



Workshop „Rietveld Refinement with Profex“

# Lesson 8: Common Refinement Challenges

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## Refinement Strategy: Words of Wisdom

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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

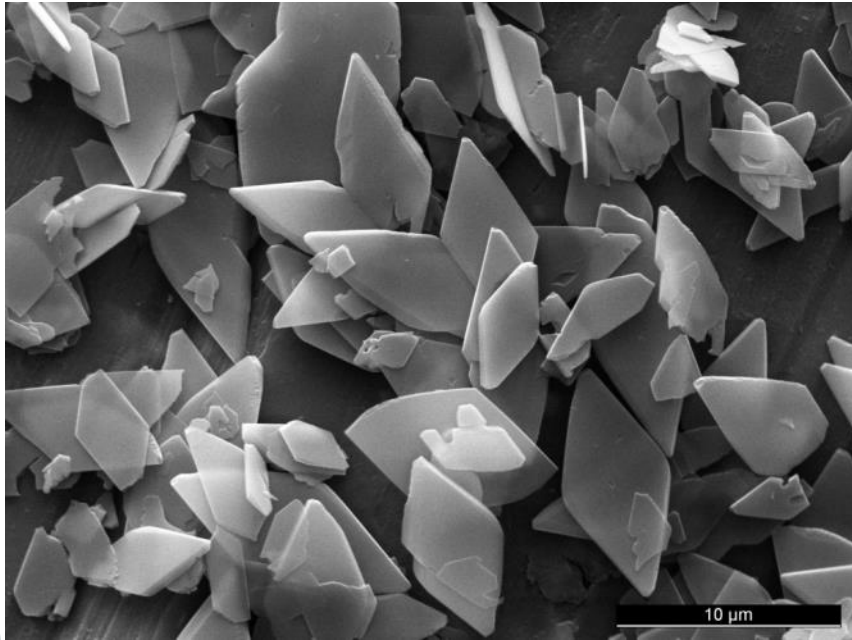
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- ▶ Example 3: Texture, preferred orientation
- ▶ Example 4: Anisotropic crystallite sizes
- ▶ Example 5: Structure refinement and electron density maps

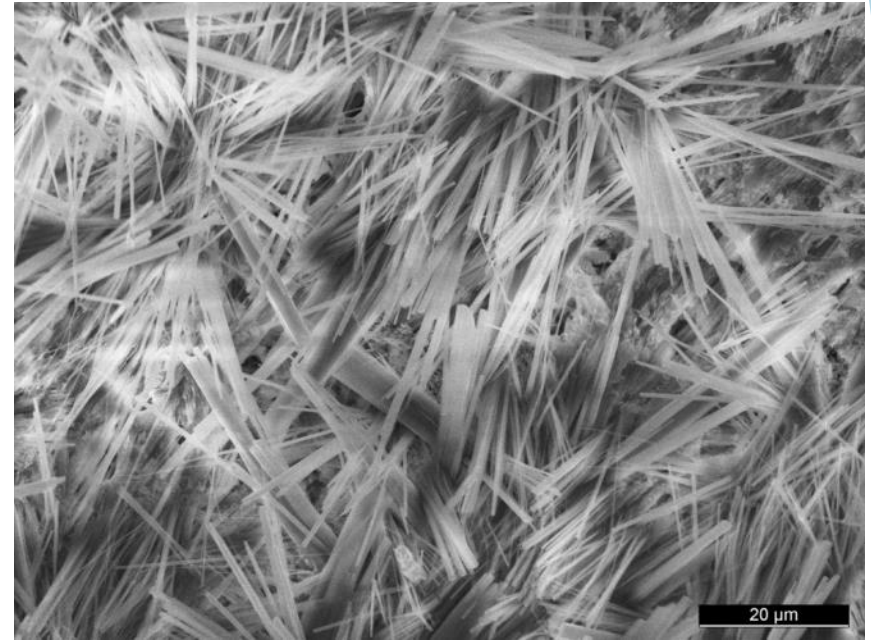


# Texture, Preferred Orientation

Images: L. Galea, RMS Foundation



Platelets lying flat



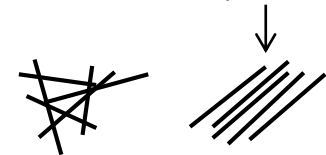
Needles, Fibers, Whiskers lying flat may point in one direction (bundles)



Random orientation



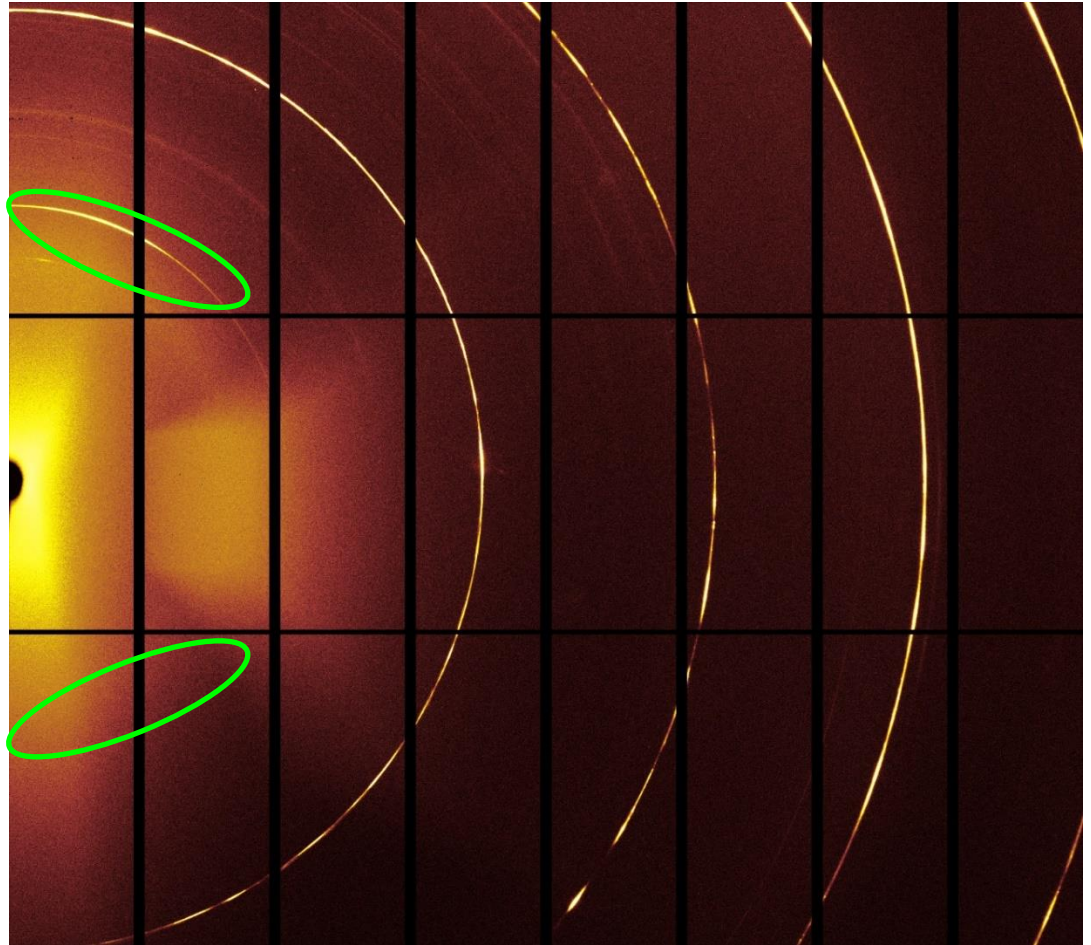
Preferred orientation



# Texture, Preferred Orientation

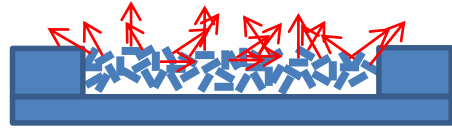
Smooth, but non-continuous  
diffraction rings

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





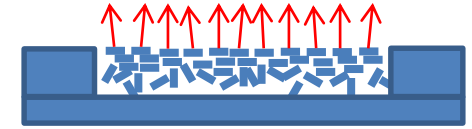
# Texture: Symmetrized Spherical Harmonics



Random density of surface normal vectors

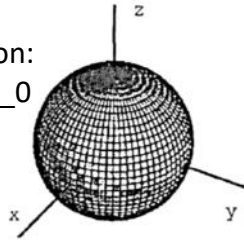
In structure files (\*.str):

GEWICHT=SPHAR $n$   
( $n=0, 2, 4, 6, 8, 10$ )

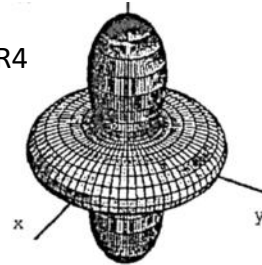


Oriented density of surface normal vectors

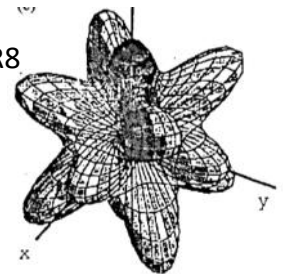
No preferred orientation:  
PARAM=GEWICHT=0.1\_0  
GEWICHT=SPHAR0



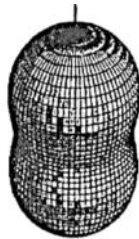
GEWICHT=SPHAR4



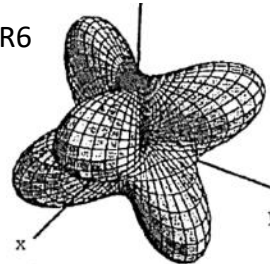
GEWICHT=SPHAR8



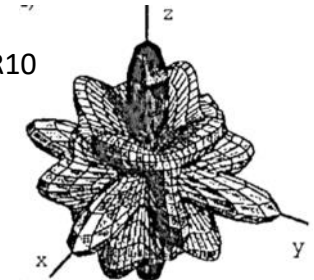
GEWICHT=SPHAR2



GEWICHT=SPHAR6

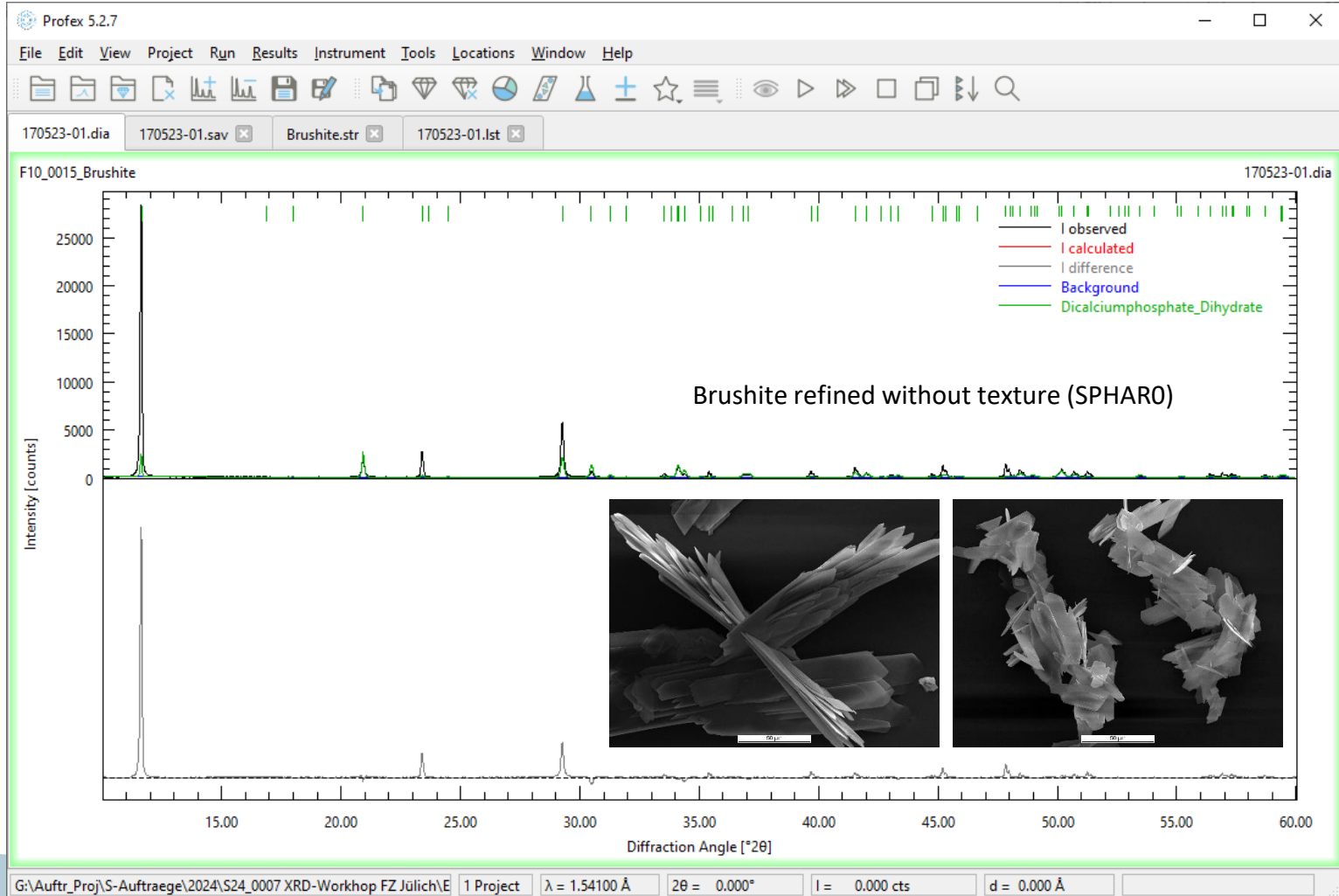


GEWICHT=SPHAR10

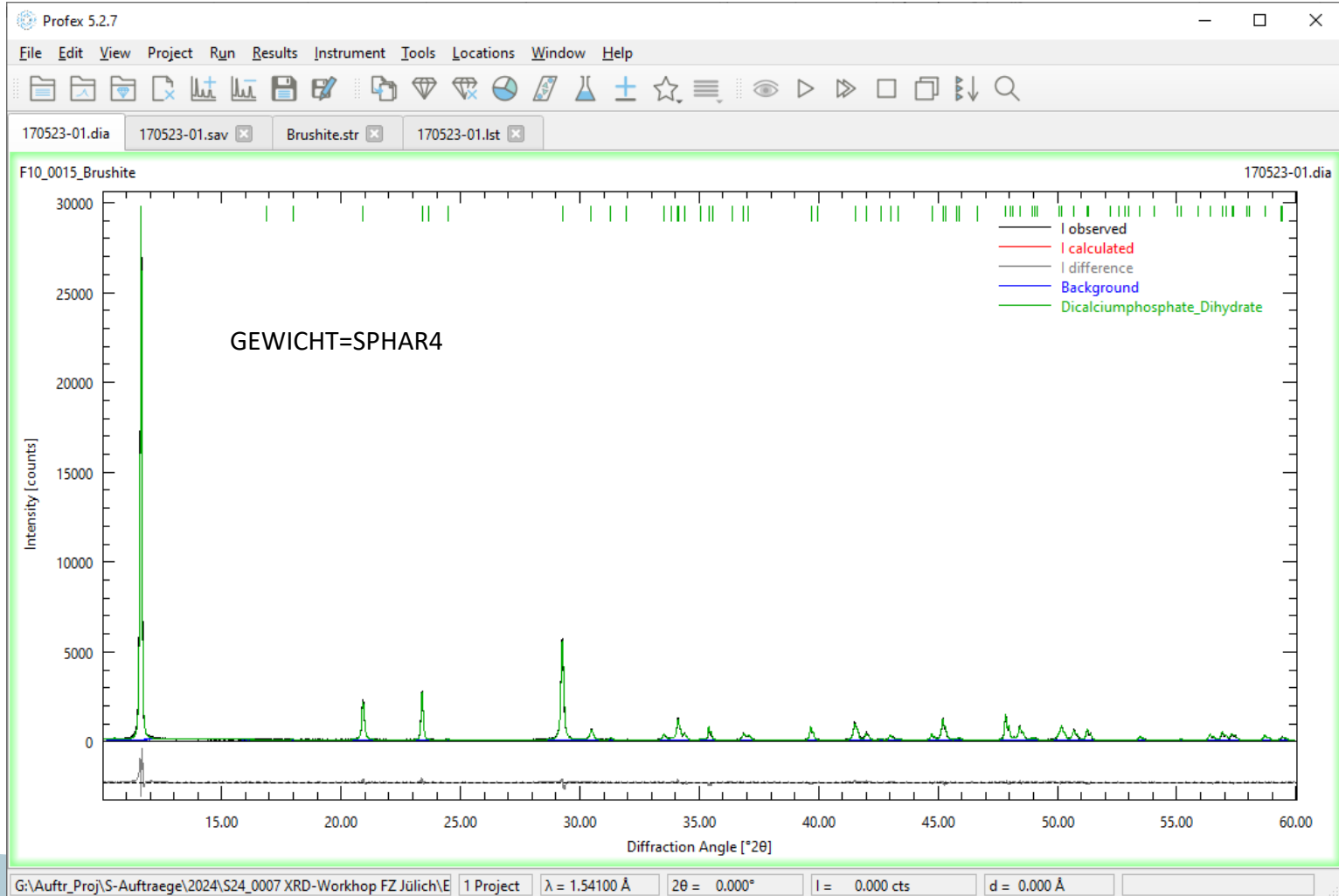


Recommendations: Keep SPHAR $n$  as low as necessary  
Do not exceed SPHAR6

# Texture, Preferred Orientation: Example 3

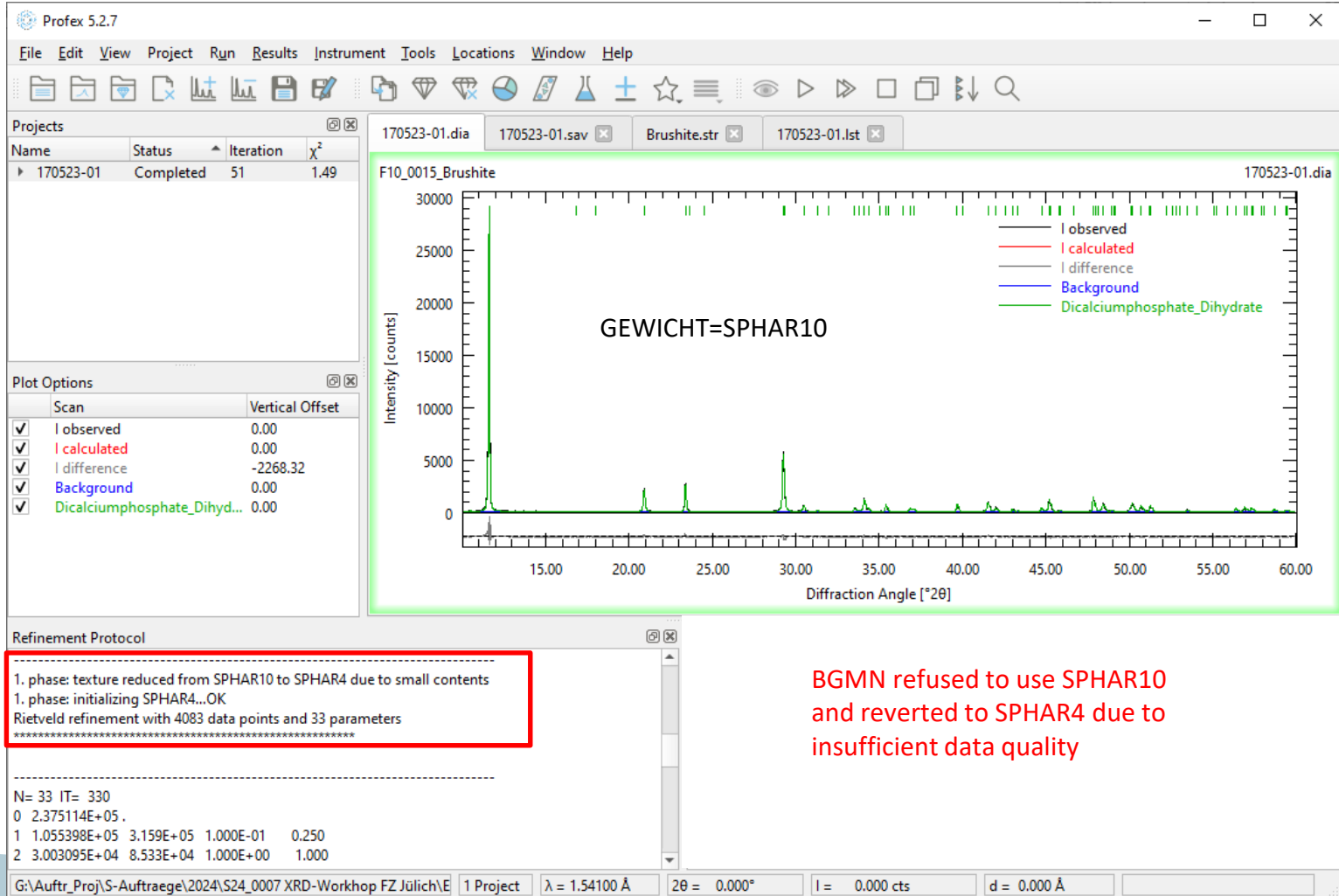


# Texture, Preferred Orientation: Example 3



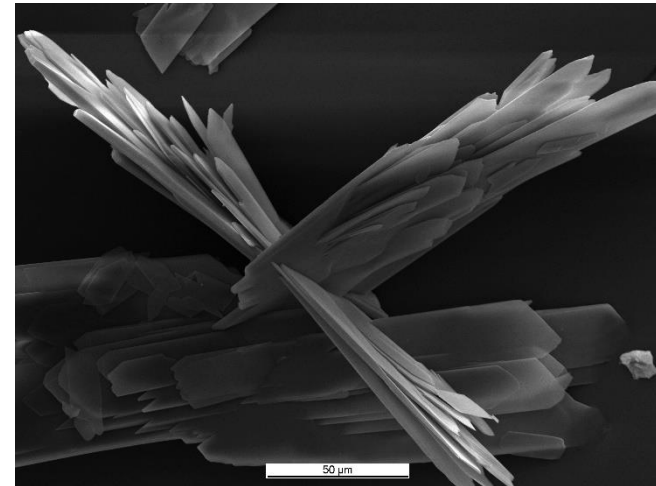


# Texture, Preferred Orientation: Example 3

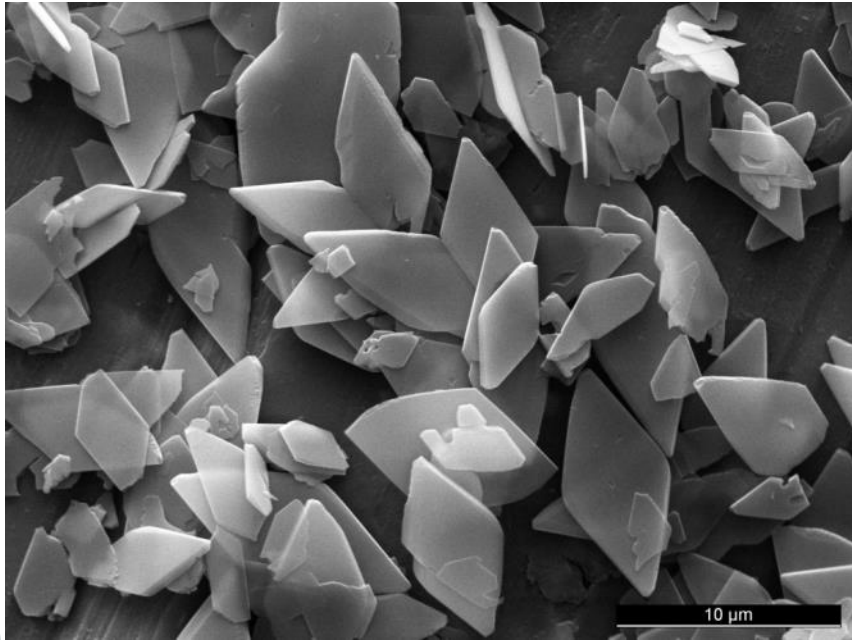


## Summary: Texture, Preferred Orientation

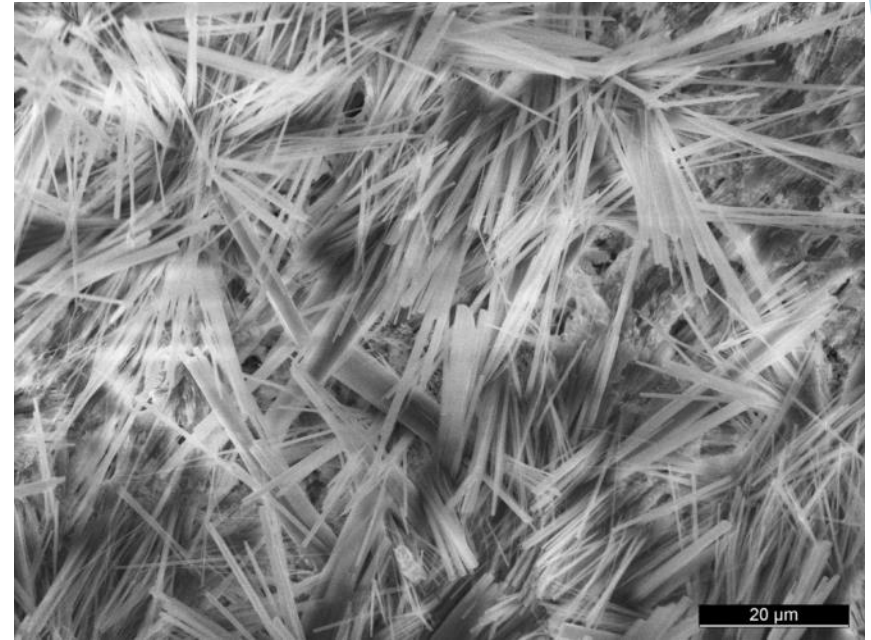
- Refine texture with  $GEWICHT=SPHARn$  if necessary ( $n=0, 2, 4, 6$ )
- Keep  $SPHARn$  as low as necessary (introduces a lot of additional refined parameters)
- Choose  $SPHARn$  based on crystal morphology and cleavage
- High  $SPHARn$  = slow and potentially unstable refinement
- Phase quantification will be biased in case of strong texture
- **Avoid texture by proper sample preparation**



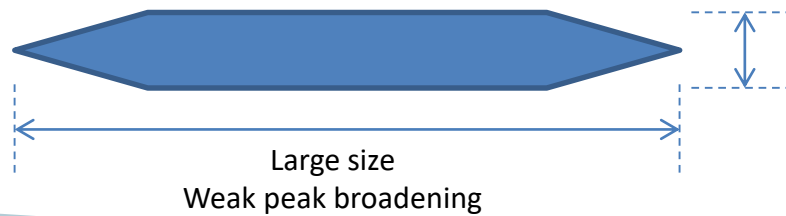
# Anisotropic Crystallite Sizes



Platelets

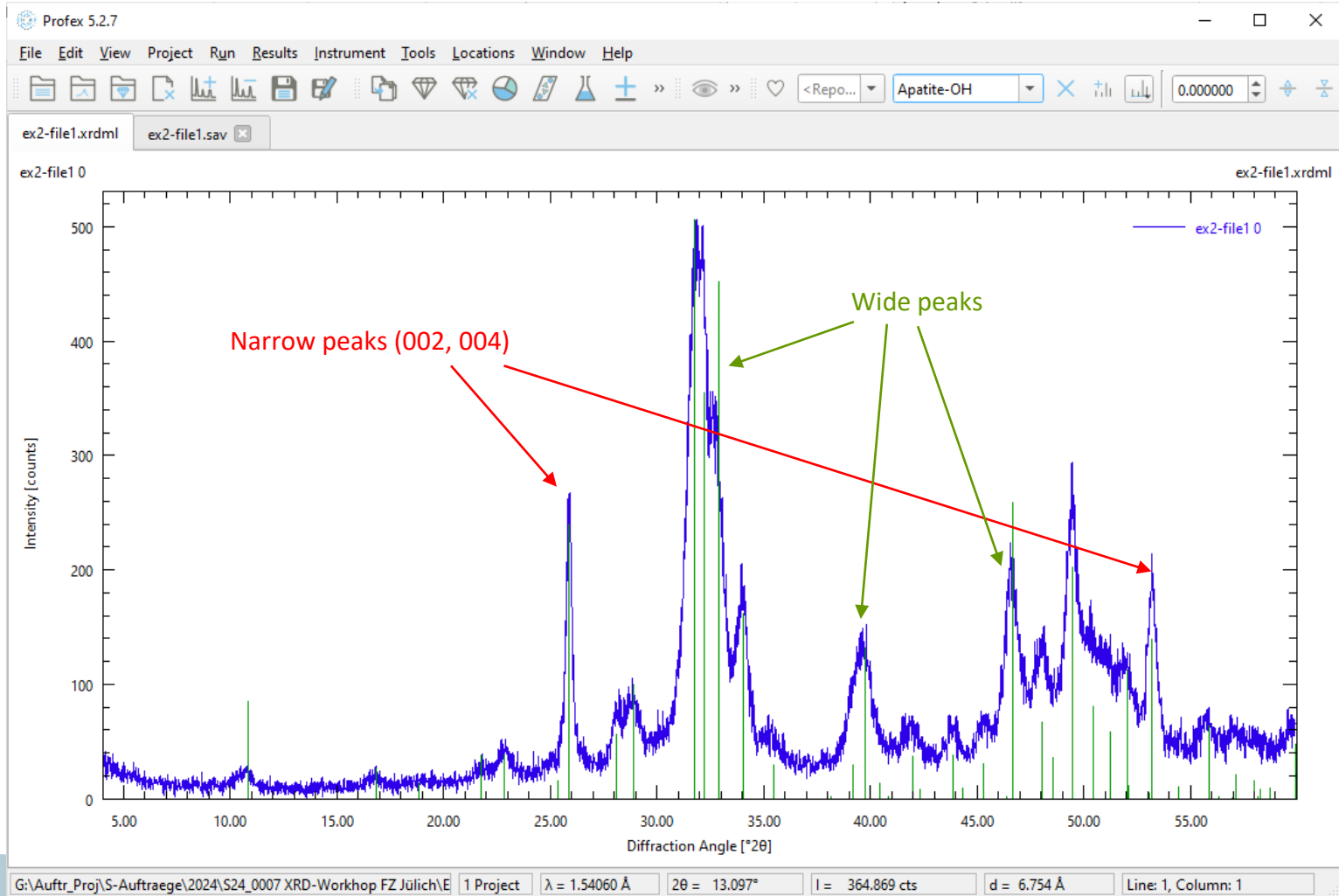


Needles, Fibers, Whiskers

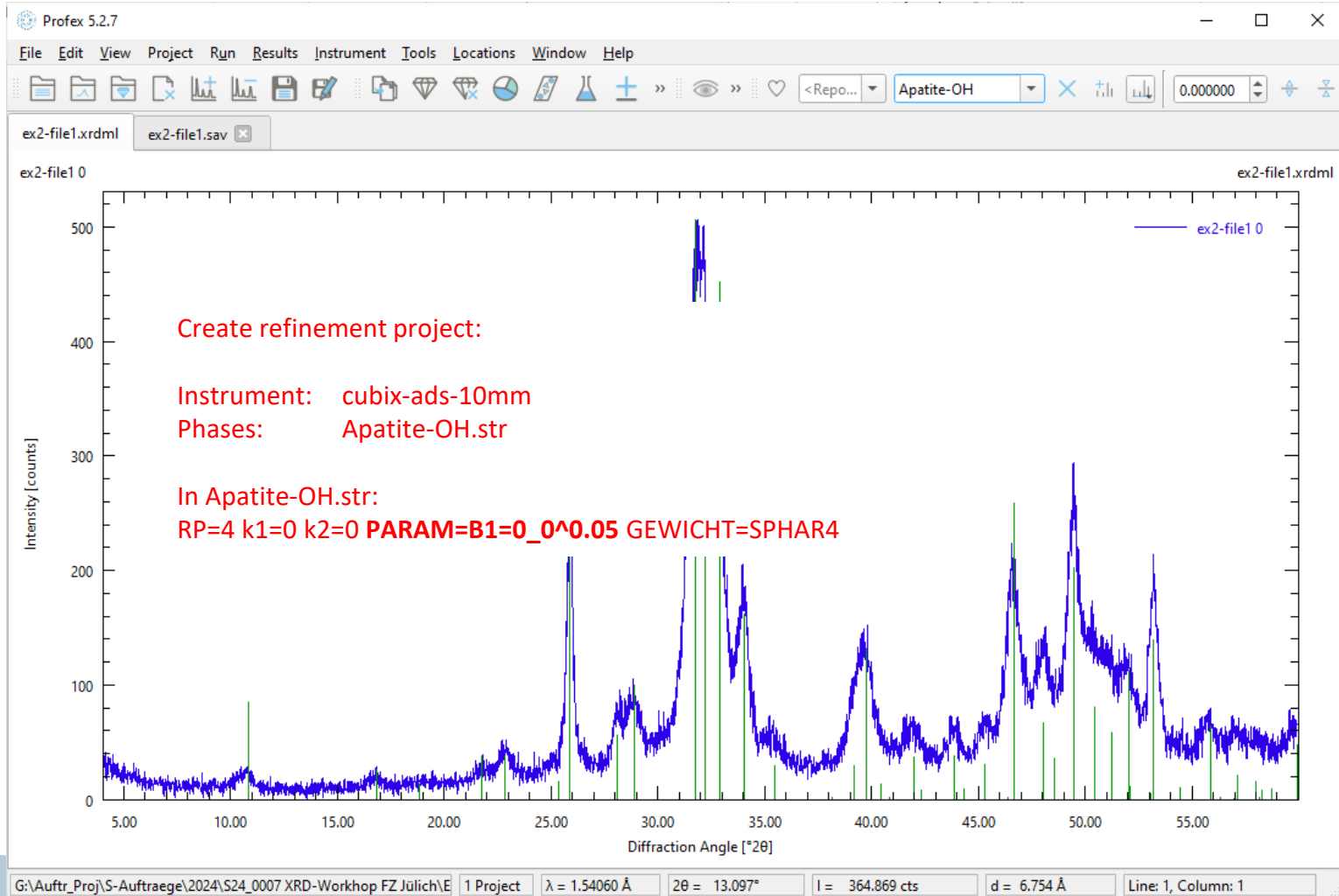


Small size  
Strong peak broadening

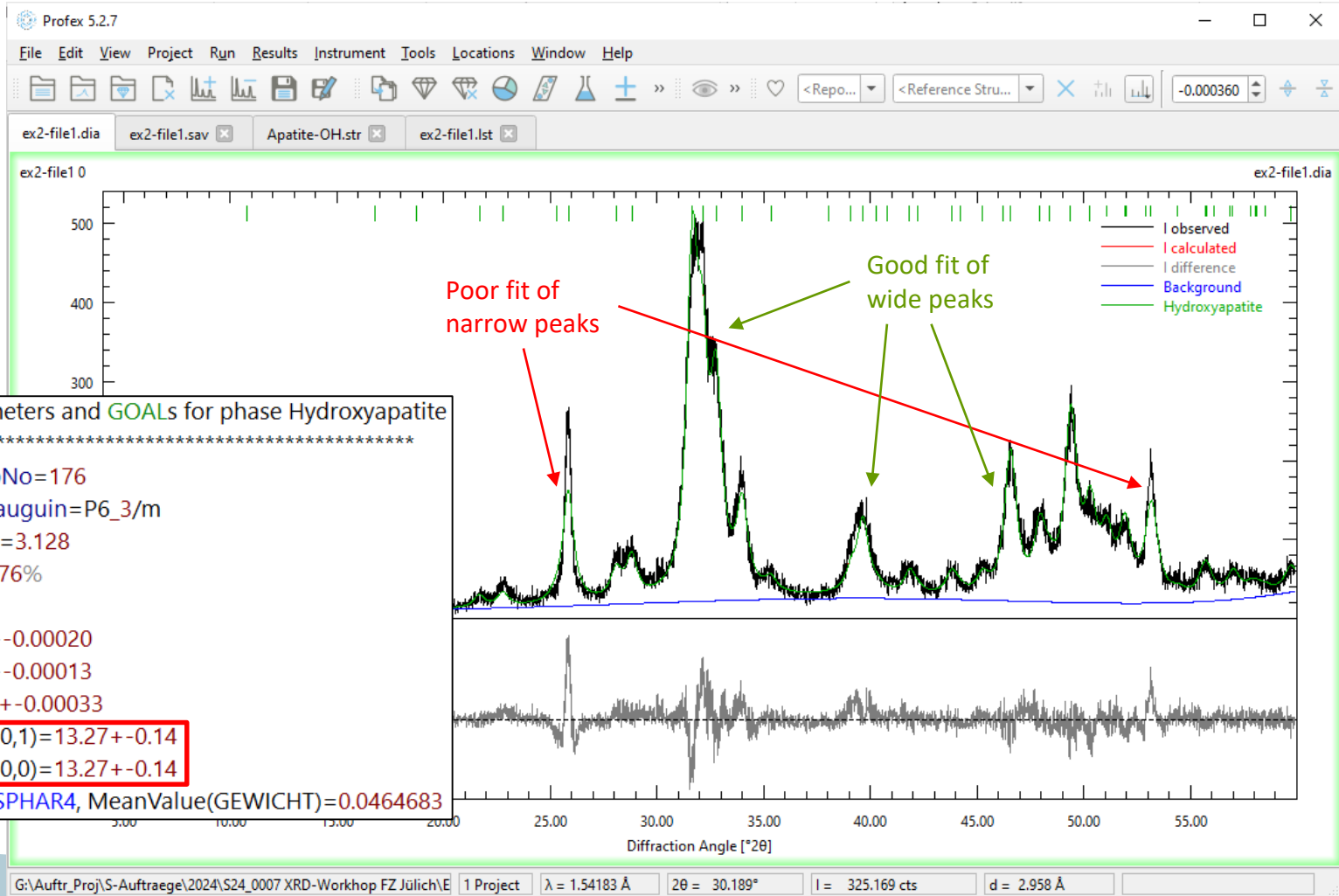
# Anisotropic Crystallite Sizes: Example 4



# Anisotropic Crystallite Sizes: Example 4



# Anisotropic Crystallite Sizes: Example 4





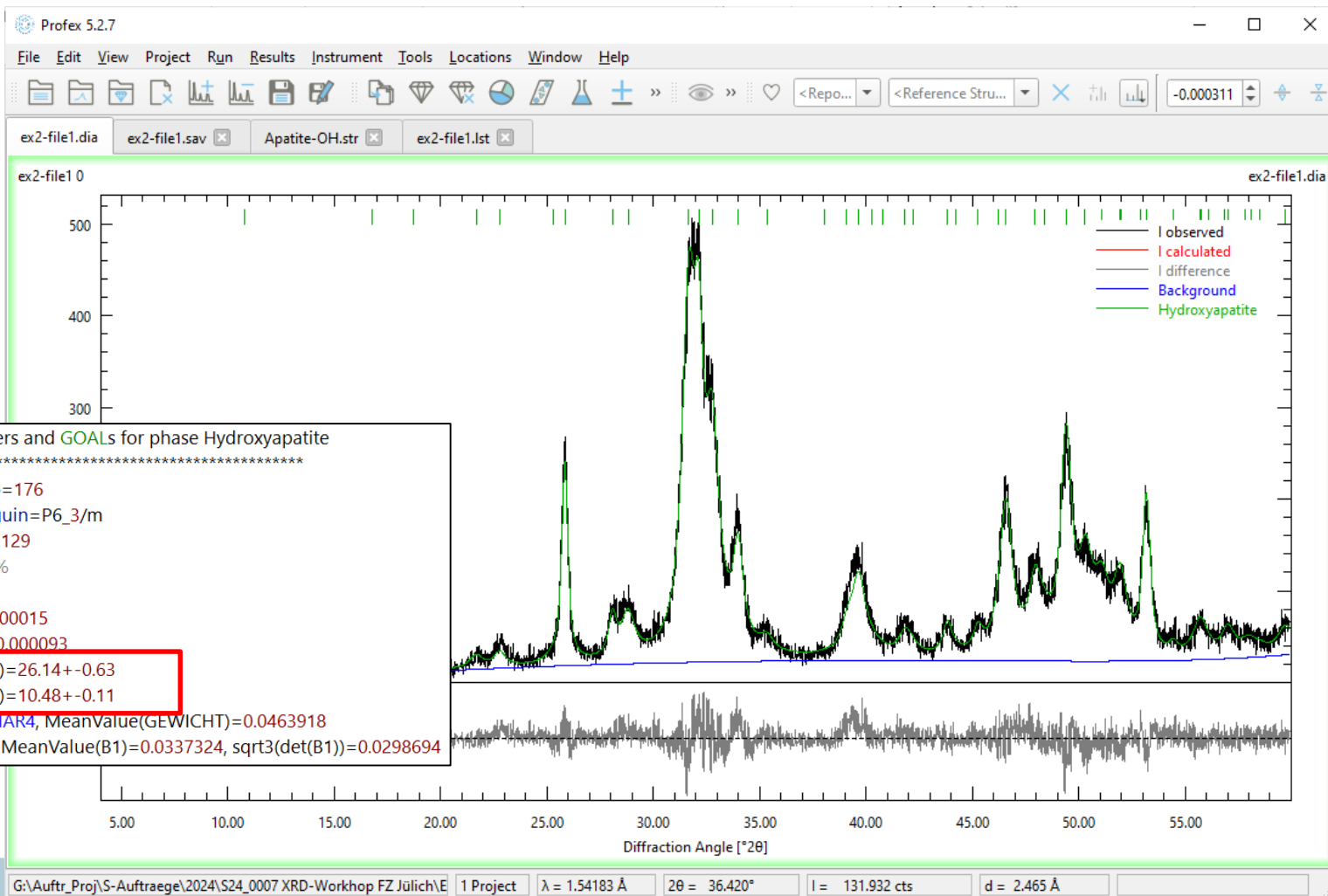
# Anisotropic Crystallite Sizes: Example 4

The screenshot shows the Profex 5.2.7 software interface. The main window displays a list of refinement parameters for a Hydroxyapatite phase. A context menu is open over the parameter `PARAM=B1=0_0^0.05`, with the option `Refine anisotropically` highlighted. The status bar at the bottom shows the current file path, project name, wavelength, 2θ, intensity, d-spacing, and the current line and column.

```
1 PHASE=Hydroxyapatite // 01-074-0565
2 MineralName=Hydroxylapatite //
3 Formula=Ca5_(PO4)3_(OH) //
4 SpacegroupNo=176 HermannMauguin=P6_3/m //
5 PARAM=A=0.9424_0.9330^0.9518 PARAM=C=0.6879_0.6810^0.6948 //
6 RP=4 k1=0 k2=0 PARAM=B1=0_0^0.05 GEWICHT=SPHARA //
7 GOAL=GrainSize(0,0,1) //
8 GOAL=GrainSize(1,0,0) //
9 GOAL:Hydroxyapatite=GEWICHT*iff
10 E=CA Wyckoff=f x=0.3333 y=0.6667 z=0.0000
11 E=CA Wyckoff=h x=0.2468 y=0.9933 z=0.0000
12 E=P Wyckoff=h x=0.3987 y=0.3685 z=0.0000
13 E=O Wyckoff=h x=0.3284 y=0.4848 z=0.0000
14 E=O Wyckoff=h x=0.5873 y=0.4651 z=0.0000
15 E=O Wyckoff=i x=0.3437 y=0.2579 z=0.0000
16 E=O(0.5000) Wyckoff=e x=0.0000 y=0.0000 z=0.0000
17 E=H(0.5000) Wyckoff=e x=0.0000 y=0.0000 z=0.0000
18
```

Profex 5.2.7  
File Edit View Project Run Results Instrument Tools Locations Window Help  
ex2-file1.dia ex2-file1.sav Apatite-OH.str ex2-file1.lst  
G:\Auftr\_Proj\S-Auftraege\2024\S24\_0007 XRD-Workshop FZ Jülich\E 1 Project λ = 1.54183 Å 2θ = 0.000° I = 0.000 cts d = 0.000 Å Line: 6, Column: 29

# Anisotropic Crystallite Sizes: Example 4



# Anisotropic Crystallite Sizes: Example 4

Anisotropic crystallite size, no micro-strain:

k1=0  
k2=0  
B1=ANISO^0.05  
GEWICHT=SPHAR4

```
Local parameters and GOALS for phase Hydroxyapatite
*****
SpacegroupNo=176
HermannMauguin=P6_3/m
XrayDensity=3.129
Rphase=11.89%
UNIT=NM
A=0.94561+-0.00015
C=0.688477+-0.000093
GrainSize(0,0,1)=26.14+-0.63
GrainSize(1,0,0)=10.48+-0.11
GEWICHT=SPHAR4, MeanValue(GEWICHT)=0.0463918
B1=ANISOLIN, MeanValue(B1)=0.0337324, sqrt3(det(B1))=0.0298694
```

Anisotropic crystallite size, isotropic micro-strain:

k1=0  
PARAM=k2=0\_0^0.0001  
B1=ANISO^0.05  
GEWICHT=SPHAR6

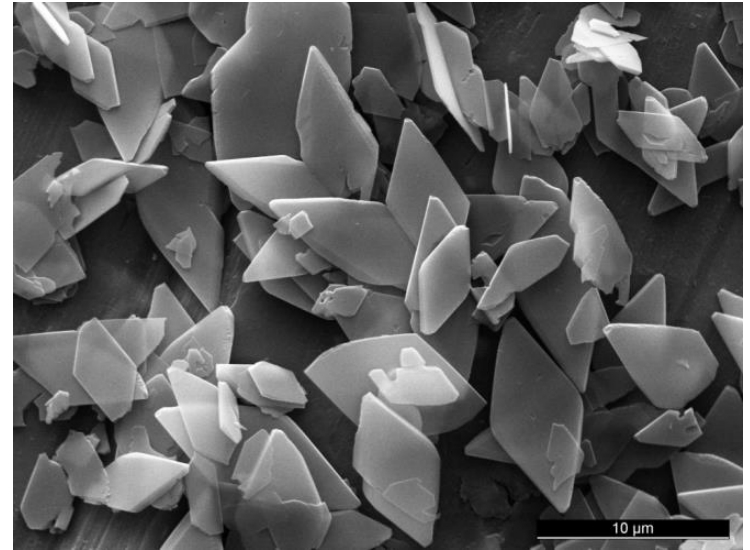
```
Local parameters and GOALS for phase Hydroxyapatite
*****
SpacegroupNo=176
HermannMauguin=P6_3/m
XrayDensity=3.130
Rphase=11.26%
UNIT=NM
A=0.94552+-0.00015
C=0.68838+-0.00010
k2=0.0000170+-0.0000020
GrainSize(0,0,1)=43.9+-2.9
GrainSize(1,0,0)=12.18+-0.23
GEWICHT=SPHAR6, MeanValue(GEWICHT)=0.0453694
B1=ANISOLIN, MeanValue(B1)=0.0282312, sqrt3(det(B1))=0.0227333
```

Warning: Strong correlation between crystallite size (B1) and micro-strain (k2)

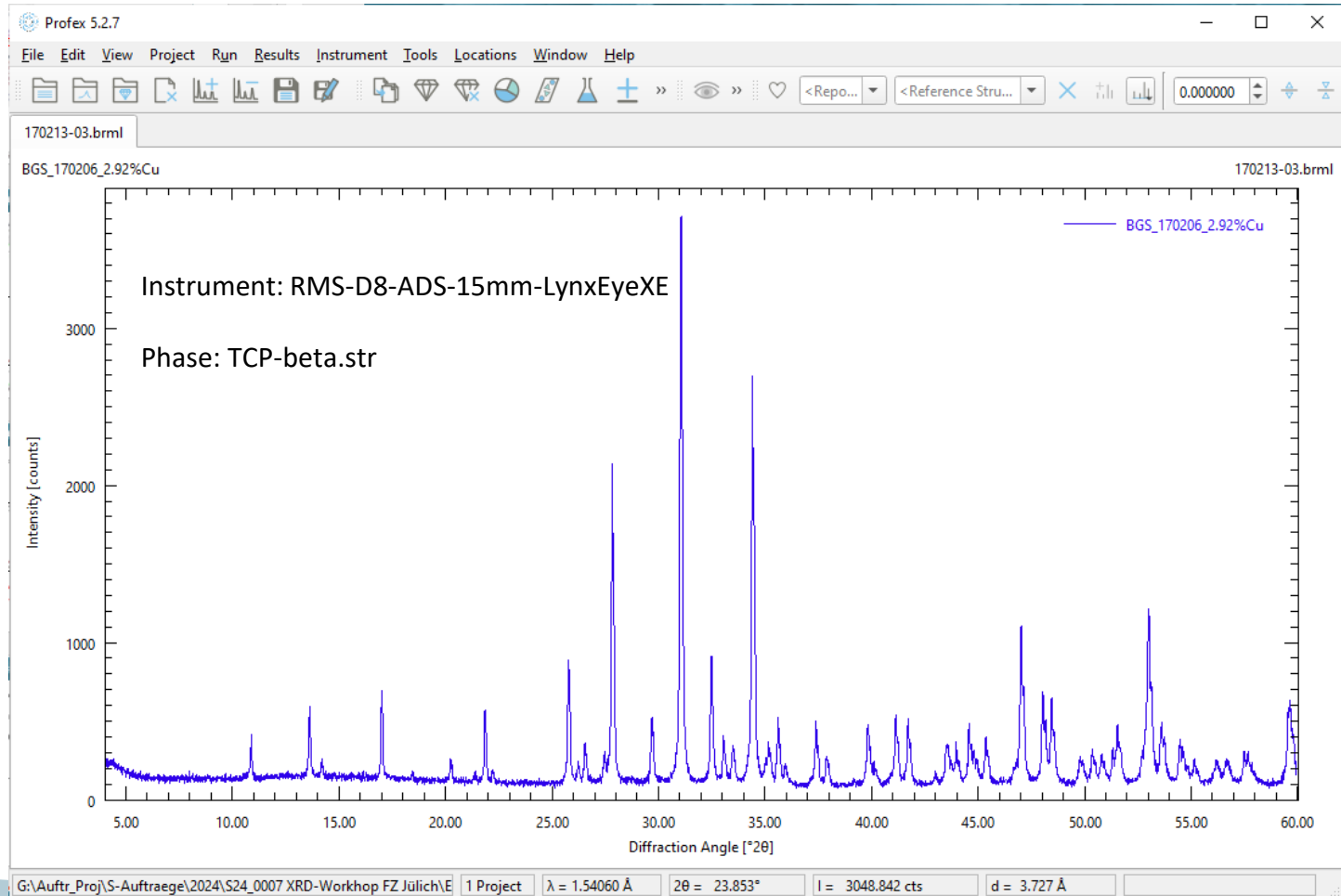
Reduce the correlation by measuring up to high 2θ angles

## Anisotropic Crystallite Sizes: Summary

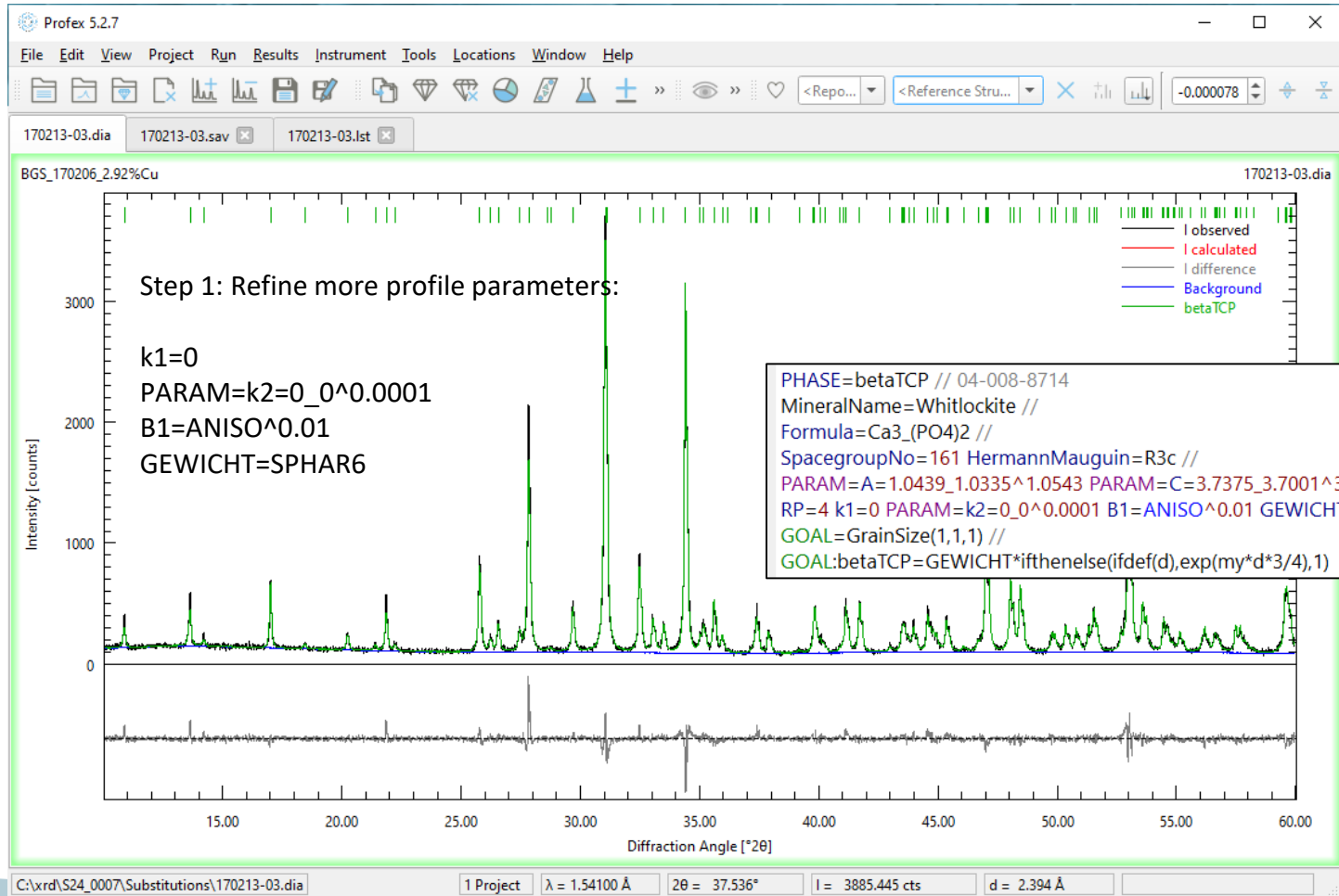
- ▶ Expected for platelet- / needle- / rod-shaped crystals
- ▶ Refined through  $B1=ANISO$  parameter
- ▶ Only use if really necessary (improvement of fit observed)
- ▶ Can be reduced to isotropic automatically by BGMN
- ▶ May correlate with  $k2$  parameter



# Structure Refinement and Electron Density Maps

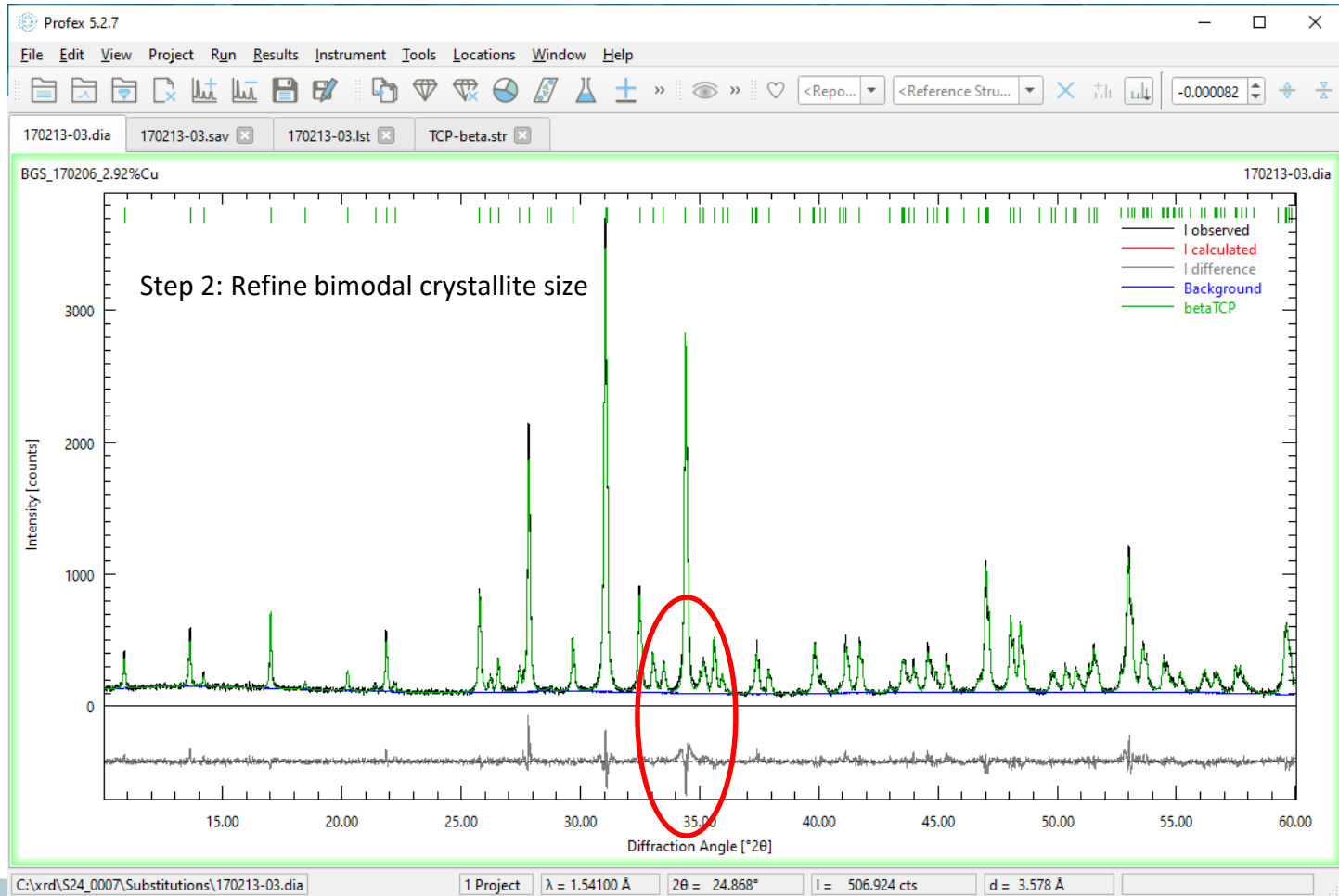


# Structure Refinement and Electron Density Maps





# Structure Refinement and Electron Density Maps



# Structure Refinement and Electron Density Maps

Profex 5.2.7

File Edit View Project Run Results Instrument Tools Locations Window Help

170213-03.dia 170213-03.sav 170213-03.lst TCP-beta.str\*

2b

Bi-modal crystallite size (STR)  
Override SPHAR limits (STR)  
Sample height displacement (SAV)

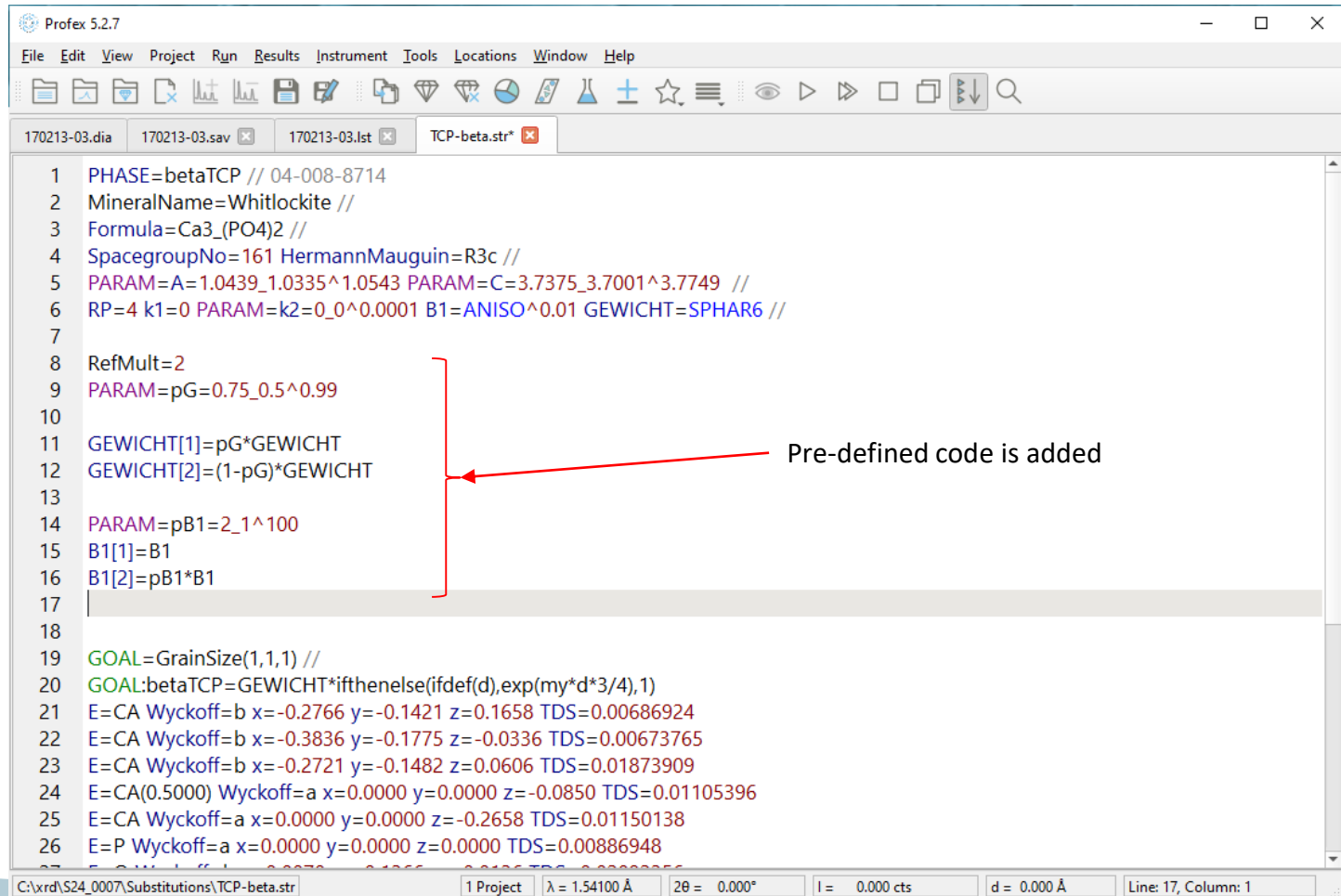
2a

```
1 PHASE=betaTCP // 04-008-8714
2 MineralName=Whitlockite //
3 Formula=Ca3_(PO4)2 //
4 SpacegroupNo=161 HermannMauguin=R3c //
5 PARAM=A=1.0439_1.0335^1.0543 PARAM=C=3.7375_3.7001^3.7749 //
6 RP=4 k1=0 PARAM=k2=0_0^0.0001 B1=ANISO^0.01 GEWICHT=SPHAR6 //
7
8
9
10 GOAL=GrainSize(1,1,1) //
11 GOAL:betaTCP=GEWICHT*ifthenelse(ifdef(d),exp(my*d*3/4),1)
12 E=CA Wyckoff=b x=-0.2766 y=-0.1421 z=0.1658 TDS=0.00686924
13 E=CA Wyckoff=b x=-0.3836 y=-0.1775 z=-0.0336 TDS=0.00673765
14 E=CA Wyckoff=b x=-0.2721 y=-0.1482 z=0.0606 TDS=0.01873909
15 E=CA(0.5000) Wyckoff=a x=0.0000 y=0.0000 z=-0.0850 TDS=0.01105396
16 E=CA Wyckoff=a x=0.0000 y=0.0000 z=-0.2658 TDS=0.01150138
17 E=P Wyckoff=a x=0.0000 y=0.0000 z=0.0000 TDS=0.00886948
18 E=O Wyckoff=b x=0.0070 y=-0.1366 z=-0.0136 TDS=0.02092356
19 E=O Wyckoff=a x=0.0000 y=0.0000 z=0.0400 TDS=0.02031823
20 E=P Wyckoff=b x=-0.3109 y=-0.1365 z=-0.1320 TDS=0.00802728
21 E=O Wyckoff=b x=-0.2736 y=-0.0900 z=-0.0926 TDS=0.02473981
22 E=O Wyckoff=b x=-0.2302 y=-0.2171 z=-0.1446 TDS=0.02316067
23 E=O Wyckoff=b x=-0.2735 y=0.0053 z=-0.1523 TDS=0.00752722
24 E=O Wyckoff=b x=-0.4777 y=-0.2392 z=-0.1378 TDS=0.01652830
25 E=P Wyckoff=b x=-0.3465 y=-0.1537 z=-0.2333 TDS=0.00526379
26 E=O Wyckoff=b x=-0.4031 y=-0.0489 z=-0.2211 TDS=0.01118555
```

C:\xrd\S24\_0007\Substitutions\TCP-beta.str 1 Project  $\lambda = 1.54100 \text{ \AA}$   $2\theta = 0.000^\circ$  I = 0.000 cts d = 0.000  $\text{\AA}$  Line: 8, Column: 1

Step 2a: Create some space after the profile parameters  
Step 2b: insert the pre-defined text block „Bi-modal crystallite size“

# Structure Refinement and Electron Density Maps

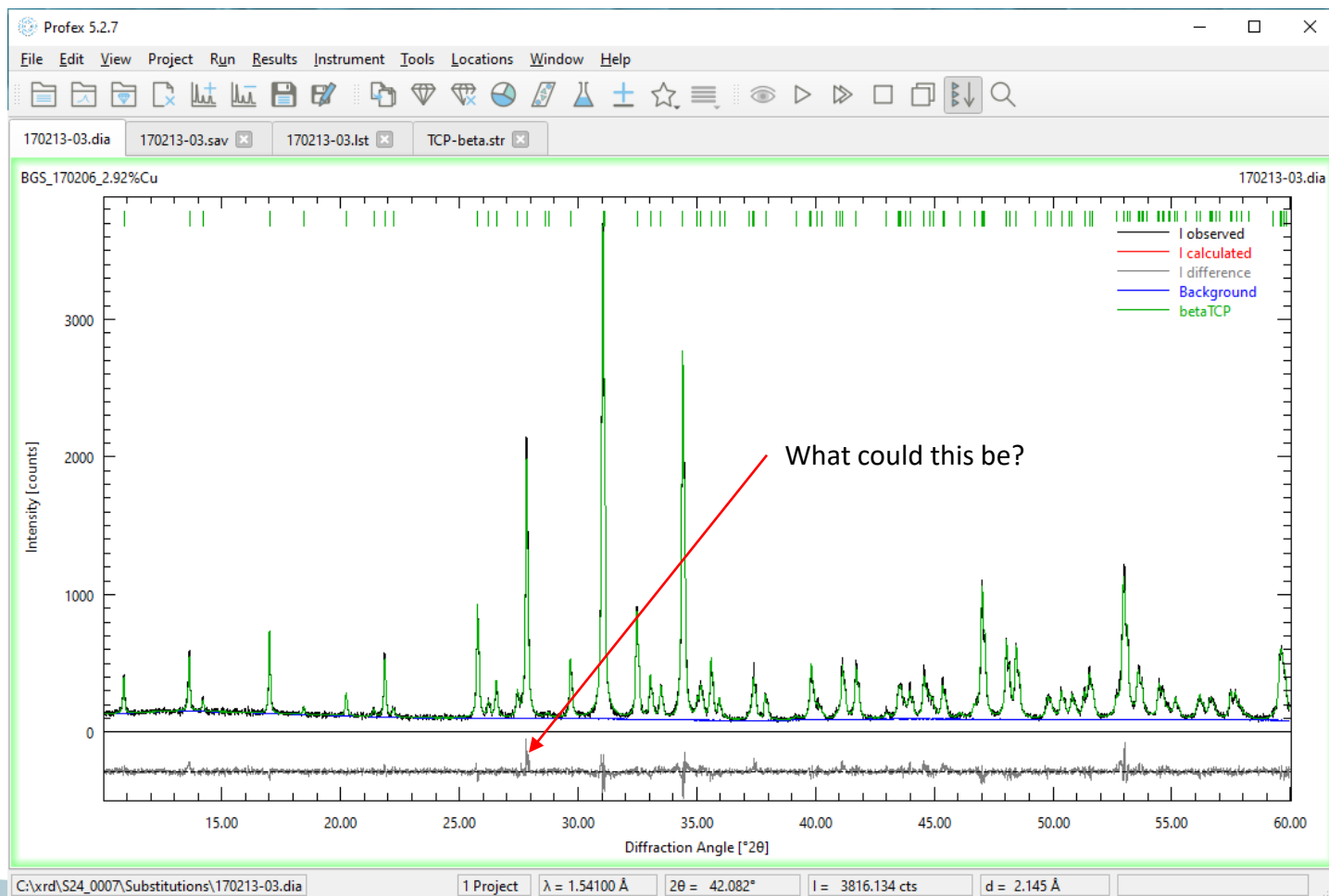


```
1 PHASE=betaTCP // 04-008-8714
2 MineralName=Whitlockite //
3 Formula=Ca3_(PO4)2 //
4 SpacegroupNo=161 HermannMauguin=R3c //
5 PARAM=A=1.0439_1.0335^1.0543 PARAM=C=3.7375_3.7001^3.7749 //
6 RP=4 k1=0 PARAM=k2=0_0^0.0001 B1=ANISO^0.01 GEWICHT=SPHAR6 //
7
8 RefMult=2
9 PARAM=pG=0.75_0.5^0.99
10
11 GEWICHT[1]=pG*GEWICHT
12 GEWICHT[2]=(1-pG)*GEWICHT
13
14 PARAM=pB1=2_1^100
15 B1[1]=B1
16 B1[2]=pB1*B1
17
18
19 GOAL=GrainSize(1,1,1) //
20 GOAL:betaTCP=GEWICHT*ifthenelse(ifdef(d),exp(my*d*3/4),1)
21 E=CA Wyckoff=b x=-0.2766 y=-0.1421 z=0.1658 TDS=0.00686924
22 E=CA Wyckoff=b x=-0.3836 y=-0.1775 z=-0.0336 TDS=0.00673765
23 E=CA Wyckoff=b x=-0.2721 y=-0.1482 z=0.0606 TDS=0.01873909
24 E=CA(0.5000) Wyckoff=a x=0.0000 y=0.0000 z=-0.0850 TDS=0.01105396
25 E=CA Wyckoff=a x=0.0000 y=0.0000 z=-0.2658 TDS=0.01150138
26 E=P Wyckoff=a x=0.0000 y=0.0000 z=0.0000 TDS=0.00886948
```

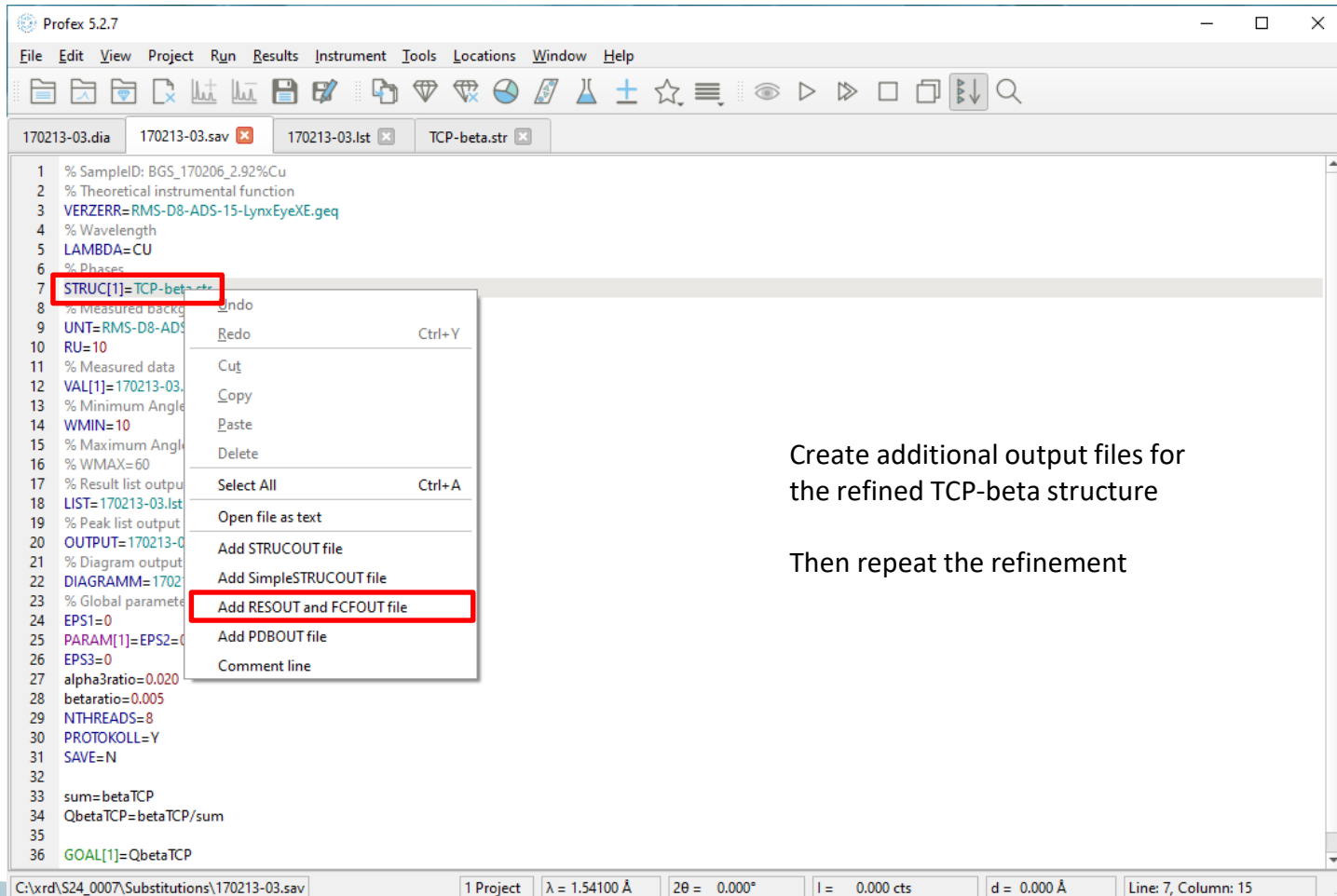
Pre-defined code is added

C:\xrd\S24\_0007\Substitutions\TCP-beta.str | 1 Project | λ = 1.54100 Å | 2θ = 0.000° | I = 0.000 cts | d = 0.000 Å | Line: 17, Column: 1

# Structure Refinement and Electron Density Maps



# Structure Refinement and Electron Density Maps



Profex 5.2.7

File Edit View Project Run Results Instrument Tools Locations Window Help

170213-03.dia 170213-03.sav 170213-03.lst TCP-beta.str

```
1 % SampleID: BGS_170206_2.92%Cu
2 % Theoretical instrumental function
3 VERZERR=RMS-D8-ADS-15-LynxEyeXE.geq
4 % Wavelength
5 LAMBDA=CU
6 % Phases
7 STRUC[1]=TCP-beta
8 % Measured background
9 UNT=RMS-D8-ADS-15-LynxEyeXE.geq
10 RU=10
11 % Measured data
12 VAL[1]=170213-03.dia
13 % Minimum Angle
14 WMIN=10
15 % Maximum Angle
16 WMAX=60
17 % Result list output
18 LIST=170213-03.lst
19 % Peak list output
20 OUTPUT=170213-03.lst
21 % Diagram output
22 DIAGRAMM=170213-03.dia
23 % Global parameters
24 EPS1=0
25 PARAM[1]=EPS2=0
26 EPS3=0
27 alpha3ratio=0.020
28 betaratio=0.005
29 NTHREADS=8
30 PROTOKOLL=Y
31 SAVE=N
32
33 sum=betaTCP
34 QbetaTCP=betaTCP/sum
35
36 GOAL[1]=QbetaTCP
```

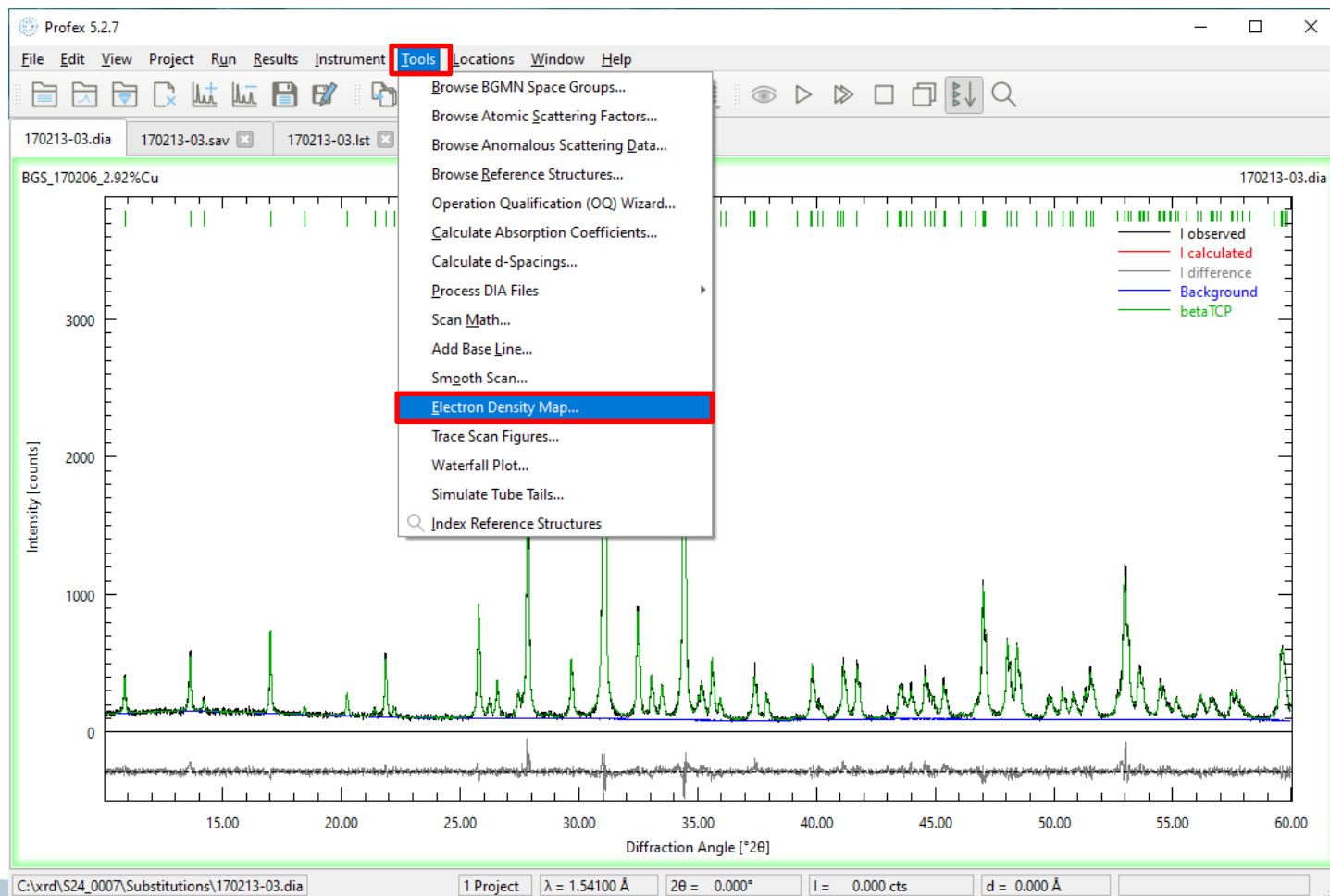
Undo  
Redo Ctrl+Y  
Cut  
Copy  
Paste  
Delete  
Select All Ctrl+A  
Open file as text  
Add STRUCOUT file  
Add SimpleSTRUCOUT file  
Add RESOUT and FCFOUT file  
Add PDBOUT file  
Comment line

C:\xrd\S24\_0007\Substitutions\170213-03.sav 1 Project  $\lambda = 1.54100 \text{ \AA}$   $2\theta = 0.000^\circ$  I = 0.000 cts d = 0.000  $\text{\AA}$  Line: 7, Column: 15

Create additional output files for the refined TCP-beta structure

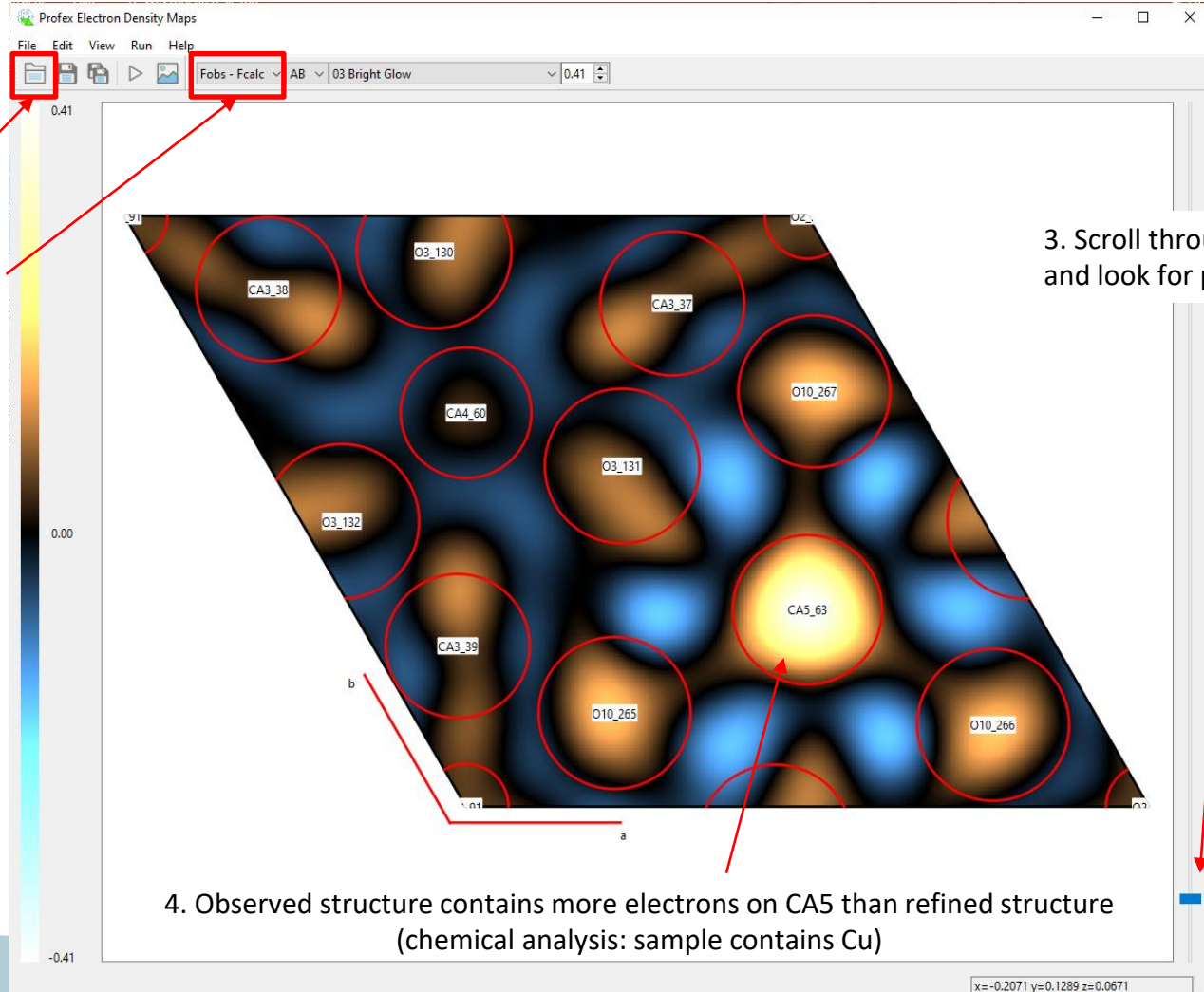
Then repeat the refinement

# Structure Refinement and Electron Density Maps





# Structure Refinement and Electron Density Maps



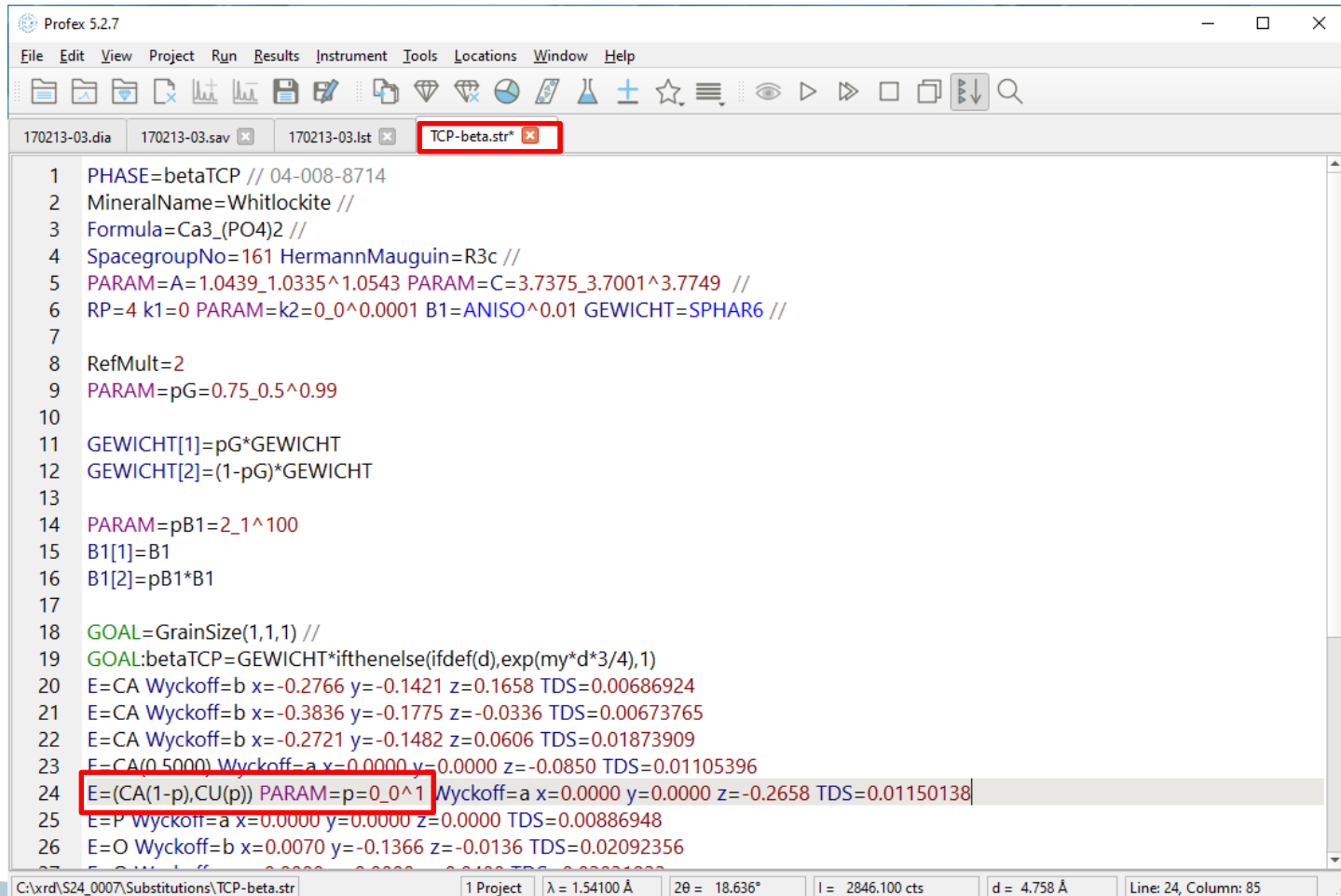
1. Load \*.fcf file

2. Set to Fobs - Fcalc

3. Scroll through the structure and look for peaks or holes

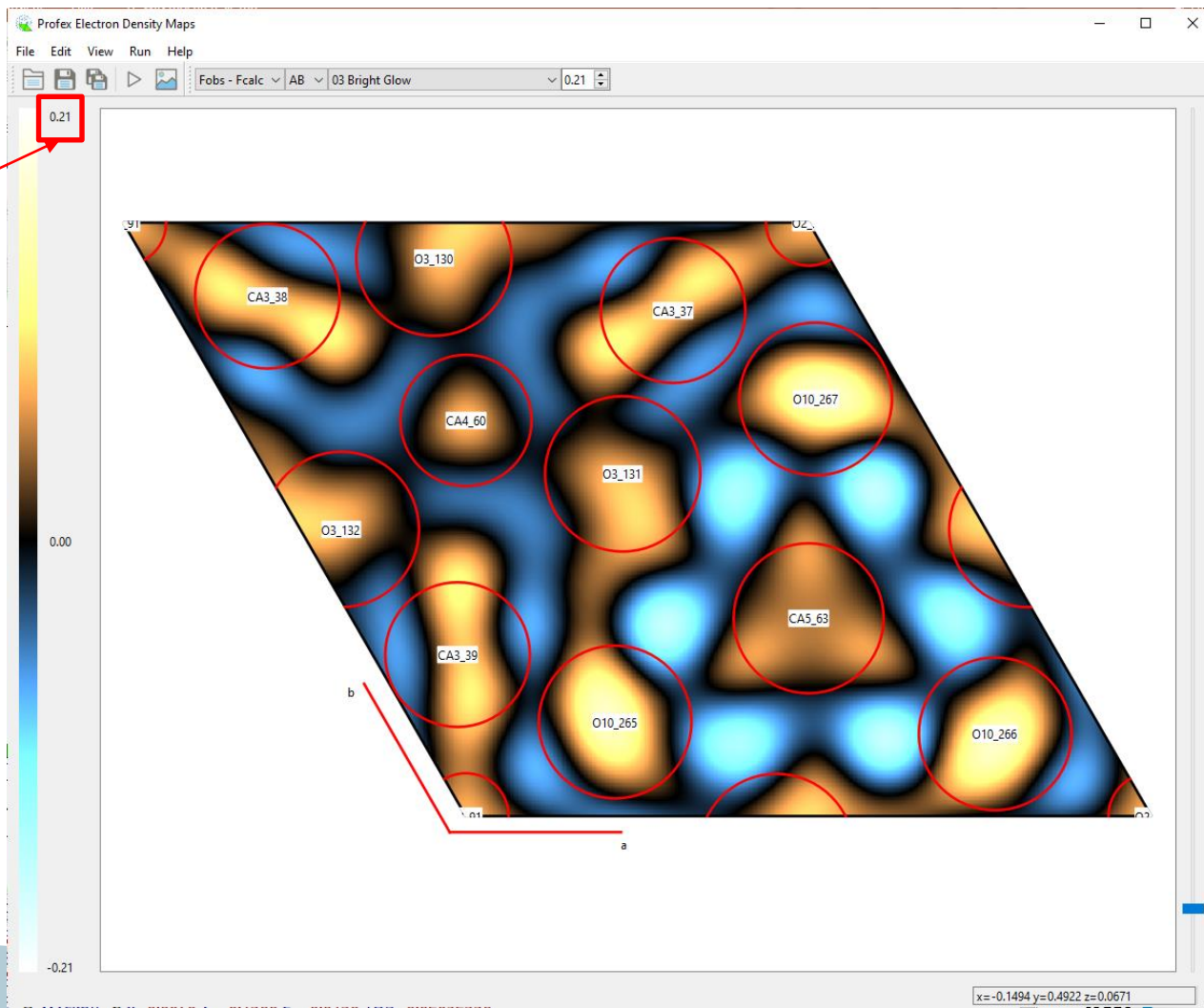
4. Observed structure contains more electrons on CA5 than refined structure (chemical analysis: sample contains Cu)

# Structure Refinement and Electron Density Maps



```
Profex 5.2.7
File Edit View Project Run Results Instrument Tools Locations Window Help
170213-03.dia 170213-03.sav 170213-03.lst TCP-beta.str
1 PHASE=betaTCP // 04-008-8714
2 MineralName=Whitlockite //
3 Formula=Ca3_(PO4)2 //
4 SpacegroupNo=161 HermannMauguin=R3c //
5 PARAM=A=1.0439_1.0335^1.0543 PARAM=C=3.7375_3.7001^3.7749 //
6 RP=4 k1=0 PARAM=k2=0_0^0.0001 B1=ANISO^0.01 GEWICHT=SPHAR6 //
7
8 RefMult=2
9 PARAM=pG=0.75_0.5^0.99
10
11 GEWICHT[1]=pG*GEWICHT
12 GEWICHT[2]=(1-pG)*GEWICHT
13
14 PARAM=pB1=2_1^100
15 B1[1]=B1
16 B1[2]=pB1*B1
17
18 GOAL=GrainSize(1,1,1) //
19 GOAL:betaTCP=GEWICHT*ifthenelse(ifdef(d),exp(my*d*3/4),1)
20 E=CA Wyckoff=b x=-0.2766 y=-0.1421 z=0.1658 TDS=0.00686924
21 E=CA Wyckoff=b x=-0.3836 y=-0.1775 z=-0.0336 TDS=0.00673765
22 E=CA Wyckoff=b x=-0.2721 y=-0.1482 z=0.0606 TDS=0.01873909
23 E=CA(0.5000) Wyckoff=a x=0.0000 y=0.0000 z=-0.0850 TDS=0.01105396
24 E=(CA(1-p),CU(p)) PARAM=p=0_0^1 Wyckoff=a x=0.0000 y=0.0000 z=-0.2658 TDS=0.01150138
25 E=P Wyckoff=a x=0.0000 y=0.0000 z=0.0000 TDS=0.00886948
26 E=O Wyckoff=b x=0.0070 y=-0.1366 z=-0.0136 TDS=0.02092356
27 E=O Wyckoff=b x=0.0000 y=0.0000 z=0.0000 TDS=0.00000000
C:\xrd\S24_0007\Substitutions\TCP-beta.str 1 Project λ = 1.54100 Å 2θ = 18.636° I = 2846.100 cts d = 4.758 Å Line: 24, Column: 85
```

# Structure Refinement and Electron Density Maps

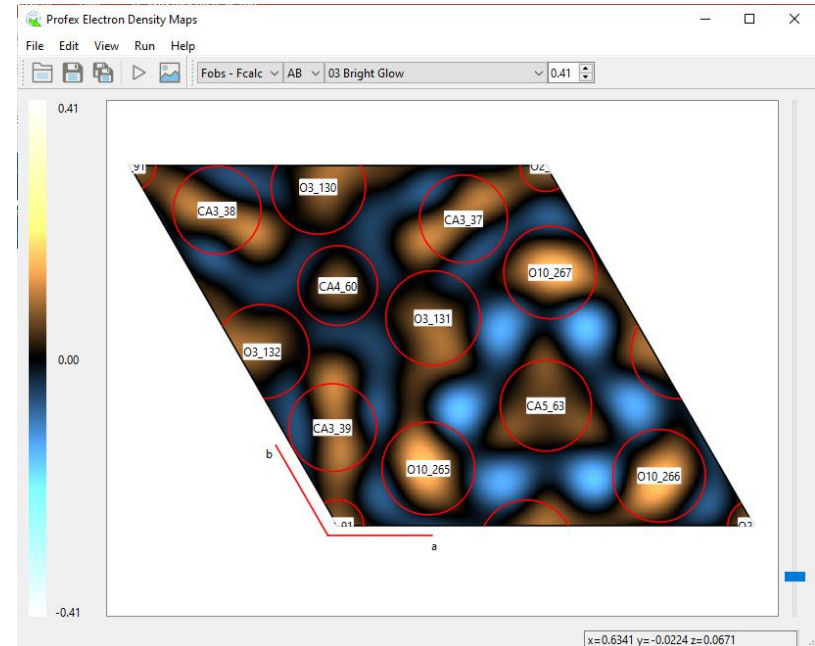


Electron peak improved from 0.41 to 0.21

# Structure Refinement and Electron Density Maps: Summary

- Electron density maps („difference Fourier maps“) visualize mismatches between measured and refined structure models.
- Add additional output files for the structure (FCF and RES) and repeat the refinement.
- Open density electron map editor from „Tools“ menu.
- Search for peaks and valleys to locate mismatches.

```
% SampleID: BGS_170206_2.92%Cu
% Theoretical instrumental function
VERZERR=RMS-D8-ADS-15-LynxEyeXE.geq
% Wavelength
LAMBDA=CU
% Phases
STRUC[1]=TCP-beta.str
FCFOUT[1]=TCP-beta-170213-03.fcf
RESOUT[1]=TCP-beta-170213-03.res
```



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Thank you for your attention!

