TMT4301 Materials Characterization
X-ray Characterization of materials

LX8-9: Extra bonus lecture – lab report

Sverre M. Selbach

Department of Materials Science and Engineering
NTNU Norwegian University of Science and Technology
Trondheim, Norway

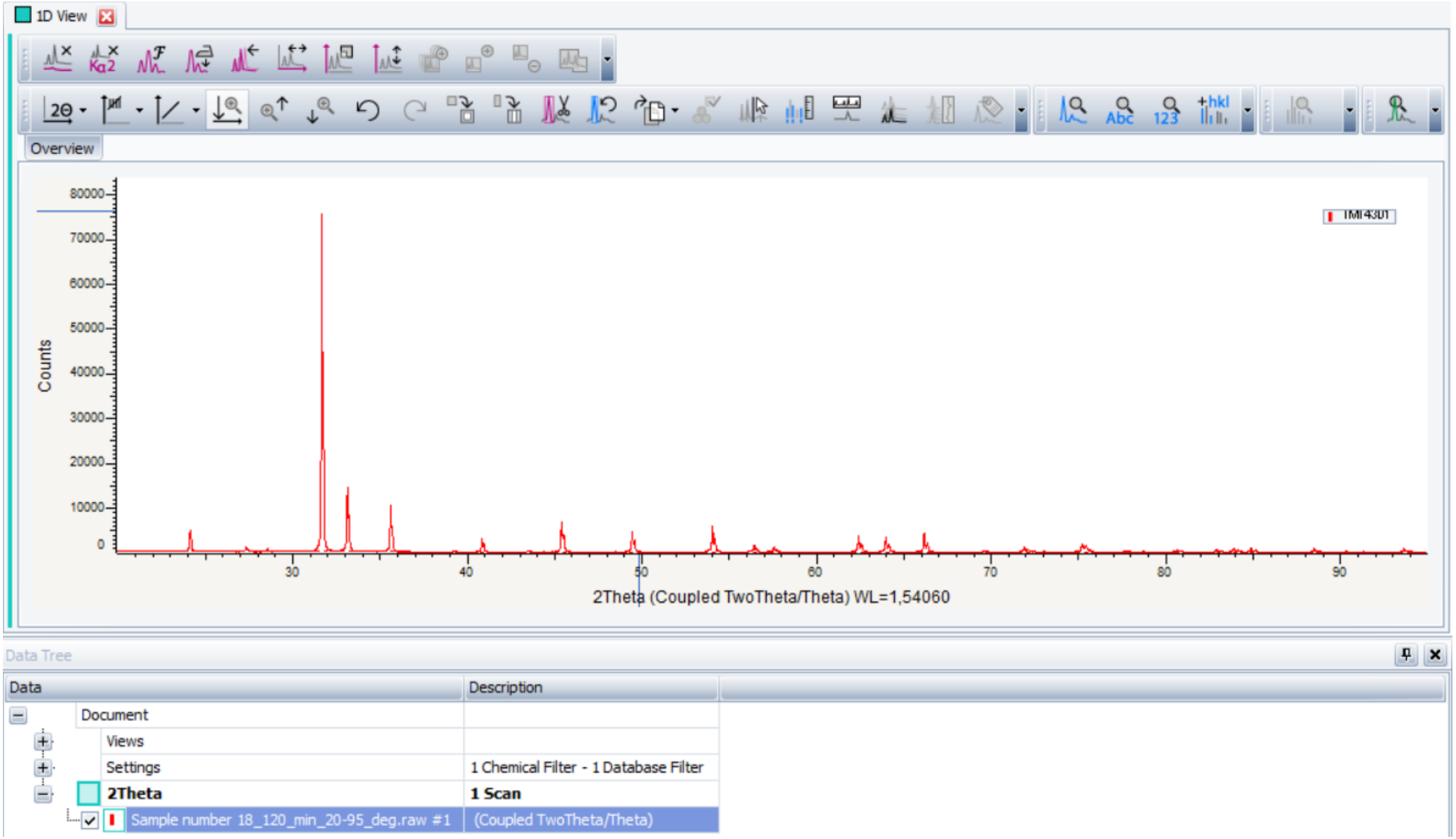
Norwegian University of Science and Technology

This lecture

- Identifying a two-phase sample in EVA
- Performing Pawley analysis of a two-phase sample in Topas
- Rietveld refinement of a two-phase sample in Topas

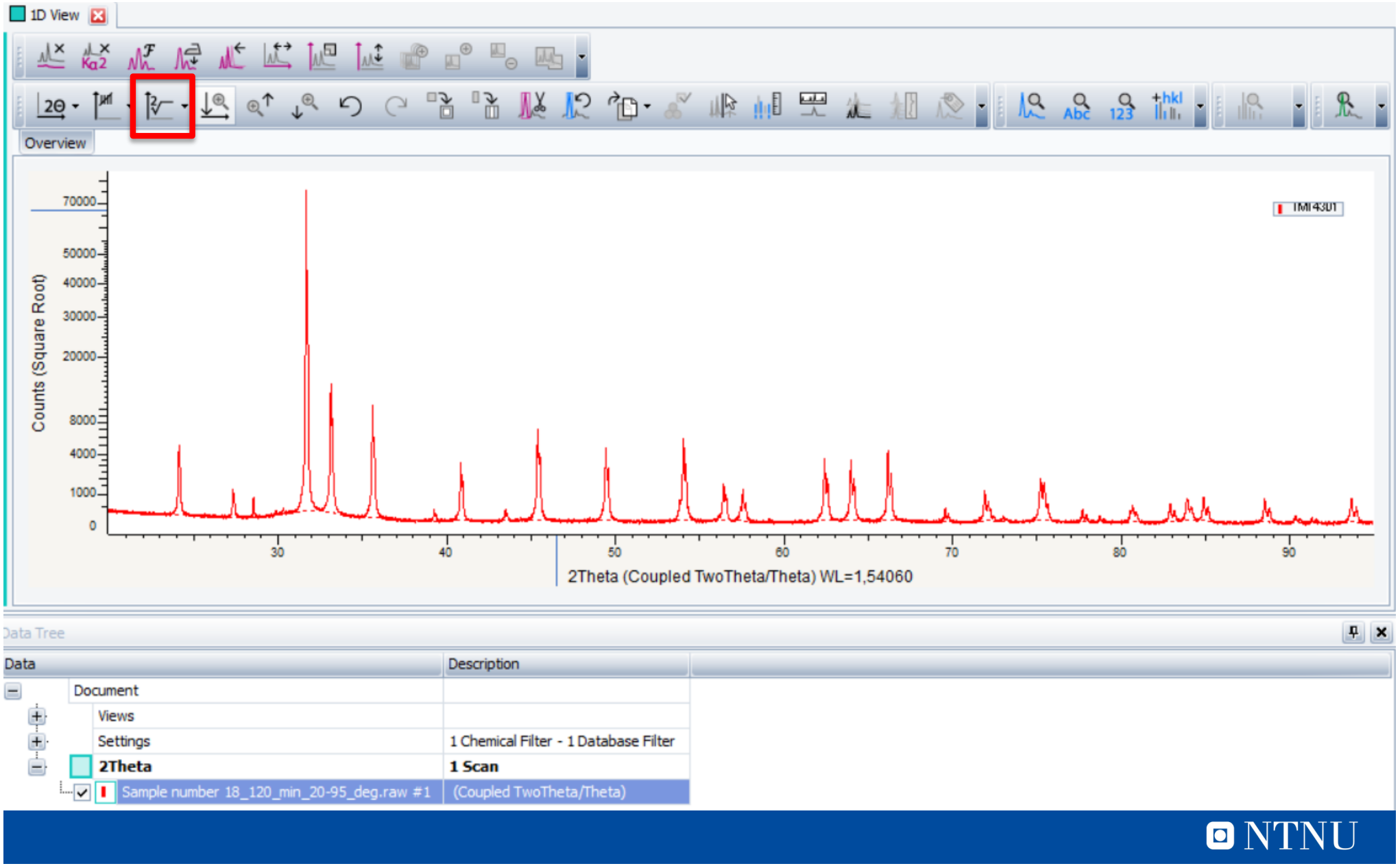
EVA

- Import a diffractogram, .raw file.



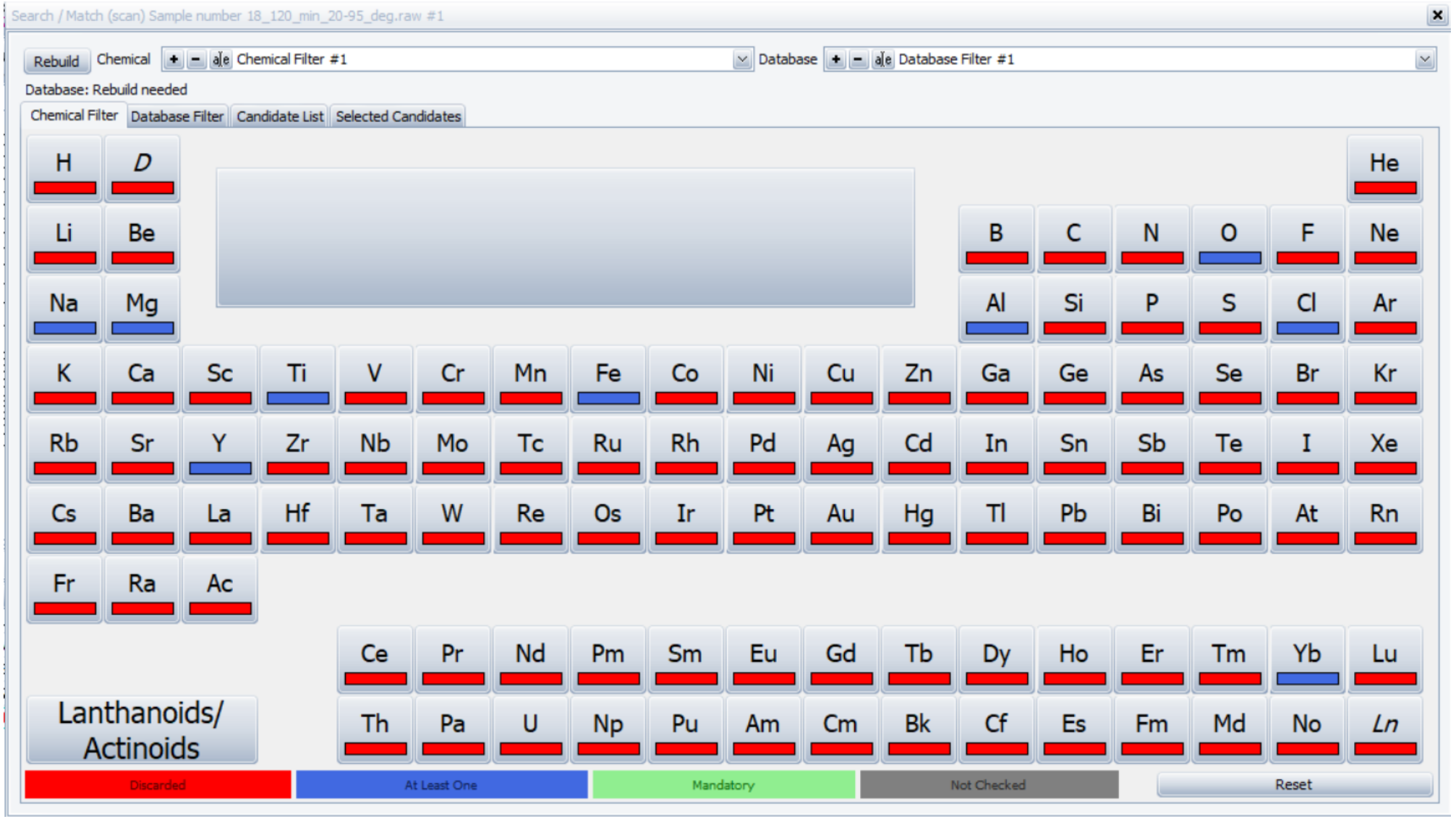
EVA

- Pro tip: use square root y-axis scaling for different peak intensities.



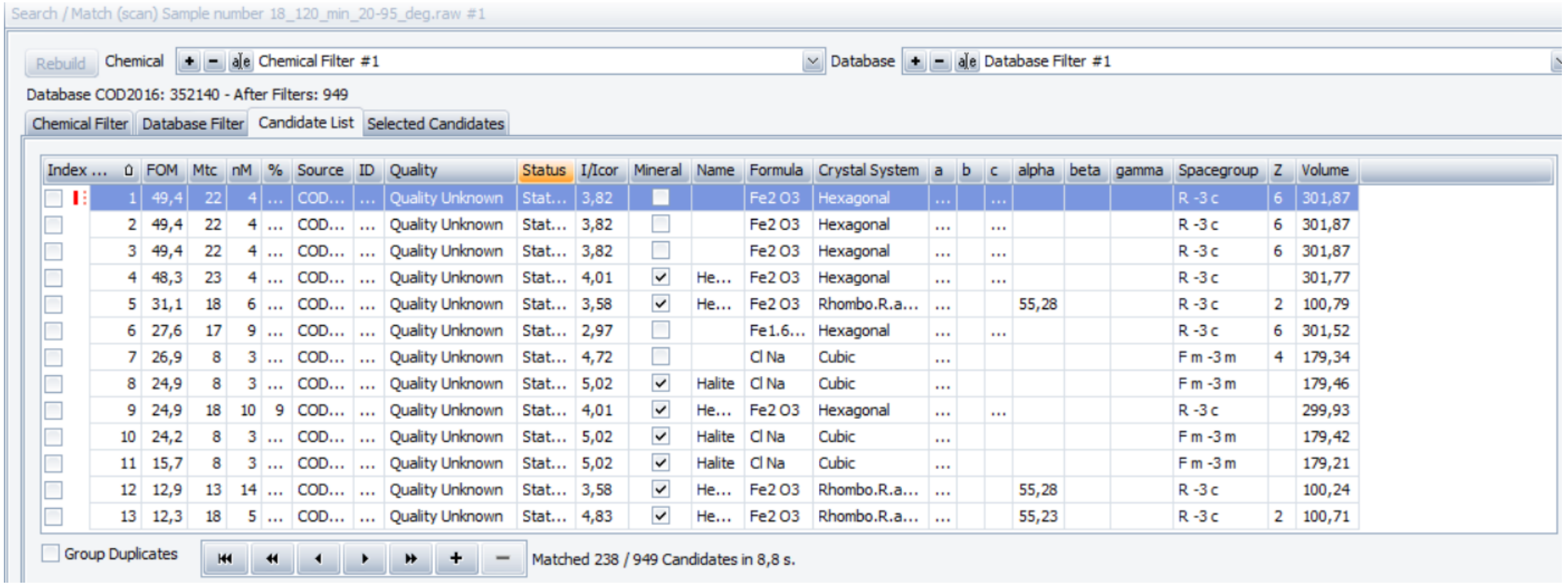
EVA – search and match

- Choose the right elements and the right conditions



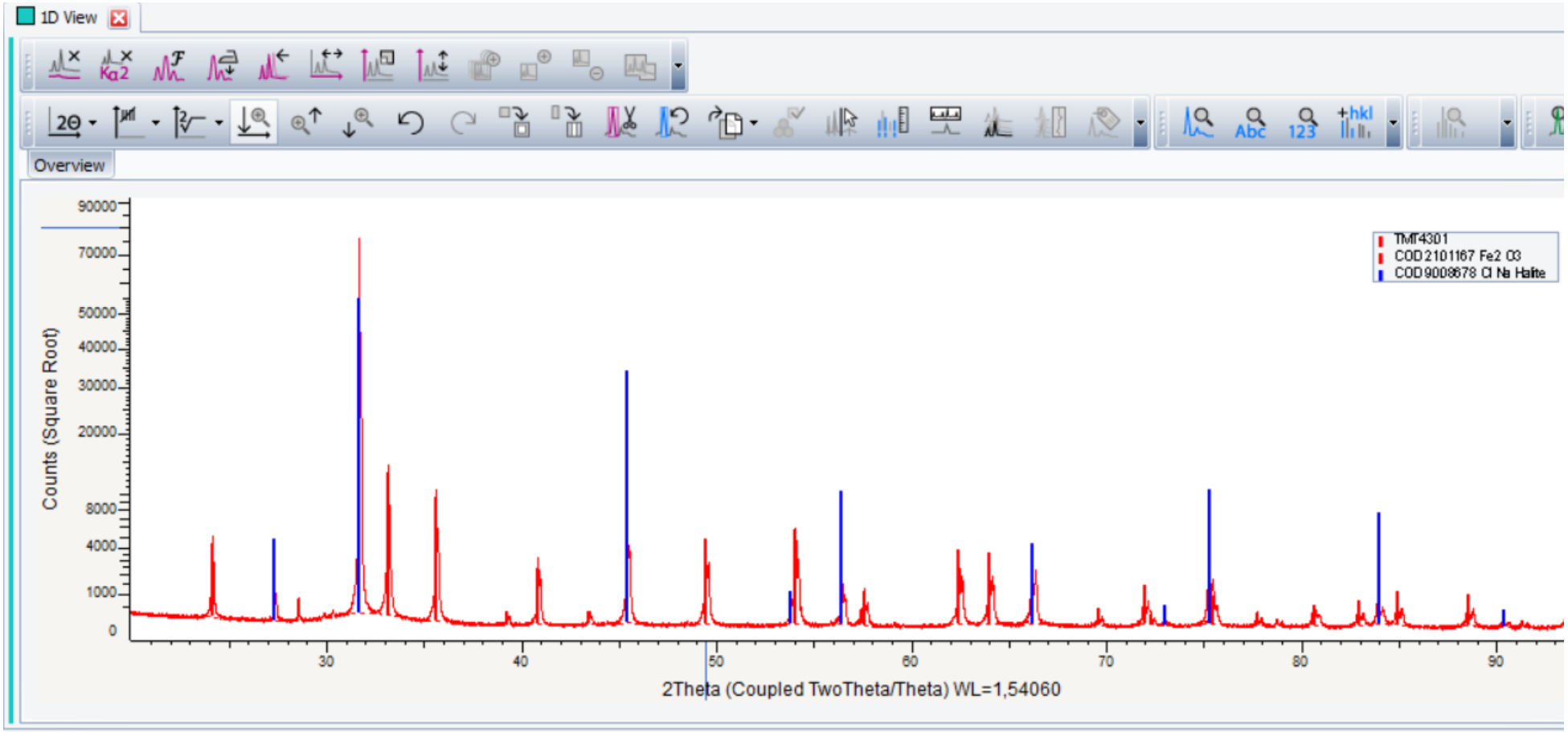
EVA – search and match

- Check promising patterns which can index some of the peaks while you search for a second which can index the rest.



Index	...	û	FOM	Mtc	nM	%	Source	ID	Quality	Status	I/Icor	Mineral	Name	Formula	Crystal System	a	b	c	alpha	beta	gamma	Spacegroup	Z	Volume
1			49,4	22	4	...	COD...	...	Quality Unknown	Stat...	3,82	☐		Fe2 O3	Hexagonal	...		...				R -3 c	6	301,87
2			49,4	22	4	...	COD...	...	Quality Unknown	Stat...	3,82	☐		Fe2 O3	Hexagonal	...		...				R -3 c	6	301,87
3			49,4	22	4	...	COD...	...	Quality Unknown	Stat...	3,82	☐		Fe2 O3	Hexagonal	...		...				R -3 c	6	301,87
4			48,3	23	4	...	COD...	...	Quality Unknown	Stat...	4,01	☑	He...	Fe2 O3	Hexagonal	...		...				R -3 c		301,77
5			31,1	18	6	...	COD...	...	Quality Unknown	Stat...	3,58	☑	He...	Fe2 O3	Rhombo.R.a...	...			55,28			R -3 c	2	100,79
6			27,6	17	9	...	COD...	...	Quality Unknown	Stat...	2,97	☐		Fe1.6...	Hexagonal	...		...				R -3 c	6	301,52
7			26,9	8	3	...	COD...	...	Quality Unknown	Stat...	4,72	☐		Cl Na	Cubic	...						F m -3 m	4	179,34
8			24,9	8	3	...	COD...	...	Quality Unknown	Stat...	5,02	☑	Halite	Cl Na	Cubic	...						F m -3 m		179,46
9			24,9	18	10	9	COD...	...	Quality Unknown	Stat...	4,01	☑	He...	Fe2 O3	Hexagonal	...		...				R -3 c		299,93
10			24,2	8	3	...	COD...	...	Quality Unknown	Stat...	5,02	☑	Halite	Cl Na	Cubic	...						F m -3 m		179,42
11			15,7	8	3	...	COD...	...	Quality Unknown	Stat...	5,02	☑	Halite	Cl Na	Cubic	...						F m -3 m		179,21
12			12,9	13	14	...	COD...	...	Quality Unknown	Stat...	3,58	☑	He...	Fe2 O3	Rhombo.R.a...	...			55,28			R -3 c		100,24
13			12,3	18	5	...	COD...	...	Quality Unknown	Stat...	4,83	☑	He...	Fe2 O3	Rhombo.R.a...	...			55,23			R -3 c	2	100,71

EVA – search and match result

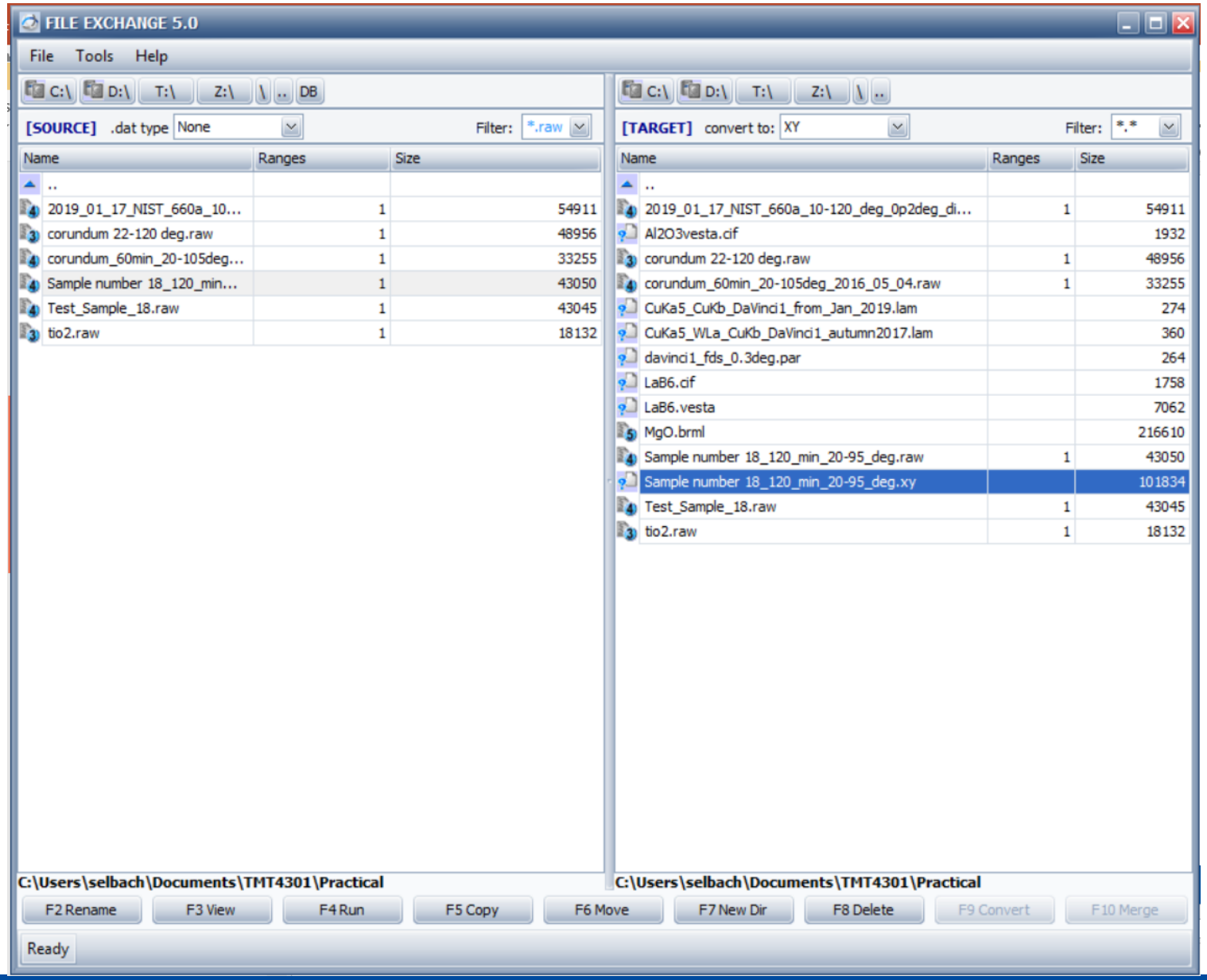


Data Tree

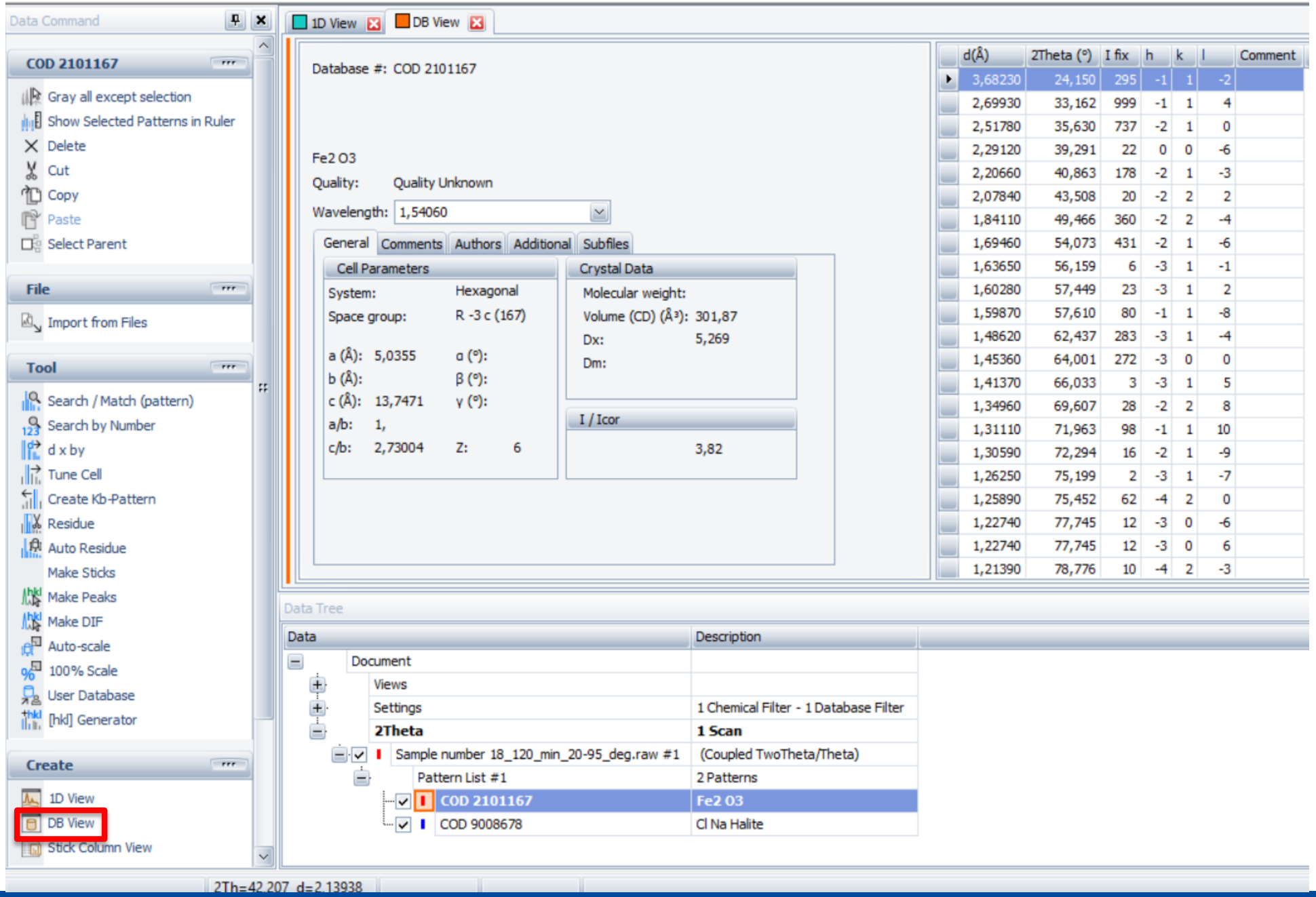
Data	Description
Document	
Views	
Settings	1 Chemical Filter - 1 Database Filter
2Theta	**1 Scan**
Sample number 18_120_min_20-95_deg.raw #1	(Coupled TwoTheta/Theta)
Pattern List #1	2 Patterns
COD 2101167	Fe2 O3
COD 9008678	Cl Na Halite

Export your data, from .raw to .xy

- You can download Bruker Diffrac FileExchange from the Odin server

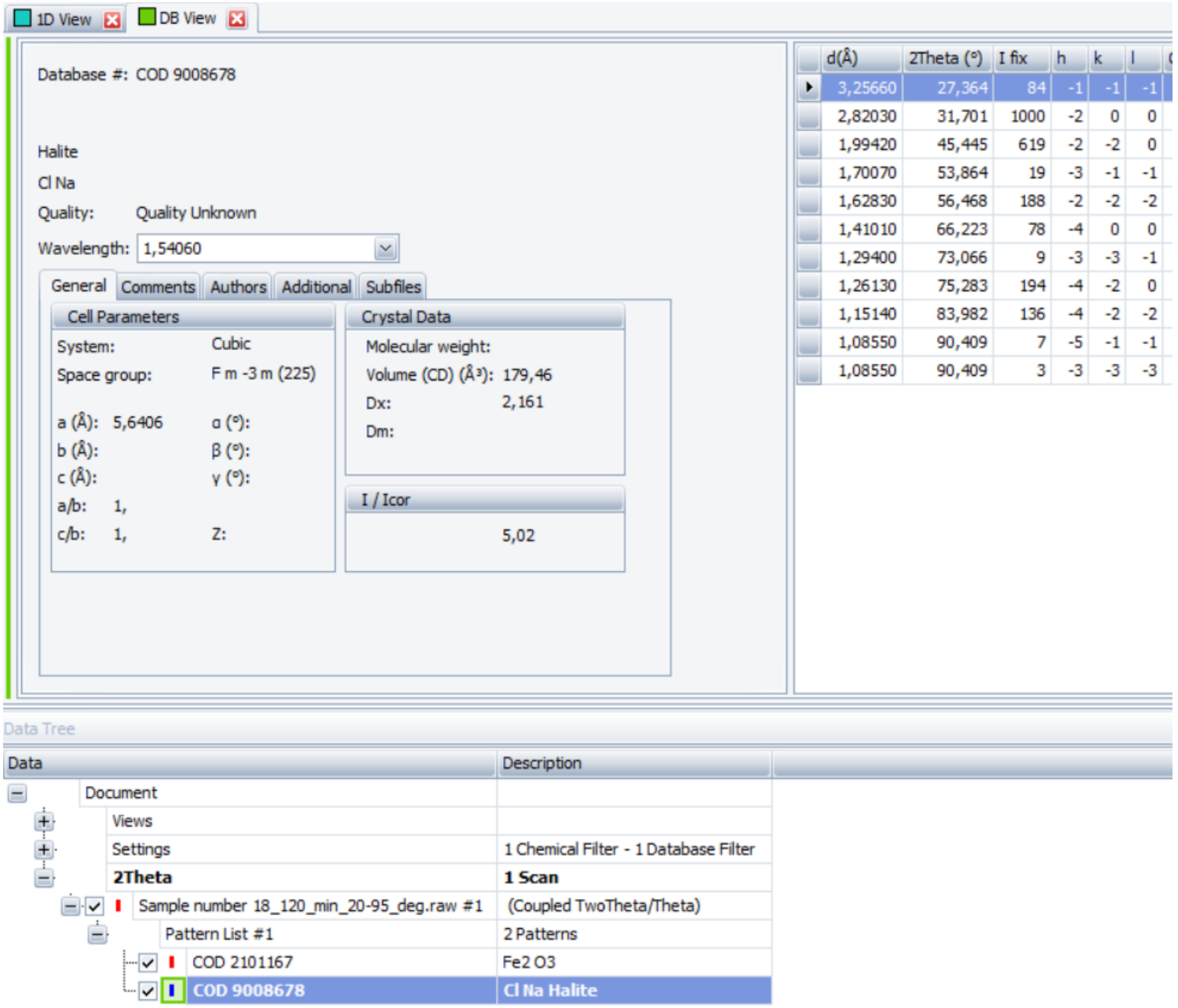


Find SG and lattice param. with EVA and COD

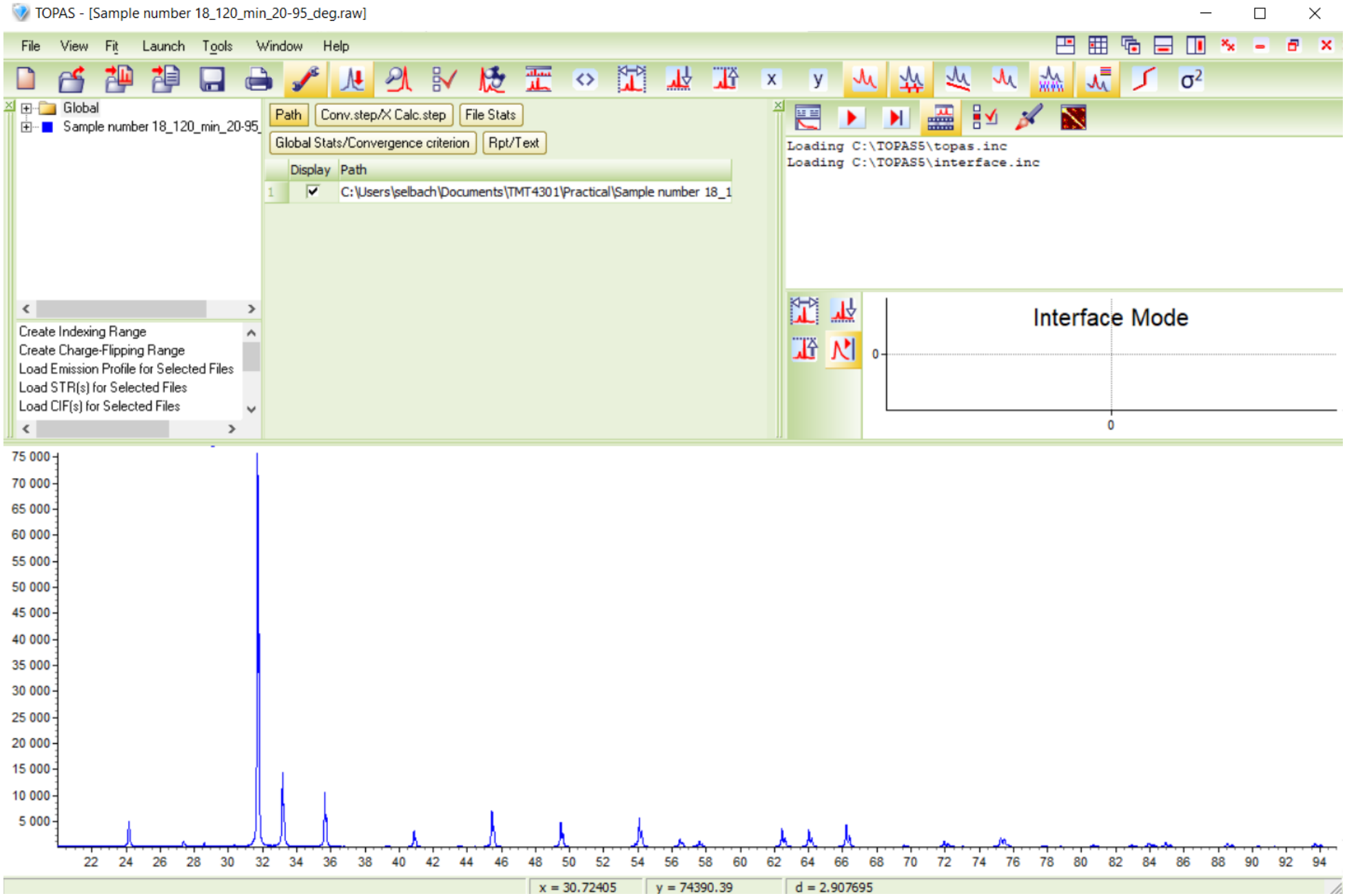


Find SG and lattice param. with EVA and COD

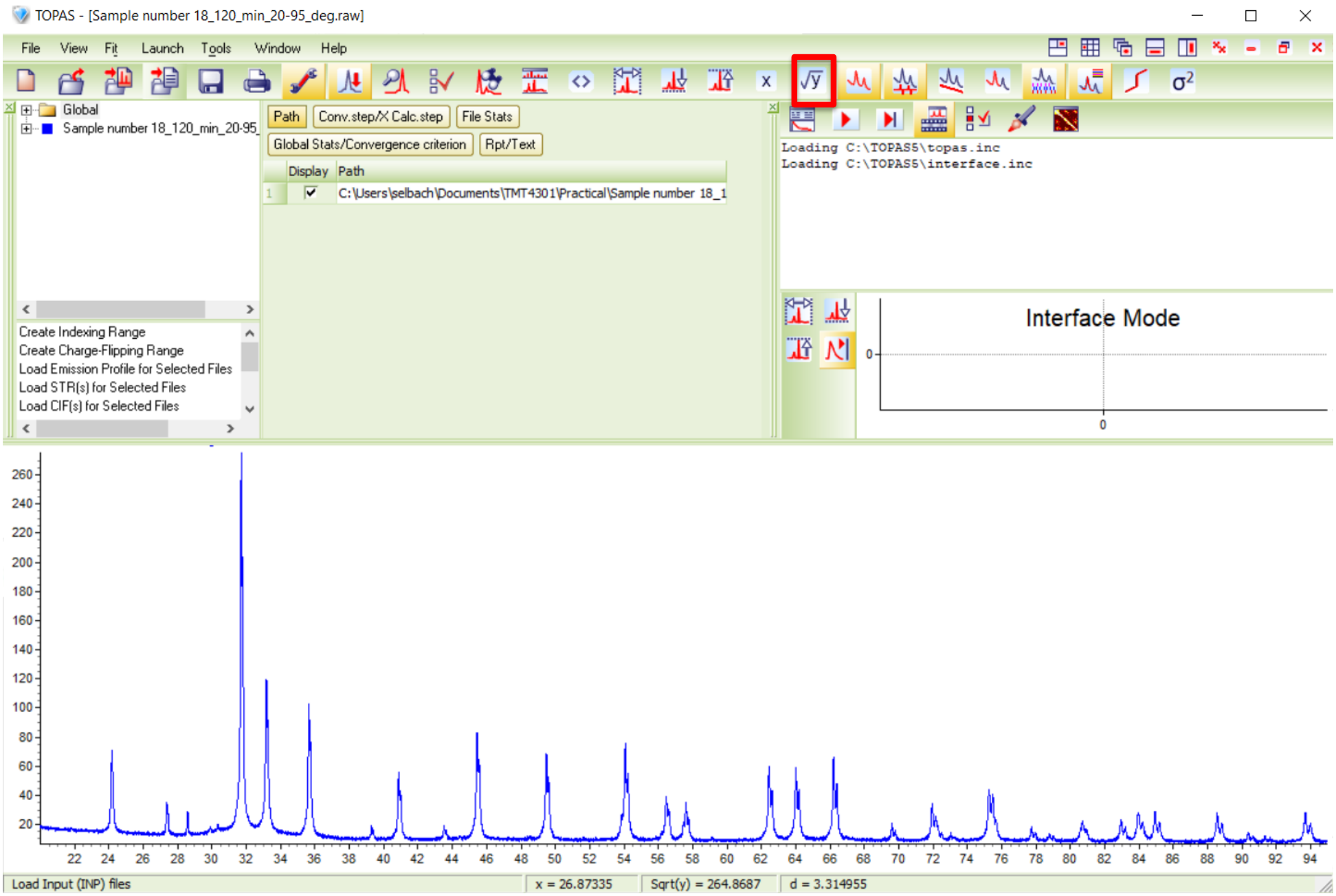
You will also find peak positions here.



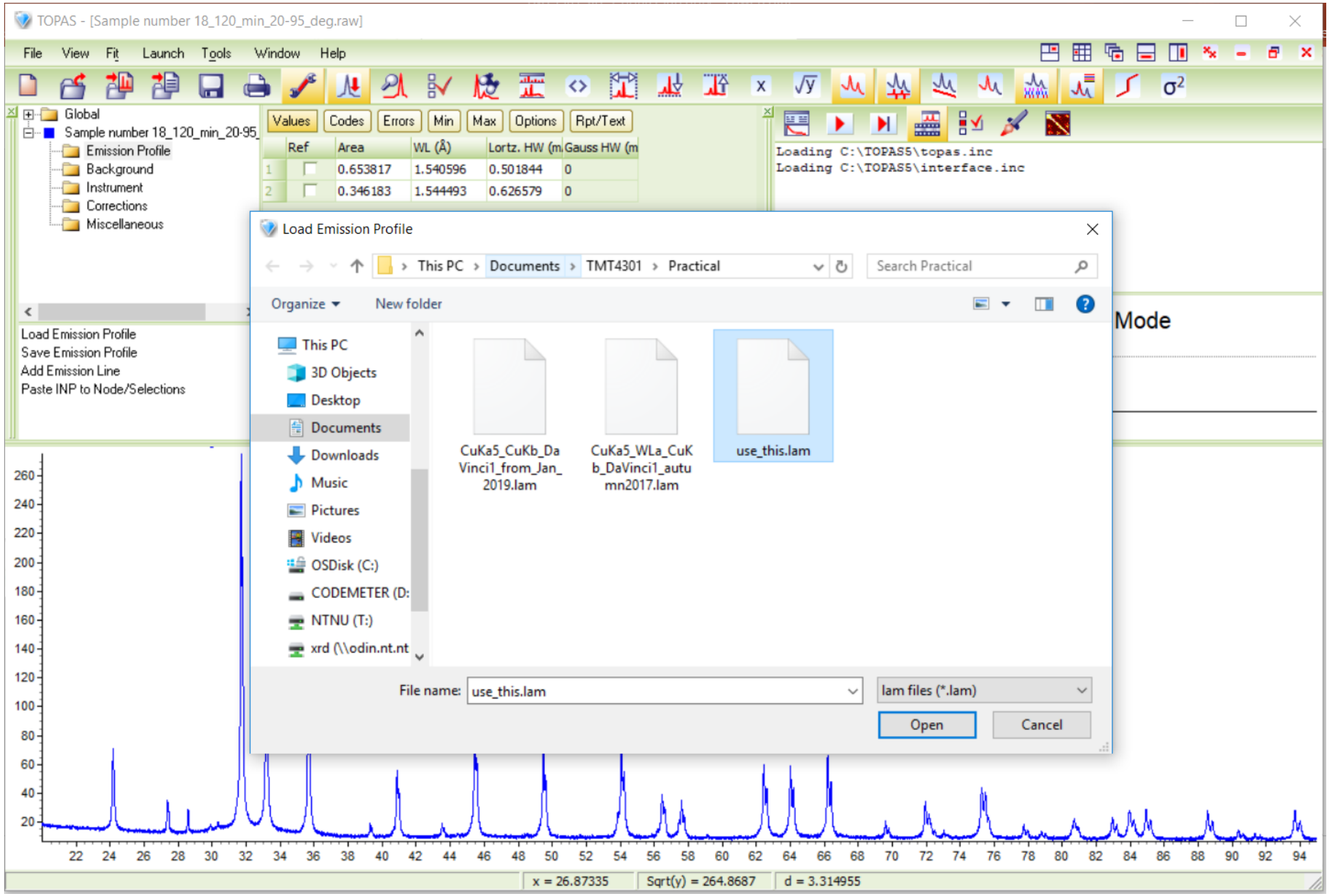
TOPAS – import a .raw file



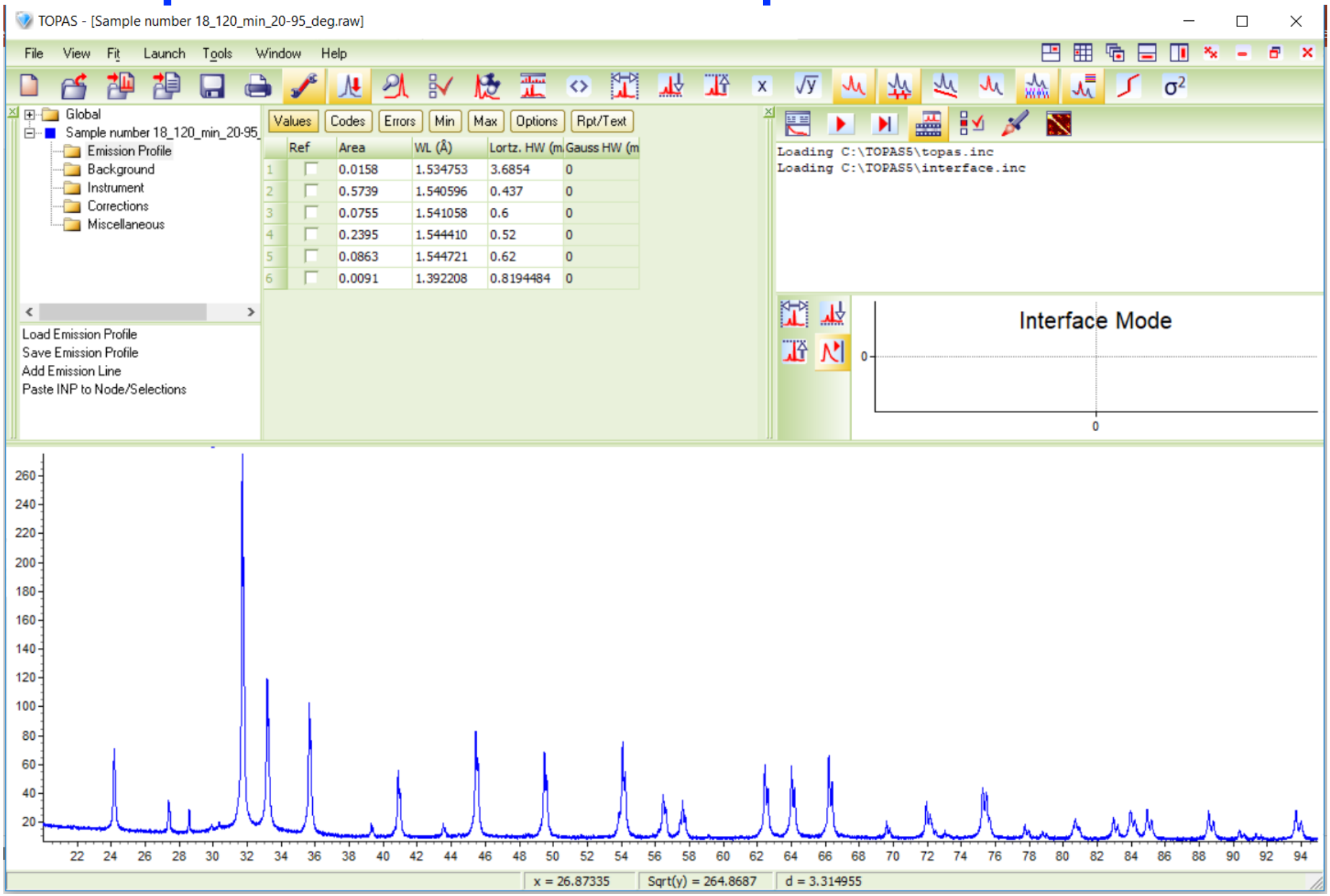
TOPAS – use square root for y-axis scaling



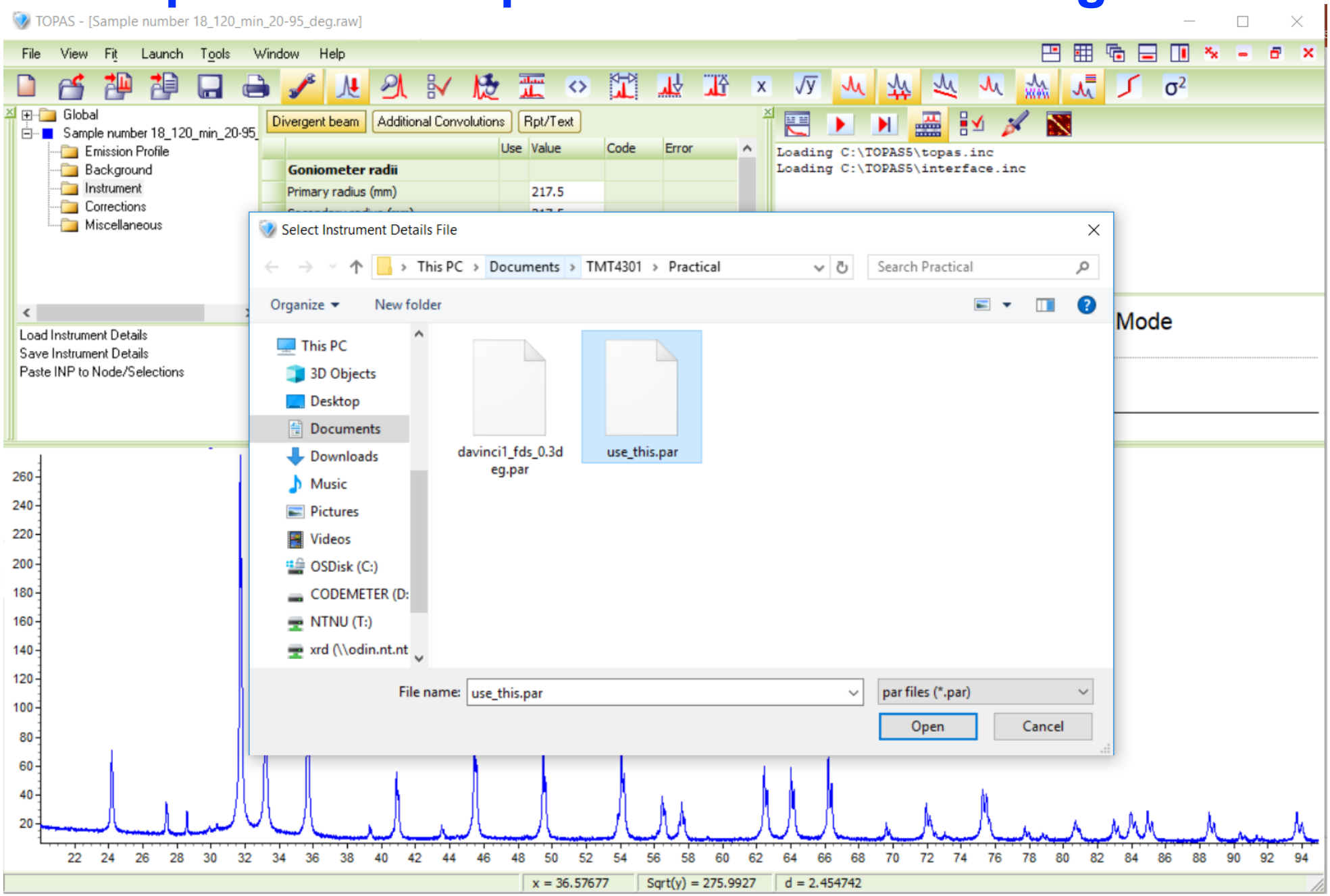
Topas – load an emission profile



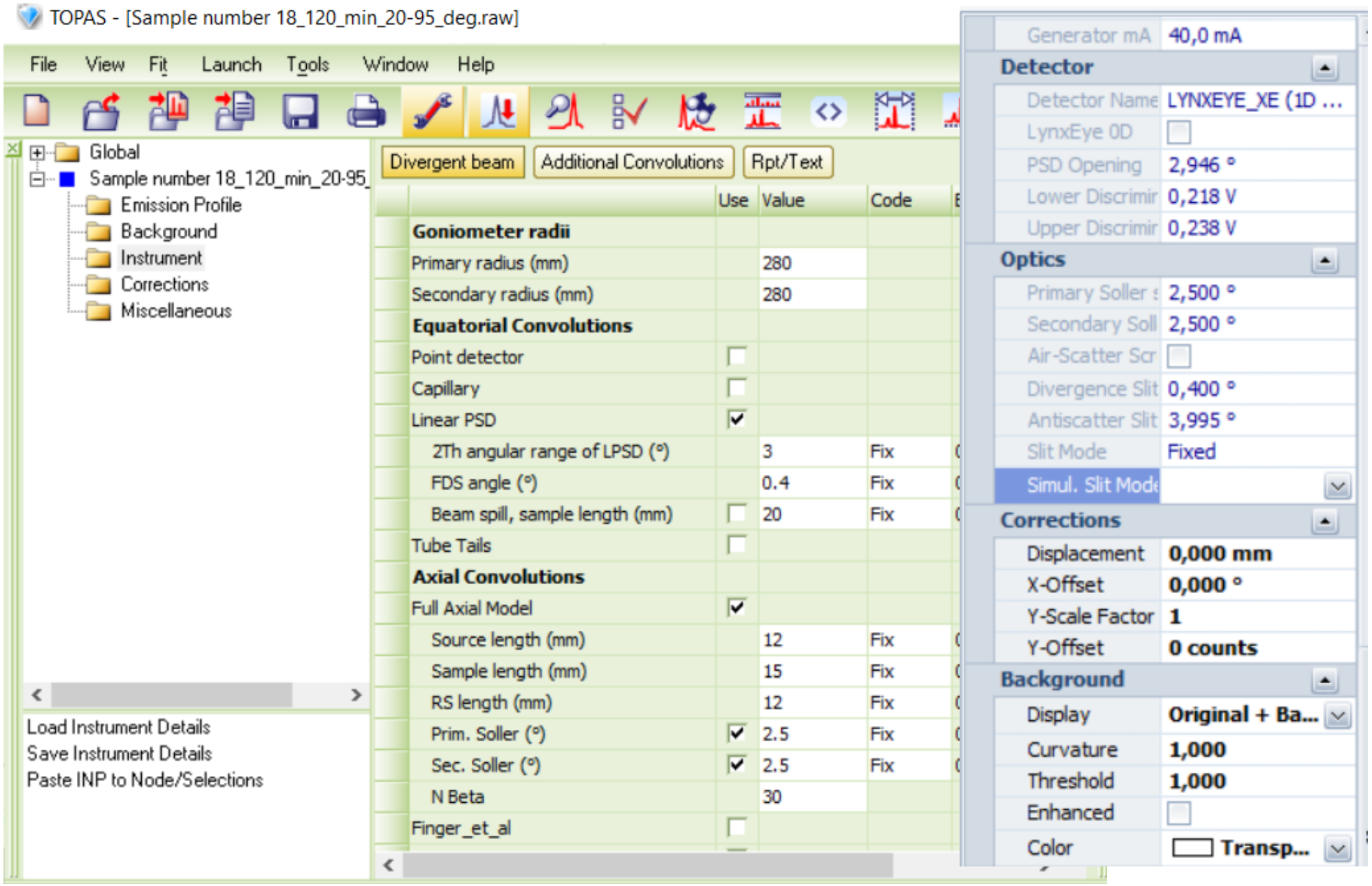
Topas – load an emission profile



Topas – load a .par instrumental settings file

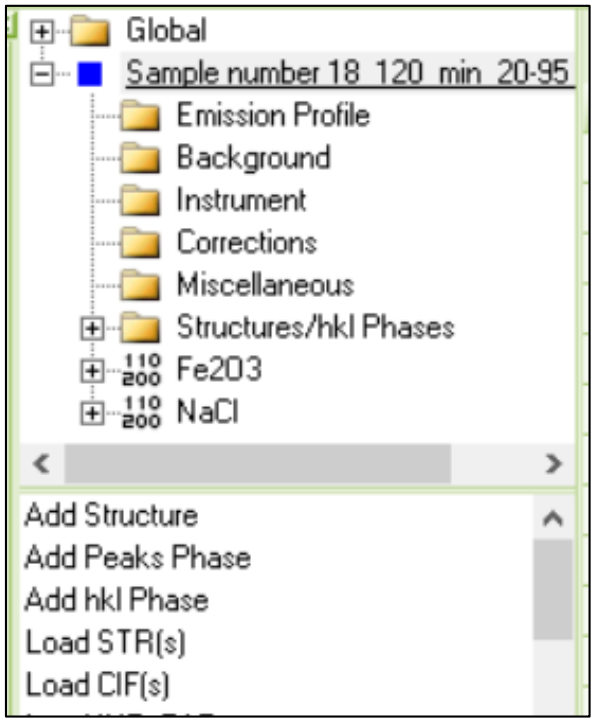


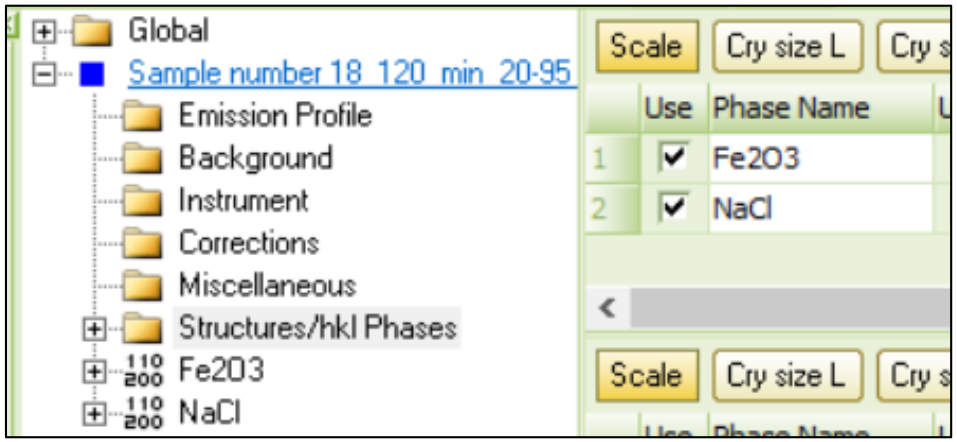
Topas – load a .par file. EVA gives you info too:

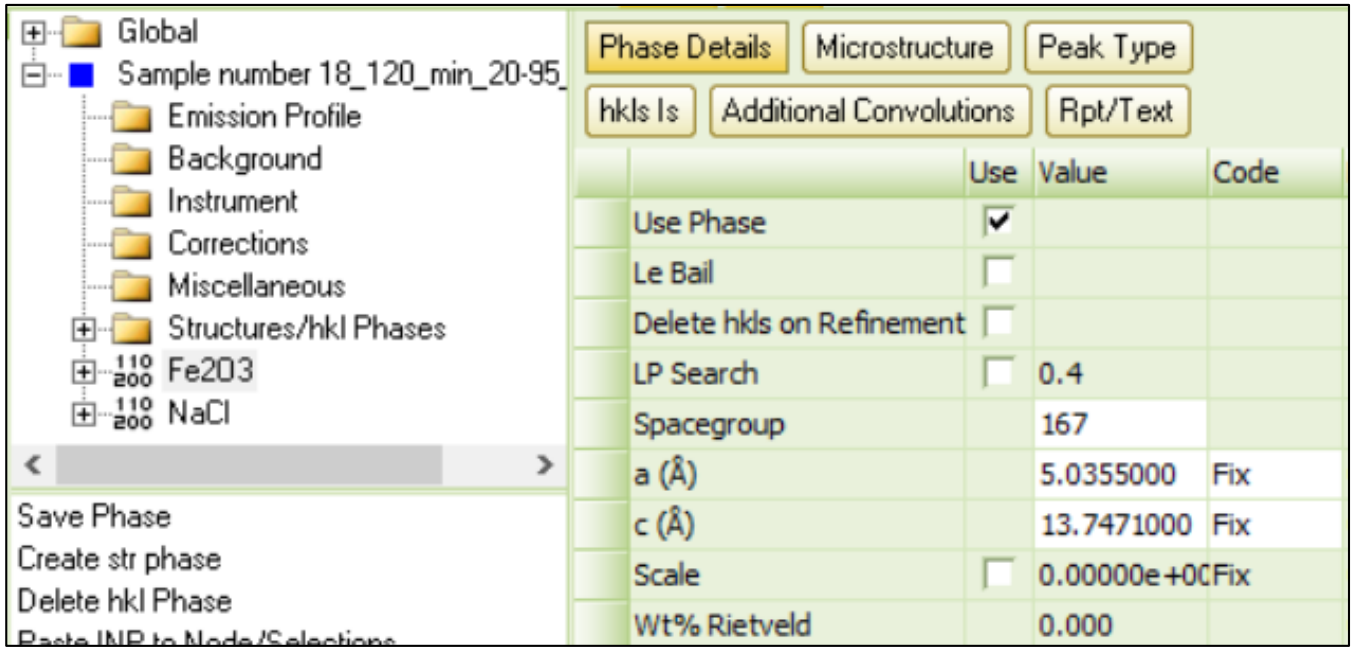


Pawley – add two hkl phases, rename them

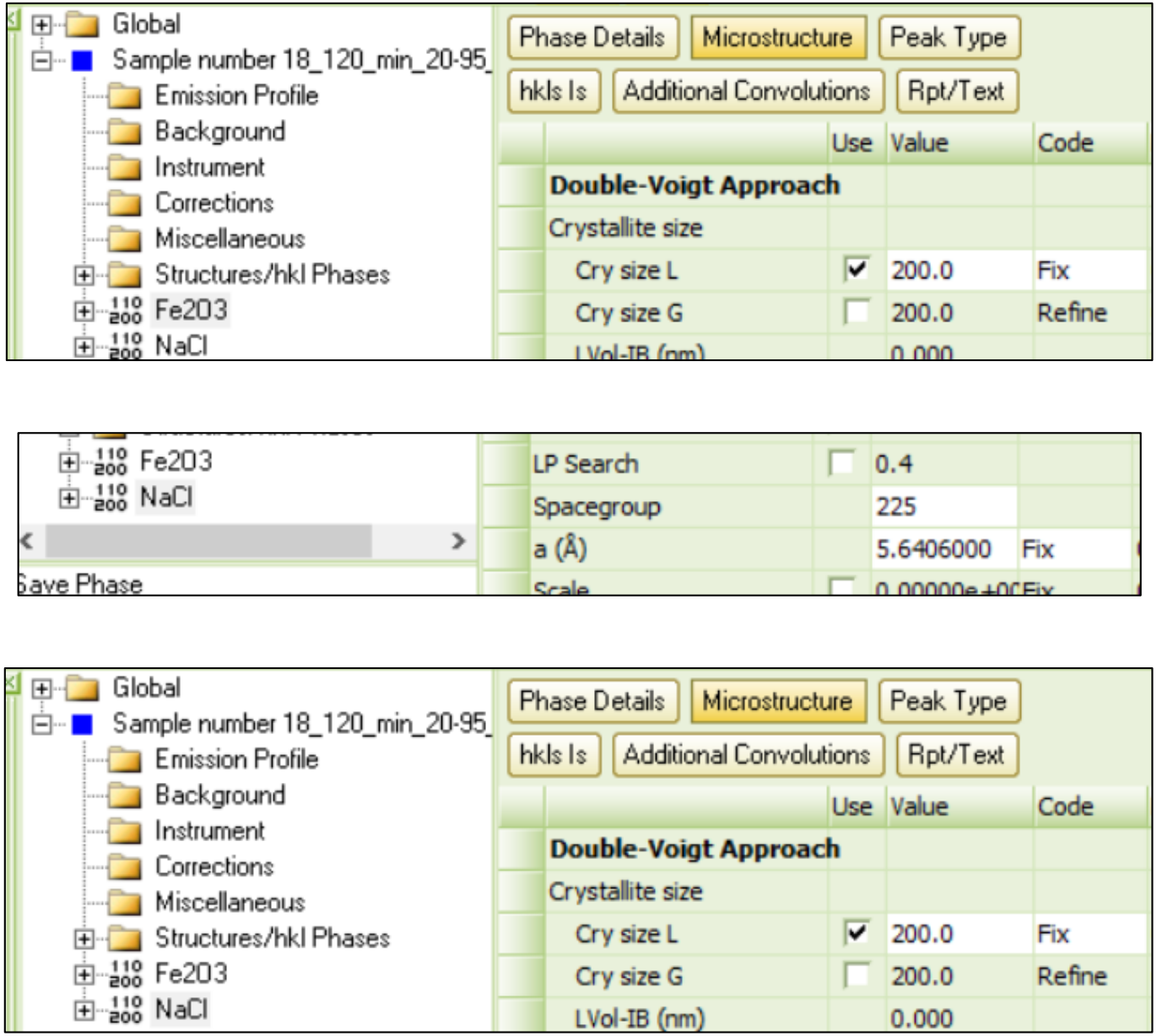
- Note context sensitive menus.





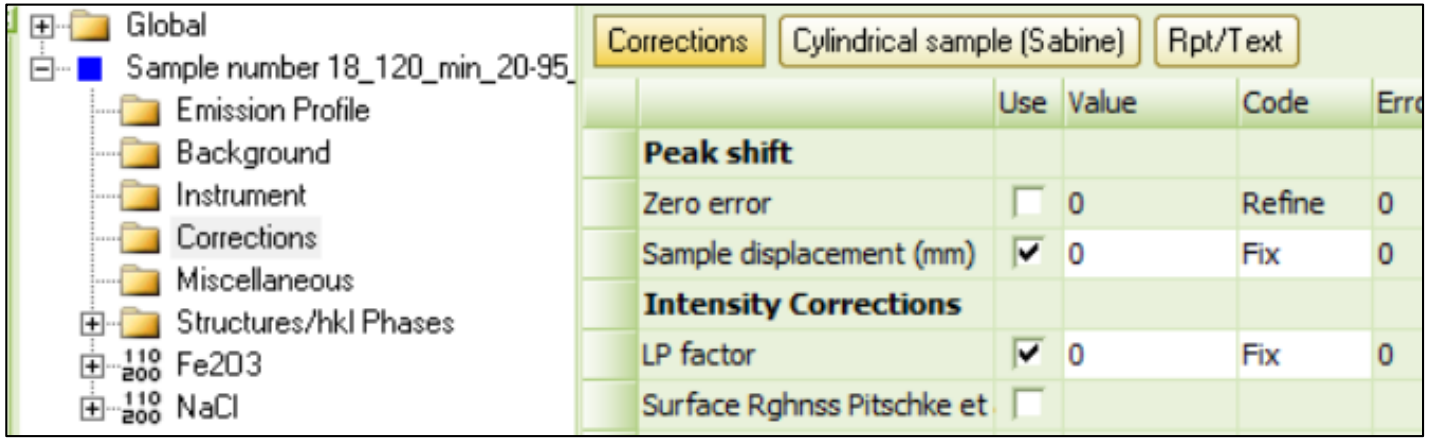


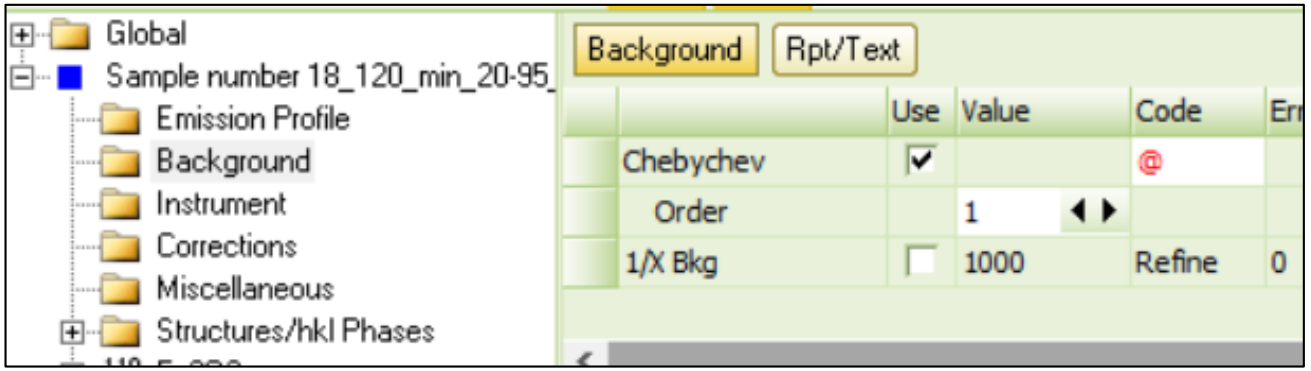
Pawley – fix all parameters first



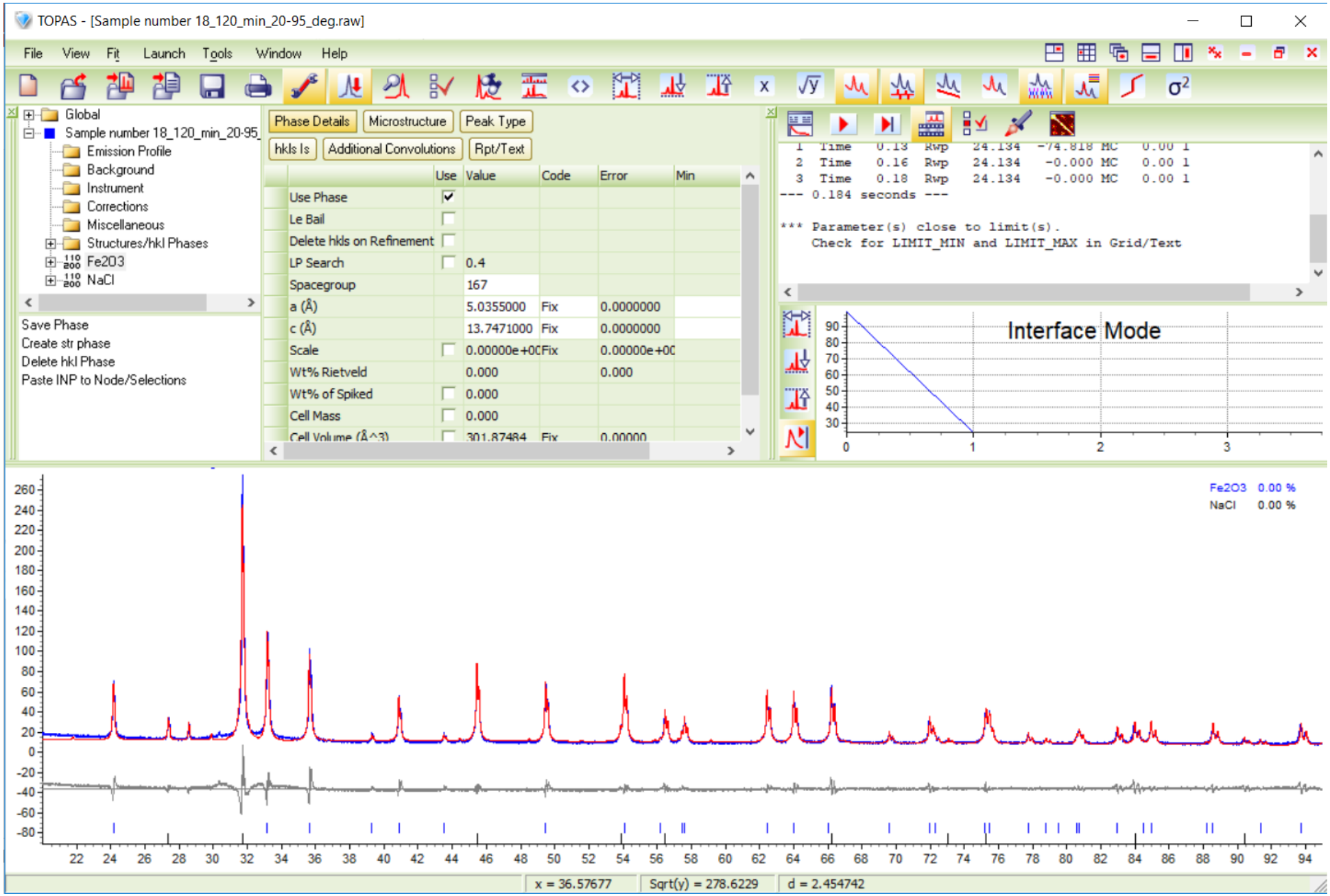
Pawley – fix all parameters first

- Exception: allow at least one variable for the background – flat background which gives a crude, but reasonable fit.



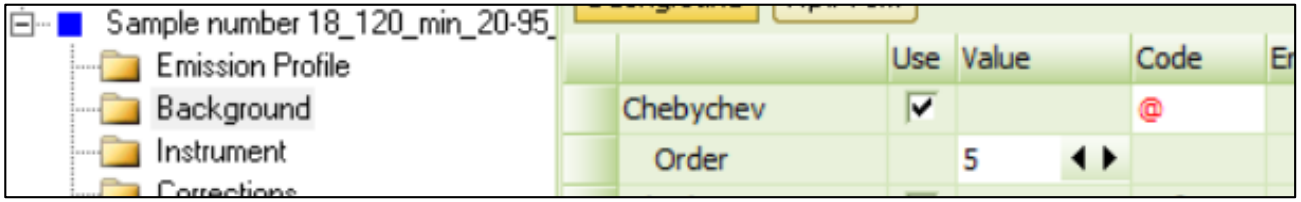


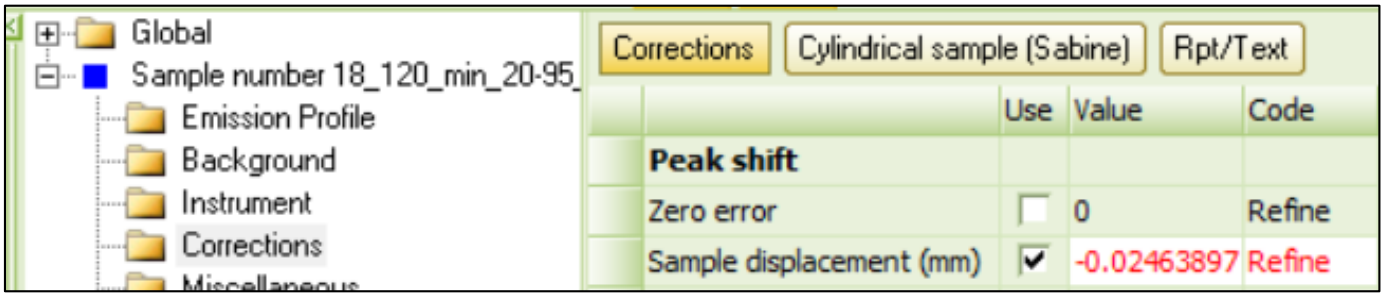
Pawley – first attempt, nothing refined

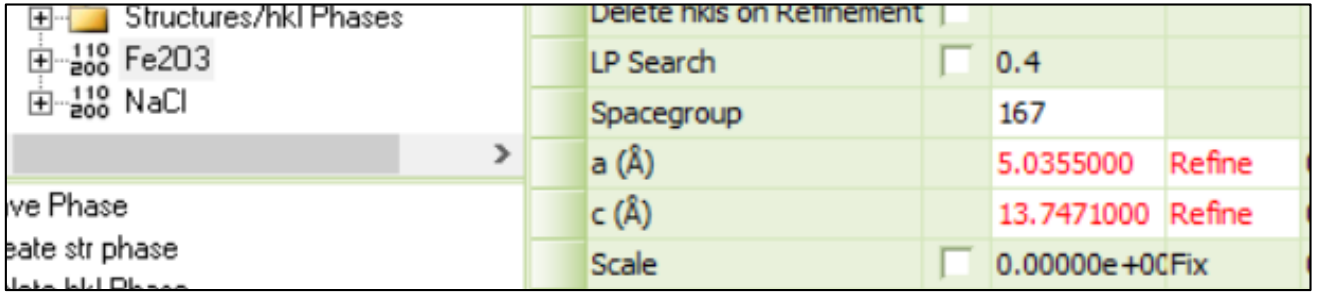


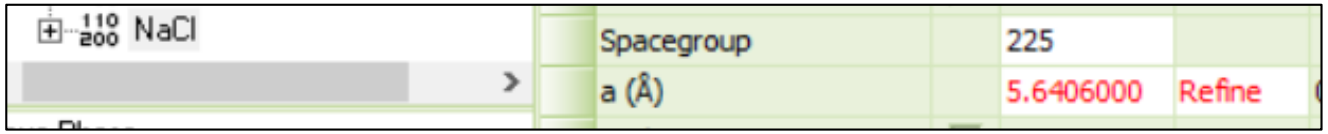
Pawley – progressively add variables

- Add more nodes to the background polynomial – be careful
- The add variables affecting *peak positions*.

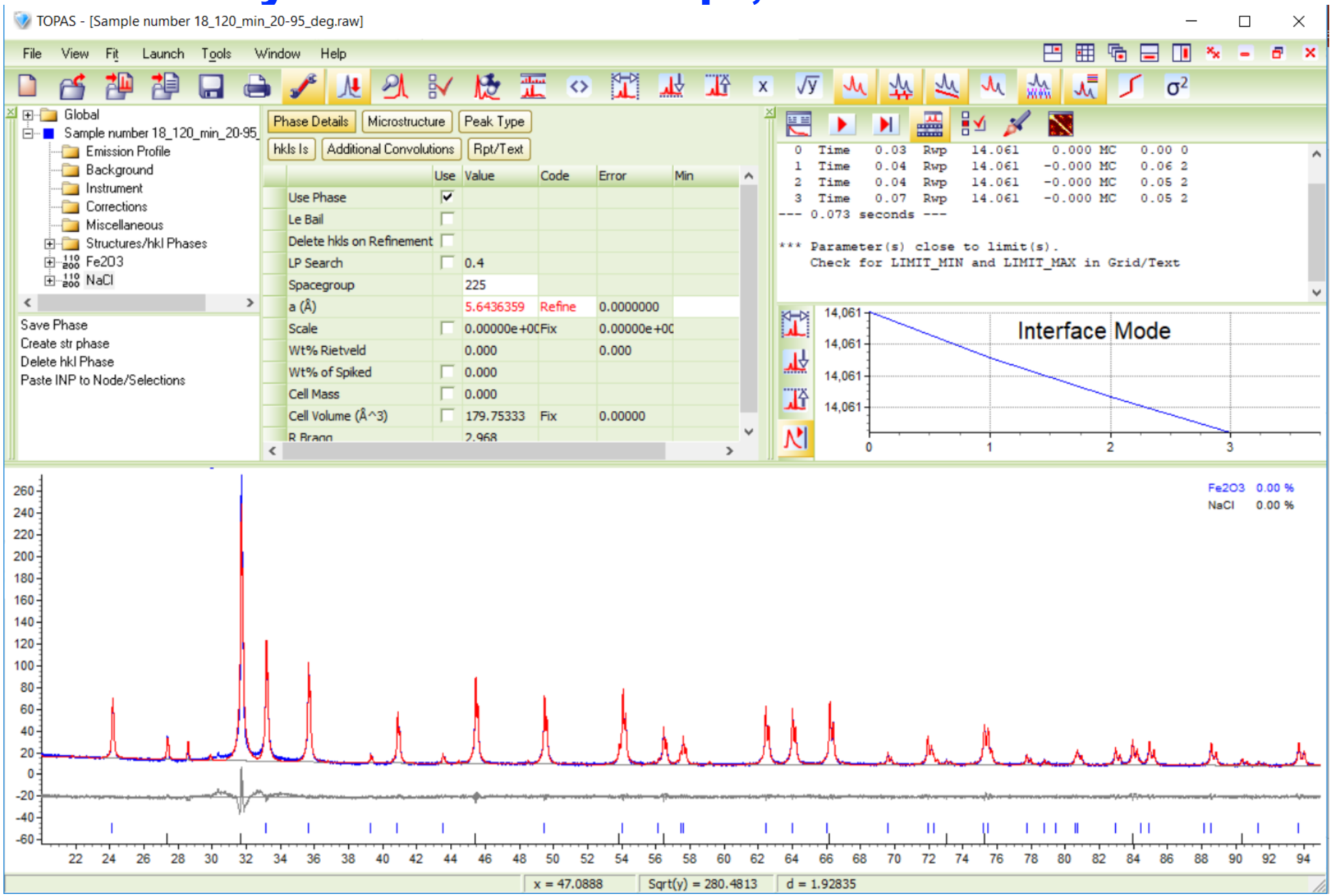




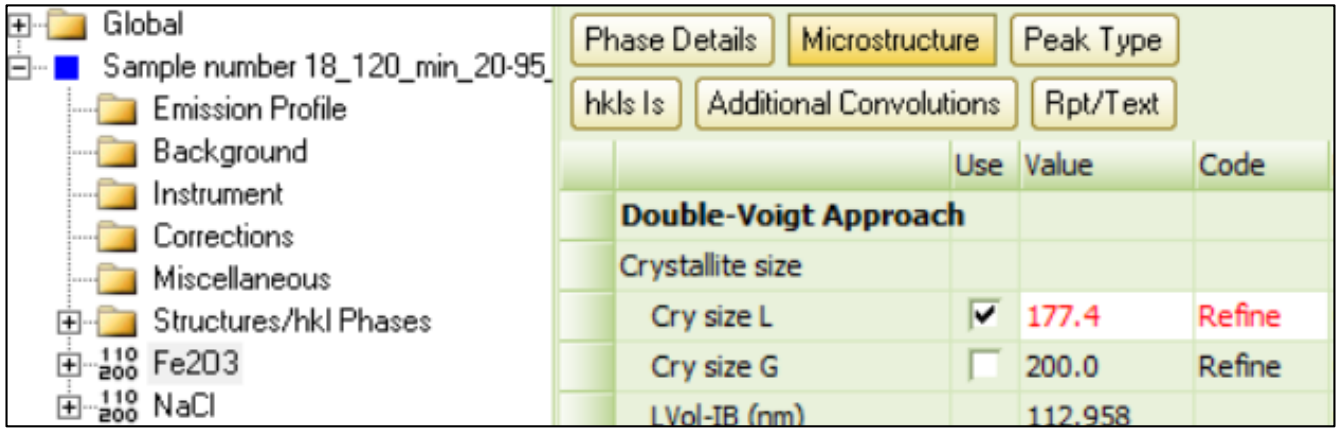


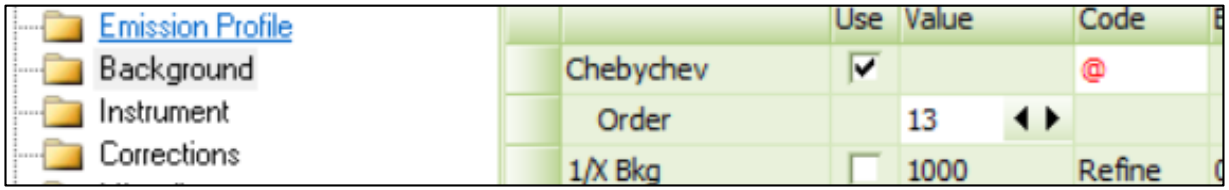


Pawley – second attempt, some variables

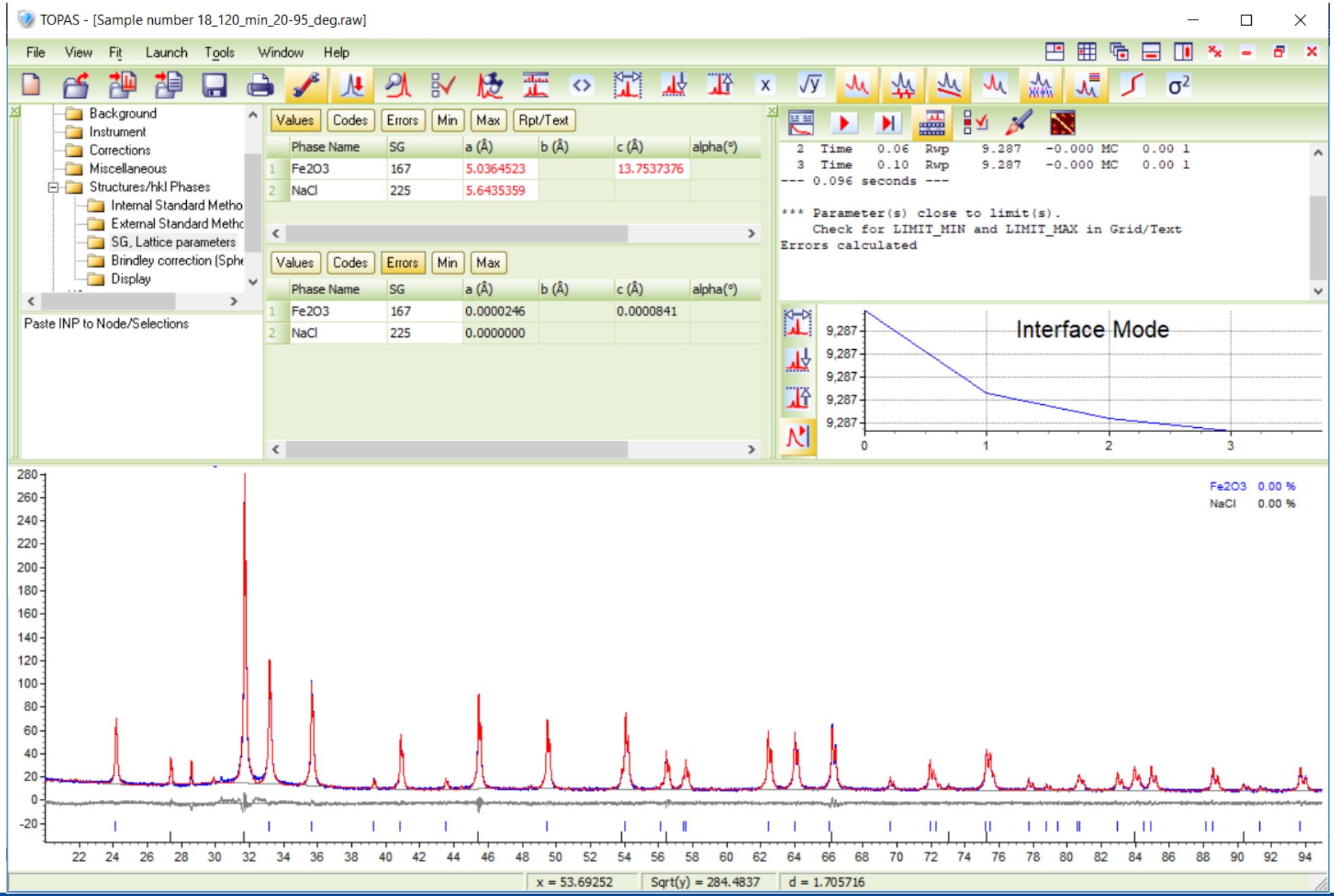


Pawley – next add variables for peak shape



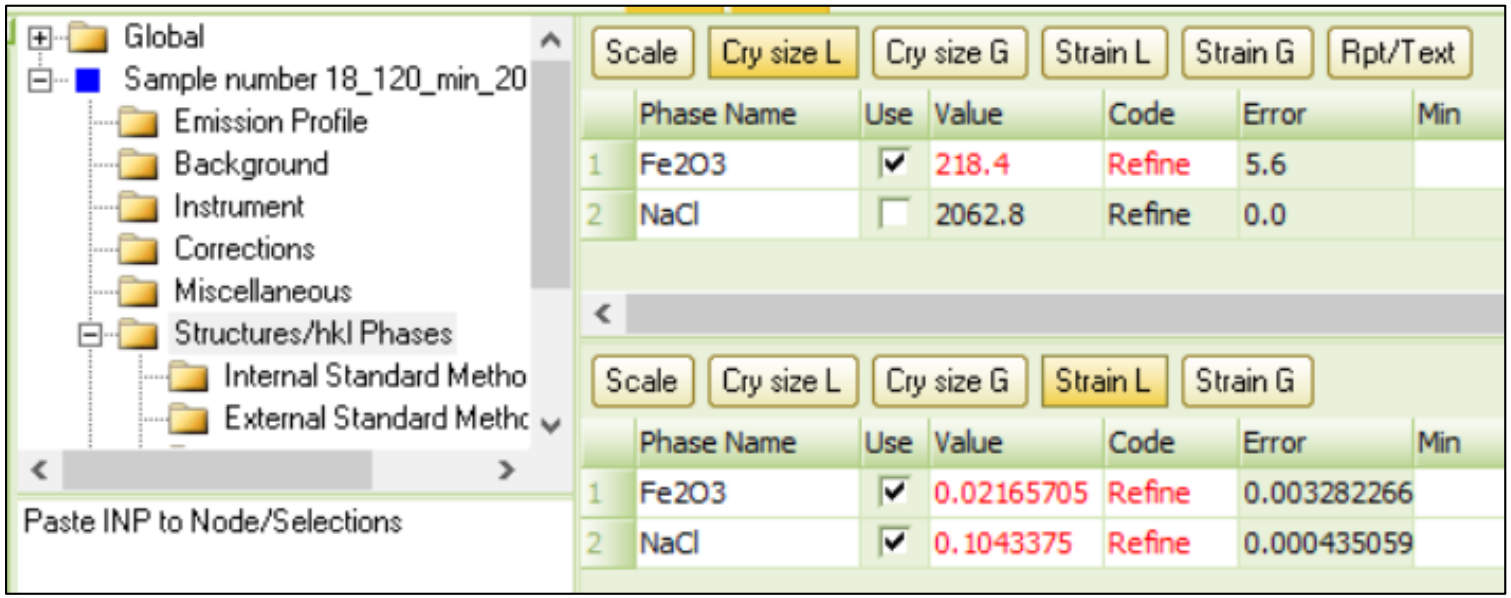


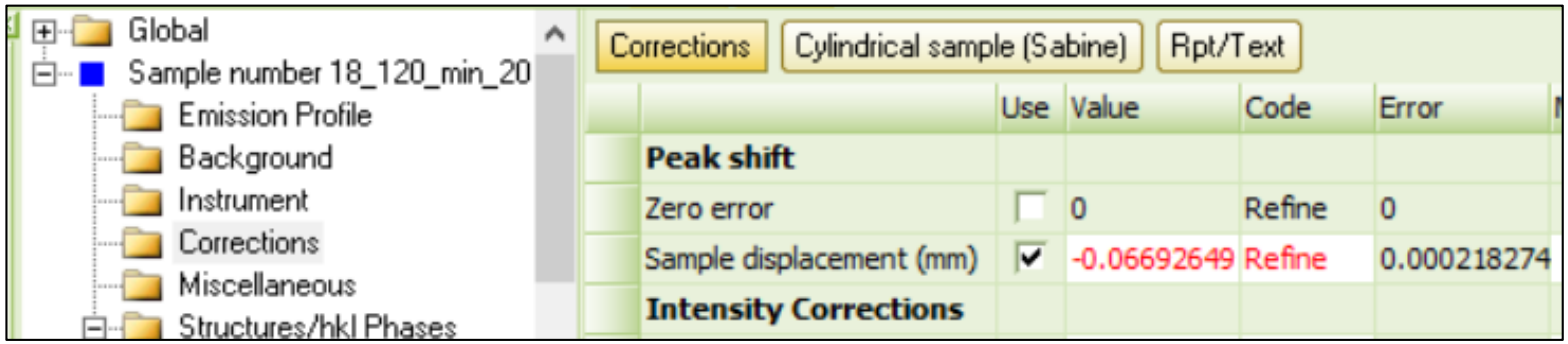
Pawley – a pretty good fit!



Pawley – summarising results

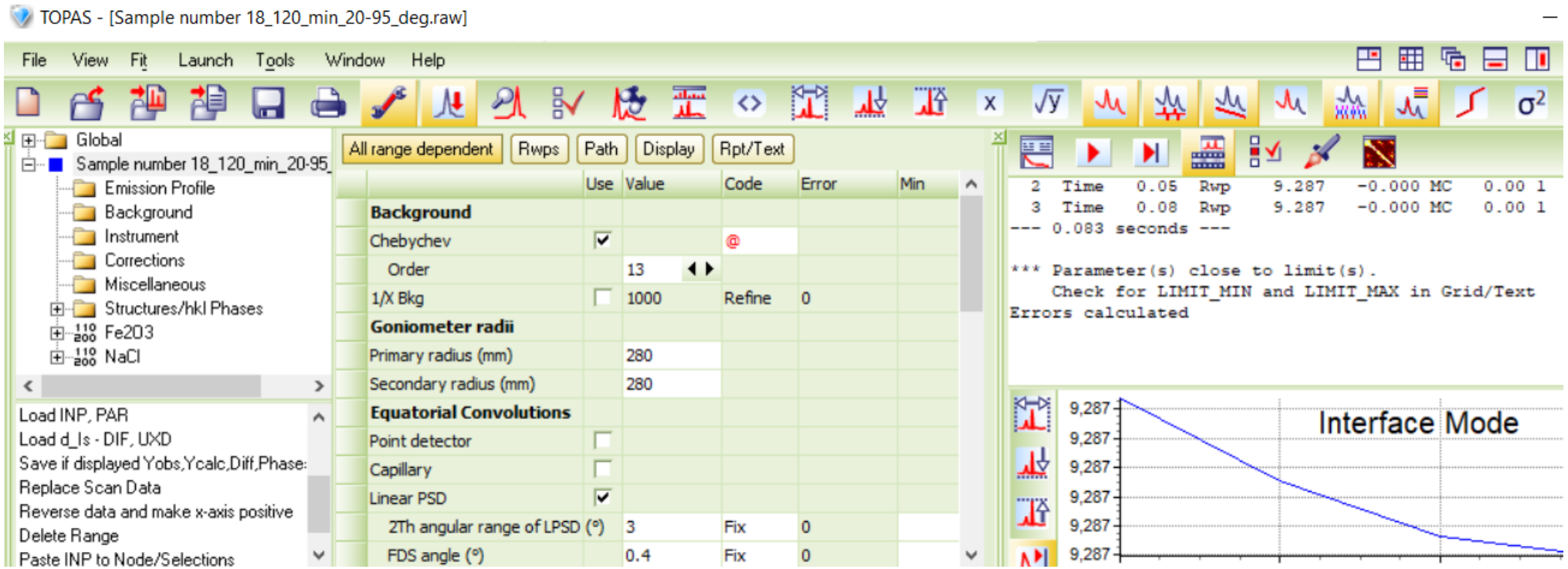
- Useful for many phases or many diffractograms (under global).





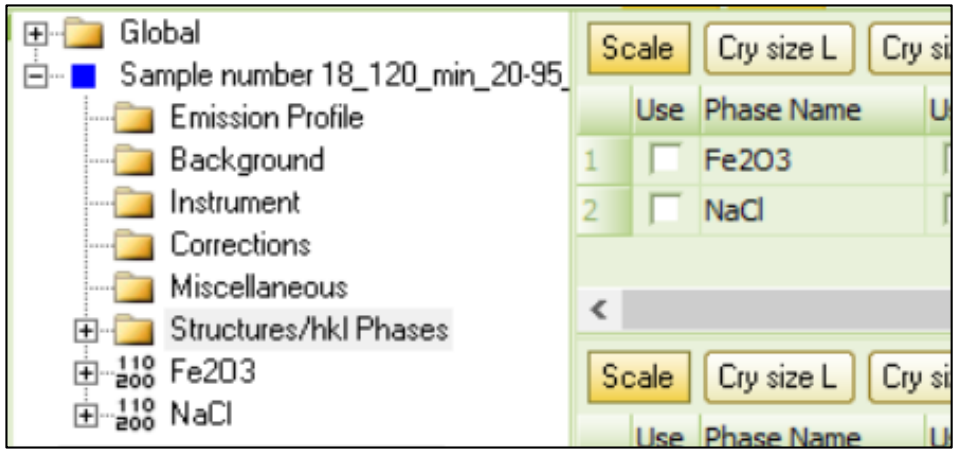
Pawley – background polynomial

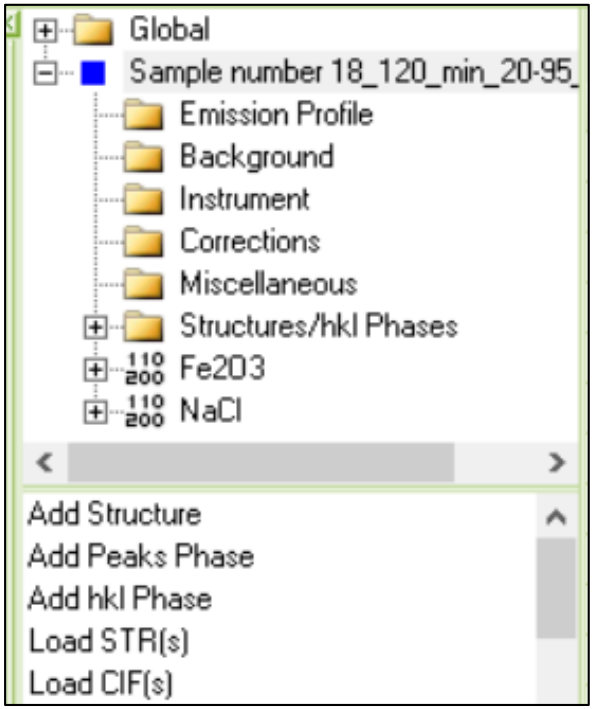
- You can add more nodes as long as the background does not fit peaks.
- E.g. 13 is a high number, but unproblematic with broad 2q range and a bulk well-crystallized sample.
- Can be problematic for small nanocrystallites – why?



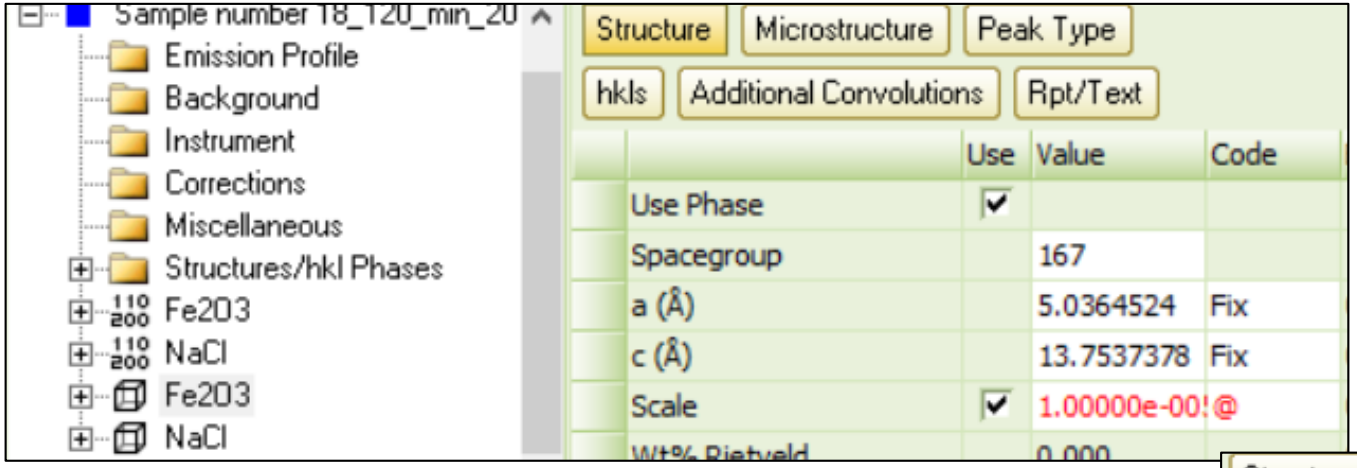
Preparing for Rietveld refinement

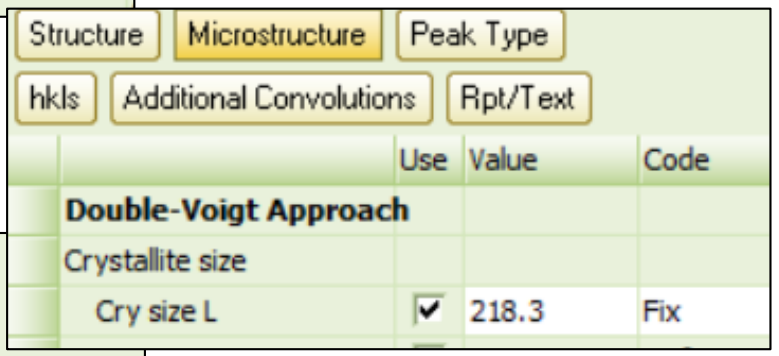
- Uncheck the hkl phases for Pawley
- Add two new structures
- You can also load a saver .str file or a downloaded .cif file
- .cif – Crystallographic Information File

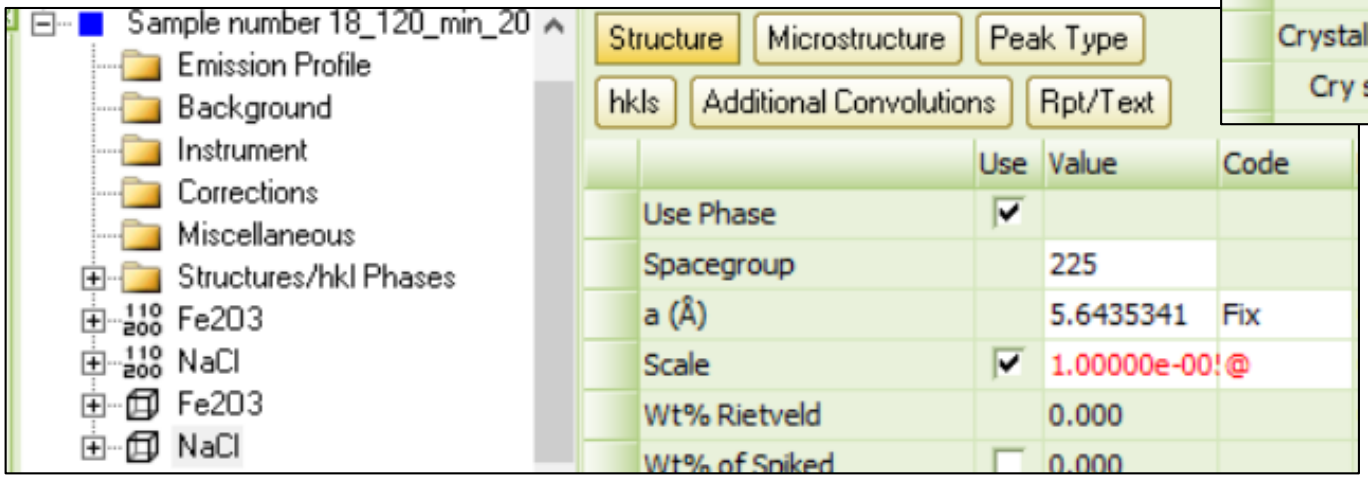


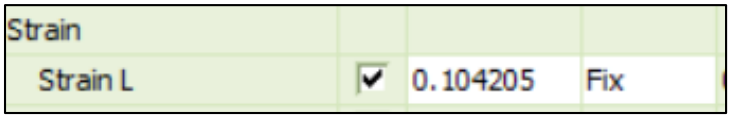


Add structures for Rietveld refinement

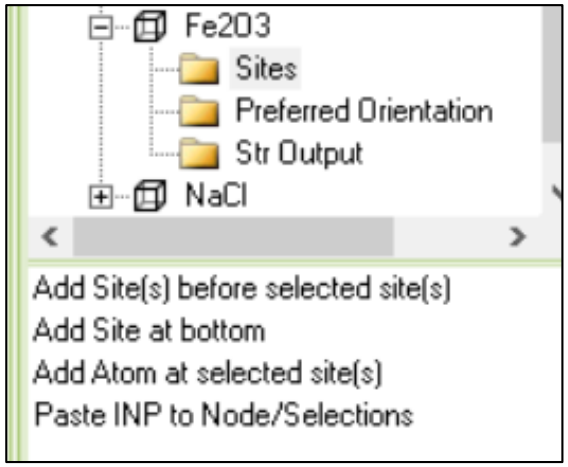


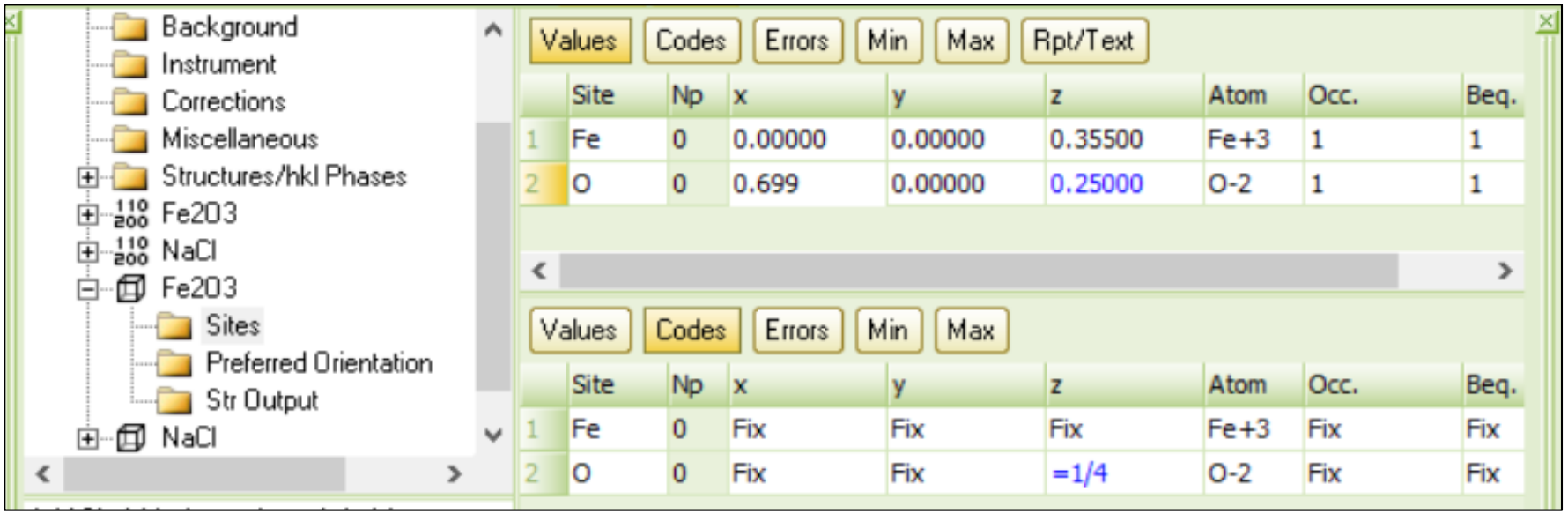




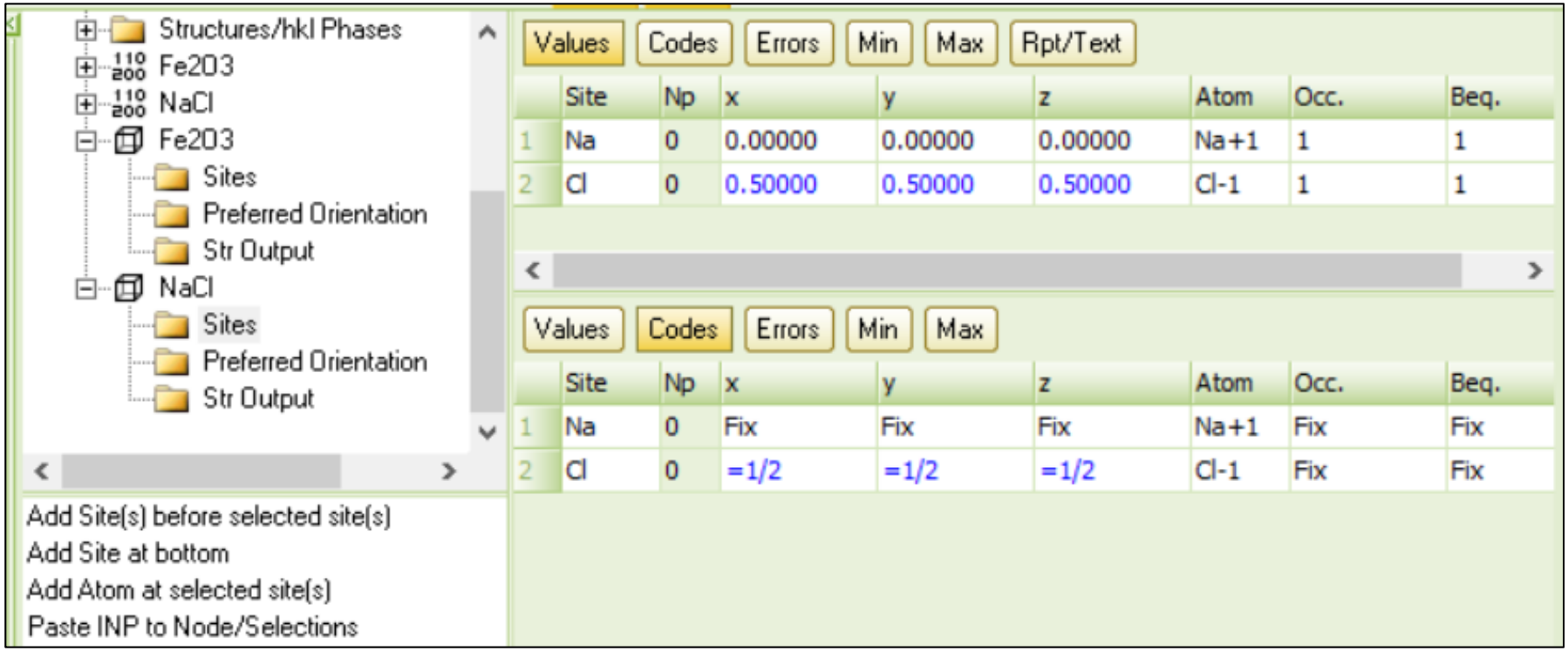


Structures for Rietveld – atomic positions

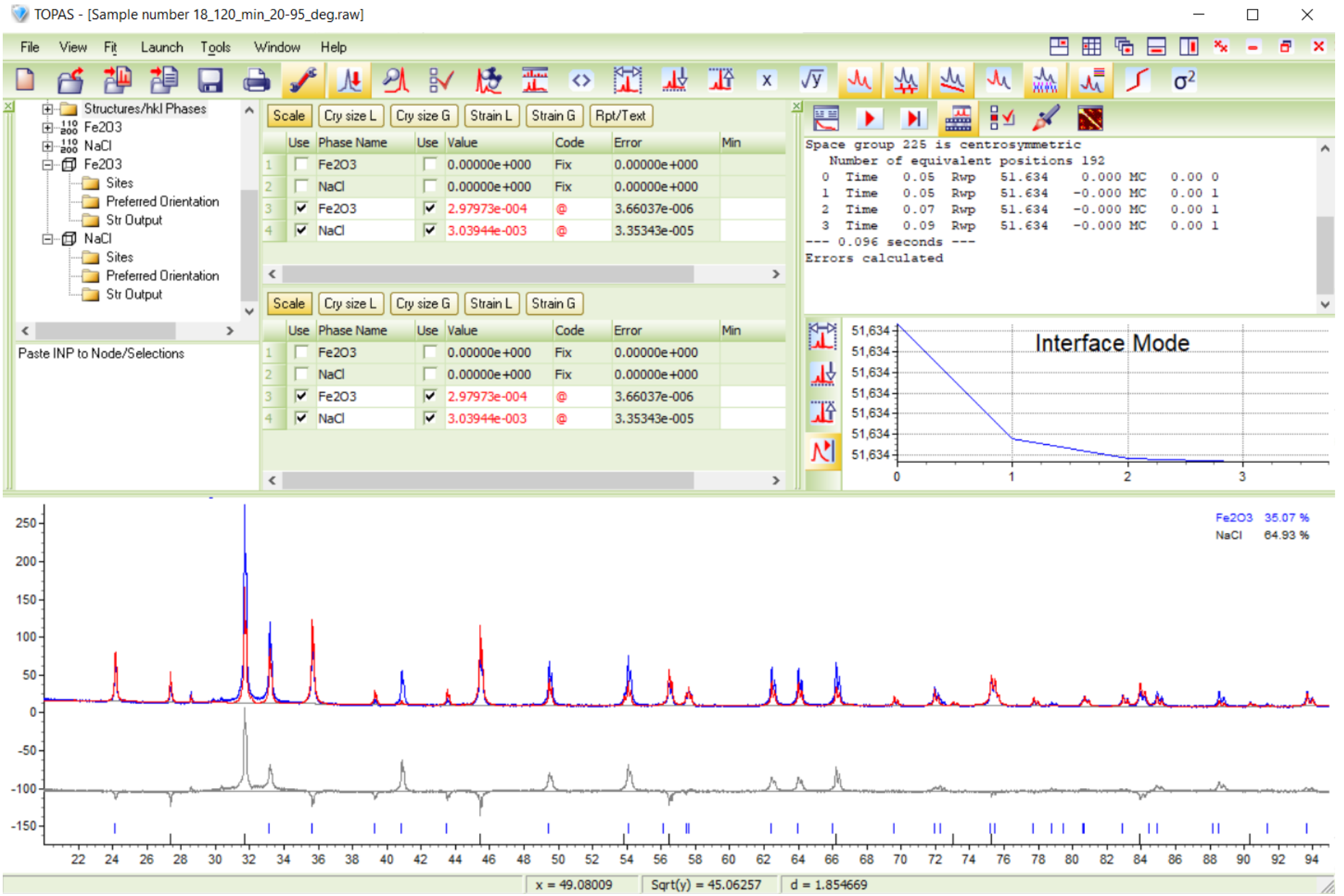




Structures for Rietveld – atomic positions

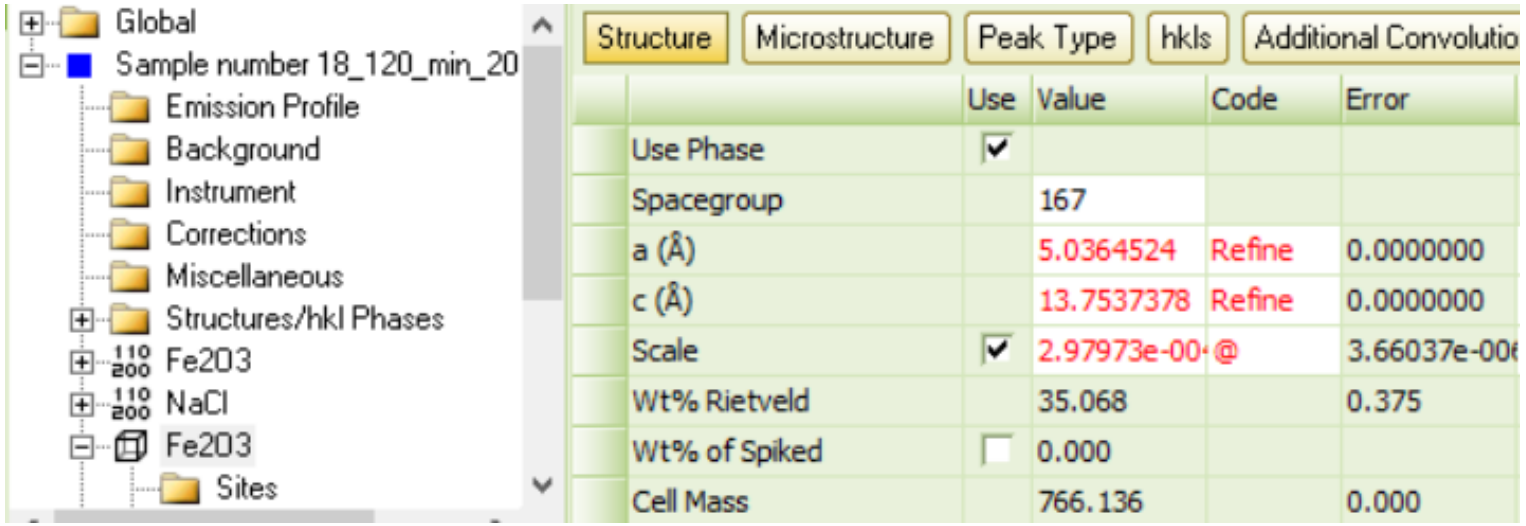


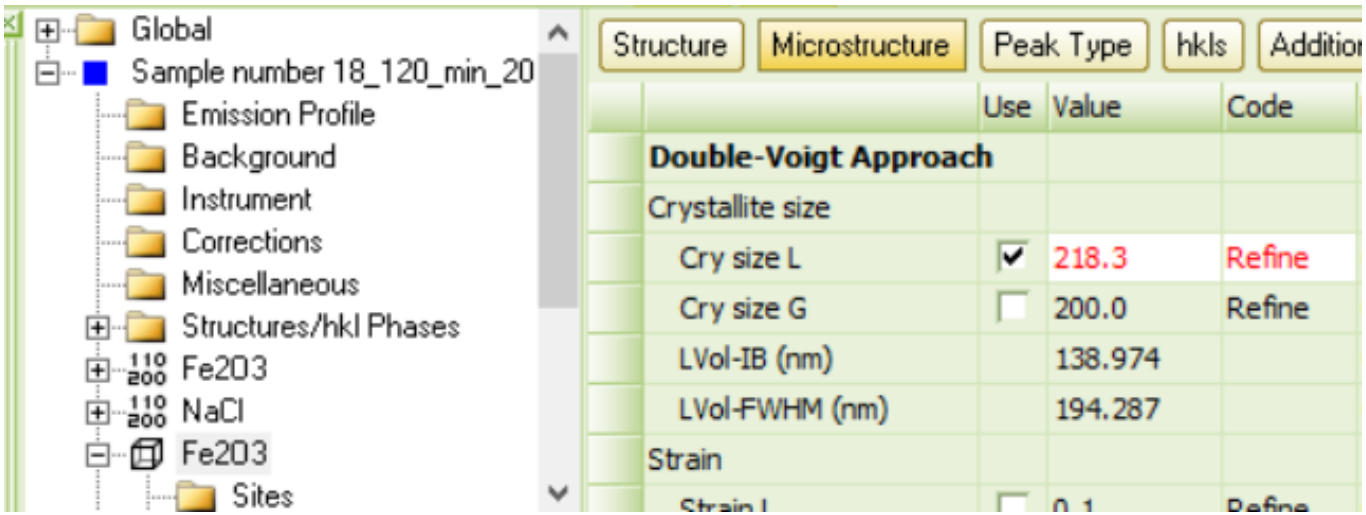
Rietveld – first attempt with Pawley results



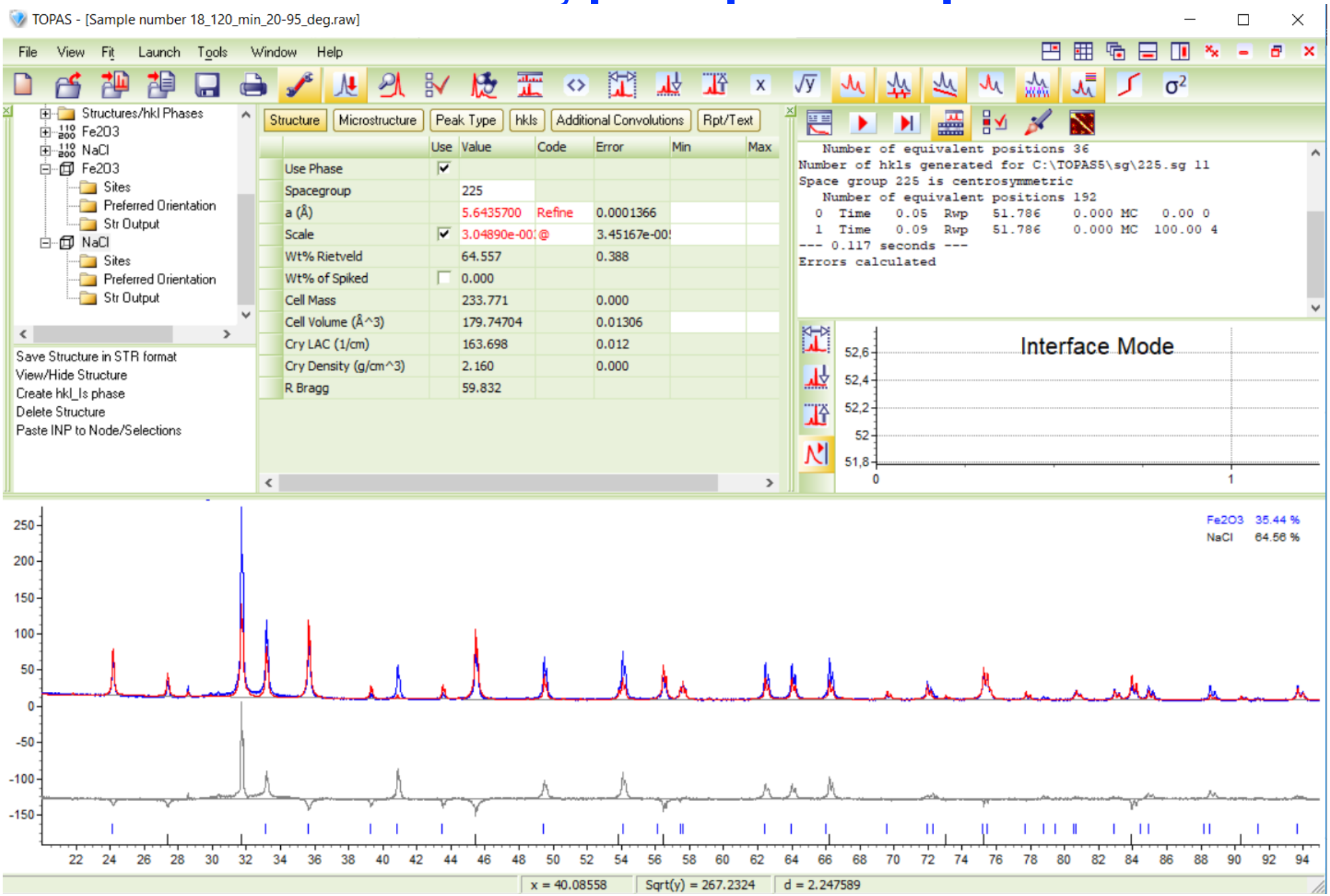
Rietveld refinement

- Start with lattice parameters – peak *positions*.
- Proceed with size/strain – peak *shapes*.



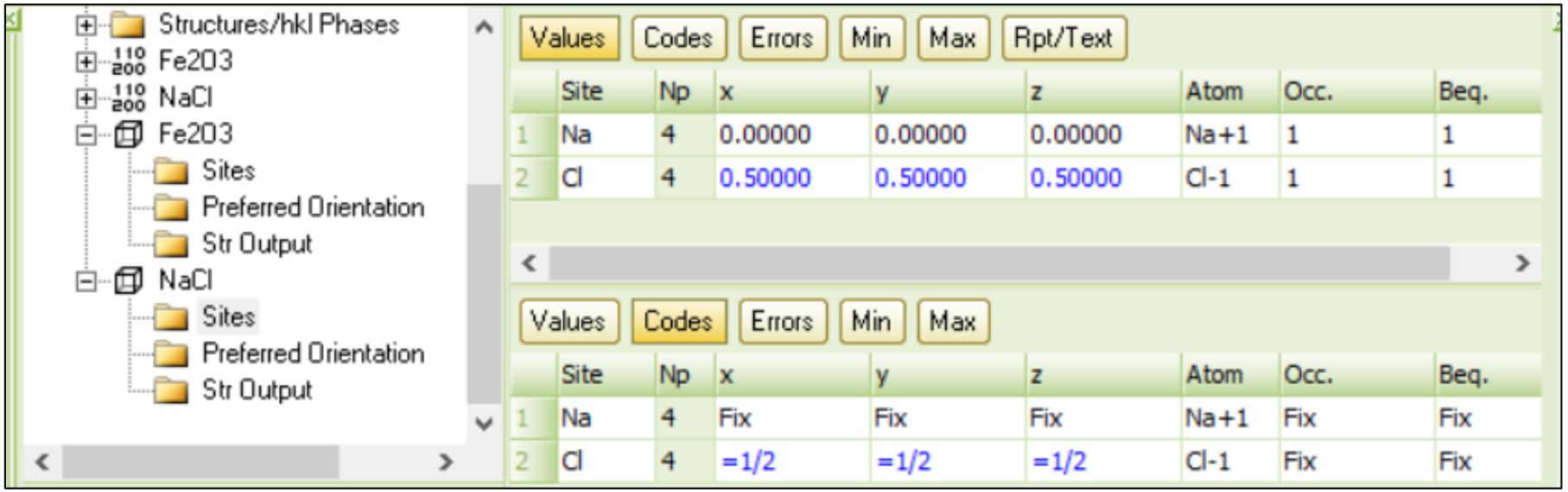


Rietveld refinement, peak pos./shape included



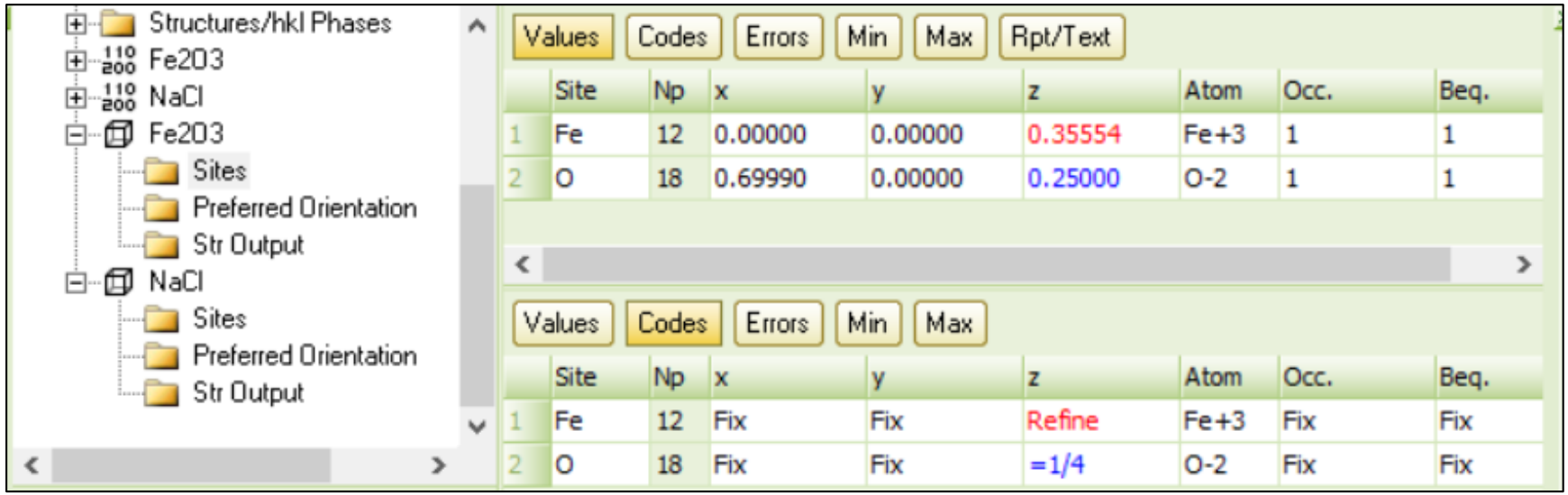
Rietveld refinement – atomic positions

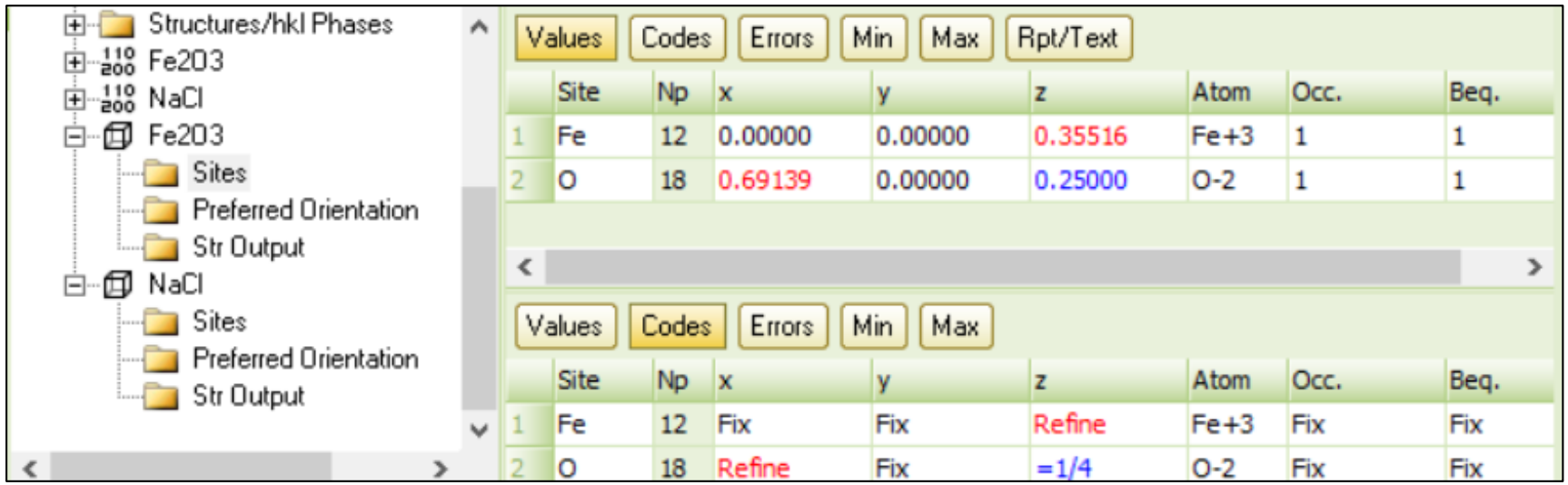
- Always start with locked atomic positions.
- Lattice parameters and size/strain MUST converge before you add atomic positions as variables.



Rietveld refinement – atomic positions

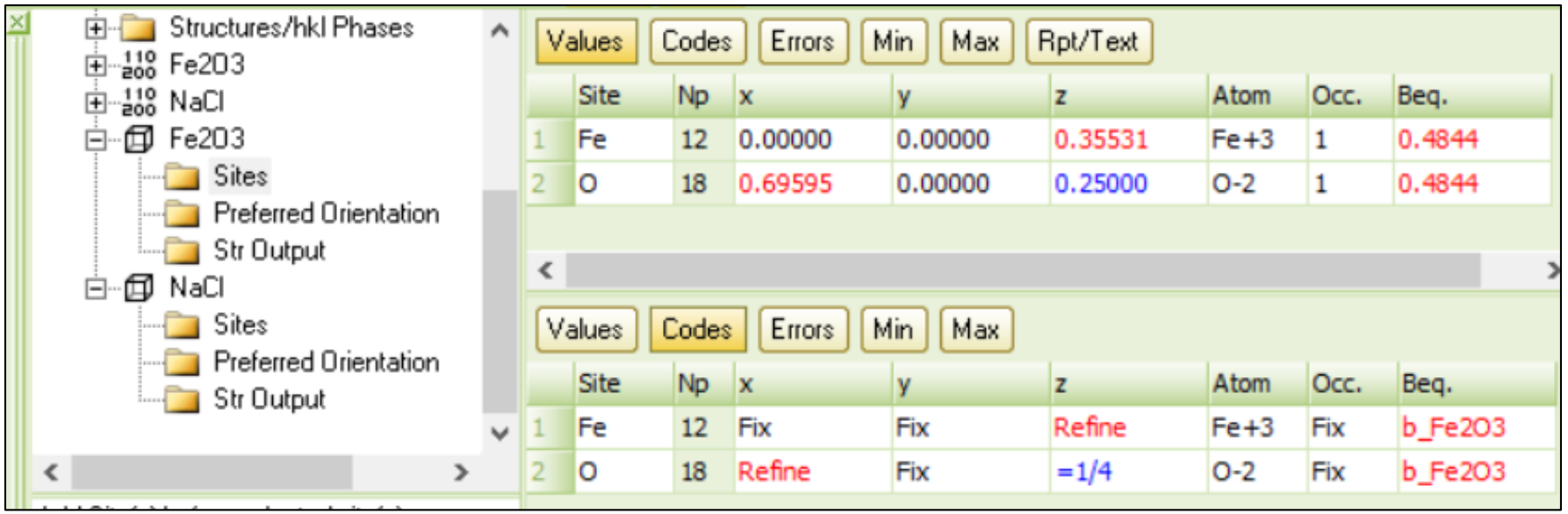
- Start with heaviest atomcs, proceed with lighter.
- If more what one Wyckoff position: start with highest multiplicity.

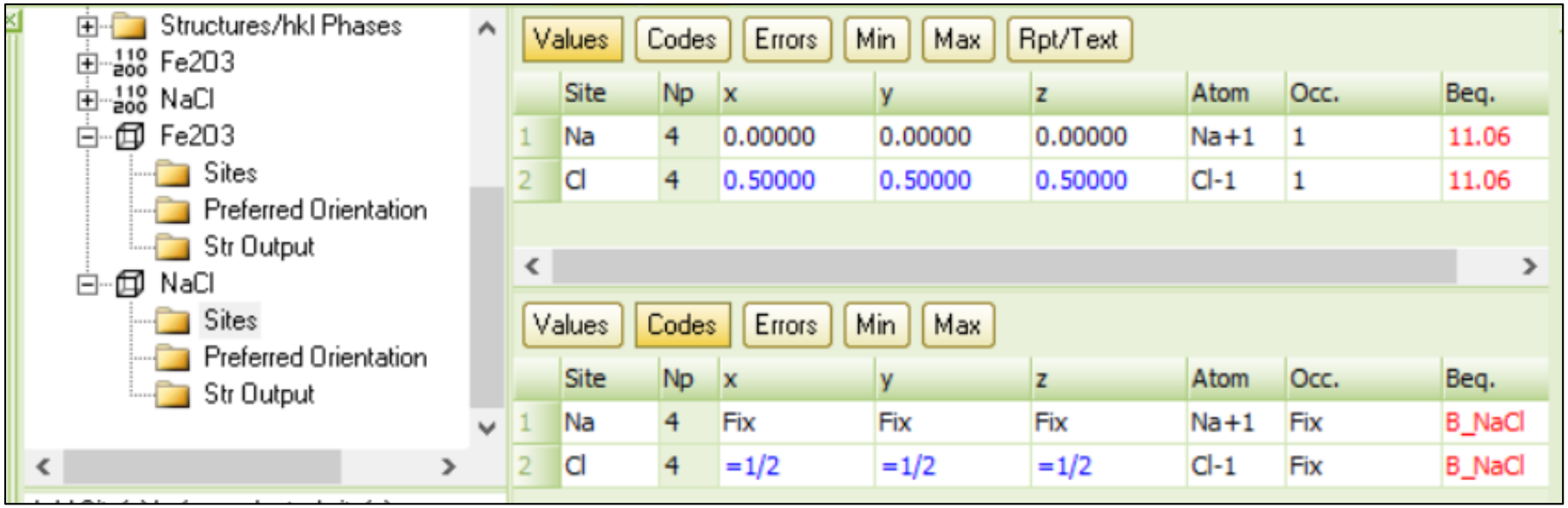




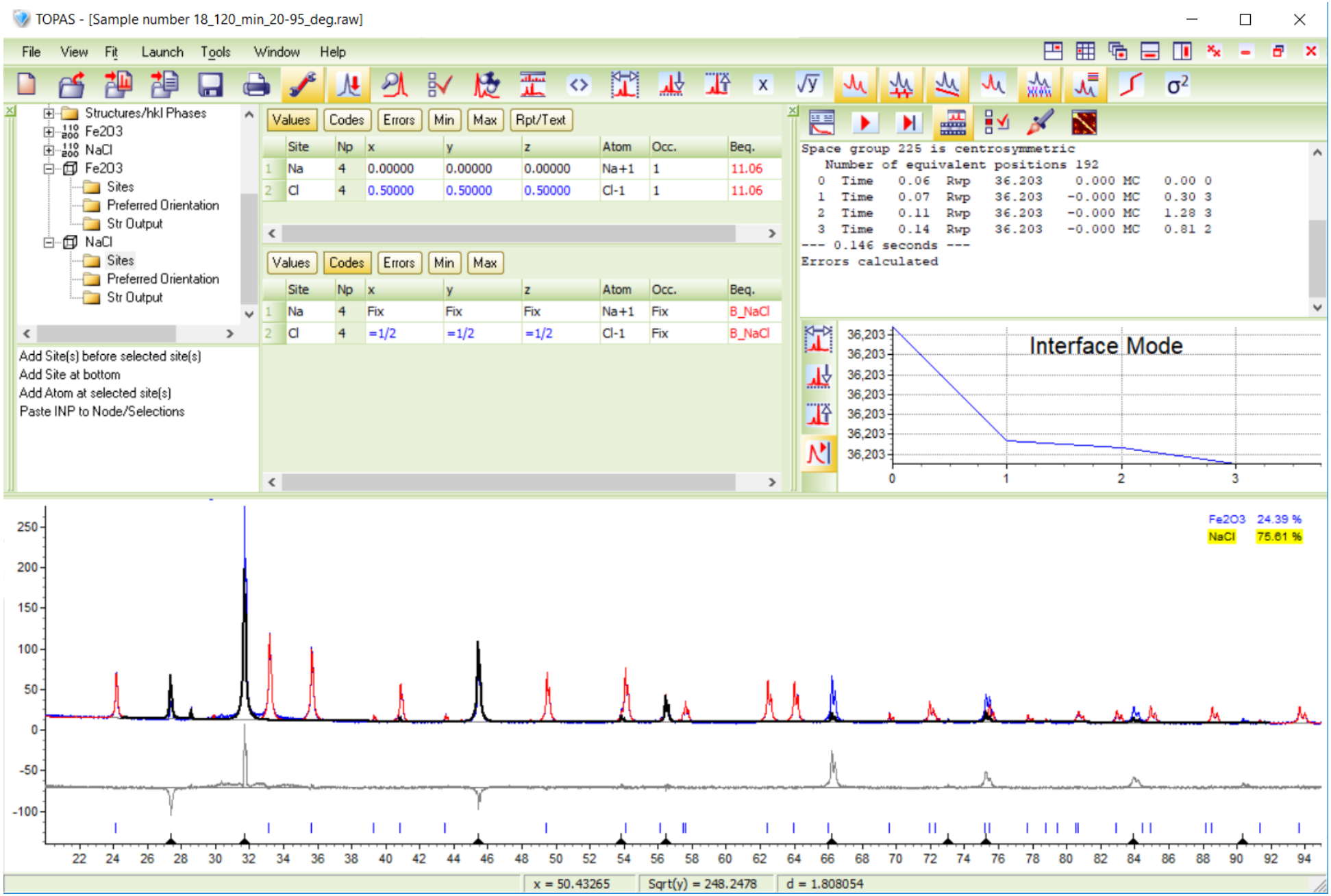
Rietveld refinement – B-factors

- Start with linking parameters, see example below.



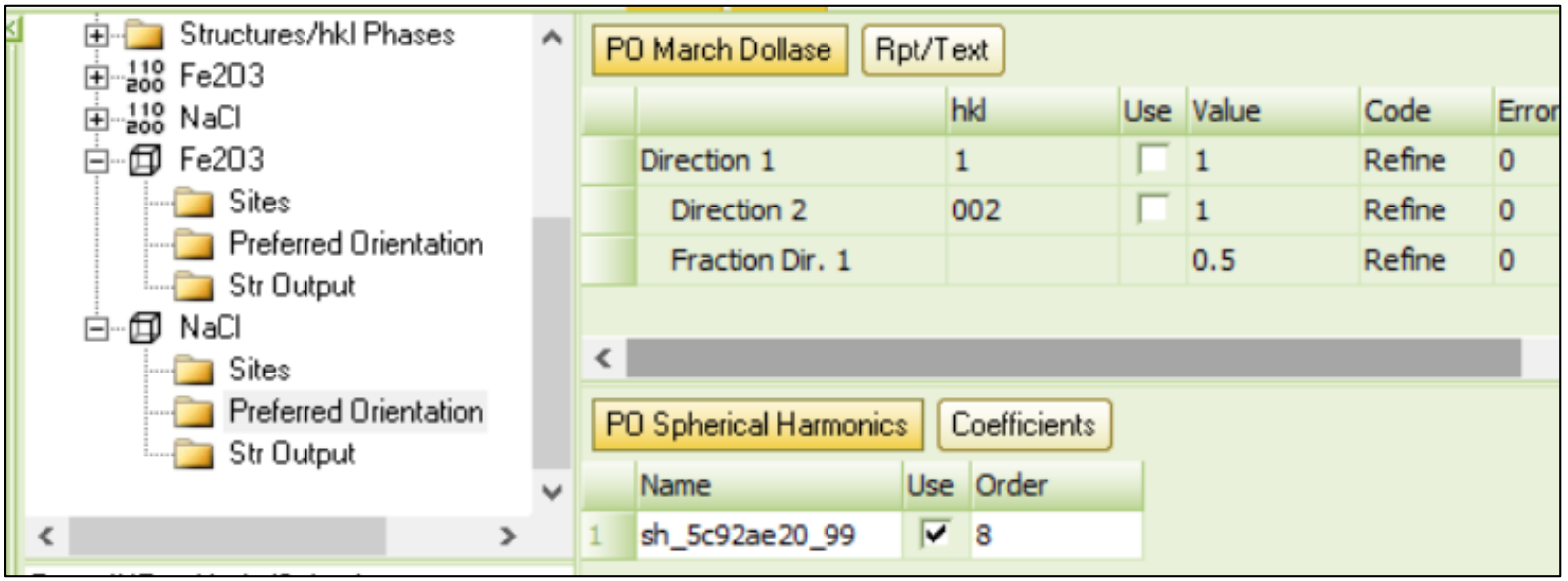


Peak intensities wrong and B-factors too high…



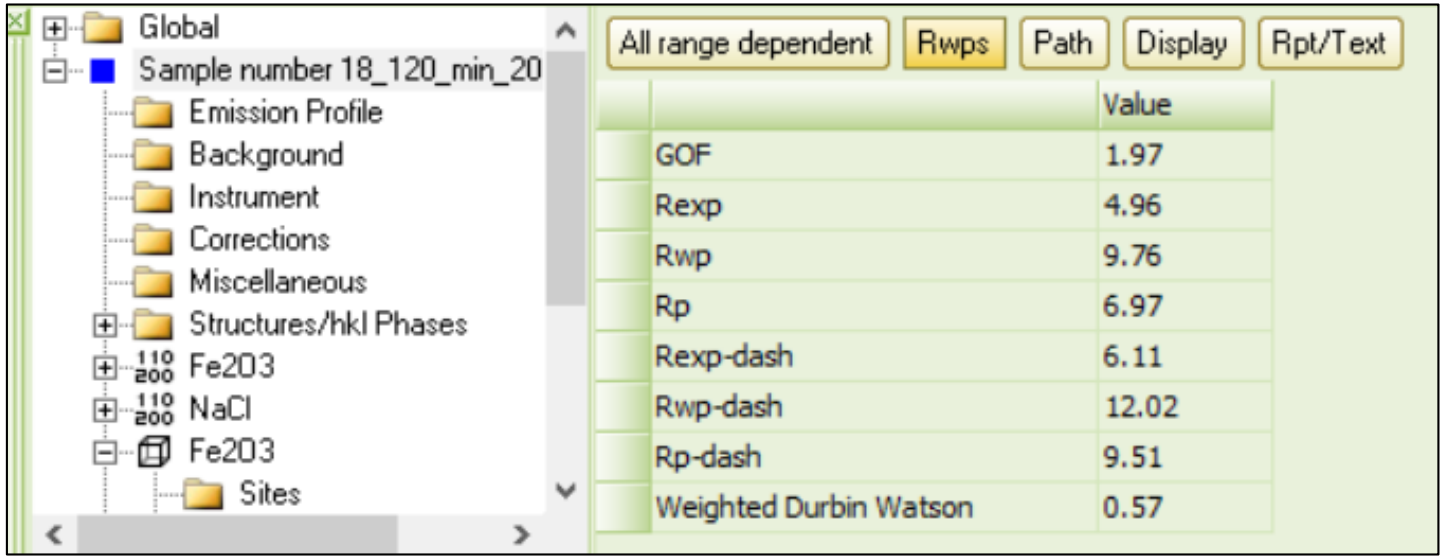
Preferential orientation in powder

- Use this with care and make sure you know what you are doing!
- (I know what I'm doing – and I made the sample…)

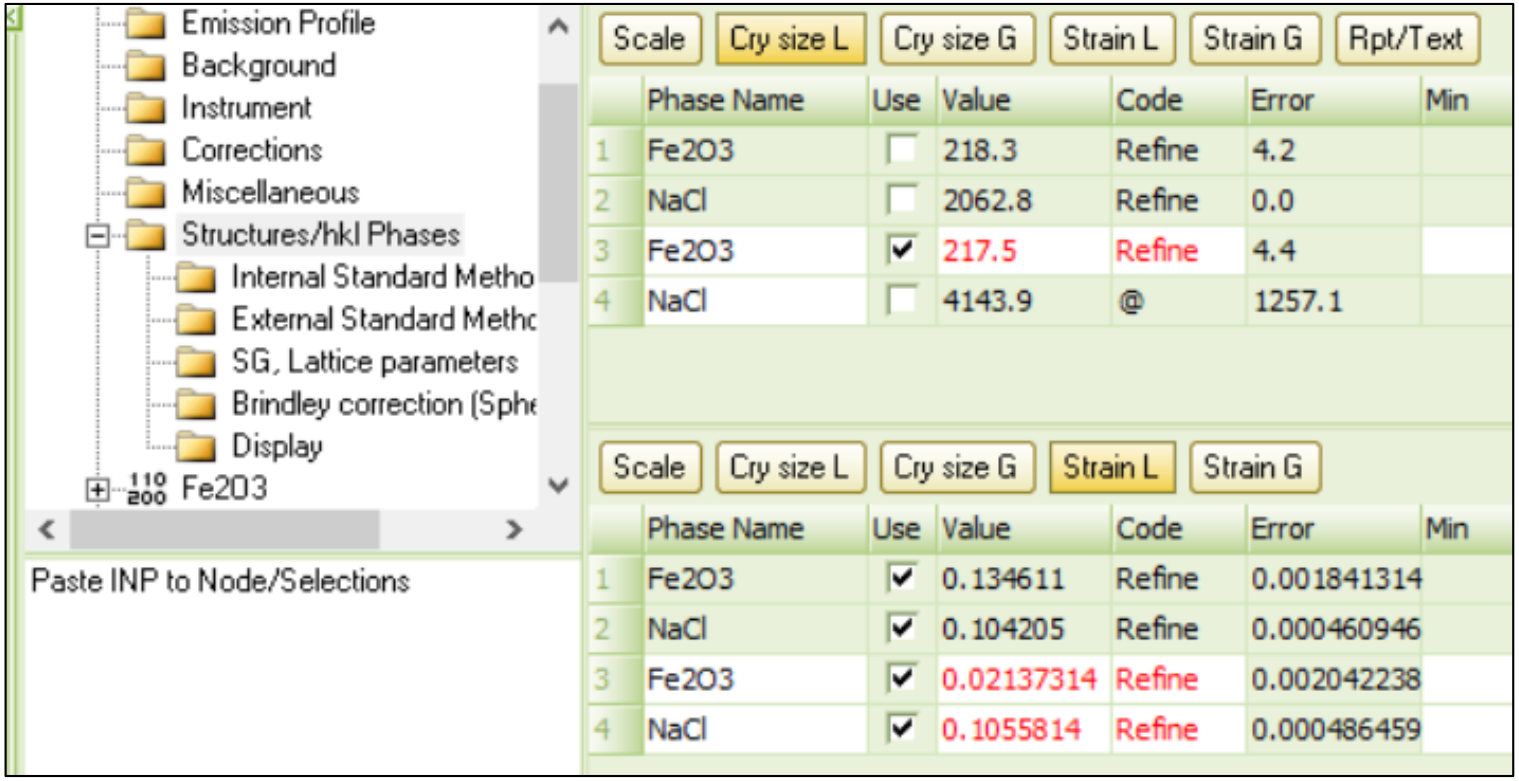


Rietveld refinement – final result

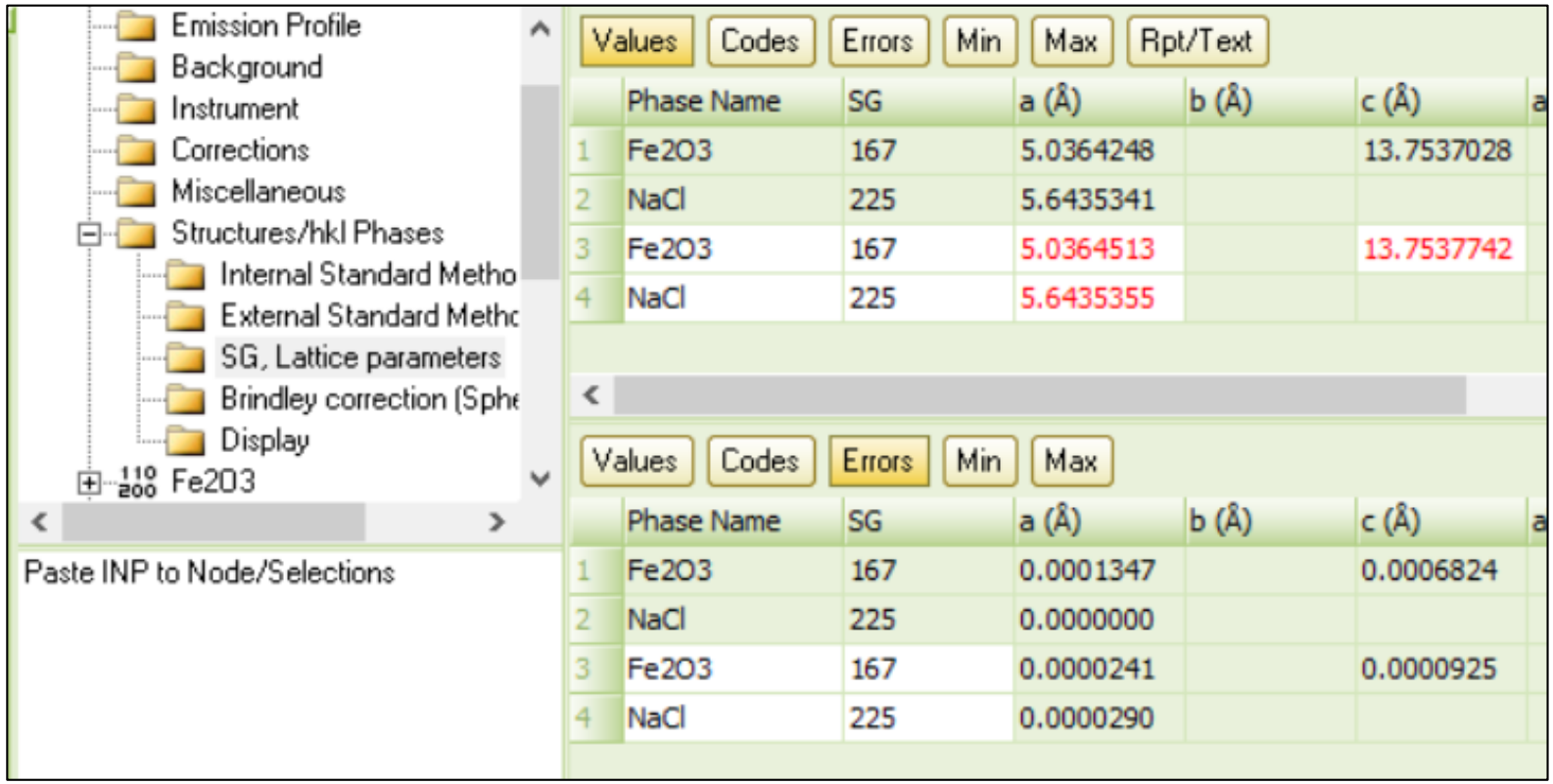
Rietveld refinement – fit statistics



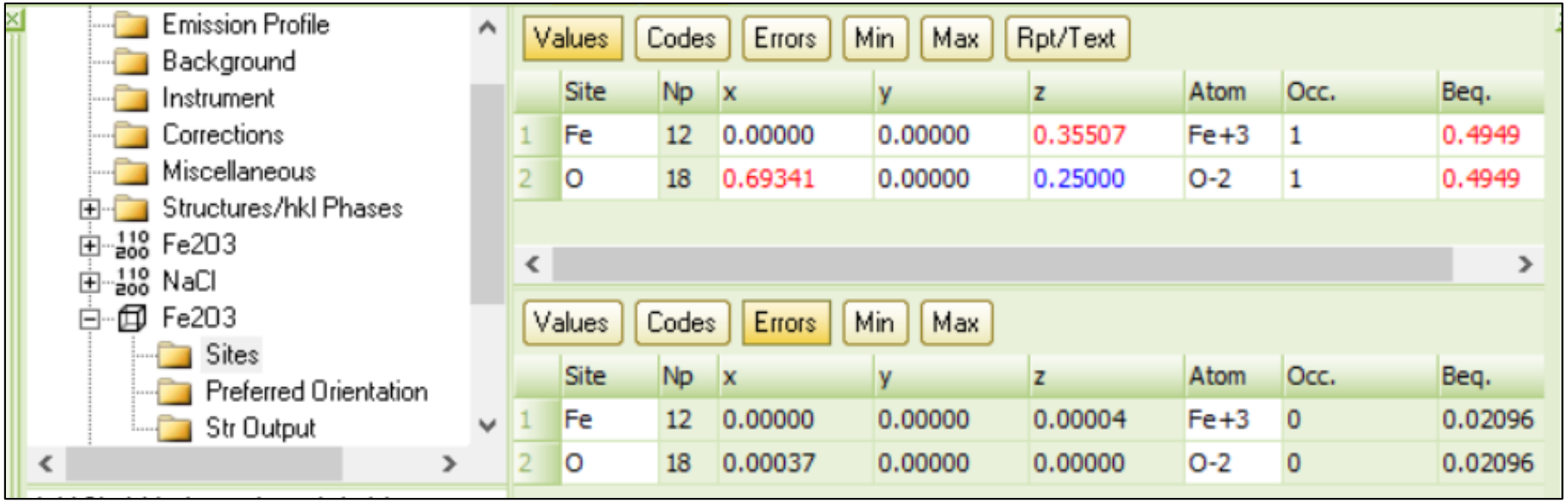
Rietveld refinement - results

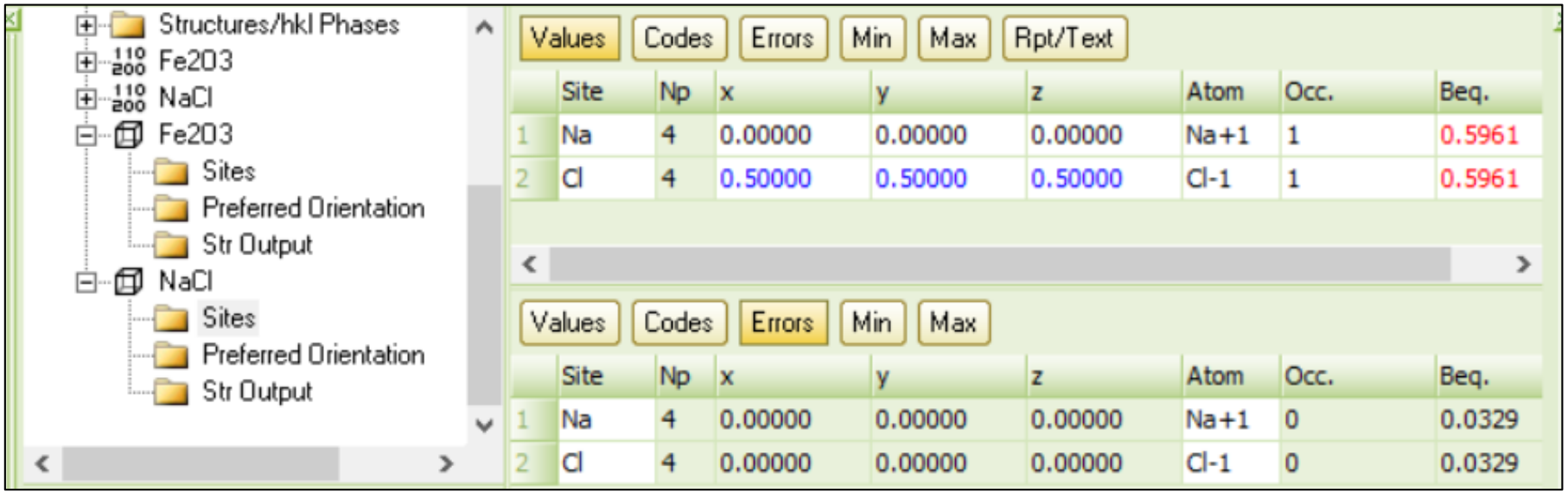


Rietveld refinement - results

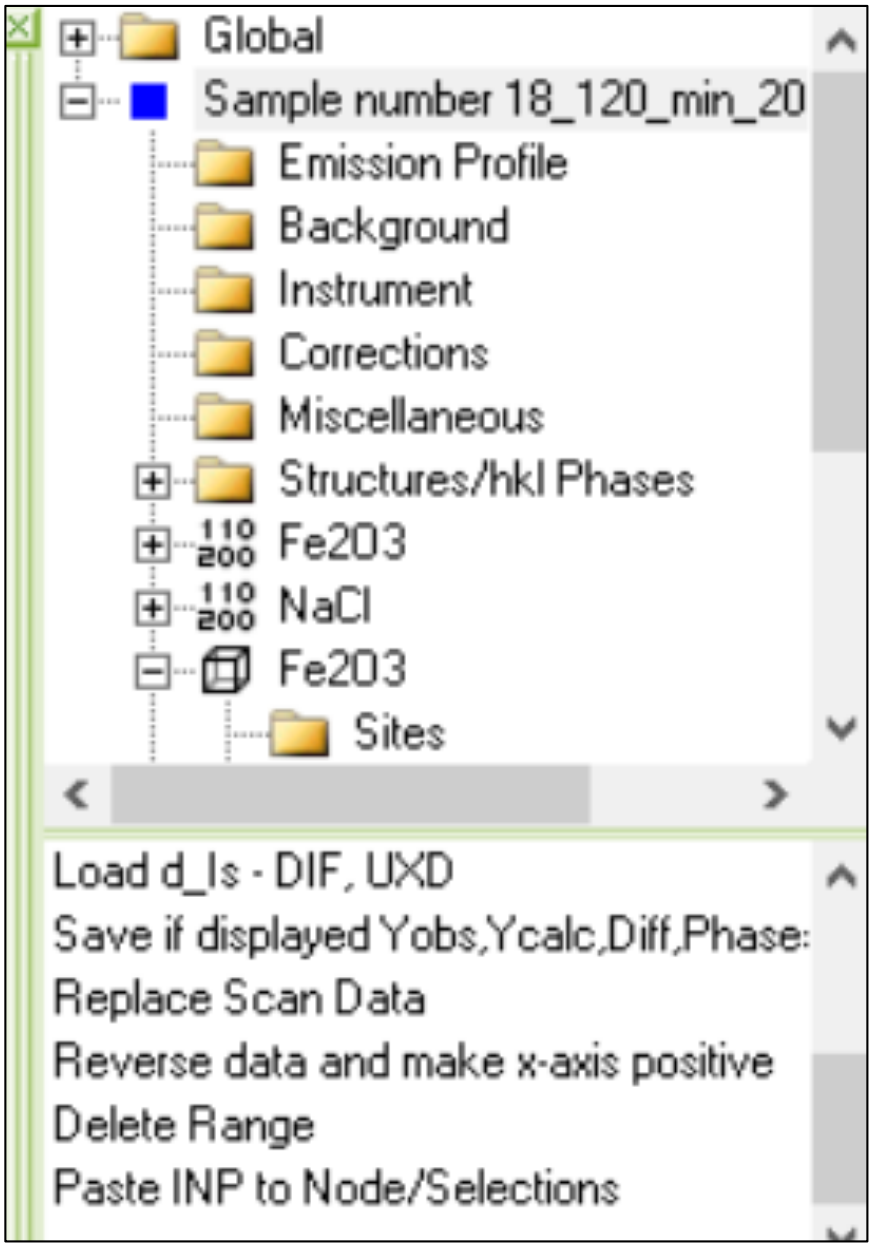


Rietveld refinement - results

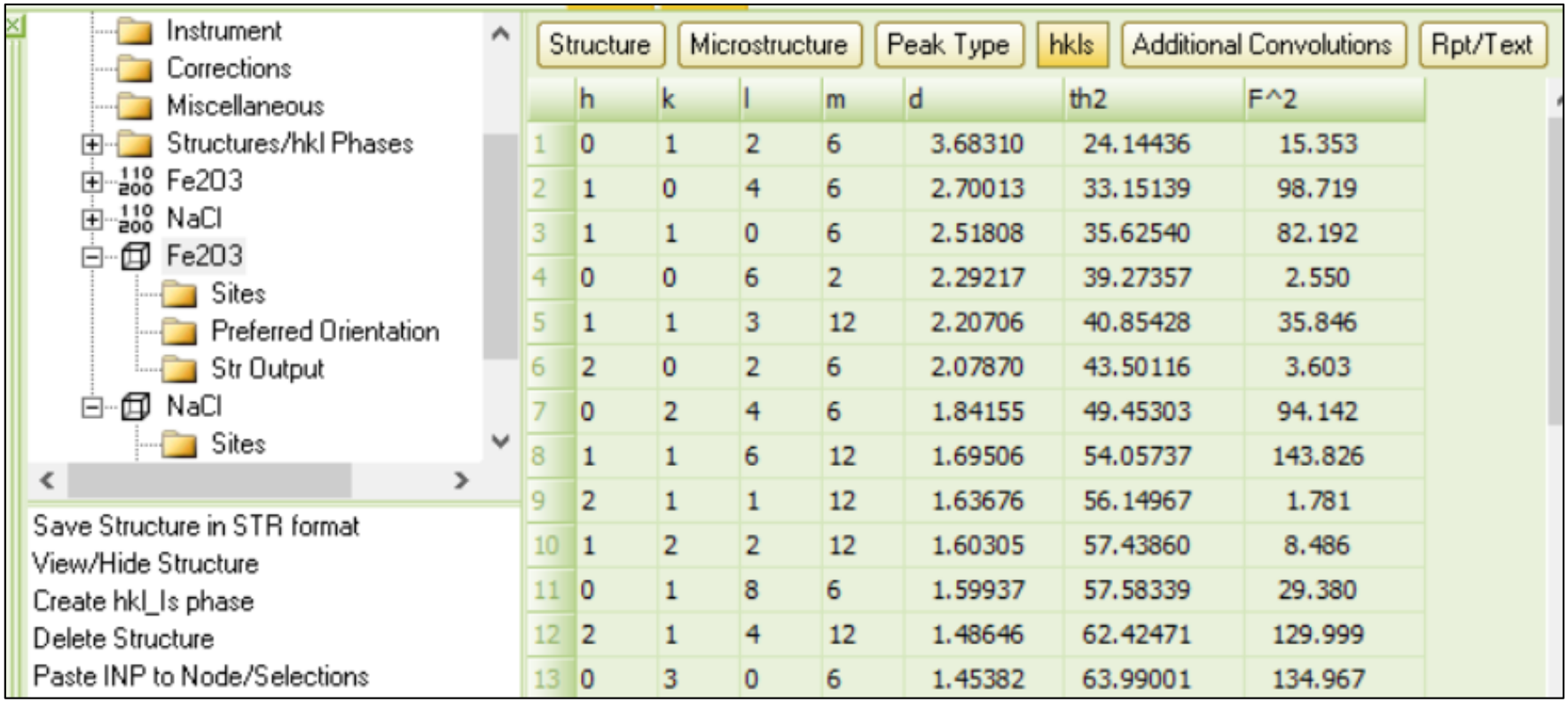




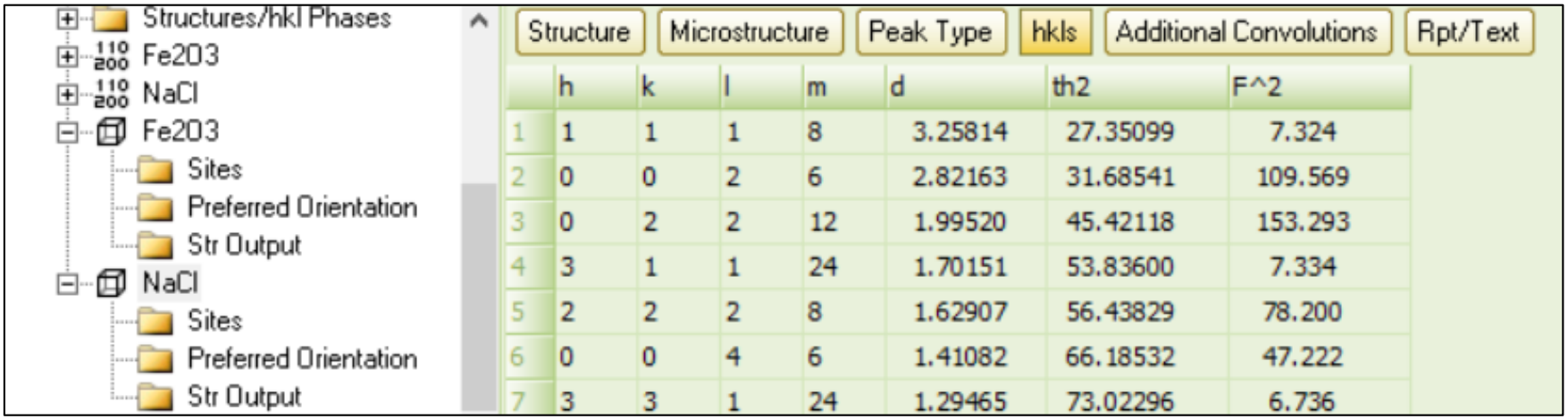
Rietveld refinement – export your data



Getting the positions of the hkl ticks



	h	k	l	m	d	th2	F^2
1	0	1	2	6	3.68310	24.14436	15.353
2	1	0	4	6	2.70013	33.15139	98.719
3	1	1	0	6	2.51808	35.62540	82.192
4	0	0	6	2	2.29217	39.27357	2.550
5	1	1	3	12	2.20706	40.85428	35.846
6	2	0	2	6	2.07870	43.50116	3.603
7	0	2	4	6	1.84155	49.45303	94.142
8	1	1	6	12	1.69506	54.05737	143.826
9	2	1	1	12	1.63676	56.14967	1.781
10	1	2	2	12	1.60305	57.43860	8.486
11	0	1	8	6	1.59937	57.58339	29.380
12	2	1	4	12	1.48646	62.42471	129.999
13	0	3	0	6	1.45382	63.99001	134.967



	h	k	l	m	d	th2	F^2
1	1	1	1	8	3.25814	27.35099	7.324
2	0	0	2	6	2.82163	31.68541	109.569
3	0	2	2	12	1.99520	45.42118	153.293
4	3	1	1	24	1.70151	53.83600	7.334
5	2	2	2	8	1.62907	56.43829	78.200
6	0	0	4	6	1.41082	66.18532	47.222
7	3	3	1	24	1.29465	73.02296	6.736

Pawley refinement – hkl phases

- Advantages:
  - Data quality requirement limited compared to Rietveld
    - Uncertainty will still depend on collection time and 2θ range
  - Lattice parameters often the most important information
    - E.g. high symmetry structures have no/little degrees of freedom in atomic positions
  - Crystallite size the essential information for nanocrystalline powder
  - Lattice strain the essential information for disordered or strained materials, or chemically complex solid solutions.
- Disadvantages:
  - No information about atomic positions or occupancies
  - No quantification of phase fractions

Rietveld refinement – structure models

- Advantages:
  - Atomic positions, occupancies and B-factors extracted.
  - Quantitative information about phase fractions obtained.
  - Necessary information to publish or report new or novel structures.
- Disadvantages:
  - High quality data necessary – long collection time and broad 2θ.
  - More variables, more possibilities of making mistakes.

General refinement strategy for Pawley

- Start with the most important things, proceed with less important when convergence is reached for the most important.
- In other words: do NOT refine all variables at once!
- TOPAS has no chemical/physical knowledge – you have.

- Set background to 3, increase it later if necessary.
- Make sure your emission profile and instrumental parameters are right.
- Make sure your simulated Bragg peaks “hit” the measured.
  - Lock size and strain with FP.
  - Follow the position of the hkl ticks.
  - Use d-spacing for the x-axis and the formulas from previous lectures and adjust the initial guess value.
  - Refine lattice parameters and sample displacement simultaneously.
- Add crystallite size and/or strain to fit the peaks shapes with FP.

General refinement strategy for Rietveld

- As for Pawley +:
- Lattice parameters (peak positions) and size/strain (peak shape) must converge before you refine atomic positions.
- ONLY refine atomic positions where the space group has a degree of freedom.
  - How do you know which positions have degrees of freedom?
  - Use fractions for high symmetry positions in codes field
  - Wyckoff sites – test with VESTA to be certain!
- Start with the position that affects the peak intensities the most.
  - Z^2 x multiplicity/stoichiometry
  - Start with the heaviest atoms
  - Reach convergence before you add progressively lighter atoms.
  - Exceptions may apply, a sound understanding is required.
- Occupancies – be careful! Examples: $PbZr_{0.2}Ti_{0.8}O_3$ and Fe_3O_4.
- Link parameters when sensible – user understanding required.
- Do not over-fit your data! Mind R_{wp}, R_{exp} and χ^2!

Take-home messages from *bonus* lecture LX8-9

- This is the essence of what you should do for your lab report.
- The nominal composition was 50% Fe_2O_3 and 50% NaCl.
  - +/- 5-10% is the typical error in mass% for Rietveld refinement.
- Serious preferred orientation of the NaCl crystallites –
  - or simply too large/few crystallites
    - Wrong peak intensities with position sensitive detector
    - Spots in Debye rings on a 2D plate detector
  - Had to use corrections to obtain a reasonable result
  - Note how the B-factors tell you if something is wrong
- Never underestimate visual inspection, more important than R-factors!
- Rietveld refinement still not trivial after 15 years…