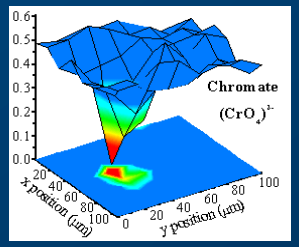
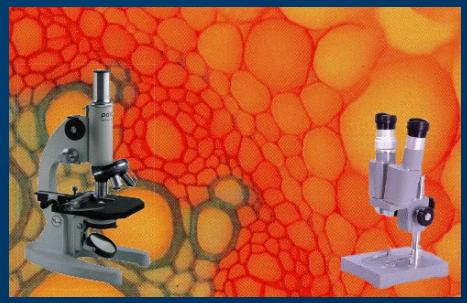
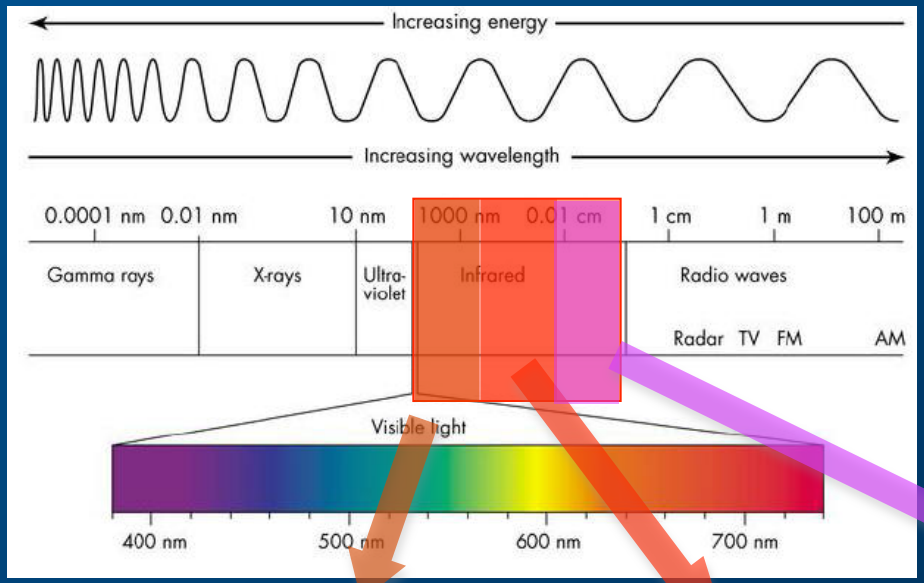




" Space , Earth and Environmental studies: why using synchrotron infrared?"

Paul DUMAS
SOLEIL Synchrotron, France
paul.dumas@synchrotron-soleil.fr

Infrared Science and energy domain



THREE MAIN IR RANGES

NEAR IR

0,8-2,5µm

(1.54 – 0.49 eV)

MID IR

2.5-25µm

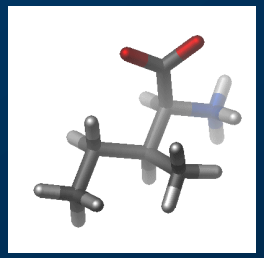
(0.49 eV – 49.5 meV)

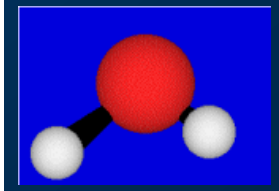
FAR IR (THz)

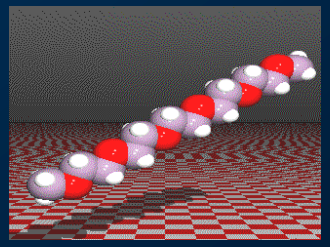
25-1000µm

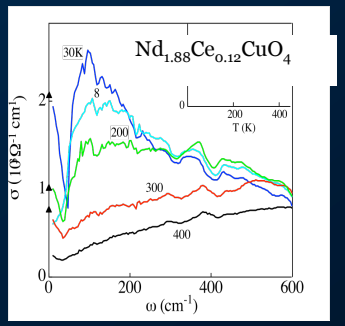
(0.49 eV – 1.2 meV)

Band combination, identification (pharmaceutical for ex.)

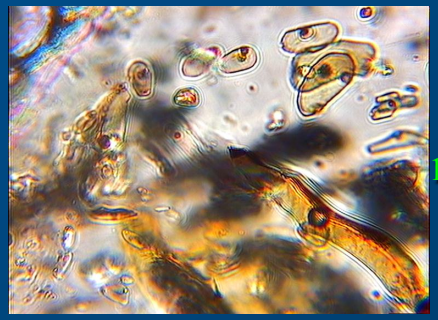


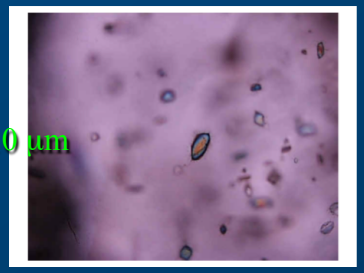






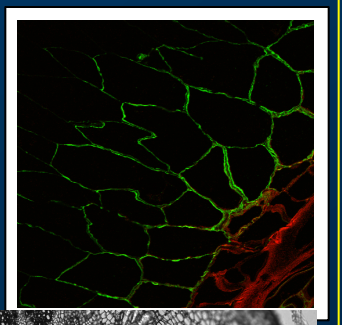
Requirements in Space , Earth and Environmental Science





Small particles, probe at the microns size level

Space particles are very tiny (µm size)



Accumulations, changes , in phytoremediation, at the micron size level

Requirements

- High quality of the spectroscopic information
- High spatial resolution
- Highest contrast fidelity

Source of infrared photons and technique

1) Synchrotron radiation: a brighter source in infrared

2) Confocal Infrared microscopy

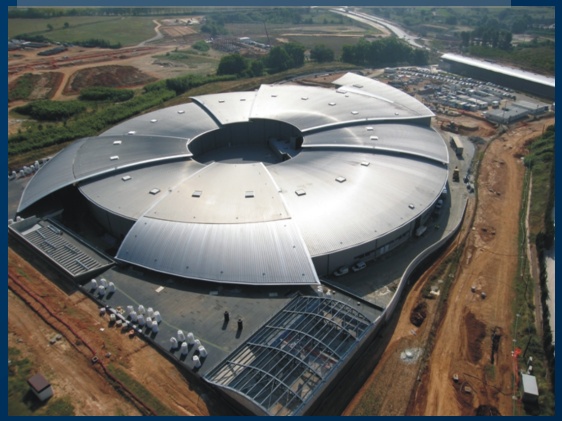
SOLEIL SYNCHROTRON

Australian Synchrotron, Melbourne
Circumference=216 m

DIAMOND , UK
Circumference=561.6 m

ESRF , Grenoble, France
Circumference=844 m

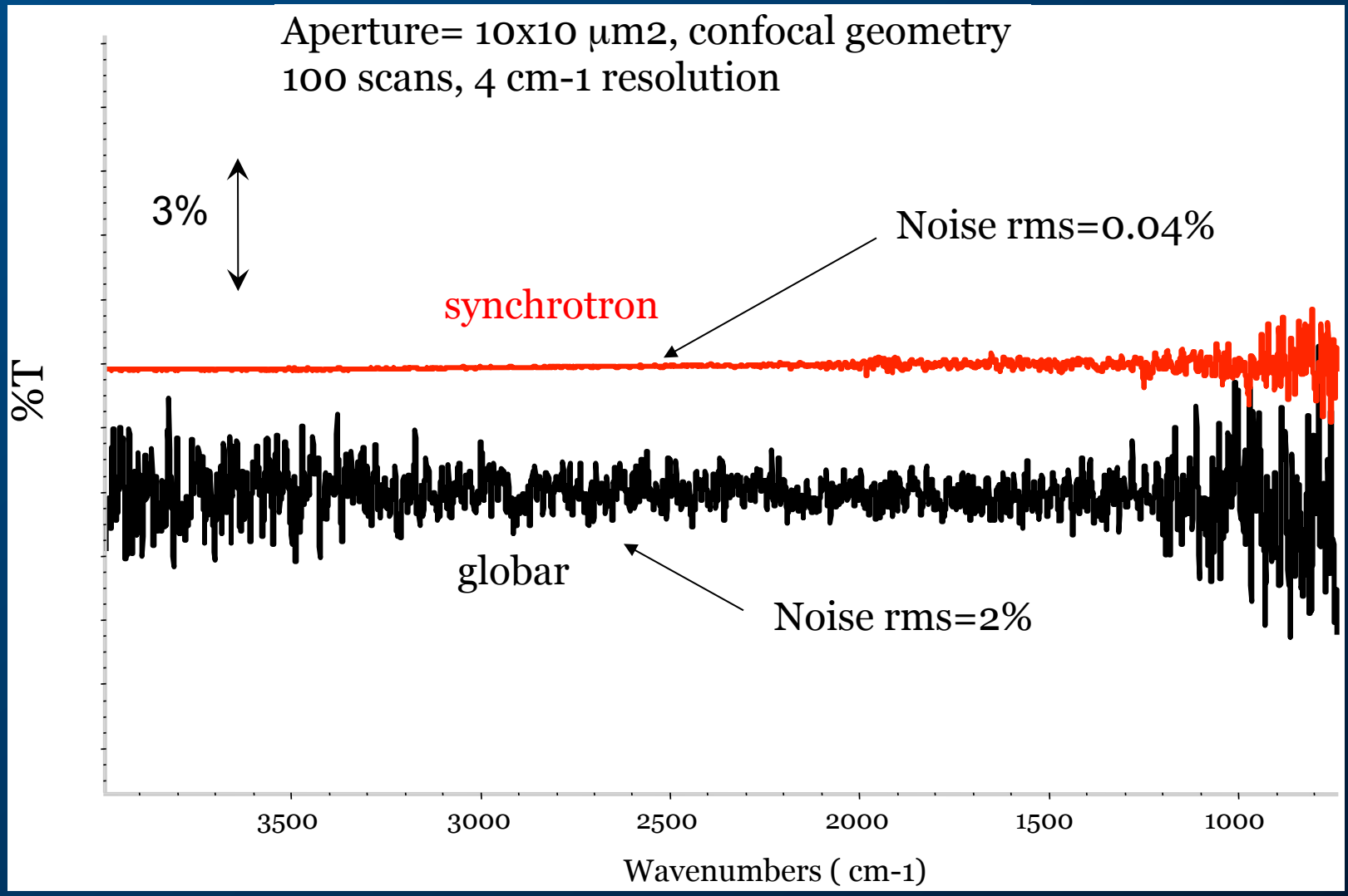
ALBA , Barcelona, Spain
Circumference=249.6



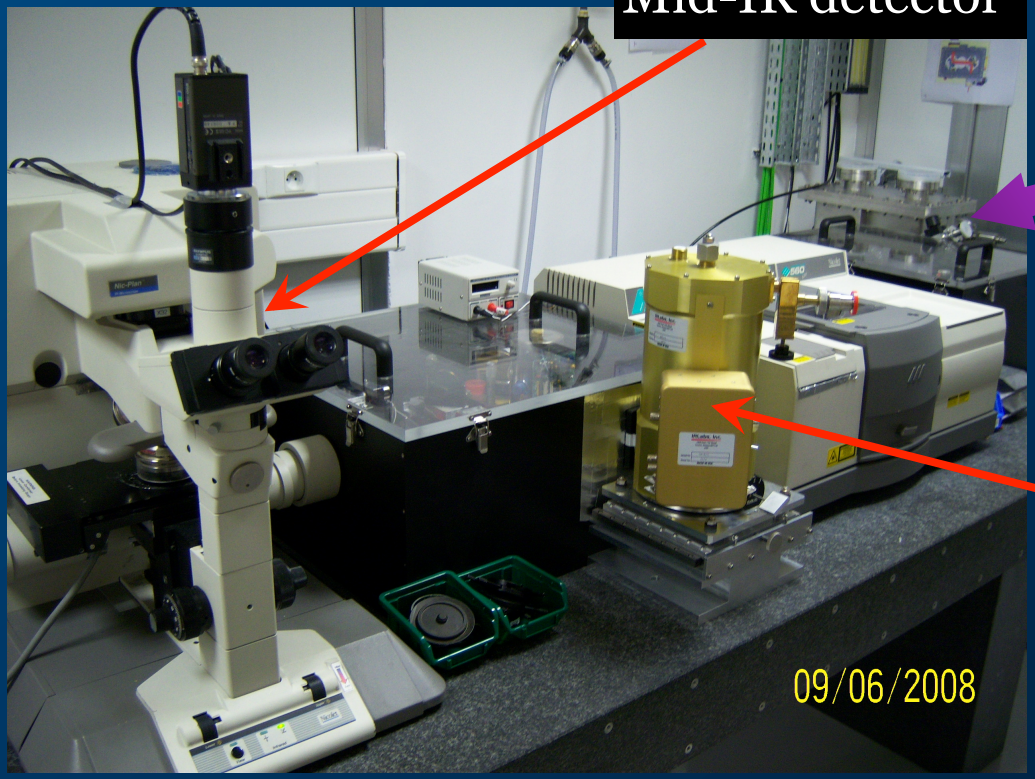
Shangai Synchrotron Facility
Circumference=345 m

Spring-8 , Japan
Circumference=1436 m

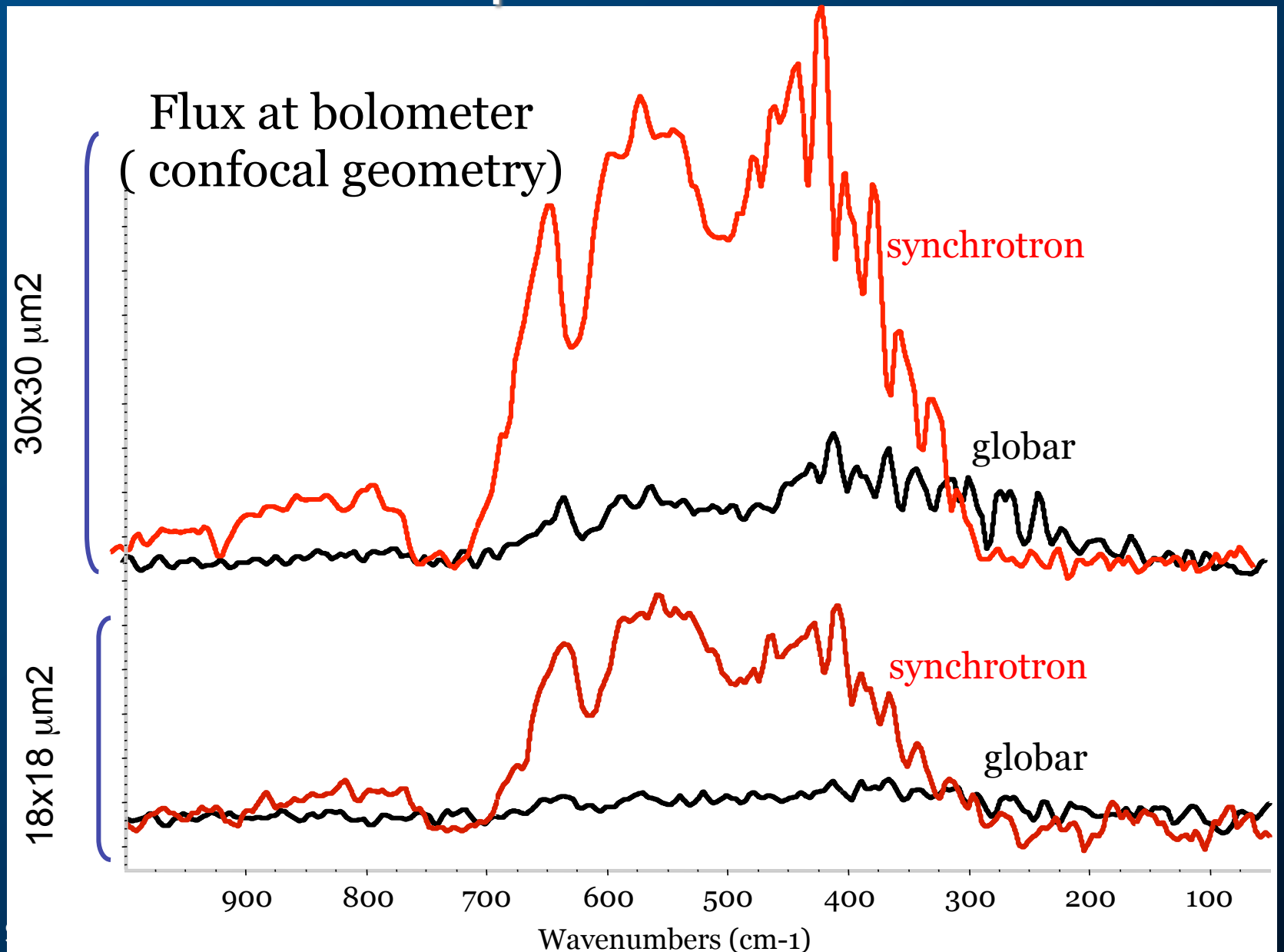
Spectral quality and data acquisition time…



Synchrotron Infrared beamlines are also exploiting , at lower spatial resolution (diffraction limit) the far-IR region:

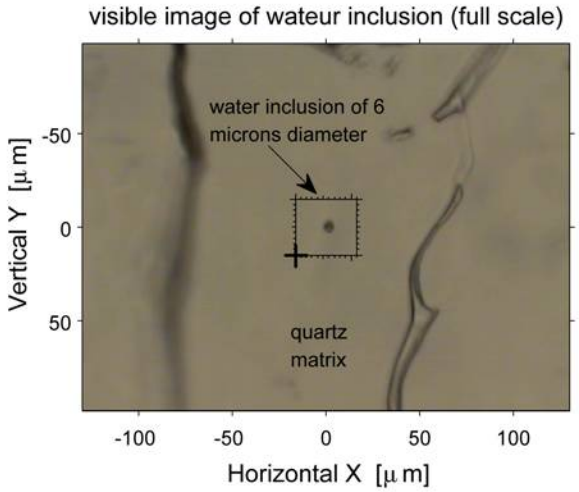


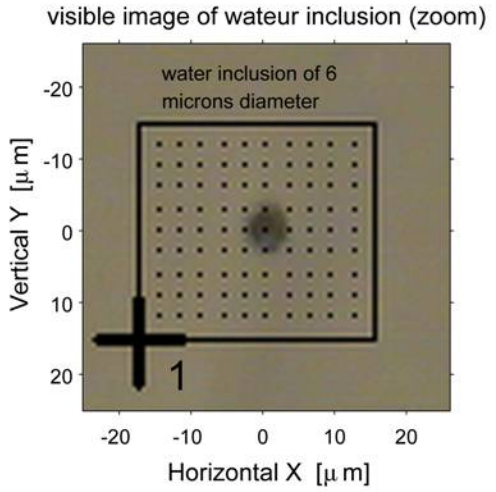
Detector signal at decreasing aperture sizes

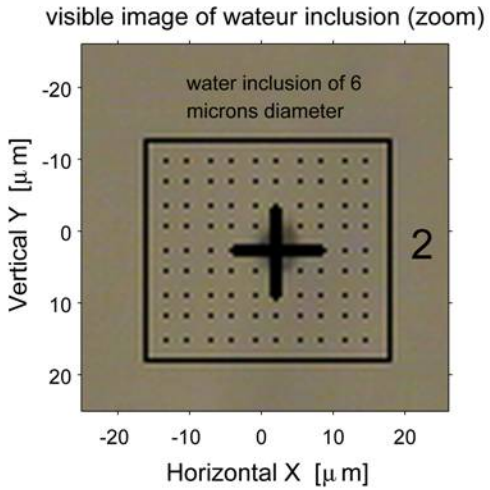


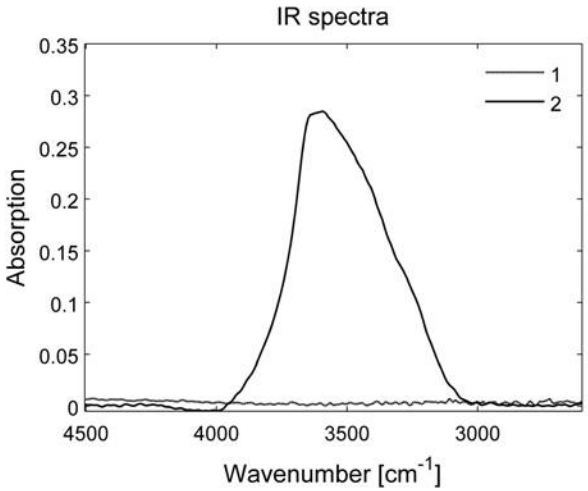
Confocality and 3D imaging

Inclusion in quartz



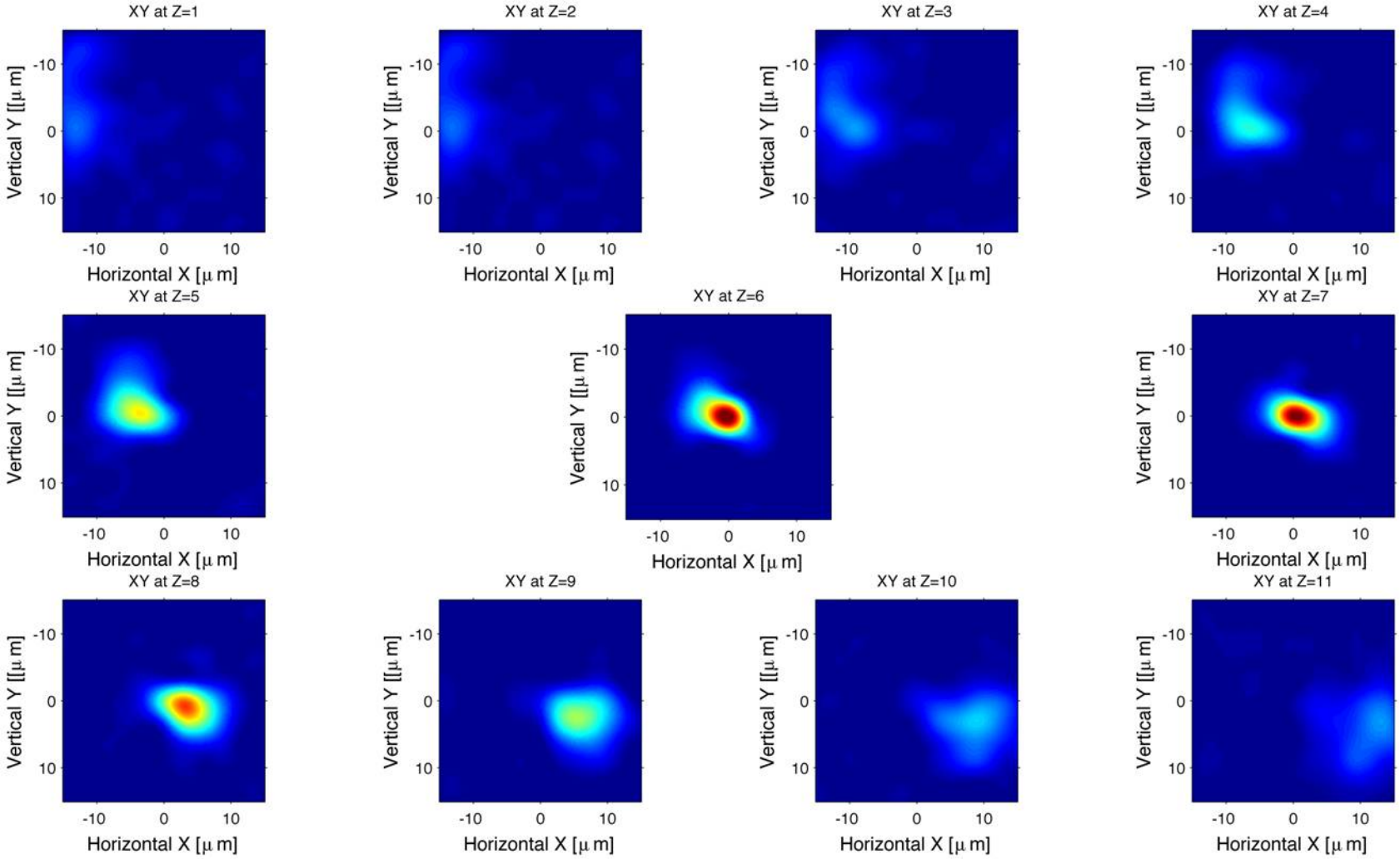




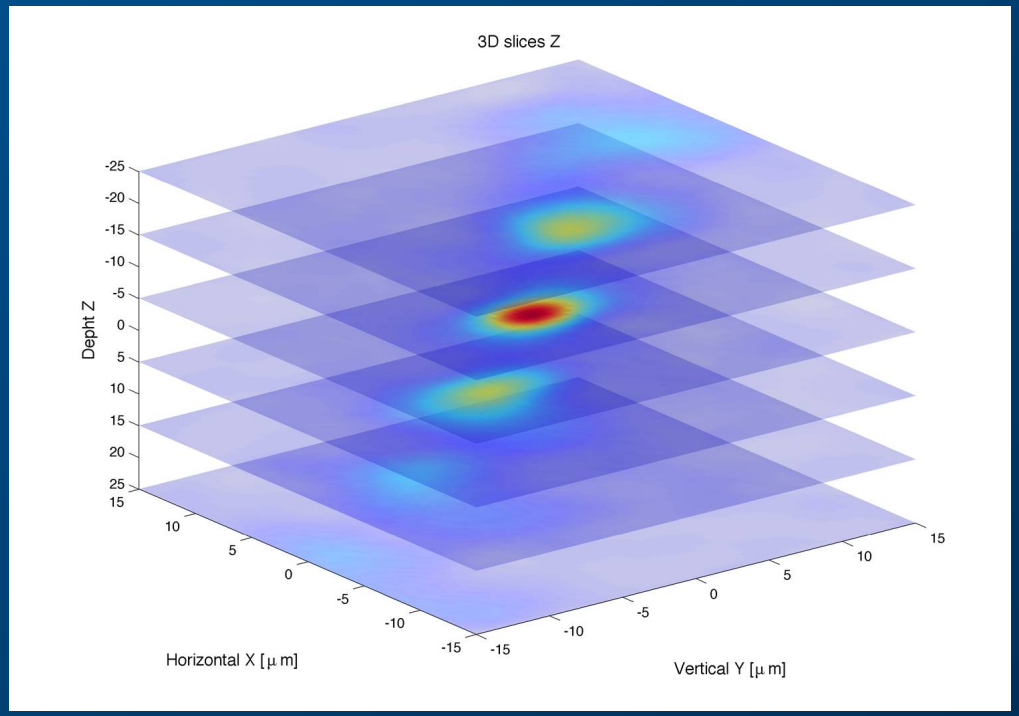


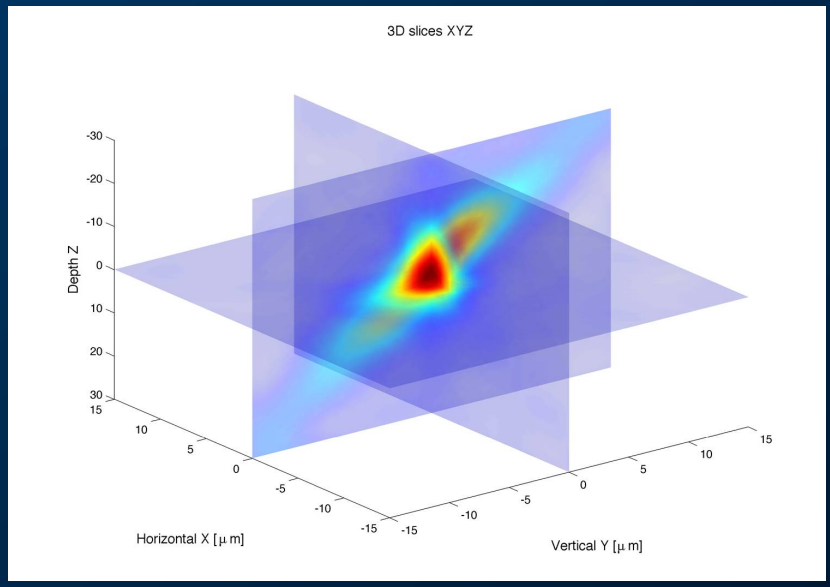
L. Mercury, F. Jamme and P. Dumas
In preparation

2D images at various Z position (step 1 µm)



3D image

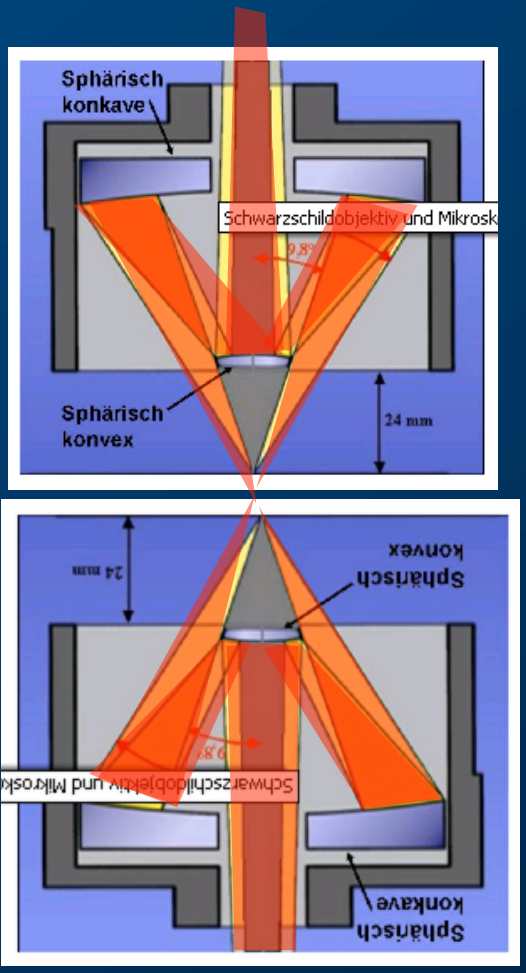

3D slices Z
Depht Z
-25
-20
-15
-10
-5
0
5
10
15
20
25
15
10
5
0
-5
-10
-15
Horizontal X [μ m]
-15
-10
-5
0
5
10
15
Vertical Y [μ m]

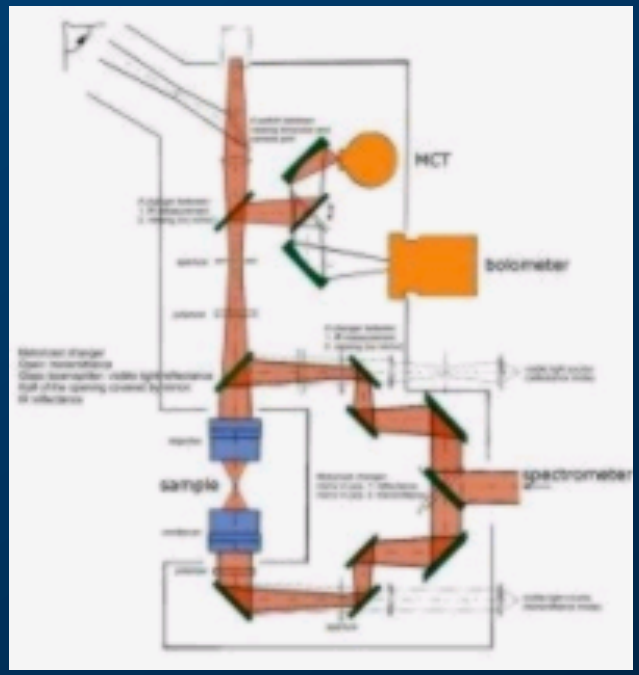

3D slices XYZ
Depth Z
-30
-20
-10
0
10
20
30
15
10
5
0
-5
-10
-15
Horizontal X [μ m]
-15
-10
-5
0
5
10
15
Vertical Y [μ m]

Sampling issues

Transmission mode

- Sample must be thin (microsectionning, microtome..)
- Embedding is one way, but embedding compound may contribute to the IR spectra
- Requires IR transparent windows (CaF2, BaF2, ZnSe, ZnS, diamond!)



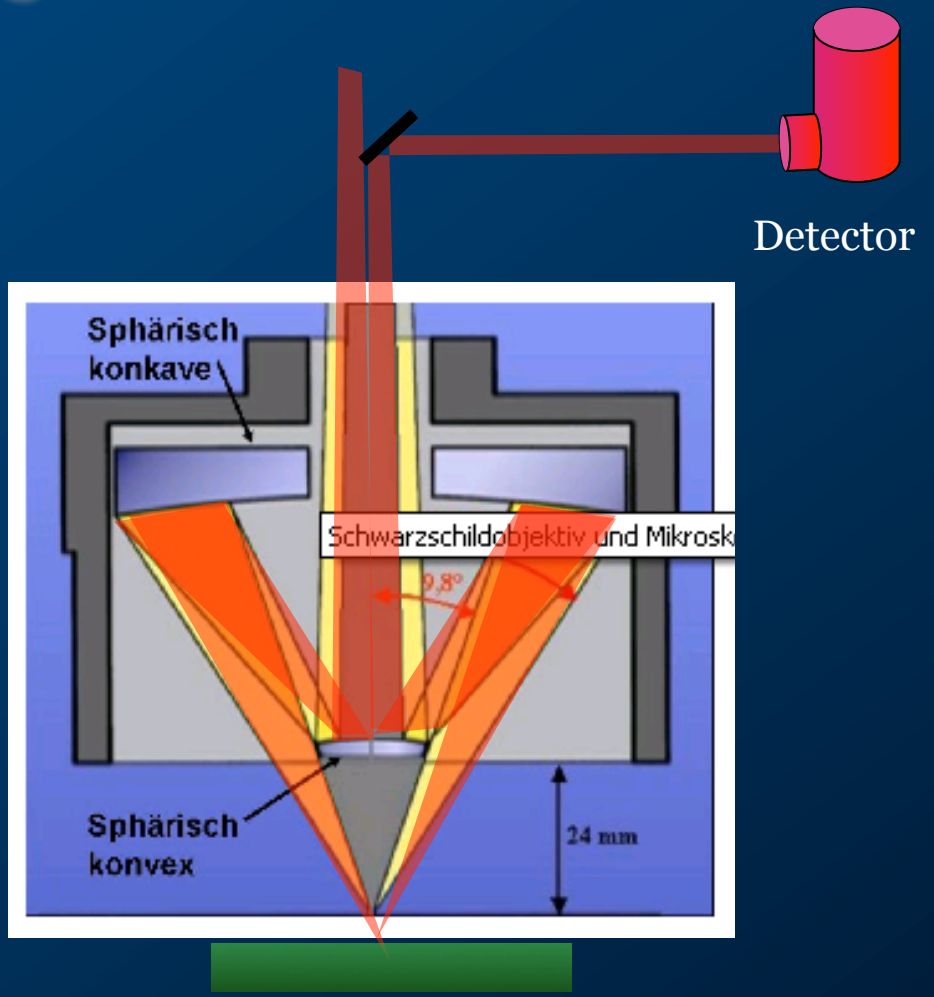


Sampling issues

Reflection mode

- Sample must be flat or flattened
(polishing..)

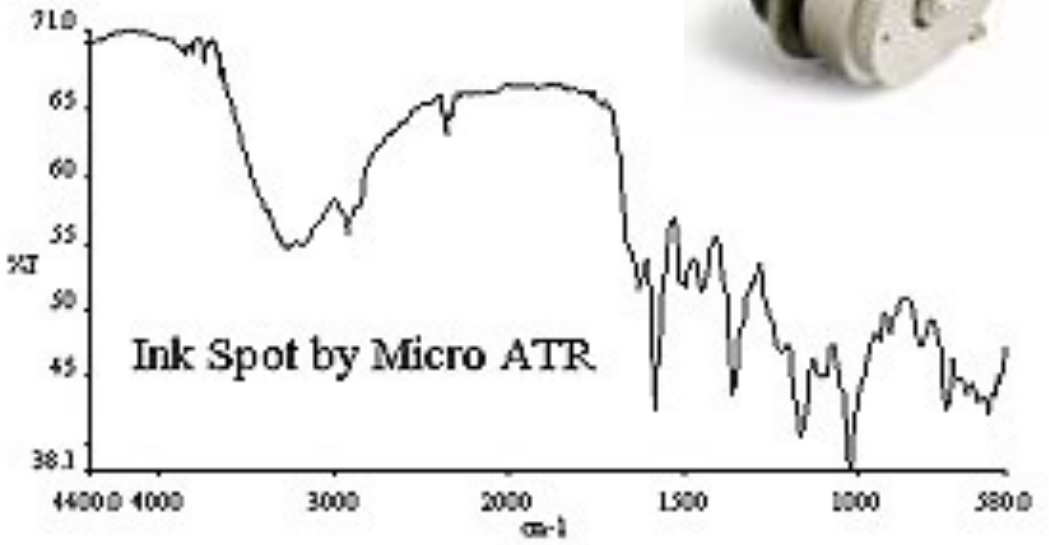
- Signal is much weaker (R %~=$[(n-1)/(n+1)]^2$



ATR Objective
(Attenuated Total Reflection)

$$d = \lambda / \{2\pi n_1 [\sin^2\theta - (n_2/n_1)^2]^{1/2}\}$$

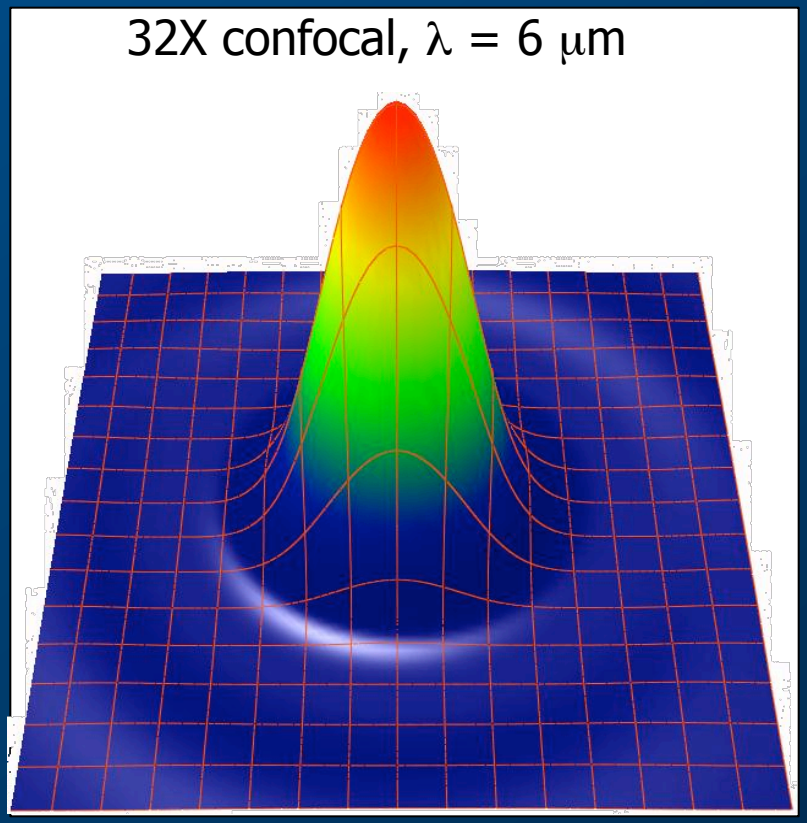
Analysis of ink on the paper

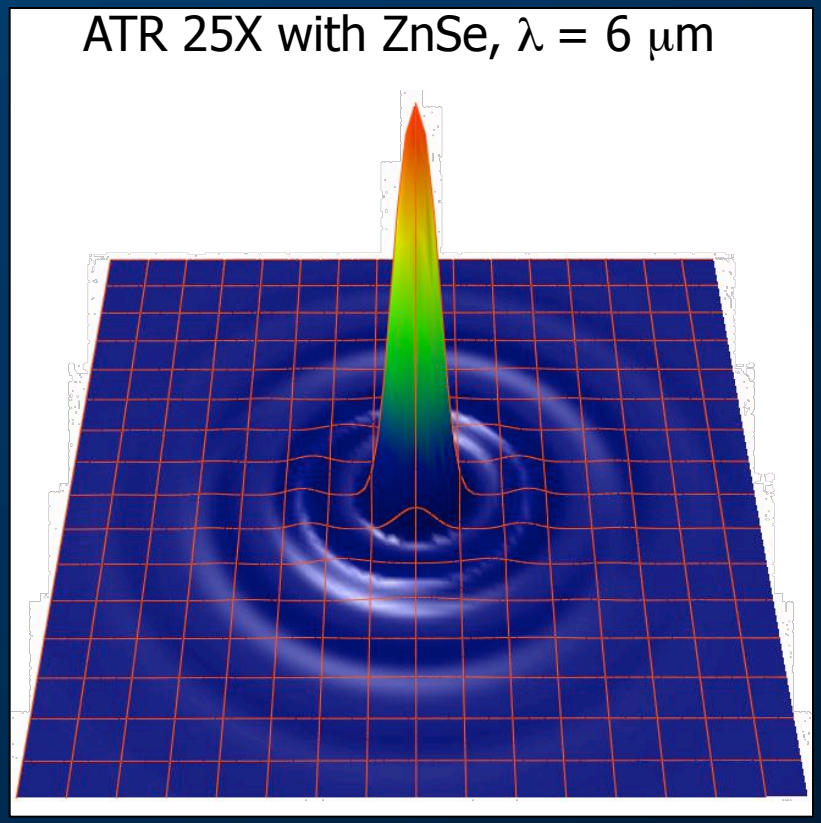


ZnSe n=2.4 d=2 μm
Ge n=4 d=0.66 μm

Attenuated total reflectance is an intrinsically confocal measurement

=> $S(x,y,\lambda) \sim (PSF)^2$, effect of diffraction rings is suppressed.



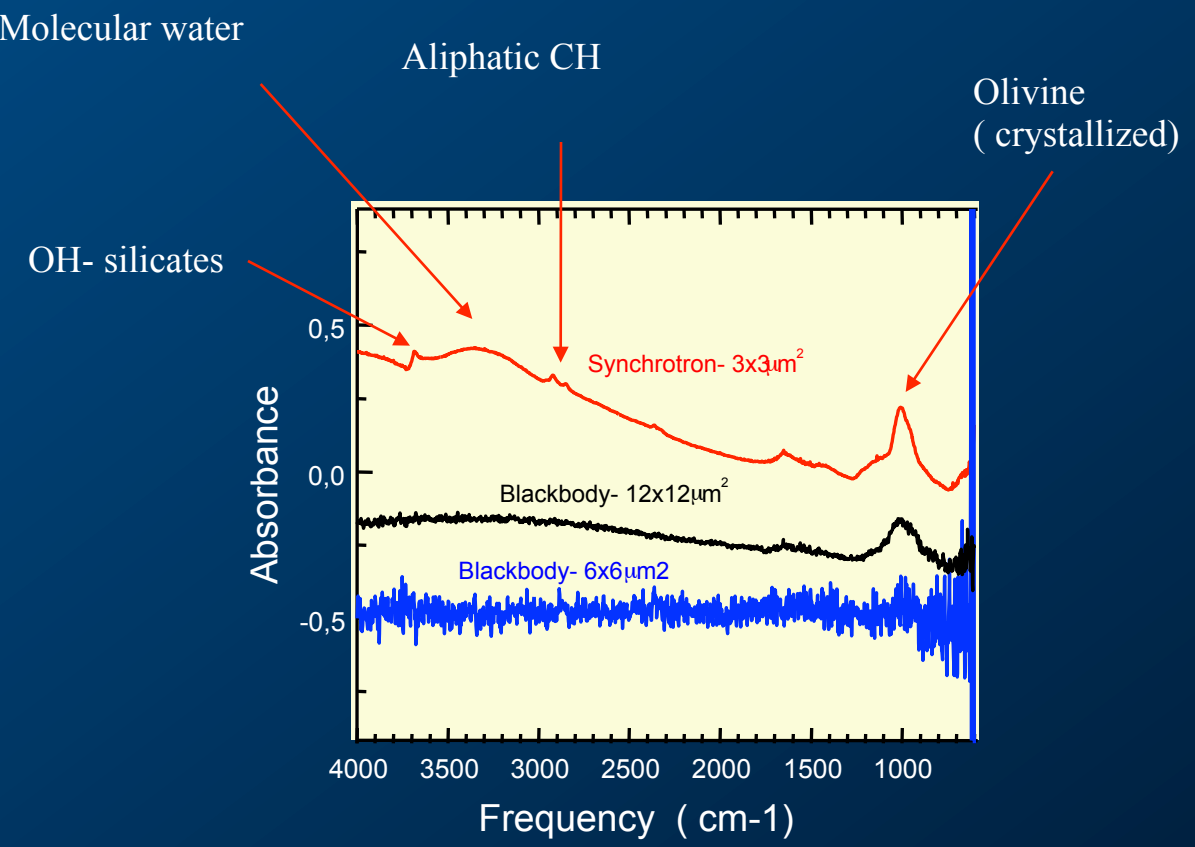


the spatial resolution is improved by a factor equal to the refractive index

Synchrotron IR micro-spectroscopy and Space Science: Interplanetary Durst Particles identification

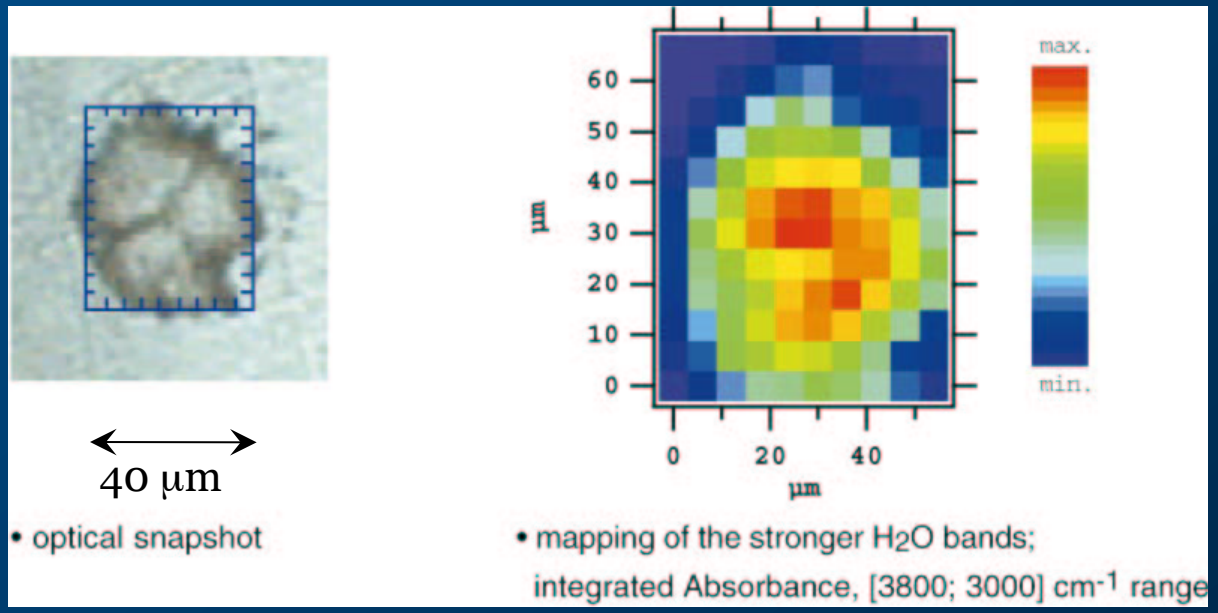
P.Dumas

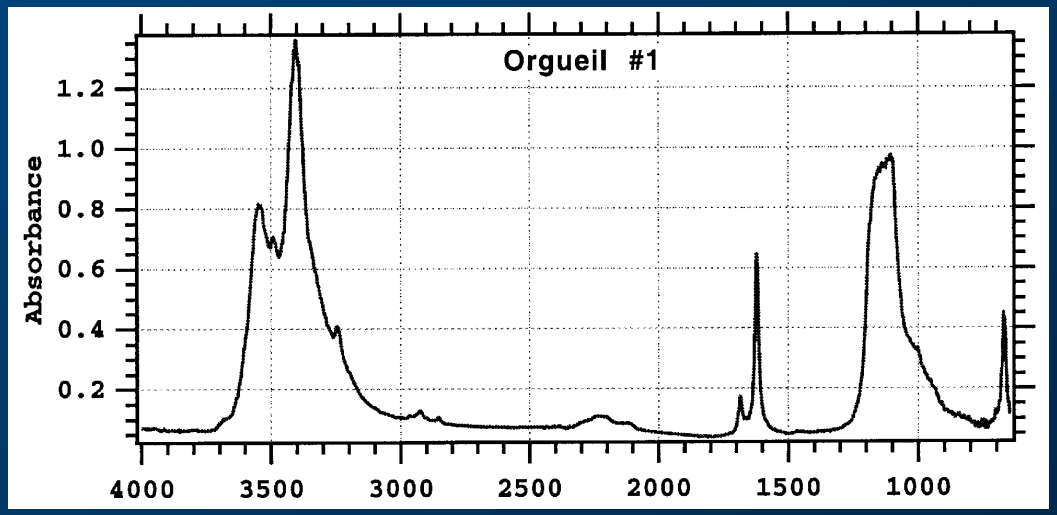
"Orgueil" particules



Ph. Raynal, L. D'Hendecourt, J. Borg, J.P. Bibring , G.P. Williams and P. Dumas

Aperture= 3x3 µm

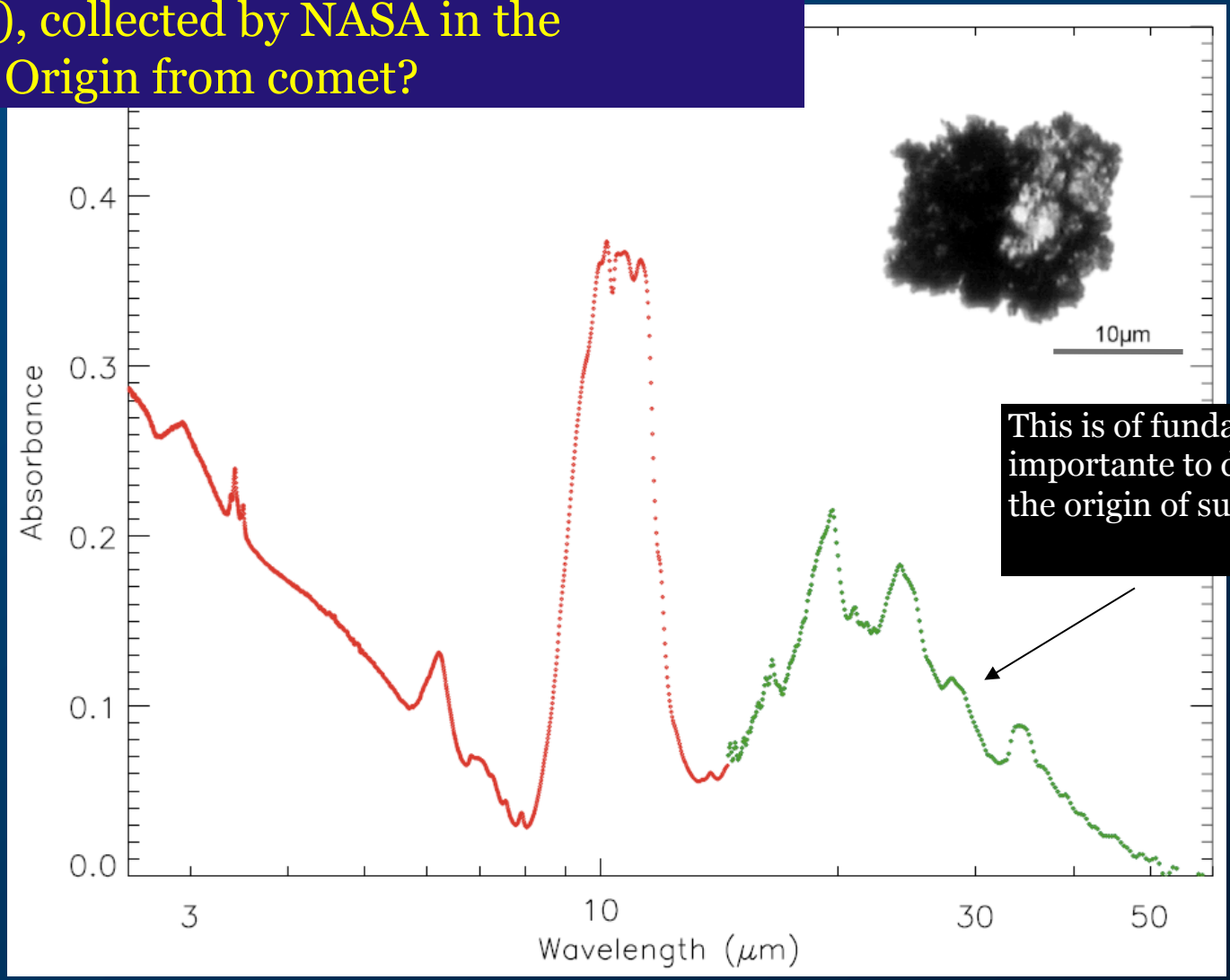




Chemical image of water distribution inside a 40 µm particle

Synchrotron far-IR microscopy

Extra terrestrial studies of Interplanetary Dust Particle (IDP), collected by NASA in the statosphere.. Origin from comet?



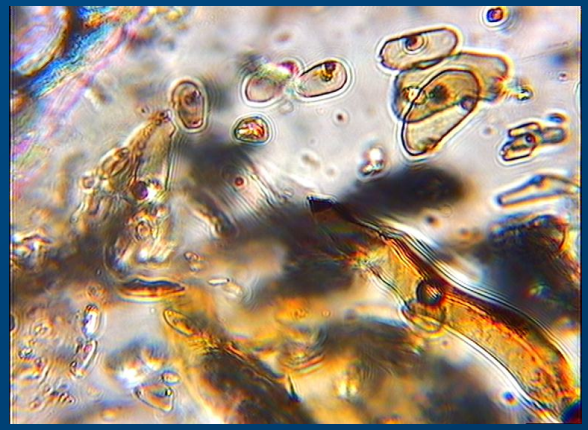
This is of fundamental importante to discriminate the origin of such particles

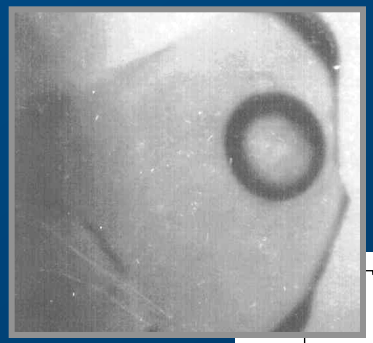
From E. Dartois, J. Borg, C.Sandt, P. Dumas .

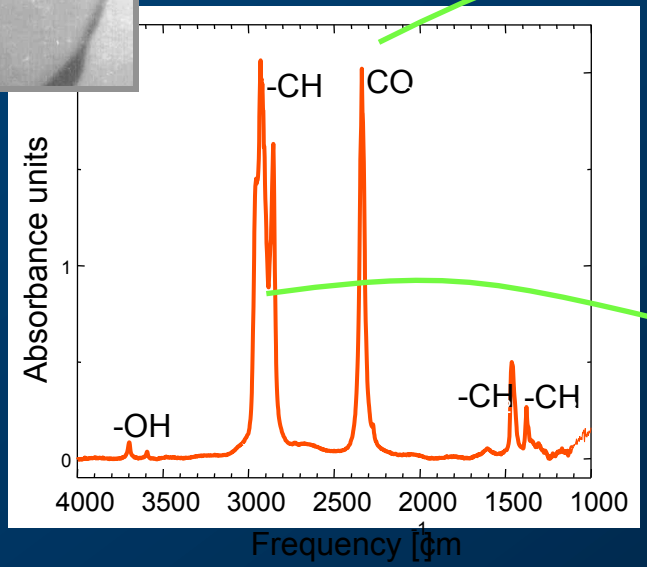
Synchrotron IR micro-spectroscopy and Earth Science: Inclusions and extreme conditions

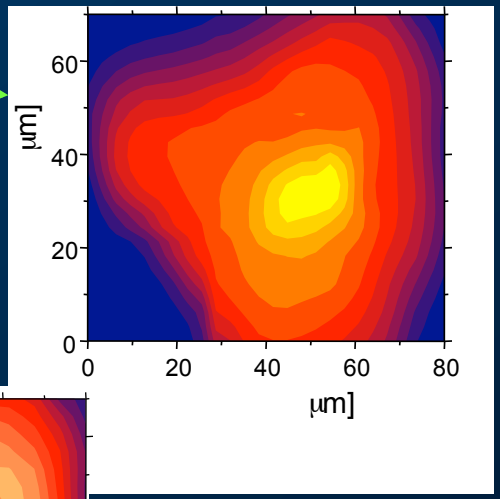
P.Dumas

Inclusions in rocks

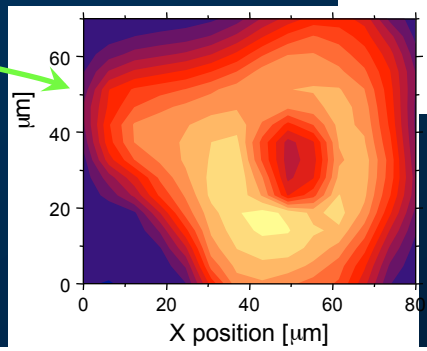








CO_2

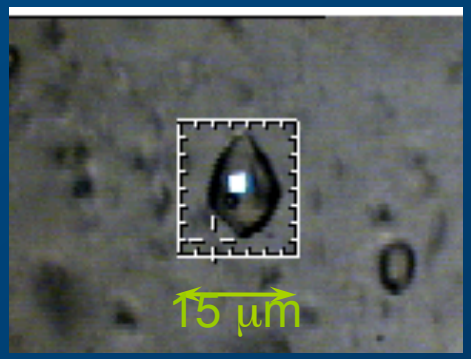


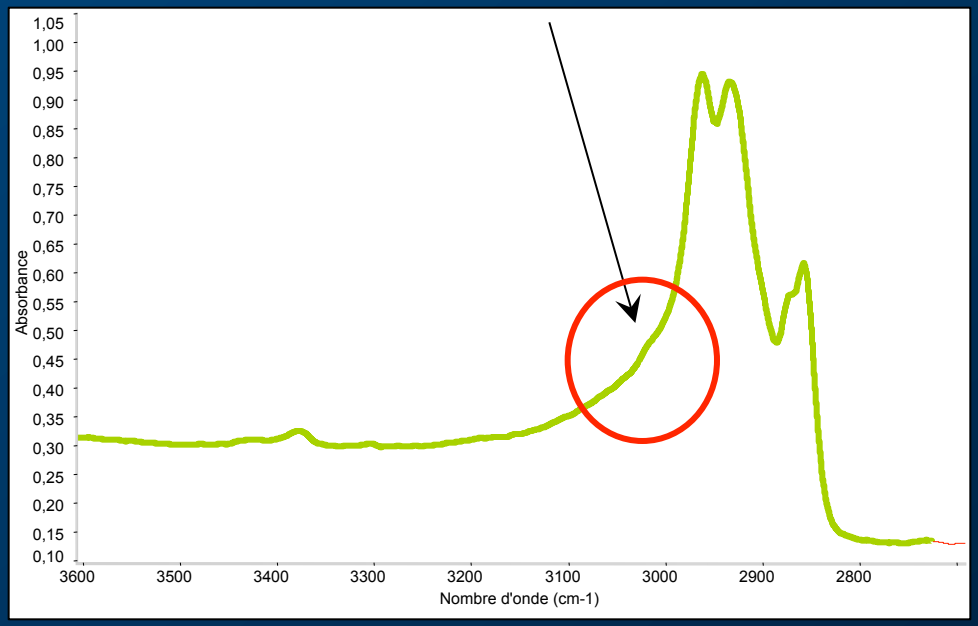
Hydrocarbons

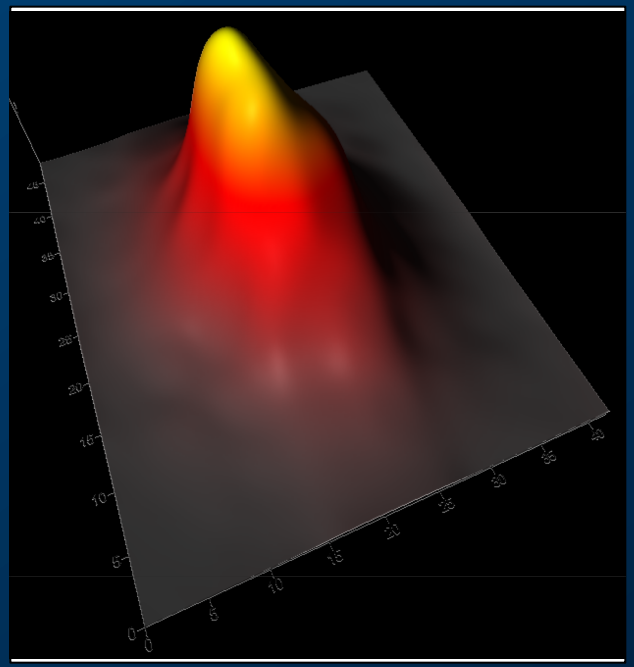
N. Guilhaumou, P. Dumas Oil & Gas Science and Technology - Rev. IFP, Vol. 60 (2005), No. 5, pp. 763-779

Inclusions in rocks

Inclusion in calcite
Benzenic C=H



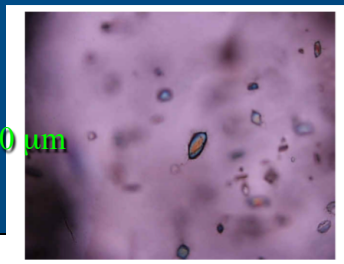




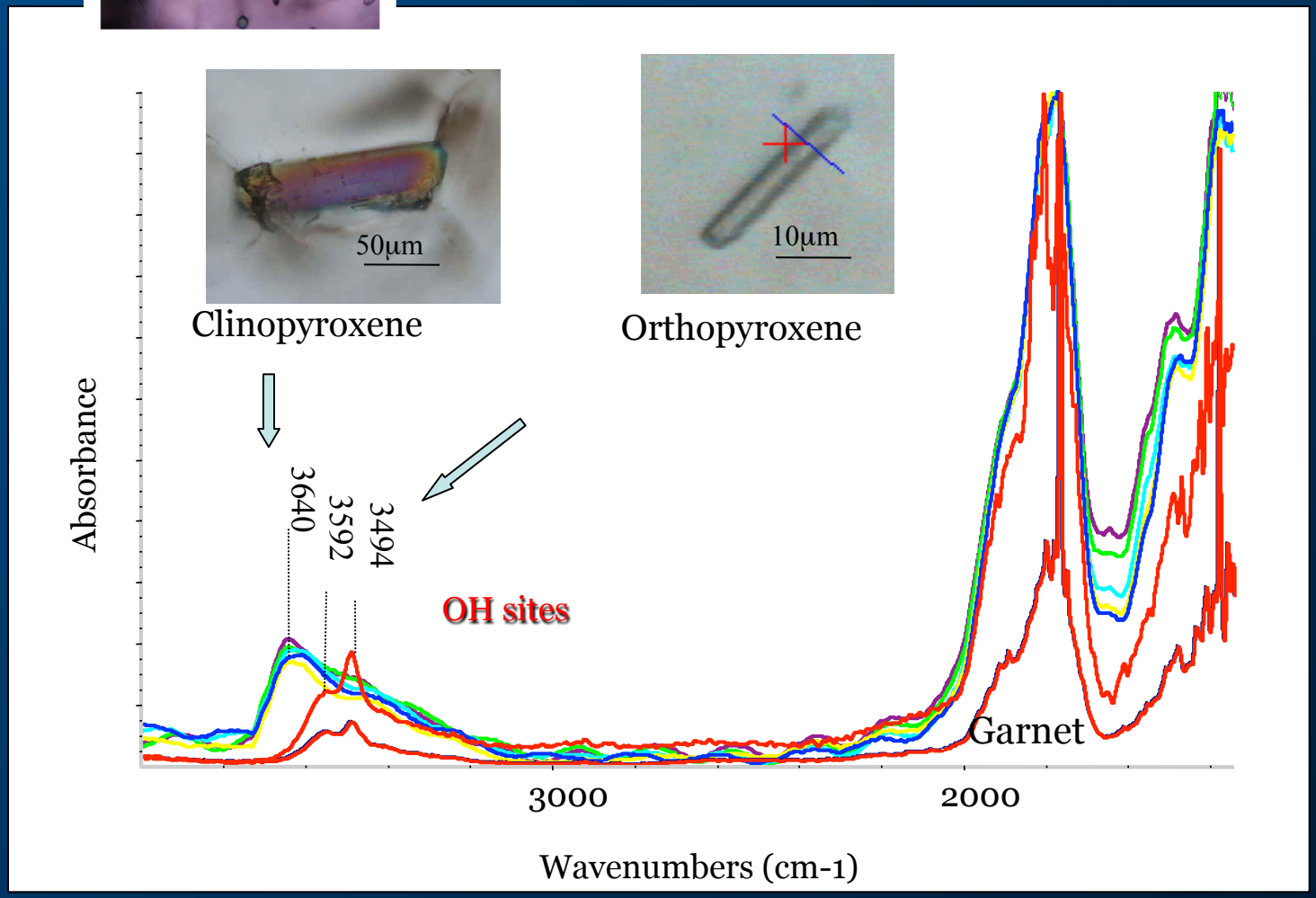
Analysis achieved with aperture, confocal, of 3x3 µm²

N. Guilhaumou et al.

Inclusions in rocks



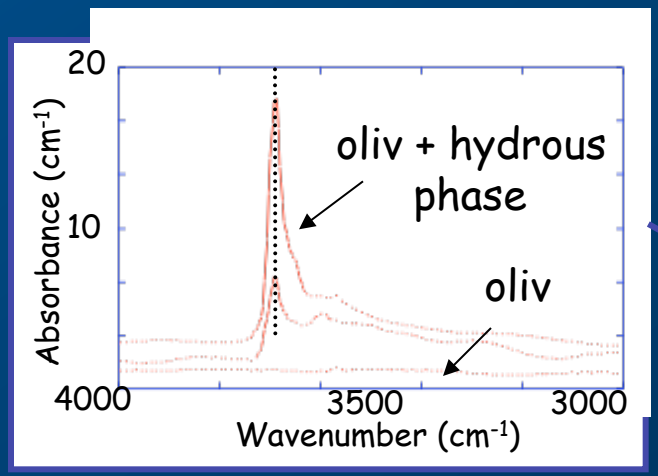
4000 to 7000 ppm wt H20
in cpx and opx, nothing garnet

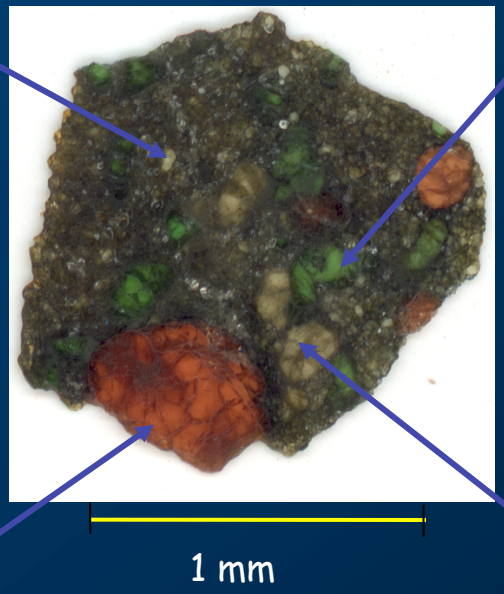


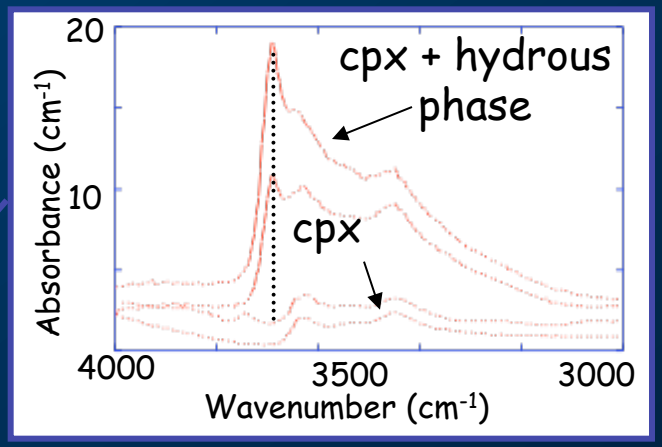
N. Guilhaumou, P. Dumas Oil & Gas Science and Technology - Rev. IFP, Vol. 60 (2005), No. 5, pp. 763-779

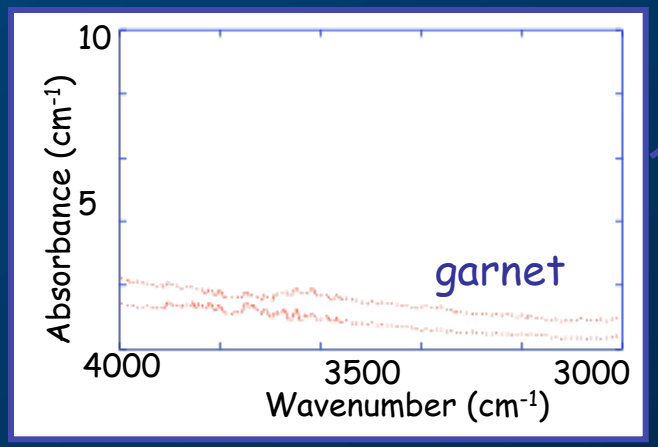
IR spectra of phases in garnet lherzolite: Example from Thaba Putsoa

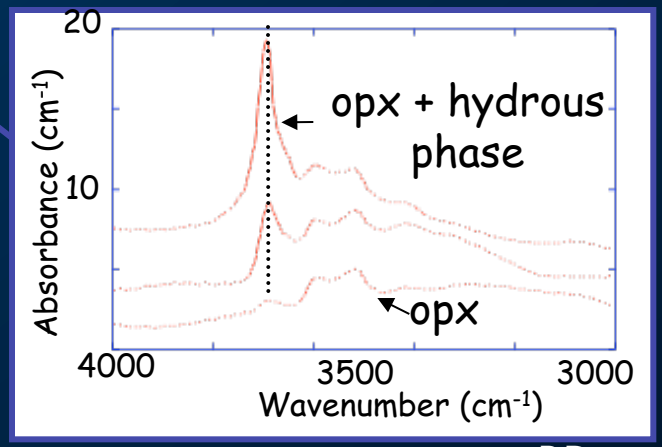
Hcpx > Hopx>> Holiv >> Hgnt (Hsp = 0)



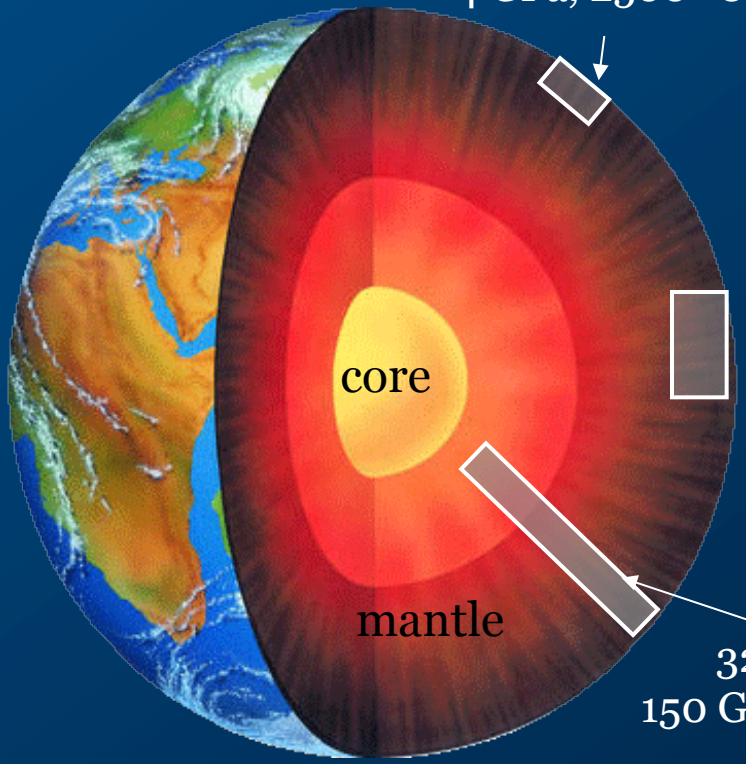








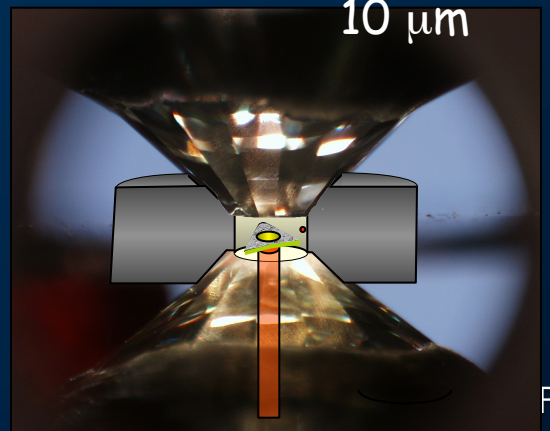
The field has been historically leaded by Earth Science discipline



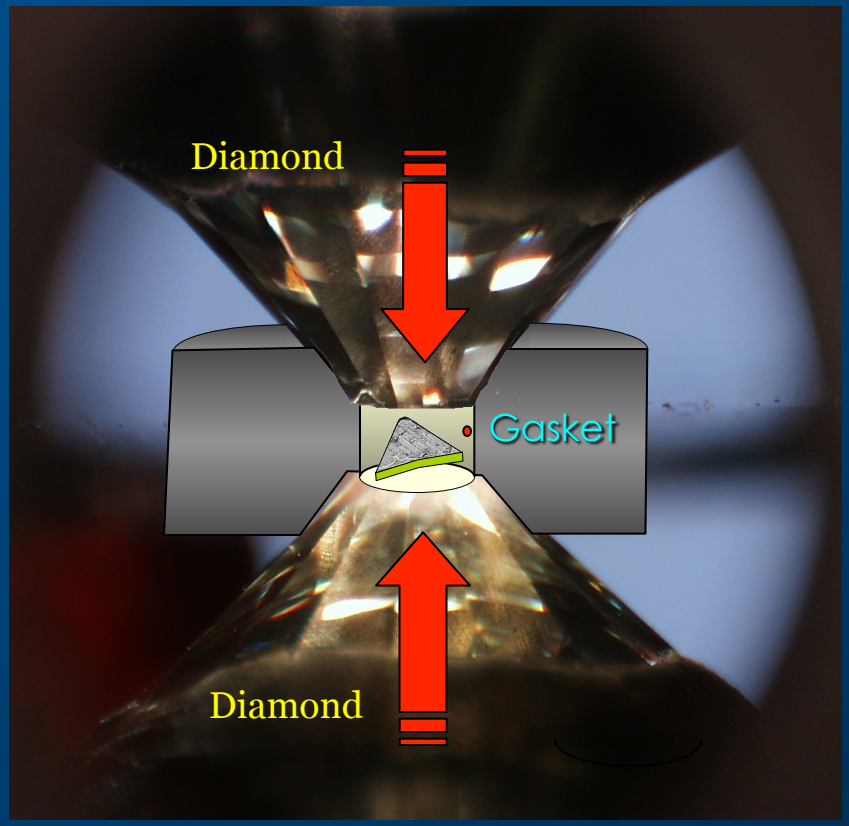
0.1 cm

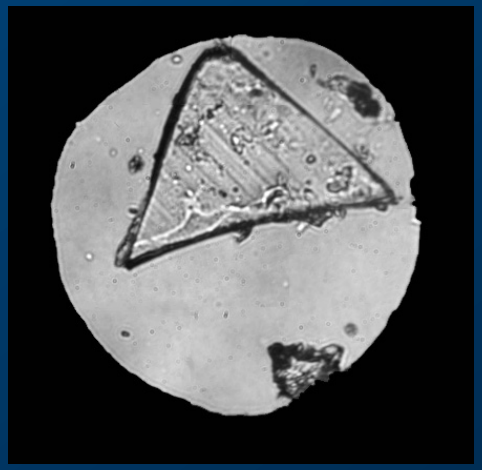
100 μm

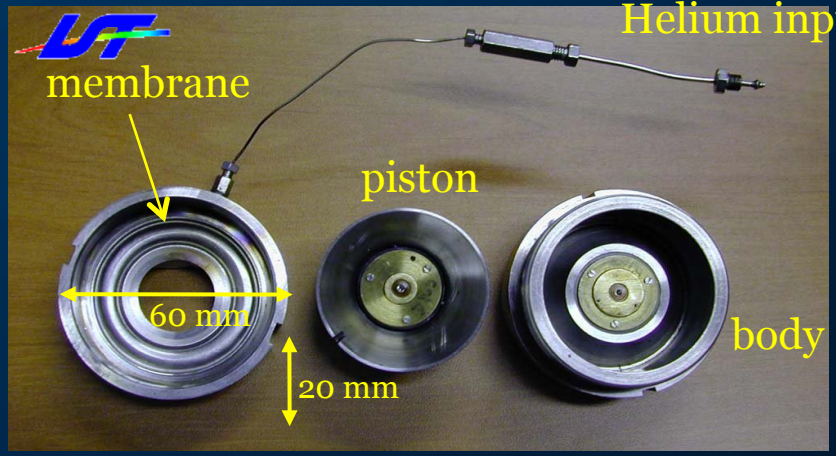
10 μm



The Diamond Anvil Cell







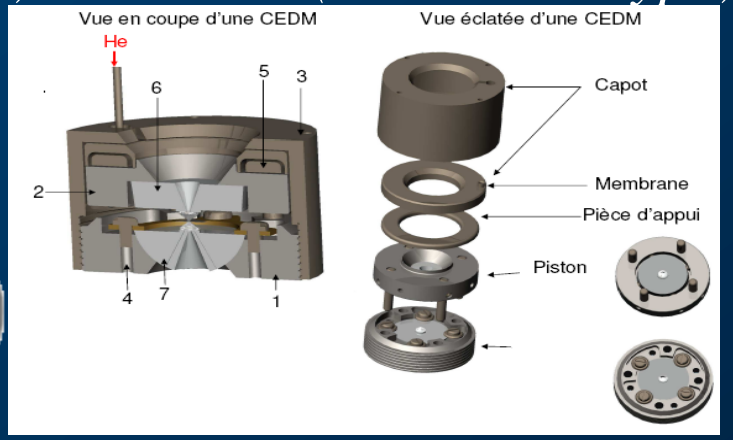
Type of DACs

Many can be accomodated with commercial optics, but not all!

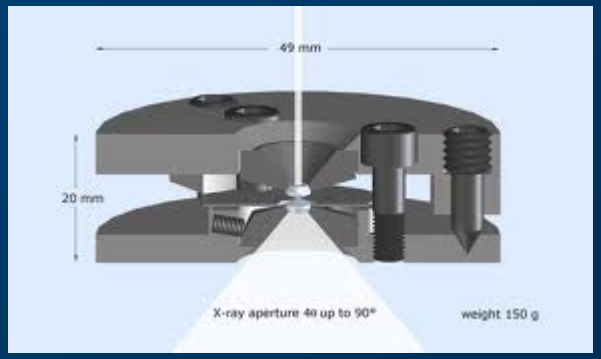
Ultra-small (Tozer)

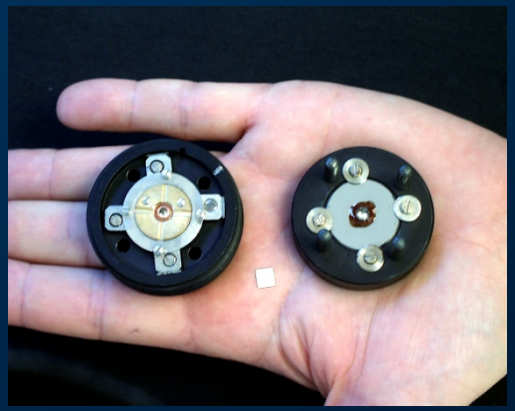
US (Mao type)

EC (Le Toullec type)

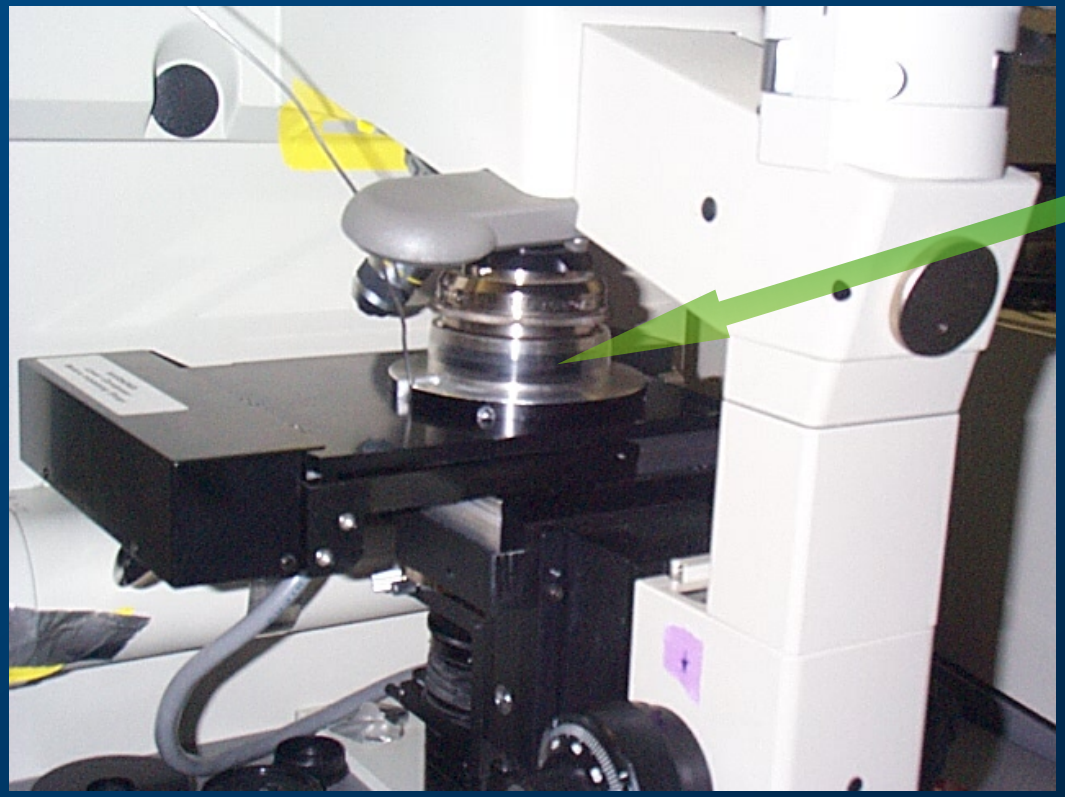


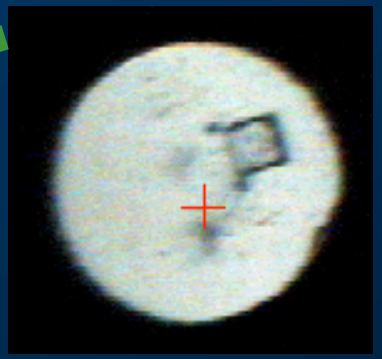
Simple (Boehler)





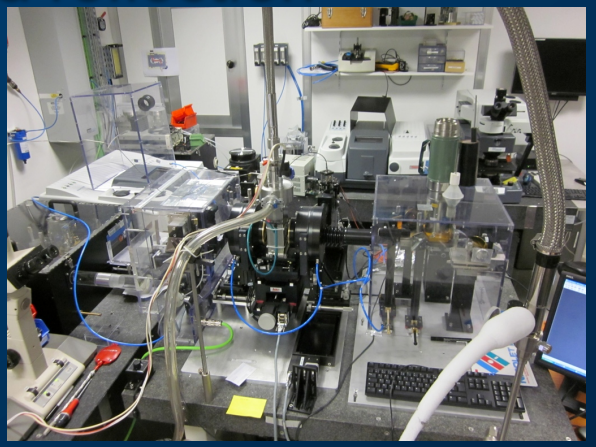
DAC cell and infrared microscope





Home made microscope

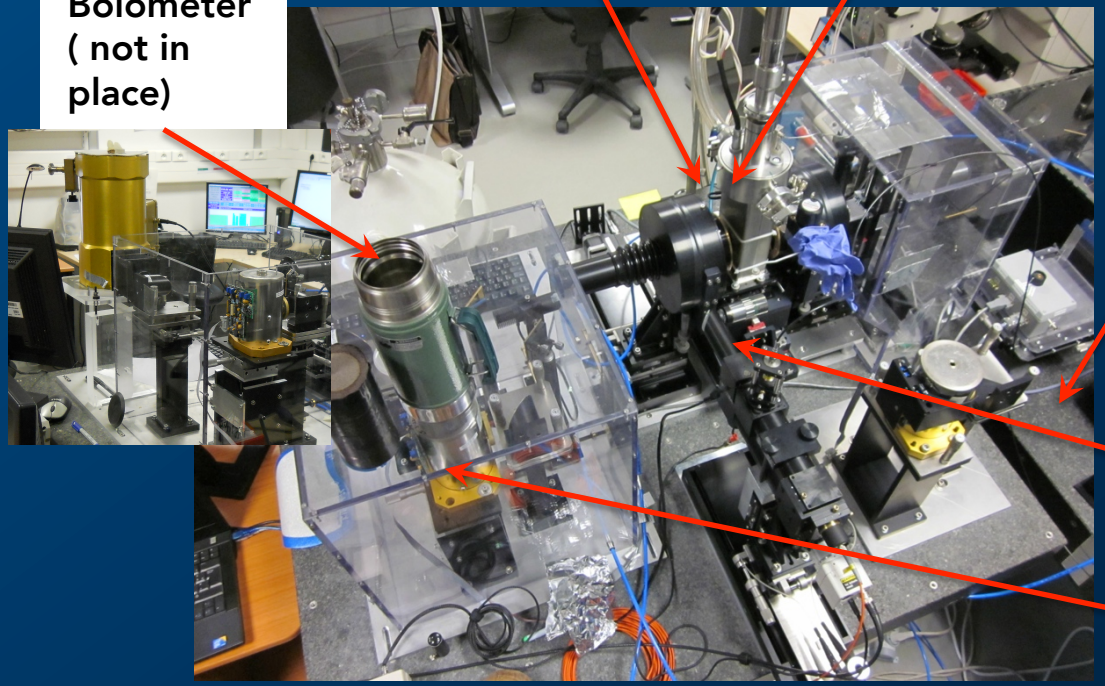
Complete Horizontal microscope , for both Raman and IR, in the mid- and far-IR, in transmission and reflection



X,Y,Z stage for aligning a cryostat-containing DAC

cryostat

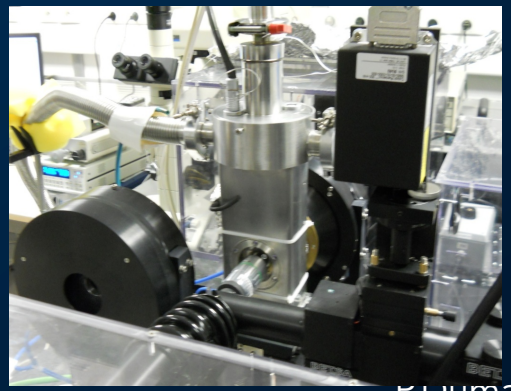
Bolometer (not in place)

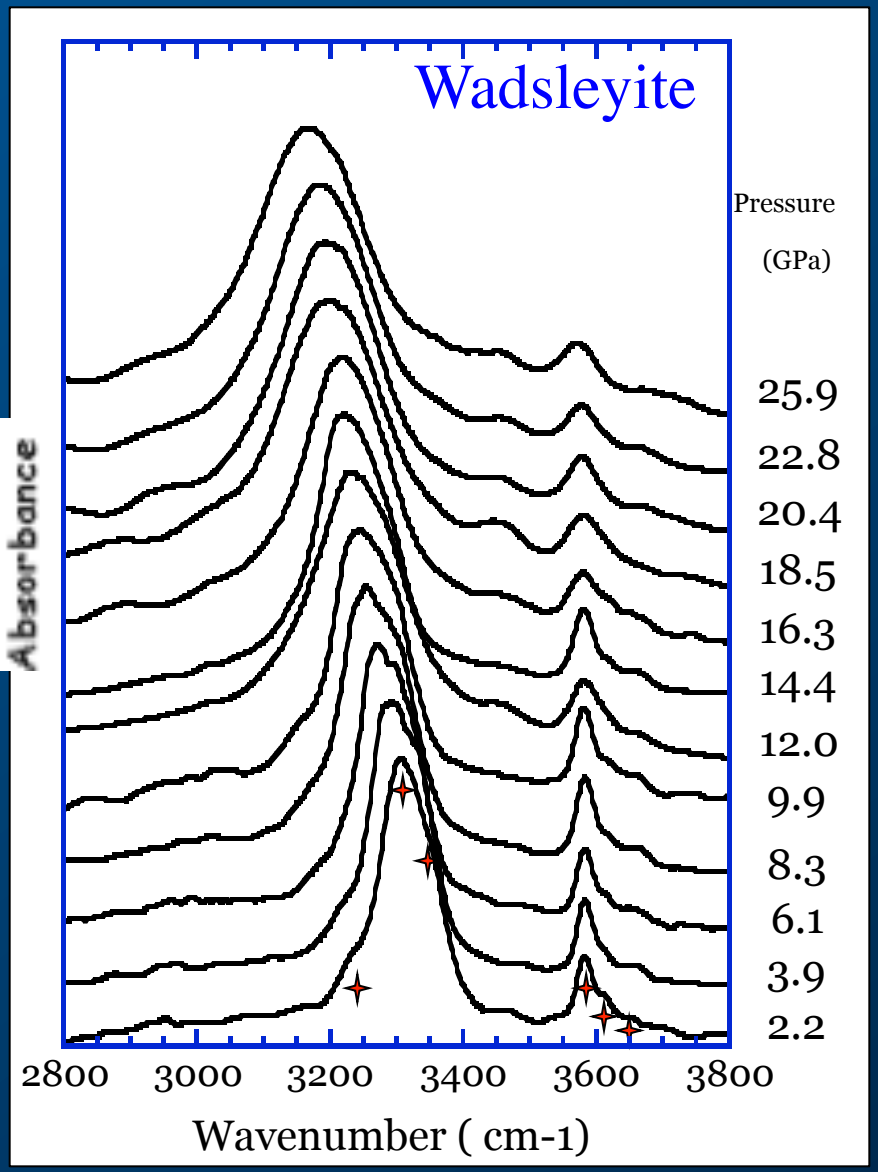


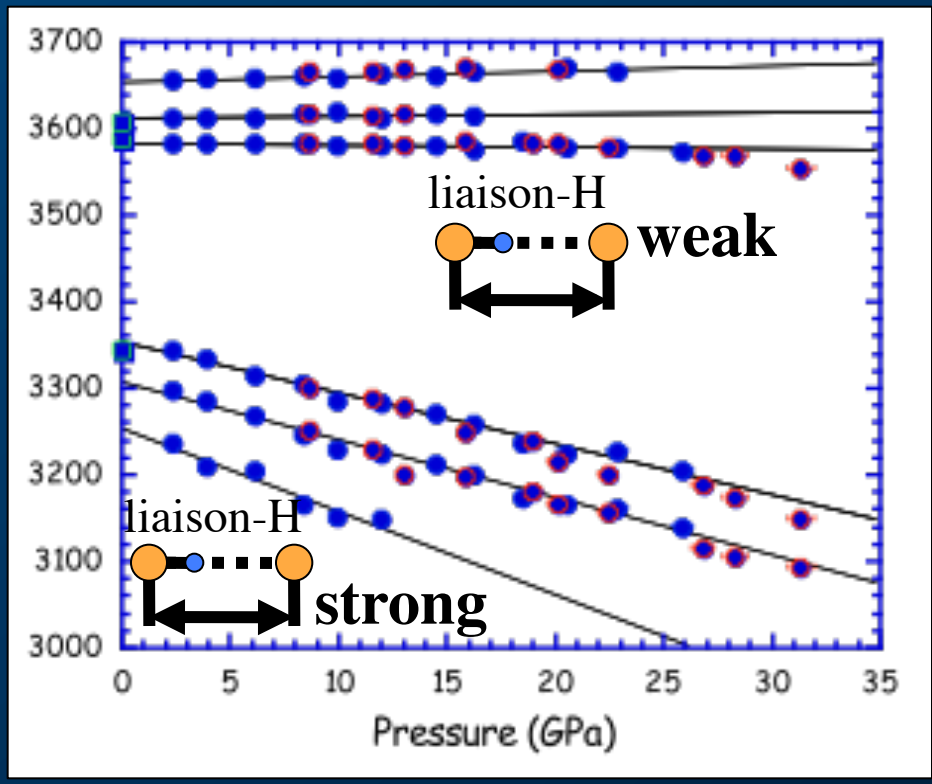
MCT + Bolometer in reflexion (not seen in the picture)

Raman Head

MCT







Corresponding to O-H…O de ~ 3.05 Å et ~ 2.85 Å

E. M. Chamorro Perez ; I. Daniel ; J.-C. Chervin; P. Dumas ; J. Bass. ; T. Inoue Physics and Chemistry of Minerals 2006, vol. 33, no7, pp. 502-510

Superionic phase of NH3

- Like Water, NH3 is a simple molecule capable of exhibiting « exotic » properties (plasticity, superionicity) under extremes conditions.

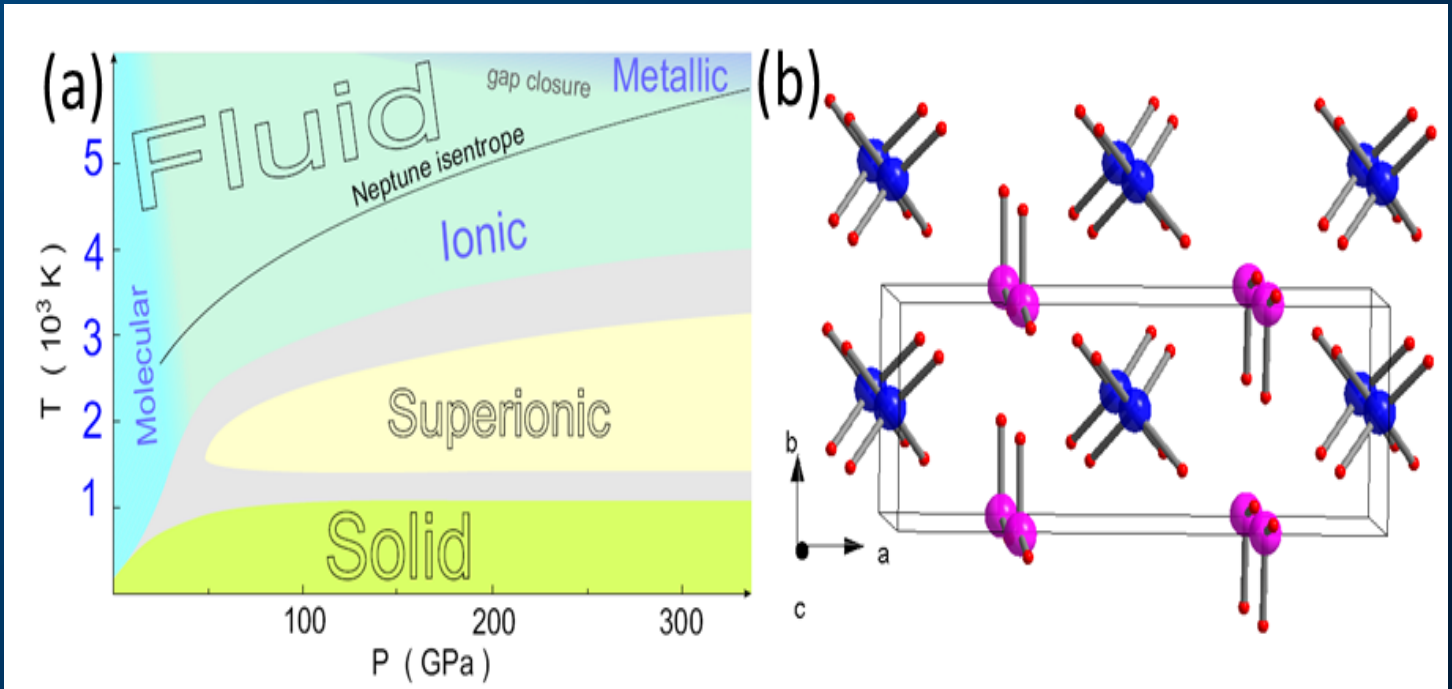
- Water and NH3 are the main constituents of Neptune, Uranus…

- In « normal » conditions, ammoniac ice is a molecular solid, with strong covalent bondings, and weak hydrogen bondings.

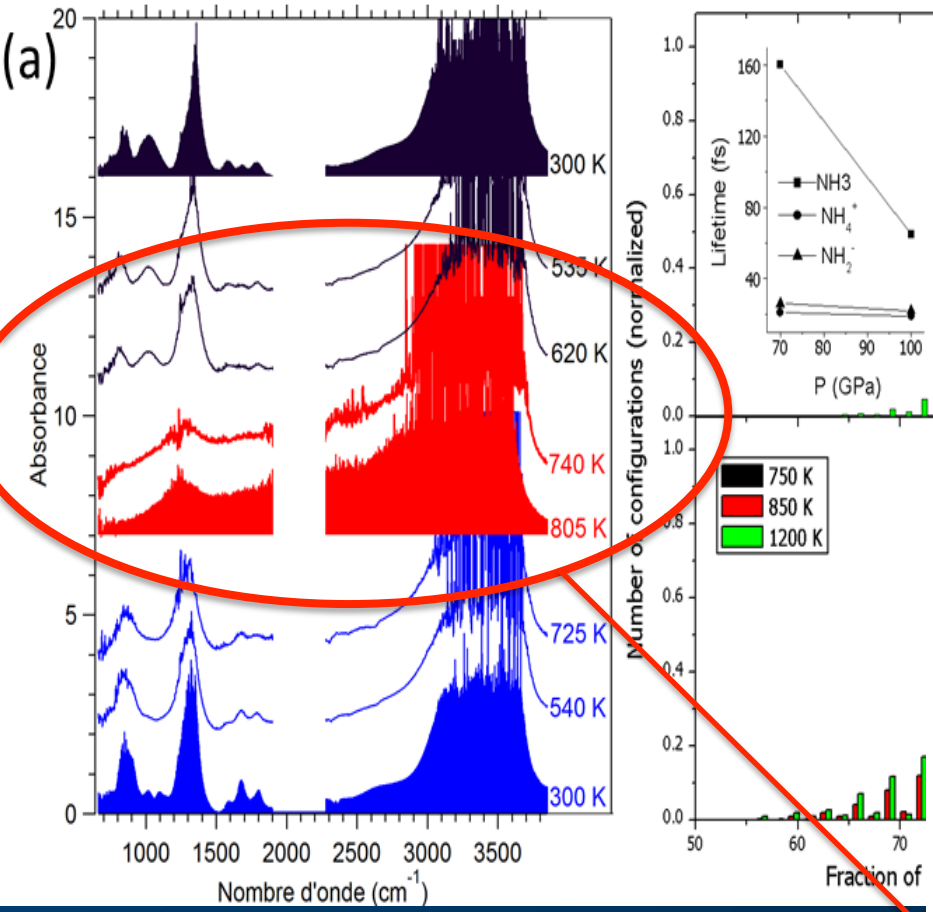
- Under high pressure (~10^6 atm or 1 Mbar) ,like in planet interior, the bondings are modified and ressemble more to ionic ones

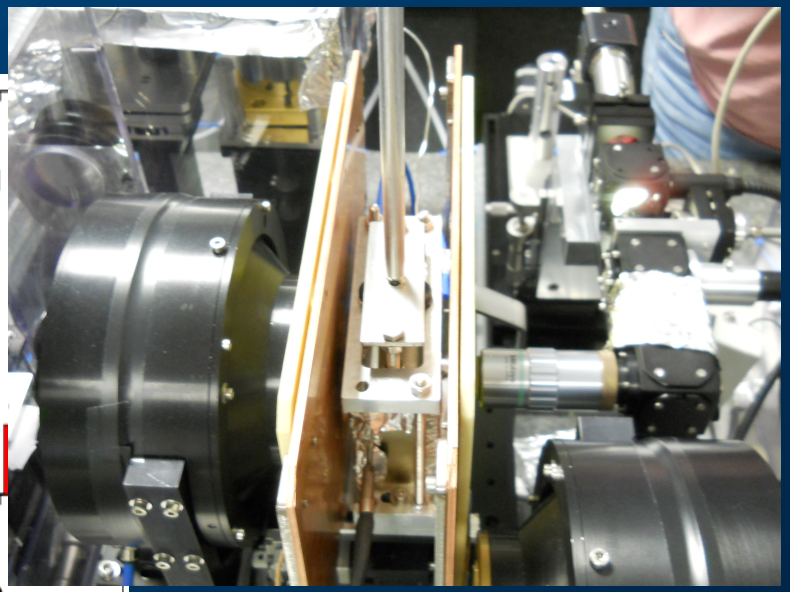
Superionic phase of NH3

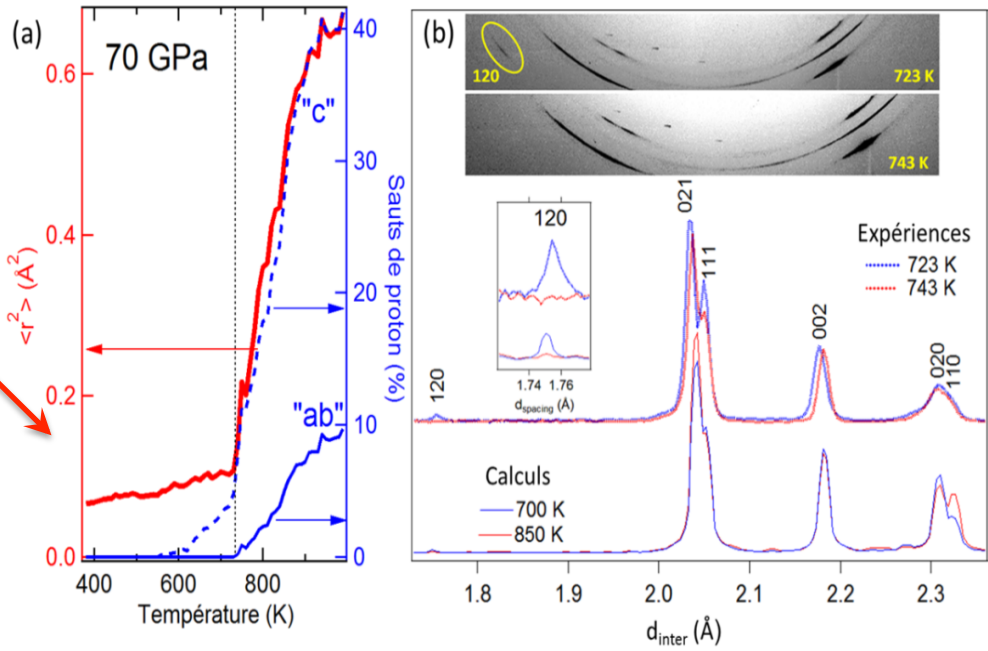
It has been predicted, at high P and high T, a superionique phase (matter exhibits simultaneously a solid and liquid character , with a high hydrogen mobility inside the nitrogen atoms network.



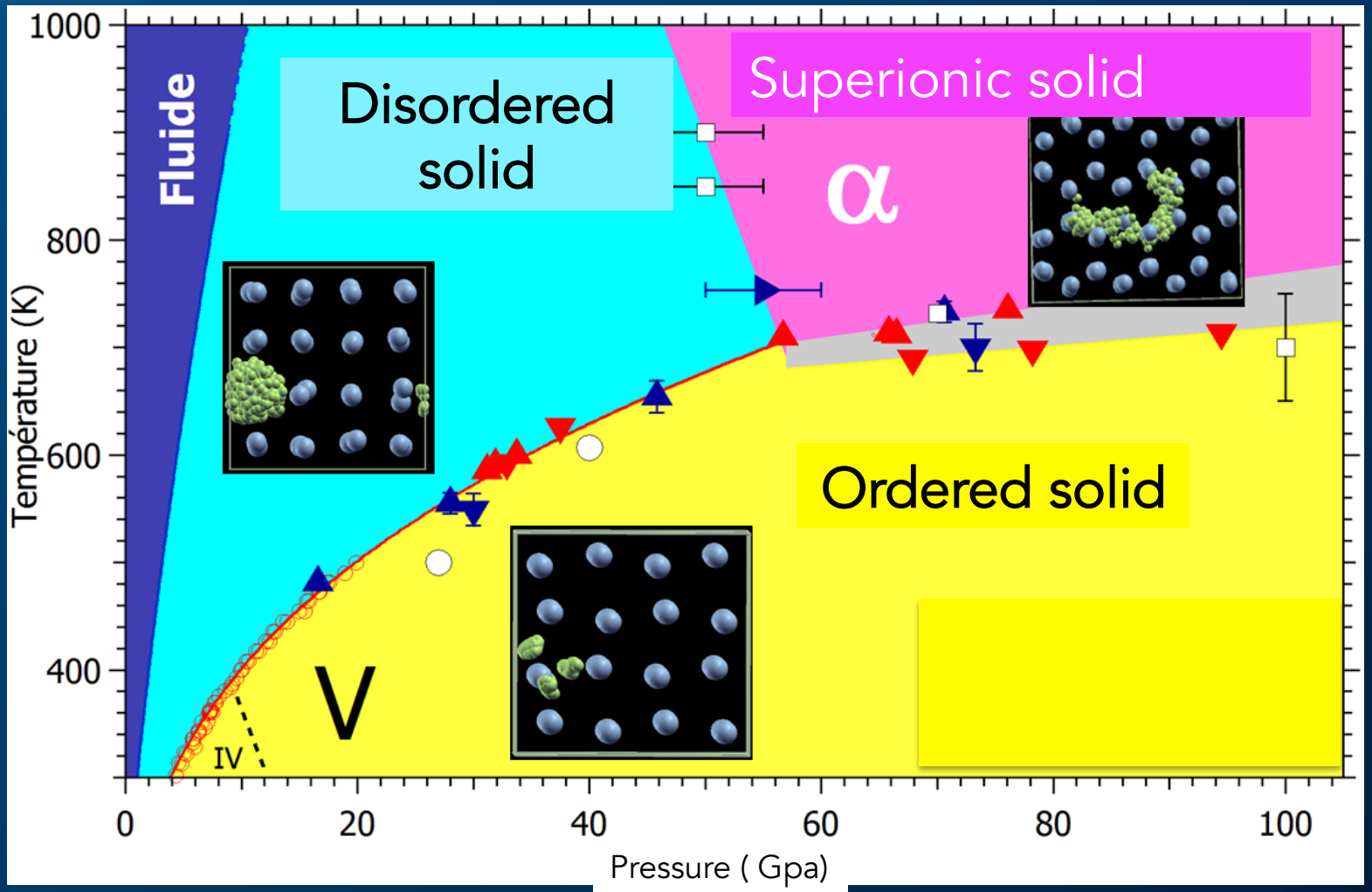
Superionic phase of NH3







Phase diagram of NH3

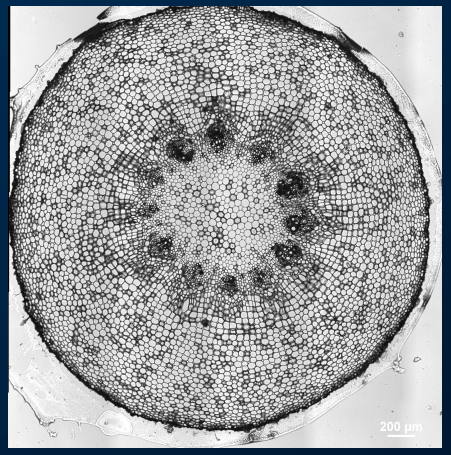


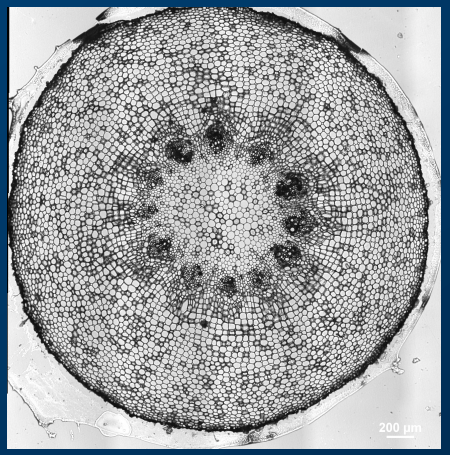
Synchrotron IR micro-spectroscopy and Environmental Science: Phytoremediation

P.Dumas

Ni-hyper accumulating and Non-hyper accumulating Roots from the plant (Senecio coronatus)

Aim : comparing and finding differences in the IR spectra of Nickel hyperaccumulating and non-hyperaccumulating genotypes of plant roots from South Africa (Senecio coronatus) growing on the same ultramafic soil, naturally enriched with Nickel, which show different response in terms of metal uptake.

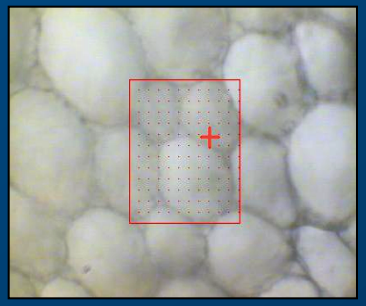


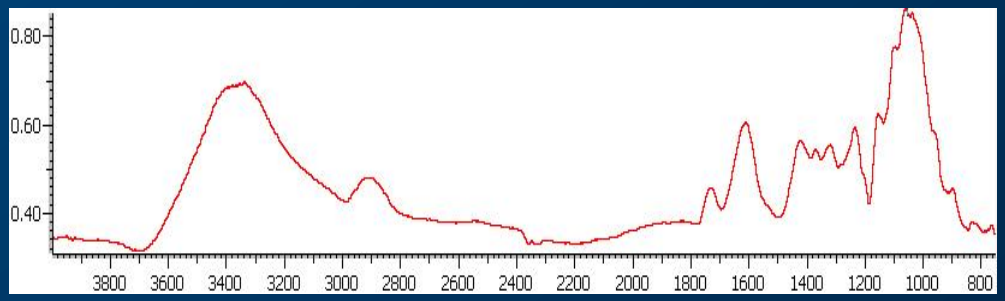


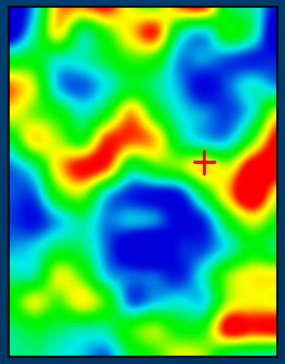
Soil contamination with heavy metals has become a worldwide problem, leading to losses in agricultural yield and hazardous health effects as they enter the food chain (Babaoglu et al). Whereby living plants are used for soil contamination uptake, this approach exploits the ability of various plant species to grow up in high metal environments while accumulating large amounts of toxic elements.

Chemical imaging at diffraction limit in the endodermis

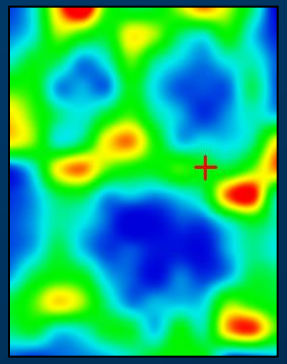
Visible Image



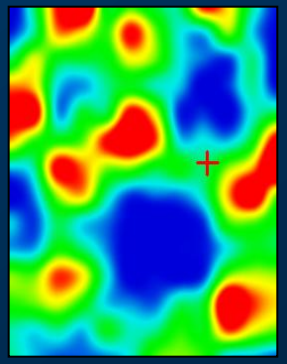




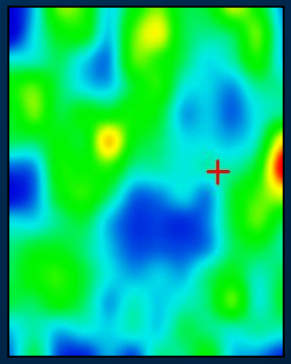
Polysaccharides



Carbohydrates



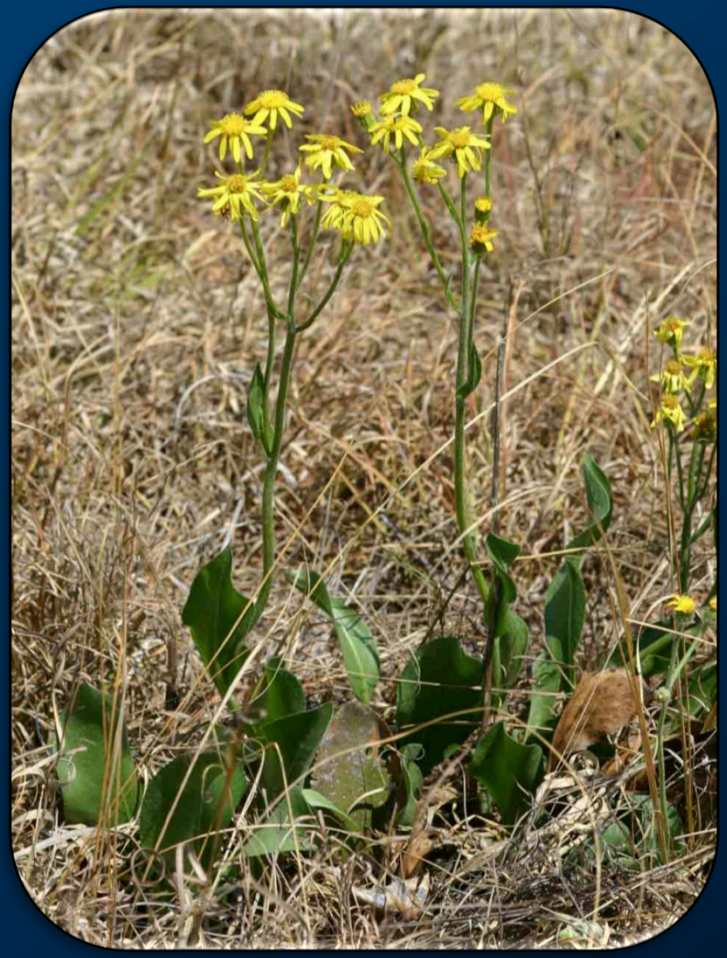
Protein



Lipids

Nickel Hyper-accumulator Roots from the Plant (*Senecio Coronatus*)

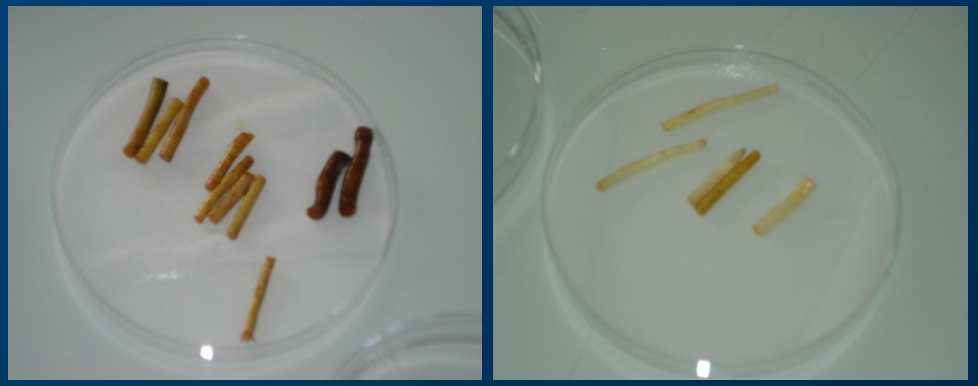
✓ **Whereby living plants are used for soil contamination uptake.**

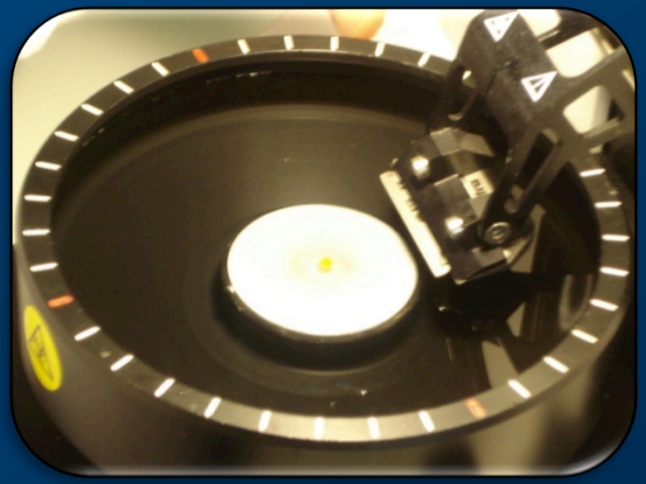


Sample Preparation

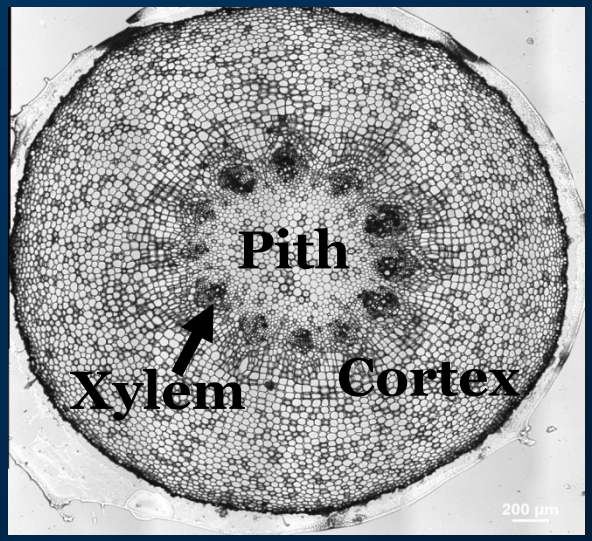
- **Sectioning roots with thickness of 50 microns**

Ni-accumulator **Non accumulator**



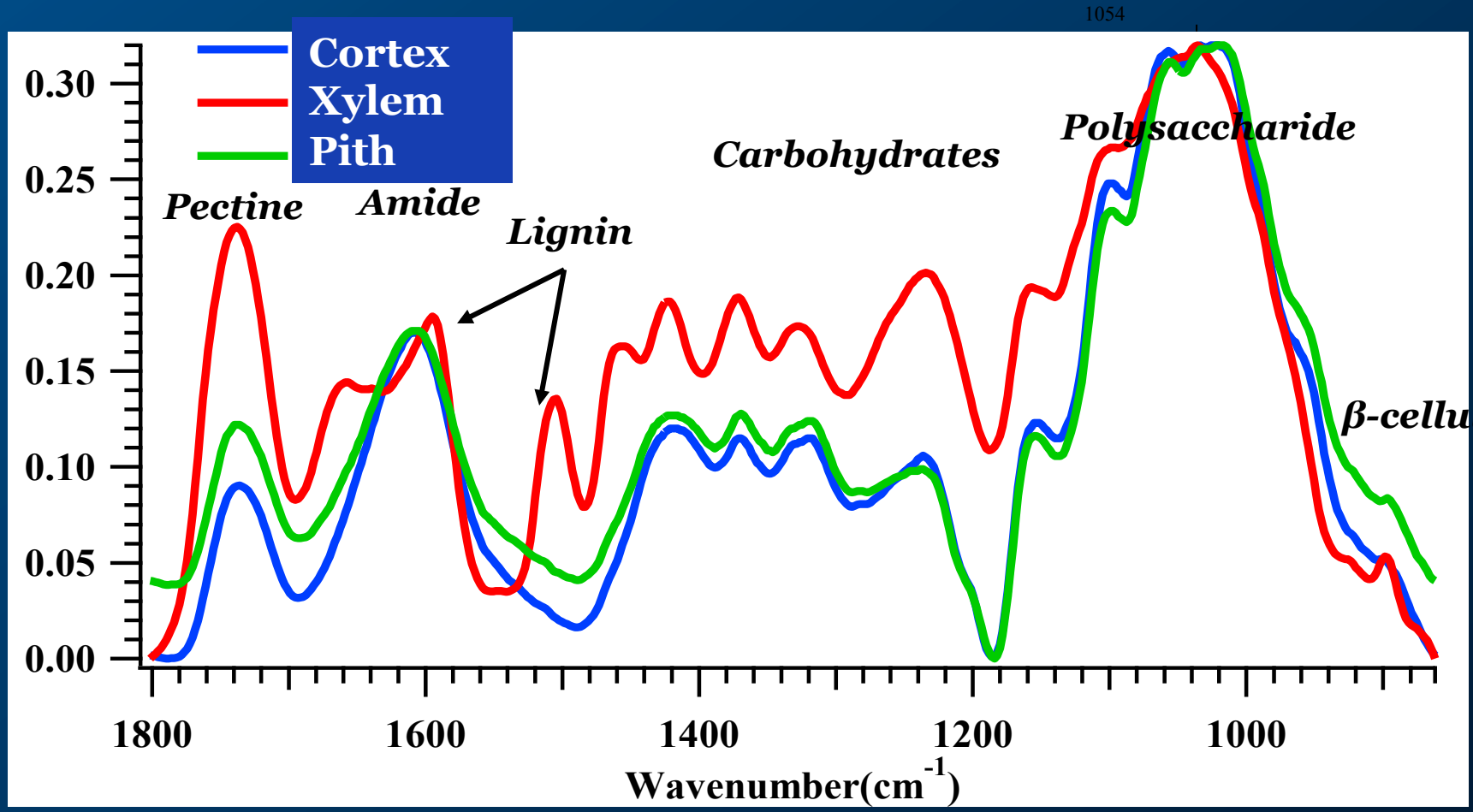


Vibratome



Microscopic view of the root Cut-cross section

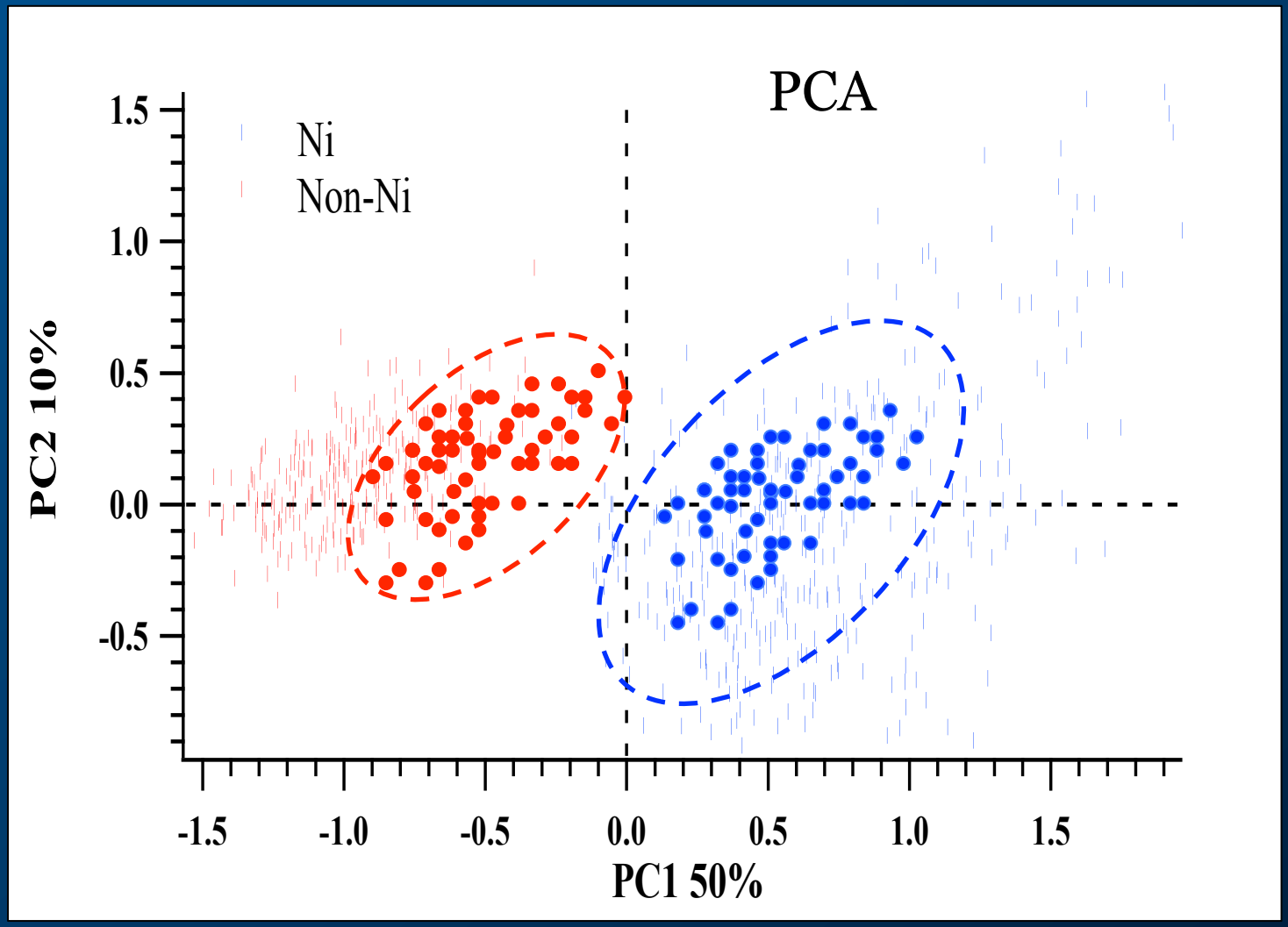
Band assignments



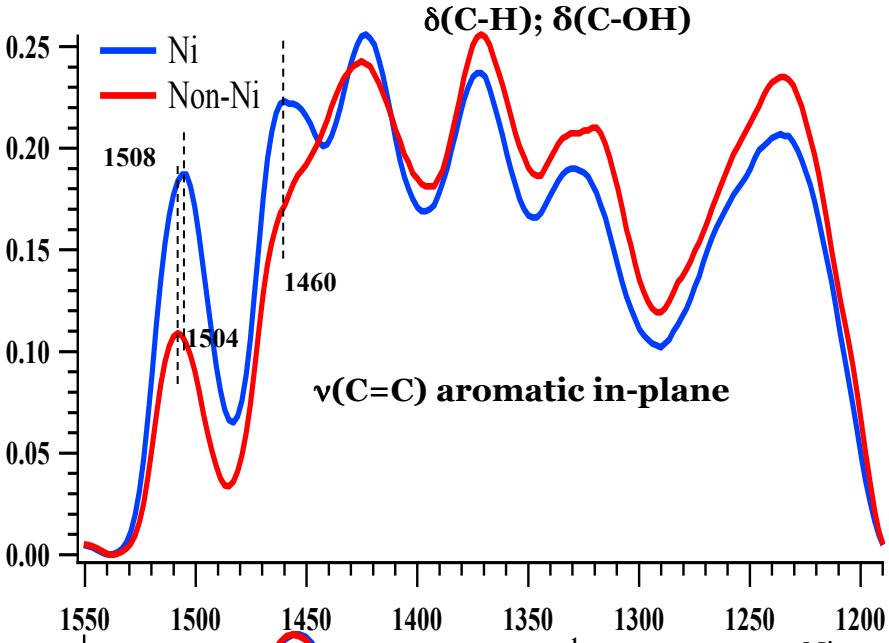
Deep into the analysis

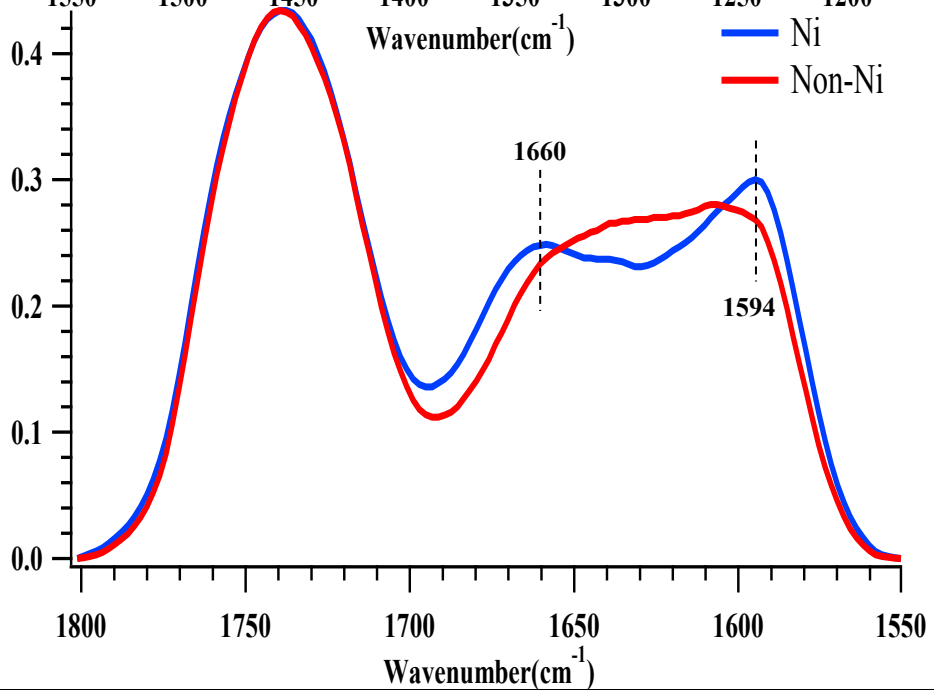
- ✓ Chemical structure of Xylem is different than the other part of roots
- ✓ **Principal Component Analysis** to compare Cortex and Xylem from both samples individually.

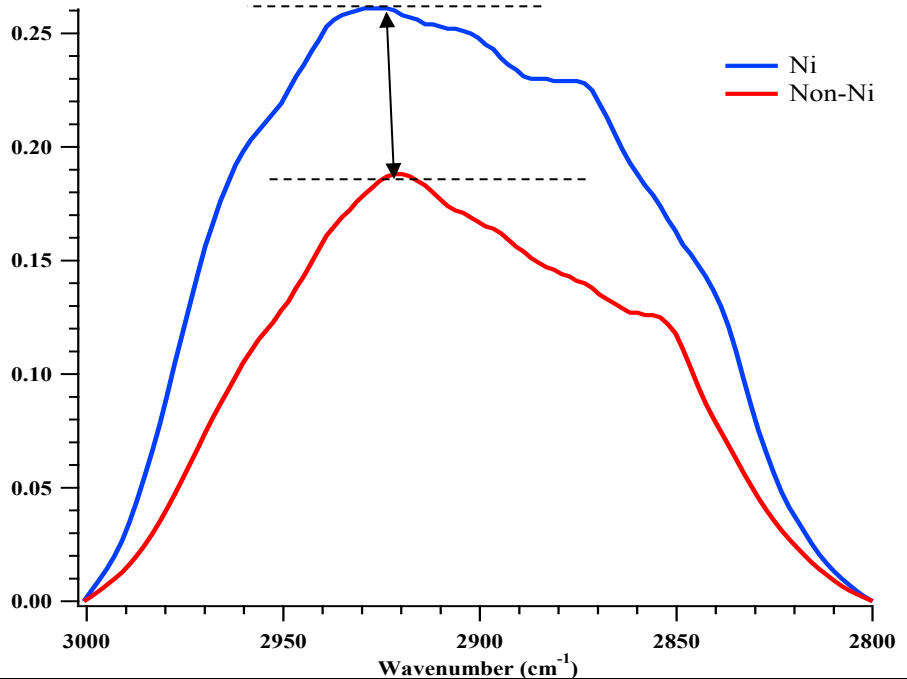
Cortex



PCA-Loadings







What was concluded?

☑ Frequency shift at the bands of Ni accumulator, structural changes:

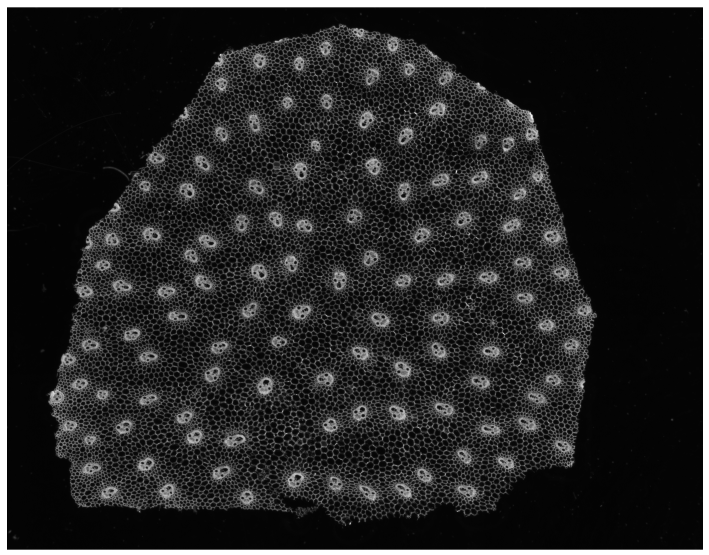
(*chemical bonding or rearrangement*).

☑ The content of pectin, lignin, and lipids bands are strongest in Ni accumulator (*natural response*).

Lignocellulose related to conversion for biofuels

P. Robert, B. Bouchet, M.F. Devaux, L. Jouanin, L. Saunier, F. Guillon INRA Nantes and Versailles
F. Jamme INRA and SOLEIL

General Context



Corn stem

The production of fuel ethanol depends almost entirely on corn grain. This industry, as well as the use of fuel ethanol itself, is rapidly expanding and beginning to increase prices of corn for food and the downstream animal products. It is important to modify plants for use as a feedstock for biofuels.

See for Ref: « Structural and chemical properties of grass lignocelluloses related to conversion for biofuels « W. F. Anderson and D. E. Akin in J Ind Microbiol Biotechnol (2008) 35:355–366

Lignocellulose related to conversion for biofuels

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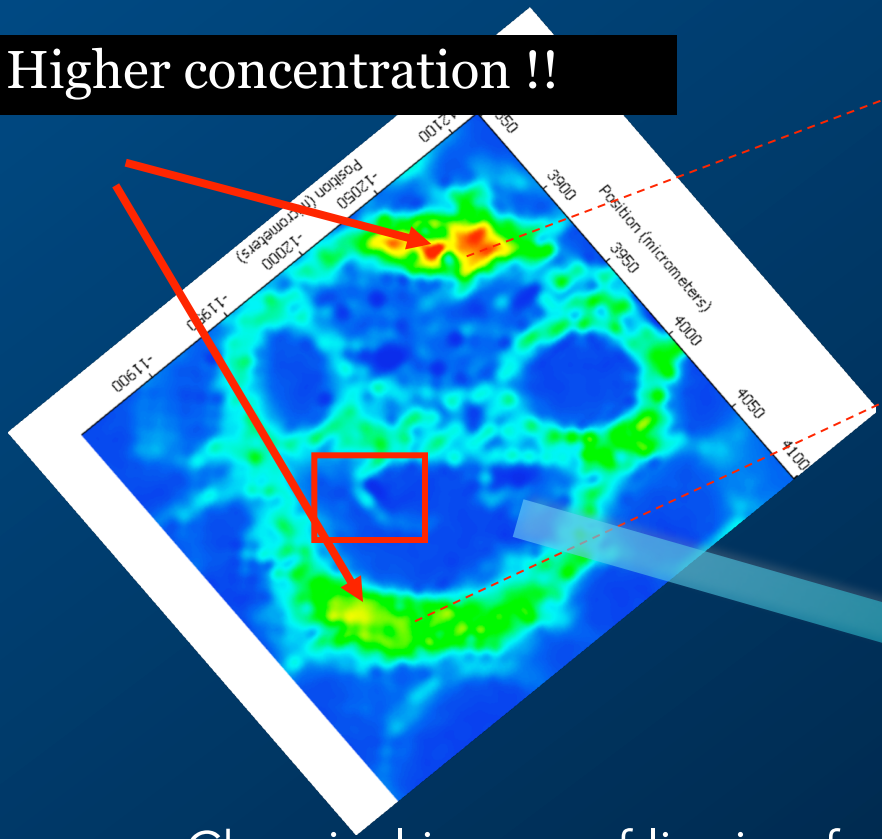
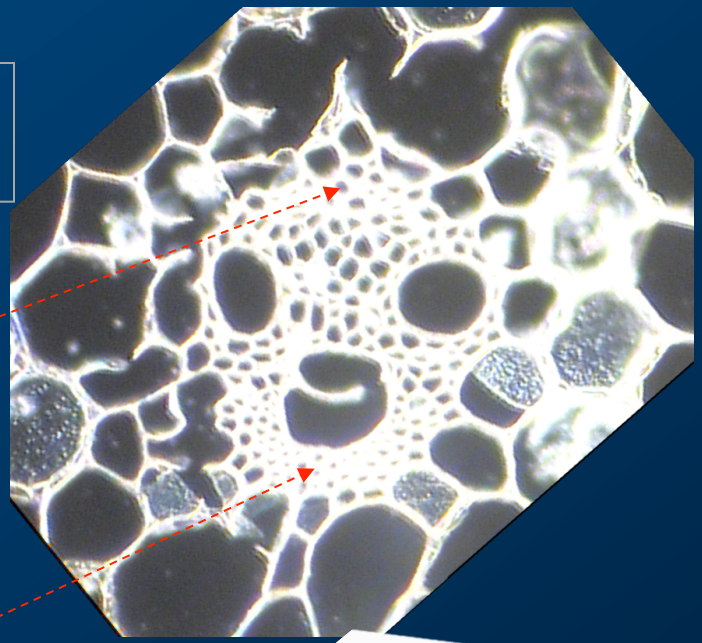
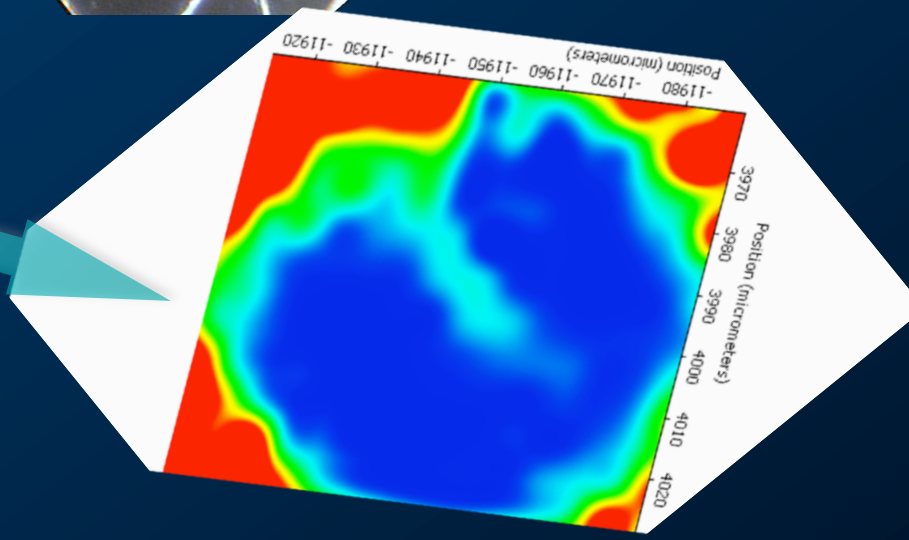
Higher concentration !!







Chemical image of lignin of modified corn stem

Summary

- There are 28 IR beamlines in the different synchrotron facilities around the world.

- There is an increasing interest in Material science in Extreme Conditions, Earth science , Space and Environmental Science

- It is essential to combine experiments, in particular with X-ray microprobes (micro-XANES, XRF, XRD…)

- Also, Raman microscope, MEB availability within the same synchrotron building is very desirable

- Sample preparation is more demanding than others discipline. Special care, tools should be taken and developed for such a purpose