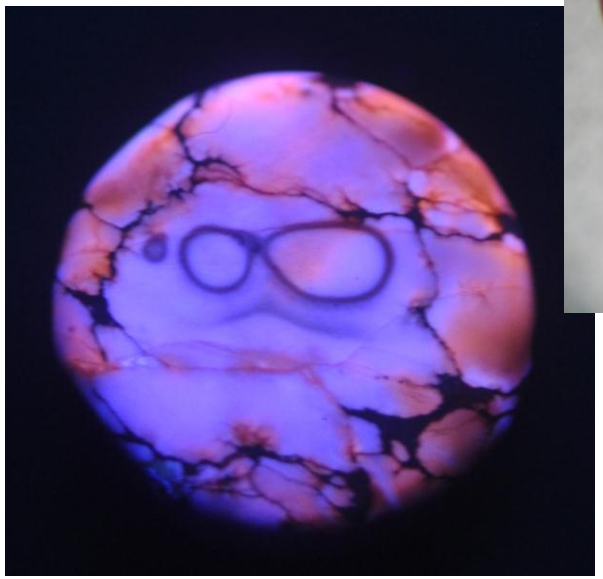




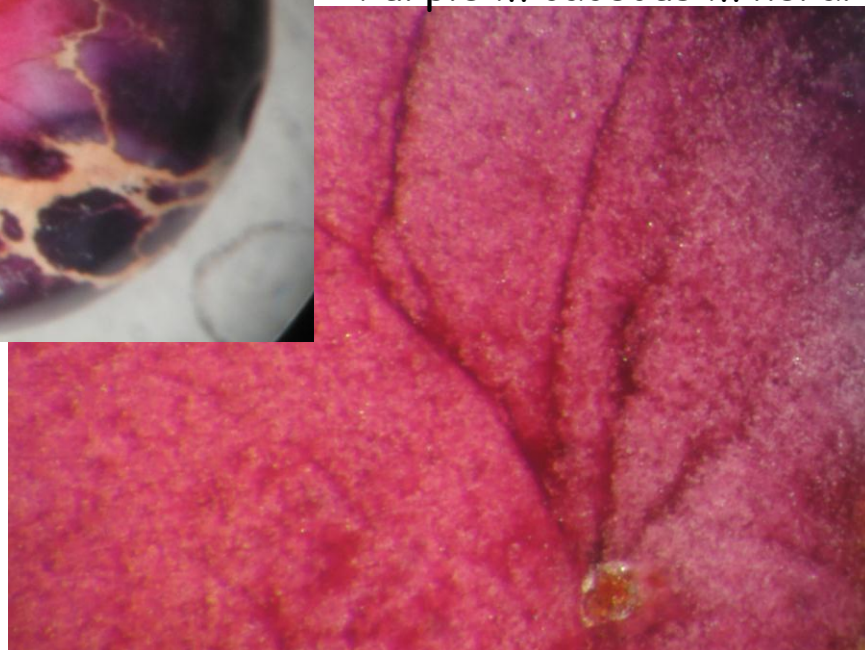


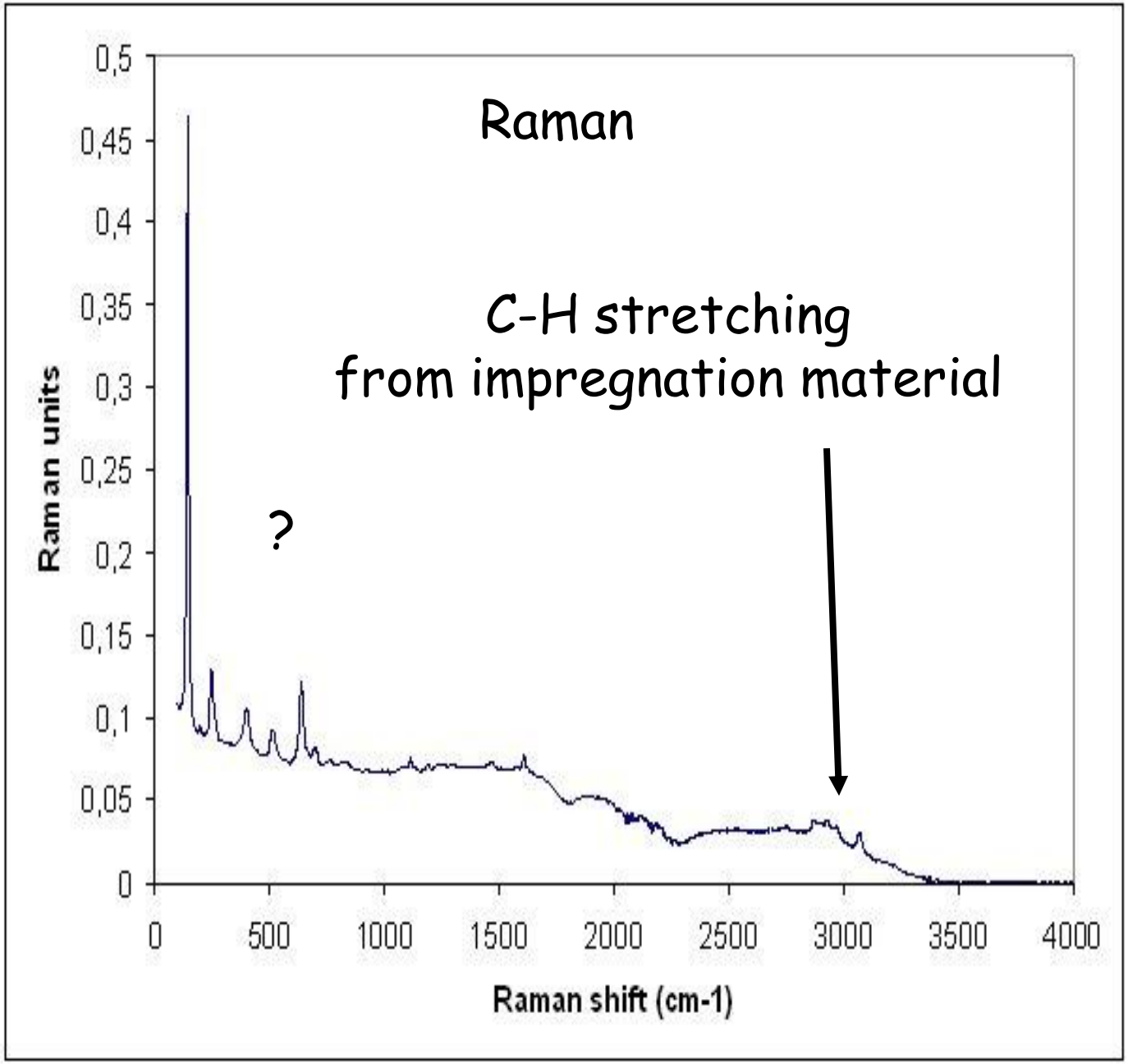
Impregnated
w « plastic »

Purple micaceous mineral



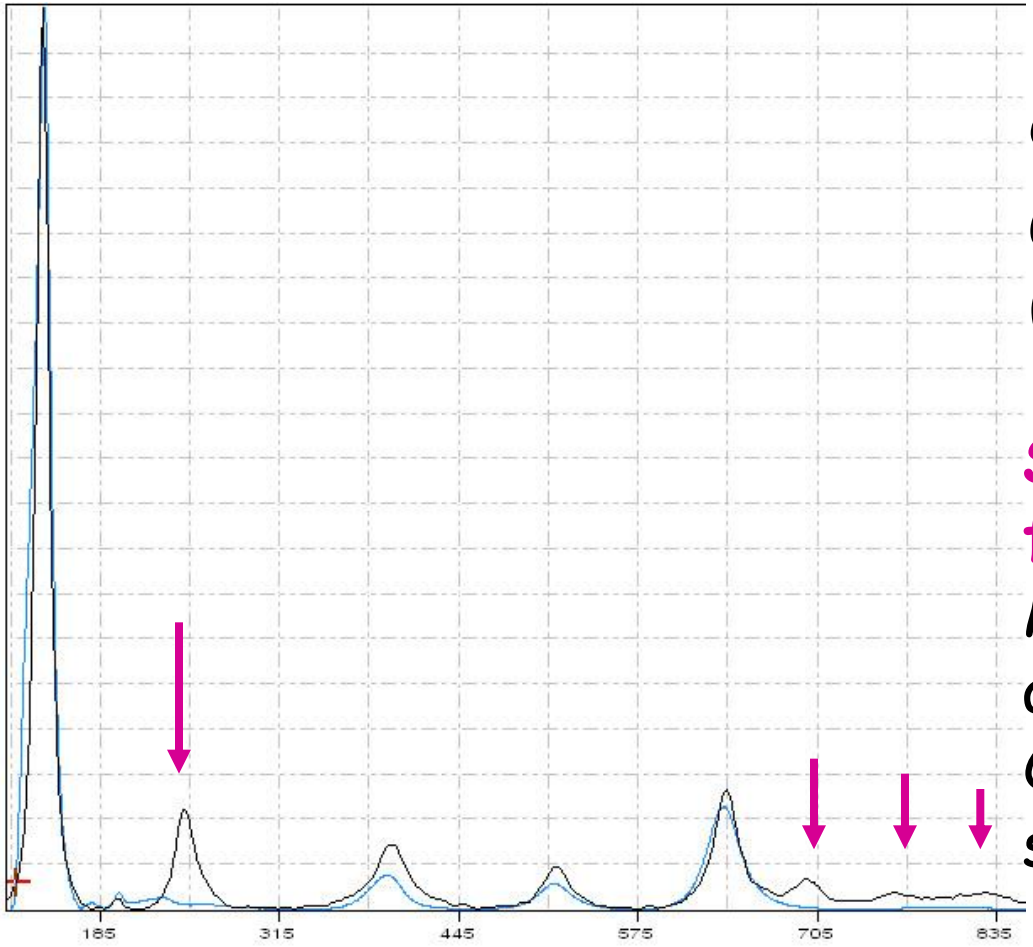
Blue and
orange LWUV
luminescence





Chemistry:
EDS
K, Al, Si, O
Ti
Traces of Mn

Possibly
Mn^{3+}: color
Mn^{2+}: orange luminescence

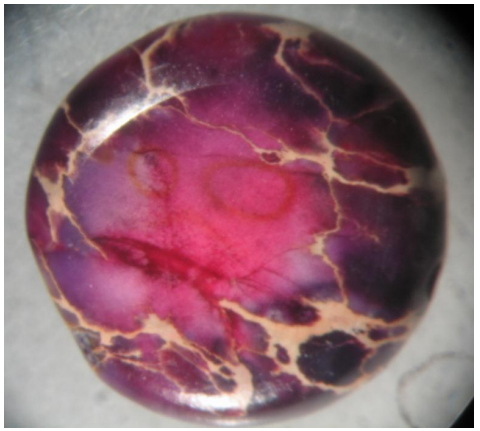


Crystal Sleuth:

Good match with **anatase**!
(green spectrum)

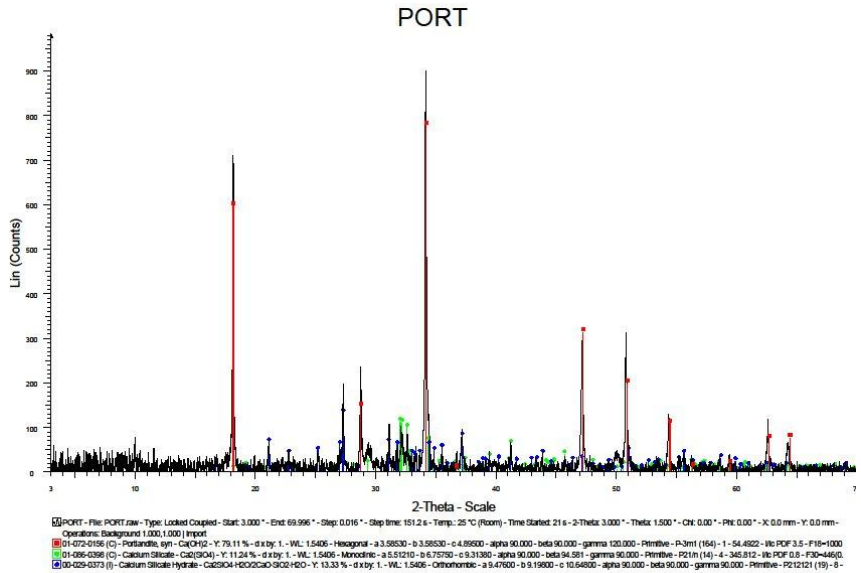
Some lines unaccounted for:
Micaceous potassium aluminosilicate
Close to muscovite but more spread

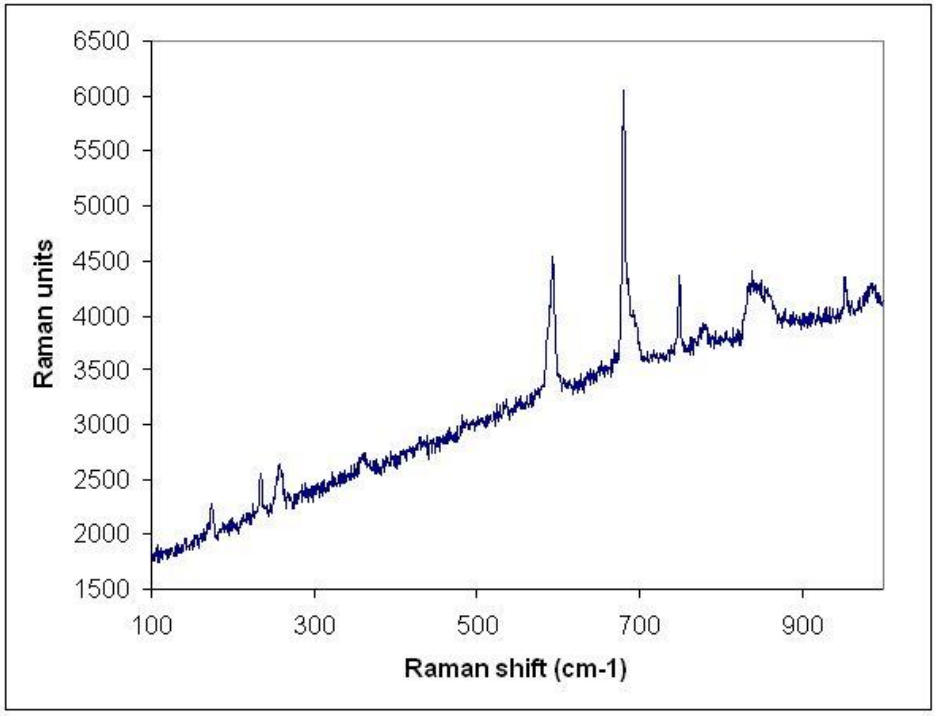
Can we manage to identify this natural material non-destructively?



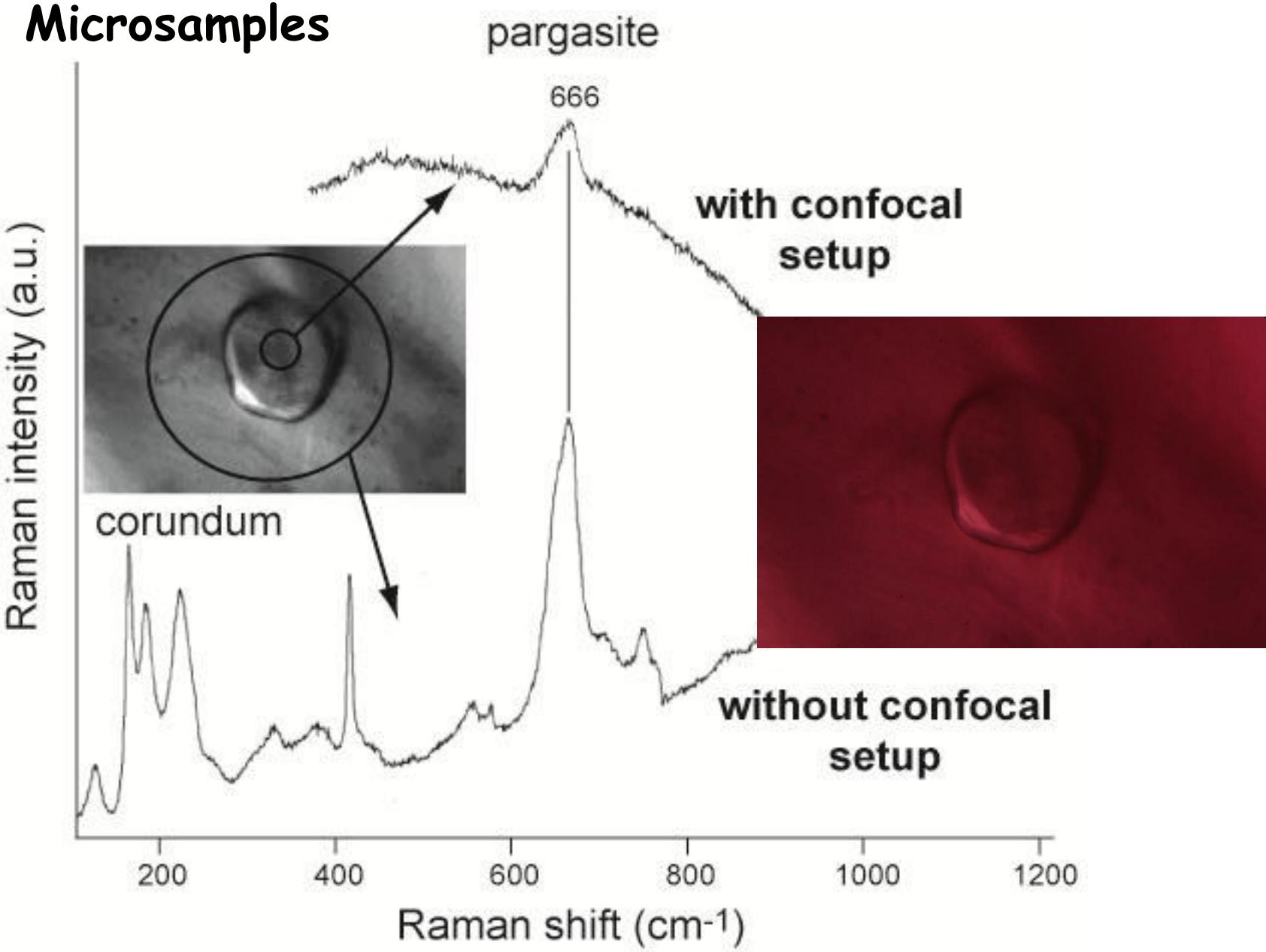
Macrosamples

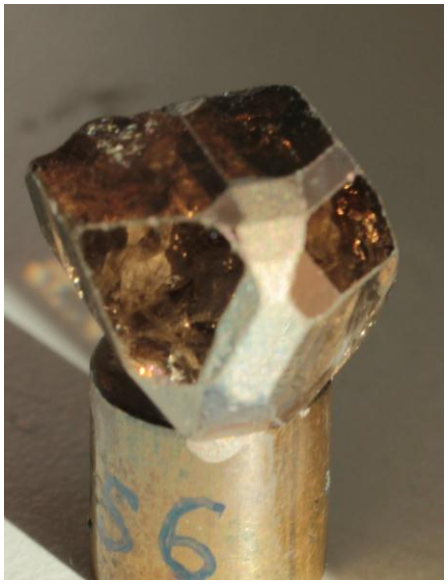
Blue portlandite
Also yellow and green
Cu doped, natural?





Microsamples

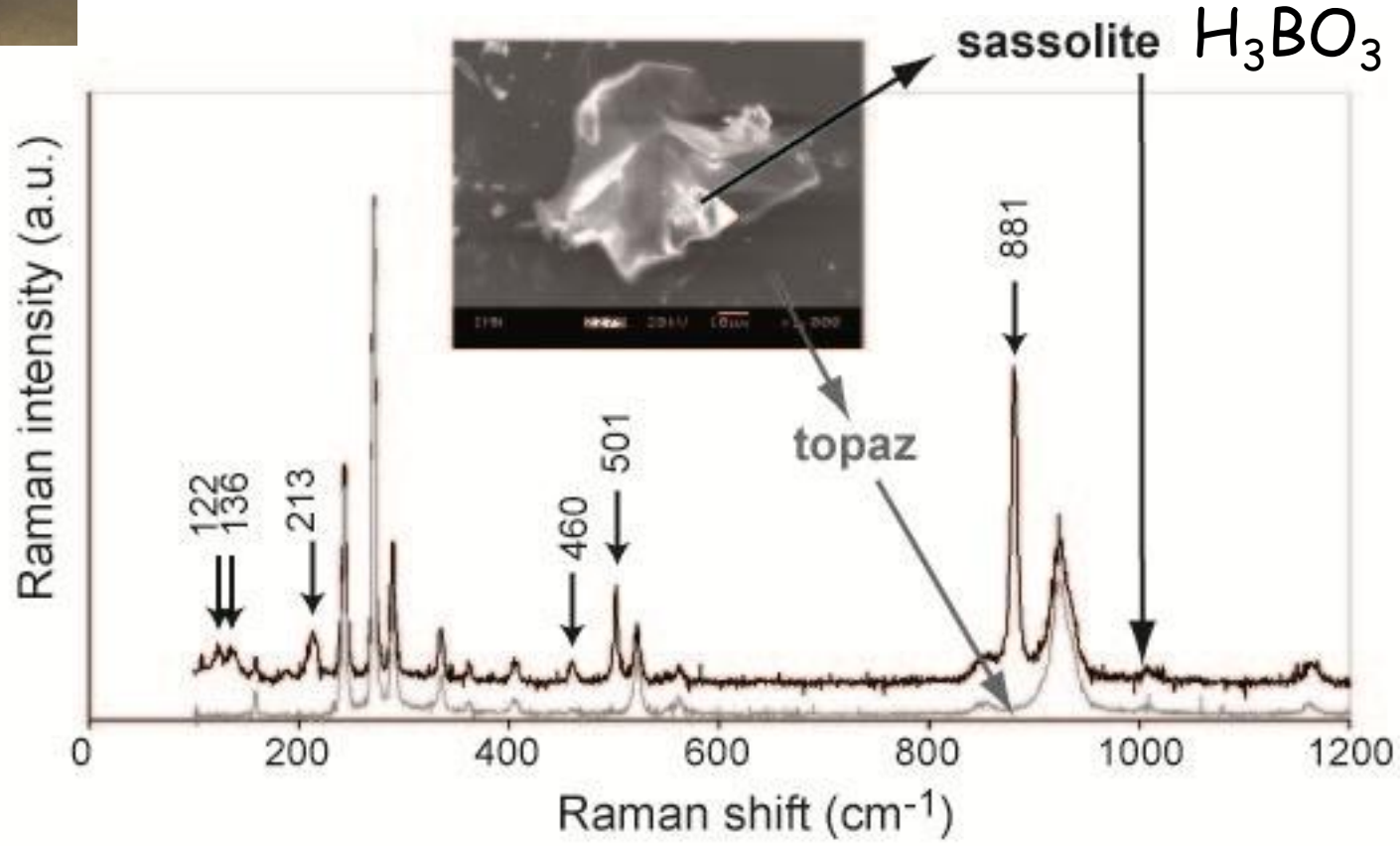


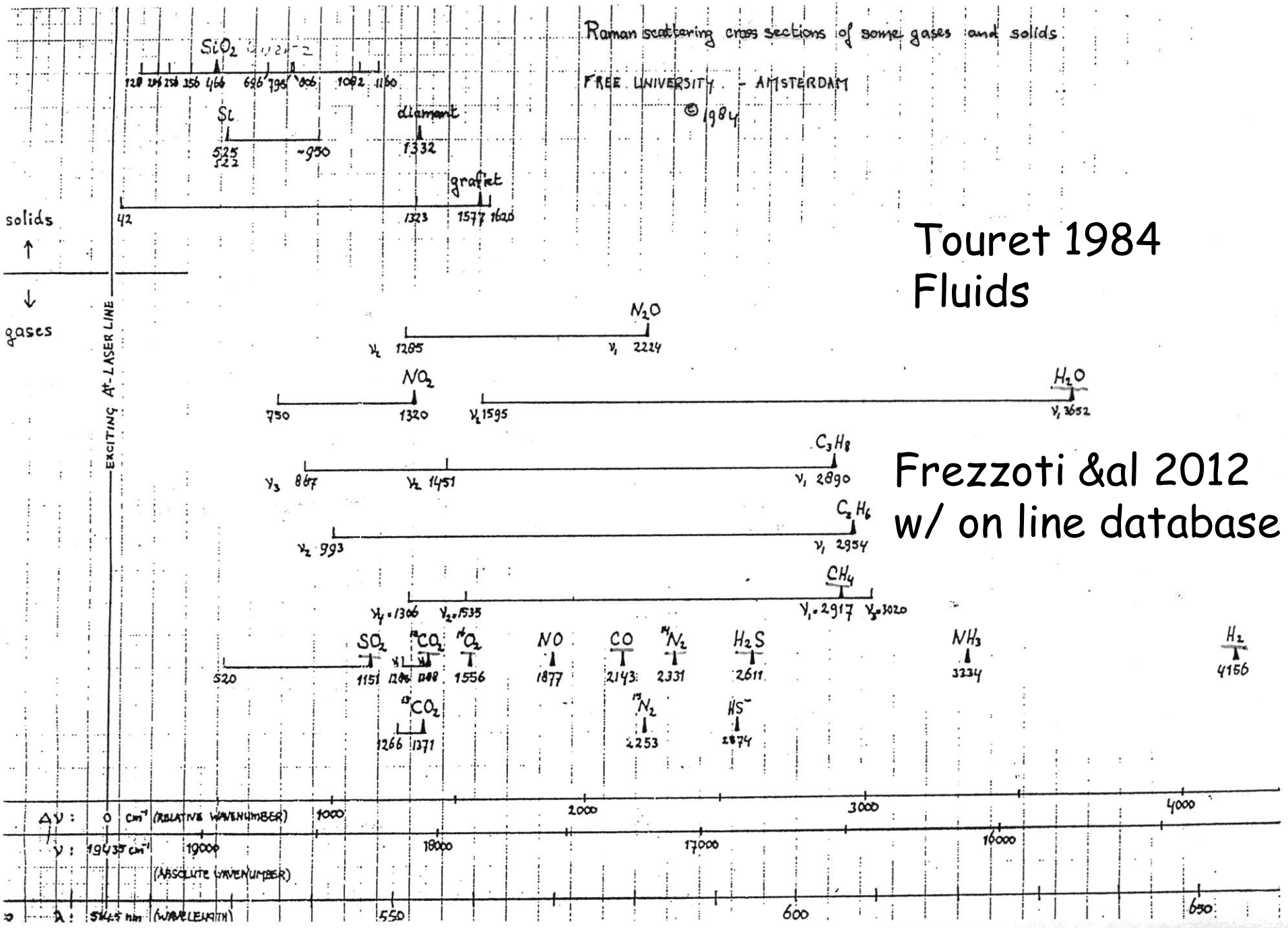


Microsamples

Identification of phases in fluid inclusions

Little exploited by gemmologists
Fluids or daughter crystals

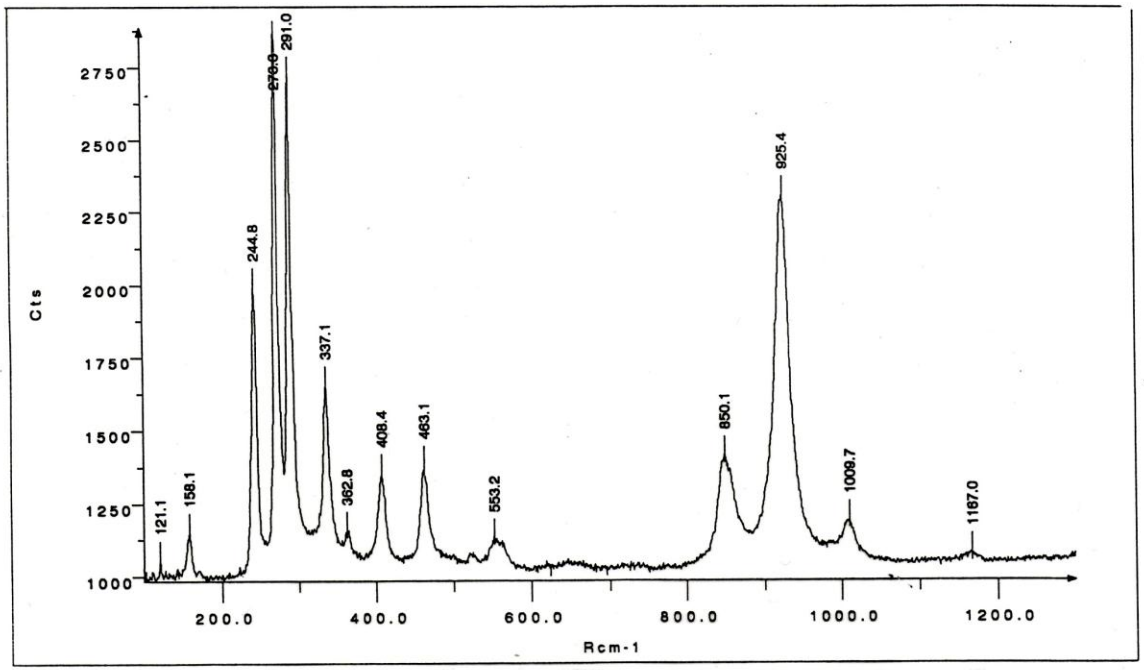




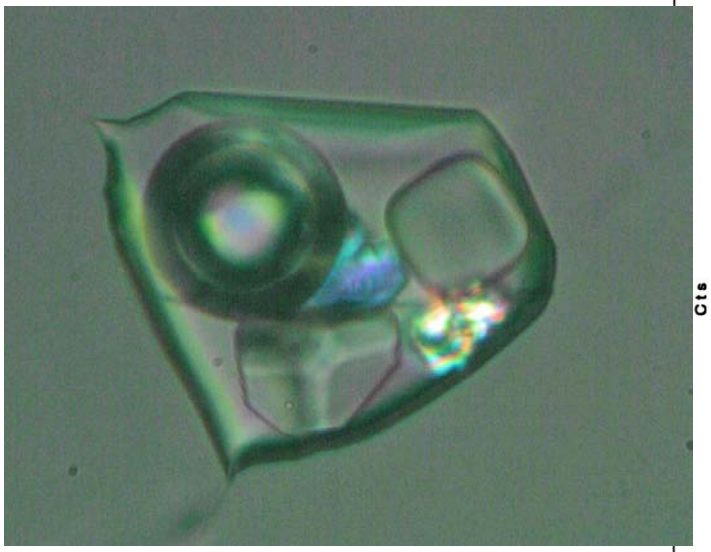
Touret 1984
Fluids

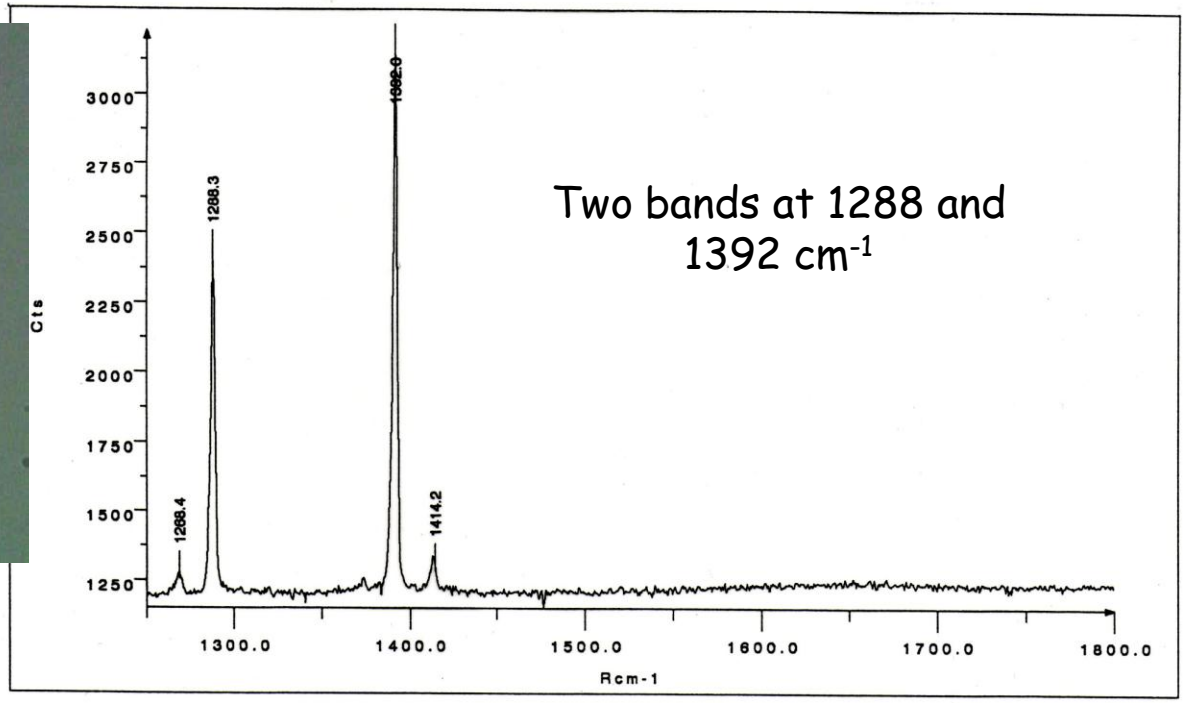
Frezzoti &al 2012
w/ on line database

Identification of phases in fluid inclusions



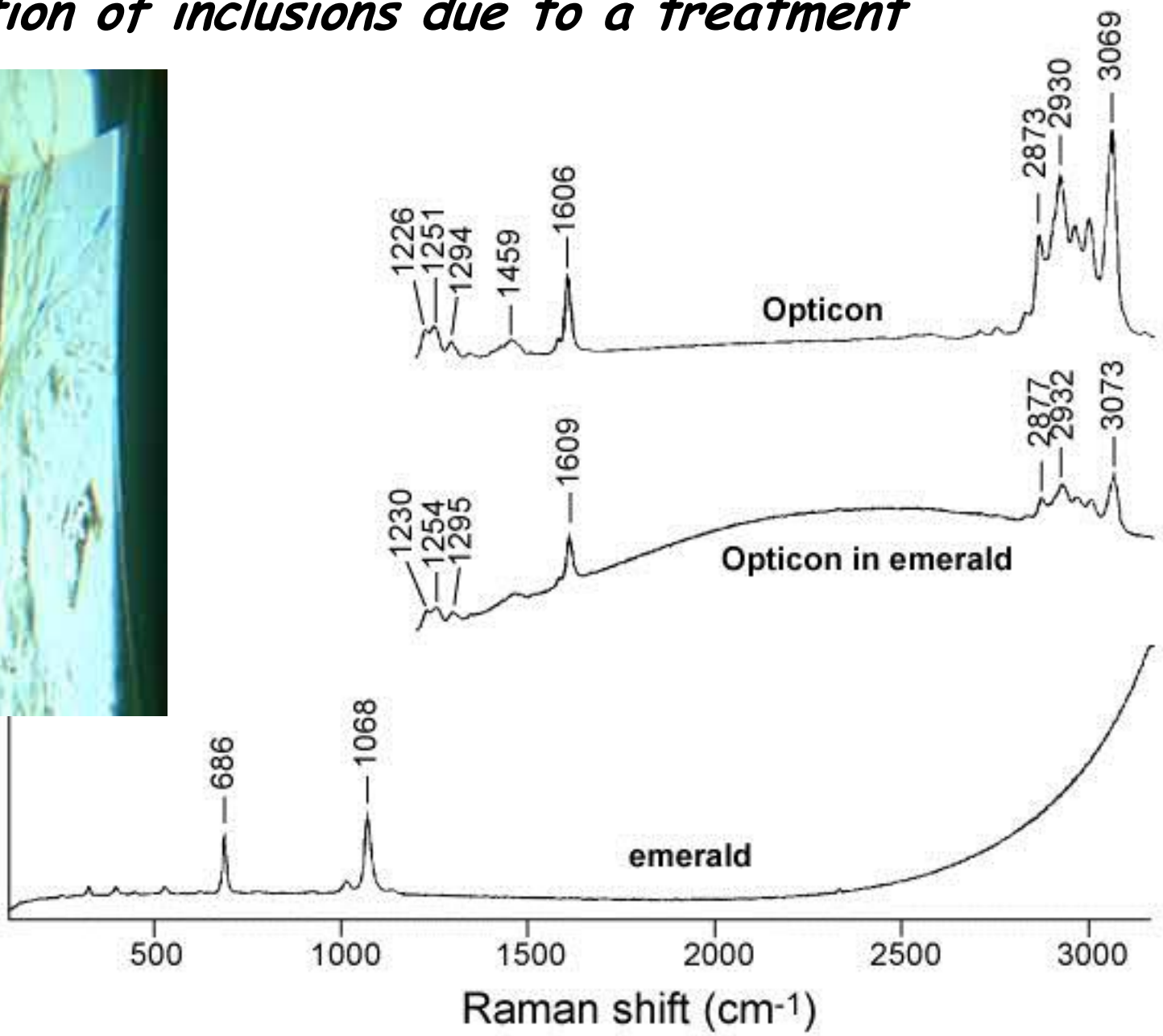
Inclusion in blue topaz





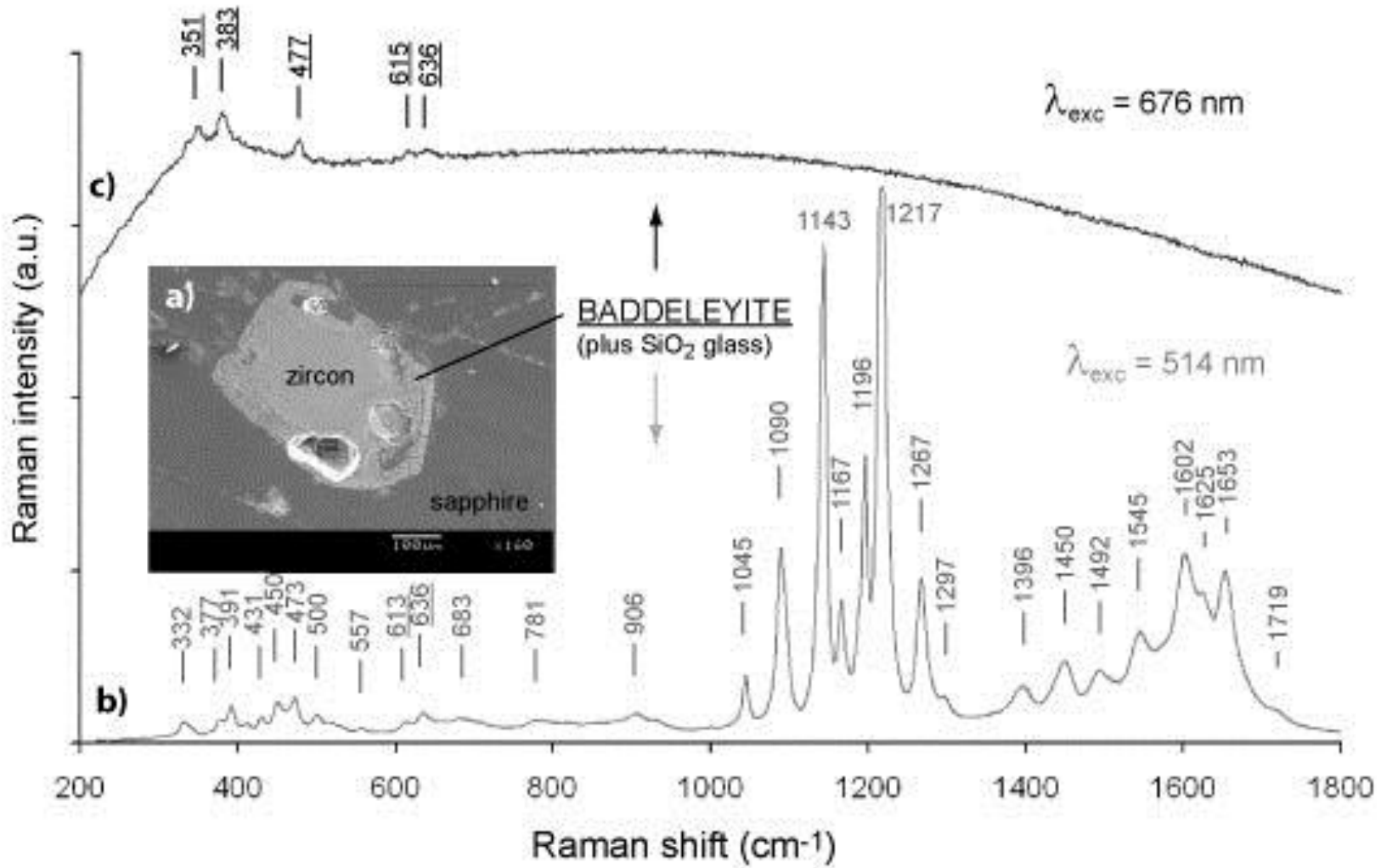
Two bands at 1288 and 1392 cm^{-1}

Identification of inclusions due to a treatment



Identification of inclusions due to a treatment

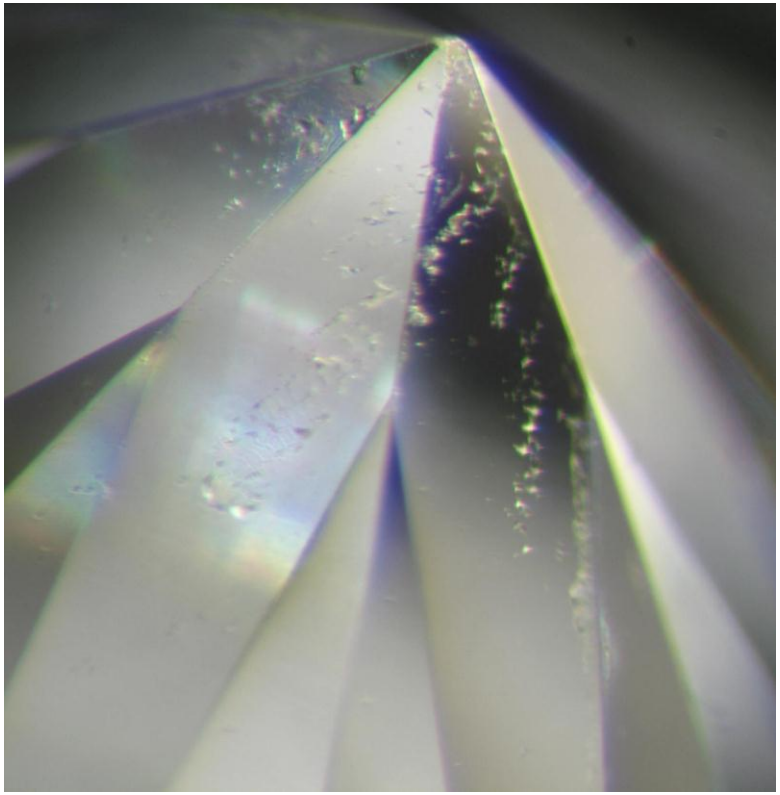
Melting of zircon inclusions: 1700 to 1850°C



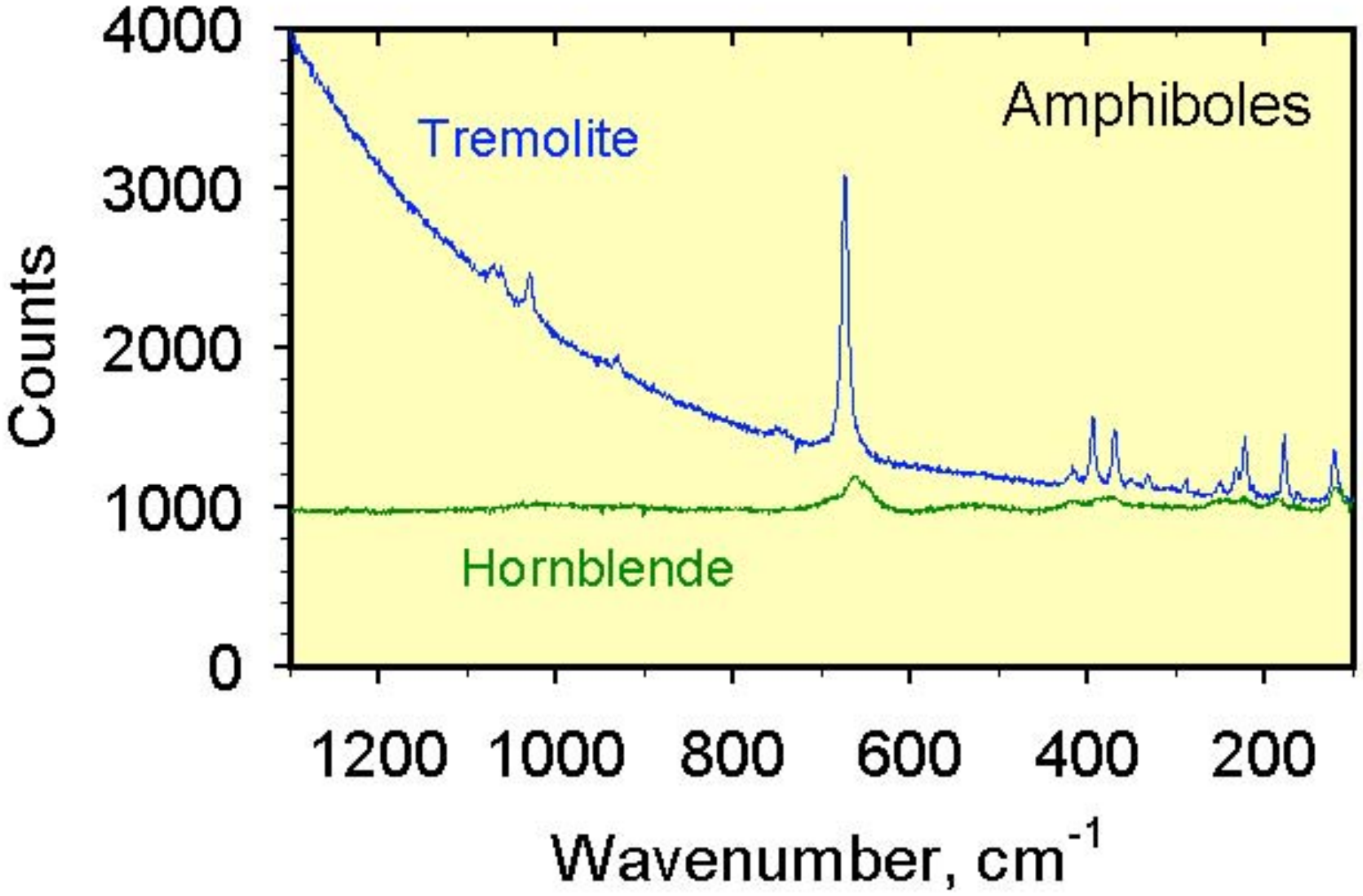
$ZrSiO_4 \Rightarrow ZrO_2 + SiO_2$

Identification of thin films covering gems

« diamond-covered »
cubic zirconia



4- Determination of order disorder: Bandwidth considerations



4- Determination of order disorder: Bandwidth considerations

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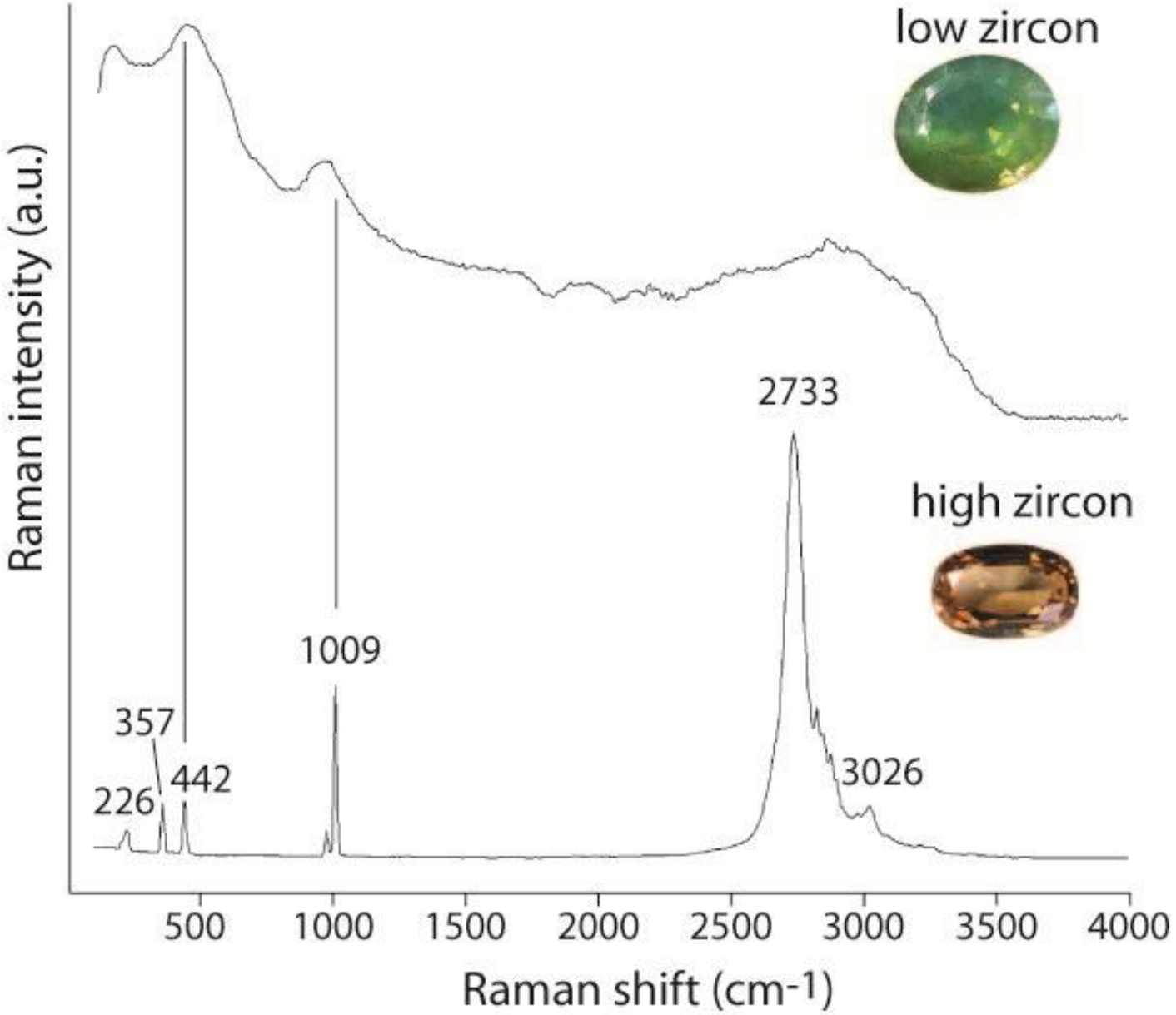
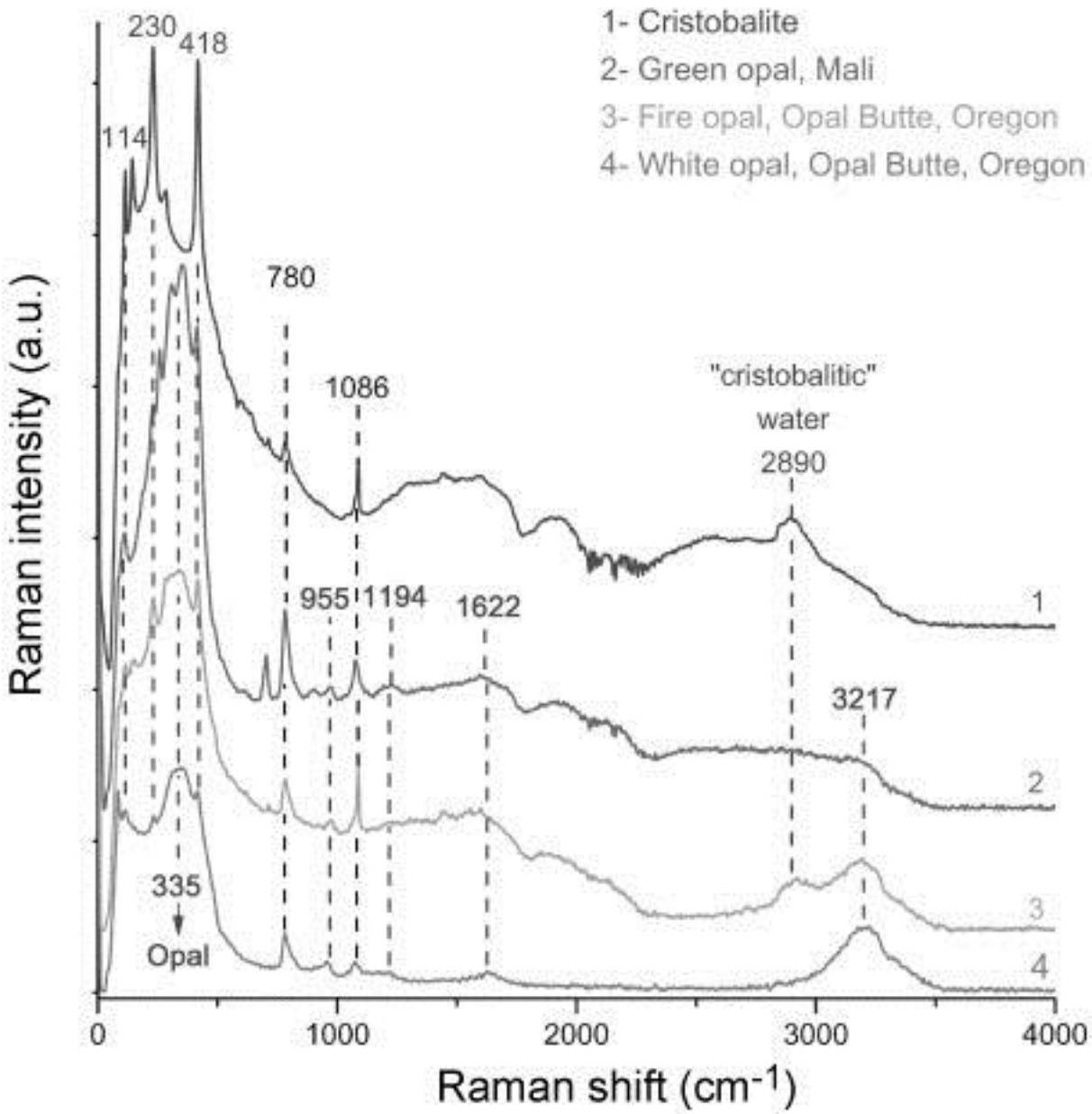


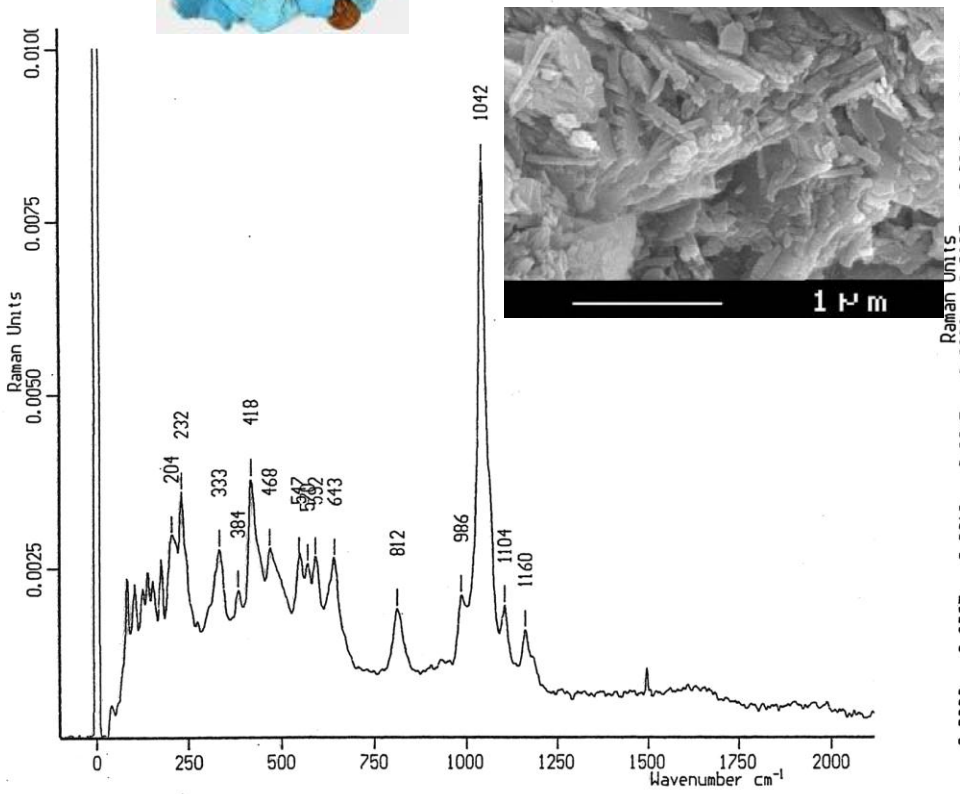
Nasdala et al. 1995

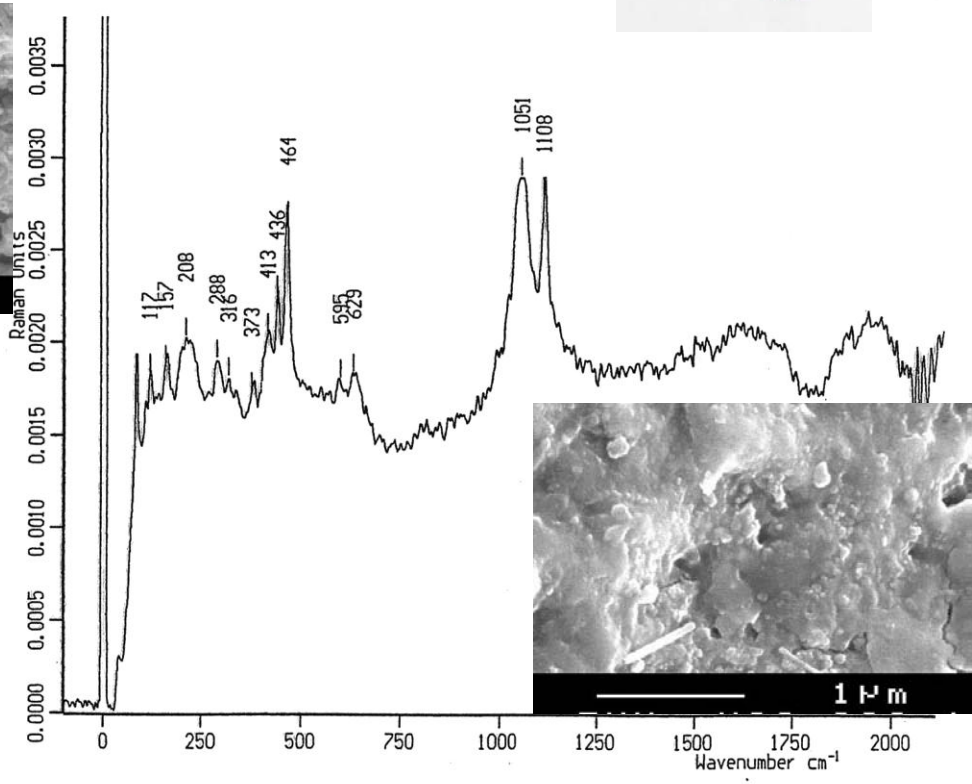
4- Determination of order disorder: Bandwidth considerations



« Blue agate »

4- Determination of order disorder: Bandwidth considerations





Natural turquoise: well cristallized, large grains, fine peaks

Synthetic turquoise: poorly cristallized, small grains, large peaks

5- Resonant Raman spectroscopy and the identification of some organic colouring agents in gems

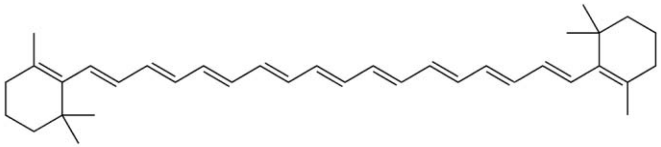
Parrodienes vs carotenoids

Parrots vs carrots

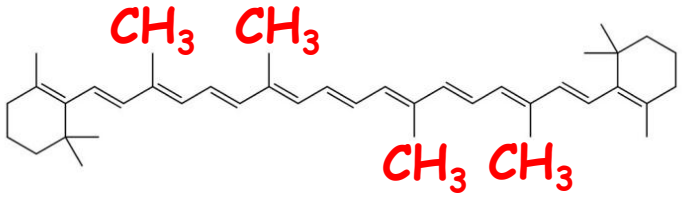
Both are oligomers of polyacetylene

End-radicals are generally of unknown nature

Parrodienes
Unsubstituted polyenes
Uncommon in nature
Pigments for N= 6 to 15



Carotenoids
Substituted polyenes
Very common in nature

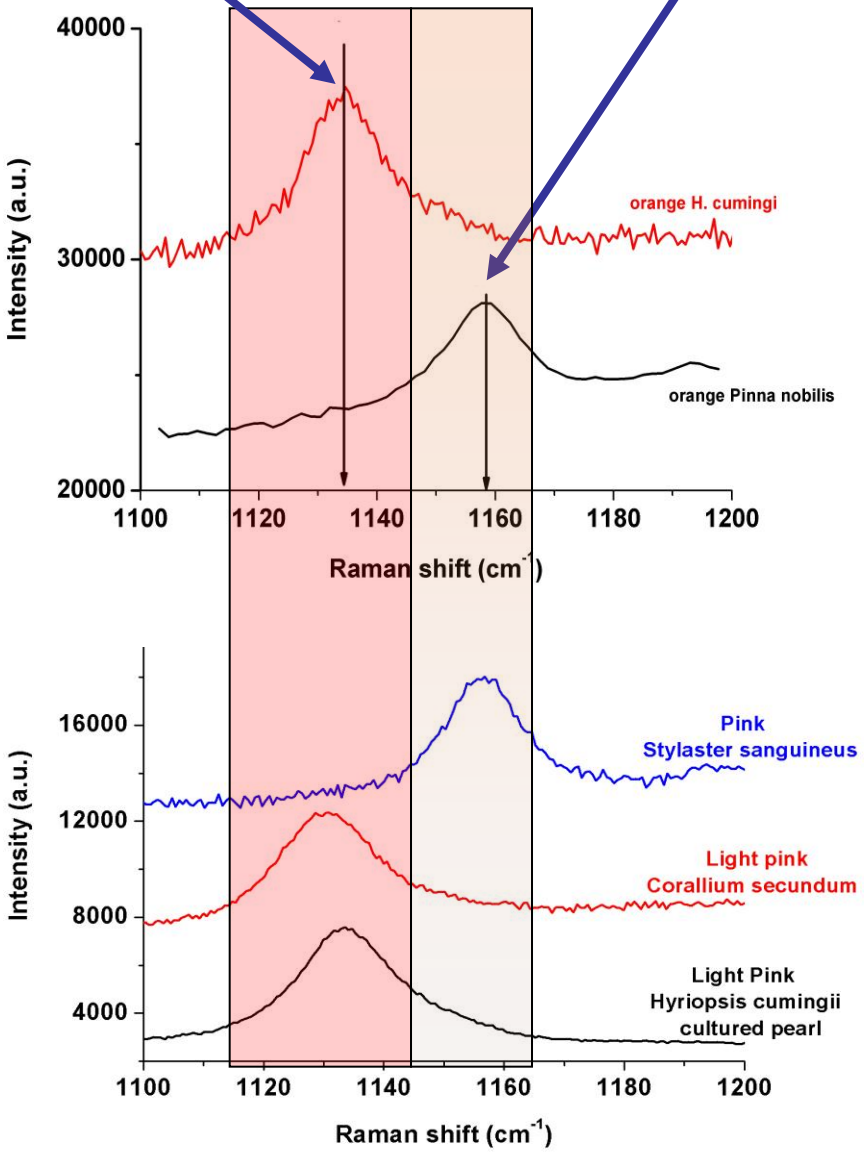


Parrodienes

1130 ±15 cm^{-1}

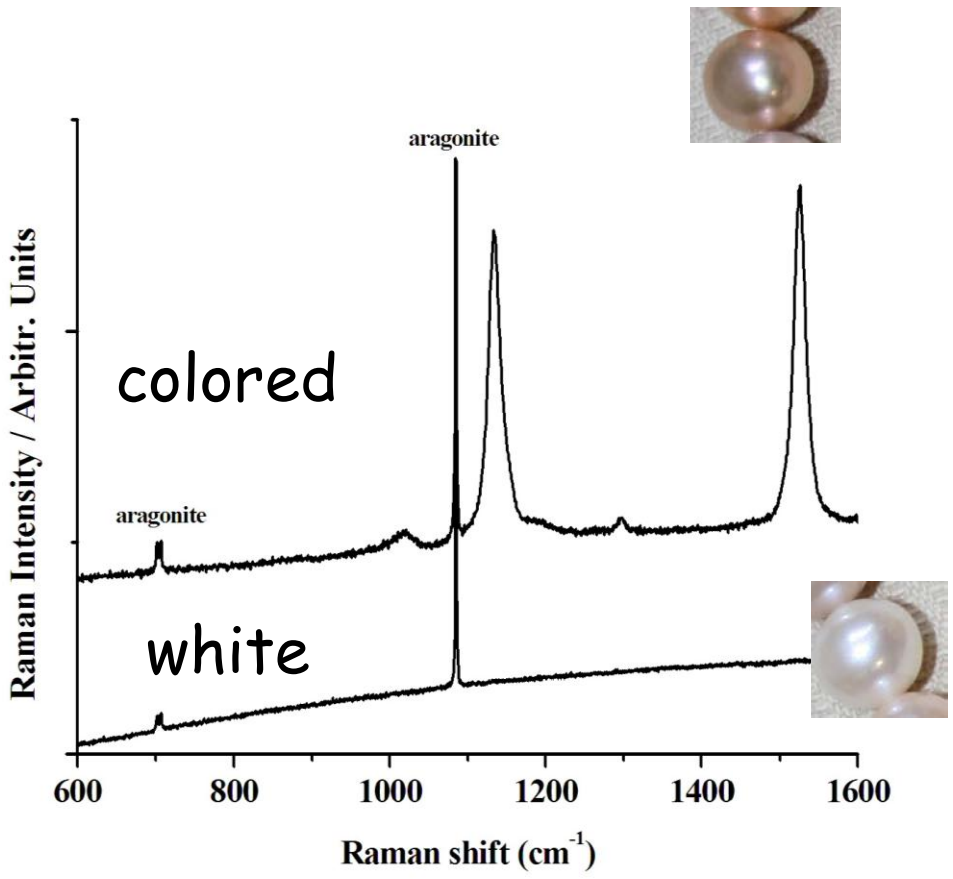
Carotenoids

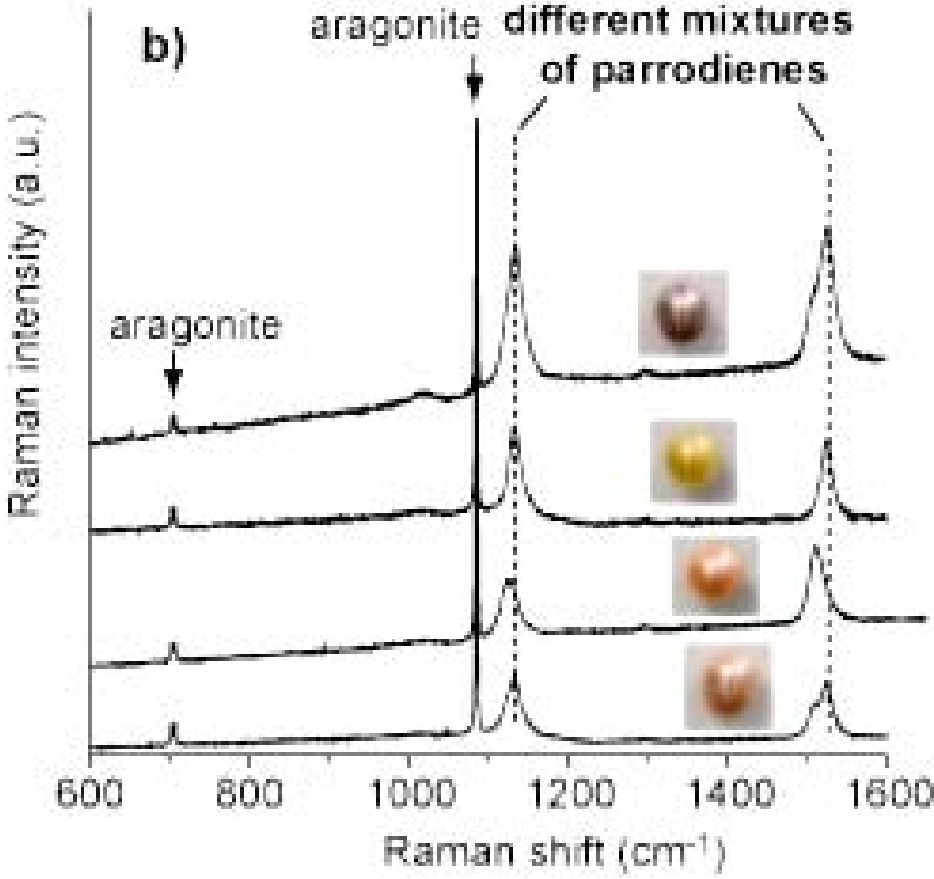
1155±10 cm^{-1}



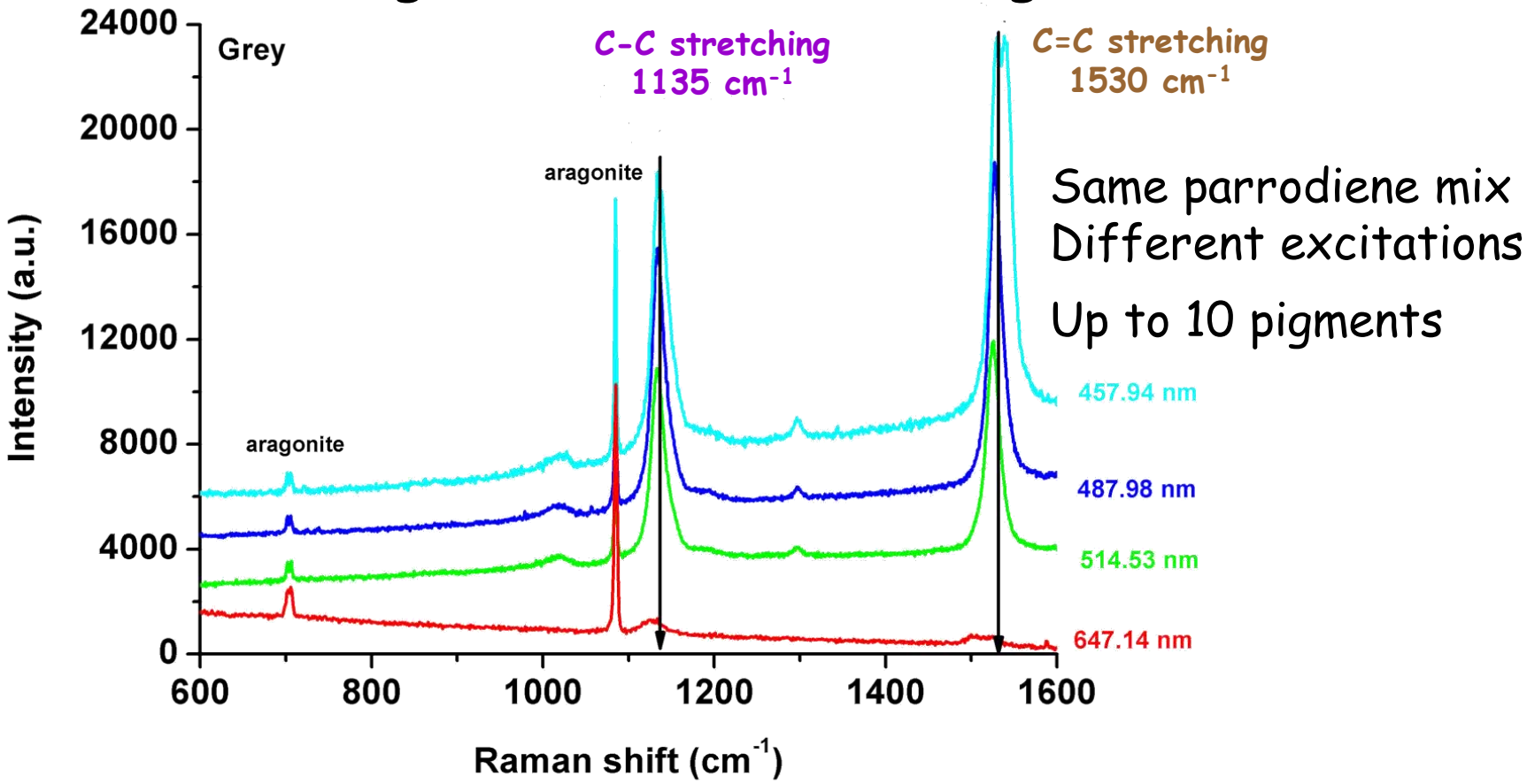
Applications to pearls and corals

Pearls Freshwater cultured pearls (FWCP)





Raman spectra of a naturally grey colored FWCP using 4 excitation wavelengths



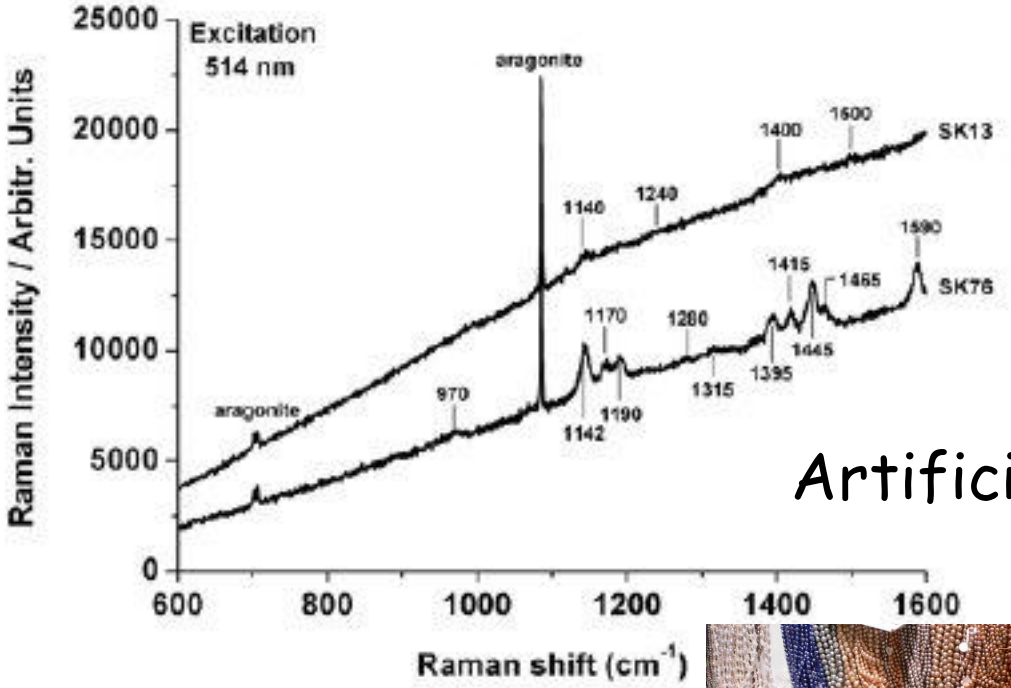
Changing excitation wavelength, variations in the position, shape and relative intensities of the two most intense bands are noted (mainly for C=C stretching band).

Exact position of C=C stretching band depends on the polyenic chain length.

Barnard et al. 2006: $\nu_1 = 97.07 \ln(1/n) + 1745$ cm^{-1} for $3 \leq n \leq 12$

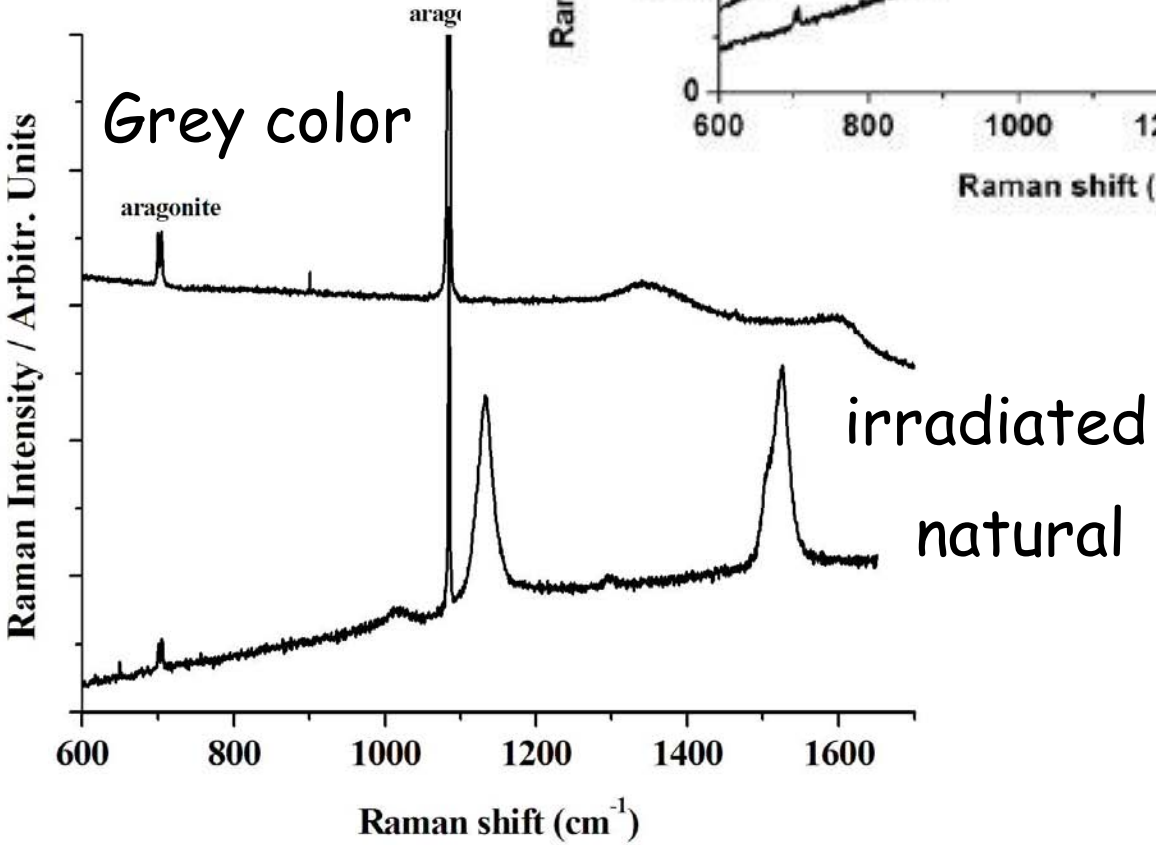
n: number of double bonds in the polyenic chain.

Detection of Treatment: Artificial coloring of pearls



Artificial dyes

Grey color



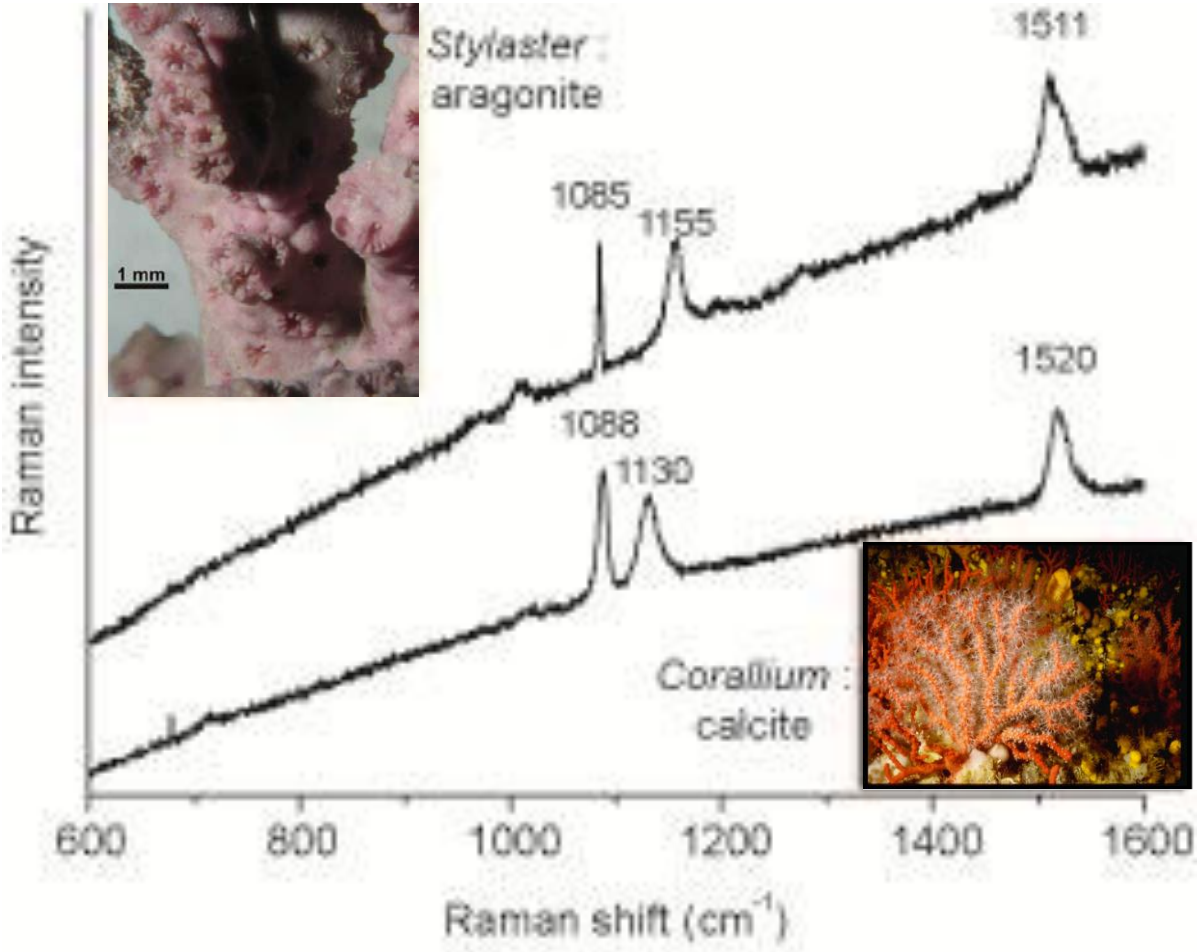
irradiated

natural

Corals

Carotenoids

Combination found only in this species for gem-quality coral



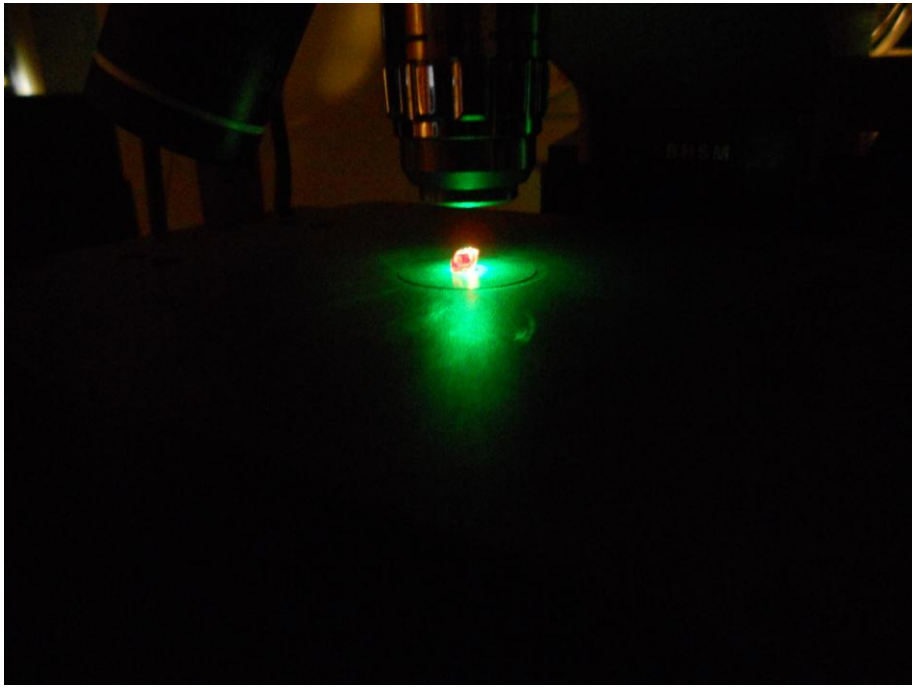
parrodienes

6 - Raman spectrometers as photoluminescence instruments for gems

Why do gemmological laboratories use Raman spectrometers for luminescence spectroscopy?

For diamond, PL more important than Raman itself!

Two spectrometers for the price of one, with limitations



Instrumentation

HeCd (325 nm), Ar+ (e.g. 488 nm and 514 nm), frequency-doubled Nd:YAG (532 nm), diode lasers (e.g. 532 nm and 785 nm)
usually a range of lasers is necessary

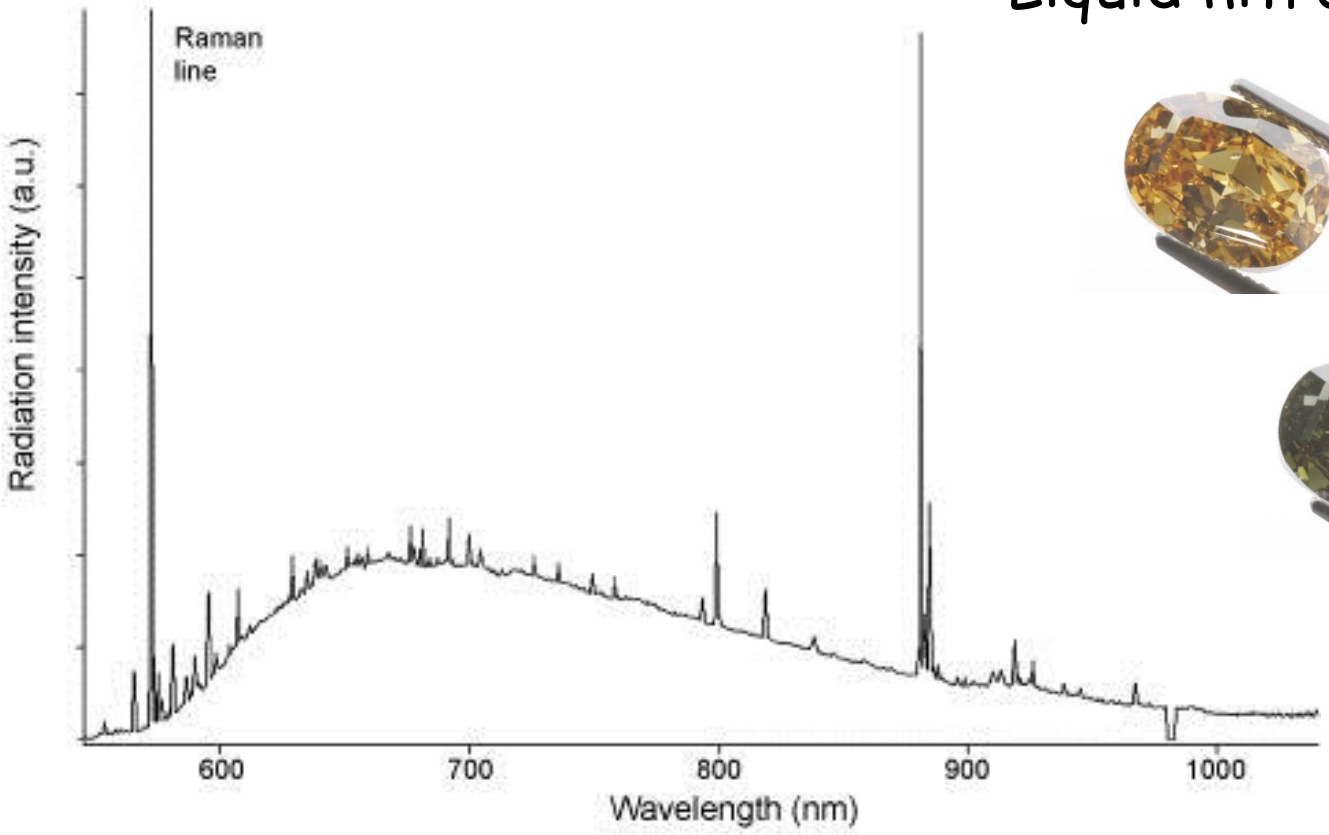
Usually as a microprobe

Usually at liquid nitrogen temperature (beware damage)

Applications to gems

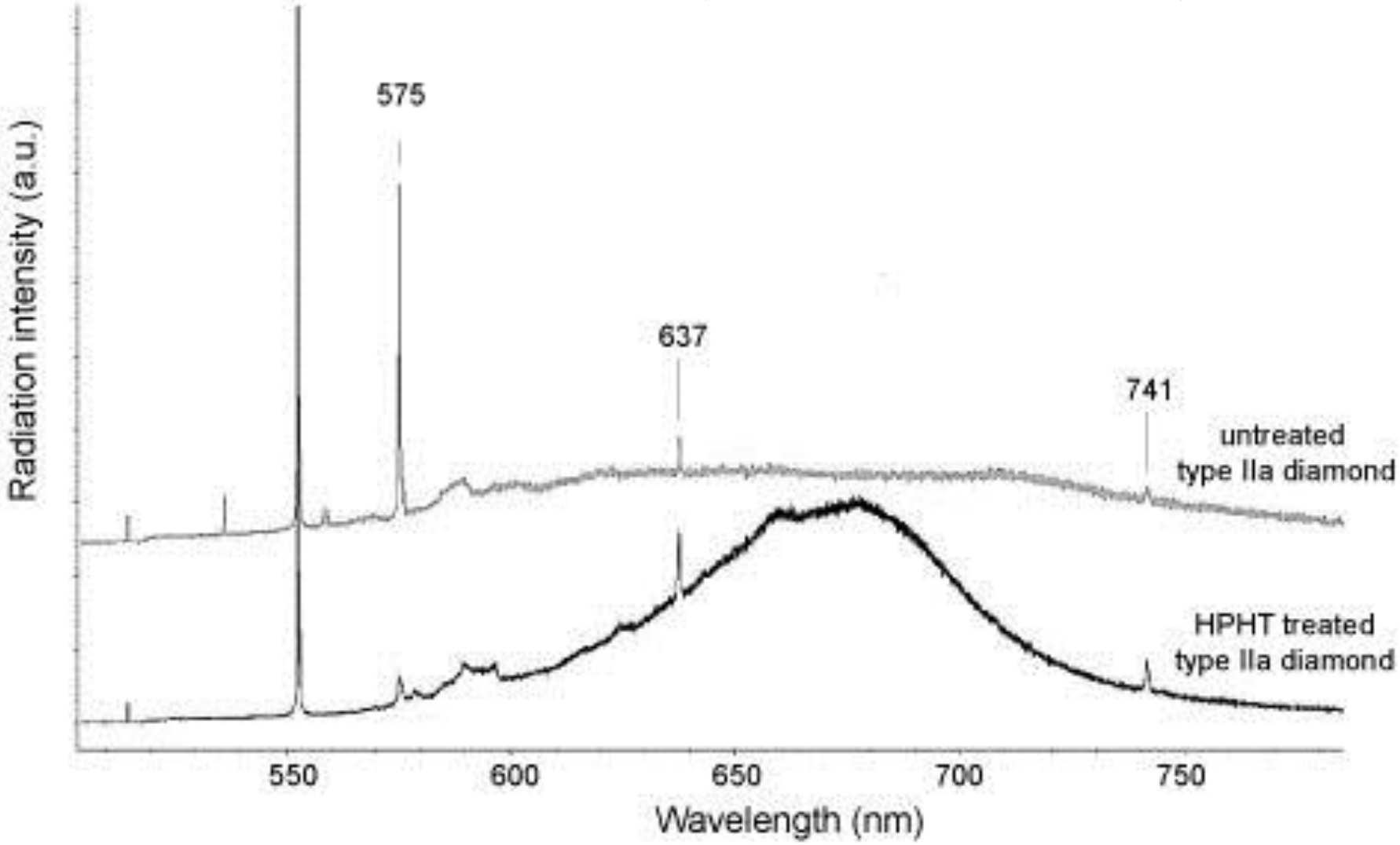
Photoluminescence spectroscopy of diamonds

Chameleon diamond
Liquid nitrogen

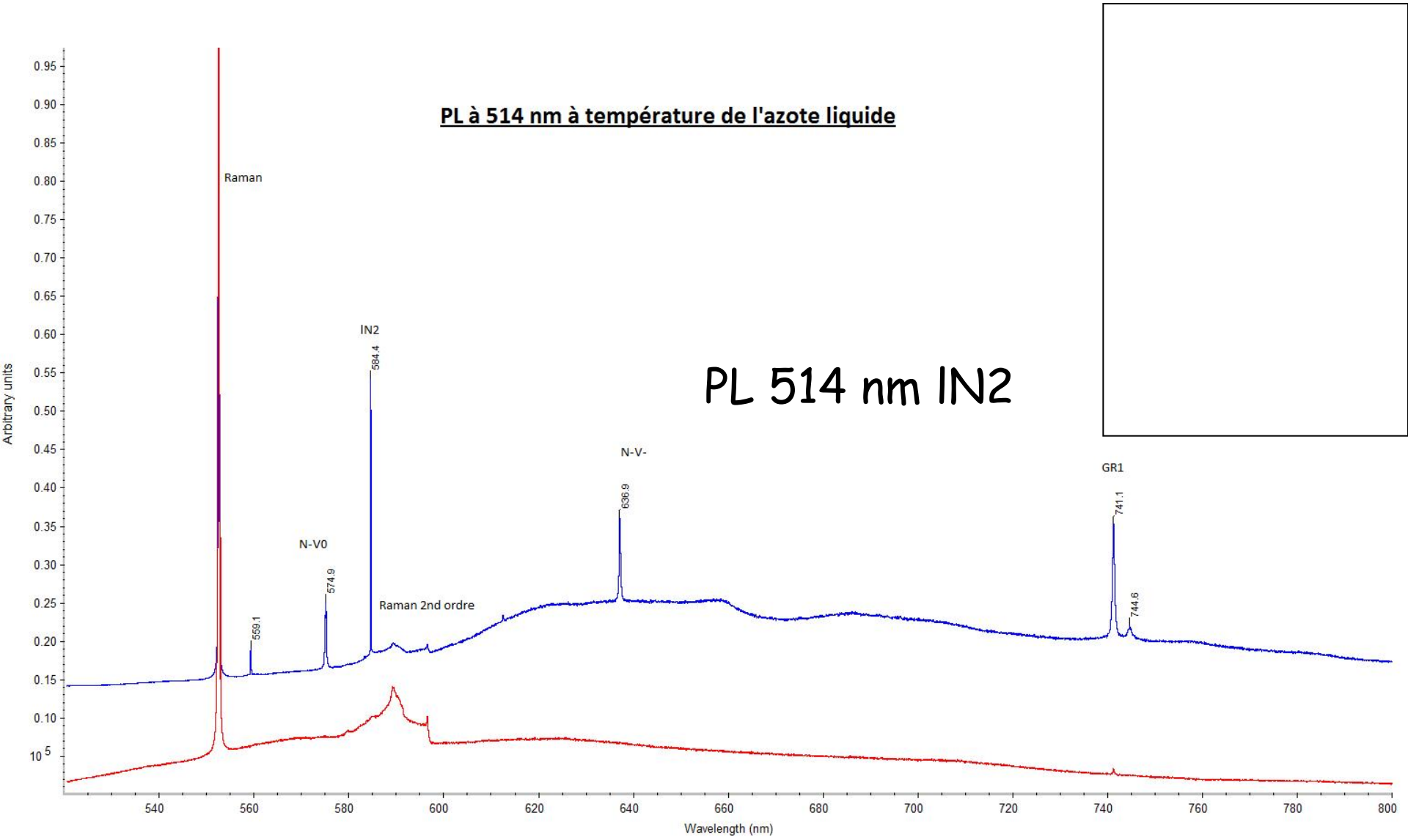


Raman and PL spectrum obtained on an echelle spectrometer
Extremely high resolution, many very sharp bands
Lots of information

Detection of HPHT treatment of diamond

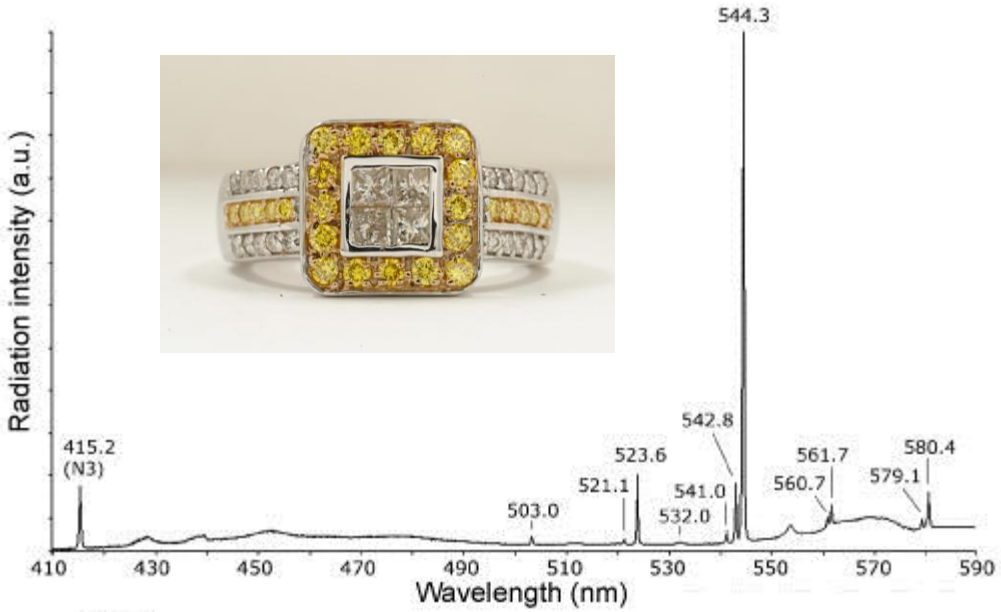


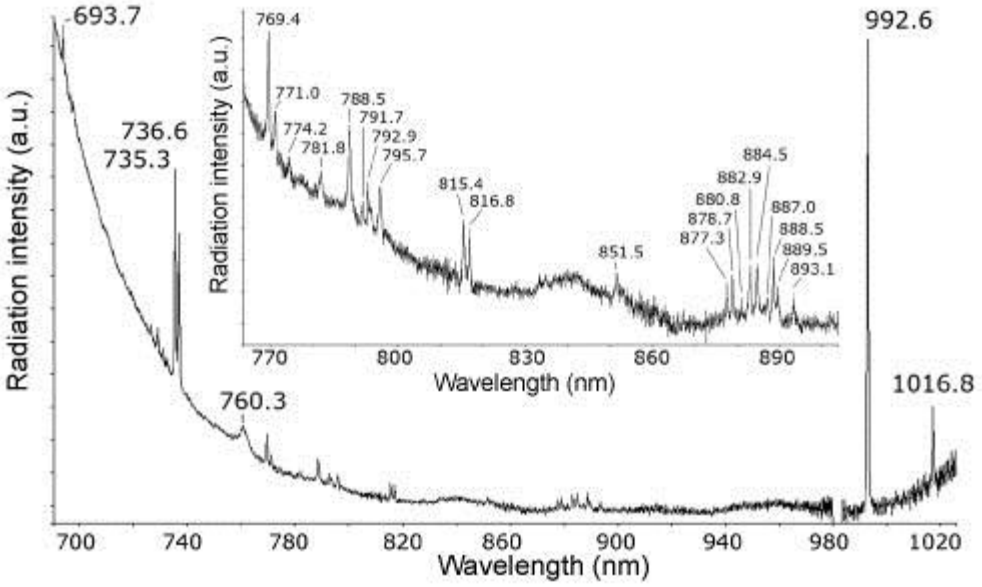
Major issue, still much developments to come



No PL may be a problem!

Identification of (small) synthetic diamond with PL



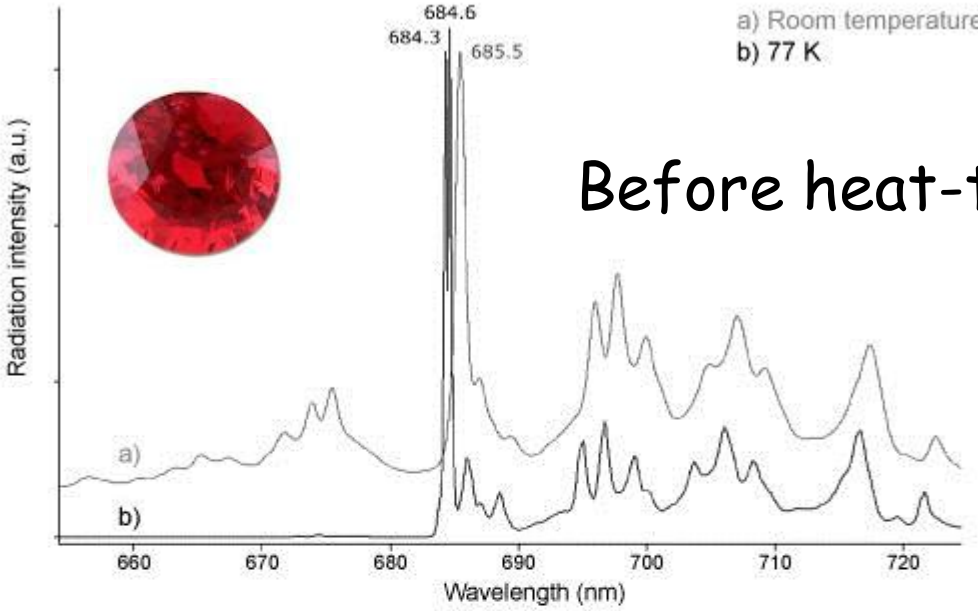


Co-related luminescence Co-N centers

Photoluminescence spectra excited by the 405 nm laser line of an irradiated HPHT and an untreated,HPHT synthetic diamond grown within a molten cobalt solvent

Photoluminescence spectroscopy of other gem materials

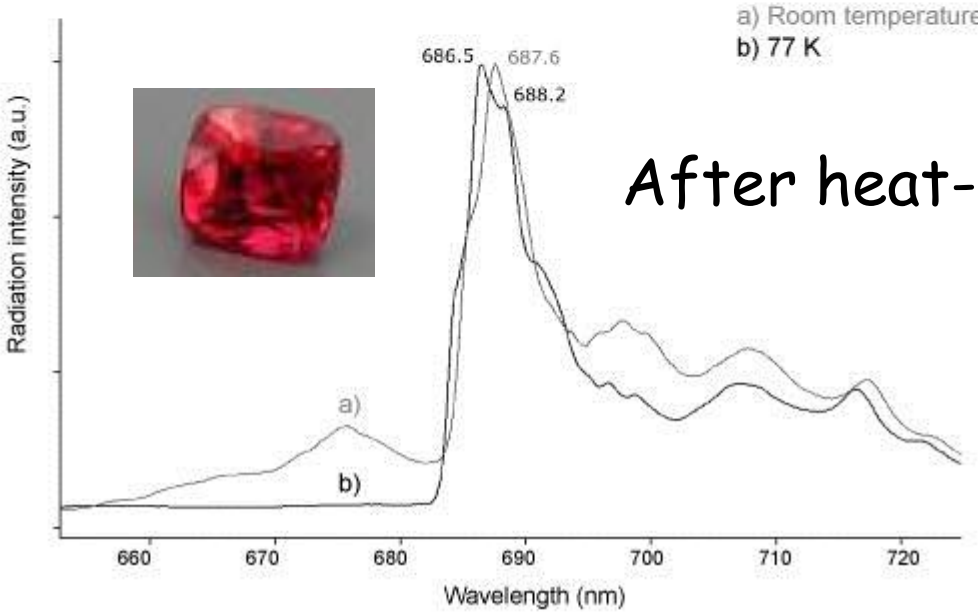
Mostly Cr^{3+}
at the moment



Before heat-treatment

Broader bands:
Increased
disorder

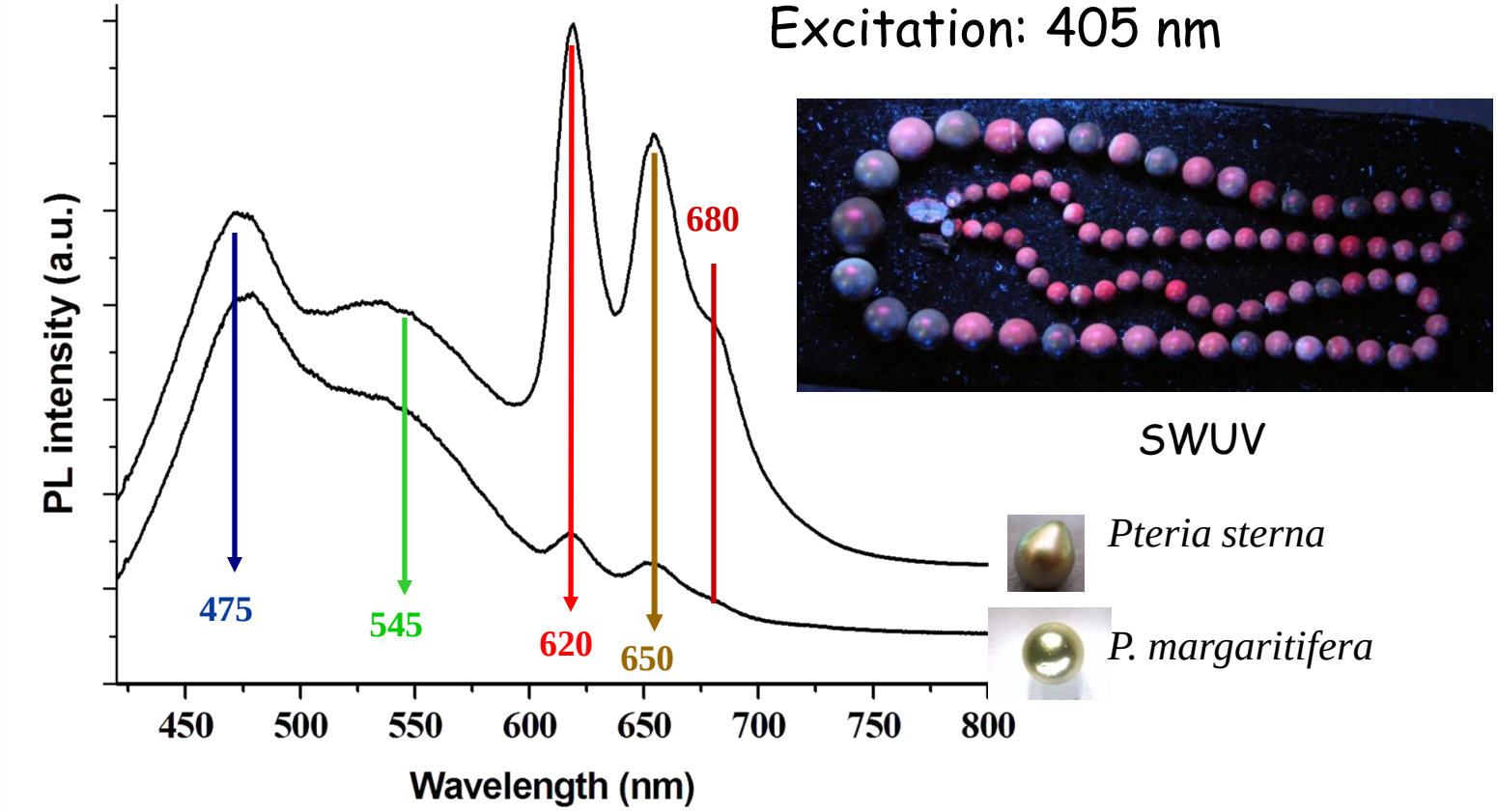
Compare to Raman of synthetic spinels



After heat-treatment

Pteria sterna vs *P. margaritifera* "Yellow"

Excitation: 405 nm



SWUV

Pteria sterna

P. margaritifera

The **PL in the blue part of *P. margaritifera* is more important** than that detected **in the red part**. Slight differences in the exact positions of PL bands (e.g. 475 and 545 nm).

Conclusions and perspectives

Essential for large gem laboratories

Alone (rarely) or in combination with other techniques

Improvement of databases necessary for gem-specific products

PL: detection of HPHT in diamond, but also colored stones, pearls

What future for small dedicated instruments?