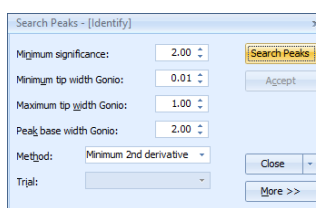
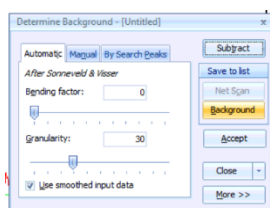
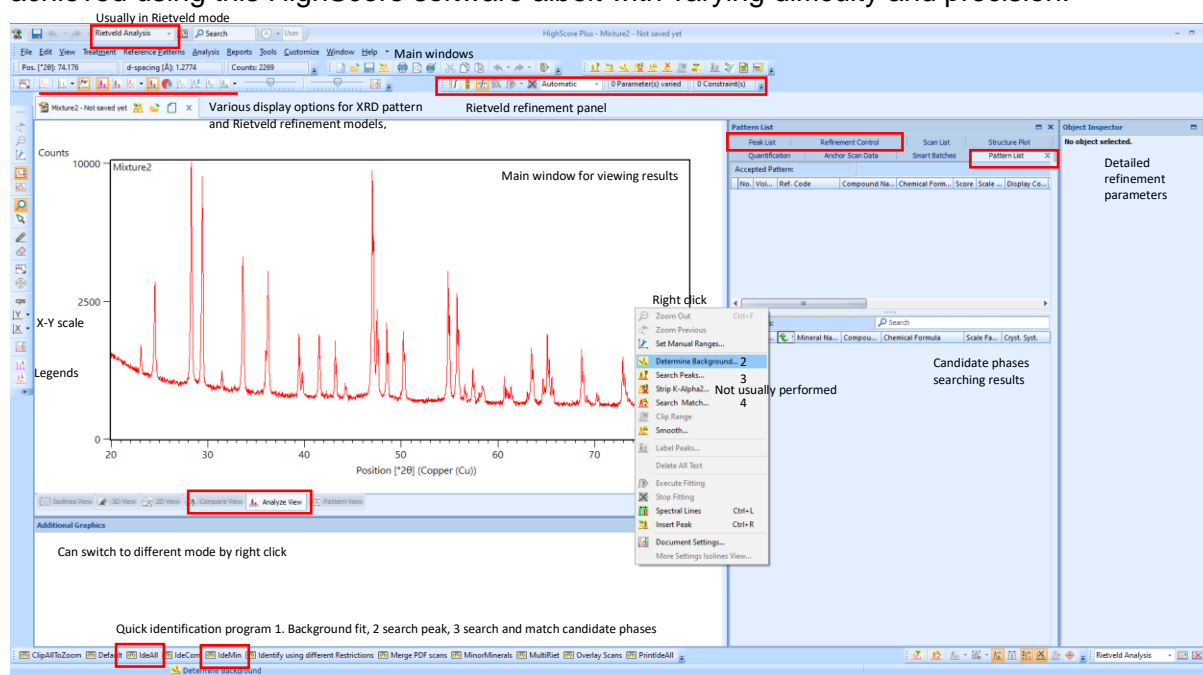


# Empyrean HighScore Rietveld refinement tutorial 2<sup>nd</sup>

2021.11.17

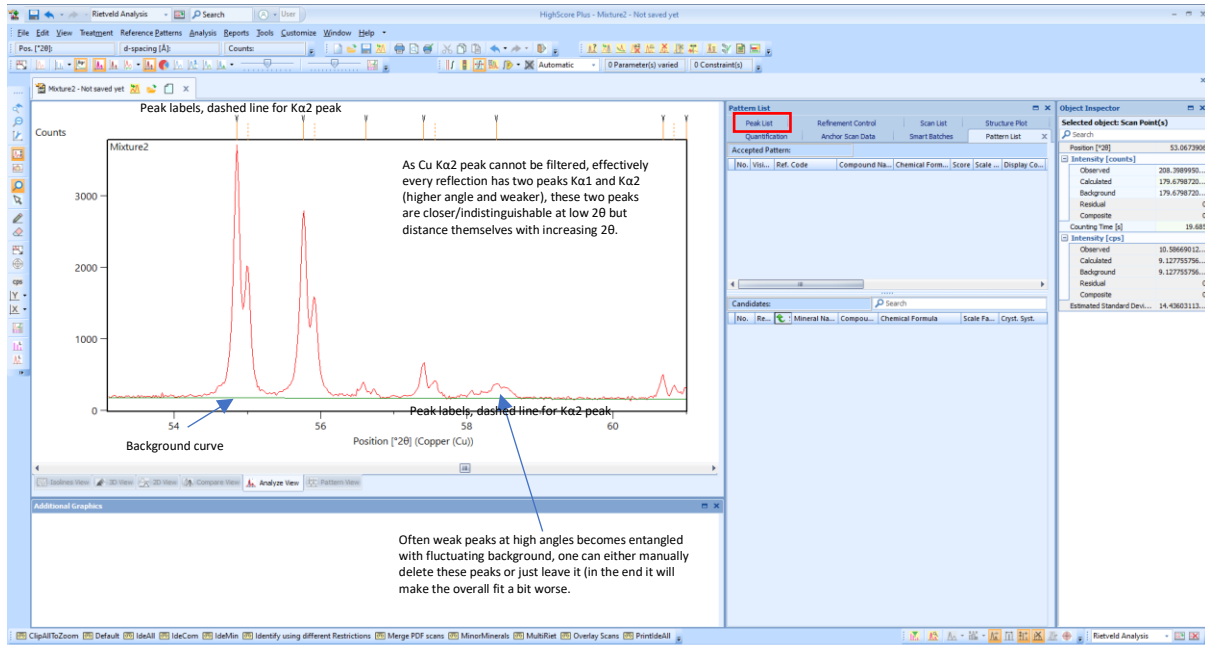
Ning Ma, NW.E69, [ning.ma@erdw.ethz.ch](mailto:ning.ma@erdw.ethz.ch) for complements/complains

Let us assume you have acquired a reasonably good powder XRD pattern and are now interested in the crystallinity, the phase identification, refining crystallographic parameters and/or estimating the phase proportions of your sample. All of this can be theoretically achieved using this HighScore software albeit with varying difficulty and precision.

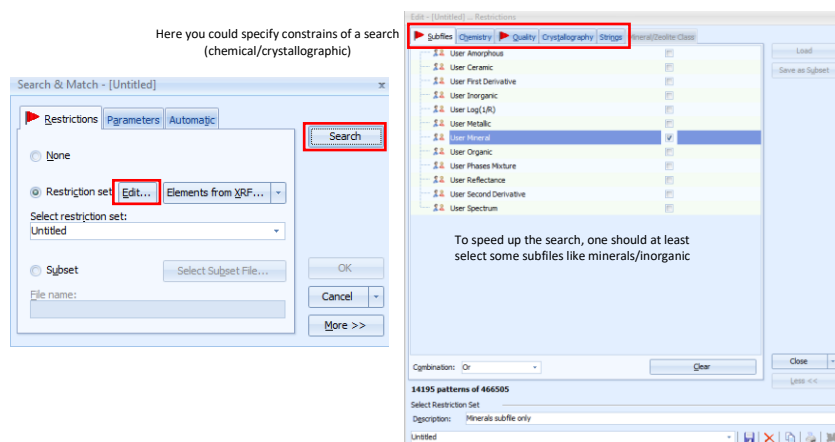


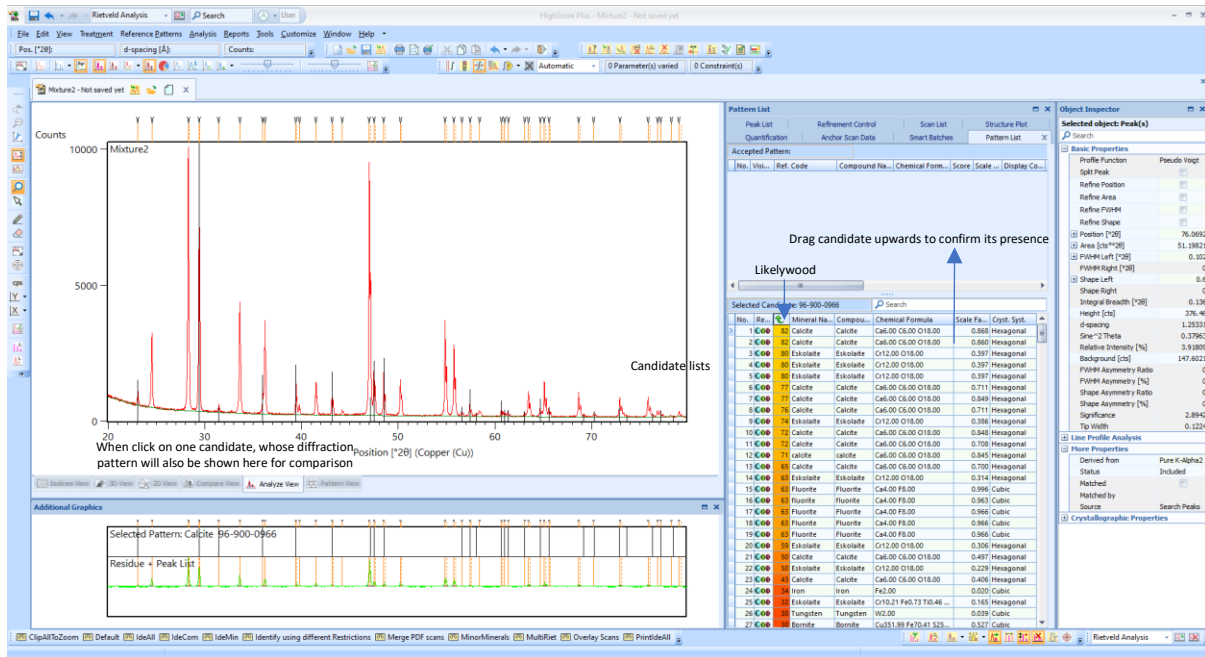
1. Load data file in high score either by dragging or File-open, (double click will only open the file in Data Viewer). One can of course load multiple files simultaneously. If you choose to load them by dragging or open different files sequentially, you will have each sample opened in separate windows, but if you wish to directly compare them on the same figure then load the first by File-open and then load all subsequent files by File-Insert. Then you can view them simultaneously under **compare view**, but for Rietveld refinement only (the first) one file can be processed under **analyze view**.
2. The first step towards a crystallographic refinement is background determination, you want to fine the position and intensity of reflections/peaks, for this you first need to determine and then remove the effect of background. Right click in the main window choose Determine background, adjust bending factor (0-20) and granularity, you will see a smooth curve generated below your XRD pattern, this is the calculated background, adjust both factors until this curve matches well your pattern, click background-accept. **Do not click subtract which will directly subtract the intensity on your pattern by calculated background, then you have changed your raw data.**

- Then you want to trace all the diffraction 'peaks', whose position ( $2\theta$  and d-spacing) and peak height (intensity) will be what we are mainly interested thereafter. Right click search peaks-accept, there are various mathematical definition one can set to a 'peak' from a fluctuating background. Usually one can just accept the default method. Once you clicked accept, numerous of small vertical arrows will be displayed above the main figure, which signifies the list of peaks the program has discovered (you can also view/select/delete them in the middle panel under peak list).



- Now we can start thinking about what minerals/phases are present in this sample. We do this by compare our pattern with existing patterns from available crystallographic database (i.e. COD 2021, PDF-2/4 etc. already installed). One can start a search either by right click and search & match or click analysis (top panel)-search and match-execute search and match. Then in the pop-out window choice Edit and put some constrains before click search and OK.



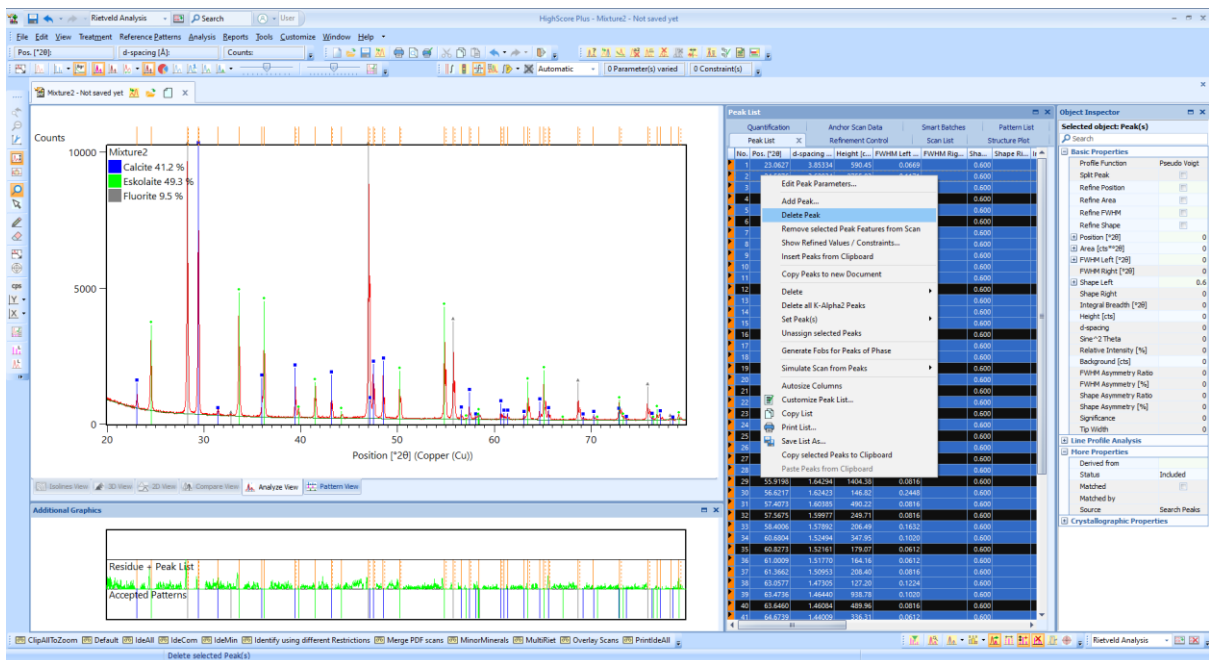


- Now you will see a list (often excessive amount) of candidates displayed in the middle-lower panel which are ranked based on the quality of match (score) to your pattern. **Compare carefully if one phase is likely present in your sample.** There are all over 100'000 XRD patterns with each containing multiple peaks, and your sample is also often a mixture. **Therefore you should first have a good estimation on the chemistry and what mineral phases you could potentially have, before dragging random weird minerals upwards into pattern list (candidate list).** Typically due to various experimental errors (temperature error, sample height displacement, preferred orientation etc, non-perfect match between sample and database i.e. for solid solutions, an olivine with different Mg# number), the experimentally measured peak position/relative intensity is somewhat deviated from the database value (usually should  $<0.3^\circ$  otherwise the program will have problem of recognition). Usually you could **starting viewing the candidates with highest scores, zoom in on the main window** to see how far the measured peak position differs from database value (and if choose the same phase with a different composition with help to reduce this difference), check the match/mismatch of respective candidates not just at one reflection but rather examine the match across the entire scan range (some mismatch is usually, the intense peaks should match reasonably well). Apart from the peak position, another important check is peak intensity. Double click on a candidate file that you find plausible, score down. You will see a table containing miller index, d-spacing,  $2\theta$  and relative intensity (% over the most intensive peak in this phase). Check if the most intense peaks (60% or above) is reasonably present in your pattern as well. **Accepting candidate phase by dragging it upwards to the upper panel (pattern list).** Afterwards, you will see a number of 'arrows' above the figure disappeared, meaning these peaks are tentatively assigned to the candidate phase and accounted for. Now repeat this process until all major peaks are accounted for. **When this is done, select all accepted patterns from 'pattern list' panel, right click and say convert pattern to phase.**



Ideally all peaks should be accounted for so no more arrows and no more high score candidates present as well. For single phase and pure compound, this should be what we aim for, but for complex mixture like rocks which are multi-phase mixture with chemical substitution, some remaining peaks are no big problems.

6. After converting pattern to phase, we need to delete all the peak list to avoid confusing in the next step, so go to peak list, select all and delete. Now we are ready to start the Rietveld refinement.



7. We now go to refinement control (middle upper panel). Rietveld refinement is a crystallographic model that fits/tries to reproduce experimentally measured XRD pattern by 1. Input one or multiple existing crystallographic models (these are the candidates that we have just selected, they provide a starting point of our refinement/model including parameters like space ground/symmetry, chemistry, site occupancy, lattice parameter, intrinsic intensity of X-ray diffraction for each reflection. It is not possible to start a Rietveld refinement without a priori crystallographic model (at least a space group), 2. Refine these parameters/models so as to better fit our experimental results (which basically the program iterates these parameters to match the shape of our XRD pattern). As you will soon find out, given the excessive number of parameters involved, the refinement strategy as well as some rational sense is critical to achieve a reasonably good result.

During sample preparation, there is often a slight error induced by sample height errors, always tick

Account for sample porosity, for our rocks, usually can just leave it

Name	In...	Refine	Value	Deviation	Code	Constra...	Maximum	Minimum
Global Variables Systematic/constant 'error'/shift' of all 2θ, since it has been pre-calibrated on instrument, so 0 is fine.								
Zero Shift [°2θ]		<input type="checkbox"/>	0	0.000000	0.00	None	0.100000	-0.100000
Specimen Displacement [mm]		<input checked="" type="checkbox"/>	0	0.000000	81.00	None	1.000000	-1.000000
Specimen Packing Factor		<input type="checkbox"/>	0	0.000000	0.00	None	1.500000	0.000000
Wavelength [Å]		<input type="checkbox"/>	1.540598	0.000000	0.00	None	0.000000	0.000000
Residual Aberration		<input type="checkbox"/>	0	0.000000	0.00	None	1.000000	0.000000
K-α2 / K-α1 Intensity Ratio		<input type="checkbox"/>	0.5	0.000000	0.00	None	1.000000	0.000000
K-β1 / K-α1 Intensity Ratio		<input type="checkbox"/>	0	0.000000	0.00	None	1.000000	0.000000
K-β2 / K-α1 Intensity Ratio		<input type="checkbox"/>	0	0.000000	0.00	None	1.000000	0.000000
K-β3 / K-α1 Intensity Ratio		<input type="checkbox"/>	0	0.000000	0.00	None	1.000000	0.000000
Tungsten L-α Intensity Ratio		<input type="checkbox"/>	0	0.000000	0.00	None	1.000000	0.000000
White Radiation & Absorption Edge								
Background Polynomial								
Flat background		<input checked="" type="checkbox"/>	0	0.000000	21.00	None	0.000000	0.000000
1/X Background		<input checked="" type="checkbox"/>	0	0.000000	11.00	None	0.000000	0.000000
1/X^2 Background		<input type="checkbox"/>	0	0.000000	0.00	None	0.000000	0.000000
Coefficient 1		<input checked="" type="checkbox"/>	0	0.000000	31.00	None	0.000000	0.000000
Coefficient 2		<input checked="" type="checkbox"/>	0	0.000000	41.00	None	0.000000	0.000000
Coefficient 3		<input checked="" type="checkbox"/>	0	0.000000	51.00	None	0.000000	0.000000
Coefficient 4		<input checked="" type="checkbox"/>	0	0.000000	61.00	None	0.000000	0.000000
Coefficient 5		<input checked="" type="checkbox"/>	0	0.000000	71.00	None	0.000000	0.000000
Calcite								
Scale factor		<input checked="" type="checkbox"/>	0.01	0.000000	21.00	None	214748364...	0.000
March-Dollase Factor 1	0.000	<input type="checkbox"/>	1	0.000000	0.00	None	1.800000	0.200
B overall		<input type="checkbox"/>	0	0.000000	0.00	None	10.000000	0.000
Extinction		<input type="checkbox"/>	0	0.000000	0.00	None	0.000000	0.000
Flat Plate Absorption Correction		<input type="checkbox"/>	0	0.000000	0.00	None	1.000000	0.000
Porosity		<input type="checkbox"/>	0	0.000000	0.00	None	0.000000	0.000
Roughness		<input type="checkbox"/>	0	0.000000	0.00	None	0.000000	0.000
Layer Displacement [mm]		<input type="checkbox"/>	0	0.000000	0.00	None	10.000000	-10.000
Layer Thickness [μm]		<input type="checkbox"/>	-1	0.000000	0.00	None	6.000000	0.001
Unit Cell								
a [Å]		<input checked="" type="checkbox"/>	4.988	0.000000	51.00	Multipl...	0.000000	0.000
b [Å]		<input type="checkbox"/>	4.988	0.000000	51.00	Multipl...	0.000000	0.000
c [Å]		<input checked="" type="checkbox"/>	17.061	0.000000	61.00	None	0.000000	0.000
alpha [°]		<input type="checkbox"/>	90	0.000000	0.00	None	0.000000	0.000
beta [°]		<input type="checkbox"/>	90	0.000000	0.00	None	0.000000	0.000
gamma [°]		<input type="checkbox"/>	120	0.000000	51.00	Multipl...	0.000000	0.000
Atomic coordinates								
Profile Variables								
Caglioti U Left		<input type="checkbox"/>	0	0.000000	0.00	None	10.000000	-1.000
Caglioti V Left		<input type="checkbox"/>	0	0.000000	0.00	None	10.000000	-1.000
Caglioti W Left		<input checked="" type="checkbox"/>	0.01	0.000000	31.00	None	10.000000	-1.000
Peak Shape 1 Left		<input checked="" type="checkbox"/>	0.6	0.000000	41.00	None	1.500000	-0.100
Peak Shape 2 Left		<input type="checkbox"/>	0	0.000000	0.00	None	0.100000	-0.100
Peak Shape 3 Left		<input type="checkbox"/>	0	0.000000	0.00	None	0.001000	-0.001

Selected object: Background	
Method	Use available background
Use Extended Backgrou...	Polynomial
Flat	Use available background
Basepoints	Basepoints
1/X	Chebyshev 1
Coefficients	
Coefficient 1	Shifted Chebyshev I
Coefficient 2	Amorphous Sinc Function
Coefficient 3	Damped Amorphous Sinc Function
Coefficient 4	
Coefficient 5	
1/X^2	

For simple samples use polynomial, tick flat, 1/x and 1-5 coefficients.

For complex mixtures, single click Global variables/background, and on the right panel click background, choose Chebyshev 1, tick 6-7 variable.

In the end you want to have a reasonable match between your measured and fitted background.

Each phase has a subfolder, the basic strategy is to refine the more abundant phases and more important parameters first, others later and do it in a progressive manner

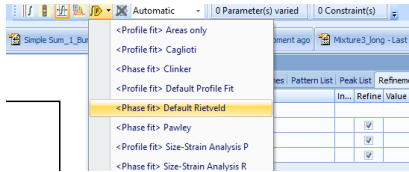
Scale factor = wt.% proportion of this phase in the entire mixture

March-Dollase factor, a model to account for preferred orientation

Unit cell parameter, tick according to crystal class, i.e. for cubic crystals only tick a.

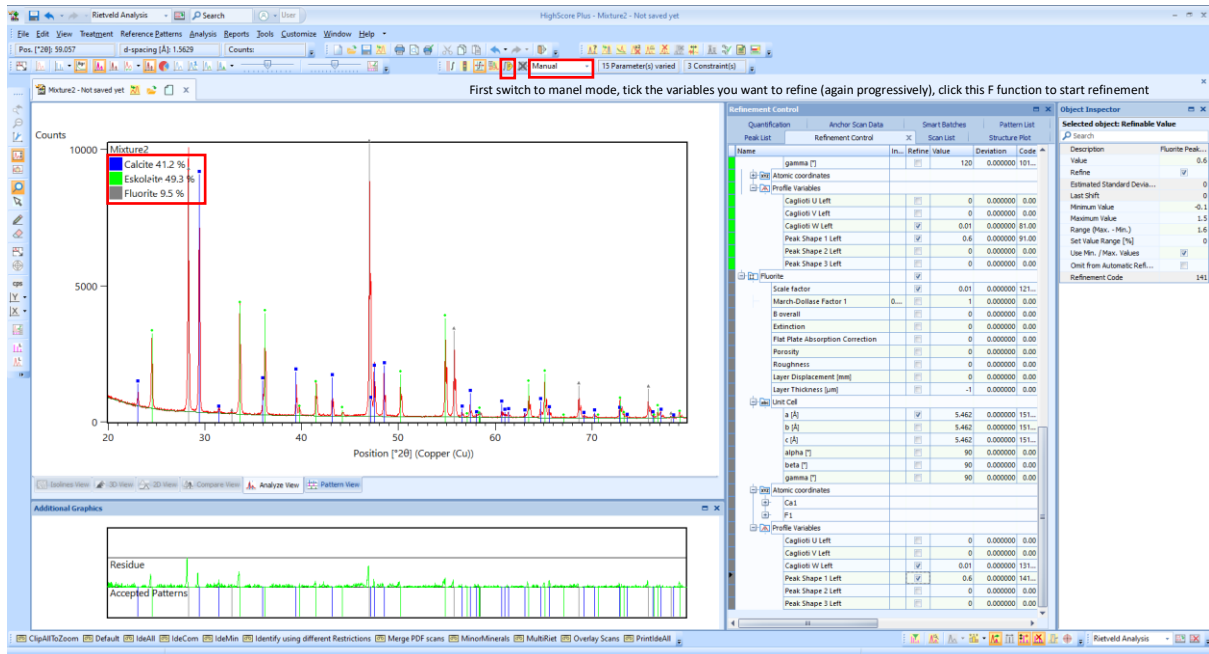
One thing, for trigonal system (e.g. quartz) the database usually treat it as hexagonal so just change a and c.

Caglioti W left and peak shape 1 left, Parameters to adjust peak shapes at high 2θ



Instead of manually selecting the parameters to refine, it is also possible to do an automatic/default Rietveld refinement by: **Under automatic mode, click F, select Default Rietveld.**  
**Note, this should only be used once you complete all previous steps, importantly converting pattern to phase, delete peak list.**

In addition, there are relatively less parameters varied in this default refinement. Therefore one should only use it to get a first and crude idea, before then manually check and refine additional parameters.



- Now to start refinement, first switch to manual mode, tick the variables you want to refine (again progressively), click this **F function** to start refinement.

Refinement sequence:

First stage: Global variables including **specimen displacement, background fitting curve** (polynomial for simple mixture, Chebyshev 1 for complex background shapes), **tick all major phases (maybe >15-20%), scale factor, unit cell parameters, profile variable-Caglioti W left, peaks shape 1 left.**

Now refine the minor phases (parameters listed above) and less critical parameters of major phases:

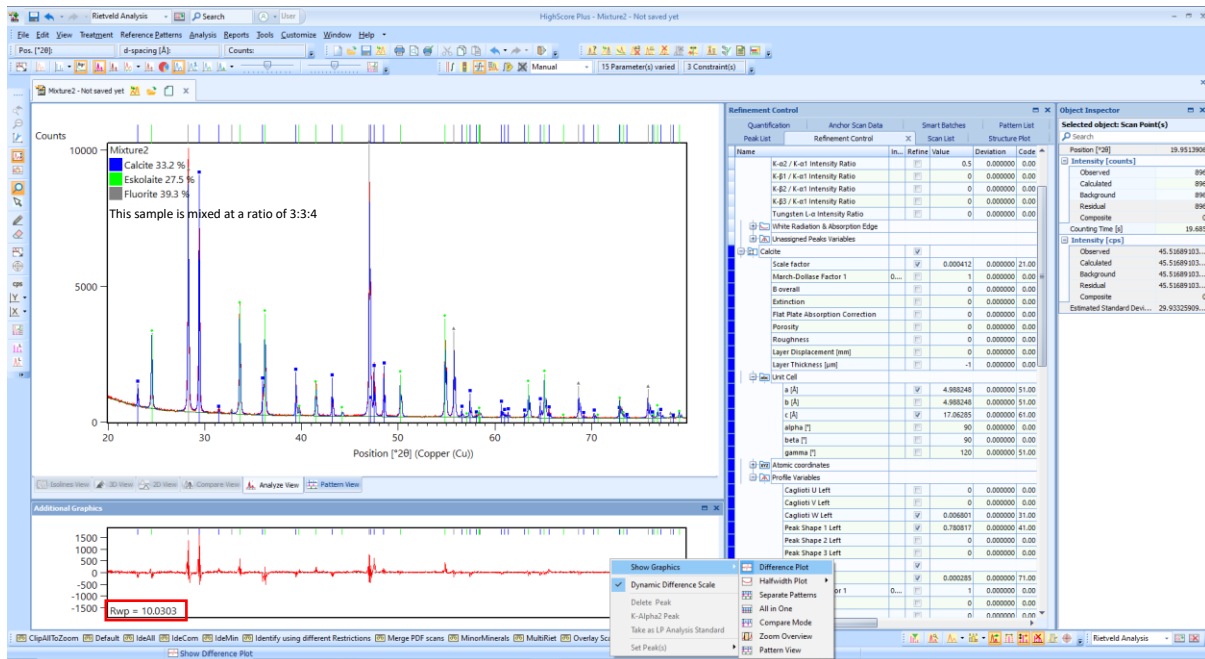
Theoretically, a typical XRD reflection should be a mixture of Gaussian+Lorentzian profile (approximately 50:50), but in practice the measured peaks tend to be more asymmetric in shape (especially the left side). Another possibility is preferred orientation of crystals (during sample preparation).

Second stage, **only for major phases, refine the asymmetry (click on phase, go to right panel, find the asymmetry item, choose split width/shape or other models), PLO (click on phase, go to right panel, find preferred orientation, use March-Dollase/spherical harmonics, specify the type or PLO, Caglioti U and V left parameters).**

Run refinement and check the fitting quality/residue at every step by right click the Left bottom panel and chose difference plot, the lower the RWP the better (optimal value 1).

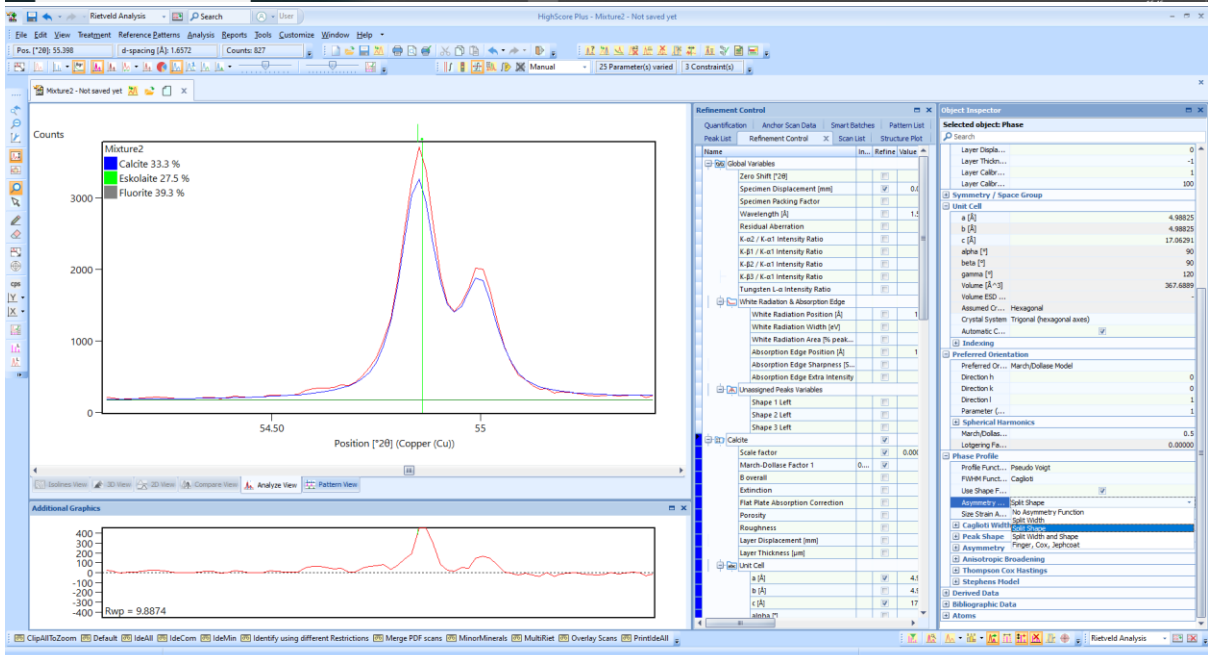
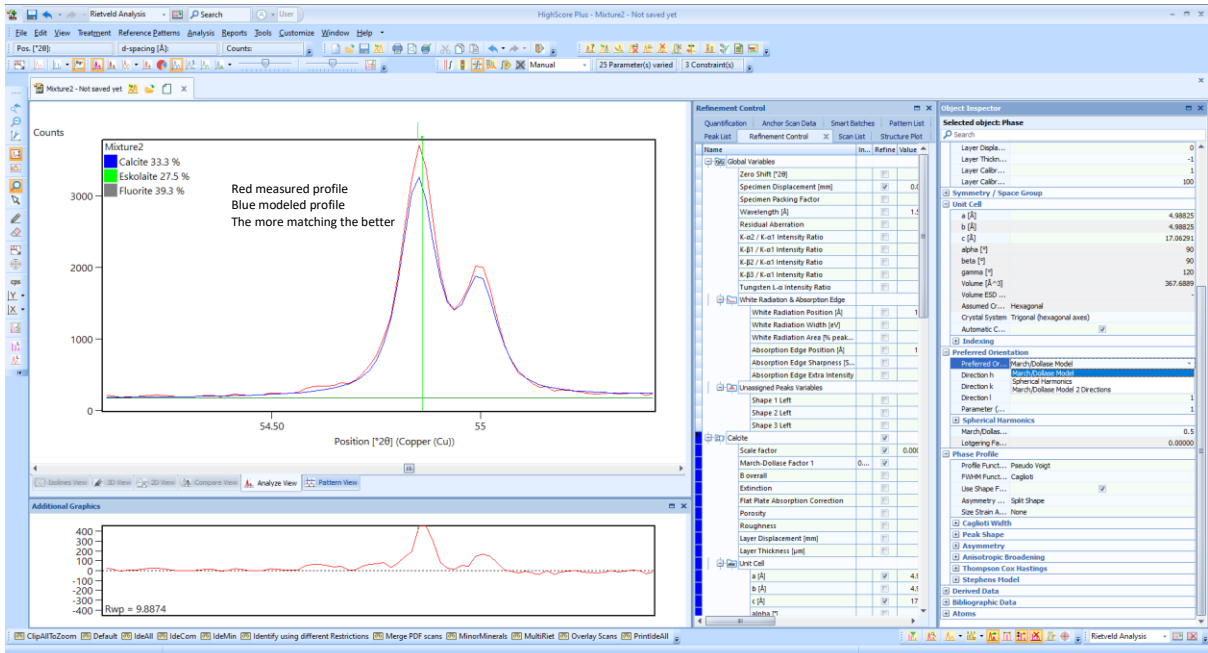
However it is always important to think about whether refining some parameters make sense. E.g. if changing a lot parameters does not improve the fit significantly then maybe it is not worthy. Typically for most mineralogical/petrological we are either interested in the crystallinity (in which case we just see if there are peaks or just a broad bump as is typically for glass), lattice parameter/chemical composition or phase proportion of mixture (model abundance of minerals in a rock). If quantitative

analysis is not desired (when you just want to know what phase can be present), then one can simply search and match the phase manually without performing the Rietveld refinement.



- The ultimate refinement model should be checked by residue (rwp value), the goodness of match between modelled profile vs. measured profile and absence of unexplainable feature (unidentified/unattributed peaks, mismatch of intensity etc.)

Finally one word about using XRD to get phase proportion, for a natural rock with multiple mineral phases which all have solid solutions, it is not always easy to find a suitable database candidate. As minerals with low symmetry has much more complicated XRD pattern, feldspar is particularly difficult to fit/refine (actually it is almost not possible to do it perfectly). Another point is the sensitivity of XRD on phase abundance, as the phase proportion is directly proportional to the refined scale factor (in addition to also other factors like PLO, chemistry), XRD is intrinsically only capable to get a model abundance for phases that scatters strong enough (only they offer at least one relatively strong reflection in your XRD pattern, which usually means they should be at least 5 wt. % or more, unless this phase scatters much stronger than others i.e. a high Z phase like Fe or Au metal). In the above mentioned example we see for very ideal mixture (3 phases, approximate proportion, all pure components with good quality database reference model) this estimation can be extremely accurate, but for a natural rock powder/mixtures 10-20% error should always be born in mind.





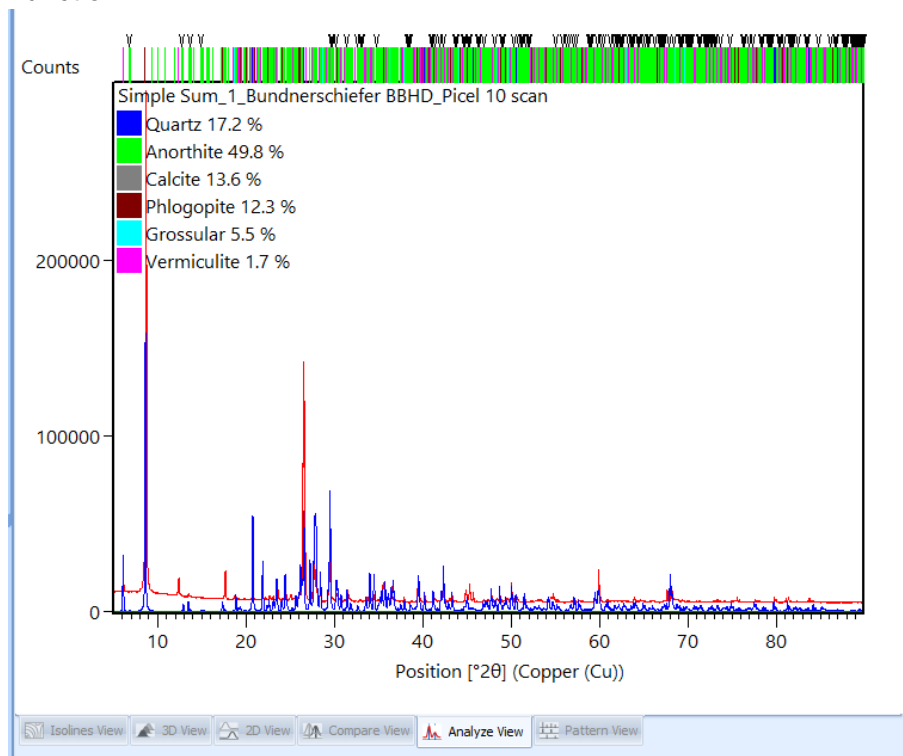
# Bug shooting

Forgot to define background

If you see something like this when starting a refinement, where modeled pattern looks completely detached from the measured one, this usually comes from the fact that you did not specify the background pattern at refinement step (different from first step).

Solution:

In refinement control, select background and fit new background using polynomial or Chebyshev function.



## About XRD database

For now we have two XRD diffraction pattern database:

PDF-2 2021 (suitable for phase identification, more mineralogical data, somewhat weird name/nomenclature for minerals, alas, **not suitable for Rietveld refinement** (not enough crystallographic information).

COD 2021, free XRD database, suitable for both phase identification and Rietveld refinement (default database).

If necessary one can switch the database under customize-manage database and just unclick the other one before activate the one you need (no compatible simultaneously).

**Please when you are done always go back to COD 2021 database.**

