TerrAnalytiX

Instrumentation function to Rietveld refinement

"Reflection on your diffraction setup"

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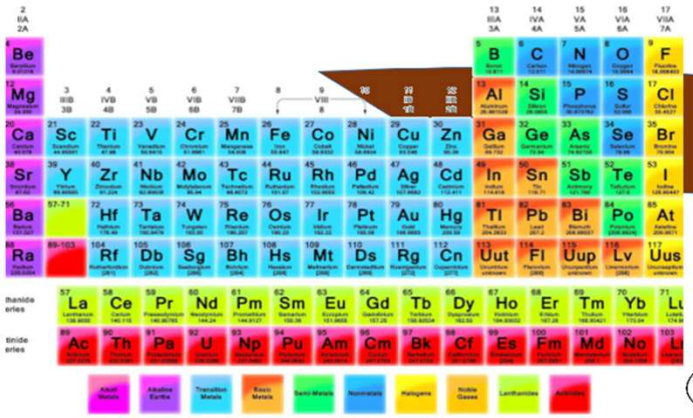
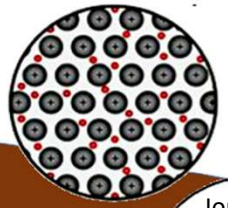
Summer school **"Combined Analysis Using Ray Scattering", 6-10 July 2026 in Caen**

What is matter ?

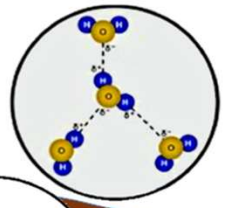
From about 100 chemical elements



Metallic bounding

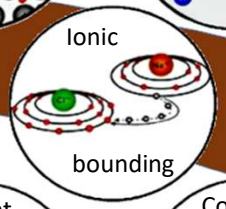


hydrogen bounding

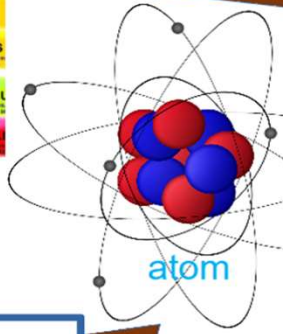


Several possibilities of assembly

Ionic

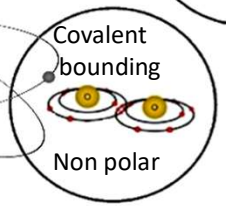


bounding



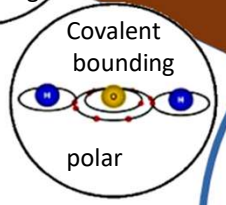
atom

Covalent bounding



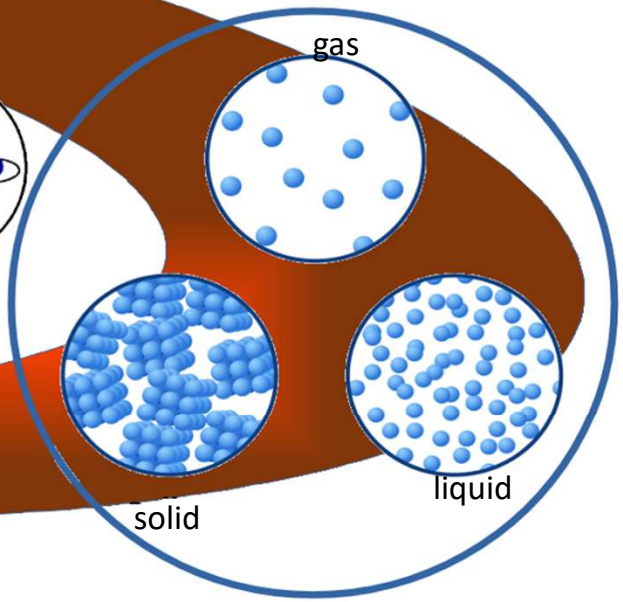
Non polar

Covalent bounding



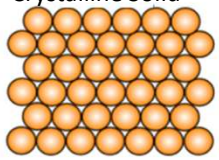
polar

3 states of matter

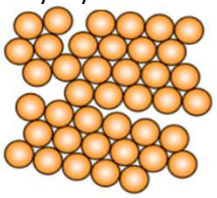


Solid organisation

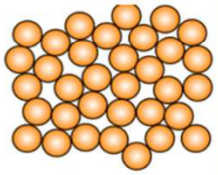
Crystalline Solid



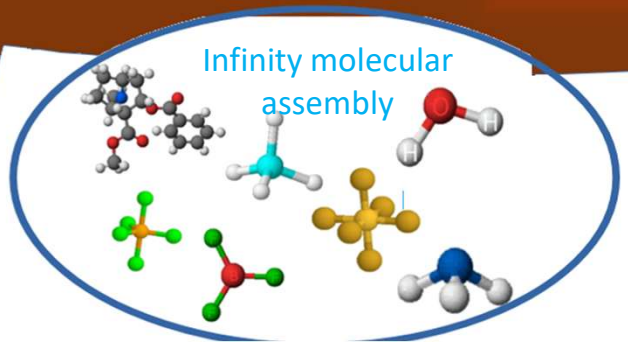
Poly-crystalline Solid



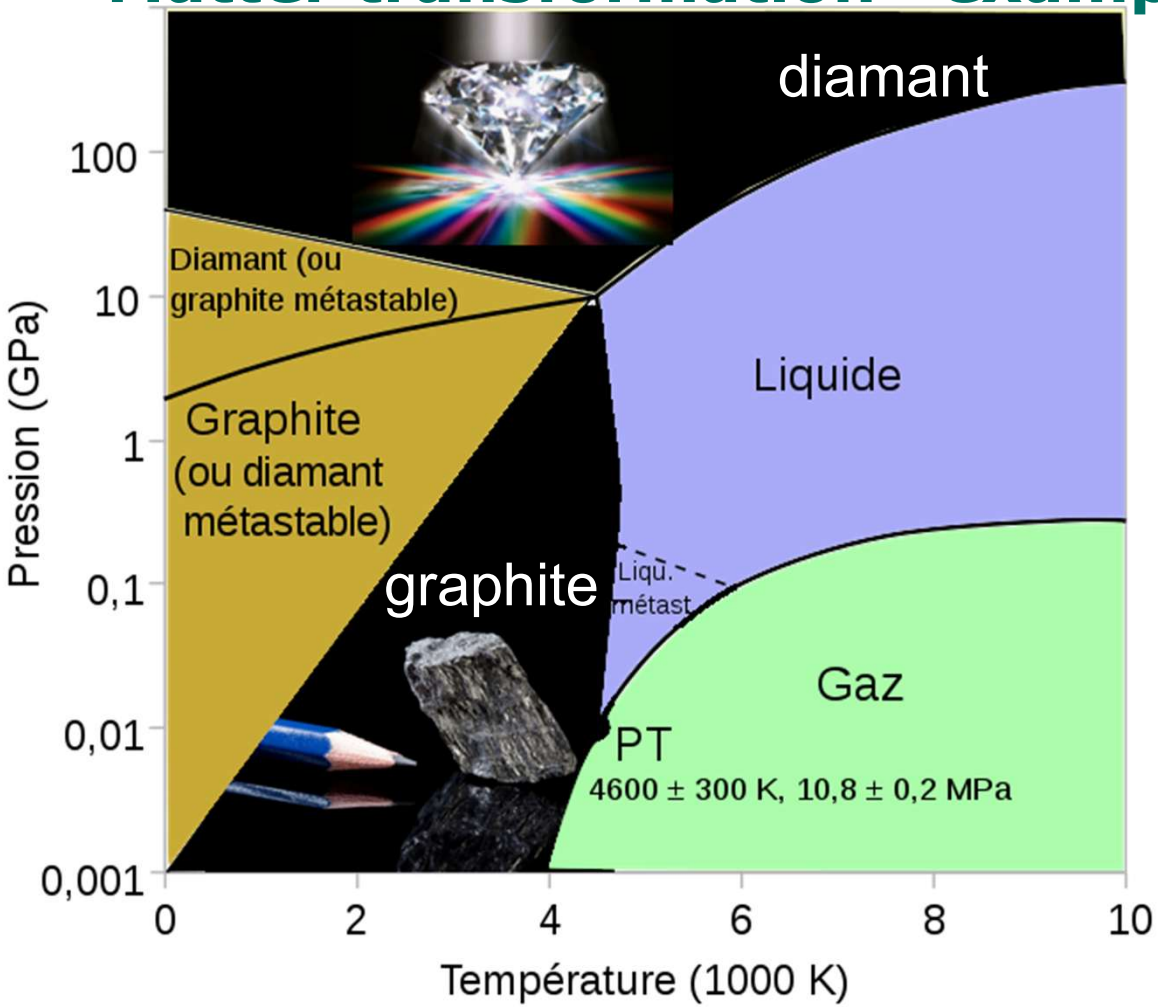
Solid glass

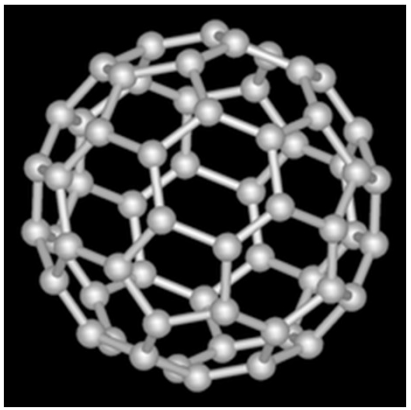


Infinity molecular assembly

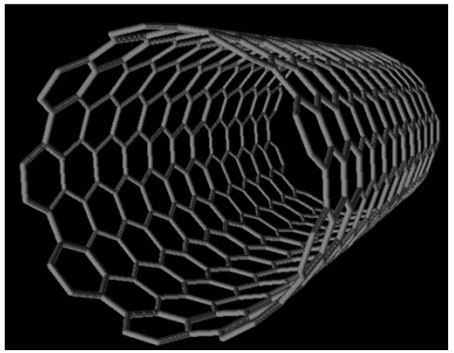


Matter transformation– example of carbone





fulleren



Carbon Nanotube

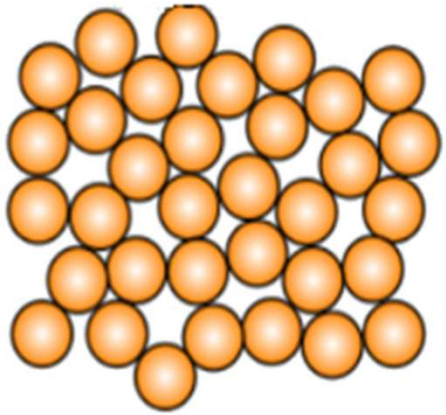
Complexity of transformation : chemical combination
=> Several possible arrangements, with physical rules

Crystallography

How solid matter is organized

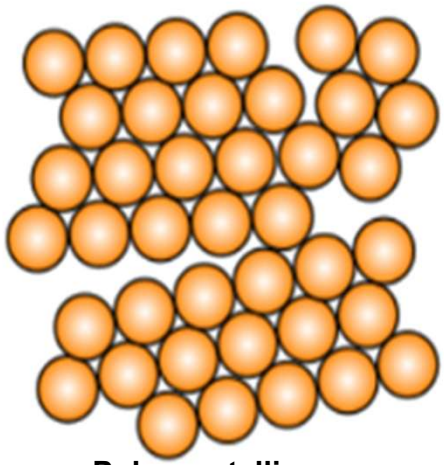
Crystallography

- A solid can be:



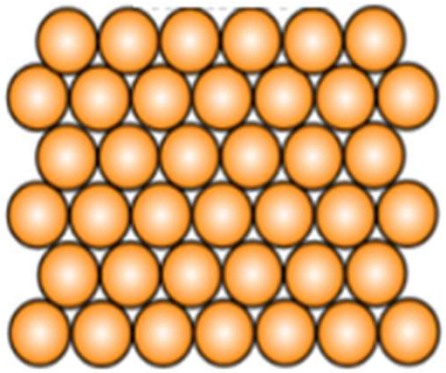
Amorphous:

Solid material, where atom does not present an order at short distance



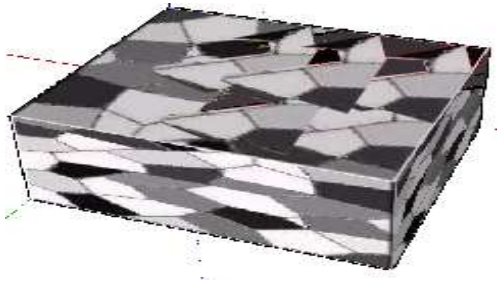
Poly crystalline:

Solid material with groups of atoms highly organized



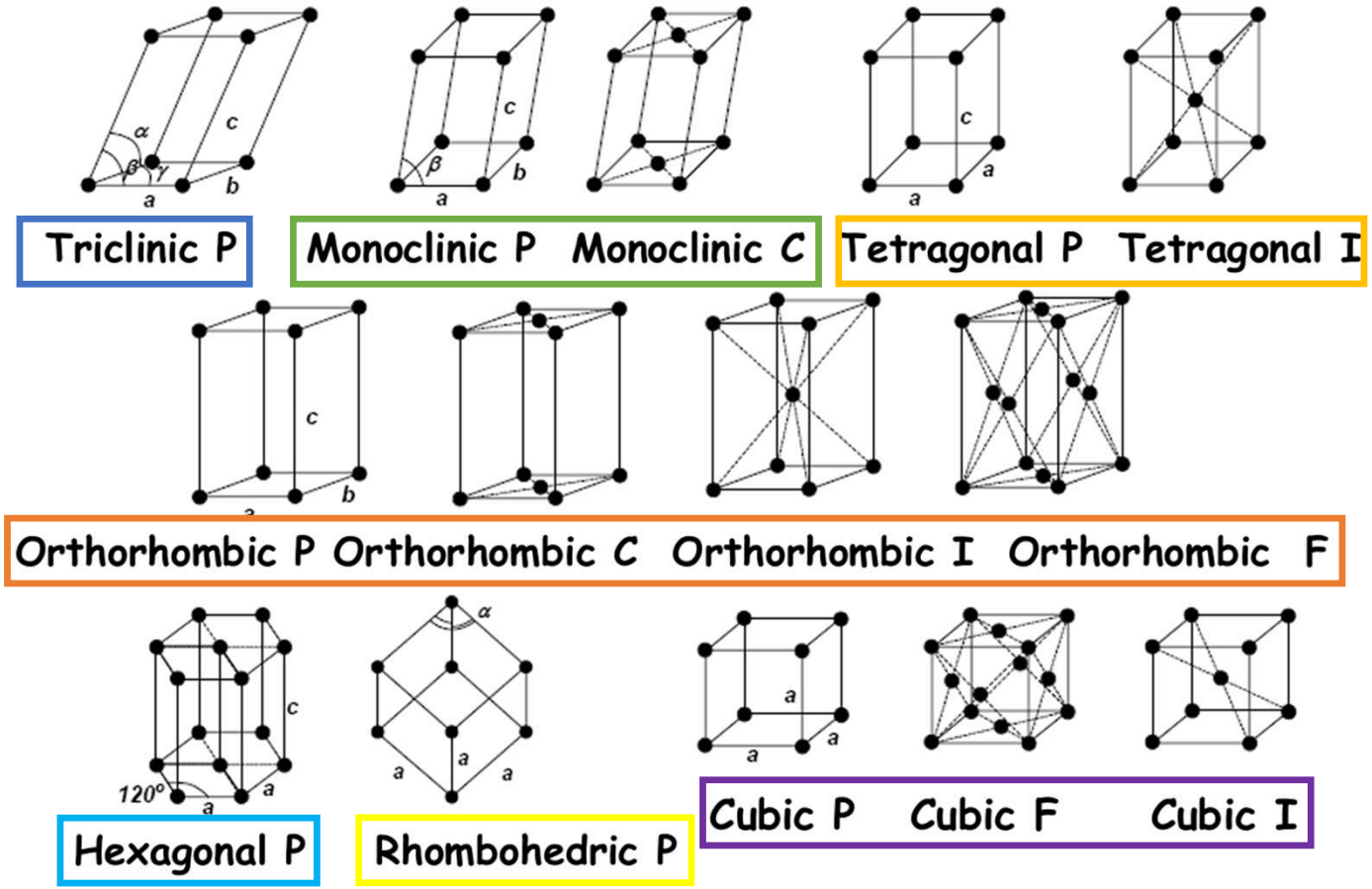
Single crystal:

Solid material (mostly) with a high degree of organization



Crystallography, how to explain the structure of matter

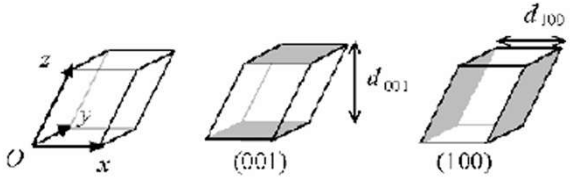
- Order is performed with 7 geometrical shapes: the **Bravais lattices**



Crystalline structure is governed by **atomic bonding** and **coordinance**.

Repetition of ordering leads to make interferences with radiation and atomic planes : **diffraction**

Cells parameters allow to characterize the geometry of the unit cell : a, b, c, α, β, γ

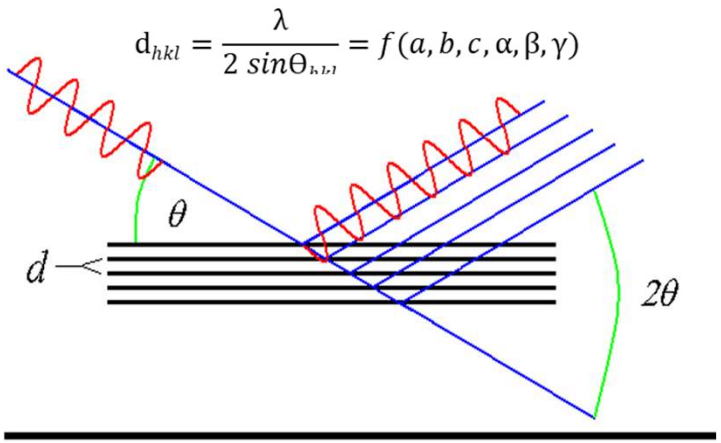


Atomic planes are identified by 3 digits (Miller index), **hkl**

X-Ray Diffraction basics

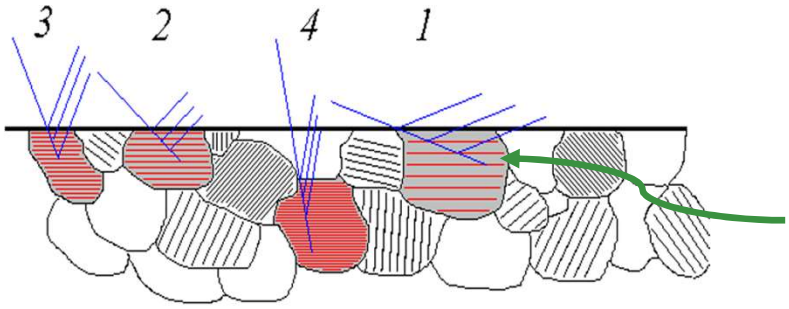
Condition of diffraction:

When wavelength of the radiation is in condition of interference with atomic planes



$Powder\ diffraction = \Sigma\ crystallite\_diffraction$

This is a poly-crystalline material



crystallite with its own orientation vs primary beam

- Planes of atoms act like a diffraction grating
- Constructive & destructive interference leads to peaks in scattered intensity
- Values of λ & d determines 2θ

Bragg's law : nλ= 2d sinθ

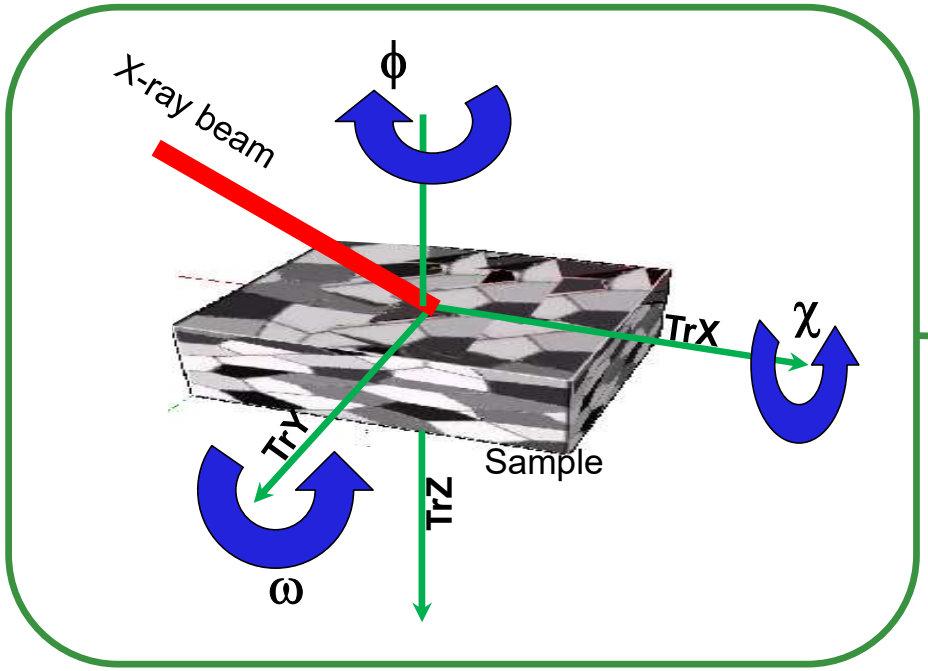
Where

- n = order of radiation
- λ= wavelength of radiation
- 2d = lattice spacing of crystallites in the powder sample for XRD
- θ = Bragg angle

X-ray diffraction

How to measure structures at the nanoscale

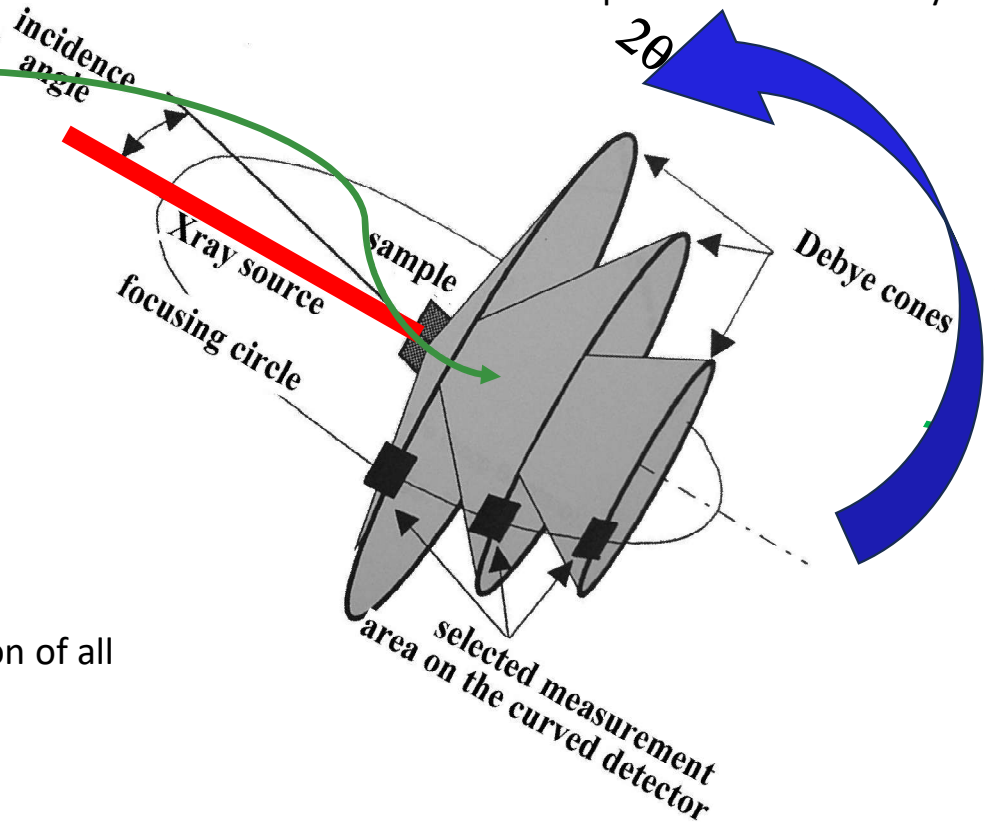
X-Ray Diffraction instrument - definitions



X-ray beam interacts with sample structure

Referential description

Sample diffracts the X-ray beam



[(IUCr) International Union of Crystallography](#) : CIF definition of all parameters used in XRD

X-Ray Diffraction pattern

A powder sample is measured by using X-ray diffractometer

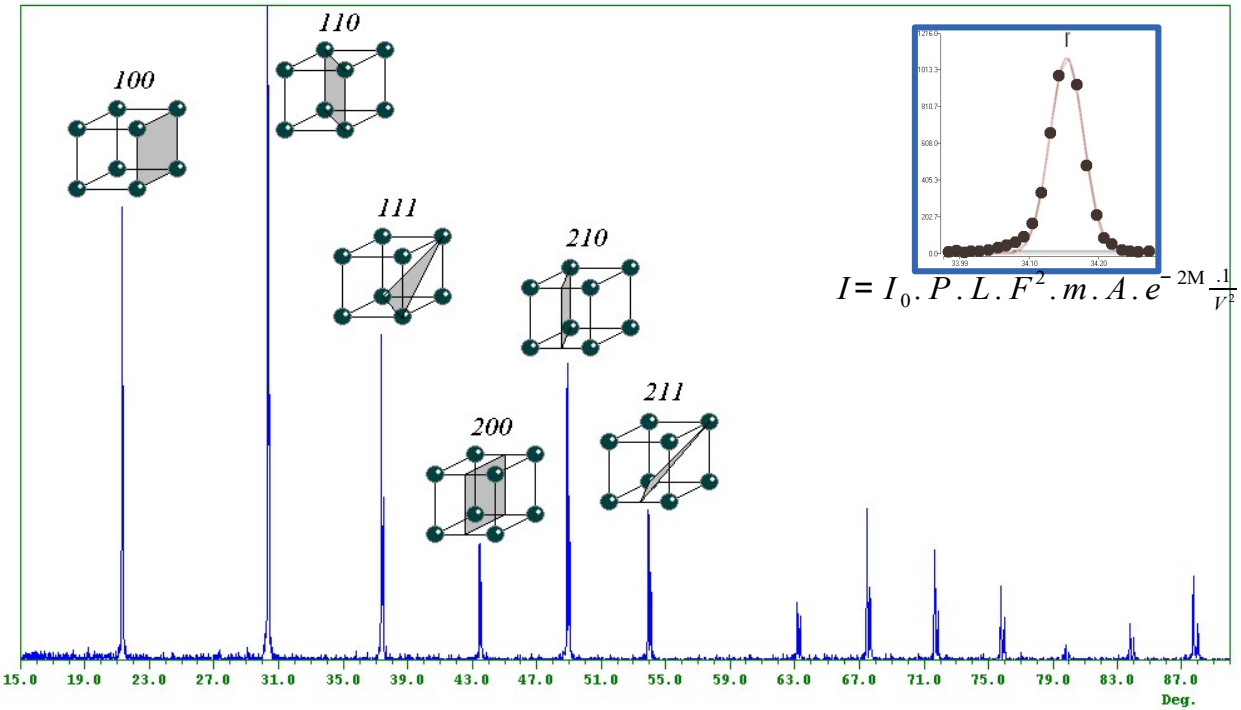
The diffractogram represents the interference function of a given materials by its periodic structure of atomic planes

Peak position → d-spacings

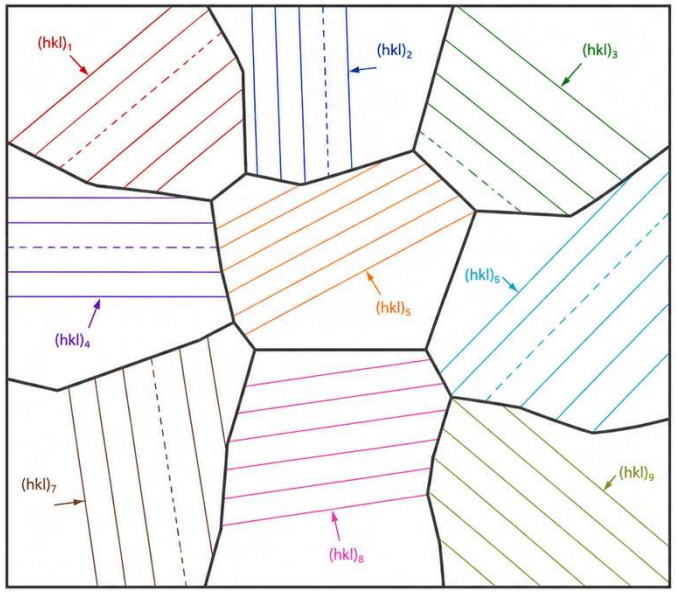
Peak intensity → nature and atomic positions in planes

Pattern will be affected by:

- The mineralogy
- The instrumental characteristics

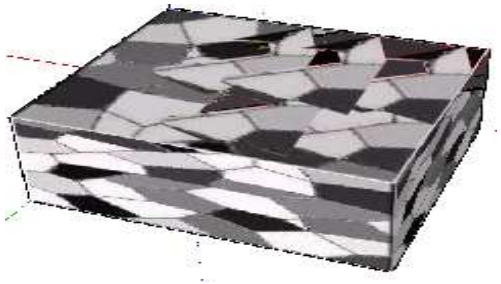


$$I = I_0 . P . L . F^2 . m . A . e^{-2M} \frac{.1}{V^2}$$

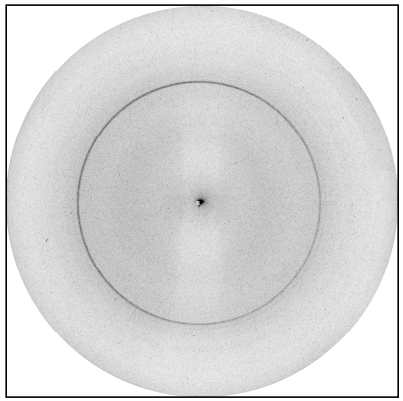


X-Ray Diffraction pattern – instrument/sample influence

A primary **X-ray beam** Enlight a sample:
- Wavelength function of the beam : $\Sigma\lambda \pm \Delta\lambda$ For instance, Cukα_1 (100) + Cukα_2(50)
- Shape and divergence of the beam : width, div width, height, div height



A **sample** receives the primary beam:
- Sample shape : bulk, powder, surface, cylinder
- Type of lighting (reflection/transmission)
- Sample positioning in the beam $(\Omega, \chi, \varphi, X, Y, Z)$
- Grain size distribution and shape, microstrains
- N phases composition
- Structural specificity: strains, texture, thin film, defects, superstructure …



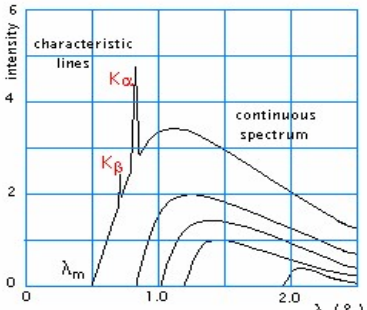
A **detection device** receives the diffracted beam:
- Detector spatial resolution
- Detector positioning $(2\theta, \xi, radius)$
- Detector characteristics (OD, 1D, 2D, and dimensions)
- Detector energy resolution

X-ray diffraction setup

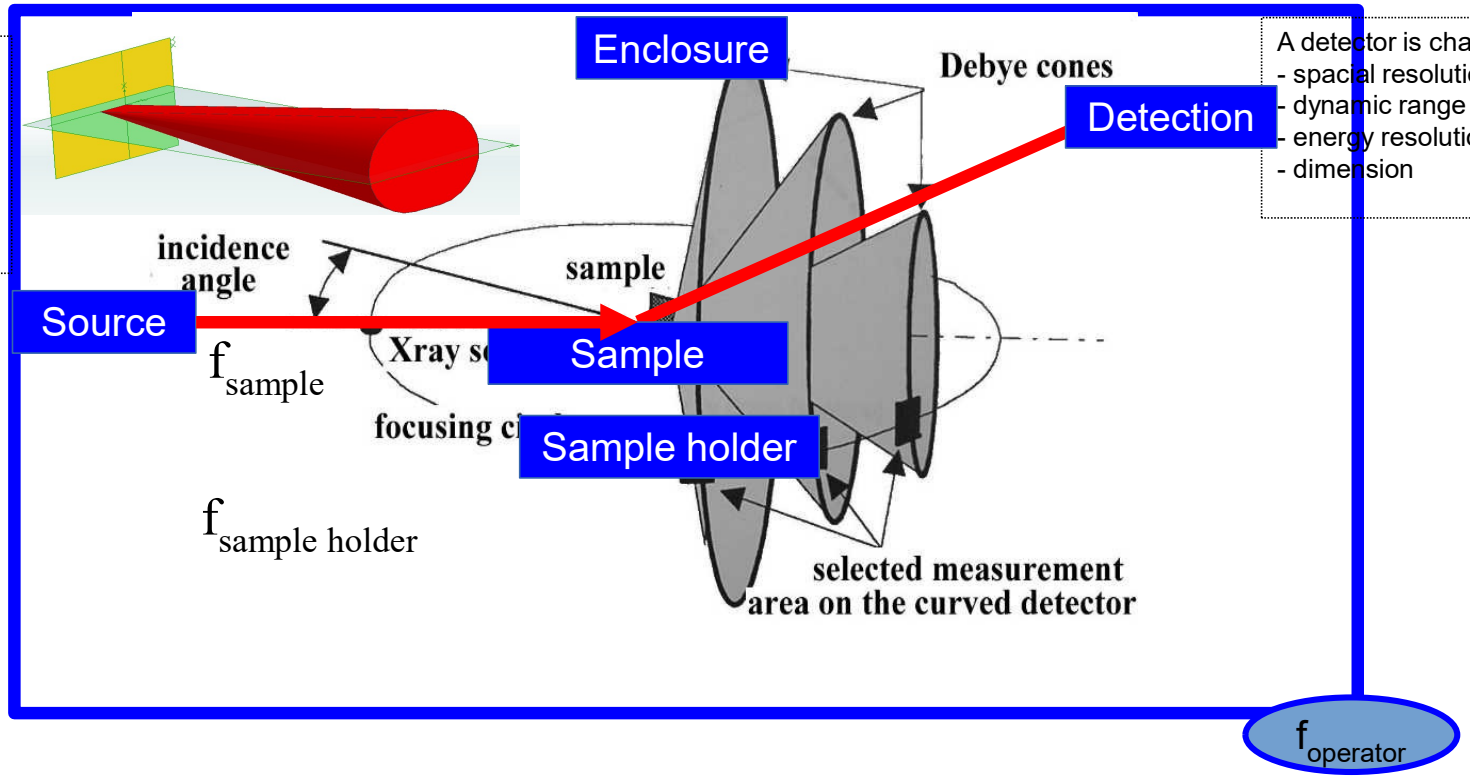
Instrument using a radiation for probing matter is defined by several functions :

A light emission characterized by :

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



Molybdenum spectrum vs the applied voltage



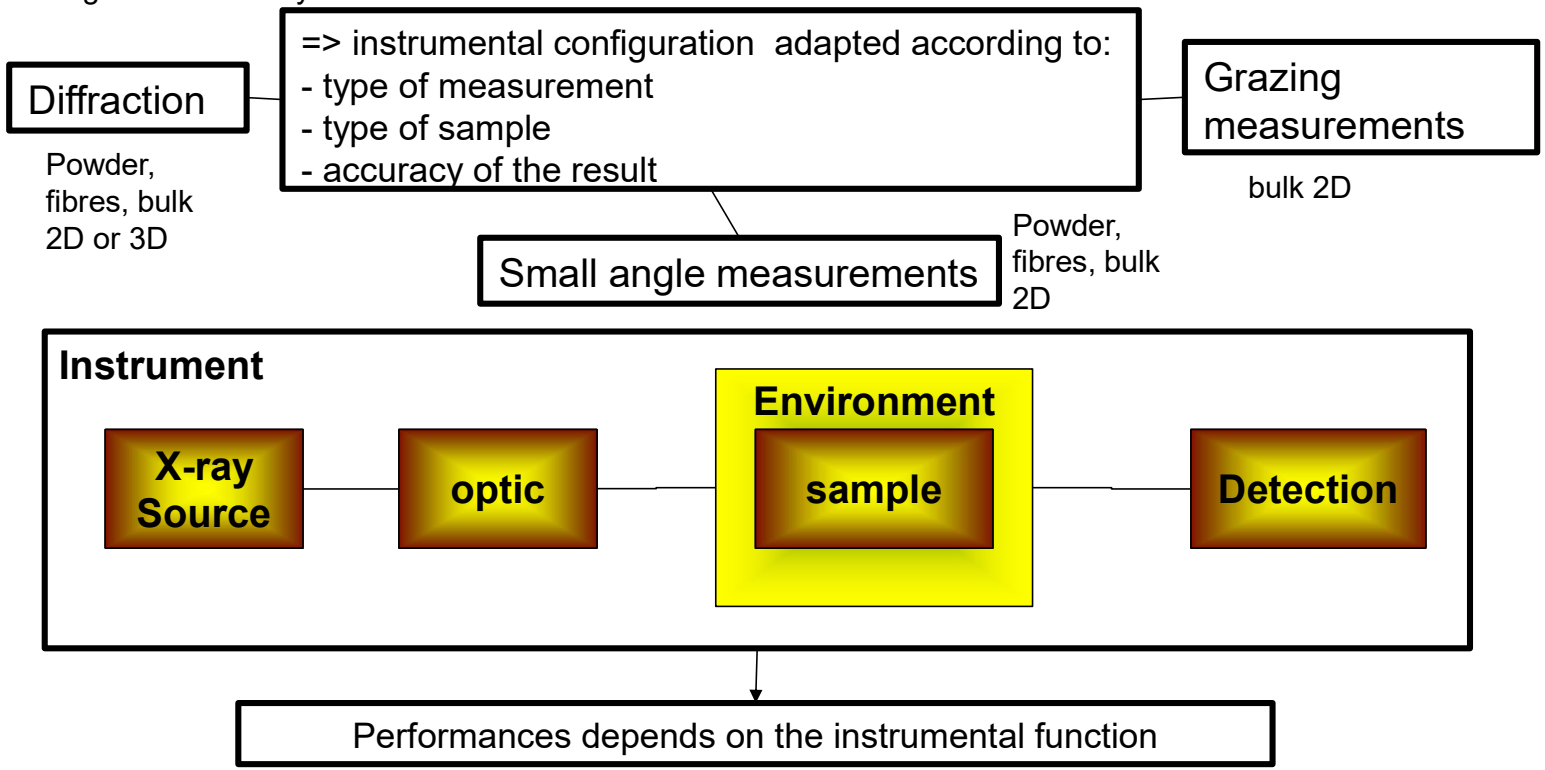
A detector is characterized by :
- spacial resolution
- dynamic range
- energy resolution
- dimension

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

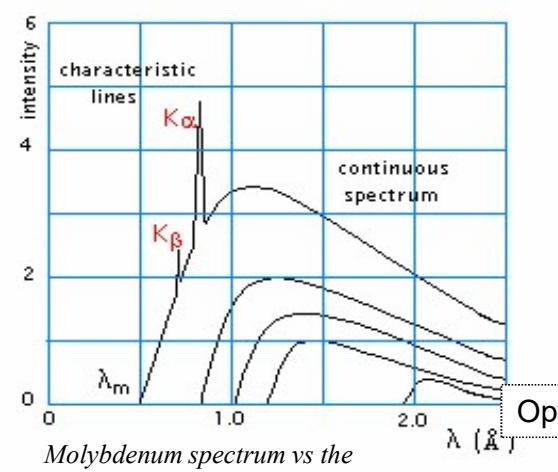
Instrumental function for XRD

Elastic coherent interaction :
reflectometry : 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 crystalline defects.



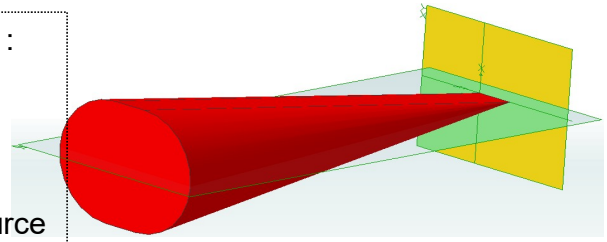
Function X-ray source



Molybdenum spectrum vs the applied voltage

A light emission characterized by :

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

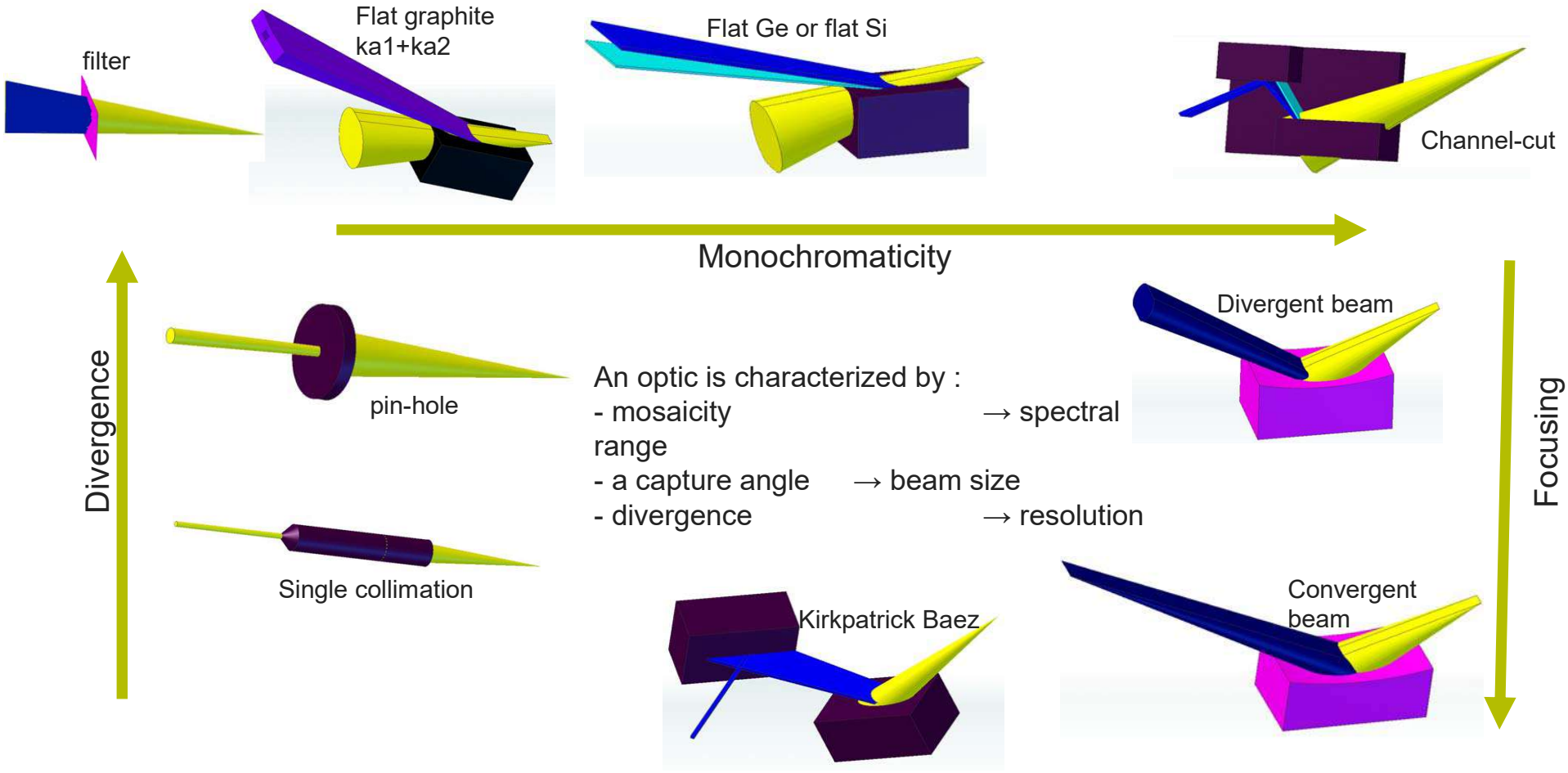


Optimizing the characteristics of a source allows to focus on a given interaction

	fluorescence	imaging	diffraction	reflection	diffusion
Spectral range	large	large	Monochromatic (excepted Laue)	monochromatic	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 ...)

Instrumental function for XRD – beam characteristics



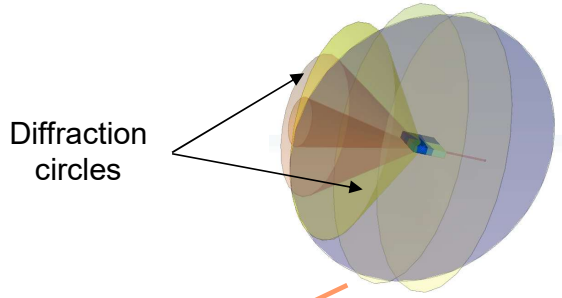
Powder vs crystal

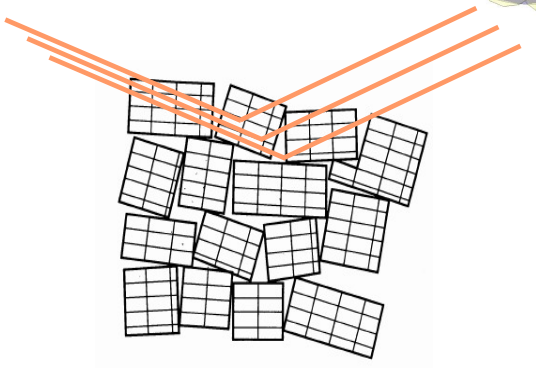
Powder sample :

- **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





Possible with ARL EQUINOX

Not possible with ARL EQUINOX

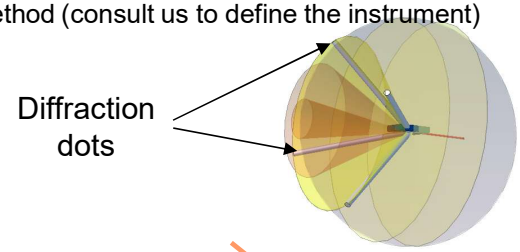
Single cristal :

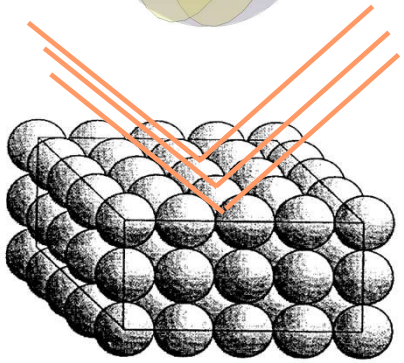
- **1 unique grain probed by X-rays**
- 1 unique diffacted signal for a given orientation of cristal

=> 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)



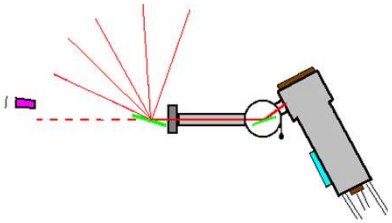


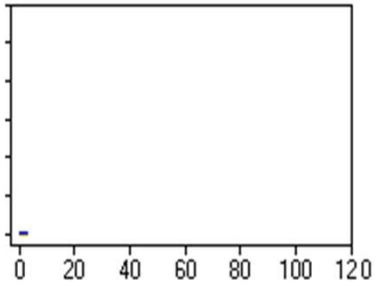
Function X-ray detection

0D Detection :

Acquisition is done Stepwise

2θ and statistics are time dependent



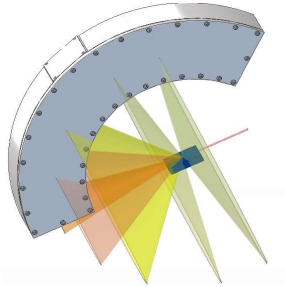


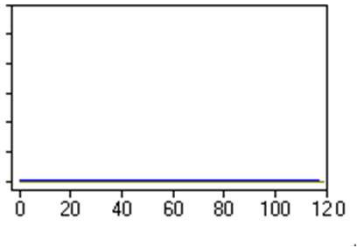
Bragg-Brentano geometry

1D Detection :

Acquisition is done in snapshots

Statistics is time dependent





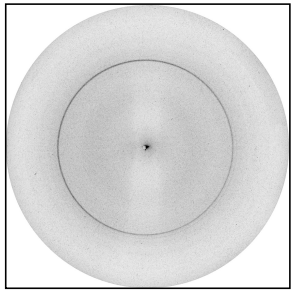
asymetric geometry

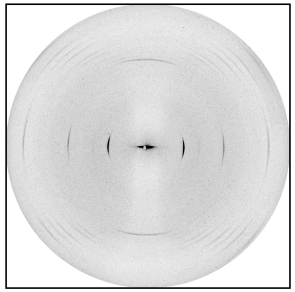
2D Detection :

Acquisition is done in snapshots

Statistics is time dependent

Texture information but point beam required





X-ray diffraction setup

Understanding how to get the result

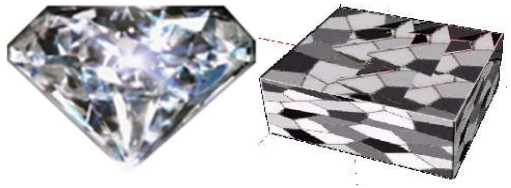
- appropriate instrumental configuration

- appropriate sample conditioning

- appropriate calibrations / corrections

$$d_{hkl} = \frac{\lambda}{2 \sin \theta_{hkl}} = \frac{h.c}{2 E_{hkl}.\sin \theta}$$

		Type of solid		
		Single crystal	Polycrystalline	d_{hkl}
Type of radiation	Monochromatic	Rotating crystal Method	Powder XRD	$\frac{\lambda}{2 \sin \theta_{hkl}}$ λ (or E) is fixed
	polychromatic	Laue Method	ED-XRD	$\frac{h.c}{2 E_{hkl}.\sin \theta'}$ θ is fixed



Single crystal

Polycristalline material

X-Ray Diffraction pattern

1rst step : determination of the instrumental function

- **Type of instrument**:
  - Bragg-Brentano diffractometer:
    - Primary beam is monochromatic and divergent on flat sample surface
      - Monochromaticity by using filter or bent monochromator
    - Sample refocuses the diffraction beam on the detection device
      - Spinner can rotate the sample in continuous φ rotation (axis perp to sample surface)
    - Sample rotates in θ angle and detector in 2θ angle
    - Detector integrate counting for a certain acquisition time

Bragg Brentano geometry

Sample is an optical component!!

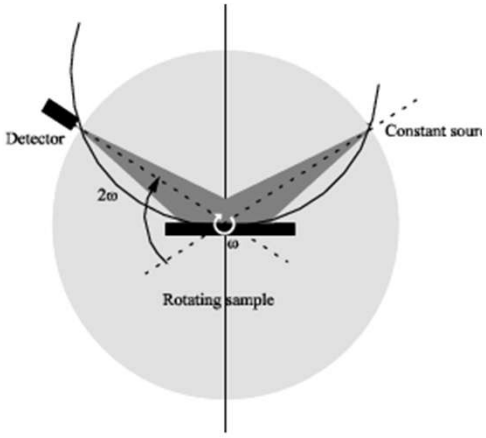


Figure 2.46. *θ-2θ Bragg-Brentano diffractometers*

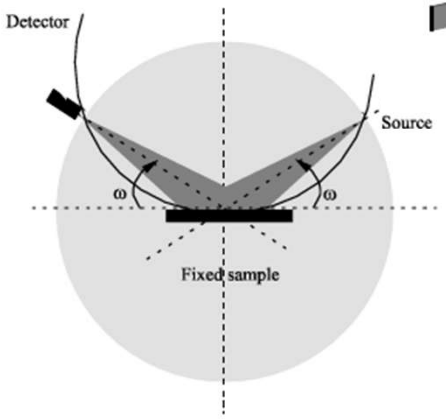


Figure 2.47. *θ-θ Bragg-Brentano diffractometer*

without optic

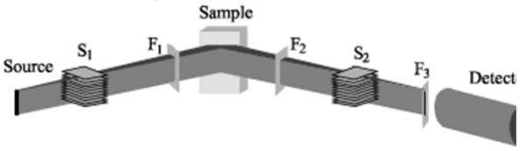
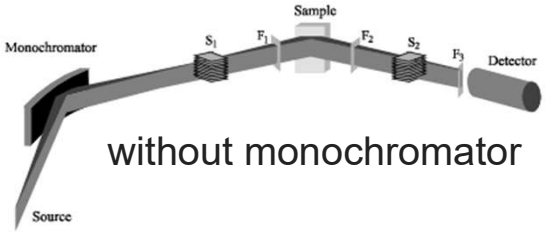


Figure 2.48. *Path of the X-ray beams in a Bragg-Brentano diffractometer*



without monochromator

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

For phase identification and quantification

From R. Guinebretiere

X-Ray Diffraction pattern

1rst step : determination of the instrumental function

- **Type of instrument**:
  - Debye-Scherrer diffractometer:
    - Primary beam is monochromatic using a bent or flat monochromator and convergent on the detector
    - Sample is measured in transmission, either inside a capillary or in between 2 transparent foils
      - Spinner can rotate the sample in continuous φ rotation (axis parallel to Ω)
    - Detector scans in 2θ angle
    - Detector integrate counting for a certain acquisition time

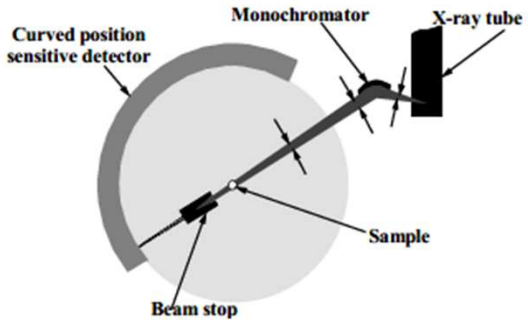


Figure 2.28. *Debye-Scherrer diffractometer equipped with a position sensitive detector*

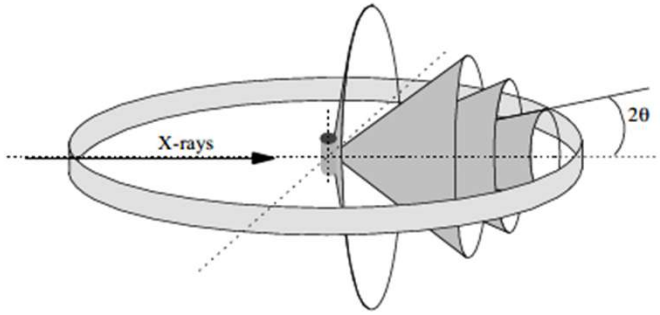


Figure 2.25. *Geometric arrangement of the Debye-Scherrer and Hull diffractometer*

For high resolution powder diffraction

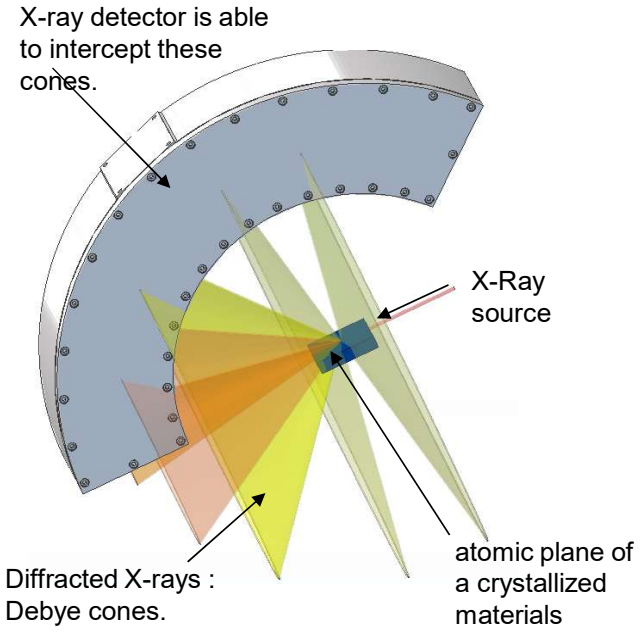
From R. Guinebretiere

X-Ray Diffraction pattern

1rst step : determination of the instrumental function

- **Type of instrument**:
  - Asymmetric geometry diffractometer:
    - Primary beam is monochromatic using a flat monochromator
    - Sample is measured in reflection at a fixed Ω angle
      - Spinner can rotate the sample in continuous φ rotation (axis perp. to Ω)
    - Detector scans in 2θ angle (PSD detector does not need to be scanned)
    - Detector integrate counting for a certain acquisition time

Well adapted for in-situ measurements, thin films, stress and texture measurements, mapping



X-Ray Diffraction pattern

1rst step : determination of the instrumental function

- **Type of instrument**:
  - Parallel beam geometry – asymmetry or $\theta/2\theta$ or $\omega\ scan$:
    - Primary beam is monochromatic using a flat monochromator
    - Sample is measured in reflection or transmission at a fixed or variable Ω angle
      - Spinner can rotate the sample in continuous φ rotation (axis perp. to Ω)
    - Detector scans in 2θ angle
    - Back optic is used
    - Detector integrate counting for a certain acquisition time

For high resolution analysis, peaks profile, rocking curves, epitaxial, reflectometry, microstrains

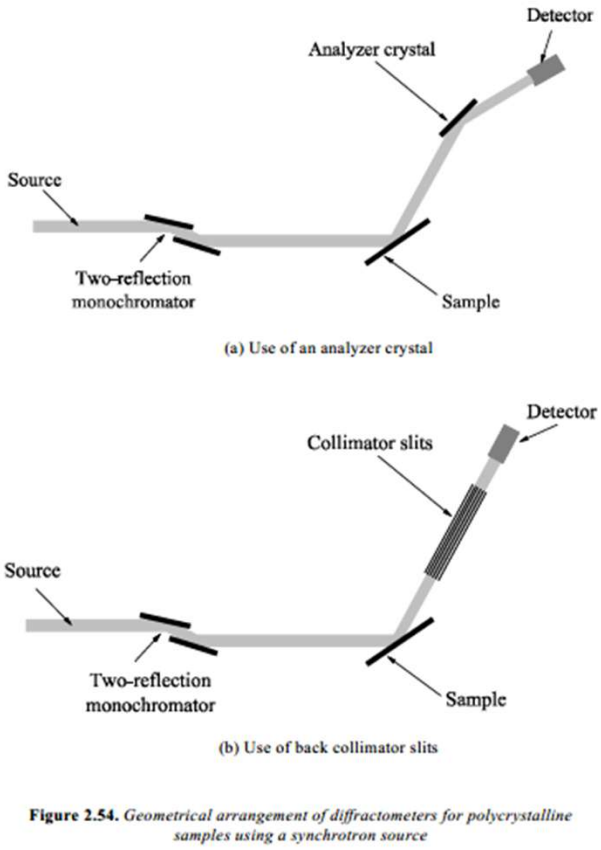


Figure 2.54. *Geometrical arrangement of diffractometers for polycrystalline samples using a synchrotron source*

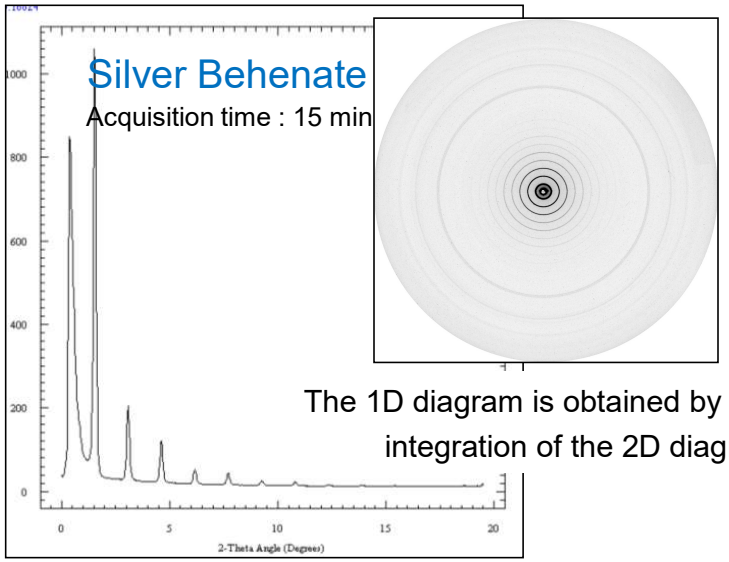
From R. Guinebretiere

X-Ray Diffraction pattern

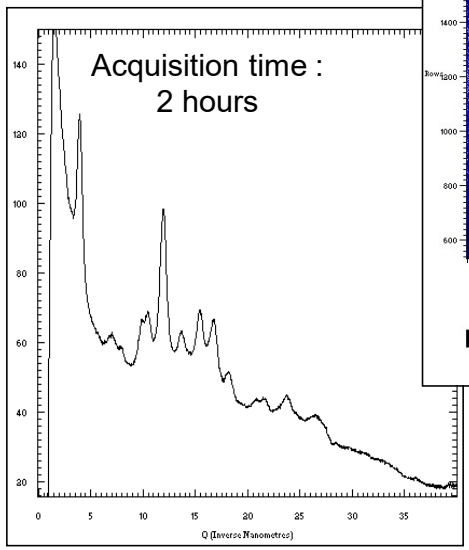
1rst step : determination of the instrumental function

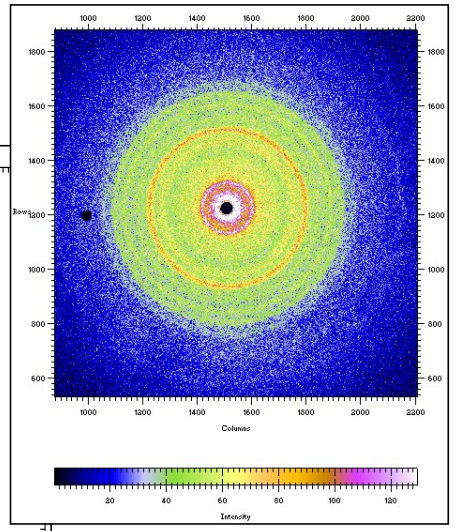
- **Type of instrument**:
  - Small Angle X-ray Scattering -SAXS:
    - Primary beam is highly collimated and preferably monochromatic using a 2D monochromator
    - Sample is measured in transmission
    - Sample is measure in reflection (GISAXS)
      - Spinner can rotate the sample in continuous φ rotation (axis perp. to Ω)
    - Detector scans in 2θ angle, far to sample to detect low 2theta

For high dhkl measurement – nanomaterials …



The 1D diagram is obtained by azimuthal integration of the 2D diagram





X-Ray Diffraction pattern

1rst step : determination of the instrumental function

- **Type of instrument**:
  - Synchrotron setup cases:
    - Primary beam is monochromatic using a flat monochromator
    - Sample is measured in reflection or transmission at a fixed Ω angle
      - Spinner can rotate the sample in continuous φ rotation (axis perp. to Ω)
    - Detector scans in 2θ angle (PSD detector does not need to be scanned)
    - Easy to use 2D detectors
    - Detector integrate counting for a certain acquisition time

Large variety of configurations with expensive components surrounding beam lines

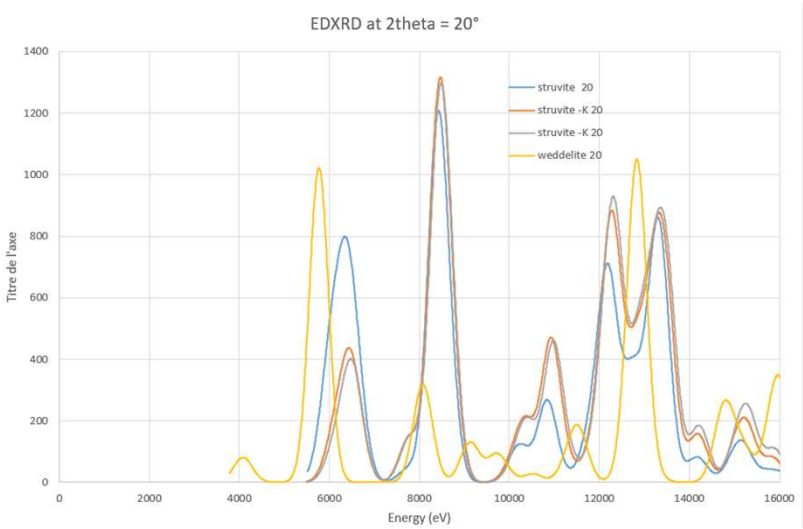
From R. Guinebretiere

X-Ray Diffraction pattern

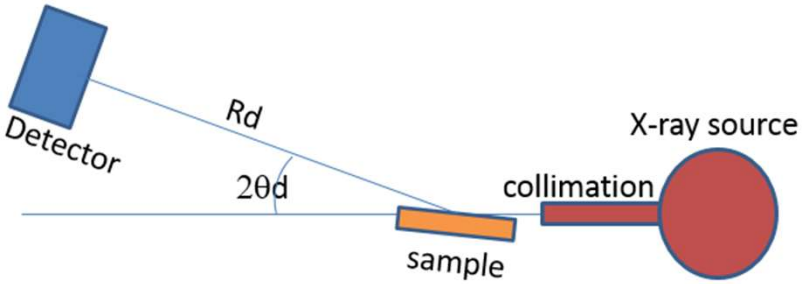
1rst step : determination of the instrumental function

- **Type of instrument**:
  - Energy dispersive diffractometer:
    - Primary beam is polychromatic and almost parallel
    - Sample is measured in reflection at a fixed Ω angle or in transmission
      - Spinner can rotate the sample in continuous φ rotation (axis perp. to Ω)
    - Detector is fixed but is able to dissociate energy
    - Detector integrate counting for a certain acquisition time

$$d_{hkl} = \frac{\lambda}{2 \sin \theta_{hkl}} = \frac{h.c}{2 E_{hkl}.\sin \theta}$$



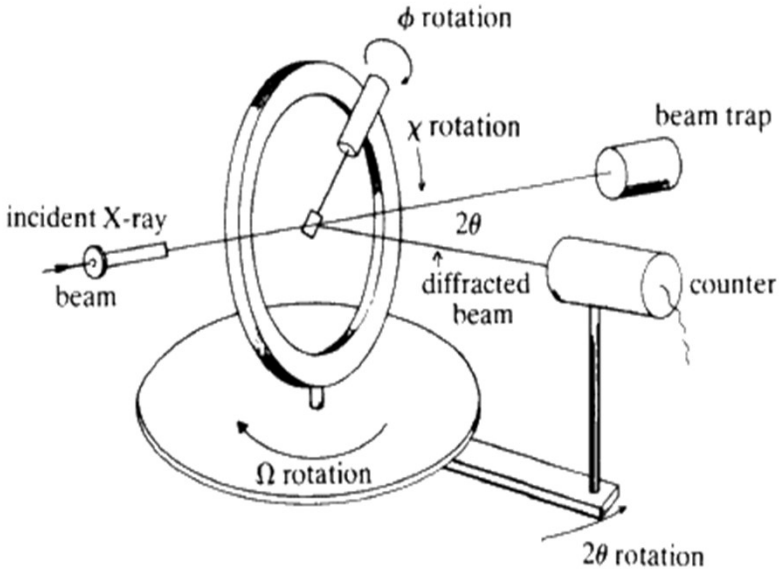
More dedicated for metals



X-Ray Diffraction pattern

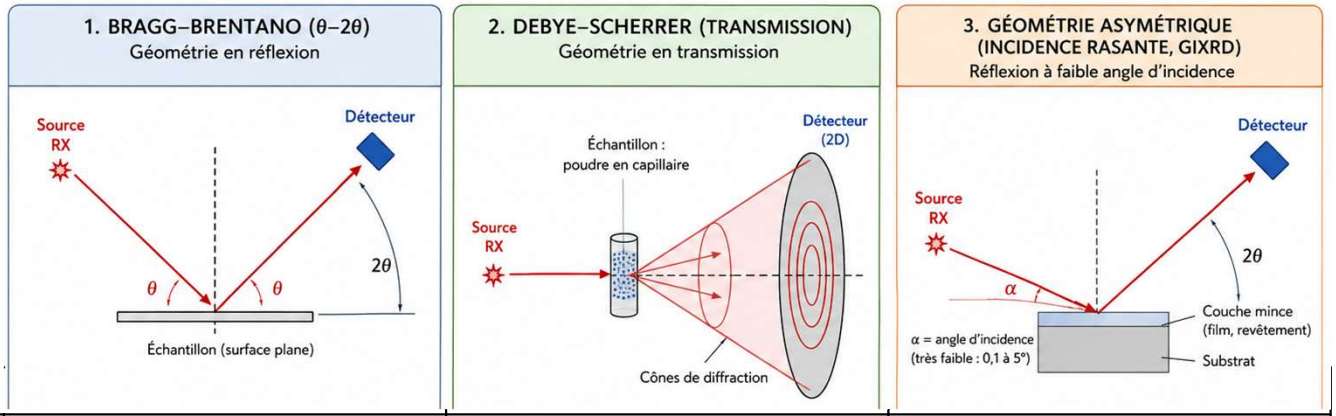
1rst step : determination of the instrumental function

- **Type of sample environment**:
  - For powder:
    - Traditionally, flat sample holder with spinner
    - Some specificities : environmental cell, furnaces, pressure, reaction chambers
  - For Thin films:
    - Accurate omega (Z,XY translation stage)
    - Collimation
  - For texture/stress:
    - 4 axis goniometer



X-Ray Diffraction pattern

Comparison of the different techniques



Mode	Reflection	Transmission	Fixed incidence in Reflection
Sample type	Bulk, powder on crucible	Powder in capillary	Bulk, powder, thin films
Beam size	large	small	small
Surface sensitivity	weak	weak	high
Texture effects	Often important	Very weak	Variables
Amount of required matter	Medium to high	Very weak	weak
Facility to use	Excellent	Medium	good
Phases quantification	Very good	Excellent	Good
Fine structural analysis	Good	Excellent	Medium
Substrate contribution	Important	NA	Weak
Large cells identification	Not good	Good	Good
Diffracting volume	Variable with 2theta	fixed	fixed
	Low 2θ, surface representative High 2θ, depth representative		Importance to scan a large surface

X-Ray Diffraction pattern

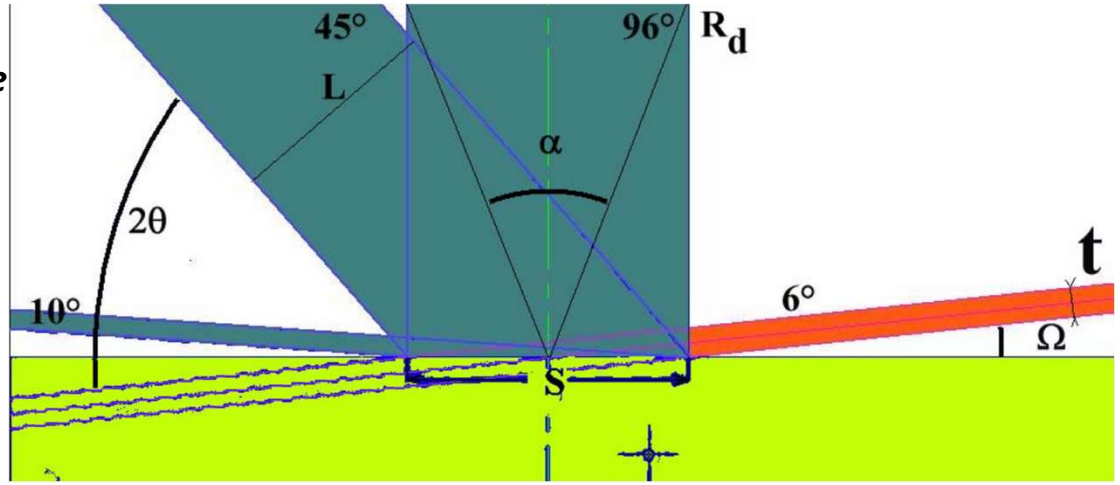
Comparison for some specific cases

Sample type	Bragg-Brentano	Debye-Scherrer	Asymmetric mode
Orientated clay	★★★★★ for d001	★★★ for identification	★
Clays' quantification	★★	★★★★★	★★
Organic transparent materials	★★	★★★★★	★★★
Large grains	★★	★★★★★	★ (depends on amount of sample to be enlighten)
Strong texture (bulk)	★★	★★★★★	★★★
Thin films	★	★★	★★★★★
Epitaxy	★	★	★★★★★

X-Ray Diffraction pattern

Asymmetric mode : Effect of Enlighted area vs incidence

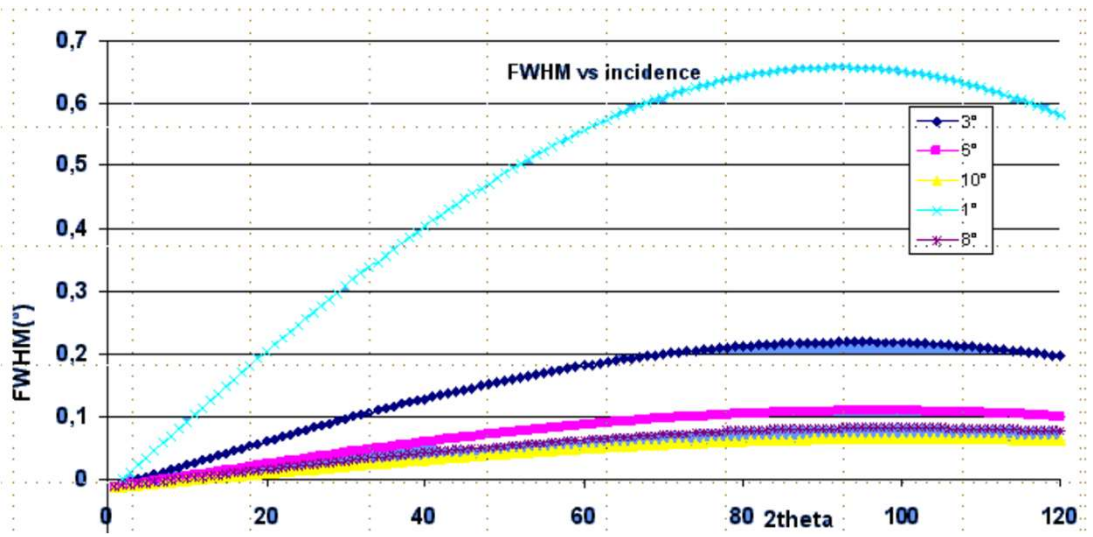
In reflection mode, when the pattern is measured with a fix incidence, peaks profile should depend on the lit surface



L = $\frac{t.\sin(2\theta-\omega)}{Sin(\omega)}$, t: beam thickness

FWHM(ω) = $\frac{t.\sin(2\theta-\omega)}{2.R_d.Sin(\omega)}$, full Width at half maximum of the peak

Lower is the incidence ω, broader will be the diffraction peaks



<u>Conclusion</u> : instrumental function should be performed for each ω configuration

The reflection mode gives more aberration than transmission mode

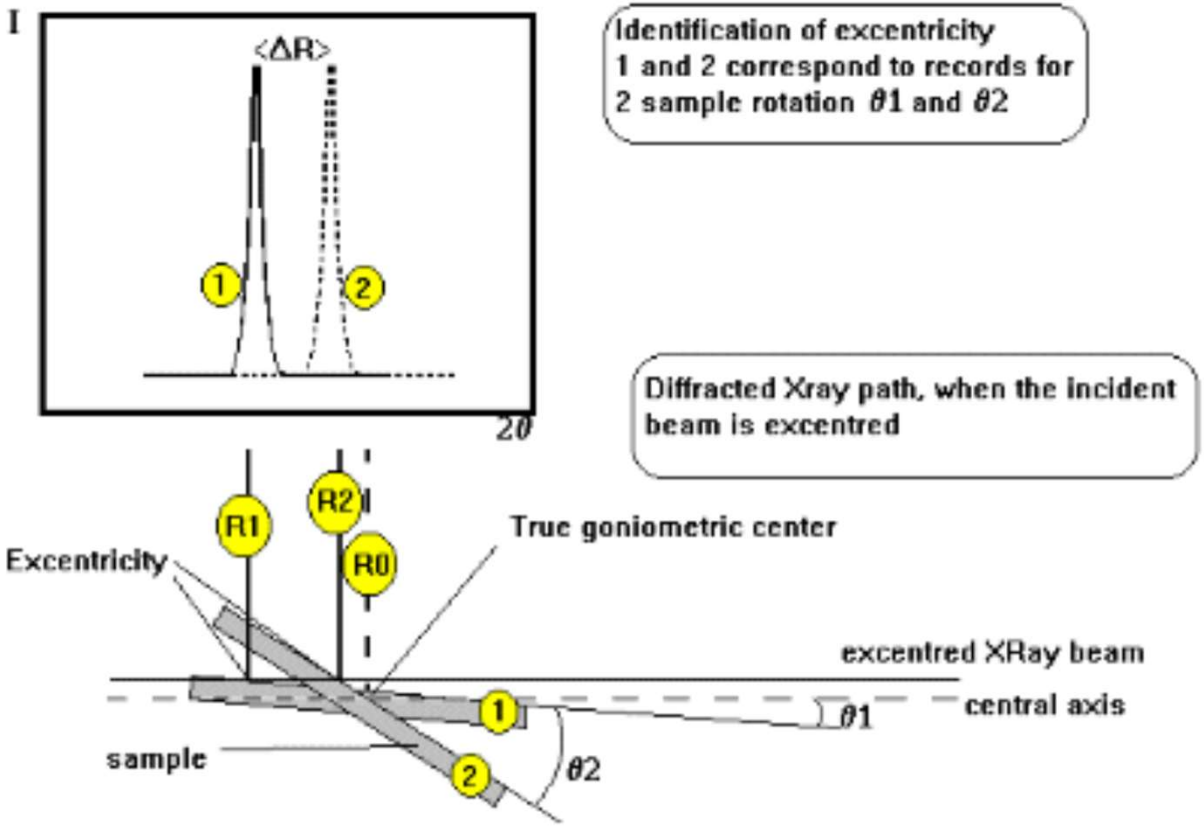
X-Ray Diffraction pattern

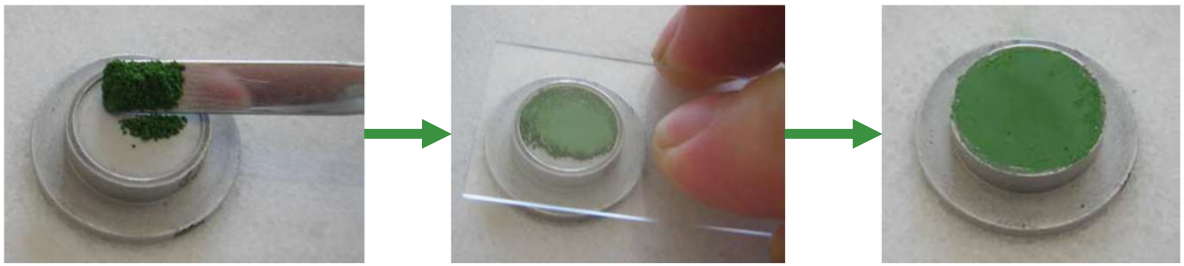
Goniometer-sample-beam alignement

The omega axis must be aligned with the diffraction axis.
If sample is low high OR beam is too high (and likewise), diffraction lines will be displaced. This is the **eccentric effect**.
Same consequences when sample absorption is too weak.

<u>Recommendation</u> : sample height adjustment by using the 2 angles method – it exists a unique Z position where 2 patterns recorded at 2 different incidences, are perfectly superimposed.

Other recommendation : be careful when preparing the sample surface

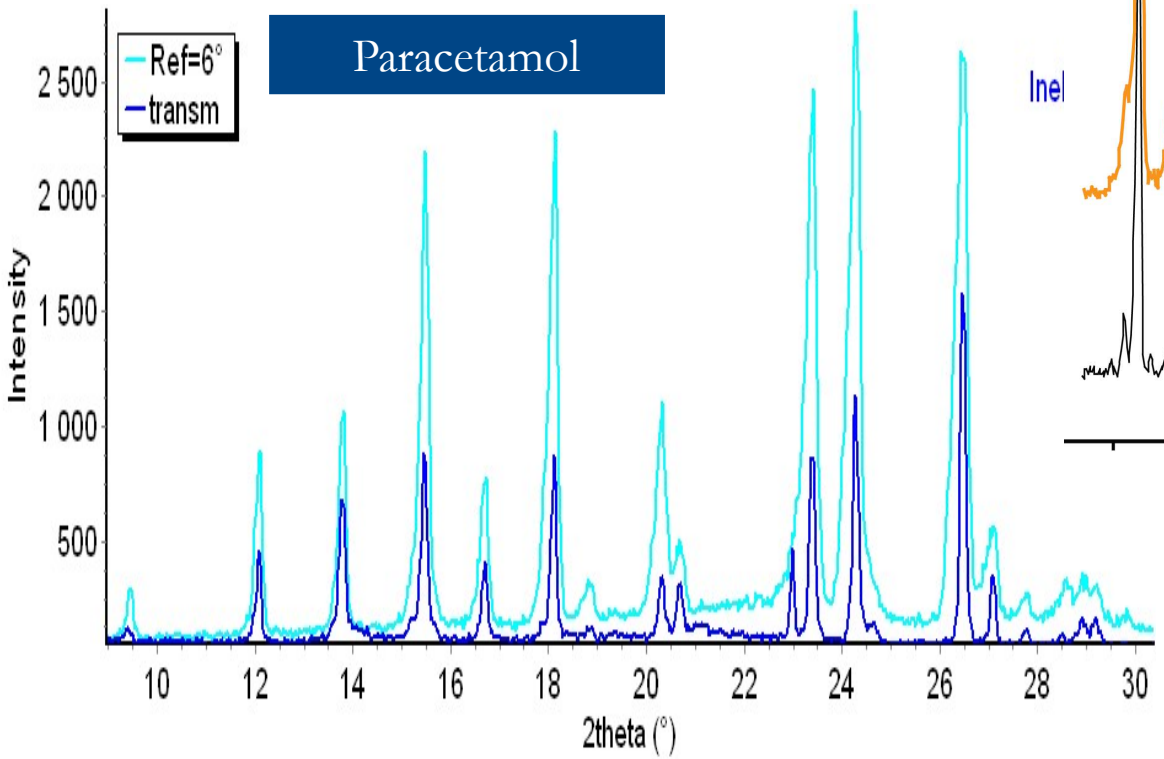


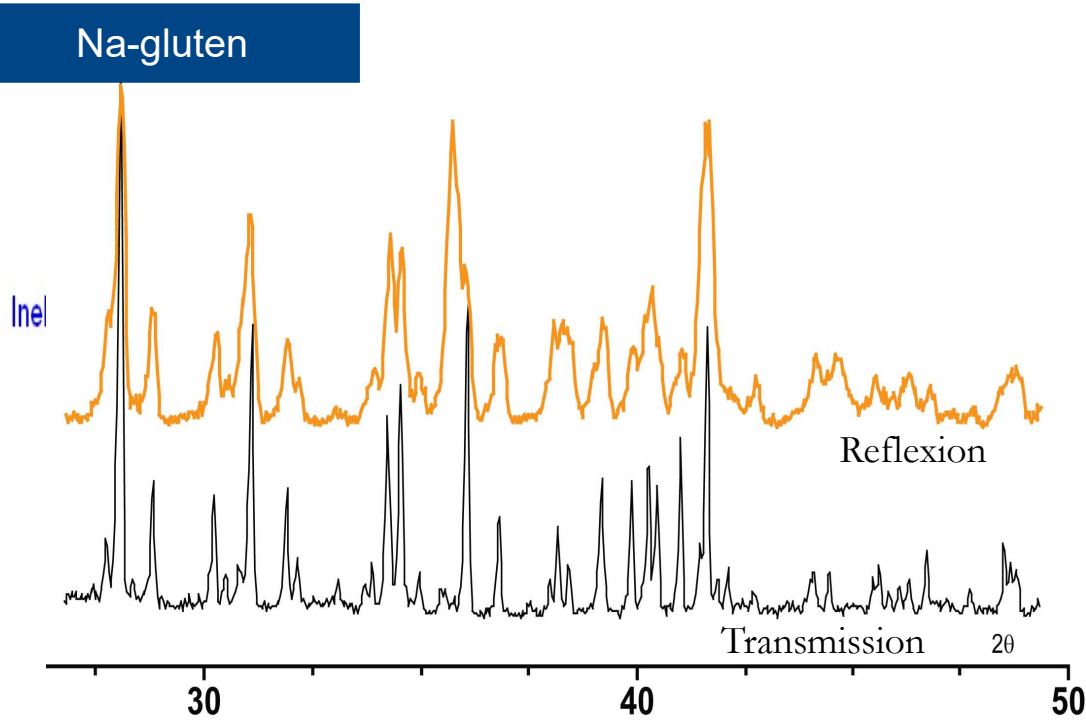


Some examples

Effect on instrumental component on pattern quality

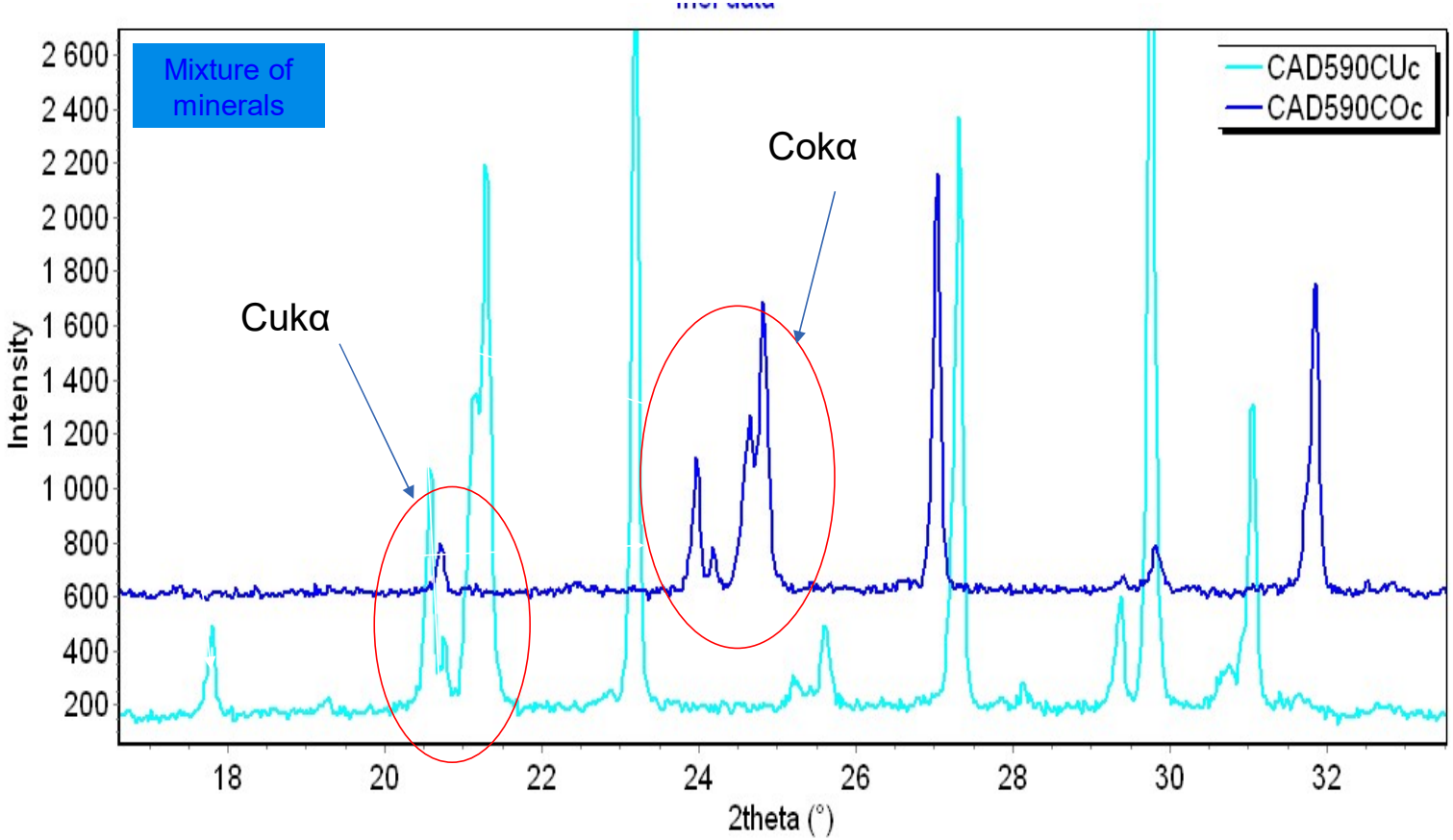
Instrumental function for XRD – effect of sample holder



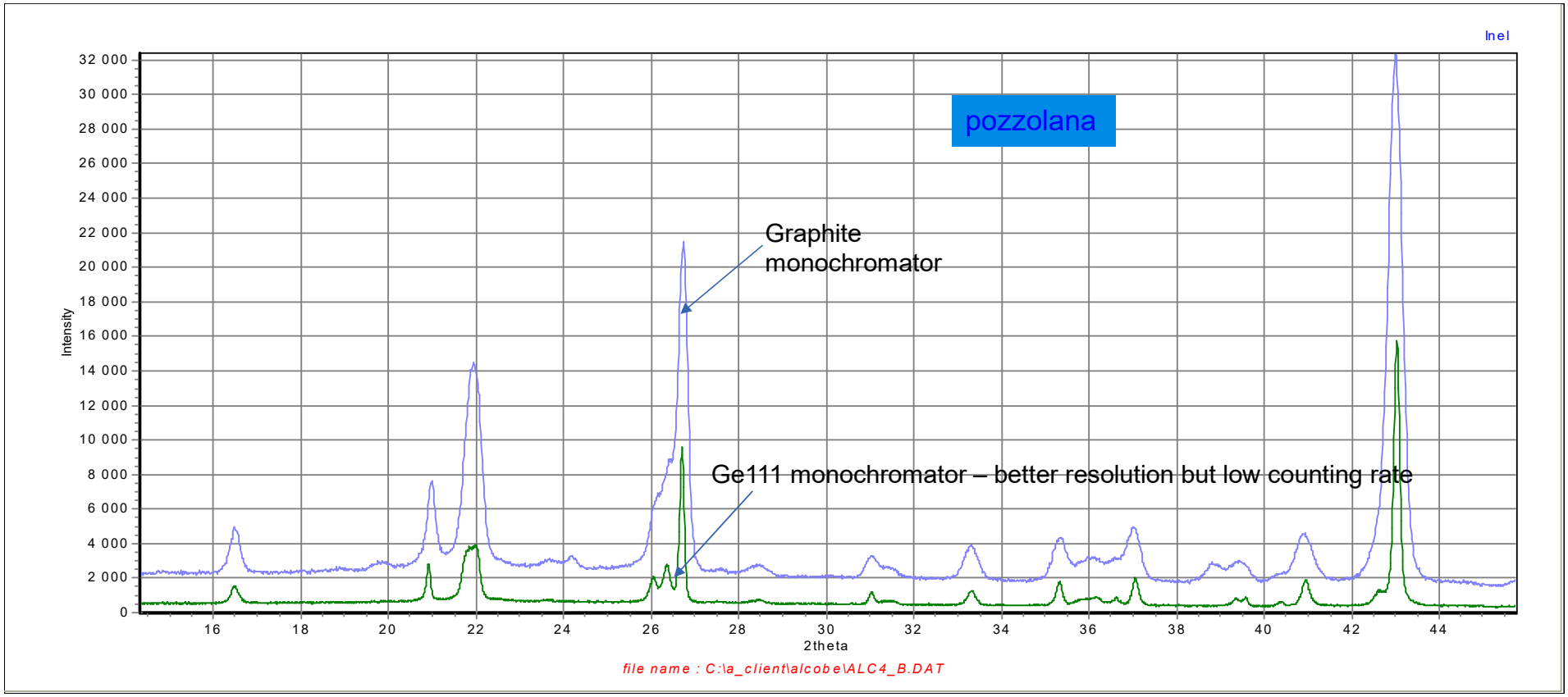


Better resolution in transmission

Instrumental function for XRD – effect of wavelength



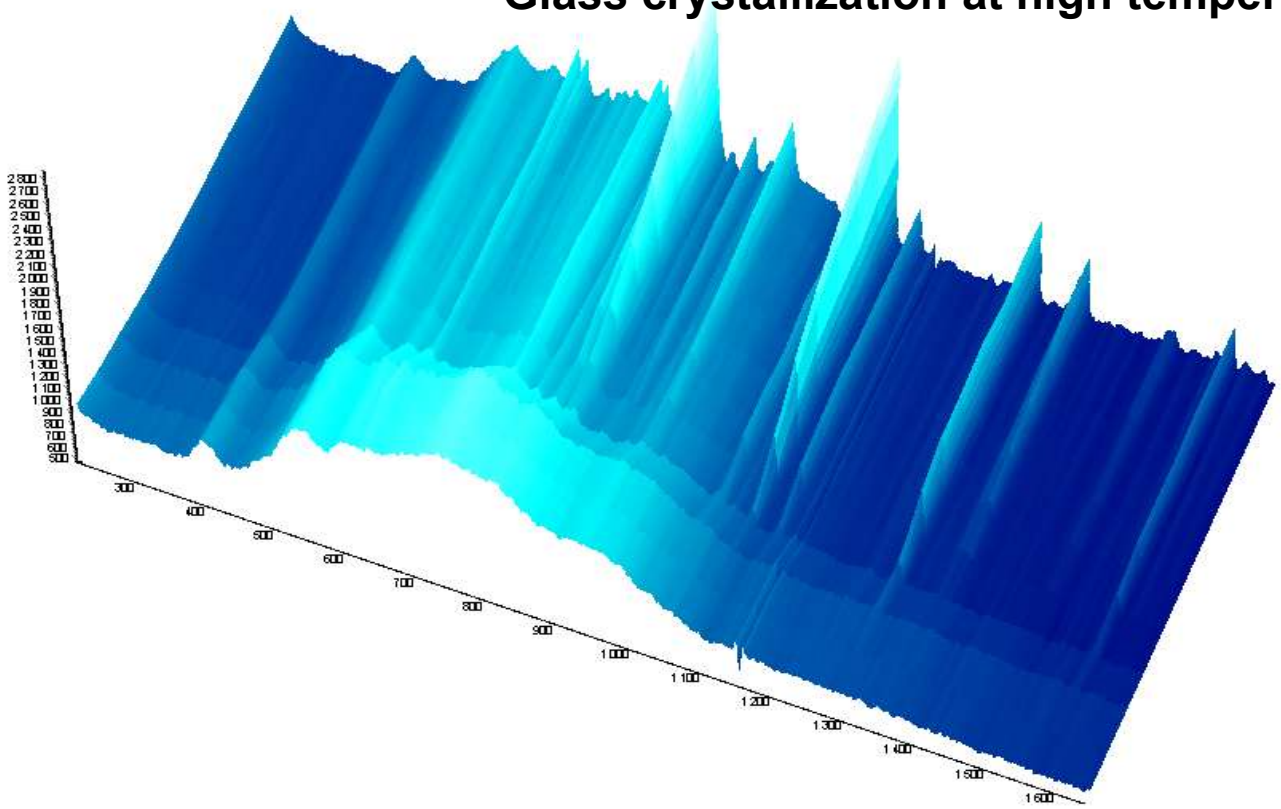
Instrumental function for XRD – effect of optic



Instrumental function for XRD – effect of optic

High flux by using elliptical mirror

Glass crystallization at high temperature

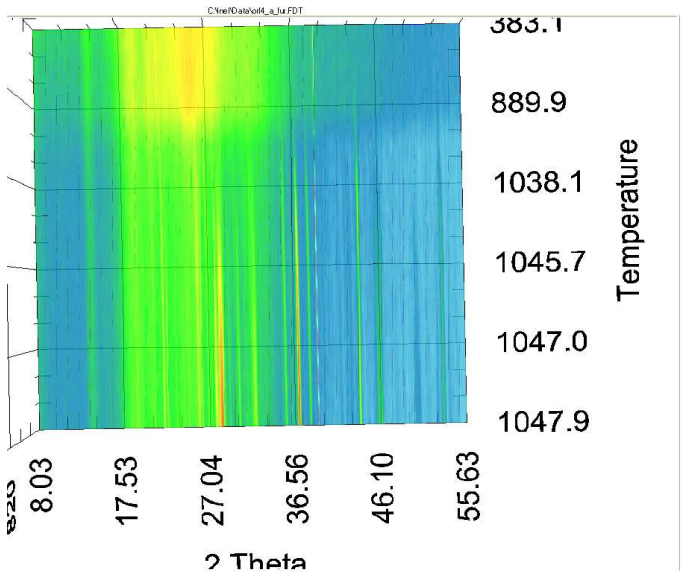


CONDITIONS :

power : 38kV – 38mA,

Furnace : FUR1200

acquisition: 3min



Some exotic devices

Because standard instruments cannot necessarly respond to any investigation requests

Instrument

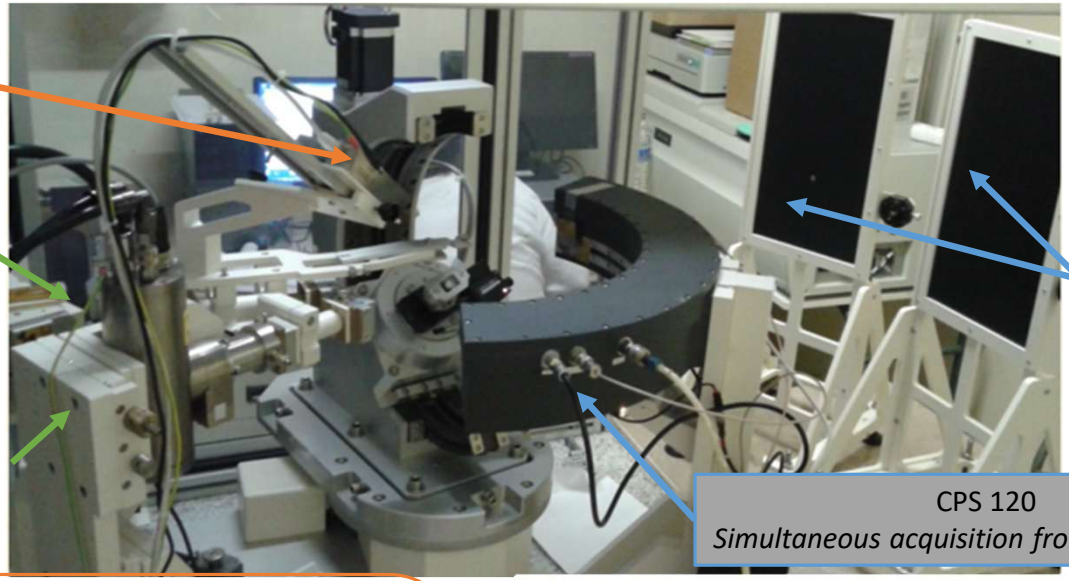
ECOCORAIL (2014-2015) - CRISMAT

INEL 4 circles diffractometer - *ANR Ecocorail*

EDX detector (spectrometry fluo)

Cu X-ray tube

Mini Source Mo



Images plate

CPS 120
Simultaneous acquisition from 0 to 120° 2ϑ

Combined analysis texture/stress/films

- ⇒ Phases identification and quantification
- ⇒ Structure resolution and refinement
- ⇒ Crystallites size and micro strains
- ⇒ Quantitative texture analysis
- ⇒ Residual stress
- ⇒ Fluo X

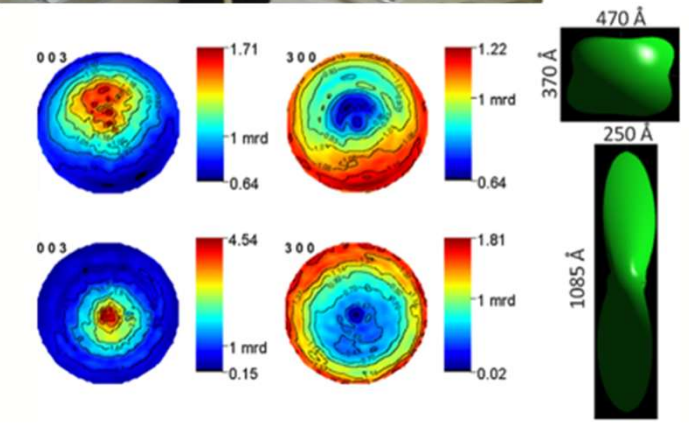


Fig. 3. {003} (left) and {300} (middle) and mean anisotropic shape of crystallites.

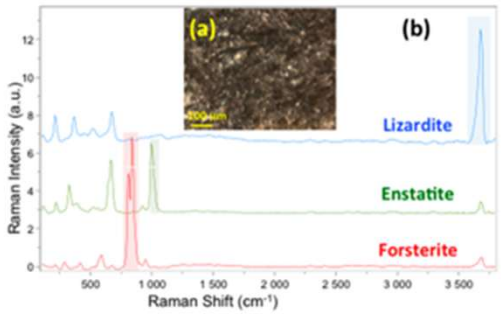
$Bi2Te_{2.4}Se_{0.6}$

Journal of the American Ceramic Society—Lognone et al.

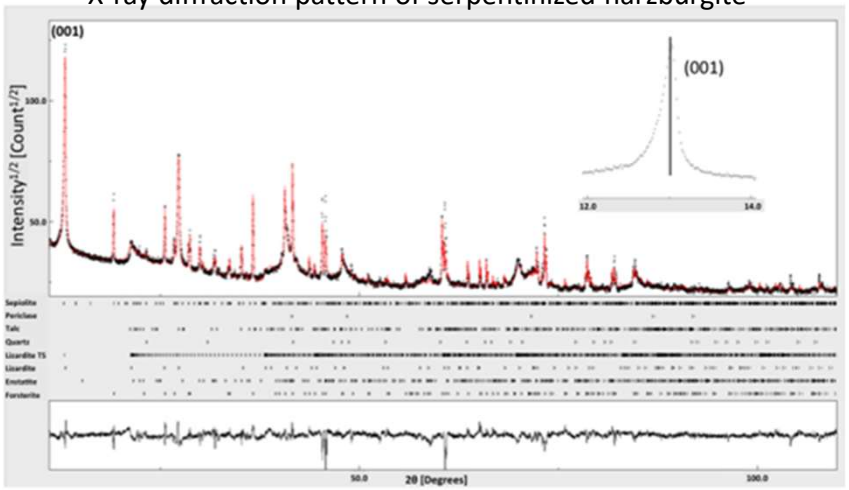
Combined analysis

ID1 Combined system- *SOLSA HORIZON H2020*

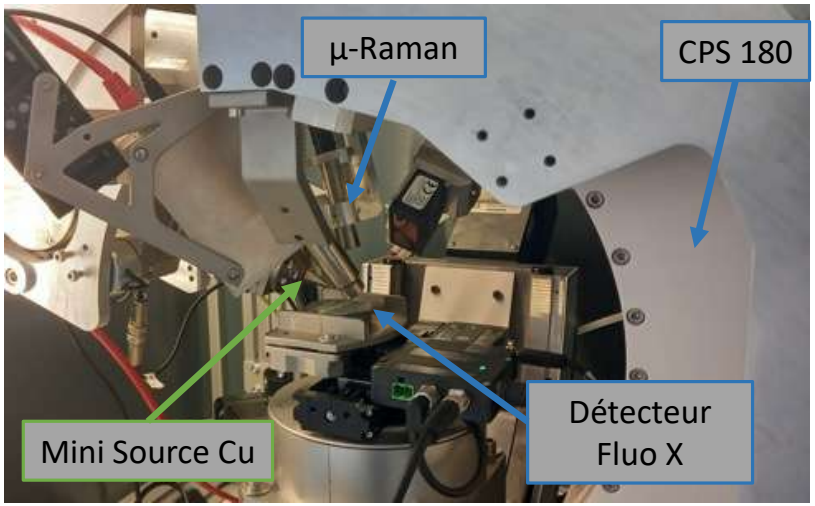
Raman spectra corresponding to lizardite, enstatite, and forsterite



X-ray diffraction pattern of serpentinized harzburgite



ACS Earth Space Chem. 2019, 3, 2237−2249



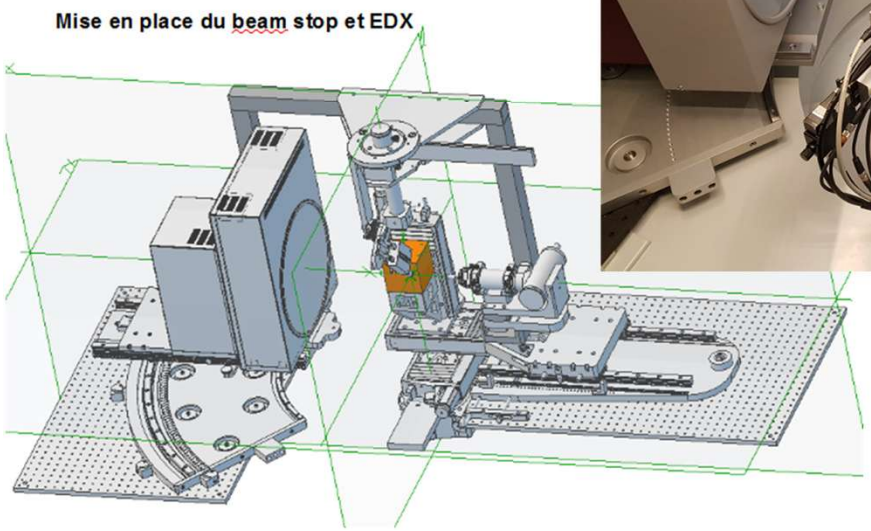
- ⇒ Phases identification and quantification
- ⇒ Structure resolution and refinement
- ⇒ Crystallites size and micro strains
- ⇒ Quantitative texture analysis
- ⇒ Residual stress
- ⇒ Fluo X
- ⇒ Raman
- ⇒ Cartographies DRX, Fluo X et Raman

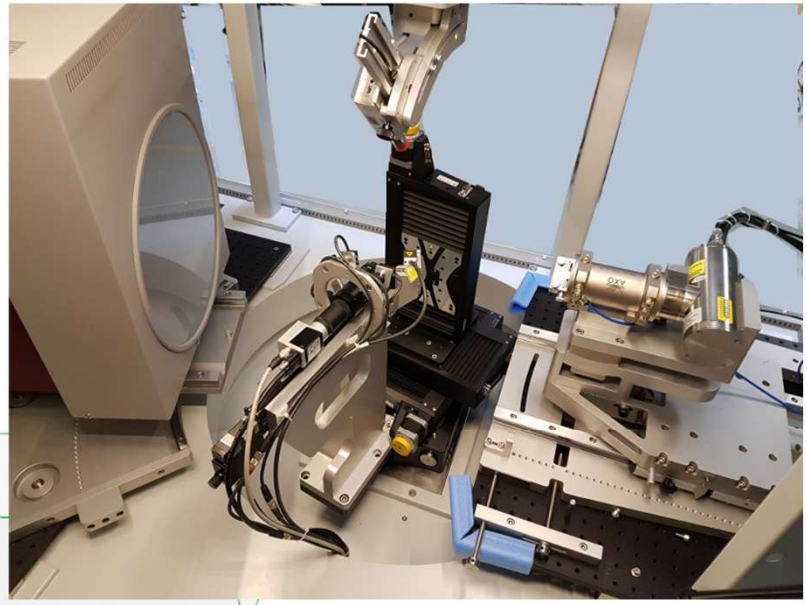
Instrument

IPANEMA (2016)

Description:

XRD-2D/XRF/Imaging combined system for archeomaterials studies





What we need from your sample

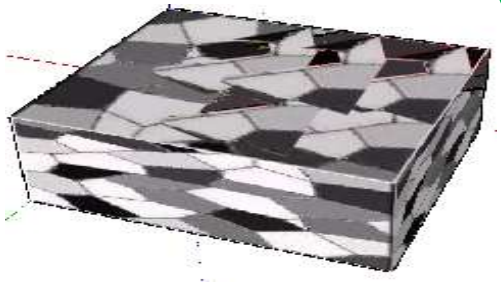
Good preparation means good results

X-Ray Diffraction basics – sample preparation

Sample preparation:

How many crystallites are necessary to estimate an appropriate characterization?

From NF EN 13925-1 “essai non destructifs – diffraction des rayons X appliquée aux matériaux polycristallins et amorphes”, about **2000** crystallites with grain size around 20 microns



BUT !

If mixture of powder, to justify a good accuracy for a phase at **5%**, it is necessary to light **40 000** crystallites!

And for **1%**, it is necessary to light **200 000** crystallites!

Without taking into account the absorption effect where a low content of low absorption phase cannot be detected in a too absorbing matrix !

Limit of detection should be considered for each mixture composition

Conclusion : low content of mineralogy is difficult to identify and quantify

Recommendation :

- Not measuring by spinning continuously on a same surface of sample
- Perform several sample preparation measured separately – measurement of large surface of sample once, and by collecting several patterns to identify the “nugget” effect (l’effet pépite).

X-Ray Diffraction basics – sample preparation

Statistic effect:

How many grains/crystallites are lighted by the beam?

for powder:

necessary to grind BUT take care to:

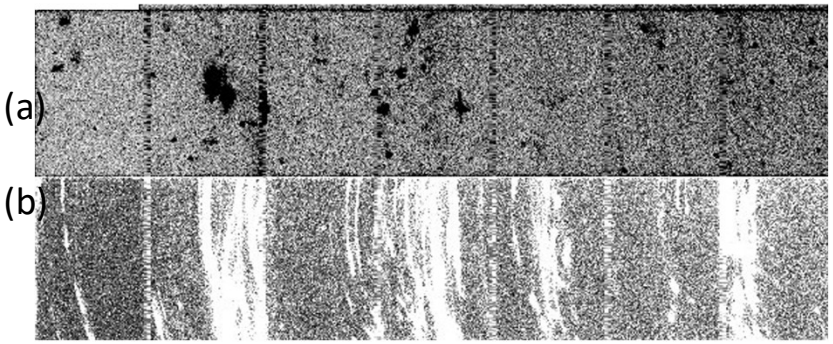
segregation effect due to hardness

mineral decomposition/transformation

how are crystallites ? Isotropic or anisotropic shape ?

is spinning efficient ?

Coarse alumina powder diffraction on 2D detector -(a) without spinning, (b) with spinning



For bulk:

if crystallites are too large, adapt device for averaging (translation stage …)

is there any texture ? Or large crystallite? => perform texture measurement

Conclusion : large crystallites are presenting large discontinuity of the Debye ring

Interpretation is difficult and quantification is not possible

Recommendation : measurement of large amount of powder in order to obtain a “smoothing” of the Debye ring -> not easy.

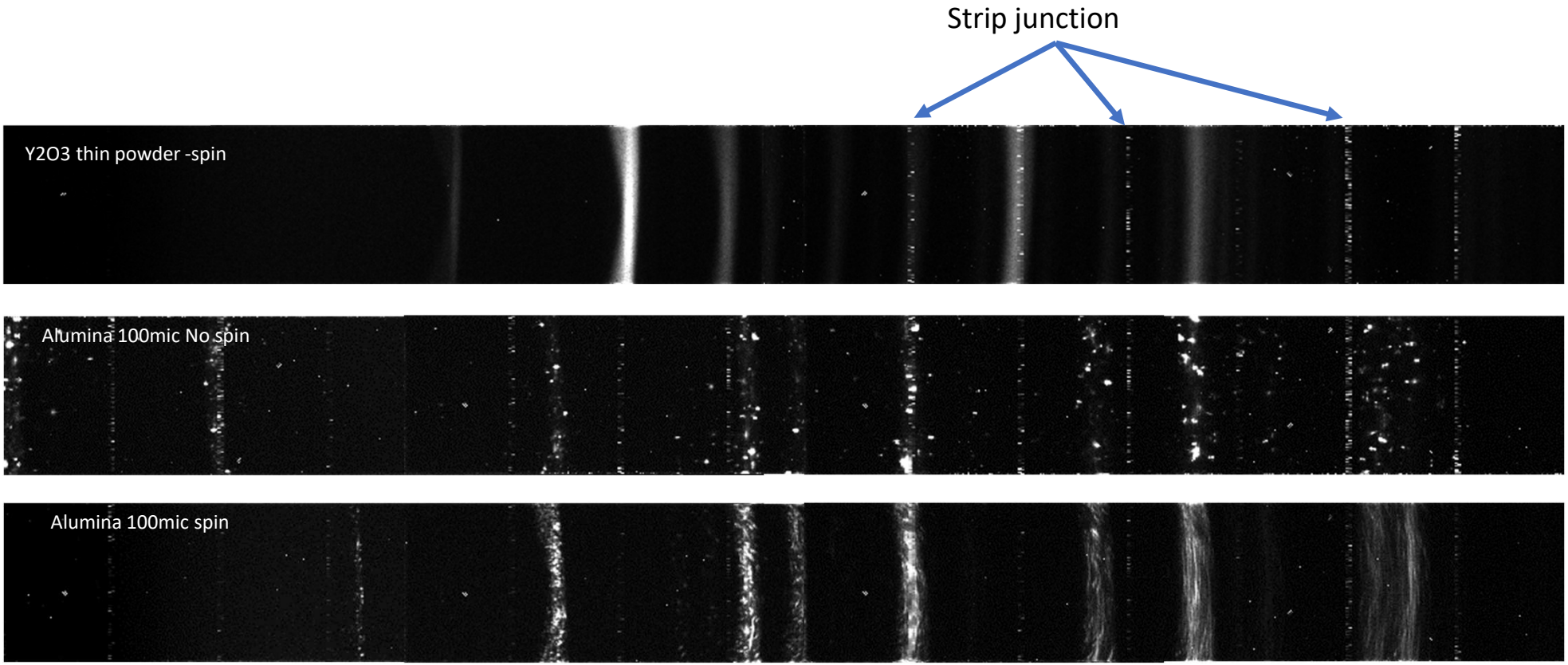
Difficult to perform on bulk material => measurement with a goniometer in detexturation mode

2D examples:

Thin powder of Y2O3 : Portion of Debye rings are continuous

Coarse alumina powder : Discontinuous Debye ring

Source : Cuka - 45KV – 0.9mA
Omega=8
Detector : REBIRX70
Tacq = 60sec



X-Ray Diffraction basics – sample preparation

Morphology effect:

Crystallites shape are often dependent to Bravais lattice:

Cubic : mostly isotropic powder BUT take care of cleavages – example Si powder, orientation 111

Tetragonal, orthorhombic or hexagonal with large c parameter will give “needles” – example: aragonite, asbestos …

Tetragonal or hexagonal with small c parameter will give “plates” – example: clays, mica

hardness effect:

Grinding mixed powder containing mineral with different hardness:

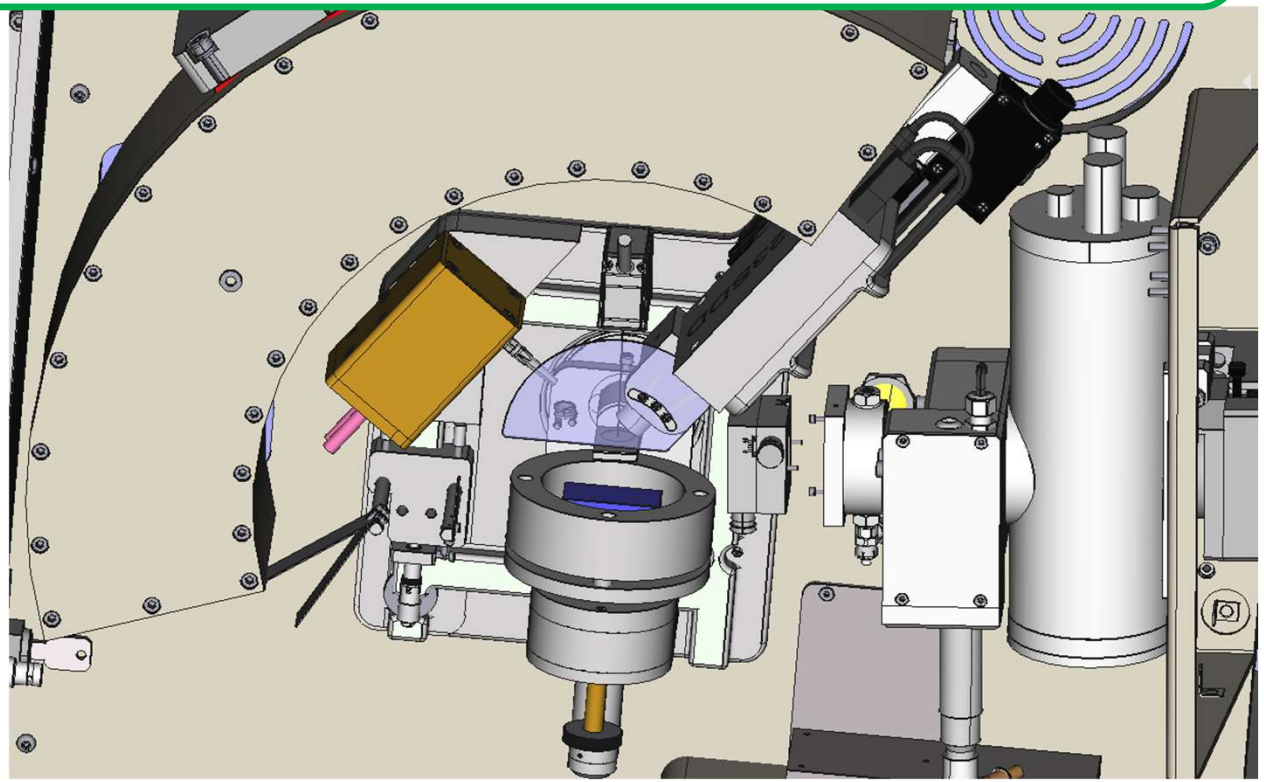
Hard mineral are grinding smooth minerals => mica decomposition

X-Ray Diffraction basics

Uncentered sample holder and combined XRD-XRF:

Allow to perform measurement on large sample area

Allow to perform both measurement simultaneously, XRD and XRF.



What we need from your instrument

Specific parameters to determine the instrumental function

X-Ray Diffraction basics

$$I_i^{calc} = S_F \sum_{j=1}^{Nphases} \frac{f_j}{V_j^2} \sum_{k=1}^{Npeaks} L_k \left|F_{k,j}\right|^2 S_j\left(2\theta_i - 2\theta_{k,j}\right) P_{k,j} A_j + bkg_i$$

Intensity of diffraction peaks:

For X-ray, mostly depends on electronic interaction and photons.

$$I_{hkl} = S.Mhkl.|F_{hkl}|^2.L_p.A.P_{hkl}.e^{-2M}$$

Instrument dependent

3 contributions:

- Structural

S : scale factor – depends on the instrument efficiency
M_{hkl} : multiplicity factor – depends on the symetry of the unit cell
F_{hkl} : structure factor – depends on structure and atoms type

$$F_{hkl} = \sum_{j=1}^{n} f_j \exp[2\pi i(hxj + kyj + lzj)]$$

$$F_{hkl(reel)} = F_{hkl(theorique)}.\exp[-B\frac{\sin\theta}{\lambda}]$$

- Instrument geometry

L_p : facteur de Lorentz-polarisation
A : facteur d'absorption

$$Lp = \frac{1 + cos^2(2\Theta)}{\cos\Theta\, sin^2\Theta}$$

- Sample geometry

P_{hkl} : Orientation préférentielle
e^{-2M} : Facteur de température

$$P_{hkl} = (G^2 cos^2\alpha_{hkl} + \frac{1}{G} sin^2\alpha_{hkl})^{-\frac{1}{2}}$$

X-Ray Diffraction basics (3/3)

Instrumental function:

Or how the setup influences the measurement

Instrument dependent

3 contributions:

$$\sigma_{instum}^2 = U \tan^2\theta + \mathrm{V} \tan\theta + W$$

$$\sigma_{exp}^2 = \sigma_{instrum}^2 + \sigma_{sample}^2$$

- Peaks width : effect of geometry, beam characteristics …
- Peak shape : depends on statistics, crystallite size, micro-strains … $\sigma_{sample} = C\,\varepsilon \tan\theta + \dfrac{K\,\lambda}{L\cos\theta}$
- Peak asymmetry : depends on instrument geometry, sample defects … several models are available

Refinement Strategy: Rietveld refinement

1- Adjustment of background and scale factor:

- Scale factor
- Background (Chebyshev polynom)

Instrument dependent

2- geometry:

- Zero offset
- excentricity

Instrument dependent

$$\Delta 2\theta = \left(\frac{180.Z}{\pi.R.\sin(\Omega)}\right)\sin(2\theta - \Omega)$$

3- profile and microstructure:

- Peak width (U, V, W)
- Crystallite size and micro strains

4- atomic structure:

- Atomic position (x, y, z)
- Thermal agitation

Quality factors:

Weighted profile R-factor, R_{wp}: Most representative of the mathematical adjustment

R_{exp}: minimal statistic expected value

Goodness of fit (GOF), χ^2: Ideally will tend toward 1

Refinement Strategy: Rietveld refinement

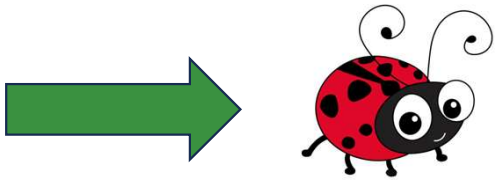
Parameters to adjust:

Factor	Influence on the peak	Parameters to adjust
Scale (S)	Global height	Phases quantity (%)
Structure (F)	Intensity ratio	Atomic coordinates
Lorentz-Pol (Lp)	Base line shape	Diffractometer geometry
Orientation (P)	Some specific peak too strong	Grains morphology
Thermal (B)	Intensity drop at high angles	Thermal agitation

Before performing Rietveld: recording standards

Determination instrumental broadening:

- Using LaB6 standard or CeO2 or Al2O3
- It is good to select a standard which fit with YOUR samples !
  - Consider the 2theta range you need
  - Consider the mean absorption factor



See determination by using MAUD

Determination peak position calibration:

- Using LaB6 standard or CeO2 or Al2O3
- It is good to select a standard which fit with YOUR samples !
  - Consider the 2theta range you need
  - Consider the mean absorption factor

Checking instrumental offsets:

- Correct sample height
- Correct beam alignment/goniometric alignment
- Correct monochromator adjustment
- Correct slits/Soller slits adjustment

Before performing Rietveld – knowing phases

1- Collect data:

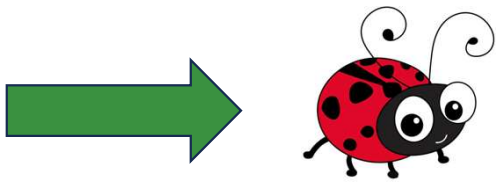
- Set Omega angle
- Acquisition time sufficient to get a smooth background

2- Do you know phases content ?

- Yes : collect the CIF files in Crystallography Open Database
- No : perform a search Match with “FPSM” for phase identification, and then collect the CIF files

3- Launch MAUD

- Open default PAR file
- Load TTX file
- Load CIF files



How Rietveld method is evoluting ?

To get better understanding in our materials

Geomaterial study case

Chemistry

C Al Ca K S Si Al Fe S K O Pb Fe Au Si N H Zn Ca As Pb Mn Mg Zn Cl As H O Mn Mg C W V N Ca P Li

Mineralogy

Quartz

SiO_2
H,Al,Li,Fe,Ti,Na,Mg,Ge,etc

Albite

$Na(AlSi_3O_8)$,
Ca, K, Mg

Muscovite

$KAl_2(AlSi_3O_{10})(OH)_2$,
Cr,Li,Fe,V,Mn,Na,Cs,
Rb,Ca,Mg,H_2O

Pyrite

FeS_2
Ni,Co,As,Cu,Zn,Ag,
Au,Tl,Se,V

Spodumene

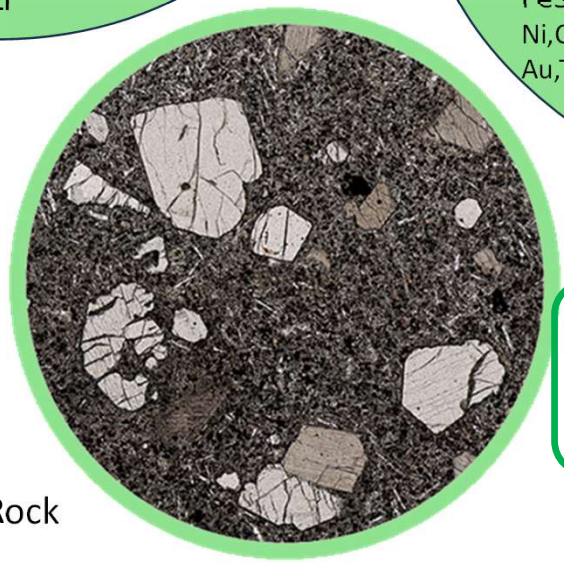
$LiAlSi_2O_6$
Fe,Mn,Mg,Ca,Na,K,H_2O

Calcite

$CaCO_3$
Mn,Fe,Zn,Co,Ba,Sr,Pb,Mg,Cu,
Al,Ni,V,Cr,Mo

Amorphe

C,H,N,P,O
Si,Mn,Fe,Zn,Co,Ba,Sr,Pb,
Mg,Cu,Al,Ni,V,Cr,Mo, etc …

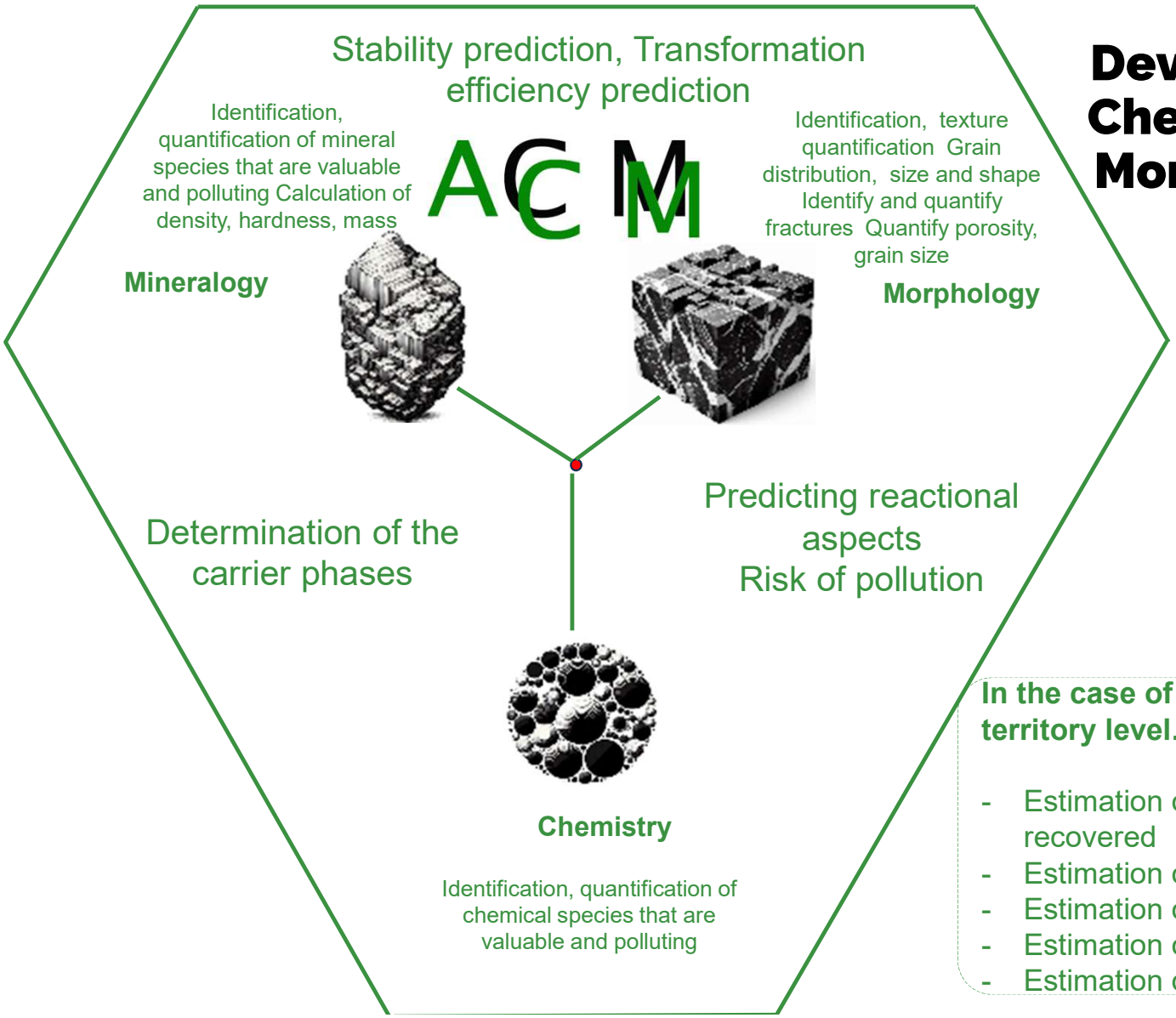


Rock

1- Geomaterials, archeomaterials, environment:

- Complex context: unknown elemental analysis, unknown mineralogy, unknown morphology

Developping Combined Chemical Mineralogical Morphological analysis



In the case of mining, summary of results at the territory level.

- Estimation of the volumes of materials to be recovered
- Estimation of the techniques used for recovery
- Estimation of costs
- Estimation of profits
- Estimation of risks

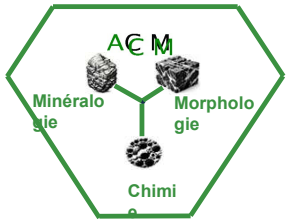
Materials expertise method

Expertise topic

- Mining
- Polluted soil
- rehabilitation
- Excavated earth

- Strategy
- documentary

In-situ measurement campaign



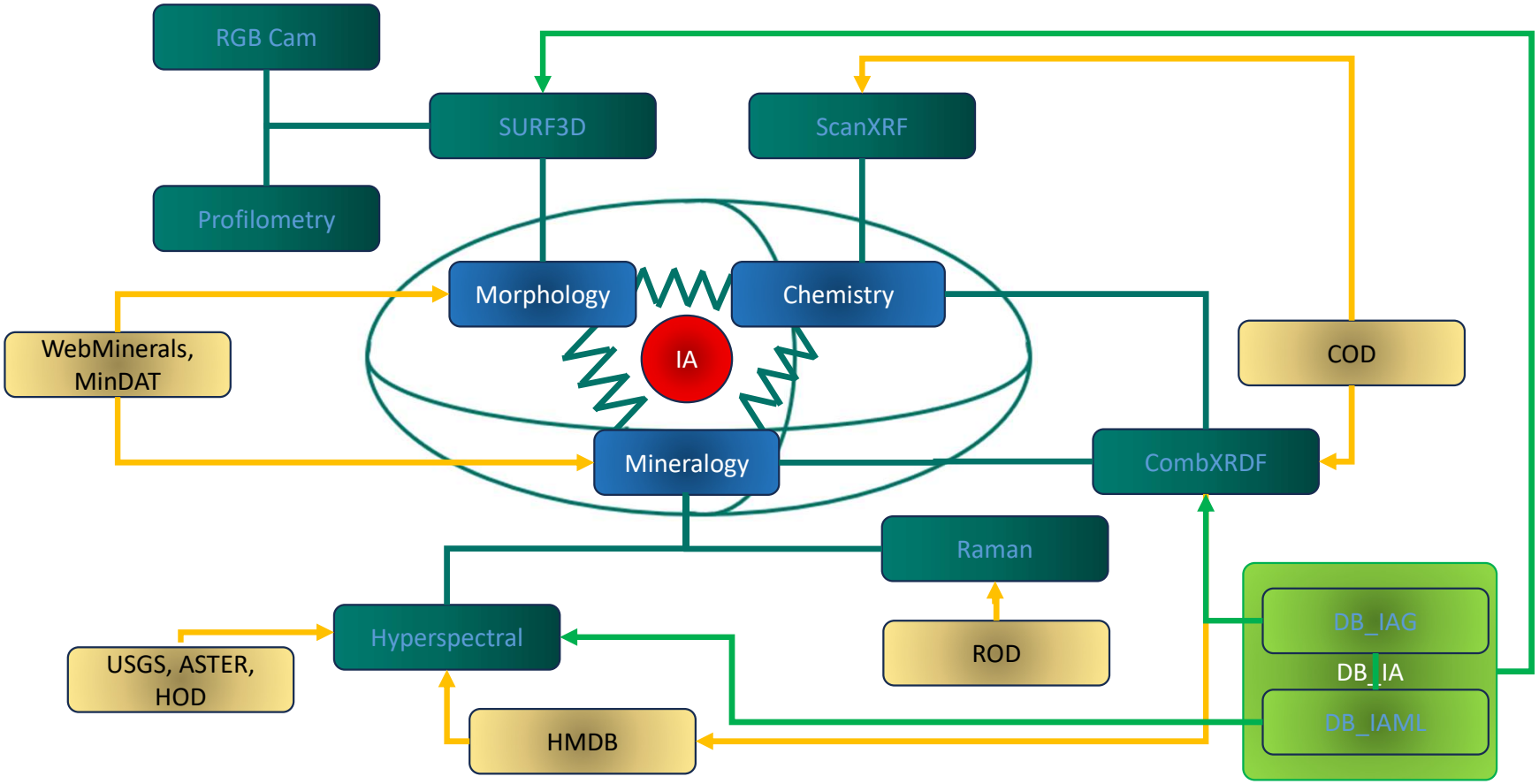
- Sampling
- Analysis
- Data treatment

Cartography and data base

Recommendations

- -
- method
- Action plan
- profits
- efforts
- perspectives
- costs

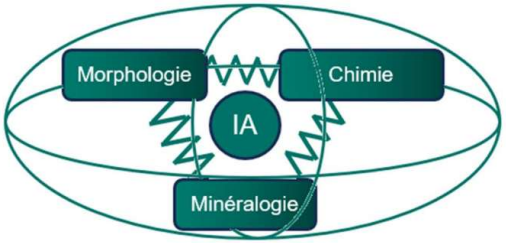
Methodoly diagram – AI integration



Combined mobile and intelligent analysis instrument for informed operational decisions.

Combined XRD – XRF

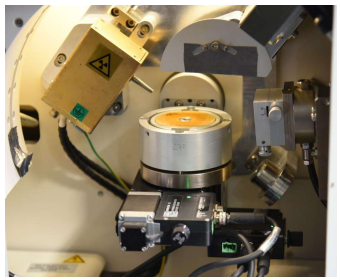
- Chemical and mineralogical quantification on the same sample
- Multiplication of measures
- Elimination of the sample preparation phase: 1 hour saving in time



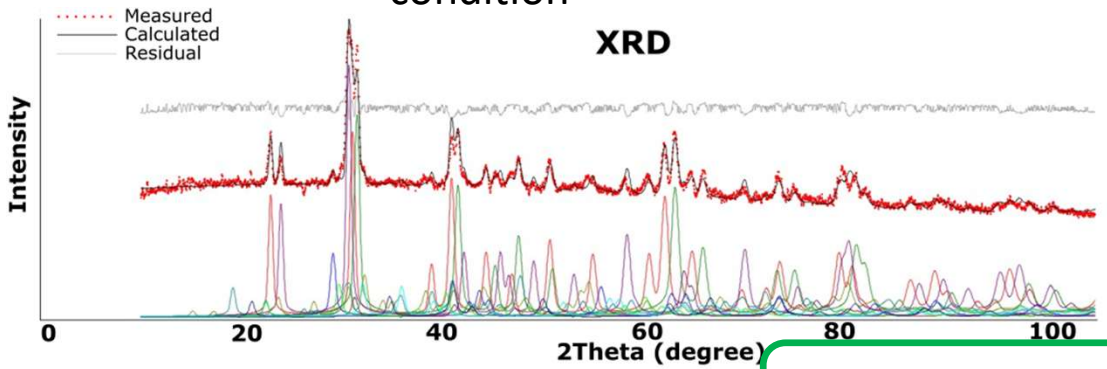
Expert decision support software suite

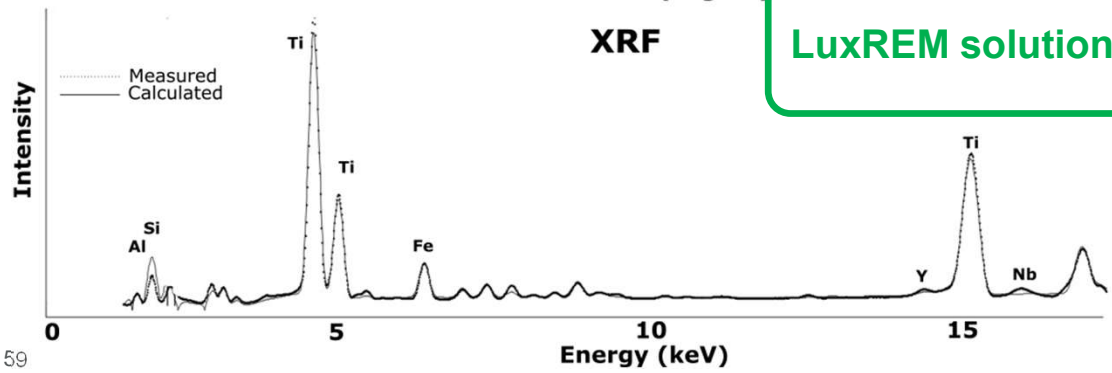
- Automation to analyze 20x more samples
- Provide indicators to field operators based on raw data
- Creation of a large mineralogical database

A novel coupled XRD and XRF technique and methodology



- Small enough to fit in the boot of a car / core logging facility
- Low power consumption, around 200W, to enable set-up in field condition





LuxREM solution

A transportable technical solution

- **Low number of moving parts, in particular the XRD that does not have a goniometer**

Simultaneous data acquisition

- **Mineralogical and chemical composition obtained in 30 minutes**
- **Unique data combination software and methodology at the core of the system**

VanLab equiped for in-field combined analysis chemistry-mineralogy

VanLab equipped with combined Mineralogy and chemistry system

Installation:

- ☞ 30 approximately
- ☞ Internal power supply

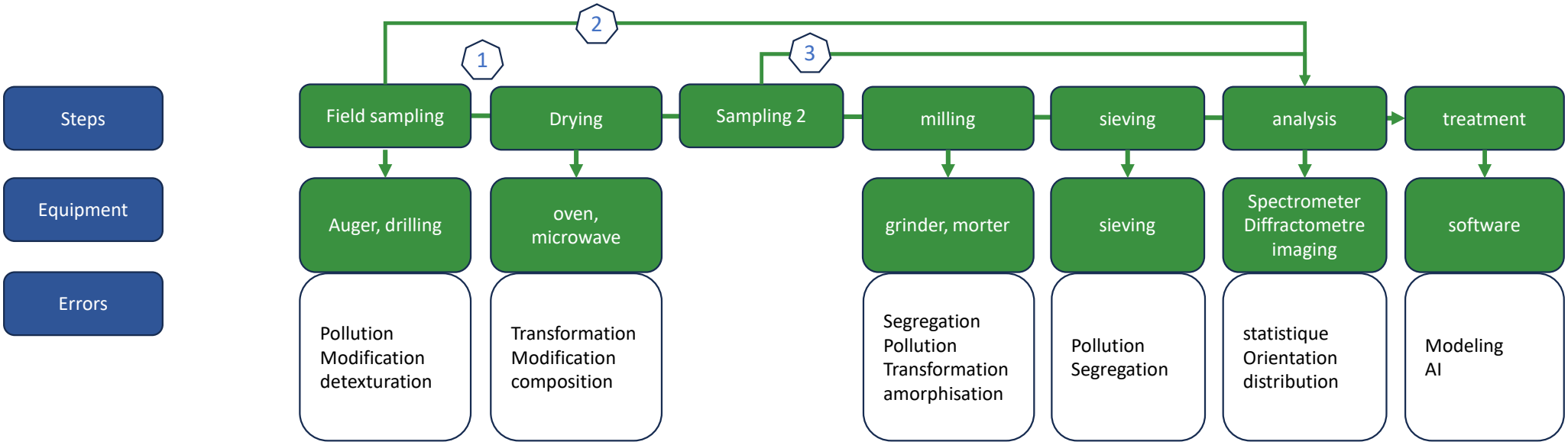
Workflow:

- ☞ Sample preparation platform
- ☞ Sample identification
- ☞ Measurement (about 4 samples per hour)
- ☞ Data treatment (LuxREM software)
- ☞ Storing data and results

Advantages:

- ☞ Tight reactivity with explorers
- ☞ Results given every 30 min (preparation, measurement, data treatment)
- ☞ mobile

Operating mode and equipment

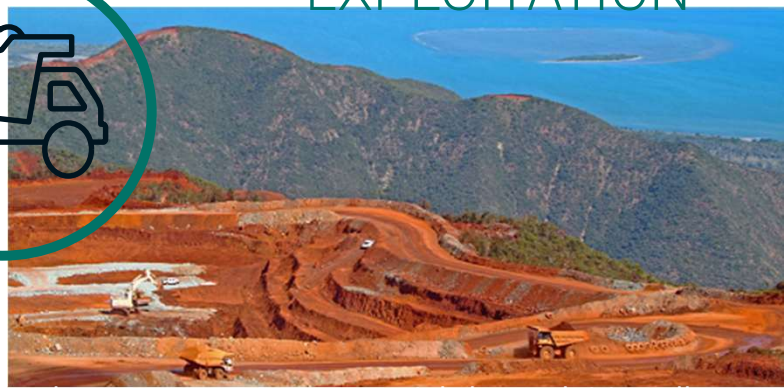


This diagram summarizes the procedure.
The standard suggests path (1), but many may have some biases.
Each step has variations:
Drying: temperature, drying time
Grinding: type of grinder, particle size to reach
Sieving: particle size to reach
These variations can have more or less impact on biases: transformation, segregation, contamination, amorphization.
This procedure was defined to minimize measurement biases for analysis: optimal statistics and low bias => good quantification.
We suggest path (1) under moderate conditions, and paths (2) and (3) when the sampled materials are fairly homogeneous. Our method makes it possible to account for minimizing measurement biases for analysis.

Rationalize materials today, By proposing new methods

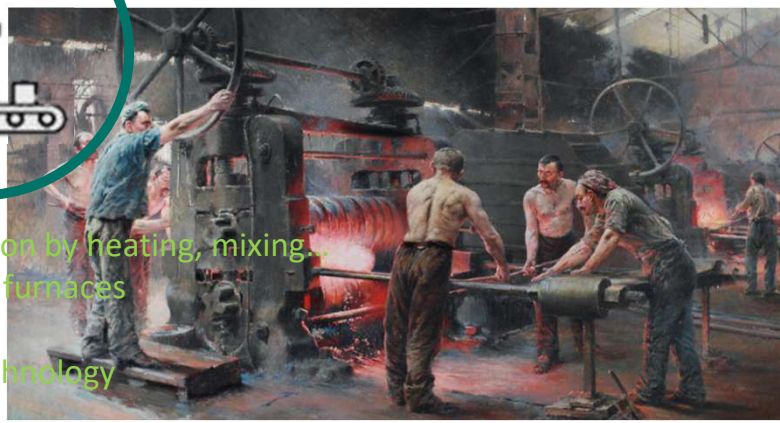
EXPLORATION

EXPLOITATION



RECYCLING

TREATMENT PROCESS

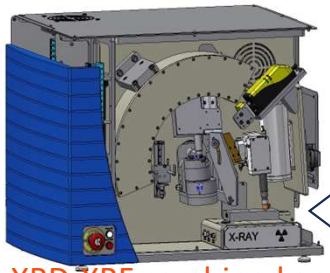


To optimize the transformation by heating, mixing…
refinery, cement plant, blast furnaces
Foundry, plastics industry,
Cosmetics, pharmacy, biotechnology
Automotive, aeronautics…
Agronomy, forestry…

Use cases

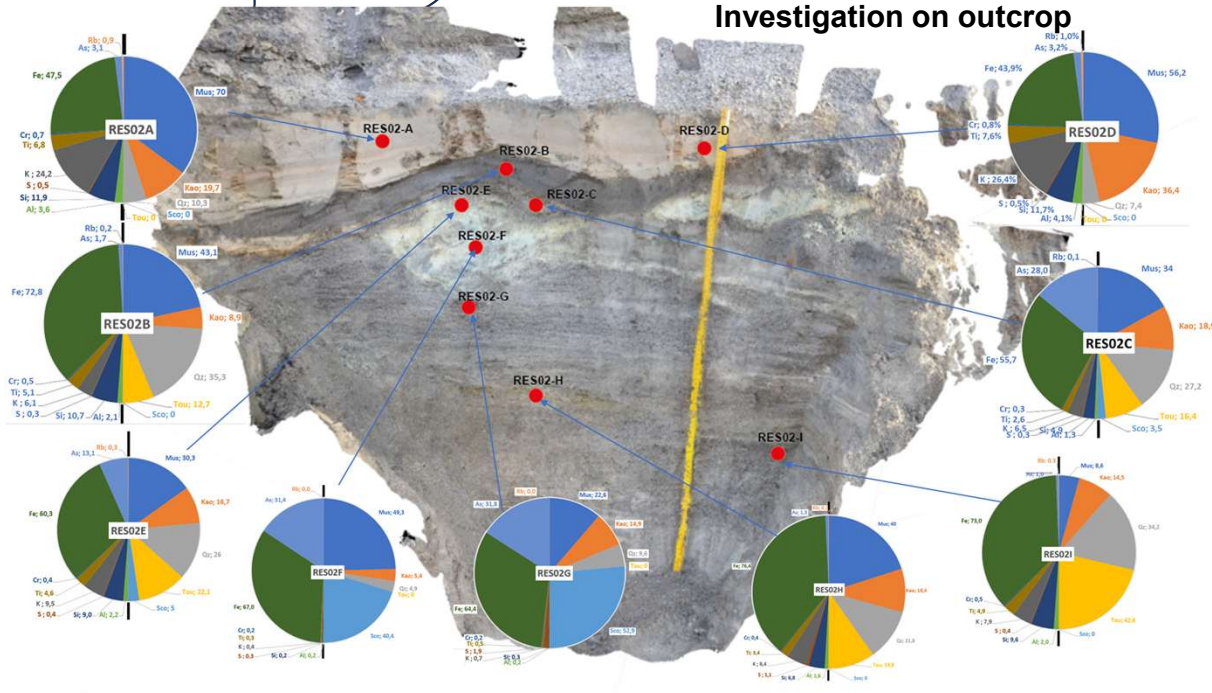
Abbaretz, old tin mine (Sn)

Installation of MODULAB next to the mine tailings



XRD-XRF combined analysis

Investigation on outcrop



- **Some results on grab samples:**

➢ Sampling, preparation and measurement of 9 samples in 3h (30 min / sample)

➢ Identification and quantification of chemical elements and their bearing phases

Use cases

Fricheco site in Marseille

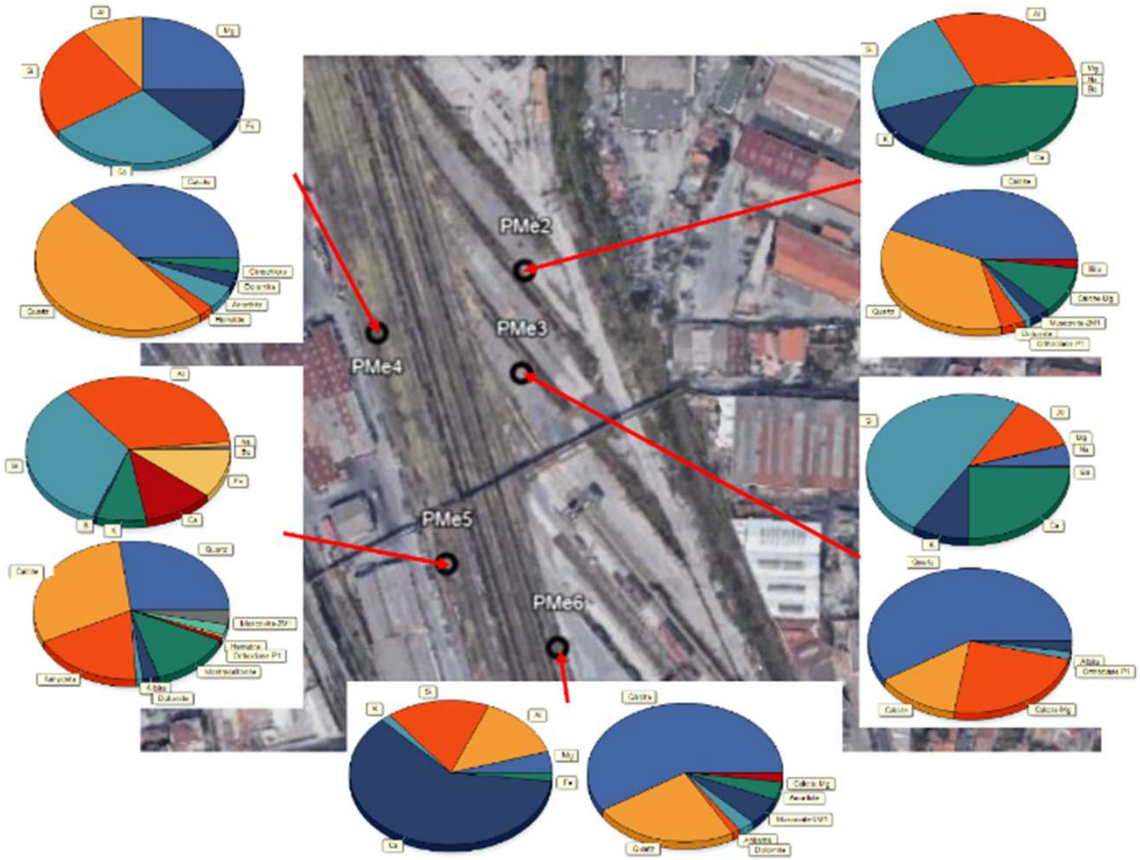
rehabilitation of an industrial site for revegetation

- Identification of pollutants
- Identification and quantification of clay
- Characterization of samples

More than 100 measurements (mineralogy and chemistry) in 3 days

Samples collection

Results



Other use cases

Envisol project : recovery of polluted soils

Collaboration project between BRGM, TerrAnalytiX and Envisol.

- Environmental mineralogical and chemical characterization
- Old mining installations in Spain

- Test on samples provided by Envisol
- Establish practices and a common database for the interpretation and valorization of data

Eramet project : mineral analysis for mining

Collaboration project between BRGM, TerrAnalytiX and Envisol.

- Mineralogical and chemical characterization of mineralized sand
- Senegal

Comparison of XRD/XRF with a laboratory system:

- 100 samples analyzed vs. 4 for the laboratory system
- Better quality of results
- Faster solution: 15min versus 24h

Good agreement between laboratory and in-field techniques

Faster and less preparation

On-site

Less expensive technique

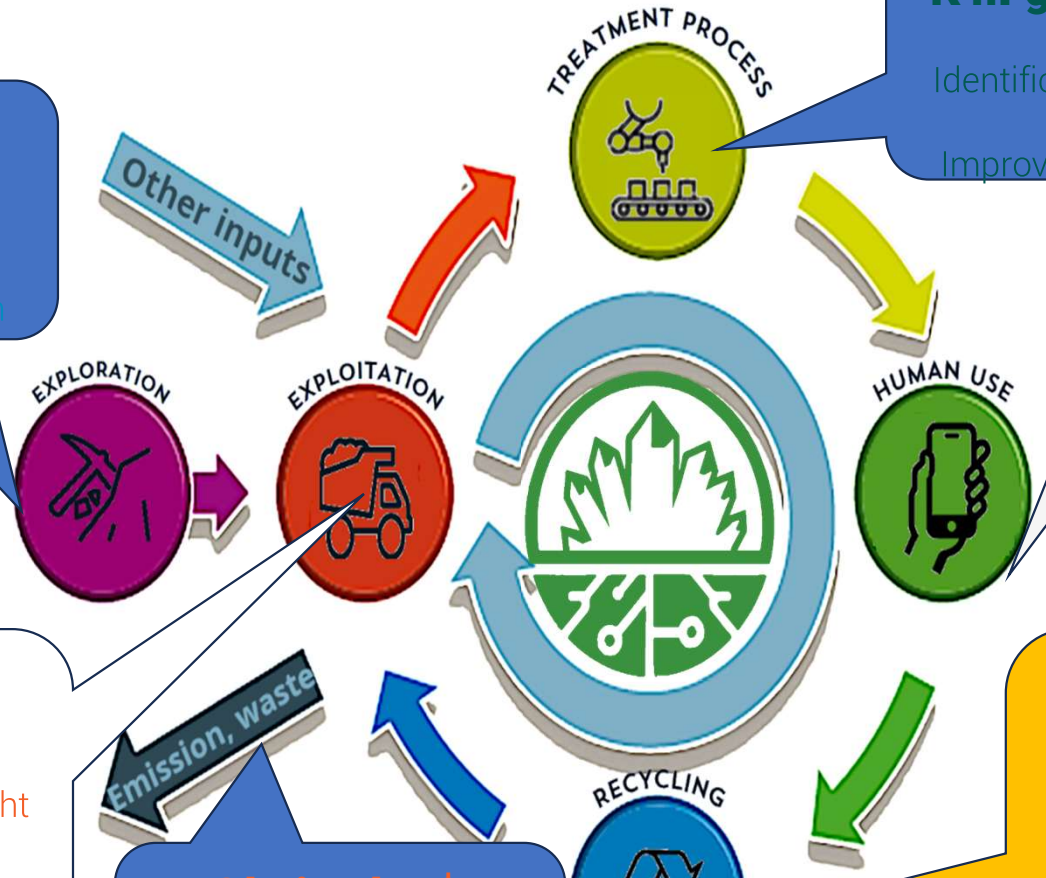
Now go to enjoy the

Rietveld refinement training !

Our values

Esgpg e rf c cvnjmp_rgml
Reliable analysis
Exploration qualification

K ml gmpg e npmbsargml
Quality Control
Identification of foreign bodies (residues)
Improved process knowledge



Our future needs are important:
We create new needs,
We must extract and recycle,
we transform enormously,
We must preserve and rationalize.

Af _p_arcpgkg e k _rrcp
To direct it towards the right outlet:
storage, treatment, waste
Sorting materials
Quality Control

?l _jwkg e $ aml rpmj
Avoiding waste by giving a value to backproduct

Af _p_arcpgkg e k _rrcp
To direct it towards the right outlet:
storage, treatment, waste
Sorting materials
Quality Control

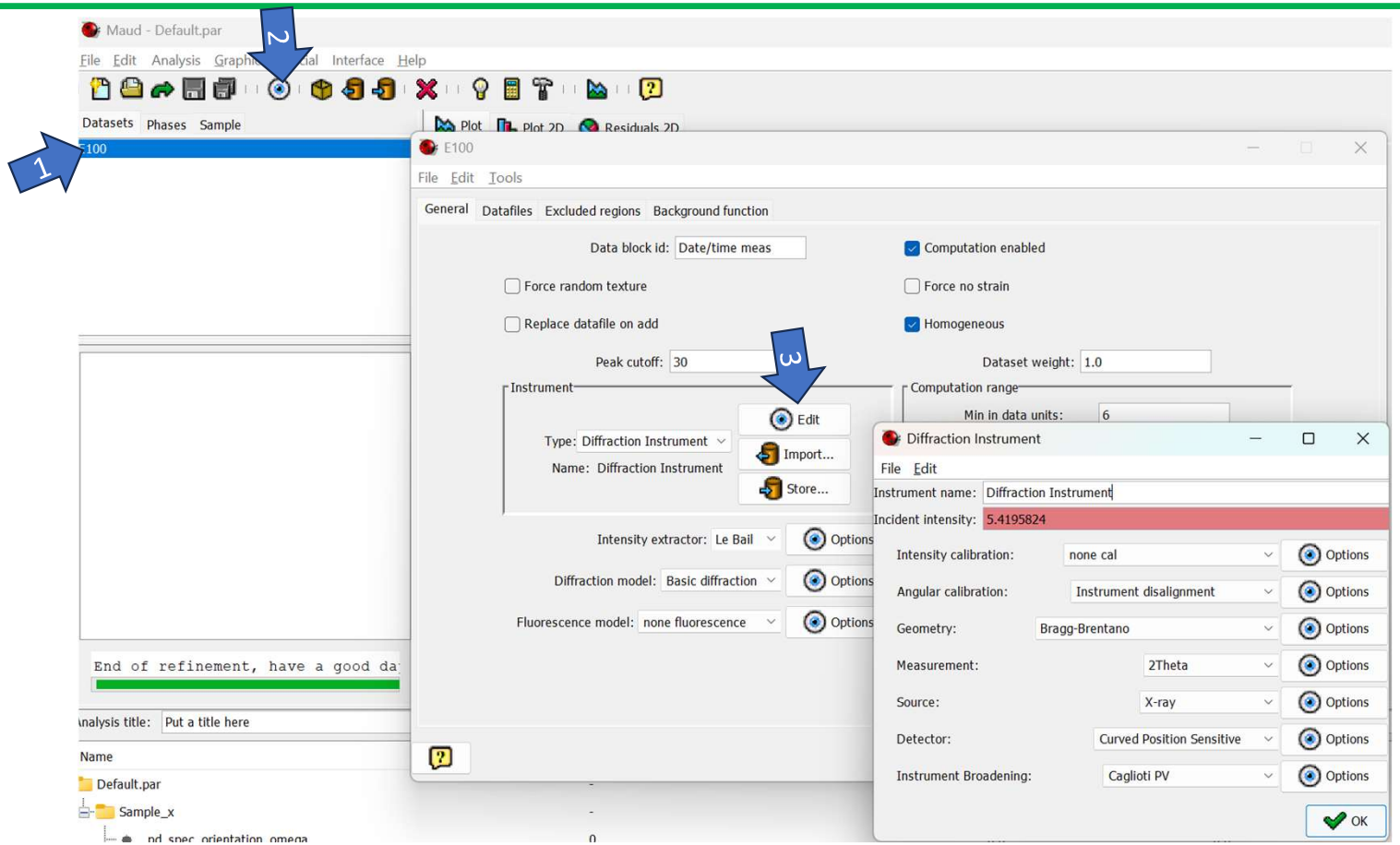
Defining Instrumental function

Basis before starting Rietveld refinement

Instrumental function - MAUD

1- Launch MAUD:

- Create instrument



Instrumental function - MAUD

2- Enter instrumental parameters:

No change

No change – zero offset to refined latter

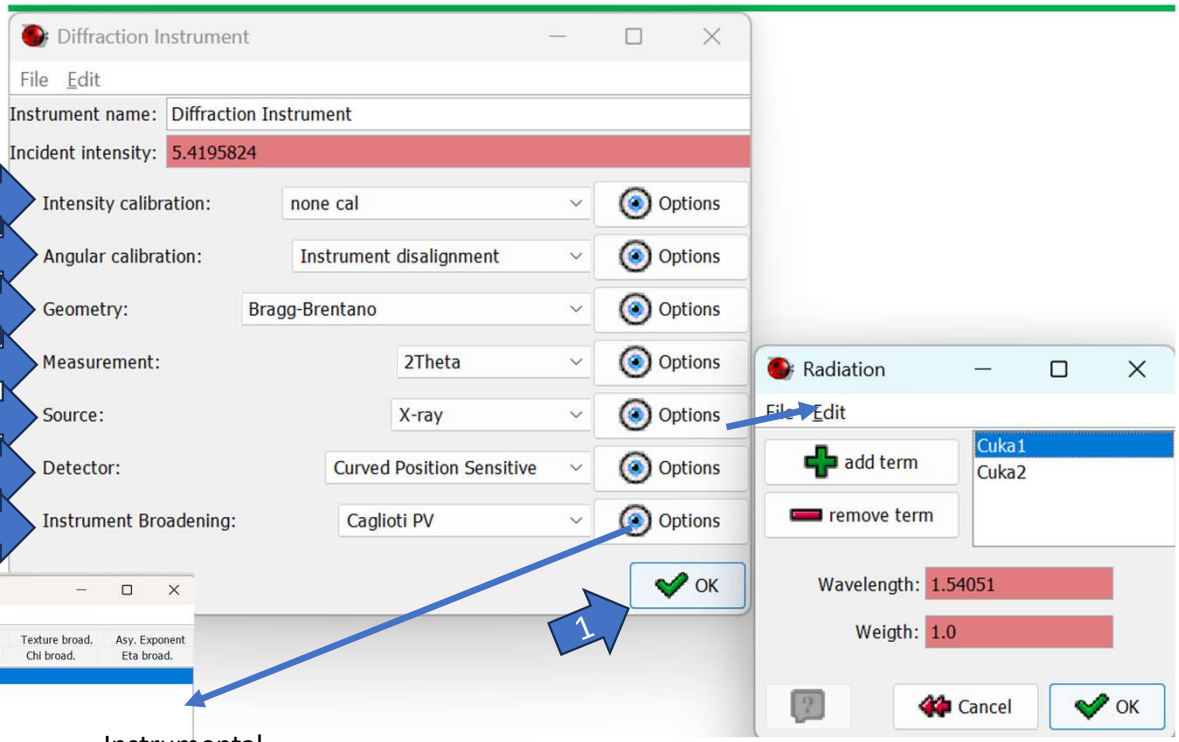
Select Bragg Brentano if reflection mode

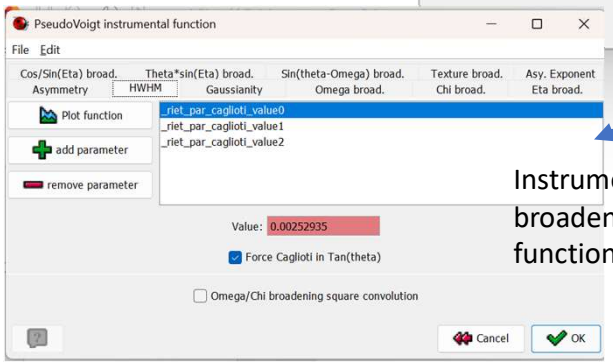
Select « 2theta » scan

Define the wavelength 2 radiations : ka1 and ka2

Select « Curved Position Sensitive » detector

To be refined latter !



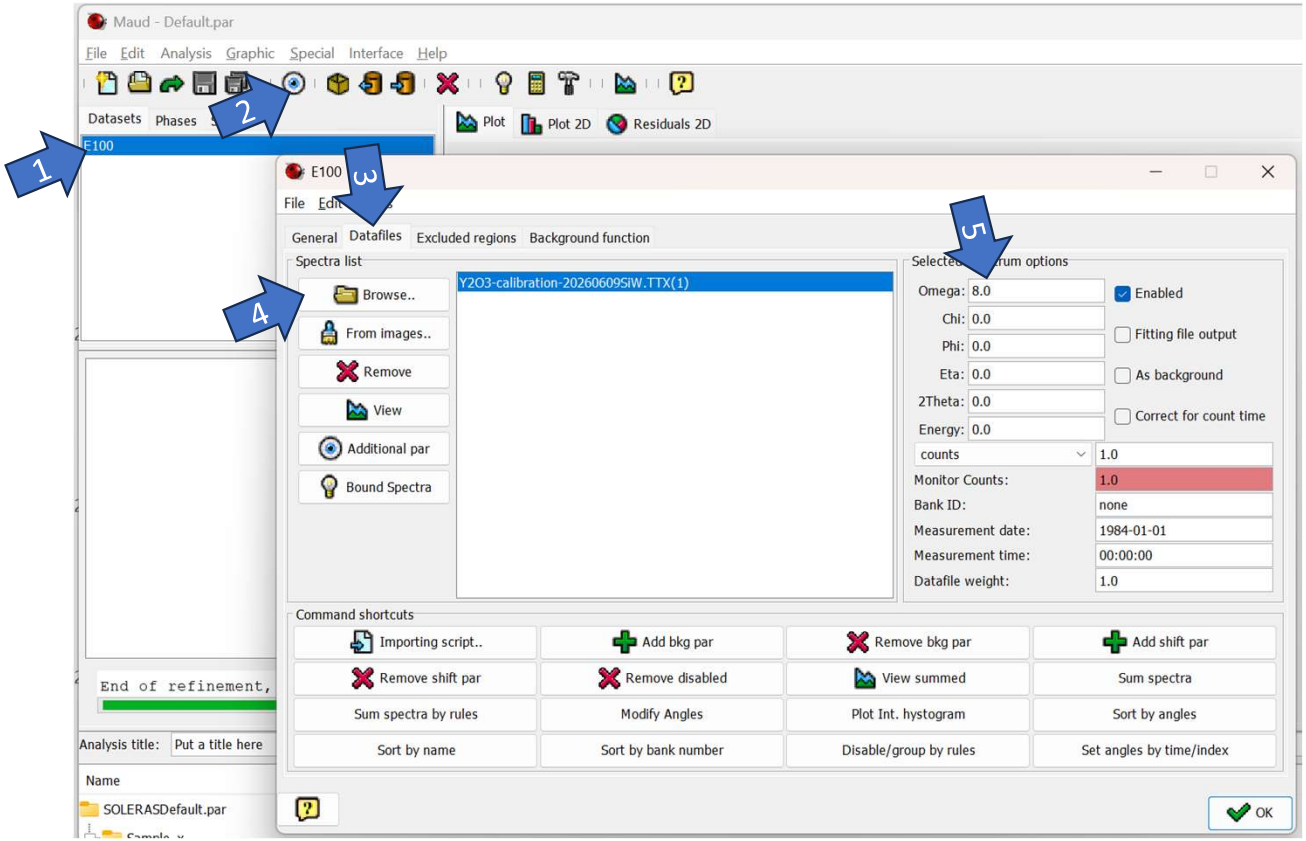


Instrumental broadening function

Instrumental function - MAUD

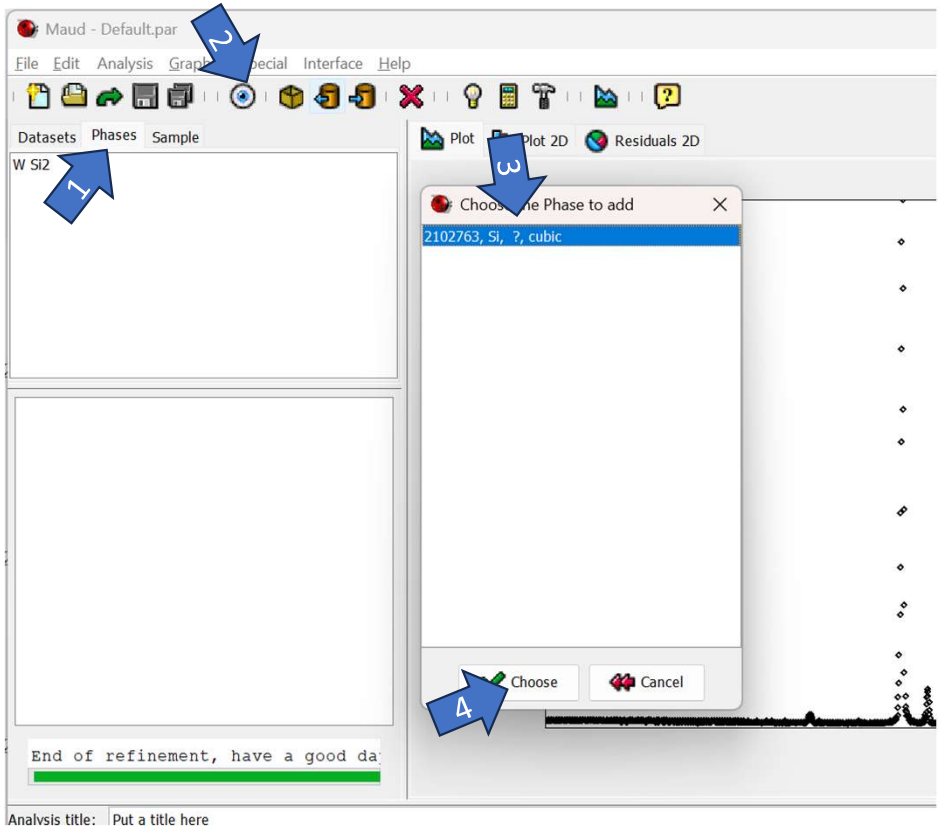
3- Load standard:

- Open TTX file and set omega to the correct value and load appropriate CIF file



Performing Rietveld - MAUD

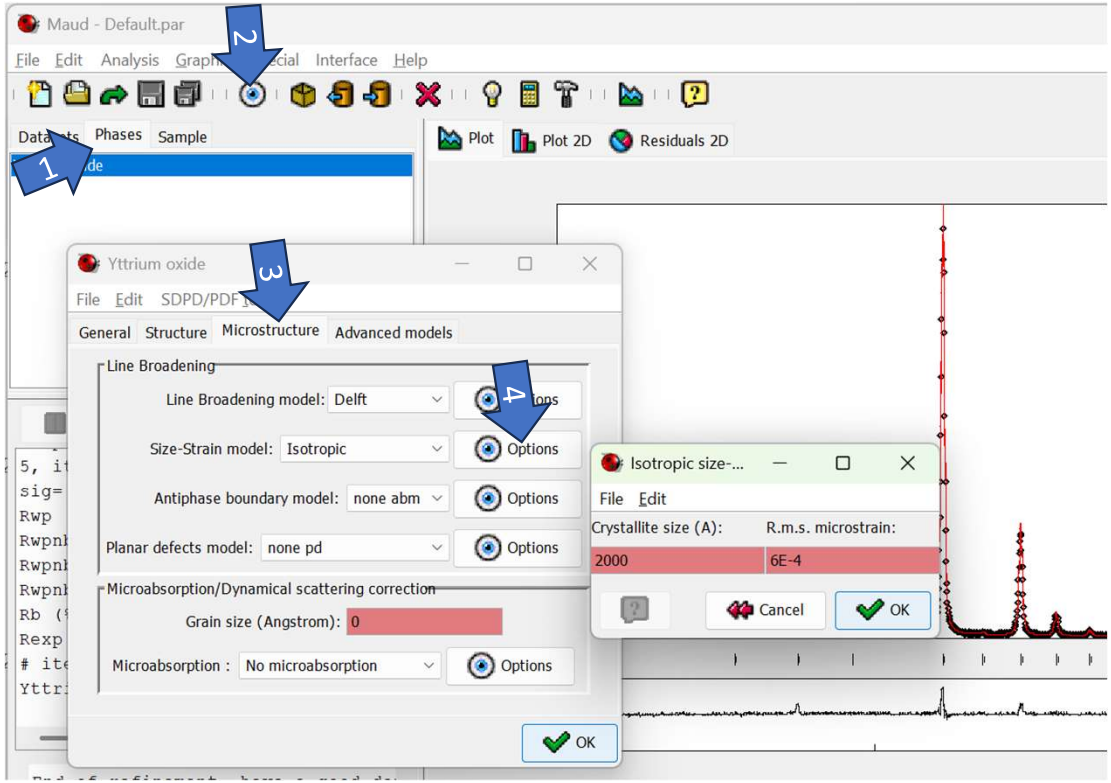
3- Load standard CIF files:



Instrumental function - MAUD

4- Fix crystallinity:

- Open standard for instrumental function – well known and cristallized sample (by default, Y2O3)

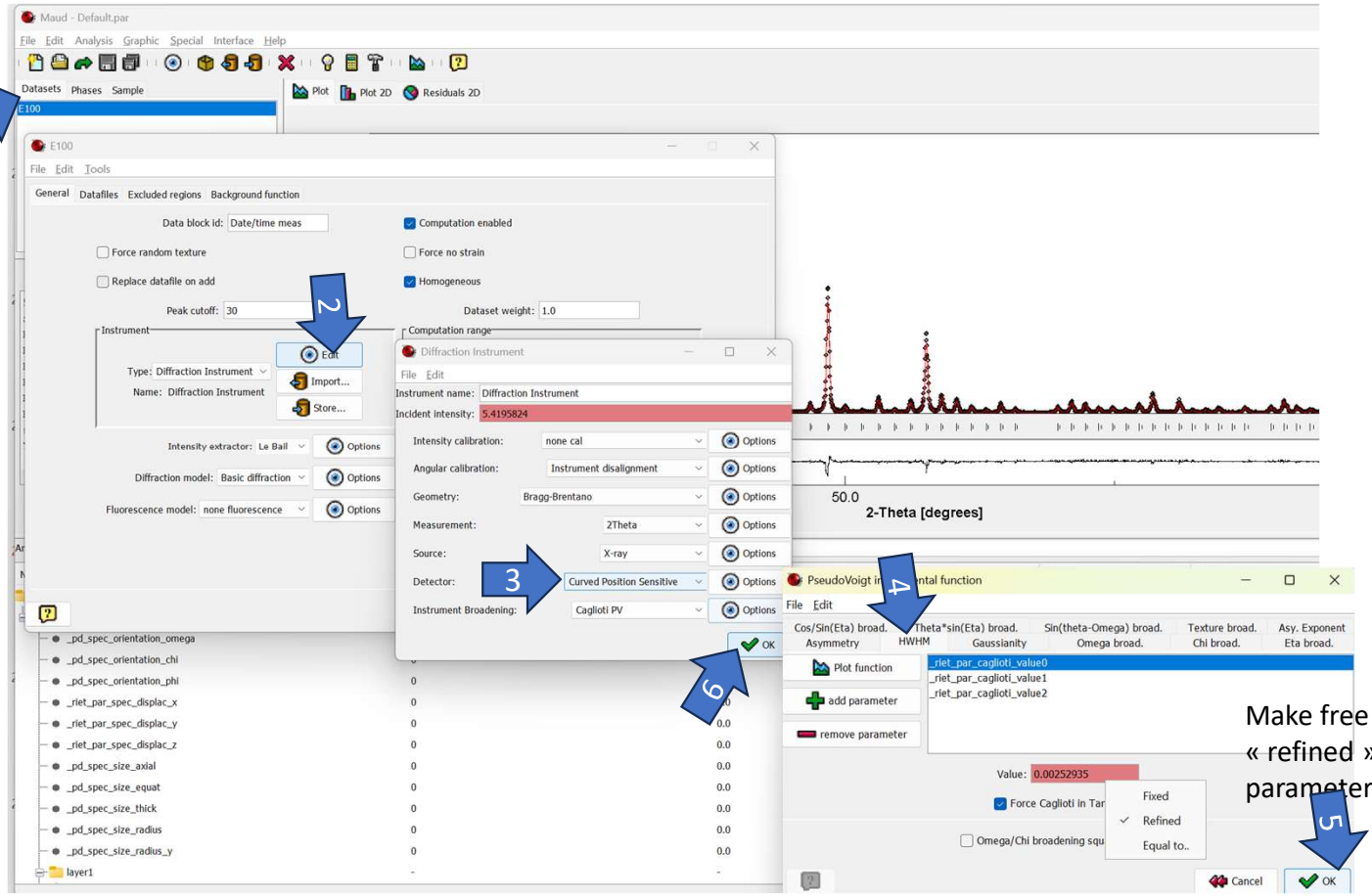


Set crystallite size to 2000

Instrumental function - MAUD

4- Refine Cagglioti:

- Open standard for instrumental function – well known and cristallized sample (by default, Y2O3)



And, finally « refine »

Make free to be « refined » the 3 parameters

Instrumental function - MAUD

5- Fix all parameter:

- Fix all parameters and save PAR file as default (name of your instrument)
- This default file will be the starting point of any of your Rietveld refinement

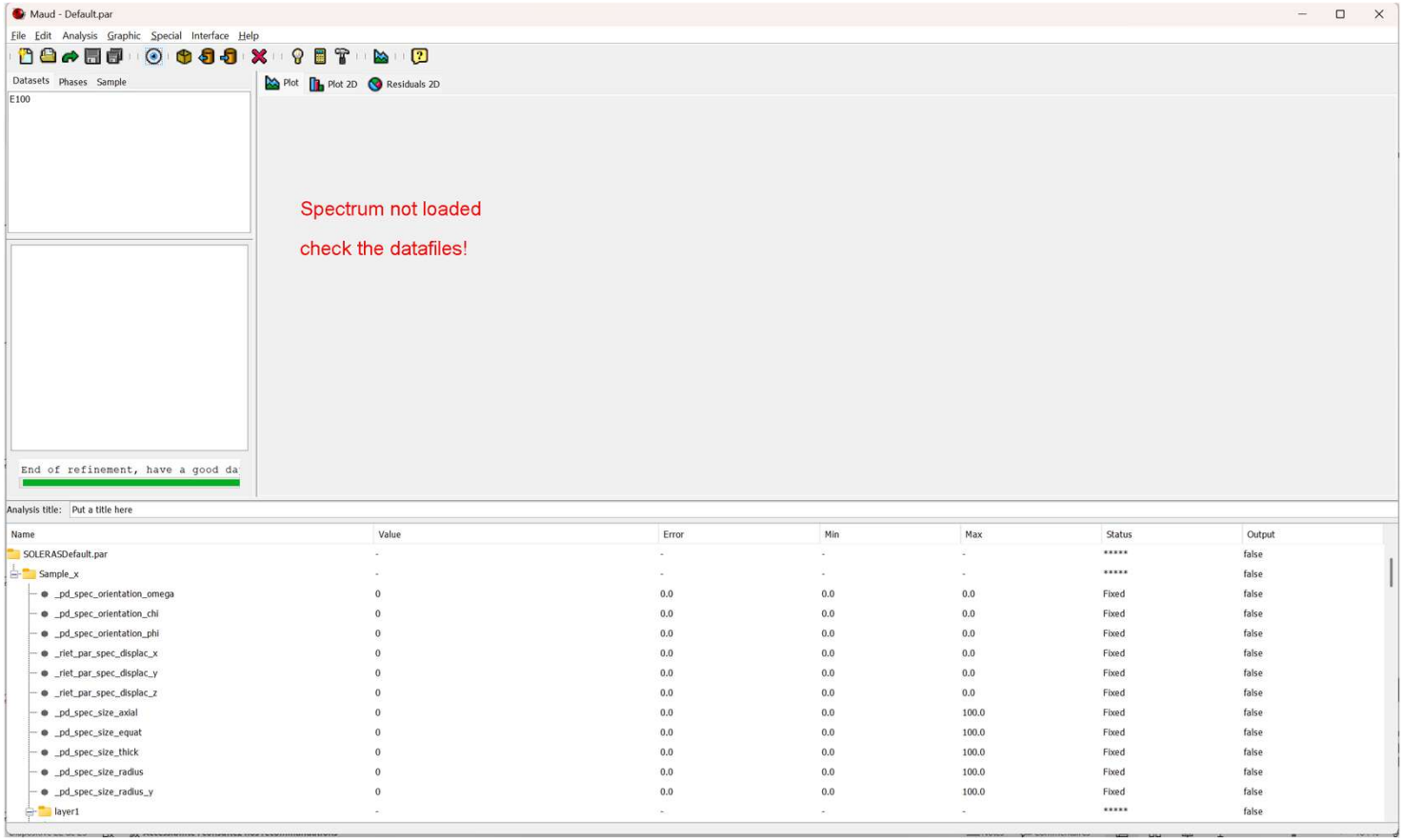
Performing Rietveld refinement

Starting from default PAR file

Performing Rietveld - MAUD

1- Launch MAUD:

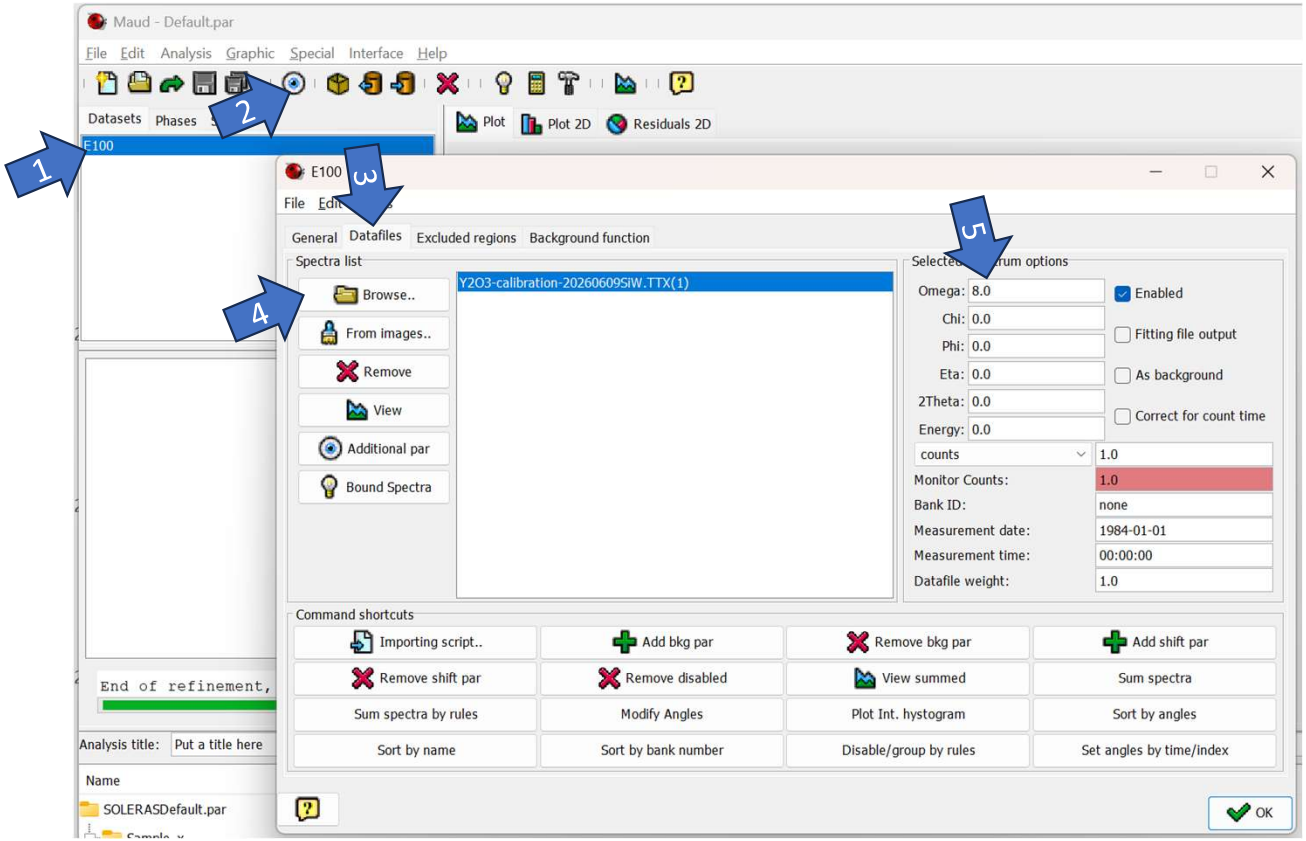
- Open DEFAULT.PAR, as defined initially of the instrumental function



Performing Rietveld - MAUD

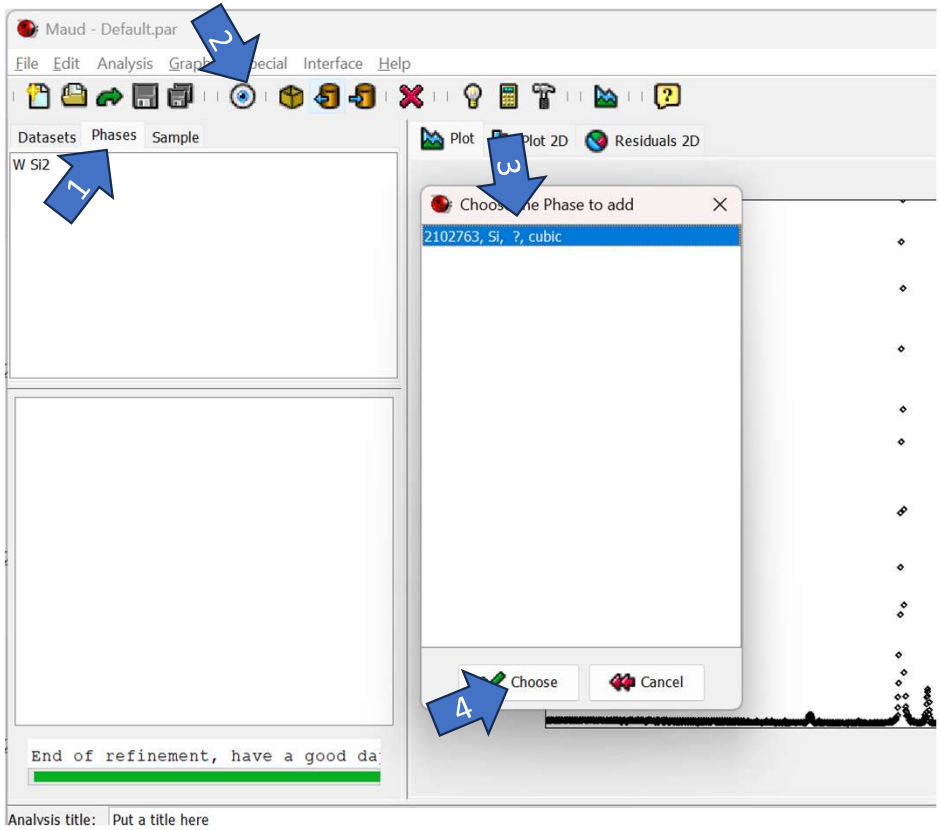
2- Launch MAUD:

- Open TTX file and set omega to the correct value



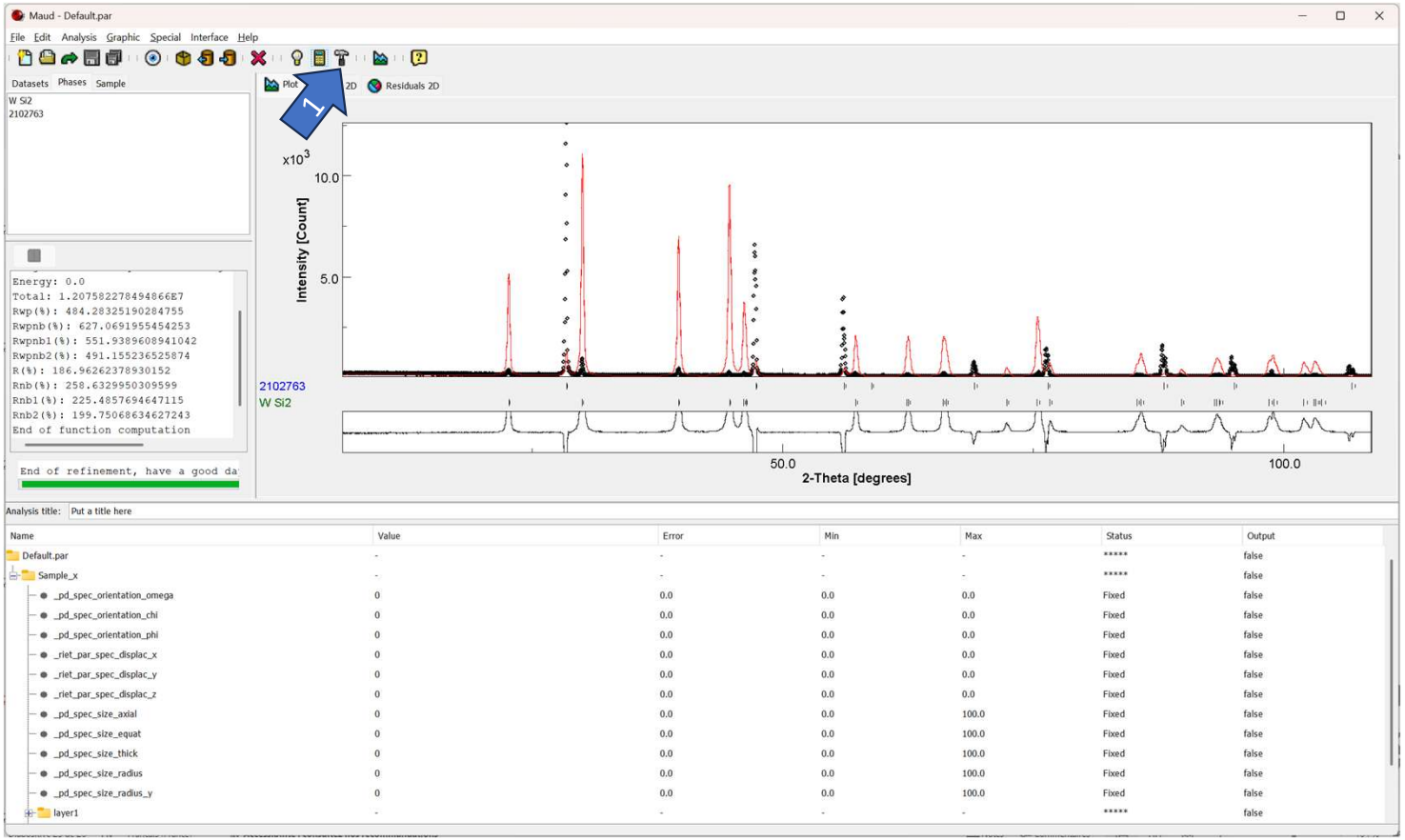
Performing Rietveld - MAUD

3- Load CIF files:



Performing Rietveld - MAUD

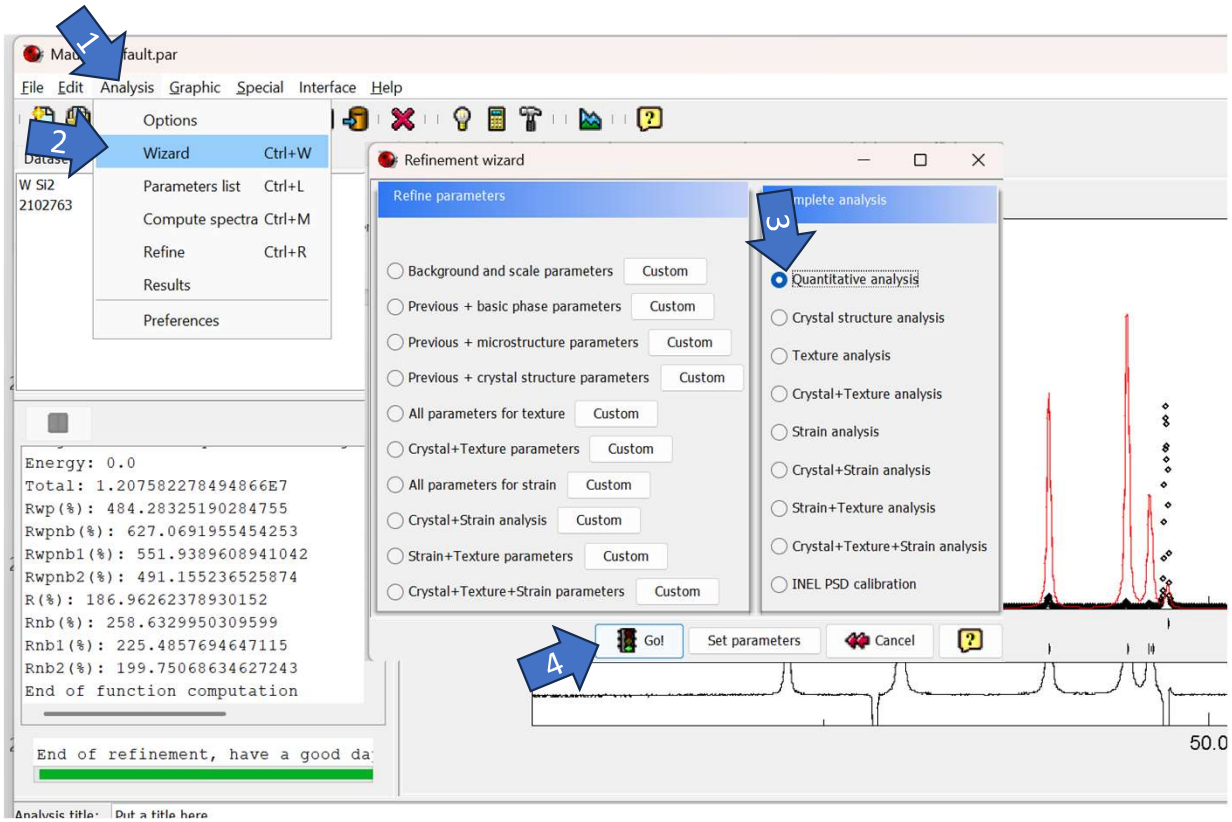
4- Pattern calculation:



Performing Rietveld - MAUD

4- quantitative analysis:

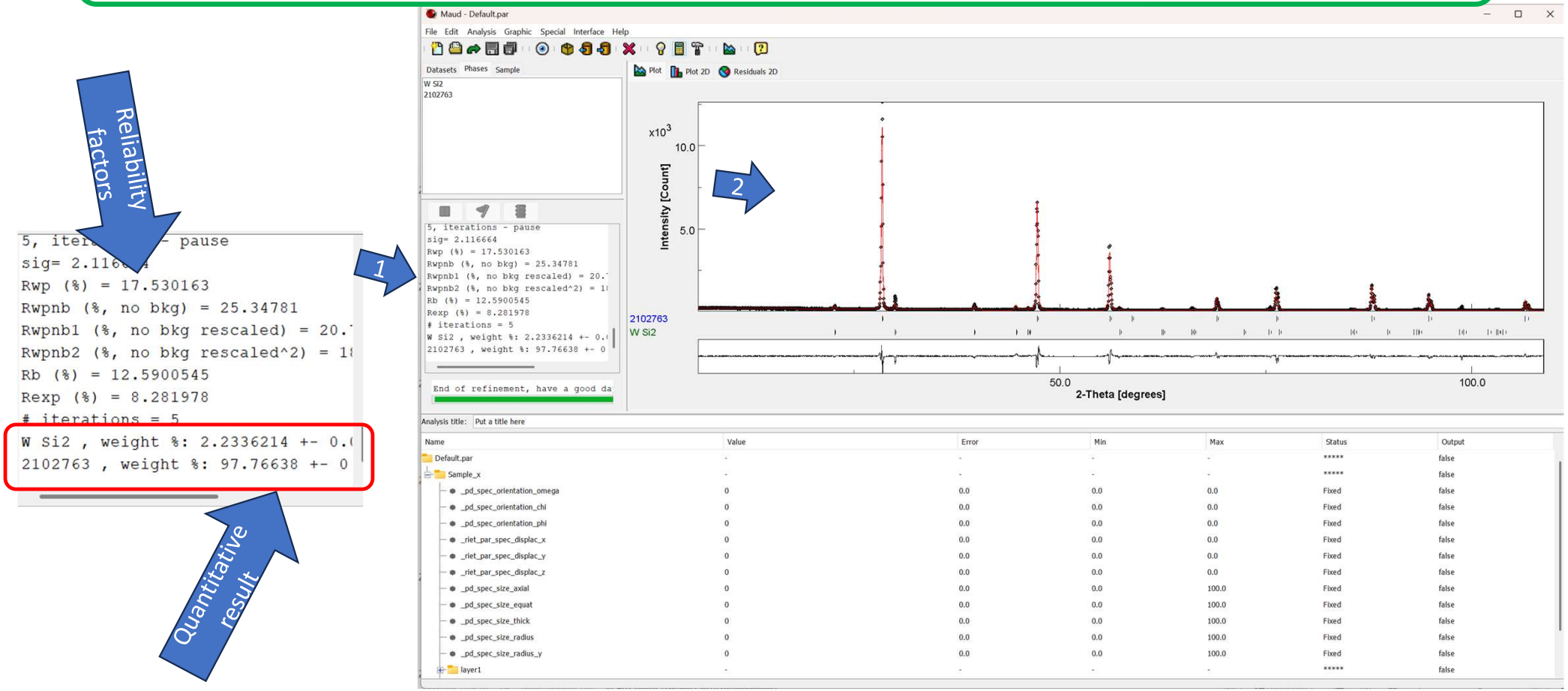
- Go !



Performing Rietveld - MAUD

5- quantitative analysis:

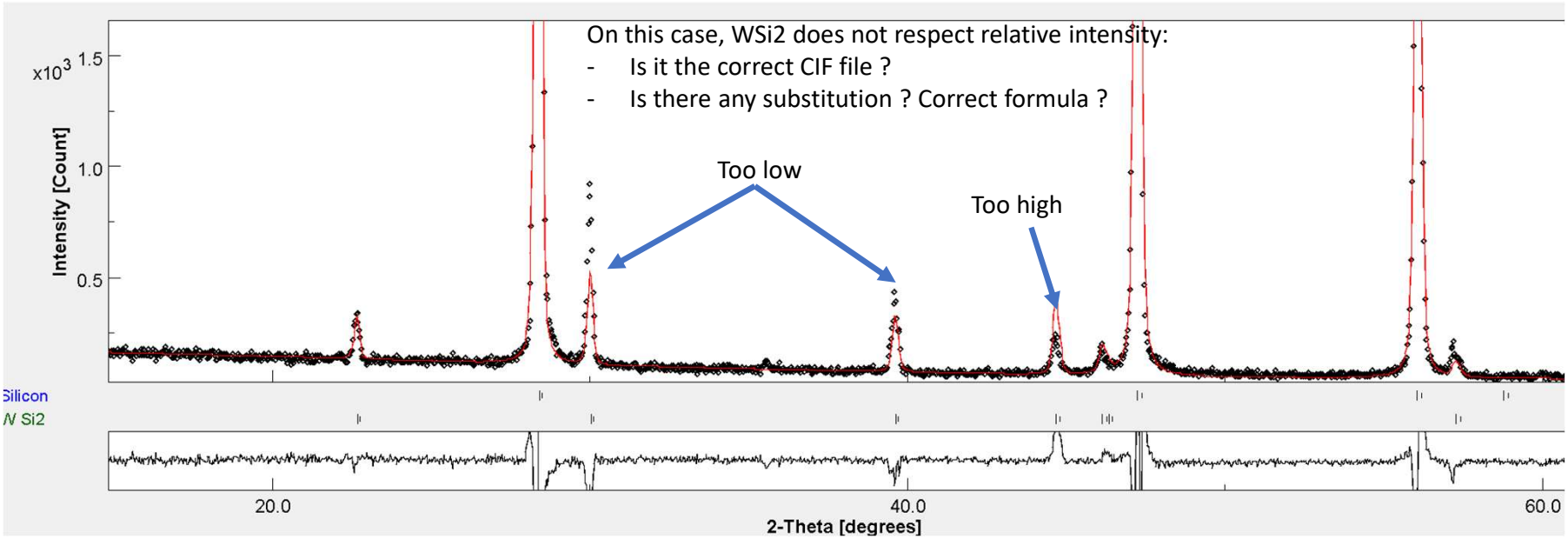
- First results



Performing Rietveld - MAUD

6- what additional refinement:

- Eccentricity
- Particle size
- Microstrains
- Cell parameters



ANNEX : wavelengths

At. No.	Element symbol	$K\alpha_2$	$K\alpha_1$	$K\beta_1$	$K\beta_2$ (*D* signifies mean of doublet)	*K* absorption edge
1	H					
2	He					
3	Li		240			226·5
4	Be		113			
5	B		67			
6	C		44			$43\cdot_{68}$
7	N		31·60			$30\cdot_{99}$
8	O		23·71			$23\cdot_{32}$
9	F		18·31			
10	Ne		14·616	14·464		
11	Na		11·909	11·617		
12	Mg		9·8889	9·558		9·5117
13	Al	8·33916	8·33669	7·981		7·9511
14	Si	7·12773	7·12528	6·7681		6·7446
15	P		6·1549	5·8038		5·7866
16	S	5·37471	5·37196	5·03169		5·0182
17	Cl	4·73050	4·72760	4·4031		4·3969
18	A	4·19456	4·19162	3·8848*		3·8707
19	K	3·74462	3·74122	3·4538		3·43645
20	Ca	3·36159	3·35825	3·0896		3·07016
21	Sc	3·03452	3·03114	2·7795		$2\cdot757_3$
22	Ti	2·75207	2·74841	2·51381		$2\cdot497_{30}$
23	V	2·50729	2·50348	2·28434		$2\cdot269_{02}$
24	Cr	2·29351	2·28962	2·08480		$2\cdot070_{12}$
25	Mn	2·10568	2·10175	1·91015		$1\cdot896_{36}$
26	Fe	1·93991	1·93597	1·75653		$1\cdot743_{34}$
27	Co	1·79278	1·78892	1·62075		$1\cdot608_{11}$
28	Ni	1·66169	1·65784	1·50010	1·48861	$1\cdot488_{02}$
29	Cu	1·54433	1·54051	1·39217†	1·38102	$1\cdot380_{43}$
30	Zn	1·43894	1·43511	1·29522	1·28366	$1\cdot283_3$
31	Ga	1·34394	1·34003	1·20784	1·19595	$1\cdot195_{67}$
32	Ge	1·25797	1·25401	1·12890	1·11682	$1\cdot116_{52}$
33	As	1·17981	1·17581	1·05726	1·04498	$1\cdot044_{97}$
34	Se	1·10875	1·10471	0·99212	0·97986	$0\cdot979_{78}$
35	Br	1·04376	1·03969	0·93273	0·92064	0·91995
36	Kr	0·9841	0·9801	0·87845	0·86609	0·86547
37	Rb	0·92963	0·92551	0·82863	0·81641	0·81549
38	Sr	0·87938	0·875214	0·78288	0·77076	0·76969
39	Y	0·83300	0·82879	0·74068	0·72874	0·72762
40	Zr	0·79010	0·78588	0·70170	0·68989	0·68877

At No.	Element symbol	$K\alpha_2$	$K\alpha_1$	$K\beta_1$	$K\beta_2$ (*D* signifies mean of doublet)	*K* absorption edge
41	Nb	0·75040	0·74615	0·66572	0·65412	0·65291
42	Mo	0·713543	0·70926	0·632253	0·62099 (*D*)	0·61977
43	Tc	0·67927*	0·67493*	0·60141*	0·59018*	(0·5891)
44	Ru	0·64736	0·64304	0·57246	0·56164	$0\cdot560_{47}$
45	Rh	0·617610	0·613245	0·54559	0·53509 (*D*)	$0\cdot533_{78}$
46	Pd	0·589801	0·585415	0·52052	0·51021	$0\cdot509_{15}$
47	Ag	0·563775	0·559363	0·49701	0·48701	$0\cdot4858_2$
48	Cd	0·53941	0·53498	0·475078	0·46531	0·46409
49	In	0·51652	0·51209	0·454514	0·444963	0·44388
50	Sn	0·49502	0·49056	0·435216	0·425900	0·42468
51	Sb	0·47479	0·470322	0·417060	0·407950	0·40663
52	Te	0·455751	0·451263	0·399972	0·391080	0·38972
53	I	0·437805	0·433293	0·383884	0·37547	$0\cdot373_{79}$
54	X	0·42043	0·41596	0·36846	0·35989	0·35849
55	Cs	0·404812	0·400268	0·354347	0·346084	0·34474
56	Ba	0·389646	0·385089	0·340789	0·332745	0·33137
57	La	0·375279	0·370709	0·327959	0·32024 (*D*)	0·31842
58	Ce	0·361665	0·357075	0·315792	0·30826 (*D*)	0·30647
59	Pr	0·348728	0·344122	0·304238	0·29690 (*D*)	0·29516
60	Nd	0·356487	0·331822	0·293274	0·28631	0·28451
61	Pm	0·3249	0·3207	0·28209	(0·2761)	(0·2743)
62	Sm	0·31365	0·30895	0·27305	0·26629	0·26462
63	Eu	0·30326	0·29850	0·26360	0·25697	0·25552
64	Gd	0·29320	0·28840	0·25445	0·24812	0·24680
65	Tb	0·28343	0·27876	0·24601	0·23960	0·23840
66	Dy	0·27430	0·26957	0·23758	0·23175	0·23046
67	Ho	0·26552	0·26083	(0·2302)	(0·2244)	0·22290
68	Er	0·25716	0·25248	0·22260	0·21715	0·21566
69	Tu	0·24911	0·24436	0·21530	(0·2101)	0·2089
70	Yb	0·24147	0·23676	0·20876	0·20363	0·20223
71	Lu	0·23405	0·22928	0·20212	0·19689	0·19584
72	Hf	0·22699	0·22218	0·19554	0·19081	0·18981
73	Ta	0·220290	0·215484	0·190076	0·18508 (*D*)	0·18393
74	W	0·213813	0·208992	0·184363	0·17950 (*D*)	0·17837
75	Re	0·207598	0·202778	0·178870	0·17415 (*D*)	0·17311
76	Os	0·201626	0·196783	0·173607	0·16899 (*D*)	0·16780
77	Ir	0·195889	0·191033	0·168533	0·16404 (*D*)	0·16286
78	Pt	0·190372	0·185504	0·163664	0·15928 (*D*)	0·15816
79	Au	0·185064	0·180185	0·158971	0·15471 (*D*)	0·15344
80	Hg	0·17992*	0·17504*	0·15439*	0·15020 (*D*)*	0·14923