RMS · · · · · · · Testing • Research • Consulting

Workshop „Rietveld Refinement with Profex“

Lesson 2: Sample Preparation and Instrument Settings

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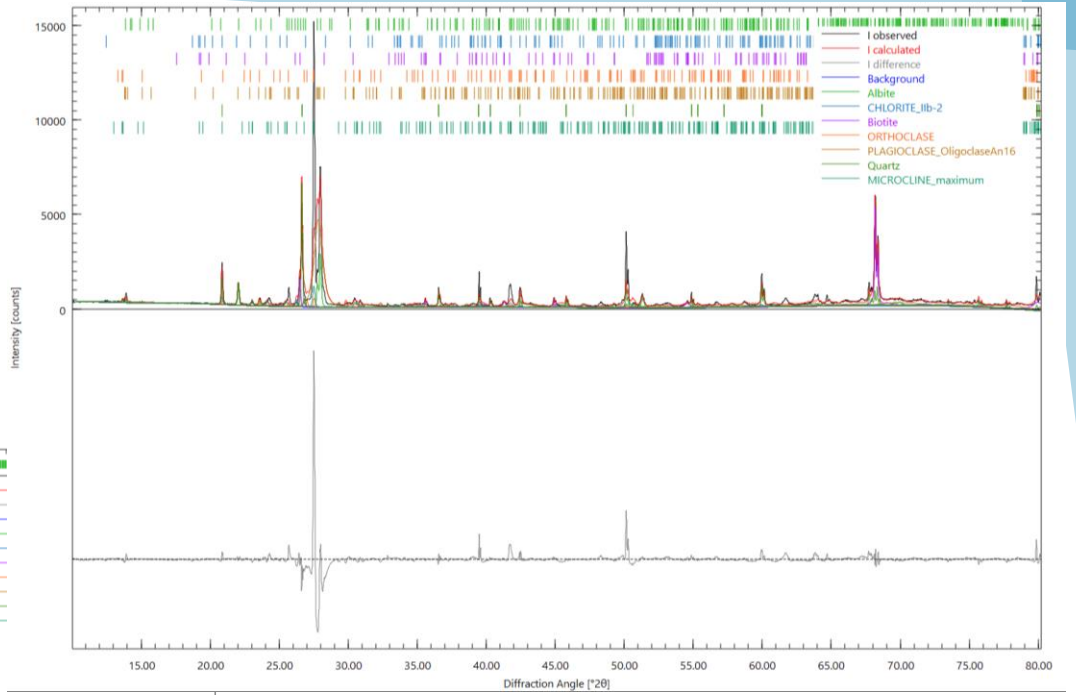
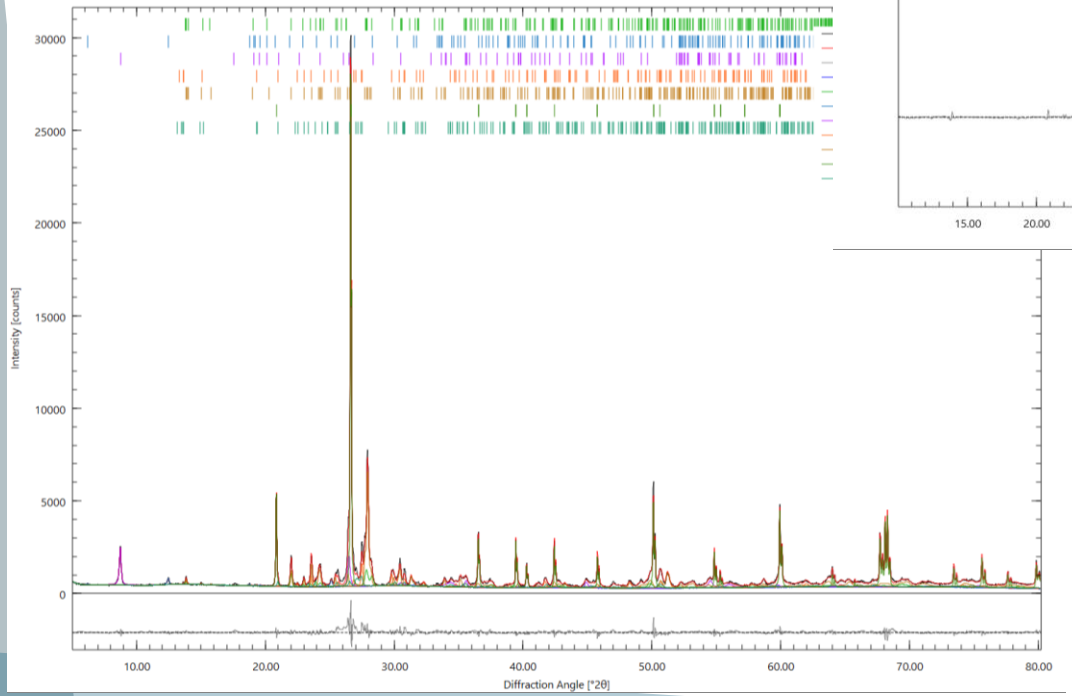
Forschungszentrum Jülich, Germany

Sample Preparation

What is different?

Only difference:
XRD sample preparation





- Same specimen
- Same XRD instrument
- Same instrument parameters
- Same refinement software
- Same refinement strategy

Sample Preparation

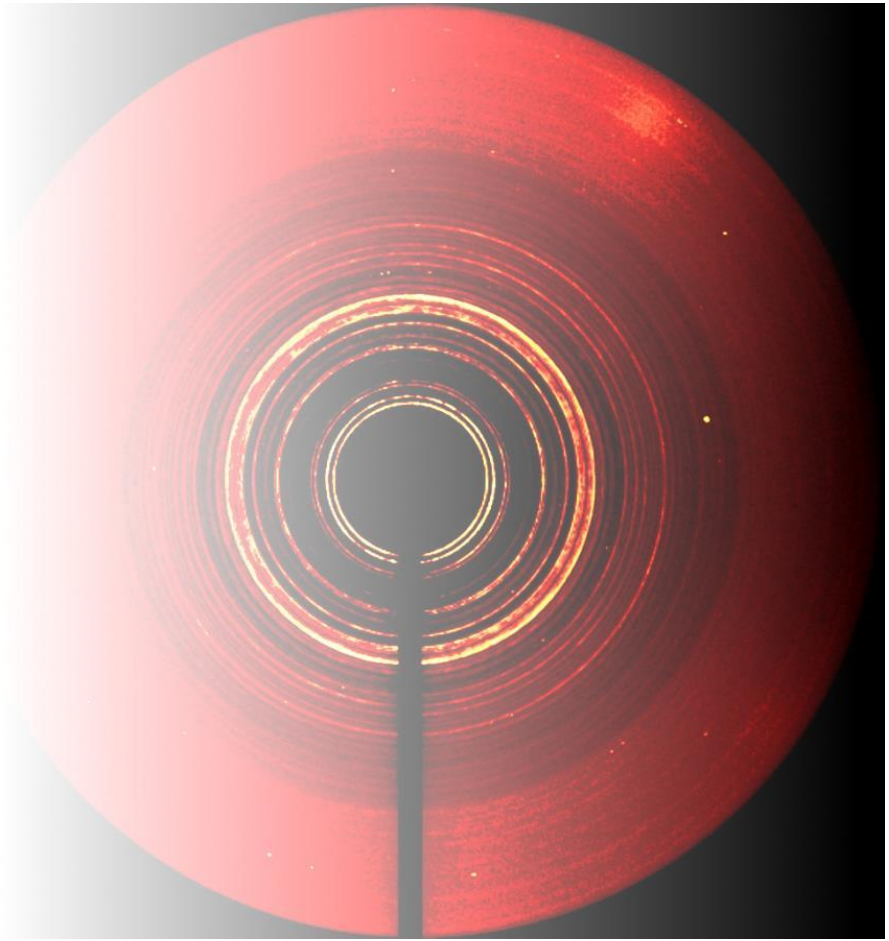
Sample preparation is **ABSOLUTELY CRUCIAL** for a good diffraction pattern!

Some problems encountered during Rietveld refinement are inherent to the sample.

Some are related to sample preparation errors.

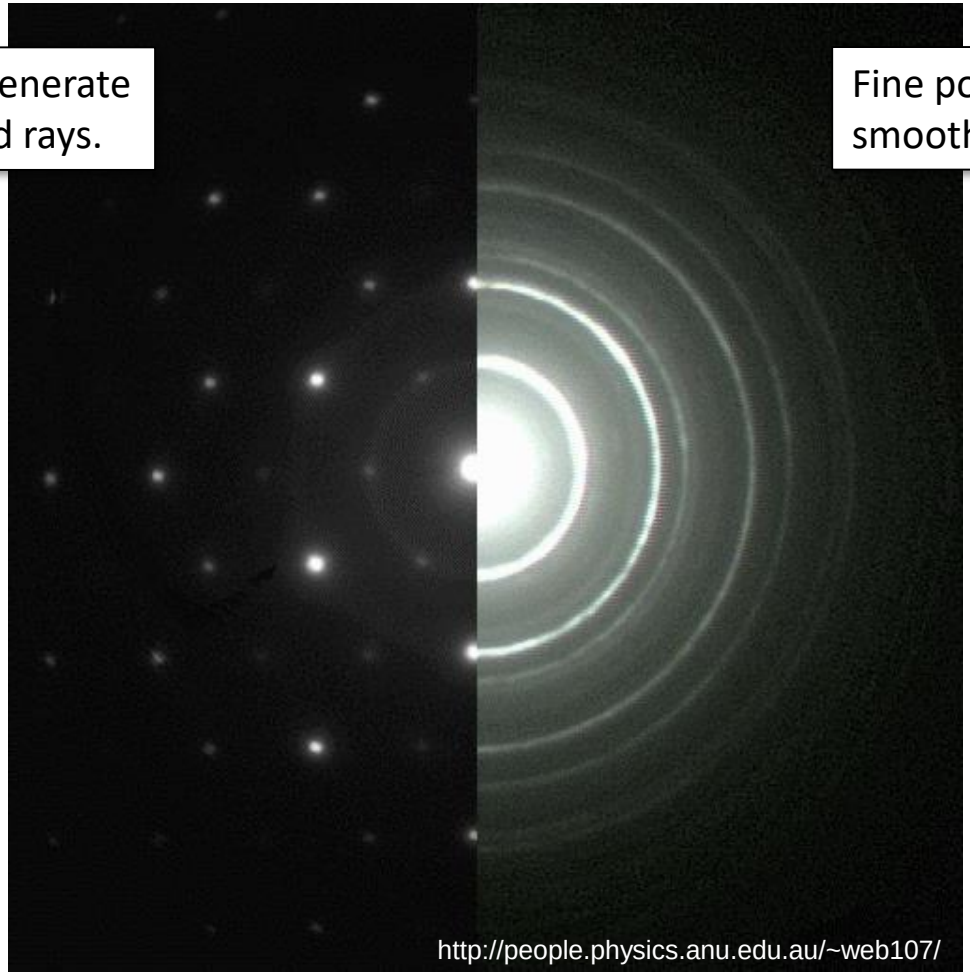
Sample-Related Problems

- Graininess
- Micro-absorption
- Texture
- Sample height displacement
- Surface roughness
- Sample transparency



Graininess

Single crystals generate spotty diffracted rays.



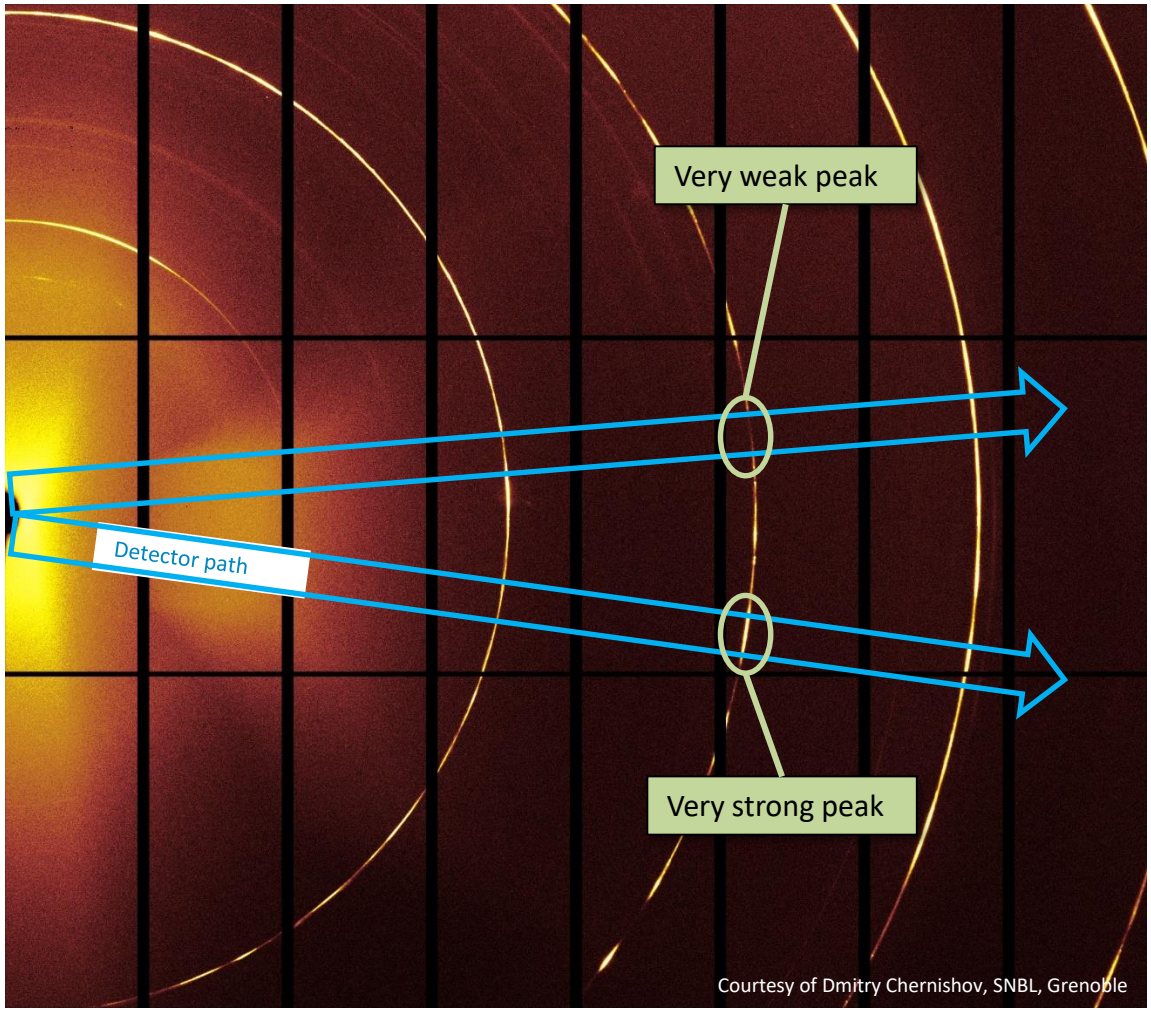
Fine powders generate smooth diffraction rings.

Graininess

Spotty diffraction rings

The same sample, at
the same 2θ position,
but different intensities!

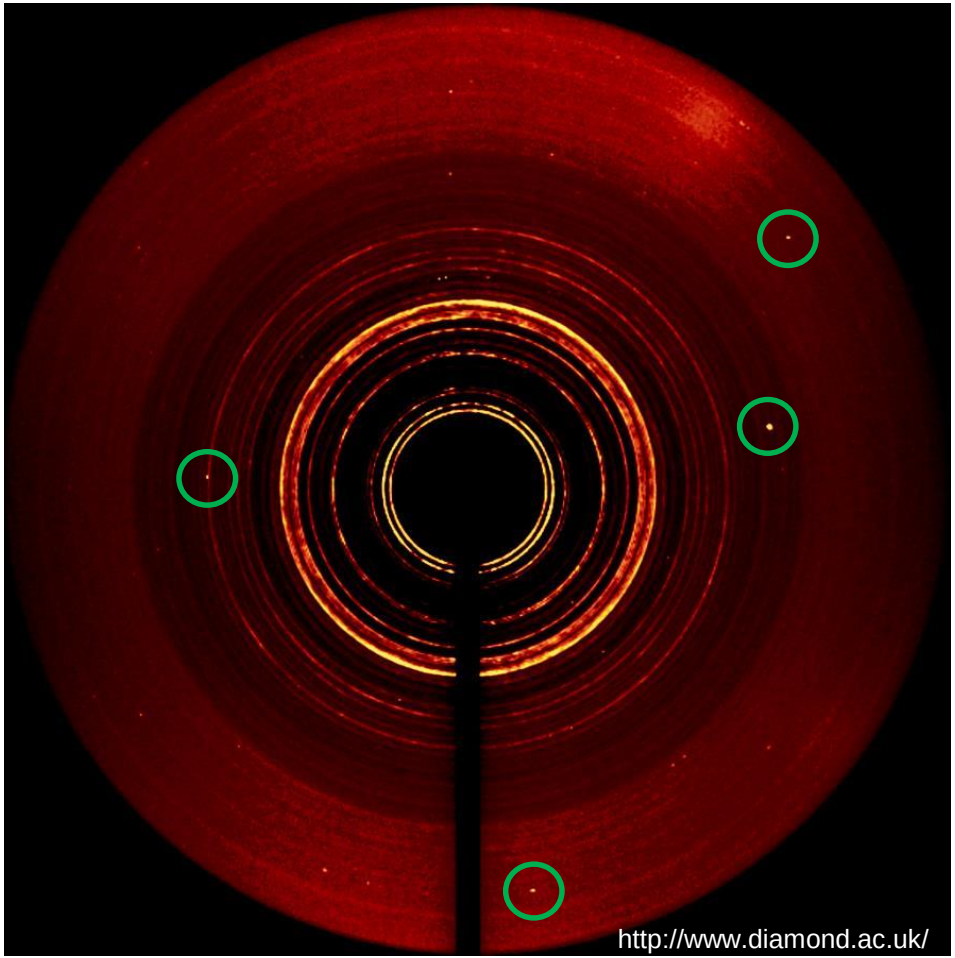
Grainy samples:
- non-reproducible intensities
- «phantom» peaks
- «missing» peaks



Graininess: Rocks in Dust

«Rocks in Dust»:
A few large crystals in a fine matrix

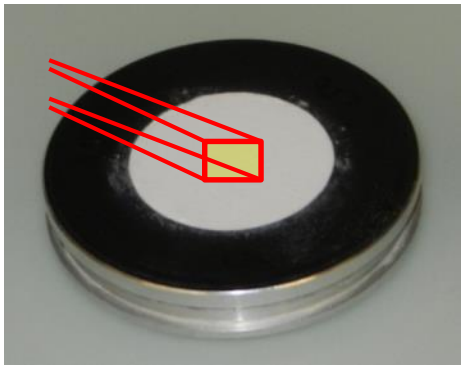
Usually invisible, but if scanned: Strong peaks out of nowhere!



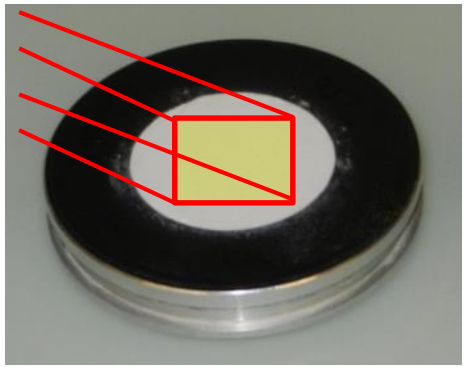
Graininess

Reducing graininess:

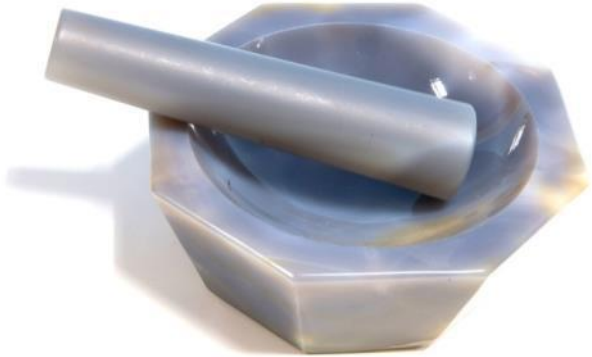
- Grinding / milling to < 10 µm (better 1 – 5 µm)
- Adjust divergence slit and beam mask for largest possible irradiated area
  (= more particles contribute to diffraction pattern)
- Use spinning sample stage
  (= better randomisation)
- Counting time per step ≥ 1 revolution of samples stage spinner



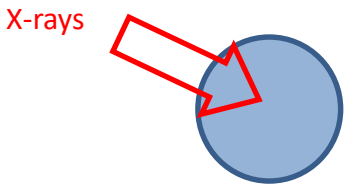
Few diffracting crystallites



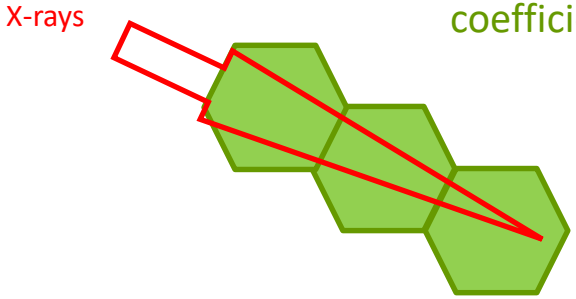
Many diffracting crystallites



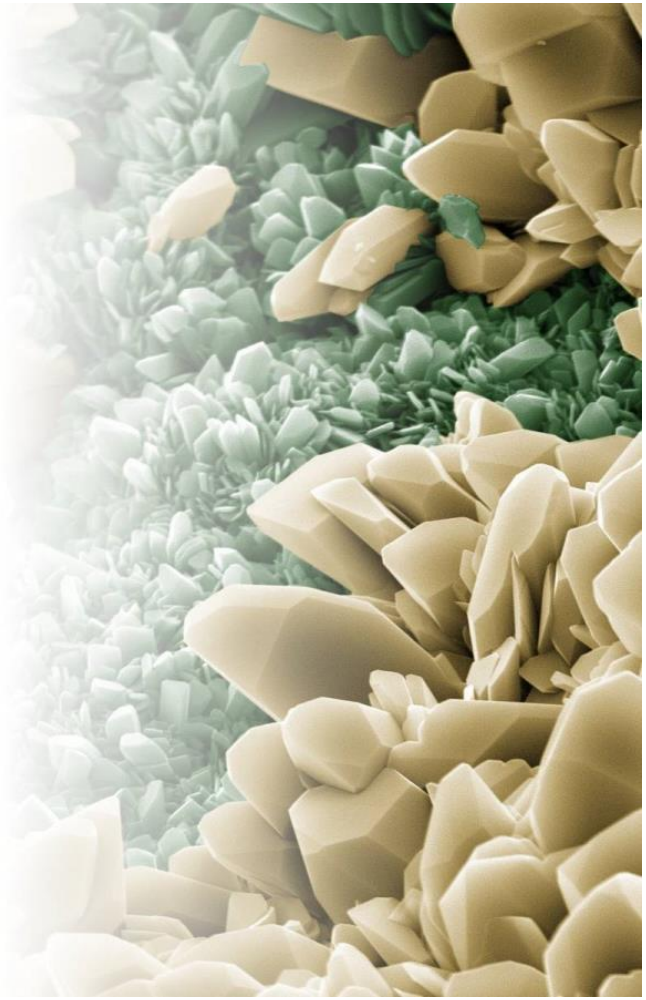
Micro-Absorption



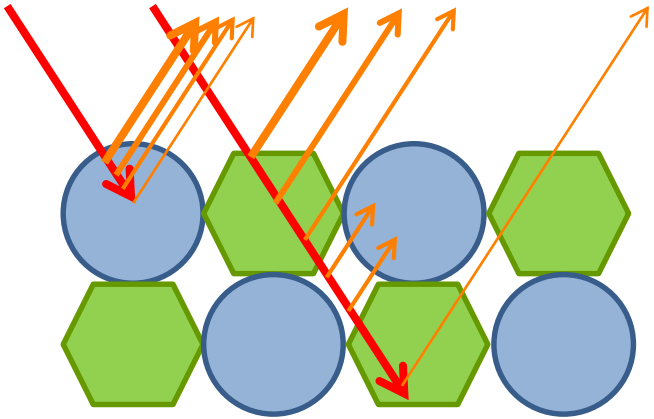
Phase 1: High absorption coefficient for X-radiation



Phase 2: Low absorption coefficient for X-radiation

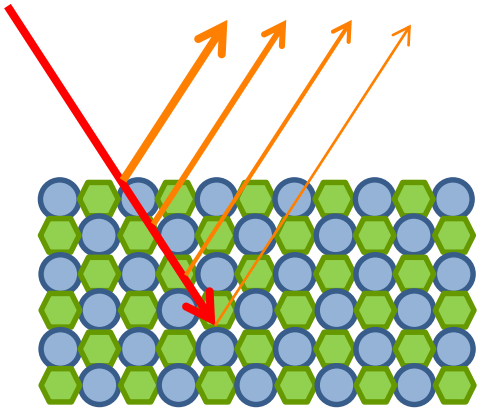


Micro-Absorption



Strong attenuation by phase 1
Large particles absorb significant part of the radiation.
→ Small volume of interaction

Weak attenuation by phase 2
→ Large volume of interaction

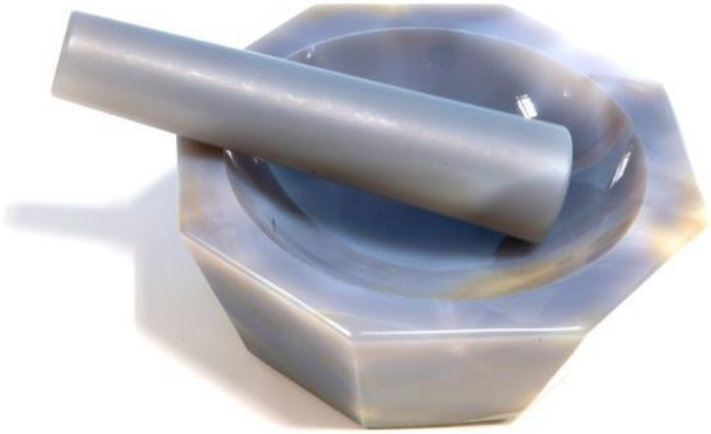


Small particles absorb insignificant part of the radiation.
→ Volumes of interaction with phases 1 & 2 are representative for phase composition

Micro-Absorption

Micro-absorption:

- Occurs in samples with…
  - … large particles (**not crystallites!**)
  - … phases with large contrast in absorption coefficients
- Leads to biased phase quantifications
- Can be reduced by grinding / milling

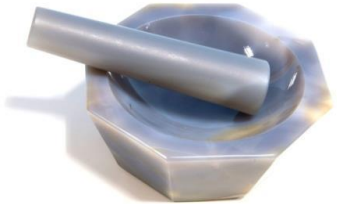


Summary: Ideal Particle Size

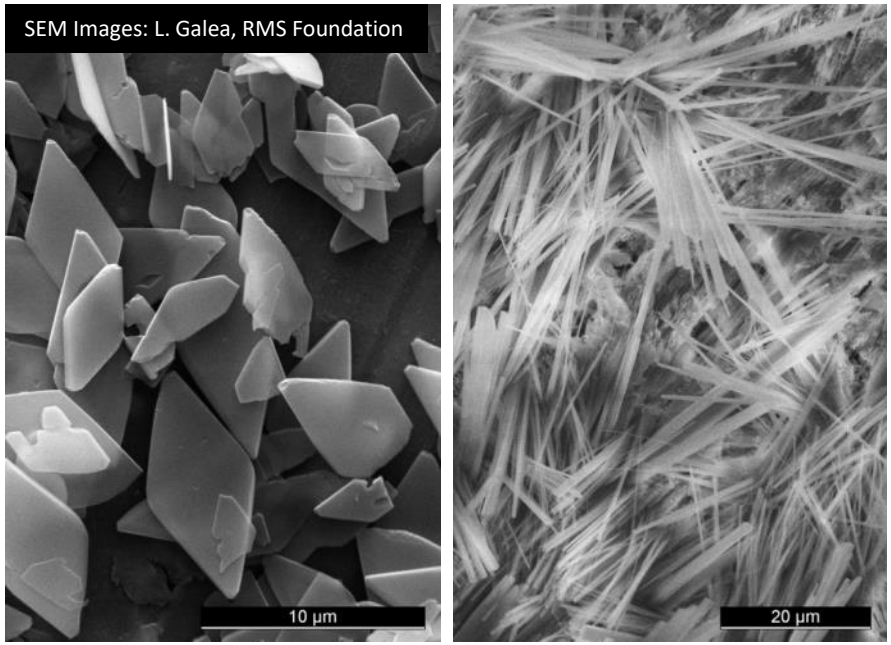
- Ideal particle and crystallite size: 1–5 µm
- Larger particles: Micro-absorption
- Larger crystallites: Grainy sample

- Caution: High-energy milling (e.g. planetary mill) generates:
  - Lattice defects and strain in the crystal structure
  - Peak broadening due to reduction of crystallite size
  - Amorphous fraction (invisible to XRD)

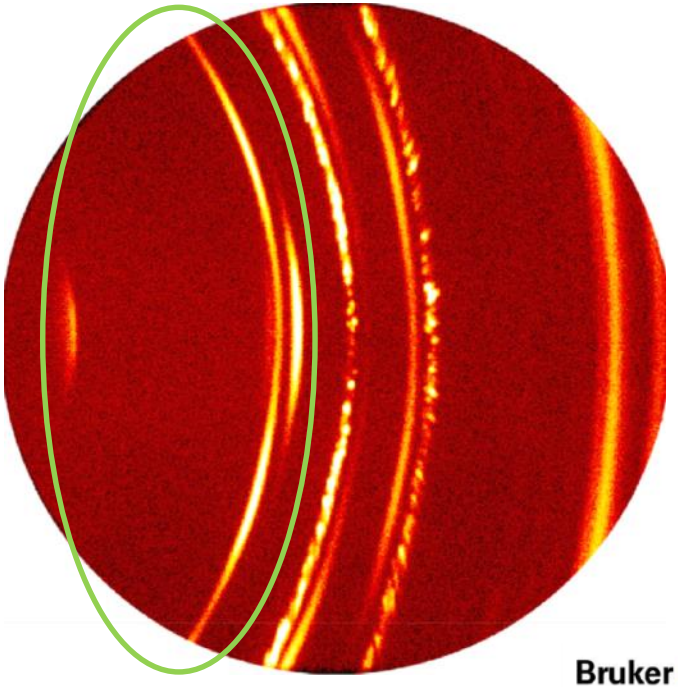
- Use manual milling (agate mortar) or specialized micronizing mill to avoid over-milling



Texture / Preferred Orientation (PO)



Platelets, Needles, Fibers, Whiskers



Random orientation

Preferred orientation

Texture / Preferred Orientation (PO)

Try to avoid orientation at the surface of the sample:

- Shave the top layer off the sample
- Use back-loading sample holder
- Disorder surface with textured stamp

- Various creative solutions can be found on the internet (involving Vaseline, hair spray, …)

PO can be corrected mathematically,
but phase quantification will be biased.
(more on this in the lesson on «Rietveld refinement»)

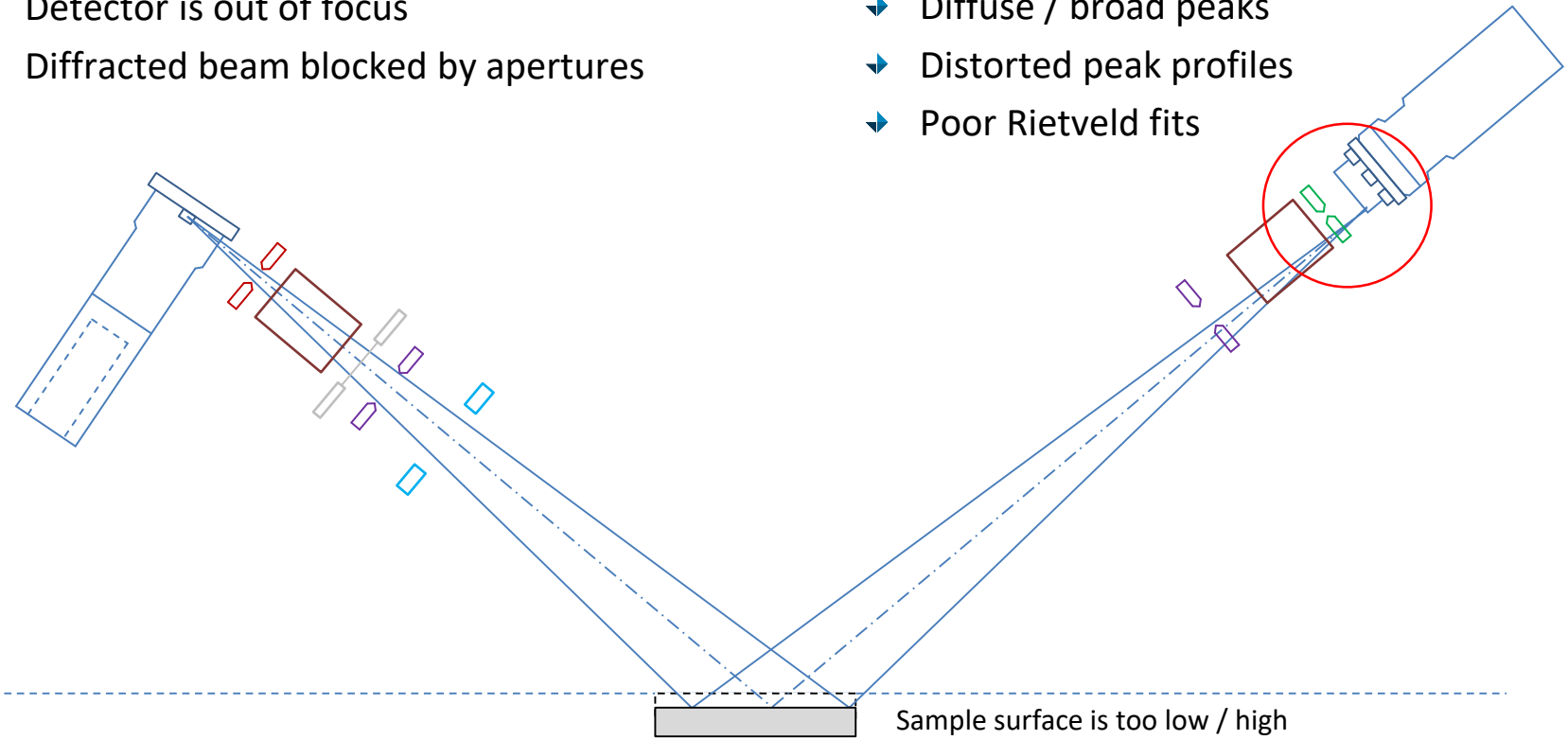
Sample Height Displacement

On the Instrument:

- Focus of diffracted beam is displaced
- Detector is out of focus
- Diffracted beam blocked by apertures

In the XRD pattern:

- 2θ shift of peaks
- Diffuse / broad peaks
- Distorted peak profiles
- Poor Rietveld fits



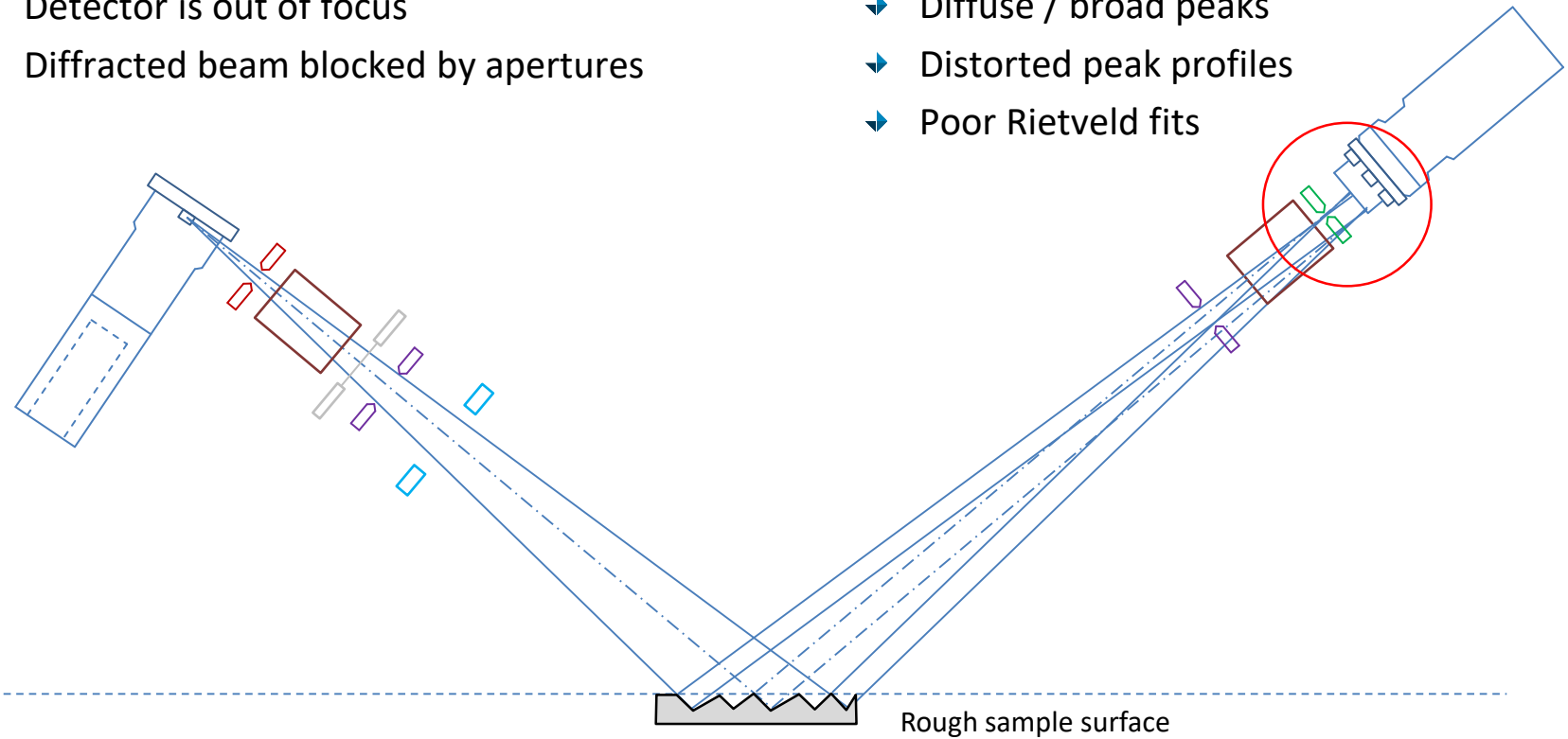
Surface Roughness

On the Instrument:

- Focus of diffracted beam is **partially** displaced
- Detector is out of focus
- Diffracted beam blocked by apertures

In the XRD pattern:

- 2θ shift of peaks
- Diffuse / broad peaks
- Distorted peak profiles
- Poor Rietveld fits



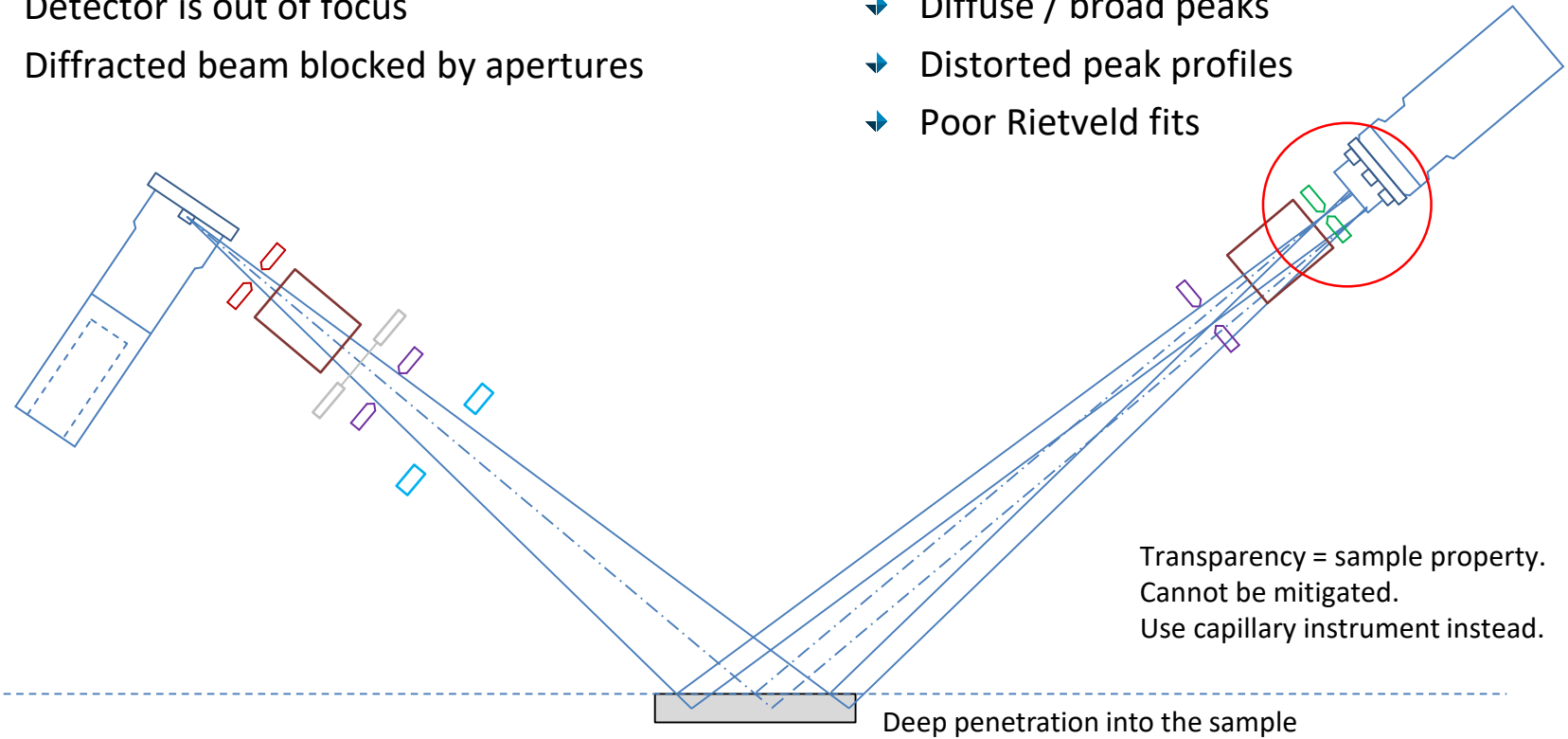
Sample Transparency

On the Instrument:

- Focus of diffracted beam is **partially** displaced
- Detector is out of focus
- Diffracted beam blocked by apertures

In the XRD pattern:

- 2θ shift of peaks
- Diffuse / broad peaks
- Distorted peak profiles
- Poor Rietveld fits



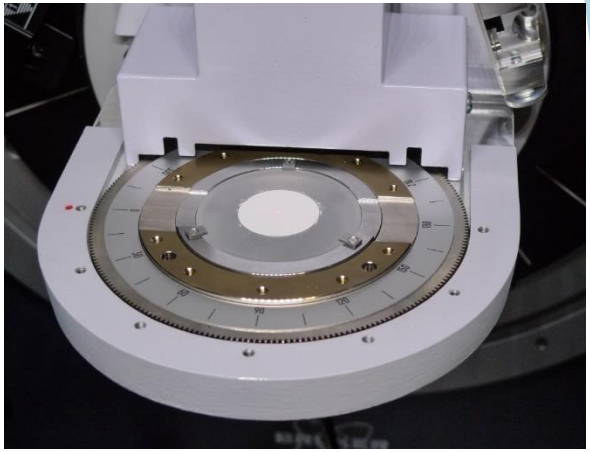
Transparency = sample property.
Cannot be mitigated.
Use capillary instrument instead.

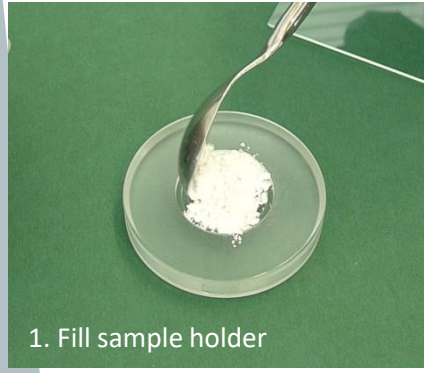
Deep penetration into the sample

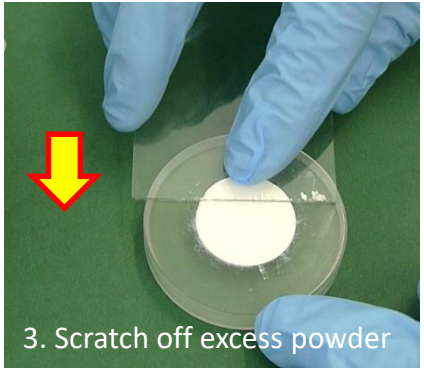
Summary: The Perfect Sample

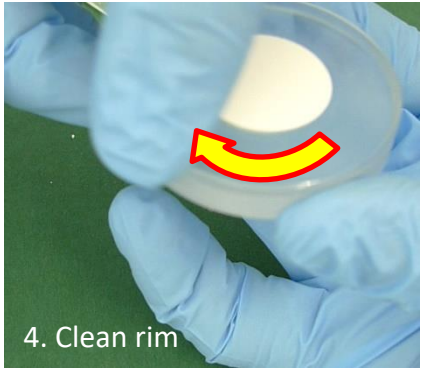
The perfect sample for Bragg-Brentano diffractometers:

- Crystallites and particles of 1-5 µm size
- Perfectly random orientation
- Perfectly flat surface
- Surface precisely centered in the goniometer
- High packing density









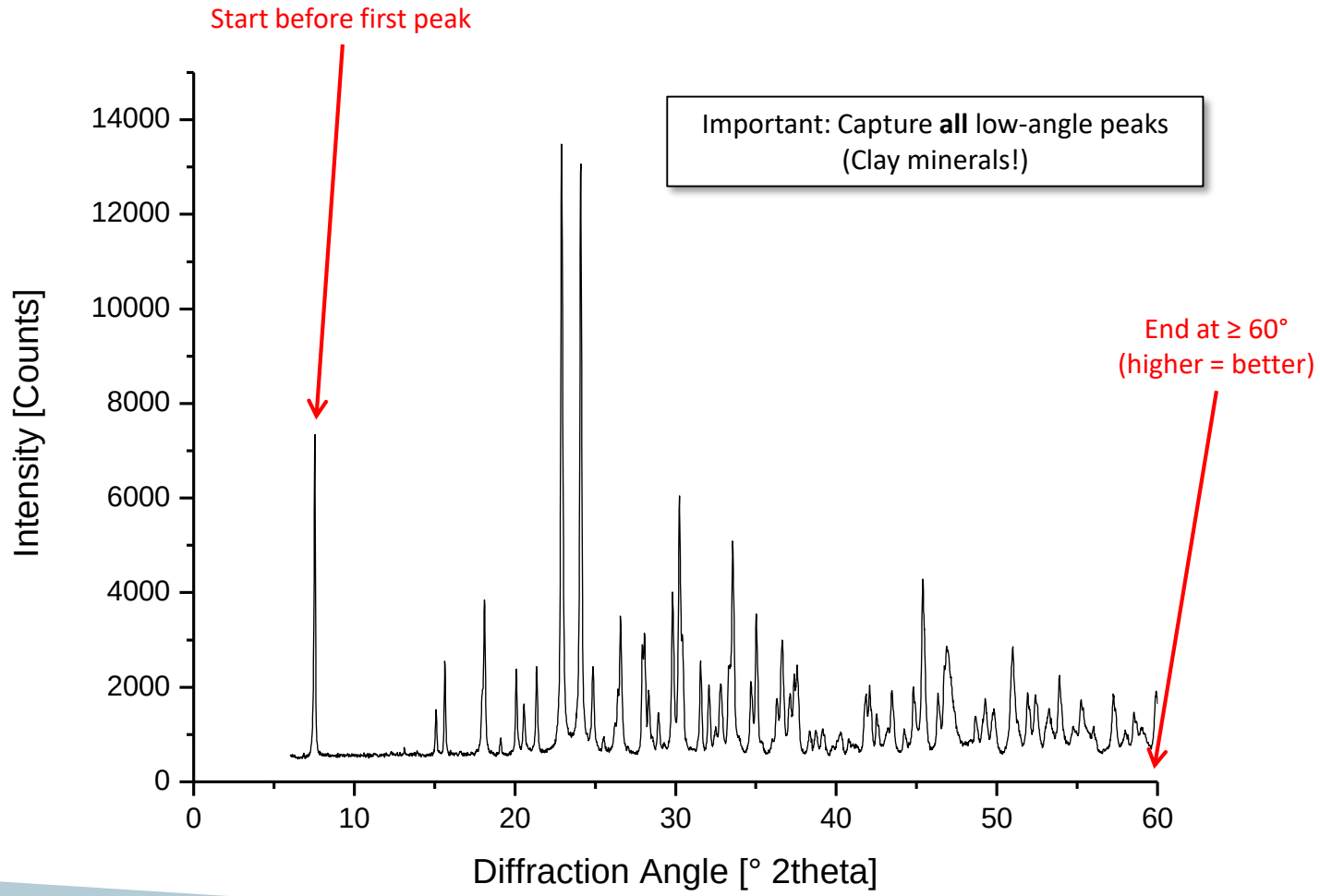
Scan Parameters

- Angular Range

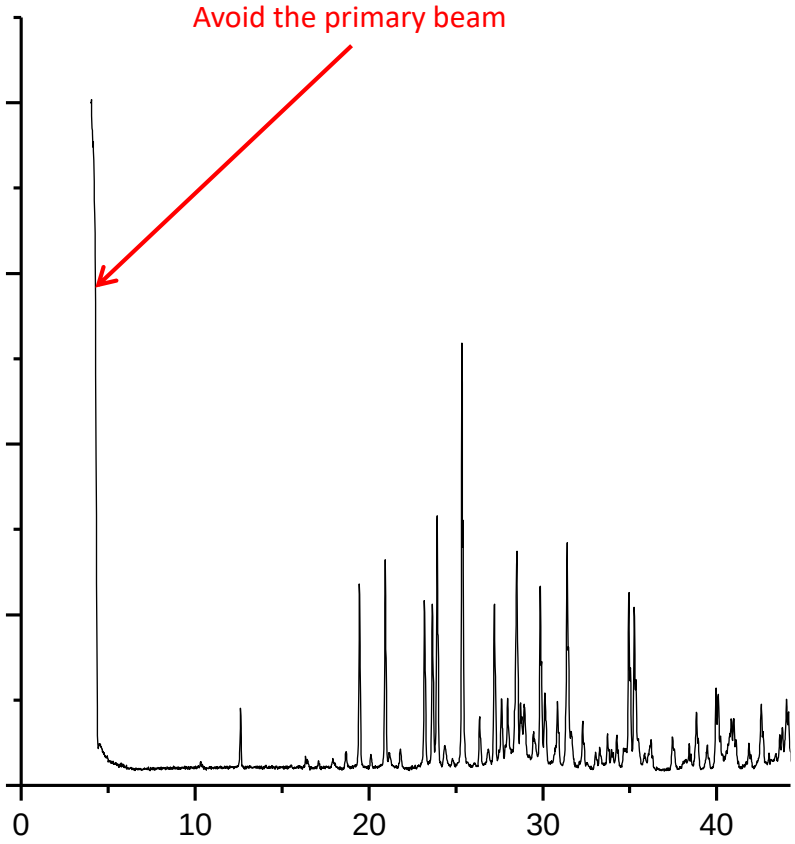
- Step Size

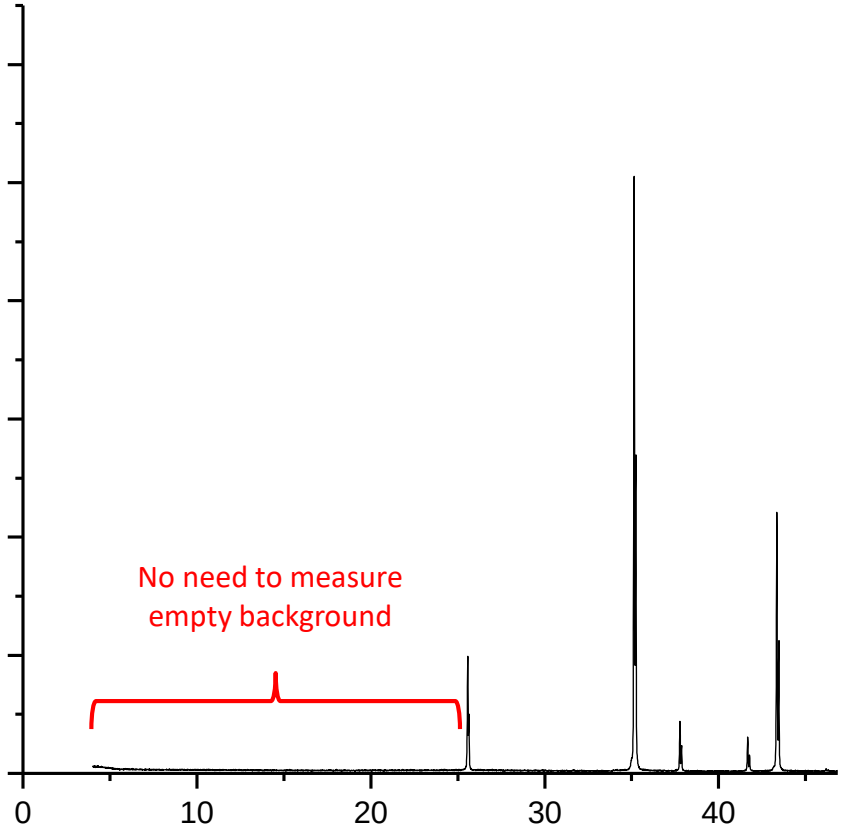
- Counting Time

Scan Parameters: Angular Range



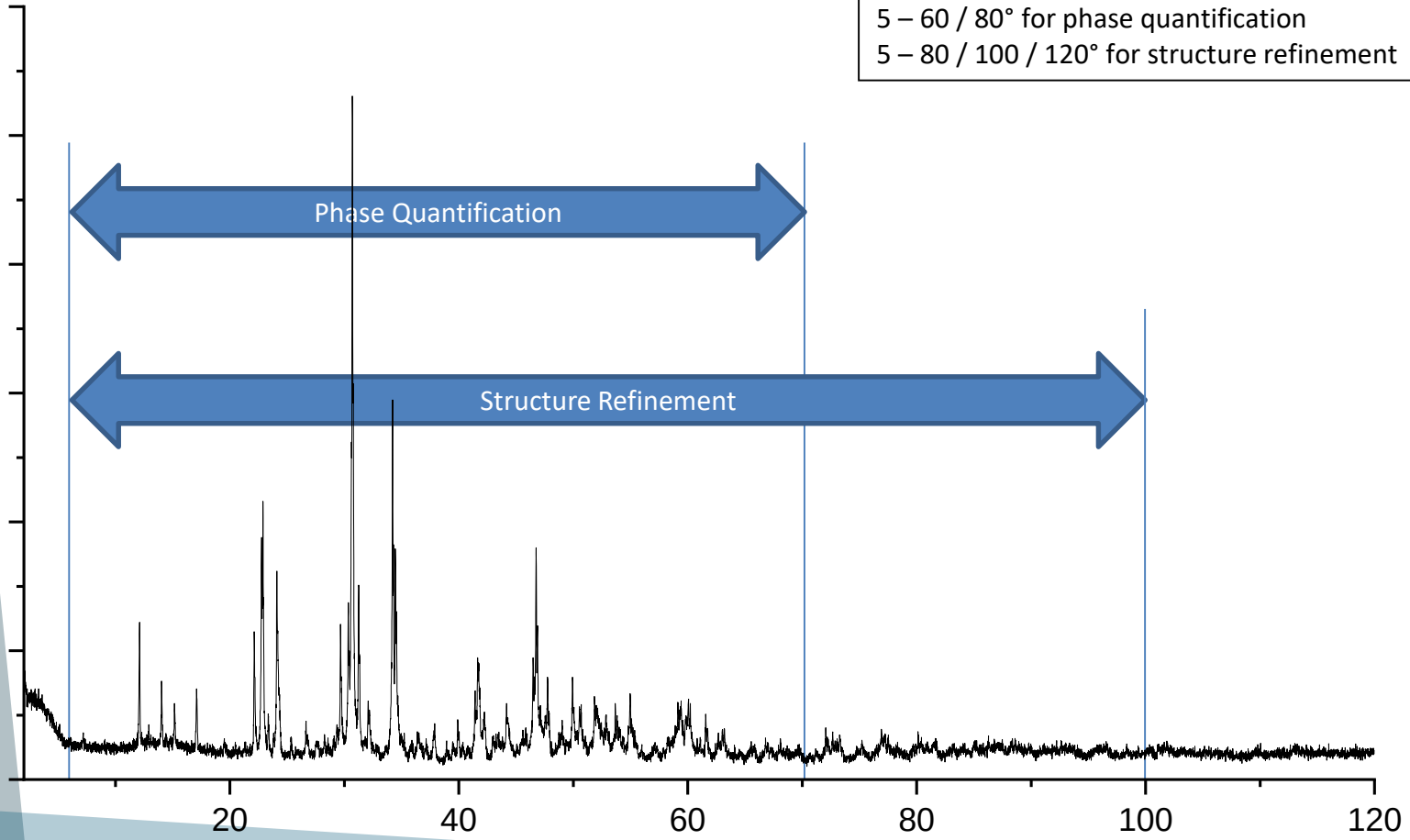
Scan Parameters: Angular Range



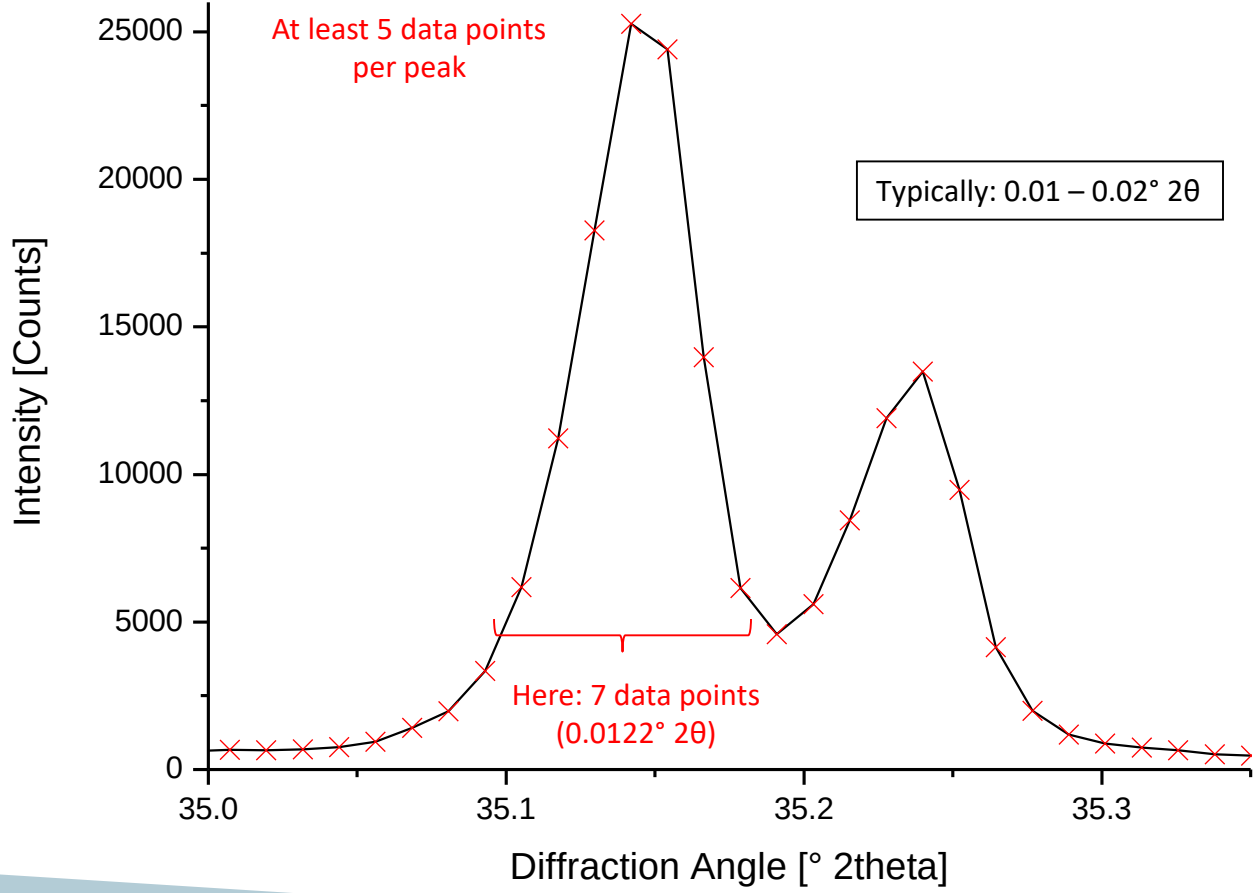


Scan Parameters: Angular Range

Recommendation (ceramics / minerals, CuKα radiation):
5 – 60 / 80° for phase quantification
5 – 80 / 100 / 120° for structure refinement

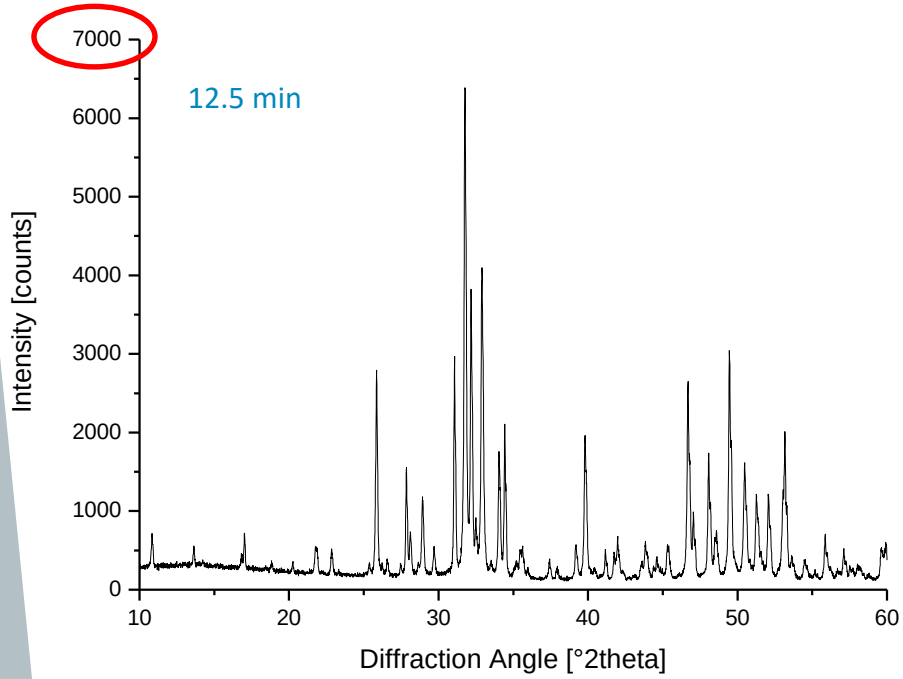


Scan Parameters: Step Size

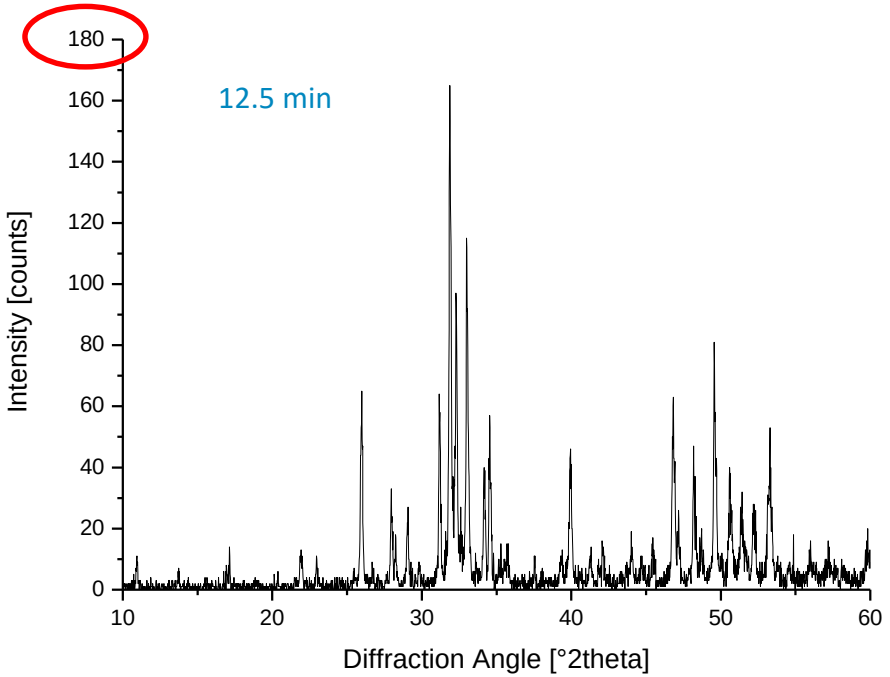


Scan Parameters: Time per Step

1D Energy dispersive Detector

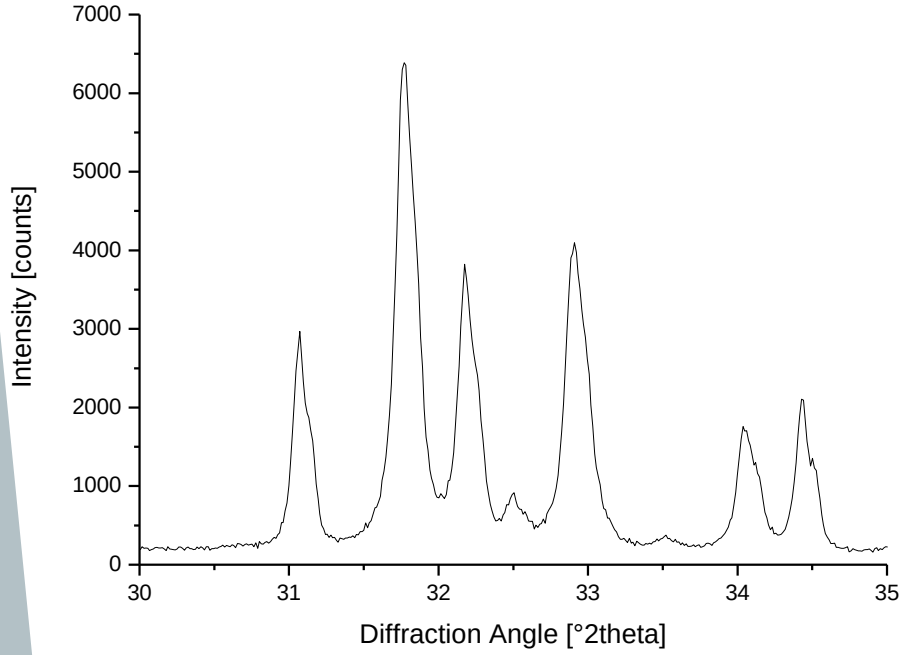


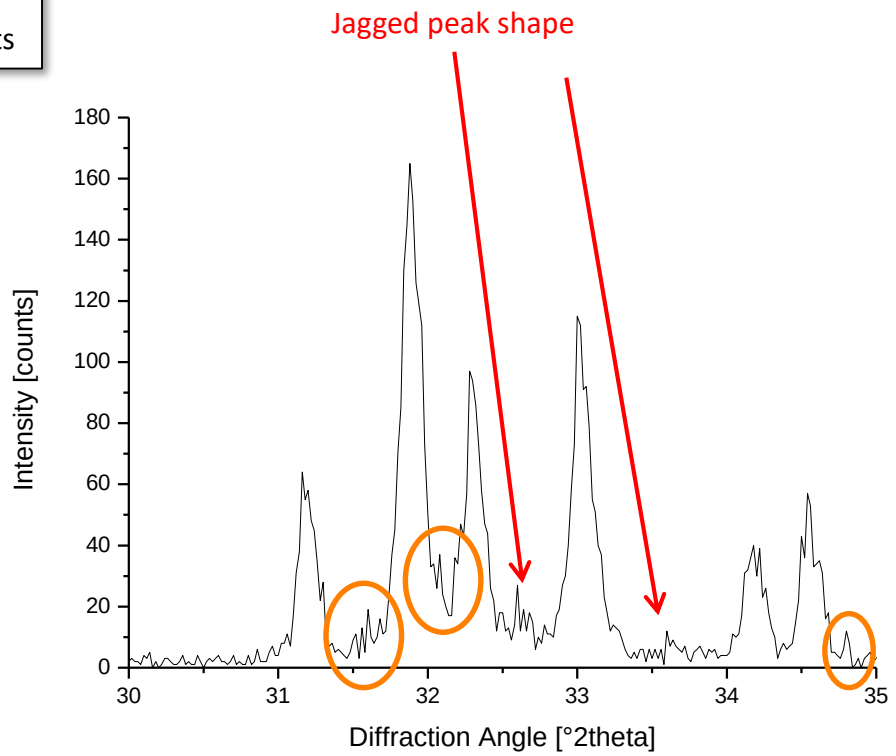
0D Detector



Scan Parameters: Time per Step

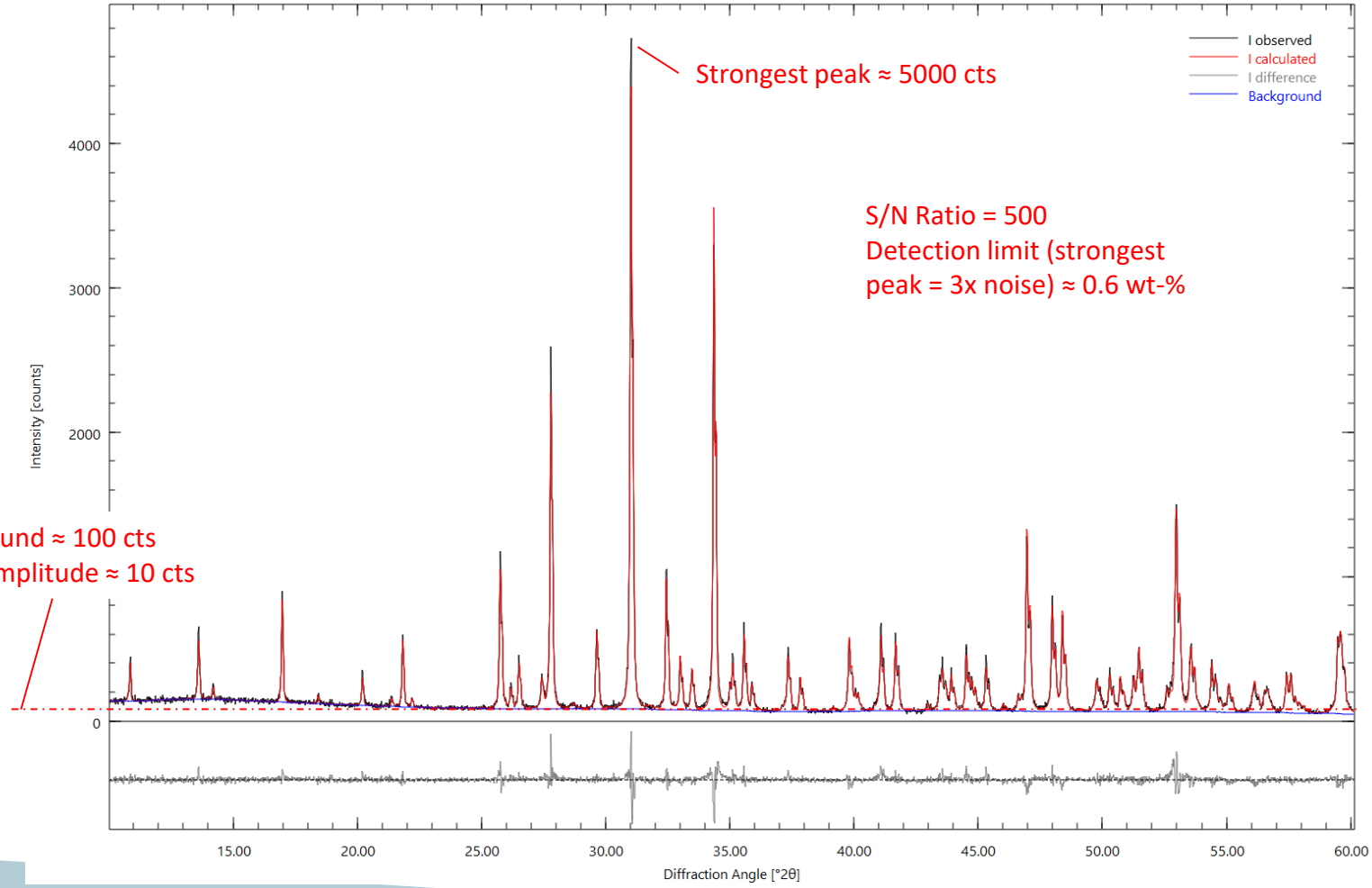
My personal rule of thumb:
Standard measurement: Strongest peak ~5000 counts
High-intensity measurement: Strongest peak >10‘000 counts



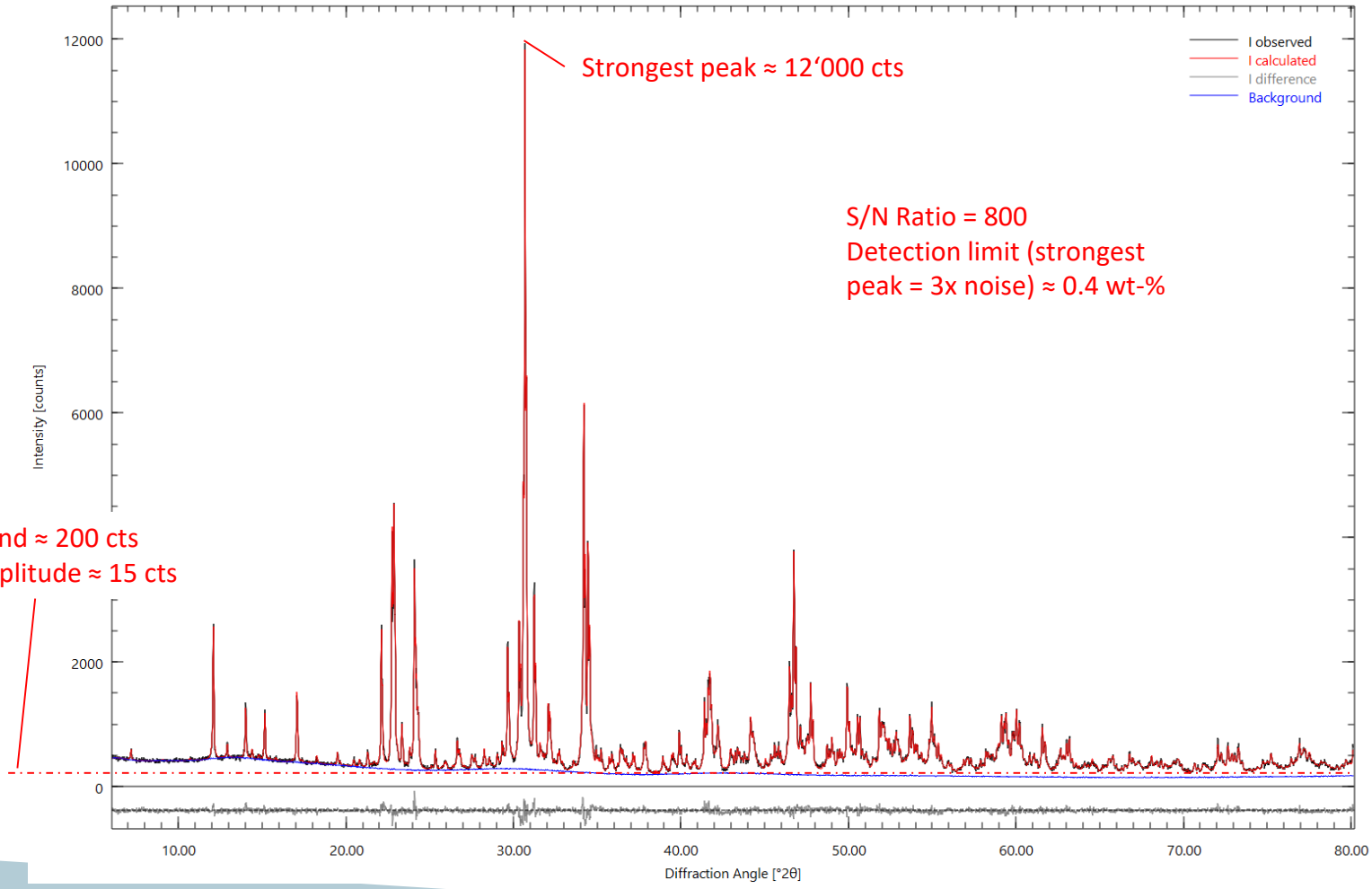


Noise or peak?

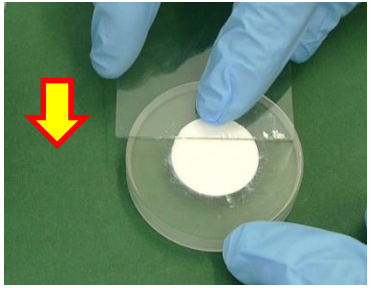
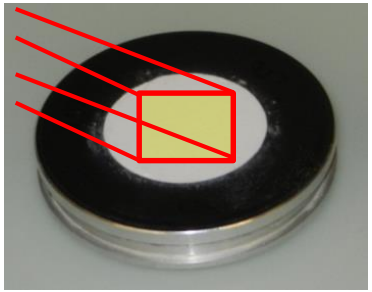
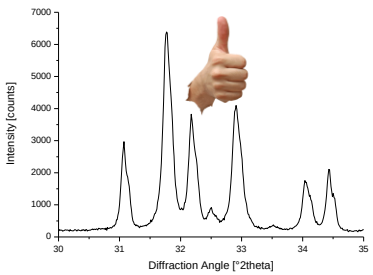
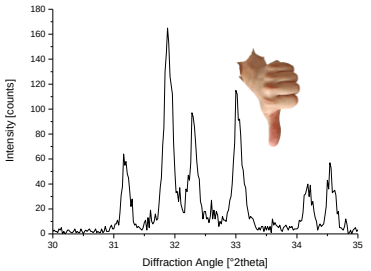
Scan Parameters: Standard S/N Ratio (0.15 sec/step LynxEyeXE Detector)



Scan Parameters: High S/N Ratio (0.50 sec/step LynxEyeXE Detector)



Summary

- Good sample preparation:
  - 1-5 µm particles
  - No texture / preferred orientation
  - Compact powder, flat surface
  - Precisely centered on the instrument
- Correct instrument setup:
  - θ-2θ parafocusing setup
  - Maximize irradiated area
- Scan parameters:
  - Capture all low-angle peaks
  - Sufficiently small step size (0.01 – 0.02°)
  - Adequate S/N ratio

= Good Datasets for Rietveld Refinement