Lesson 3
“How-To” Session

Nicola Döbelin
RMS Foundation, Bettlach, Switzerland

Refinement Strategy: Words of Wisdom

Always refining everything
may lead to good fits,
but the results may be useless.

Release parameters one by one.
When the fit doesn't improve anymore,
don't try to extract more information.

Chose your refinement strategy wisely.
Ask yourself if the results make
physical sense.

Examples

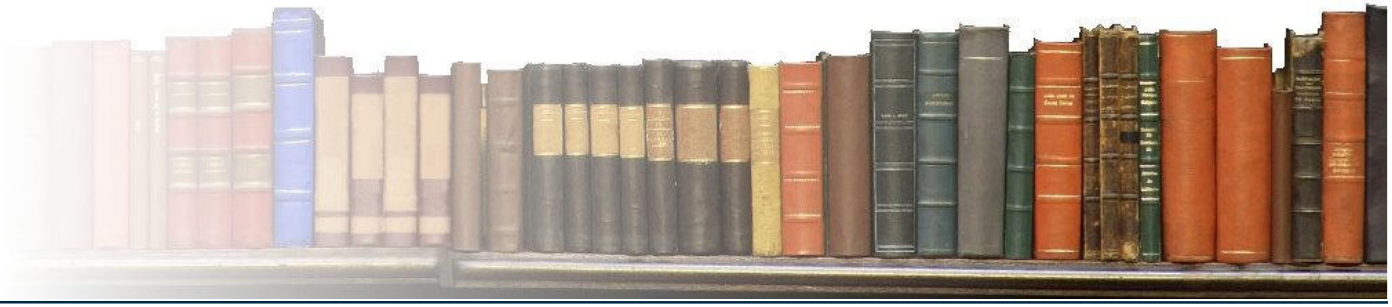
Example 1: Texture, preferred orientation

Example 2: Anisotropic crystallite sizes

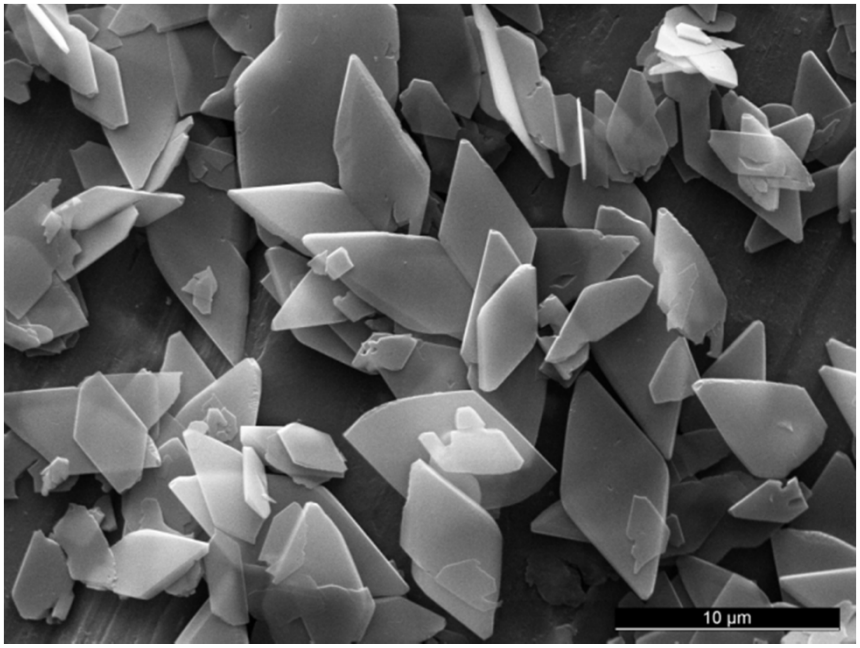
Example 3: Non-existent phases

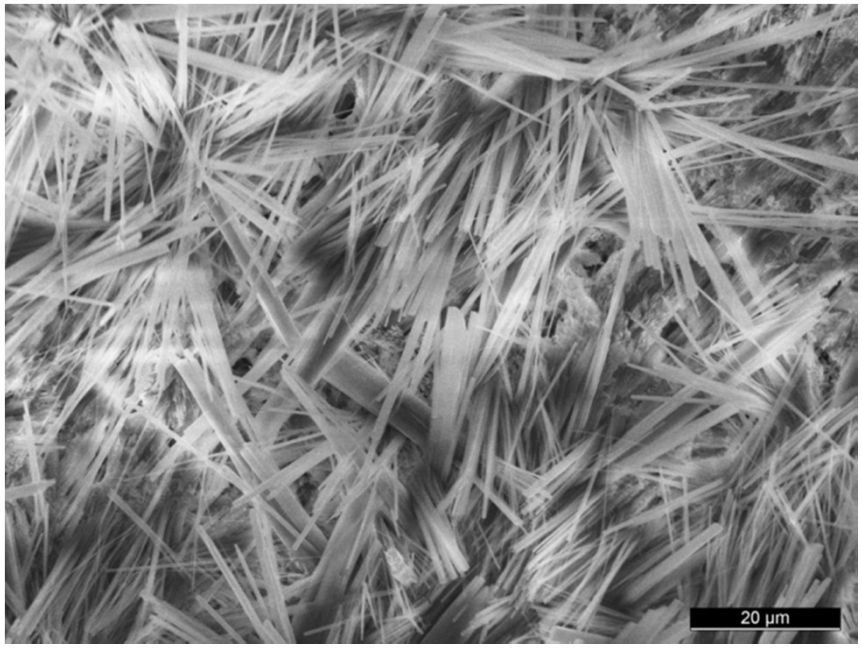
Example 4: Micro-absorption and Brindley correction

Example 5: Amorphous Content



Texture, Preferred Orientation





Platelets

lying flat

Needles, Fibers, Whiskers

lying flat
may point in one direction (bundles)

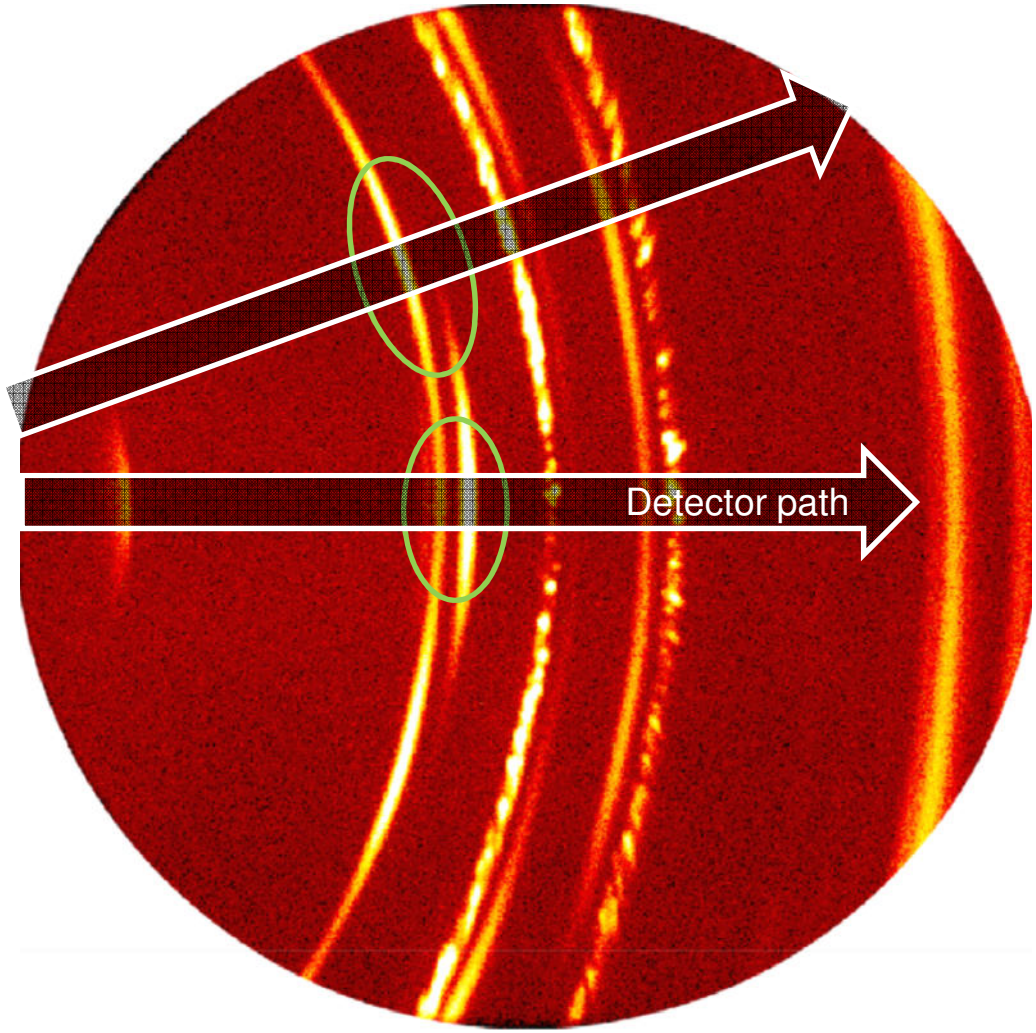
Random orientation

Preferred orientation

Images: L. Galea, RMS Foundation

Texture, Preferred Orientation

Smooth, but non-continuous diffraction rings



Some orientations are over-represented, others are under-represented.

Bruker AXS

Texture: Symmetrized Spherical Harmonics

In structure files (*.str) change:

PARAM=GEWICHT=0.1_0

to

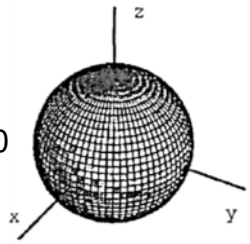
GEWICHT=SPHAR*n*

(n=0, 2, 4, 6, 8, 10)

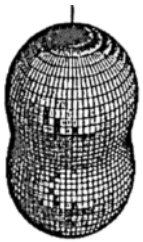
No preferred orientation:

PARAM=GEWICHT=0.1_0

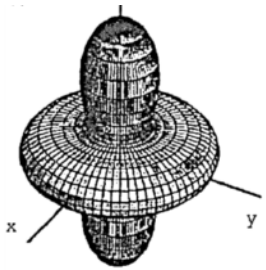
GEWICHT=SPHAR0



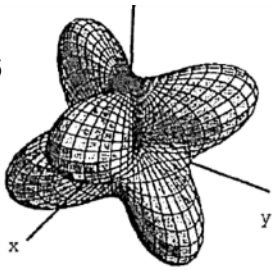
GEWICHT=SPHAR2



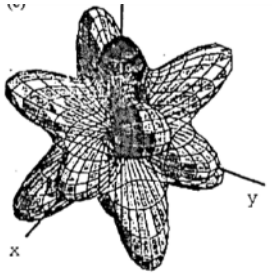
GEWICHT=SPHAR4



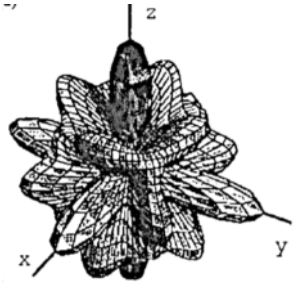
GEWICHT=SPHAR6



GEWICHT=SPHAR8



GEWICHT=SPHAR10



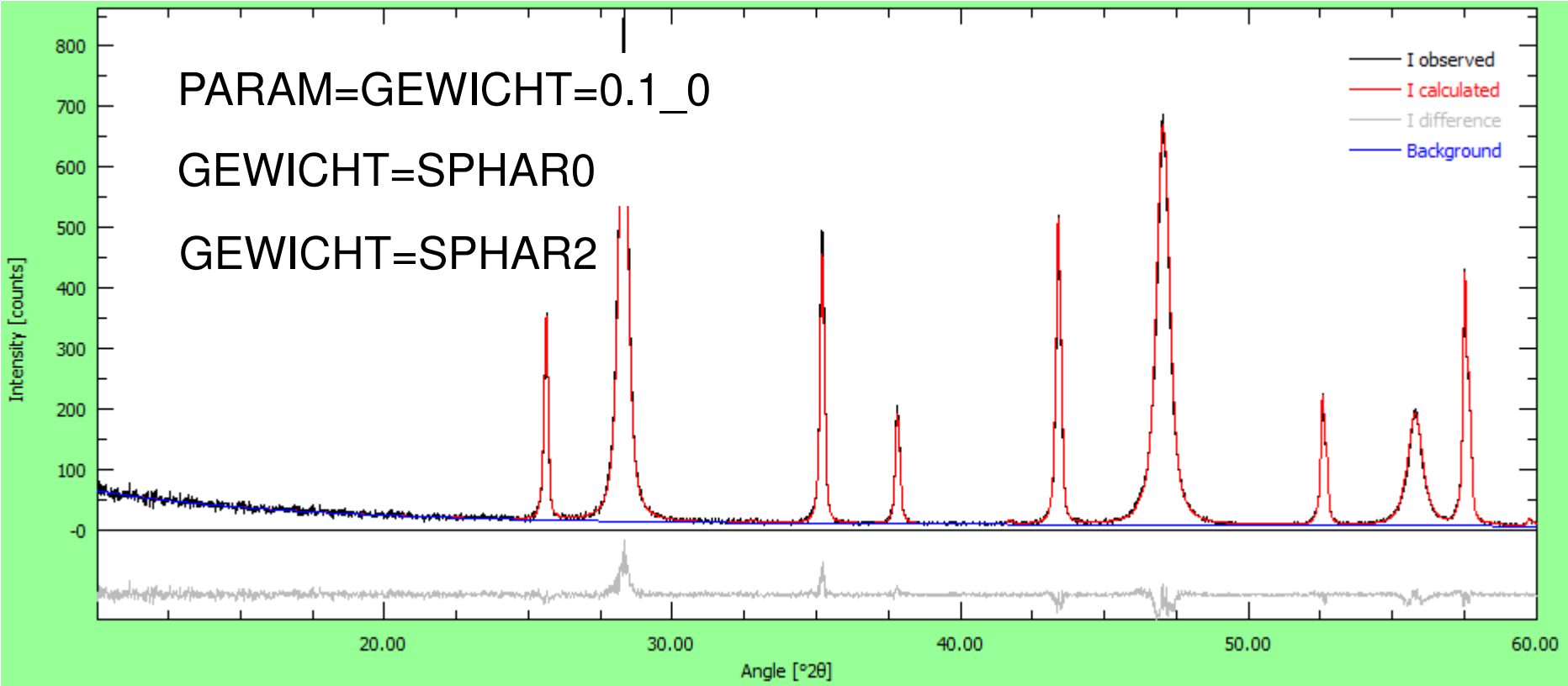
Järvinen, M. Materials Science Forum [278-281], 1998, 184-199.

Example 1 - Texture

Instrument: pw1800-fds

Phases: Corundum, Fluorite

Both phases: RP=4 PARAM=k1=0_0^1 PARAM=k2=0_0 PARAM=B1=0_0^0.03 PARAM=GEWICHT=0.1_0 //

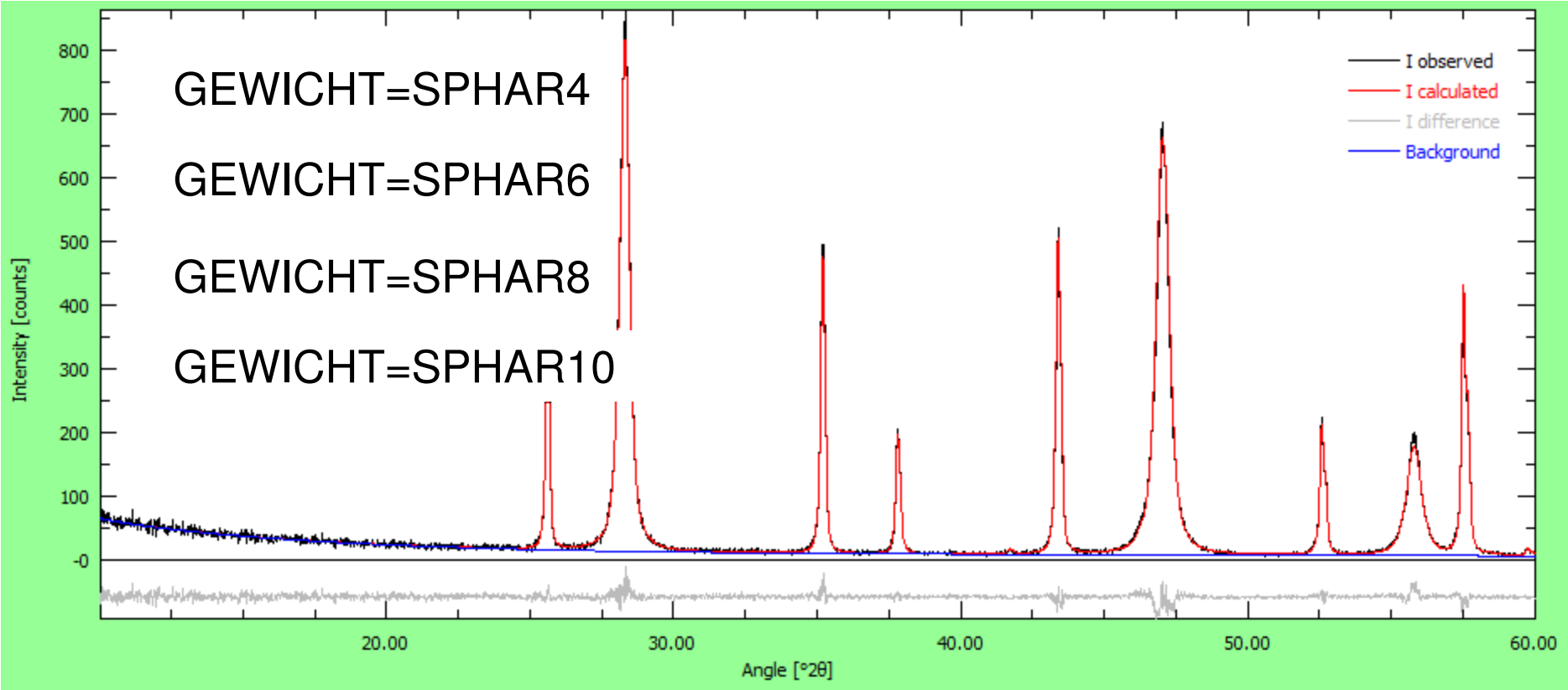


Example 1 - Texture

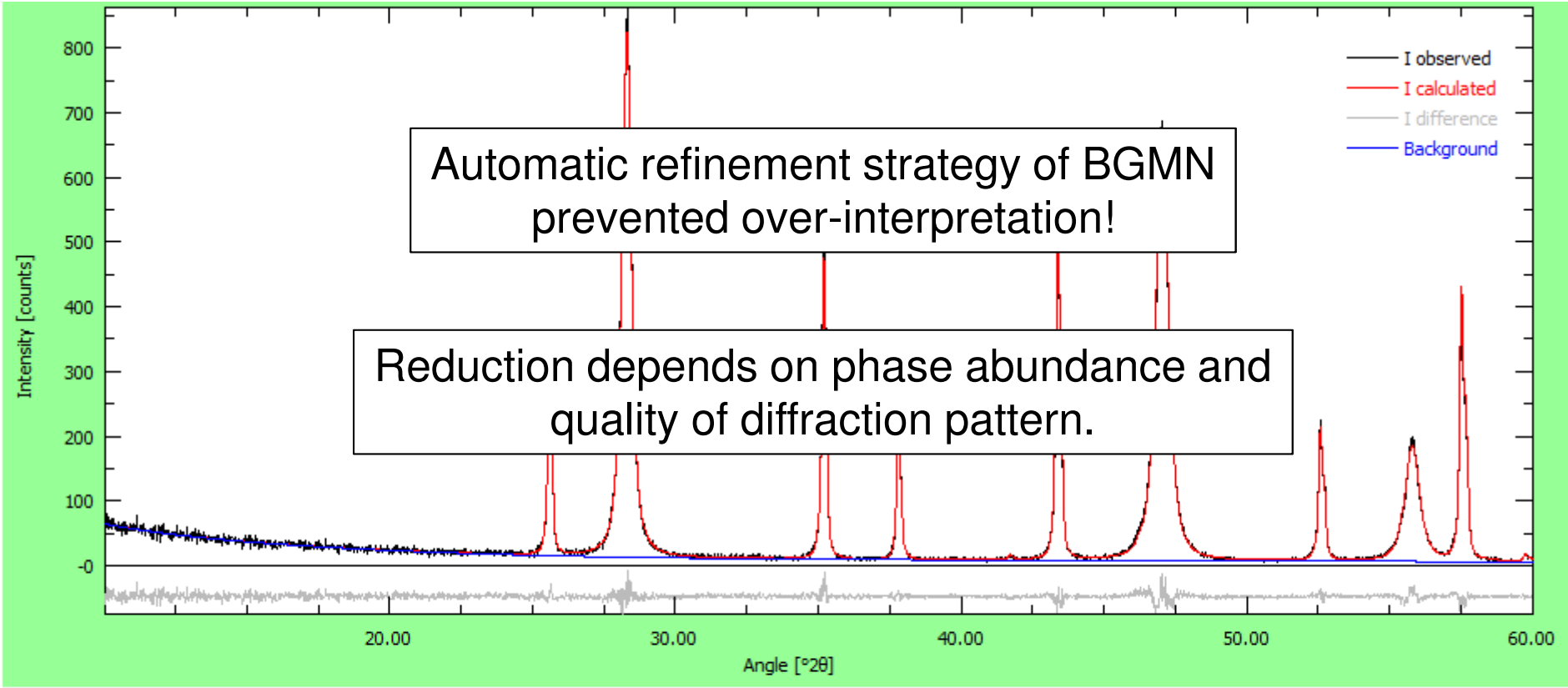
Instrument: pw1800-fds

Phases: Corundum, Fluorite

Both phases: RP=4 PARAM=k1=0_0^1 PARAM=k2=0_0 PARAM=B1=0_0^0.03 GEWICHT=SPHAR4 //



Example 1 - Texture




```
--------------------------------------------------------------------------------
1. phase: texture reduced from SPHAR10 to SPHAR4 due to small contents
2. phase: texture reduced from SPHAR10 to SPHAR6 due to small contents
1. phase: initializing SPHAR4...OK
2. phase: initializing SPHAR6...
OK
```

!

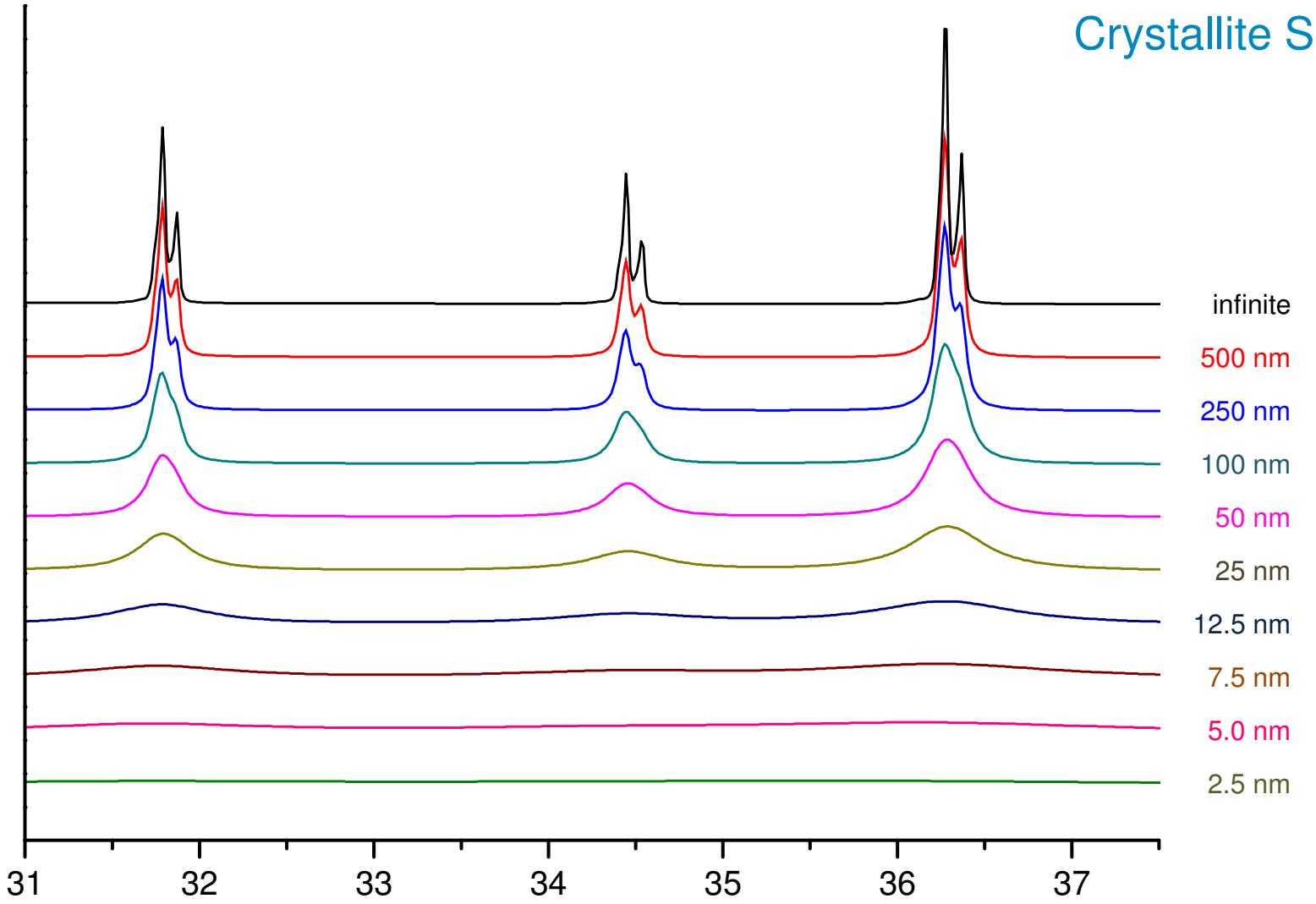
Example 1 - Texture

- Refining «GEWICHT» with symmetrized spherical harmonics functions allows to model texture / preferred orientation.
- Complexity of the polynome can be set in structure file (SPHAR*n*).
- High order introduce large number of refined parameters. (→ slow refinement, may get unstable)
- Automatic refinement strategy will protect from over-interpretation.

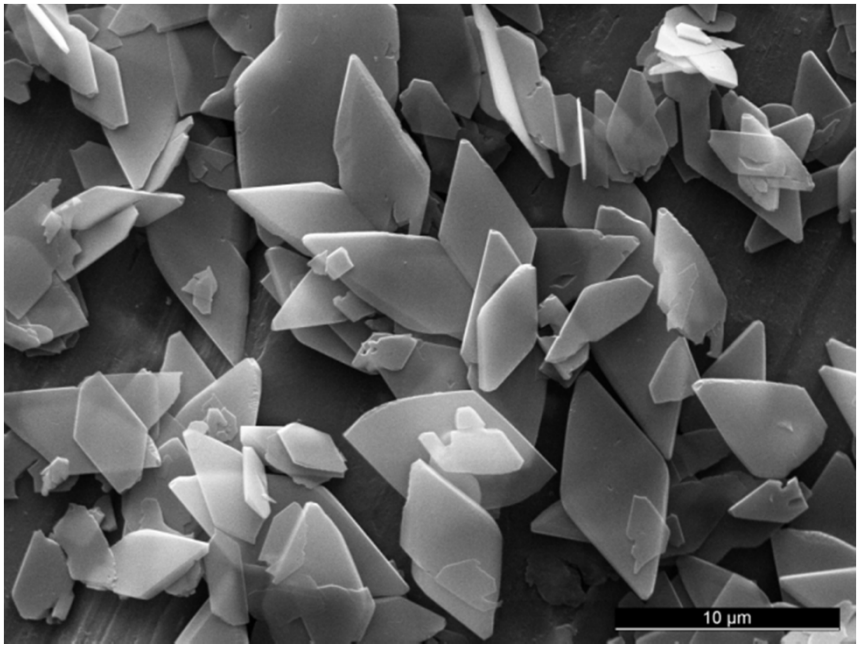
Recommendation:

- Use a moderate order of SPHAR polynomes in your structure files (e.g. SPHAR4)
- Let BGMN reduce the order if necessary
- Only increase the order if the fit really improves

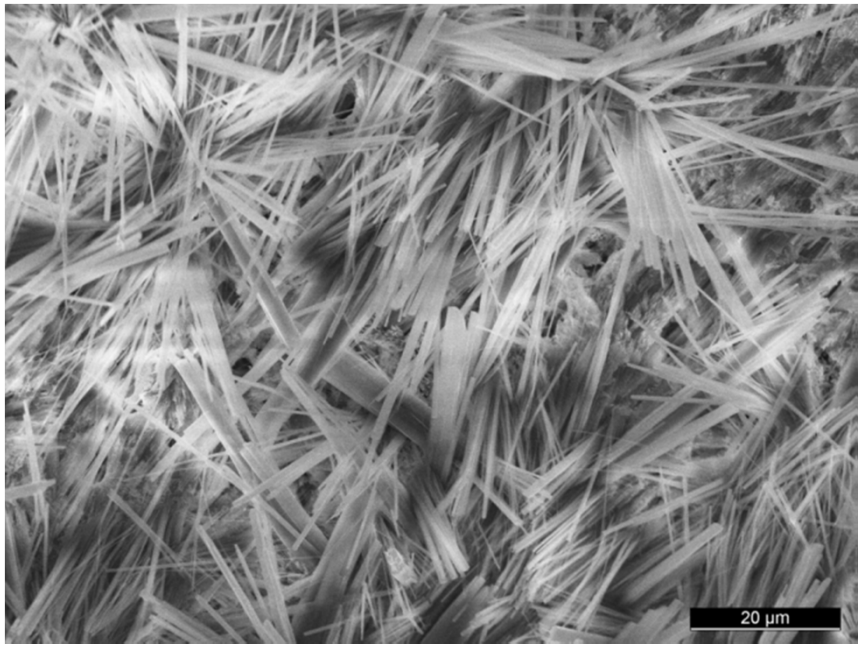
Anisotropic Crystallite Sizes



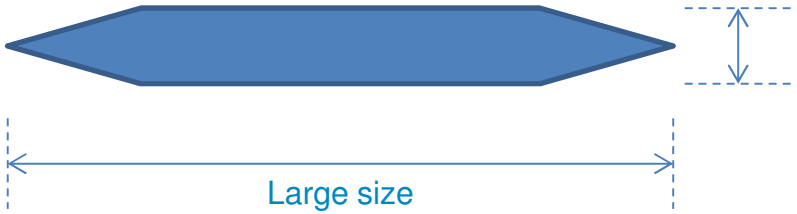
Anisotropic Crystallite Sizes



Platelets

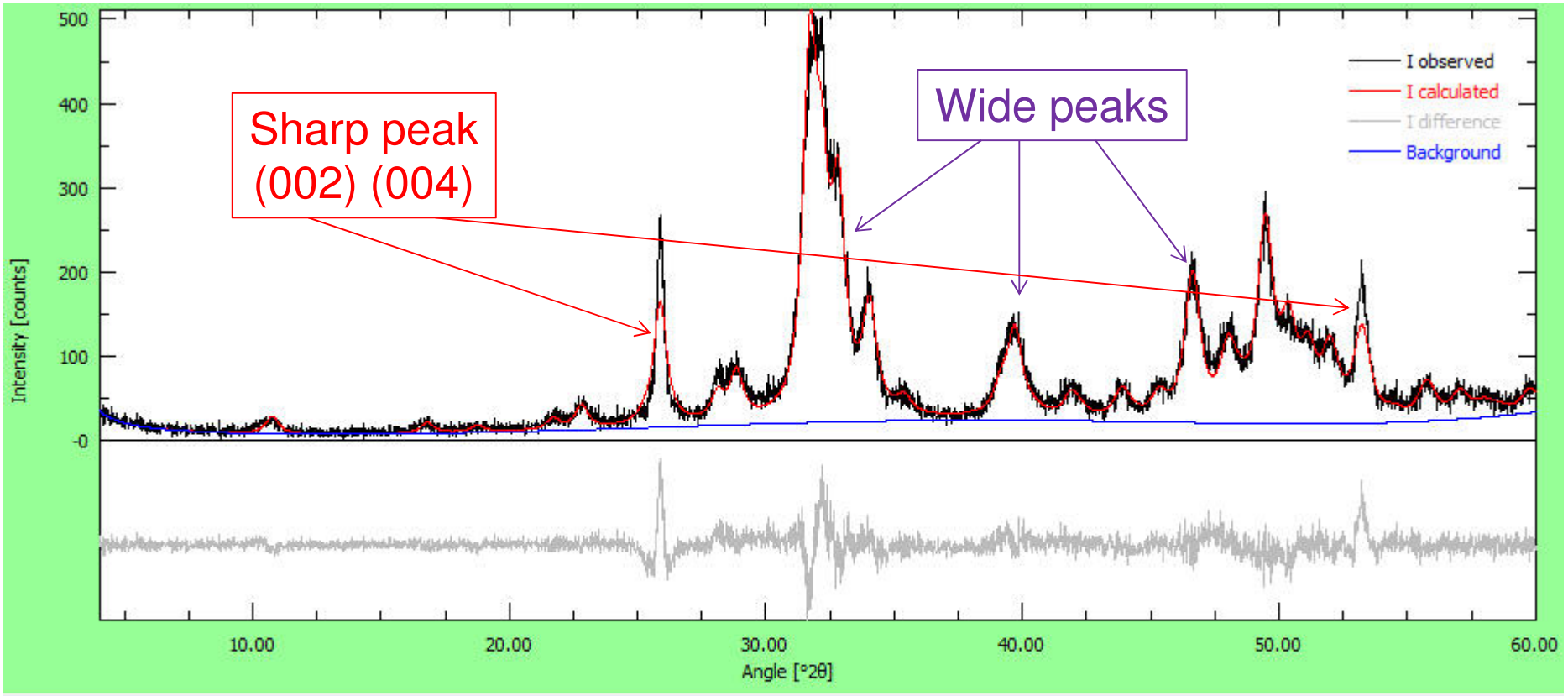


Needles, Fibers, Whiskers



Images: L. Galea, RMS Foundation

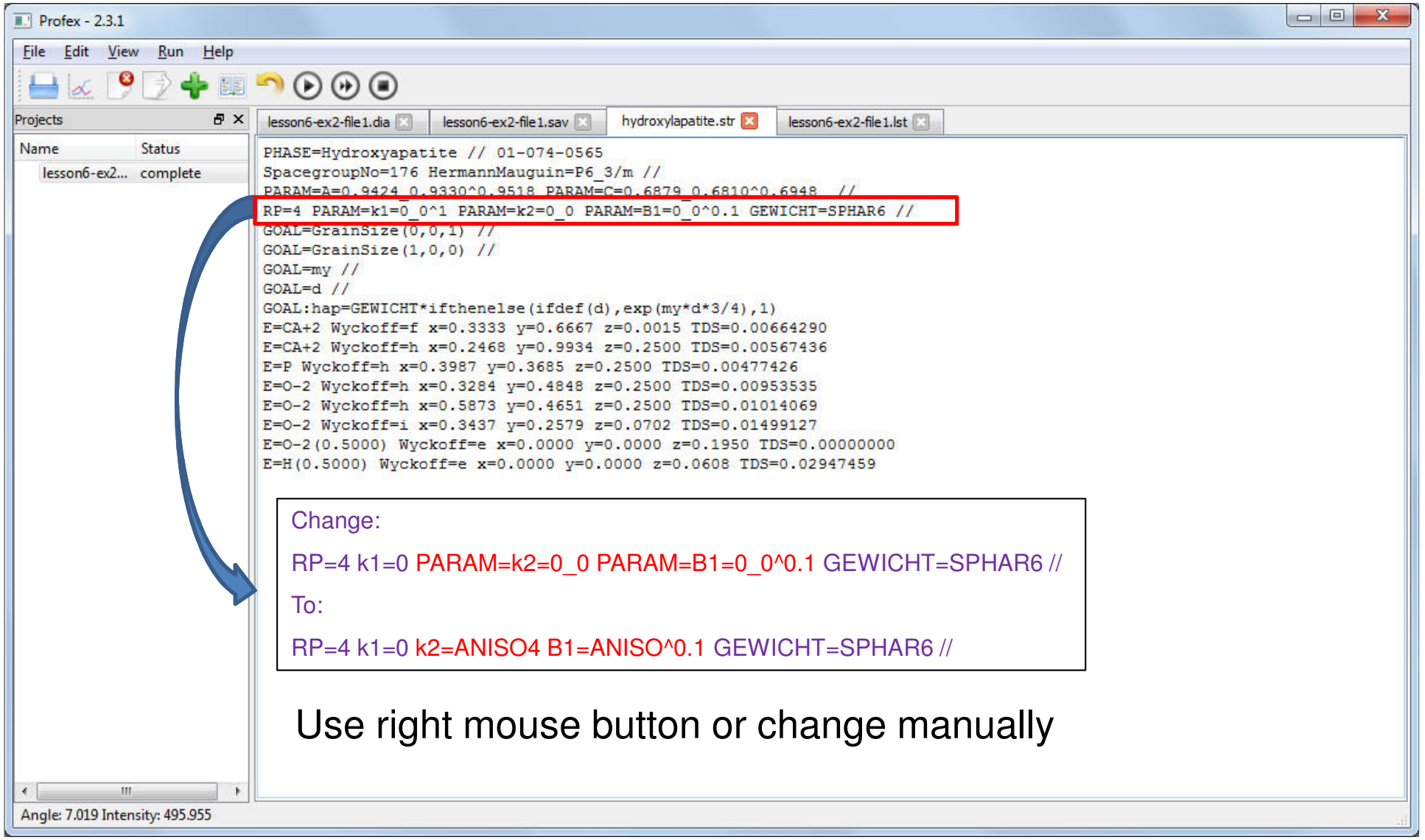
Example 2 – Anisotropic Crystallite Size



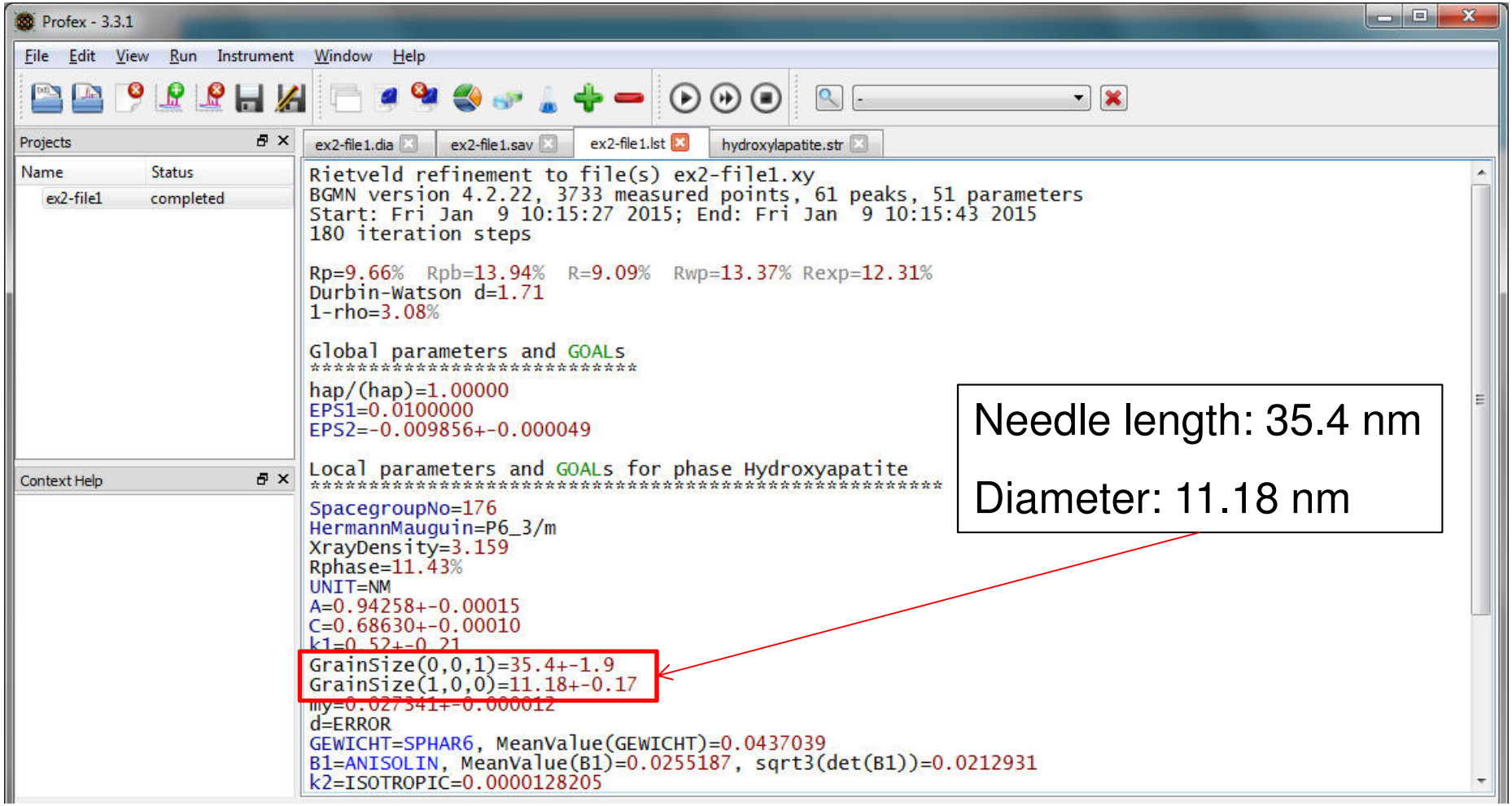
Sample lesson6-ex2-file1 (C:/xrd/S12_0008/Examples/Lesson 6/Example 2/lesson6-ex2-file1.lst)

Phase	R_{Phase} [%]	Quantity [wt-%]	Mean Gewicht [a.u.]	Crystallite Sizes [nm]	Density [g/cm³]
Hydroxyapatite	14.91	100.00	0.044979	(0,0,1)14.22 (1,0,0)14.22	3.159

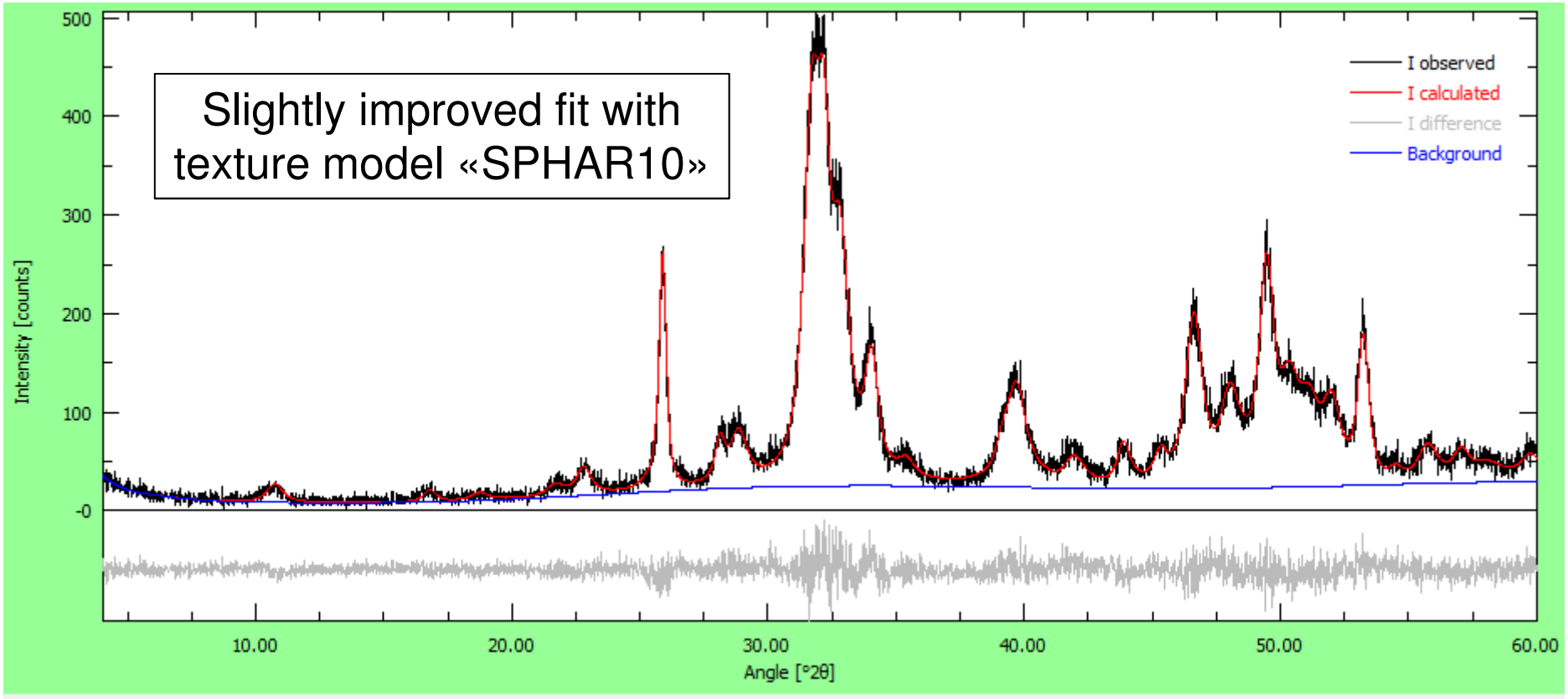
Example 2 – Anisotropic Crystallite Size



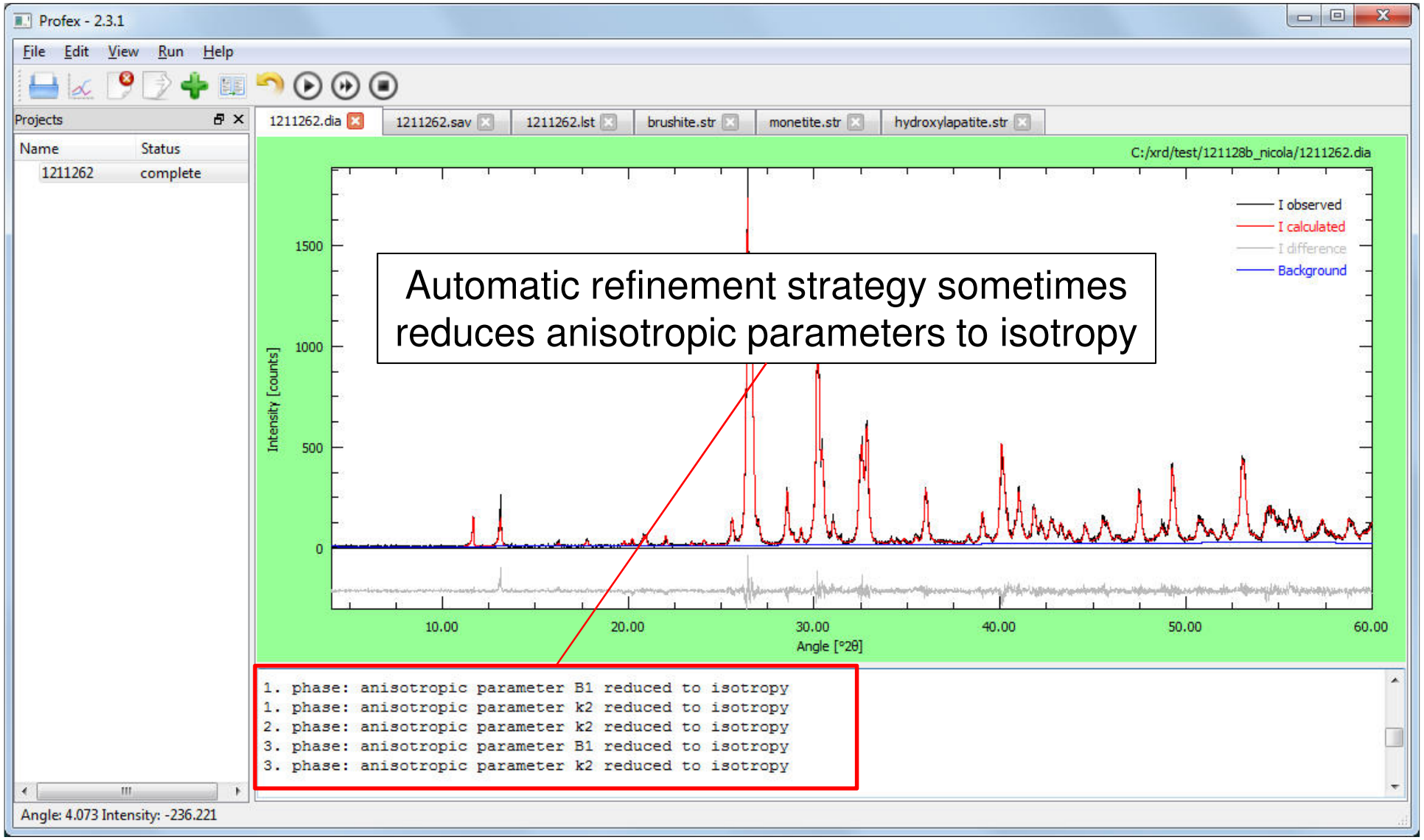
Example 2 – Anisotropic Crystallite Size



Example 2 – Anisotropic Crystallite Size



Example 2 – Anisotropic Crystallite Size



Example 2 – Anisotropic Crystallite Size

Refine anisotropic crystallite sizes with «B1=ANISO»

Refine anisotropic micro-strain with «k2=ANISO4»

Recommendation:

- Do not refine micro-strain anisotropically unless it improves the fit
- Refine peak broadening anisotropically (B1=ANISO^0.01), let BGMN handle the reduction to isotropy
- Check if the upper limit of B1 was reached. If yes:
  - increase the limit…
  - … or see next example (non-existent phases)

Example 3 – Non-existent Phases

Experimental design:

Step 1:

- α-TCP prepared at 1350 °C
- Traces of β-TCP may have formed during cooling

Step 2:

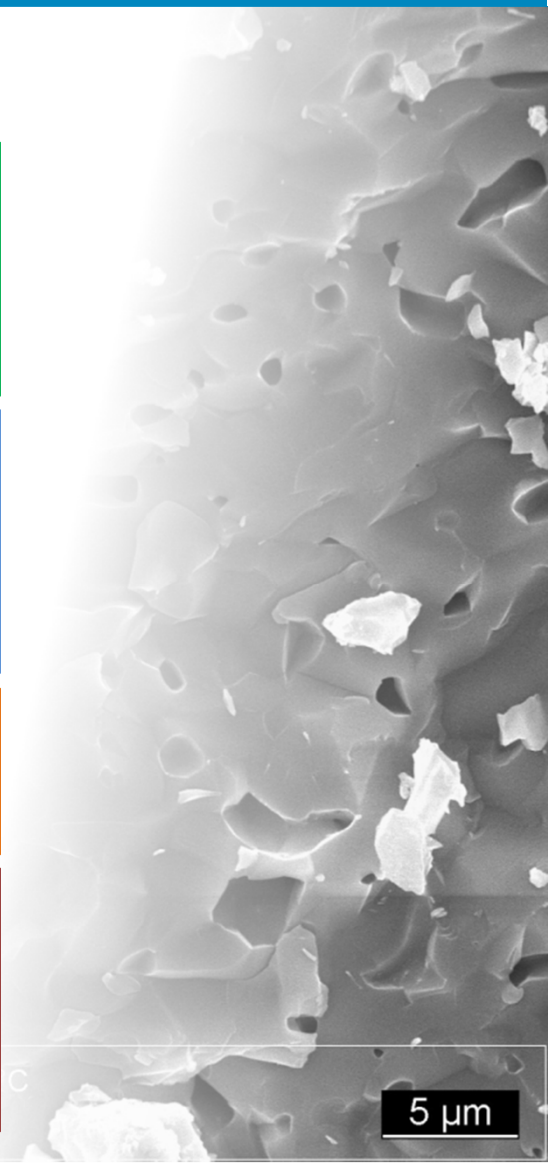
- α-TCP hydrated to Hydroxylapatite
- β-TCP (if present) remains

Question:

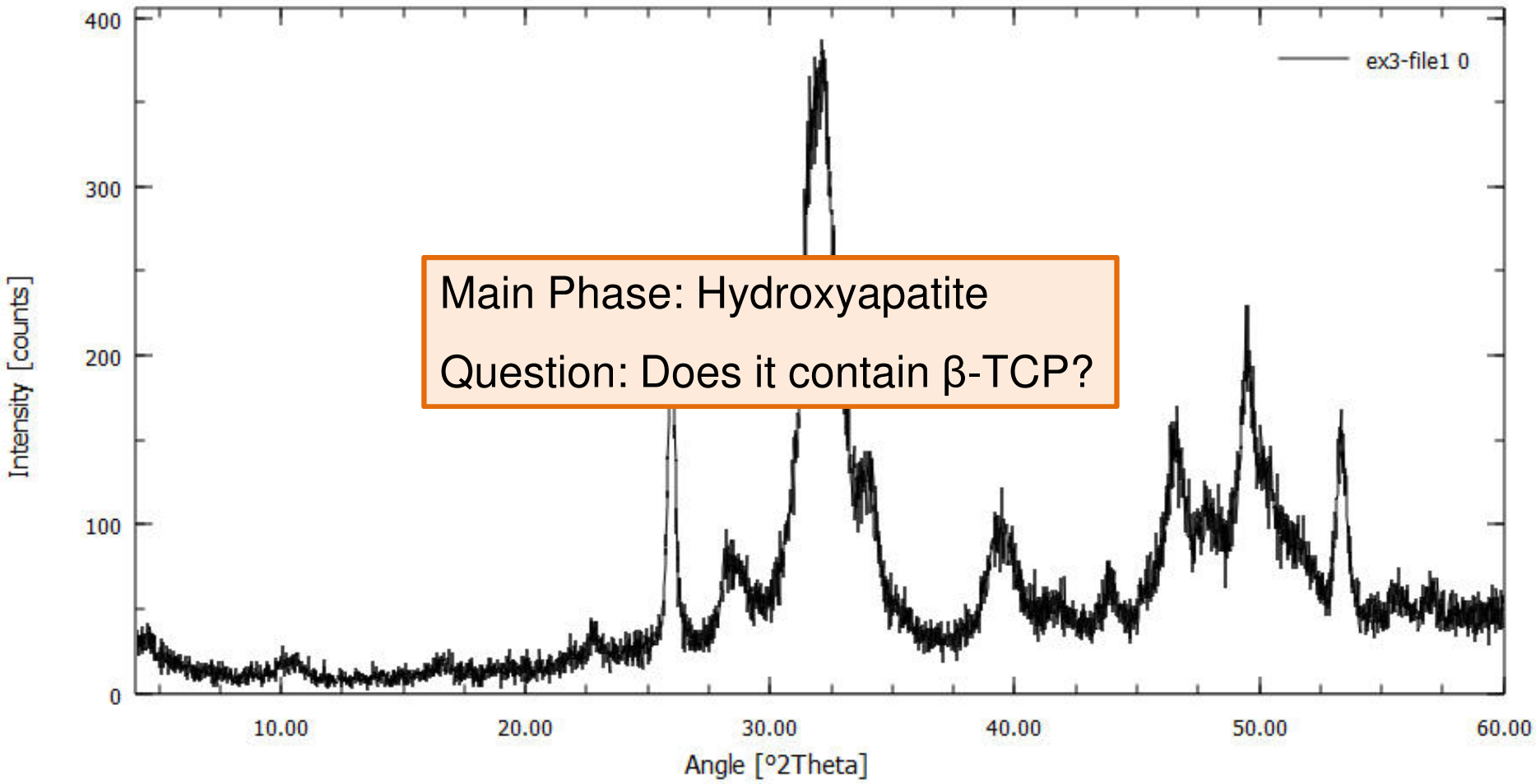
- Is β-TCP present after setting?

Background Information:

- If β-TCP is present, it has formed at ~1000°C
- Must be highly crystalline with large crystallites



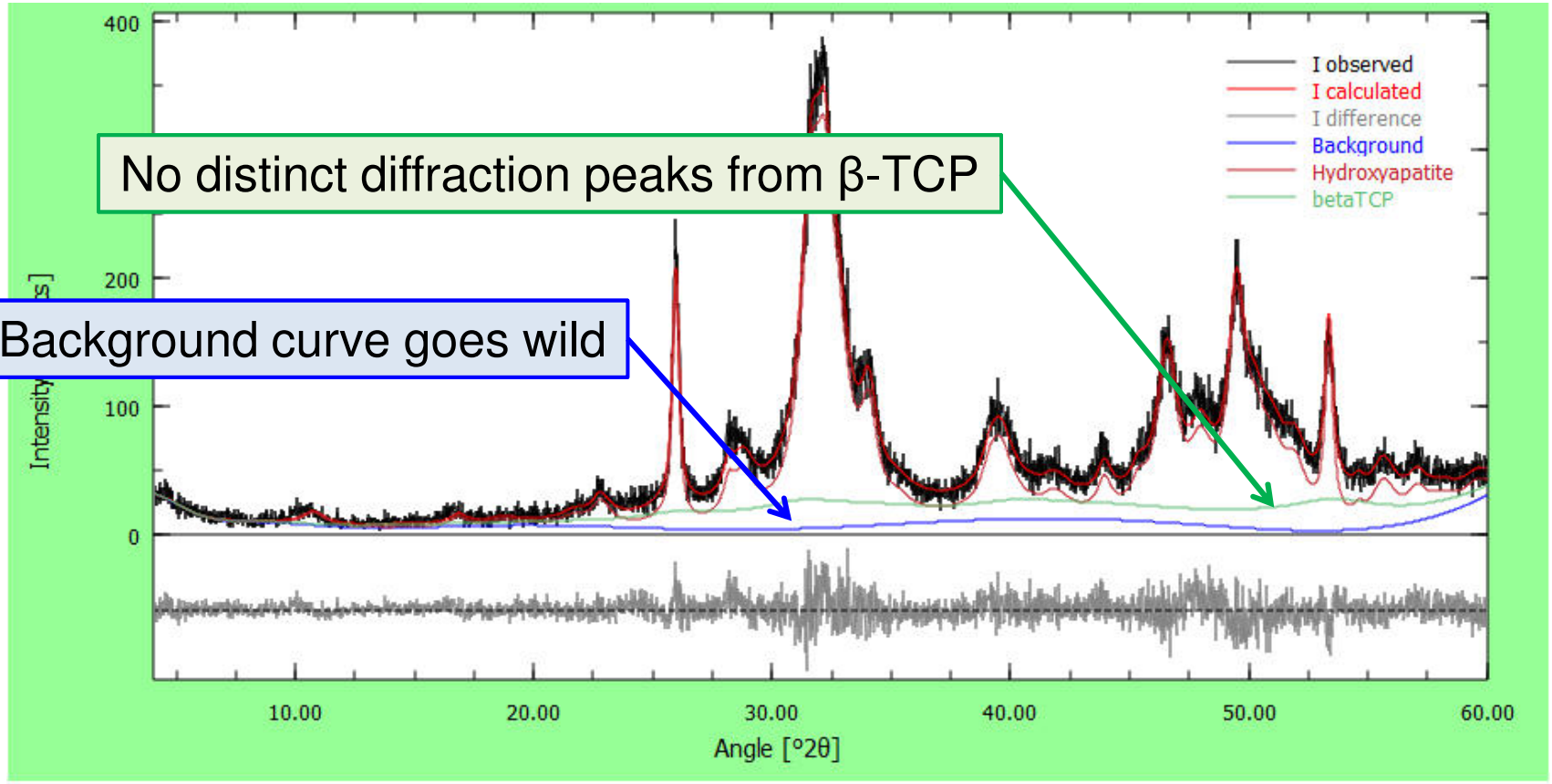
Example 3 – Non-existent Phases



Main Phase: Hydroxyapatite

Question: Does it contain β-TCP?

Example 3 – Non-existent Phases



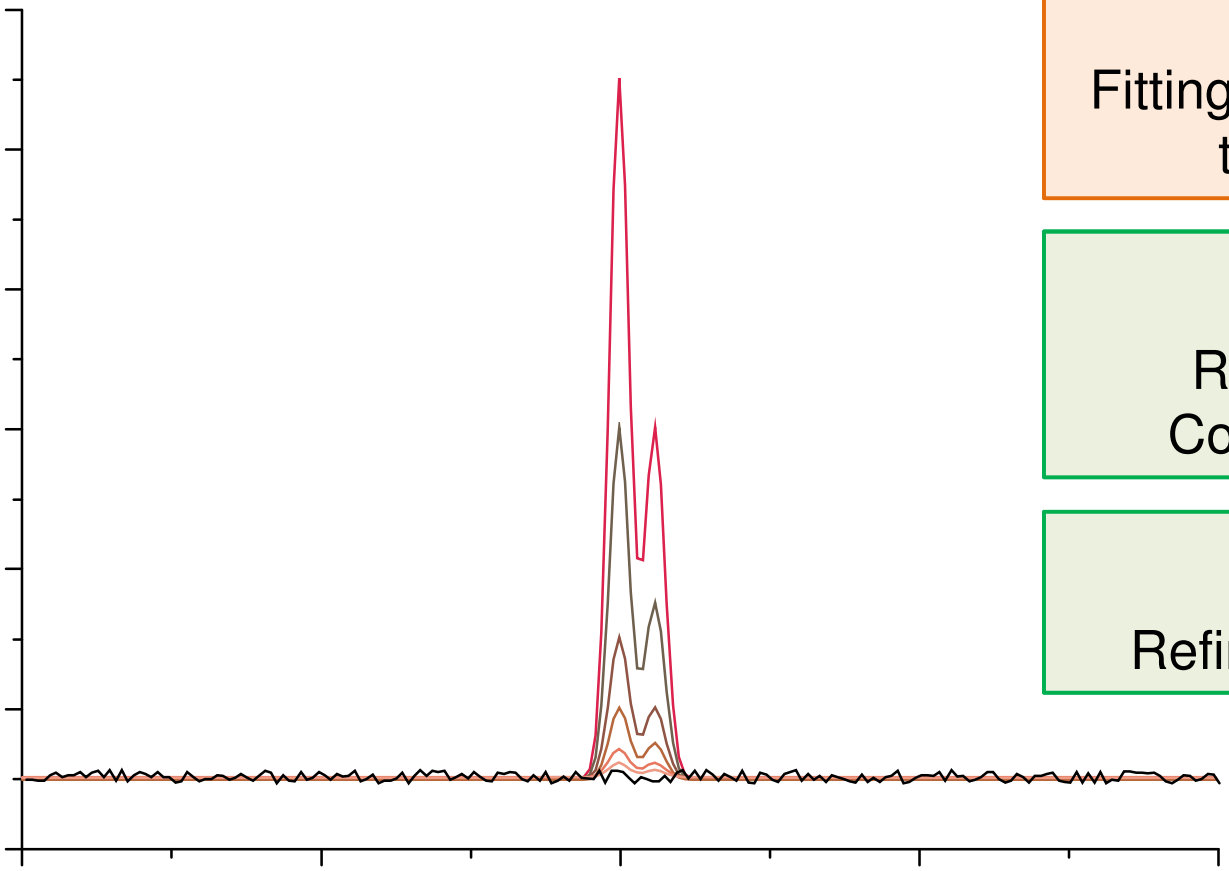
Global Parameters and GOALs

C:\Users\doebelinn\Desktop\Examples-Test\Lesson 7\Example 3\ex3-file1.lst
R_{wp}=14.08%, R_{exp}=12.93%, X^2=1.0889

Parameter / Goal	Value	ESD
hap/(hap+betaTCP)	0.762	0.051
betaTCP/(hap+betaTCP)	0.238	0.051

23.8 wt-% betaTCP (totally wrong!)

Example 3 – Non-existent Phases



Problem:

Refining non-existing phases
=
Fitting a calculated pattern
to random noise

Solution 1:

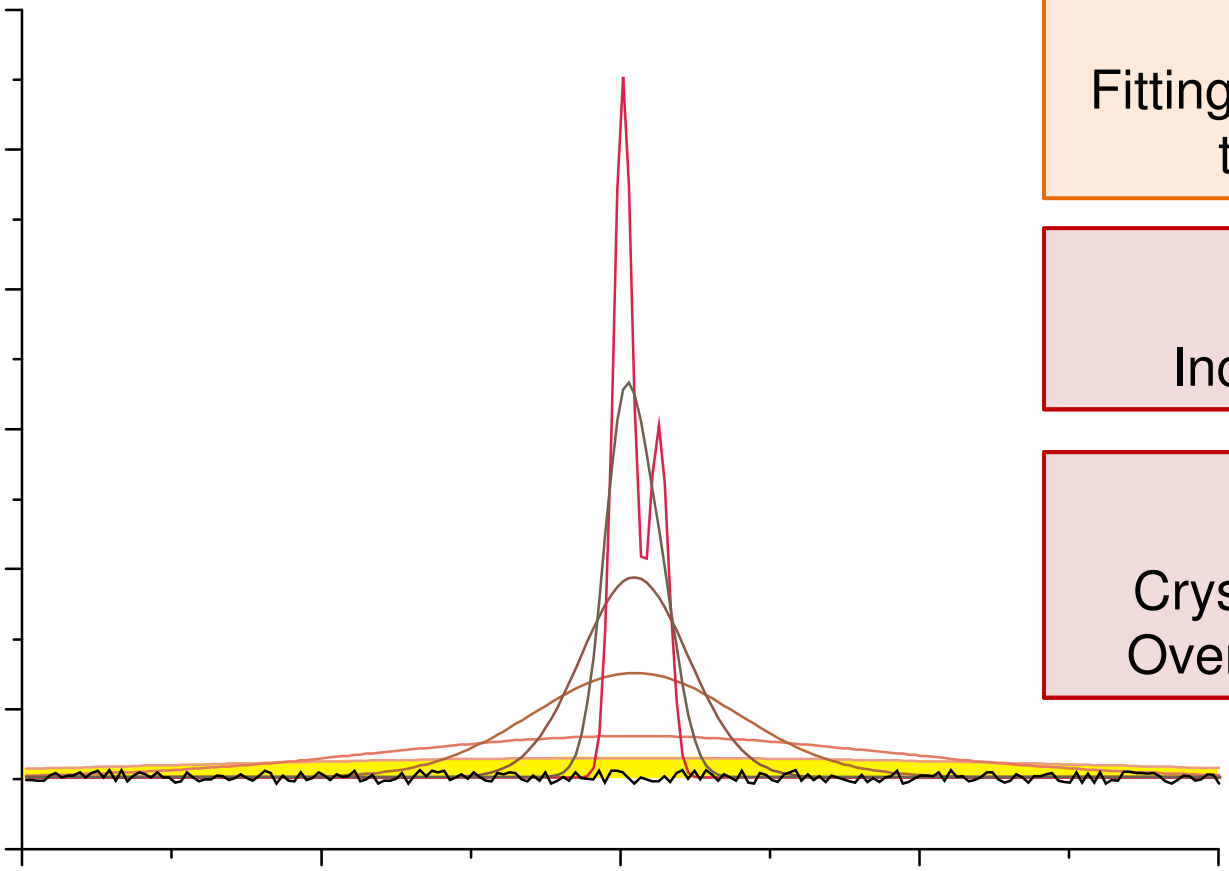
Reducing intensity
Constant peak width

Result:

Refined quantity → 0 %

Correct result

Example 3 – Non-existent Phases



Problem:

Refining non-existing phases
=
Fitting a calculated pattern
to random noise

Solution 2:

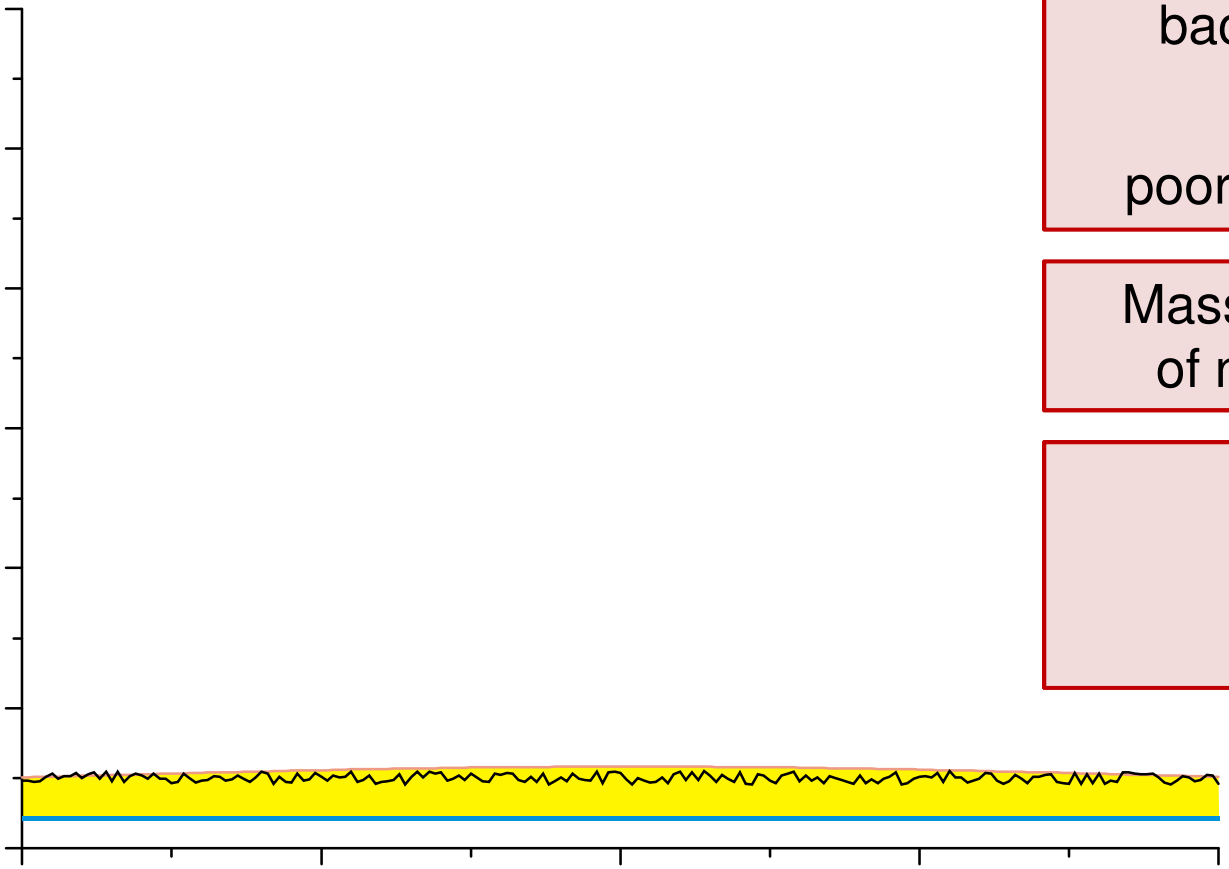
Increase peak width

Result:

Crystallite Size → 0 nm
Over-estimated quantity

Wrong result

Example 3 – Non-existent Phases



Even worse:

No anchor points for background anymore

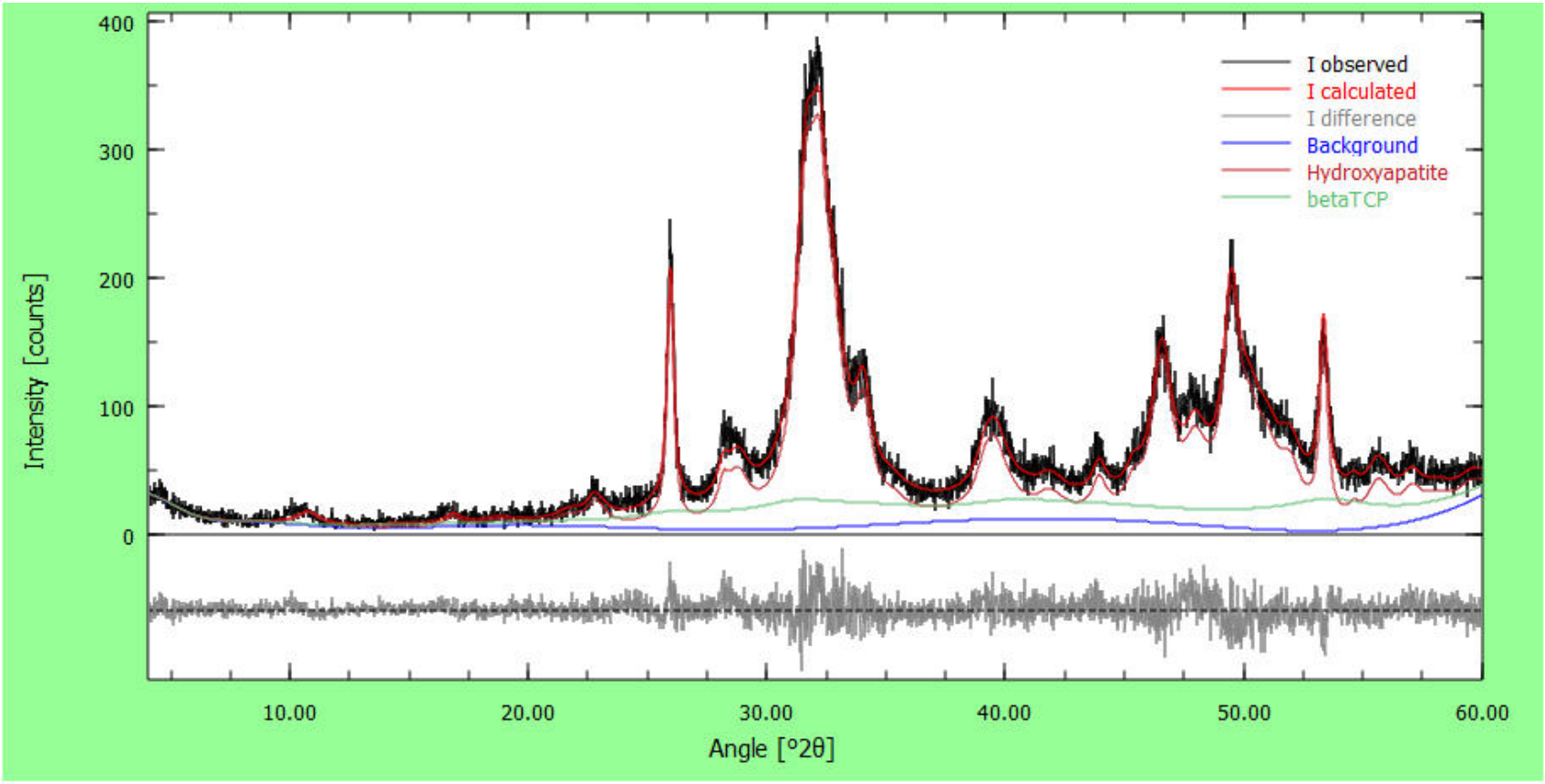
Background is poorly/randomly defined

Massive over-estimation of non-existing phase

Result:

Totally wrong!
Unpredictable!

Example 3 – Non-existent Phases



Global Parameters and GOALs

C:\Users\doebelinn\Desktop\Examples-Test\Lesson 7\Example 3\ex3-file1.lst
R_{wp}=14.08%, R_{exp}=12.93%, X^2=1.0889

Parameter / Goal	Value	ESD
hap/(hap+betaTCP)	0.762	0.051
betaTCP/(hap+betaTCP)	0.238	0.051

GrainSize(1,1,1) = 2.47+-0.44

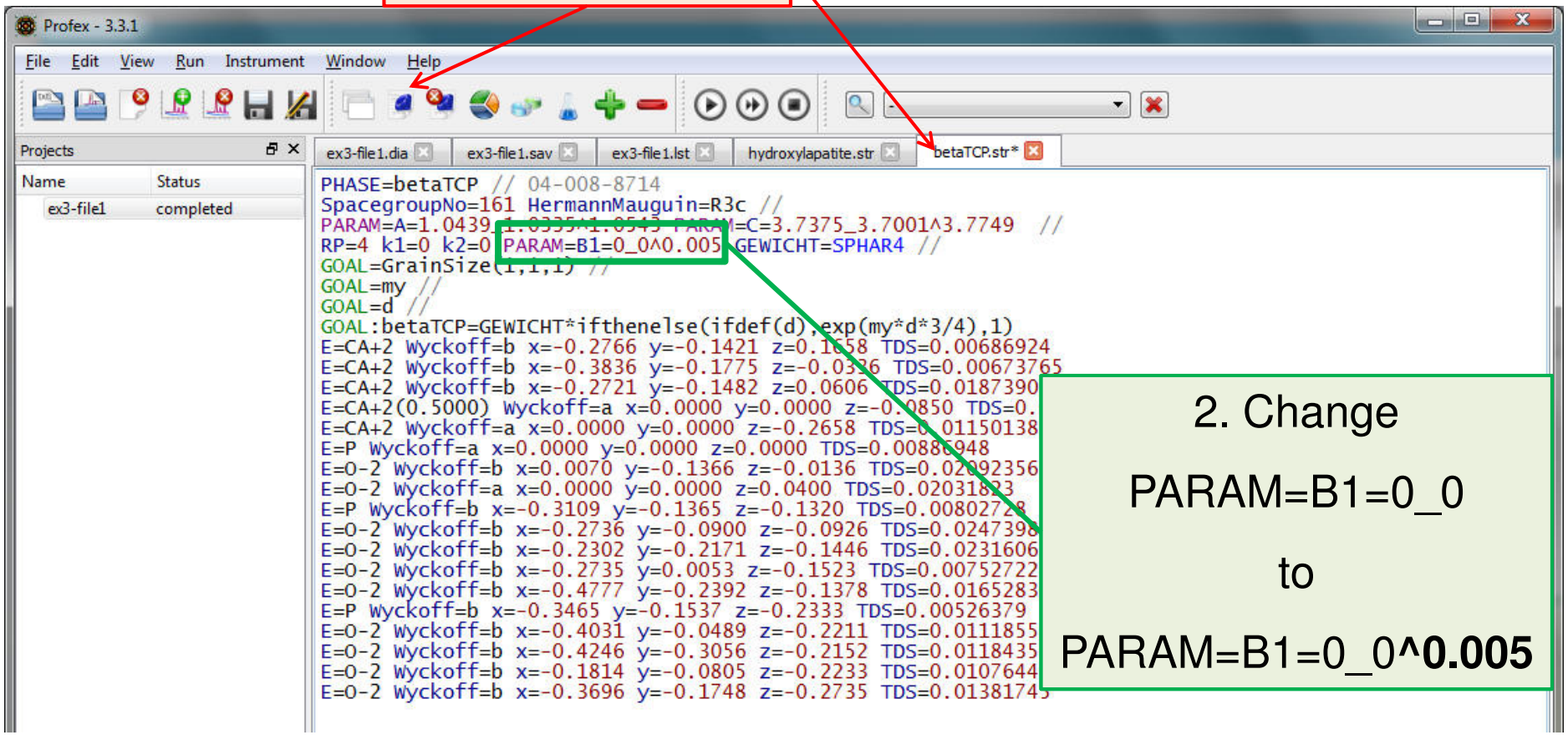
Example 3 – Non-existent Phases

Solutions:

- Use a reasonable upper limit for B1 (peak broadening, crystallite size)
- Don’t trust very small crystallite sizes (e.g. < 20 nm)
- Repeat the refinement without the questionable phase
  (Does the fit really look worse? Or just as good?)
- Use additional information:
  - Sintered samples: very small crystallites are unlikely
  - Cement samples: very small crystallites are reasonable

Example 3 – Non-existent Phases

1. Edit betaTCP.str



2. Change

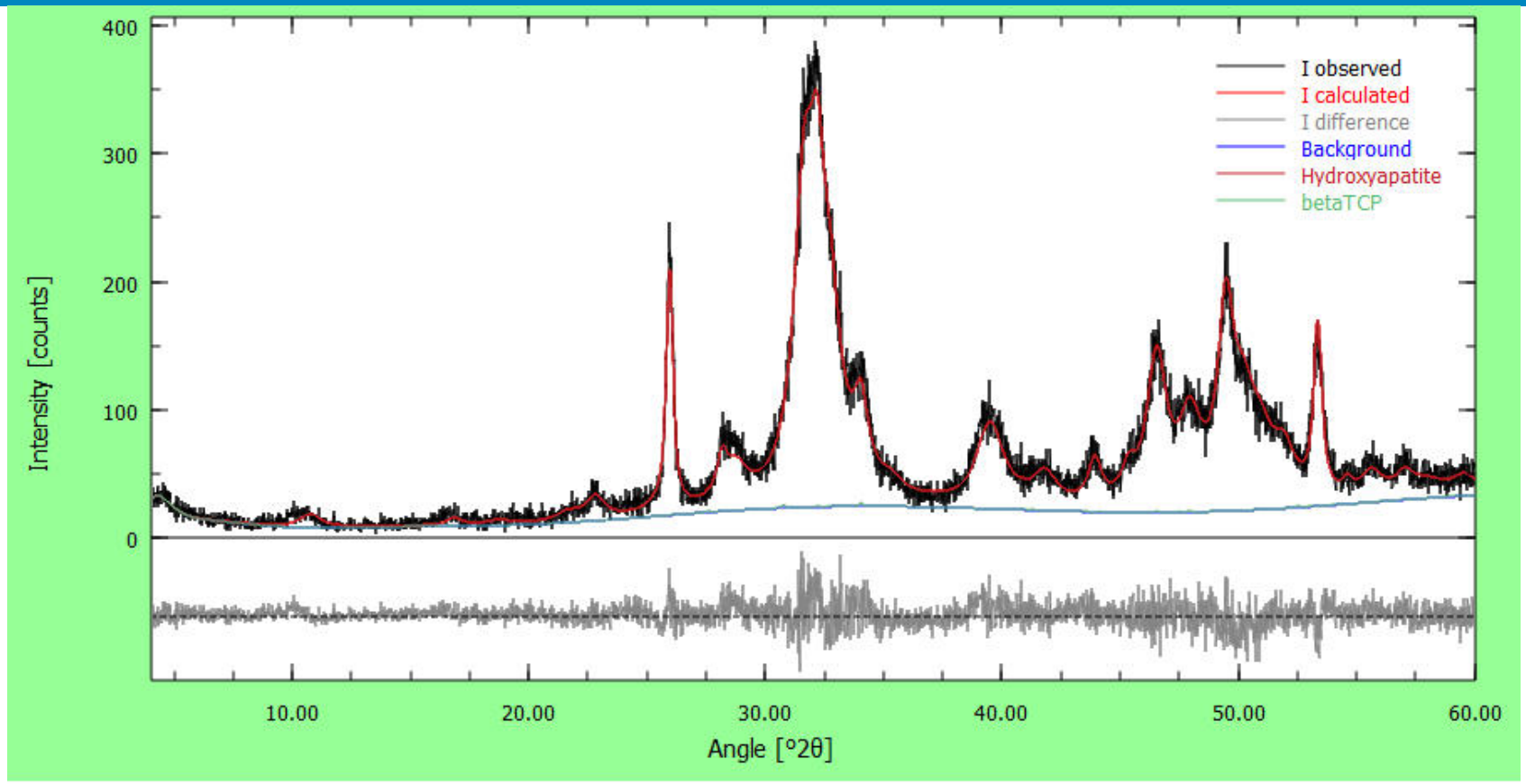
PARAM=B1=0_0

to

PARAM=B1=0_0**^0.005**

3. Run Refinement…

Example 3 – Non-existent Phases



Global Parameters and GOALs

C:\Users\doebelinn\Desktop\Examples-Test\Lesson 7\Example 3\ex3-file1.lst
R_{wp}=14.23%, R_{exp}=12.94%, X^2=1.0997

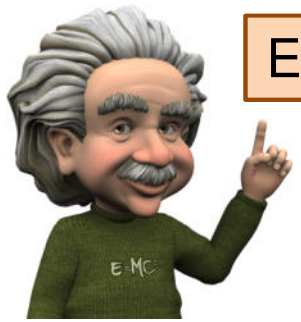
Parameter / Goal	Value	ESD
hap/(hap+betaTCP)	0.9973	0.0021
betaTCP/(hap+betaTCP)	0.0027	0.0021

< 1 % vs. 23.8 %!

Example 3 – Non-existent Phases

How to choose the upper limit for B1?

Upper limit B1	Crystallite Size β-TCP	Quantity β-TCP
None	2 nm	23.8 wt-%
0.1	4 nm	14.6 wt-%
0.05	8 nm	7.0 wt-%
0.01	42 nm	0.4 wt-%
0.005	85 nm	0.8 wt-%
0.001	424 nm	0.2 wt-%
0.0005	849 nm	0.2 wt-%
0	∞	0.2 wt-%



Educated Guess!

Sample was sintered at 1350°C:

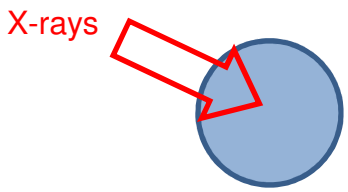
→ Crystallites of several 100 nm diameter expected

→ Any other useful data available?

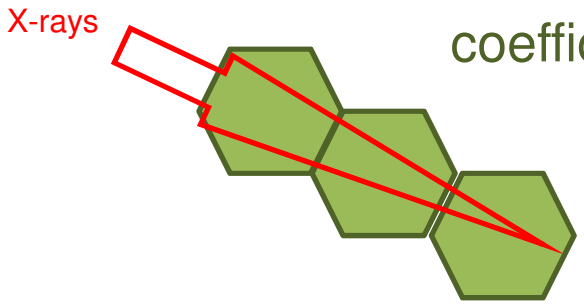
→ Other samples which **do** contain β-TCP?

→ Before cement reaction?

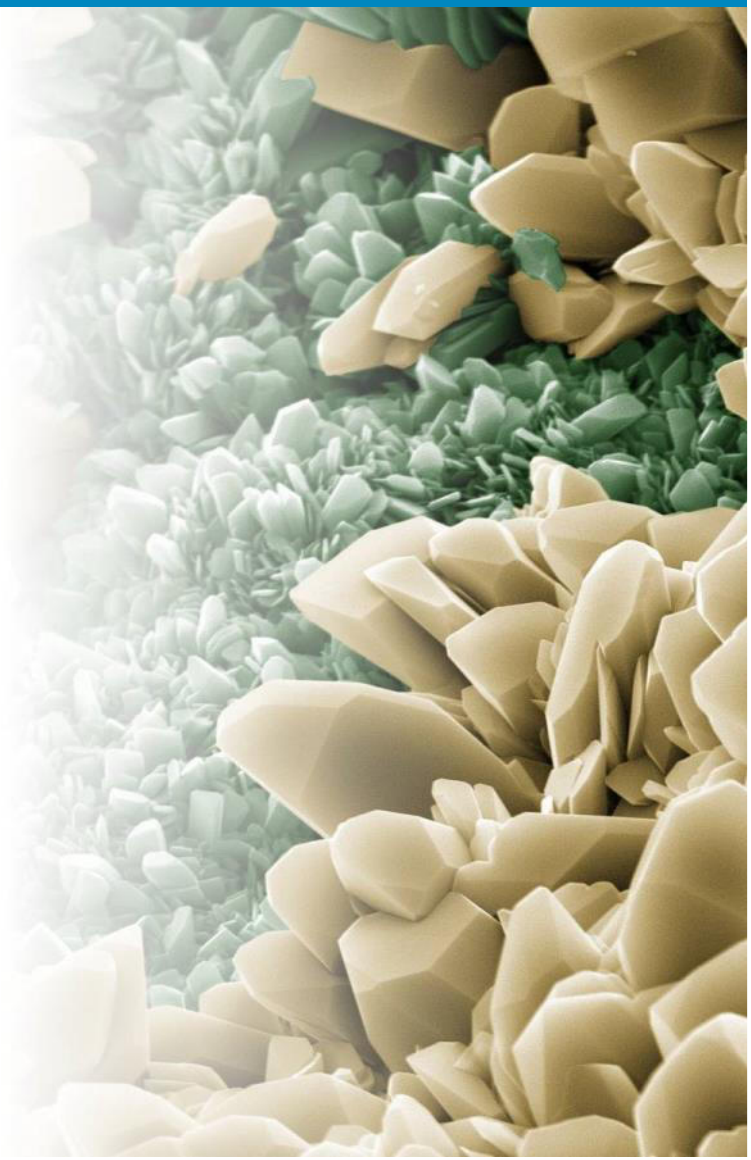
Micro-absorption



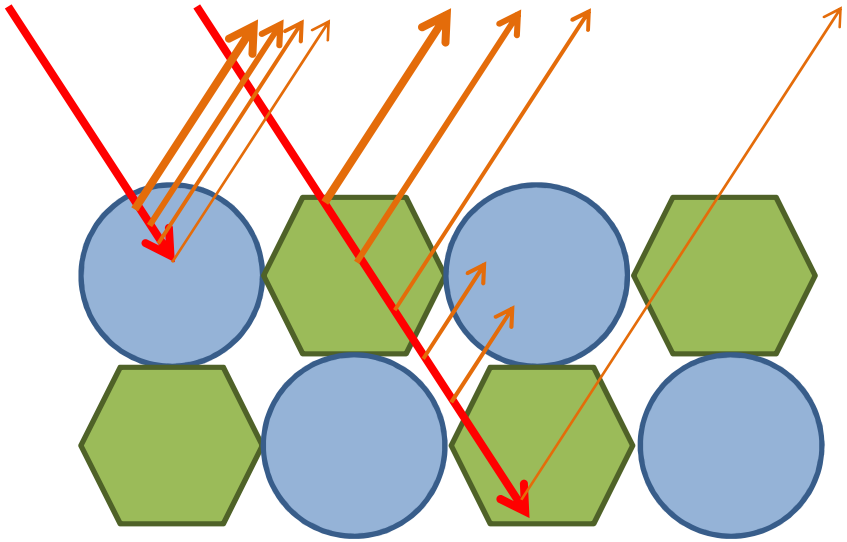
Phase 1: High absorption coefficient for X-radiation

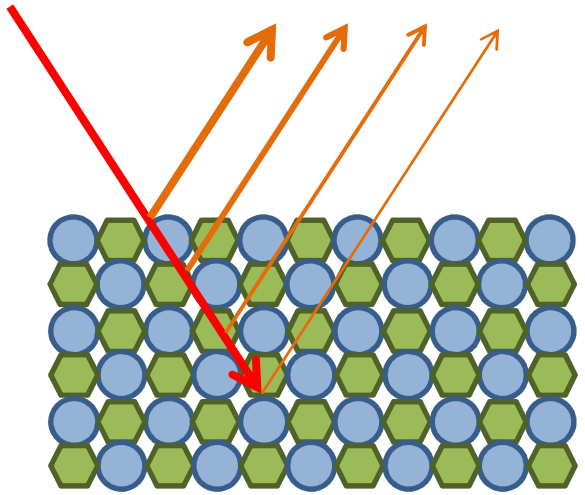


Phase 2: Low absorption coefficient for X-radiation



Micro-absorption





Strong attenuation by phase 1

Large particles absorb significant part of the radiation.

→ Small volume of interaction

Weak attenuation by phase 2

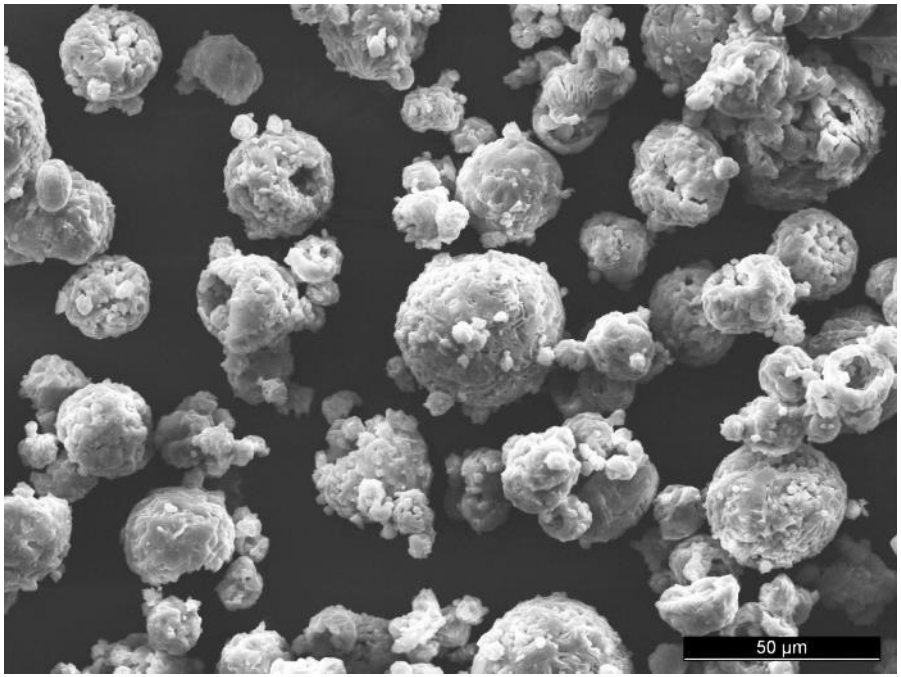
→ Large volume of interaction

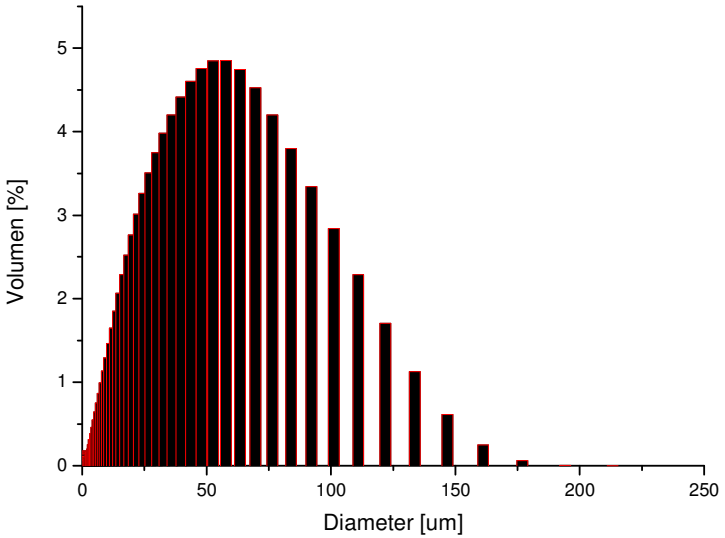
Small particles absorb insignificant part of the radiation.

→ Volumes of interaction with phases 1 & 2 are representative for phase composition

Micro-absorption and Brindley Correction

Micro-absorption can be corrected,
but mean particle* size must be known.





*not crystallite size

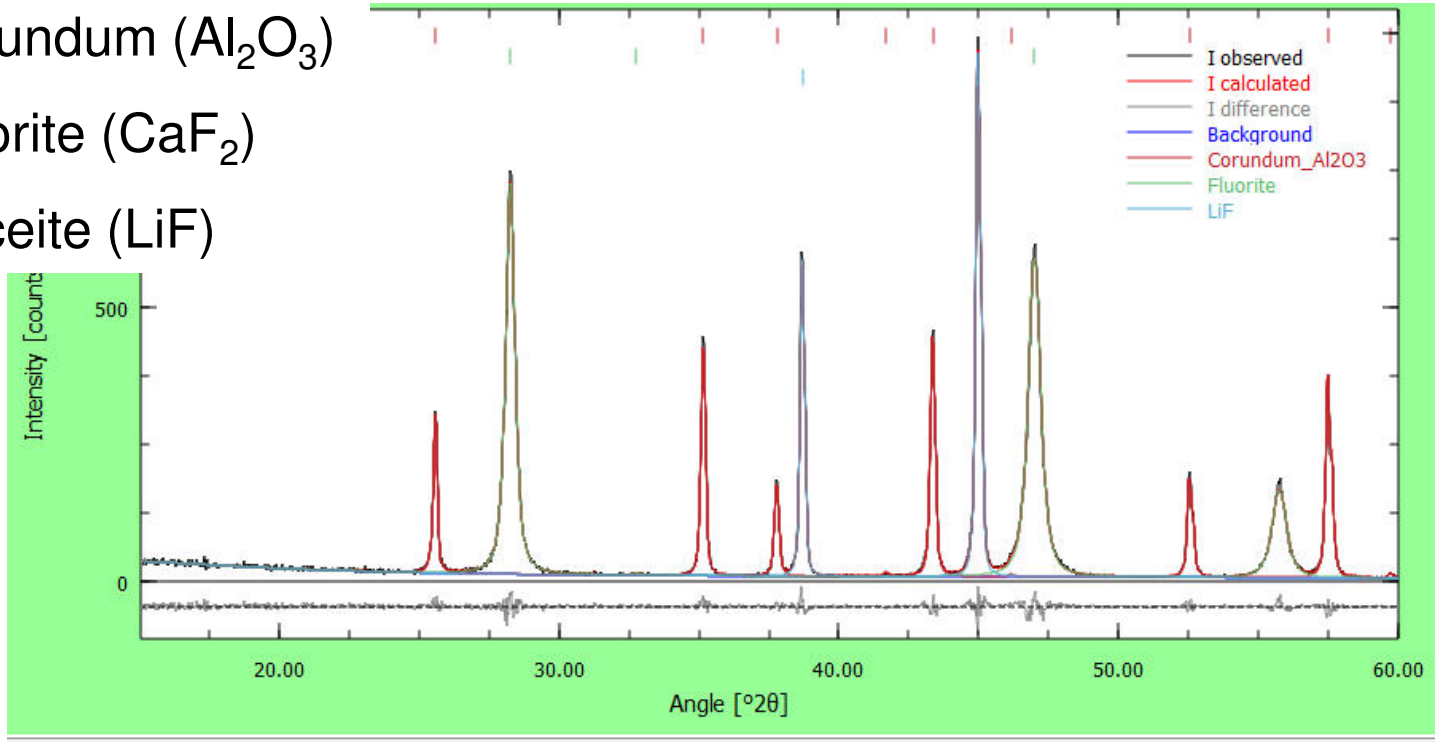
Example 4 – Micro-Absorption

Reference mixture:

33.33 wt-% Corundum (Al_2O_3)

33.33 wt-% Fluorite (CaF_2)

33.33 wt-% Griceite (LiF)



Global Parameters and GOALs

C:\Users\doebelinn\Desktop\Examples-Test\Lesson 7\Example 4\ex4-file1.lst

R_{wp}=7.54%, R_{exp}=13.39%, X^2=0.5631

Parameter / Goal	Value	ESD
corundum/(corundum+fluorite+lif)	0.3348	0.0038
fluorite/(corundum+fluorite+lif)	0.3001	0.0029
lif/(corundum+fluorite+lif)	0.3651	0.0034

Wrong phase quantities

Example 4 – Micro-Absorption

Add mean particle diameter (µm) to structure files:

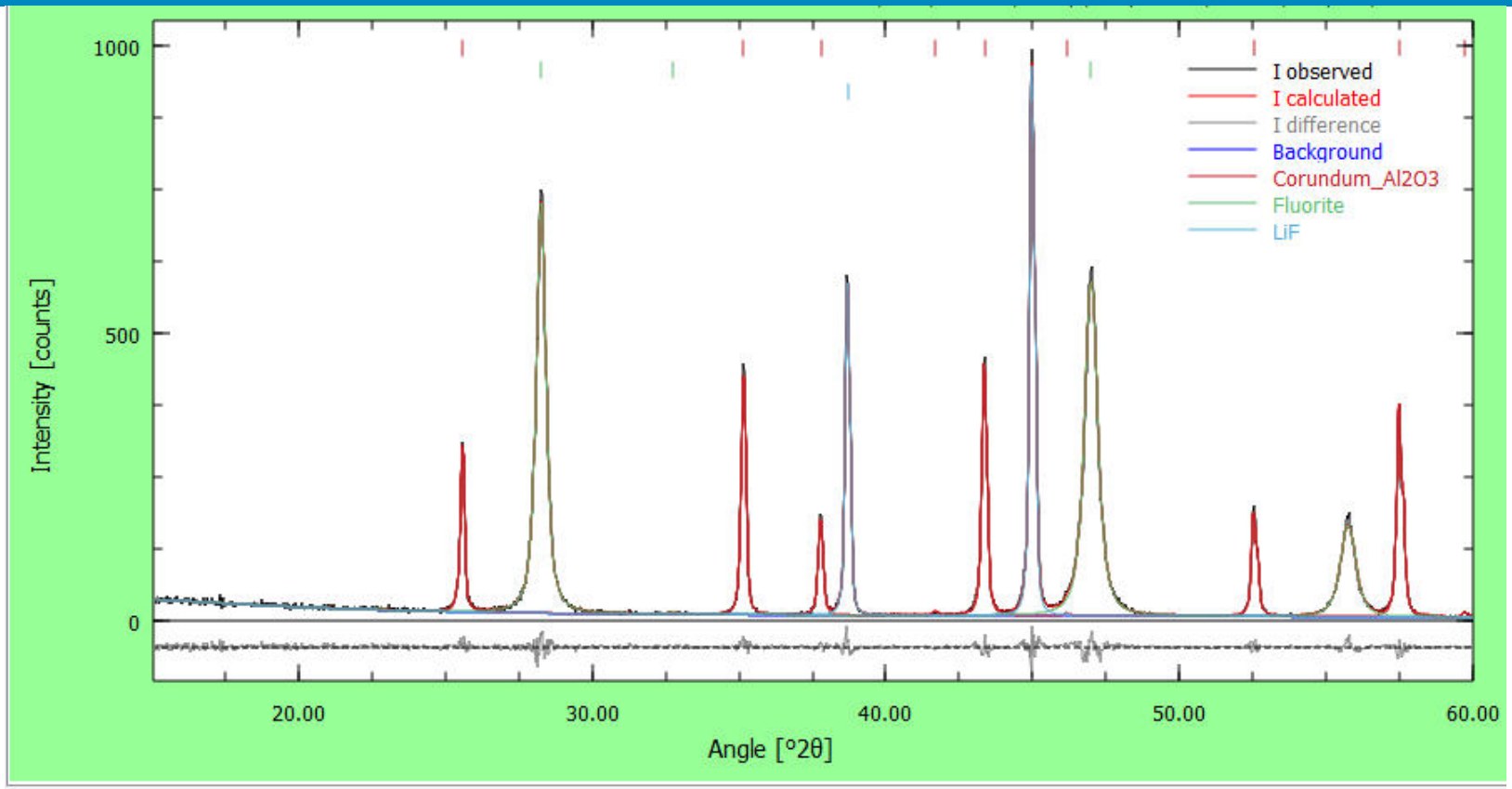
lesson5-ex4-file1.dia | lesson5-ex4-file1.sav | lesson5-ex4-file1.lst | **Corundum.str** | Fluorite.str | LiF.str

```
PHASE=Corundum_Al2O3 // 04-004-2852
SpacegroupNo=167 Setting=1 HermannMauguin=R-32/c //
PARAM=A=0.4760_0.4712^0.4808 PARAM=C=1.2993_1.2863^1.3123  //
RP=4 PARAM=k1=0_0^1 k2=ANISO4 B1=ANISO^0.01 GEWICHT=SPHAR8 //
GOAL=GrainSize(1,1,1) //
d=12 //
GOAL=d //
GOAL=my //
GOAL:corundum=GEWICHT*ifthenelse(ifdef(d),exp(my*d*3/4),1)
E=AL Wyckoff=c x=0.0000 y=0.0000 z=0.3522 TDS=0.00224764
E=O-2 Wyckoff=e x=0.3062 y=0.0000 z=0.2500 TDS=0.00271875
```

Corundum: 12 µm
Fluorite: 10 µm
LiF: 9 µm

my (µ) = mass absorption coefficient
(calculated automatically by BGMN)

Example 4 – Micro-Absorption



Global Parameters and GOALs

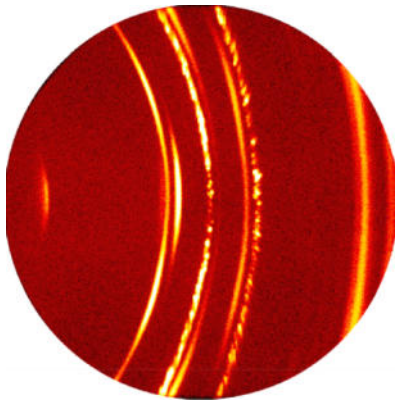
C:\Users\doebelinn\Desktop\Examples-Test\Lesson 7\Example 4\ex4-file1.lst
R_{wp}=7.54%, R_{exp}=13.39%, X^2=0.5631

Parameter / Goal	Value	ESD
corundum/(corundum+fluorite+lif)	0.3337	0.0038
fluorite/(corundum+fluorite+lif)	0.3347	0.0031
lif/(corundum+fluorite+lif)	0.3317	0.0033

Example 4 – Micro-Absorption

Micro-Absorption and Brindley correction:

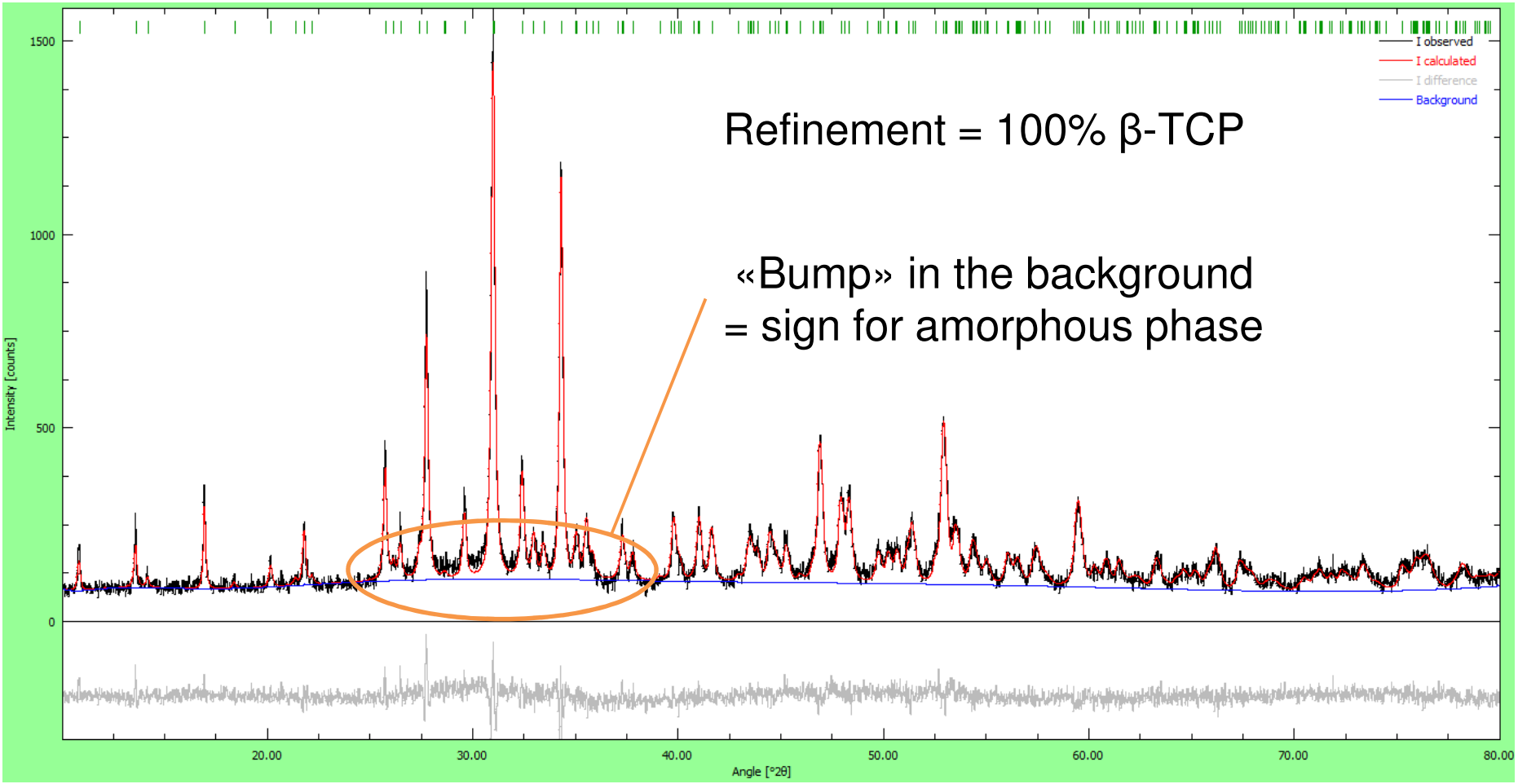
- Try to avoid the problem in the first place (keep particle size close to 1 µm)
- Additional information (particle size from SEM, PSD analysis) required for all refined phases!
- Large particles still lead to grainy diffraction patterns. Brindley-correction does **not** solve this problem!



Bruker AXS

Example 5 – Amorphous Content

Question: Does this sample contain amorphous material?



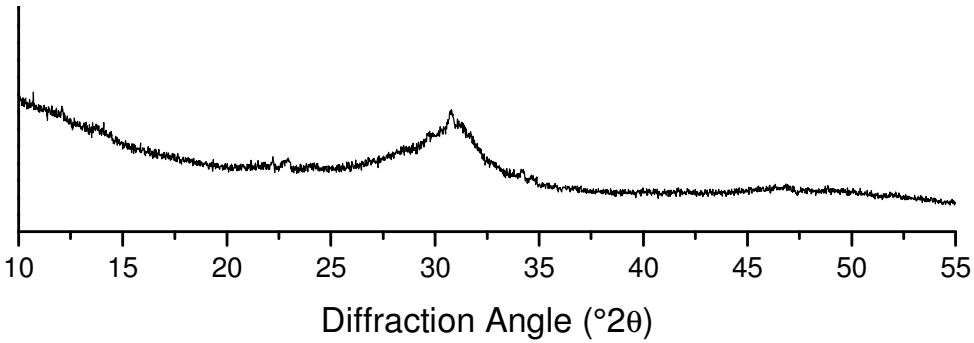
Example 5 – Amorphous Content

Problem: Amorphous phases

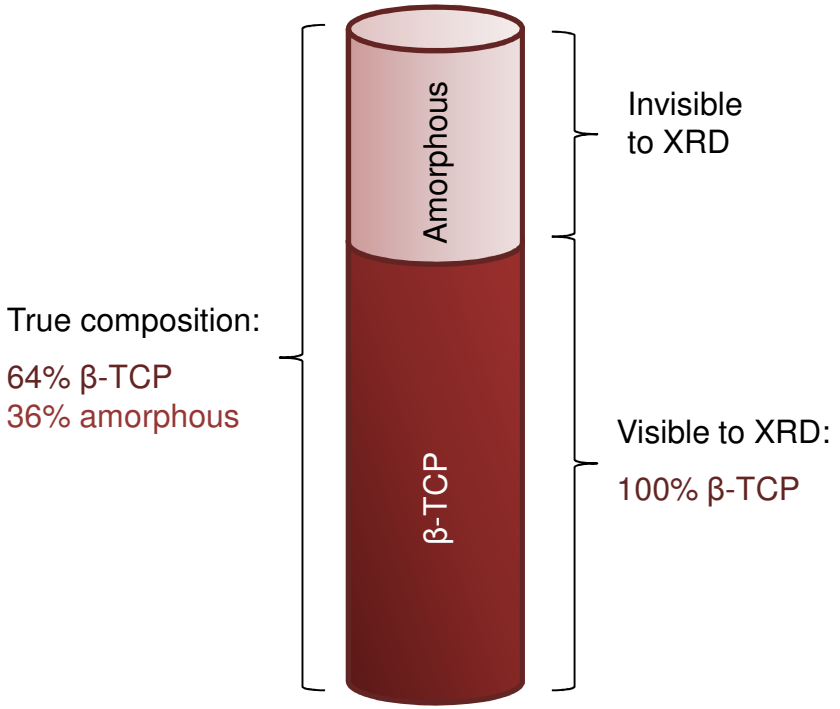
- Don’t procude a distinct diffraction pattern
- Create a broad bump around 30° 2θ

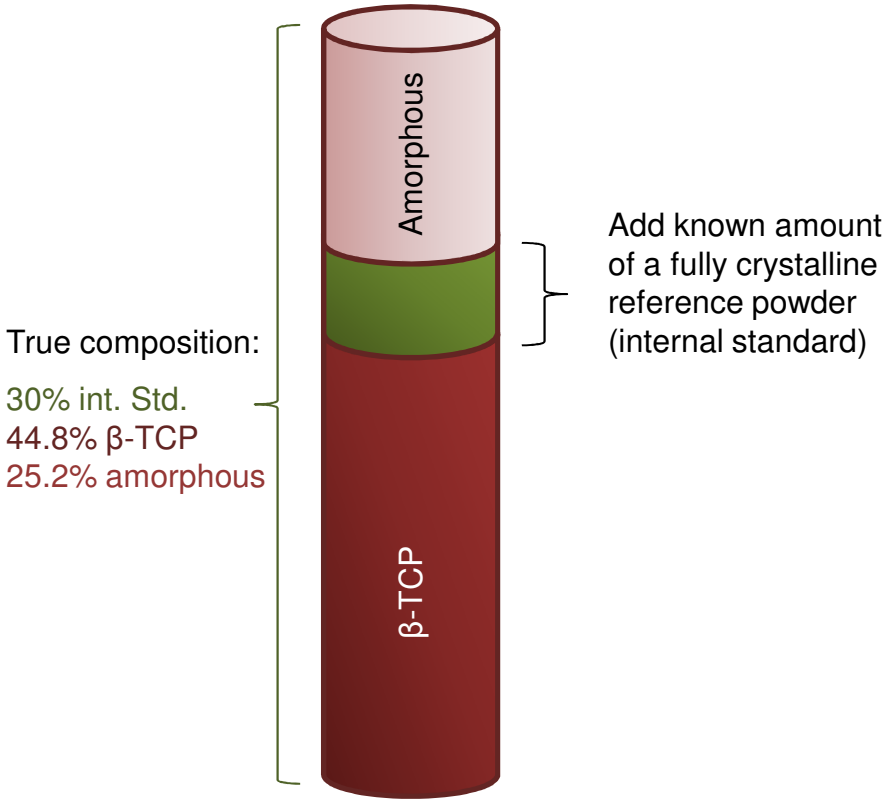
Most common solution:

Internal Standard



Example 5 – Amorphous Content

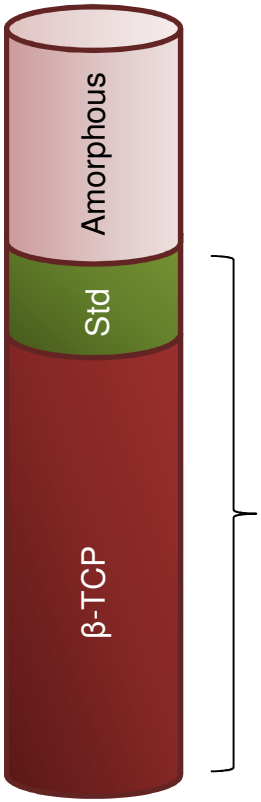




Example 5 – Amorphous Content

True composition:

30% standard
44.8% β-TCP
25.2% amorphous



Visible to XRD

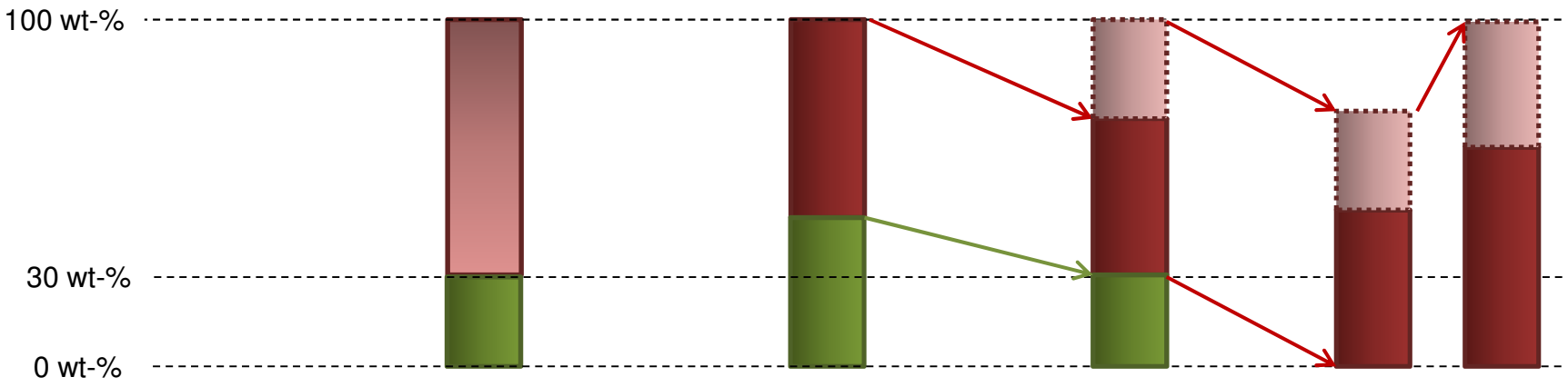
Visible to XRD:

59.9% β-TCP
40.1% int. Std.

(=100%)

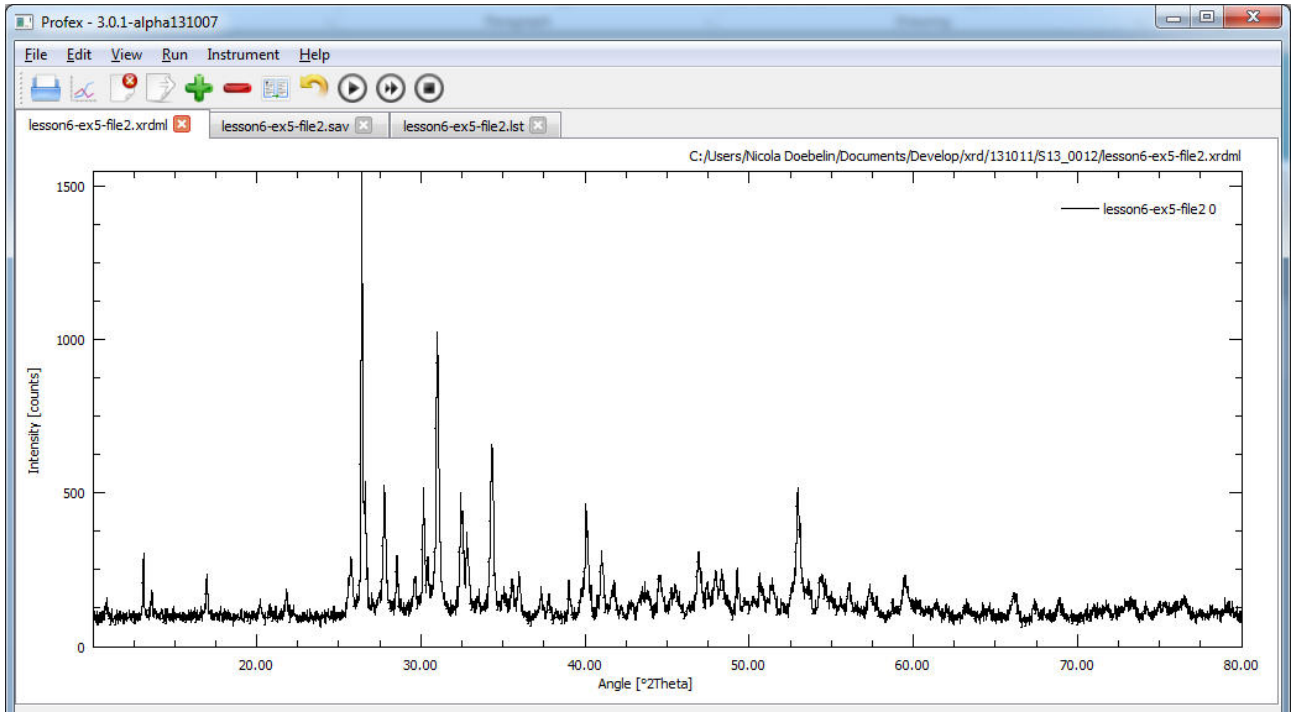
Example 5 – Amorphous Content

Phase	Mixed	Refined	Normalized to int. Std.	Normalized w/o int. Std.
Amorphous	? (Σ = 70.0 wt-%)	-	Fill up to 100% = 25.2 wt-%	36 wt-%
β-TCP	?	59.9 wt-%	59.9 * 0.748 = 44.8 wt-%	64 wt-%
Internal Standard	30.0 wt-%	40.1 wt-%	40.1 * 0.748 = 30.0 wt-%	-

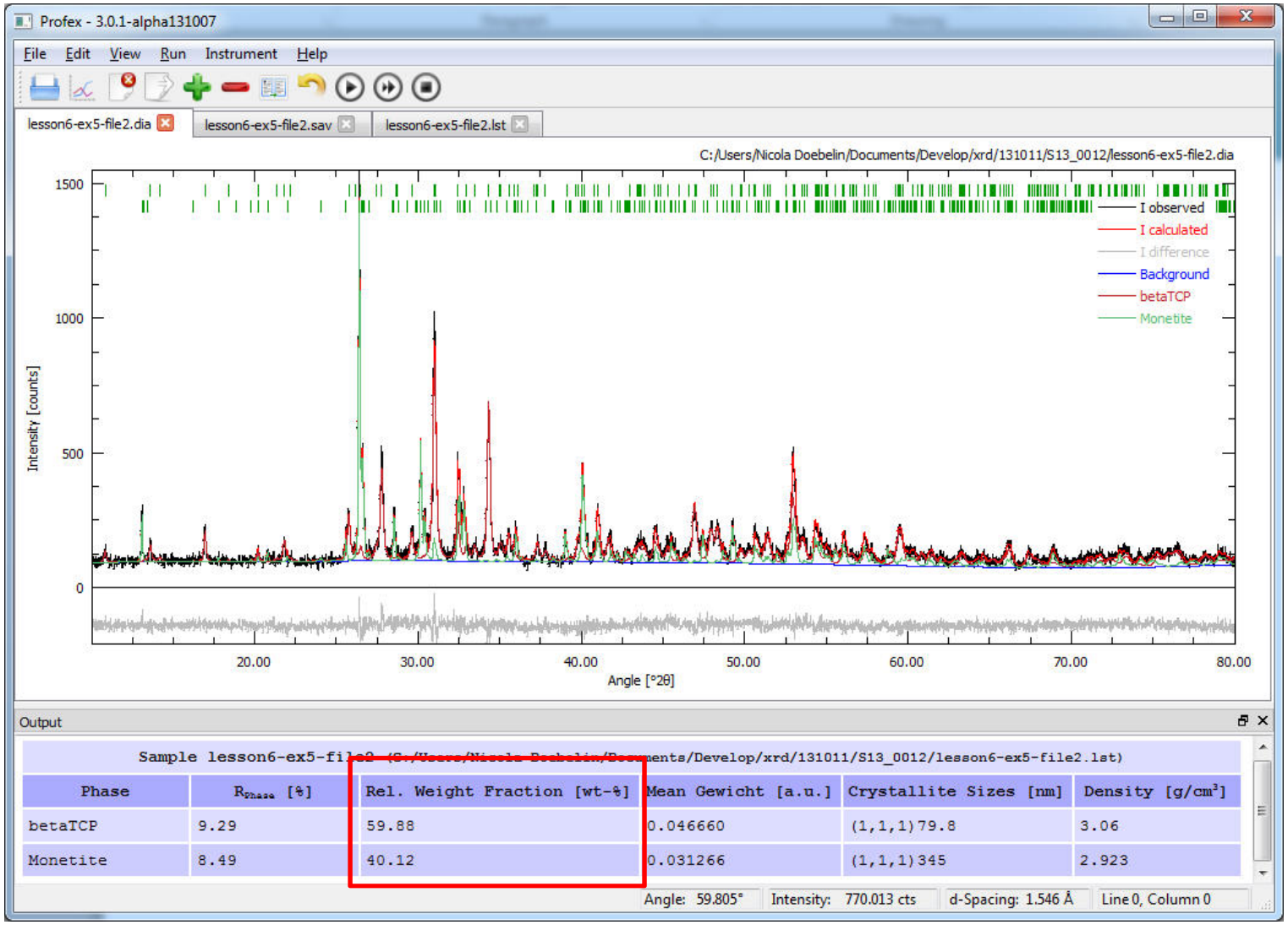


Example 5 – Amorphous Content

Example 5 File 2		
Sample	β-TCP + amorphous phase	70 wt-%
Internal Standard	Monetite	30 wt-%

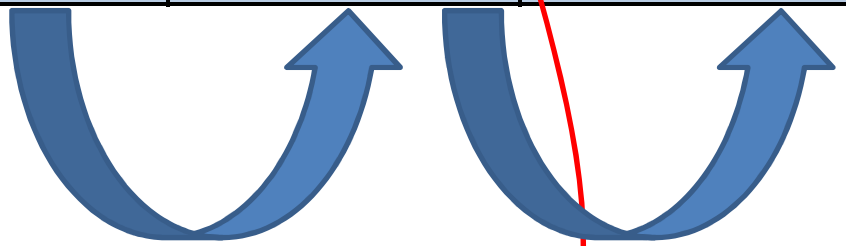


Example 5 – Amorphous Content



Example 5 – Amorphous Content

Phase	Mixed	Refined	Normalized to int. Std.	Normalized w/o int. Std.
Amorphous	?	-	25.22	36.03
b-TCP	?	59.88	44.78	63.97
Internal Standard	30.00	40.12	30.00	-



$* \frac{30.00}{40.12}$

$* \frac{100.00}{70.00}$

Gap between (44.78 + 30)% and 100%

Example 5 – Amorphous Content

Challenge: Selection of internal standard material:

- Must be 100% crystalline
- Simple structure (cubic)
- No texture or micro-absorption problems
- Absorption coefficient similar to matrix
- Absolutely homogeneous mixing
- Must not react with sample matrix

Common materials:

- Si
- LiF

Monetite was a bad choice:

- Triclinic
- Large crystals (micro-absorption)
- Severe texture effects