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Workshop „Rietveld Refinement with Profex“

Lesson 8: Common Refinement Challenges

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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.

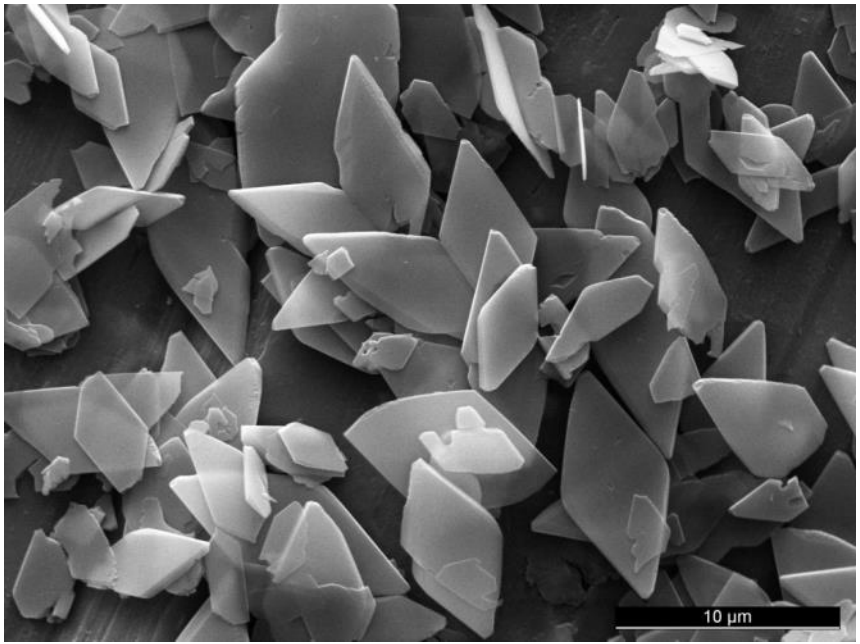
Chose your refinement strategy wisely.
Ask yourself if the results make
physical sense.

Examples

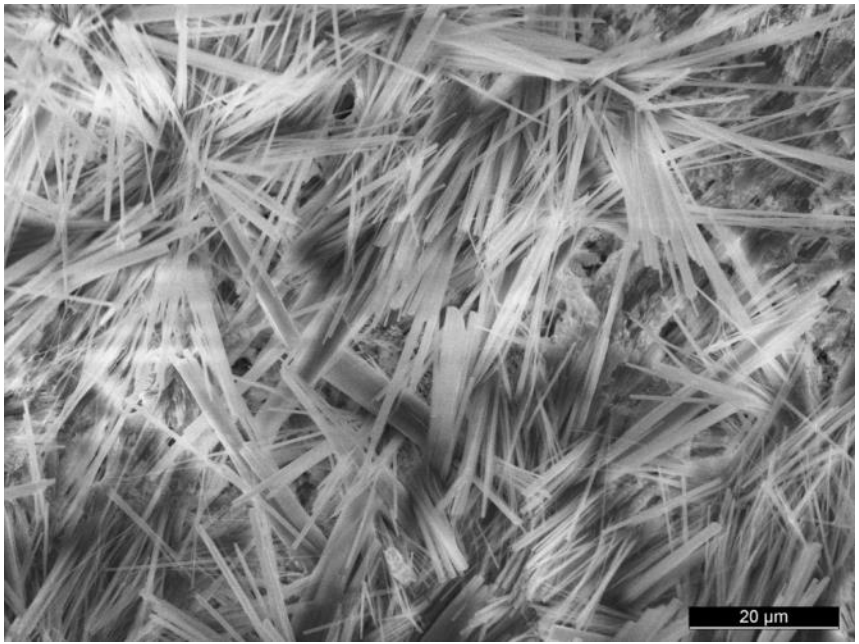
- Example 3: Texture, preferred orientation
- Example 4: Anisotropic crystallite sizes
- Example 5: Structure refinement and electron density maps

Texture, Preferred Orientation

Images: L. Galea, RMS Foundation



Platelets lying flat



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

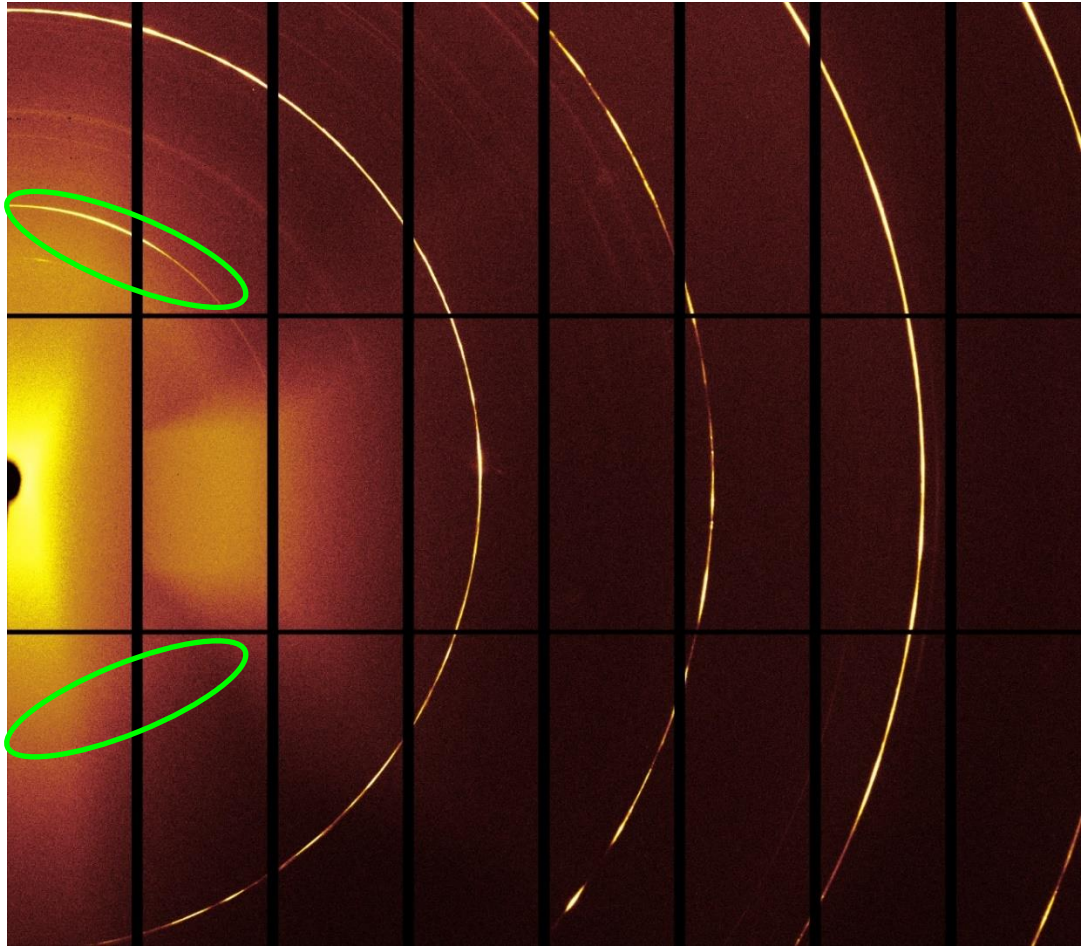
Random orientation

Preferred orientation

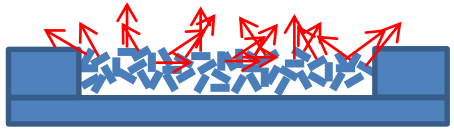
Texture, Preferred Orientation

Smooth, but non-continuous diffraction rings

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



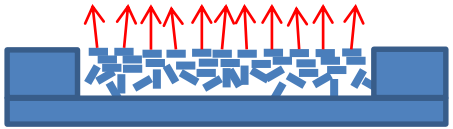
Texture: Symmetrized Spherical Harmonics



Random density of surface normal vectors

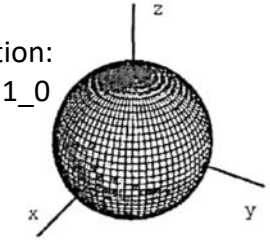
In structure files (*.str):

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

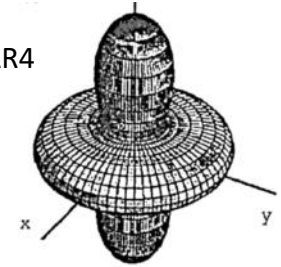


Oriented density of surface normal vectors

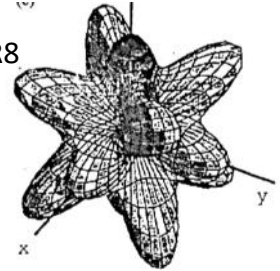
No preferred orientation:
PARAM=GEWICHT=0.1_0
GEWICHT=SPHAR0



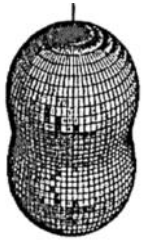
GEWICHT=SPHAR4



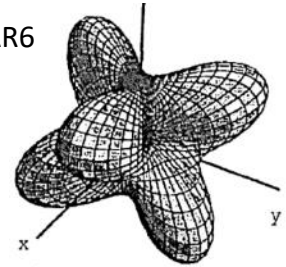
GEWICHT=SPHAR8



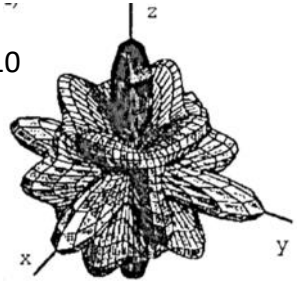
GEWICHT=SPHAR2



GEWICHT=SPHAR6



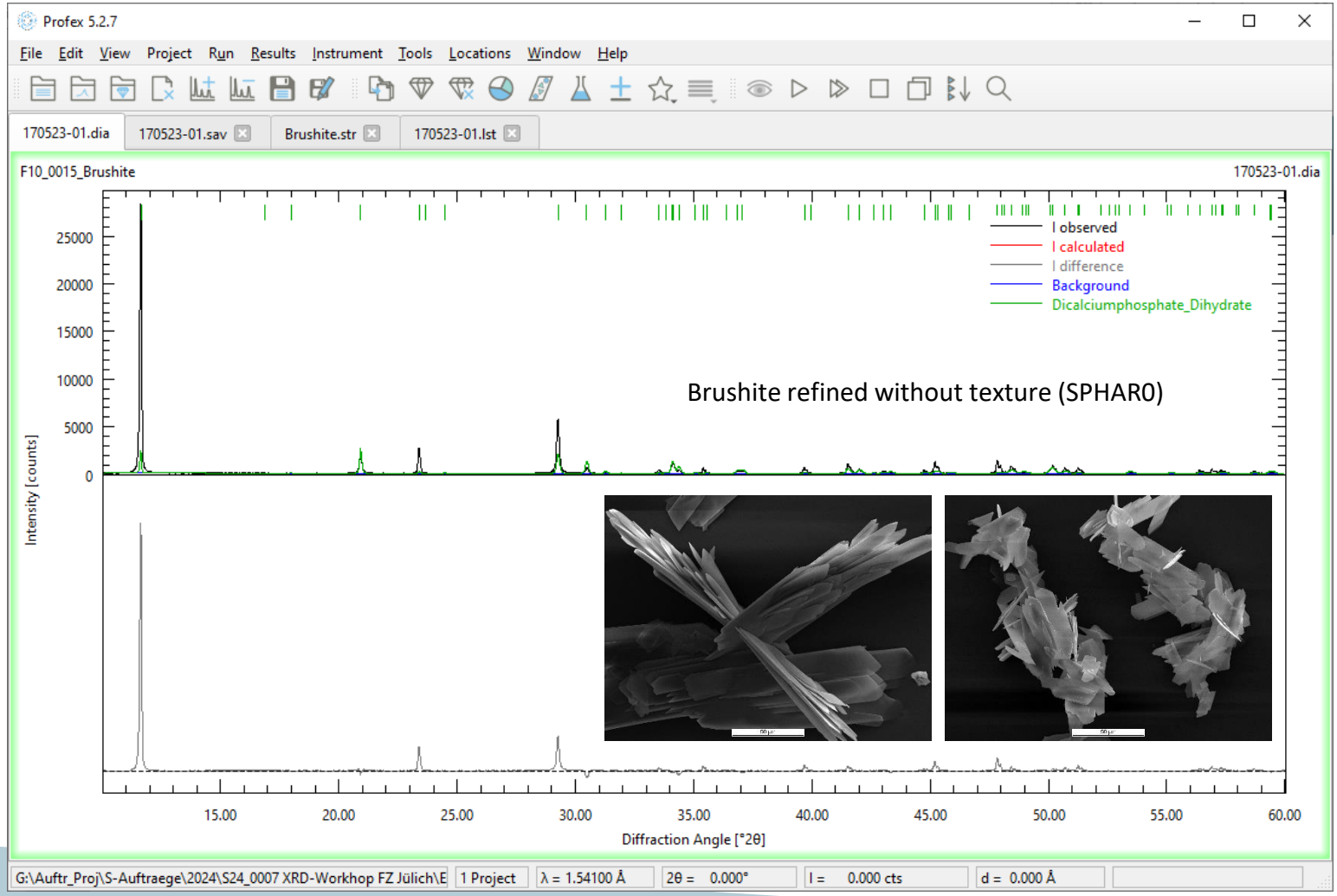
GEWICHT=SPHAR10



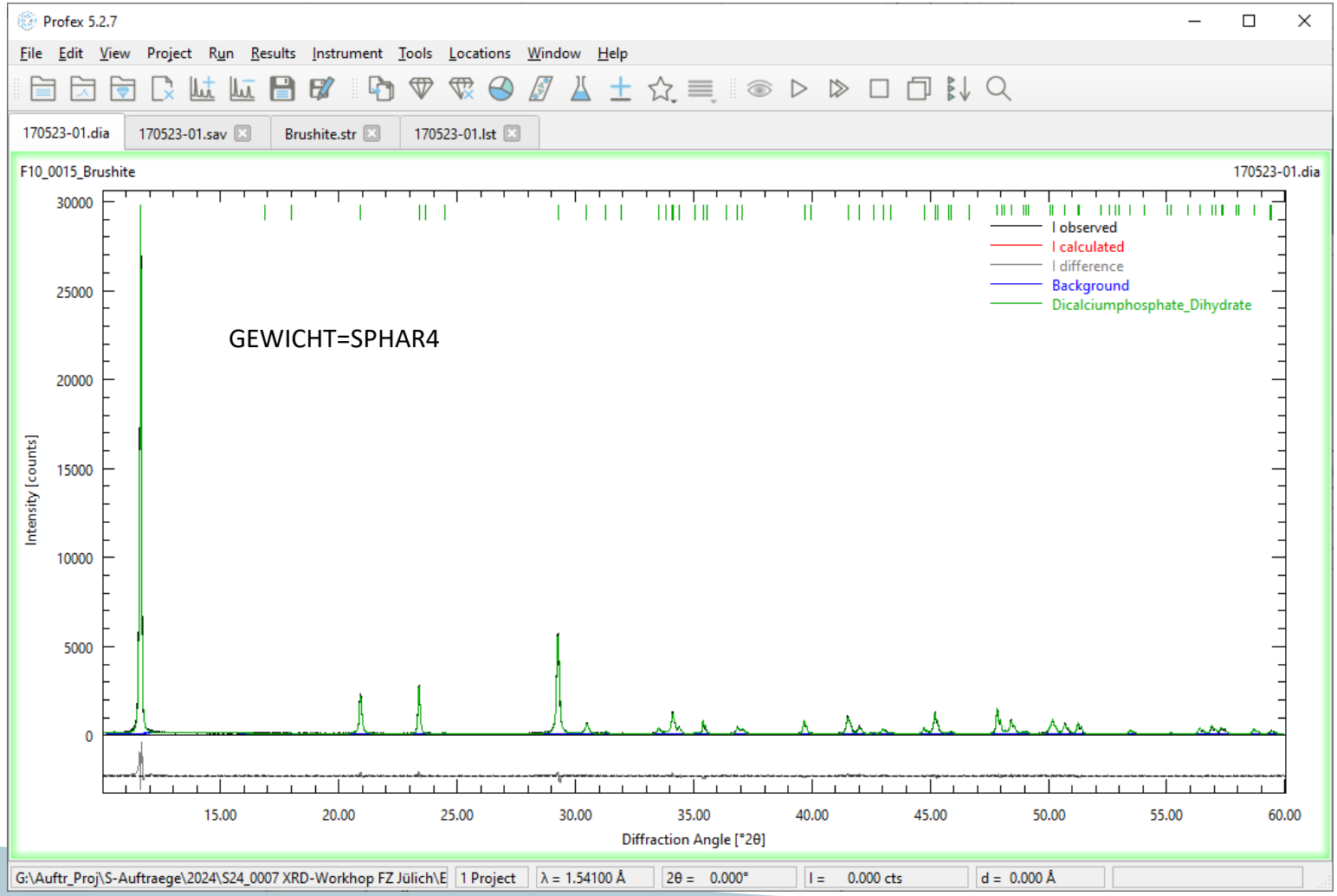
Recommendations: Keep SPHARn as low as necessary
Do not exceed SPHAR6

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

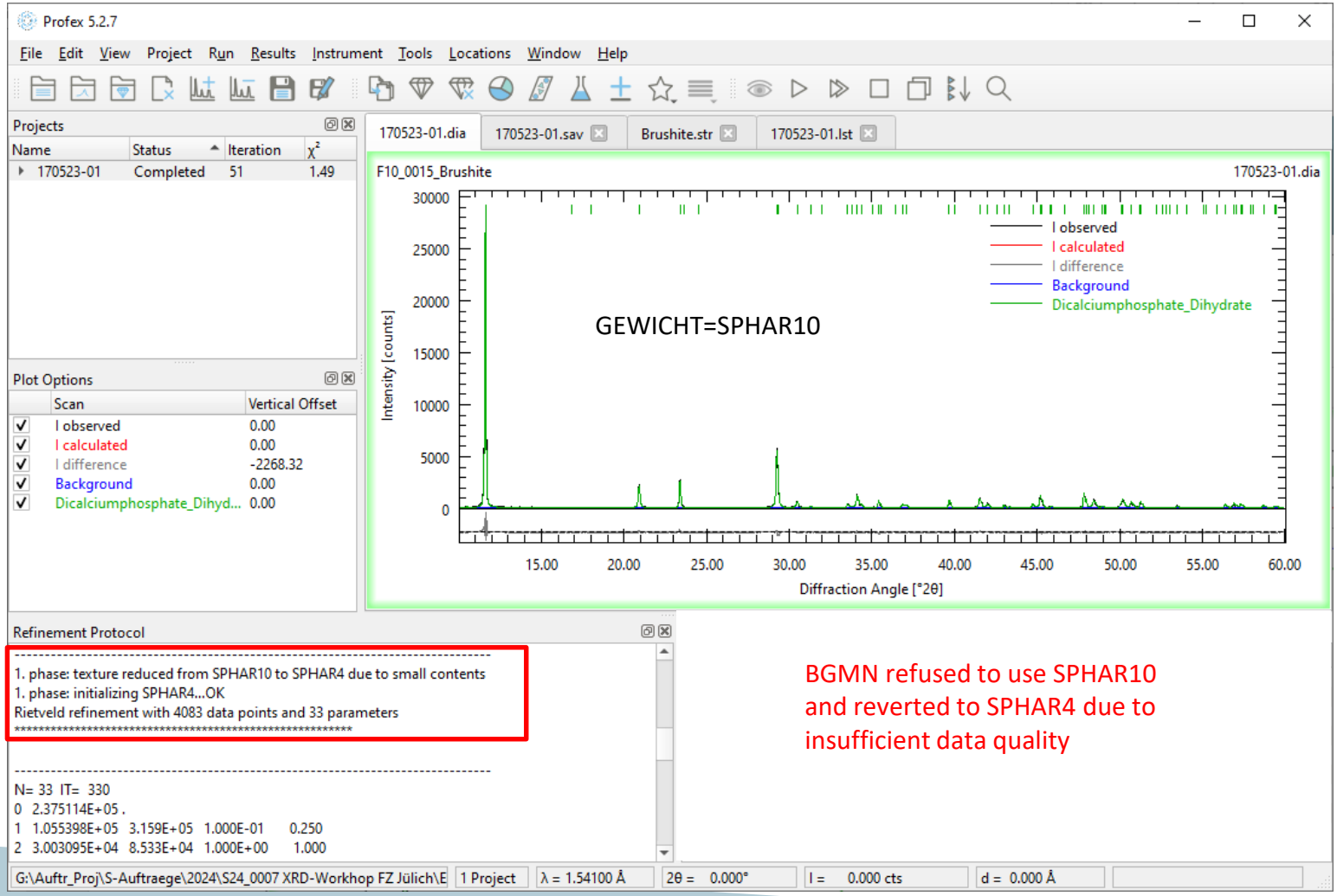
Texture, Preferred Orientation: Example 3



Texture, Preferred Orientation: Example 3



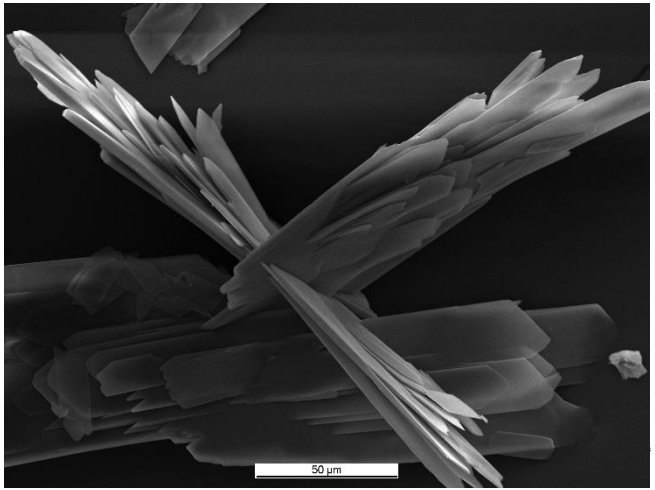
Texture, Preferred Orientation: Example 3



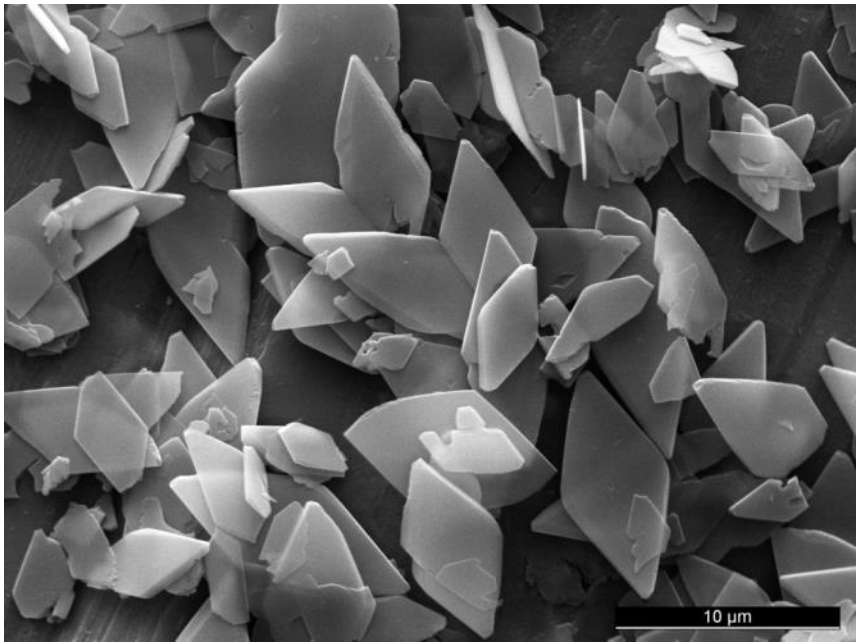
BGMN refused to use SPHAR10 and reverted to SPHAR4 due to insufficient data quality

Summary: Texture, Preferred Orientation

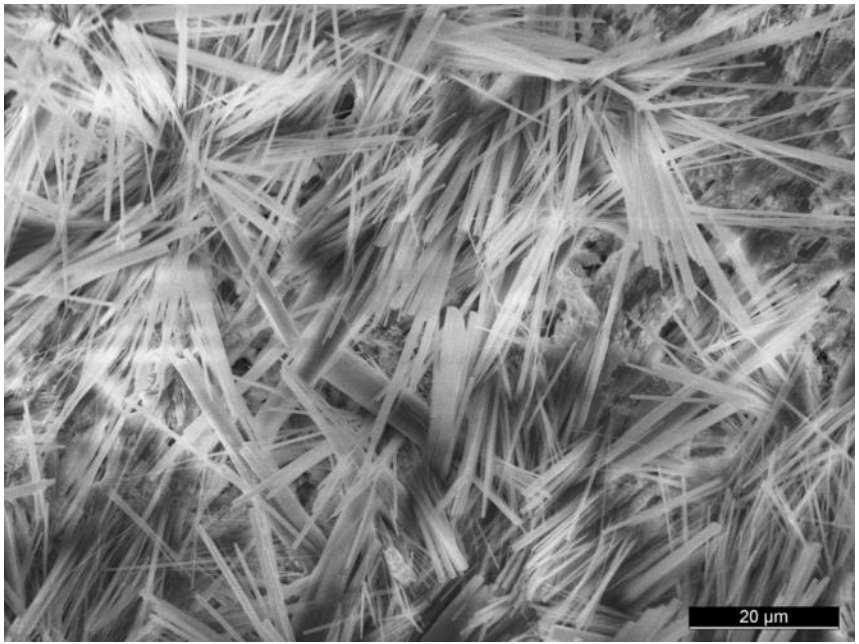
- Refine texture with GEWICHT=SPHARn if necessary (n=0, 2, 4, 6)
- Keep SPHARn as low as necessary (introduces a lot of additional refined parameters)
- Choose SPHARn based on crystal morphology and cleavage
- High SPHARn = slow and potentially unstable refinement
- Phase quantification will be biased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



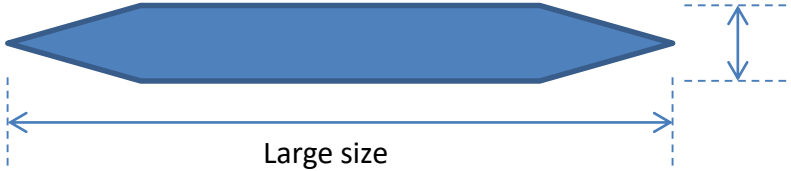
Anisotropic Crystallite Sizes



Platelets



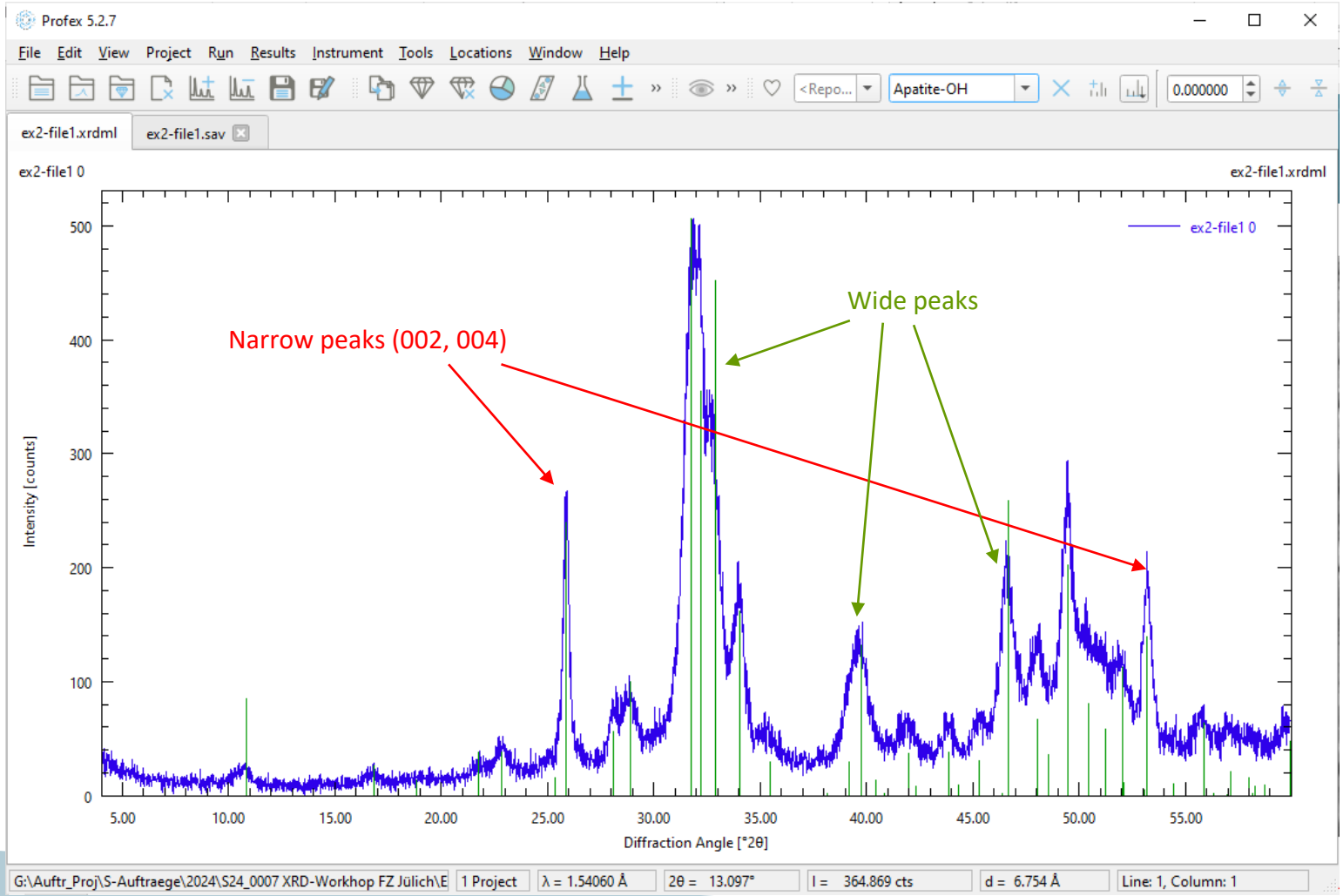
Needles, Fibers, Whiskers



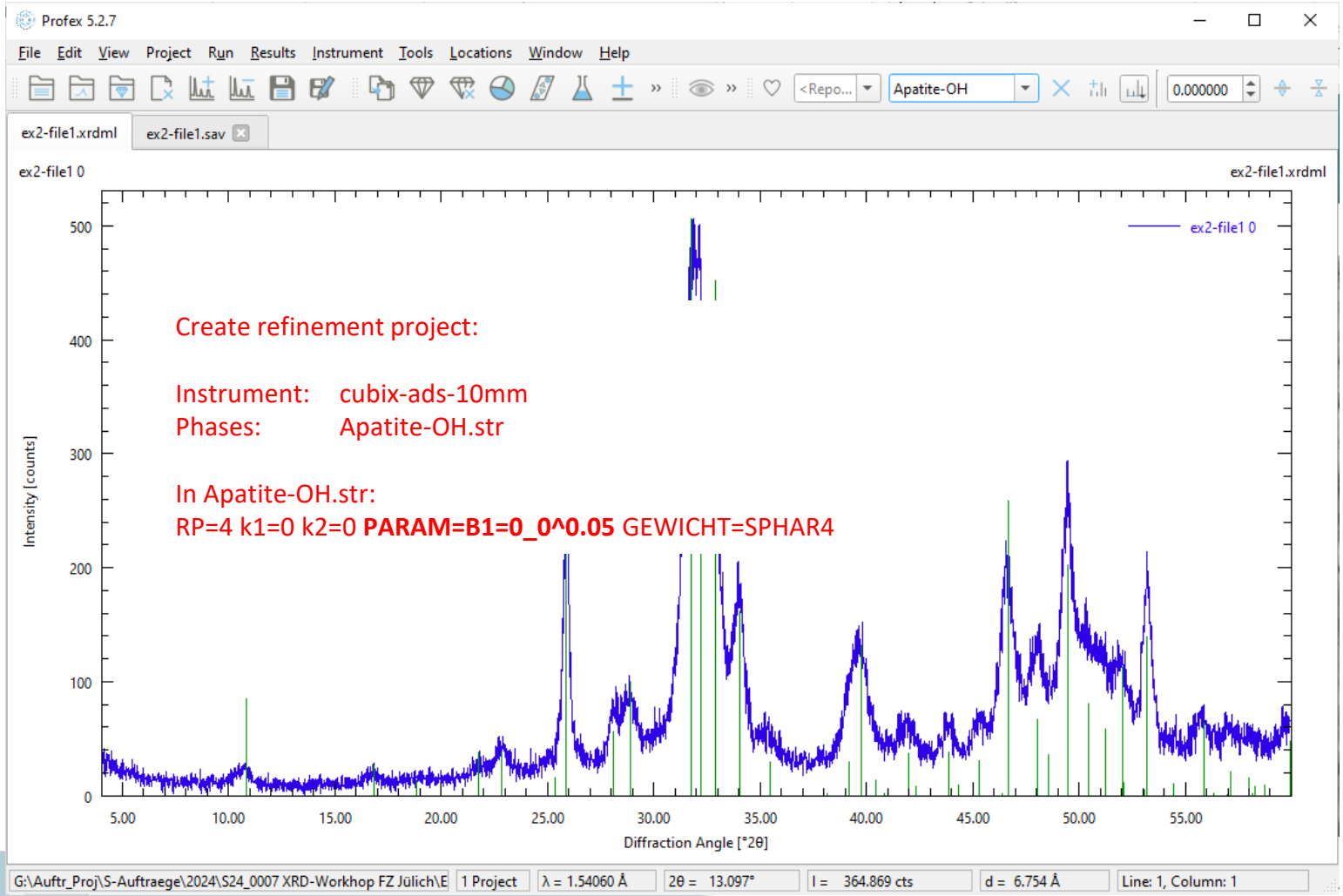
Large size
Weak peak broadening

Small size
Strong peak broadening

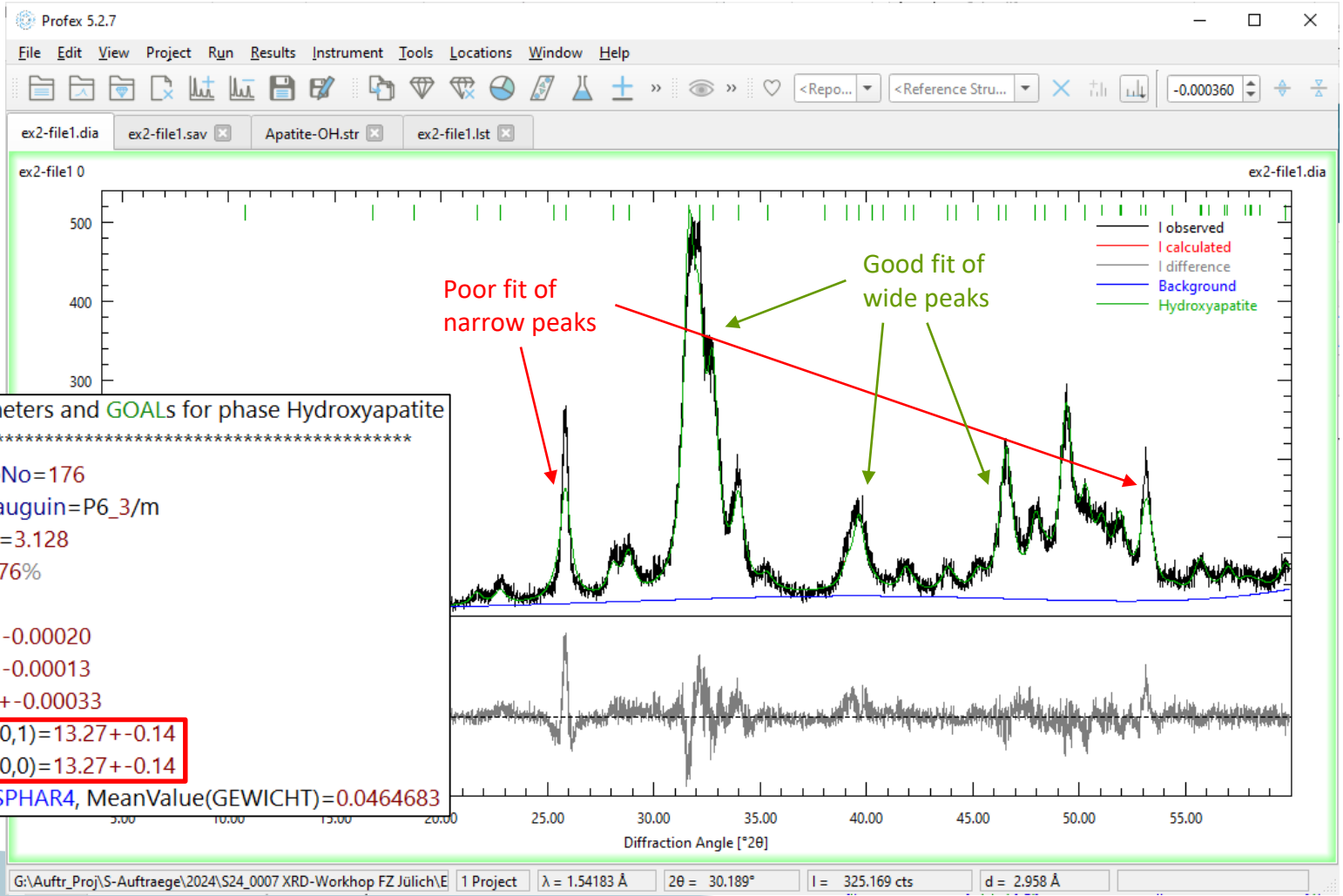
Anistropic Crystallite Sizes: Example 4



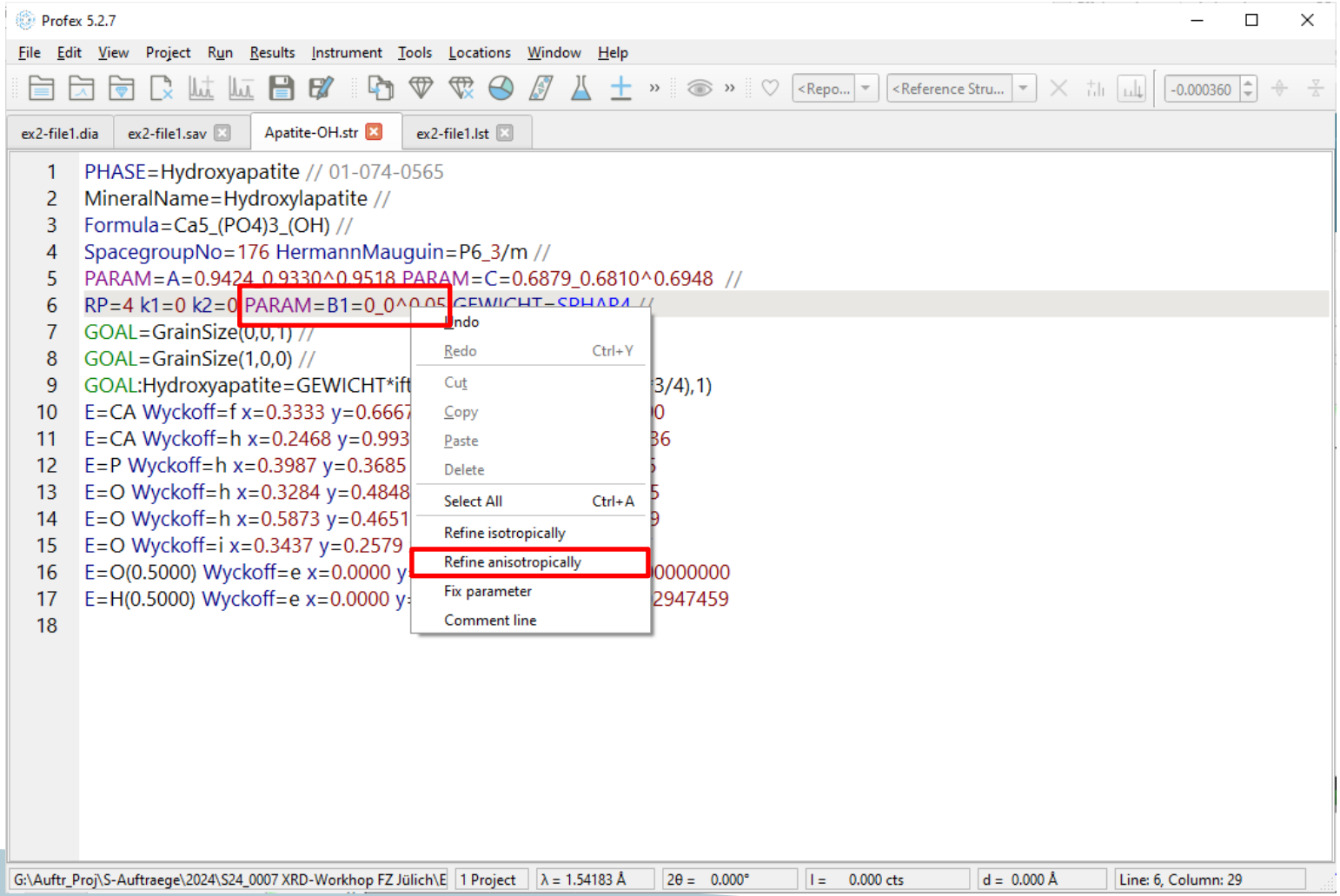
Anistropic Crystallite Sizes: Example 4



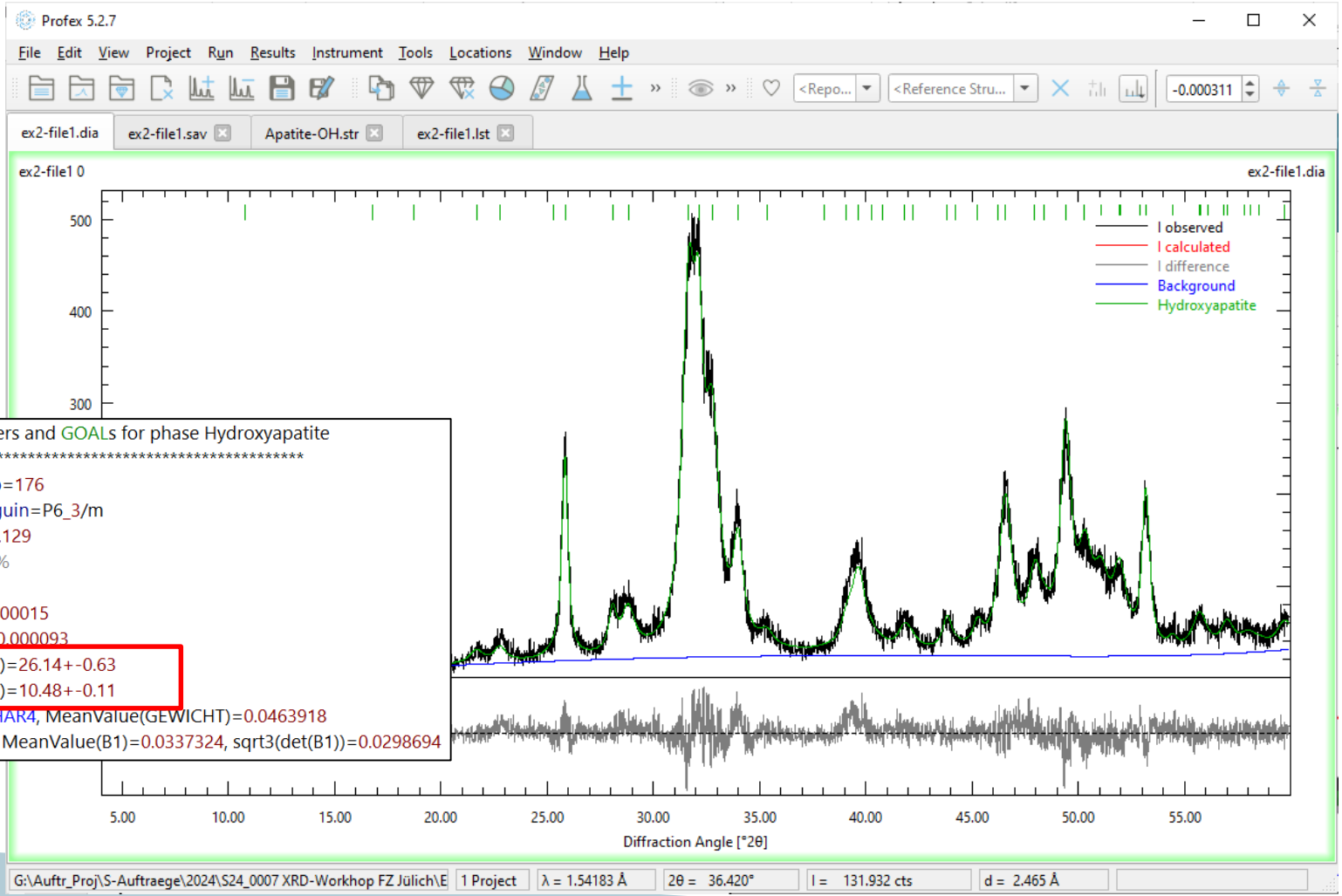
Anistropic Crystallite Sizes: Example 4



Anistropic Crystallite Sizes: Example 4



Anistropic Crystallite Sizes: Example 4



Anistropic 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

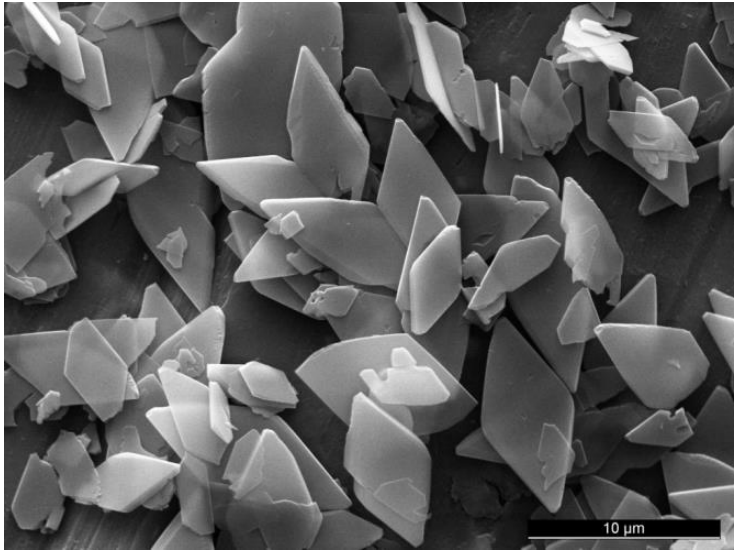
Local parameters and GOALs for phase Hydroxyapatite
****
SpacegroupNo=176
HermannMauguin=P6_3/m
XrayDensity=3.130
Rphase=11.26%
UNIT=NM
A=0.94552+-0.00015
C=0.68838+-0.00010
k2=0.0000170+-0.0000020
GrainSize(0,0,1)=43.9+-2.9
GrainSize(1,0,0)=12.18+-0.23
GEWICHT=SPHAR6, MeanValue(GEWICHT)=0.0453694
B1=ANISOLIN,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

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

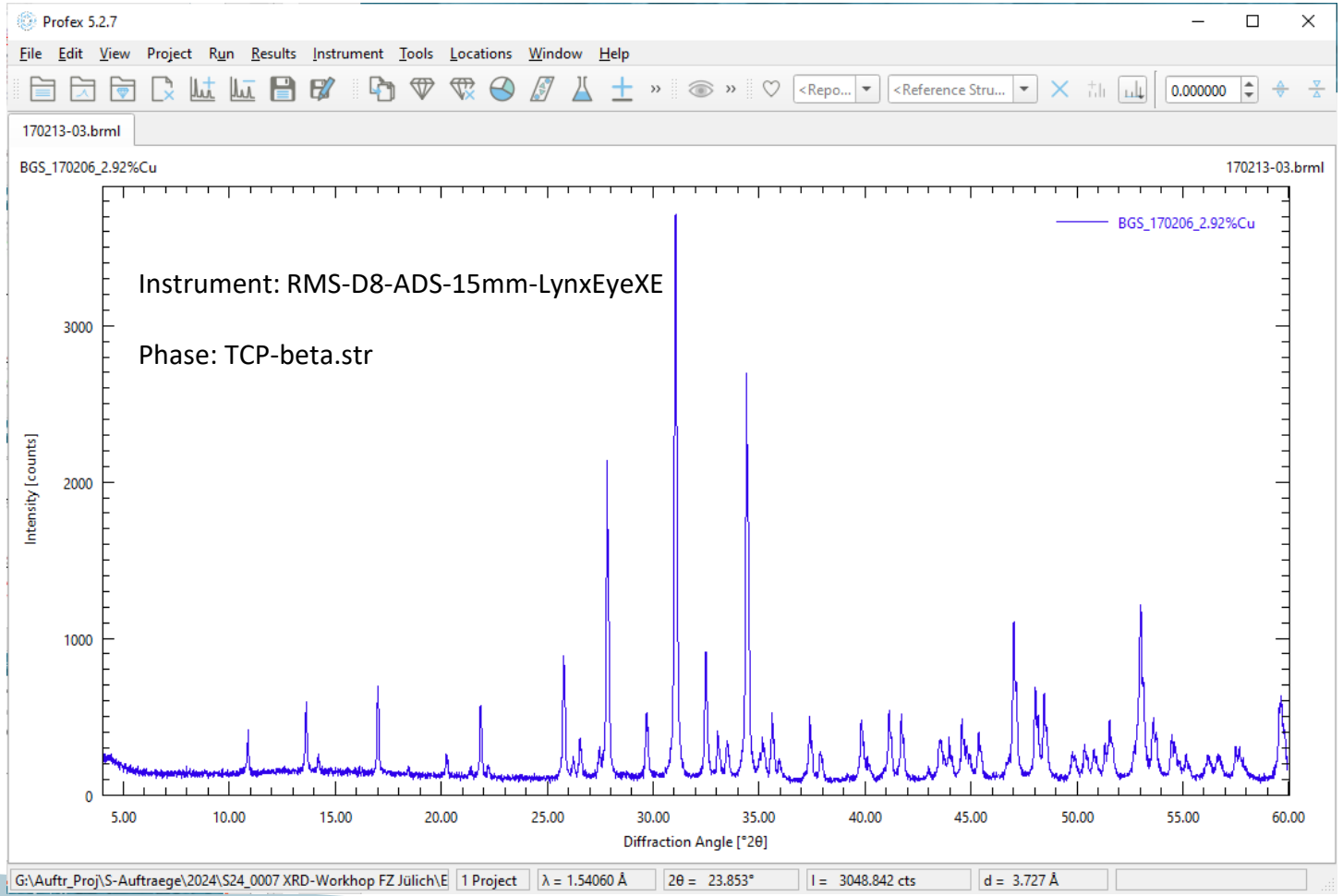
Reduce the correlation by measuring up to high 2θ angles

Anisotropic Crystallite Sizes: Summary

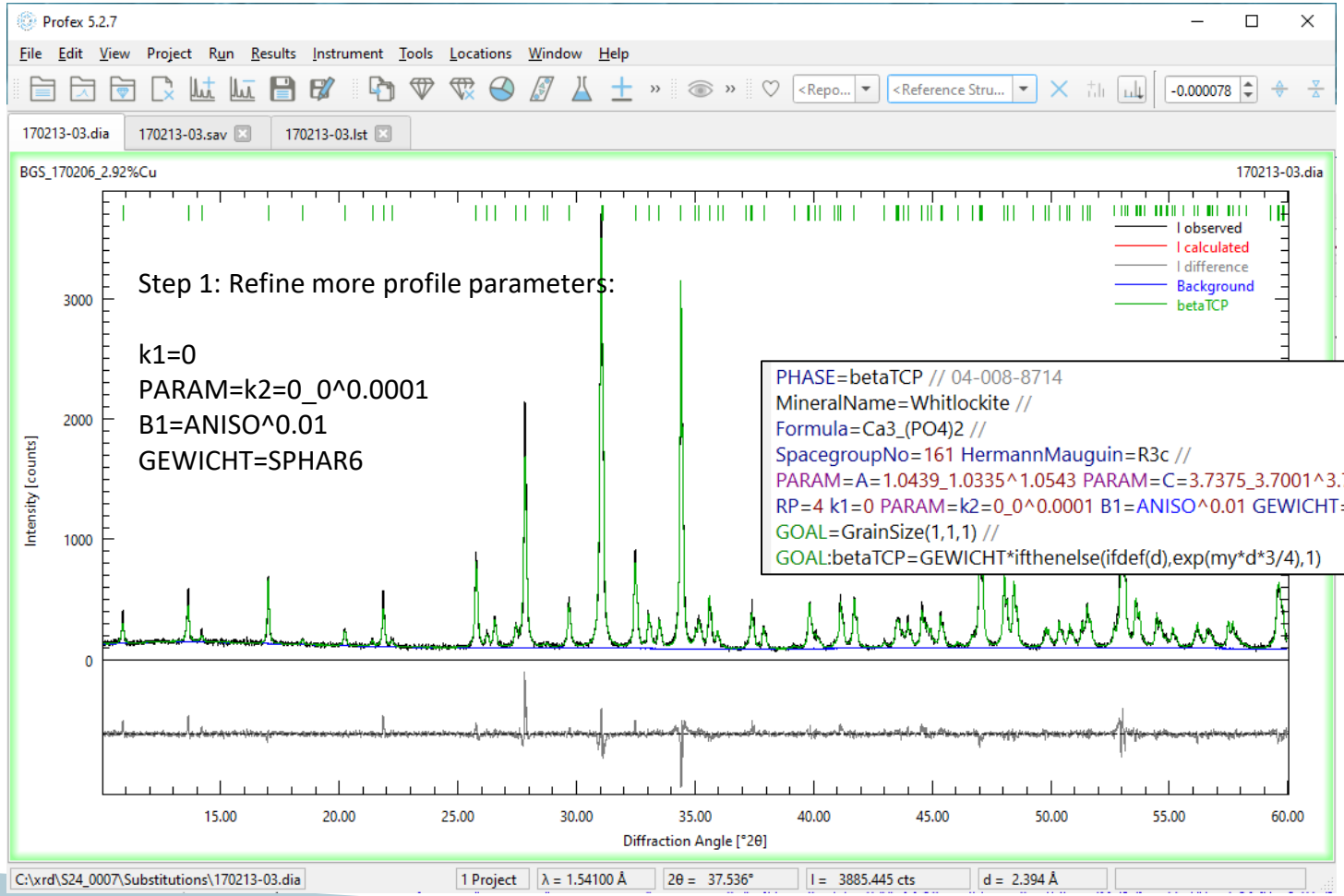
- Expected for platelet- / needle- / rod-shaped crystals
- Refined through B1=ANISO parameter
- Only use if really necessary (improvement of fit observed)
- Can be reduced to isotropic automatically by BGMN
- May correlate with k2 parameter



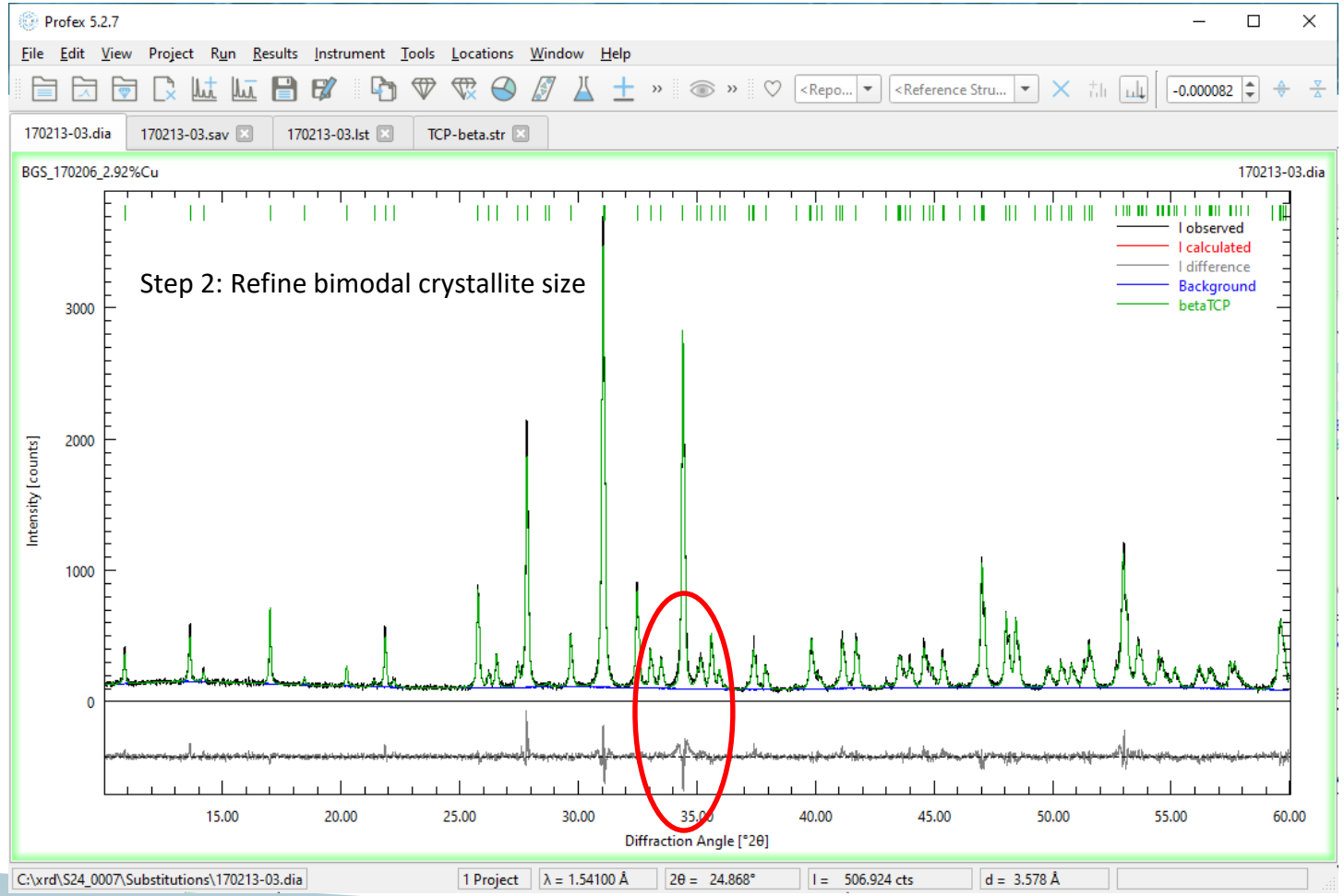
Structure Refinement and Electron Density Maps



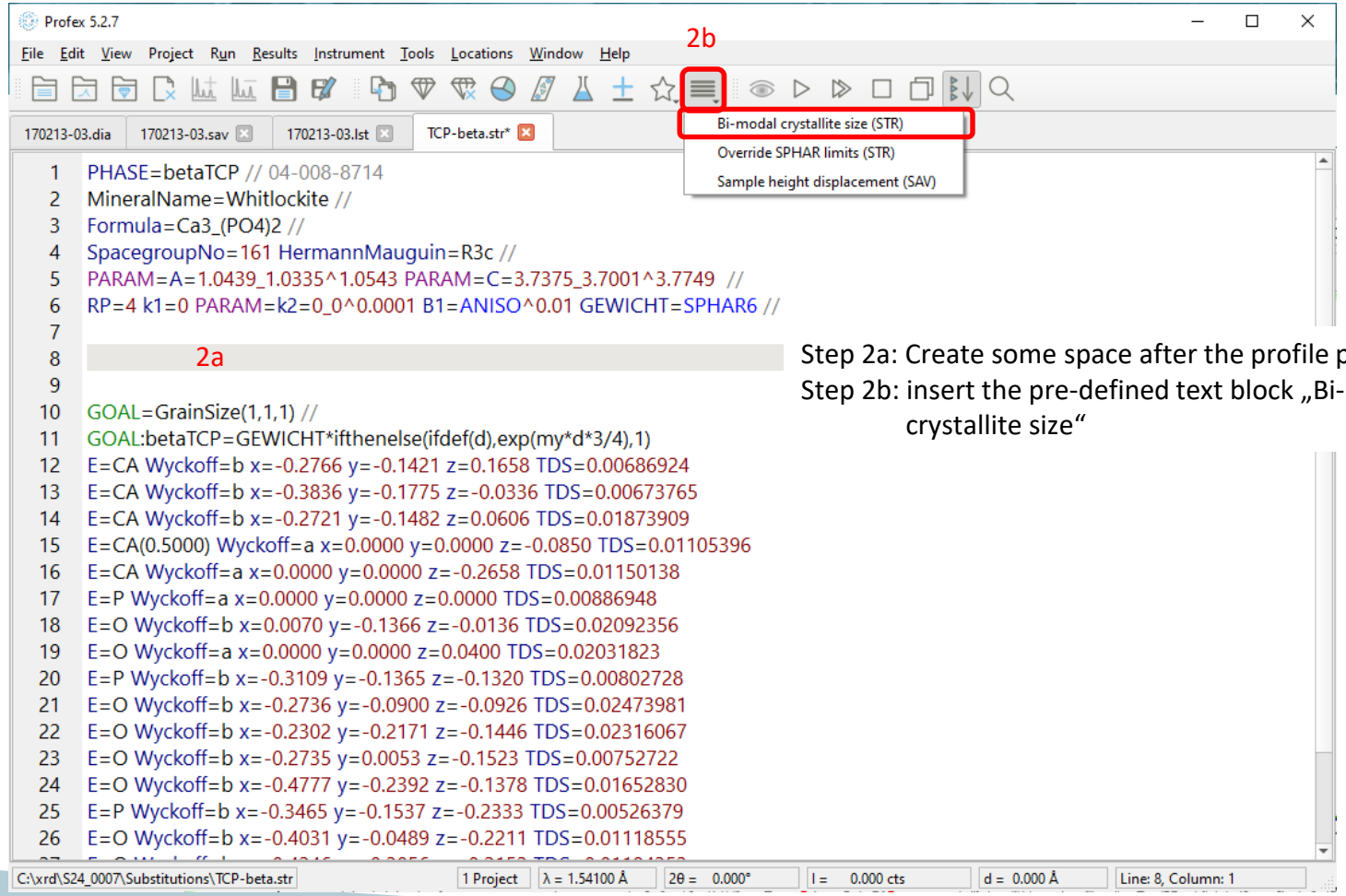
Structure Refinement and Electron Density Maps



Structure Refinement and Electron Density Maps



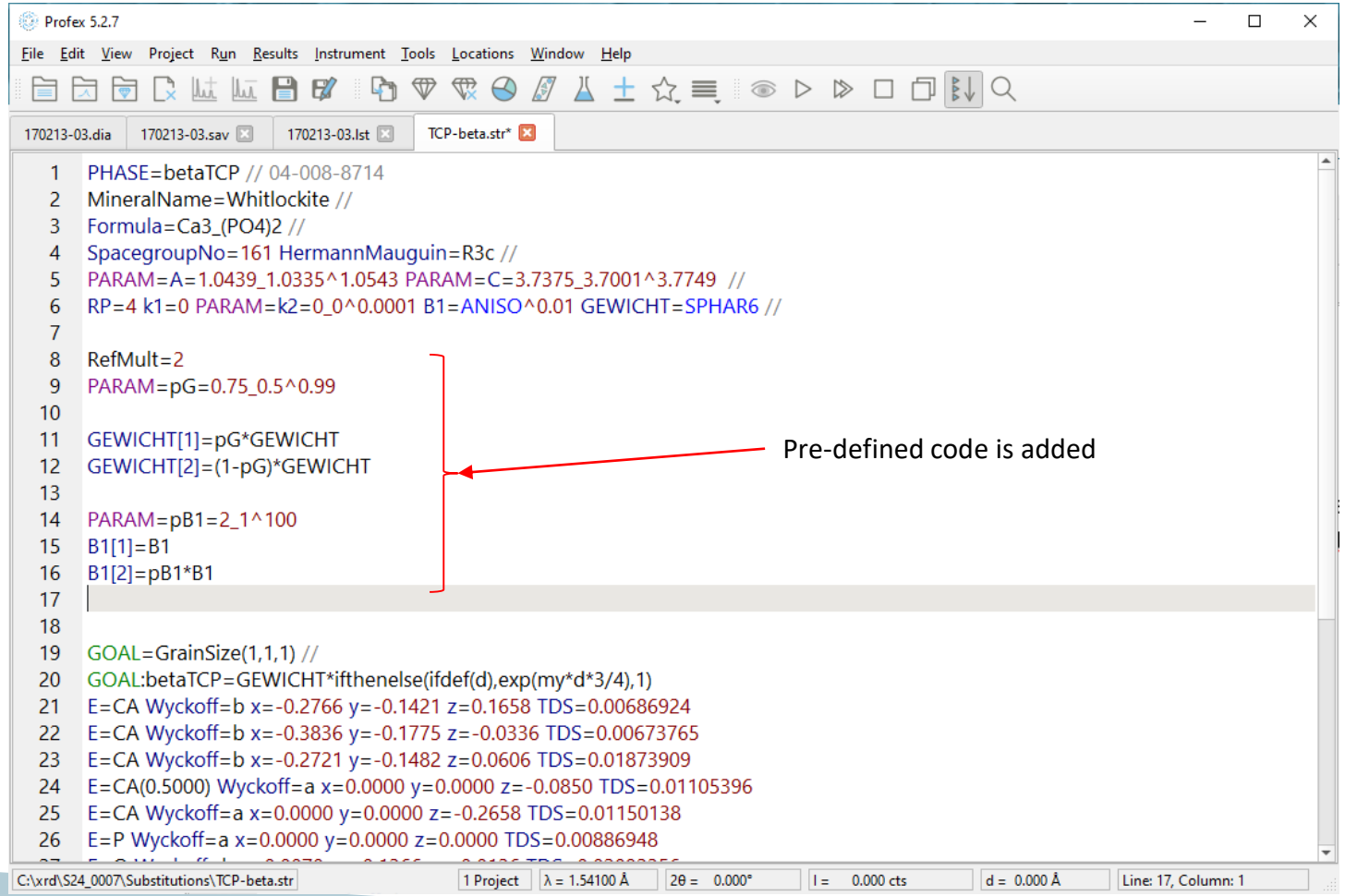
Structure Refinement and Electron Density Maps



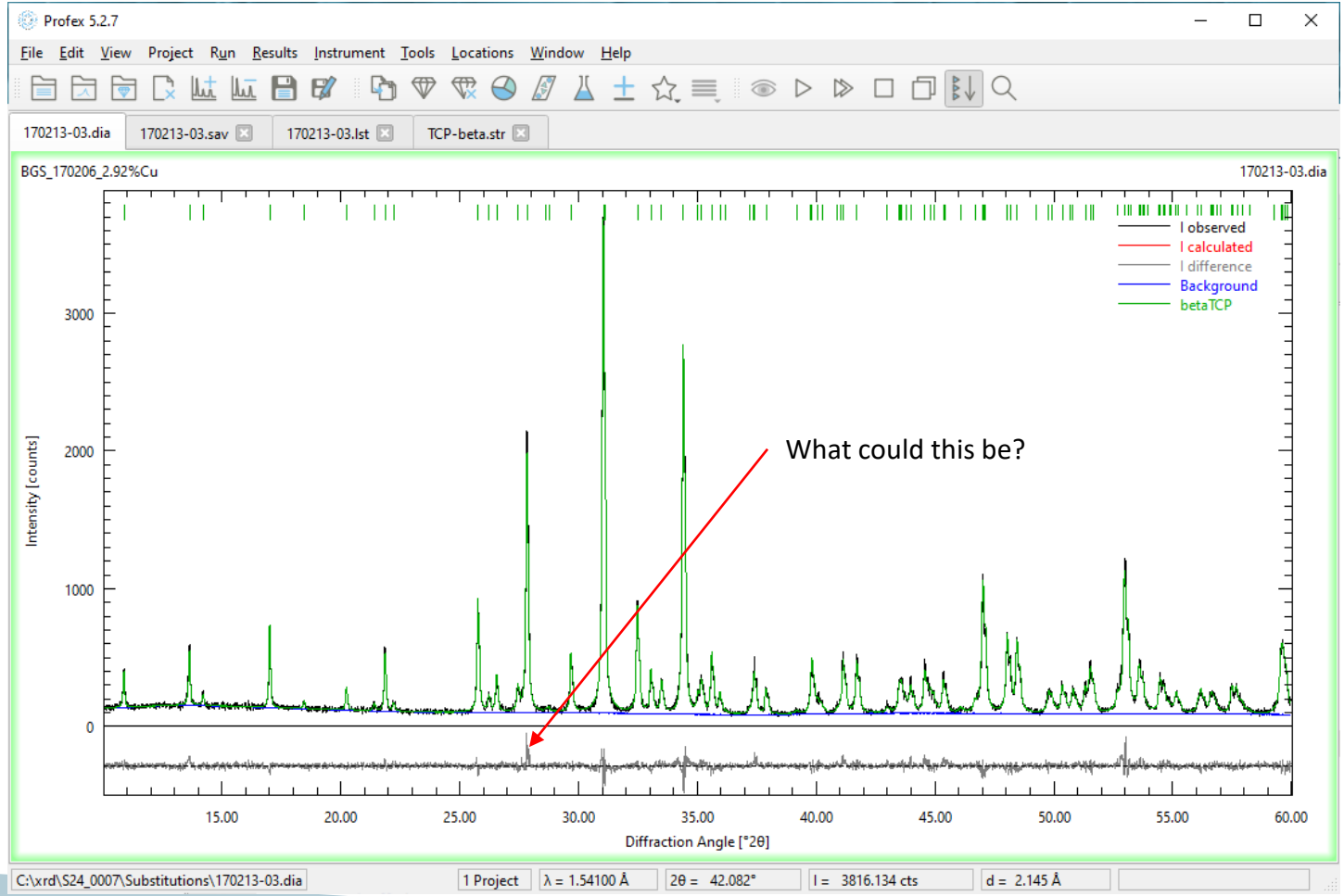
Step 2a: Create some space after the profile parameters

Step 2b: insert the pre-defined text block „Bi-modal crystallite size“

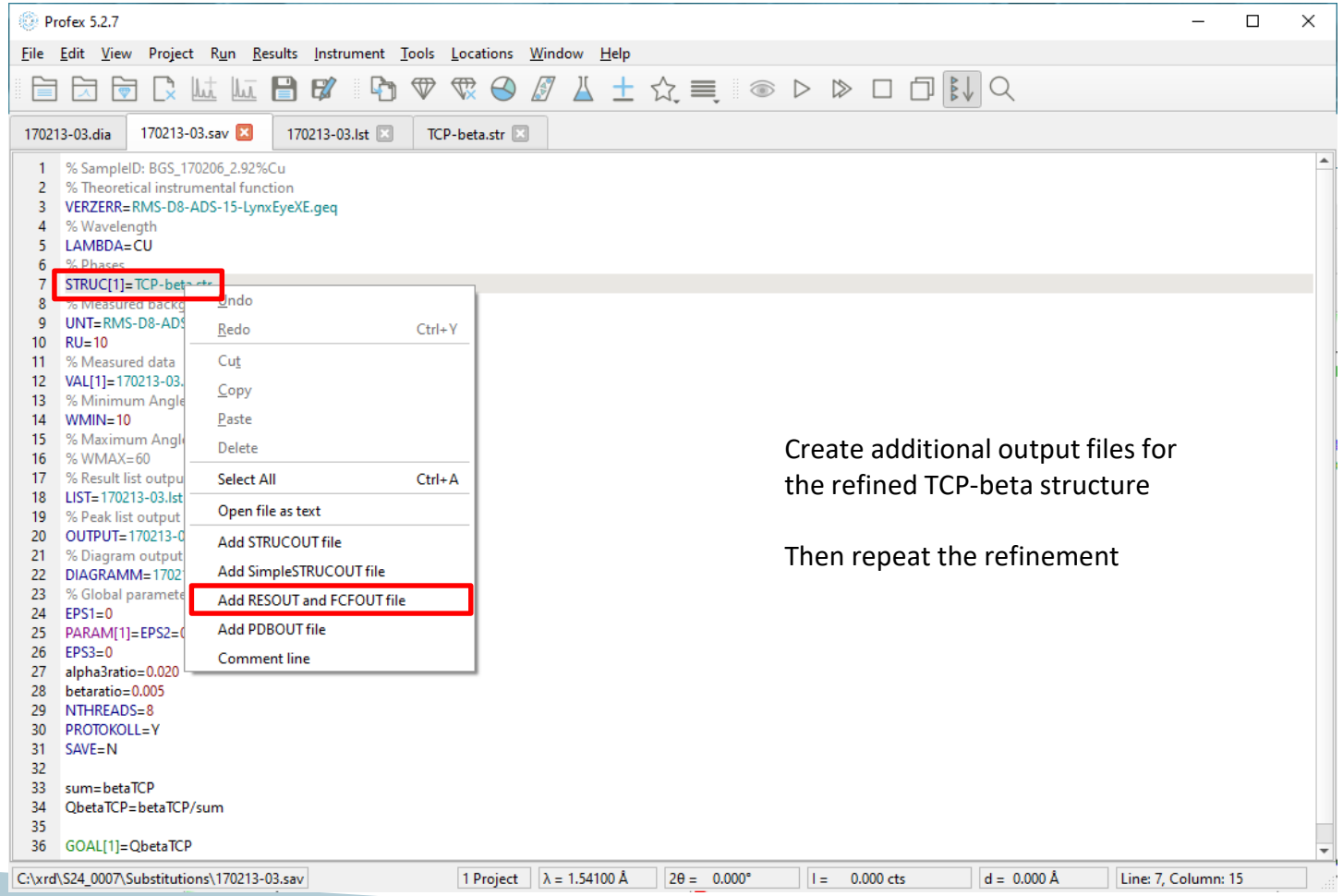
Structure Refinement and Electron Density Maps



Structure Refinement and Electron Density Maps



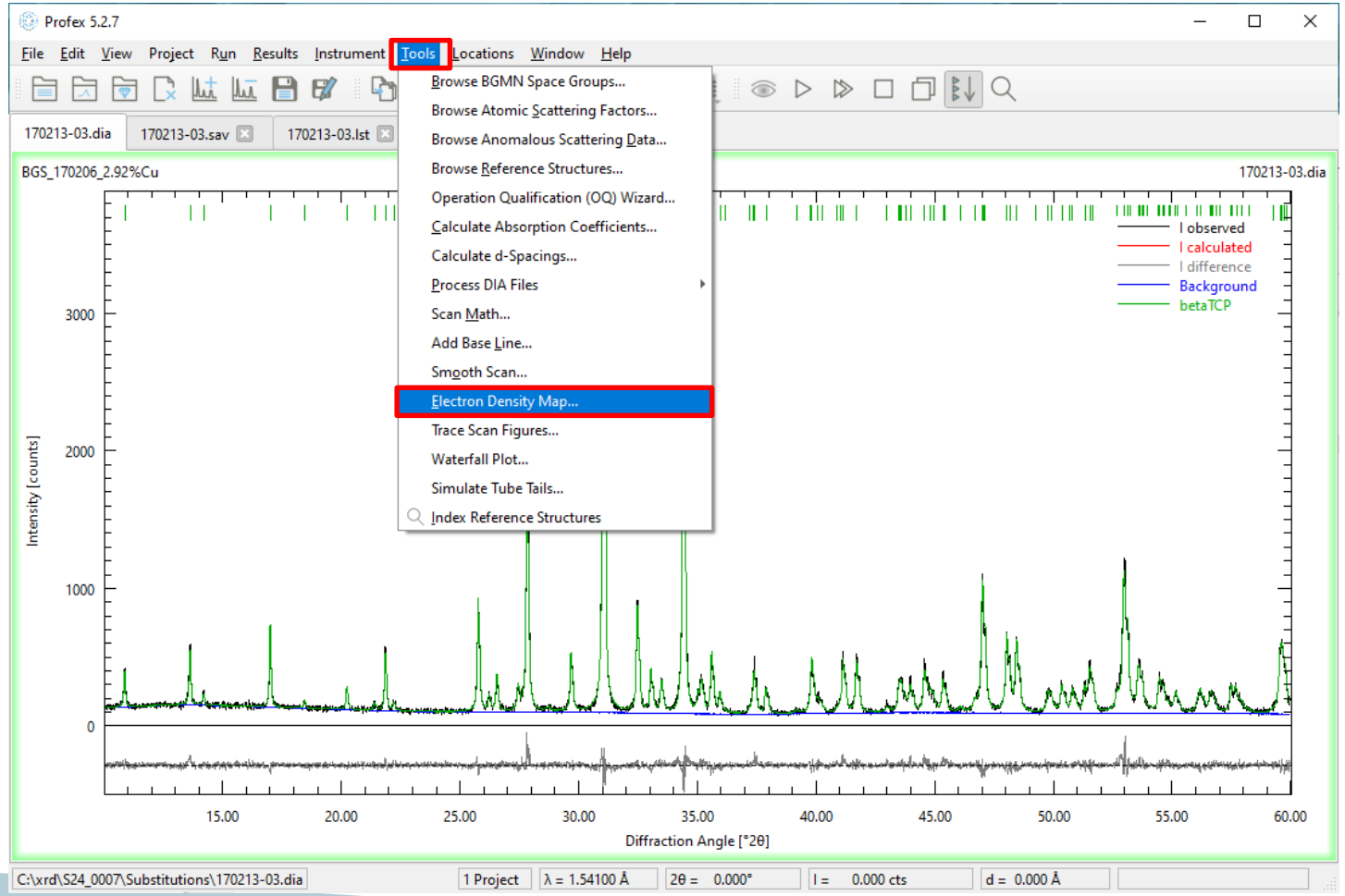
Structure Refinement and Electron Density Maps



Create additional output files for the refined TCP-beta structure

Then repeat the refinement

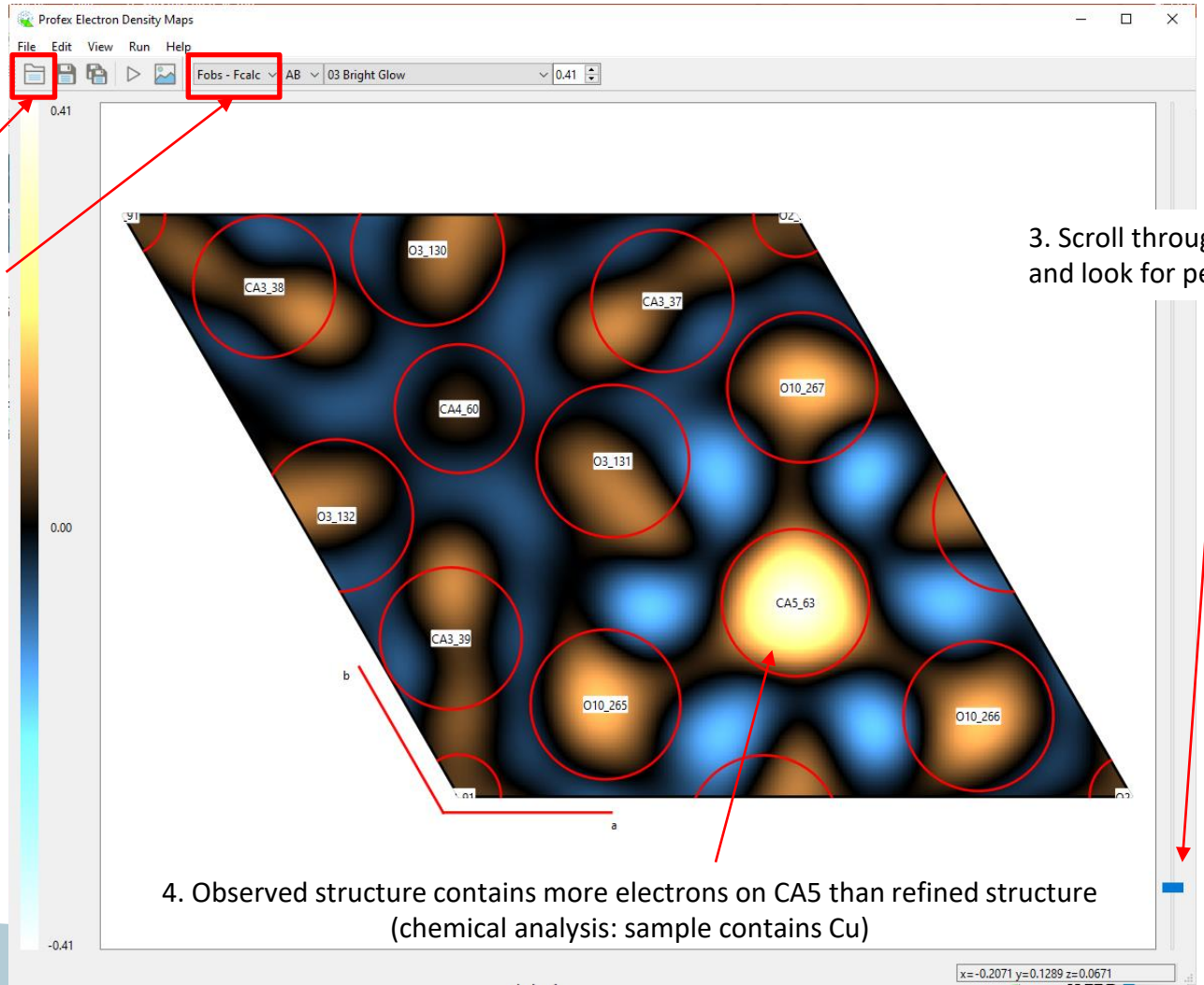
Structure Refinement and Electron Density Maps



Structure Refinement and Electron Density Maps

1. Load *.fcf file

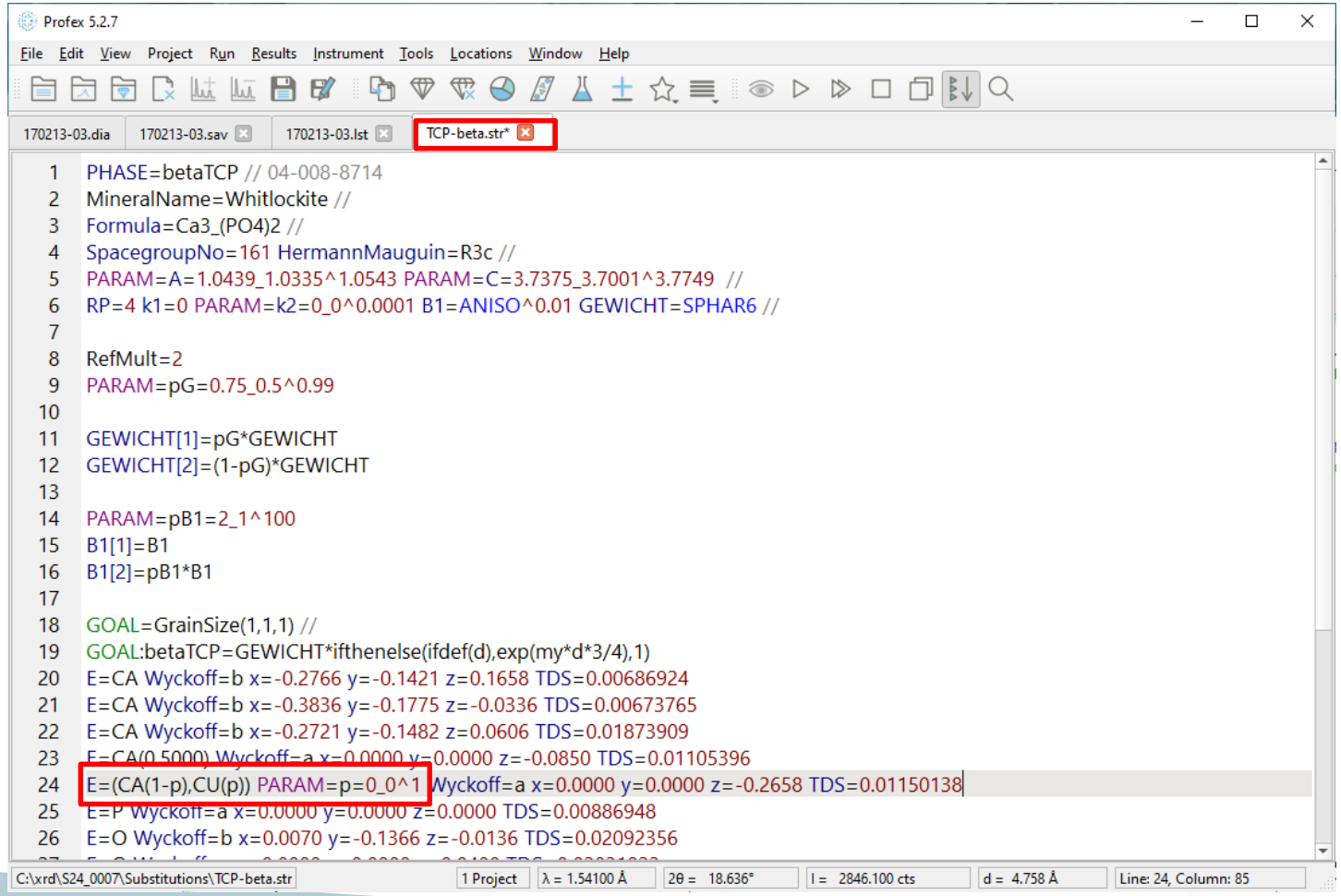
2. Set to Fobs - Fcalc



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

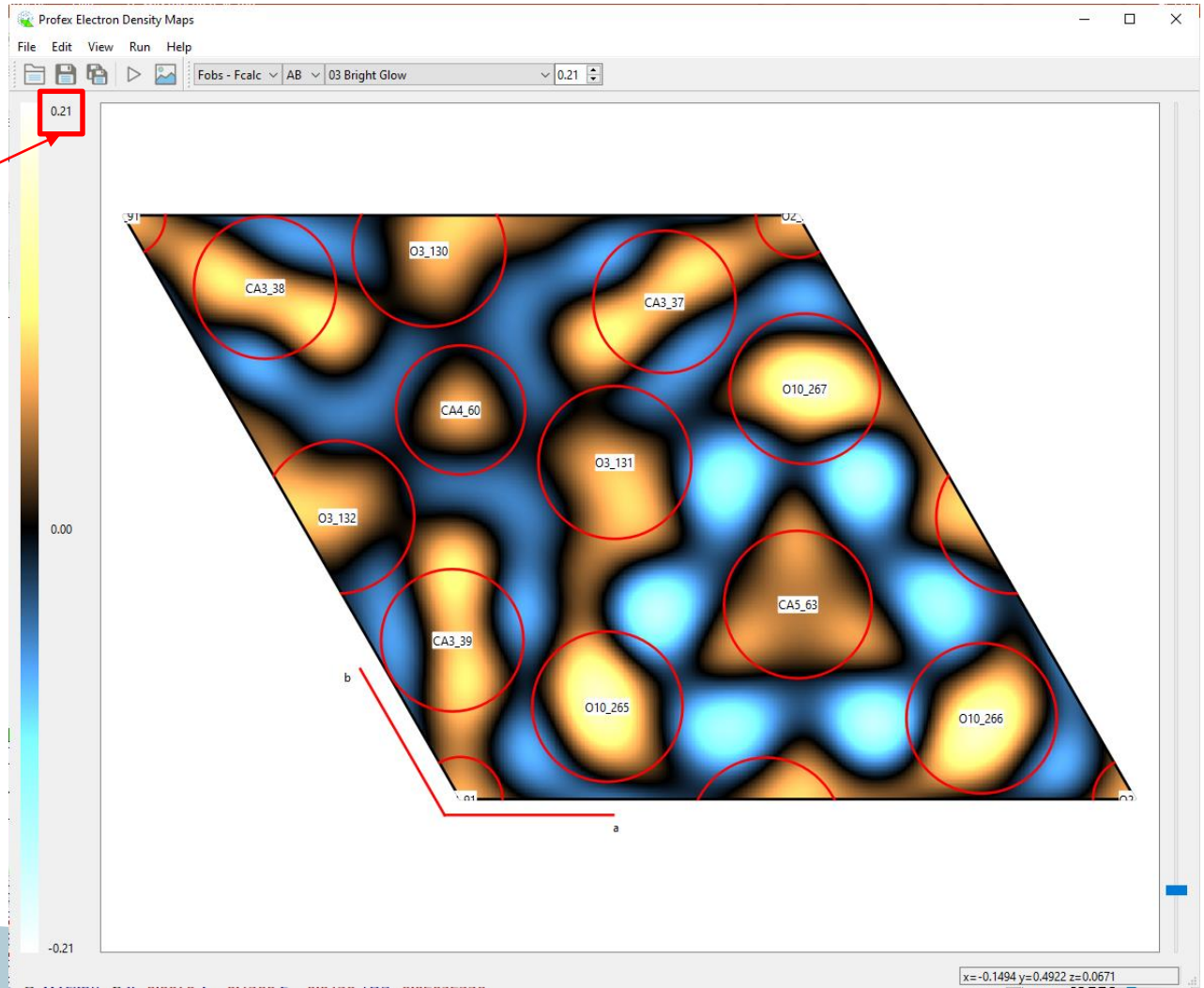
4. Observed structure contains more electrons on CA5 than refined structure (chemical analysis: sample contains Cu)

Structure Refinement and Electron Density Maps



Structure Refinement and Electron Density Maps

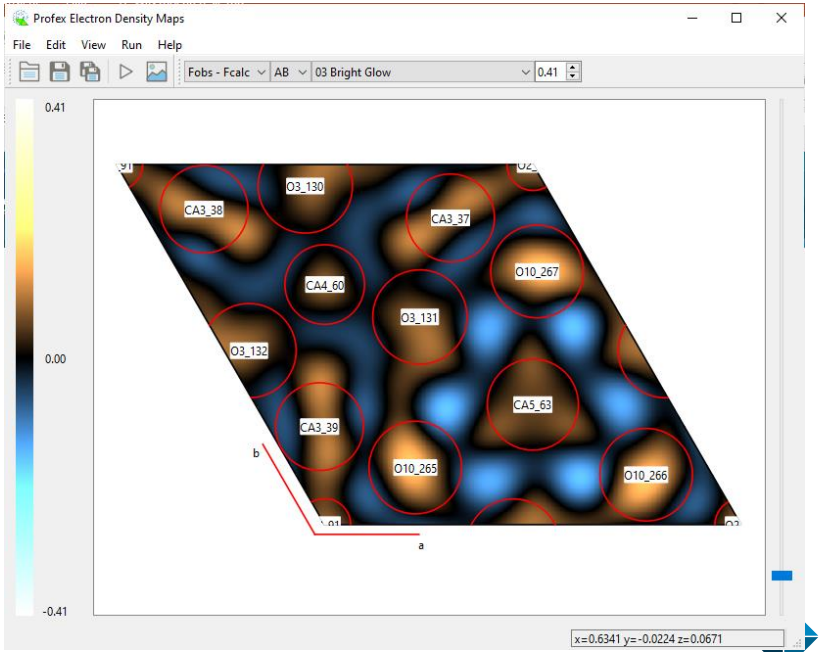
Electron peak improved from 0.41 to 0.21



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
```



Thank you for your attention!