INEL INNOV

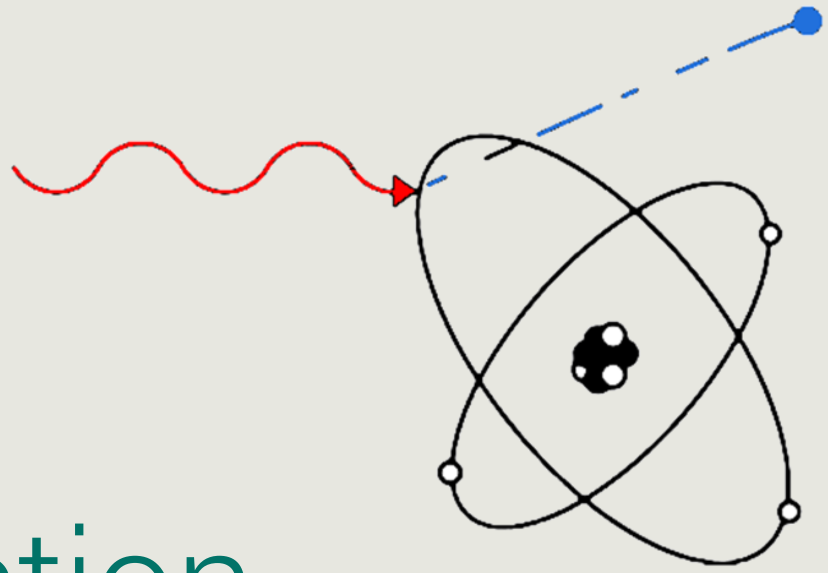
13th workshop

« Combined Analysis Using X-Ray Scattering »

Instrumentation

July 3rd -7th 2023, Caen

Henry PILLIERE
INEL INNOV

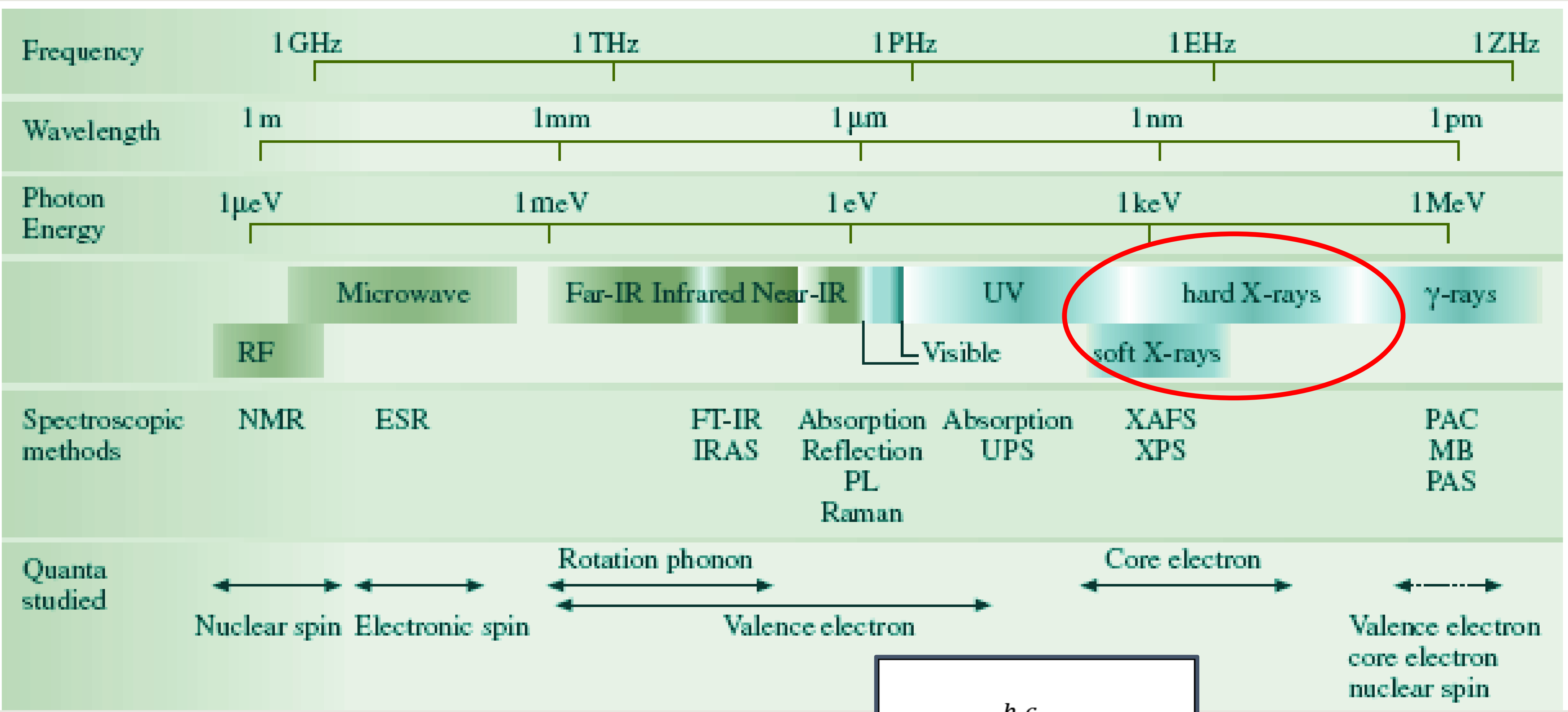


Wave matter Interaction

When a photon does encounter an atomic particle, it transfers energy to the particle. The energy may be reemitted back the way it came (reflected), scattered in a different direction or transmitted forward into the material.

Wave matter interaction

The energy of photons used for optical spectroscopic measurements of various quanta



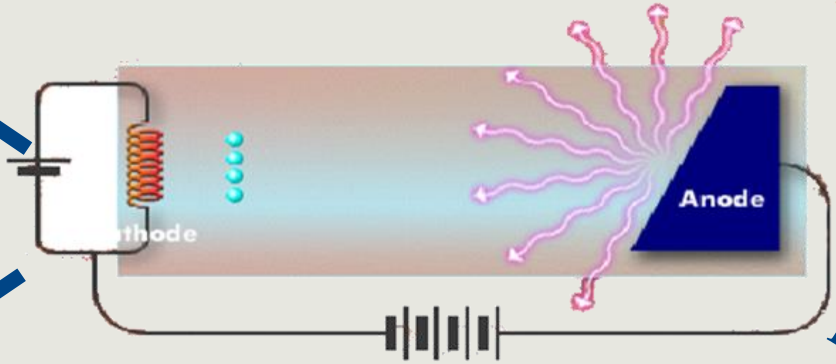
$$E = \frac{h.c}{\lambda} = h.\,v$$

EHz : exahertz (10^{18}) - ZHz : zettahertz (10^{21}) - YHz : yottahertz (10^{24})

Wave matter interaction

The energy of photons used for optical spectroscopic measurements of various quanta

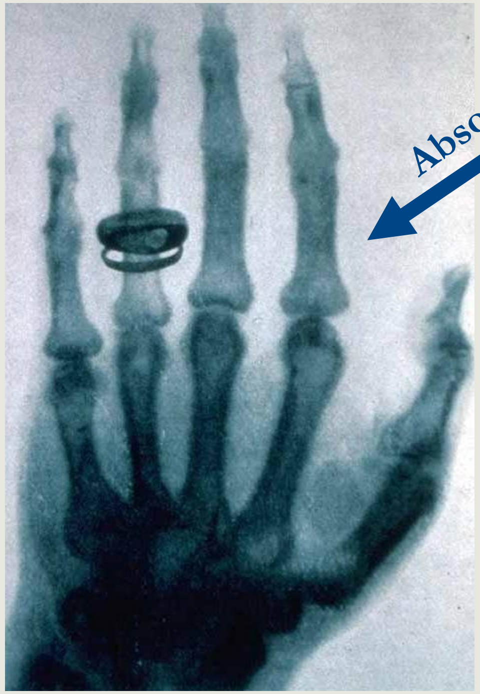
X-rays Production : classically by excitation of external electronic level with electron beam



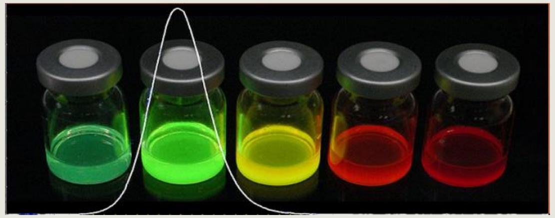
Reflection

Diffusion

Absorption

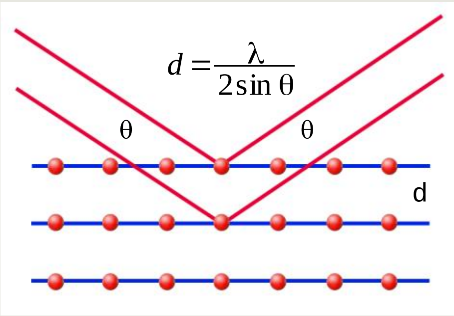


fluorescence



Diffraction

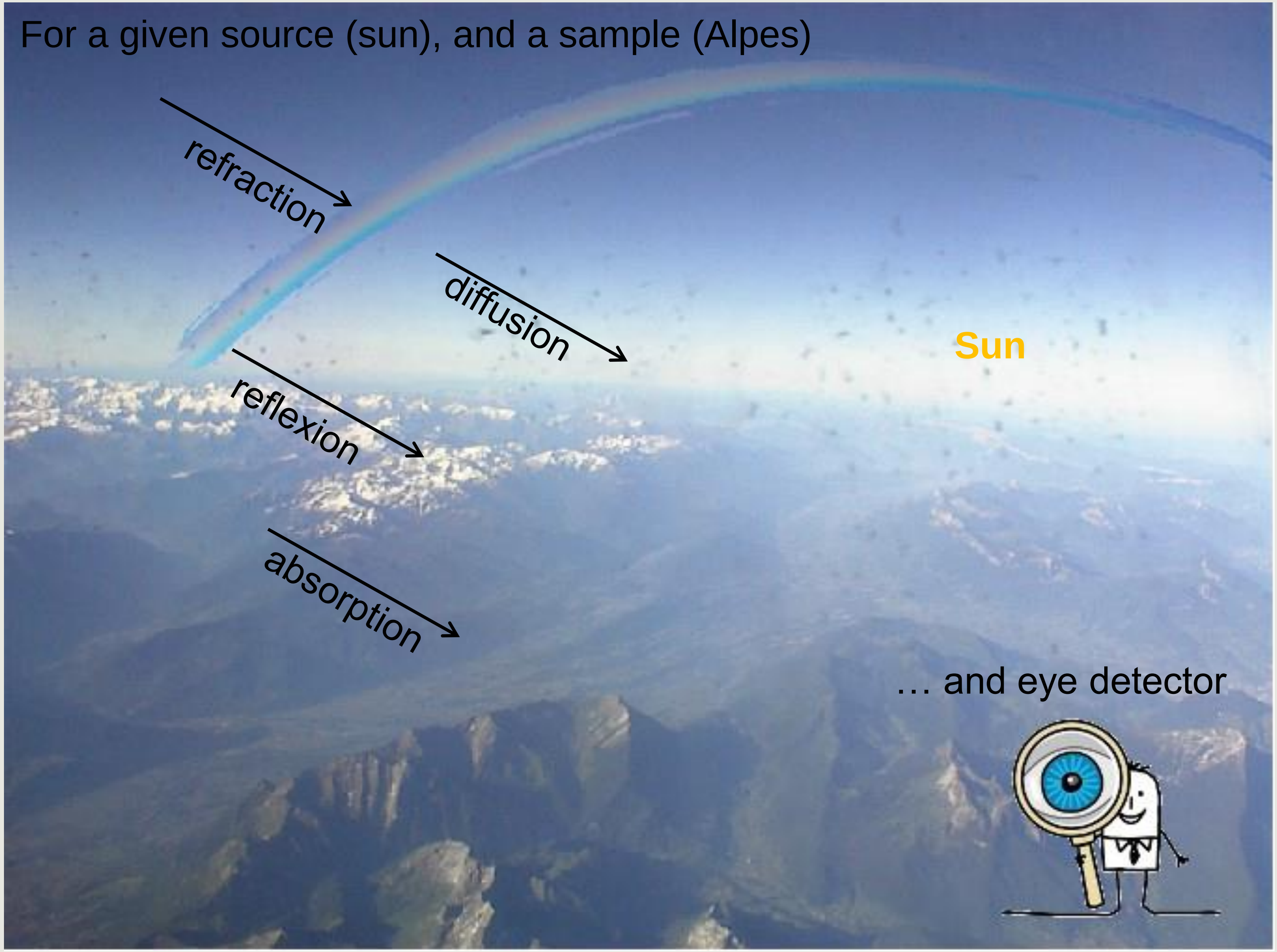
Bragg's law



Wave matter interaction

Instrumentations using radiation for material analysis need to be optimized :

- source characteristics
- detection characteristics
- sample environment
- mechanical design



Wave matter interaction

We can propose instruments for this expertise:

- X-ray diffraction : phase analysis, identification and quantification of phase
- X-ray diffusion (SAXS) : nanoparticles morphology
- X-ray fluorescence : elemental analysis
- X-ray imaging : image of X-ray absorption
- X-ray reflection : nanometric coating analysis

Focus on X-ray diffraction

Wave matter interaction

Which material is able to diffract ?

Anything which has a structure at the nanometric scale, with enough contrast.

Structure : ordering at the atomic scale
Then, mostly crystallized material in bulk or powder but even in liquid cristals or in smoke

Contrast : X-ray interacts with electronic level
Then, heavy atoms => high contrast

Each tool or instrument is designed to fulfill a task

According to its characteristics, it will be used in a defined range ...

Or

A tool or an instrument can be designed according to the definition of a need ...

Instrument

A hammer is designed according to the type of nail, and for the destination

=> Same type of instrument can have different design depending on the application

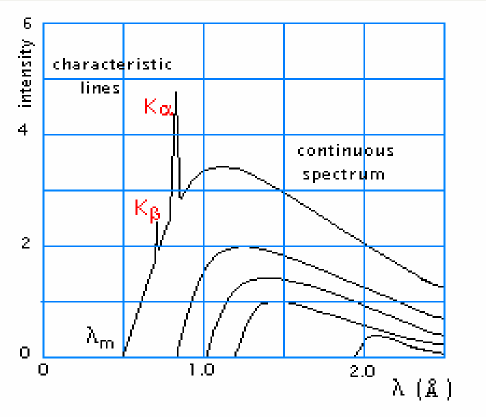
Instrument is designed for the need we are looking for. It allows to measure and quantify physical parameters (length, weight, power, energy, time...)

X-ray diffraction instrument

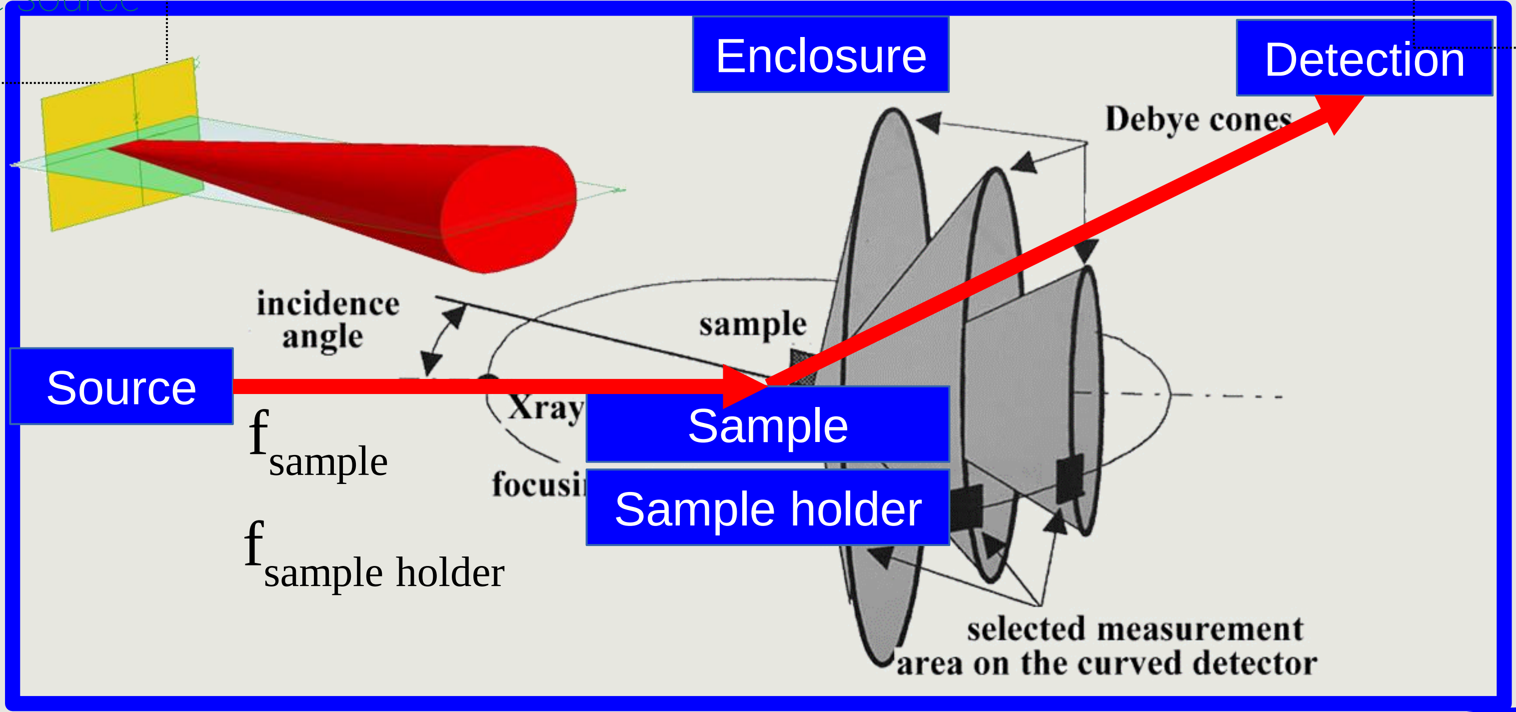
A light emission characterized by :

- a spectral range
- a solid angle
- intensity
- dimension and shape of the source

A detector is characterized by :
- spacial resolution
- dynamic range
- energy resolution
- dimension



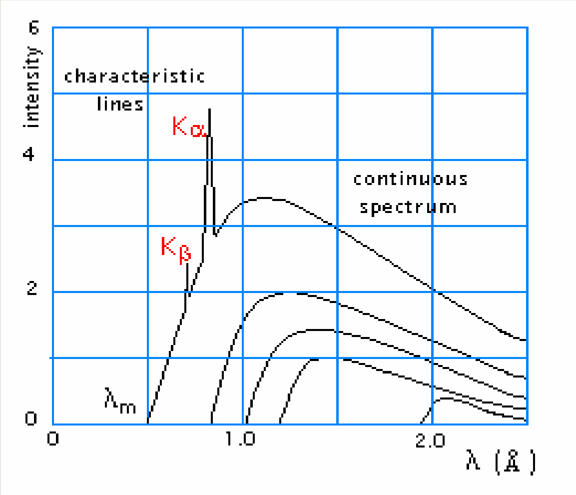
Molybdenum spectrum vs the applied voltage



$f_{operator}$

Most instruments using radiation corresponds to this scheme :
XRD – XRF- FTIR- Raman-UV ...

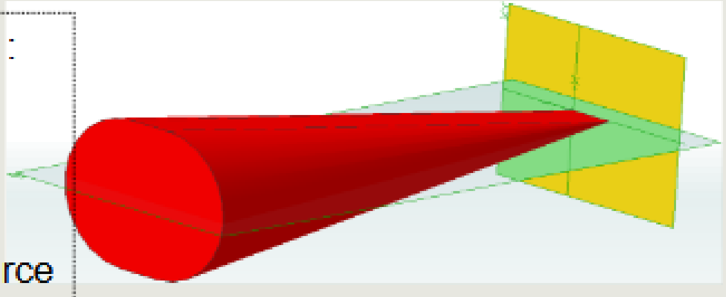
X-ray diffraction instrument



Molybdenum spectrum vs the applied voltage

A light emission characterized by :

- a spectral range
- a solid angle
- intensity
- dimension and shape of the source



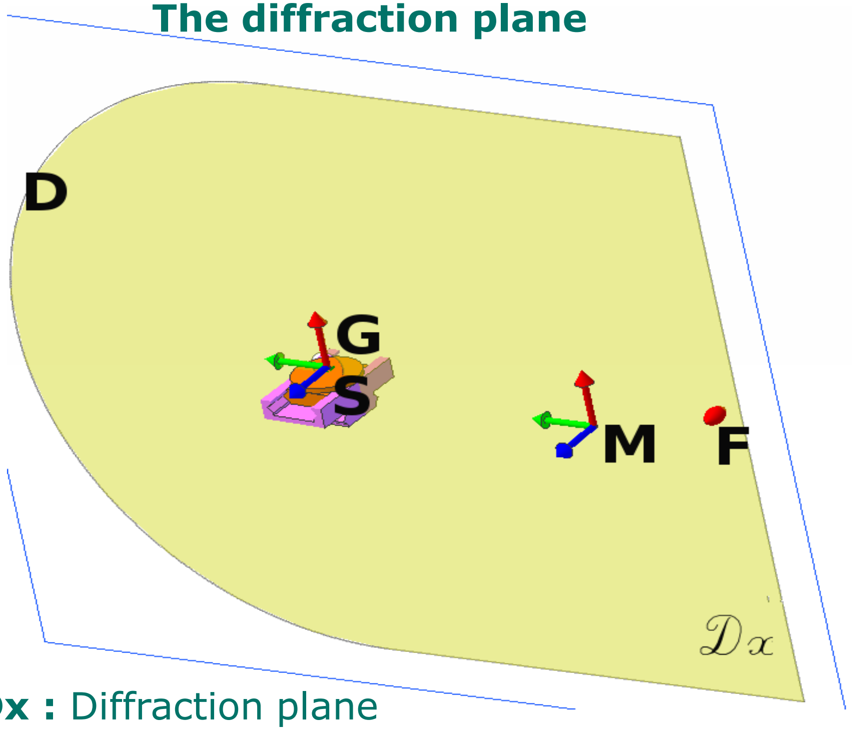
Optimizing the characteristics of a source allows to focus on a given interaction

	fluorescence	imaging	diffraction	reflection	diffusion
Spectral range	large	large	Monochromatic (excepted Laue)	monochromati c	monochromatic
Solid angle	Few degrees	Large (60°)	Small to parallel or focusing	Very small	Very small or focusing
Source size	Small or large	Small for resolution improvment	small	small	small
Source shape	point/linear	point	Point or linear	linear	Point or linear

This is achieved by using appropriate optics (1D, 2D, monochromator, mirror, collimator, slits ...)

X-ray diffraction instrument

The diffraction plane



Dx : Diffraction plane
F : focus of the source
M: Optical position (monochromator, mirror), involving a primary beam deviation
G : Goniometer center where is localized the sample
S : Sample position
D : Diffraction device
Dir X: Direction of the primary beam
Dir Y: Direction perpendicular to the diffraction plane (axial direction)
Dir Z: Direction perpendicular to the sample surface (equatorial direction)

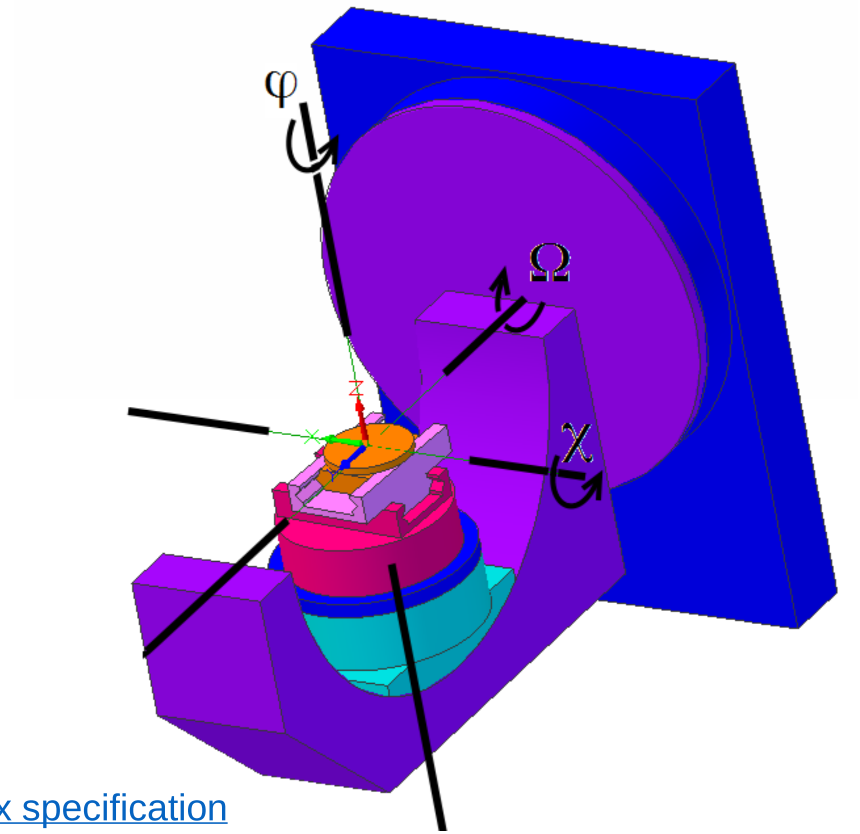
The Goniometer

Sample orientation is defined by 3 Eulerian angles:

- "Ω" angle is the incident angle on the sample surface
- " φ" angle is the rotation belongs the normal axis to the sample surface
- "χ" angle allows to tilt sample belongs the axis intercept of the diffraction plane and sample surface

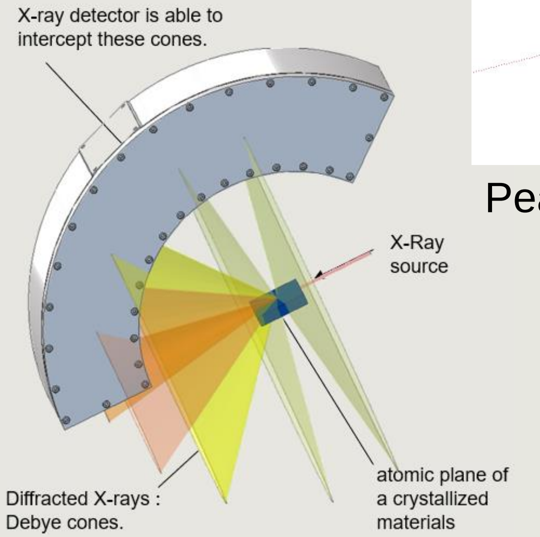
Remark:

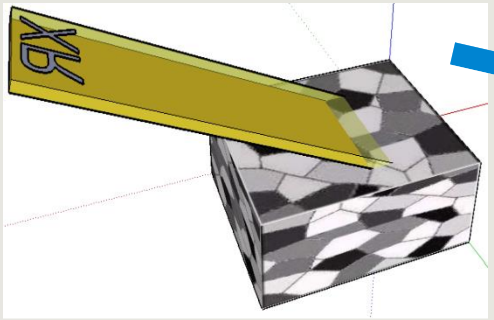
- "2θ" angle belongs to the detection part

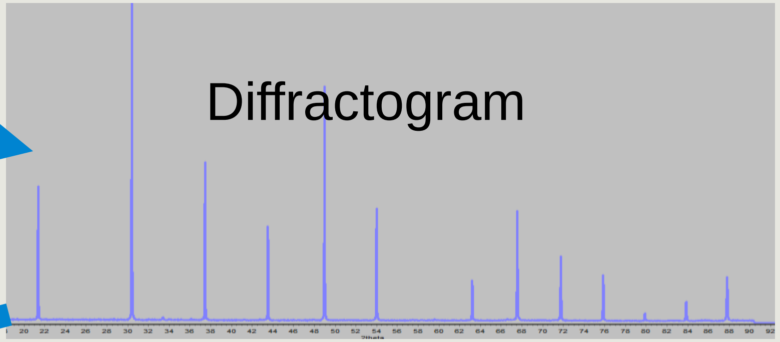


See CIF format: [(IUCr) CIF 1.1 syntax specification]

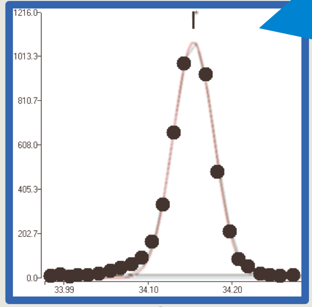
X-Ray diffraction, what kind of informations







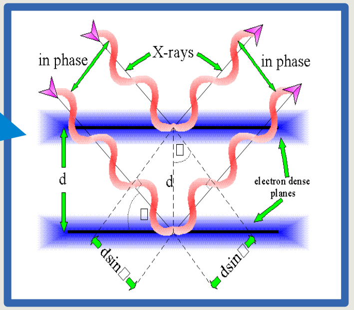
Peak intensity/shape



$$I = I_0 . P . L . F^2 . m . A . e^{-2M} \frac{.1}{V^2}$$

Overall analysis of peaks shape, position and intensity and background function

Peak position



$$\lambda = 2d_{hkl} \sin(\theta_{hkl})$$

What is the composition?	Phase identification
and how much?	Phases quantification
what is the crystallite size and morphology?	Particles size,
Is-there any constrains inside crystallite?	micro strains
Or in the overall sample?	Stress analysis
Is there an organization at the crystallite scale?	Preferred orientation (powder) or texture (bulk)
And can we quantify a distribution? Pole figures,	ODF
Structure, organization of electronic density levels :	cell parameters, valence, atomic occupation, ...
What is the structural modification of my sample vs physical parameters (P, T...)?	dilatation, phase transition
Structural anisotropy :	stress, texture, thin film characterization ...

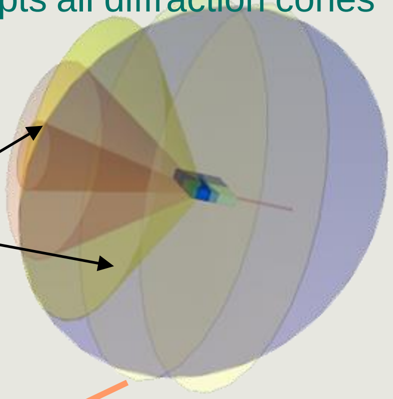
X-Ray diffraction, powder vs crystal

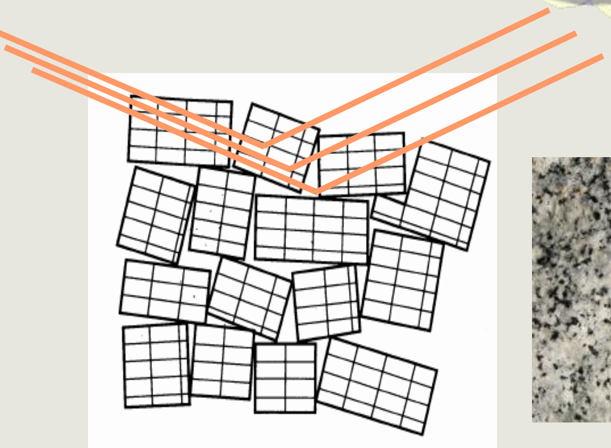
Powder sample :

- **Large number of grains probed by X-rays**
- Grains are small according to beam size (20µm)
- Each grain is able to diffract according to its orientation

=> several diffracted beam for a fixed sample orientation

Diffraction plane intercepts all diffraction cones





Powder diffractometer setup

Oriented polycrystal :

- large number of crystallite having a rule for organization

Texture diffractometer setup

Single crystal diffractometer setup

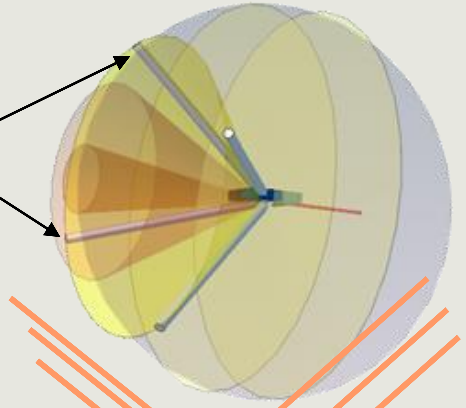
Single cristal :

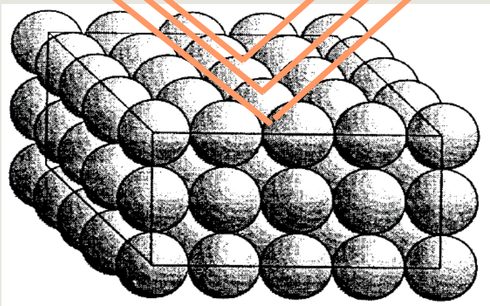
- **1 unique grain probed by X-rays**
- 1 unique diffacted signal for a given orientation of cristal

=> only possibilities to record several diffracted beam

- Moving cristal by using a goniometer and monochromatic beam
- Not moving cristal, but using a polychromatic beam

→ Laue method (consult us to define the instrument)



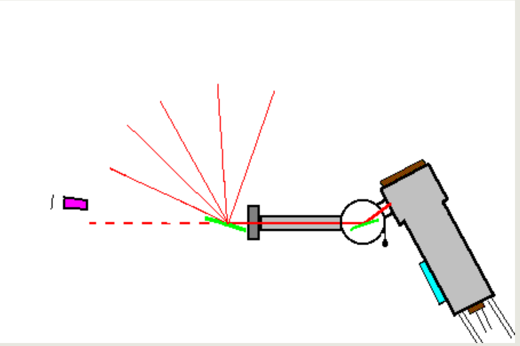


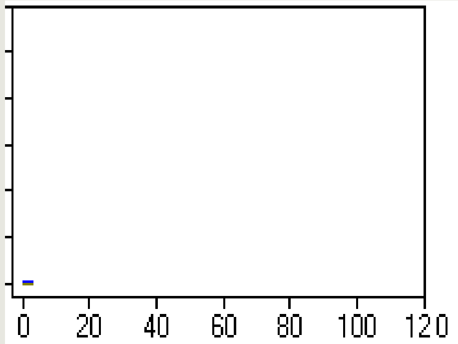
X-Ray diffraction, detection types

0D Detection :

Acquisition is done Stepwise

2θ and statistics are time dependent



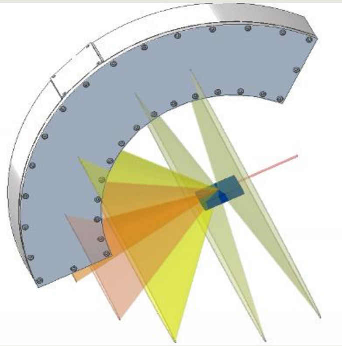


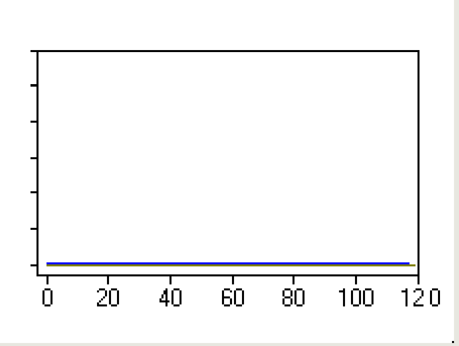
Bragg-Brentano geometry

1D Detection :

Acquisition is done in snapshots

Statistics is time dependent





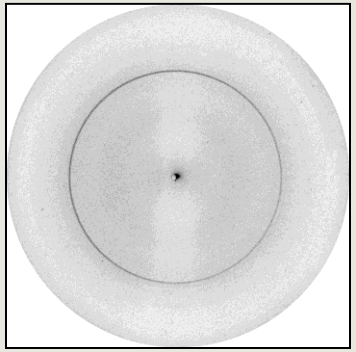
asymetric geometry

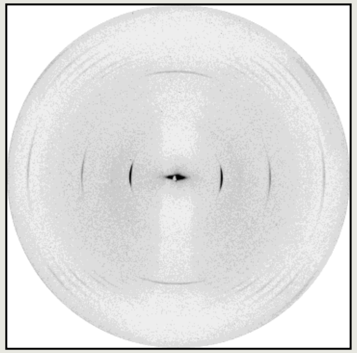
2D Detection :

Acquisition is done in snapshots

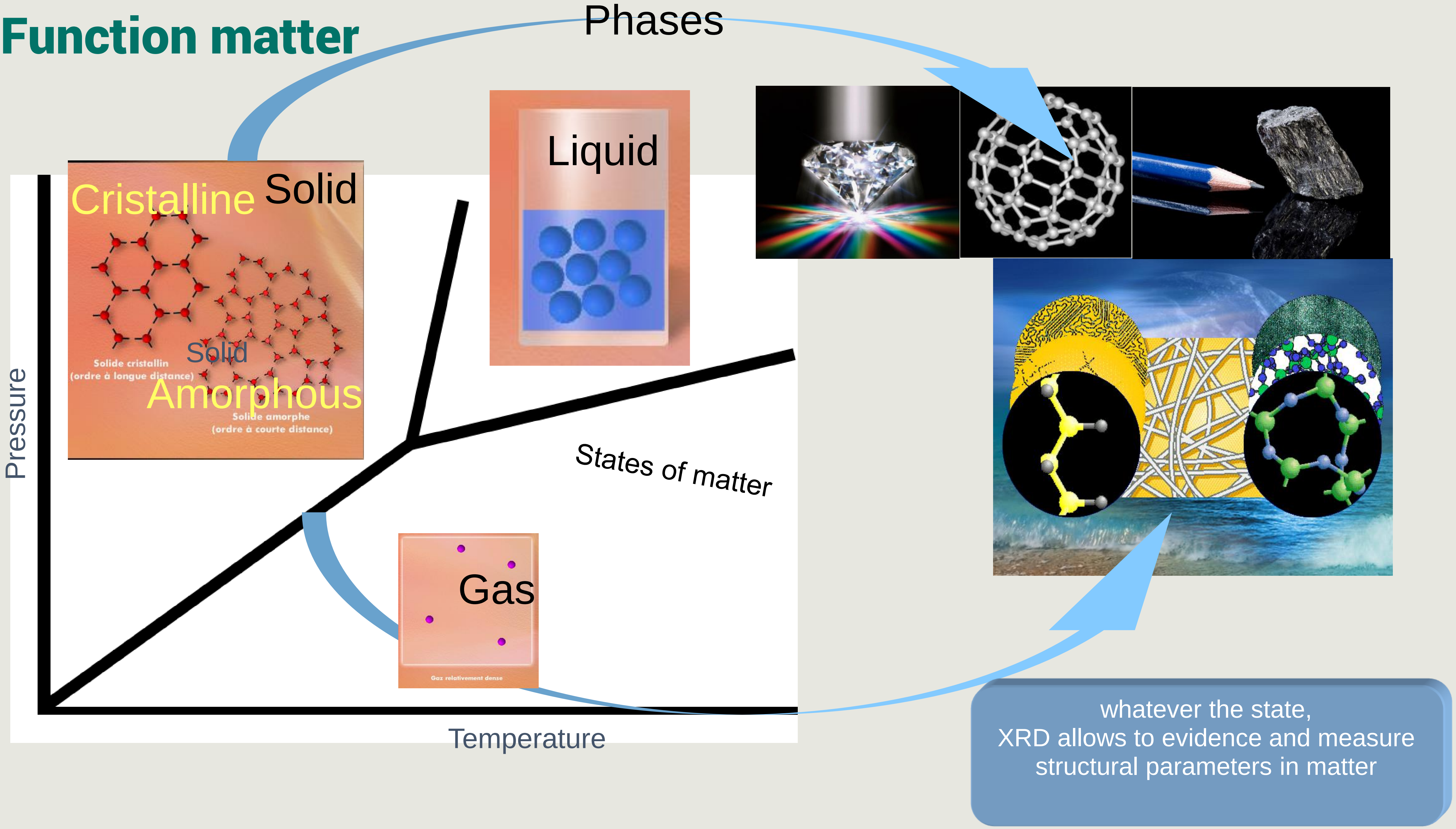
Statistics is time dependent

Texture information but point beam required





Function matter



Instrumental function for XRD

- **Instrumental function is governed by all components of the XRD instrument :**
  - - source characteristics
  - - optics and collimation
  - - detection device
  - - sample environment

- **XRD components should be compatible to each other**
  - Example : 1D optic is not recommended with a 2D detector (equatorial aberration)

- **The good knowledge of the instrumental function allows to estimate as well the quality of the result**
- Example : absorption correction or LP correction are not the same in Bragg Brentano or in Debye Scherrer

- **The instrument must be adapted to the requested measurement**
- Example : performing transmission measurement with Bragg-Brentano XRD is not appropriate

- **Instrumental conditions must be correctly chosen (reproducibility of results)**
- Example : choose of the appropriate wavelength vs sample

- **Use of appropriate standards**

Example : in reflection, eccentricity is influenced by transparency. Using standard with same absorption can correct this

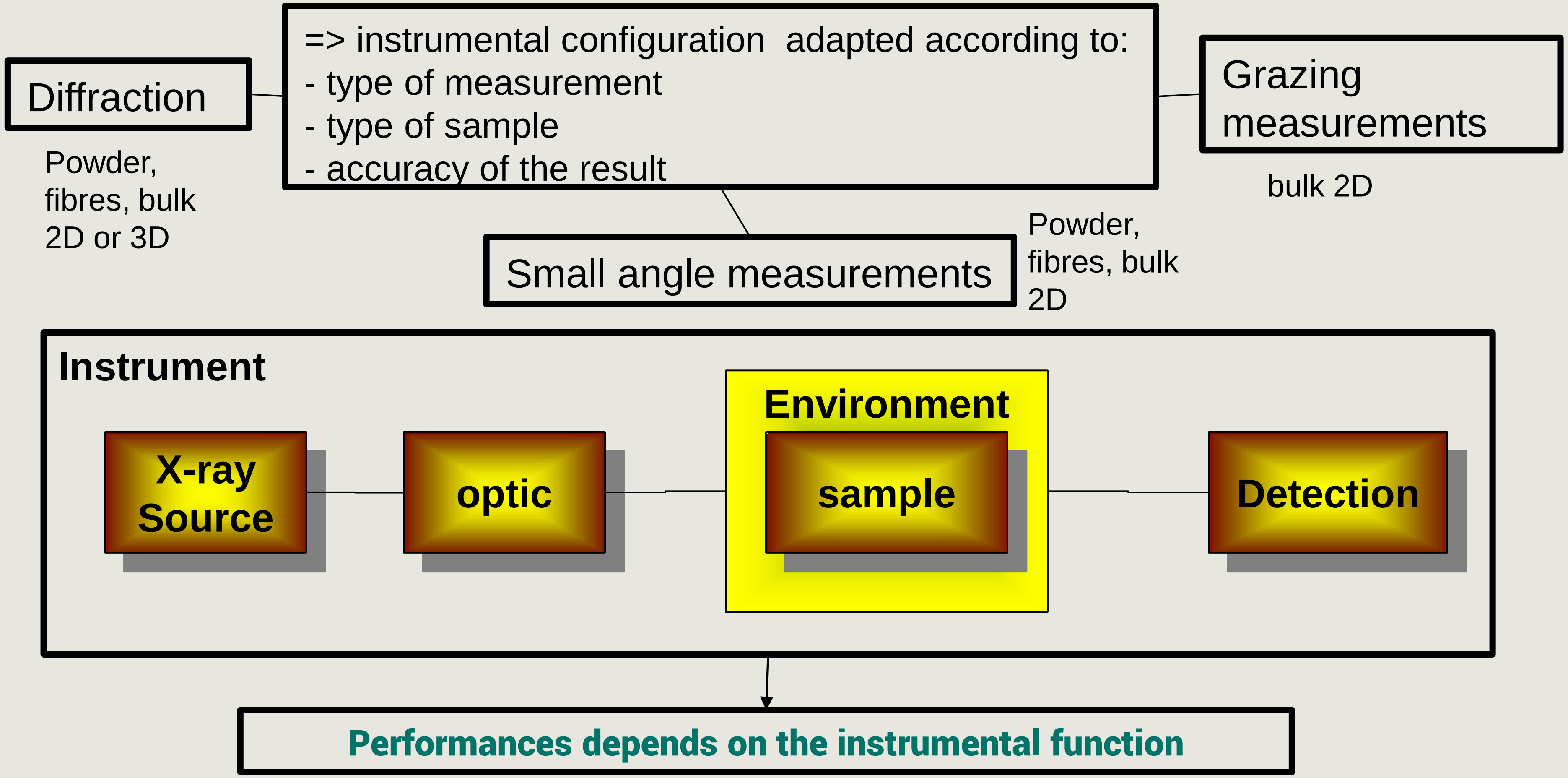
Instrumental function for XRD

Elastic coherent interaction :

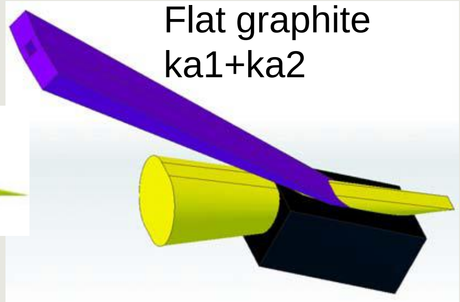
reflectometrie : investigation on thin film for measuring thickness, roughness and density
diffraction : investigation on phases
absorption : imaging and radiography.

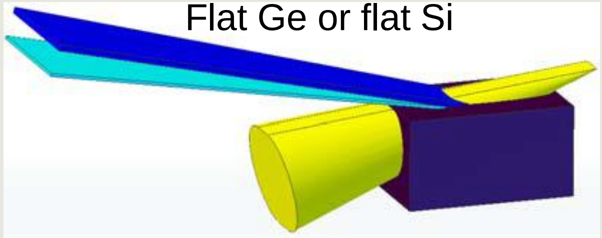
Incoherent elastic interaction :

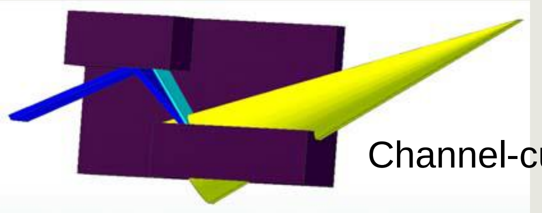
diffusion by a rough surface or cristalline defects.



Instrumental function for XRD – beam characteristics





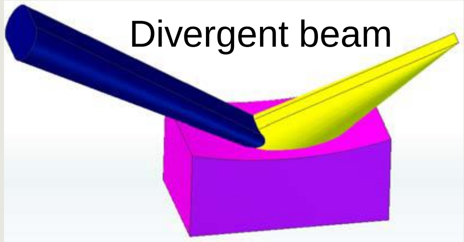


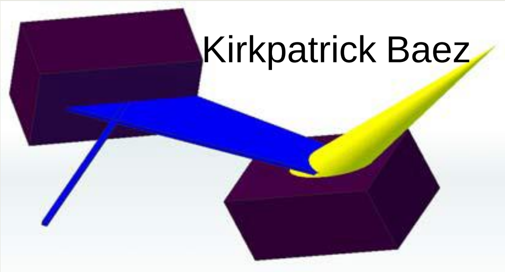
Monochromaticity

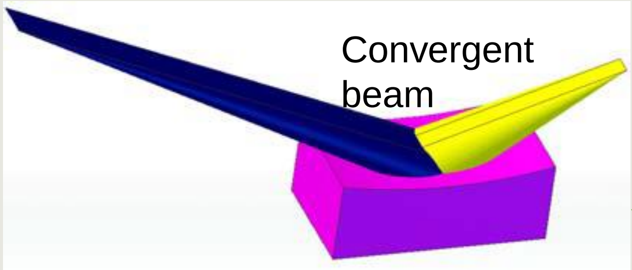
Divergence

An optic is characterized by :
- mosaicity → spectral range
- a capture angle → beam size
- divergence → resolution

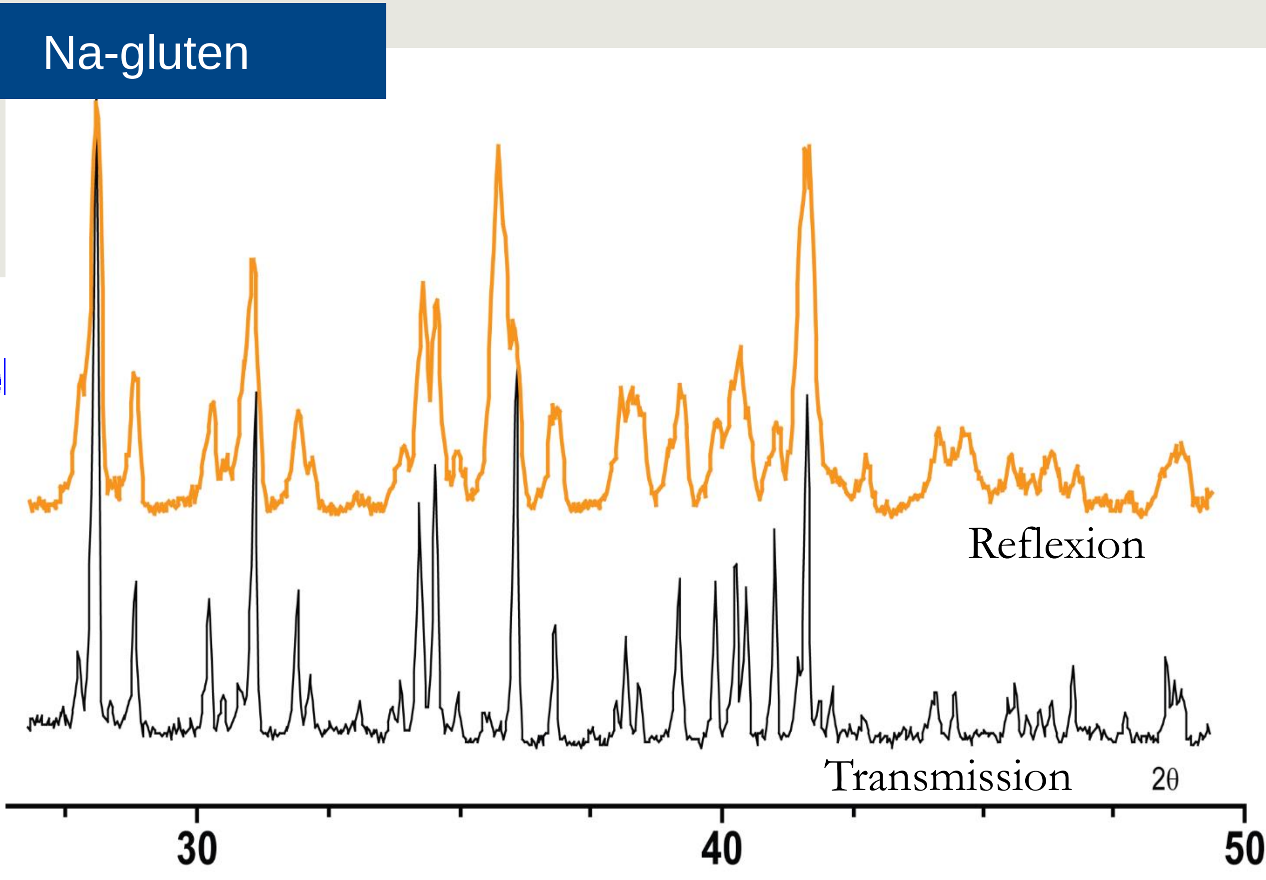
Focusing

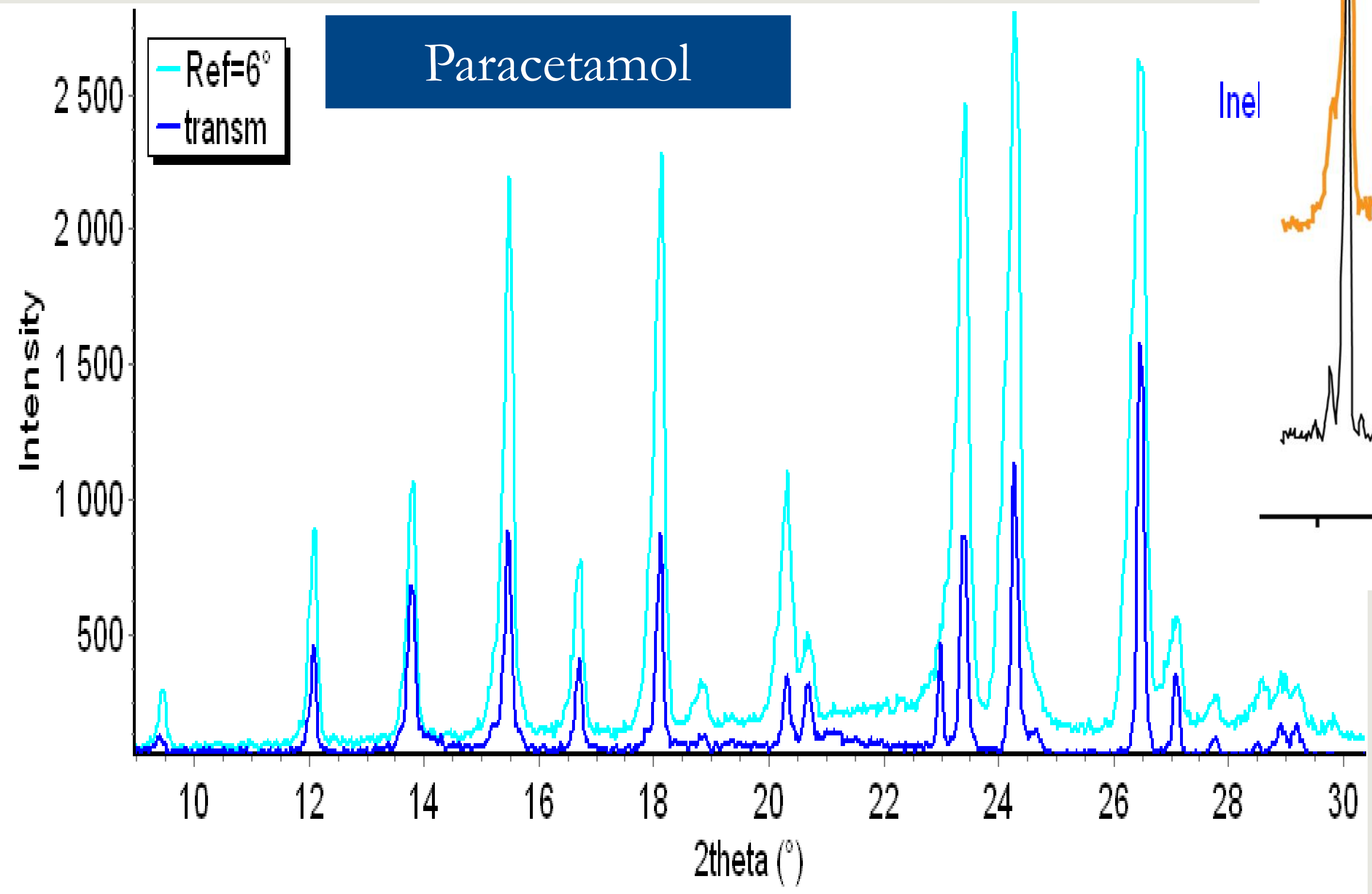






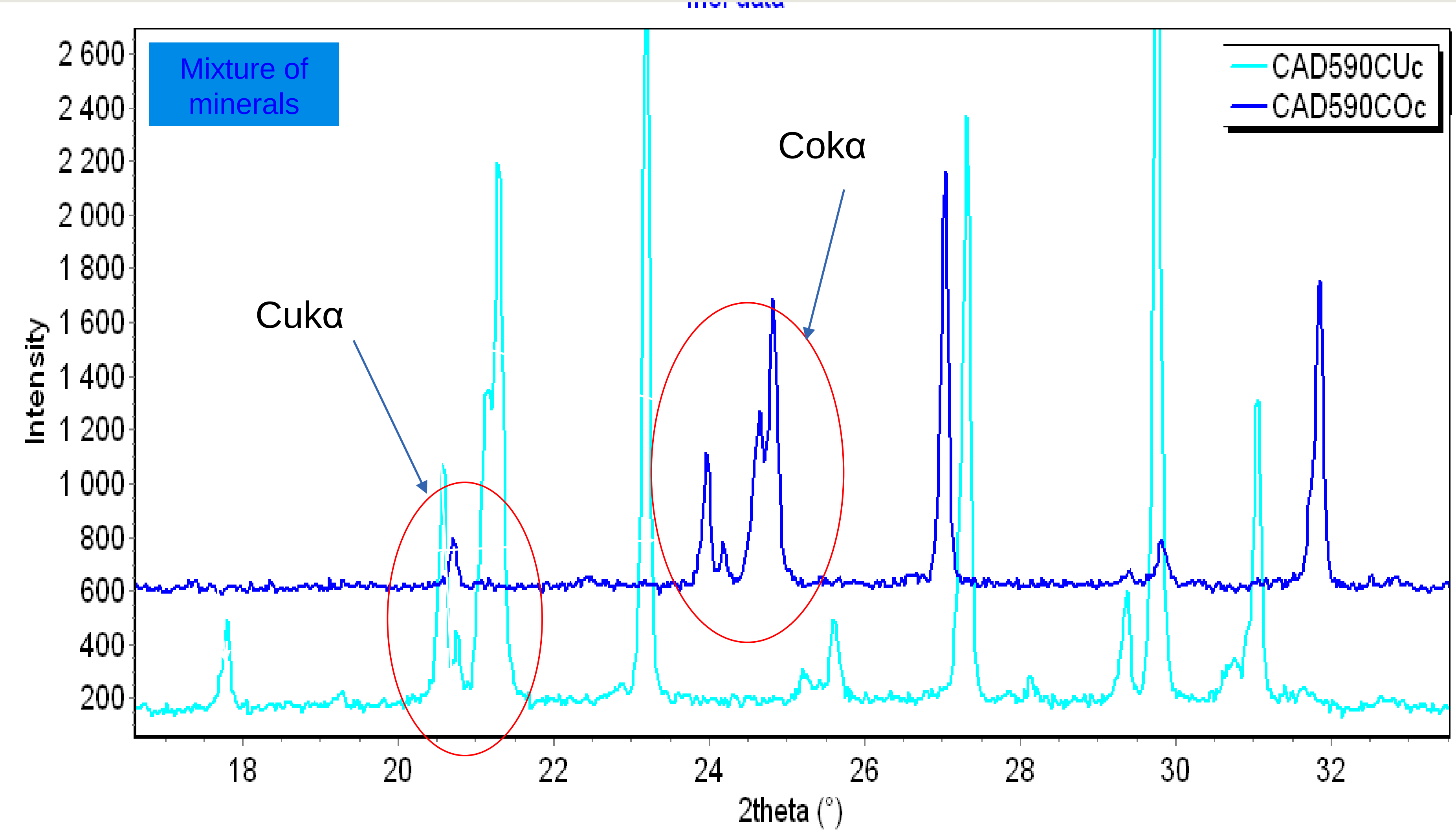
Instrumental function for XRD – effect of sample holder



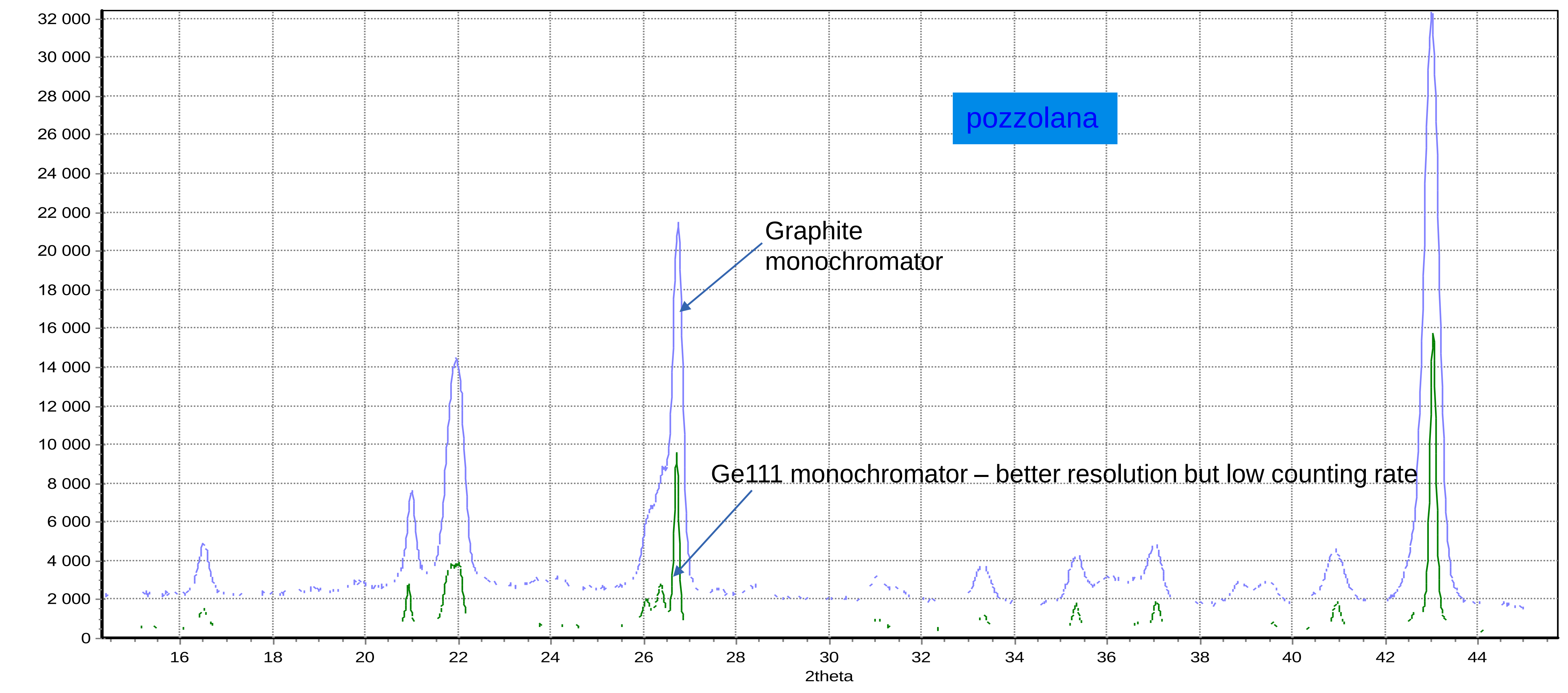


Better resolution in transmission

Instrumental function for XRD – effect of wavelength



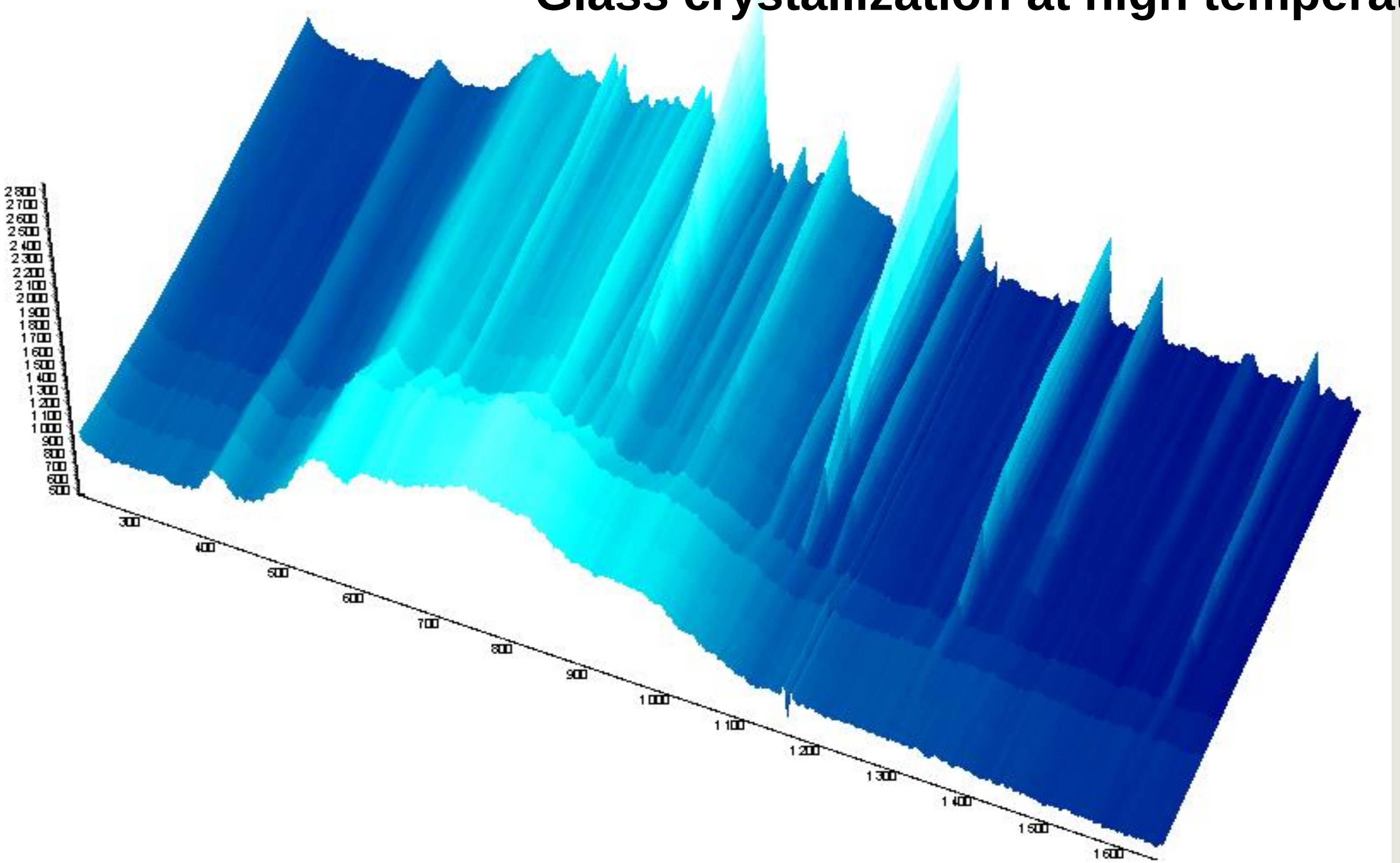
Instrumental function for XRD – effect of optic type



Instrumental function for XRD – effect of optic

High flux by using elliptical mirror

Glass crystallization at high temperature

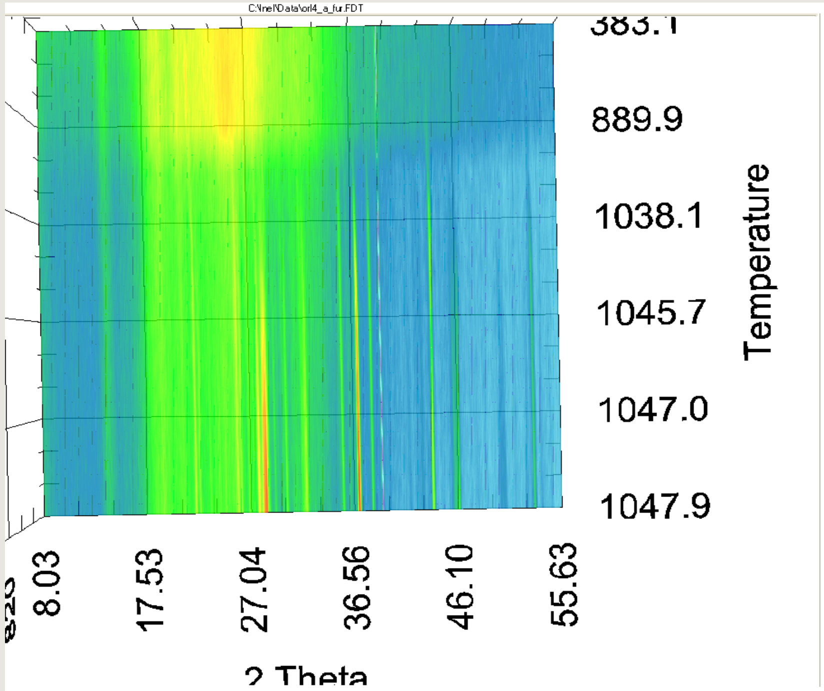


CONDITIONS :

power : 38kV – 38mA,

Furnace : FUR1200

acquisition: 3min



X-ray diffraction setup

Understanding how to get the result

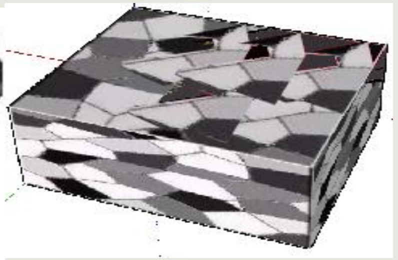
- appropriate instrumental configuration

- appropriate sample conditioning

- appropriate calibrations / corrections

		Type of solid	
		Single crystal	polycrystalline
Type of radiation	monochromatic 	Rotating crystal Method	Powder XRD
	polychromatic 	Laue Method	ED-XRD

Single crystal



Polycristalline material

XRD for polycrystal with monochromatic beam – focusing geometry

Debye Scherrer geometry

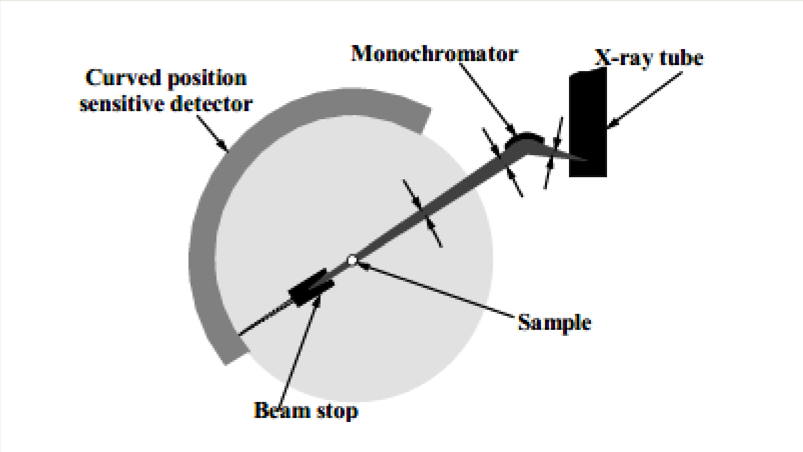


Figure 2.28. *Debye-Scherrer diffractometer equipped with a position sensitive detector*

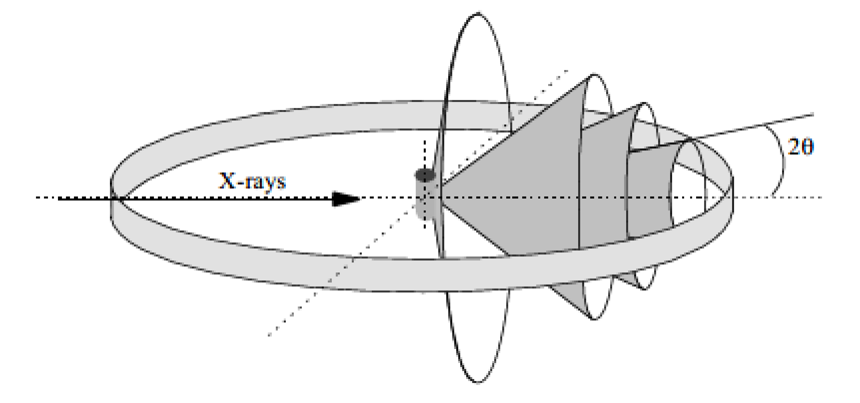


Figure 2.25. *Geometric arrangement of the Debye-Scherrer and Hull diffractometer*

Bragg Brentano geometry

Sample is an optical component!!

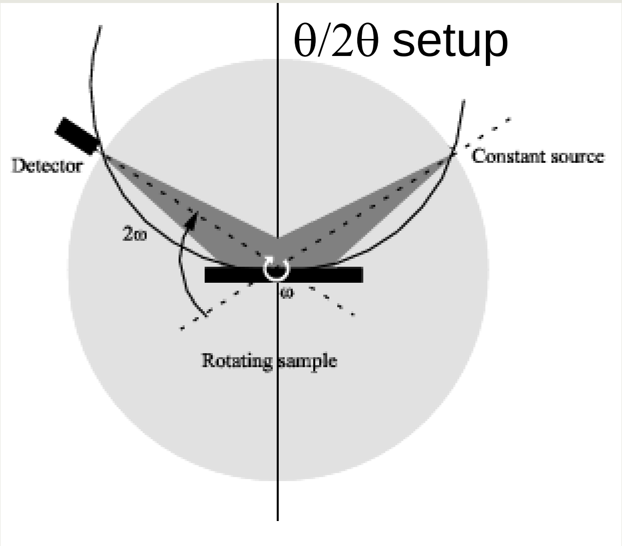


Figure 2.46. *θ-2θ Bragg-Brentano diffractometers*

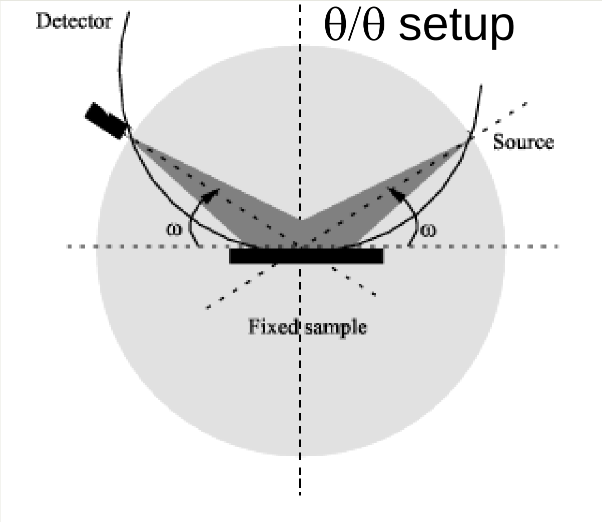


Figure 2.47. *θ-θ Bragg-Brentano diffractometer*

without optic

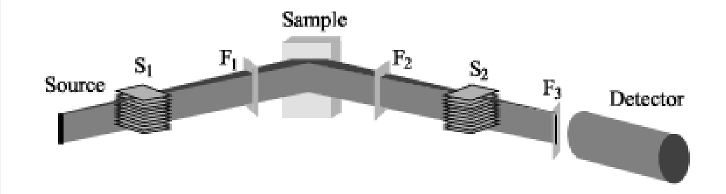
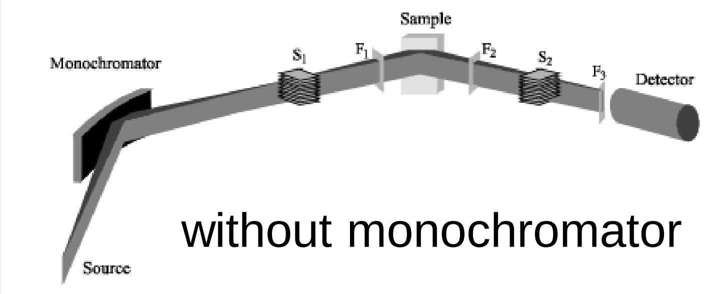


Figure 2.48. *Path of the X-ray beams in a Bragg-Brentano diffractometer*



without monochromator

Figure 2.51. *Path of the X-ray beams in a Bragg-Brentano diffractometer equipped with a front monochromator*

From Guinebretière

XRD for polycrystal with monochromatic beam – parallel beam geometry

Parallel beam geometry
With flat cristals (1, 2 or 4 bounds)

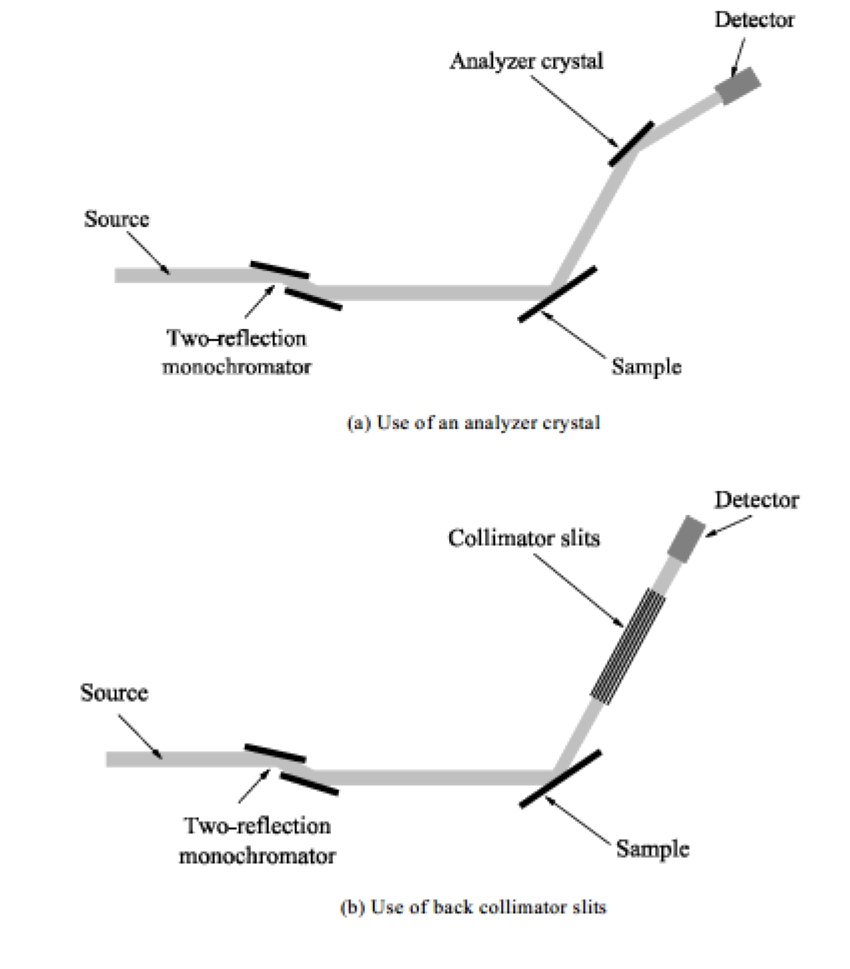


Figure 2.54. *Geometrical arrangement of diffractometers for polycrystalline samples using a synchrotron source*

Parallel beam geometry
With parabolic (or elliptic) mirror

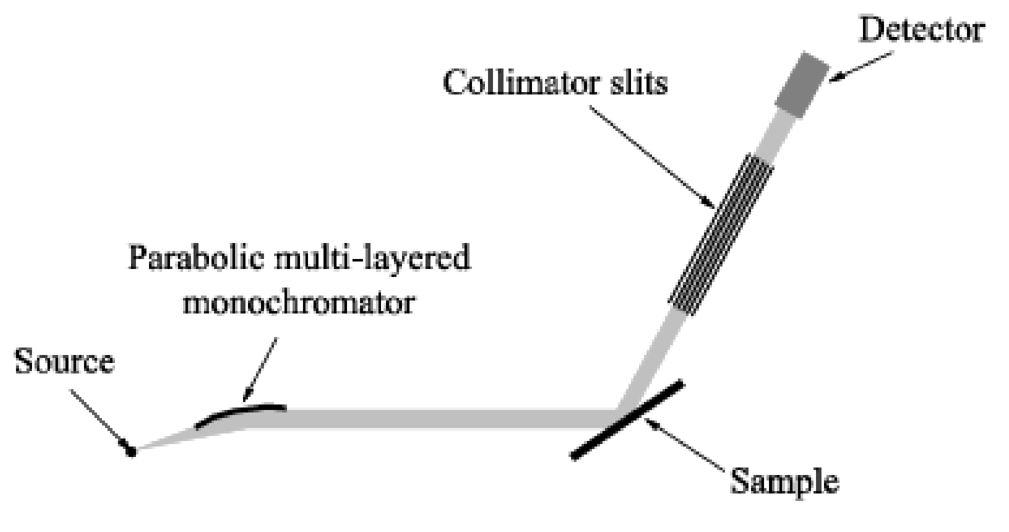


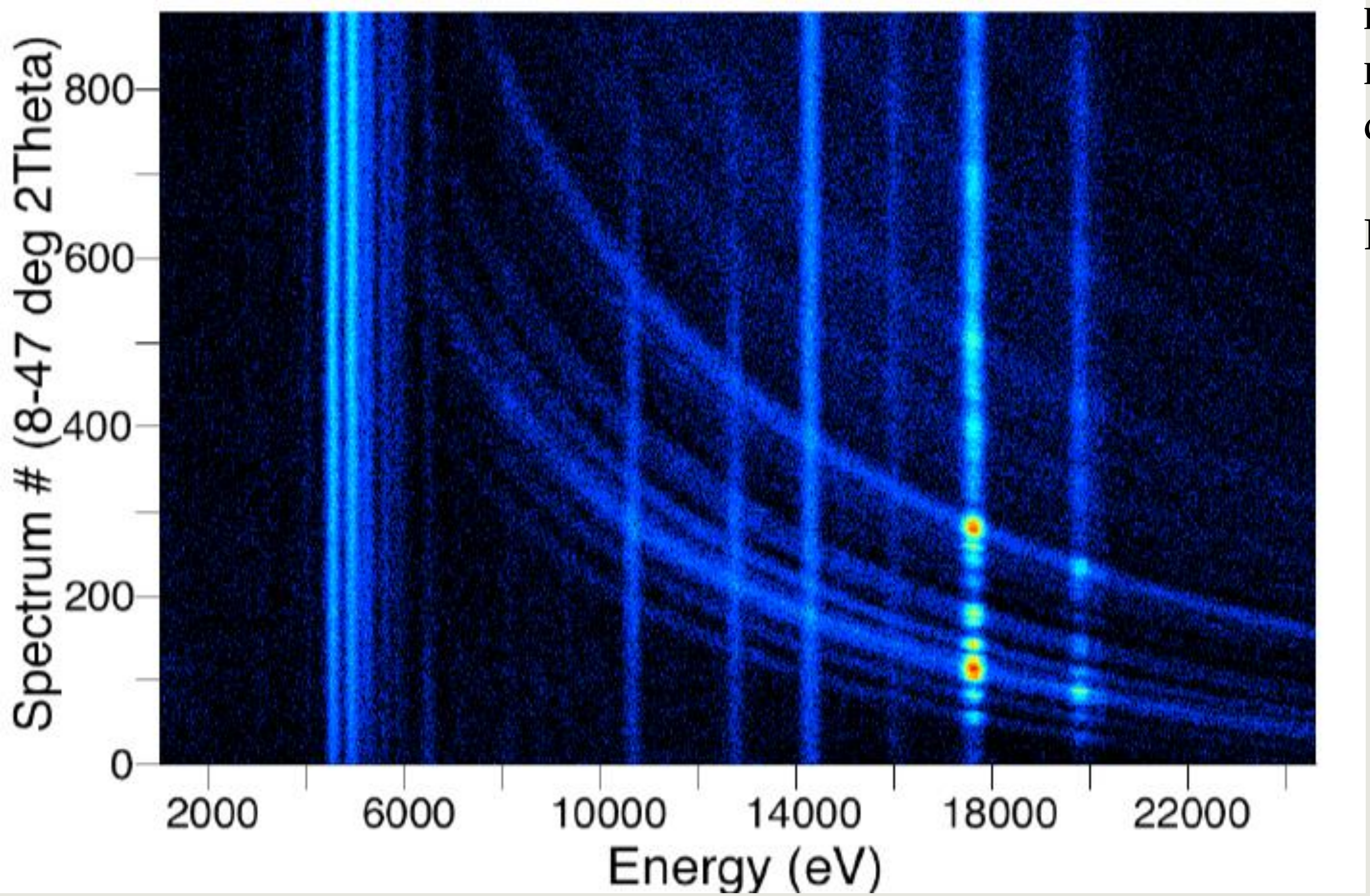
Figure 2.55. *Parallel geometry configuration in the laboratory*

From Guinebretière

XRD for polycrystal with polychromatic beam – parallel beam geometry

1- Structural information are diffracted by all the wavelength
2- Elements are emitting fluorecence signal

Need to have a detector with a **spacial detection**, able to dissociate **energy**



XRD-XRF angle-energy map
(raw data)

Angle-energy map measured for a BaSO4 rich sample using Mo radiation not monochromatised and scanning the SDD detector from 5 to 47. in 2θ.

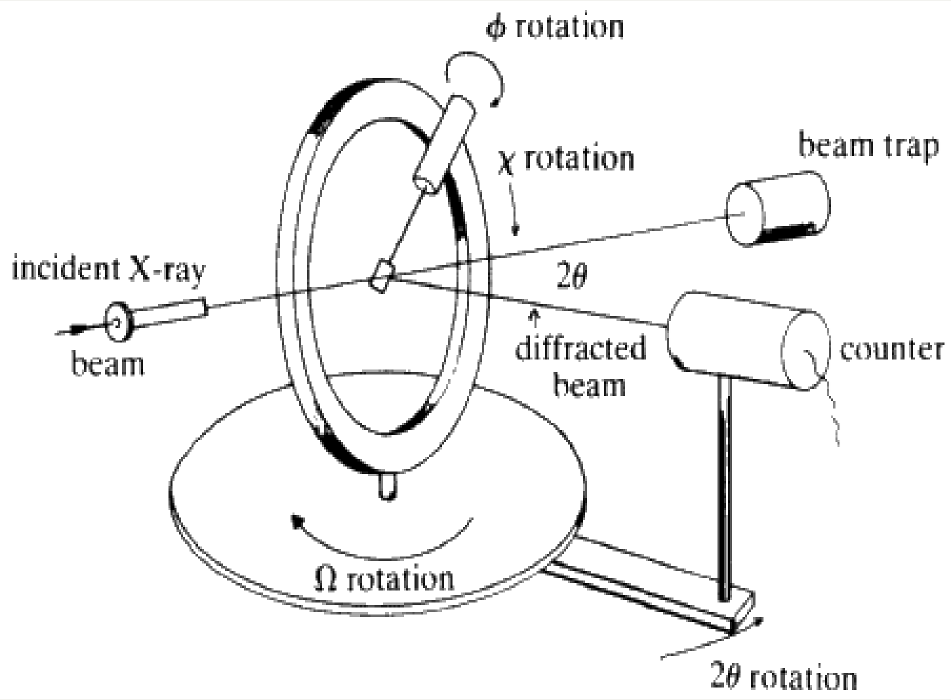
Ref. L. Lutterotti, U. Trento

Expected characteristics:
- 50mm Strip detector, composed by 100microns (could be 50?) linear pixel width
- High dynamic per pixel
- Each pixel is able to measure EDX with a resolution better then 180eV
- Light weight and low consumption
- No gas needed
- Real time detector with low dead time
- Possibility to combine several detectors in order to cover a larger intercept of the Debye cones
- Efficiency for energy range from 1keV to 30keV

XRD for single crystal with monochromatic beam – parallel beam geometry

Parallel beam geometry

With flat cristals (1, 2 or 4 bounds)



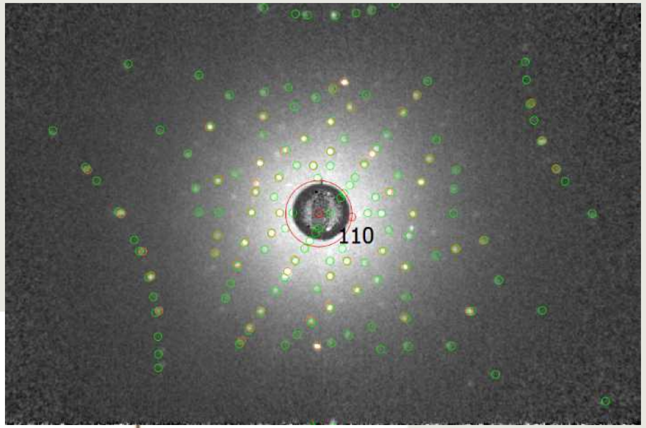
Sample hold by appropriate goniometer

Different type of configuration

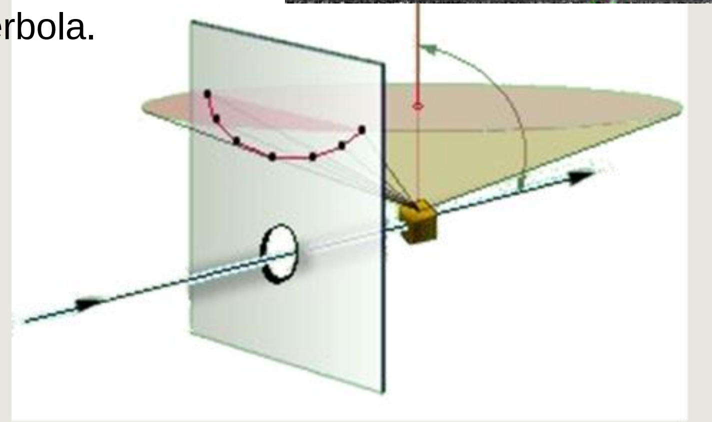
XRD for single crystal with polychromatic beam – parallel beam geometry

The Laue method is mainly used to determine the orientation of large single crystals. White radiation is reflected from, or transmitted through, a fixed crystal.
The diffracted beams form arrays of spots, that lie on curves on the film. The Bragg angle is fixed for every set of planes in the crystal. Each set of planes picks out and diffracts the particular wavelength from the white radiation that satisfies the Bragg law for the values of *d* and θ involved.

Experimental
There are two practical variants of the Laue method, the back-reflection and the transmission Laue method:

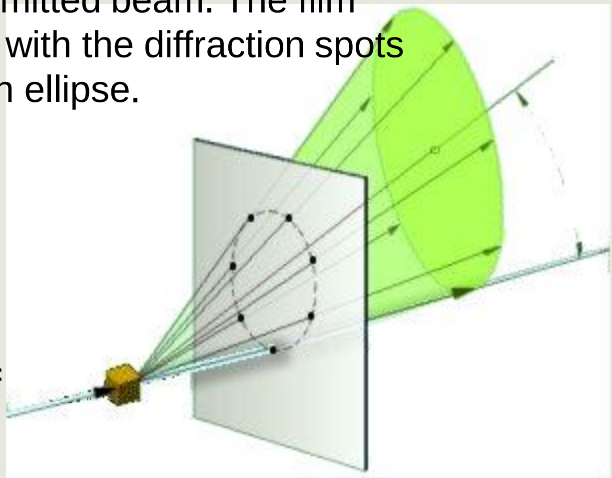


Back-reflection Laue
In the back-reflection method, the film is placed **between** the x-ray source and the crystal. The beams which are diffracted in a backward direction are recorded.
One side of the cone of Laue reflections is defined by the transmitted beam. The film intersects the cone, with the diffraction spots generally lying on an hyperbola.



Transmission Laue
In the transmission Laue method, the film is placed **behind** the crystal to record beams which are transmitted through the crystal.
One side of the cone of Laue reflections is defined by the transmitted beam. The film intersects the cone, with the diffraction spots generally lying on an ellipse.

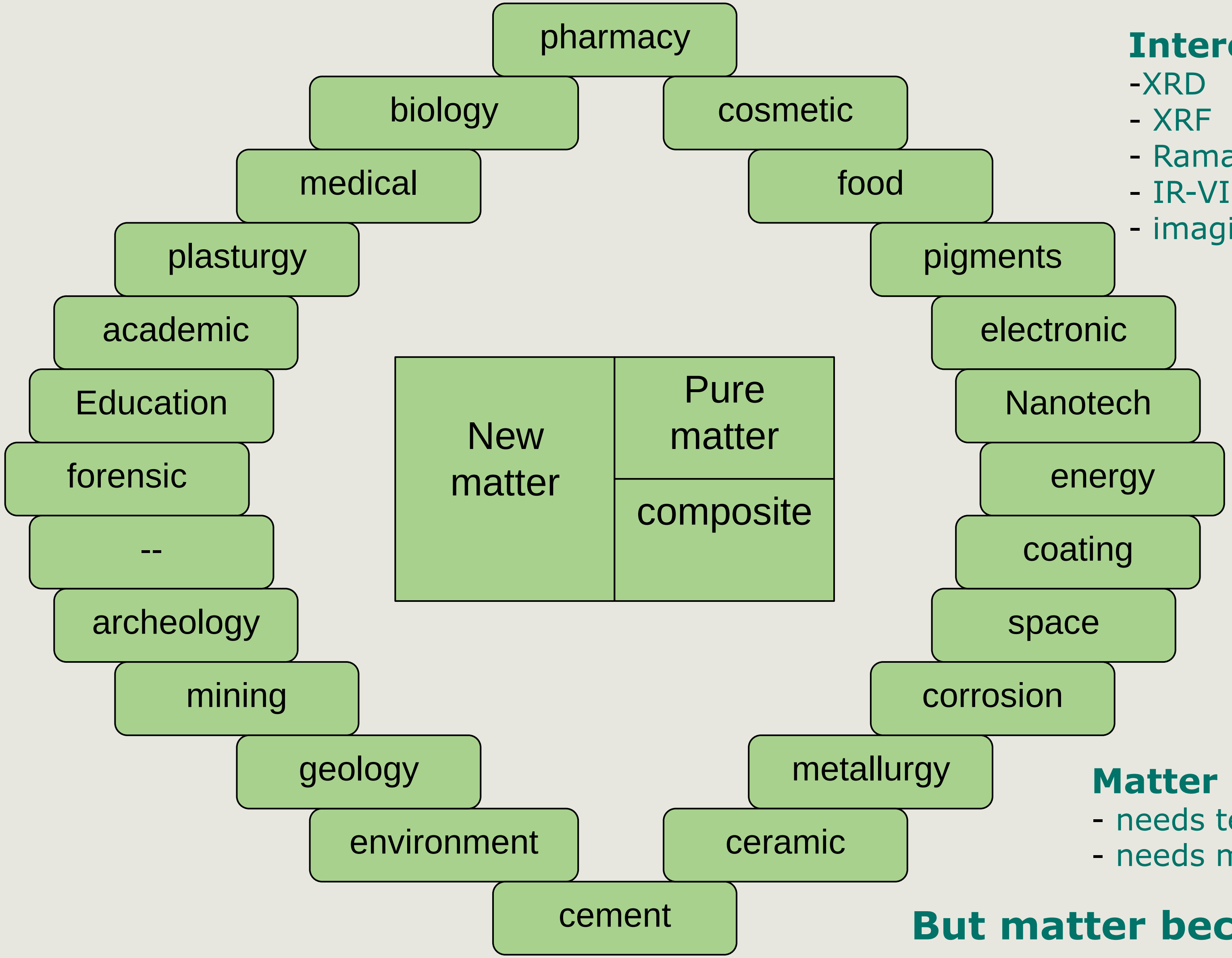
Case of



Application fields

Wide domains in material science

Application fields



Interest for using non destructive analytics
-XRD
- XRF
- Raman spectroscopy
- IR-VIS-UV spectroscopy
- imaging (RGB, hyperspectral, radiography …)

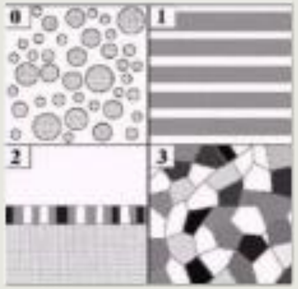
Many application fields
- Academic
- private research
- quality control
- in field analysis

Matter is the center of interest for customer
- needs techniques for characterization
- needs methodology (procedures, norms …)

But matter becomes more complex !

Matter organisation at different scales

Mineral, organic, vegetal, animal ...
All can be complex arrangements



0-D : thin powder
1-D : fiber stacking
2-D : multi-layer coating
3-D : bulk agglomerate

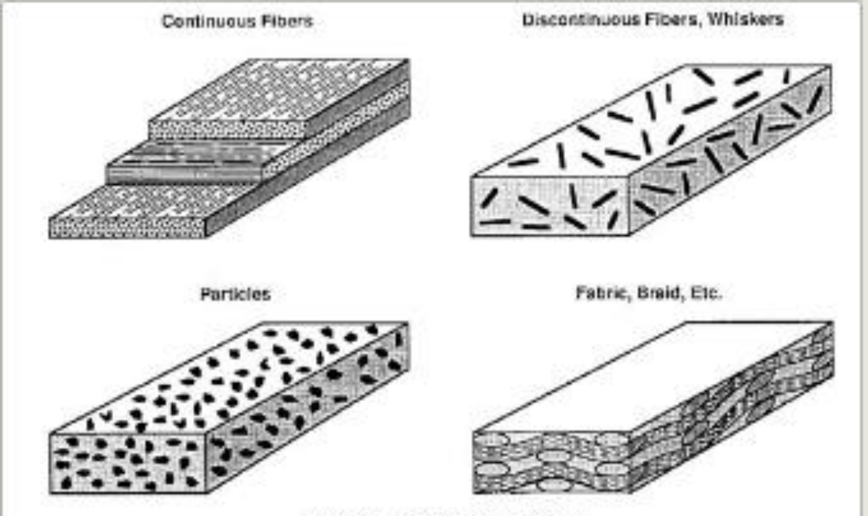
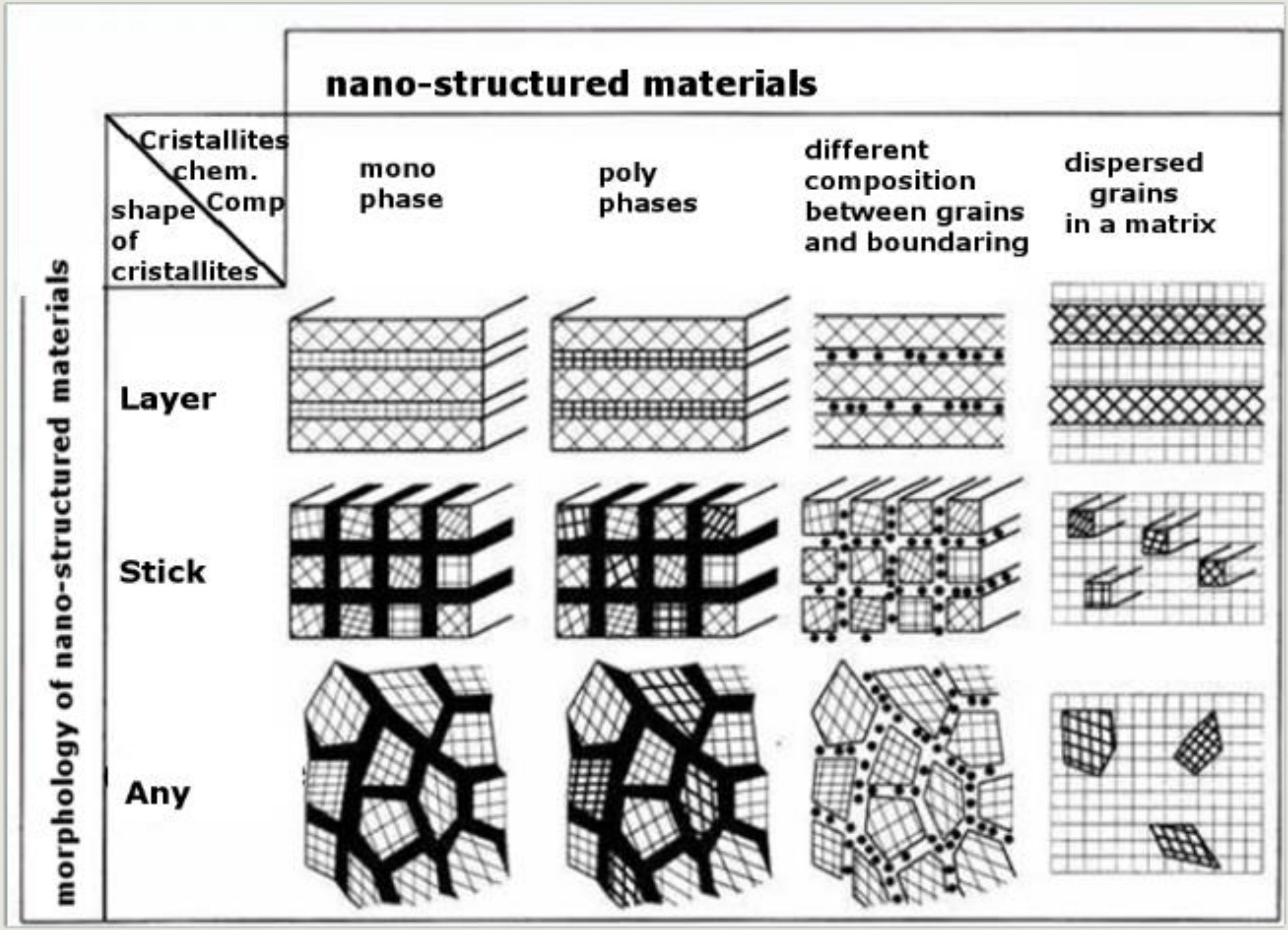


Figure 1 Reinforcement forms.



H. Gleiter, Acta. Mater. 48 (2000) 1-29

Matter, different structure at different scales

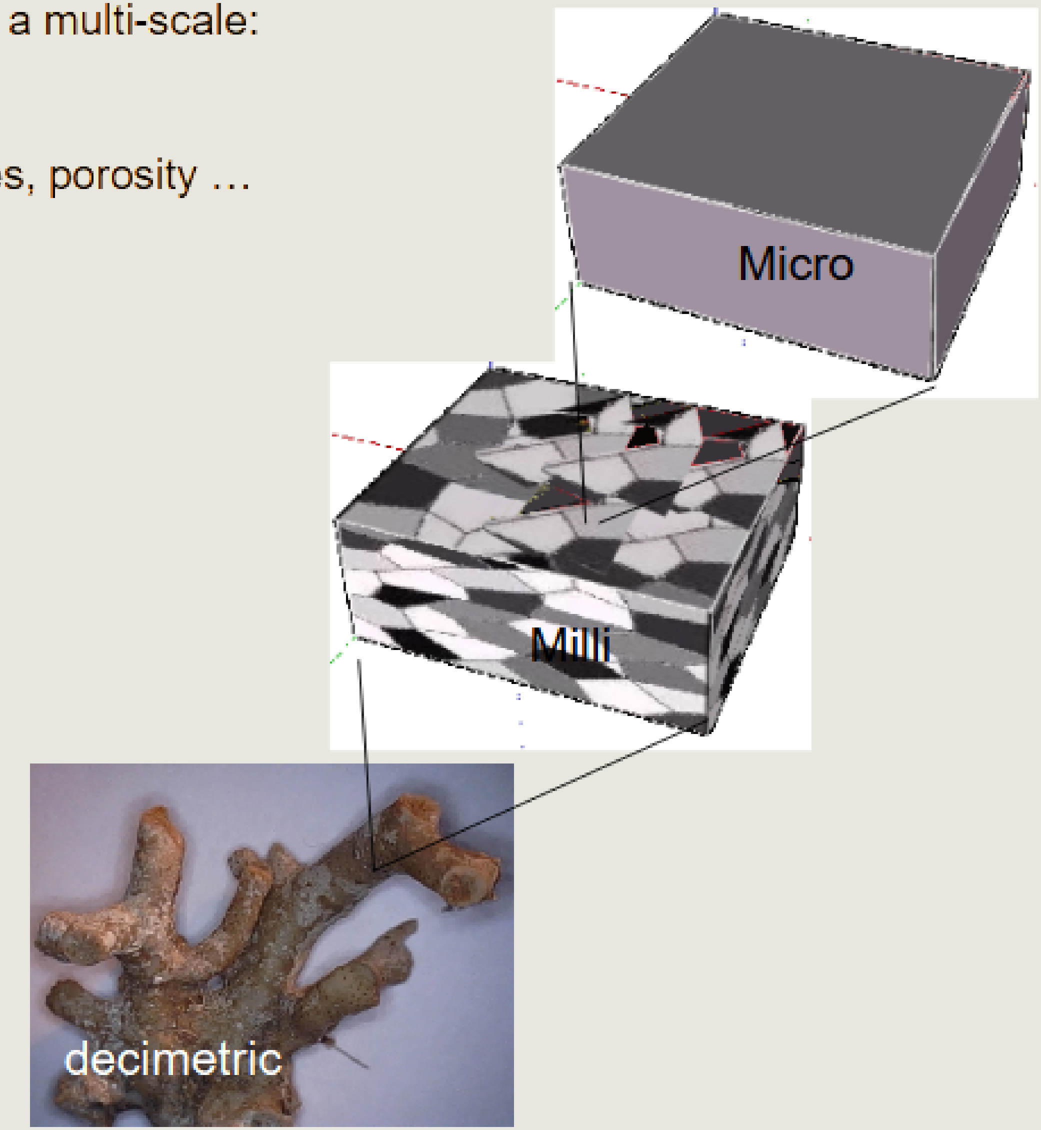
Multi-scale strategy

For a better understanding, correlations should be done at a multi-scale:

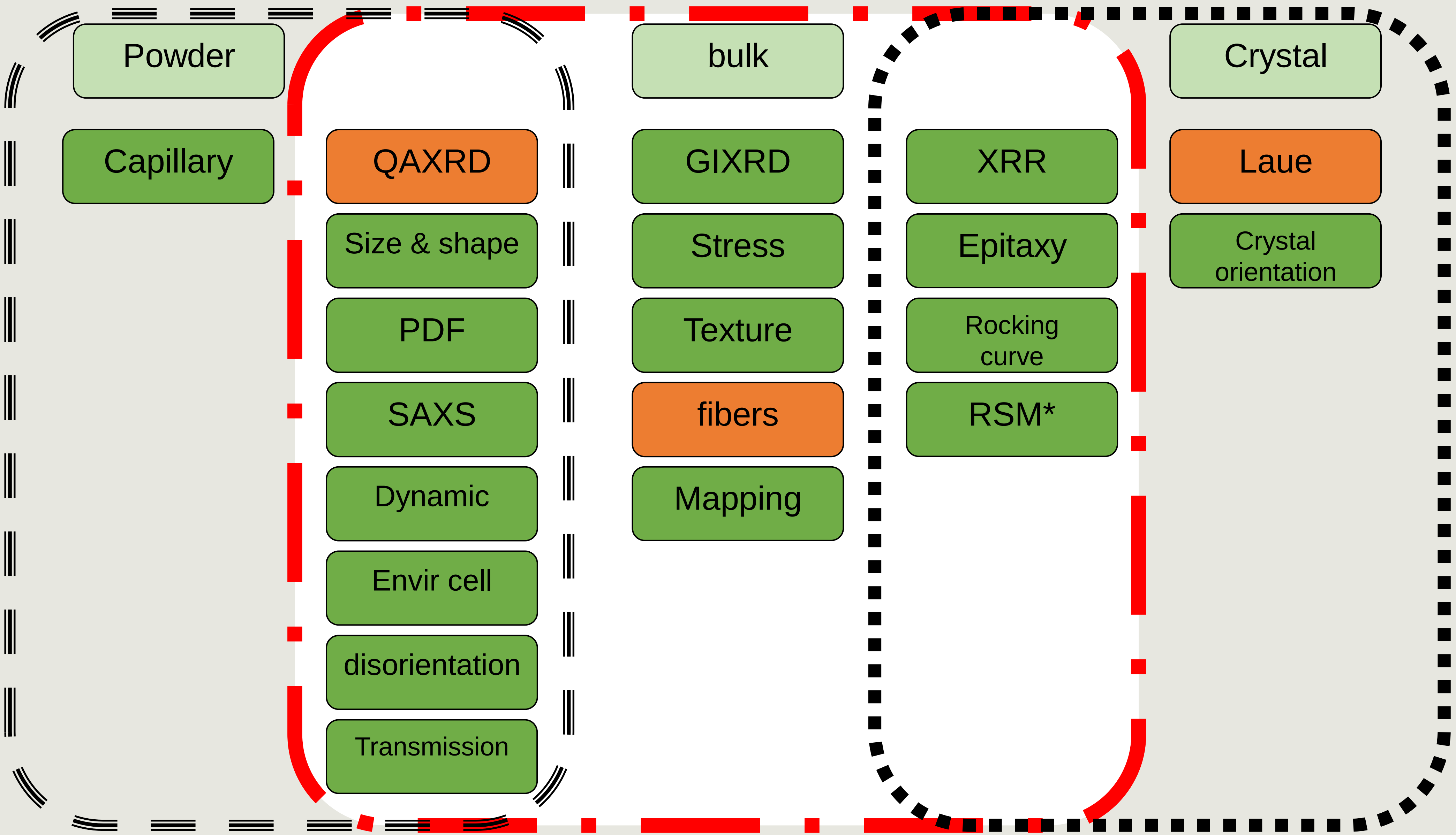
CM – sample scale: profiling + imaging
Identification of global texture of sample, surfaces, porosity …

MM - grain scale : XRD + XRF
Characterization of surfaces composition
Σ=> phases and Σ elements

MIC – micro grain scale: Raman
Identification of individual phases
=> individual phase distribution



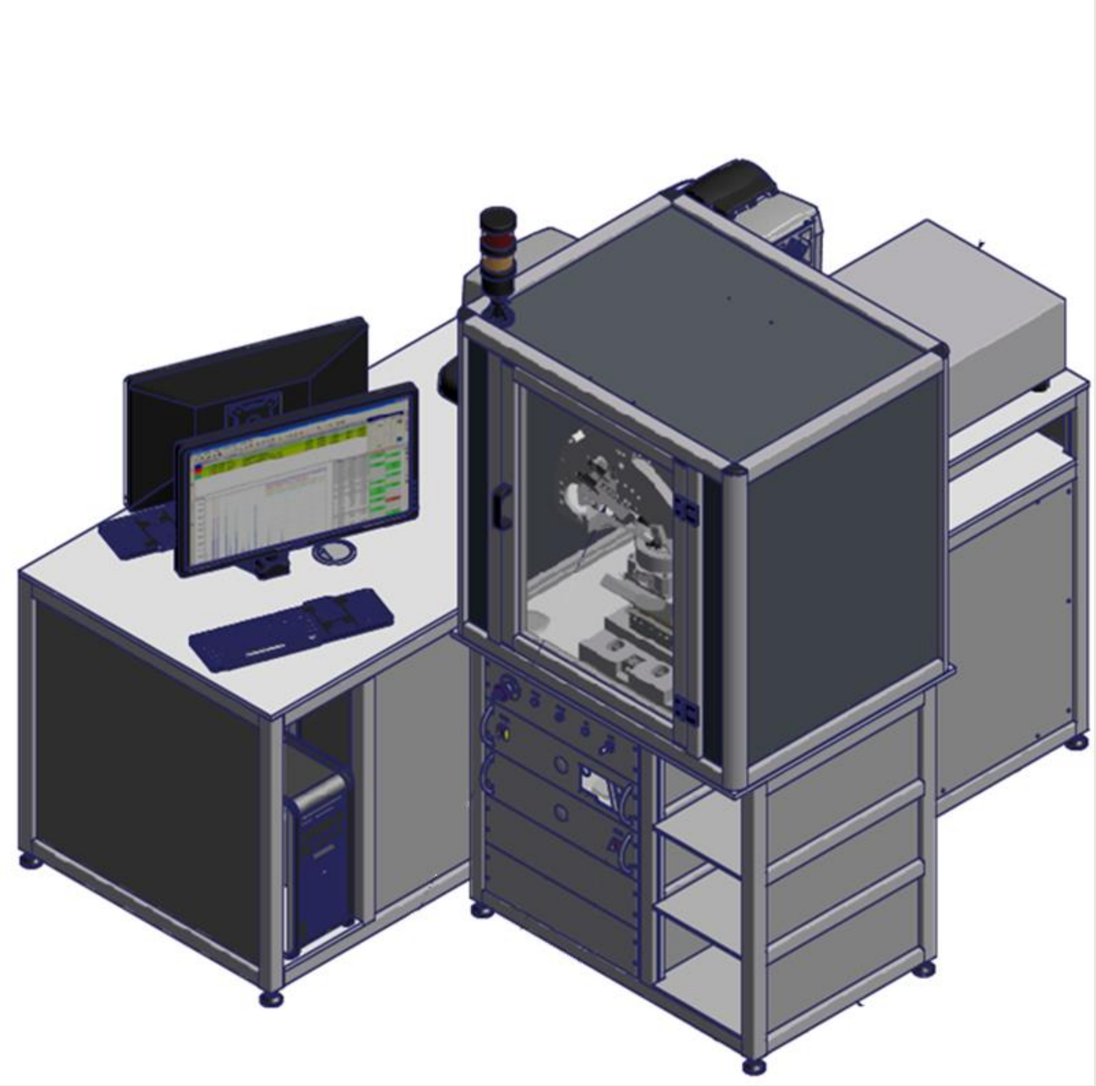
XRD analytic techniques



Combined instruments

A way to automate material charaterization

Combined analytics, ID1 (SOLSA project)



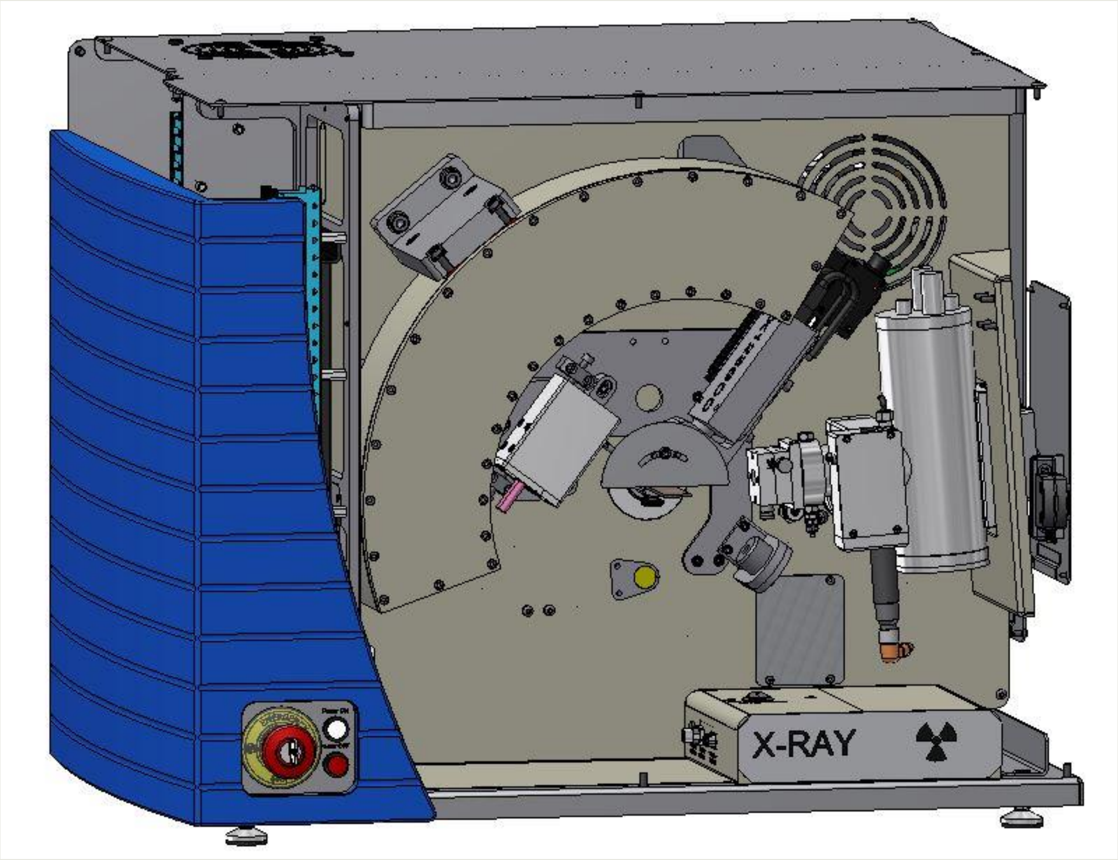
XRD designed by INEL
- X-ray source (Cu)
- Multilayer optics and collimation
- CPS 180 detection
- motioned around the sample for omega axis

XRF designed
- SDD detector

Raman spectrometer
- fiber

Sample holder
- texture goniometer : chi, phi, Z, X and Y

Combined analytics, ID2b (SOLSA project)



- **XRD on the basis of Equinox 100, developed by INEL**
  - - X-ray source (Cu, Co, Mo)
  - - Multilayer optics and collimation
  - - CPS 180 detection

- **XRF designed for SOLSA project**
  - - 4W X-ray source (Mo)
  - - SDD detector

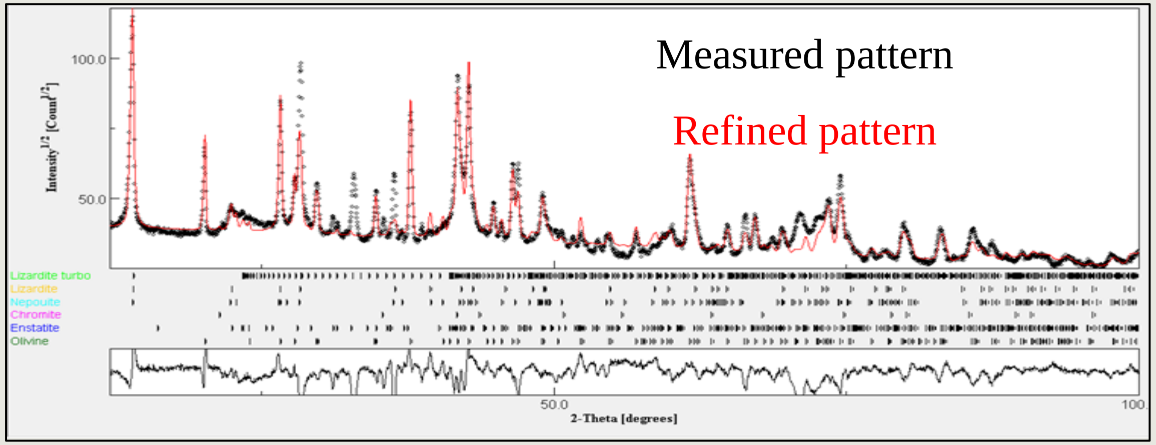
- **Sample holder**
  - - In reflection
  - - able to perform simultaneous XRD/XRF measurement

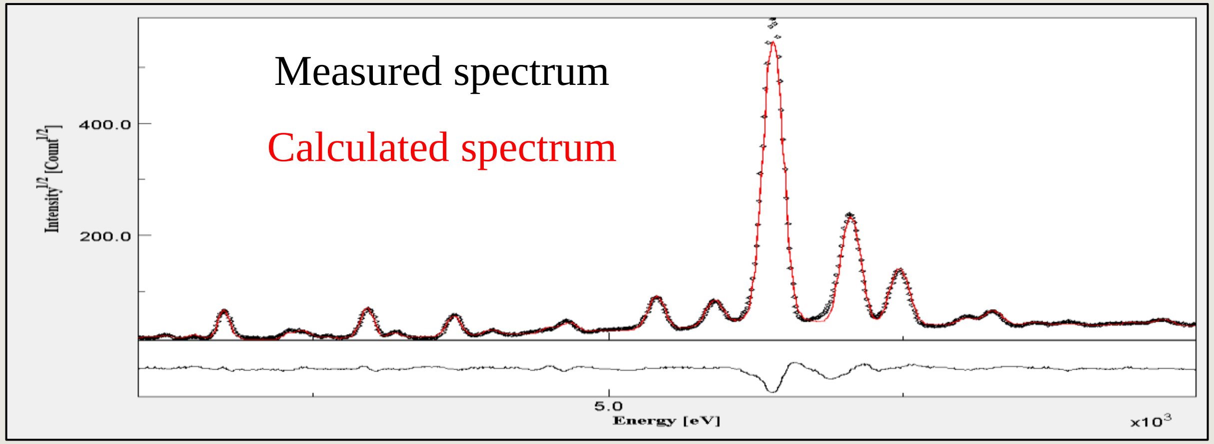
LUXREM Software designed by University of Trento

- - simultaneous acquisition
- - simultaneous data treatment by Rietveld

Combined refinement XRD-XRF

- Results on powder from Harzburgite H10, using Maud **Rietveld** SW: combined XRD/XRF





phase	Olivine	Lizardite	Lizardite turbostratique	Népouite	Talc	Enstatite	Chromite
Proportion (%)	58,48	15,23	16,48	6,98	0	2,77	0,06

chemical	Mg	Fe	Cr	Si	O	Ca	Cu	Mn	Zn	Ni	Al	Ti
Proportion (%)	15,83	8,35	0,25	18,08	52,74	0,39	0,02	0,14	0,01	0,20	3,28	0,04

chemical	H	Cl	TOTAL
Proportion (%)	0,62	0,06	100,00

Combined analysis for industry

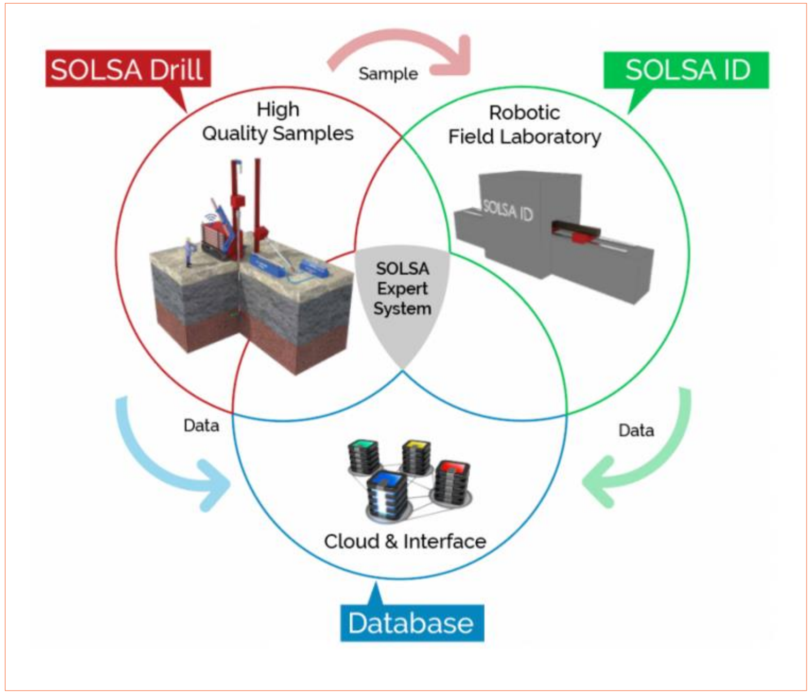
A way to automate material charaterization

Promotion of the SOLSA research project

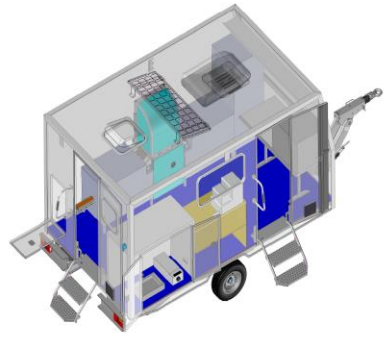
SOLSA, a H2020 collaborative research project

with :

- **Eramet**, coordinator
- **BRGM**
- **Inel - Thermo Fisher**
- Eijkelkamp
- CNRS-CRISMAT
- Univ. de Trento
- Univ. de Verona
- Univ. de Vilnius
- TU Delft



SOLSA



MODULAB
REAL TIME ANALYSIS ON SITE

EC INNOVATION RADAR

Identification of innovention potential by EU

INEL INNOV

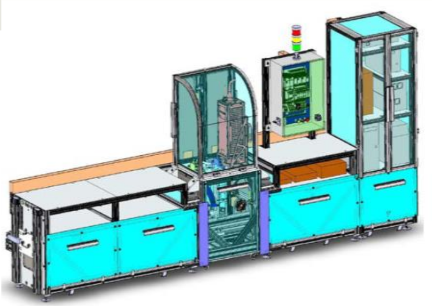
Designed startup to valorize the products

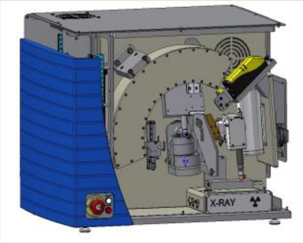
The Innovation Radar

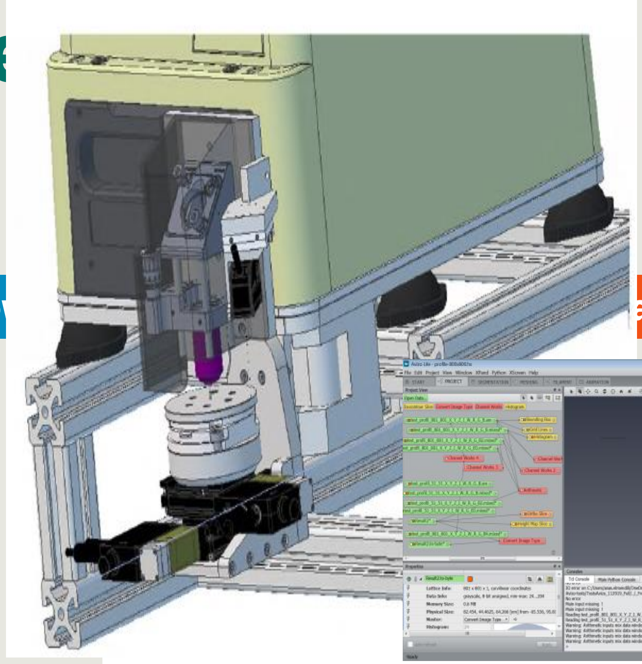
INEL INNOV

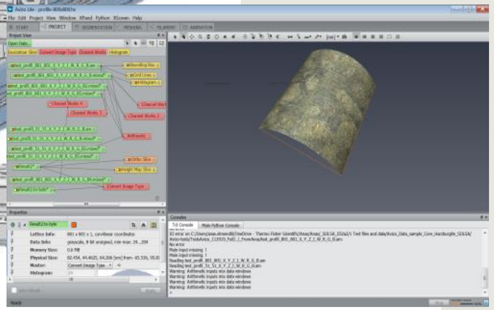
In field analytical solutions for mining e

On line analysis : drilled core scanner	Discrete analysis on pov	atments







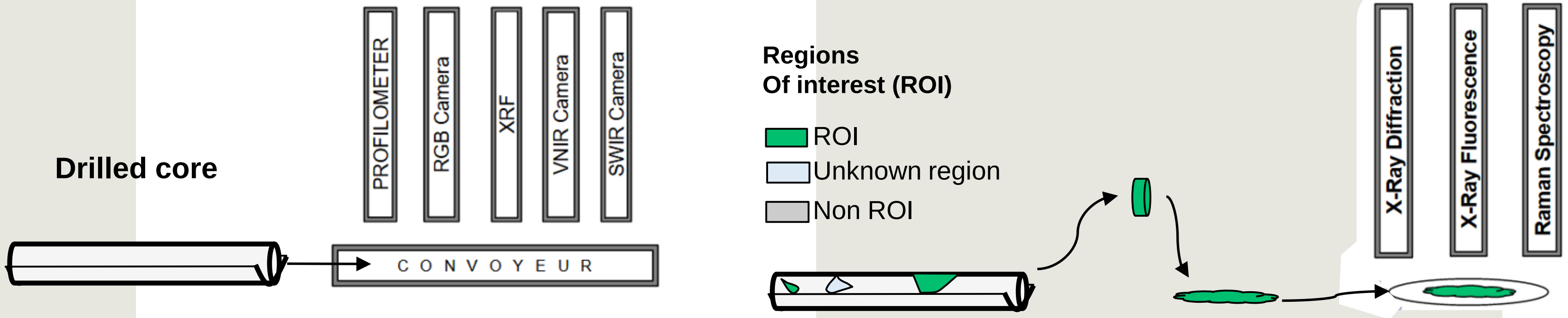


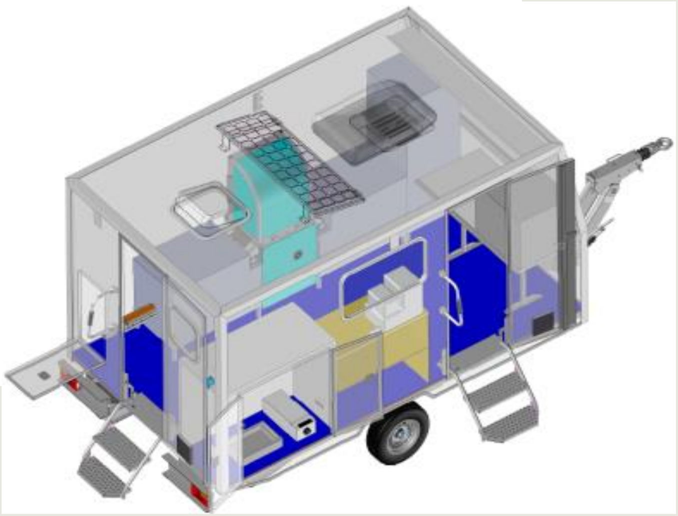
10' — Combined analysis to identified region of interest

10' — Sampling and preparation

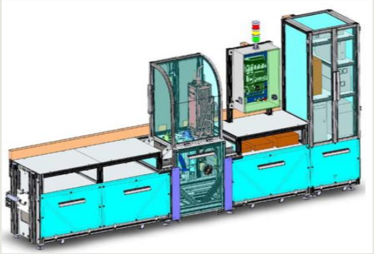
10' 10' — Combined analysis for chemical and mineralogical quantification

10' — Expert software for combined analysis



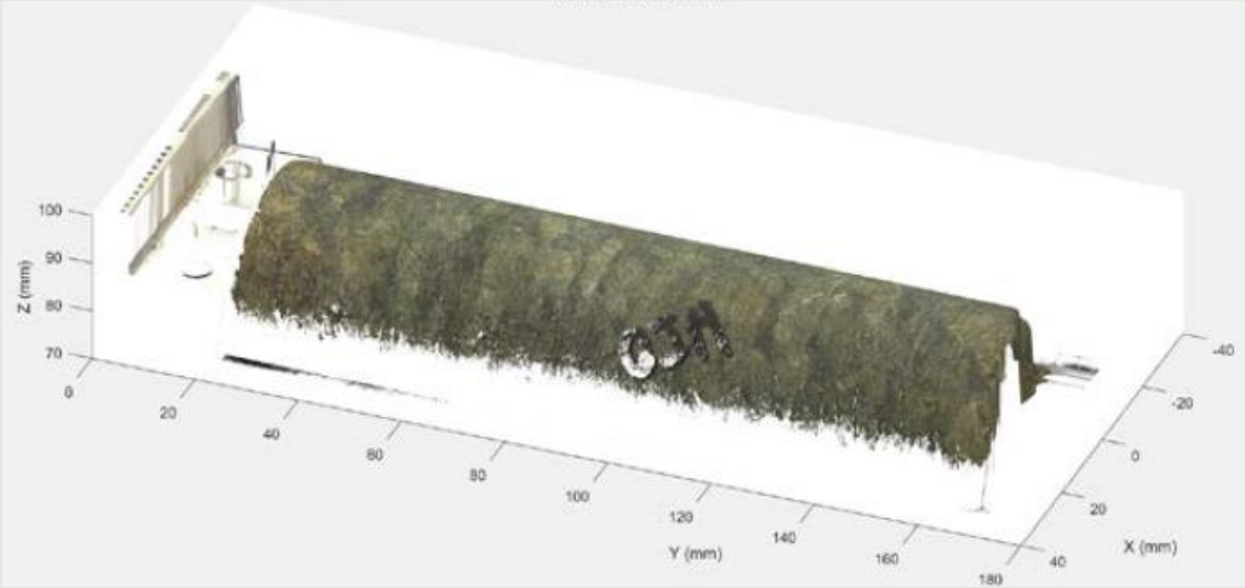


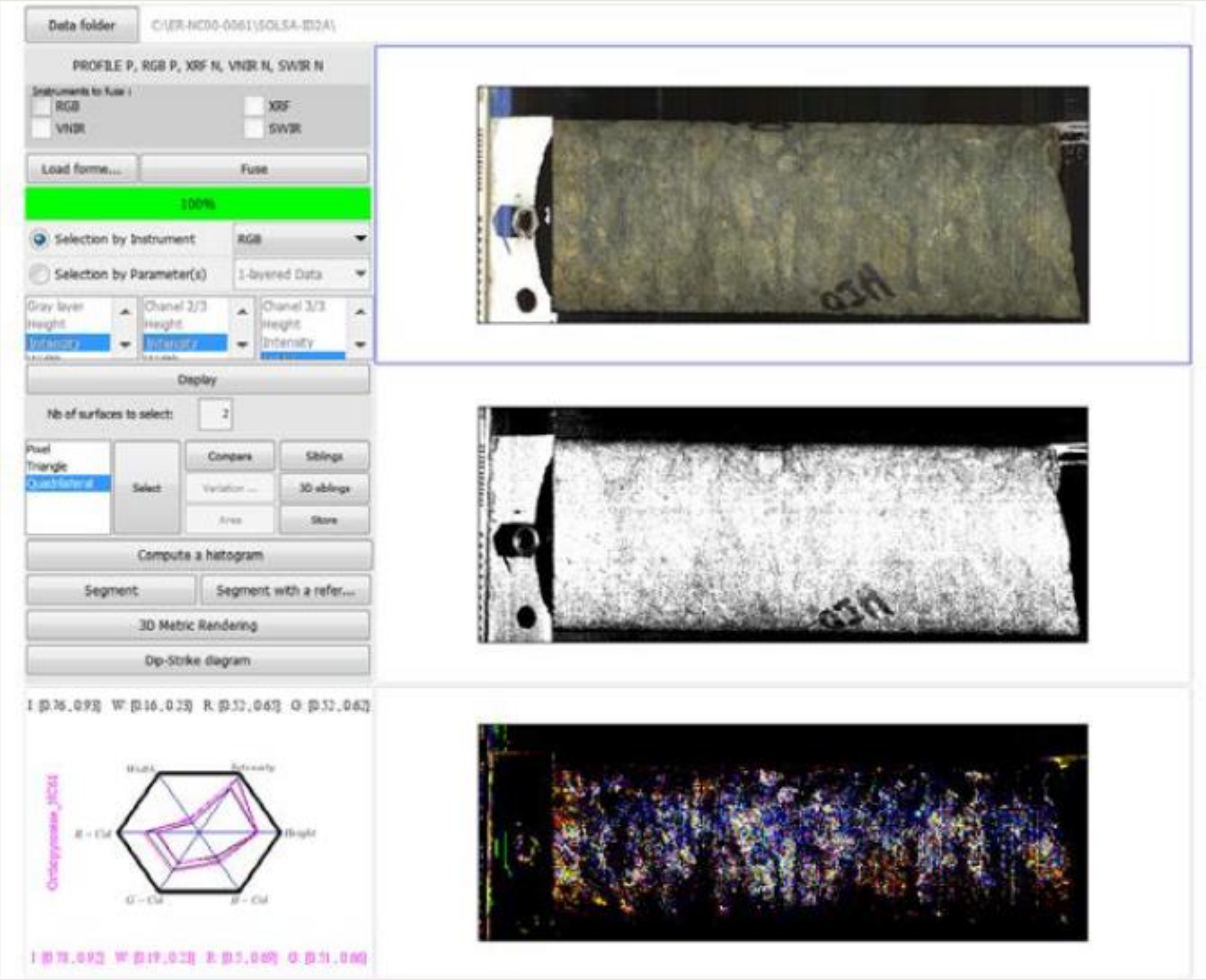
Drilled core scanner with combined techniques



MORPHOLOGY AND MINERAL TEXTURE

→ RGB images and profilometer data: segmentation

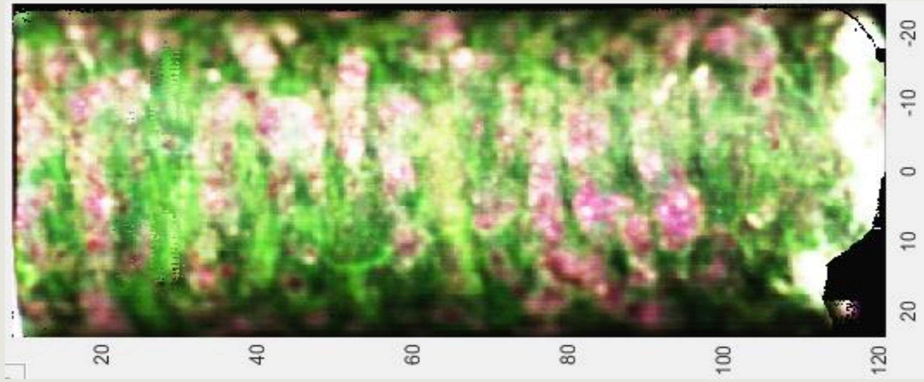




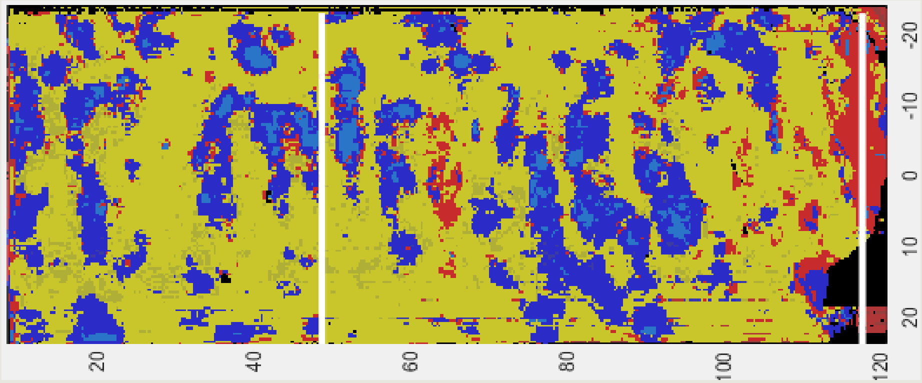
DRILLED CORE SCANNER: MORPHOLOGY AND MINERALOGY

→ Combined data treatment : example on harzburgite sample

- Hyperspectral images data treatment

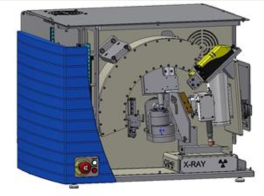


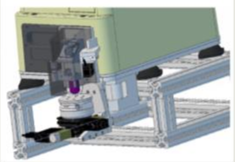
Minerals	Error	Color	Prop
Olivine-Serpentine	0		56.56
Olivine-Serpentine-Sm...	0		4.57
Pyroxene	0		2.73
Pyroxene-Serpentine	0		23.3
Pyroxene-Serpentine-...	0		0.07
Pyroxene-Serpentine-...	0		0.16
Serpentine	0		7.82



- Local investigation by selecting targeted area
- Segmentation by comparing with referenced samples
- Global investigation :
  - Histogramme,
  - Structural data (faults, fractures…), …
- Detection:
  - Mineralogy (Hyperspectral)
  - Shape/grain size
  - Roughness
  - Surface estimate → m²
  - …

CHEMICAL AND MINERALOGICAL DISCRETE COMBINED ANALYSIS





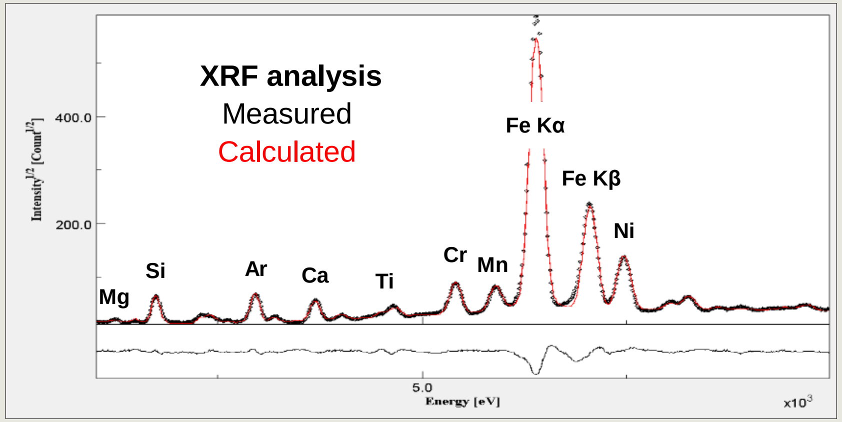
example on a sample of harzburgite ground into a powder

Chemical and mineralogical quantification:

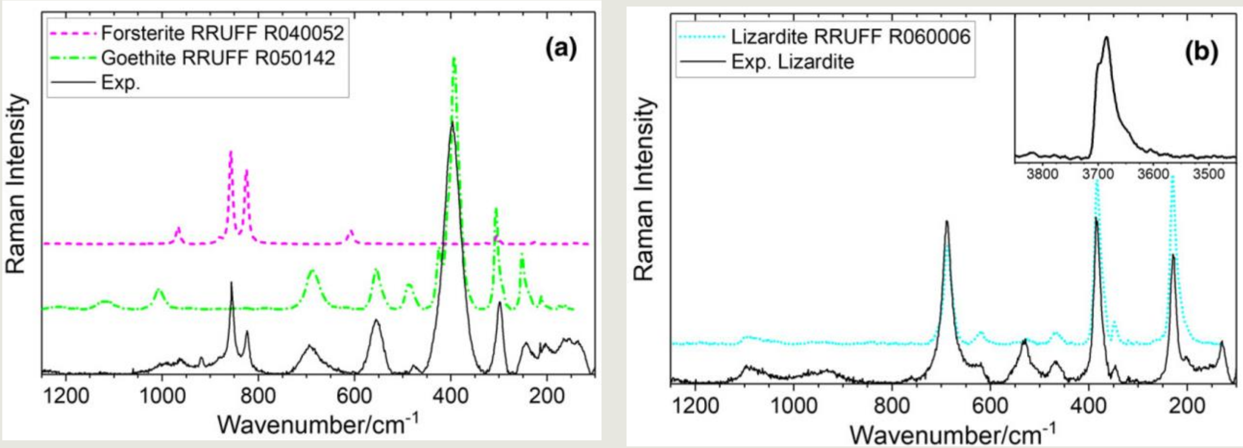
1. Chemical elements identification (XRF)

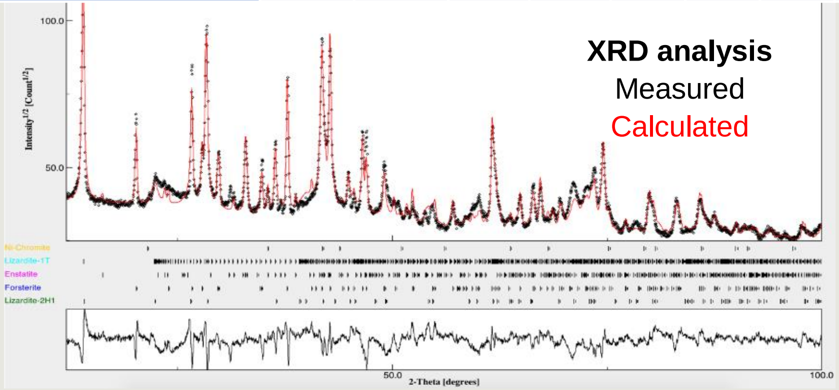
Selection of the possible phases in the XRD DB and Raman from the identified elements

1. "Rietveld Search-Match" treatment by using the selected phases



Identified chemical element	Mg	Si	Ca	Ti	Cr	Mn	Fe	Ni
Minilab Proportion (%)	23,30	19,95	0,39	0,04	0,27	0,14	9,53	0,15
Lab. Proportion (%)	**25,27**	**18,65**	**0,25**		**0,22**	**0,09**	**6,12**	**0,22**





Secchi et al. (2018)
El Mendili et al. (2019)

Raman analysis

- Shows that serpentine is **lizardite**
- Confirms the presence of **forsterite, enstatite and chromite**
- **goethite** is also detected(very small amount)

Phases	Lizardite	Forsterite	Enstatite	Ni-Chromite	Quartz
Minilab Proportion (%)	42 ± 1	45 ± 2	12 ± 1	1 ± 1	-
Lab. Proportion (%)	**46**	**41**	**13**	**-**	**trace**

COMBINED ANALYSIS, A WAY TO AUTOMATE MATERIAL CHARACTERIZATION

INEL INNOV

BENEFITS OF MODULAB

Reliability benefit

→ Good accuracy compared to laboratory analyses

ECONOMIC BENEFIT

→ Analysis is **50 to 100 times** cheaper

TIME BENEFIT

→ Automated approach to concentrate labor on other tasks

→ Up to **20 times** more analyzed sample

TECHNOLOGICAL BENEFIT

→ Systematic banking of large amounts of data

ORGANISATIONNAL BENEFIT

→ Lesser dependence on external providers

→ Real time adjustment of the industrial parameters to optimize the process

ENVIRONNEMENTAL BENEFIT

→ Limitation of sample transport

THANKS FOR ATTENTION

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