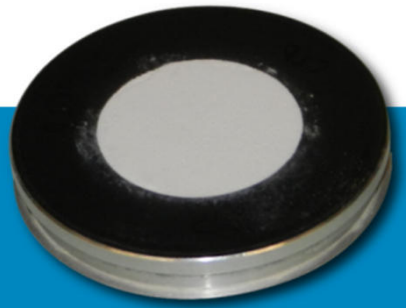
Lesson 3
Sample Preparation



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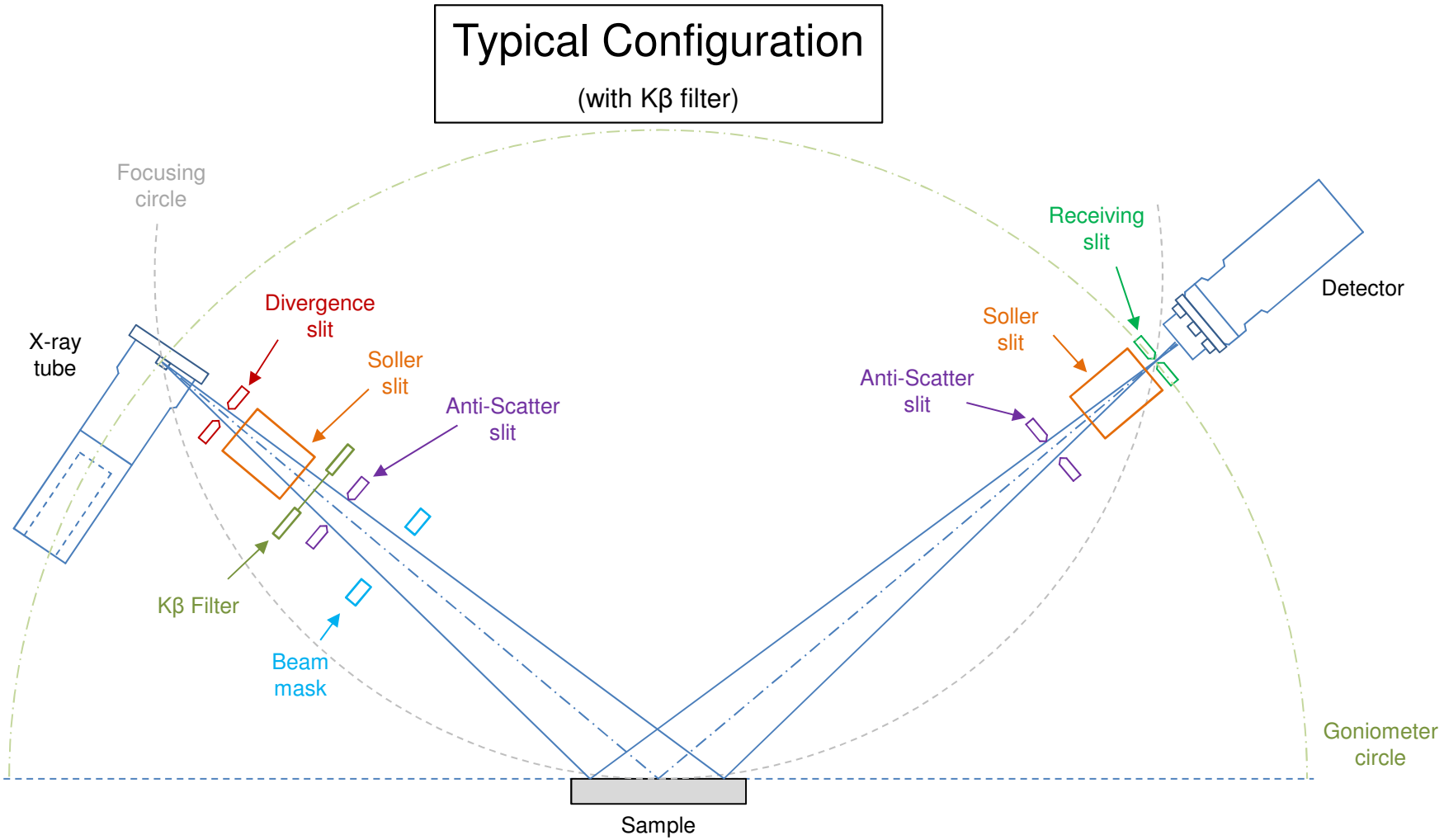
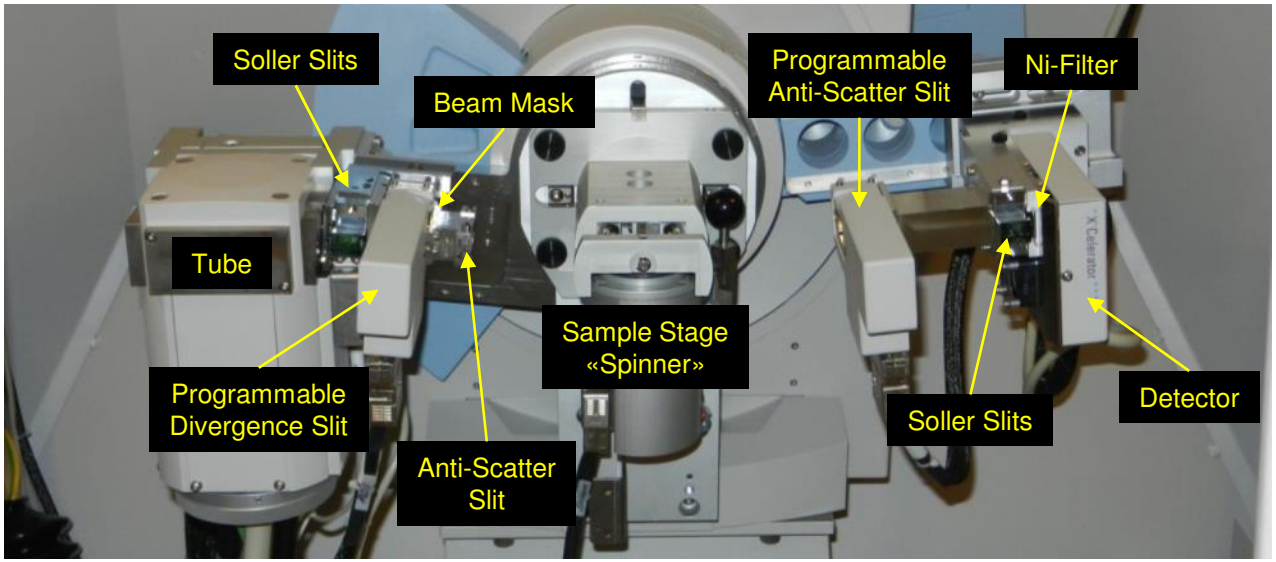
Repetition: Bragg-Brentano Diffractometer



Repetition: Instrument Configuration

- Many optical elements = many options to optimize data quality

- How to find the best configuration?



Sample Preparation

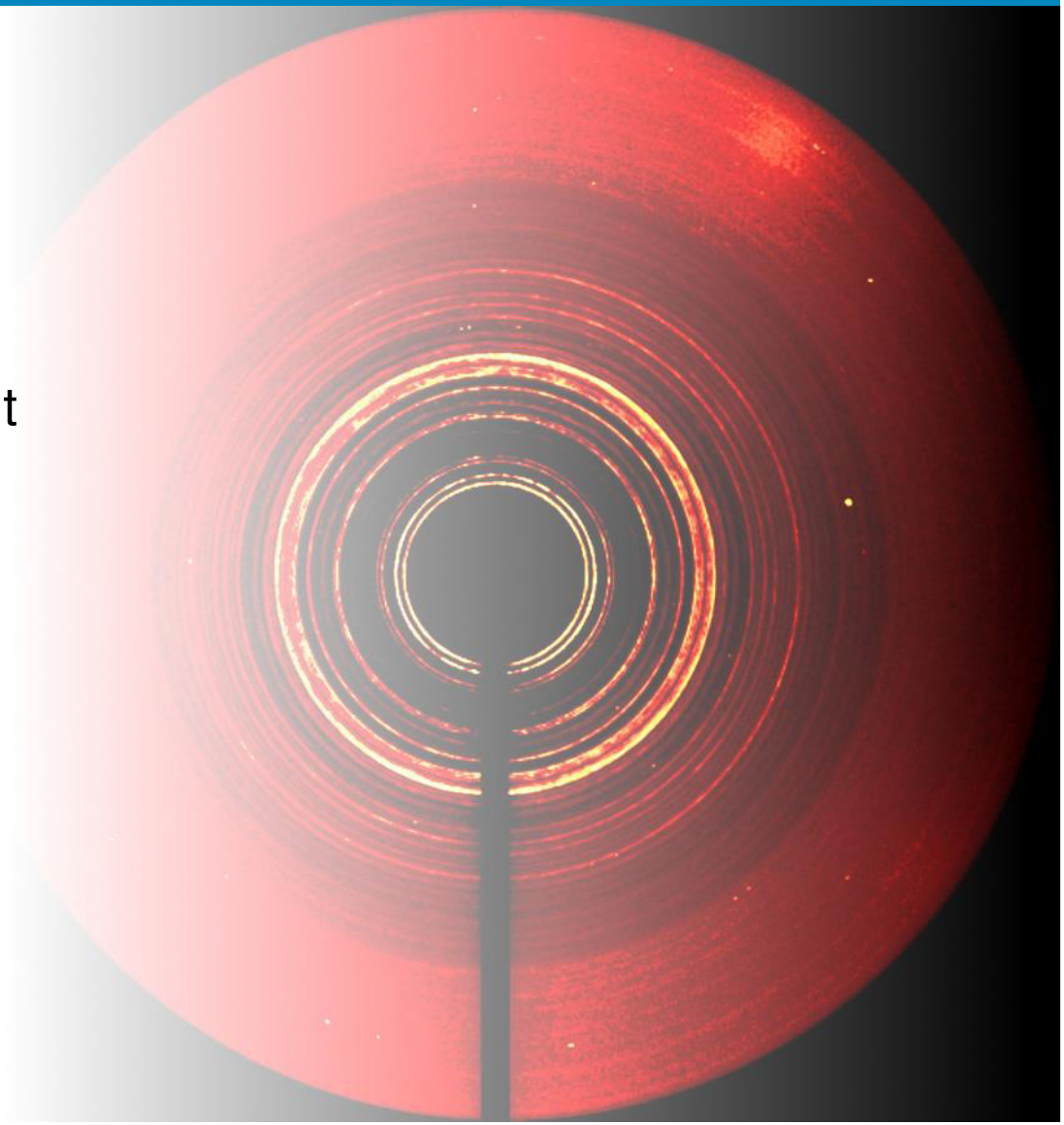
Sample preparation is **ABSOLUTELY CRUCIAL**
for a good diffraction pattern!

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

Some are related to sample preparation errors.

Problems

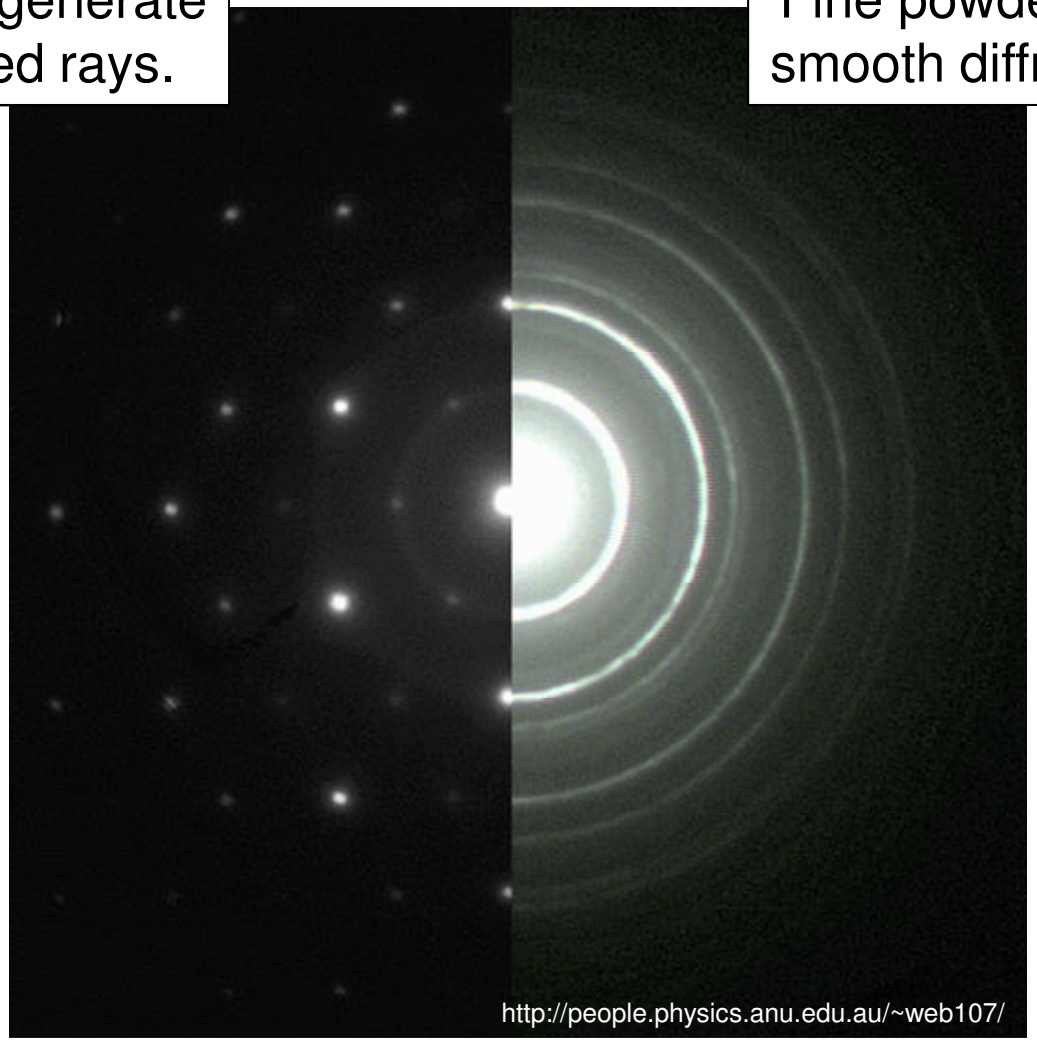
- Graininess
- Micro-absorption
- Texture
- Sample height displacement
- Surface roughness
- Sample transparency



Graininess

Single crystals generate spotty diffracted rays.

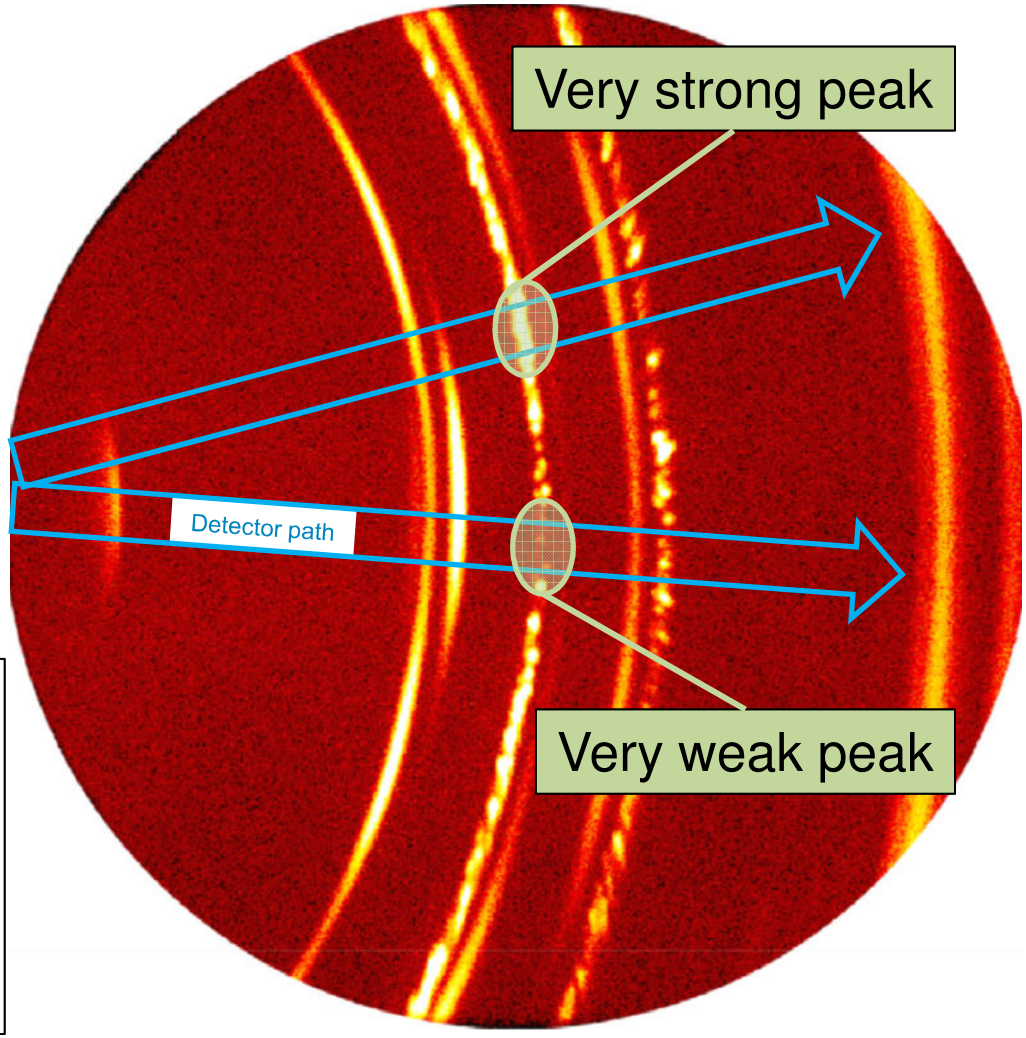
Fine powders generate smooth diffraction rings.



Graininess

Spotty diffraction rings

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



Grainy samples:

- non-reproducible intensities
- «phantom» peaks
- «missing» peaks

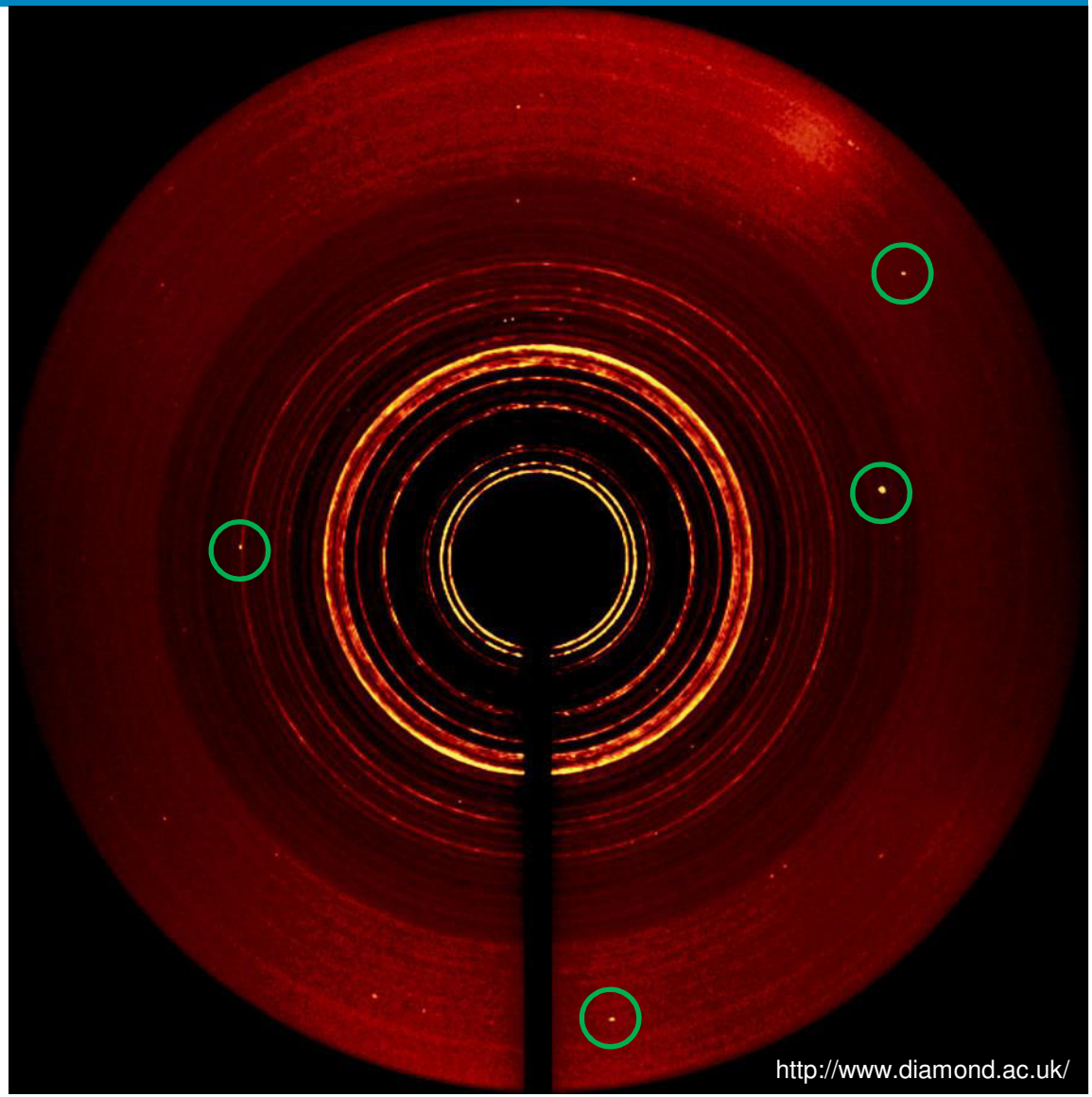
Bruker AXS

Graininess: Rocks in Dust

«Rocks in Dust»:

A few large crystals in a fine matrix

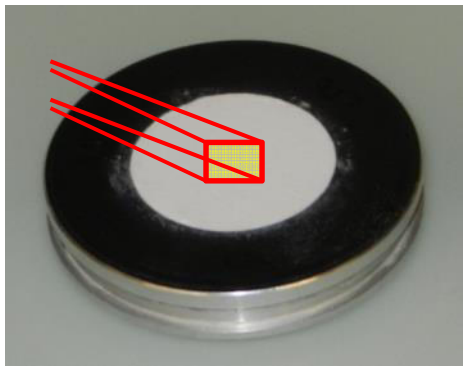
Usually invisible, but if scanned: Strong peaks out of nowhere!



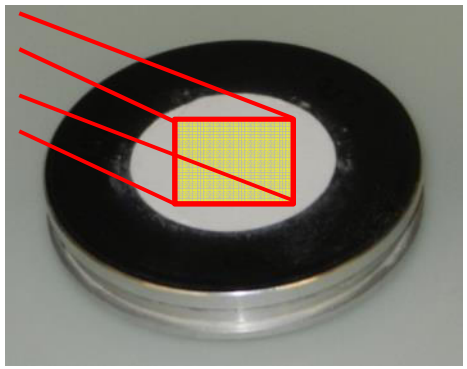
Graininess

Reducing graininess:

- Grinding / milling
- 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

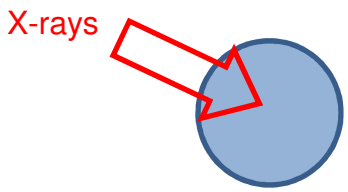


Few diffracting crystallites

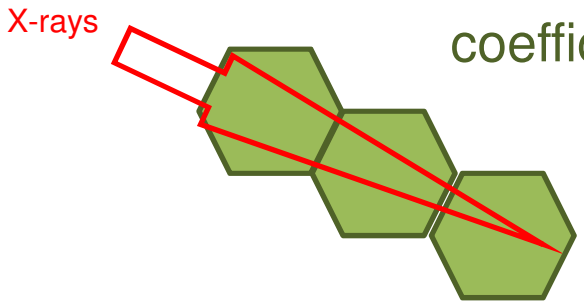


Many diffracting crystallites

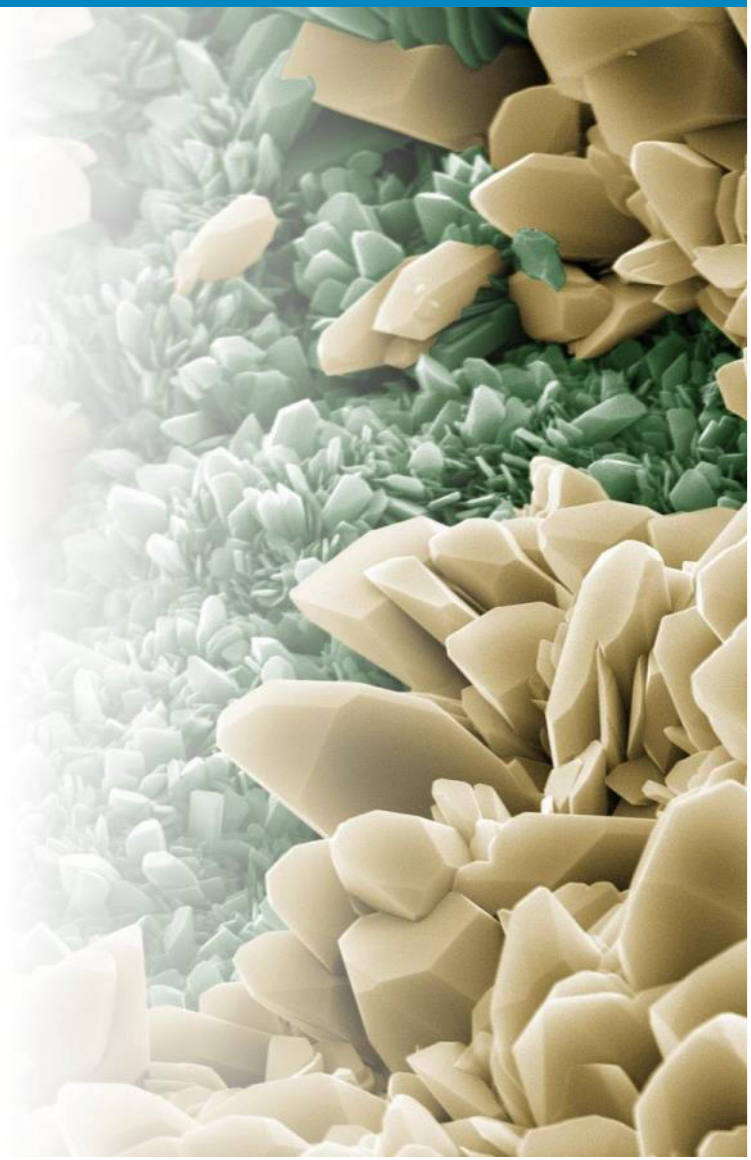
Micro-absorption



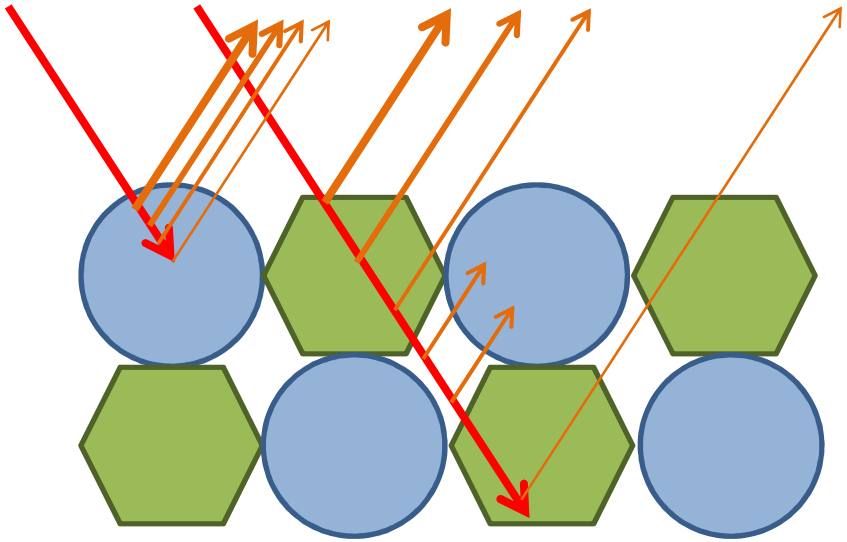
Phase 1: High absorption coefficient for X-radiation

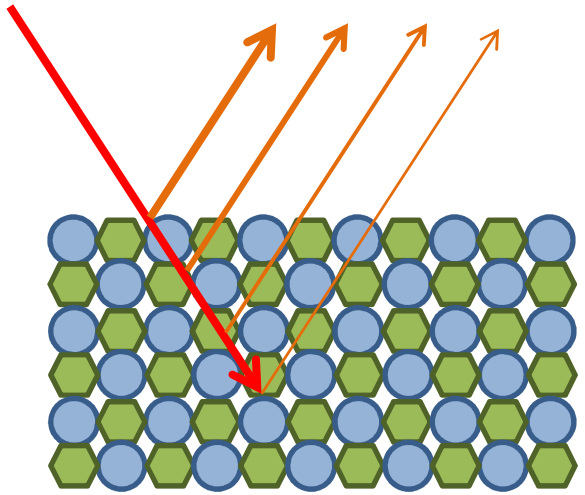


Phase 2: Low absorption coefficient for X-radiation



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

Reducing micro-absorption:

- Grinding / milling to reduce particle size

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)

- Manual milling in agate mortar is usually recommended

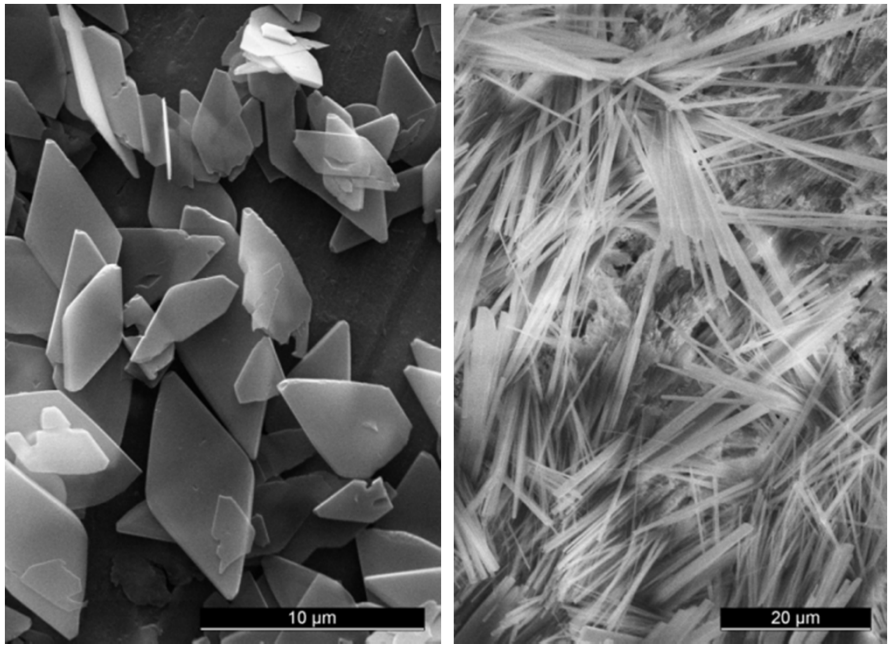
Automatic mill for XRD

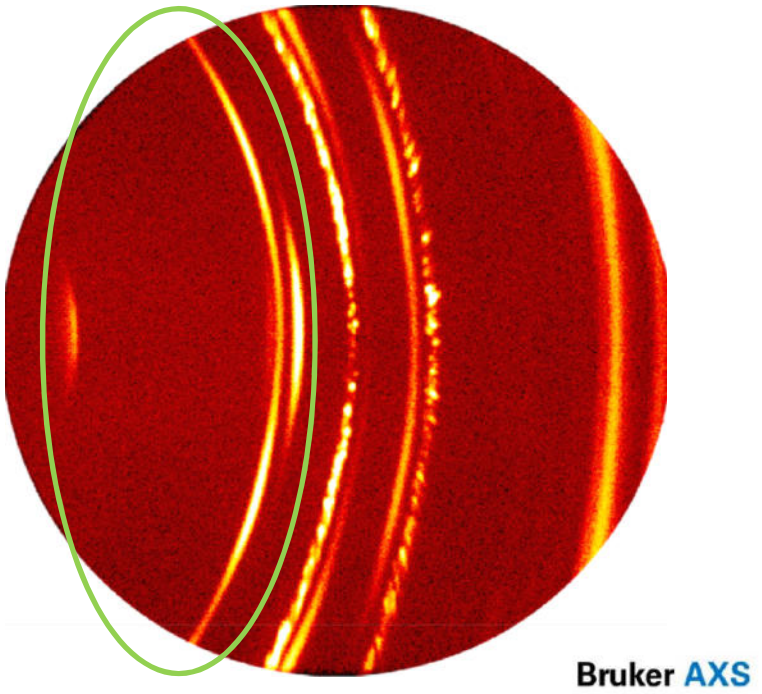
«Industry standard» for automatic XRD sample milling:

McCrone Micronizing Mill

http://www.powderbulksolids.com

Texture, Preferred Orientation





Platelets, Needles, Fibers, Whiskers

Random orientation

Preferred orientation

SEM Images: L. Galea, RMS Foundation

Texture, Preferred Orientation

Try to avoid orientation at the surface of the sample:

- Press powder without «rubbing» the surface
- Use back-loading sample holder
- Disorder surface with textured stamp

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

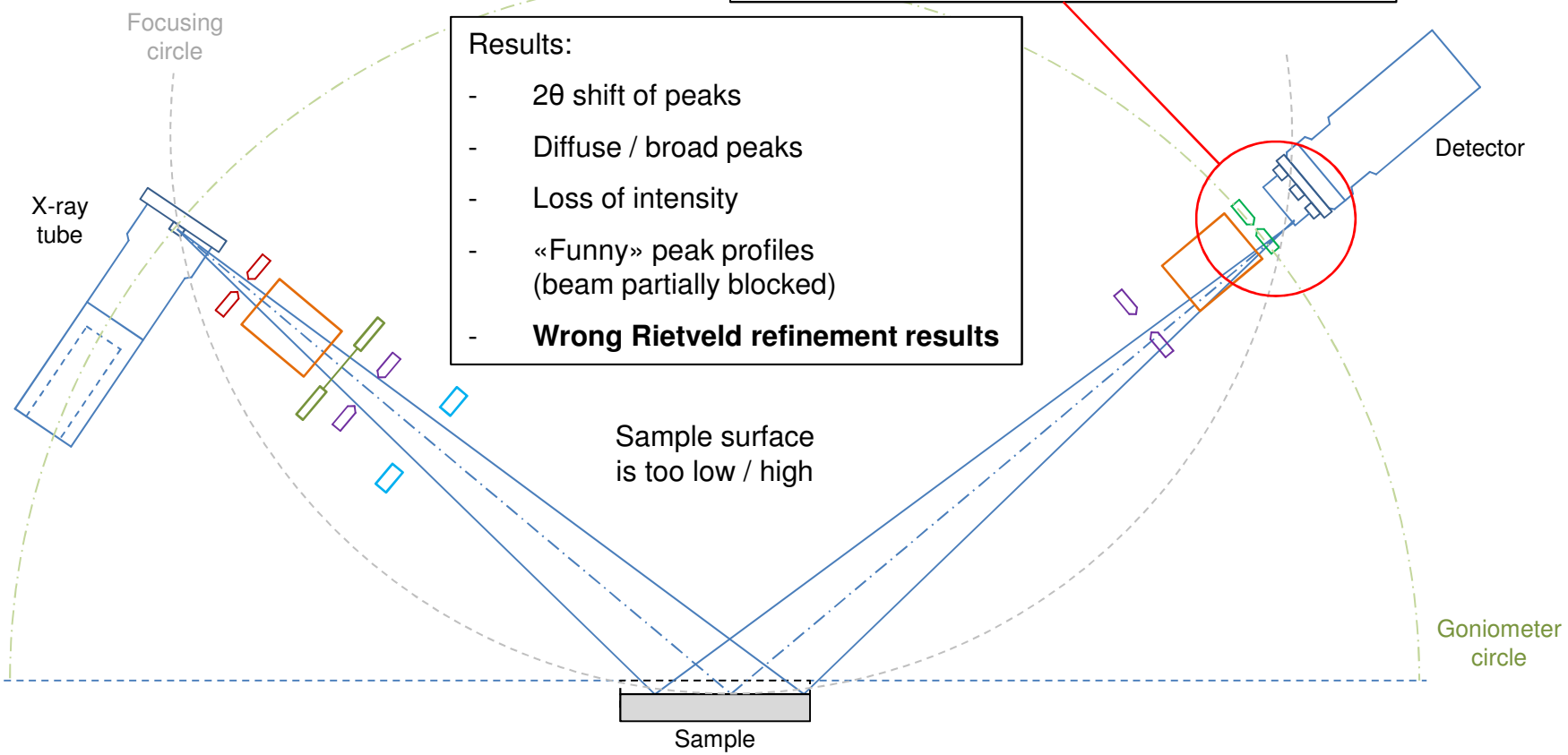
PO can be corrected mathematically, but phase quantification will be biased.
(more on this in the lesson on «Rietveld refinement»)

Sample Height Displacement

- Focus of diffracted beam is displaced
- Receiving slit / 1D / 2D detector out of focus
- Diffracted beam blocked by optical elements

Results:

- 2θ shift of peaks
- Diffuse / broad peaks
- Loss of intensity
- «Funny» peak profiles (beam partially blocked)
- **Wrong Rietveld refinement results**

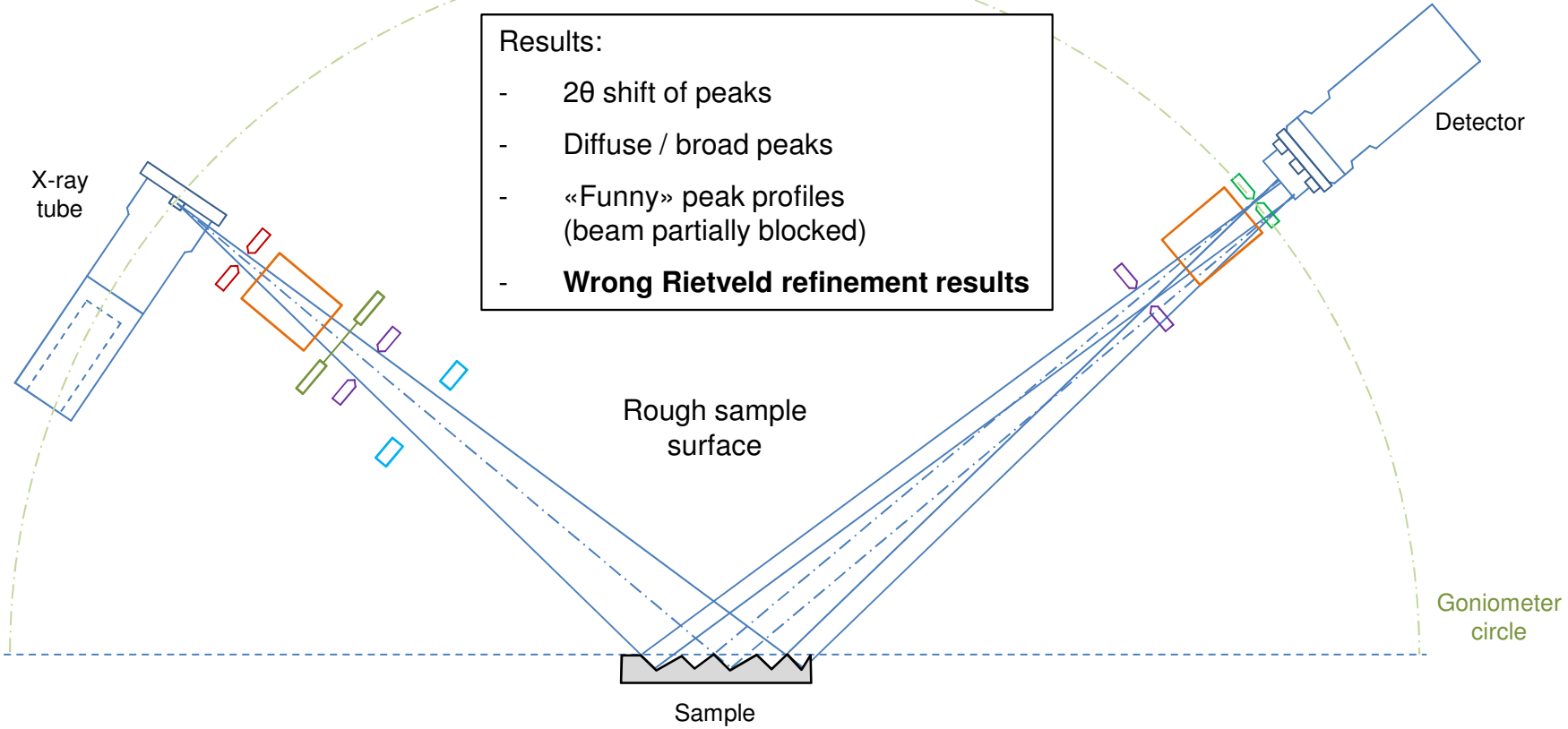


Rough Sample Surface

- Diffraction signals from different surface levels
- Focus of diffracted beam is **partially** displaced
- Receiving slit / 1D / 2D detector out of focus

Results:

- 2θ shift of peaks
- Diffuse / broad peaks
- «Funny» peak profiles (beam partially blocked)
- **Wrong Rietveld refinement results**

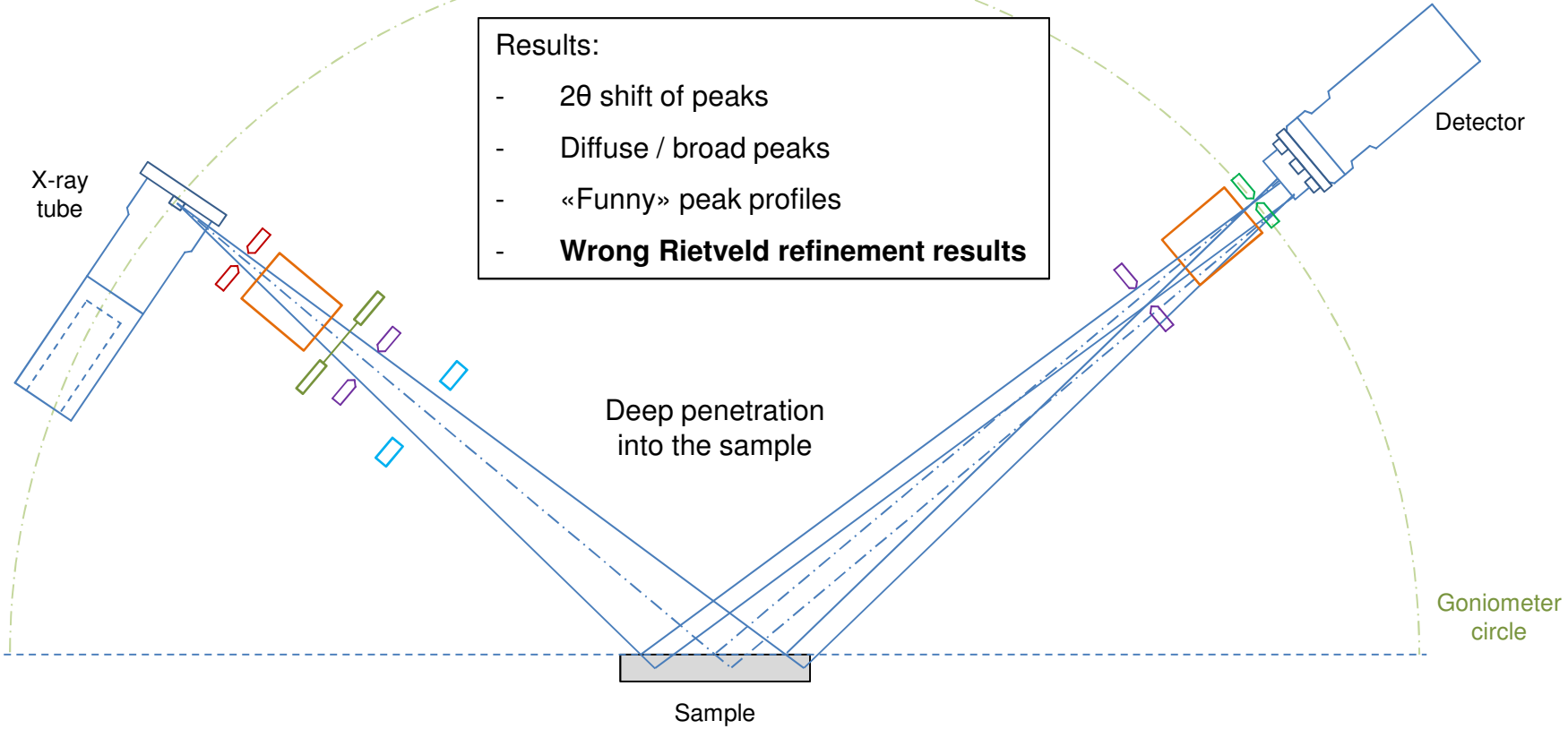


Sample Transparency

- Diffraction signals from different surface levels
- Focus of diffracted beam is partially displaced
- Receiving slit / 1D / 2D detector out of focus

Results:

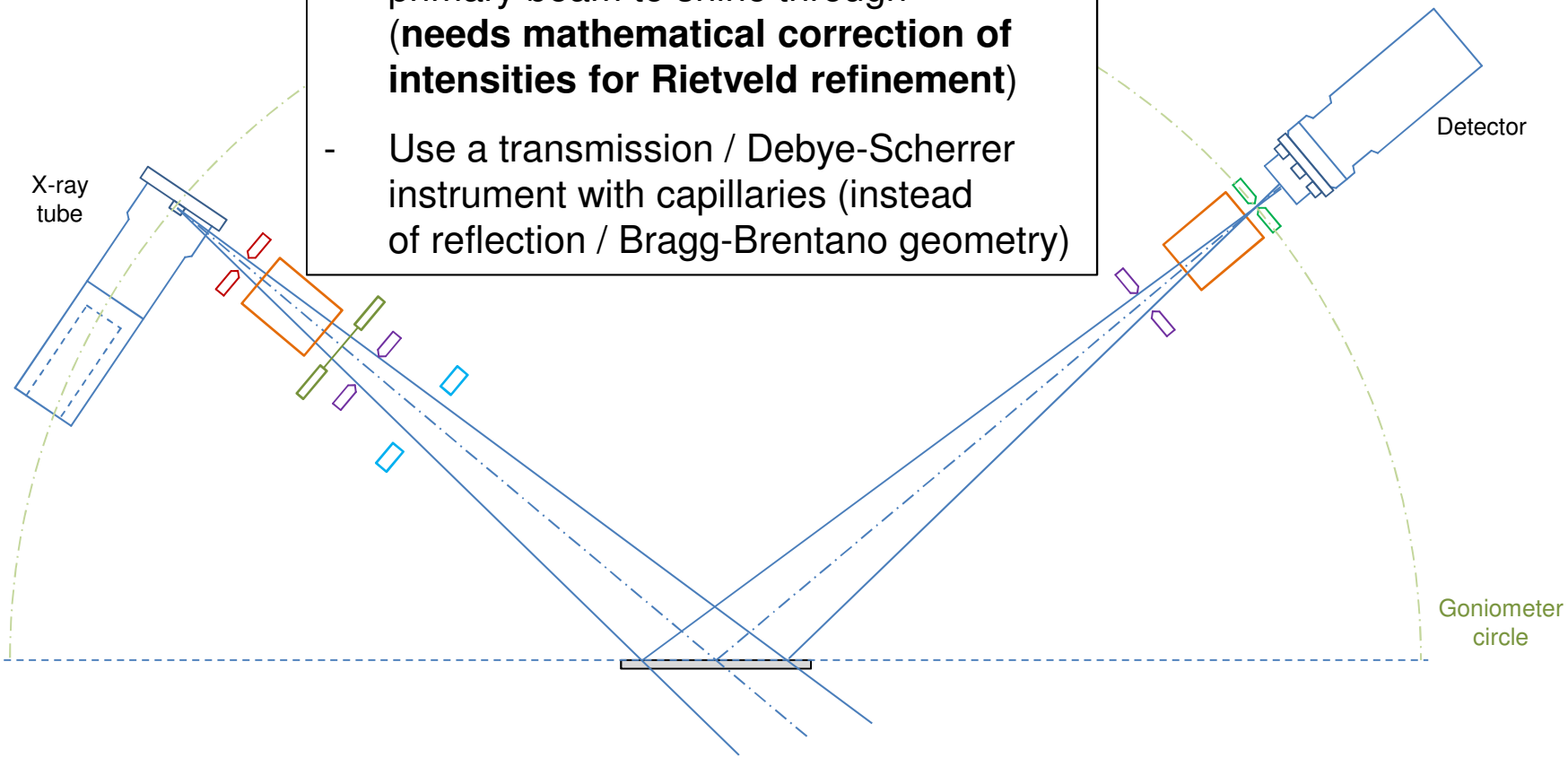
- 2θ shift of peaks
- Diffuse / broad peaks
- «Funny» peak profiles
- **Wrong Rietveld refinement results**



Sample Transparency

Possible solutions:

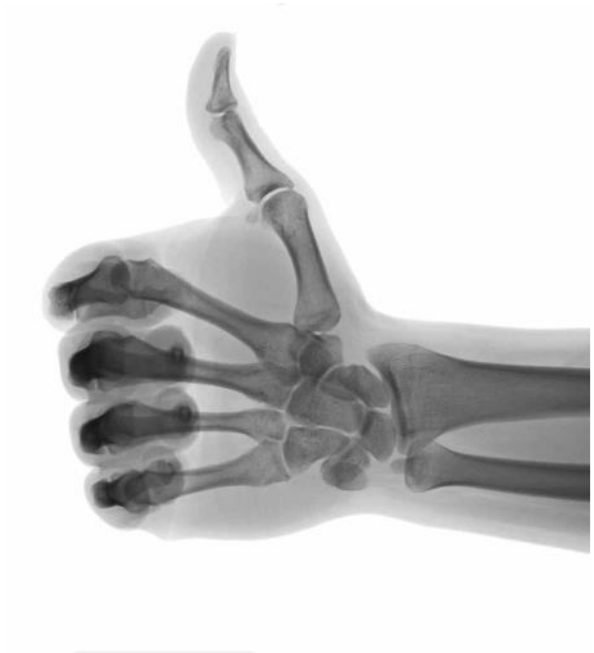
- Use very thin sample, allow the primary beam to shine through (**needs mathematical correction of intensities for Rietveld refinement**)
- Use a transmission / Debye-Scherrer instrument with capillaries (instead of reflection / Bragg-Brentano geometry)



Summary: The Perfect Sample

The perfect sample for Bragg-Brentano diffractometers:

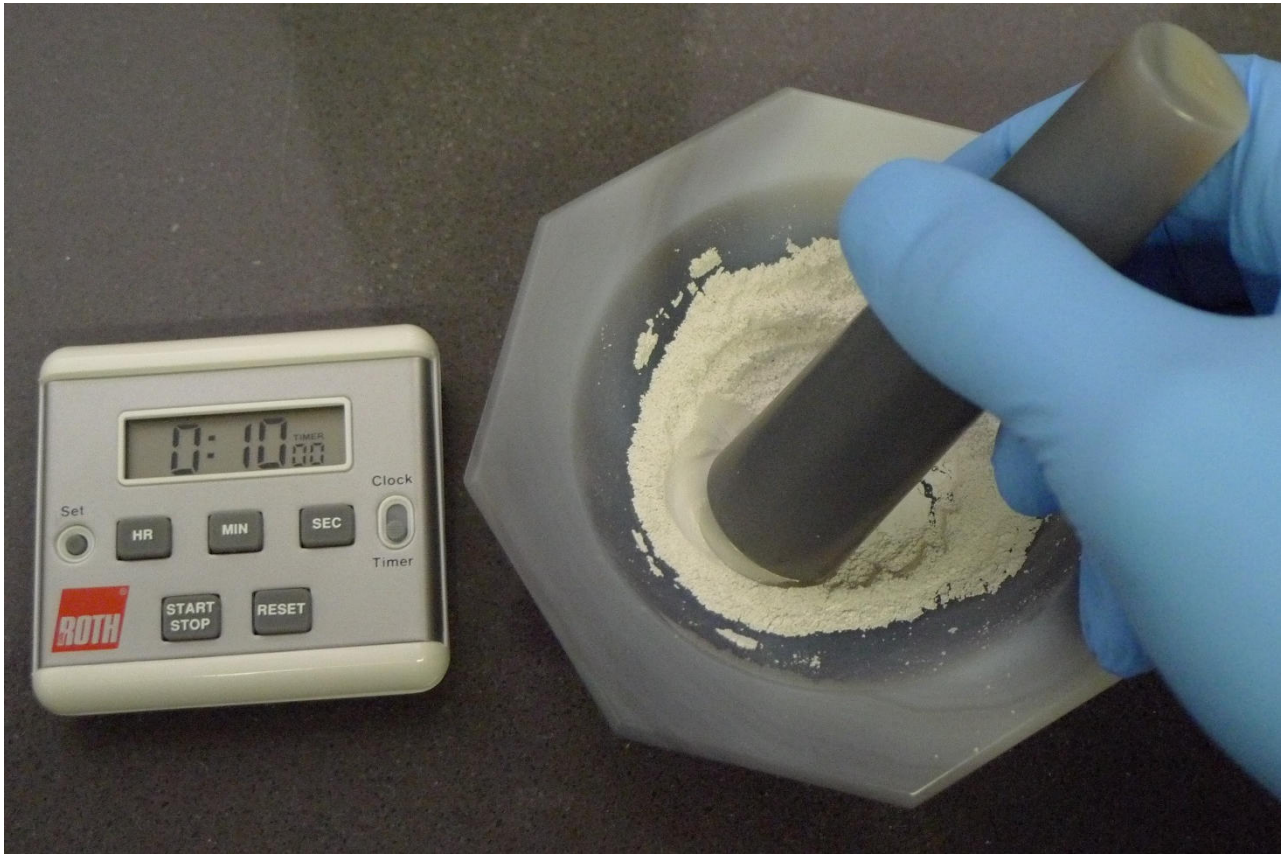
- Crystallites and particles of 1-5 µm size
- Perfectly random orientation
- Perfectly flat surface
- Surface precisely centered in the goniometer
- High packing density
- At least 1 mm thick layer of material



Good sample preparation practice

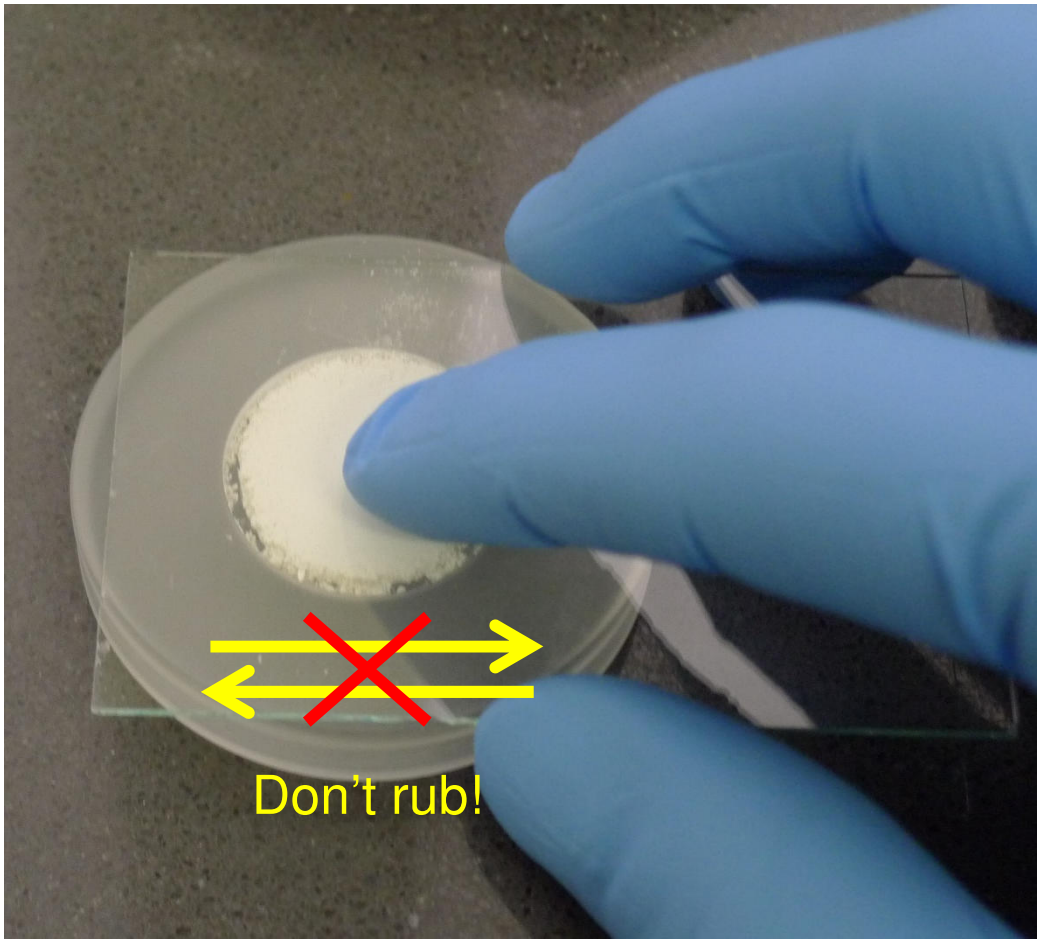
- Sample (crushed, ~1 g)
- Agate mortar + pestil
- Glass plate
- Sample holder

Good sample preparation practice



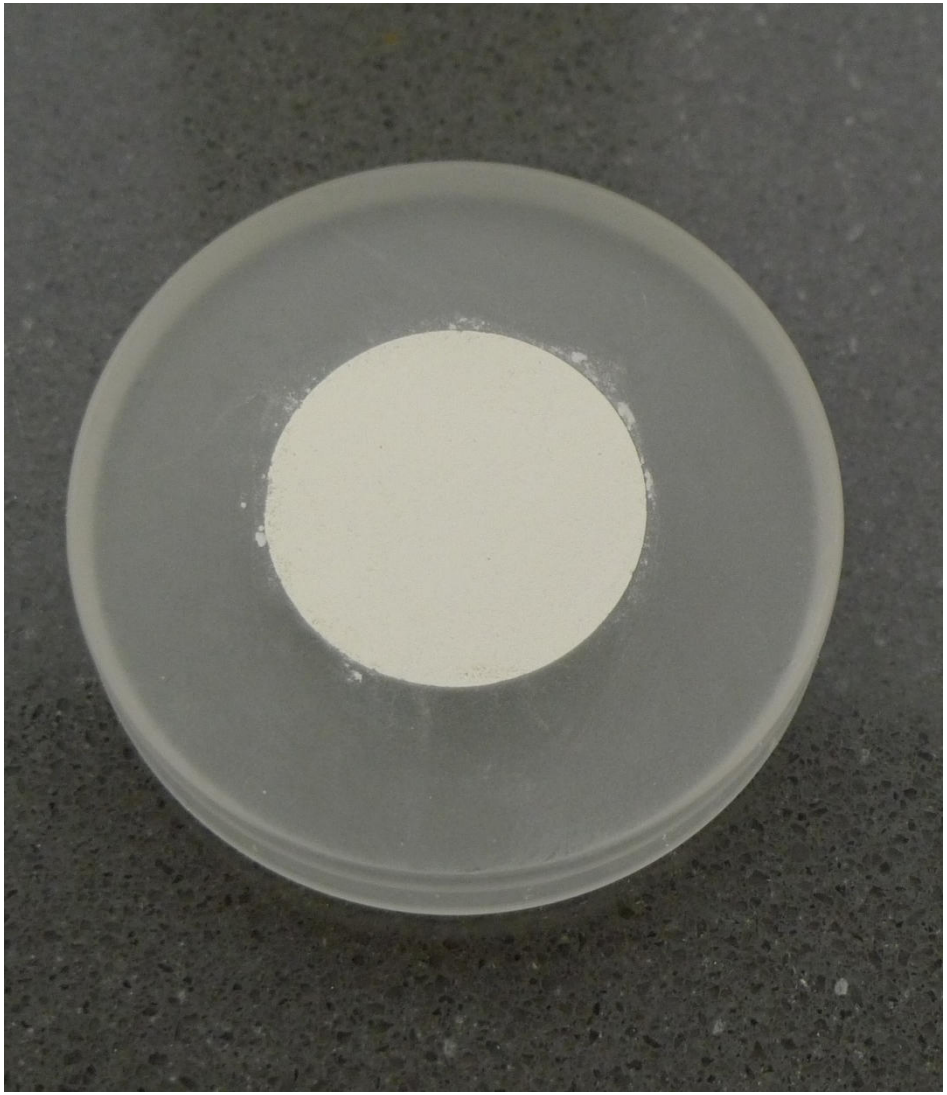
- Mill to < 5 µm
- Rock and tough ceramic samples: 10 minutes

Good sample preparation practice



- Scratch off excess material with the glass plate

Good sample preparation practice



- Perfectly flat surface
- Flush with rim
- Clean rim