JOINT RESEARCHER MEETING
Pushing the boundaries of advanced materials characterization
Heverlee – June 3, 2022

Shine on you crazy materials: Raman microscopy for advanced material characterization

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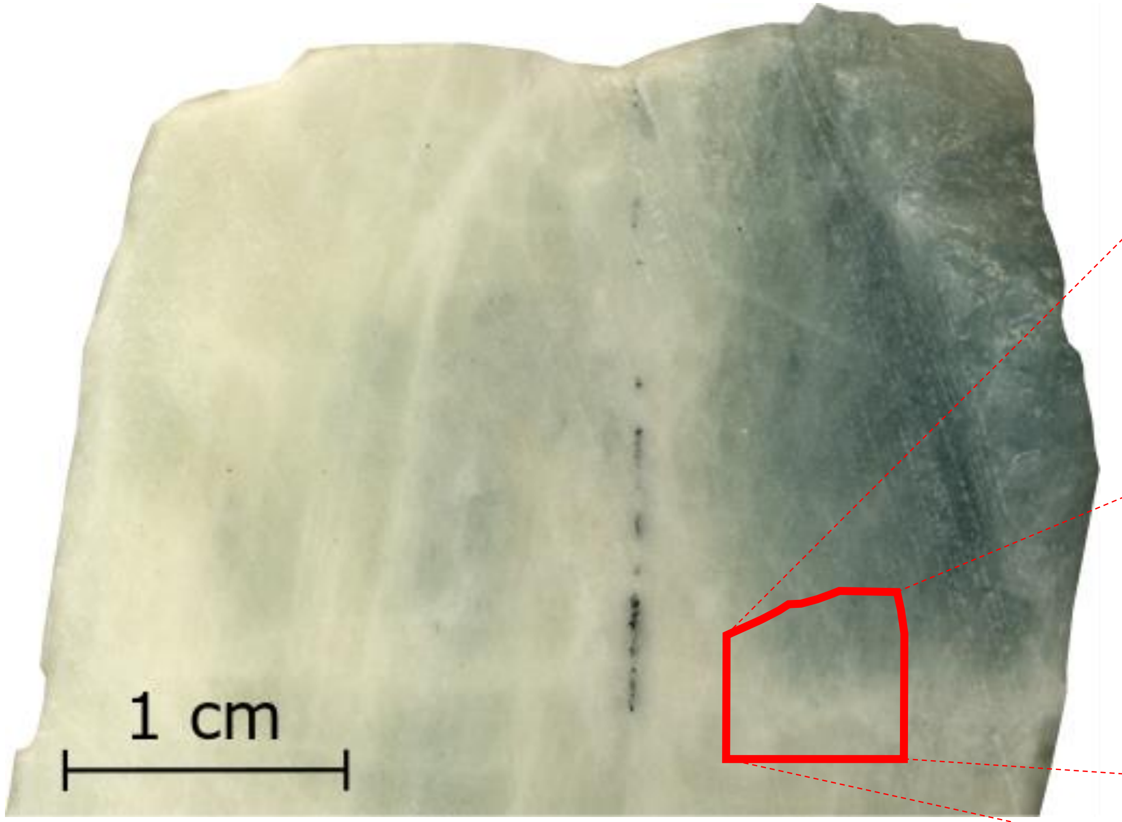
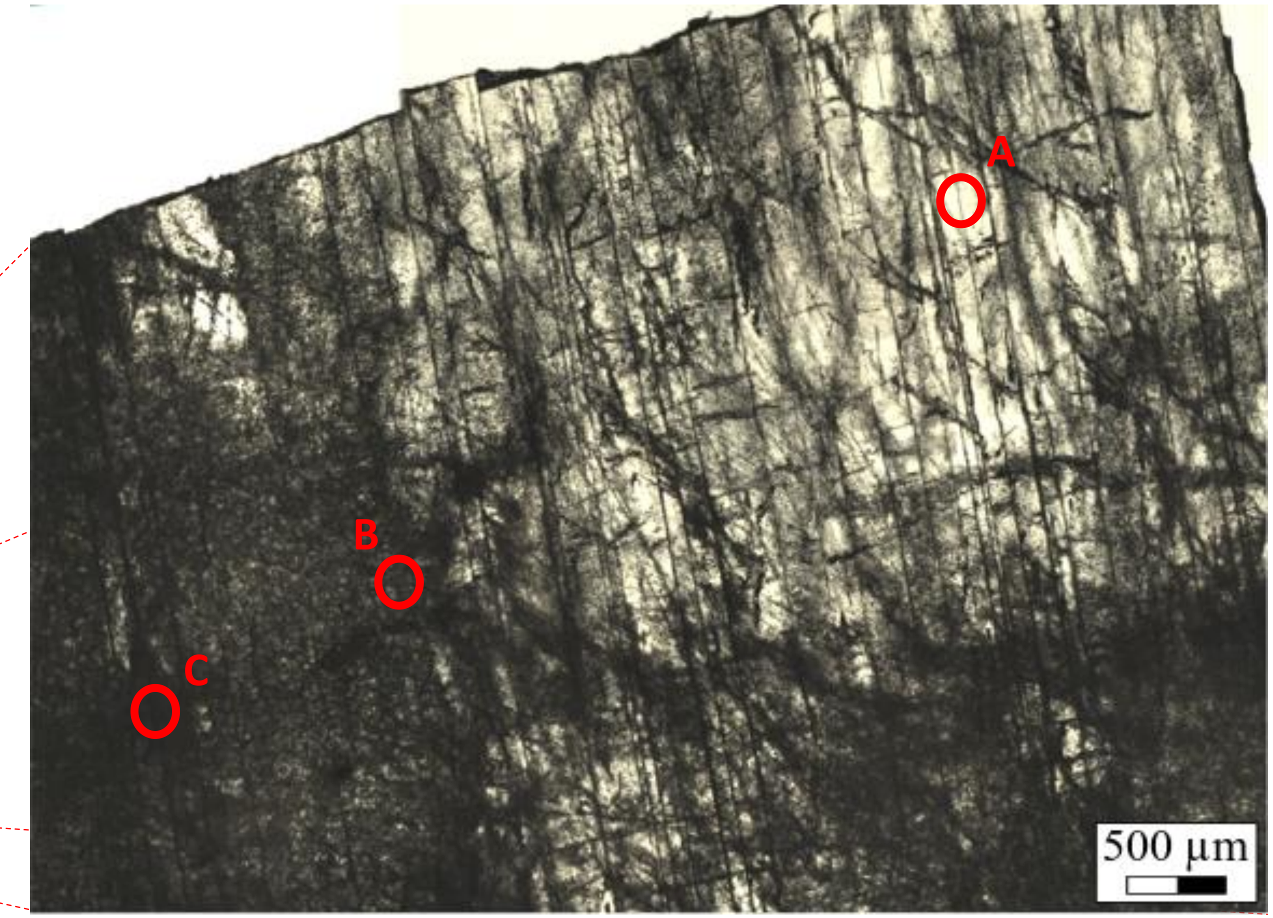
How can we investigate complex materials?



Hard rock lithium ore



C: P_2O_5 = 56.9 wt%
Al_2O_3 = 43.1 wt%

B: P_2O_5 = 57.4 wt%
Al_2O_3 = 41.0 wt%
F = 1.6 wt%

A: P_2O_5 = 53.8 wt%
Al_2O_3 = 40.8 wt%
F = 5.41 wt%

How can we investigate complex materials?

- **Afmite**, $Al_3(OH)_4(H_2O)_3(PO_4)(PO_3OH)\cdot H_2O$
- **Amblygonite**, $LiAl(PO_4)F$
- **Augelite**, $Al_2(PO_4)(OH)_3$
- **Berlinite**, $Al(PO_4)$
- **Bolivarite**, $Al_2(PO_4)(OH)_3\cdot 4H_2O$
- **Evansite**, $Al_3(PO_4)(OH)_6\cdot 8H_2O$
- **Fluellite**, $Al_2(PO_4)F_2(OH)\cdot 7H_2O$
- **Fluorwavellite**, $Al_3(PO_4)_2(OH)_2F\cdot 5H_2O$
- **Kingite**, $Al_3(PO_4)_2F_2(OH)\cdot 7H_2O$
- **Kobokoboite**, $Al_6(PO_4)_4(OH)_6\cdot 11H_2O$
- **Metaschoderite**, $Al(PO_4)\cdot 3H_2O$
- **Metavariscite**, $Al(PO_4)\cdot 2H_2O$
- **Mitryaevaite**, $Al_5(PO_4)_2[(P,S)O_3(OH,O)]_2F_2(OH)_2\cdot 14.5H_2O$
- **Montebrasite**, $LiAl(PO_4)(OH)$
- **Planerite**, $Al_6(PO_4)_2(PO_3OH)_2(OH)_8\cdot 4H_2O$
- **Redondite**, $Al(PO_4)\cdot 2H_2O$
- **Sasaite**, $Al_6(PO_4)_5(OH)_3\cdot 36H_2O$
- **Senegalite**, $Al_2(PO_4)(OH)_3\cdot H_2O$
- **Trolleite**, $Al_4(PO_4)_3(OH)_3$
- **Vantasselite**, $Al_4(PO_4)_3(OH)_3\cdot 9H_2O$
- **Variscite**, $Al(PO_4)\cdot 2H_2O$
- **Vashegyite**, $Al_{11}(PO_4)_9(OH)_6\cdot 38H_2O$
- **Wavellite**, $Al_3(PO_4)_2(OH)_3\cdot 5H_2O$

23 possible minerals!!

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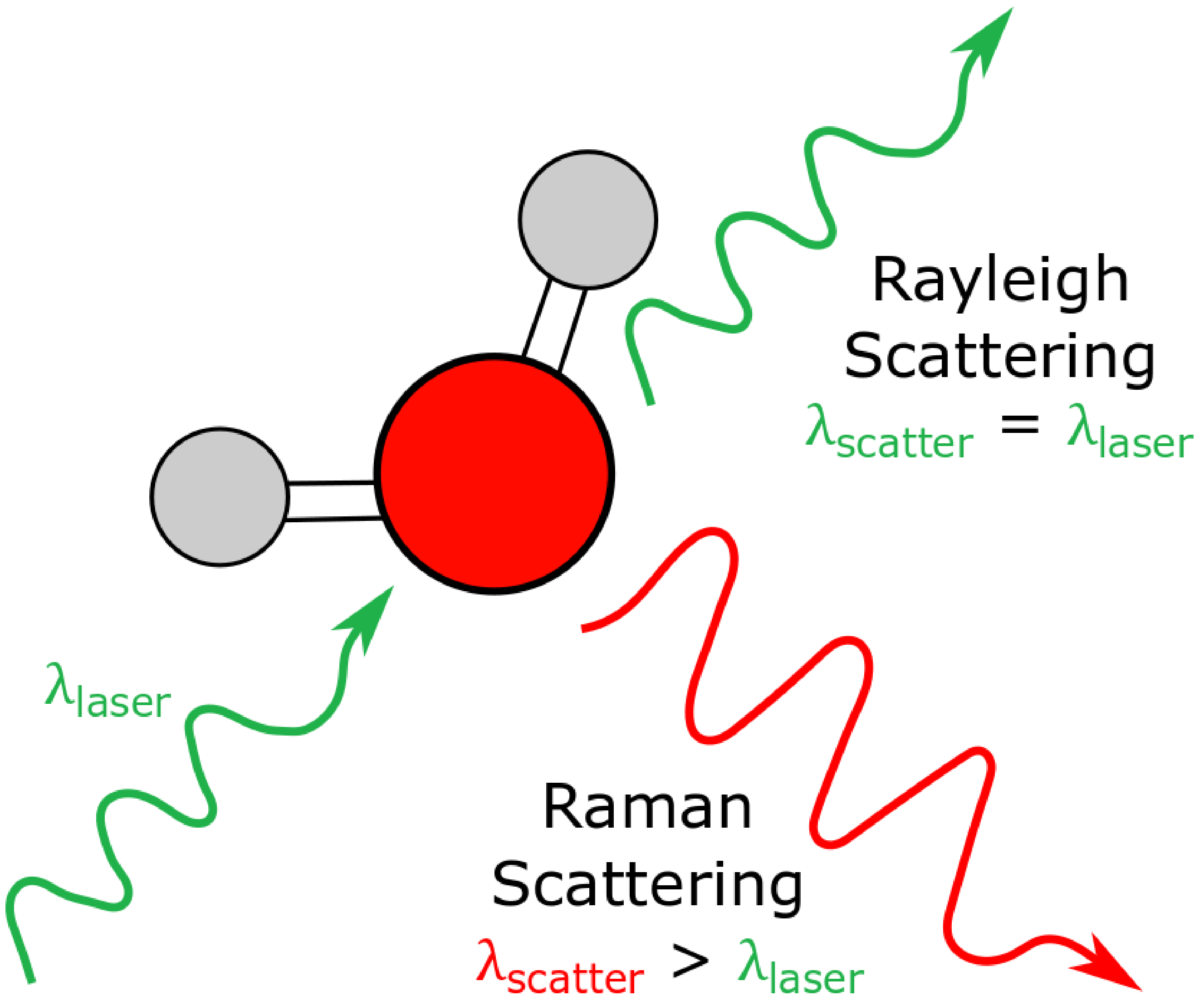
Raman spectroscopy!

Non-destructive *in situ* analysis

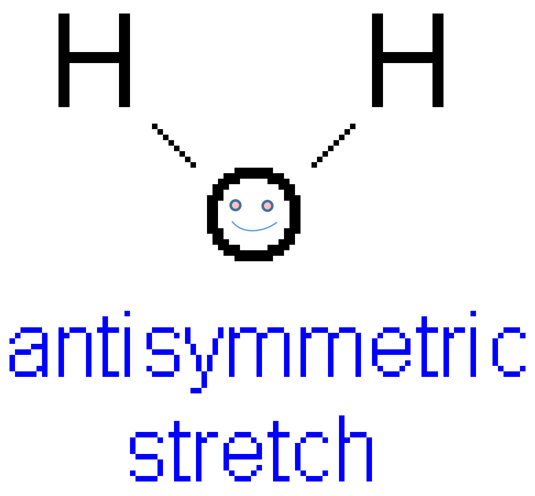
Multipurpose use:
- → solid / liquid / gas
- → inorganic / organic
- → crystalline / amorphous

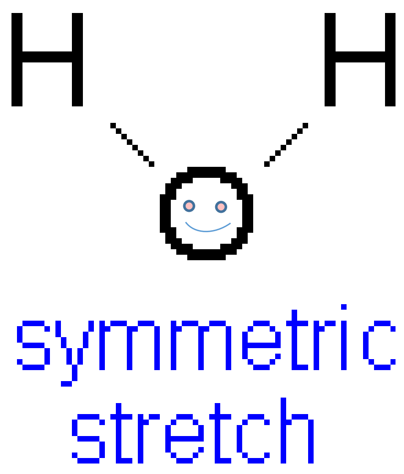
No sample preparation required

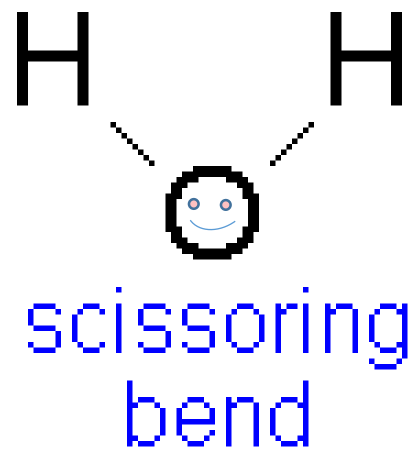


Raman spectroscopy

Vibrational spectroscopy (bond vibration energies)





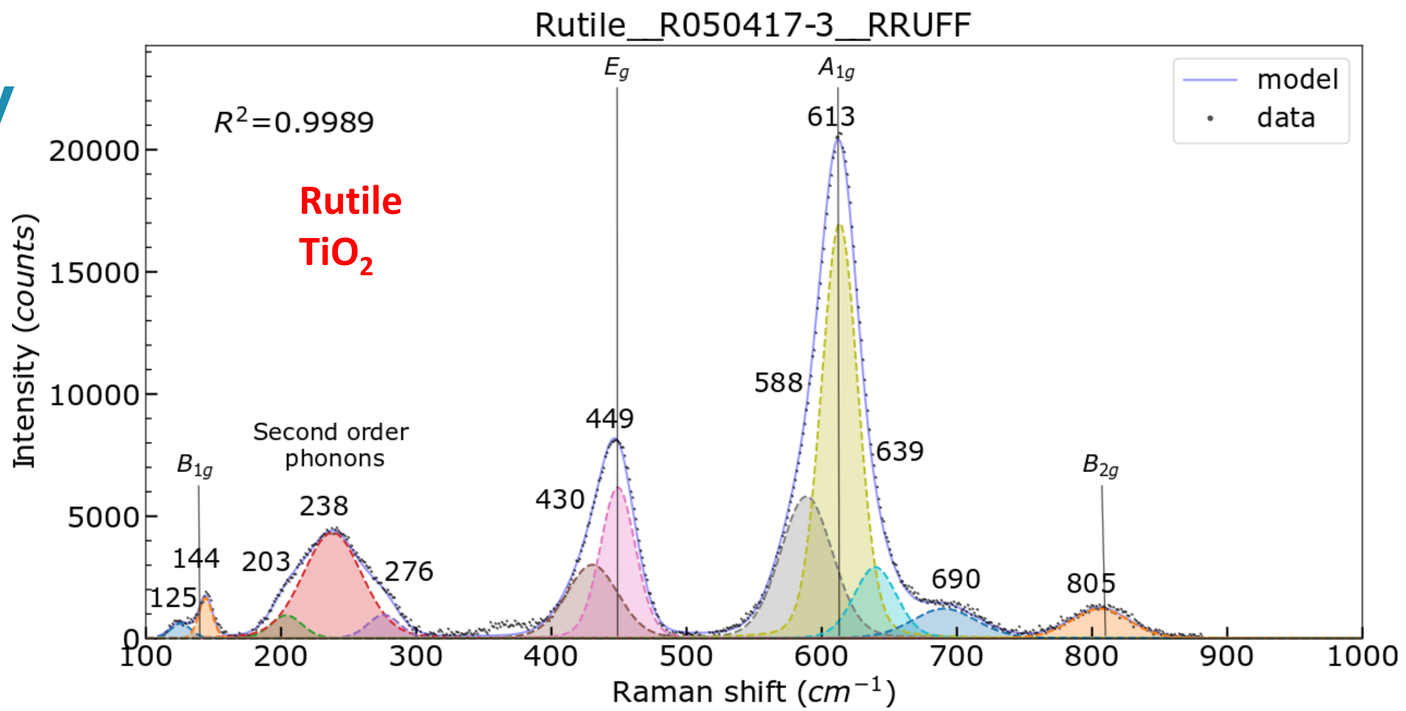


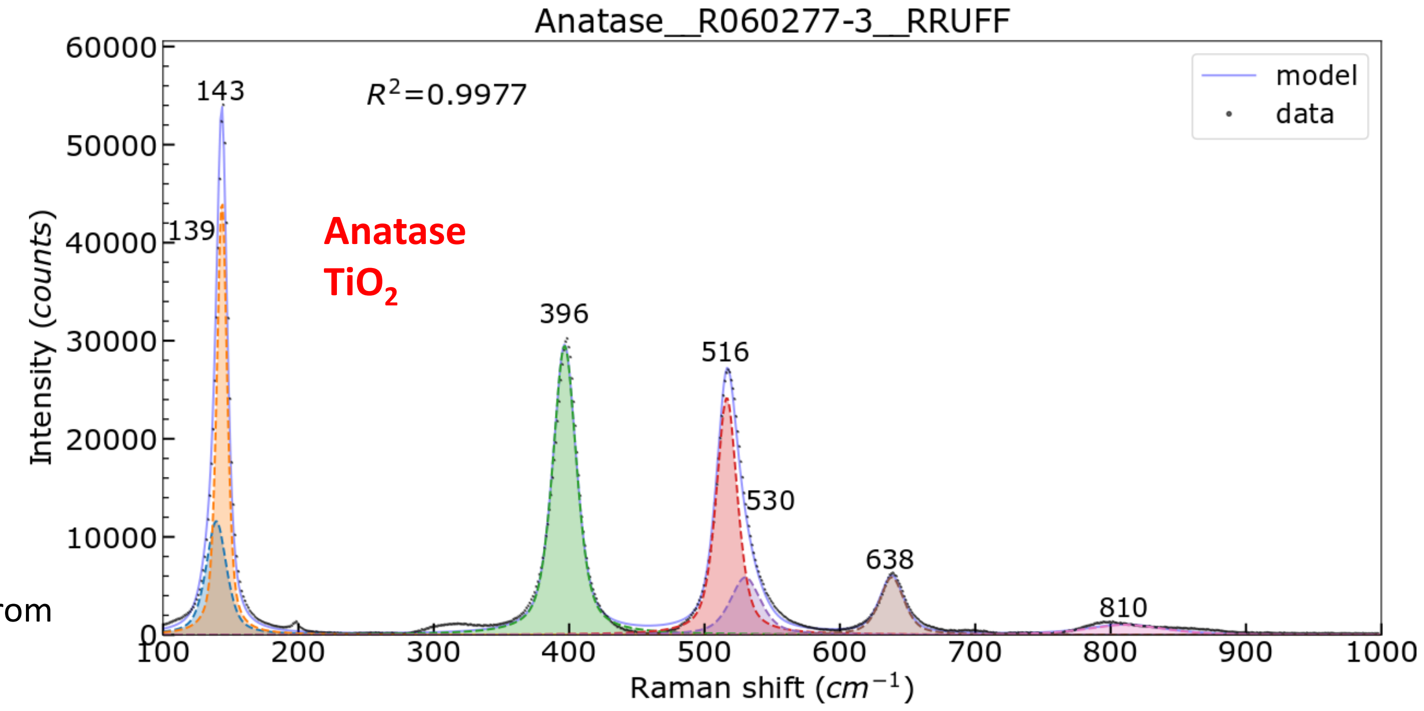
Source:
https://chem.libretexts.org/Bookshelves/Physical_and_Theoretical_Chemistry_Textbook_Maps/Supplemental_Modules_(Physical_and_Theoretical_Chemistry)/Spectroscopy/Vibrational_Spectroscopy/Vibrational_Modes/Introduction_to_Vibrations

Raman spectroscopy

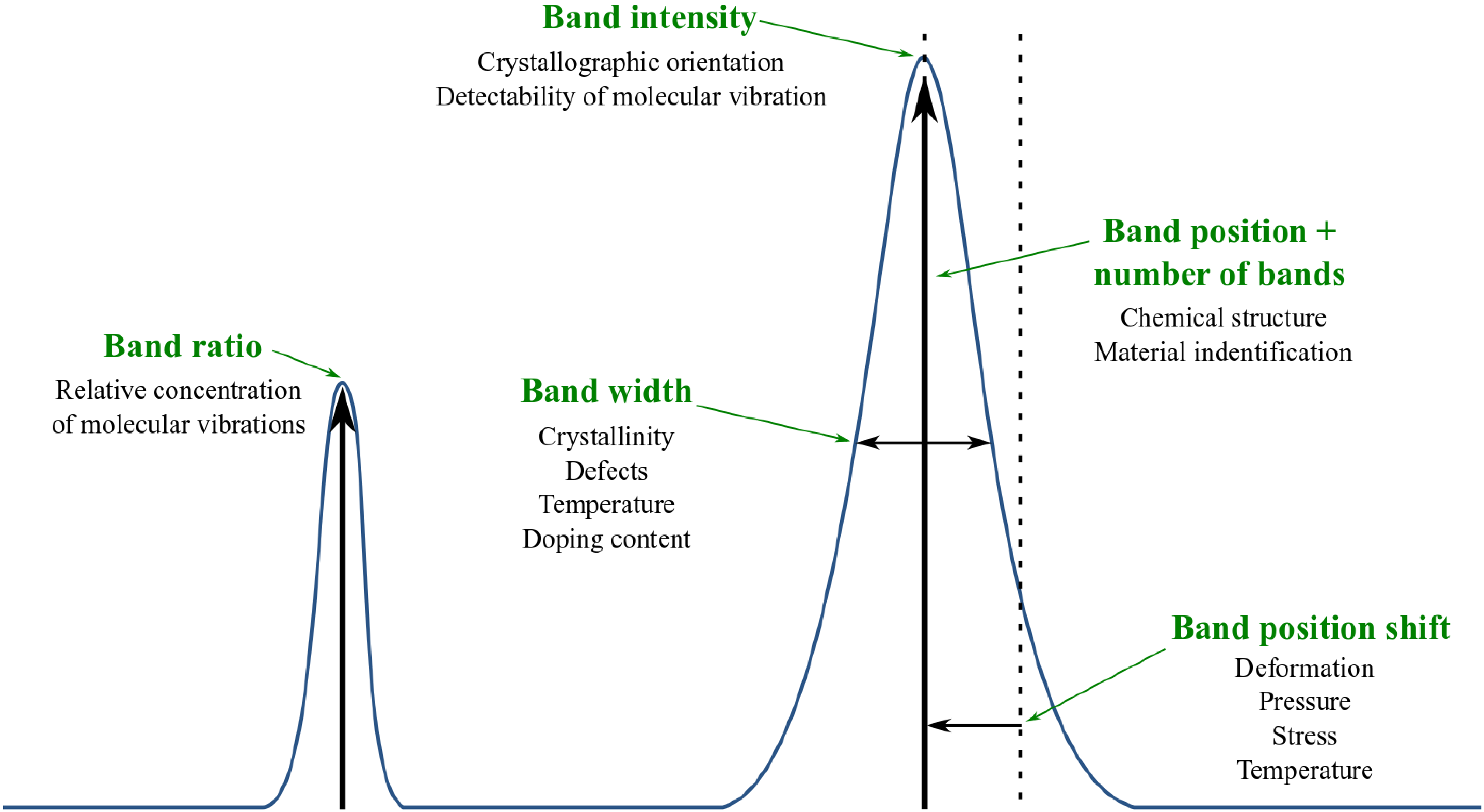
Molecular structure information

not purely chemical!





Analyses extracted from the RRUFF database



Band intensity
Crystallographic orientation
Detectability of molecular vibration
Band position +
number of bands
Chemical structure
Material indentification
Band ratio
Relative concentration
of molecular vibrations
Band width
Crystallinity
Defects
Temperature
Doping content
Band position shift
Deformation
Pressure
Stress
Temperature

Horiba LabRAM HR Evolution @ KU Leuven

Ultra-fast Raman imaging (SWIFT® and DuoScan®)

Multilaser capacity
→ 532 nm, 633 nm and 785 nm

Two grating options
→ 150 or 1800 grooves/mm

True confocal microscope

High performance spectrometer
→ 800 mm focal length

EMCCD Detector

Automated XYZ stage
→ Linkam heating-freezing stage

532 nm - semiconductor, catalysts, biological, polymers, minerals & general purpose
633 nm – corrosion, PL materials
785 nm - polymers, biological & light sensitive materials

project RAMAN-SIM2 - FWO Grant No I000718N

Horiba LabRAM HR Evolution @ KU Leuven

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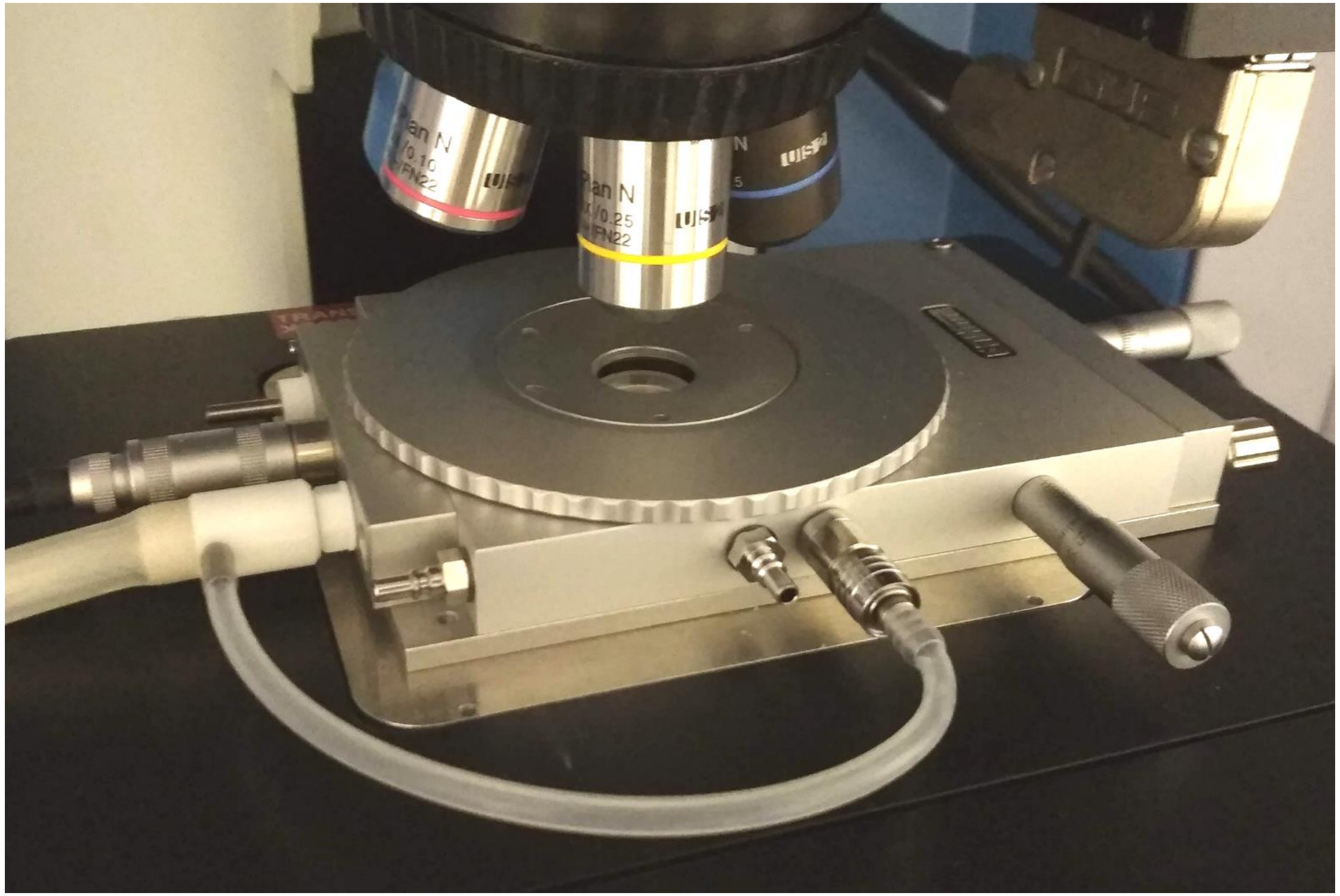


project RAMAN-SIM2 - FWO Grant No I000718N

Strengths

- Fast fingerprinting of complex materials
- Non-contact and non-destructive
- No sample preparation

Weaknesses

- Some materials are Raman inactive
- Not a bulk measurement
- Issues with photoluminescence

Opportunities

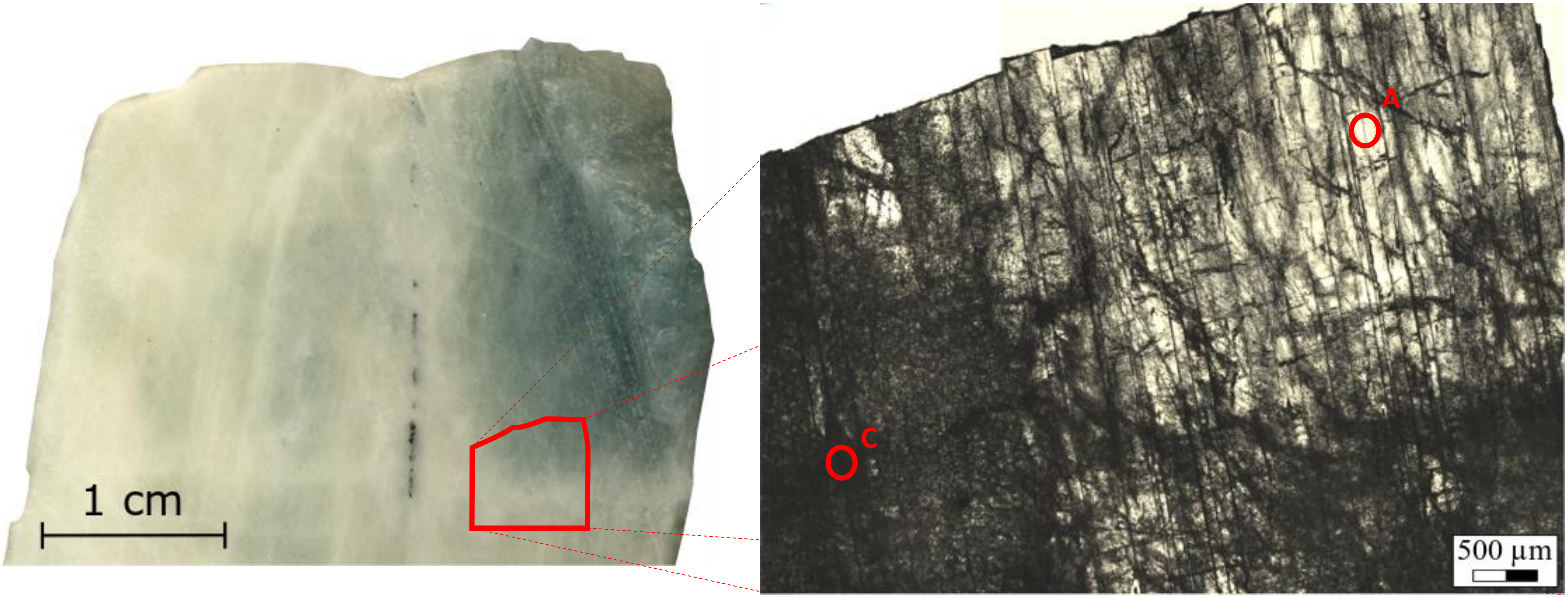
- Fast developing technique
- Mostly unexplored in many fields
- Highly customizable setup

Threats

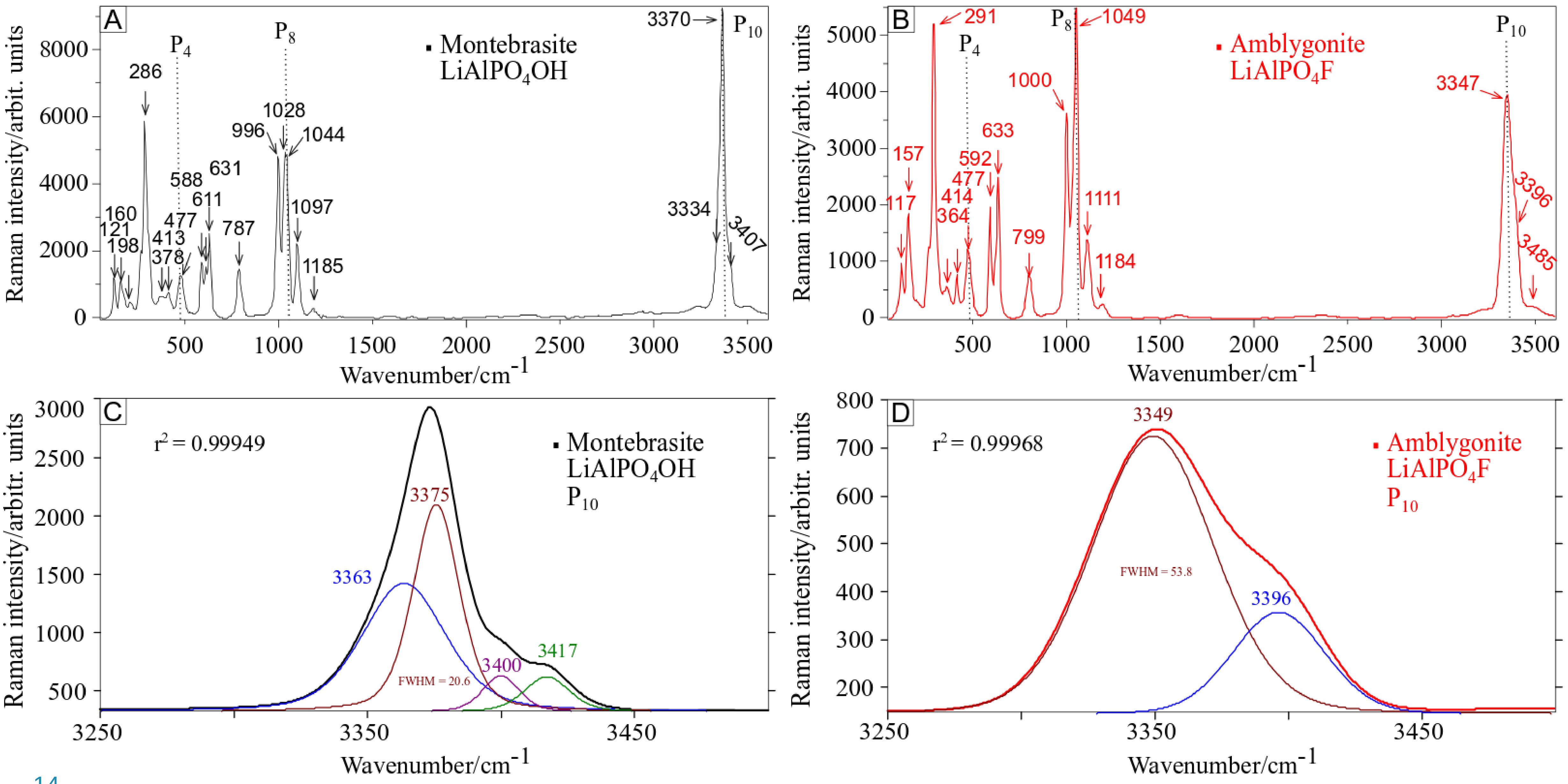
- Comparison with database is required
- Quantitative composition is not straightforward

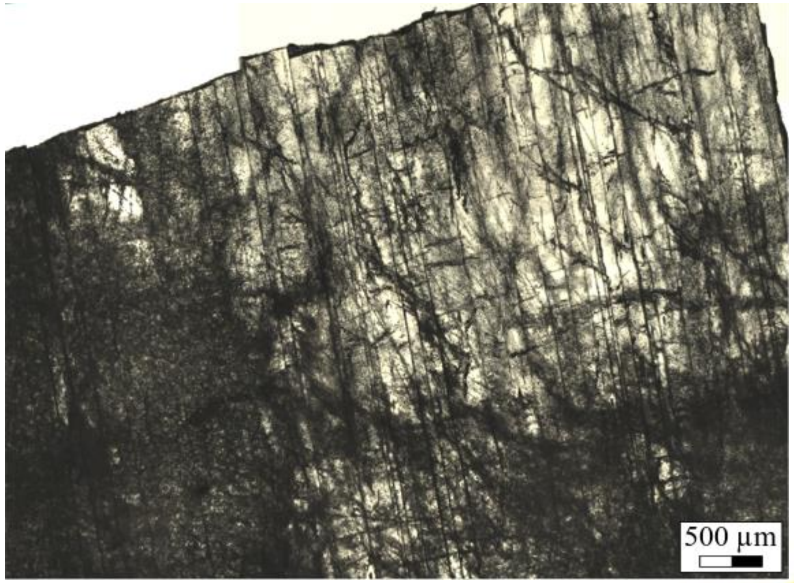
Applications

Case 1: Lithium ore sample characterization
Li phosphates
Montebrasite ($LiAlPO_4OH$) – amblygonite ($LiAlPO_4F$)

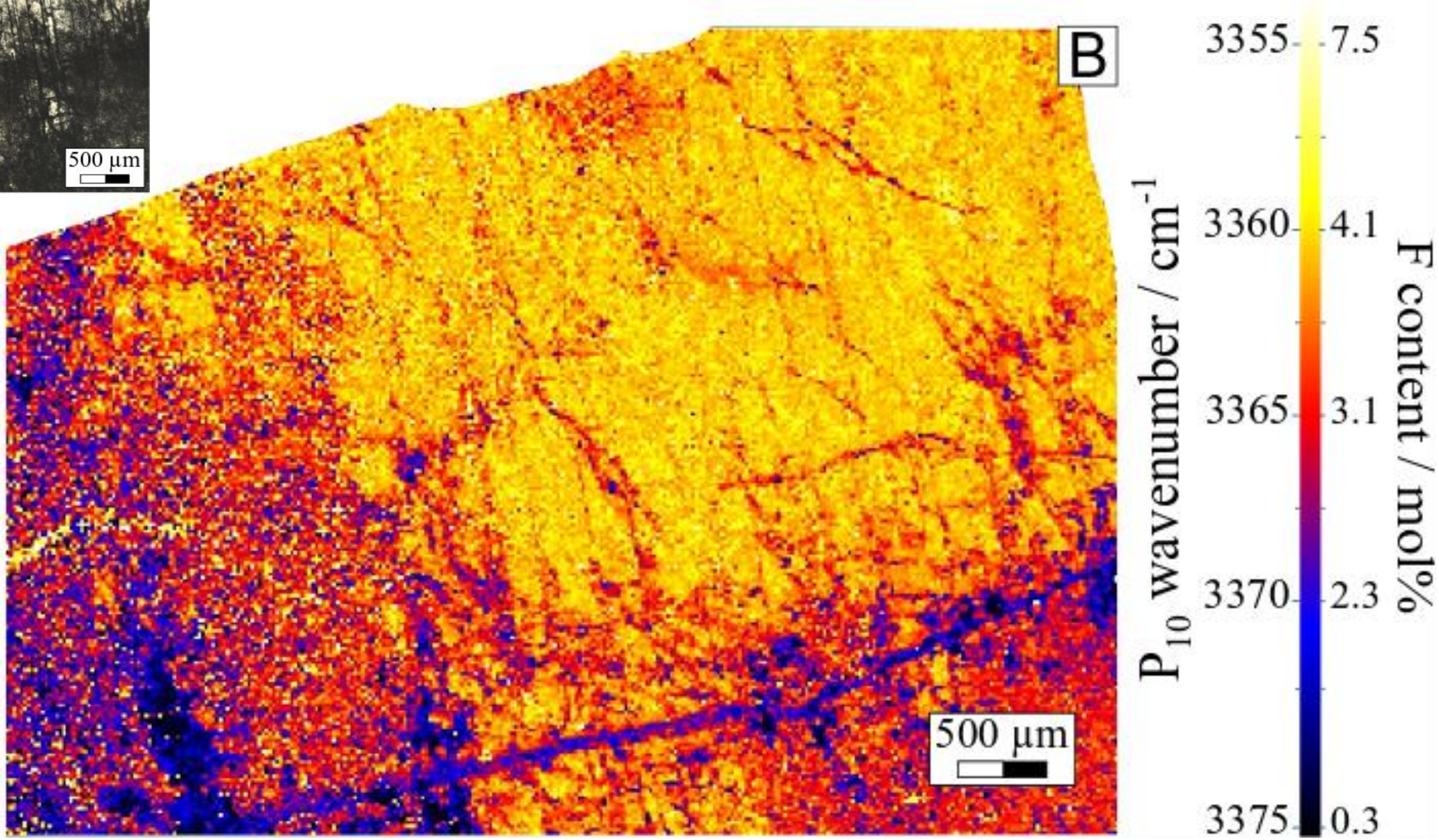

1 cm
A
C
500 µm

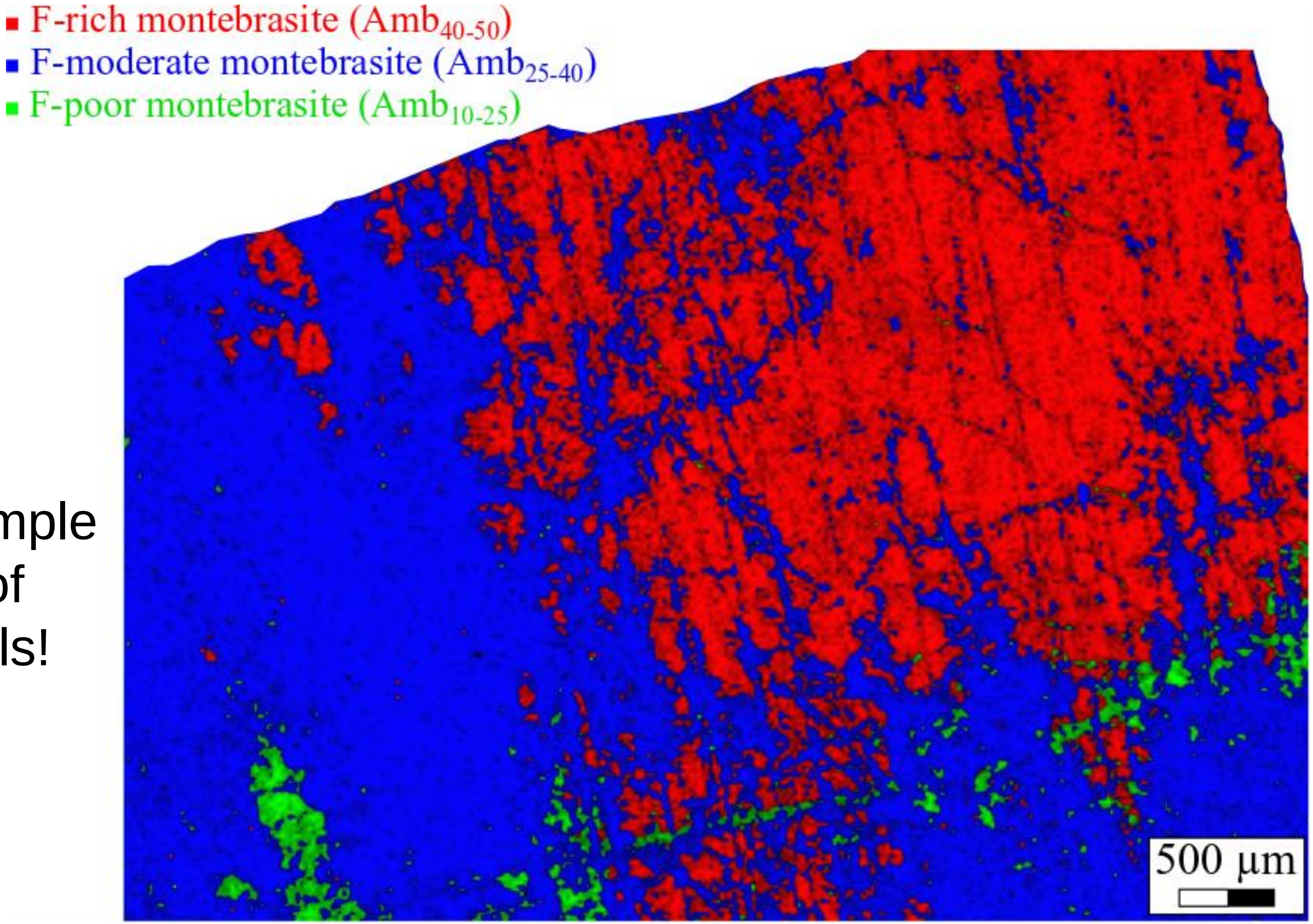
Modified from Araujo et al. (2021) *Journal of Raman Spectroscopy 52(3)*





Modified from Araujo et al. (2021) *Journal of Raman Spectroscopy 52(3)*

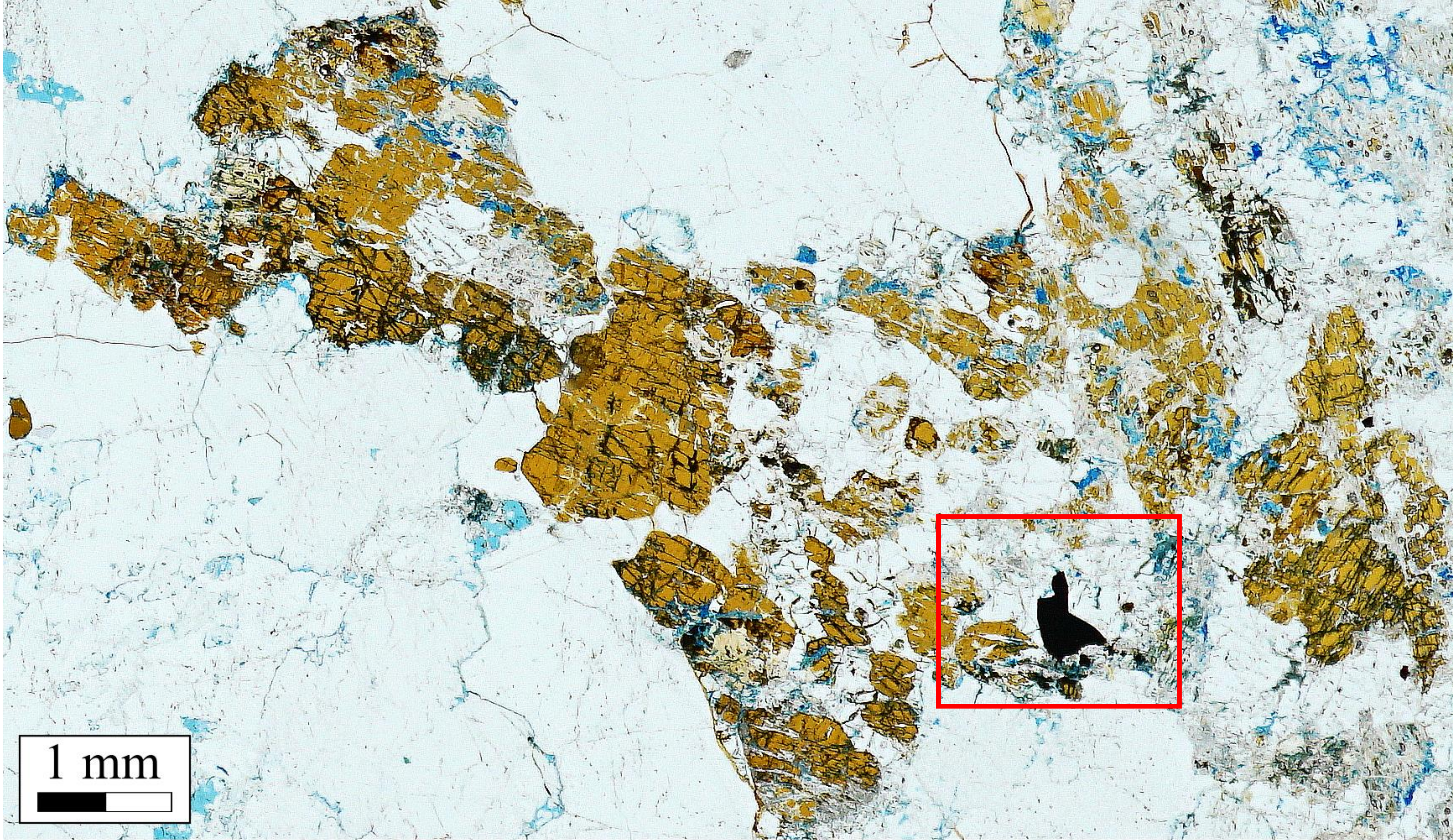




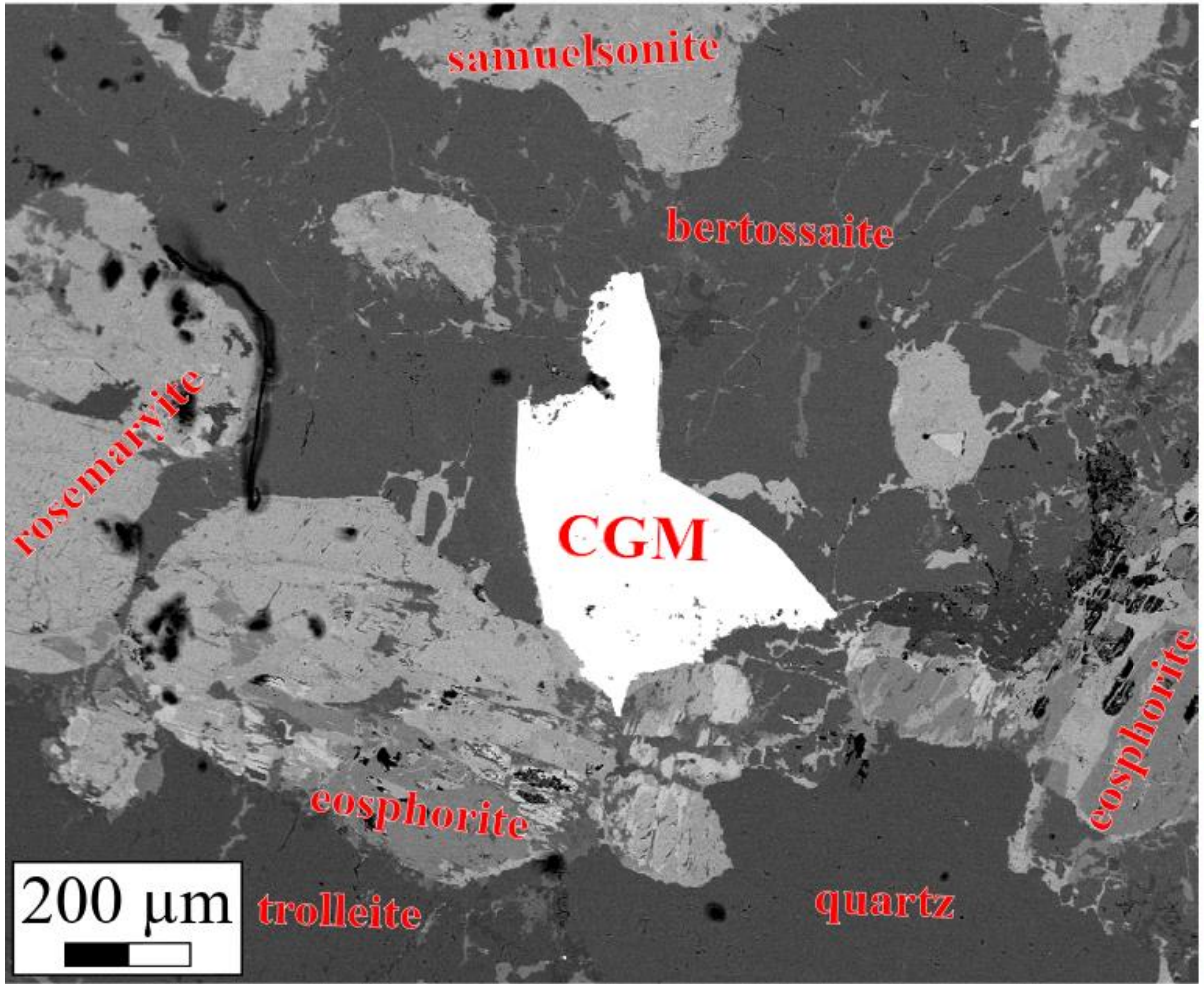
The whole sample is composed of lithium minerals!

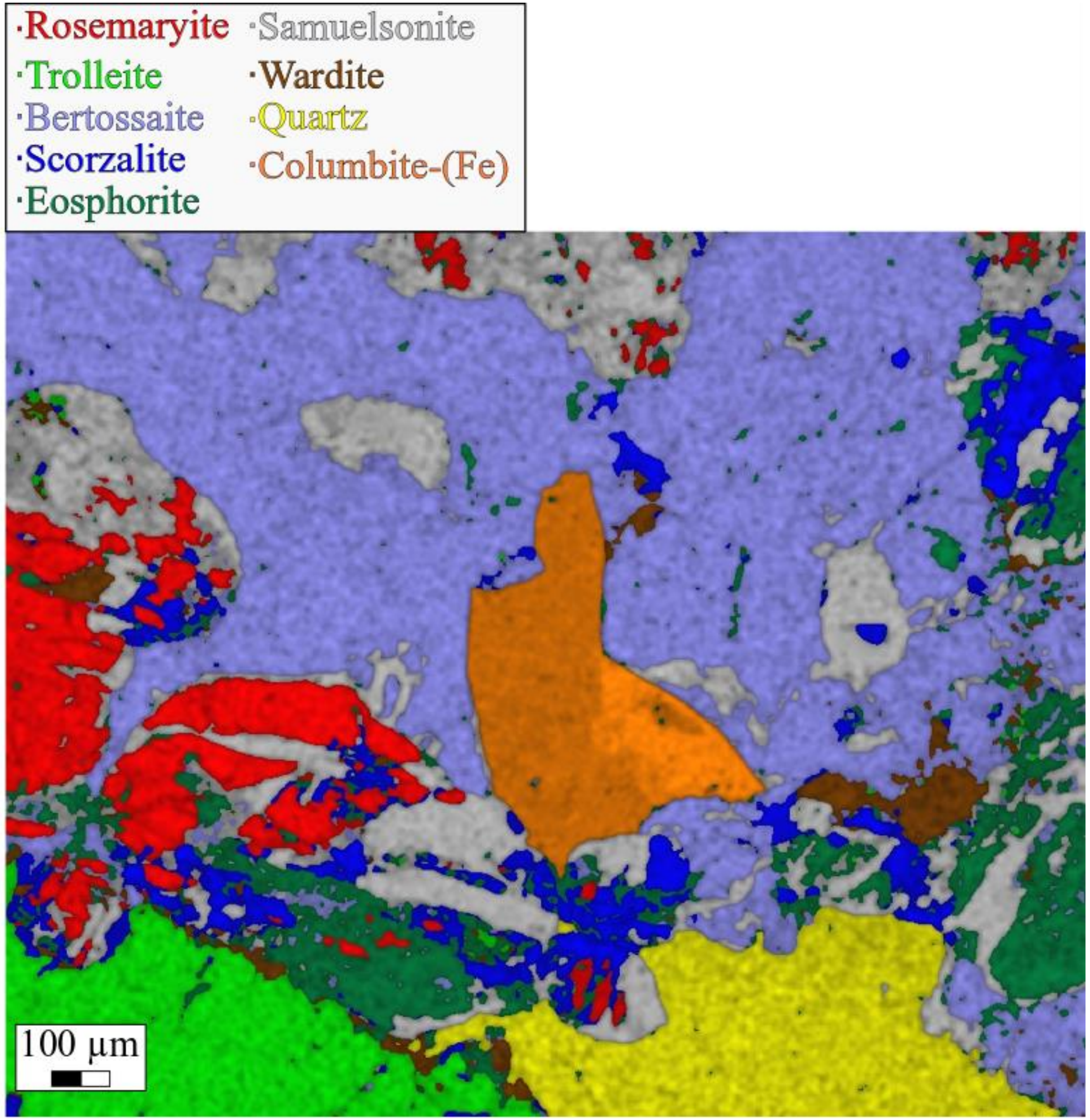
Modified from Araujo et al. (2021) *Journal of Raman Spectroscopy 52(3)*

Case 2: Complex mineral assemblages

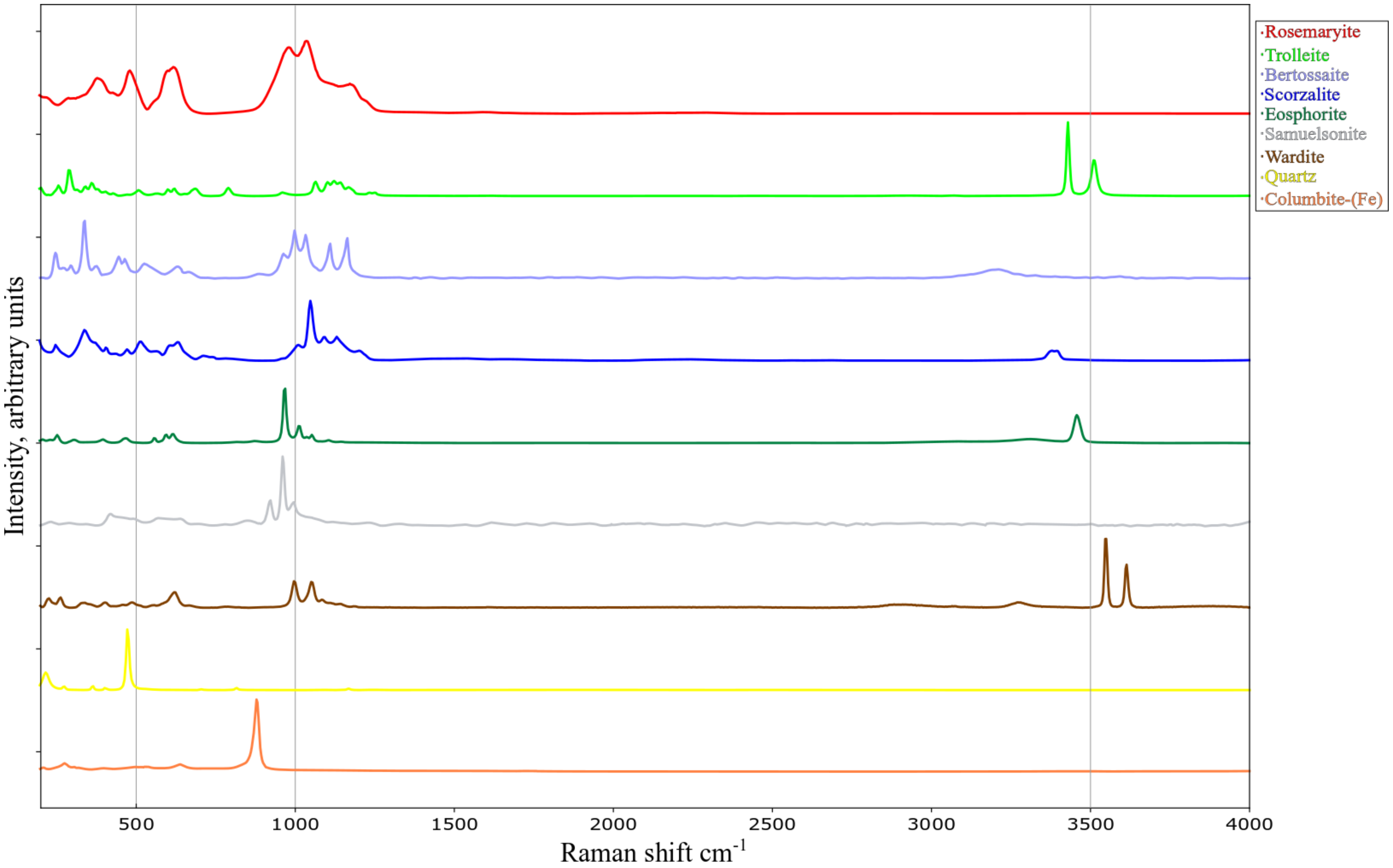


1 mm

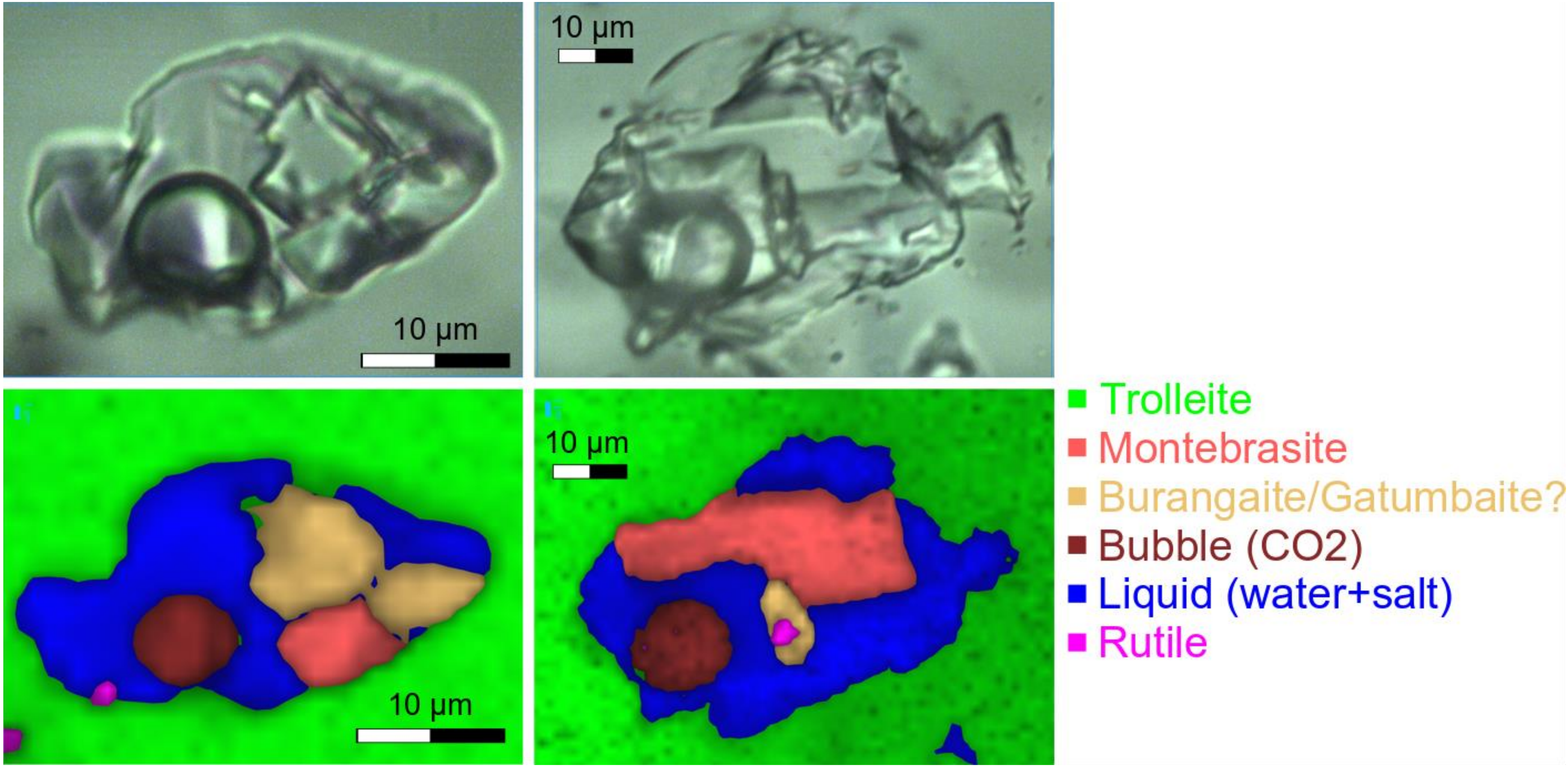




Modified from Araujo et al. (2022) *American Mineralogist*



Rosemaryite
Trolleite
Bertossaite
Scorzalite
Eosphorite
Samuelsonite
Wardite
Quartz
Columbite-(Fe)
Intensity, arbitrary units
500
1000
1500
2000
2500
3000
3500
4000
Raman shift cm-1


10 µm
10 µm
10 µm
10 µm
Trolleite
Montebrasite
Burangaite/Gatumbaite?
Bubble (CO2)
Liquid (water+salt)
Rutile

Other applications

- Solute concentrations in solutions
- Analysis of gas and fluids composition
- Stress-induced modifications
- Carbon tubes and graphene layers
- Forensic studies
- Art and heritage

Access to the lab

- Chem&Tech building (Celestijnenlaan 200F) – room 00.172
- Reservations via the "Booked" scheduler (http://booked.sim2.be)
- Dedicated users:
  - **Geology:** Fernando Prado Araujo
  - **MTM (and chemical engineering):** Pieter L'Hoëst
  - **Chemistry:** Jakob Bussé and Gerrit Van Haele

Type of user	Cost per half day (8-14h or 14-20h)
Internal, KU Leuven academic	€ 20
External, non-KU Leuven academic	€ 75
Non-academic or industry partner	€ 250 (€500 with operator)
Training (mandatory for new users)	€ 850 (one-time fee – full day)

Conclusions

- Raman spectroscopy is a **fast**, **reliable**, and **easy** material fingerprinting technique
- Raman images can be used to map **spatial variations** within complex materials
- Raman microscopy provides **versatile** and **high-resolution** analyses, complementary to more conventional techniques

Thank you!!

Comments and questions:
fernando.pradoaraujo@kuleuven.be

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