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Raman spettroscopy as gemmological tool

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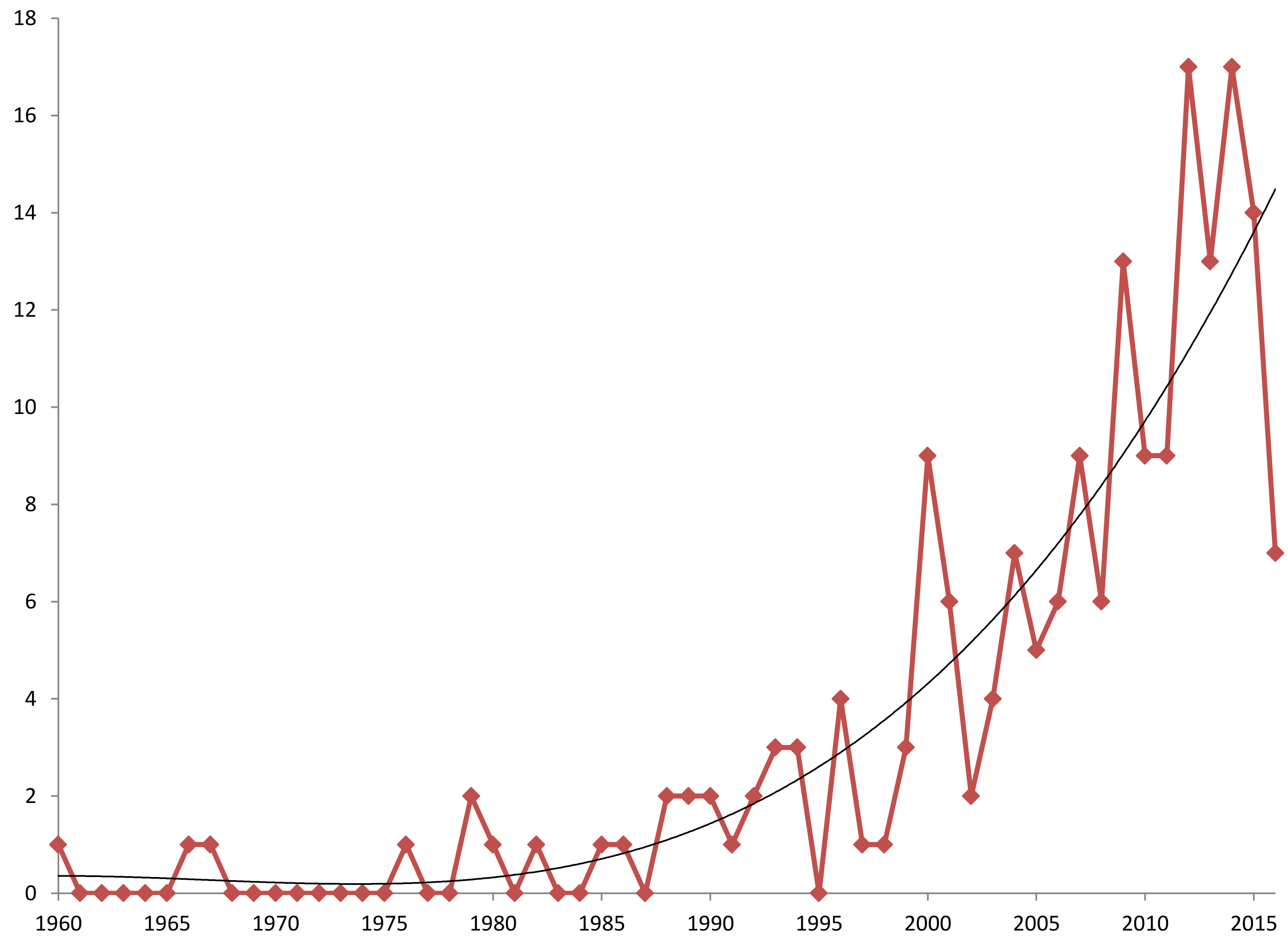
The interest of the scientific community for this topic is recently increased as evidenced by the rise of the number of published article …..

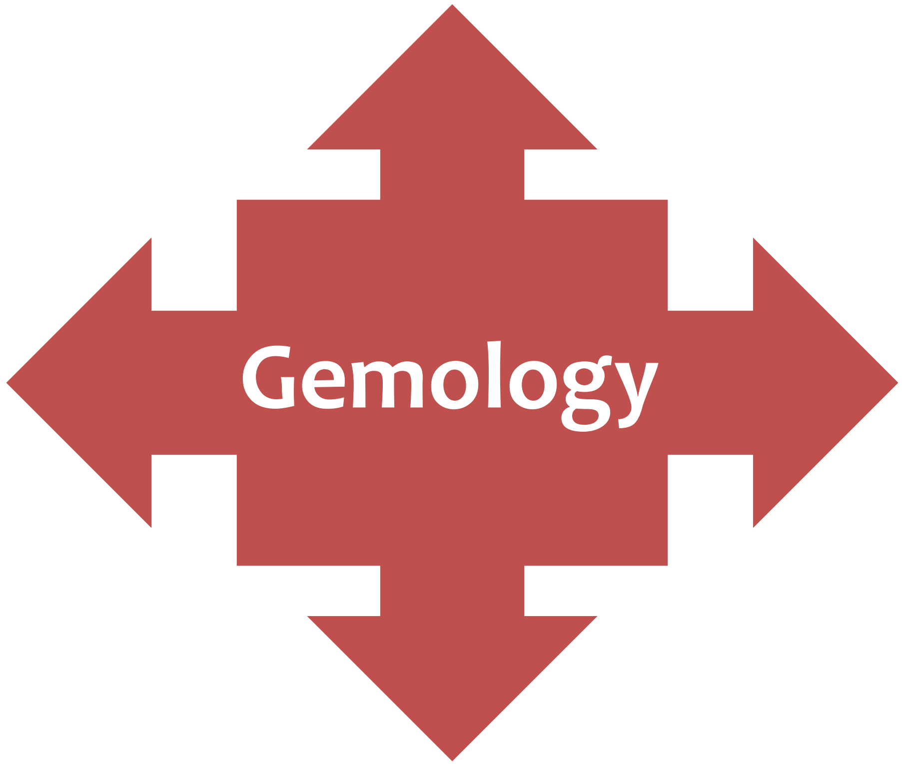


(SCOPUS)

The study of gems covers several disciplines:

geology, mineralogy and crystallography

chemistry, physics



art, history, and archaeology.

economic aspects

MUSEUM COLLECTIONS

London Museum

HISTORICAL AND ARCHAEOGICAL JEWELS

Since ancient times, gems were used for personal adornment (jewels) and to decorate various types of precious objects, such as royal insignia or liturgical objects.

Sicilian jewels preserved in important museum and churches

***Catania**, Museo Diocesano XIX secolo*

***Messina**, Museo M. Accascina XIV - XVII secolo*

***Militello in Val di Catania**, Museo di* S. Nicolò - XIX secolo

***Palermo**, Tesoro della Cattedrale –*
Corona di Costanza d'Aragona 1200

***Trapani**, Museo Pepoli* - XVII secolo

***Catania**, tesoro di Sant'Agata*

WHY ARE IMPORTANT SCIENTIFIC STUDIES ON GEMS?

For Cultural Heritage Sciences	For trades
ancient and modern artworks	Contemporaney gems and jewels

Knowledge and conservation

Identification, origin
(Imitations, syntetic gems)
Provenance
Enhancement treatments

Knowledge of economic value

WHAT IS A GEM?

It characterized by exceptional **beauty, rarity, preciosity and durability**

Many gems are well-defined mineral species, such as diamond (C);

most gemstones are **silicates** (beryl, topaz and zircon);

the second most represented class is

oxides (ruby and sapphire).

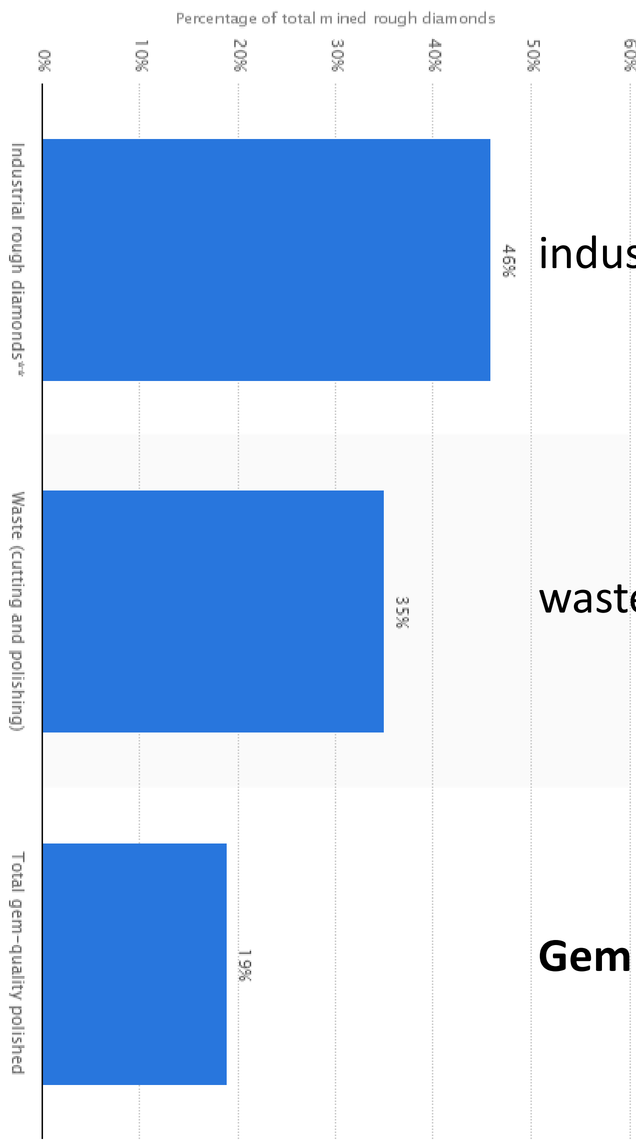
Not only crystals:

- Organogen materials (amber, corals, pearls)
- Amorphous (glass)

Qualities of gems

- **Rarity**
- Size
- Purity
- Quality
- Color
- Trasparency
- Luster

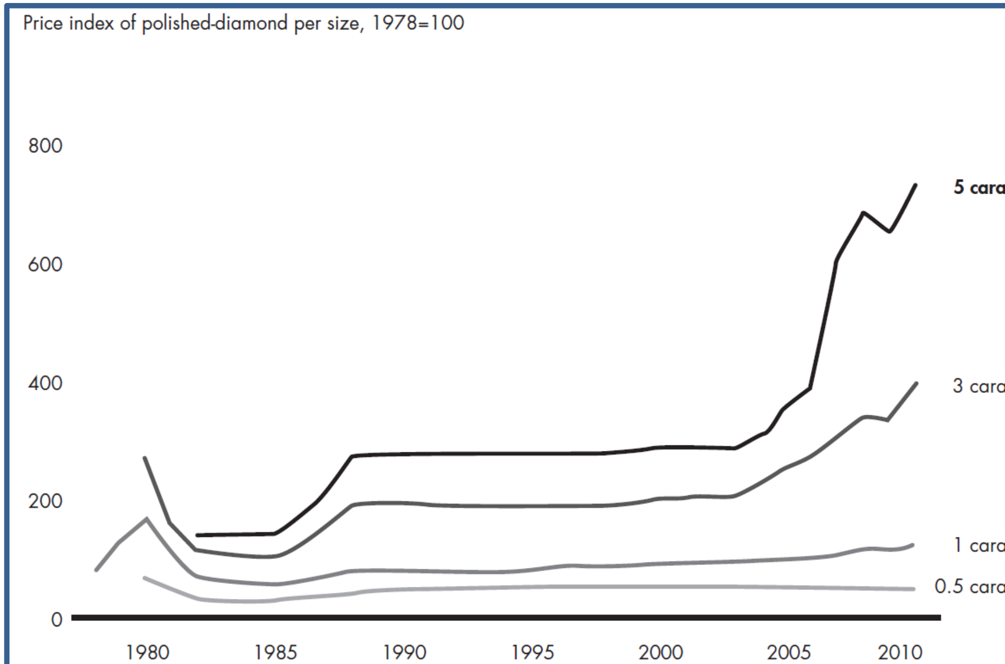
Diamond is a quite rare mineral.



industrial use

waste

Gem quality

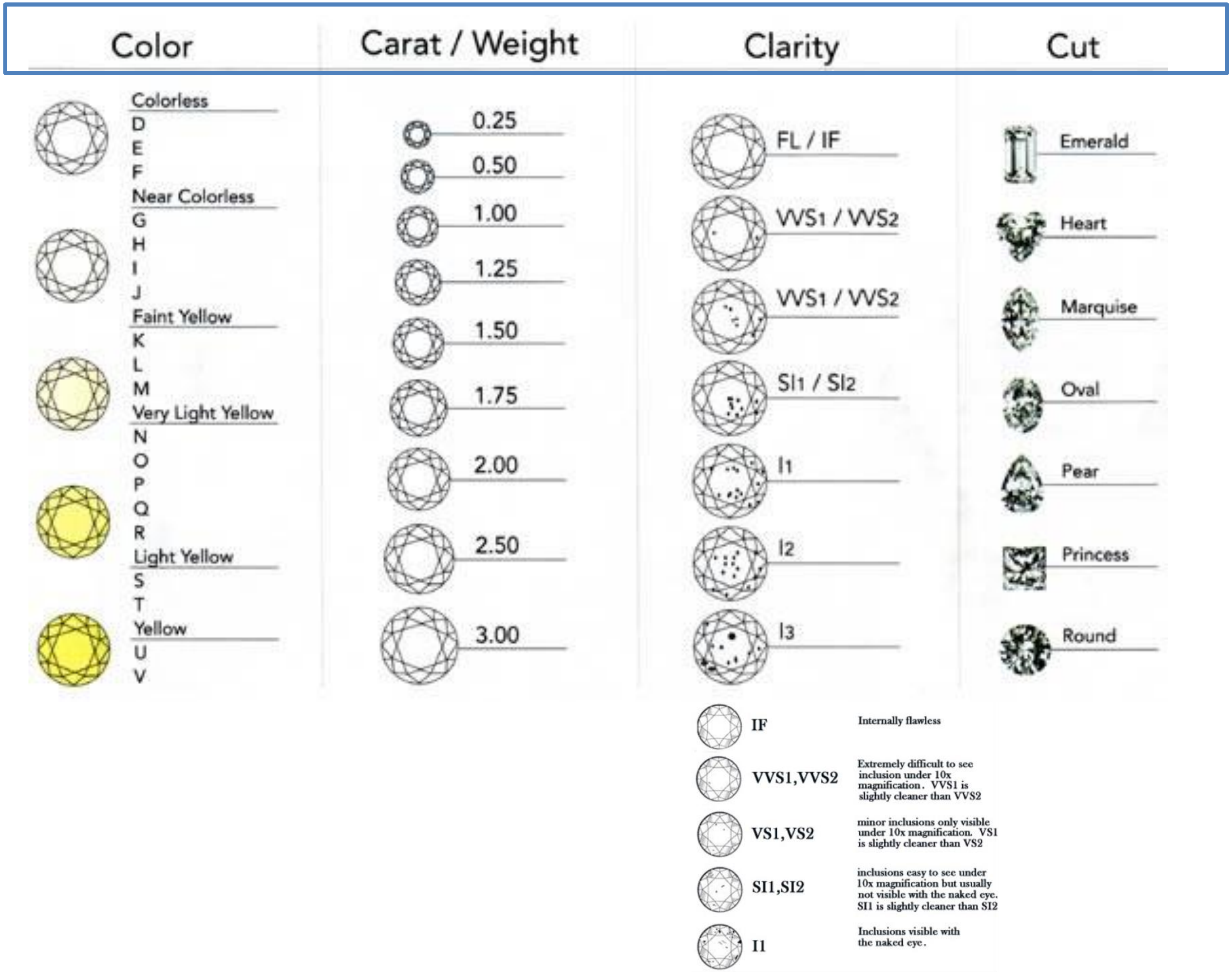


The value of diamond is strongly exponentially related to the stone dimension…

carat

- Rarity
- Size
- purity
- Quality
- Color
- Trasparency
- Luster

Parameters which determine the value of a **diamond: carat, colour, clarity, cut**



LUSTER & TRASPARENCY

Luster:

Pyrite (in shist): **metallic;**

diamond: **adamantine;**

fire agate: **vitreous**

Fluorite: **subvitreous**

nephrite jade: **greasy;**

amber: **resinous**

Pearl: **pearly;**

tiger'seye: **silky**

Trasparency:

Citrine: **transparent**;

Prehnite: **semi-transparent**;

chrysoprase: **translucent**;

sugilite: **opaque**

Idiochromatic gems

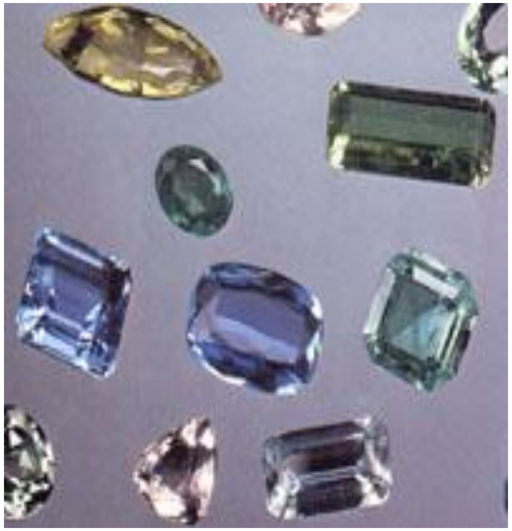
Peridot

rhodocrosite

cuprite

malachite

Allochromatic Gems



A good example is **beryl**, found in many colored varieties:

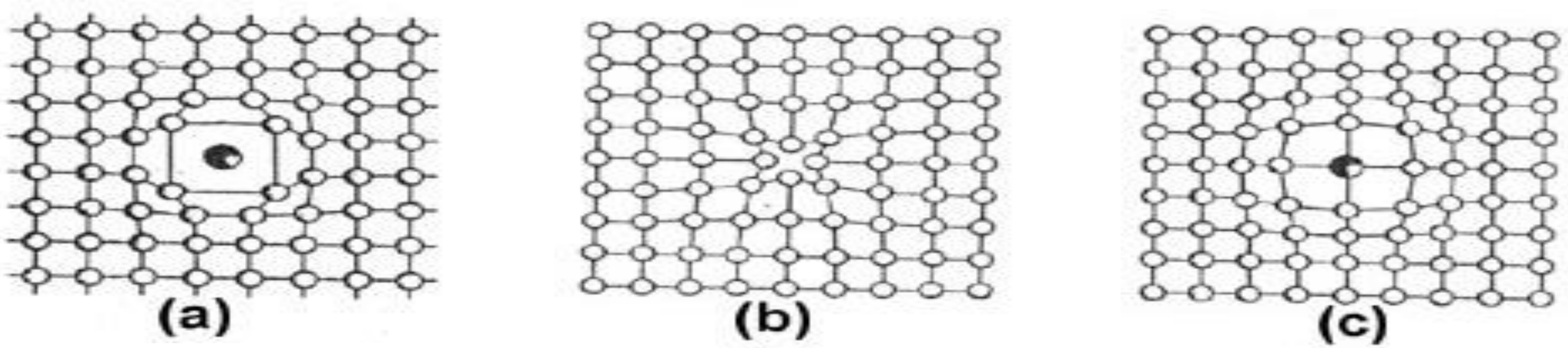
- **green emerald**
- **blue aquamarine**
- **pink morganite**
- **yellow heliodor**
- and the colorless **goshenite**.

1. chromophore elements: Ti, Fe, Cr, Co, Mn, Ni.

Allochromatic gems – example Beryl:

- **green emerald** due to chromium ions Cr^{3+} and vanadium replacing aluminum,
- **blue aquamarine** due to the simultaneous presence of Fe^{2+} and Fe^{3+},
- **pink morganite** due to manganese,
- **yellow heliodor** due to Fe–O charge transfer,
- and the colorless **goshenite**.

2. imperfections of the cristal lattice



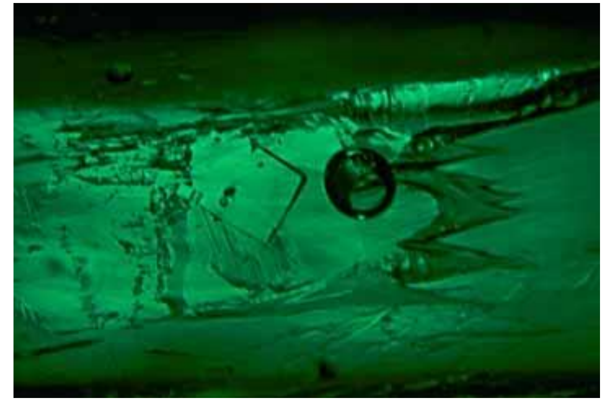
a) punctual defects of interstitial atoms or ions

b) electronic-hole (formed by heating or by irradiation)

c) atoms which replace the original ones but have a different radius.

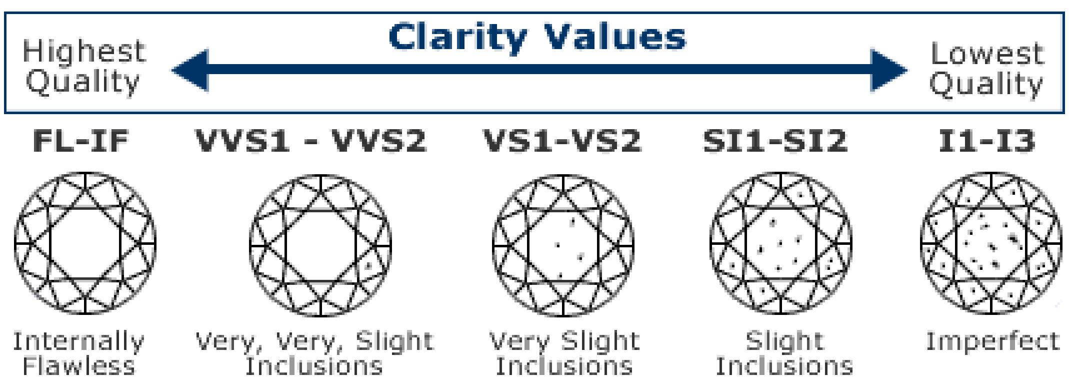
INCLUSIONS: ACCEPTED vs. NOT ACCEPTED

Natural gems may show typical **inclusions** related to environment formation

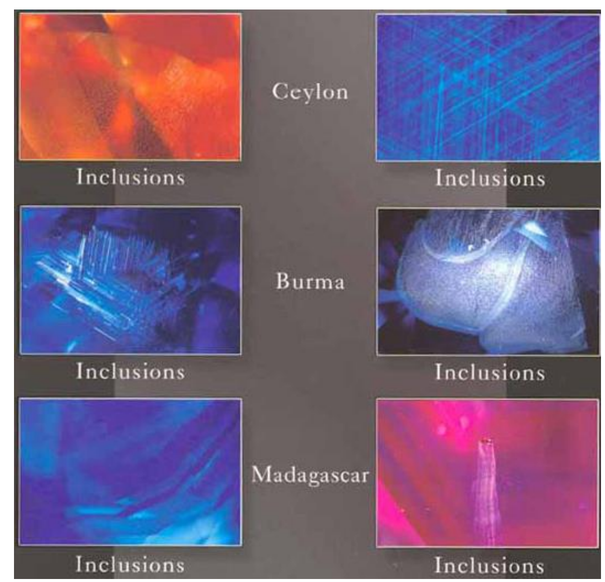


In general, ***the inclusions are unwanted***!

Diamond with inclusion



*In some cases, the inclusions are **accepted** for emerald, ruby and sapphire, if they do not decrease too much transparency.*



INCLUSIONS: when they increase the gem value

in some semiprecious gems, inclusions may increase the economic value

Quartz with dendritic inclusions

rutile needles in quartz

tiger eye: a variety of quartz with a fibrous structure containing inclusions of crocidolite

star sapphire: the inclusions are arranged according to a geometrical pattern, giving rise to bright lines

COMPOSITION vs. APPEARANCE

natural gems
Organic and inorganic

Very precious

Common ….very similar to precious ones: **natural simulant**

natural gems treated in laboratory: **treated gems**

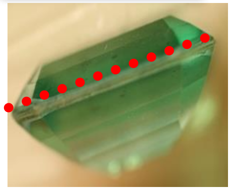
Artificial gems
In laboratory

Different chemical composition (sometimes they are not present in nature)

very similar chemical composition of the natural counterpart: **syntetic simulant**

assembled gems

two or more layers of different types of gems: **duplet- triplet**



HOW IS IT POSSIBLE STUDY GEMS?

Traditional gemological methods

- *Binocular Microscope*
- *Polariscope*
- *Refractometer*
- *Specific Gravity Liquids*

these analytical methods, even carried out by a trained jeweler, cannot give unambiguous answers such as problems related to origin, provenance and treatments.

Advanced scientific methods:

- *X ray diffraction (XRD)*
- *Infrared spectroscopy (FTIR)*
- *Neutron Diffraction (ND)*
- *Nuclear magnetic resonance (NMR)*
- *Laser induced breakdown spectroscopy (LIBS)*
- *X Ray fluorescence (P XRF)……..*

ADVANCED SCIENTIFIC METHODS:

Non-destructive and non-invasive analysis …great value of the studied objects, ….mounted on jewels

Elizabeth Taylor's famous Ruby Collection

Queen Elizabeth's Burmese ruby tiara

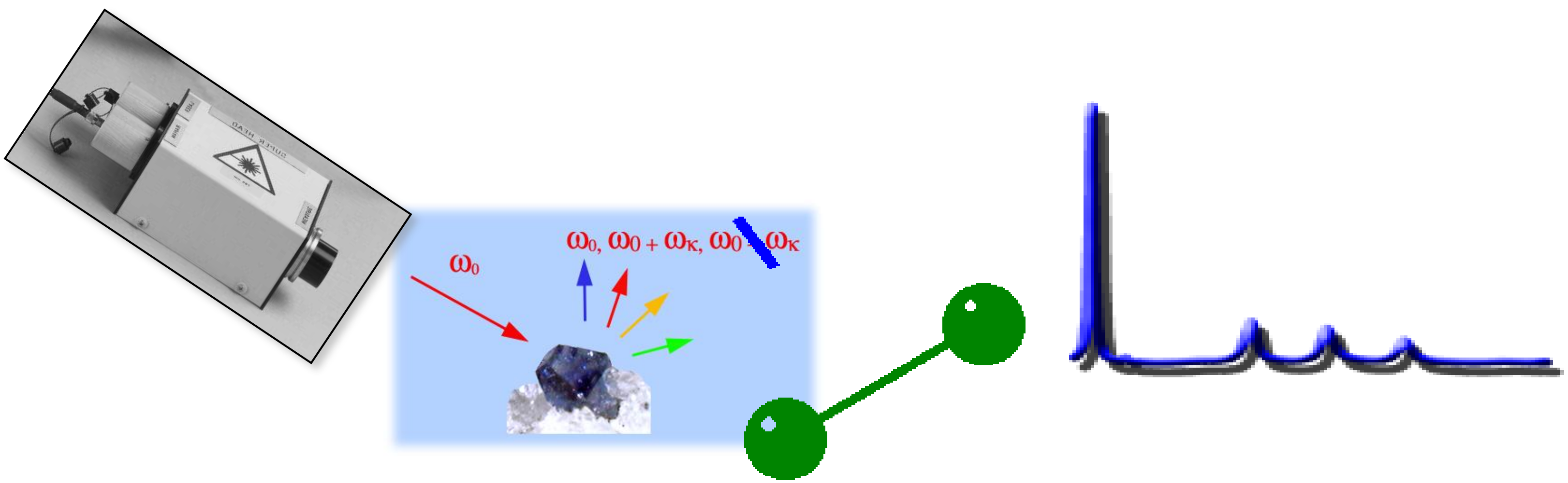
Delong star ruby
100,32 ct

Alan Caplan Ruby or the Mogok Ruby -15.97 ct

RAMAN SPECTROSCOPY

Molecular spectroscopic technique able to give back information on composition, chemical environment, molecular bonds and structure of a gaseous, liquid or solid (both crystalline and amorphous).

Based on the «Raman effect»: is the inelastic scattering of a photon. It was discovered by C. V. Raman



Peter Vandenabeele Practical Raman Spectroscopy: An Introduction. Wiley

Why Raman and Gems?

Raman spectroscopy is an ideal method for the examination of gems (also marketable gemstones)

it is particularly appreciated, being a completely

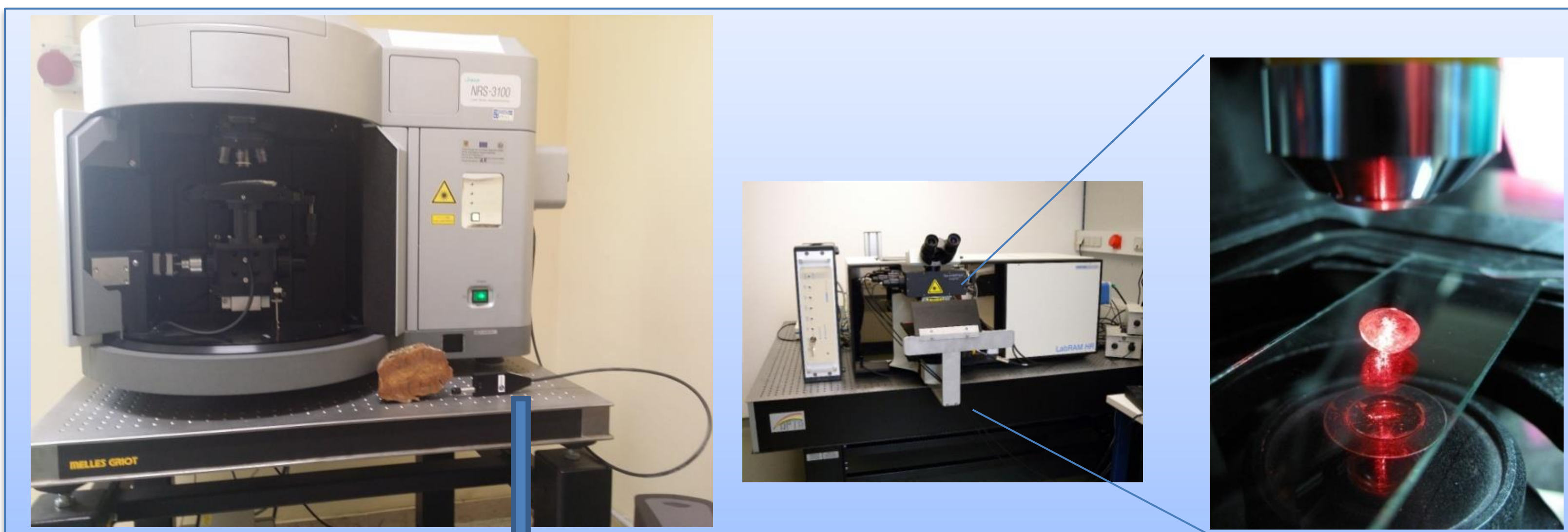
- ✓ non-destructive analysis , not requiring any sample preparation
- ✓ non invasive,
- ✓ High resolution
- ✓ short measurement

RAMAN SPECTROSCOPY: LABORATORY INSTRUMENTS

The instrumentation for Raman spectroscopy may be divided into two families: **laboratory** usually equipped with a microscope and multiple laser lines,….external optic fiber **and portable systems**

Microscale investigation:

- ✓ Identification of **gems**
- ✓ Identification and characterization of **inclusions**
- ✓ Identification of **treatments**



Micro-Raman spectroscopy with **external optical fiber** may examine both loose and mounted stones.

RAMAN SPECTROSCOPY: PORTABLE RAMAN SPECTROMETER

- ✓ In situ measurements;
- ✓ Good spatial resolution (1-3 cm^{-1})
- ✓ **Preliminary identification** of gems

…..allows the analysis of objects that cannot be moved, such as gems mounted on historic and archaeological artifacts preserved in a museum

Sequence of the topics:

1. Identification
2. treatments
3. Natural vs syntetic simulant
4. Provenance and genesis
5. Organic materials
6. Historical and archaeogical

   Jewels Collection.

Collaborations:

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Paolo Mazzoleni
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Consiglio Nazionale delle Ricerche

Donatella Capitani

Danilo Bersani
Pier Paolo Lottici

UNIVERSITEIT GENT

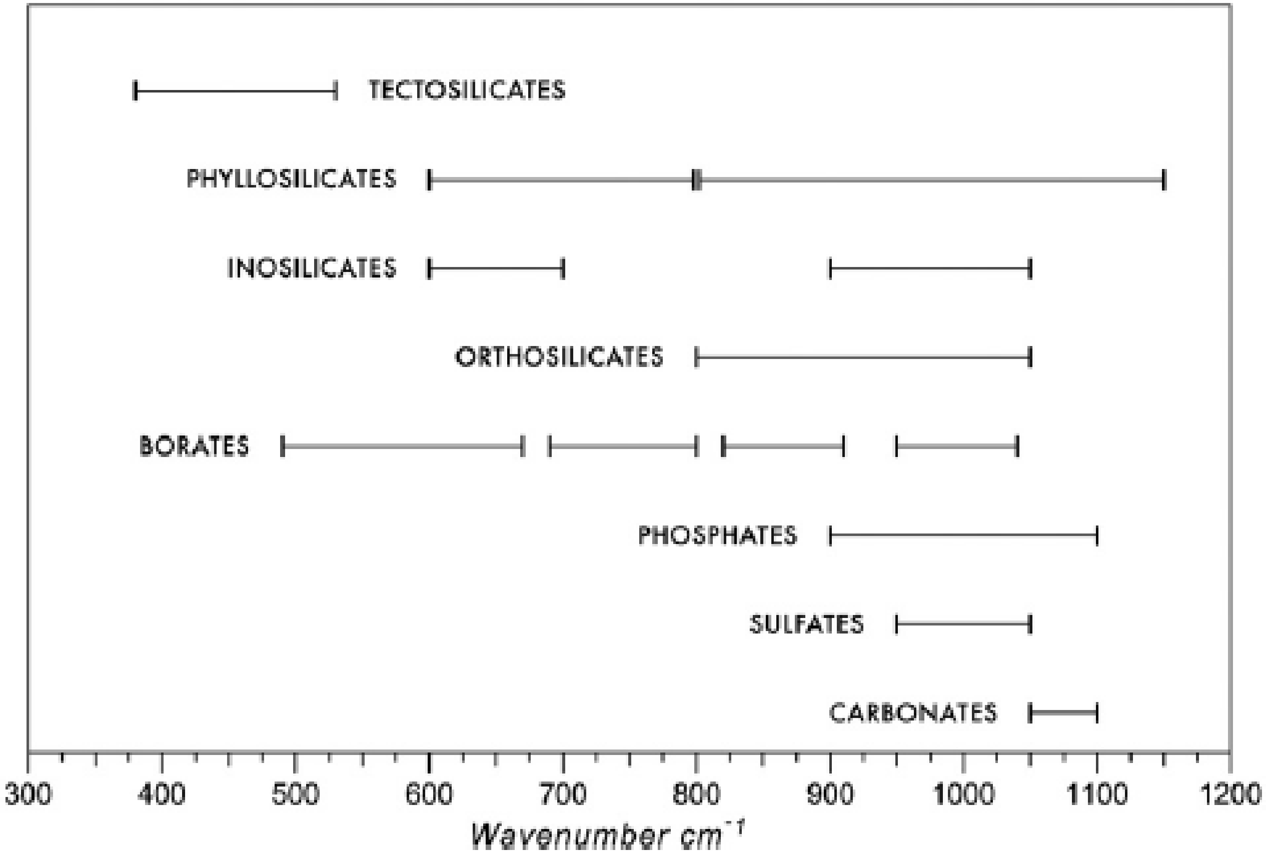
Peter Vandenabeele

Jan Jehlička

MUSEO REGIONALE
P. ORSI -SIRACUSA

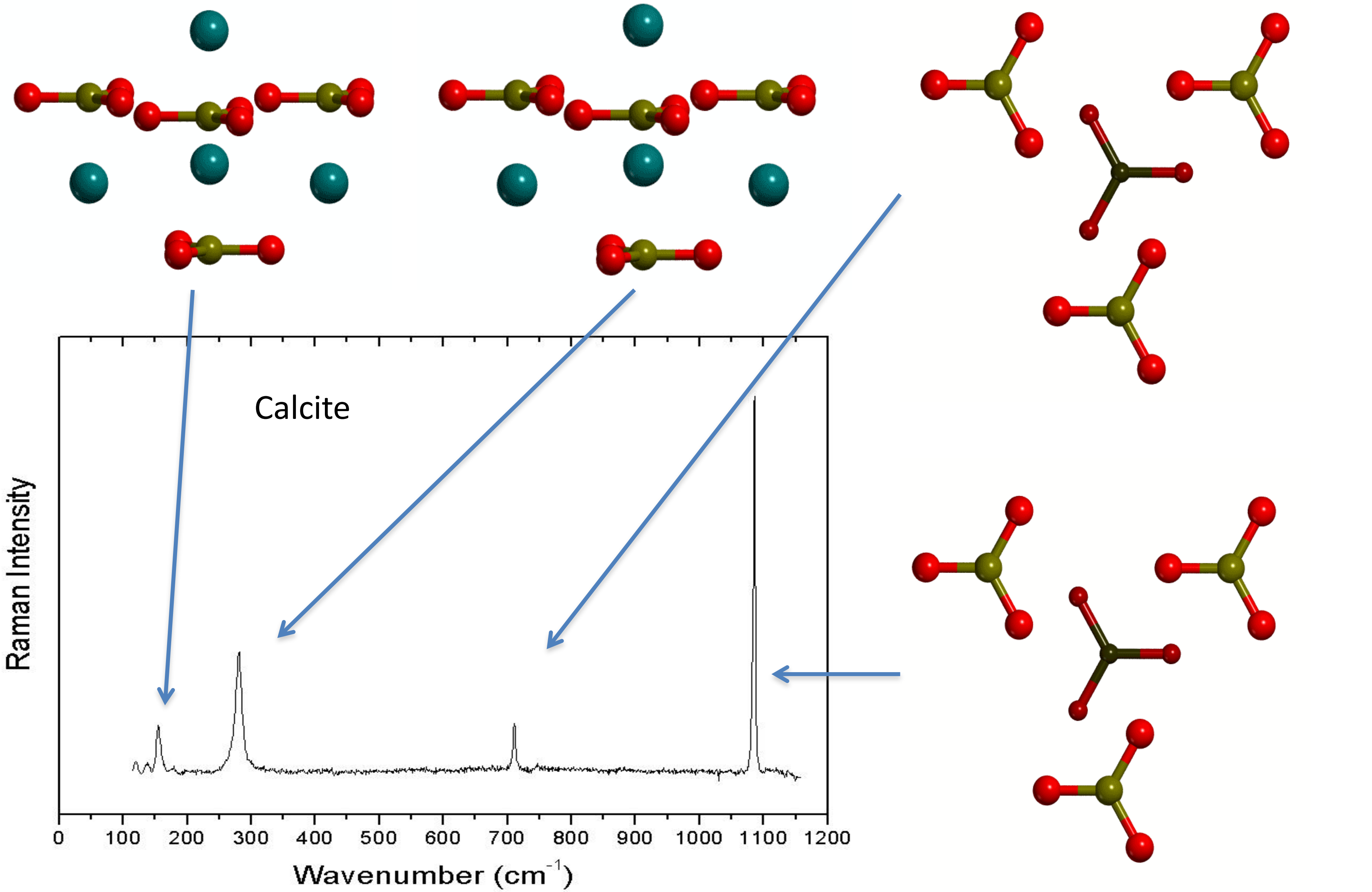
THE FIRST QUESTION: **WHAT'S THAT???**

Each mineral classes present characteristic raman bands



M.L. Frezzotti et al. / Journal of Geochemical Exploration 112 (2012) 1–20

RAMAN SPECTRUM

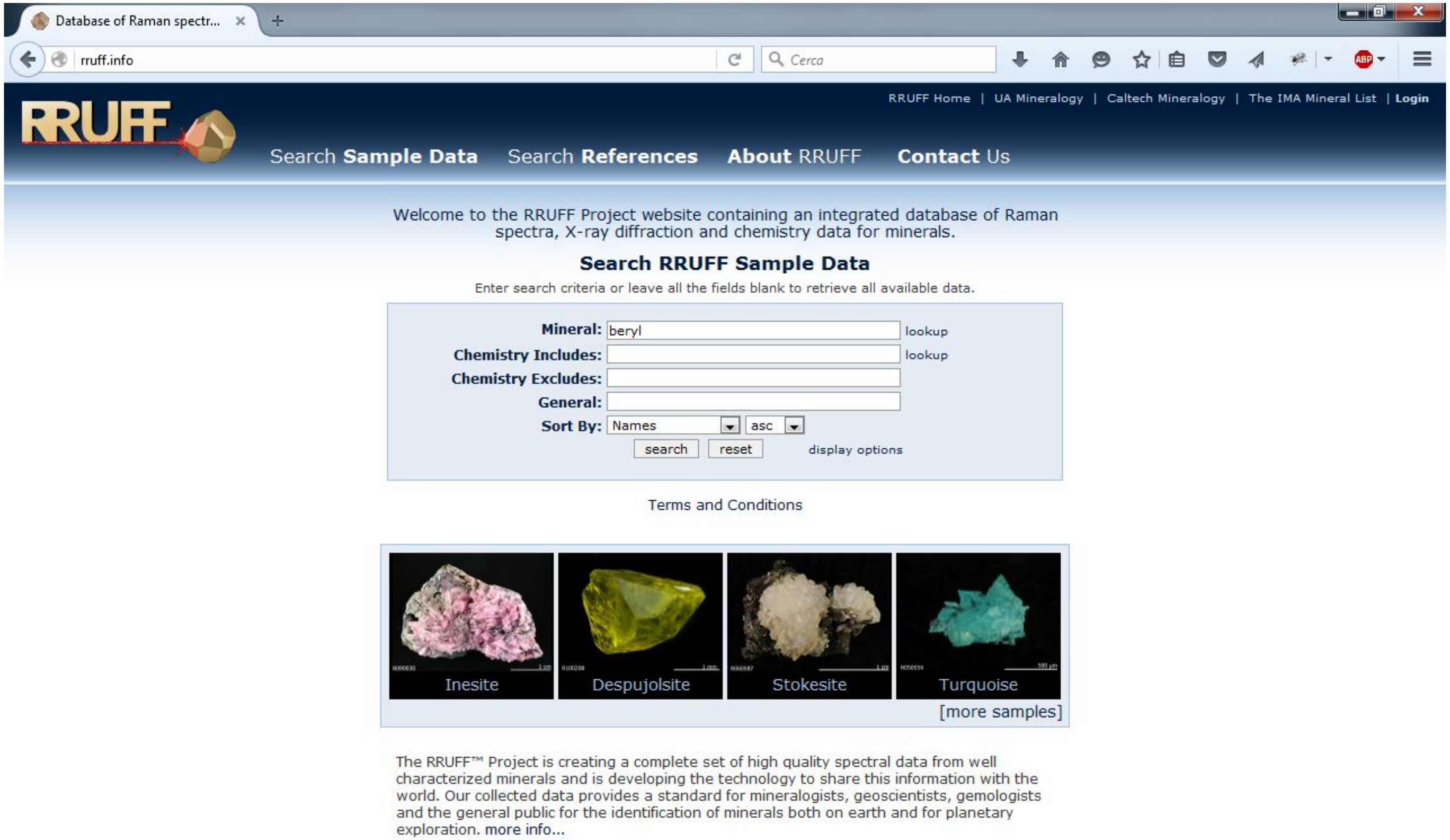


software Crystal (UNITO)

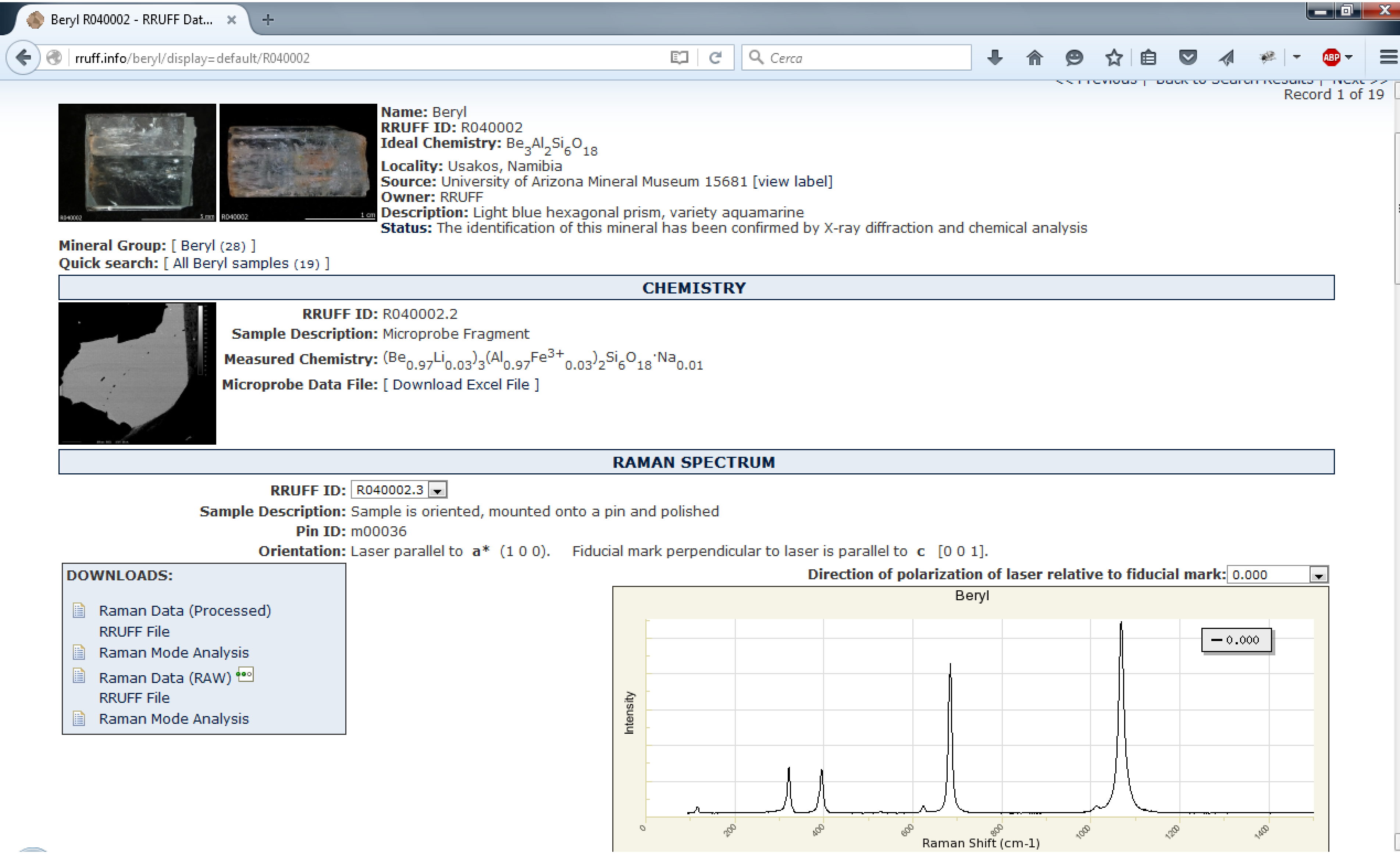
GEMS IDENTIFICATION

The standard way to give an answer by means of Raman spectroscopy is by **comparison** of the **spectral fingerprint** of the gem with spectra of **standard minerals**.

the availability of a **large database of Raman spectra** of mineral species is constantly increasing in time, so this question is often easy to answer using Raman spectroscopy.

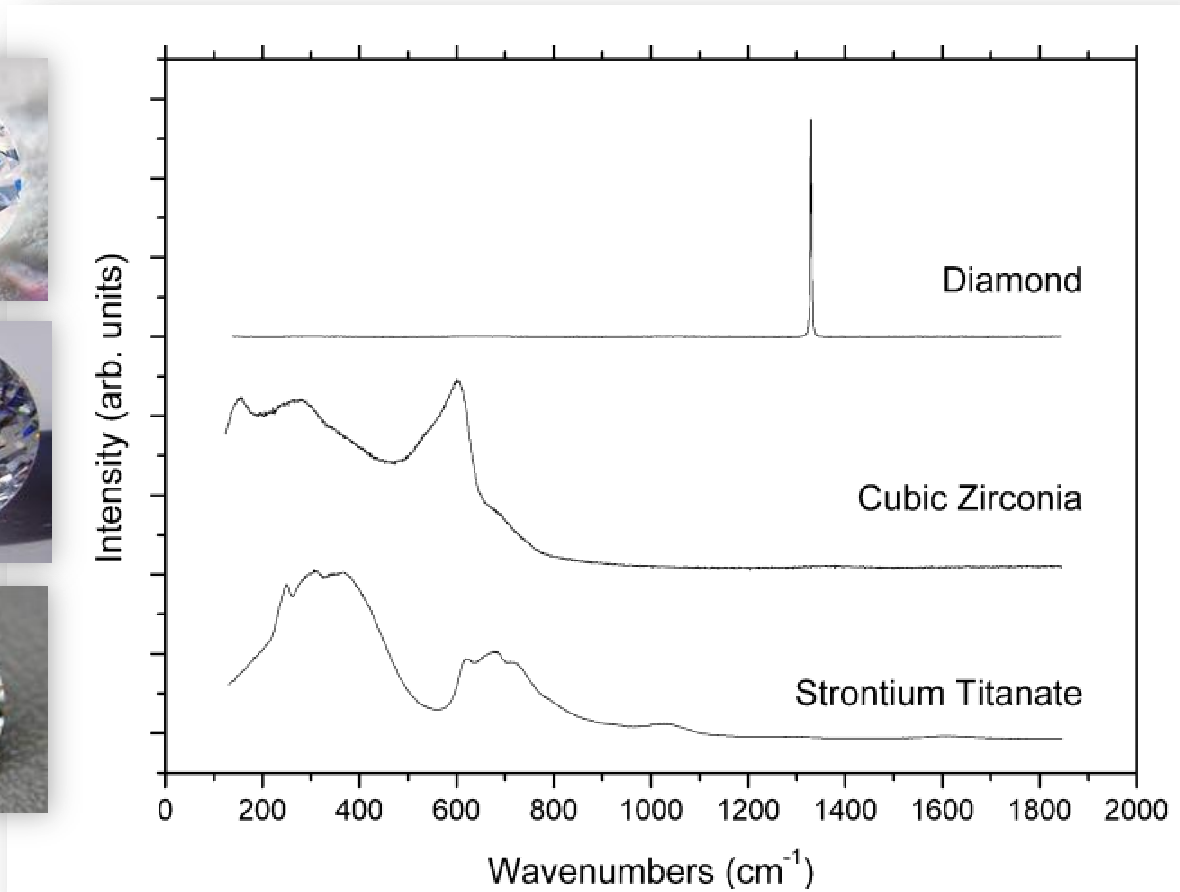


On-line database: RRUFF



Identification: comparison with references

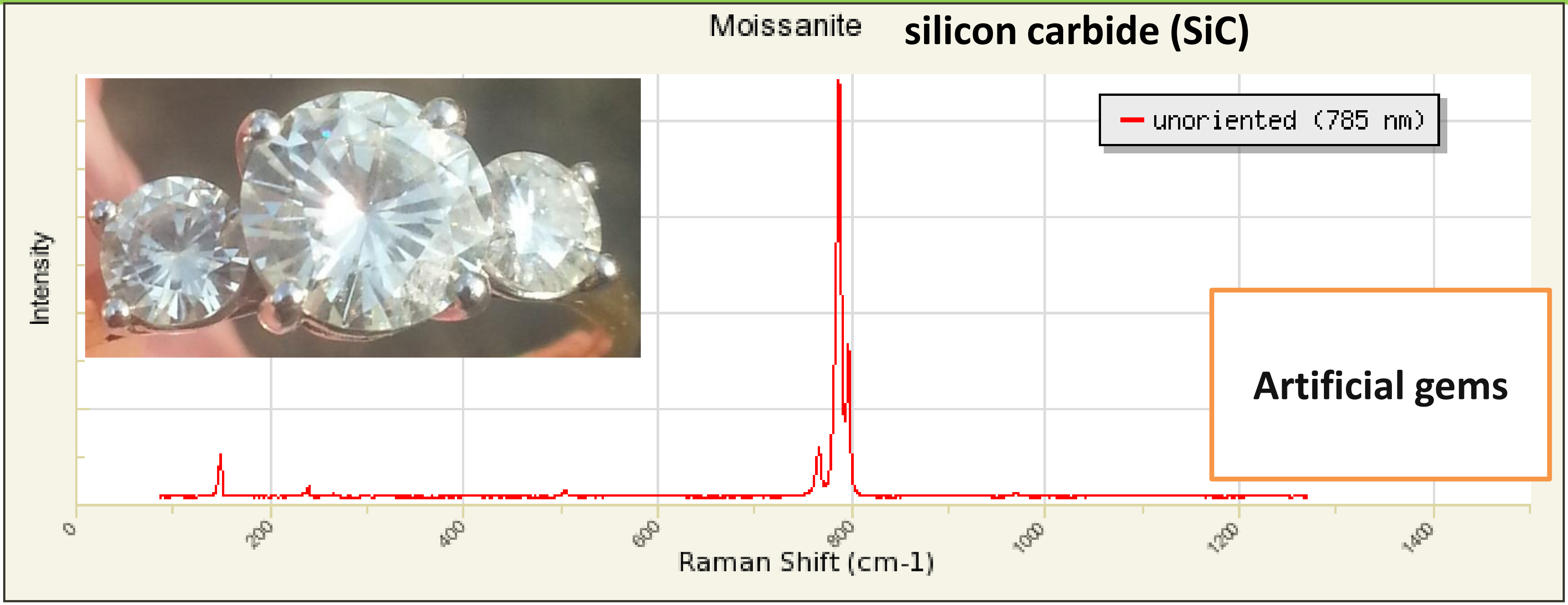
The detection of **imitations** is often an easy task using Raman spectroscopy, owing to **different compositions** compared with the real gems, as is the case of cubic zirconia, used as an imitation (simulant) of diamond (Aponik et al. 1998) and of strontium titanate.

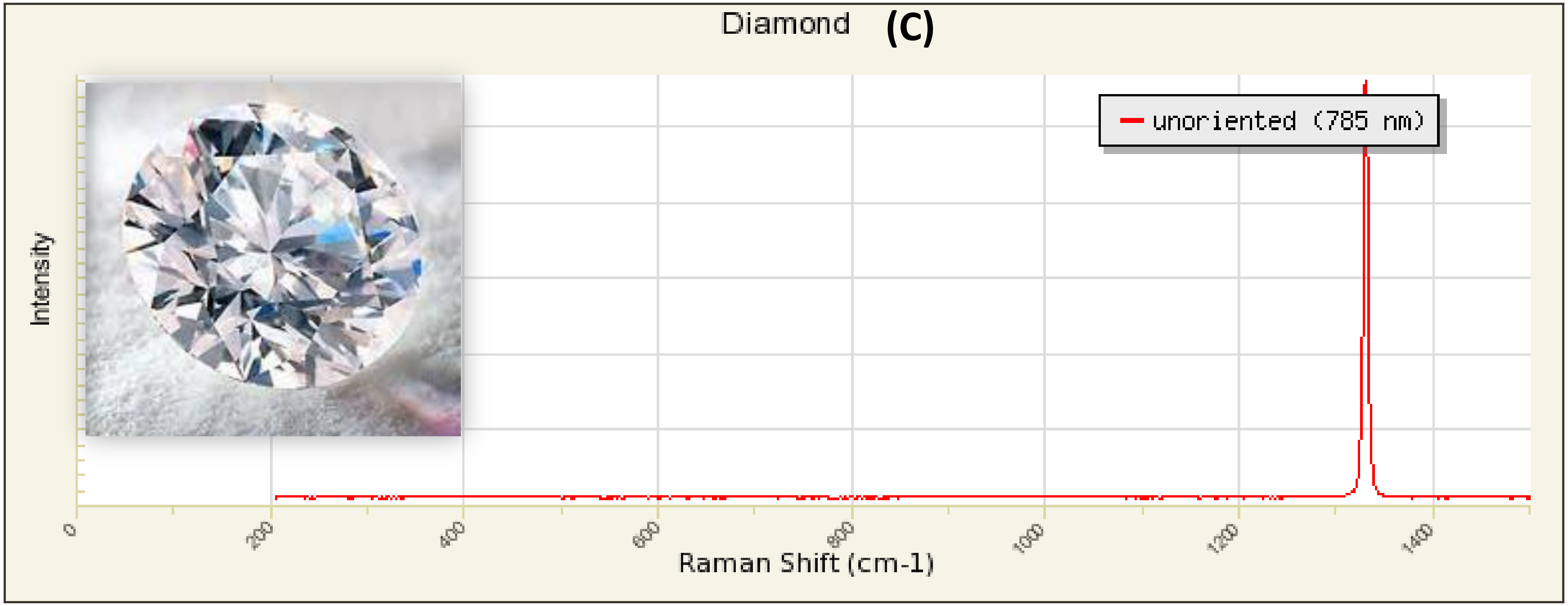


Natural gem

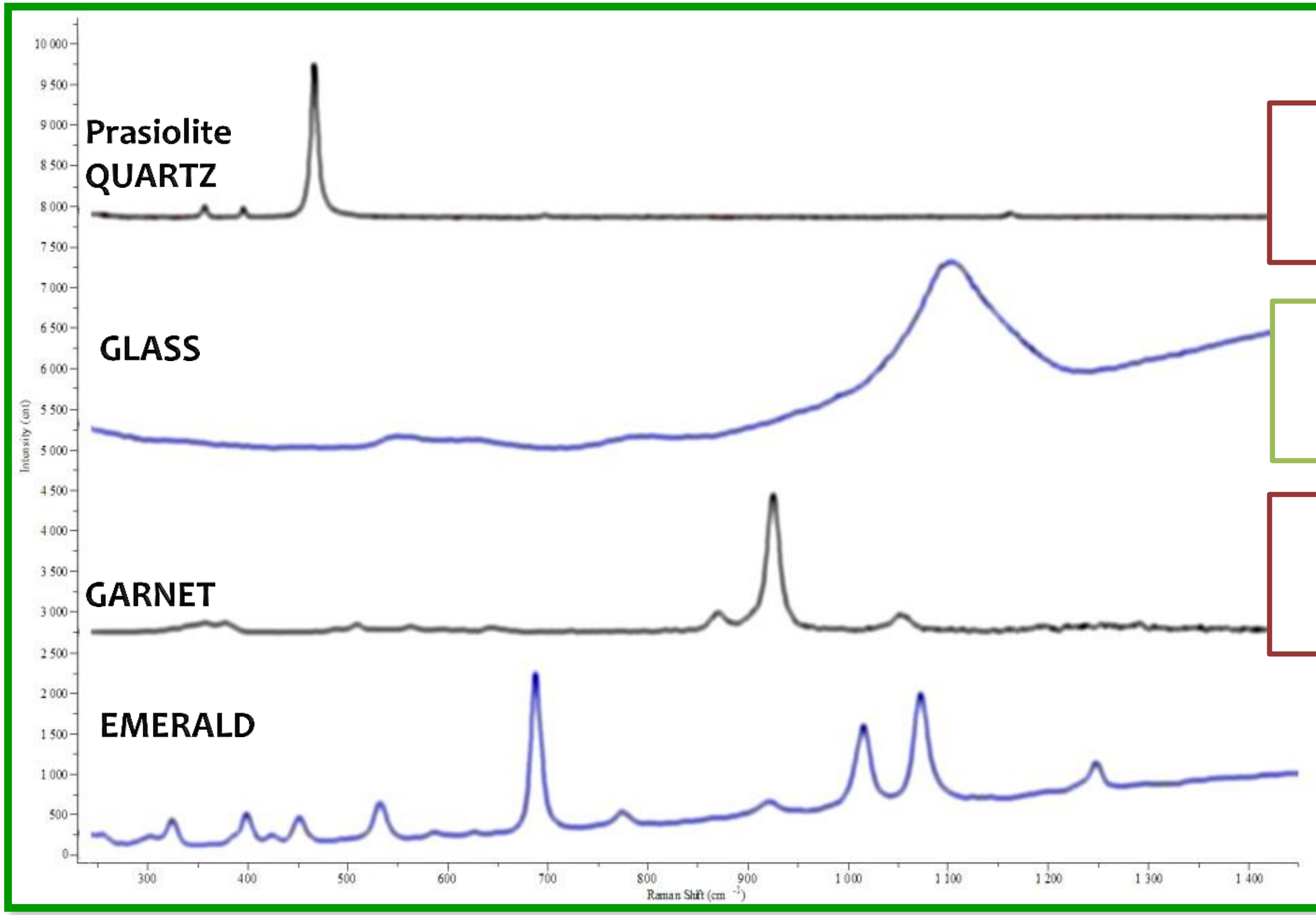
Simulant gems

Bersani D. Lottici P. Applications of raman spectroscopy to gemology Anal. Bioanl Chem. 2010 397 2631- 2646


Moissanite
silicon carbide (SiC)
unoriented (785 nm)
Artificial gems
Intensity
Raman Shift (cm-1)
0
200
400
600
800
1000
1200
1400


Diamond
(C)
unoriented (785 nm)
Intensity
Raman Shift (cm-1)
0
200
400
600
800
1000
1200
1400

Identification of the green gems: comparison with references



Simulant natural gems

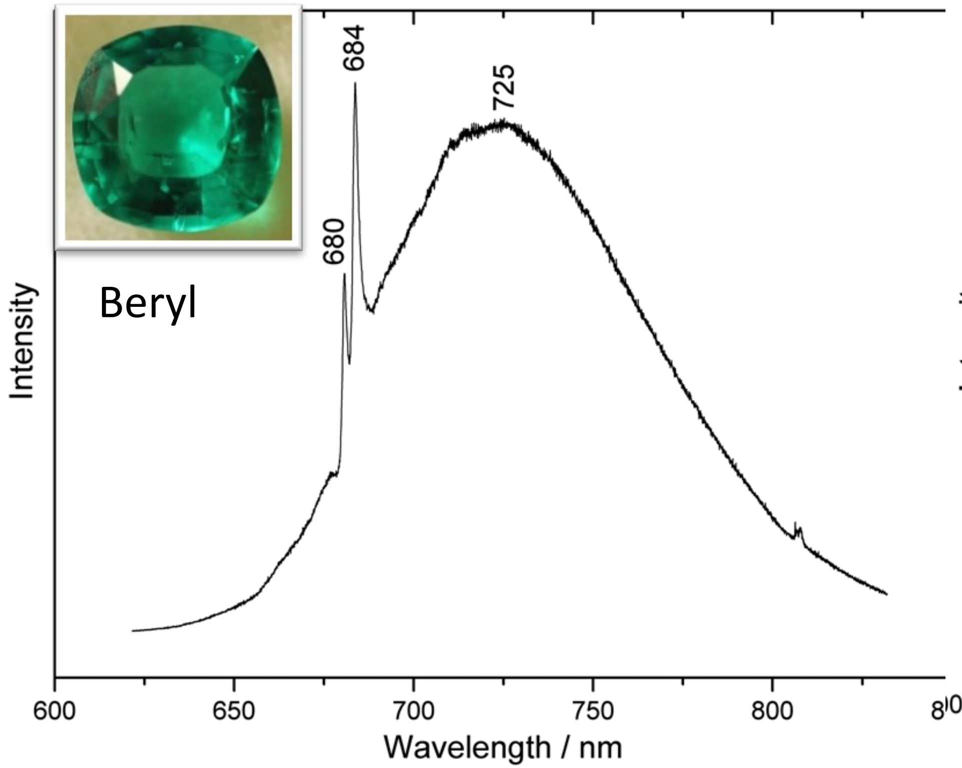
Artificial gems

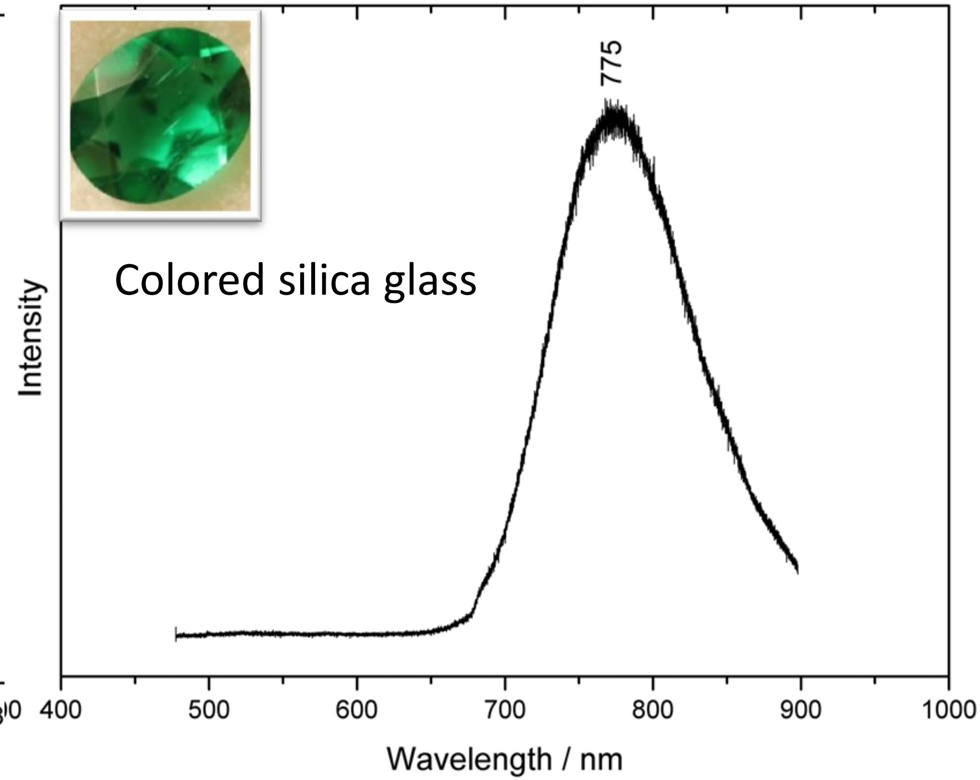
Simulant natural gems

Emerald or artificial or simulant?

Bersani B, Azzi G, Lambruschi E, Barone G, Mazzoleni P, Raneri S, Longobardo U, Lottici PP (2014): **Characterization of emeralds by micro-Raman spectroscopy**. *Journal of Raman Spectroscopy*, 45, 1293–1300. doi: 10.1002/jrs.4524

Identification of the green gems: photoluminescence





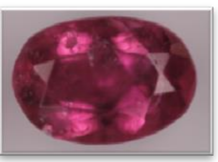
photoluminescence spectra of gems

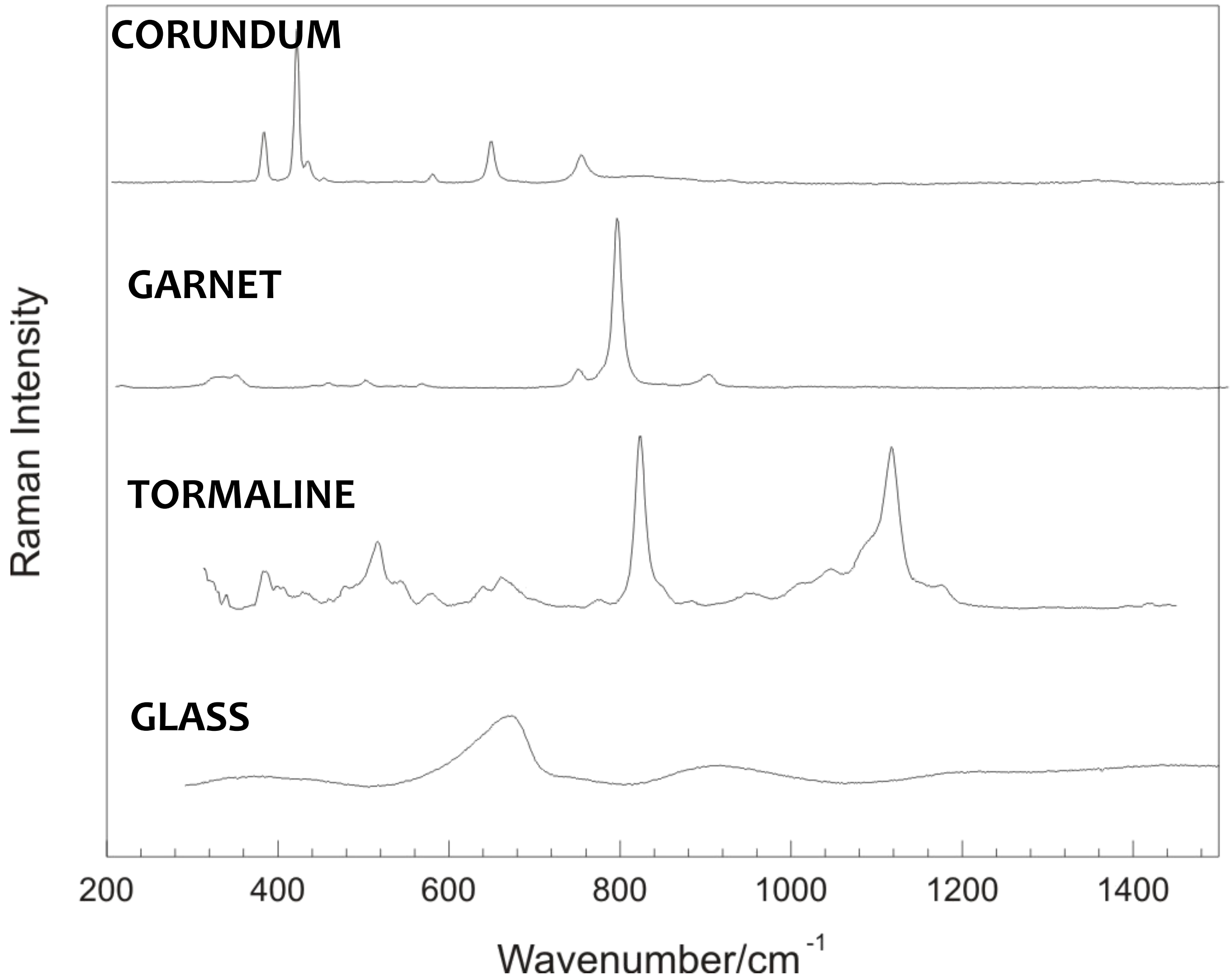
The beryl nature of this gem is confirmed by the photoluminescence spectra: the narrow lines at 680 and 684 nm are characteristic of Cr3+ emission in a beryl structure, whereas the broad band centered at about 725 nm is attributed to Fe3+

the photoluminescence spectrum is broad and structureless, as expected for amorphous or glassy materials.

Bersani B, Azzi G, Lambruschi E, Barone G, Mazzoleni P, Raneri S, Longobardo U, Lottici PP (2014): **Characterization of emeralds by micro-Raman spectroscopy**. *Journal of Raman Spectroscopy*, 45, 1293–1300. doi: 10.1002/jrs.4524

Identification of the red gems: comparison with references



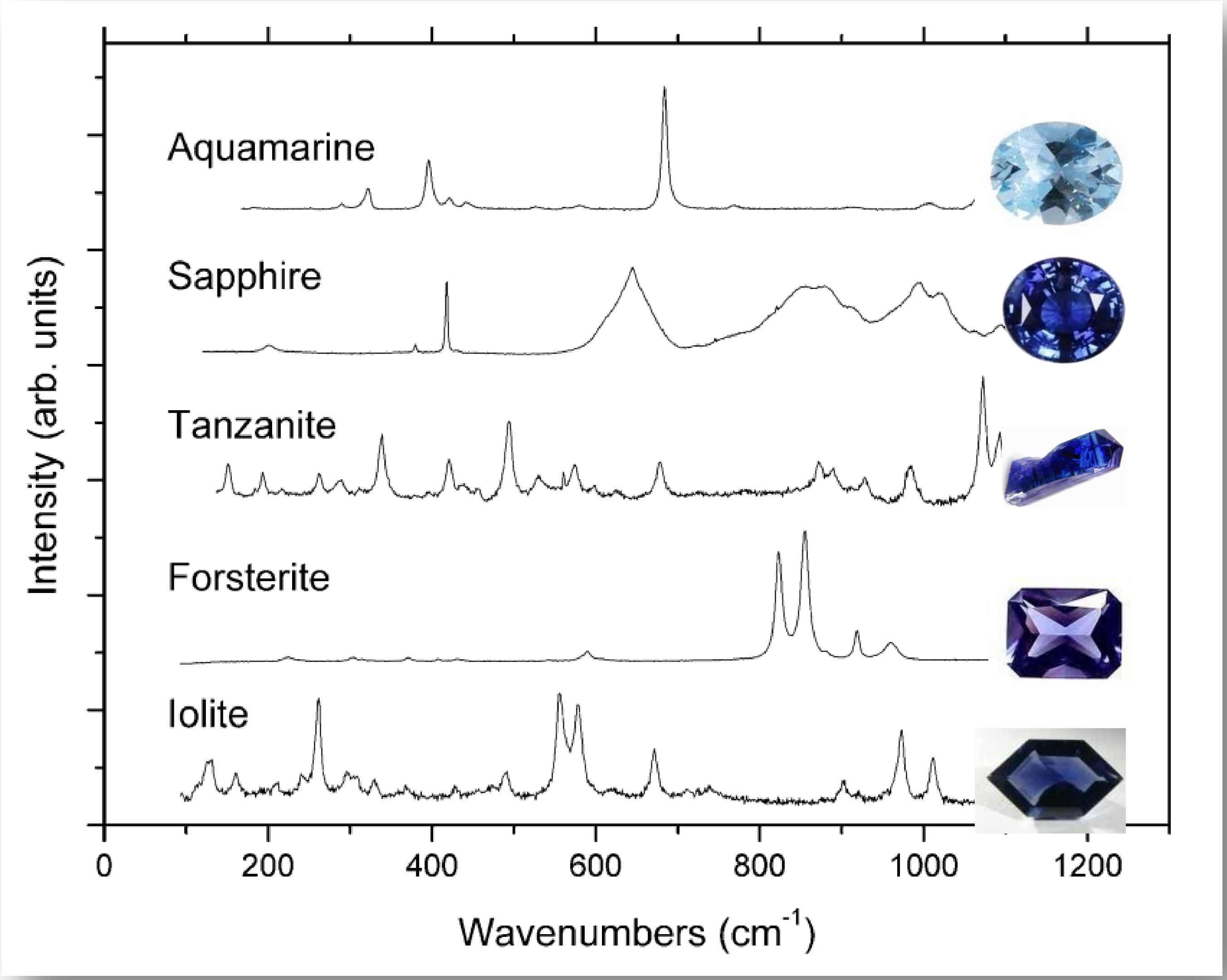


Simulant natural gems

Artificial gems

G. Barone, D. Bersani,P. P. Lottici, P. Mazzoleni, S. Raneri and U. Longobardo. (2016) Red gemstone characterization bymicro-Raman spectroscopy: the case of rubies and their imitations. DOI 101002jrs4919

Identification of the blue gems: comparison with references

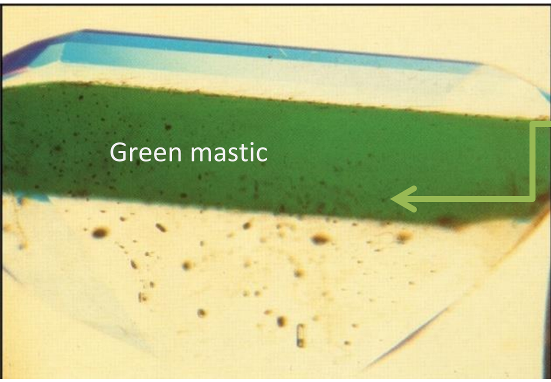


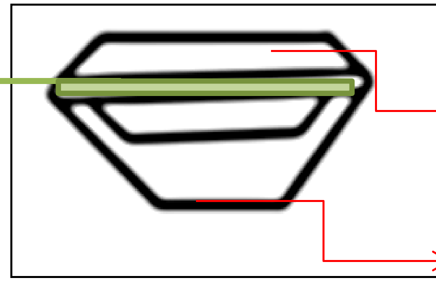
Simulant natural gems

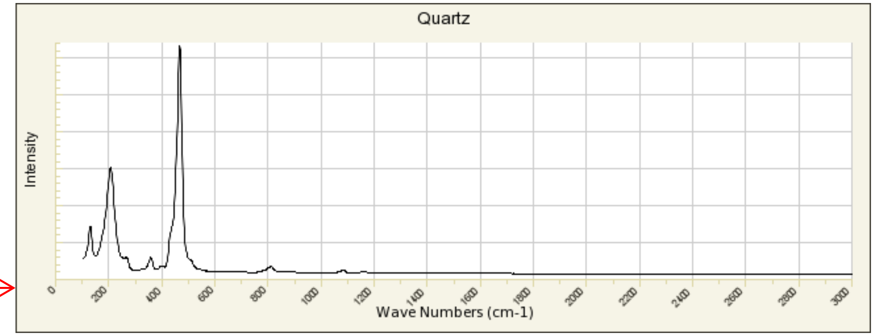
Sapphire or simulant?

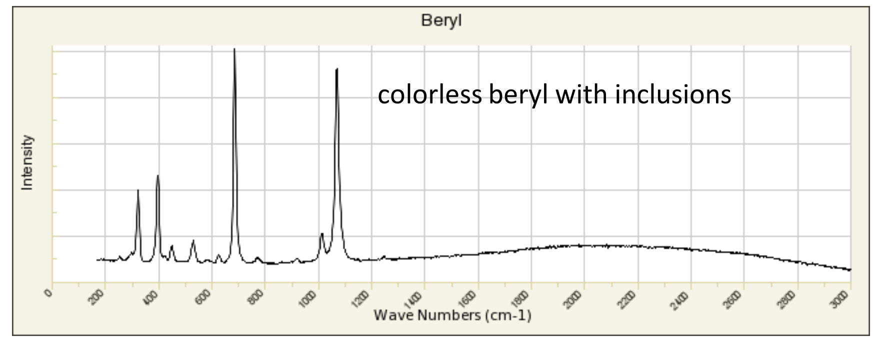
Barone G, Bersani D, Crupi V, Longo F, Longobardo U, Lottici PP, Aliatis I, Majolino D, Mazzoleni P, Raneri S, Venuti V (2014): A portable vs. micro-Raman equipment comparison for gemmological purposes: the case of sapphires and their imitations. Journal of Raman Spectroscopy, 45, 1309-1317.

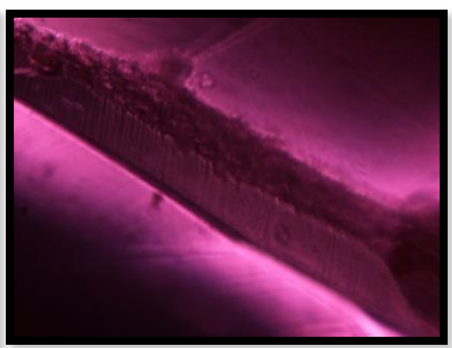
Identification of assembled gems

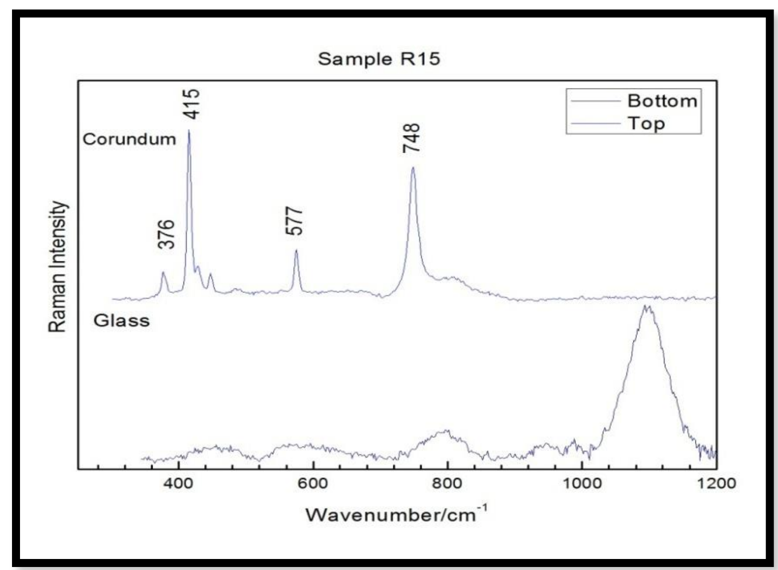












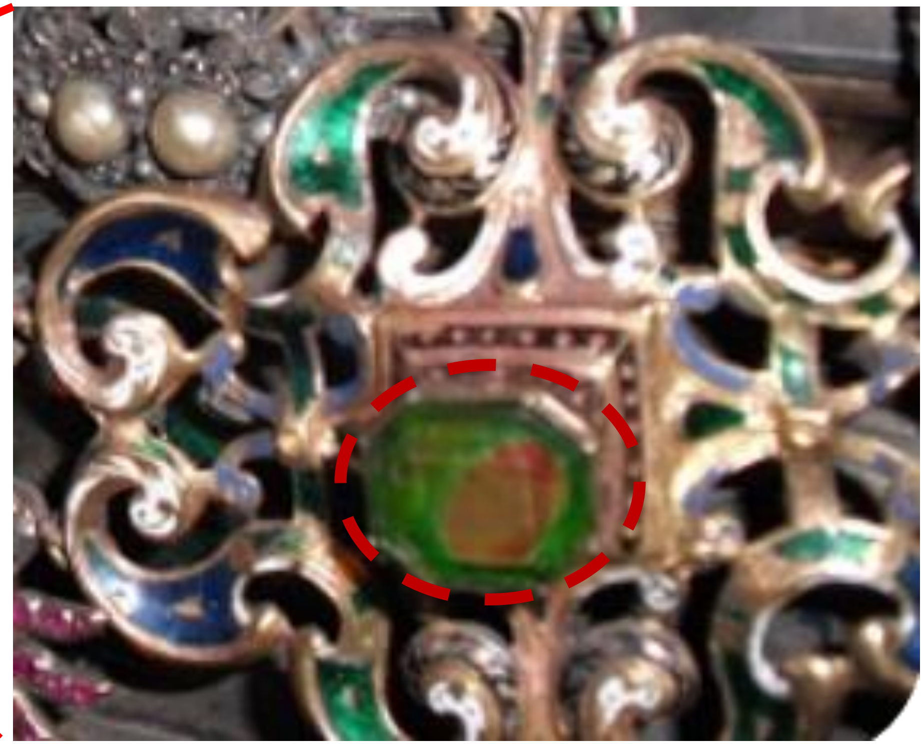
G. Barone, D. Bersani, P. P. Lottici, P. Mazzoleni, S. Raneri and U. Longobardo. (2016) Red gemstone characterization bymicro-Raman spectroscopy: the case of rubies and their imitations. DOI 101002jrs4919

Identification of composite gems ..in monted gems

S. Agata (Catania, Sicily)

Photo Ugo Longobardo

Assembled gems



Degradation of the glue

2 TREATMENTS

natural gems treated in laboratory: **treated gems**

most of the gems are not completely “natural.”

different types of treatments are used to obtain a more agreeable aspect, in terms of transparency and color.

important to distinguish between:

- **untreated gems**,
- gems that have received **treatments** which are considered **acceptable** by the gem market,
- and gems that have received heavy treatments, **not acceptable** by the market.

Bersani D. Lottici P. Applications of raman spectroscopy to gemology Anal. Bioanl Chem. 2010 397 2631- 2646

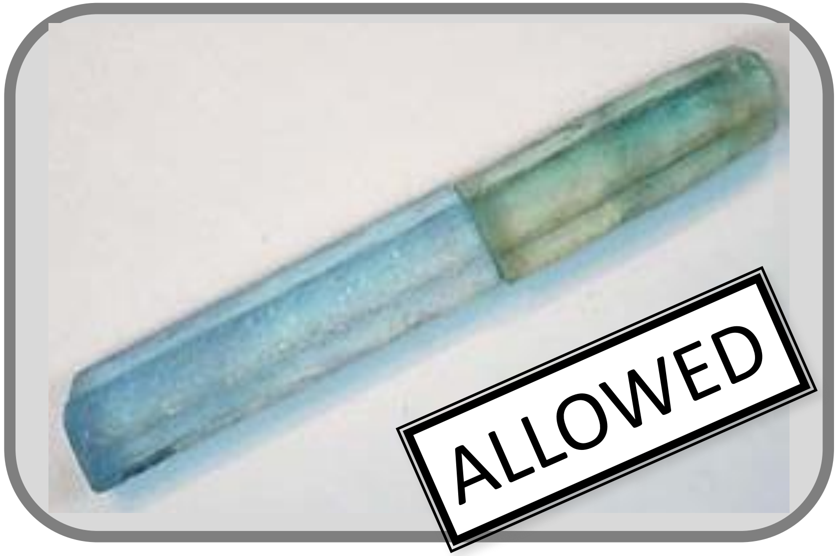
Some enhancement treatments

	Diamond	Beryl (Emerald, Aquamarine)	Chrysoberyl (Alexandrite)	Corundum (Ruby, Sapphire)	Jade (Jadeite, Nephrite)	Opal	Quartz (Rock crystal, Amethyst, Citrine)	Topaz	Tourmaline	Pearl (Cultured)
Methods to change color										
Irradiation	Occasional	Rare		Occasional			Common	Common	Rare	Rare
Heating	Occasional	Common		Common			Common	Common	Rare	Rare
Chemical bleaching					Common					Common
Surface coating	Rare	Rare		Rare	Common		Occasional	Occasional		Occasional
Dyeing		Rare		Rare	Occasional	Occasional	Occasional	Rare		Occasional
Color diffusion				Occasional				Occasional		
Heating at high pressure	Occasional									
Methods to change clarity										
Filling cracks or cavities	Occasional	Common	Rare	Occasional			Rare		Rare	
Remove inclusions	Occasional			Rare						
Quench crackling				Rare			Rare			
Impregnation					Common	Occasional				

J. E. Shigley, GEOLOGIJA. 2008. Vol. 50. No. 4(64). P. 227–236

- **Irradiation**
- **Heating**
- Chemical bleaching
- **Surface coating**
- **Dyeing**.
- **Color diffusion**
- **Filling cracks or cavities**
- Remove inclusions
- Quench cracklig
- impregnation

As an example, most gem sellers accept as **normal** the **heating** of blue-green-shaded **beryls to obtain blue aquamarine** (Shigley 2008)



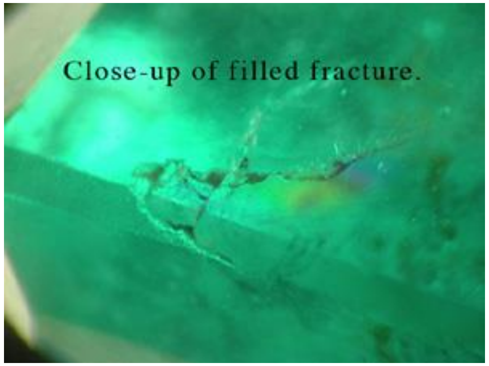
Comparison of treated and untreated aquamarine pieces cut from the same stone.

whereas **ion diffusion** used to **modify the color of a corundum** is usually not acceptable and is considered as **fraudulent** (Emmet et al. 2003).

Bersani D. Lottici P. Applications of raman spectroscopy to gemology Anal. Bioanl Chem. 2010 397 2631- 2646

fissure fillings cracks or cavities is one of the most used gem treatments, usually accepted among jewelers (corundum, emerald…diamond)

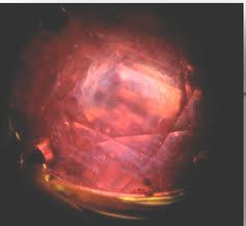
Many substances are used: oils, waxes, Canada balsams, and epoxy resins such as Opticon and Permasafe (Kiefert et al. 2000).

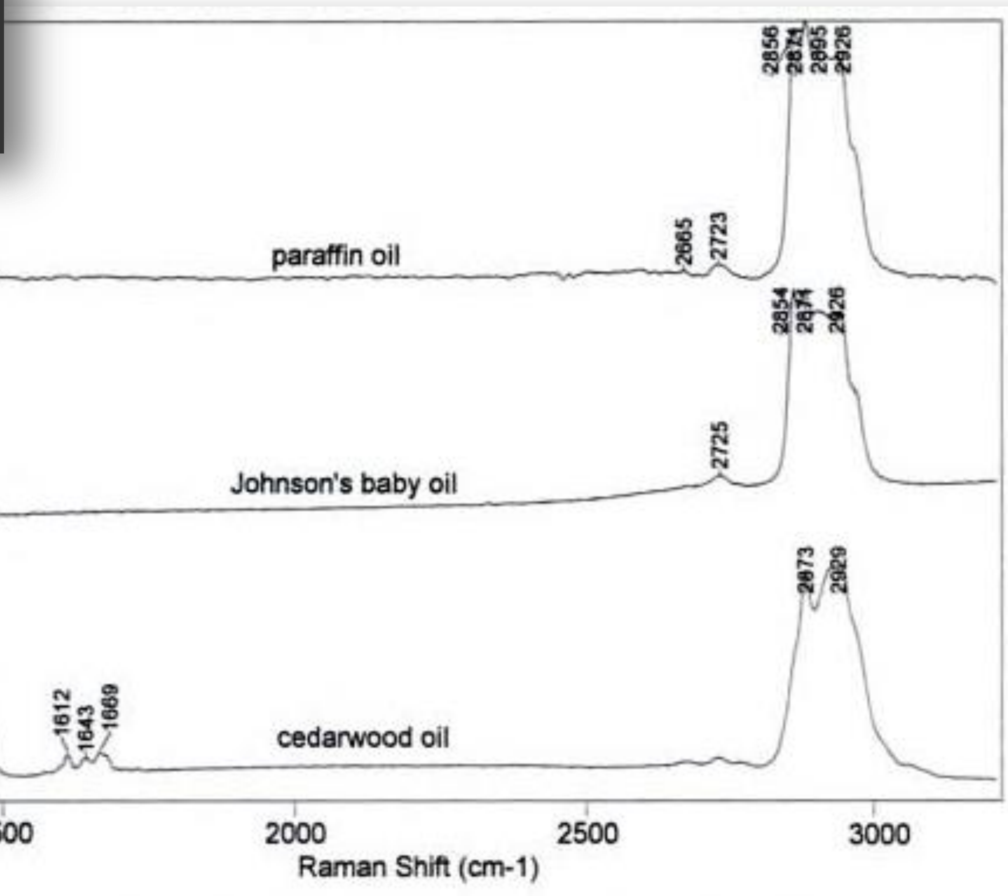


- some substances (such as oils) are **accepted** in the trade as fillers, ….are **removable**
- other such as epoxy resins, are **not accepted** because after polymerization their **removal is very difficult** (Kiefert et al. 2000).

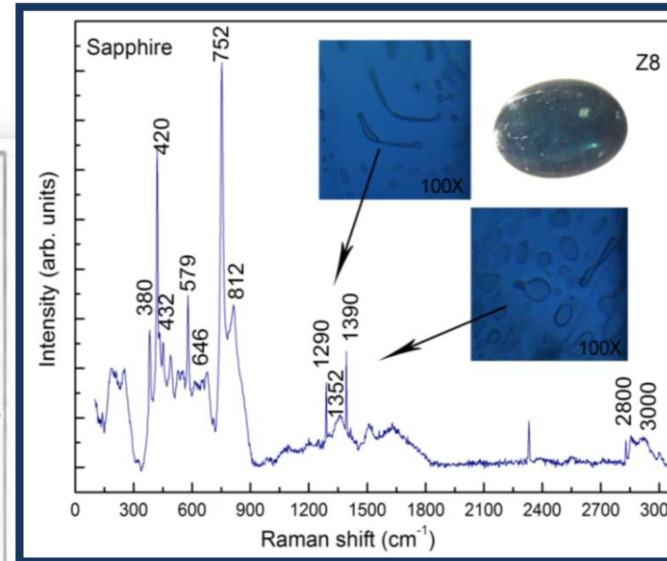
The characterization of the filler is important….

"ALLOWED" FILLERS



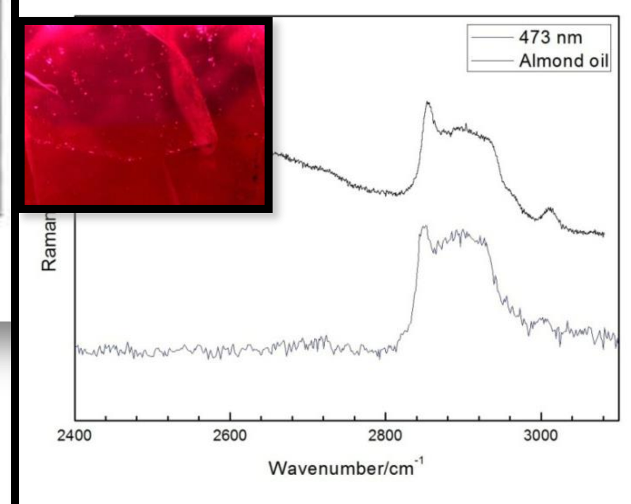


Kiefert L, Hanni HA, Ostertag T (2001) In: Lewis IR, Edwards HGM (eds) Handbook of Raman spectroscopy: from the research laboratory to the process line. Marcel Dekker, New York, pp 469–490;



Barone G. et al (2014): Journal of Raman Spectroscopy, 45

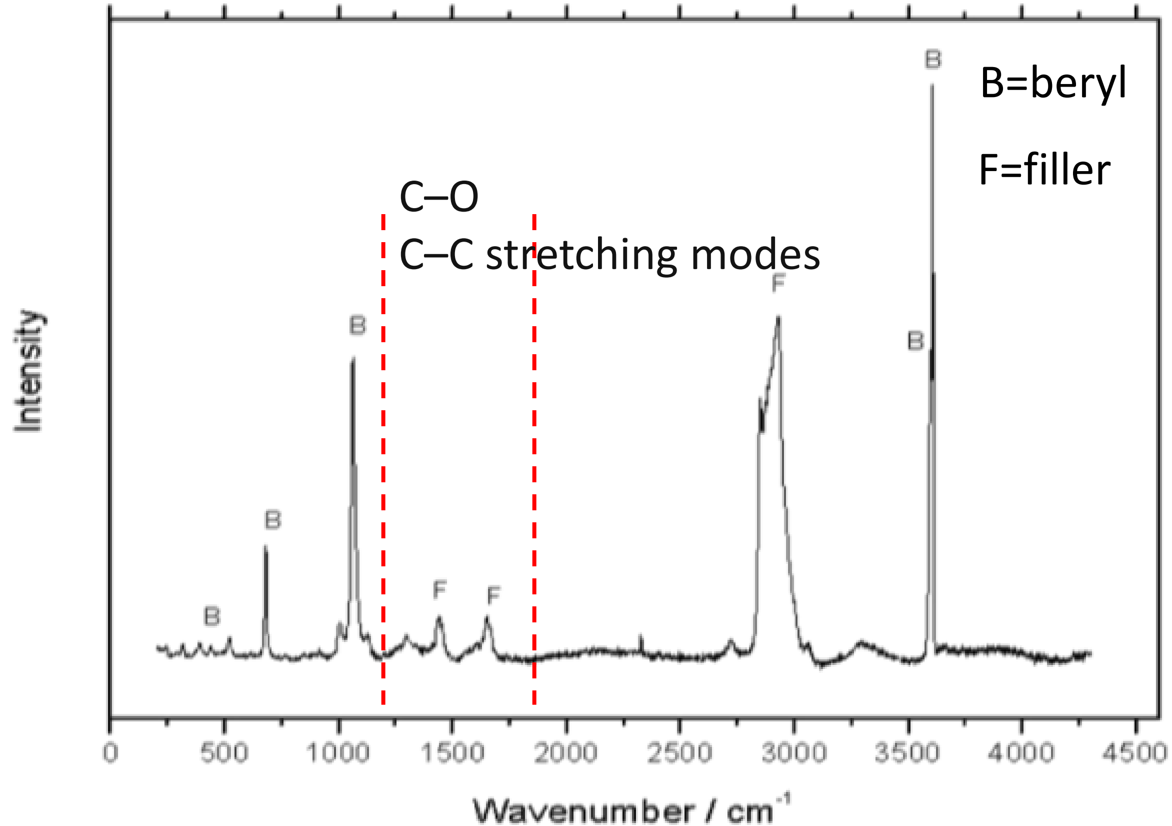
Oil paraffin used as filler



G. Barone, D. Bersani,P. P. Lottici, P. Mazzoleni, S. Raneri and U. Longobardo. (2016) Red gemstone characterization bymicro-Raman spectroscopy: the case of rubies and their imitations. DOI 101002jrs4919

“ALLOWED” FILLERS

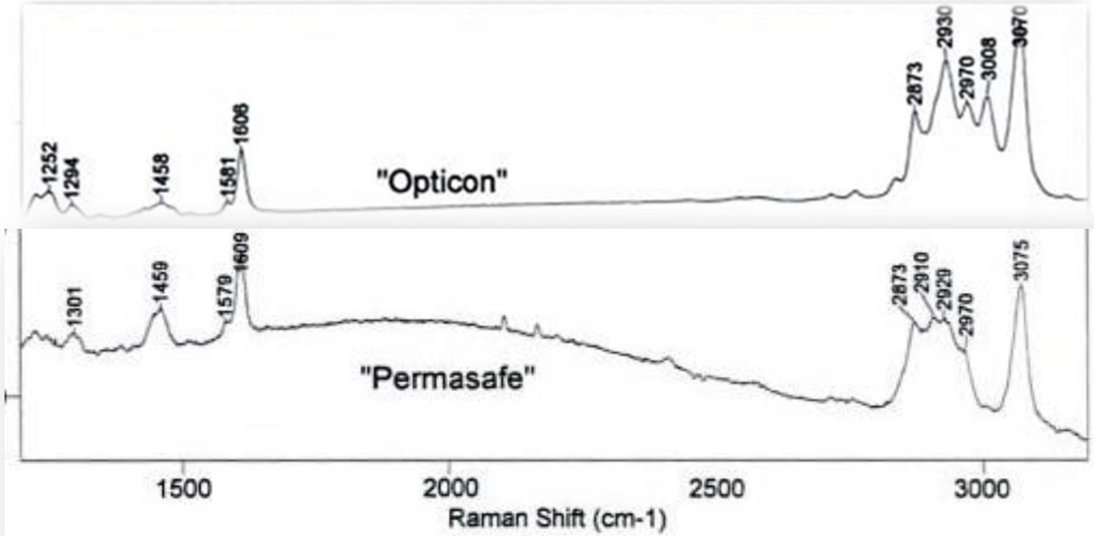
Most common treatment: oiling/filling. «**Allowed**» fillers: non-polymerised

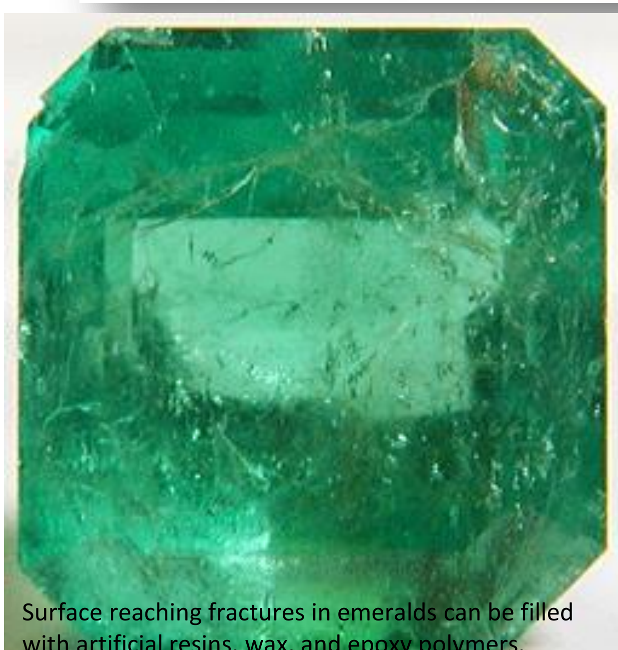


Spectrum similar to paraffin oil, «Johnson’s Baby »

Bersani B, Azzi G, Lambruschi E, Barone G, Mazzoleni P, Raneri S, Longobardo U, Lottici PP (2014): **Characterization of emeralds by micro-Raman spectroscopy**. *Journal of Raman Spectroscopy*, 45, 1293–1300. doi: 10.1002/jrs.4524

“NOT-ALLOWED” FILLERS





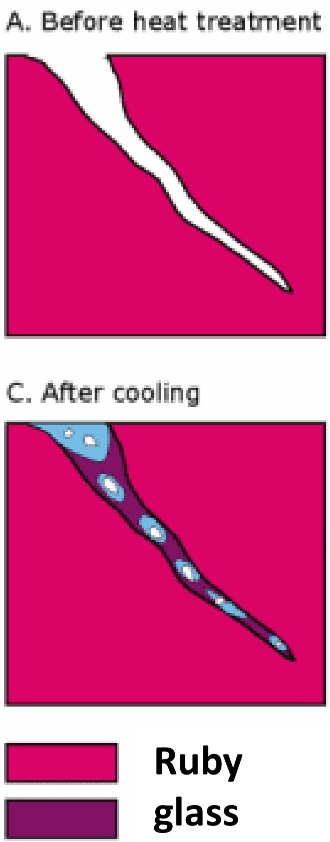
Surface reaching fractures in emeralds can be filled with artificial resins, wax, and epoxy polymers.

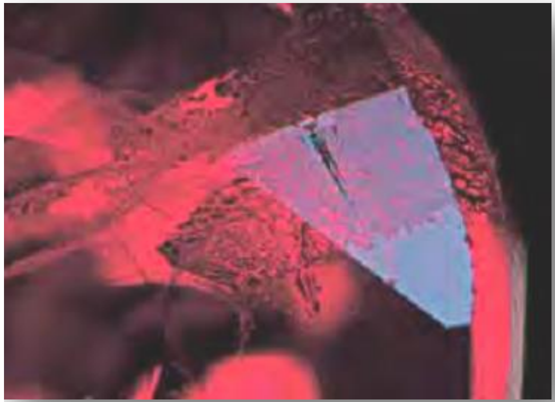
treated emerald

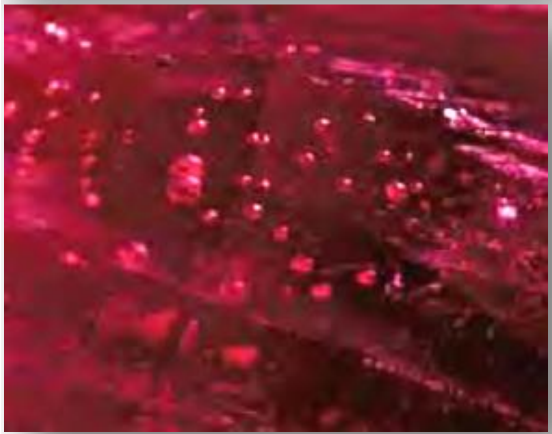
Kiefert L, Hanni HA, Ostertag T (2001) In: Lewis IR, Edwards HGM (eds) Handbook of Raman spectroscopy: from the research laboratory to the process line. Marcel Dekker

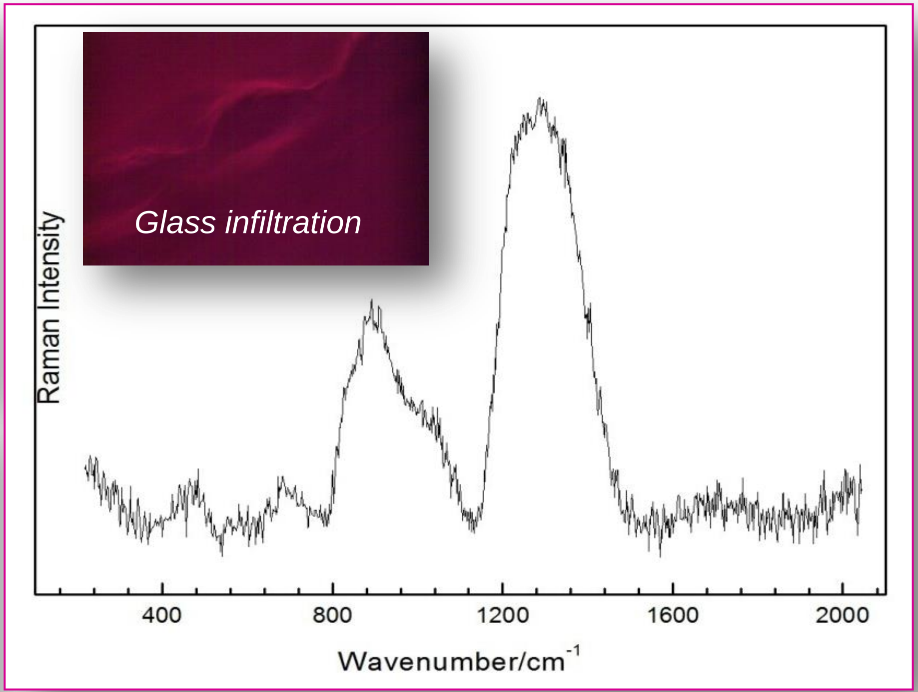
"NOT-ALLOWED" FILLERS

Not only organic materials are used to fill fissures: some highly fractured rubies are filled with high-refractive-index glass to improve their clarity (McClure et al. 2006).









The presence of glass filler is showed by the typical raman bands.

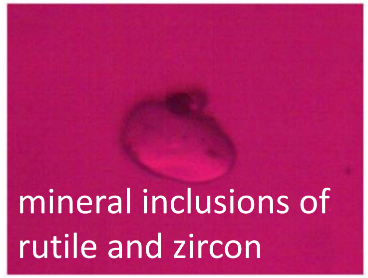
G. Barone, D. Bersani,P. P. Lottici, P. Mazzoleni, S. Raneri and U. Longobardo. (2016) Red gemstone characterization bymicro-Raman spectroscopy: the case of rubies and their imitations. DOI 101002jrs4919

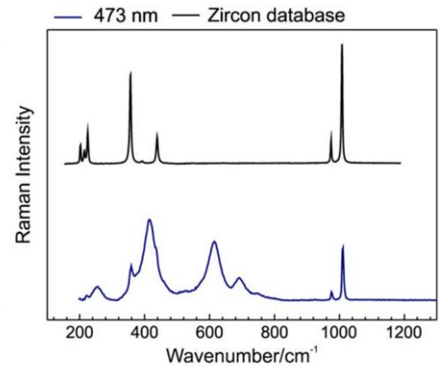
INVASIVE TREATMENTS

natural ruby subjected to heat treatment and glass filling

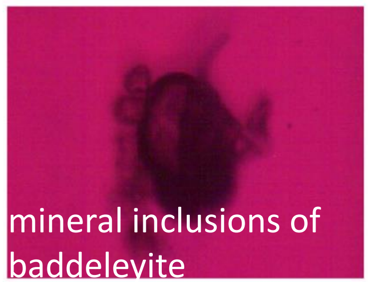
a)

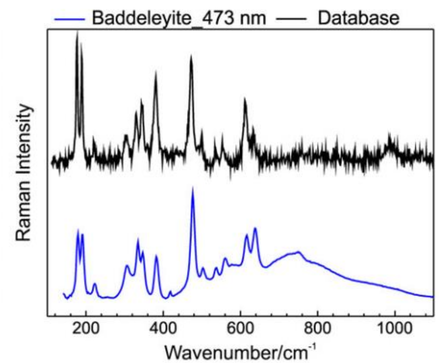
b)



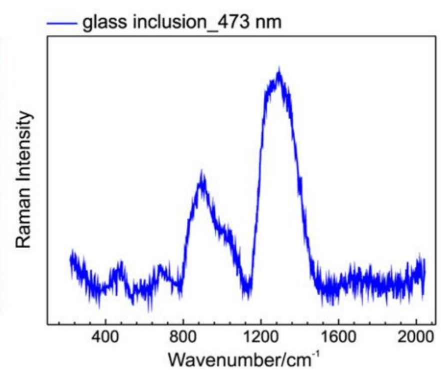


c)





d)

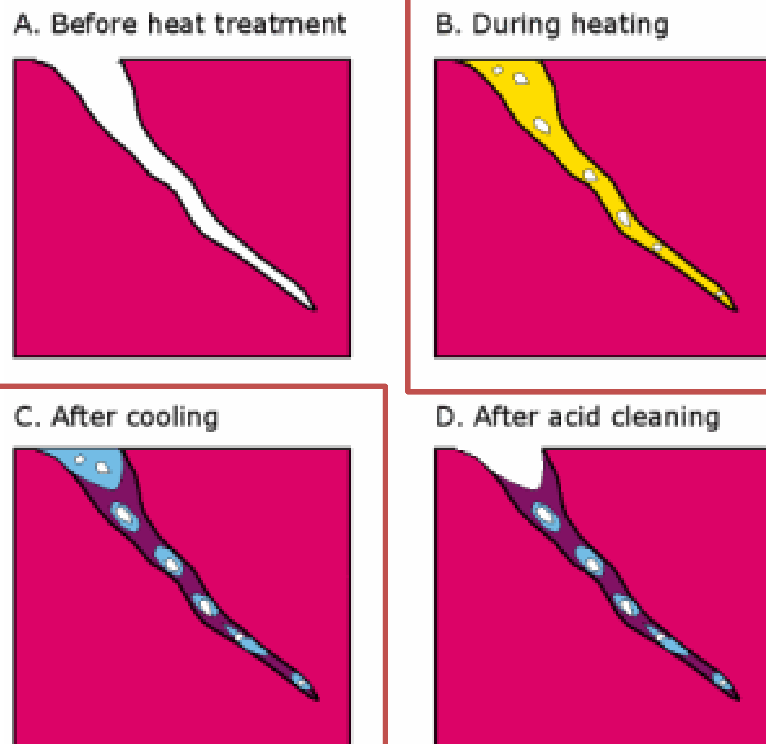


Inclusions in (a) samples R9 and relative micro-Raman spectra acquired by using the 473-nm line

G. Barone, D. Bersani,P. P. Lottici, P. Mazzoleni, S. Raneri and U. Longobardo. (2016) Red gemstone characterization bymicro-Raman spectroscopy: the case of rubies and their imitations. DOI 101002jrs4919

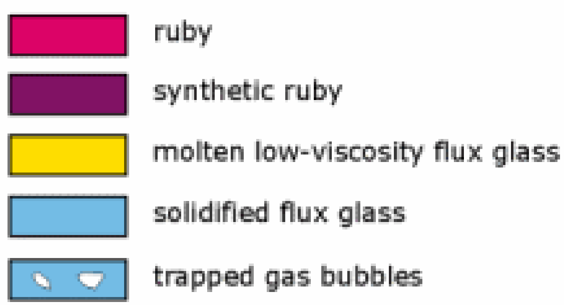
"NOT-ALLOWED" TREATMENTS

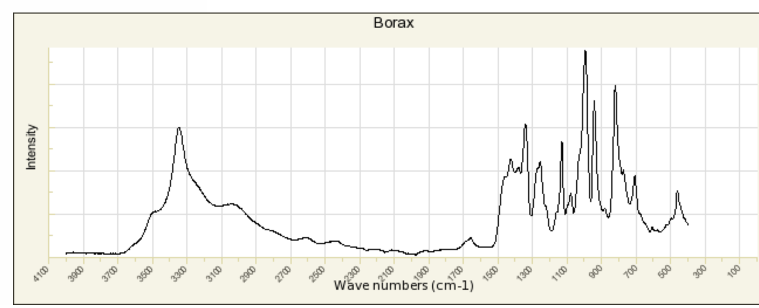
"flux healing" of fractures in Ruby obtained by partial surface melting to hide fractures…



B. the **fracture are filled with a low viscosity glass rich in flux agents** such as borax, calcium borate, and calcium or sodium phosphate. This substances produce the melting of the corundum

C. after the cooling the fracture will be filled by **synthetic rubies** recognizable for the inclusion of solidified flux glass.





Micro-Raman spectroscopy could be used to find traces of flux agents

NATURAL vs. SYNTHETIC SIMULANT

natural gems
Organic and inorganic

Artificial gems
In laboratory

assembled gems

Very precious

natural simulant

treated gems

without a corresponding in nature

similar chemical composition of the natural counterpart: **syntetic simulant**

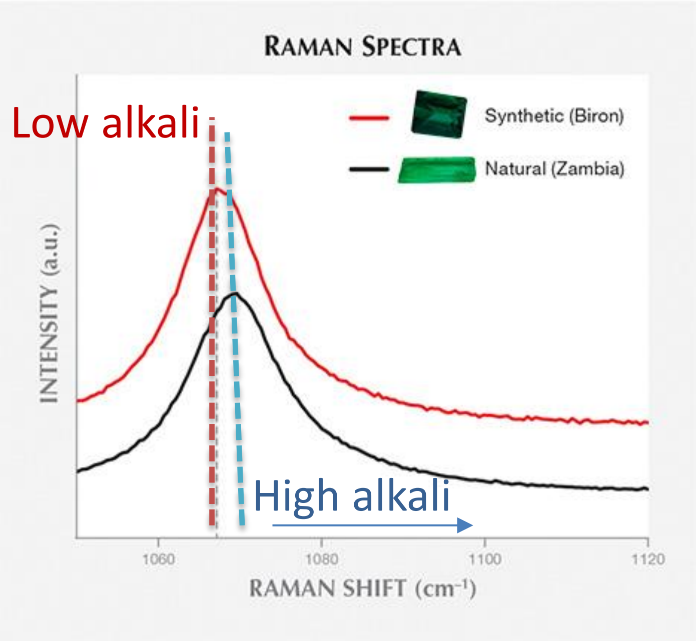
two or more layers of different types of gems: **duplet- triplet**

Is it possible distinguish with the Raman spectroscopy a natural gem from its synthetic simulant since they have very similar composition and structure?

IDENTIFICATION OF SYNTHETIC SIMULANT

Characteristic Raman features: alkali content in emeralds

in the case of emeralds, the band at 1070 cm^{-1} can discriminate the origin of the beryl. The frequency and the width of this band are expected to increase with the amount of alkali:



Type	Content of alkali	frequency and width
I	Low alkali	1068-1070 cm-1 sharper
II	High alkali	1069-1073 cm-1 width 18-26 cm-1
Hydrothermal syntetic	alkali-free water	1067- 1068 cm-1 width 11-14 cm-1

in **low alkali** emeralds, it shifts to lower wavenumbers and becomes sharper.

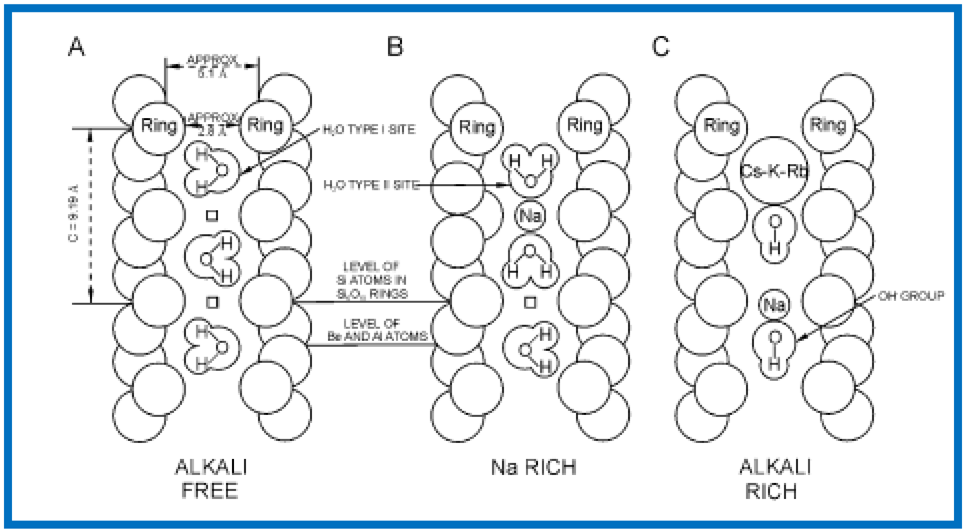
in **high alkali emeralds**, it is broader and it is found at higher wavenumbers,

In **hydrothermal synthetic emeralds**, it shows the lowest width and wavenumber.

IDENTIFICATION OF SYNTHETIC SIMULANT

Characteristic Raman features: water types in emeralds

The other region useful for our aim is near **3600 cm^{-1}** where we can see the effects of **water vibration**.



Type I Type II

In beryl structure it is possible recognized **two types of water in the channel cavities:**

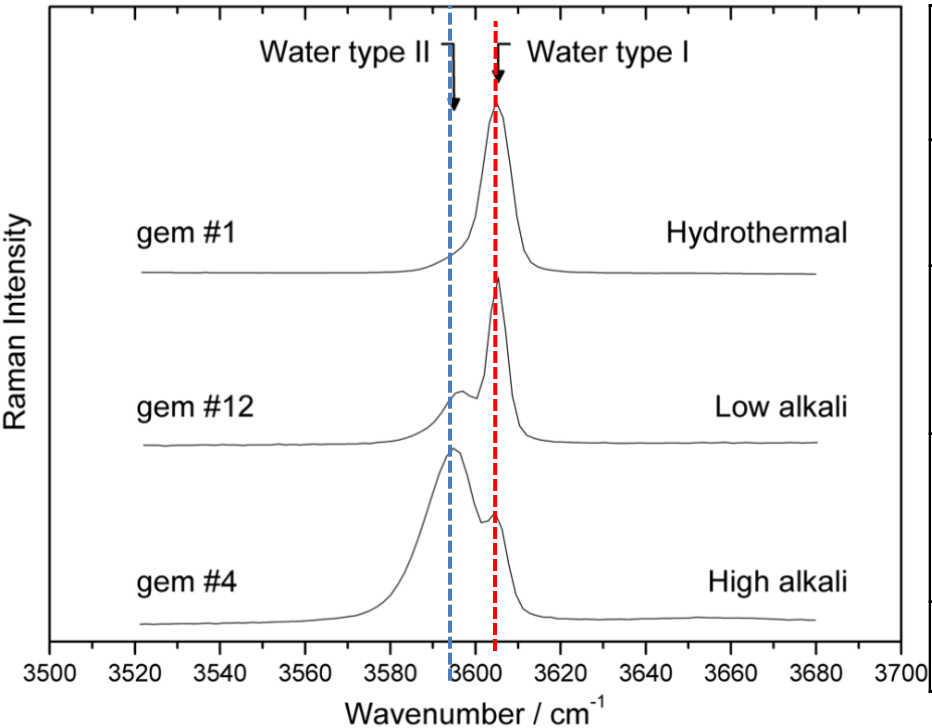
Type I: H2O molecules are found alone and the H–H 'vector' is parallel to the c-axis of the emerald crystal

Type II: water molecules are associated with nearby alkali ions forcing the H–H vector to be perpendicular to the c-axis

The raman spectra register these difference in water vibrations…..

IDENTIFICATION OF SYNTHETIC SIMULANT

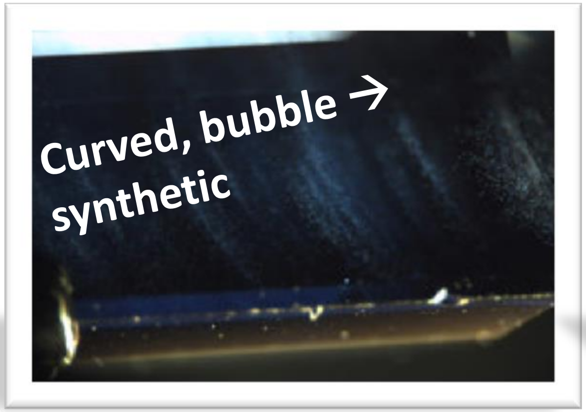
Characteristic Raman features: alkali content in emeralds

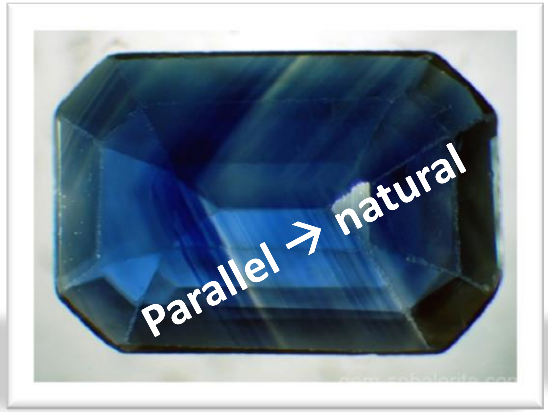


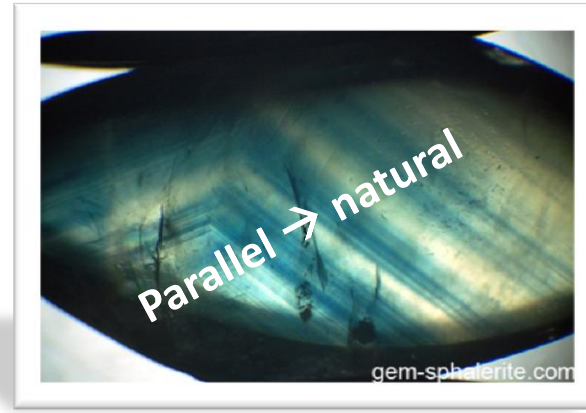
Type	Content of alkali	frequency and width	OH stretching
I	Low alkali	1068-1070 cm-1 sharper	3608 cm-1
II	High alkali	1069-1073 cm-1 width 18-26 cm-1	3598 cm-1
Hydrothermal syntetic	**alkali-free water**	1067- 1068 cm-1 width 11-14 cm-1	3608 cm-1
Flux grown syntetic			Absence of water

WHEN COMPOSITION AND STRUCTURE ARE SIMILAR IN NATURAL AND SYNTHETIC GEMS….

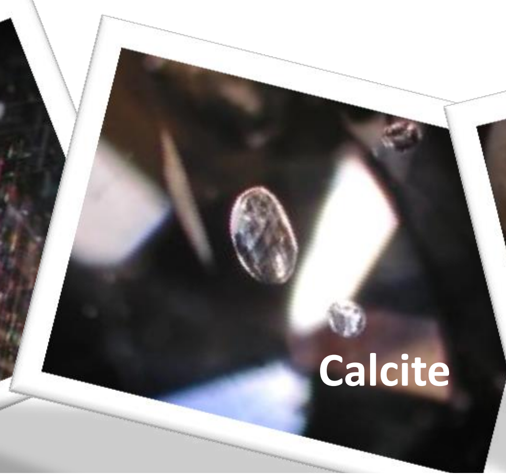
GROWTH LINES

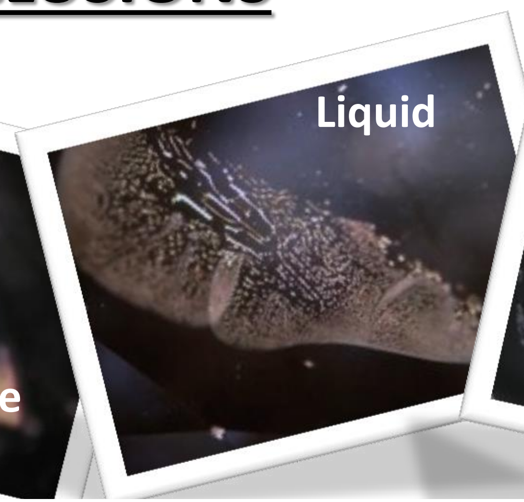






INCLUSIONS





but not always the inclusions allow to distinguish natural from synthetic .... because there is an attempt to reproduce the inclusions

Natural vs. synthetic: SAPPHIRE

Natural: inclusions in sapphire

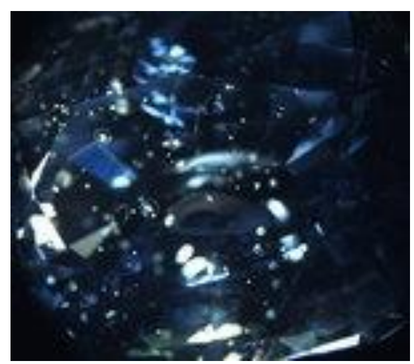
spinel

Needle rutile silky net

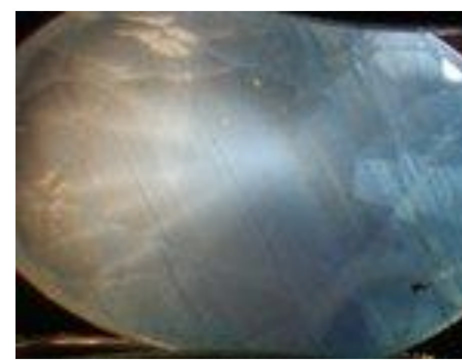
Syntetic: inclusions in sapphire

Zaffiro sintetico Chatham

Treated inclusions in sapphire

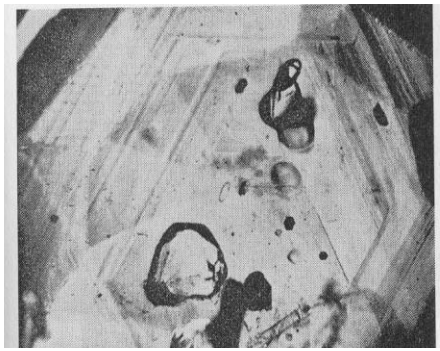
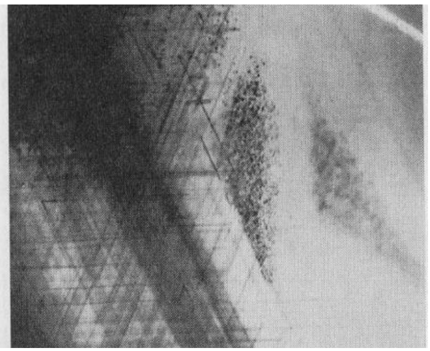


Many included crystal surrounded by tension halos due to heating.



heat treated Thai blue sapphire

Natural vs. synthetic: RUBIES

Natural: inclusions in Burmese rubies (are the most valuable) a) of crystals and zoning in ruby; b) "Silk" ruby


un-heated Mogok ruby a) rounded calcite guest crystals; b) Apatite and calcite guest crystals reflecting

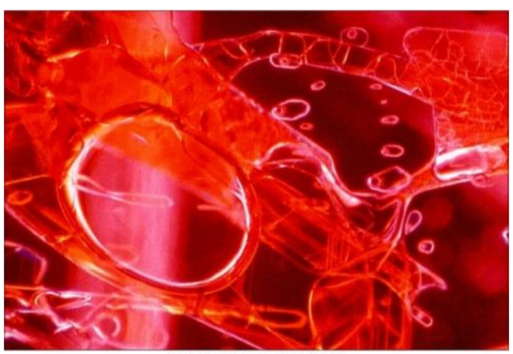
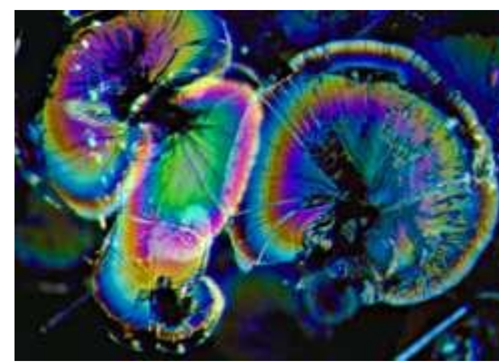


FOTO 10 - Rubino sintetico DOUROS
Le inclusioni mostrate sono tipiche esclusive nella sintesi Douros e non sono state mai osservate né in rubini naturali né in quelli artificiali. Residui da fondente. Luce a campo scuro, 100x.

Inclusions in **synthetic** ruby DOUROS

Heat **treated** Mong Hsu ruby

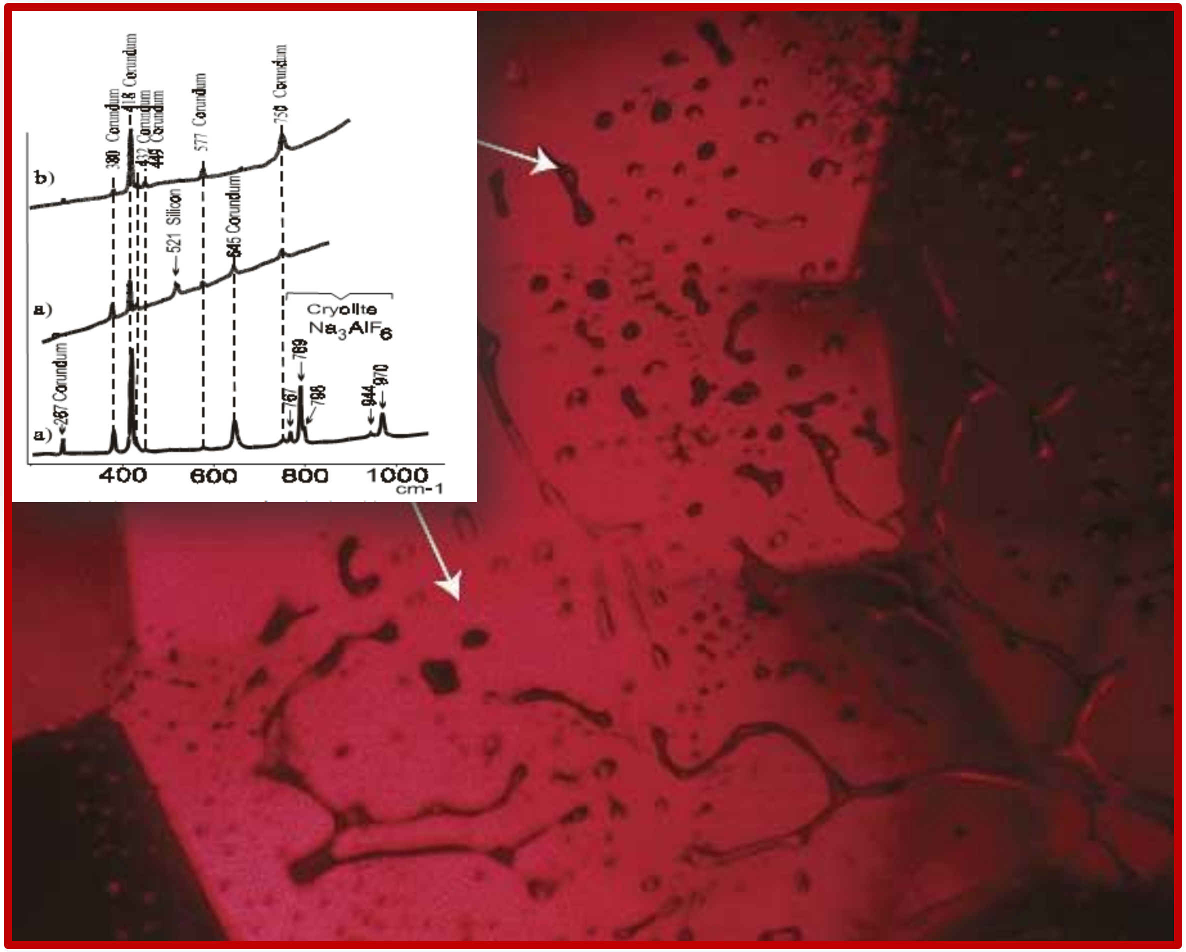


Discoid fractures caused by heat treatment in an Australian sapphire;

When synthesis remains appear….

Delé et al. 1997

identified the **synthetic corundum** produced by the flux method by looking for the presence in gems of **inclusions of flux, such as cryolite, tungstates, and polymolybdates.**



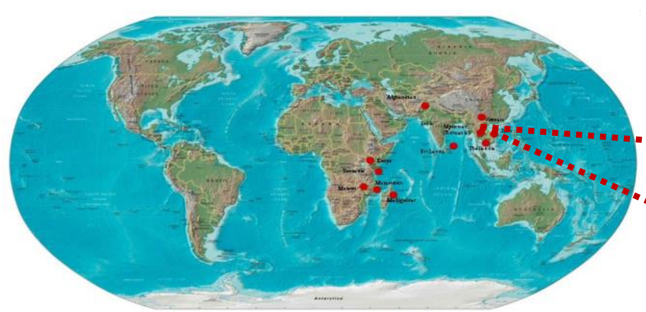
4 PROVENANCE AND GENESIS

different Provenance → **different economic value!!!!**

The investigation of the provenance of gems by means of Raman spectroscopy could be done in two ways:

A. **study of solid or fluid** inclusions….. characteristic of different paragenesis

B. study of slight variations in the vibrational spectra related **to small differences in composition or the presence of elements typical of some localities or geological environments** (Moroz et al 2000, Lodinski et al 2005).



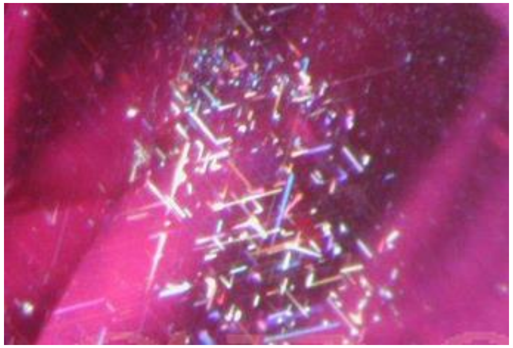
*the pigeon's blood red shade of expensive **Mogok rubies:** to some bluish tint Möng Hsu rubies - two major problems: 1) is dense silk clouds and a strong purplish color, blue cores; 2) are heavily fractured*

Provenance and genesis: SOLID AND FLUID INCLUSIONS Rubies

Delè et al. 1997, Sutherland et al. 2008 , Anderson 1994....provided a non exaustive list of the most common **inclusions** in **ruby** from some classic localities:

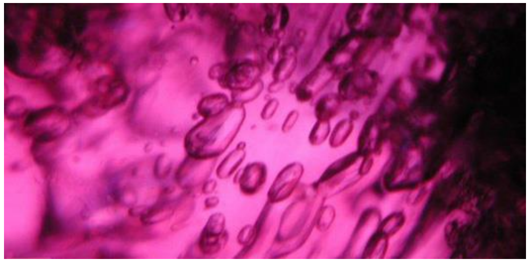
Solid inclusions	Geological setting	localities
Feather +/- liquid inclusion +/- cavities and twinning of laminae (corundum, black zircon)/ **pyroxene and nepheline**/ Boehmite)	**volcanic veins**	**Thailand** (ex Siam)
Needles Rutile **(**Silk) and rutile, mica./ vermouth effect/ **spinel, calcite, amphibole**	**metamorphic carbonates**	**Mogok (Burma, Myanmar)**
quartz and apatite/calcite, dolomite, rutile, diaspore, phlogopite and zircon	**metasomatic seams**	**Vietnam**
nebulous alignments and Feather		Kashimir
zircon inclusions surrounded by dark halos. Feather and twinning of color		Sri Lanka

Bold: mineral inclusions characteristic of different parageneses



Silk in Ruby from **Mogok**

Unheated Ruby from **Mogok** hosting rutile prisms, 49x



Elongated inclusion in ruby from **Mogok**

Calcite crystal inclusion in ruby from **Mogok**

Bohemite needle with “satellite” secondar feathers in unheted ruby from **Mogok**

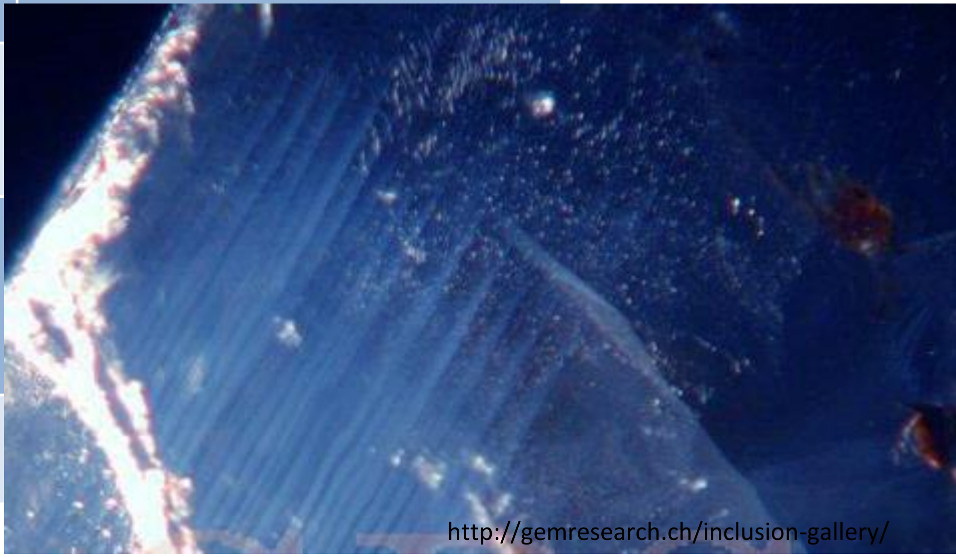
Robert Webster Gemme Zanichelli . http://gemresearch.ch/inclusion-gallery/

Provenance and genesis: SOLID AND FLUID INCLUSIONS - Sapphire

Anderson 1994

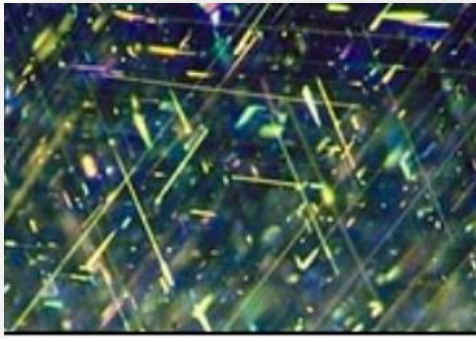
Solid inclusions/growth bands	Geological setting	localities
Plagioclase with polisintetic gemination . +/-pyroclore	Basaltic origin	Thailand, Cambogia
«silk» of rutile	metamorphic carbonates	Myanmar (Birmania) Mogok
linear growth bands	gold-bearing sands	Montana (USA) High Ti and low Fe
Feather and Color zoning /Mica, Hm, phase lq, Pyroclore and garnet. linear growth bands	Basaltic origin	Australia High Fe and low Ti
Liquid inclusions, «Feather»/ tourmaline, silk, tr mica	Pegmatite, Magmatism or thermal metamorphism	
«Feather» and «Fly wings». zircon inclusions surrounded by dark halos 3 phases (lq+ gas+ Hm). asterie	gneiss	
Bohmite Al(OH)3 Apatite		

non exaustive list of the most common **inclusions** in **sapphire** from some classic localities

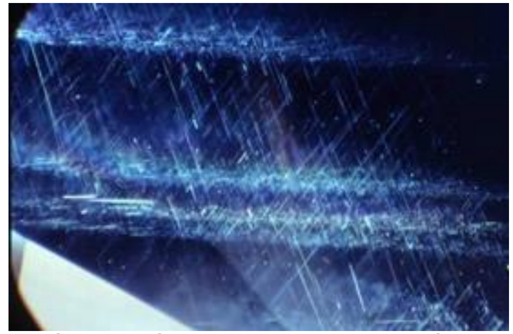


Fluid inclusion feathers «fingerprints» in sapphire from **Sri Lanka**

Provenance and genesis: SOLID AND FLUID INCLUSIONS Sapphire

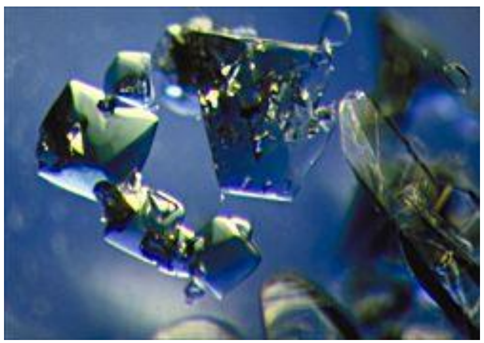


Myanmar Sapphire

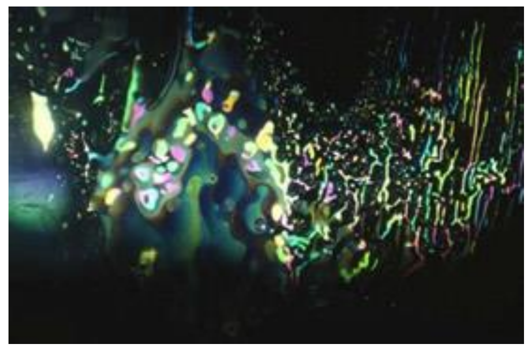


Unheated **Myanmar** Sapphire with oriented rutile needles (silk)

Healed feather in a **Myanmar** Sapphire

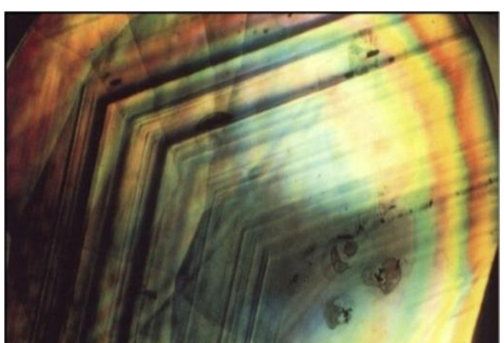


Spinel octahedra in a blue sapphire from **Sri Lanka**;



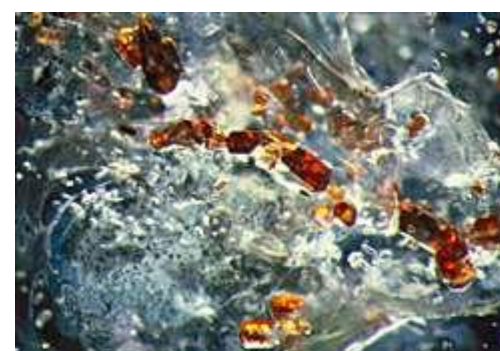
Healing feather in a Sapphire from **Thailand**, 70x

sapphire from **Thailand** with an included radioactive mineral, 100x



Angular growth zoning in sapphires from **Australia**.

http://www.pillarandstone.com/inclusion.html



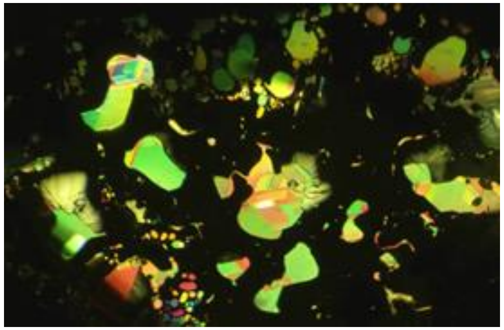
Primary rutile crystals (orange) in a sapphire from **Montana**;

Provenance and genesis: SOLID AND FLUID INCLUSIONS Emerald

Solid inclusions	Geological setting	localities
Rare inclusions (two phase)	pegmatites	Brasile
Pirite and three phase inclusion (*Chivor*) three phase inclusion: gas liquid and halite +/- parisite (Muzo)	pegmatites	Colombia
mica, actinolite +/-Carbon inclusion	micaschist and choritic schist	Siberia
Tremolite, mica	pegmatites	Austria
Two phases "a virgola" (liquid inclusion with gas bubble)	pegmatites	India
Mica +/- iron oxide +/- graphite (Transvaal)	Biotite schist a biotite, clorite e attinolite	Sud Africa
Mica and two phase inclusions and cavities	Pegmatite and micaschist	Tanzania
tremolite	pegmatites	Zimbawe
Mica biotite, rare feather +/- pyrolusite, amphibole, tourmaline, three phase inclusion	pegmatites	Zambia
Mica biotite, actinolite and calcite	pegmatites	Australia

non exaustive list of the most common **inclusions** in **emerald** from some classic localities

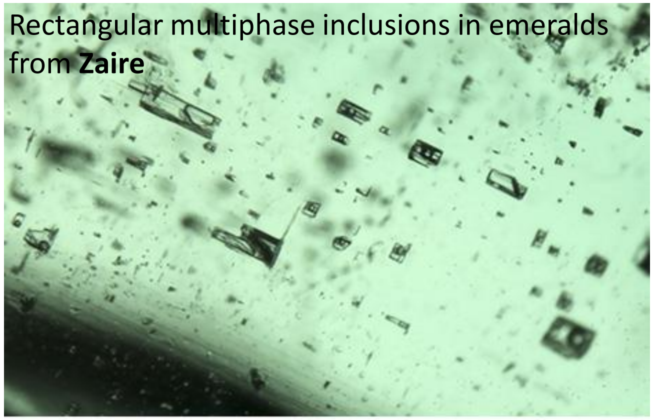
Three-phase inclusion in an Emerald from **Colombia**



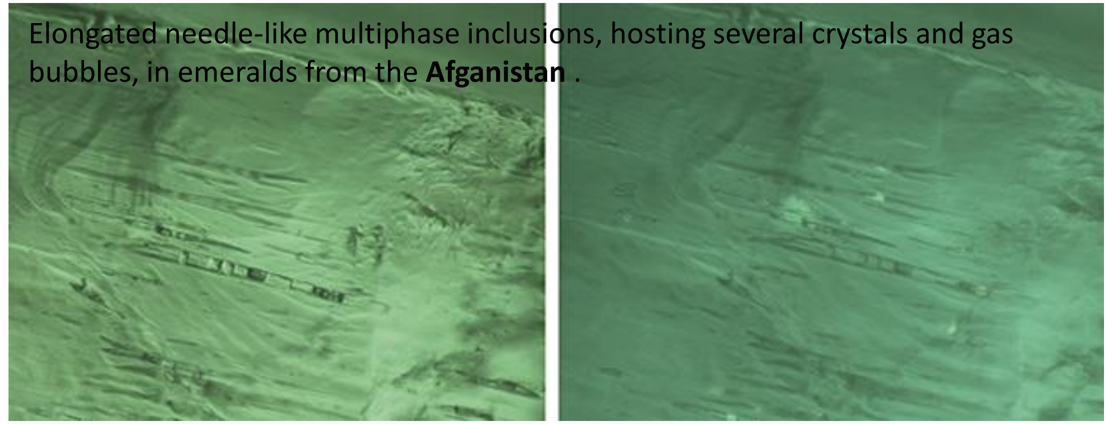
Feather with fluids in a Beryl from **Madagascar**, 70x.

Anderson 1994

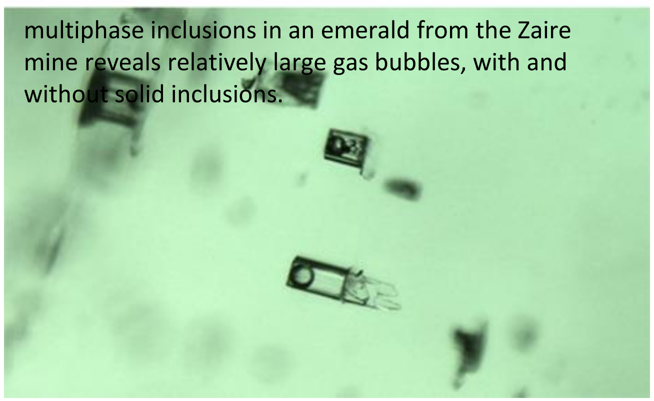
Provenance and genesis: SOLID AND FLUID INCLUSIONS Emerald



Rectangular multiphase inclusions in emeralds from **Zaire**

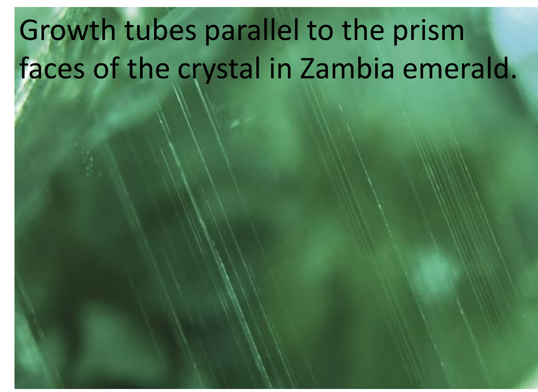


Elongated needle-like multiphase inclusions, hosting several crystals and gas bubbles, in emeralds from the **Afganistan** .



multiphase inclusions in an emerald from the Zaire mine reveals relatively large gas bubbles, with and without solid inclusions.

Rectangular cavities with tails are sometimes found in **Indian Emeralds.**



Growth tubes parallel to the prism faces of the crystal in Zambia emerald.

inclusion pyrolusite emerald Zambia

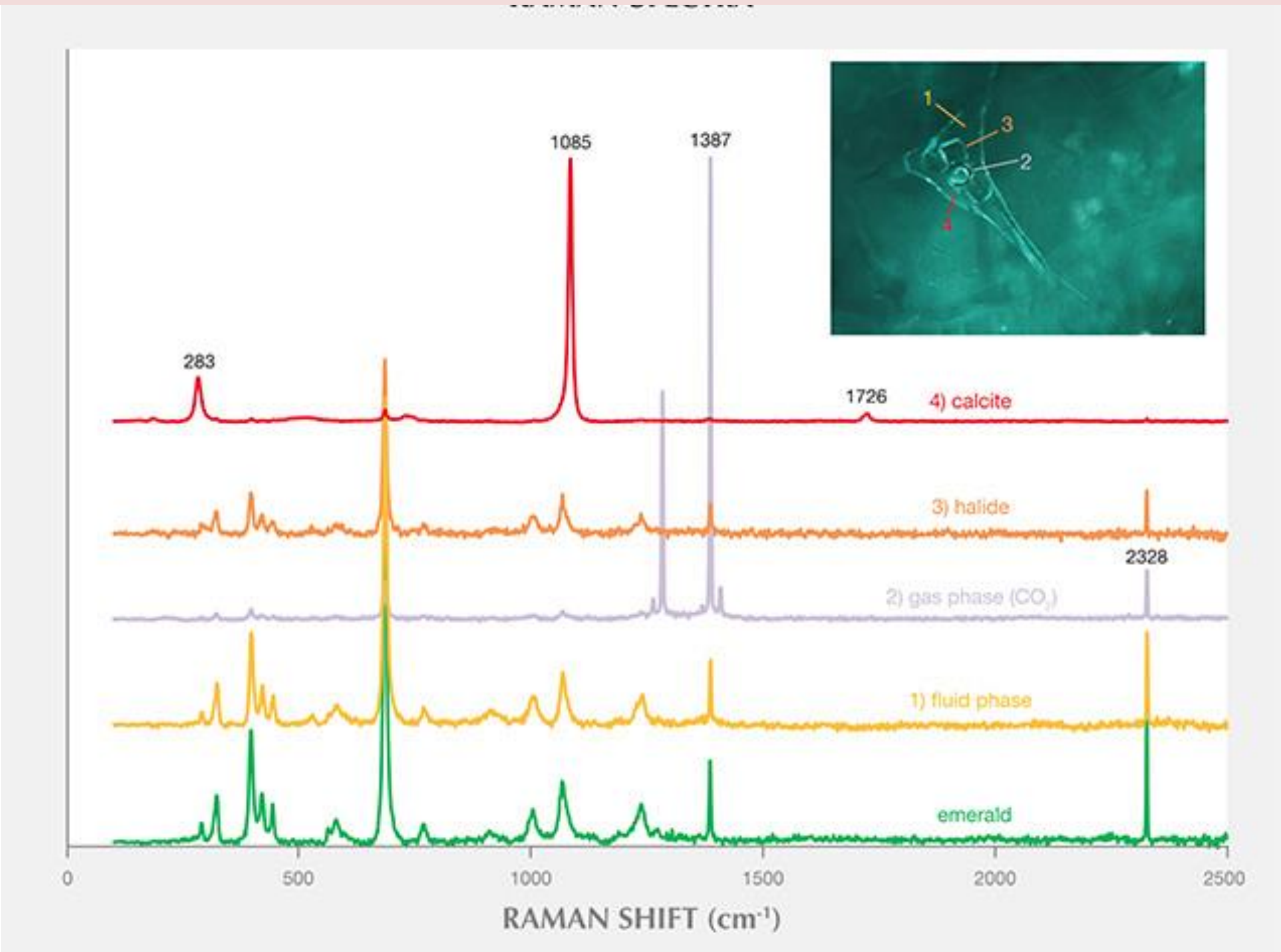
Inclusion amphibole in emerald Zambia

Inclusion tourmaline.in emerald Zambia

http://www.pillarandstone.com/inclusion.html

http://www.gia.edu/gems-gemology/summer-2014-saeseaw-three-phase-inclusions-emerald

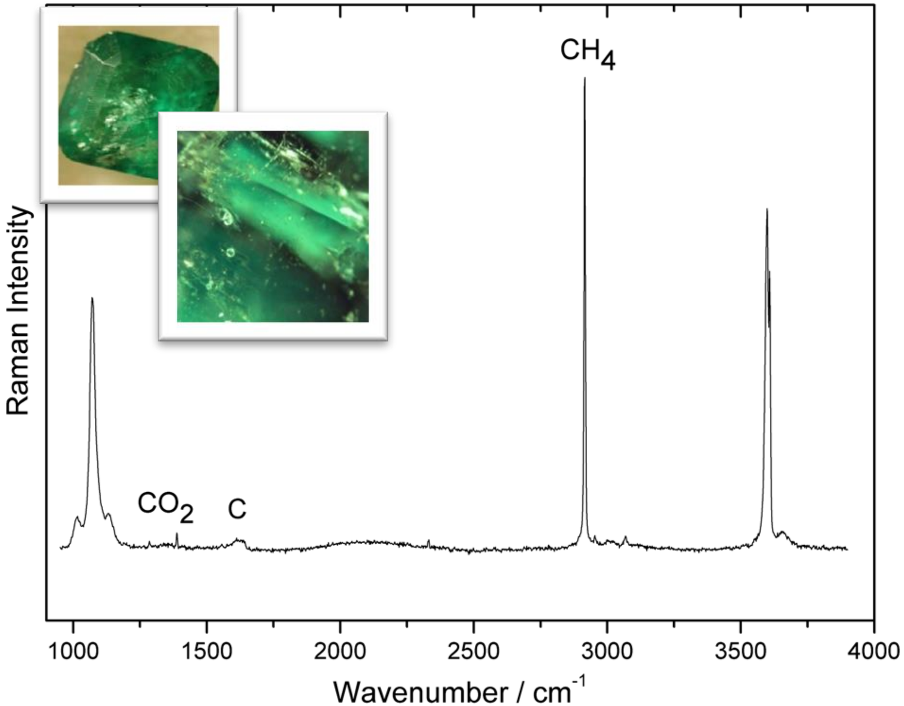
Provenance and genesis: SOLID AND FLUID INCLUSIONS Emerald



This Musakashi (**Zambia**) emerald. Raman spectroscopy was used to identify the host emerald (green), the CO_2 gas bubble (purple), the square halide crystal (orange), and the smaller carbonate crystal (red).

http://www.gia.edu/gems-gemology/summer-2014-saeseaw-three-phase-inclusions-emerald

Provenance and genesis: SOLID AND FLUID INCLUSIONS



Raman spectrum of a **tri-phase inclusion**

The very strong band of methane CH_4 (2915 cm^{-1}) together with weaker bands of CO_2 and carbonaceous material (1610 cm^{-1}) are visible.

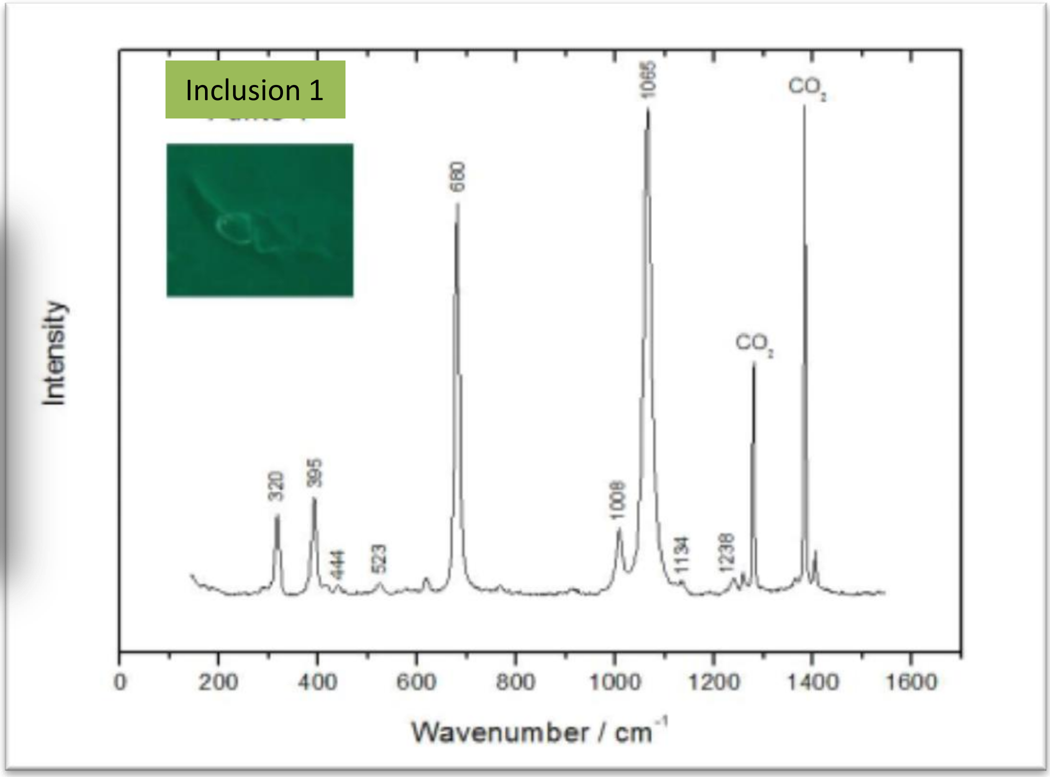
In addition to CO_2 density, it is possible to evaluate the CO_2/CH_4 ratio to obtain further information on the genesis (Novak 1971)

Bersani B, Azzi G, Lambruschi E, Barone G, Mazzoleni P, Raneri S, Longobardo U, Lottici PP (2014): **Characterization of emeralds by micro-Raman spectroscopy**. *Journal of Raman Spectroscopy*, 45, 1293–1300. doi: 10.1002/jrs.4524

Two- phase Inclusion in green gems (liquid with gas bubble)

the analysis of fluid inclusion can give very detailed information on the nature of the gemstone

Fluid inclusions



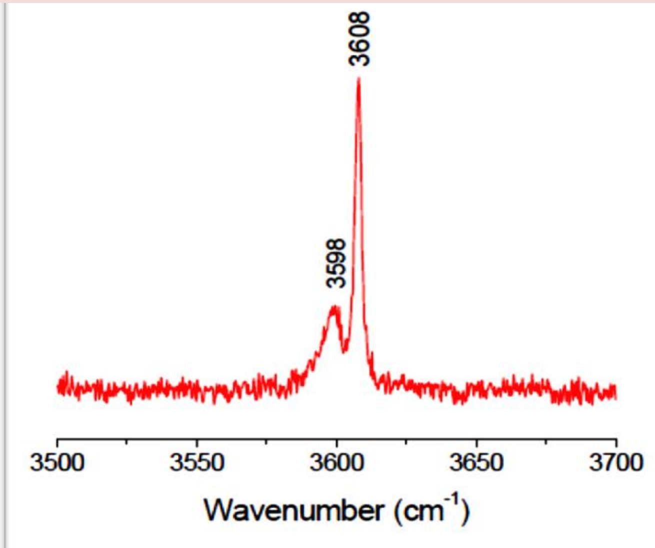
In the microphotograph is showed a liquid inclusion with a gas bubble (two-phase inclusion) inside a emerald. The peak testify the presence of CO_2.

Bersani B, Azzi G, Lambruschi E, Barone G, Mazzoleni P, Raneri S, Longobardo U, Lottici PP (2014): **Characterization of emeralds by micro-Raman spectroscopy**. *Journal of Raman Spectroscopy*, 45, 1293–1300. doi: 10.1002/jrs.4524

Provenance and genesis: OTHER RAMAN FEATURES

For **beryl**, the relationship between raman spectra and alkali contents may constrain also the provenance of the gem

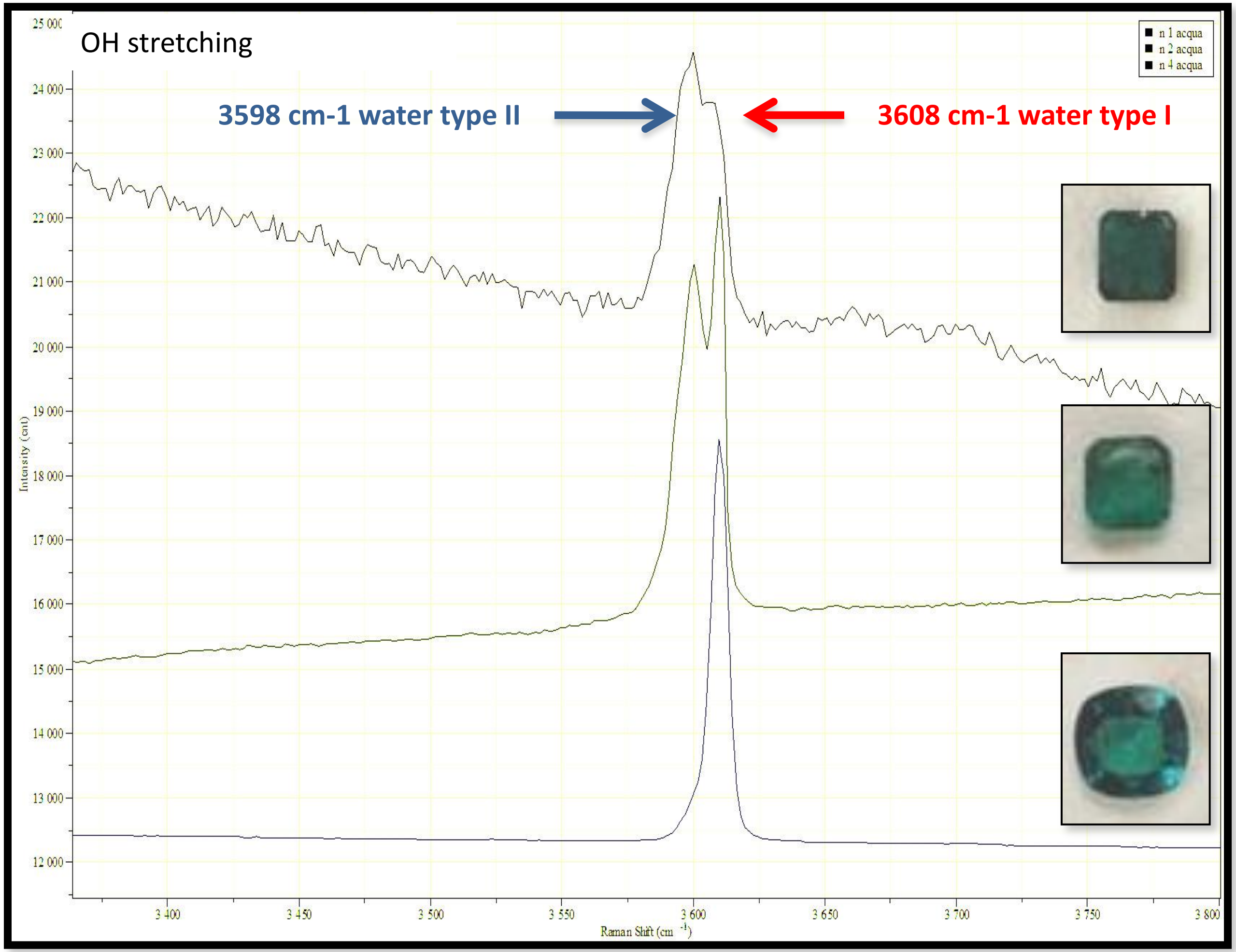
DOPO LA 65



Beryl may be classified in three groups….provenance

Type	Content of alkali	frequency and width	OH stretching	provenance
I	Low alkali Alkali poor	1068-1070 cm-1 sharper	3608 cm-1	host rocks pegmatite
II	High alkali Alkali rich	1069-1073 cm-1 width 18-26 cm-1	3598 cm-1	host rocks mica schist and gneiss
Hydrothermal syntetic	alkali-free water	1067- 1068 cm-1 width 11-14 cm-1	3608 cm-1	

Provenance and genesis: OTHER RAMAN FEATURES



natural high-alkali schist type: host rocks mica schist and gneiss

a natural low-alkali : host rocks pegmatite

Hydrothermal syntetic

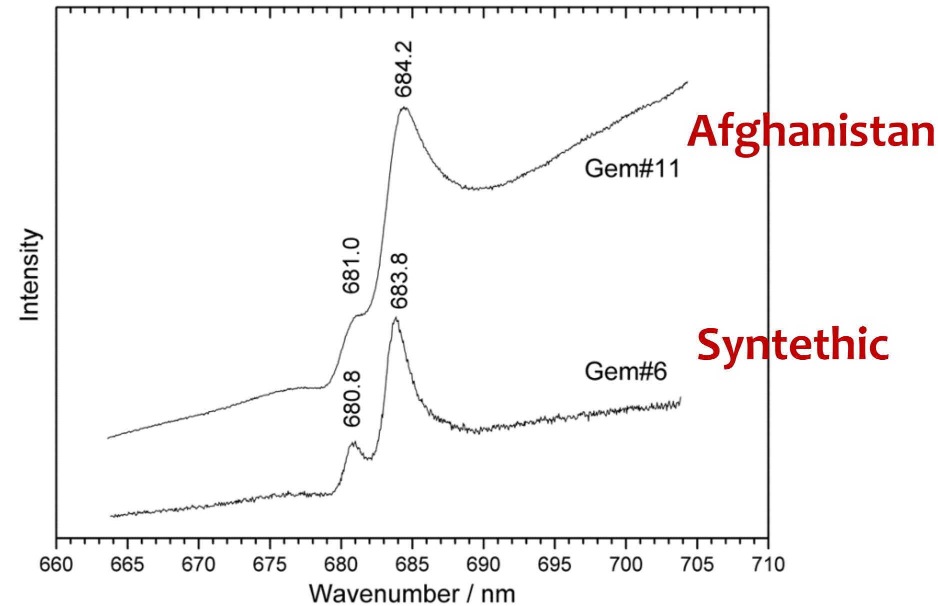
The presence and the intensity of the band at 3598 cm1, as well as the I_{3598}/I_{3608} ratio, depend on the amount of alkali ions.

Provenance: A) variations in vibrational spectra ..Kind of water in the beryl channels

Bersani B, Azzi G, Lambruschi E, Barone G, Mazzoleni P, Raneri S, Longobardo U, Lottici PP (2014) JRS 45, 1293–1300. doi: 10.1002/jrs.4524

Provenance and genesis: OTHER RAMAN FEATURES

in emerald Cr^{3+} (substituting Al^{3+}) generates two **photoluminescence bands** in **the visible part of the spectrum,** at 680nm and 684 nm, that could be used, according to Moroz et alii as a tool for the determination of the provenance of natural emeralds.



As an example, the spectra of gem #11 and gem #6 are compatible with the pattern reported for an Afghanistan sample and a synthetic product, respectively. We compared the photoluminescence spectra of the studied emeralds with those published by Moroz.

Provenance studies are highly complex and only the combination of many techniques can give reliable results. Actually, the existing database of photoluminescence spectra of emeralds is not sufficient for gemmological scopes

4 ….. PROVENANCE AND GENESIS

different Provenance → **different economic value!!!!**

The investigation of the provenance of gems by means of Raman spectroscopy could be done in two ways:

A. study of solid or fluid inclusions

B. study of slight variations in the vibrational spectra related **to small differences in composition or the presence of some elements typical of some localities or geological environments** (Moroz et al 2000, Lodinski et al 2005).

Provenance and Genesis - COMPOSITIONAL ANALYSIS

Garnet Group

$X^{2+}_{3}Z^{3+}_{2}(SiO_4)_3$

This isomorph group is usually divided into two series:

Pyrope

Almandine

Spessartine

Uvarovite

Andradite

Grossular

Pyrope

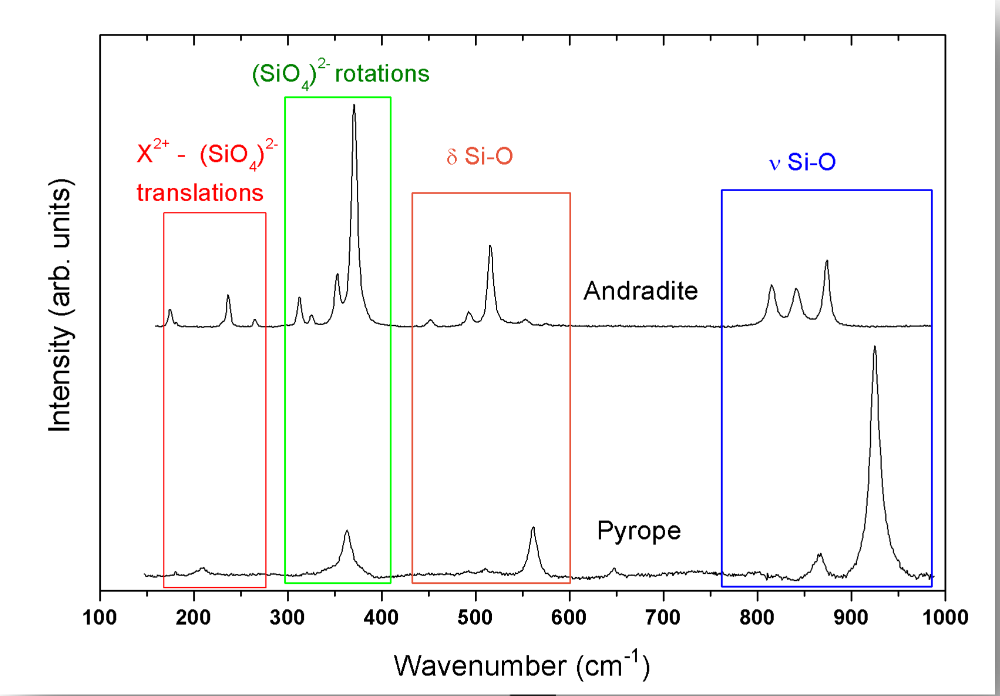
Almandine

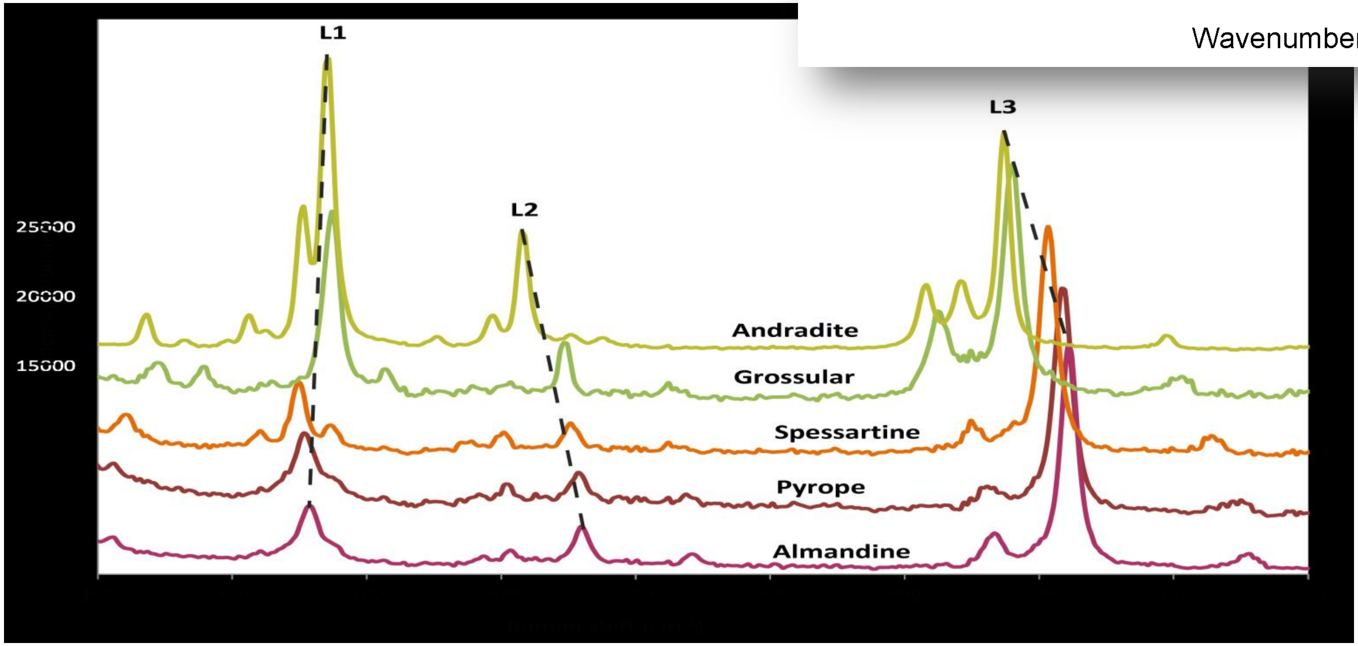
tsavorite

demantoid

Provenance and Genesis - COMPOSITIONAL ANALYSIS

For gemological study obtain, the composition of garnet allow to constra the provenance of the gemstone



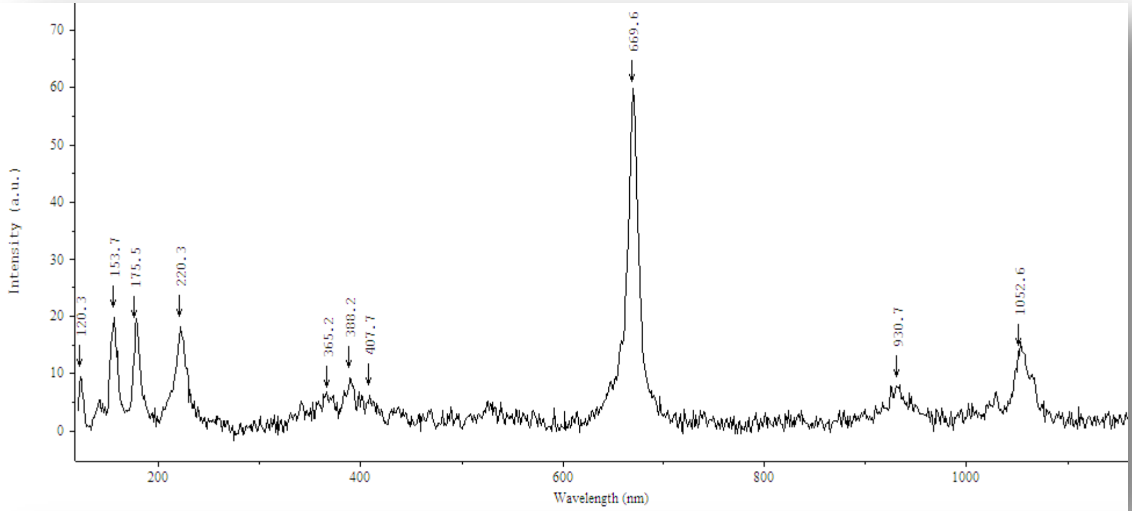


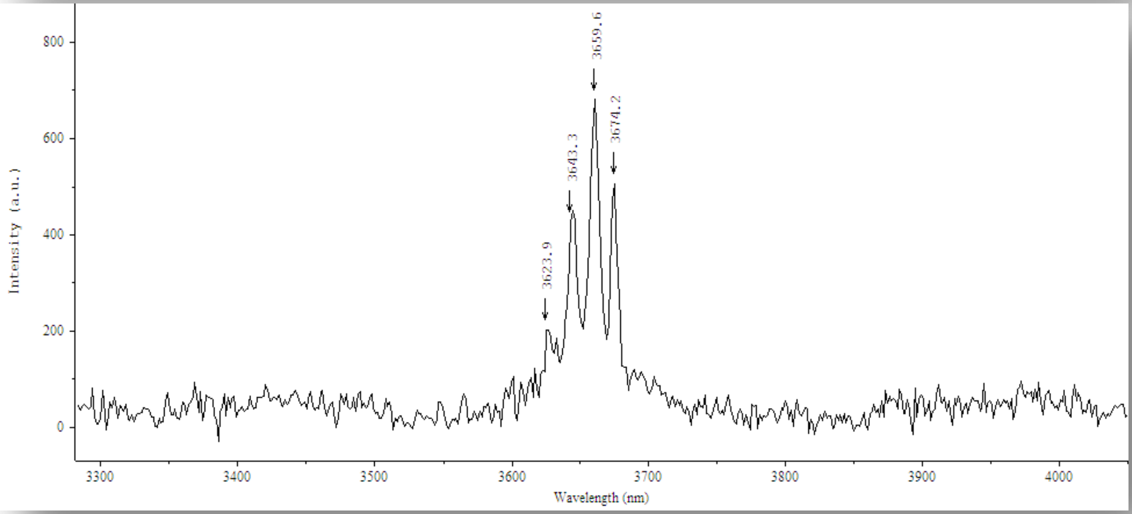
Bersani et al. 2009 calculate the composition of garnet that better reproduces the frequencies measured in the Raman spectrum of the sample with the use of **MIRAGEM** software.

Raman spectra of garnet minals. Three the most intense lines are marked L1, L2, L3. Serov et al.

Provenance and Genesis - COMPOSITIONAL ANALYSIS

Nephrite is a variety of **tremolite–actinolite of the amphibole group**, used in jewelry as a green semiprecious stone.





nephrite

$(Ca_2(Mg^{2+},Fe^{2+})_5Si_8O_{22}(OH)_2)$

Series *tremolite (Mg-rich term)*

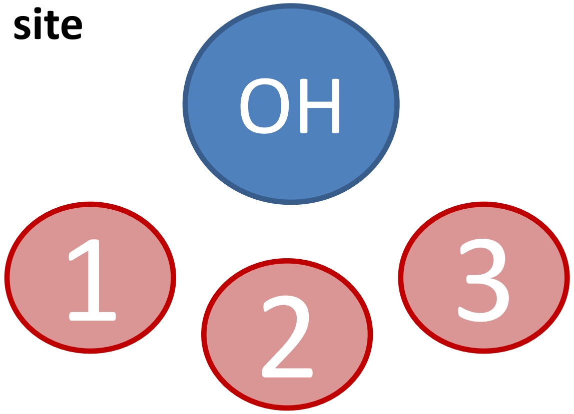
- ferroactinolite (Fe-rich term).

to the identification of materials, the variable iron and magnesium contents were investigated.

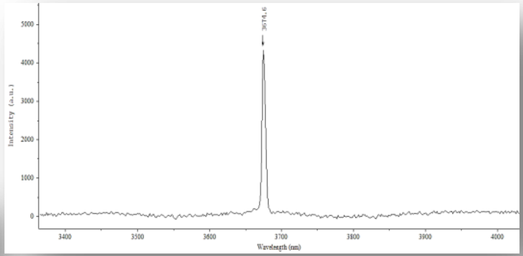
Provenance and Genesis - COMPOSITIONAL ANALYSIS

The fine structure of the **OH stretching vibration band of the Raman spectra of nephrite** depends on the electronegativity of the bonded cations. The study of this fine structure allows **estimation of the cation distribution in nephrite**, which is responsible for the **coloration**, and is associated with different **geological conditions** and so can help in provenance studies.

Different Mg, Fe occupancies around the OH site

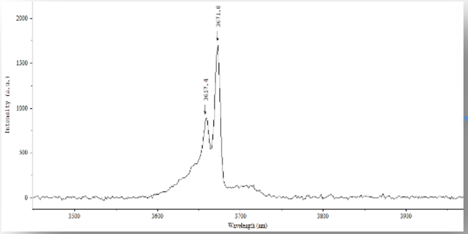


Campolongo



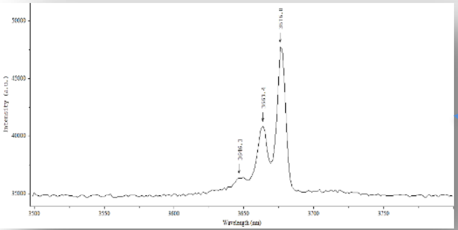
Tremolite: 1,2,3 = Mg (Mg, Mg, Mg)

Pizzo Bandiera



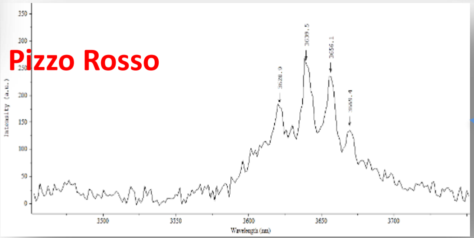
as Fe increases: Mg, Mg, Fe

Alpe Rosso



Mg, Fe, Fe

Pizzo Rosso



Fe, Fe, Fe

5 ORGANIC GEMS

ORGANIC GEMS: AMBER

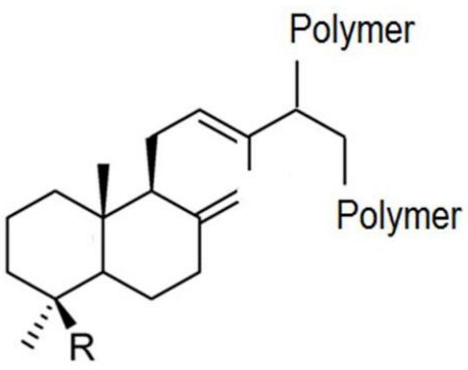
- Amber is fossil resins widely used since ancient times for manufacturing jewels. Its formation is due to polymerization of terpenoid compounds.

- The **physical properties and the aspect of amber** are strongly variable depending on both the **biological origin and the geological environment** in which the oxidative processes of maturation have took place.

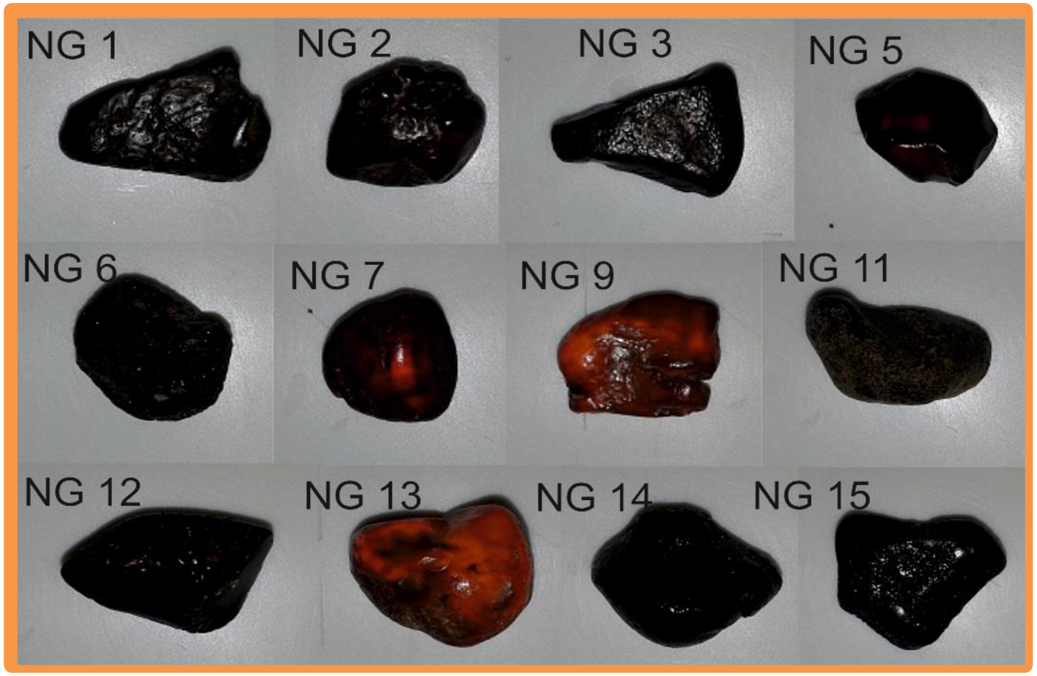
Barone, Mazzoleni, Raneri, Longobardo

Consiglio Nazionale delle Ricerche

Capitani, Proietti



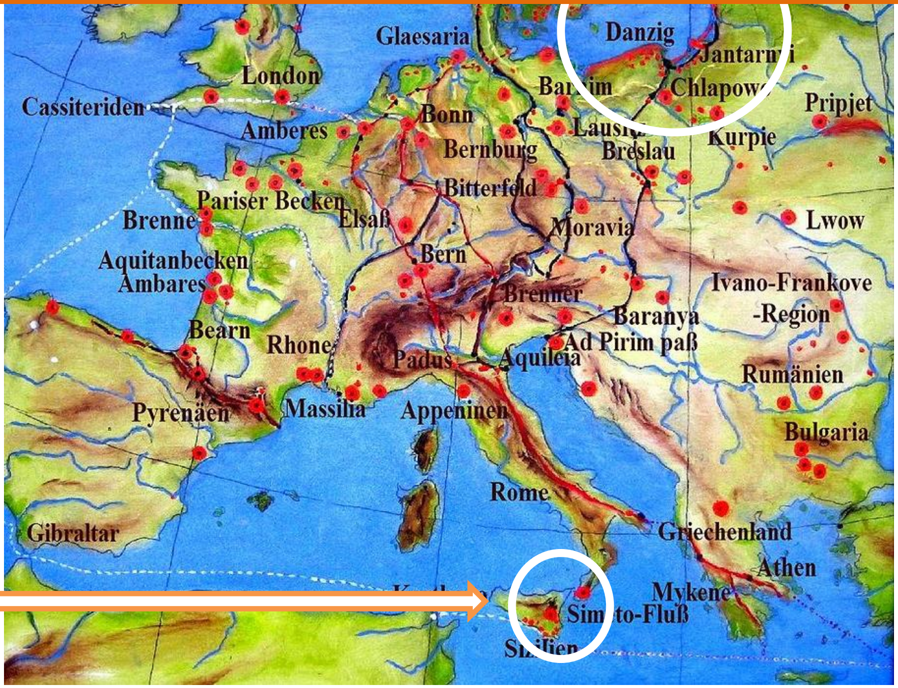
R: CH_3;
R: $COOCH_3$



Ambers are formed by complex macromolecular structure such as the polymer that characterised the more common amber class

ORGANIC GEMS: AMBER

diffused fossil resins come from the **Baltic region of Northern Europe** and **Dominican Republic**.



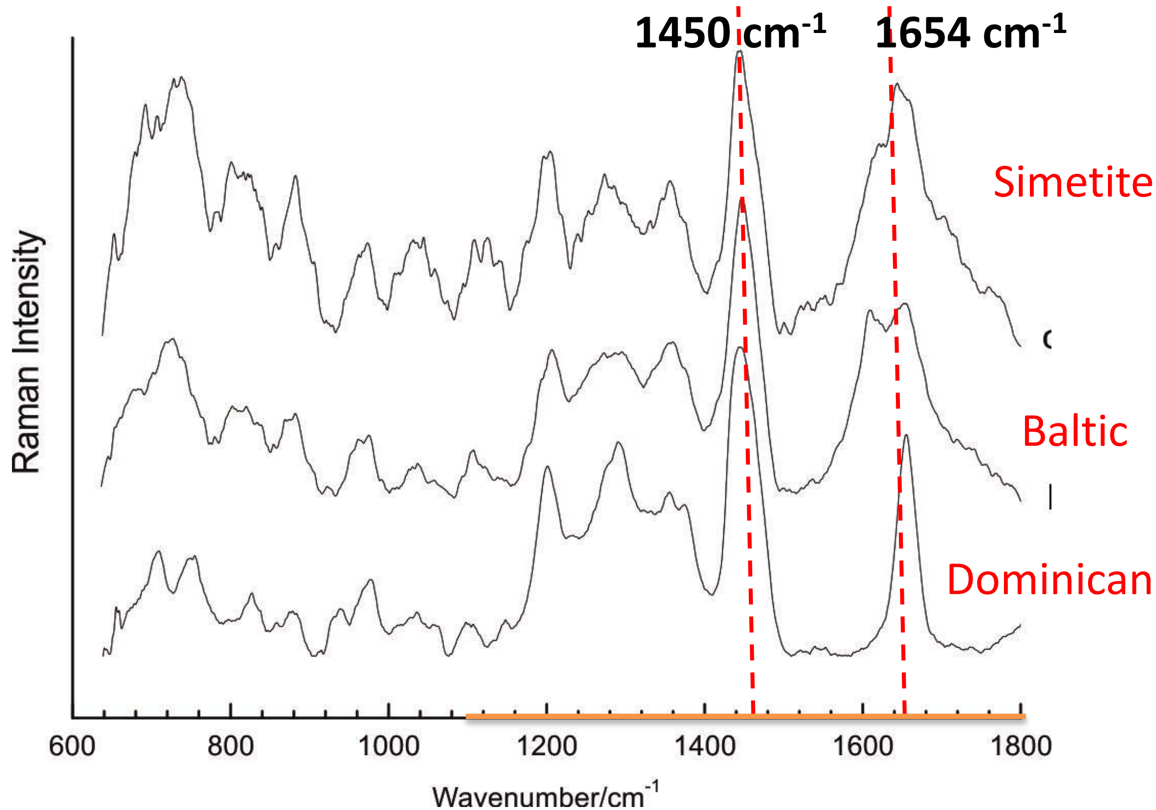
Sicily is a source of a rare and fashionable amber, named **Simetite, considered as one of the most valuable in the world for its physical-chemical properties and rarity.**

Historical sources testify that it has been used since ancient times for local jewelers but in the last two centuries the demand of Sicilian amber exceeded the supply.

ORGANIC GEMS: AMBER

The non-crystalline nature of amber prevent the use of many analytical techniques.

μ-Raman spectroscopy is really a useful tools in characterizing Amber, allowing to obtain the chemical fingerprint of different fossil resins and supplying useful information on maturation degree.



The most important spectroscopic region is that between 1800-1100 cm^{-1} range, where the C - C stretching modes due to CH_2 and CH_3 groups are observable.

the greater the band at 1450 cm^{-1} with respect to that at 1654 cm^{-1}, the more mature is the resin.

Barone, Capitani, Mazzoleni, Proietti, Raneri, Longobardo, Di Tullio. **13C Solid State NMR and μ-Raman Spectroscopic Characterization of Sicilian Amber. Accepted Appl. Spectroscopy 2016**

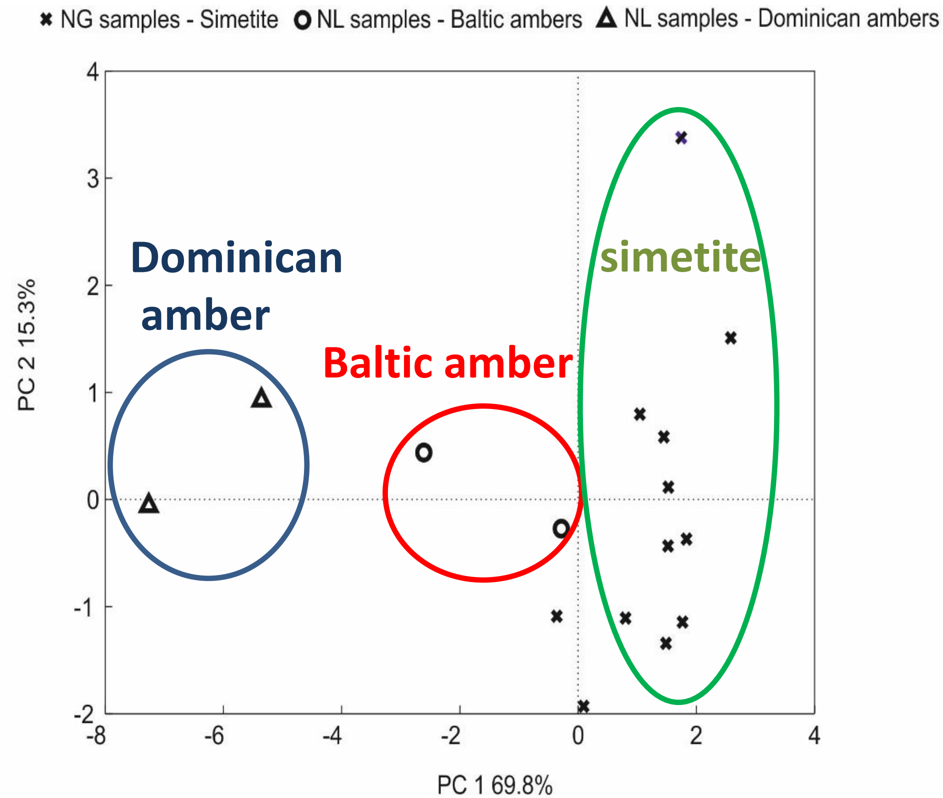
ORGANIC GEMS: AMBER

The complexity of Raman spectra make difficult to recognized the differences among ambra samples from the three studied sites.

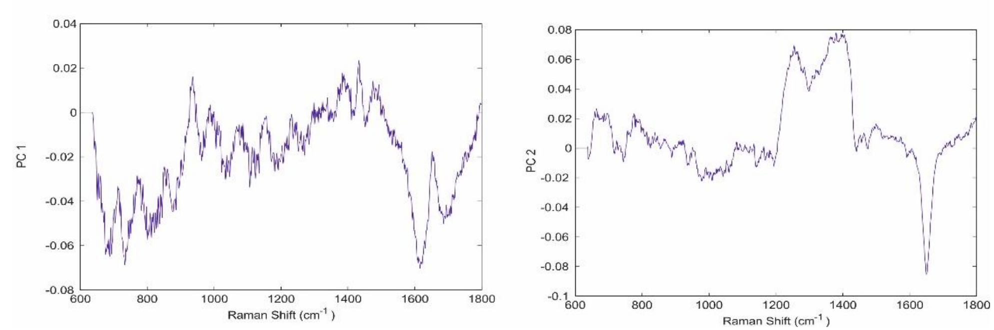
Principal Component Analysis (PCA) applied on spectral data allow us simplified the analysis enhancing the discriminant power of Raman.

Five principal components accounting for the 96% of the total variability were determined.

By considering the scores of the first two PCs, namely PC1 providing for 69.8% and PC2 for 15.3%, a good discrimination, mainly influenced by the PC1



Scores of the principal component variables



PC1 and PC2 plot of the loadings

Barone, Capitani, Mazzoleni, Proietti, Raneri, Longobardo, Di Tullio. **13C Solid State NMR and µ-Raman Spectroscopic Characterization of Sicilian Amber. Accepted Appl. Spectroscopy 2016**

6

HISTORICAL AND ARCHAEOGICAL JEWELS COLLECTIONS

Barone Mazzoleni Raneri

Vandenabeele

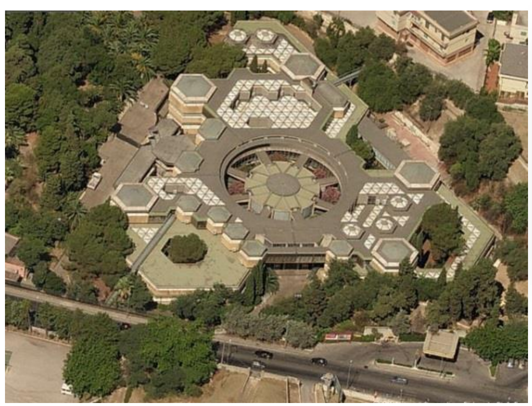
Jehlička

Bersani Lottici

Application of Portable Raman equipments

jewelry collections preserved in **Messina Museum** of the **17th/18th Century**

Barone G, Bersani D, Jehlička J, Lottici PP, Mazzoleni P, Raneri S, Vandenabeele P, Di Giacomo C, Larinà G (2014). Journal Raman Spectroscopy. DOI: 10.1002/jrs.4649.



jewelry collections preserved in **Paolo Orsi Regional Museum (Siracusa)** of **the Hellenistic-Roman period**

G. Barone, P. Mazzoleni, S. Raneri, D. Bersani, J. Jehlička, P. P. Lottici, P. Vandenabeele, G. Lamagna, A. M. Manenti. Raman investigation on precious jewelry collections preserved in **Paolo Orsi Regional Museum (Siracusa)** by using portable

Historical and archaeogical Jewels Collection. Museum of Messina and Siracuse: equipments

RockHound™ Handheld Spectrometer for the Geologist — DeltaNu

Handheld instrument (1.9 kg)
785 nm diode laser for excitation,
Max power 120 mW
Spectral range of 200–2000 cm1.

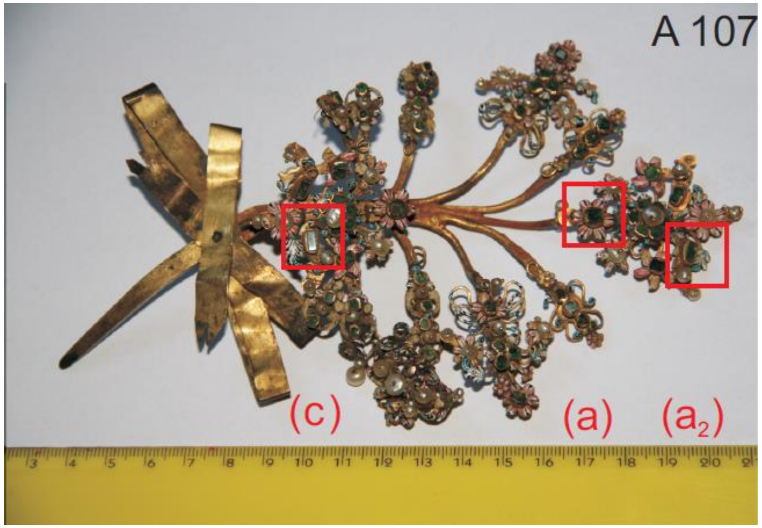
EZRAMAN-I-DUAL-G HIGH SENSITIVITY DUAL-WAVELENGTH RAMAN ANALYZER

785nm Diode Laser. Laser Output Power: ~400 mW. Spectral Coverage: ~250 to 2,350 cm-1
Average Optical Resolution: 6 cm-1

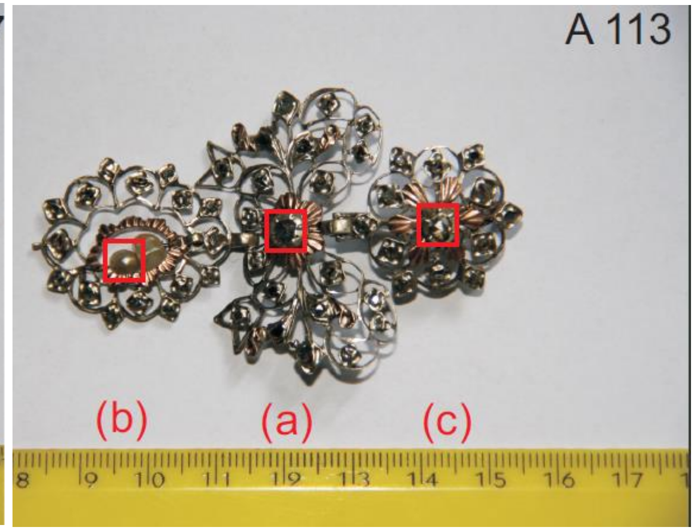
532nm Laser. Laser Output Power: ~100 mW. Spectral Coverage: ~250 to 3,200 cm-1. Average Optical. Resolution: 7 cm-1

- ❑ Identify natural and simulant gems. Verify the correct autoptic classification.
- ❑ Clarify some problems linked to nomenclature of the minerals such as for varieties of quartz
- ❑ Highlight treatments

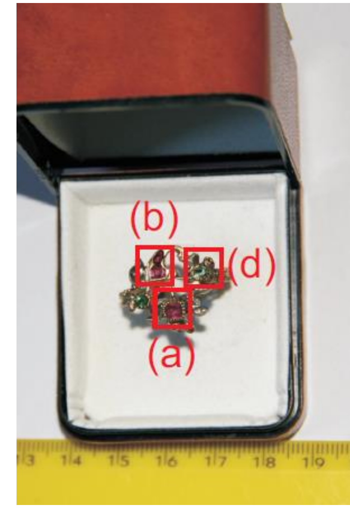
Messina Regional Museum



Autopitic classification emerald

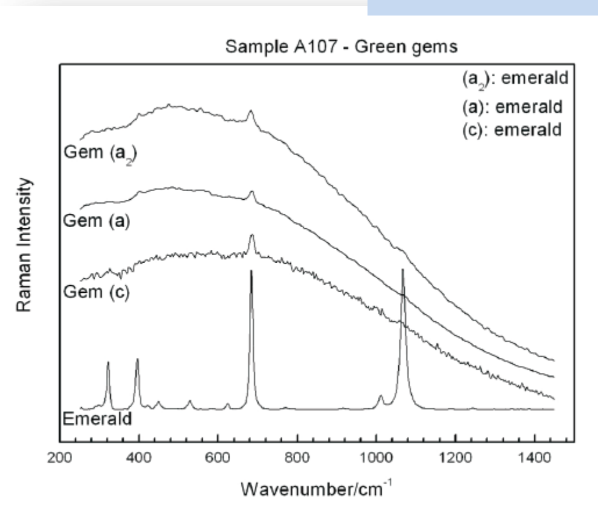


Autopitic classification diamond and pearls

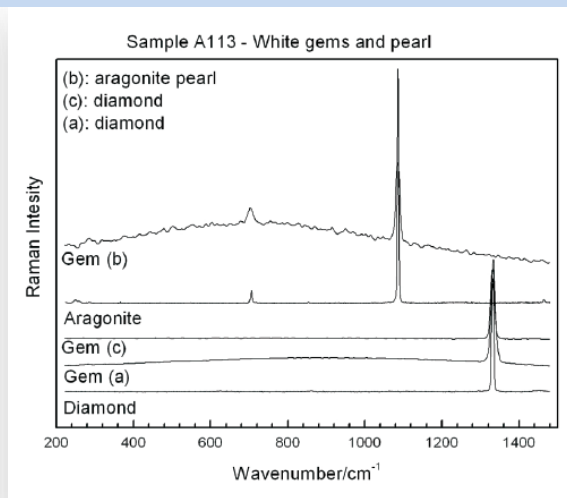


Autopitic classification emerald and rubies

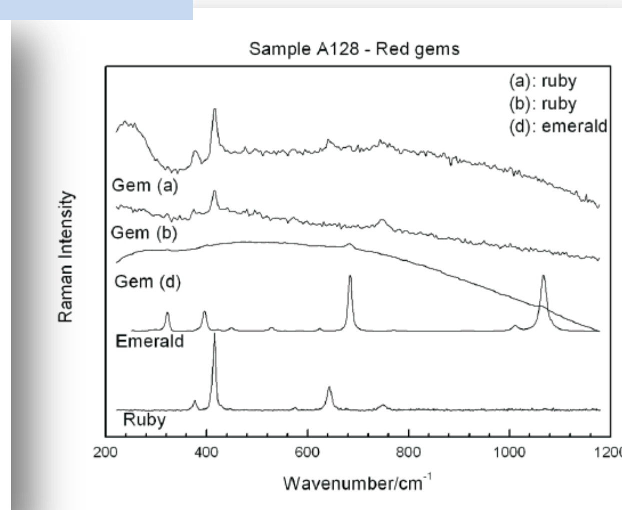
confirmed the autoptic classification



EMERALDS A 107



DIAMOND and ARAGONITE PEARL A 113

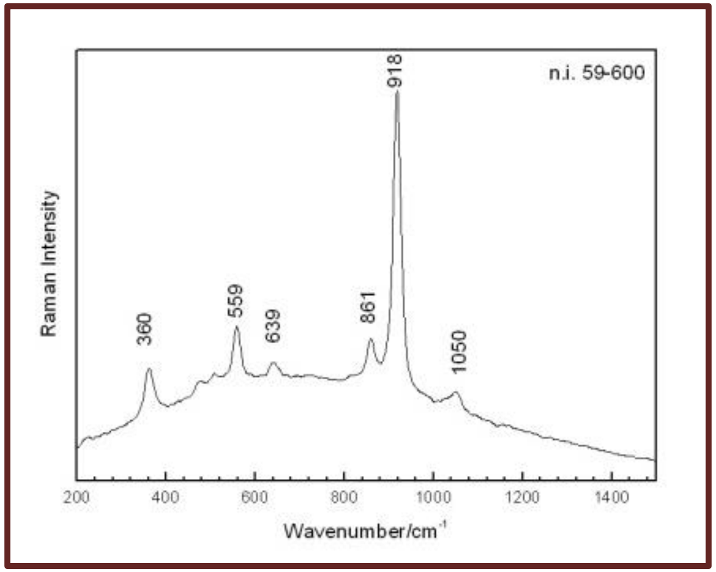


RUBIES and EMERALD A 128

Part 6A: NATURAL VALUABLE GEMS

Siracusa Regional Museum

59-600: gold ring with garnet



1577 Naxos: gold necklace with 3 stones

55079: gold ring with 2 fishes engraved in a garnet

All analyzed garnets have very similar bands position: similar composition.

Miragem software: all garnets consist of prevalent **pyrope** (70% - 80%) ±10%.

Possible common provenance.

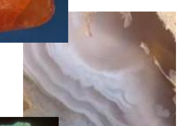
G. Barone, P. Mazzoleni, S. Raneri, D. Bersani, J. Jehlička, P. P. Lottici, P. Vandenabeele, G. Lamagna, A. M. Manenti Raman investigation on precious jewelry collections preserved in Paolo Orsi Regional Museum (Siracusa, Sicily) by using portable equipment Applied Spectroscopy, special issue on cultural heritage 2016

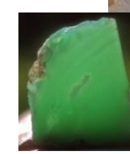
Part 6B: QUARTZ VARIETIES

Quartz varieties

SiO_2

- **Macrocrystalline* Quartz** or simply "Quartz"
  - **Rock Crystal**, **Amethyst**, Ametrine, Aventurine, Blue Quartz, Citrine, Eisenkiesel, Milky Quartz, Pink Quartz, **Prase**, Prasiolite, Rose Quartz, Smoky Quartz, Tiger's, Hawk's, Cat's Eye
- **Microcrystalline** or Cryptocrystaline*** Quartz** or simply **Chalcedony**
  - "Fibrous" Varieties: Agate, **Carnelian**, **Chalcedony**, **Chrysoprase**, **Onyx**, Plasma, Sard
  - "Grainy" Varieties: **Chert**, Flint, Jasper, Heliotrope, Plasma





chalcedony has been divided into several optically distinct types characterized by different impurities and colors

**Varieties that develop visible crystals or are made of large intergrown crystals*
***Compact varieties made of tiny crystal grains that are visible in an optical microscope*
(quartz is in the form of crystals that are smaller than 30 microns in size)
****Dense varieties whose structure cannot be resolved in an optical microscope*

opaque Microcrystalline: diasper

Siracusa Regional Museum

Eros engraved on amethyst 15226. Syracuse Museum

Eros holding a horn of plenty engraved on amethyst 21118. Syracuse Museum

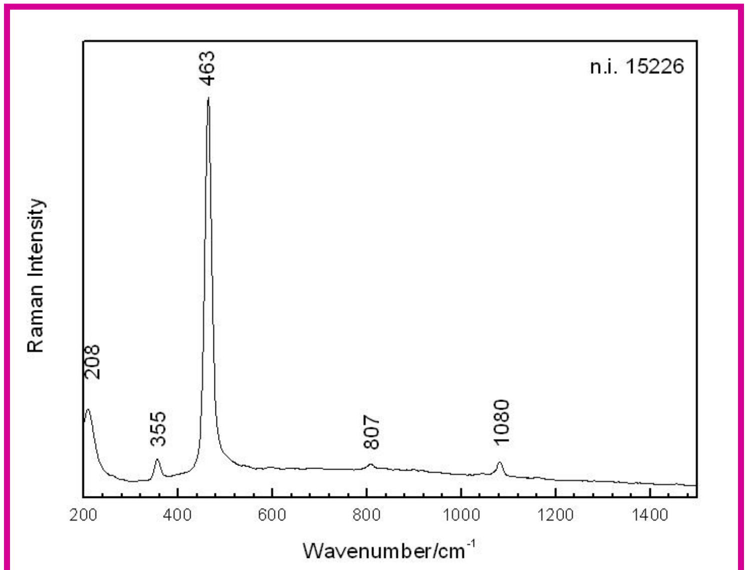
Quartz varieties

SiO_2

Macrocrystalline* Quartz

or simply "Quartz"

Rock Crystal, **Amethyst**, Ametrine, Aventurine, Blue Quartz, Citrine, Eisenkiesel, Milky Quartz, Pink Quartz, Prase, Prasiolite, Rose Quartz, Smoky Quartz, Tiger's, Hawk's, Cat's Eye



monocrystalline variety of **quartz** has been recognized.

Part B: QUARTZ VARIETIES

Siracusa Regional Museum

17269

two butterfly and inscription engraved on **carnelian**

23390

Autoptic classification
Soldier engraved on **carnelian**

15062

Eros engraved on **carnelian**

38868

Hermes and a child Dionysus engraved on **carnelian**

36267

soldiers engraved on **carnelian**

Quartz varieties

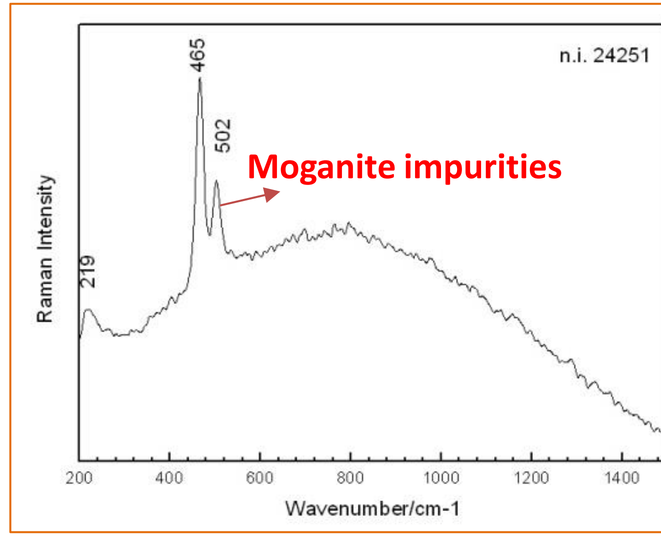
SiO_2

Microcrystalline** or Cryptocrystaline*** Quartz

or simply **Chalcedony**

"Fibrous" Varieties:

Agate, **Carnelian, Chalcedony,** Chrysoprase, Onyx, Plasma, Sard

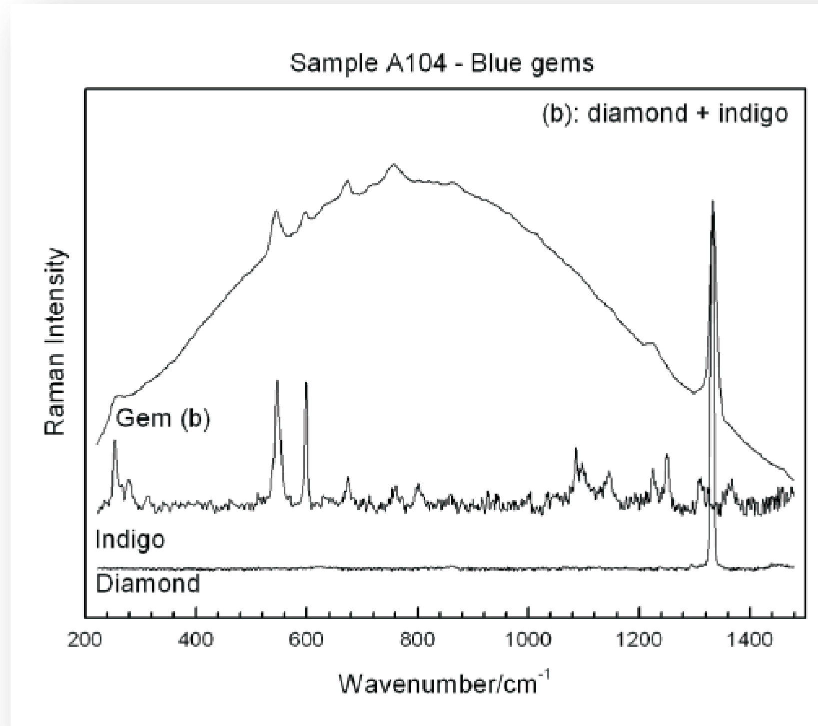


Chalcedony (carnelian agate)=
Quartz + Moganite + fluorescence

G. Barone, P. Mazzoleni, S. Raneri, D. Bersani, J. Jehlička, P. P. Lottici, P. Vandenabeele, G. Lamagna, A. M. Manenti Applied Spectroscopy, special issue on cultural heritage 2016

Messina Regional Museum

Autopitic classification diamond

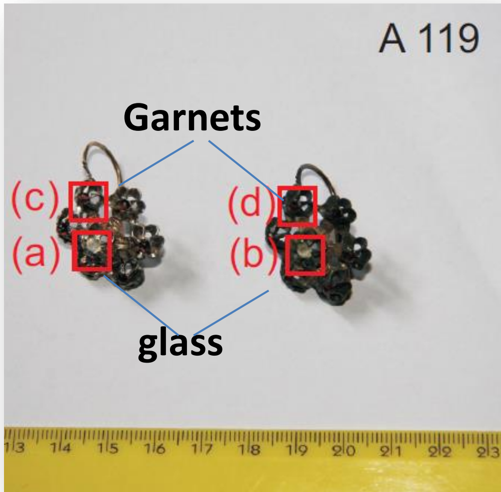


A 104 DIAMOND and INDIGO – Messina Regional Museum

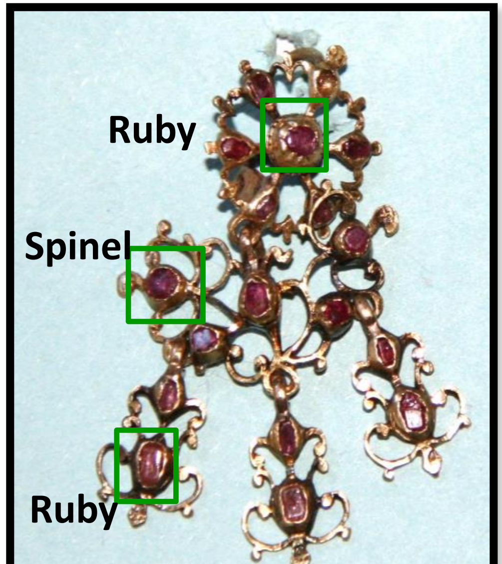
Barone, G., Bersani, D., Jehlička, J., Lottici, P.P., Mazzoleni, P., Raneri, S., Vandenabeele, P., Di Giacomo, C., Larinà, G. (2015) Journal of Raman Spectroscopy, 46 (10), pp. 989-995.

Part 6D: NATURAL vs. SIMULANT - NATURAL vs. ARTIFICIAL

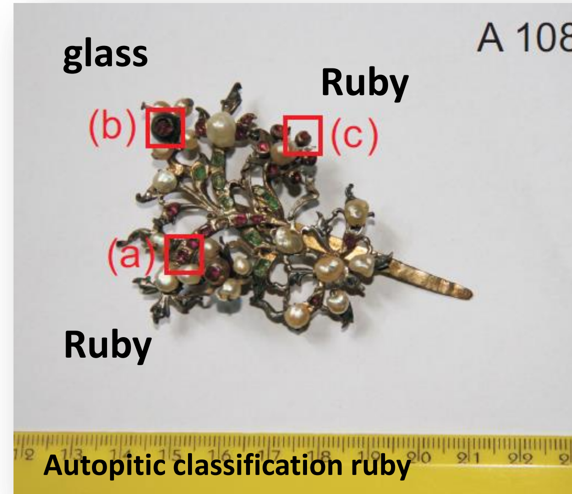
Messina Regional Museum



Autopitic classification diamond and ruby

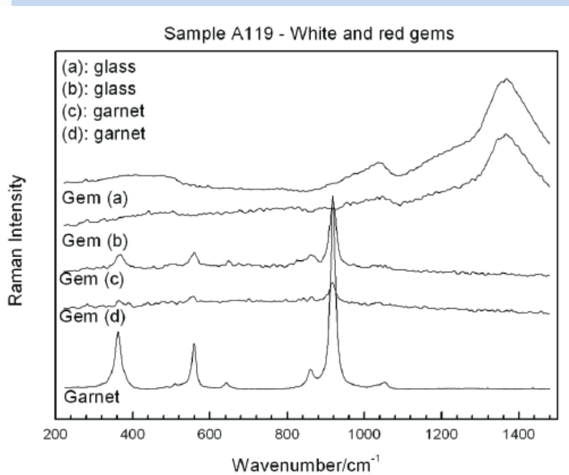


Autopitic classification ruby

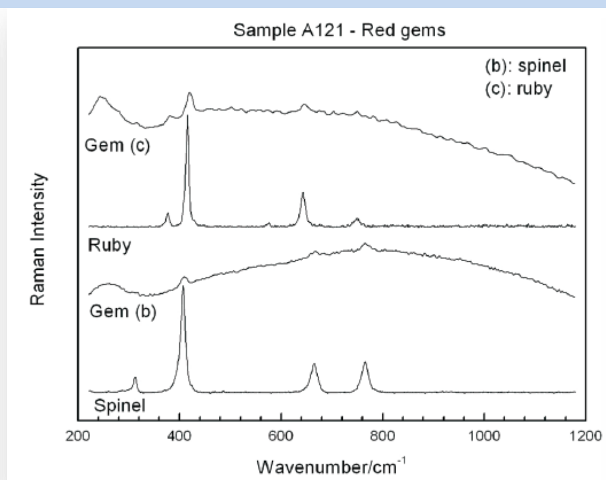


Autopitic classification ruby

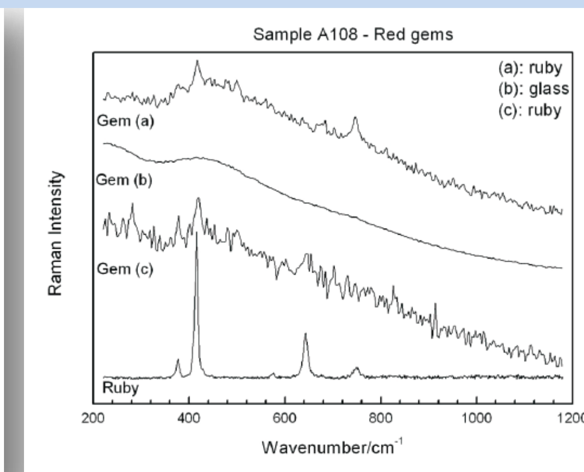
Misclassification: no diamond and ruby … glass and garnet… .



GLASS and GARNETS – A119



RUBY and SPINEL – A121

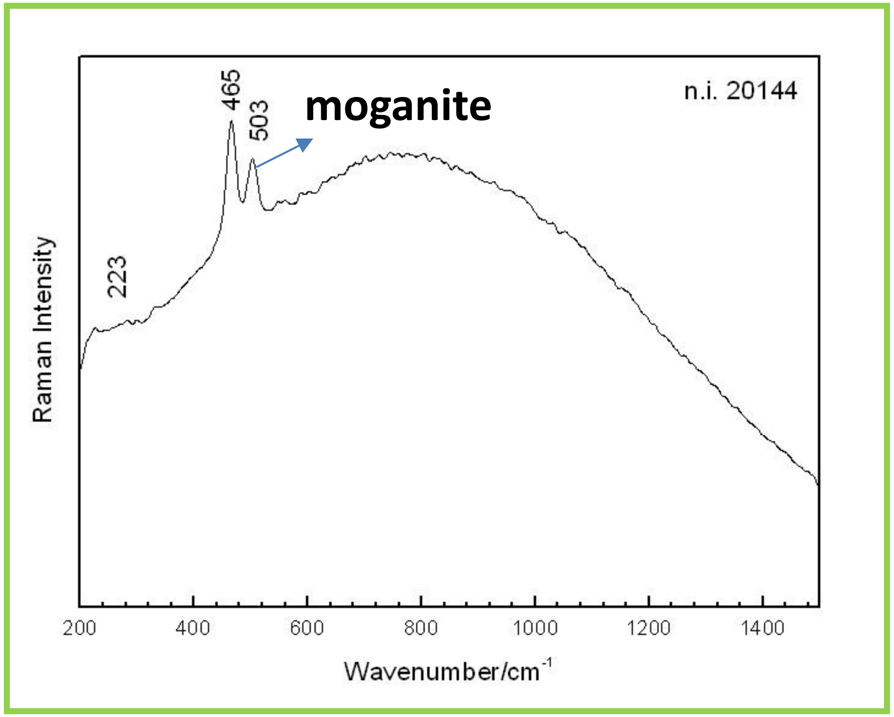


RUBY and GLASS – A108

Part 6D: NATURAL vs. SIMULANT - NATURAL vs. ARTIFICIAL

Siracusa Regional Museum

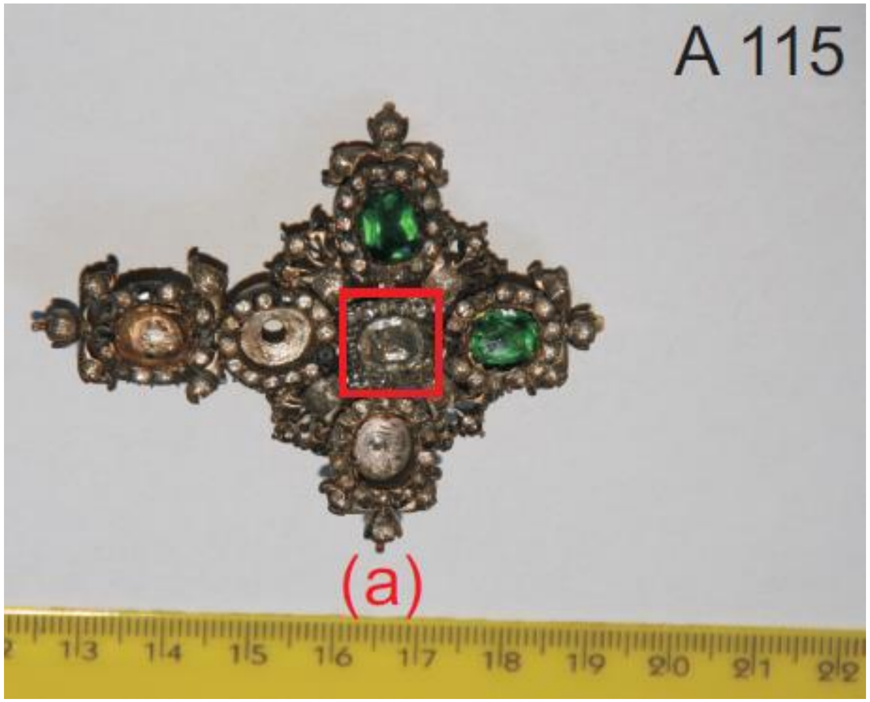
Autopitic classification ring with emerald 20144



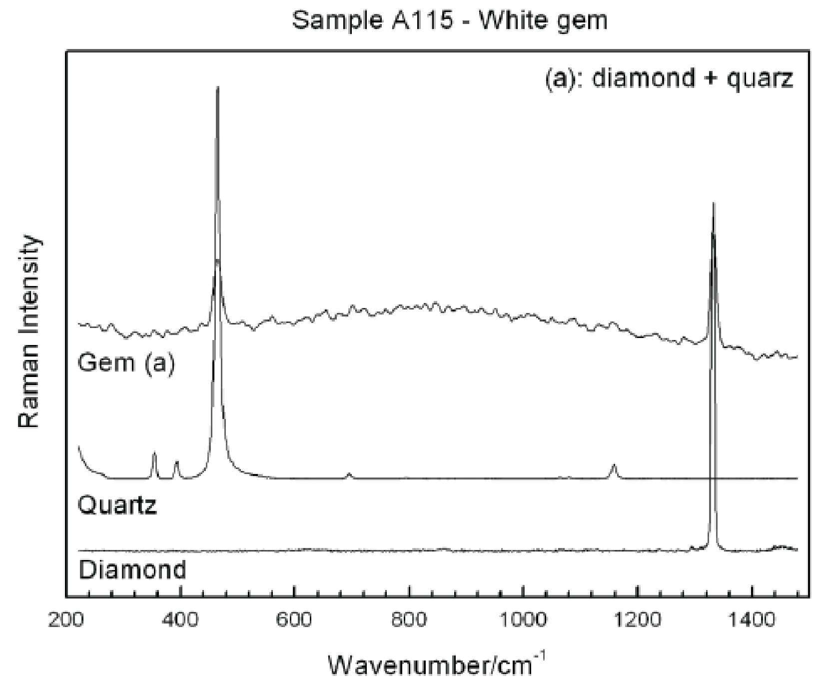
20144 green Chalcedony: quartz+ moganite + fluorescence

Misclassification: no emerald … green chalcedony

Messina Regional Museum



Autopitic classification diamond

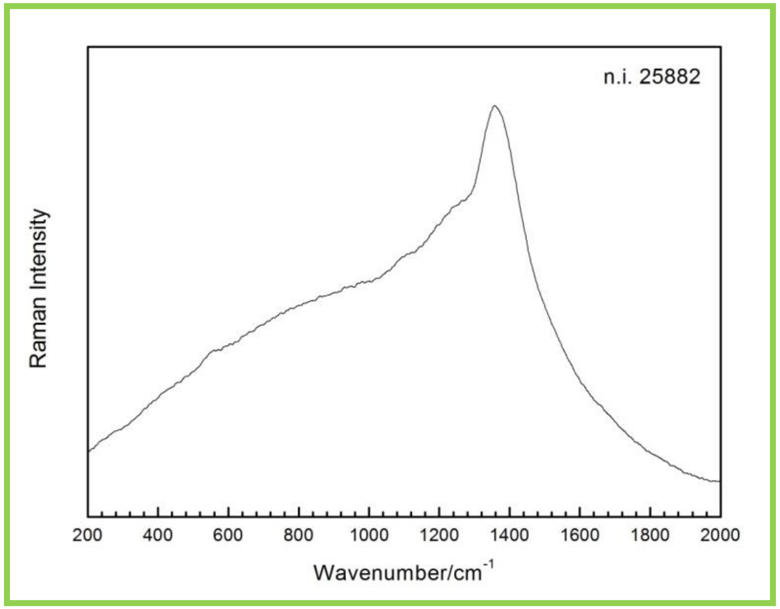


A115 Diamond and quartz: DOUBLET

Misclassification: no diamond … doublet

Siracusa Regional Museum

Autopitic classification gold ring with Caesar's head in amethyst 25882



Broad bands + fluorescence: **glass**

Misclassification: no ametyst… glass

Obsidian (volcanic glass) is sometimes cut as gem. During the **Roman Empire obsidian** was largely used to create exclusive **jewels**, vessels, mirrors and sculpture.

This gem was imitated by a cheap and easier workable **black man-made glass**.

It is extremely difficult to visually distinguish natural obsidian from man-made glass imitations.

Recently, **Raman spectroscopy was used with this aim**.

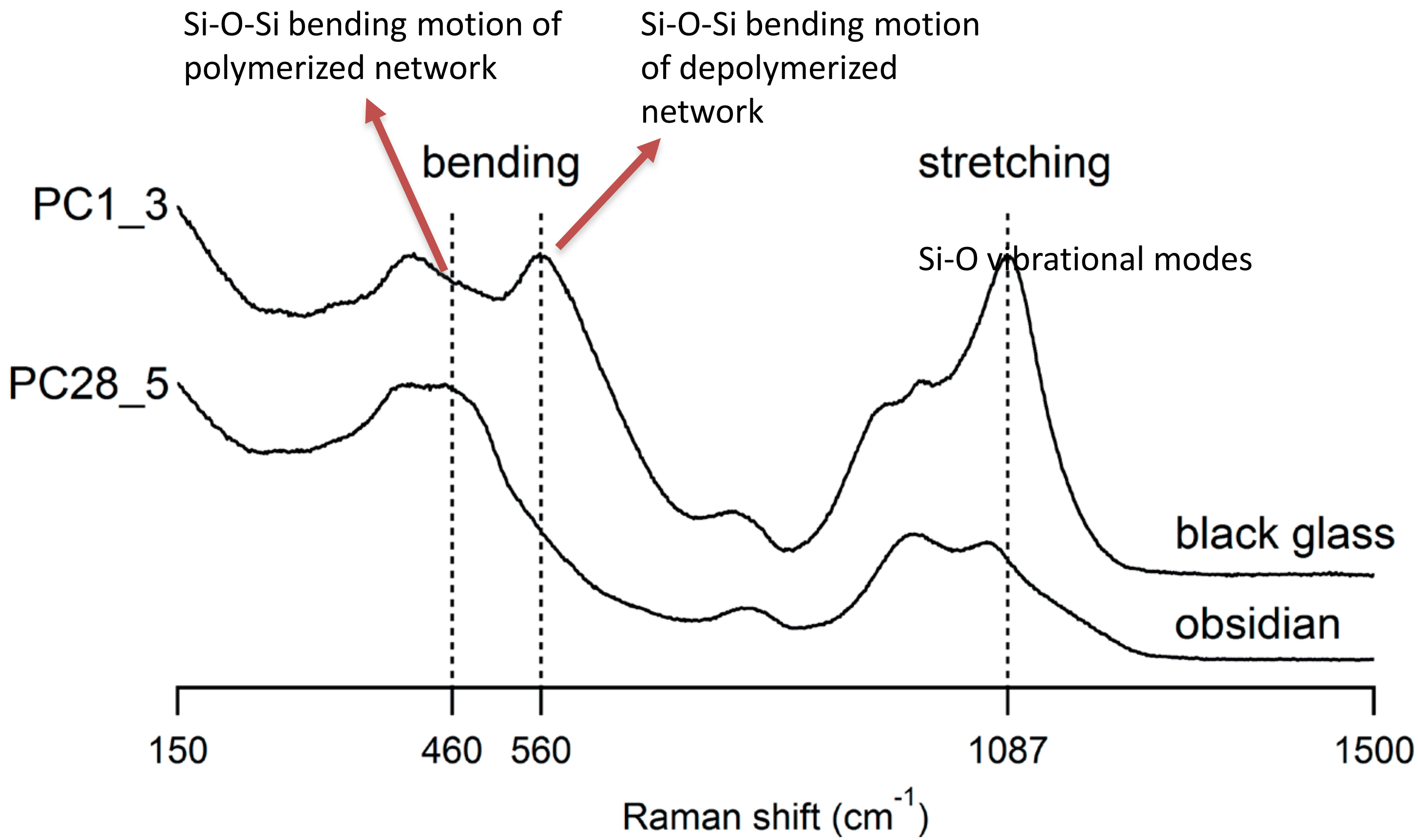
Gem with an Athlete about 500 B.C.
The J. **Paul Getty Museum**

A ROMAN OBSIDIAN MAGIC GEM CIRCA 2ND CENTURY A.D. **Paul Getty Museum**

Obsidian (volcanic glass) of Lipari (Sicily)

Part 6F: OBSIDIAN vs. ARTIFICIAL GLASS

Lipari Eolian Museum



The polymerization degree, due to the constructive and destructive elements abundances, permit to distinguish natural and man-made glasses by mean of Raman Spectra:

Obsidians are highly polymerised with strong 460 cm-1 band and weak stretching band

Man-made glass with strong 560 and 1000 cm-1 bands

Natural obsidians are characterised by higher SiO_2 and Al_2O_3 (constructive elements of network) and low Na_2O (destructive elements of network) than man-made glass. Cagno et al. Per Min.

Thanks for the attention!!!