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Testing · Research · Consulting

BGMN/Profex User Meeting 2019

New Features in Profex 4
Part 2

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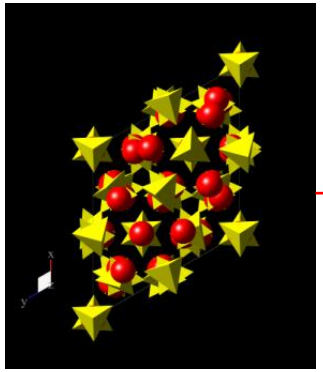
New Features in Profex 4

- GUI changes
- Search / Match
- Peak detection
- Interaction with QualX / Match!

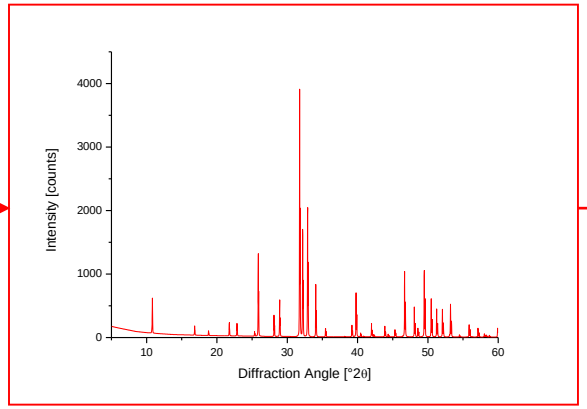
- Electron-density maps
- Drawing crystal structures with Vesta / Mercury
- Customizing report layouts

Rietveld Refinement

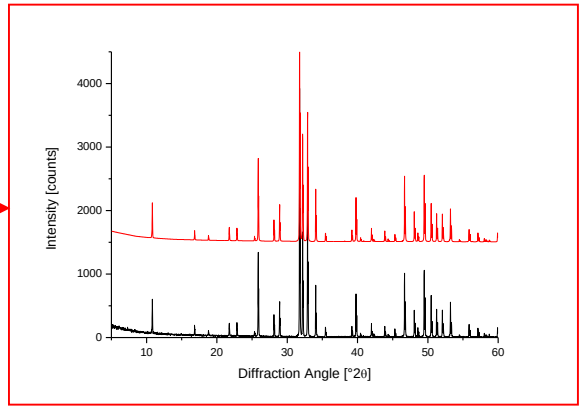
Known structure model



Calculate theoretical diffraction pattern



Compare with measured pattern

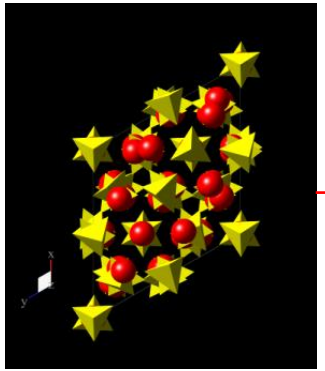


Optimize structure model, repeat calculation

Minimize differences between calculated and observed pattern by least-squares method

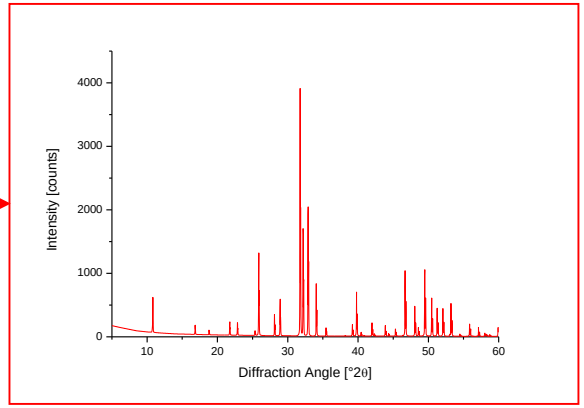
Rietveld Refinement

Direct space



Fourier transformation

Reciprocal space



Spacial arrangement of electron clouds (Scattering factors)

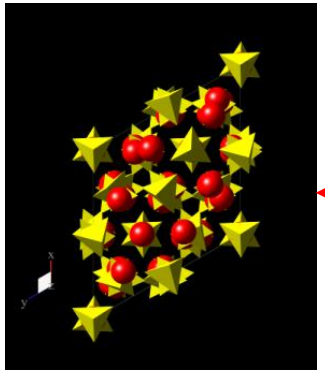
Calculated structure factors F_{calc}

Minimize difference between $|F_{obs}|$ and $|F_{calc}|$

Structure Solution

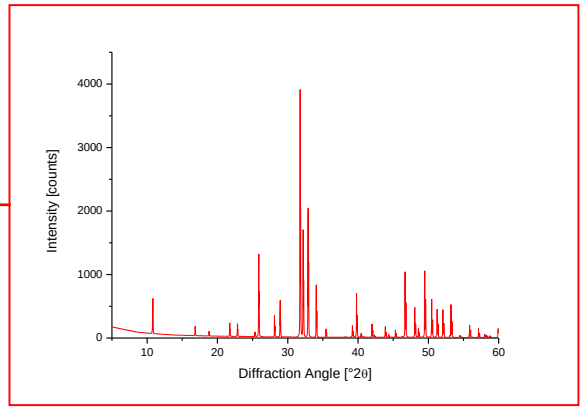
Direct space

Reciprocal space



?

Fourier
Synthesis



Spacial arrangement of
electron clouds
(Scattering factors)

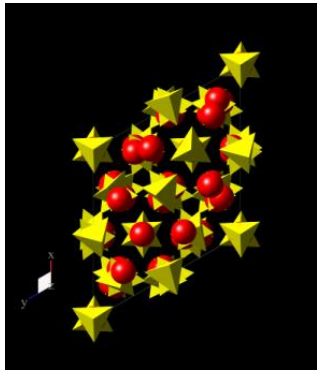
Measured
structure factors F_{obs}

$|F_{obs}|$

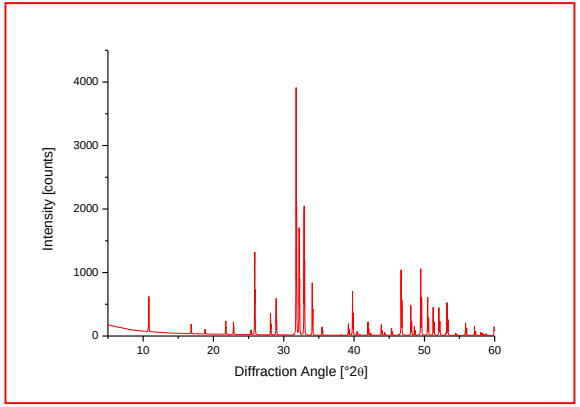
F_{hkl} is a complex number
We measure the amplitude $|F_{obs}|$
but not the phase ϕ_{obs}

Fourier Synthesis

Direct space



Reciprocal space



Calculated structure factor phases ϕ_{calc}

Measured structure factor amplitudes $|F_{obs}|$

Fourier Synthesis

Electron density distribution

Fourier Synthesis

http://pd.chem.ucl.ac.uk/pdnn/refine2/fourier.htm

«F_{obs} Fourier map»: Calculated from ϕ_{calc} and $|F_{obs}|$:

$$\rho(x,y,z) = \frac{1}{V} \cdot \sum_{hkl} |F_{obs}| \cdot \cos[2\pi(hx + ky + lz) - \phi_{calc}]$$

«F_{calc} Fourier map»: Calculated from ϕ_{calc} and $|F_{calc}|$:

$$\rho(x,y,z) = \frac{1}{V} \cdot \sum_{hkl} |F_{calc}| \cdot \cos[2\pi(hx + ky + lz) - \phi_{calc}]$$

«Difference Fourier map»: Calculated from ϕ_{calc} and $|F_{obs}| - |F_{calc}|$:

$$\rho(x,y,z) = \frac{1}{V} \cdot \sum_{hkl} (|F_{obs}| - |F_{calc}|) \cdot \cos[2\pi(hx + ky + lz) - \phi_{calc}]$$

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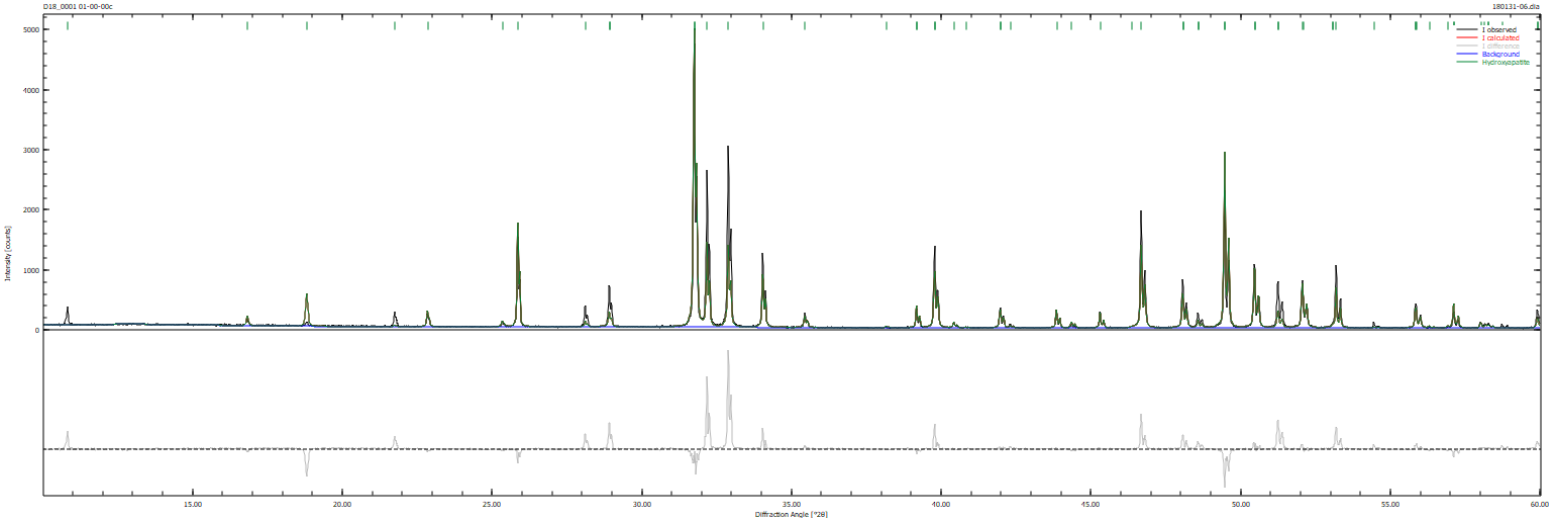
Difference Fourier Maps



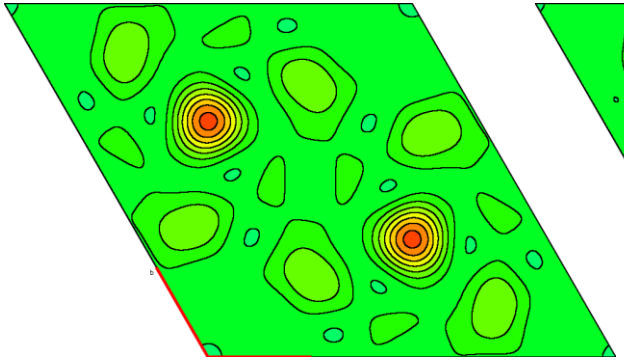
$$\rho(x,y,z) = \frac{1}{V} \cdot \sum_{hkl} (|F_{obs}| - |F_{calc}|) \cdot \cos[2\pi(hx + ky + lz) - \phi_{calc}]$$

Misfits ($|F_{obs}| \neq |F_{calc}|$) in the refinement (reciprocal space)
can be visualized in the crystal structure (direct space)

Electron Density Maps

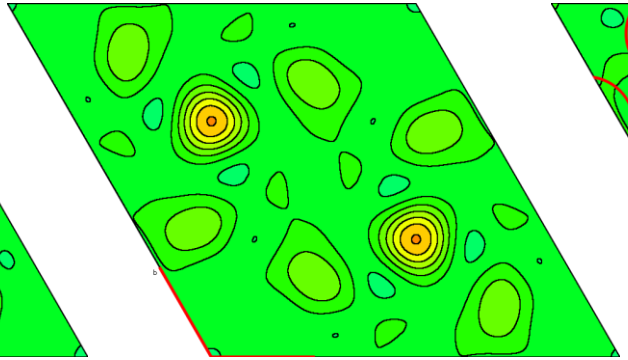
Observed electron density

F_{obs}



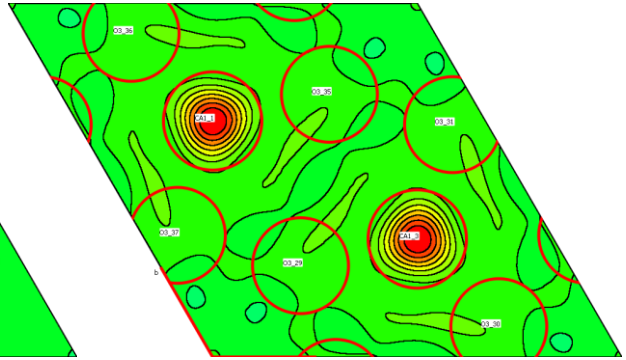
Refined electron density

F_{calc}



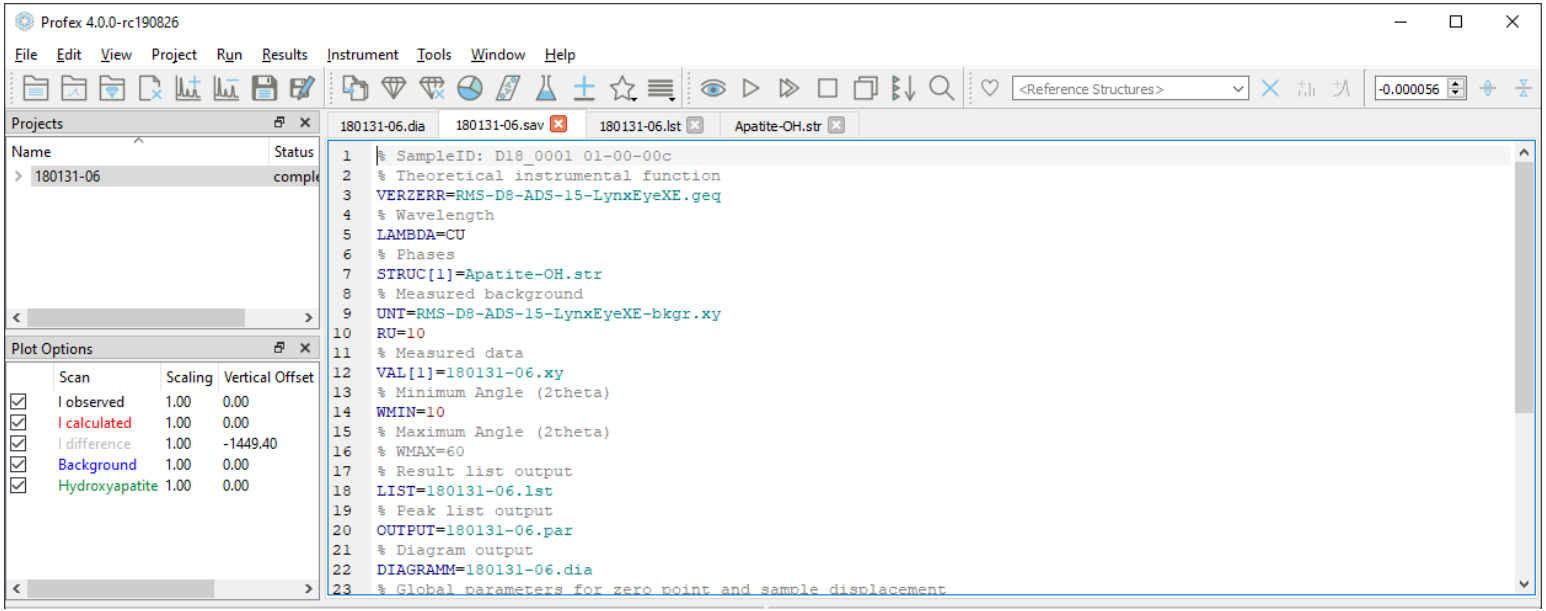
Difference on Ca1 site

$F_{obs} - F_{calc}$



stretched

Electron Density Maps

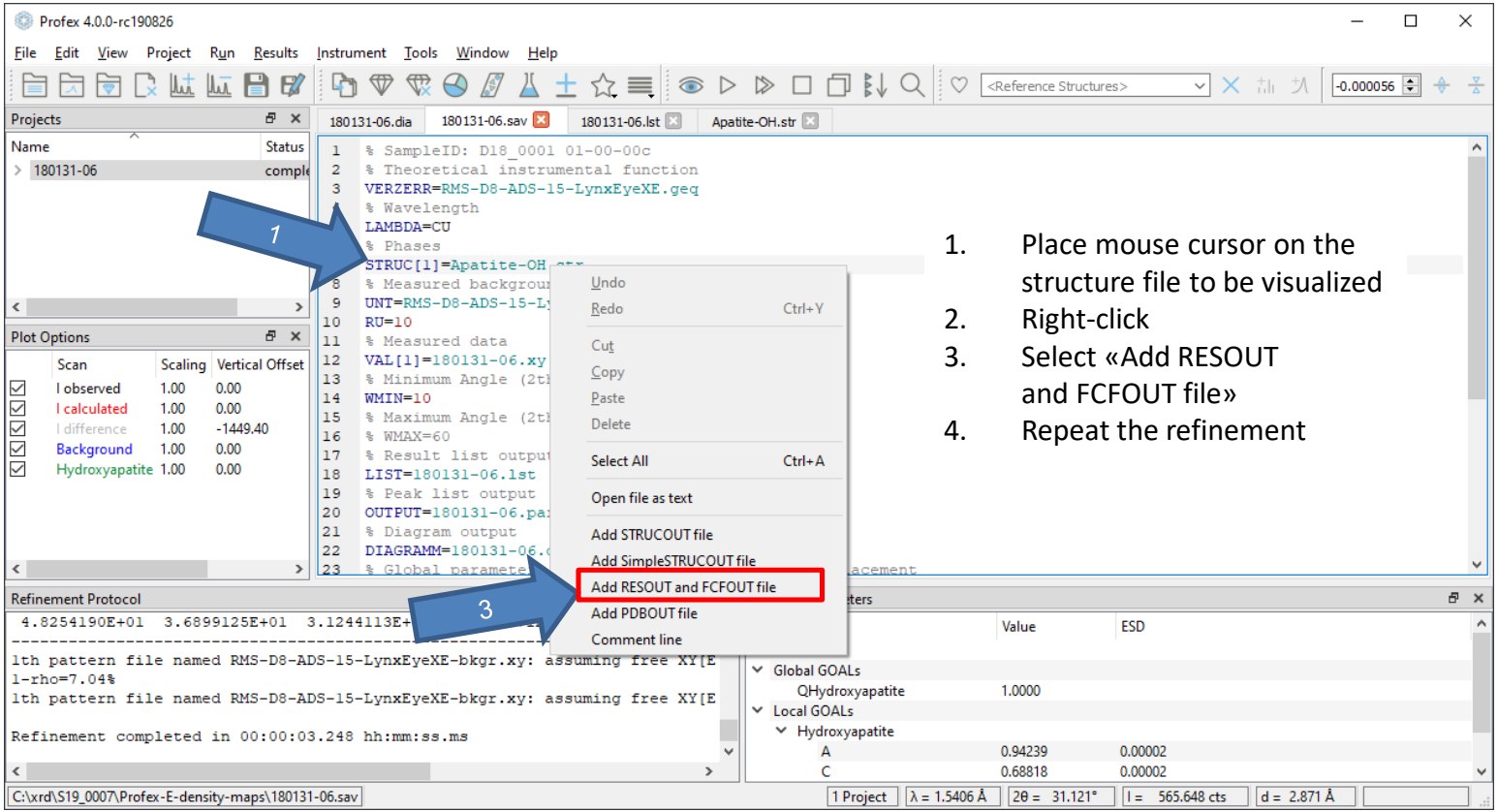


Generate two more output files:

*.res: Contains the refined structure in ShelX format

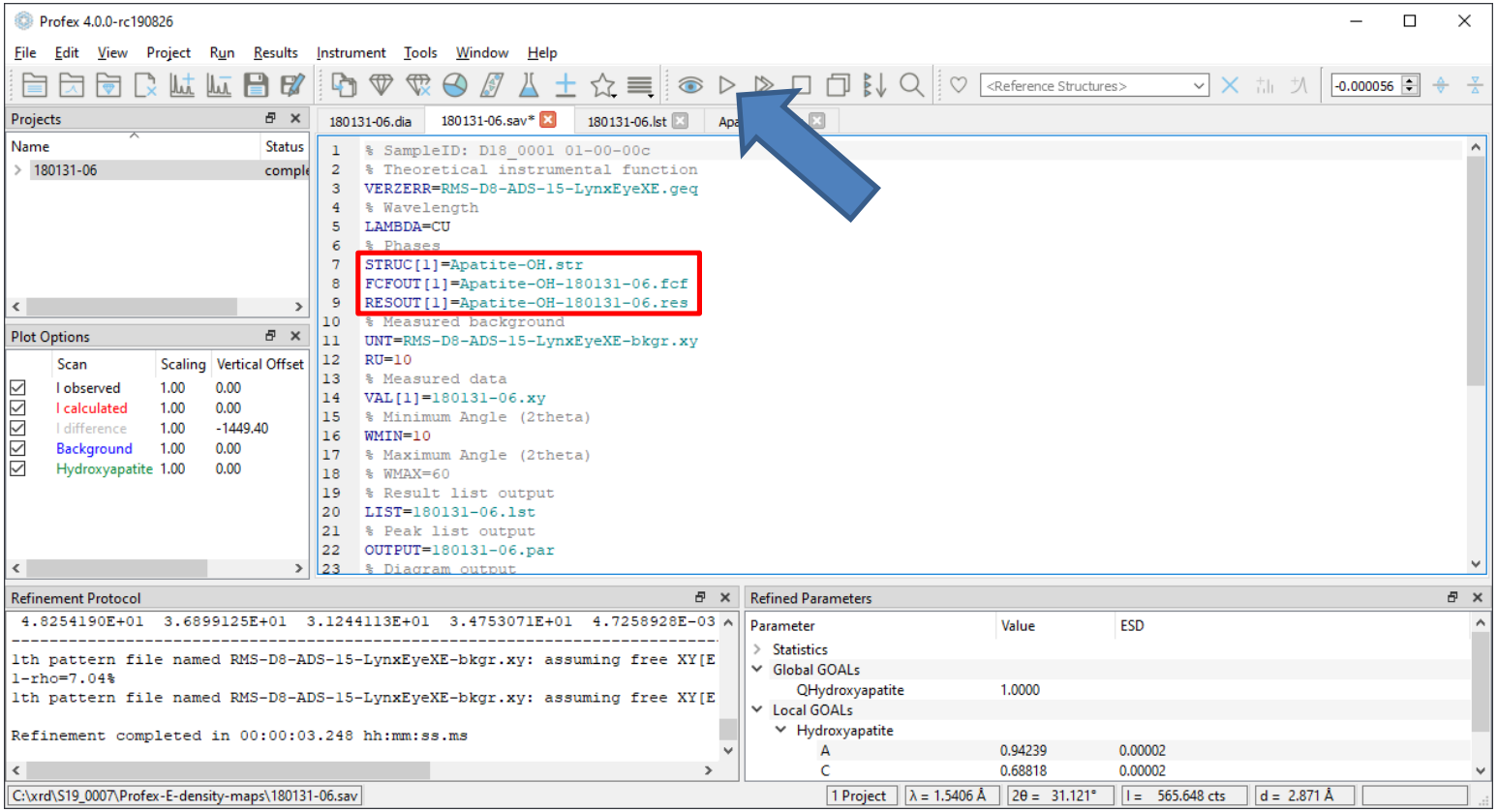
*.fcf: Contains $|F_{obs}|$, $|F_{calc}|$, and ϕ_{calc} in ShelX format

Electron Density Maps



1. Place mouse cursor on the structure file to be visualized
2. Right-click
3. Select «Add RESOUT and FCFOUT file»
4. Repeat the refinement

Electron Density Maps



Electron Density Maps

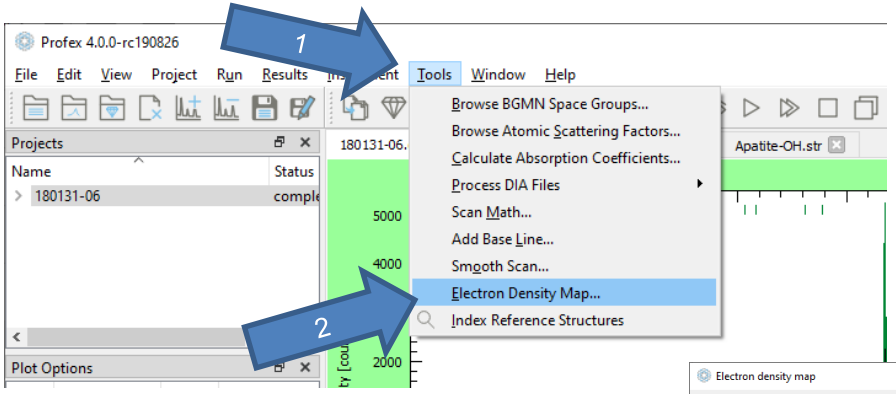
Apatite-OH-180131-06.res

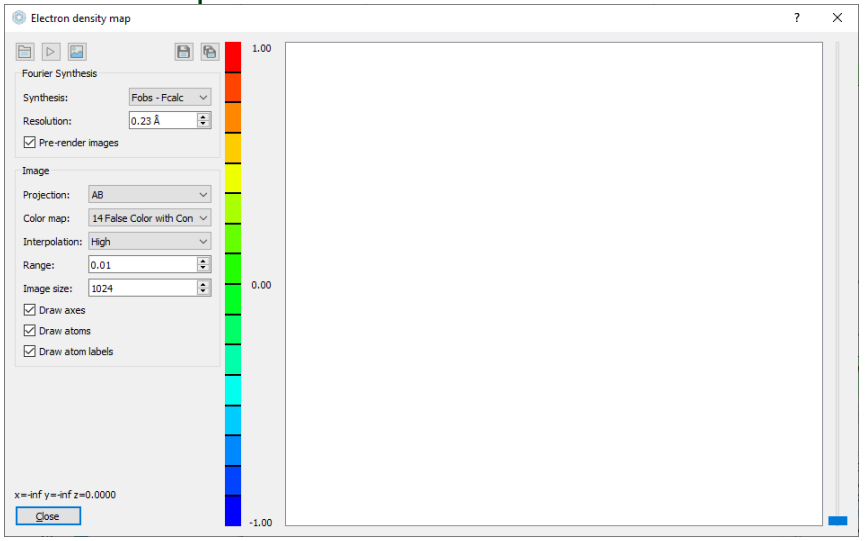
```
TITL P6_3/m No.176 Hydroxyapatite
CELL 1.54100 9.42393 9.42393 6.88182  90.000  90.000 120.000
ZERR    2.00 0.00008 0.00008 0.00006   0.000   0.000   0.000
LATT -1
SYMM -Y, X-Y, Z
SYMM -X+Y, -X, Z
SYMM -X, -Y, Z+0.5
SYMM Y, -X+Y, Z+0.5
SYMM X-Y, X, Z+0.5
SYMM -X, -Y, -Z
SYMM Y, -X+Y, -Z
SYMM X-Y, X, -Z
SYMM X, Y, -Z+0.5
SYMM -Y, X-Y, -Z+0.5
SYMM -X+Y, -X, -Z+0.5
SFAC CA MG P O H
UNIT 6 4 6 26 2
CA1      1   0.33333   0.66667   0.00150   0.00000   0.00841
MG1      2   0.33333   0.66667   0.00150   0.33333   0.00841
CA2      1   0.24680   0.99340   0.25000  10.50000   0.00719
P1       3   0.39870   0.36850   0.25000  10.50000   0.00605
O1       4   0.32840   0.48480   0.25000  10.50000   0.01208
O2       4   0.58730   0.46510   0.25000  10.50000   0.01284
O3       4   0.34370   0.25790   0.07020  11.00000   0.01899
O4       4   0.00000   0.00000   0.19500   0.16667   0.00000
H1       5   0.00000   0.00000   0.06080   0.16667   0.03733
END
```

Apatite-OH-180131-06.fcf

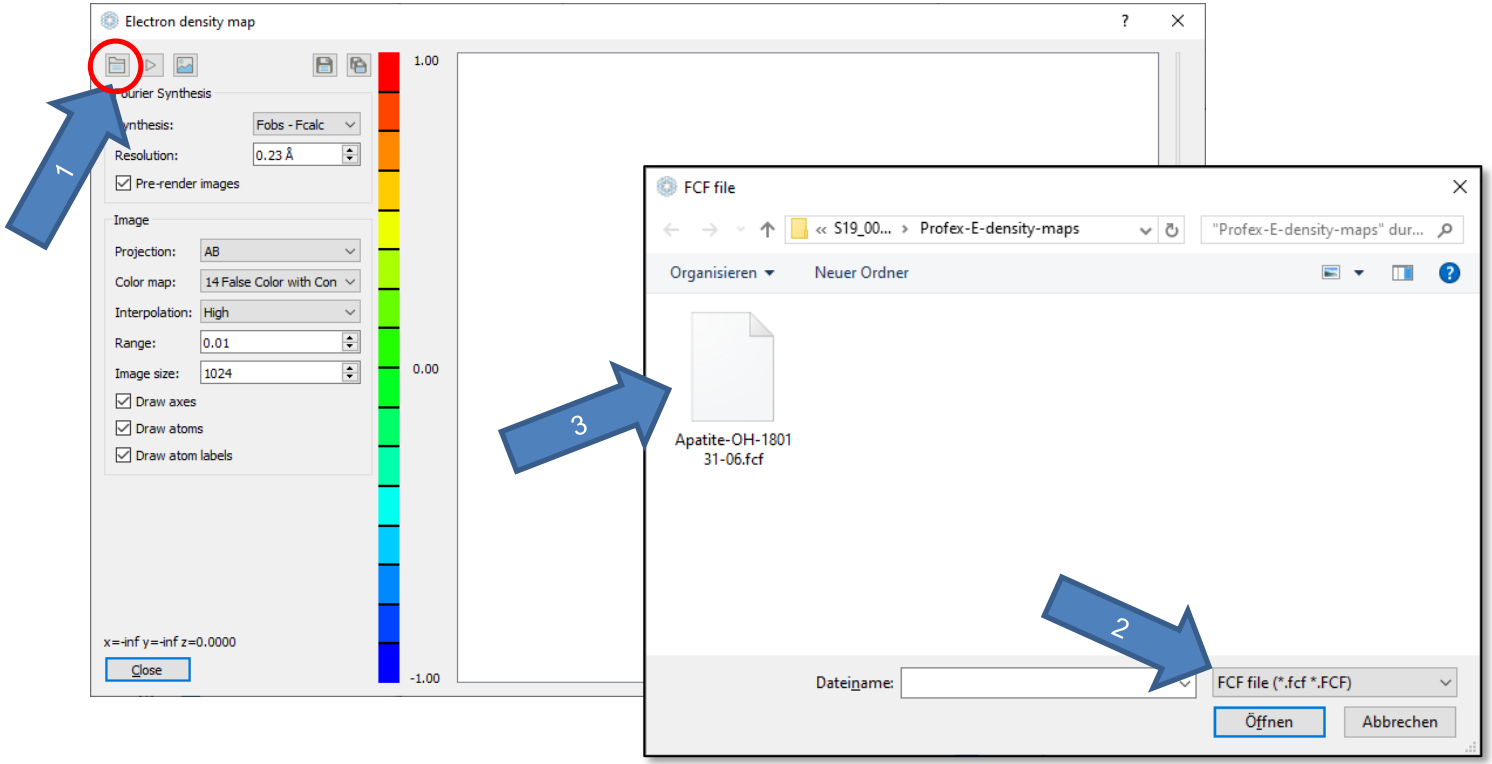
```
   1  -1   0      18.90       5.76 180.00
   1   0   0      18.90       5.76 180.00
  -1   1   0      18.90       5.76 180.00
  -1   0   0      18.90       5.76 180.00
   0   1   0      18.90       5.76 180.00
   0  -1   0      18.90       5.76 180.00
   1  -1   1      15.58      12.83 180.00
   1  -1  -1      15.58      12.83   0.00
   1   0   1      15.58      12.83   0.00
   1   0  -1      15.58      12.83 180.00
  -1   1   1      15.58      12.83   0.00
  -1   1  -1      15.58      12.83 180.00
  -1   0   1      15.58      12.83 180.00
  -1   0  -1      15.58      12.83   0.00
   0   1   1      15.58      12.83 180.00
   0   1  -1      15.58      12.83   0.00
   0  -1   1      15.58      12.83   0.00
   0  -1  -1      15.58      12.83 180.00
   2  -1   0      31.55      41.80 180.00
  -2   1   0      31.55      41.80 180.00
   1  -2   0      31.55      41.80 180.00
   1   1   0      31.55      41.80 180.00
  -1   2   0      31.55      41.80 180.00
  -1  -1   0      31.55      41.80 180.00
   2  -2   0      31.20      14.56 180.00
   2   0   0      31.20      14.56 180.00
…
```

Electron Density Maps

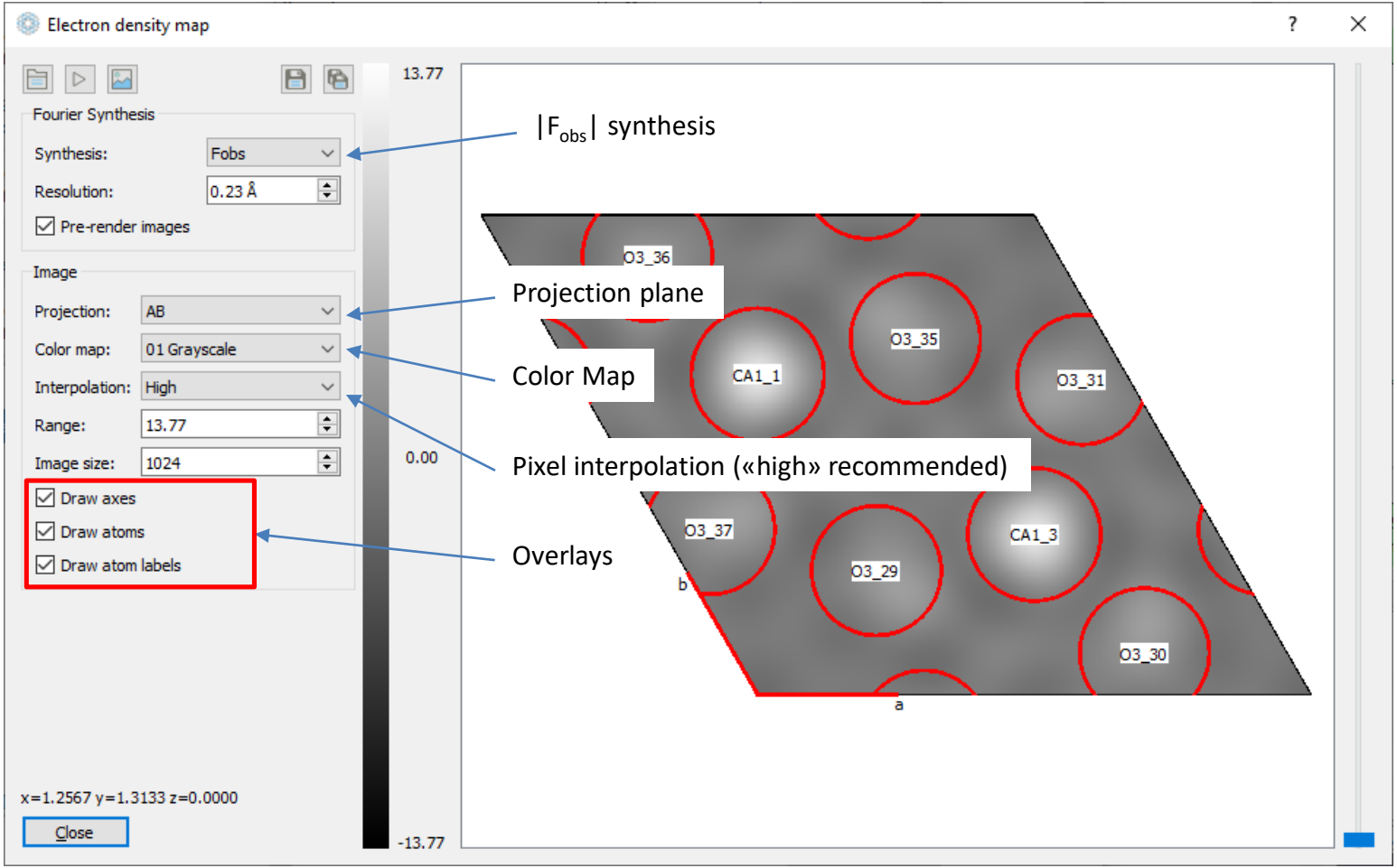




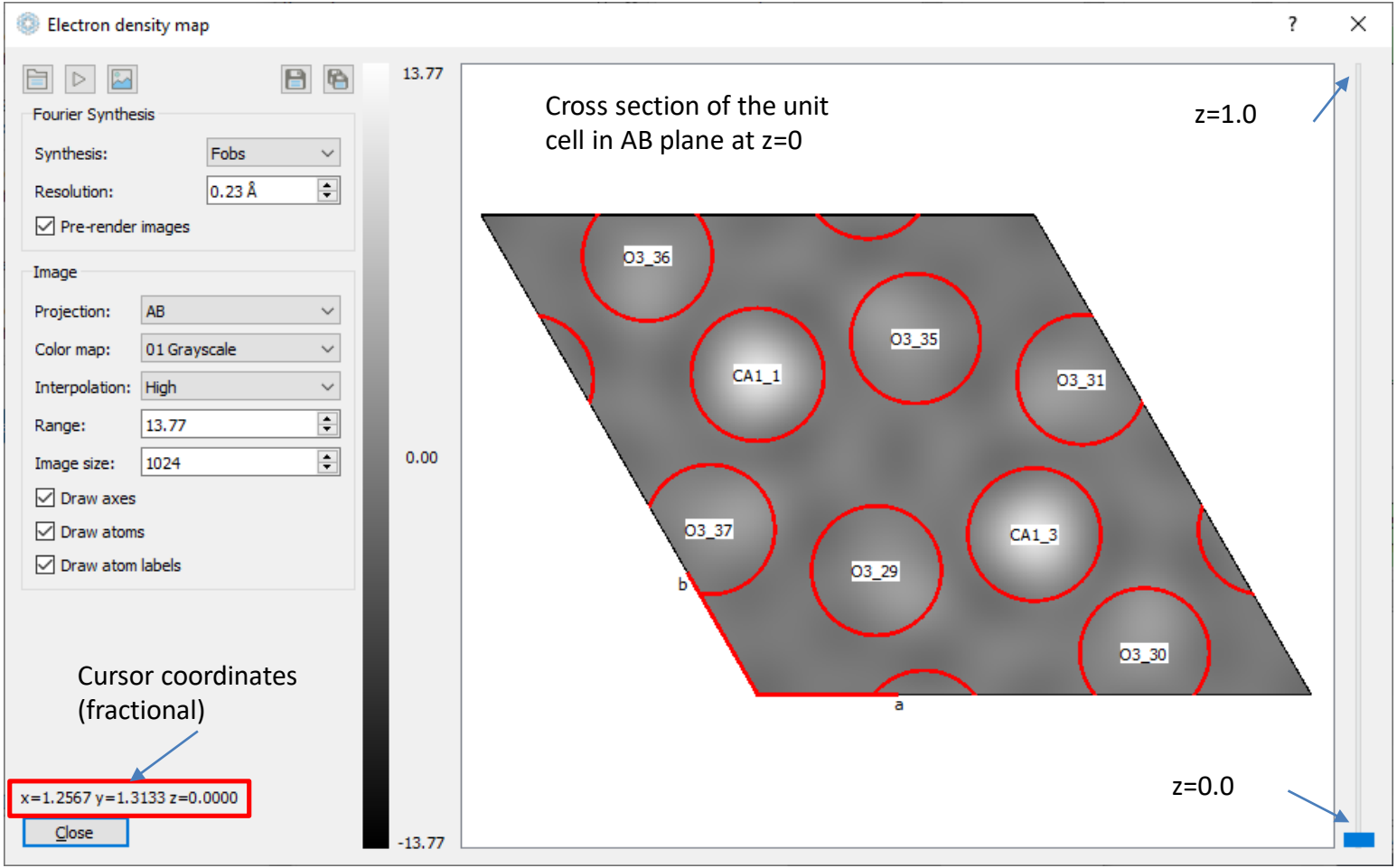
Electron Density Maps



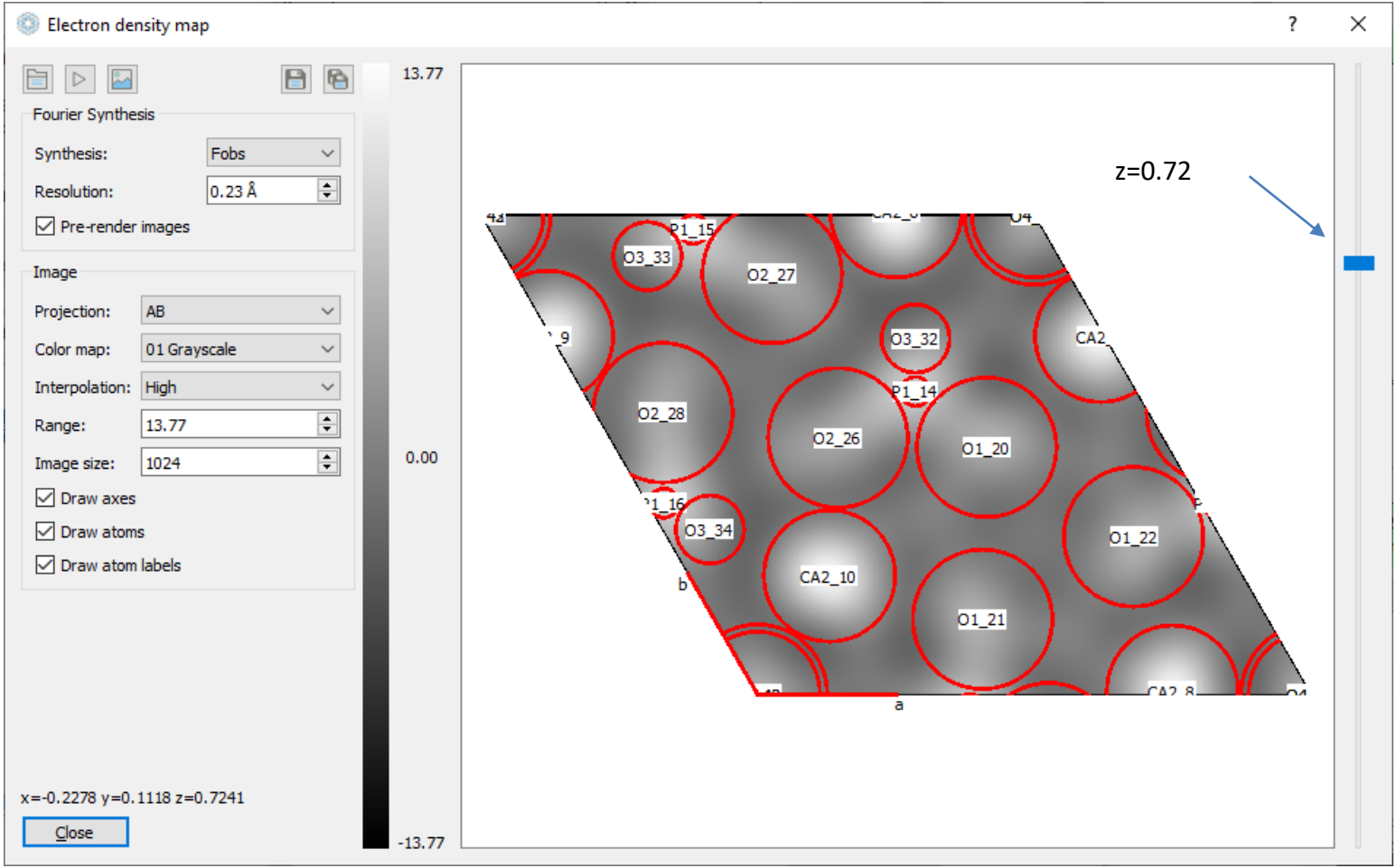
Electron Density Maps



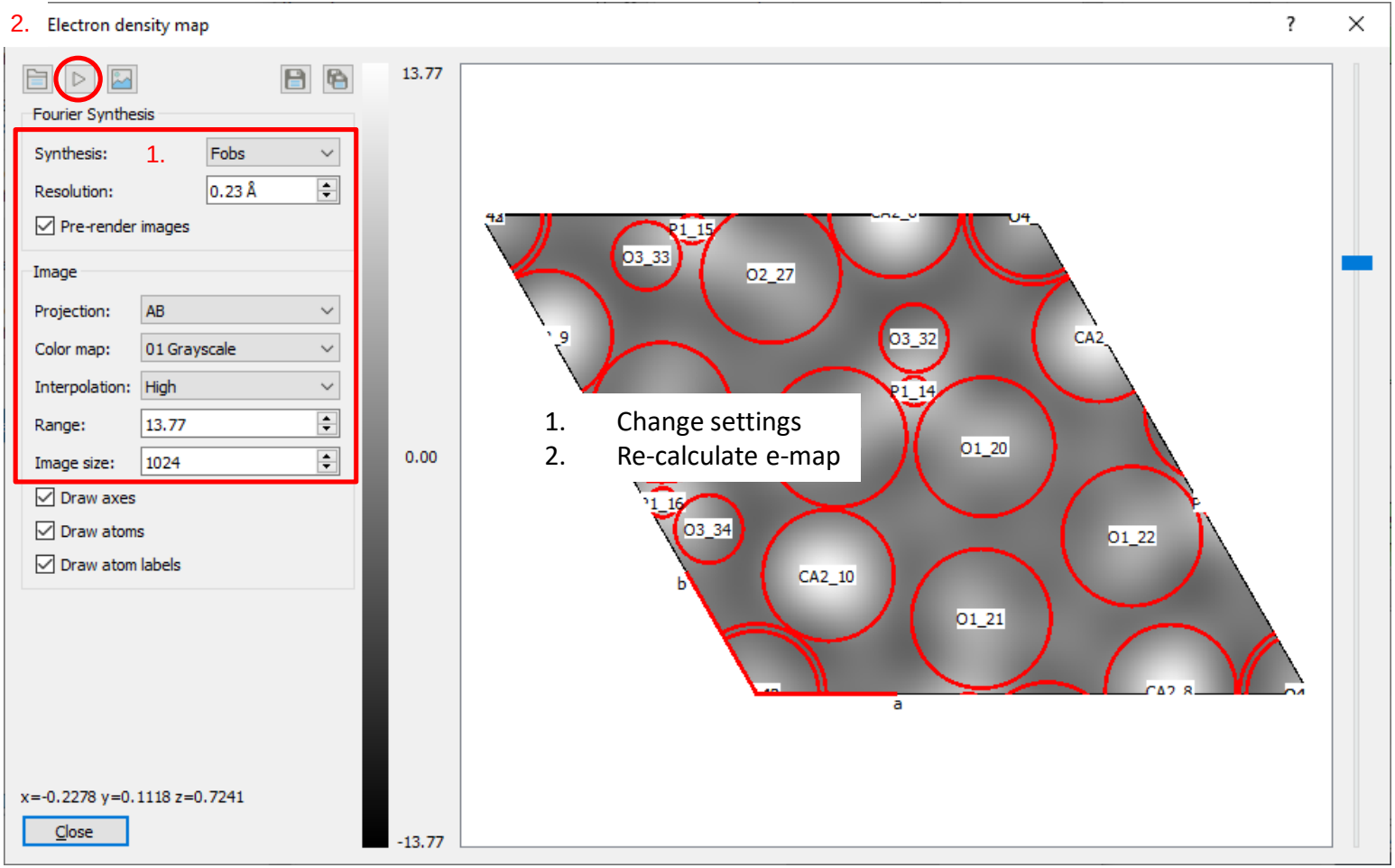
Electron Density Maps



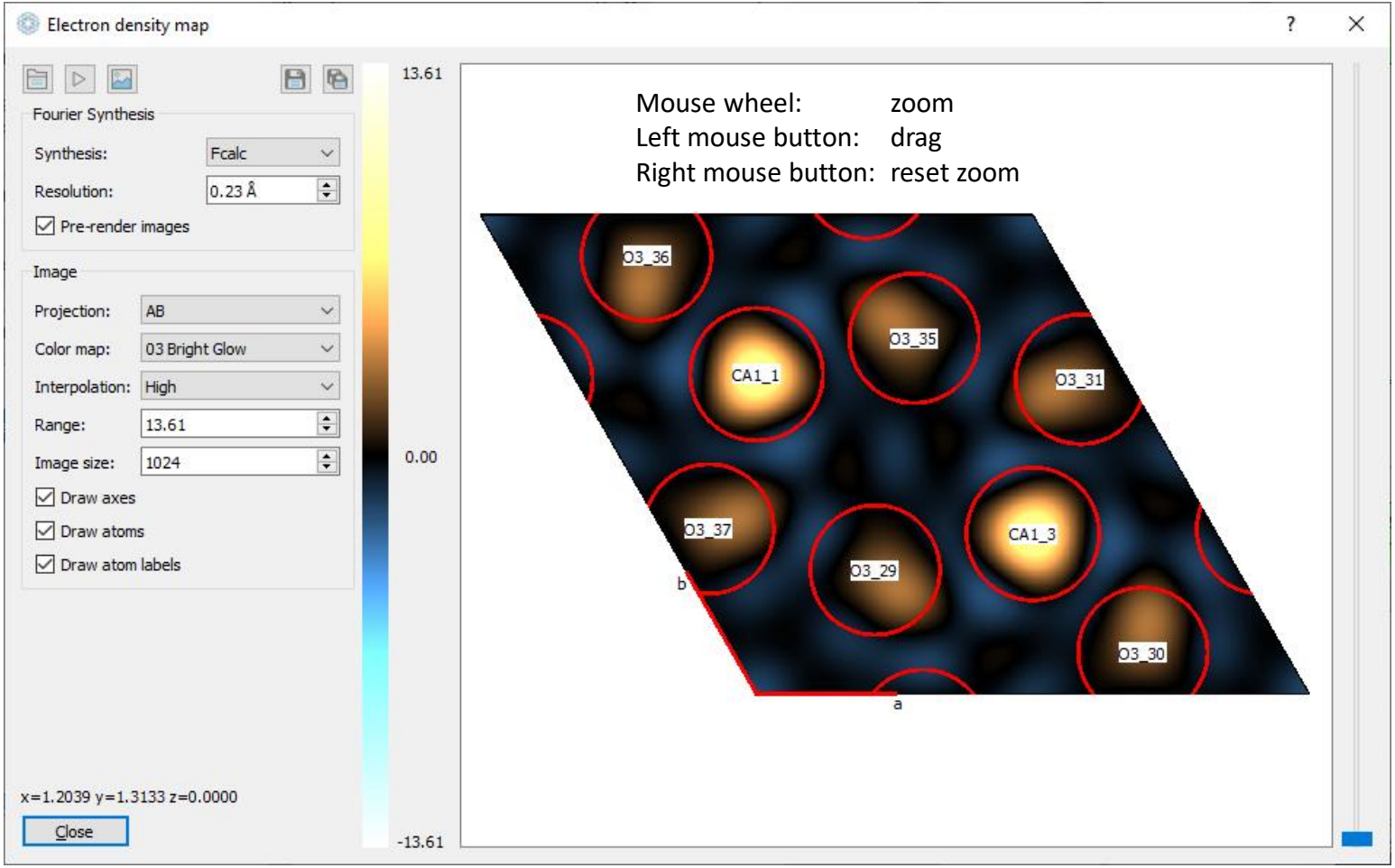
Electron Density Maps



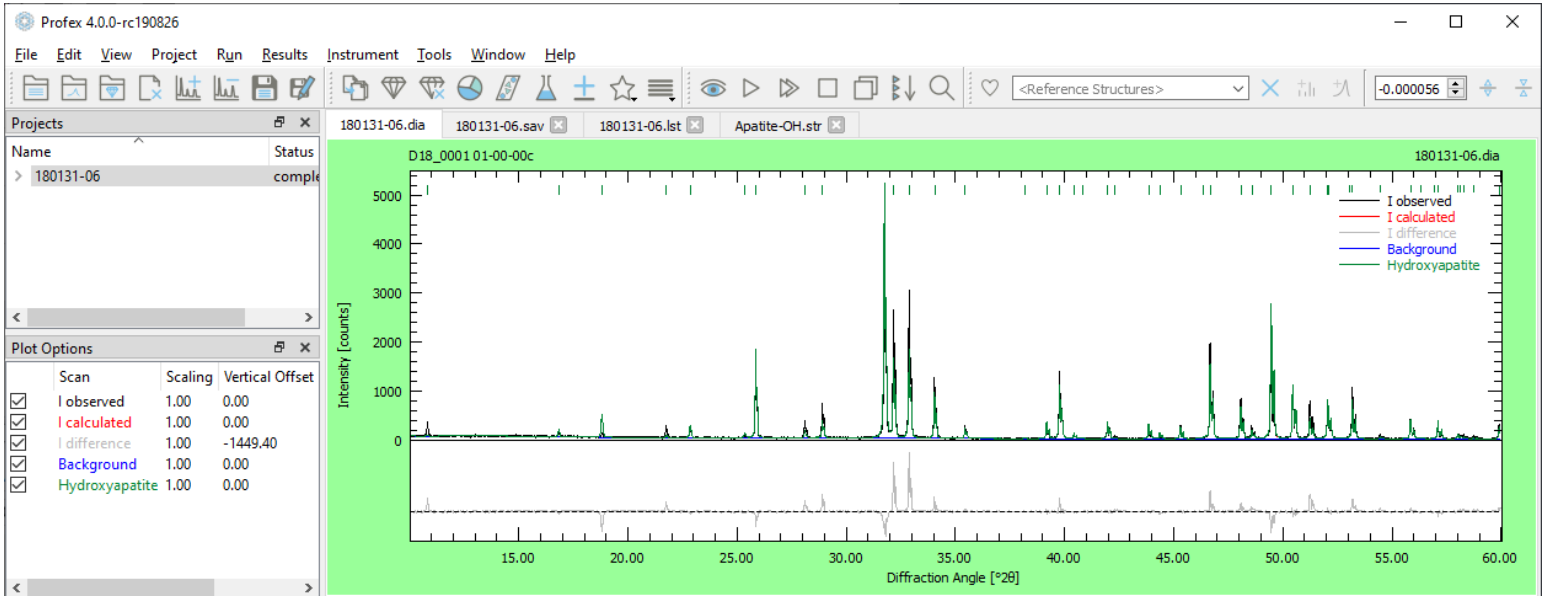
Electron Density Maps



Electron Density Maps



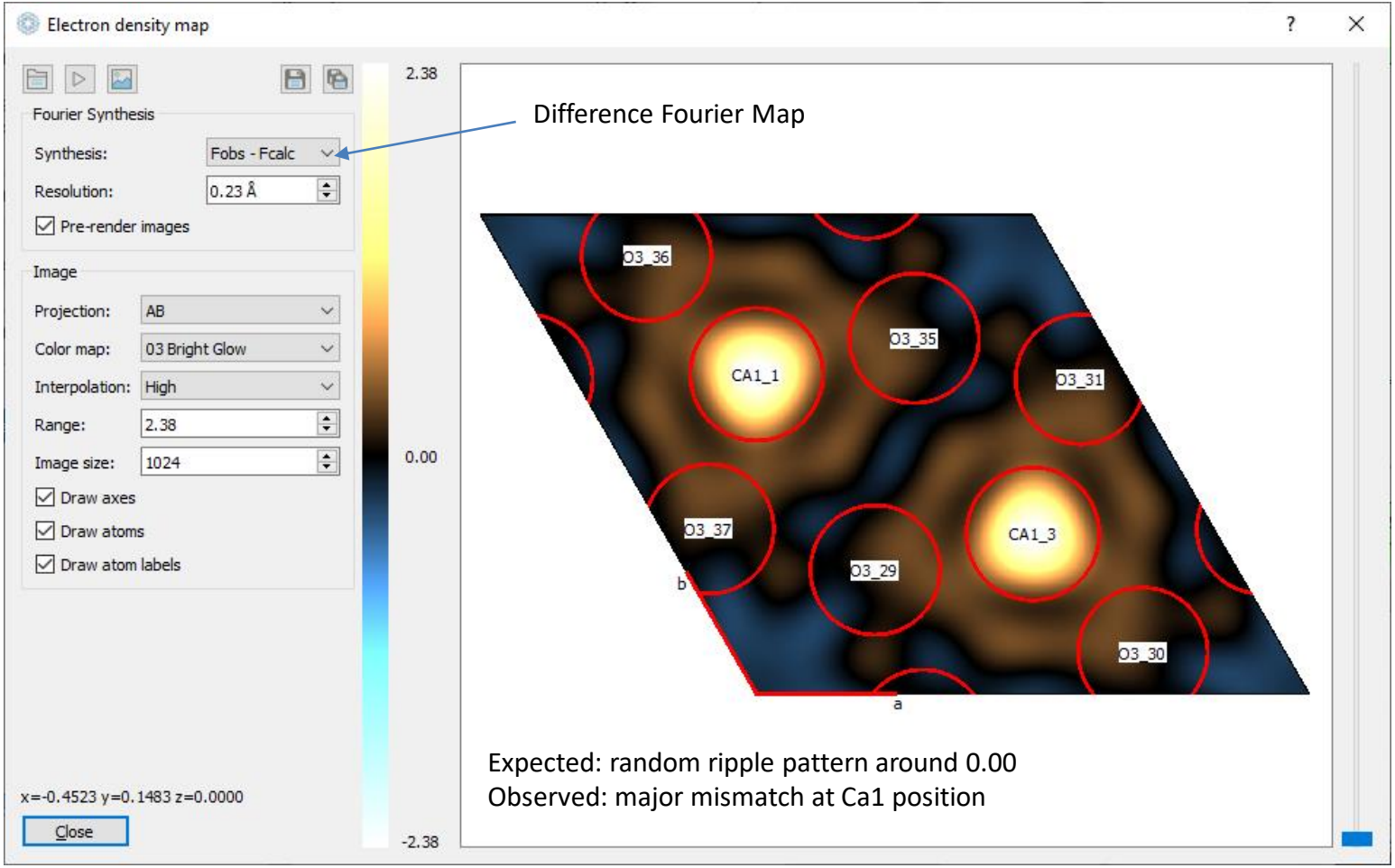
Electron Density Maps



Where does the mismatch come from?

→ Compute Difference Fourier Map

Electron Density Maps



Difference Fourier Map

1. Fix refinement of Ca1 position
2. Repeat the refinement
3. Re-calculate Difference Fourier Map
4. Check for improvement

```
PHASE=Hydroxyapatite // 01-074-0565
MineralName=Hydroxylapatite //
Formula=Ca5_(PO4)3_(OH) //
SpacegroupNo=176 HermannMauguin=P6_3/m //
PARAM=A=0.9424_0.932976^0.951824 PARAM=C=0.6879_0.6810^0.6948 //
RP=4 k1=0 PARAM=k2=0_0^0.0001 B1=ANISO^0.05 GEWICHT=SPHAR4 //
GOAL=GrainSize(0,0,1) //
GOAL=GrainSize(1,0,0) //
GOAL:Hydroxyapatite=GEWICHT*ifthenelse(ifdef(d),exp(my*d*3/4),1)
E=(CA(0),MG(1)) Wyckoff=f x=0.3333 y=0.6667 z=0.0015 TDS=0.00664290
E=CA Wyckoff=h x=0.2468 y=0.9934 z=0.2500 TDS=0.00567436
E=P  Wyckoff=h x=0.3987 y=0.3685 z=0.2500 TDS=0.00477426
E=O  Wyckoff=h x=0.3284 y=0.4848 z=0.2500 TDS=0.00953535
E=O  Wyckoff=h x=0.5873 y=0.4651 z=0.2500 TDS=0.01014069
E=O  Wyckoff=i x=0.3437 y=0.2579 z=0.0702 TDS=0.01499127
E=O(0.5) Wyckoff=e x=0.0000 y=0.0000 z=0.1950 TDS=0.00000000
E=H(0.5) Wyckoff=e x=0.0000 y=0.0000 z=0.0608 TDS=0.02947459
```

Ca1 is completely substituted with Mg

(to generate a massive mismatch)

Difference Fourier Map

Instead of changing it back to 100% Ca, lets refine the Ca / Mg ratio:

```
E=(CA(0),MG(1)) Wyckoff=f x=0.3333 y=0.6667 z=0.0015 TDS=0.00664290
```

Step 1: Parametrize the site occupancy factors.
Keep the site fully occupied but with variable Ca / Mg ratio.

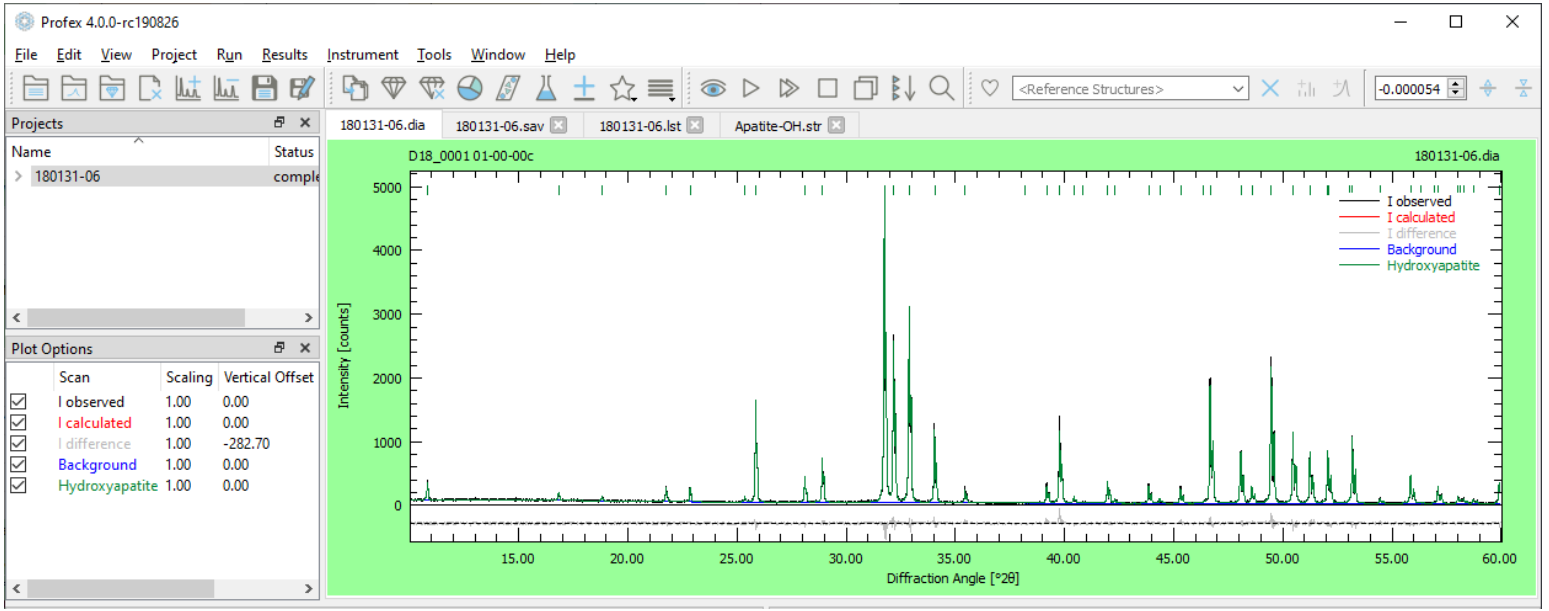
```
E=(CA(p),MG(1-p)) p=0 Wyckoff=f x=0.3333 y=0.6667 z=0.0015 TDS=0.00664290
```

Step 2: Refine p between 0 and 1.

```
E=(CA(p),MG(1-p)) PARAM=p=0_0^1 Wyckoff=f x=0.3333 y=0.6667 z=0.0015 TDS=0.00664290
```

Step 3: Repeat the refinement.
Recalculate the Difference Fourier Map.

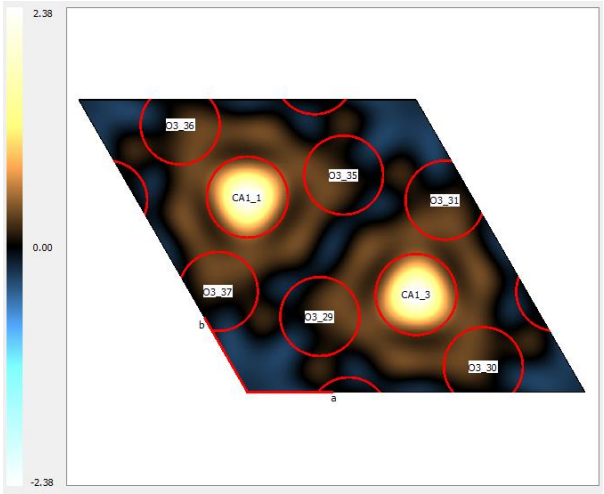
Difference Fourier Map



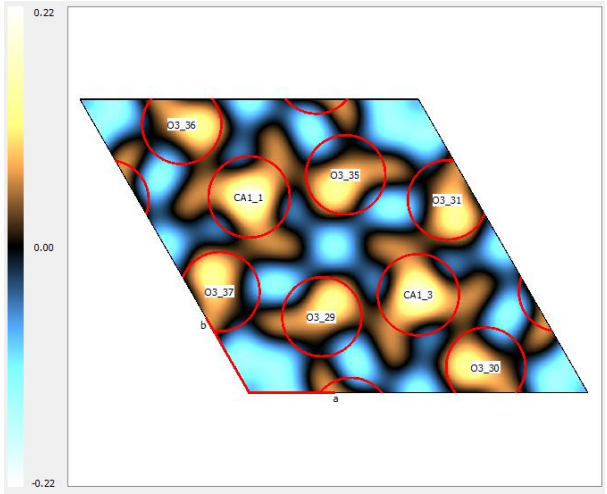
Mismatch in diffraction pattern is gone

Difference Fourier Map

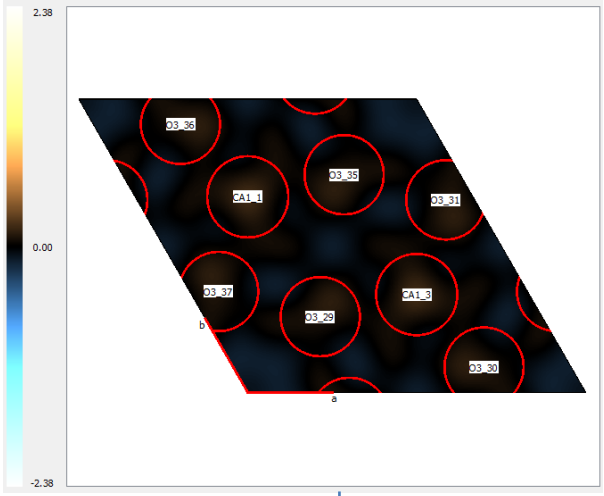
100% Mg substitution



Refined Mg substitution



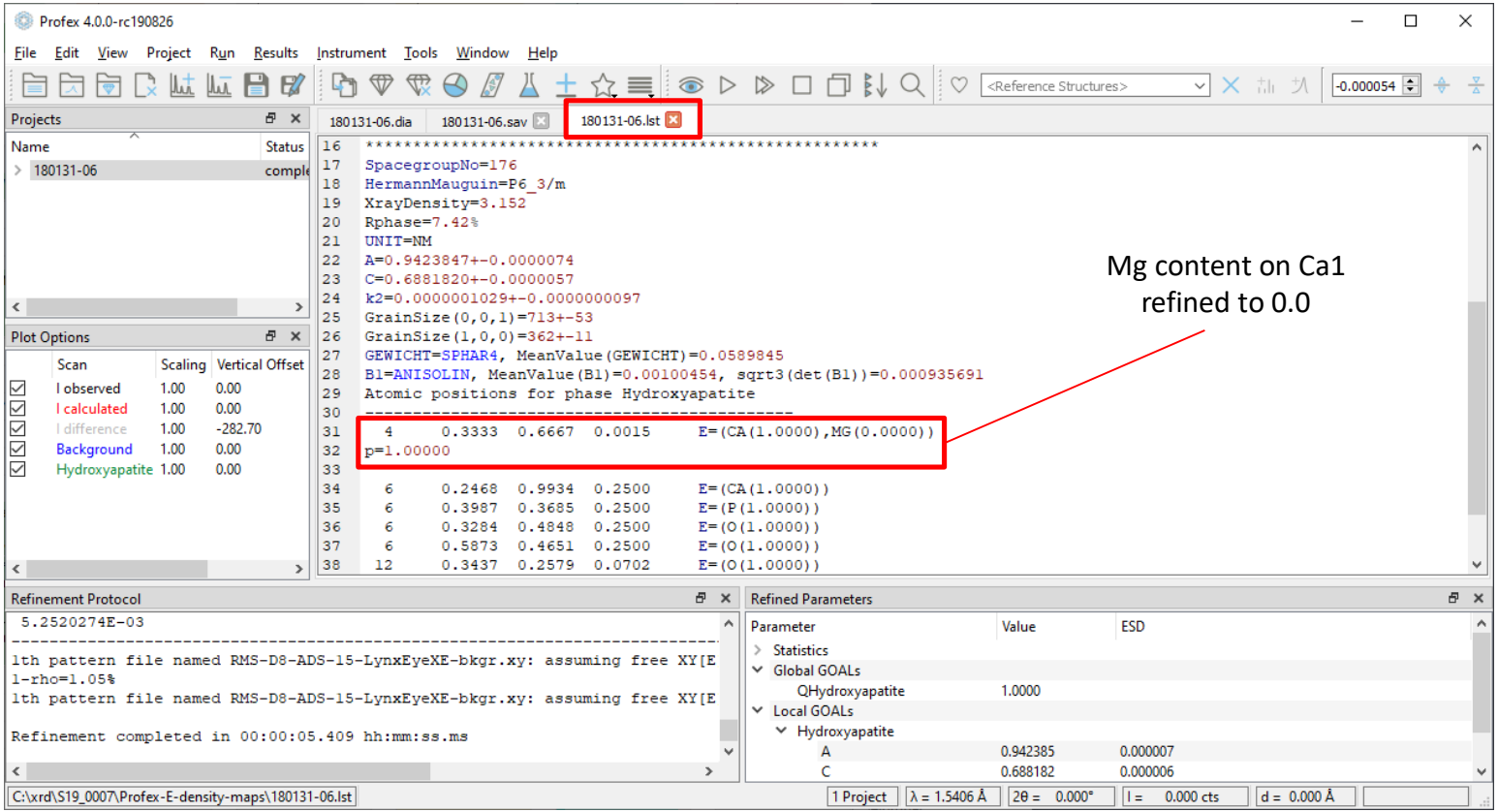
Refined Mg substitution
with range -2.38 to 2.38



Set «range» to 2.38
Click «Render images»

Massive improvement

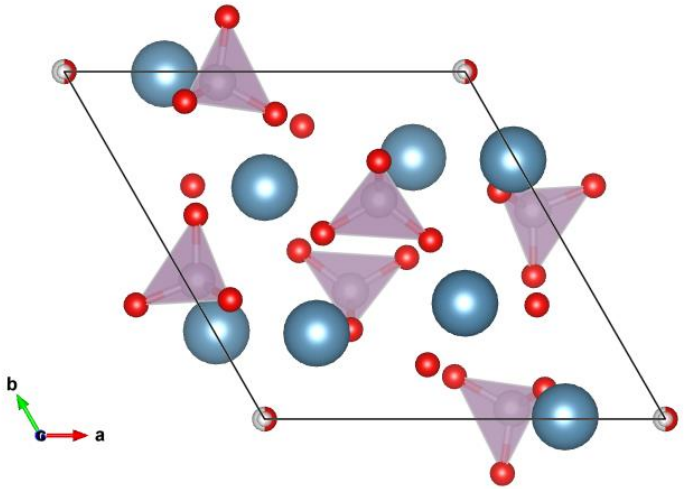
Difference Fourier Map



Drawing Crystal Structures

Visualizing refined crystal structures

1. Refine structural parameters (atomic coordinates)
2. Export refined crystal structure data in CIF format
3. Import in structure visualization program



Works with any visualization program supporting CIF input files.
Tested with: Vesta [1], Mercury [2], Diamond [3]

[1] http://www.jp-minerals.org/vesta/en/
[2] https://www.ccdc.cam.ac.uk/solutions/csd-system/components/mercury/
[3] https://www.crystalimpact.com/diamond/Default.htm

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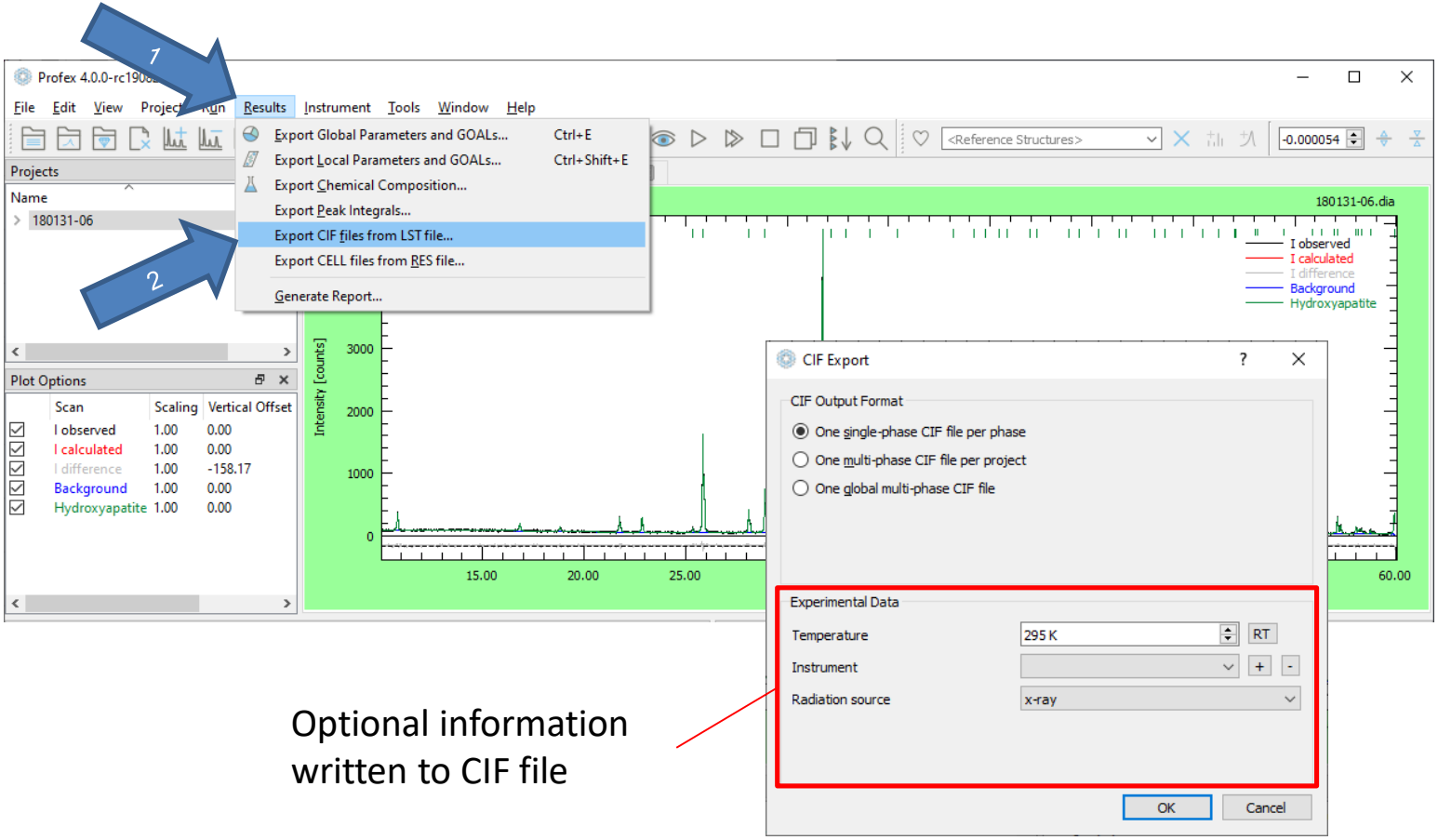
Drawing Crystal Structures

Example «Profex-structure-visualization»:

1. Open Apatite-OH.str
2. Refine unit cell and profile parameters k2, B1, GEWICHT
3. Refine Mg substitution on both Ca sites
4. Refine all general atomic coordinates (except for H site)
5. Refine all TDS (except for H site)

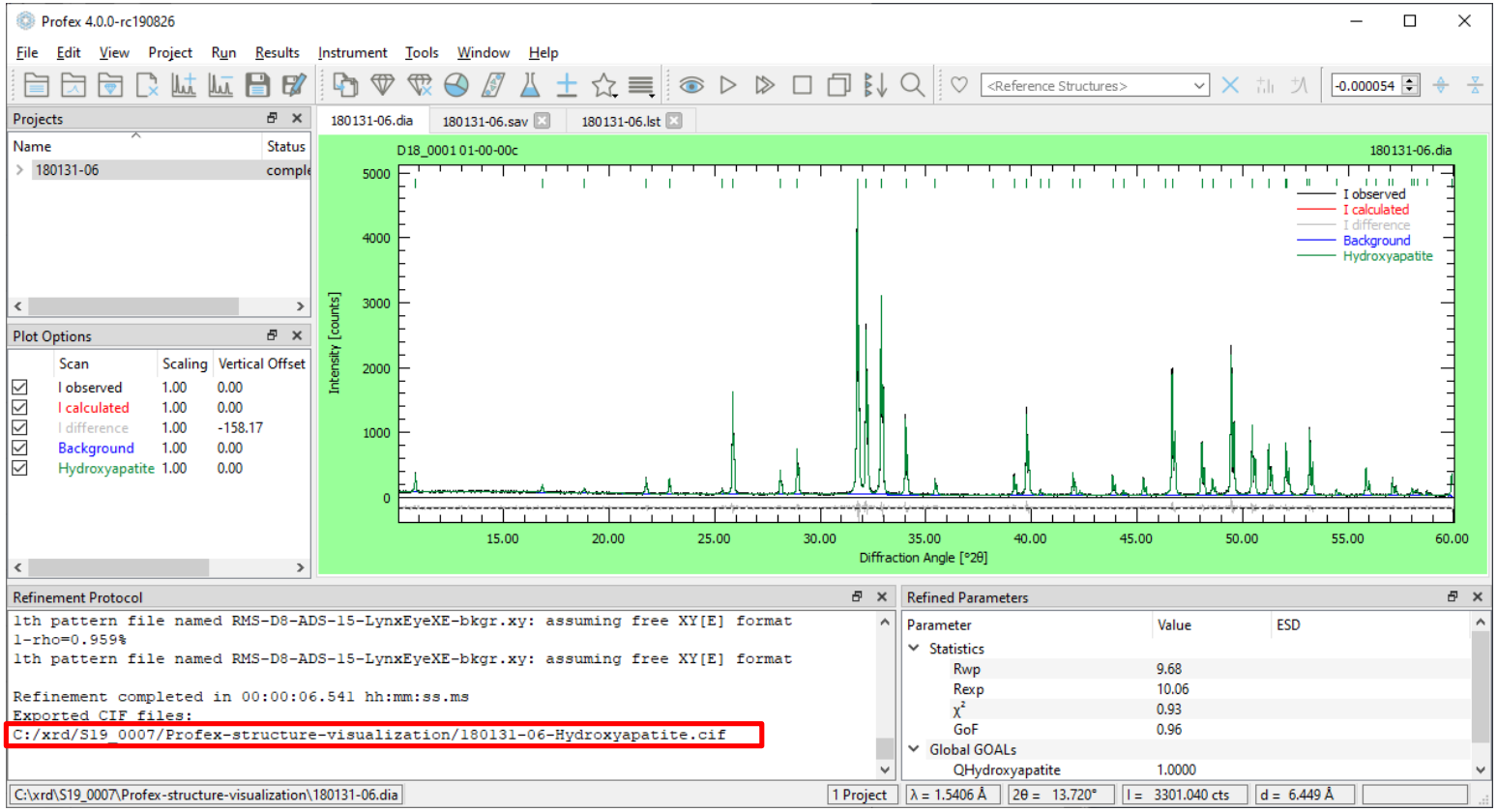
```
PHASE=Hydroxyapatite // 01-074-0565
MineralName=Hydroxylapatite //
Formula=Ca5_(PO4)3_(OH) //
SpacegroupNo=176 HermannMauguin=P6_3/m //
PARAM=A=0.9424_0.932976^0.951824 PARAM=C=0.6879_0.6810^0.6948 //
RP=4 k1=0 PARAM=k2=0_0^0.0001 B1=ANISO^0.05 GEWICHT=SPHAR4 //
GOAL=GrainSize(0,0,1) //
GOAL=GrainSize(1,0,0) //
GOAL:Hydroxyapatite=GEWICHT*ifthenelse(ifdef(d),exp(my*d*3/4),1)
E=(CA(p),MG(1-p)) PARAM=p=0_0^1 Wyckoff=f x=0.3333 y=0.6667 PARAM=z=0.0015_-0.0485^0.0515 PARAM=TDS=0.006643_0^0.02
E=(CA(p),MG(1-p)) PARAM=p=0_0^1 Wyckoff=h PARAM=x=0.2468_0.1968^0.2968 PARAM=y=0.9934_0.9434^1.0434 z=0.2500 PARAM=TDS=0.005674_0^0.02
E=P Wyckoff=h PARAM=x=0.3987_0.3487^0.4487 PARAM=y=0.3685_0.3185^0.4185 z=0.2500 PARAM=TDS=0.004774_0^0.02
E=O Wyckoff=h PARAM=x=0.3284_0.2784^0.3784 PARAM=y=0.4848_0.4348^0.5348 z=0.2500 PARAM=TDS=0.009535_0^0.02
E=O Wyckoff=h PARAM=x=0.5873_0.5373^0.6373 PARAM=y=0.4651_0.4151^0.5151 z=0.2500 PARAM=TDS=0.010141_0^0.02
E=O Wyckoff=i PARAM=x=0.3437_0.2937^0.3937 PARAM=y=0.2579_0.2079^0.3079 PARAM=z=0.0702_0.0202^0.1202 PARAM=TDS=0.014991_0^0.02
E=O(0.5000) Wyckoff=e x=0.0000 y=0.0000 PARAM=z=0.1950_0.1450^0.2450 TDS=0.00000000
E=H(0.5000) Wyckoff=e x=0.0000 y=0.0000 z=0.0608 TDS=0.029475
```

Drawing Crystal Structures

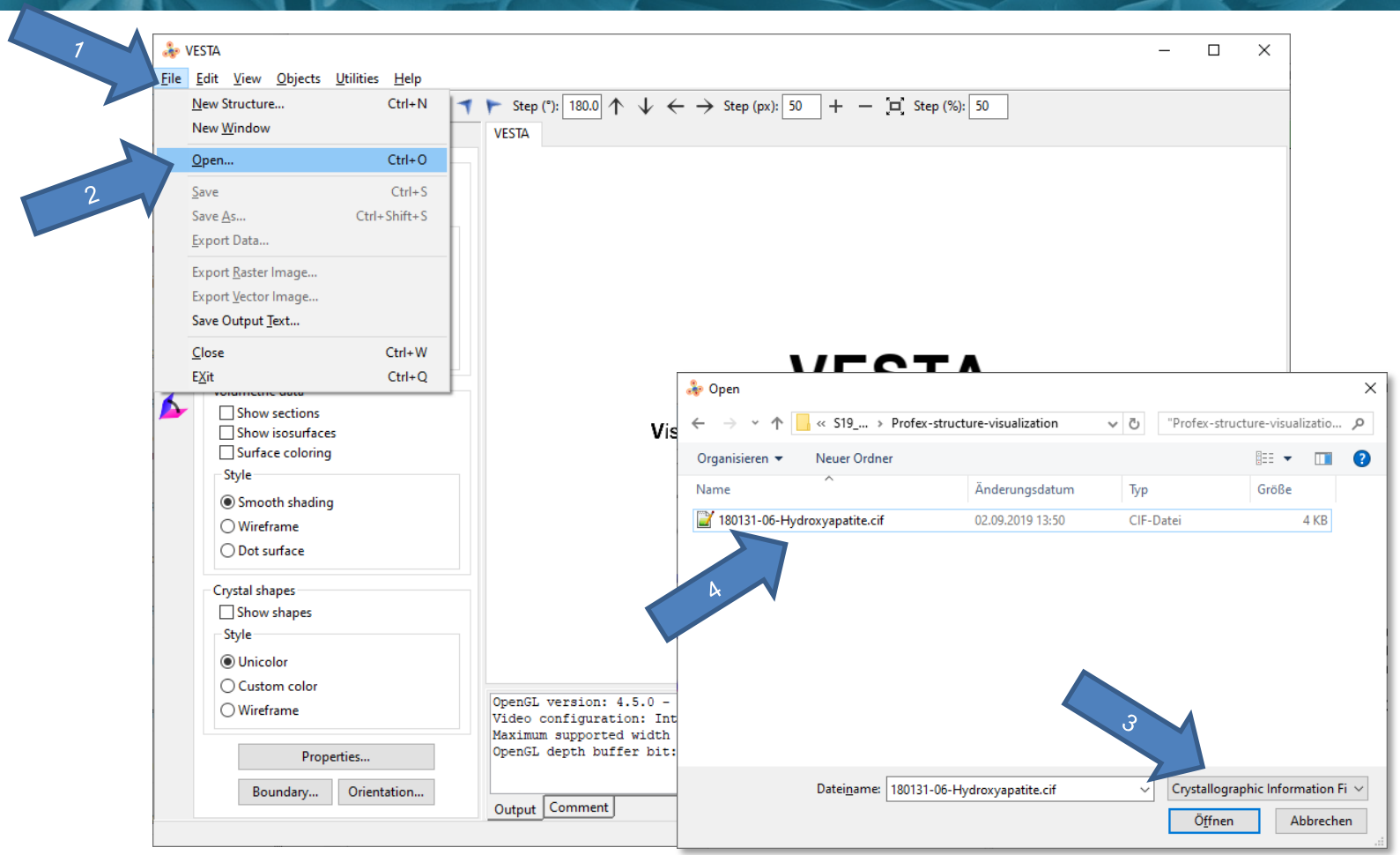


Optional information written to CIF file

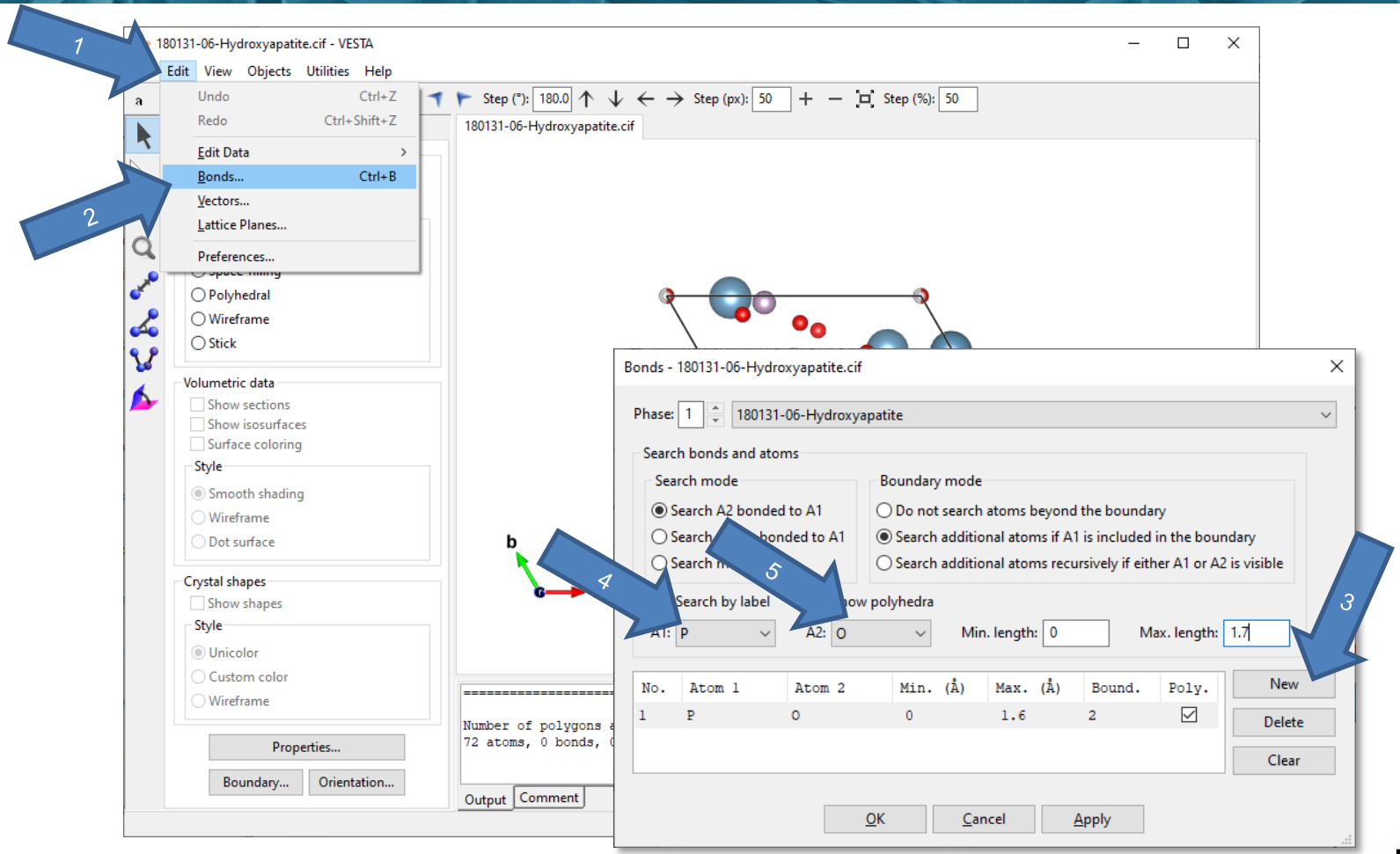
Drawing Crystal Structures



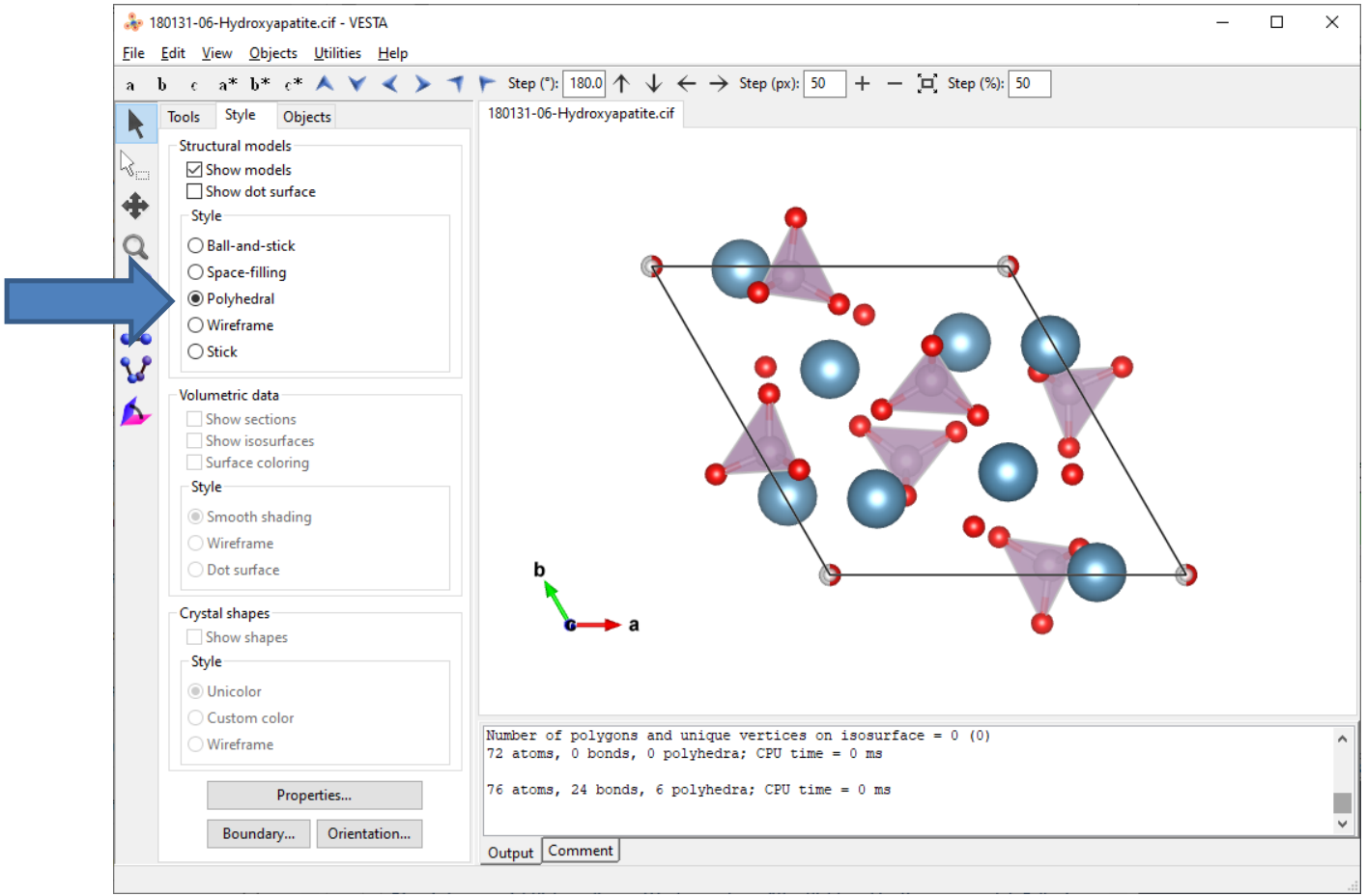
Drawing Crystal Structures



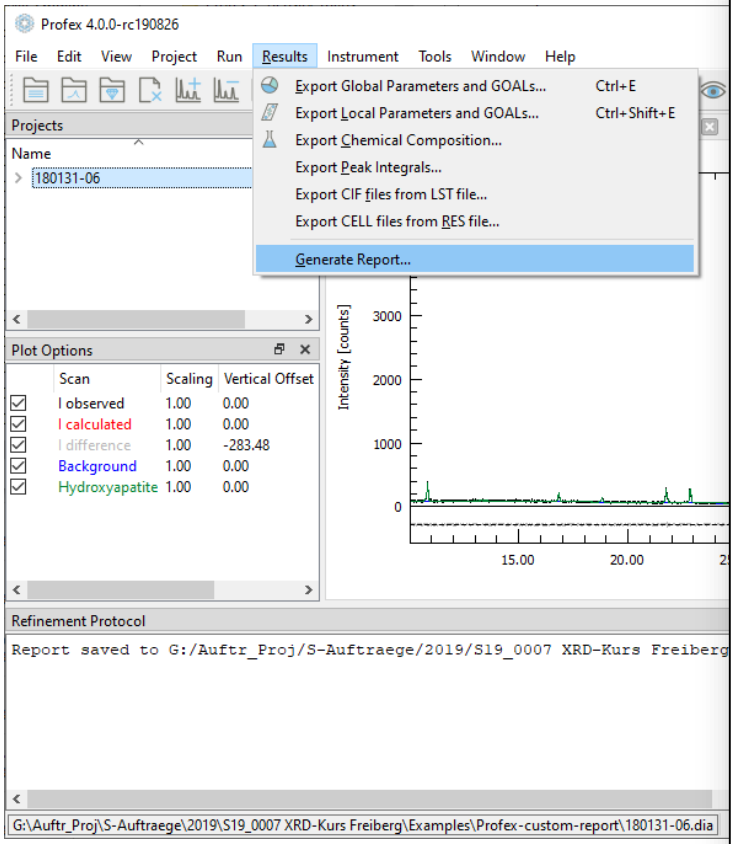
Drawing Crystal Structures

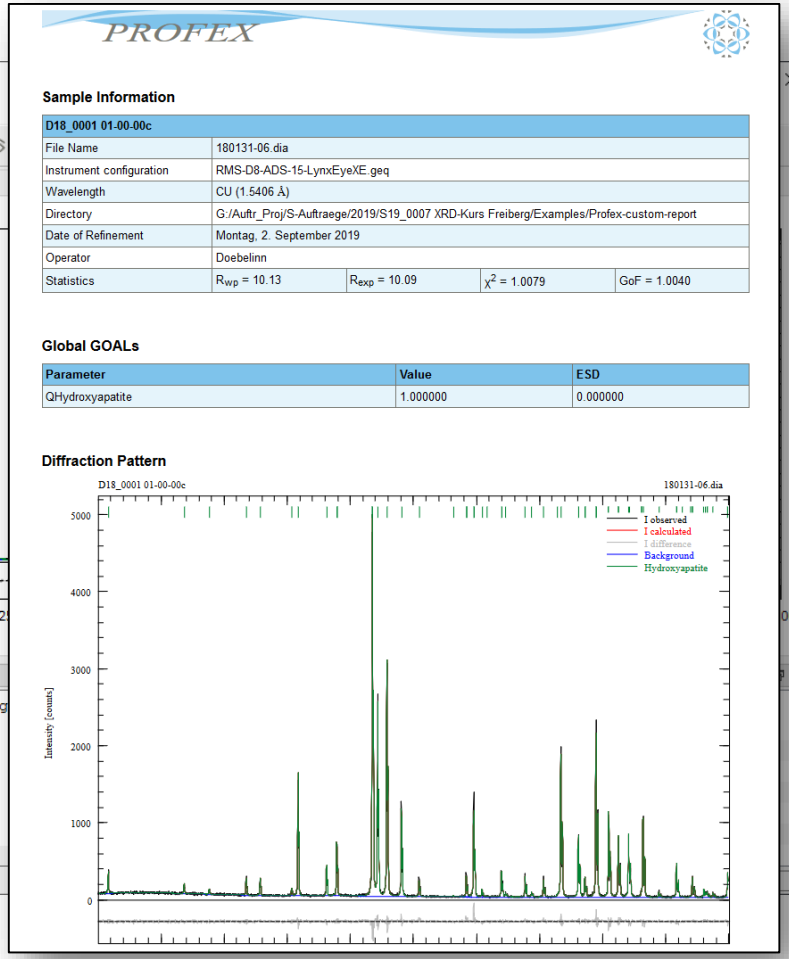


Drawing Crystal Structures



Custom Refinement Reports





Custom Refinement Reports

PROFEX

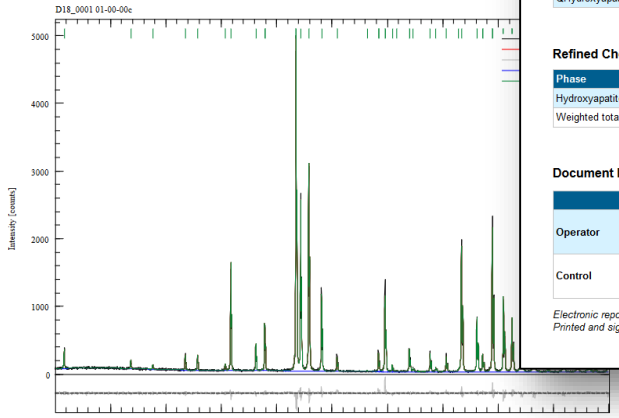
Sample Information

D18_0001 01-00-00c	
File Name	180131-06.dia
Instrument configuration	RMS-D8-ADS-15-LynxEyeXE.geq
Wavelength	CU (1.5406 Å)
Directory	G:/Auftr_Proj/S-Auftraege/2019/S19_0007 XRD-Kurs Freiberg/Examples/Profex-
Date of Refinement	Montag, 2. September 2019
Operator	Doebelinn
Statistics	R_{wp} = 10.13	R_{exp} = 10.09	χ^2 = 1.0079	G

Global GOALs

Parameter	Value	ESD
QHydroxyapatite	1.000000	0.000000

Diffraction Pattern



RMS

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Sample Information

D18_0001 01-00-00c				
File Name	180131-06.dia			
Instrument configuration	RMS-D8-ADS-15-LynxEyeXE.geq			
Wavelength	CU (1.5406 Å)			
Directory	G:/Auftr_Proj/S-Auftraege/2019/S19_0007 XRD-Kurs Freiberg/Examples/Profex-custom			
Date of Refinement	Montag, 2. September 2019			
Operator	Nicola Döbelin			
Statistics	R_{wp} = 10.13	R_{exp} = 10.09	χ^2 = 1.0079	GoF = 1

Global GOALs

Parameter	Value	ESD
QHydroxyapatite	1.000000	0.000000

Refined Chemical Composition

Phase	Phase Quantity (wt-%)	H2O (wt-%)	MgO (wt-%)	P2O5 (wt-%)	C
Hydroxyapatite	100.00	1.79	0.00	42.39	5
Weighted total	100.00	1.79	0.00	42.39	5

Document Release

	Name	Date / Signature
Operator	.....	.....
Control	.....	.....

Electronic reports/certificates distributed as PDF files do not contain original signatures and therefore are for information
Printed and signed reports/certificates are the only valid documentation.

TECHNISCHE UNIVERSITÄT BERGAKADEMIE FREIBERG
The University of Resources, Since 1765.

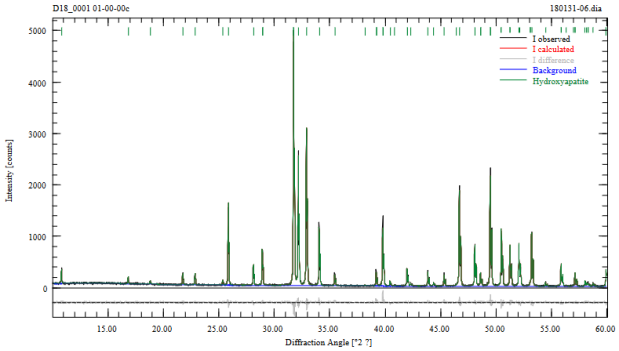
Sample Information

D18_0001 01-00-00c				
File Name	180131-06.dia			
Instrument configuration	RMS-D8-ADS-15-LynxEyeXE.geq			
Wavelength	CU (1.5406 Å)			
Directory	G:/Auftr_Proj/S-Auftraege/2019/S19_0007 XRD-Kurs Freiberg/Examples/Profex-custom-report			
Date of Refinement	Montag, 2. September 2019			
Operator	Nicola Döbelin			
Statistics	R_{wp} = 10.13	R_{exp} = 10.09	χ^2 = 1.0079	GoF = 1.0040

Global GOALs

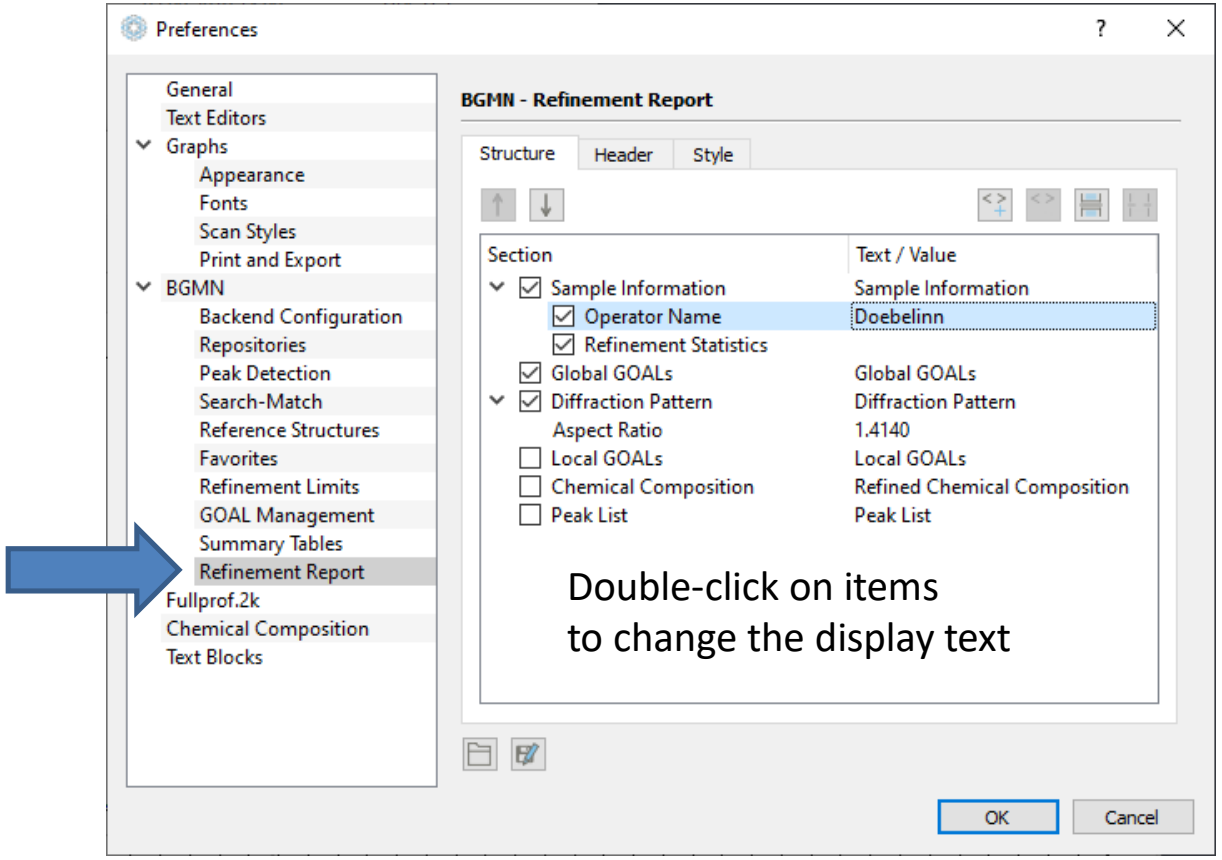
Parameter	Value	ESD
QHydroxyapatite	1.000000	0.000000

Diffraction Pattern

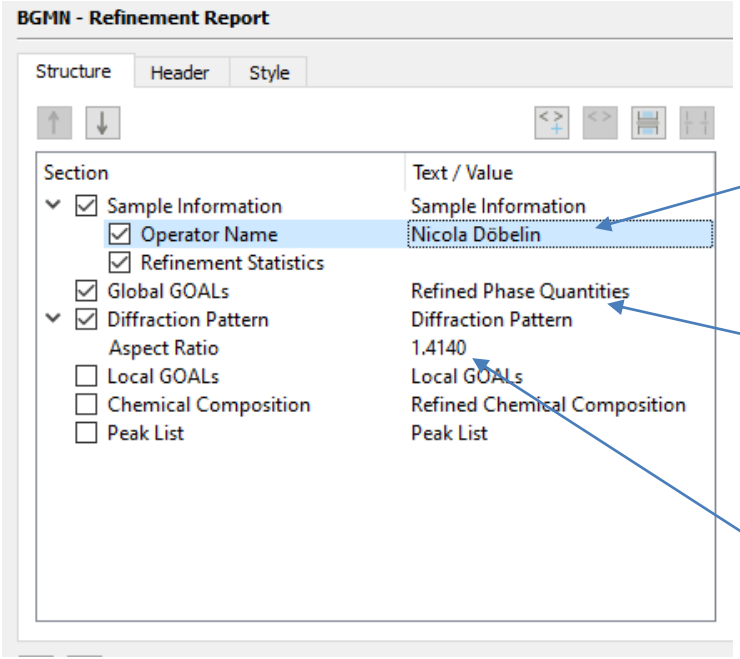


RMS

Custom Refinement Reports – Document structure



Custom Refinement Reports – Document structure



Use correct operator name

Change «Global GOALs» to «Refined Phase Quantities»

Aspect ratio of diffraction pattern determines the height of the graph (width is always the full page width).

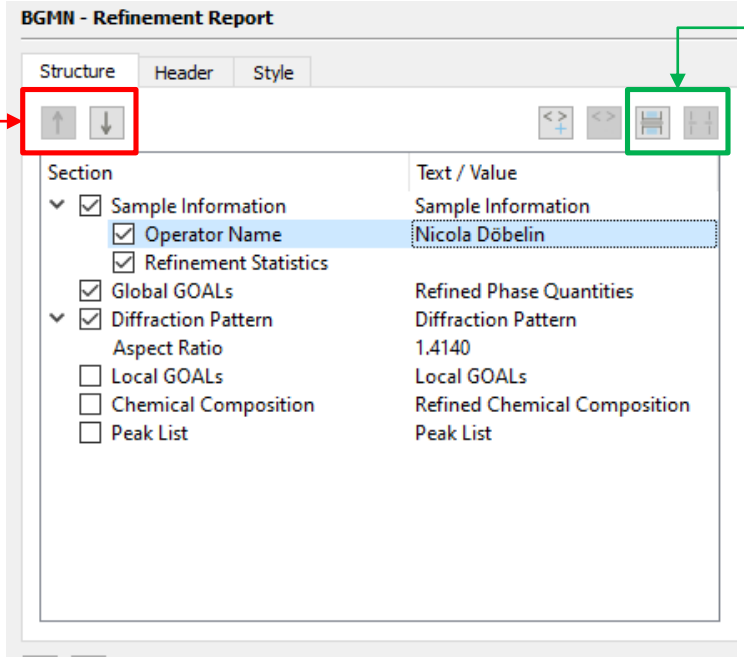
1.2

1.414

1.8

2.0

Custom Refinement Reports – Document structure

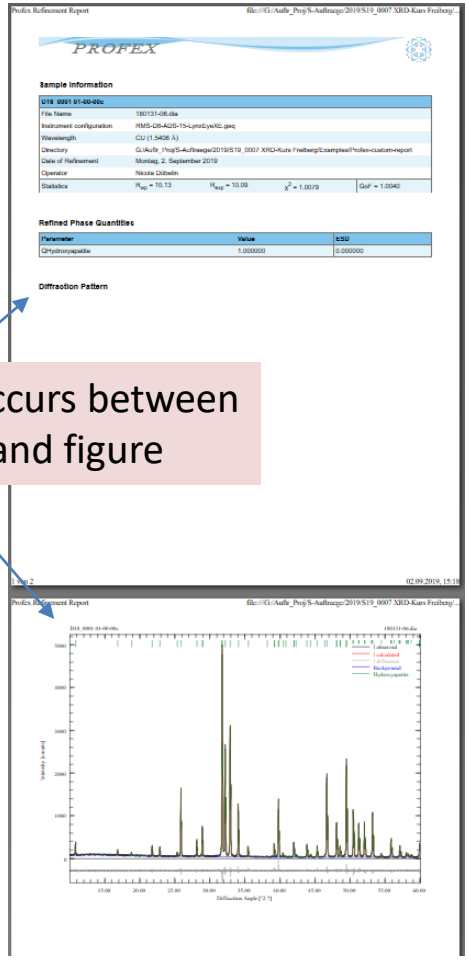


Insert / remove page break after selected item

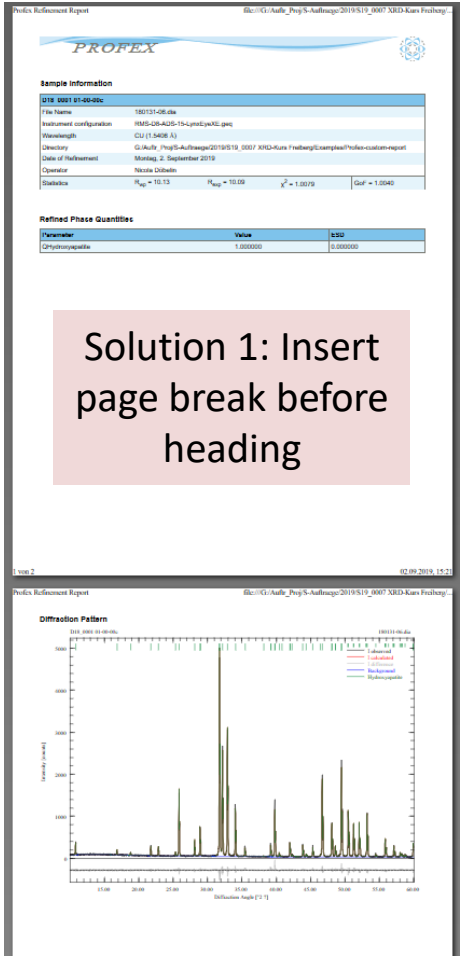
Move selected item up/down

Custom Refinement Reports – Document structure

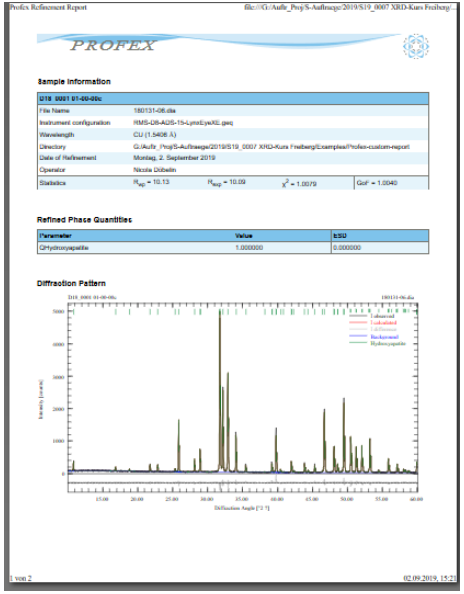
Page break occurs between heading and figure



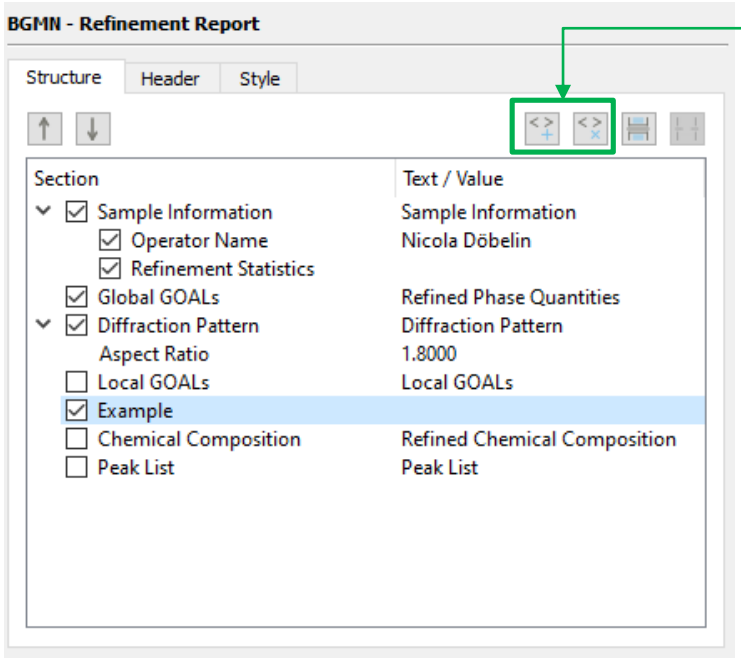
Solution 1: Insert page break before heading



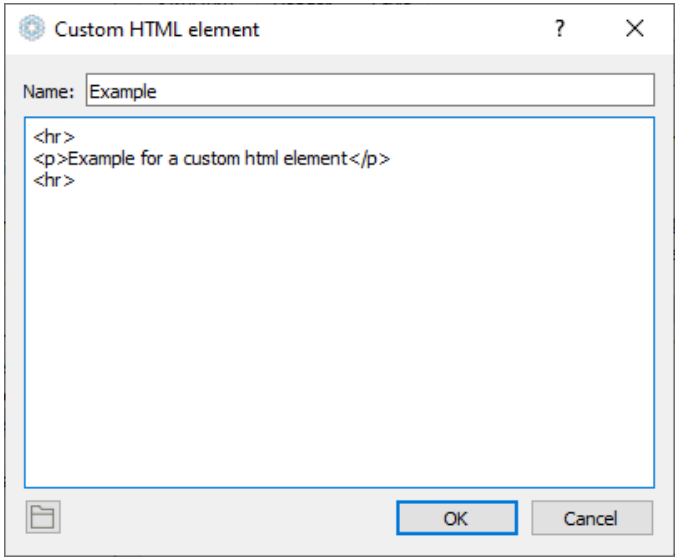
Solution 2: Increase aspect ratio of figure



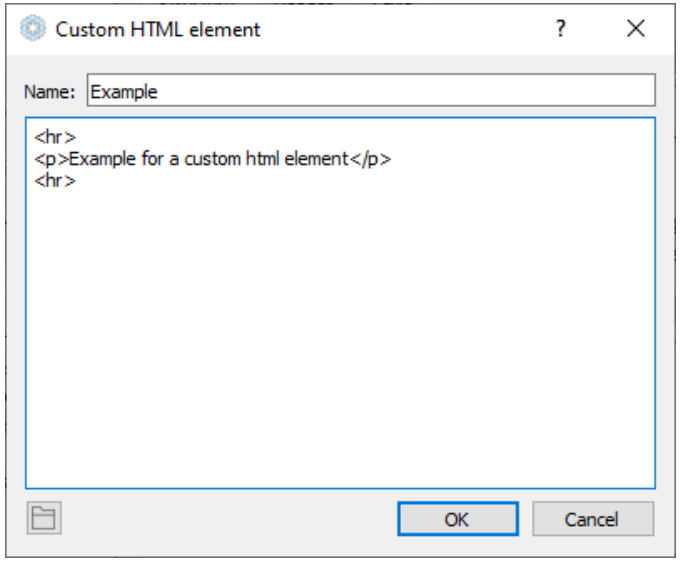
Custom Refinement Reports – Document structure

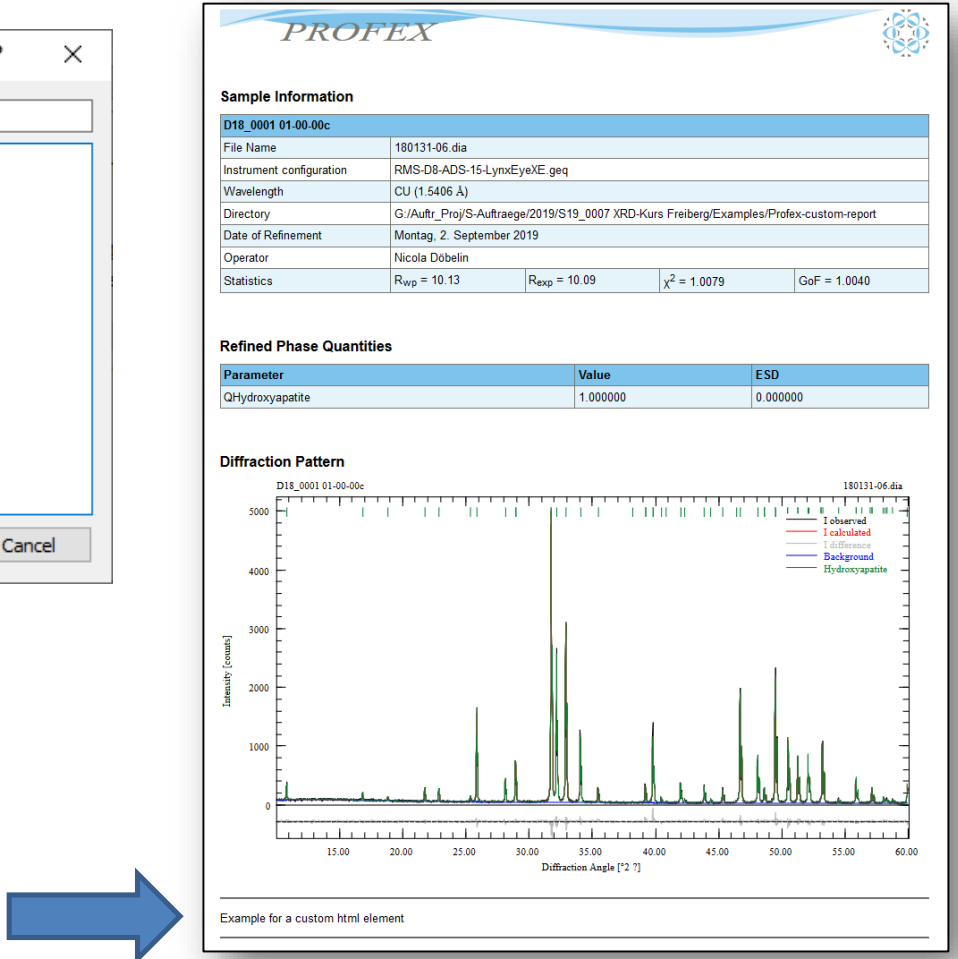


Insert / remove a custom HTML element



Custom Refinement Reports – Document structure





PROFEX

Sample Information

D18_0001 01-00-00c				
File Name	180131-06.dia			
Instrument configuration	RMS-D8-ADS-15-LynxEyeXE.geq			
Wavelength	CU (1.5406 Å)			
Directory	G:/Auftr_Proj/S-Auftraege/2019/S19_0007 XRD-Kurs Freiberg/Examples/Profex-custom-report			
Date of Refinement	Montag, 2. September 2019			
Operator	Nicola Döbelin			
Statistics	R_{wp} = 10.13	R_{exp} = 10.09	χ^2 = 1.0079	GoF = 1.0040

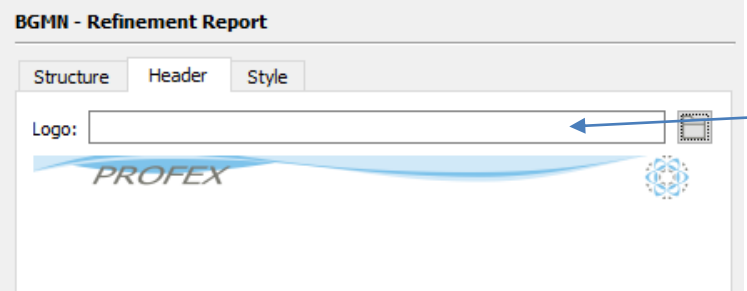
Refined Phase Quantities

Parameter	Value	ESD
QHydroxyapatite	1.000000	0.000000

Diffraction Pattern

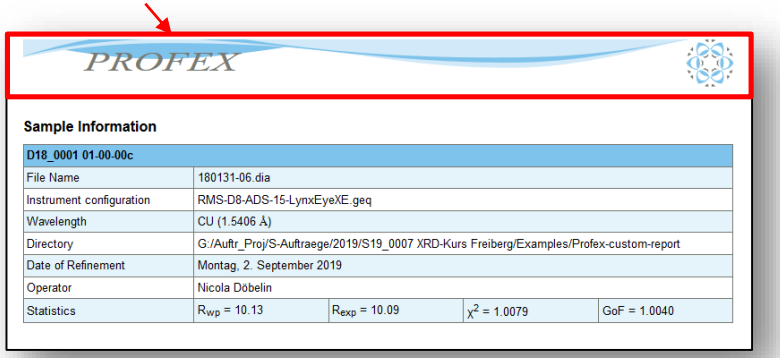
Example for a custom html element

Custom Refinement Reports – Banner



Specify banner file or leave empty for default Profex banner

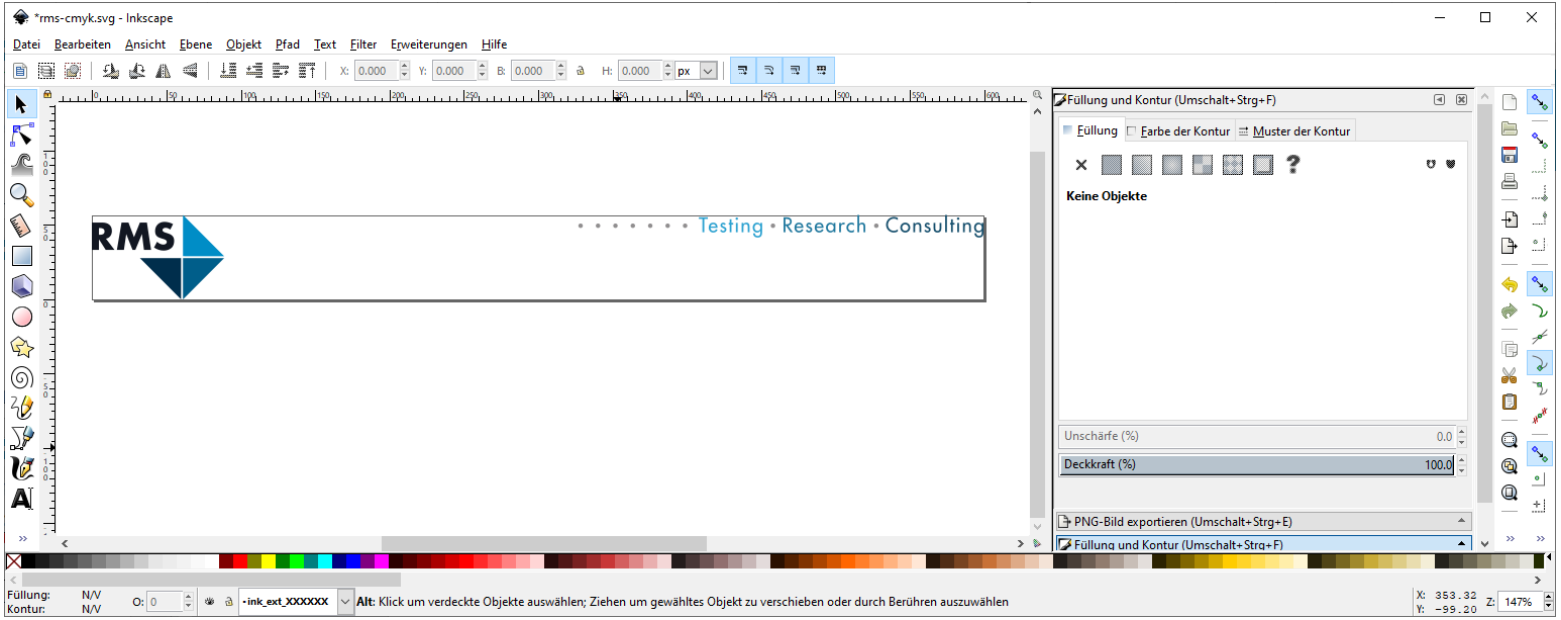
Banners appear at the top of the report and span the entire page width



Banners must be saved in SVG format (no other formats supported)

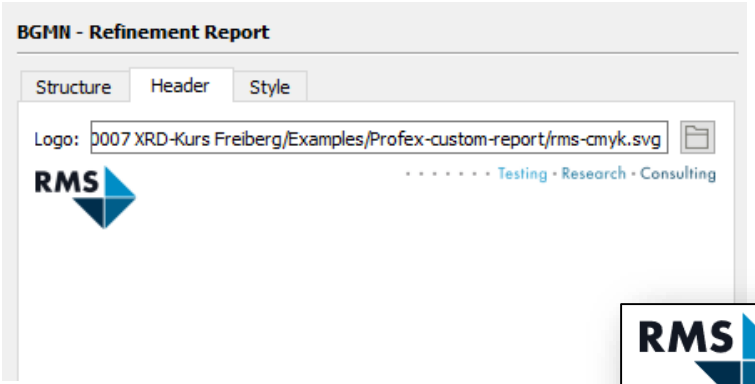
Custom Refinement Reports – Banner

Inkscape: Free software to create SVG graphs
https://inkscape.org/de/



Create a new document of approximately 160x15 mm
Save in default format (*.svg)

Custom Refinement Reports – Banner



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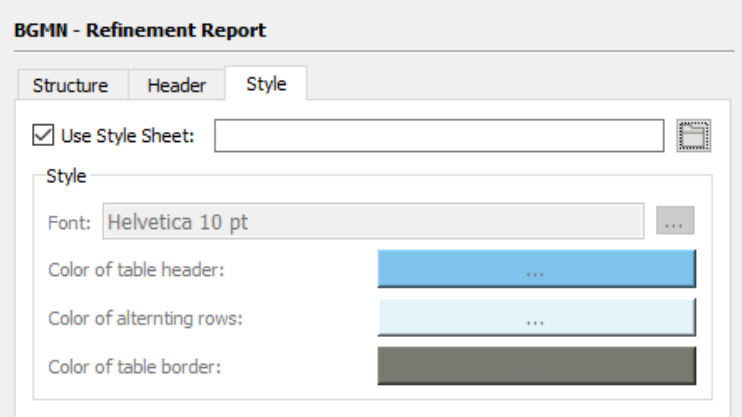
Sample Information

D18_0001 01-00-00c				
File Name	180131-06.dia			
Instrument configuration	RMS-D8-ADS-15-LynxEyeXE.geq			
Wavelength	CU (1.5406 Å)			
Directory	G:/Auftr_Proj/S-Auftraege/2019/S19_0007 XRD-Kurs Freiberg/Examples/Profex-custom-report			
Date of Refinement	Montag, 2. September 2019			
Operator	Nicola Döbelin			
Statistics	R_{wp} = 10.13	R_{exp} = 10.09	χ^2 = 1.0079	GoF = 1.0040

RMS

Custom Refinement Reports

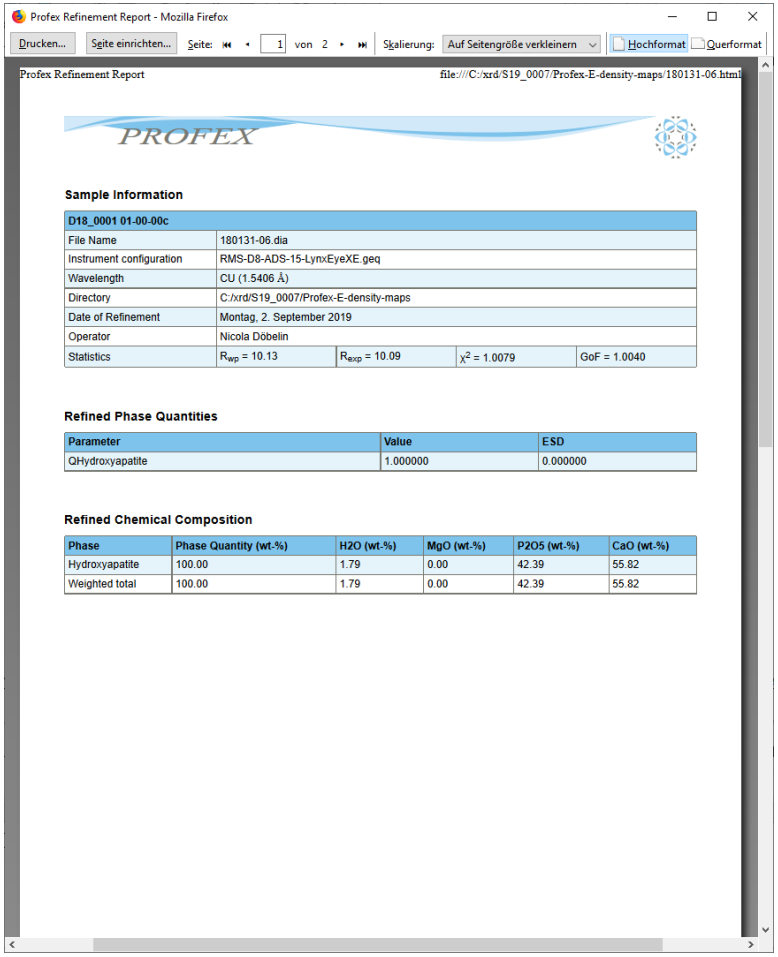


Style sheets are a technology used in web design (CSS)
→ Not covered here
(https://www.w3schools.com/Css/)

Two options for colors / style:

- Specify a CSS file
  (enable «Use Styls Sheet»)
- Select table colors directly
  (disable «Use Style Sheet»)

Custom Refinement Reports



Sample Information

D18_0001 01-00-00c				
File Name	180131-06.dia			
Instrument configuration	RMS-D8-ADS-15-LynxEyeXE.geq			
Wavelength	CU (1.5406 Å)			
Directory	C:/xrd/S19_0007/Profex-E-density-maps			
Date of Refinement	Montag, 2. September 2019			
Operator	Nicola Döbelin			
Statistics	R_{wp} = 10.13	R_{exp} = 10.09	χ^2 = 1.0079	GoF = 1.0040

Refined Phase Quantities

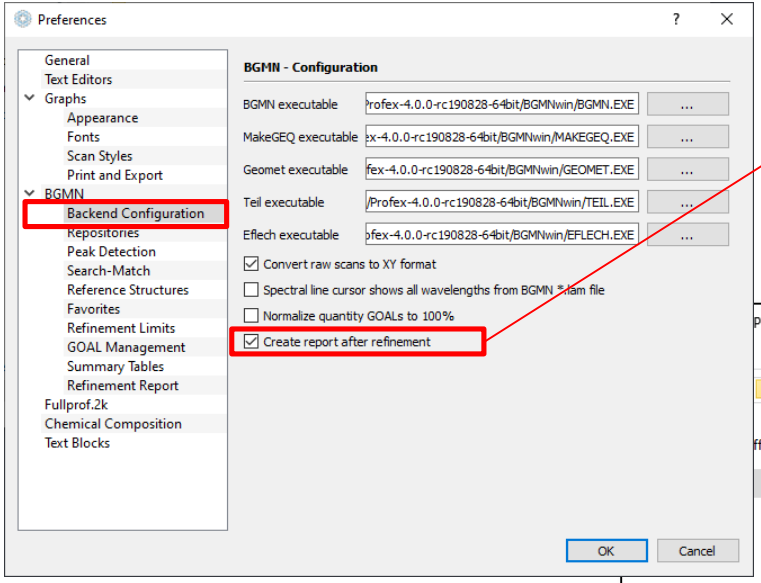
Parameter	Value	ESD
QHydroxyapatite	1.000000	0.000000

Refined Chemical Composition

Phase	Phase Quantity (wt-%)	H2O (wt-%)	MgO (wt-%)	P2O5 (wt-%)	CaO (wt-%)
Hydroxyapatite	100.00	1.79	0.00	42.39	55.82
Weighted total	100.00	1.79	0.00	42.39	55.82

Use a web browser to print reports to paper or PDF

Custom Refinement Reports



Check to automatically create a report after each refinement