

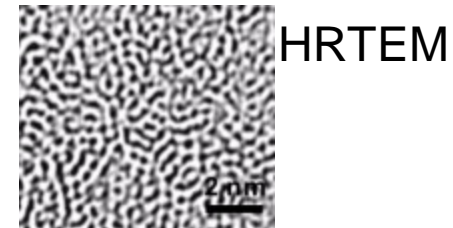
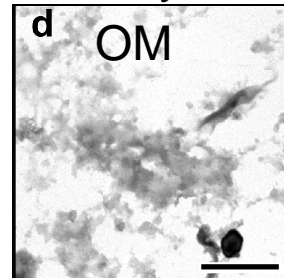
Quantitative X-Ray Diffraction

X'Pert Highscore Plus
Rietveld Module

Principles of X-Ray diffraction

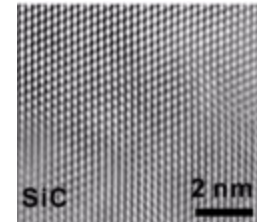
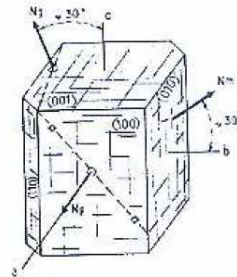
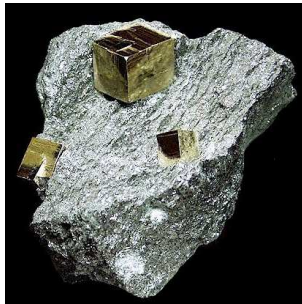
There is two types of solid material:

- Amorphous: Atoms are randomly arranged in a define volume



<http://www.nano.drexel.edu/research/projects/cdc>

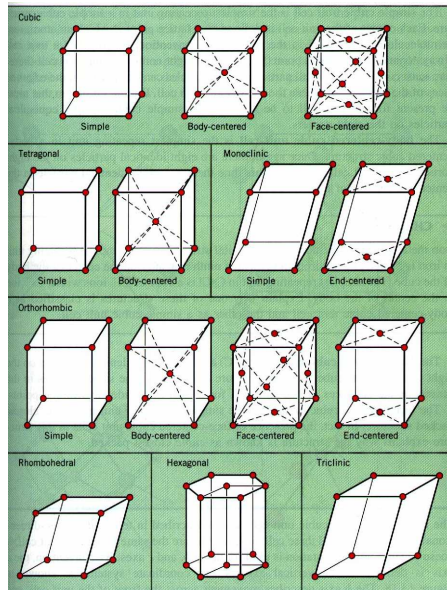
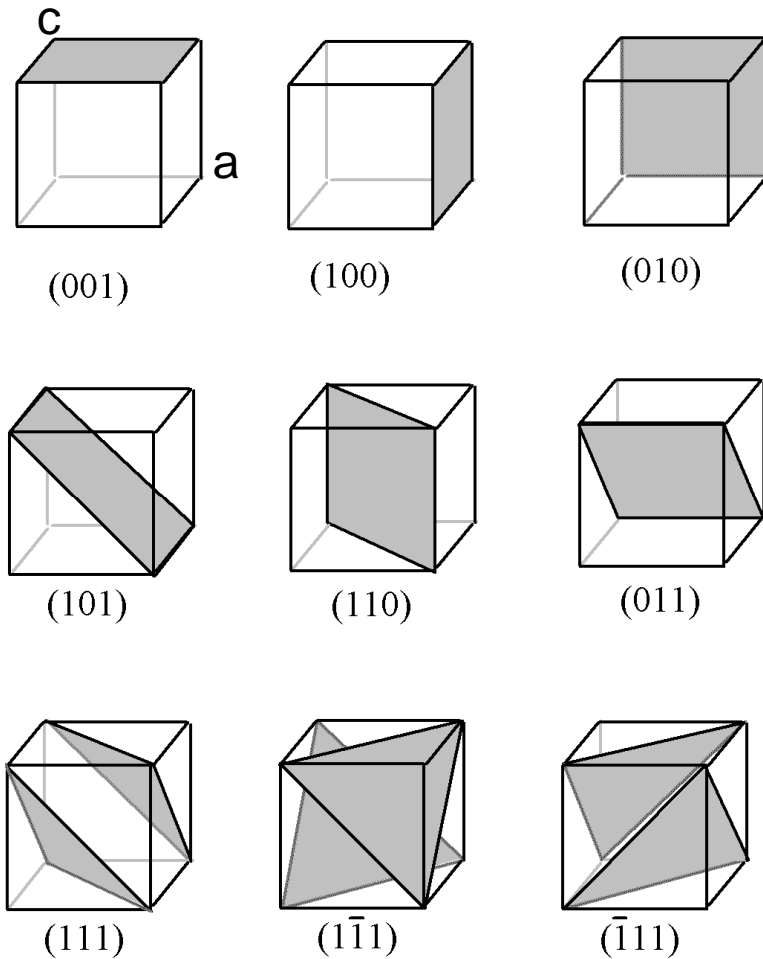
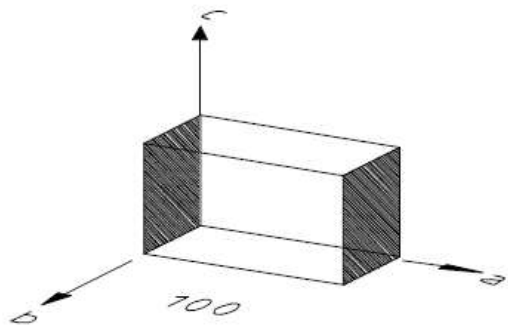
- Crystalline: Atoms are arranged in a regular pattern in a define volume. This pattern is a repetition of a given smaller pattern called the "unit cell"



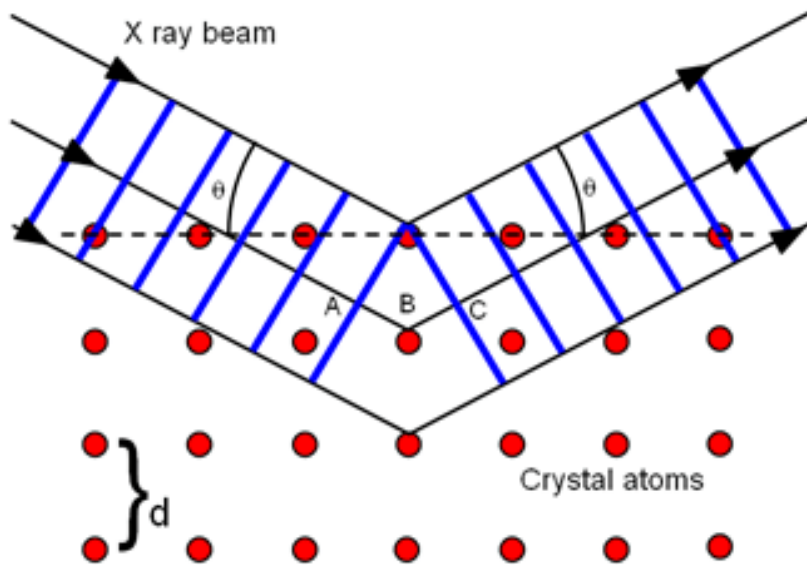
<http://www.nano.drexel.edu/research/projects/cdc>

The unit cell

Always defined by three axes: a, b & c which help defining the h, k, l plans



X-Ray diffraction



BRAGG LAW

$$2d(\sin\theta) = \lambda_0$$

where:

d = lattice interplanar spacing of the crystal

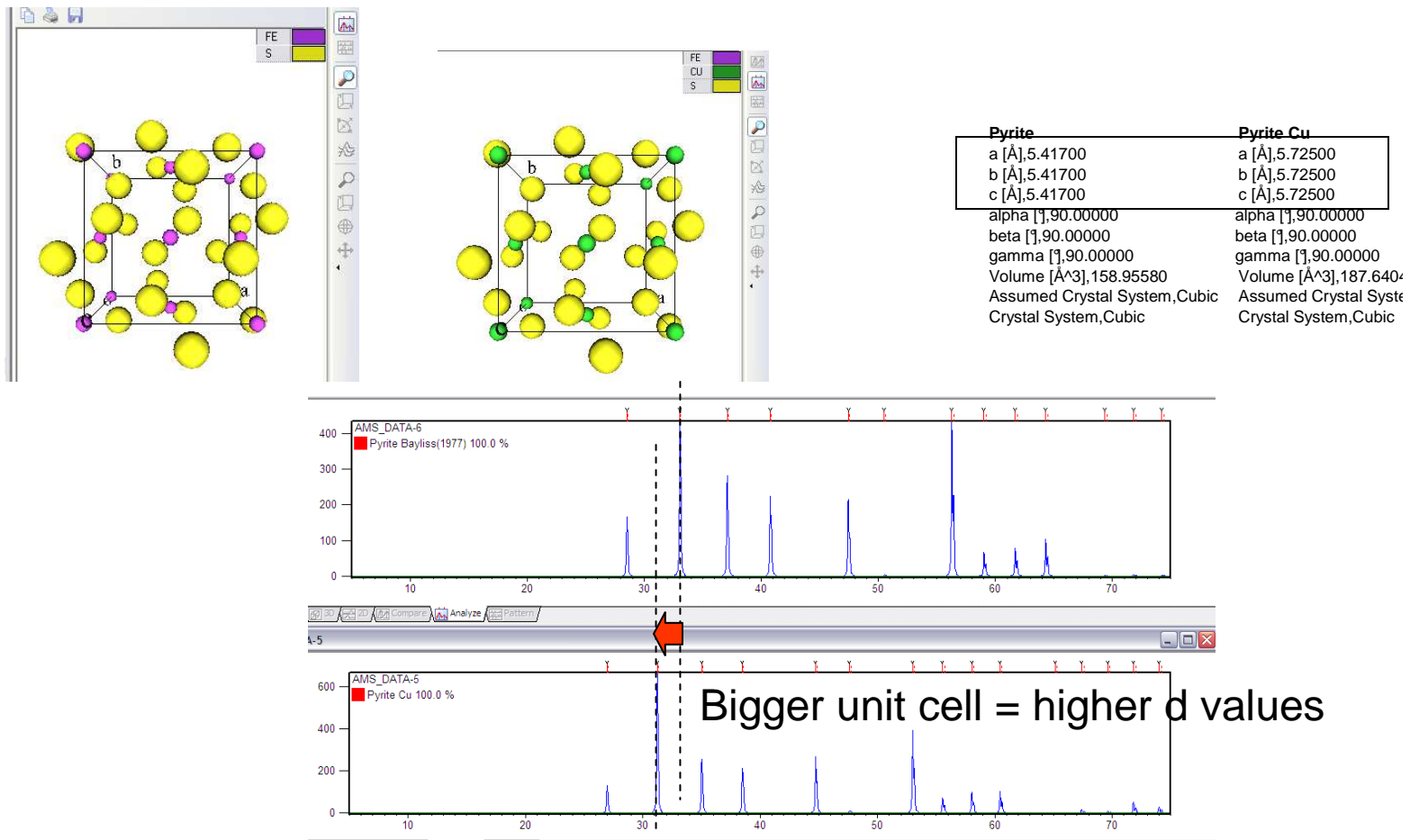
θ = x-ray incidence angle (Bragg angle)

λ = wavelength of the characteristic x-rays

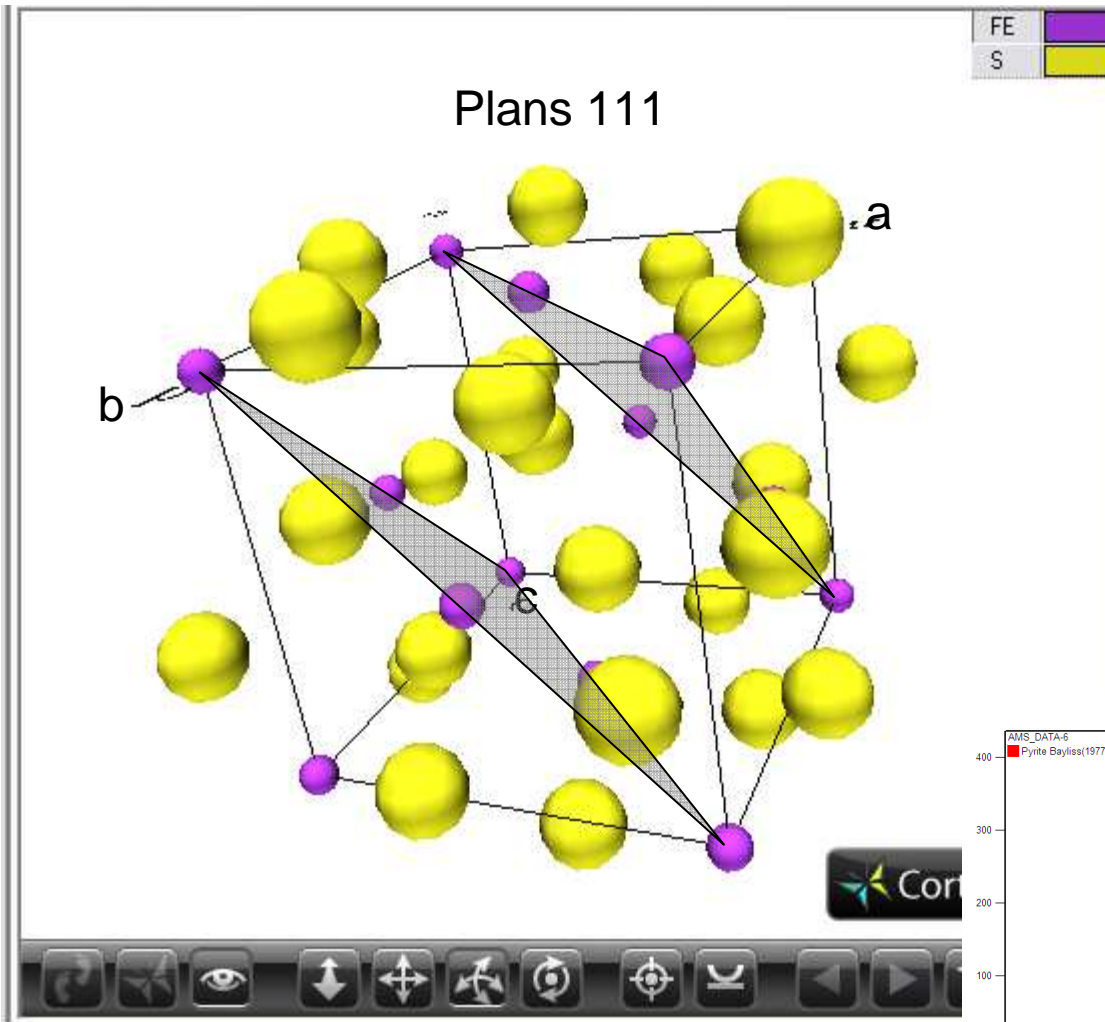
Moreover, the electronic configuration of the atoms respond differently to the incident wavelength given rise to differences in intensities.

X-Ray diffraction

Therefore for a given structure, a single pattern of reflections is possible



X-Ray diffraction

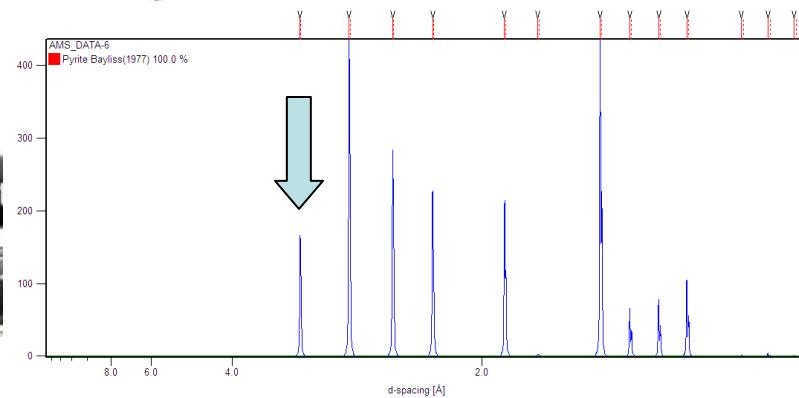


$$d = (\sqrt{a^2 + b^2}) / 2$$

$$d = 3.83 \text{ \AA}$$

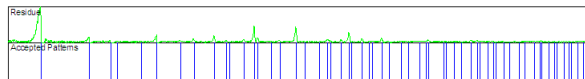
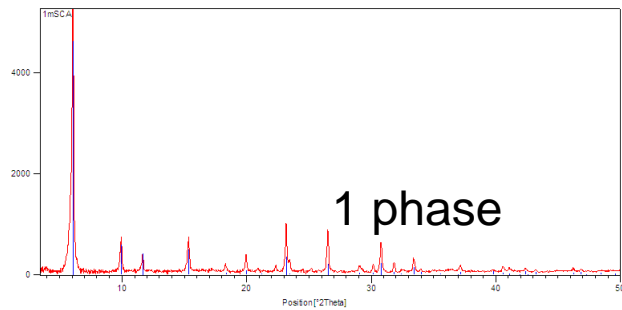
Minus the atomic radius of Fe
(0.64\AA)

$$d = 3.19 \text{ (approx)}$$

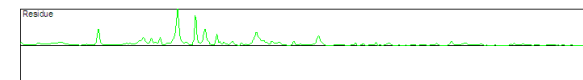
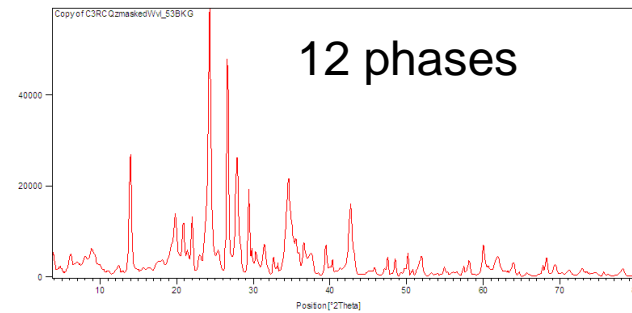
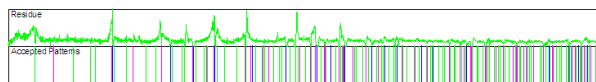
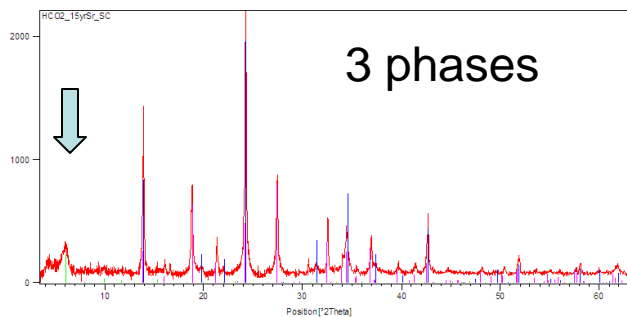
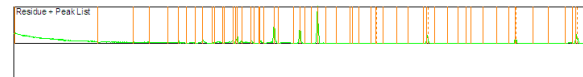
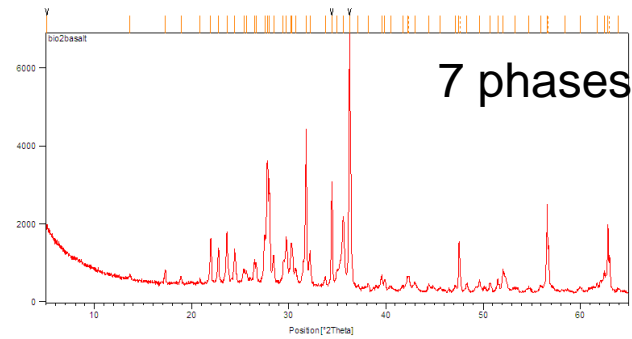


X-Ray diffraction

- In a classical powder diffraction pattern the sample is a mixture of mineral and the diffractogram reflects the addition of the single phase patterns.



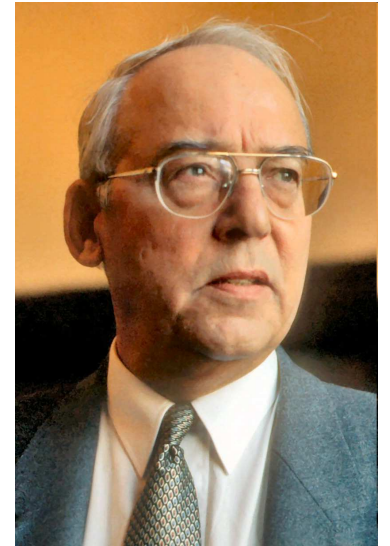
Page: 1 of 1



Principles of Rietveld refinement

From wikipedia:

- **Rietveld refinement** is a technique devised by [Hugo Rietveld](#) for use in the characterisation of [crystalline](#) materials. The height, width and position of the reflections can be used to determine many aspects of the materials structure.
- **The Rietveld method uses a [least squares](#) approach to refine a theoretical line profile until it matches the measured profile.**



Principles of Rietveld refinement

The base parameters were:

- The peak shape
- The peak width
- The preferred orientation

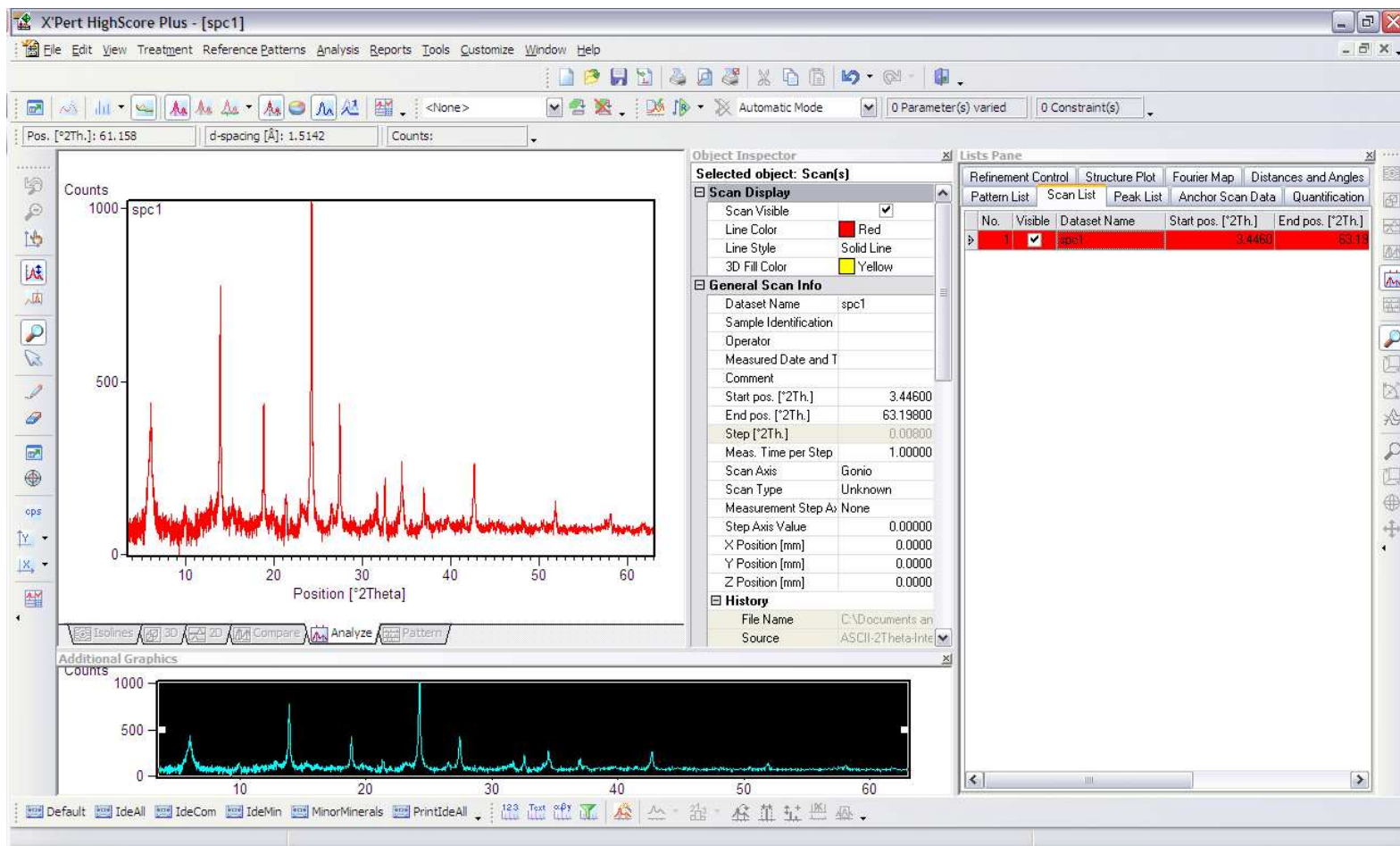
The initial publi can be found here:

<http://www.ccp14.ac.uk/ccp/web-mirrors/hugorietveld/xtal/paper2/paper2.html>

Rietveld refinement in highscore

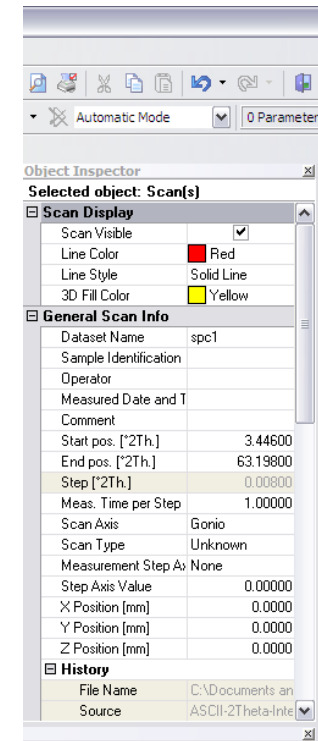
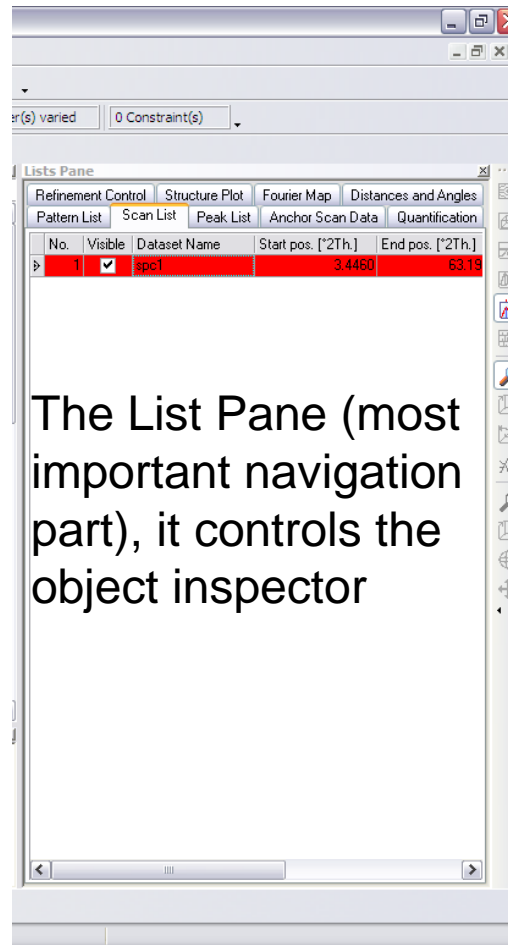
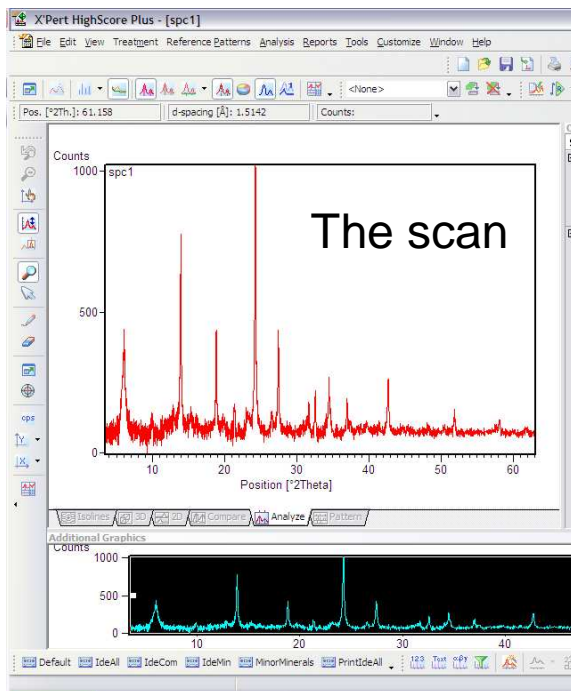
The Highscore plus interface

1. Open Highscore
2. Open spc1.asc
3. Select spc1 in Scan list tab



Rietveld refinement in highscore

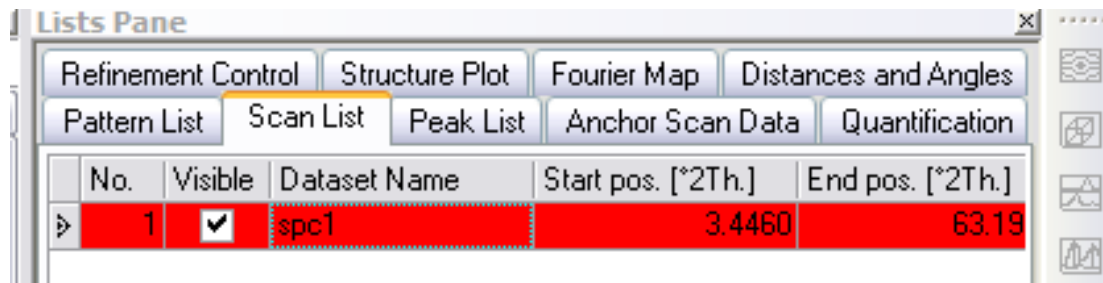
The Highscore plus interface



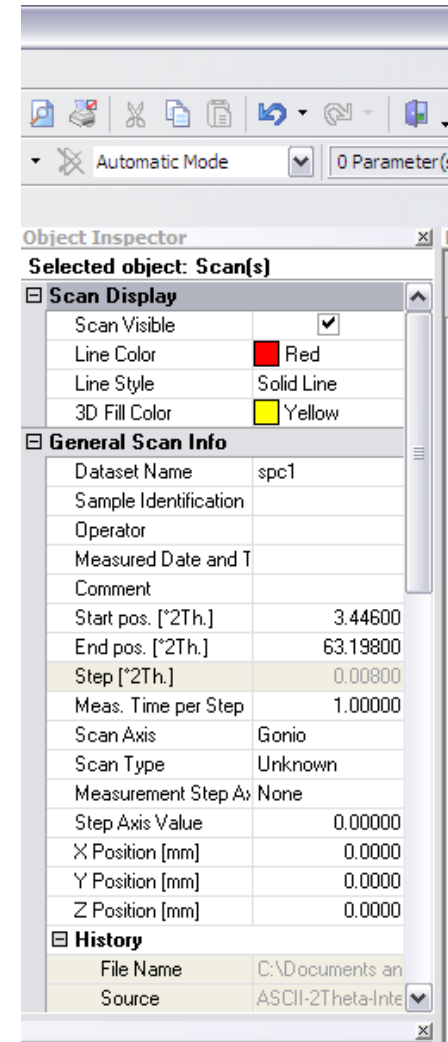
The object inspector provide important informations

Rietveld refinement in highscore

The Highscore plus interface

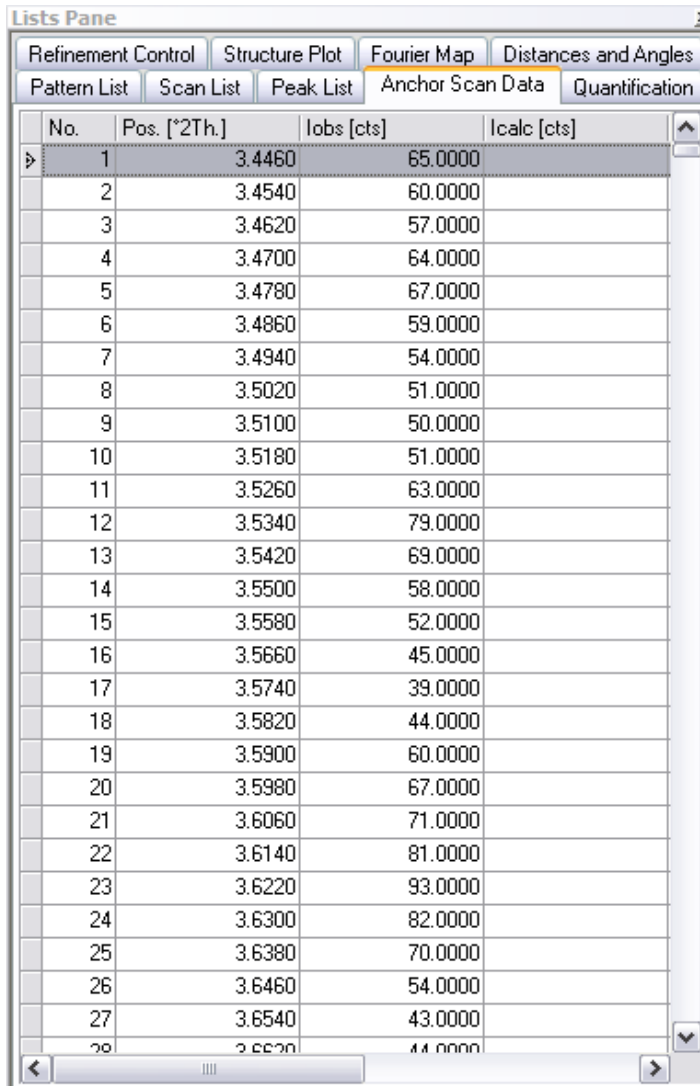


The scan tab allow to select the spectrum.
In the corresponding object inspector, you can modify the name, the color the starting/ending positions of the scan.



Rietveld refinement in highscore

The Highscore plus interface

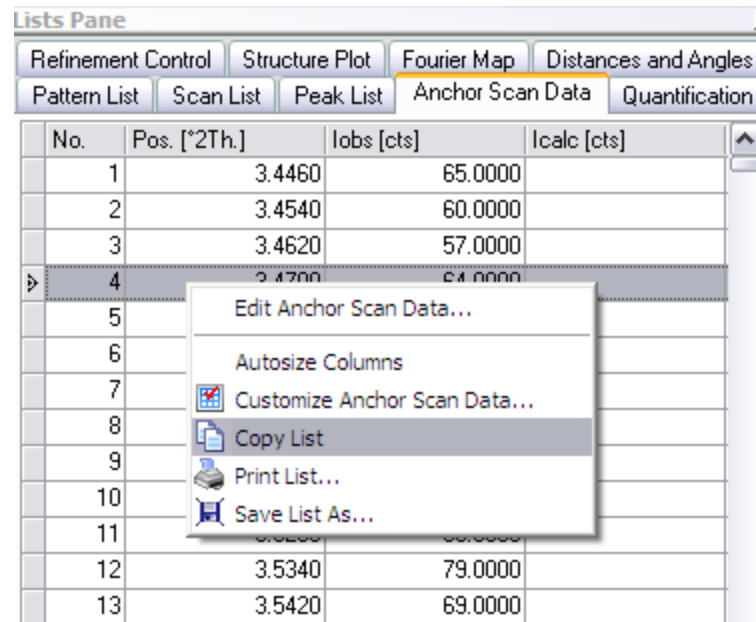


The screenshot shows the 'Lists Pane' window in Highscore Plus. The 'Anchor Scan Data' tab is selected. The table below shows the data for the first 28 scans.

No.	Pos. [$^{\circ}$ 2 θ .]	Iobs [cts]	Icalc [cts]
1	3.4460	65.0000	
2	3.4540	60.0000	
3	3.4620	57.0000	
4	3.4700	64.0000	
5	3.4780	67.0000	
6	3.4860	59.0000	
7	3.4940	54.0000	
8	3.5020	51.0000	
9	3.5100	50.0000	
10	3.5180	51.0000	
11	3.5260	63.0000	
12	3.5340	79.0000	
13	3.5420	69.0000	
14	3.5500	58.0000	
15	3.5580	52.0000	
16	3.5660	45.0000	
17	3.5740	39.0000	
18	3.5820	44.0000	
19	3.5900	60.0000	
20	3.5980	67.0000	
21	3.6060	71.0000	
22	3.6140	81.0000	
23	3.6220	93.0000	
24	3.6300	82.0000	
25	3.6380	70.0000	
26	3.6460	54.0000	
27	3.6540	43.0000	
28	3.6620	44.0000	

The Anchor scan data tab (very important) provides the actual numerical data of the displayed graph.

Right click on the list allows to copy the data that you can paste in excel



The screenshot shows the 'Lists Pane' window in Highscore Plus. The 'Anchor Scan Data' tab is selected. A context menu is open over the table, highlighting the 'Copy List' option. The table below shows the data for the first 13 scans.

No.	Pos. [$^{\circ}$ 2 θ .]	Iobs [cts]	Icalc [cts]
1	3.4460	65.0000	
2	3.4540	60.0000	
3	3.4620	57.0000	
4	3.4700	64.0000	
5	3.4780	67.0000	
6	3.4860	59.0000	
7	3.4940	54.0000	
8	3.5020	51.0000	
9	3.5100	50.0000	
10	3.5180	51.0000	
11	3.5260	63.0000	
12	3.5340	79.0000	
13	3.5420	69.0000	

Rietveld refinement in highscore

The Highscore plus interface

Structure plot allows to visualize the structure of the refined compound.

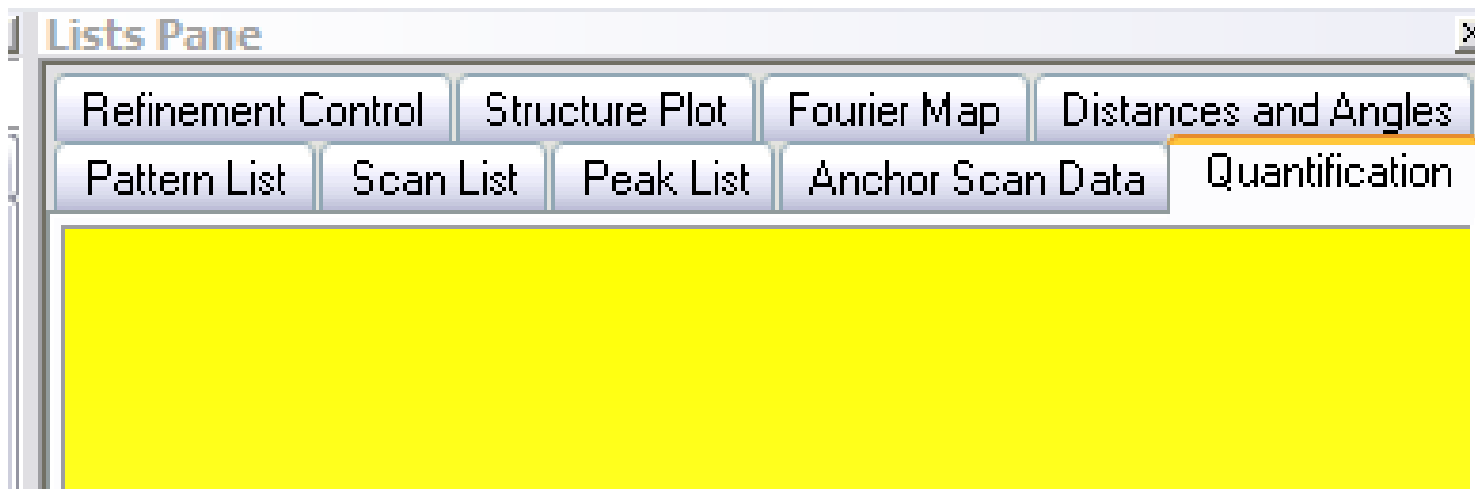
Refinement control is the most important tab for quantification.

The pattern tab is used when doing a characterization of the peaks.

We will use those 3 tabs a lot.

Fourier Map and distances and angles do not interest us.

The quantification tab is a joke.



Rietveld refinement in highscore

- In Highscore go to help and type Rietveld

+ Rietveld Analysis

The **Rietveld** method is a **full-pattern fit method**. The measured profile and a calculated profile are compared. By the variation of many parameters the difference between the two profiles is minimized. In order to perform a **Rietveld** refinement you need structure data for all phases present in your sample.

Some **Rietveld** basics are explained here:

- [Start and Stop](#) of a **Rietveld** refinement
- [Rietveld parameters manipulation](#)

The following analytical tasks are covered by a **Rietveld** refinement:

- **Quantitative phase analysis**, especially useful for complex diffractograms with a lot of peak overlap, less suitable for concentrations < about 0.5 %.
- Determination of the **Amorphous Content**, requires the addition of a crystalline standard and a measurement covering a certain 2θ range.
- **Crystallite size / micro strain analysis**, requires the measurement and refinement of a size / strain standard. To determine both properties simultaneously you need a measurement up to very high 2θ angles.
- **LE BAIL fit**, to confirm or test the unit cell and space group of a phase by fitting it to measured data and to extract structure factors. This is also the first step to determine an unknown crystal structure from powder diffraction data.
- **HKL file fit**, to quantify phases with unknown structures, based on a standard sample with known concentrations.

Rietveld refinement in highscore

- 2nd in the help list: the parameters

The screenshot shows the 'HighScore Plus Online Help' window. The left sidebar contains a search bar with 'rietveld' entered and a list of 88 topics. The main content area is titled 'All Rietveld Parameters' and includes an overview paragraph, a list of parameter groups, and a table of 'Global Parameters'.

All Rietveld Parameters

This is an overview of **all** parameters ruling a **Rietveld** refinement. Many of these parameters are for the experienced user only, and need not to be changed in general.

The following tables contain all parameters in logical groups.

- [Global Parameters](#)
- [Background Parameters](#)
- [General Phase Parameters](#)
- [Phase Cell Parameters](#)
- [Phase Atom Parameters](#)
- [Phase Profile Parameters](#)
- [Phase Bibliographic Data](#)
- [Phase Space Group Data](#)

Global Parameters:

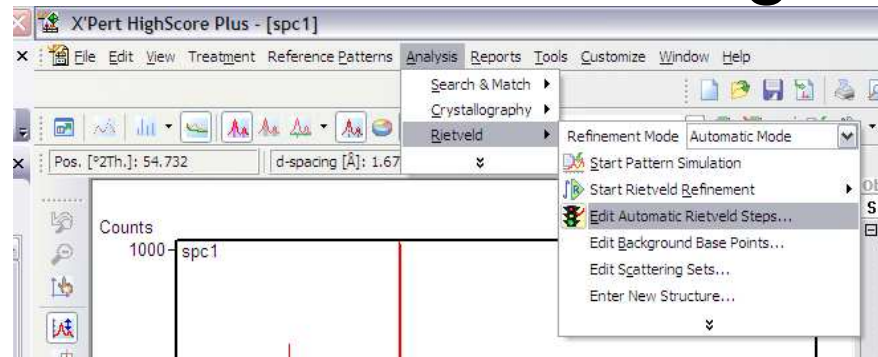
Parameter:	Auto-Refine:	Description:	[unit]:	Default:	Min.:	Max.:
Refinable Global Parameters						
Specimen Displacement	Yes	Height displacement of the sample.	[mm]	0	-1E16	1E18
DifC (wavelength)	Yes	Wavelength for X-ray or neutron diffraction experiments. TOF experiment constant: TOF = DifC*d + DifA*d**2 + Zero.	[Å] or [μs]	1.540598	-1E16	1E18
DifA	No	TOF experiment constant: TOF = DifC*d + DifA*d**2 + Zero.	[μs]	0	-1E16	1E18
Zero Shift	Yes	Zero shift of the instrument.	[°2θ]	0	-1	+1
Marquardt Start Value	Yes	Set value or start value for the Marquardt algorithm.	-	0	-1E16	1E18
Rietveld Settings:						
Absorption Correction Type:						
Flat Plate		Surface roughness correction after UEBIAN & EDMICH	On			

Rietveld refinement in highscore

- We can change a lot of parameters but many of them **MUST** not be change.
- Don't allow a parameter to change without knowing what it physically means.
Changing some parameters will create crazy phases fitting perfectly but falsely the data.

Rietveld refinement in highscore

- The parameters we can change are here:



Automatic Rietveld Steps - [default lattice big min shifts]

Org.No.	Parameters varied	Min. Shift/ESD	Used
1	Scale factor	0.10000	<input checked="" type="checkbox"/>
2	Flat background	0.10000	<input checked="" type="checkbox"/>
3	Zero shift	0.20000	<input checked="" type="checkbox"/>
4	Lattice parameters	0.90000	<input checked="" type="checkbox"/>
5	More background	0.10000	<input checked="" type="checkbox"/>
6	W (Halfwidth)	0.20000	<input checked="" type="checkbox"/>
7	Preferred orientation	0.10000	<input type="checkbox"/>
8	Atomic coordinates (x,y,z)	0.30000	<input type="checkbox"/>
9	Site occupancy factor and B i	0.30000	<input checked="" type="checkbox"/>
10	U, V (Halfwidth)	0.10000	<input type="checkbox"/>
11	Peak shape parameters	0.10000	<input type="checkbox"/>
12	B anisotropic	0.10000	<input type="checkbox"/>
13	Absorption	0.10000	<input type="checkbox"/>
14	Extinction	0.10000	<input type="checkbox"/>

Min. shift/ESD 0.1
Switch off after: False
Used: True

Buttons: Close, More >>

Order of steps

parameter

Switch/unswitch after used.

Activation box

Shift steps

Rietveld refinement in highscore

- Meaning of the parameters:

Automatic Rietveld Steps - [default lattice big min shifts]

Org.No.	Parameters varied	Min. Shift/ESD	Used
1	Scale factor	0.10000	<input checked="" type="checkbox"/>
2	Flat background	0.10000	<input checked="" type="checkbox"/>
3	Zero shift	0.20000	<input checked="" type="checkbox"/>
4	Lattice parameters	0.90000	<input checked="" type="checkbox"/>
5	More background	0.10000	<input checked="" type="checkbox"/>
6	W (Halfwidth)	0.20000	<input checked="" type="checkbox"/>
7	Preferred orientation	0.10000	<input type="checkbox"/>
8	Atomic coordinates (x,y,z)	0.30000	<input type="checkbox"/>
9	Site occupancy factor and B i:	0.30000	<input checked="" type="checkbox"/>
10	U, V (Halfwidth)	0.10000	<input type="checkbox"/>
11	Peak shape parameters	0.10000	<input type="checkbox"/>
12	B anisotropic	0.10000	<input type="checkbox"/>
13	Absorption	0.10000	<input type="checkbox"/>
14	Extinction	0.10000	<input type="checkbox"/>

- ➔ Modify the scale of each phase to better fit
- ➔ Flatten the background to get rid of amorphous
- ➔ Shift the spectrum to correct systematic error
- ➔ Modify the lattice parameters
- ➔ Add background to correct small angle uncertainties
- ➔ Variation of the principal halfwidth coefficient
- ➔ Modify peaks intensity to allow pref orient of plates
- ➔ Modify atom positions
- ➔ Modify site occupancy and general displacement
- ➔ Variation of the 2 other halfwidth coefficients
- ➔ Modify the "gaussianity" of the peaks
- ➔ Vary degree of freedom of atoms in the structure
- ➔ Unvoluntary absorption of radiations (e.g. from Cu)
- ➔ Due to interference between diffractions

Rietveld refinement in highscore:

To start a refinement we need a good characterization of the phases.

Ideal with the dbs

w/o:

Building a reference library.

Building a reference library

Several websites compile XRD data on reference minerals:

- The American Mineralogist Crystal Structure Database -free

<http://rruff.geo.arizona.edu/AMS/amcsd.php>

- The Mincrust Database (russian acad. of sci.) -free

<http://database.iem.ac.ru/mincryst/index.php>

- ICSD –not free anymore...

http://www.fiz-karlsruhe.de/icsd_home.html

Also any published structure can be added to your reference library

Building a reference library

Lets take some, the first example concerns zeolite minerals.


1. Go to <http://rruff.geo.arizona.edu/AMS/amcsd.php>
2. Search Faujasite – 4 records matching
3. Lets go to the first one (Baur, 1964).
4. The data represents the position of the atoms in the structure and the occupations when there is substitutions.
5. Click on **Download CIF data**
6. Open with X'Pert
7. The phase appears in the refinement control tab under the name global.
8. Rename it in the object inspector
9. Check the validity of the phase:
By simulating pattern




American Mineralogist

4 matching records for this search.

Faujasite-Na

 Baur W H

 American Mineralogist 49 (1964) 697-704

On the cation and water positions in faujasite
24.74 24.74 24.74 90 90 90 *Fd3m
.125 .125 .125

atom	x	y	z	occ	Biso
Si	.12544	.94655	.03626	.7	1.2
Al	.12544	.94655	.03626	.3	1.2
Na	.0699	.0699	.0699	.150	2.6
Ca	.0699	.0699	.0699	.075	2.6
O1	.1742	.1742	.9680		2.8
O2	.1773	.1773	.3232		2.5
O3	.2527	.2527	.1435		2.5
O4	.1053	.8947	0		2.8
OH5	.1673	.1673	.1673		3.2
OH6	.272	.272	.272	.333	3.9

[Download AMC data \(View Text File\)](#)
[Download CIF data \(View Text File\)](#)
[Download diffraction data \(View Text File\)](#)
[View Jmol 3-D Structure](#)

Do not close the widow

Building a reference library

Lets take some, the first example concerns zeolite minerals.


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2. Search Faujasite – 4 records matching
3. Lets go to the first one (Baur, 1964).
4. The data represents the position of the atoms in the structure and the occupations when there is substitutions.
5. Click on **(view text file)** beside Download CIF data
6. Go back
7. Click on **Download CIF data**
8. Open with X'Pert
9. The phase appears in the refinement control tab under the name global.
10. Rename it in the object inspector
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By simulating pattern




American Mineralogist

4 matching records for this search.

Faujasite-Na

 Baur W H

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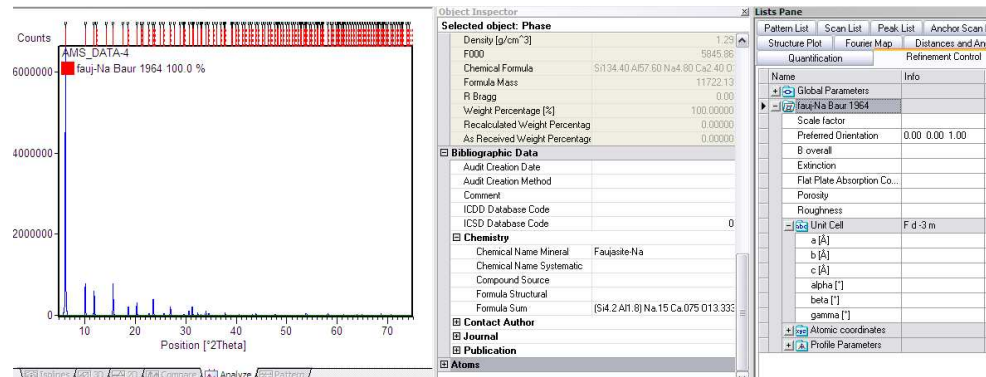
On the cation and water positions in faujasite
24.74 24.74 24.74 90 90 90 *Fd3m
.125 .125 .125

atom	x	y	z	occ	Biso
Si	.12544	.94655	.03626	.7	1.2
Al	.12544	.94655	.03626	.3	1.2
Na	.0699	.0699	.0699	.150	2.6
Ca	.0699	.0699	.0699	.075	2.6
O1	.1742	.1742	.9680		2.8
O2	.1773	.1773	.3232		2.5
O3	.2527	.2527	.1435		2.5
O4	.1053	.8947	0		2.8
OH5	.1673	.1673	.1673		3.2
OH6	.272	.272	.272	.333	3.9

[Download AMC data \(View Text File\)](#)
[Download CIF data \(View Text File\)](#)
[Download diffraction data \(View Text File\)](#)
[View JMOL 3-D Structure](#)

Do not close the widow

Building a reference library



10. Check the pattern with the XRD data from the database and the CIF text file for the formula.

11. By right-clicking on the name of the phase in the refinement control tab we can select “add all phases to reference database” which add the phase in your personal database.

12. Lets add more minerals in the dbs.

Sodalite from ballirano (last in the list)

Cancrinite from Fechtelkord (first in the list)

Fayalite from Birle et al (first)

Augite from Bindi (first)

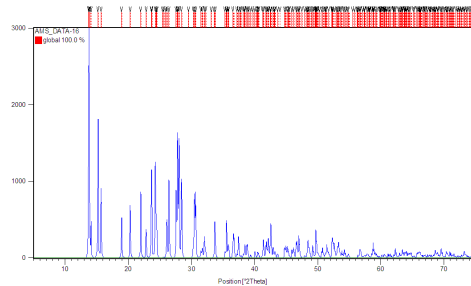
Do not close the widow

Building a reference library

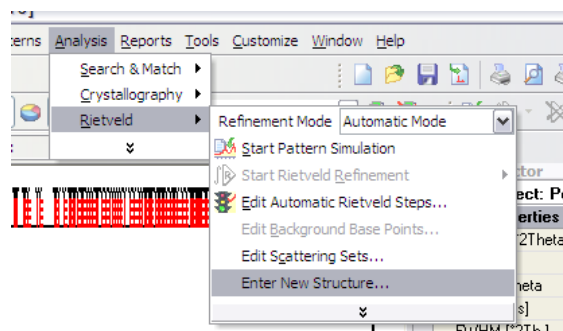
13. The particular case of the plagioclase.

Plagio are published with a C-1 unit cell which is not a standard space group.

1. Search for Andesine
2. download CIF file: not a Pg !!



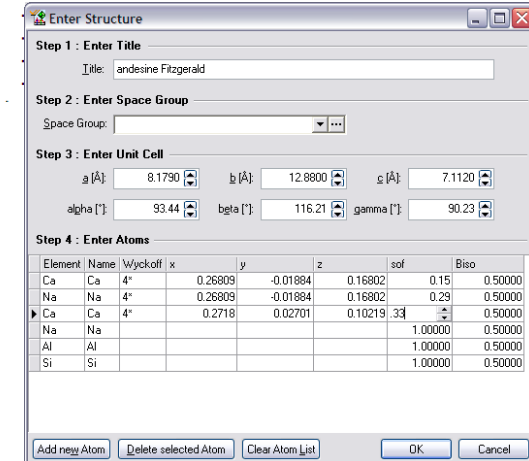
3. we need to enter the data manually.



4. Ensuite right click on the phase and select "standardize phase" We now get a Pg

```

Andesine
FitzGerald J D, Parise J B, Mackinnon I D R
American Mineralogist 71 (1986) 1399-1408
Average structure of an An48 plagioclase from the Hogarth Ranges
Sample: Neutron data
8.179 12.880 7.112 93.44 116.21 90.23 C-1
atom  x      y      z  occ B(1,1) B(2,2) B(3,3) B(1,2) B(1,3) B(2,3)
CaM'  .26809 -.01884 .16802 .15 .00680 .00790 .01366 -.00217 .00509 -.00404
NaM'  .26809 -.01884 .16802 .29 .00680 .00790 .01366 -.00217 .00509 -.00404
CaM'' .27180 .02701 .10219 .33 .00547 .00528 .01478 .00176 .00160 -.00342
NaM'' .27180 .02701 .10219 .23 .00547 .00528 .01478 .00176 .00160 -.00342
AlT1o .00694 .16420 .21481 .51 .00462 .00183 .00479 -.00035 .00210 .00029
SiT1o .00694 .16420 .21481 .49 .00462 .00183 .00489 -.00035 .00210 .00029
AlT1m .00346 .81651 .23115 .32 .00474 .00192 .00473 .00094 .00214 .00029
SiT1m .00346 .81651 .23115 .68 .00474 .00192 .00473 .00094 .00214 .00029
AlT2o .68601 .10893 .31813 .32 .00417 .00151 .00607 .00033 .00195 .00025
SiT2o .68601 .10893 .31813 .68 .00417 .00151 .00607 .00033 .00195 .00025
AlT2m .68193 .87892 .35638 .32 .00403 .00156 .00570 .00028 .00199 .00044
SiT2m .68193 .87892 .35638 .68 .00403 .00156 .00570 .00028 .00199 .00044
OAl  .00387 .13025 .98101 .01141 .00352 .00750 .00086 .00582 .00103
OAl2 .58279 .99186 .27868 .00564 .00183 .00930 .00010 .00270 .00075
OBo  .81405 .10547 .19149 .00830 .00268 .01365 -.00045 .00646 -.00007
OBm  .81627 .85251 .24428 .00829 .00361 .01864 .00081 .00777 -.00067
OCo  .0411 .00040
OCm  .0194 -.00009
ODo  .0127 .00069
ODm  .0004 -.00069
    
```



5. Add file to references

Do not close the widow

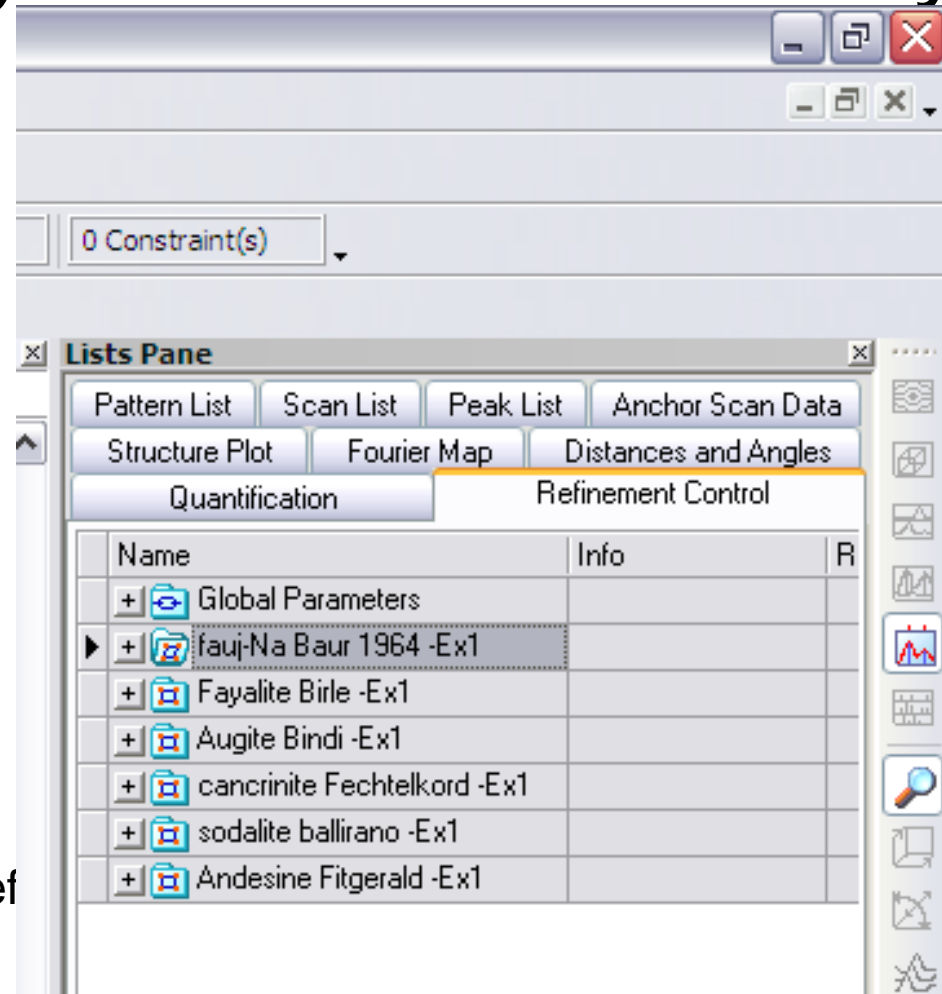
Building a crystal structure library

We should have 6 minerals

Copy them in a single window
(right click → copy to ...)

Then Save file As
Struct_Ex1 in .CRY format

If not done, “add all phases to ref
library”



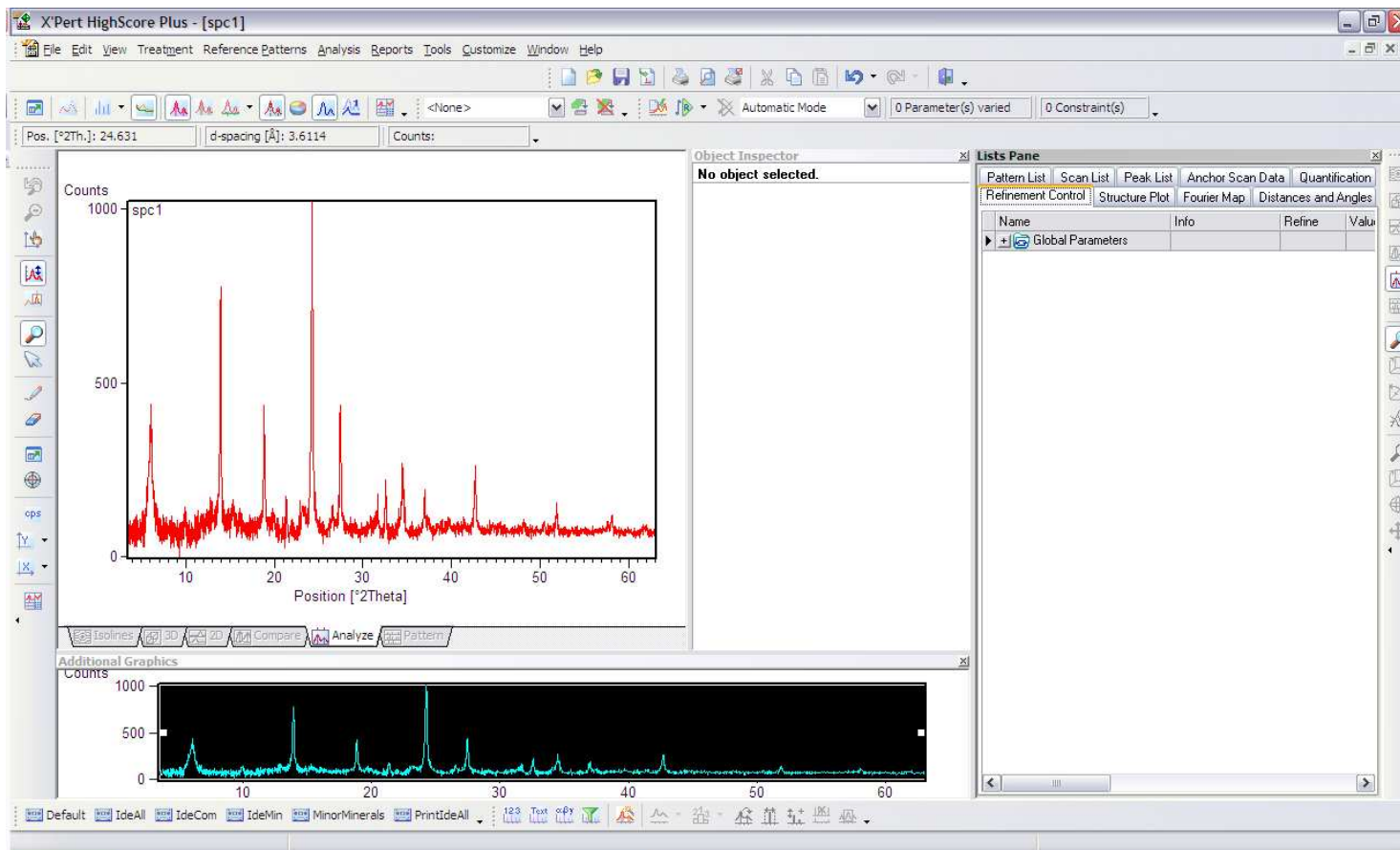
Rietveld refinement in highscore:

EXERCICE 1

Quantification of homogeneous nucleation of
hyper alkaline solution

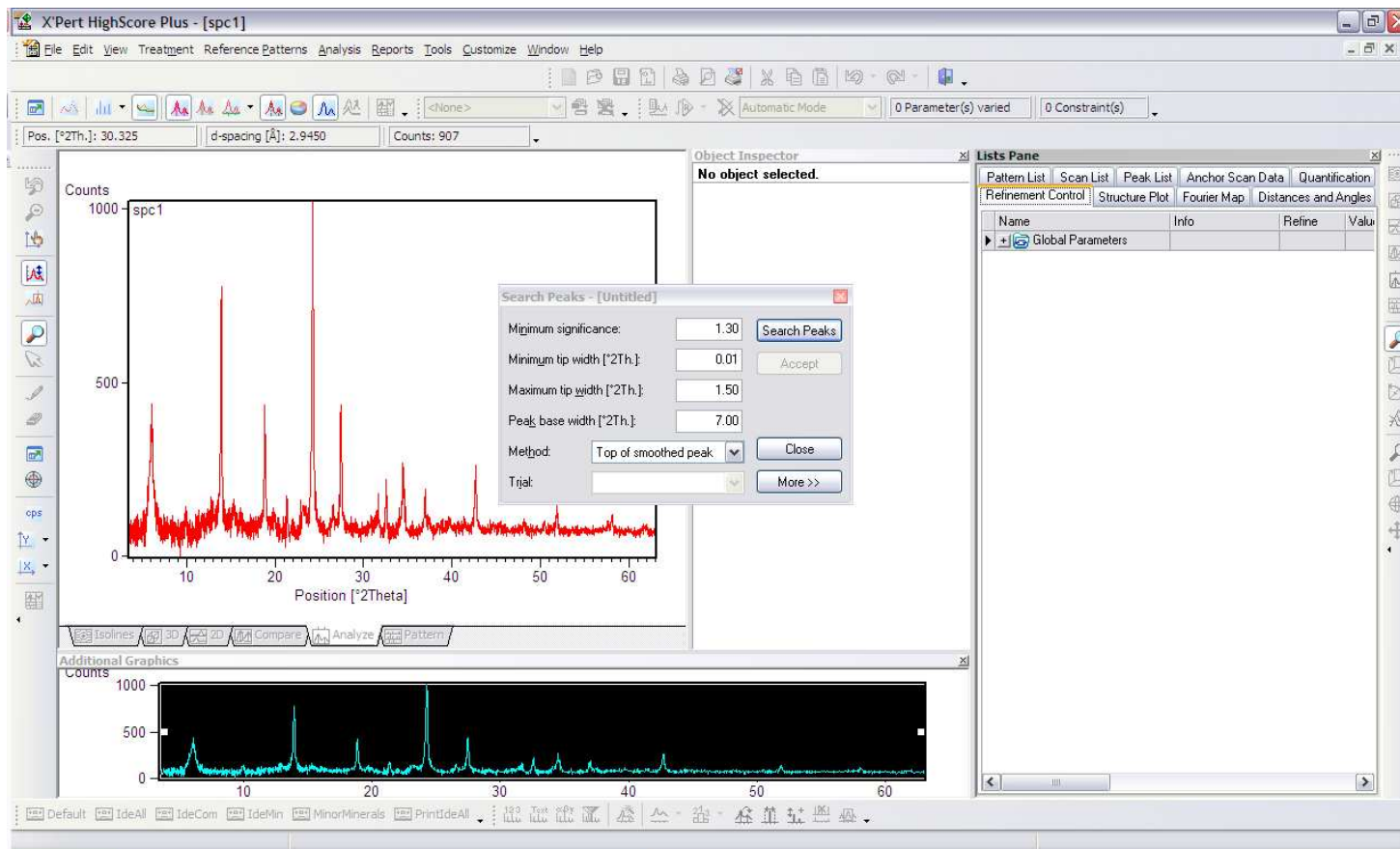
EXERCICE 1

1. Open spc1



EXERCICE 1

1. Go to Treatment → Search Peaks → Accept



EXERCICE 1

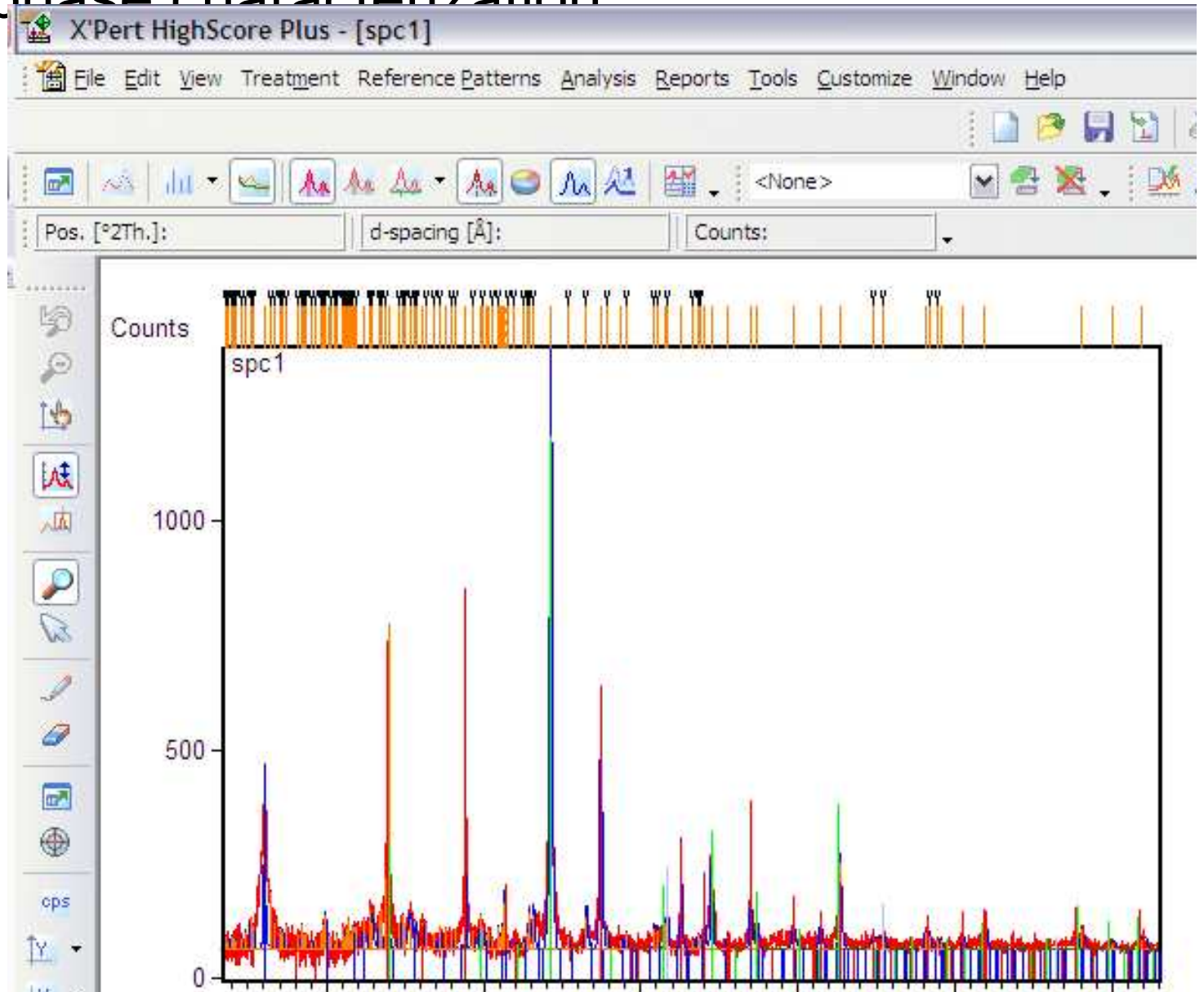
1. Go to analysis → Search and Match → Execute Search and Match → Search → OK

The screenshot displays the X'Pert HighScore Plus software interface. The main window shows a diffraction pattern plot with 'Counts' on the y-axis (0 to 1000) and 'Position [°2Theta]' on the x-axis (0 to 40). The plot is labeled 'spc1'. A 'Search & Match' dialog box is open, showing the 'Parameters' tab. The 'Data source' is set to 'Profile Data'. The 'Scoring scheme' is set to 'Multi phase'. The 'Auto residue' and 'Match intensity' checkboxes are checked. The 'Known γ Theta shift [°2Th.]' is set to 0. The 'Object Inspector' shows the 'Selected object: Peak(s)' with properties: Position [°2Theta] 13.69447, d-spacing 6.46102, $\text{Sine}^2 \text{Theta}$ 0.01421, Height [cts] 159.00. The 'Lists Pane' shows a table of candidates:

No.	Ref. Code	Score	Compound Name	Chemical Formula
1	99-000-0002	48	NO3 cancrinite	Si6.00 Al
2	99-000-0018	48	NO3 cancrinite	Si6.00 Al
3	99-000-0084	45	cancrinite Fechtel...	Na7.92 Si
4	99-000-0022	42	Cancrinite (Fechte...	O33.54 F
5	99-000-0017	42	NO3-cancrinite Bu...	Si6.00 Al
6	99-000-0001	39	nitrate sodalite	Si6.00 Al
7	99-000-0061	39	Lazurite (AMCSD, ...	Na39.08
8	99-000-0034	37	global	Ca0.96 N
9	99-000-0063	36	NO3 sodalite (Buh...	Si6.00 Al
10	99-000-0012	36	labradorite mincys...	Na3.84 C
11	99-000-0037	34	global	Na2.00 Si
12	99-000-0038	34	global	Na2.00 Si
13	99-000-0062	33	Sodalite (AMSCD, ...	Na5.28 K
14	99-000-0085	33	sodalite ballirano ...	Na5.28 K
15	99-000-0039	32	Albite (AMC Prewit...	Na2.00 Si
16	99-000-0052	31	Piemontite (AMSC...	Ca3.74 S

EXERCICE 1

1. Do the phase characterization



EXERCICE 1

1. Go to File → Insert → Select Struct_Ex1 →
Select the 3 phases of interest

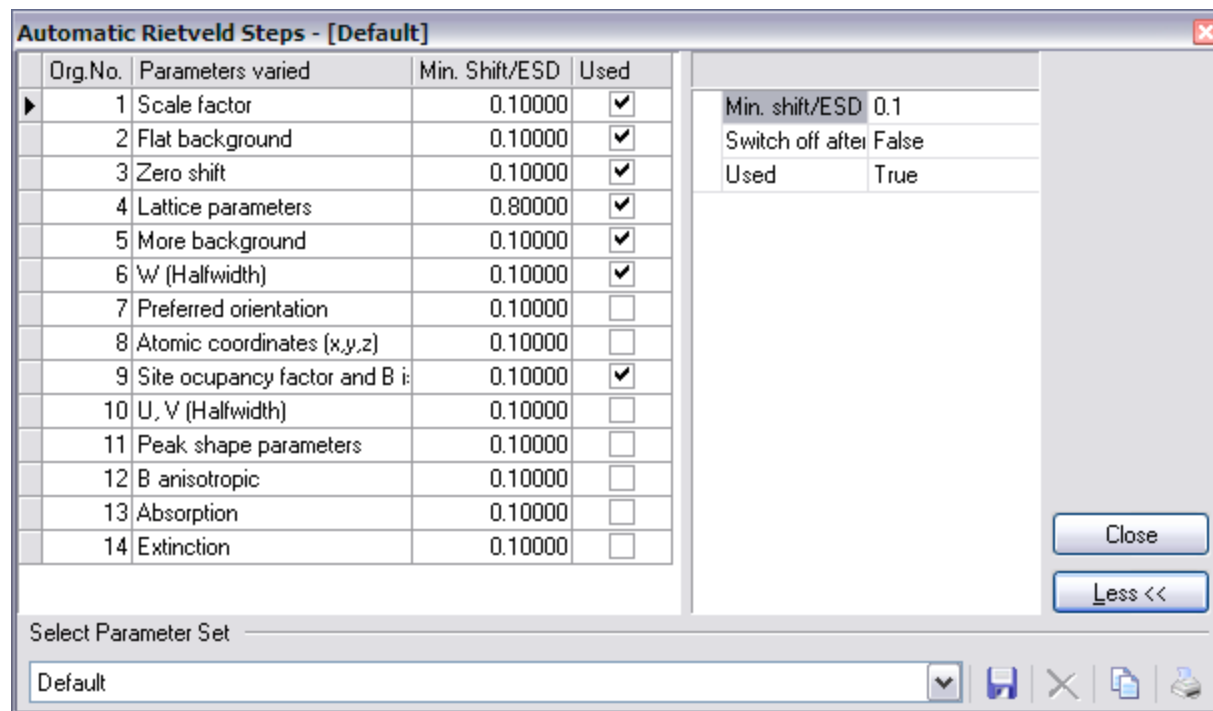
The screenshot displays the X'Pert HighScore Plus software interface. The main window shows a diffraction pattern with 'Counts' on the y-axis (0 to 1000) and 'Position [°2Theta]' on the x-axis (0 to 20). A red line represents the experimental data, and a black line represents the reference pattern. The 'Object Inspector' panel on the right shows the selected object: 'Peak(s)' with properties: Position [°2Theta] = 3.62182, d-spacing = 24.37569, and Sine² 2 Theta = 0.00100. The 'Lists Pane' on the right shows a table with columns: Name, Info, Refine, and Value. A dialog box titled 'CIF / CRYSTIN Import Structures' is open, displaying a table of structures:

No.	Use	Name	Formula	Space group	Comment
1	<input type="checkbox"/>	fauj-Na Baur 1964 -Ex1	(Si4.2 Al1.8) Na.15	Fd3-mZ	Comment not found
2	<input type="checkbox"/>	Fayalite Birlé -Ex1	(Fe1.844 Mg.078 Mn)Pnma		Comment not found
3	<input type="checkbox"/>	Augite Bindi -Ex1	Ca.61 Fe.13 Mg.43	C12/c1	Comment not found
4	<input type="checkbox"/>	canorinite Fechtelkord -Ex1	Na3.96 Si3 Al3 O15.	P63	Comment not found
5	<input type="checkbox"/>	sodalite ballirano -Ex1	Na2.64 K.7 Ca.616	P4-3n	Comment not found
6	<input type="checkbox"/>	Andesine Fitzgerald -Ex1	Ca0.96 Na1.04 Al2.	P1-	Comment not found

The dialog box has 'Invert Selection', 'OK', and 'Cancel' buttons. The 'Additional Graphics' panel at the bottom shows 'Residuals + Peak List' and 'Accepted Patterns'.

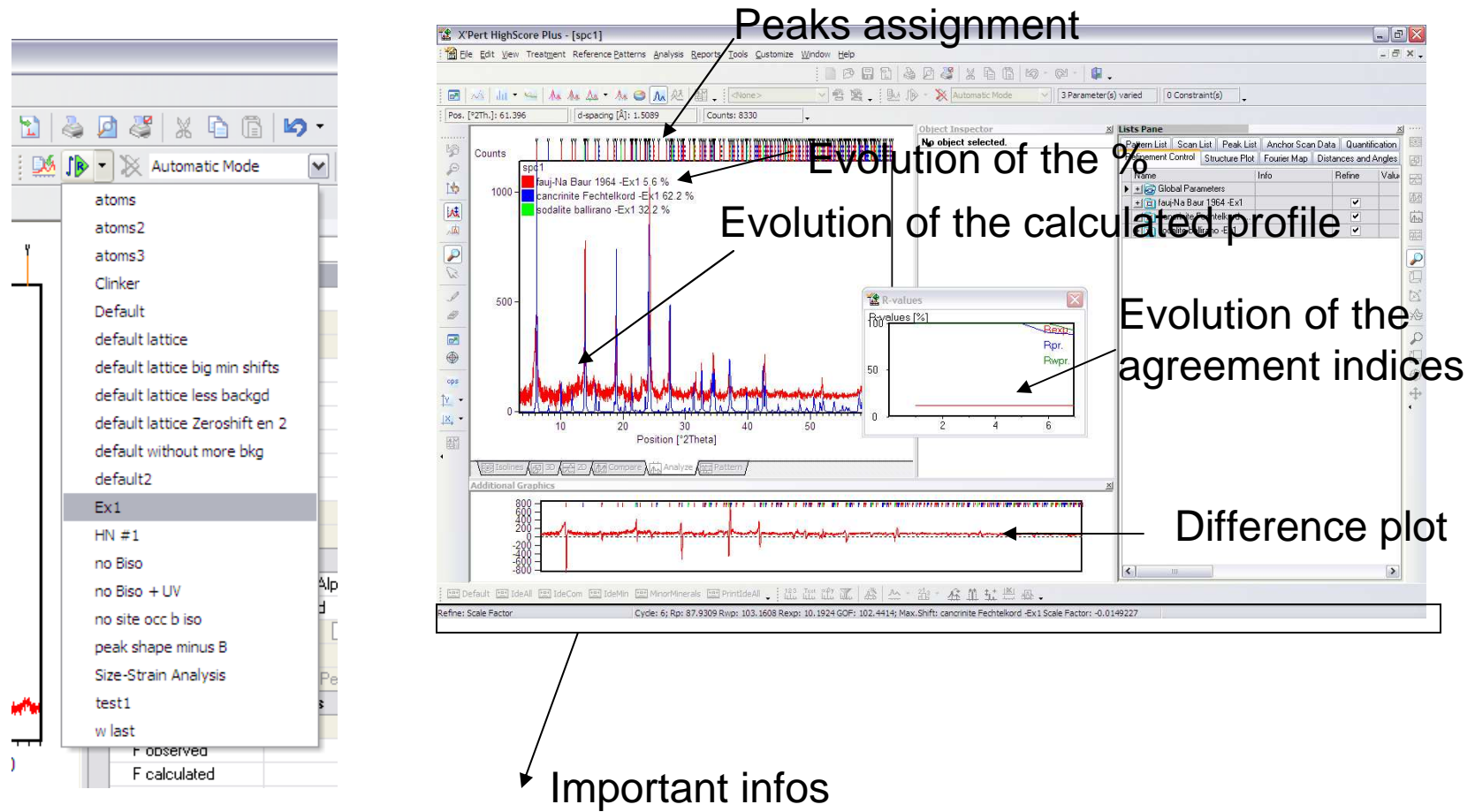
EXERCICE 1

1. Phases are now in the Refinement Control Tab
2. Let's look at the parameters. Open the automatic Rietveld steps, deselect all except the first one. Then click more, disc icon and name Ex1



Exercise 1

1. We are testing the effect of the first param
2. Run rietveld: That modified the peak intensities

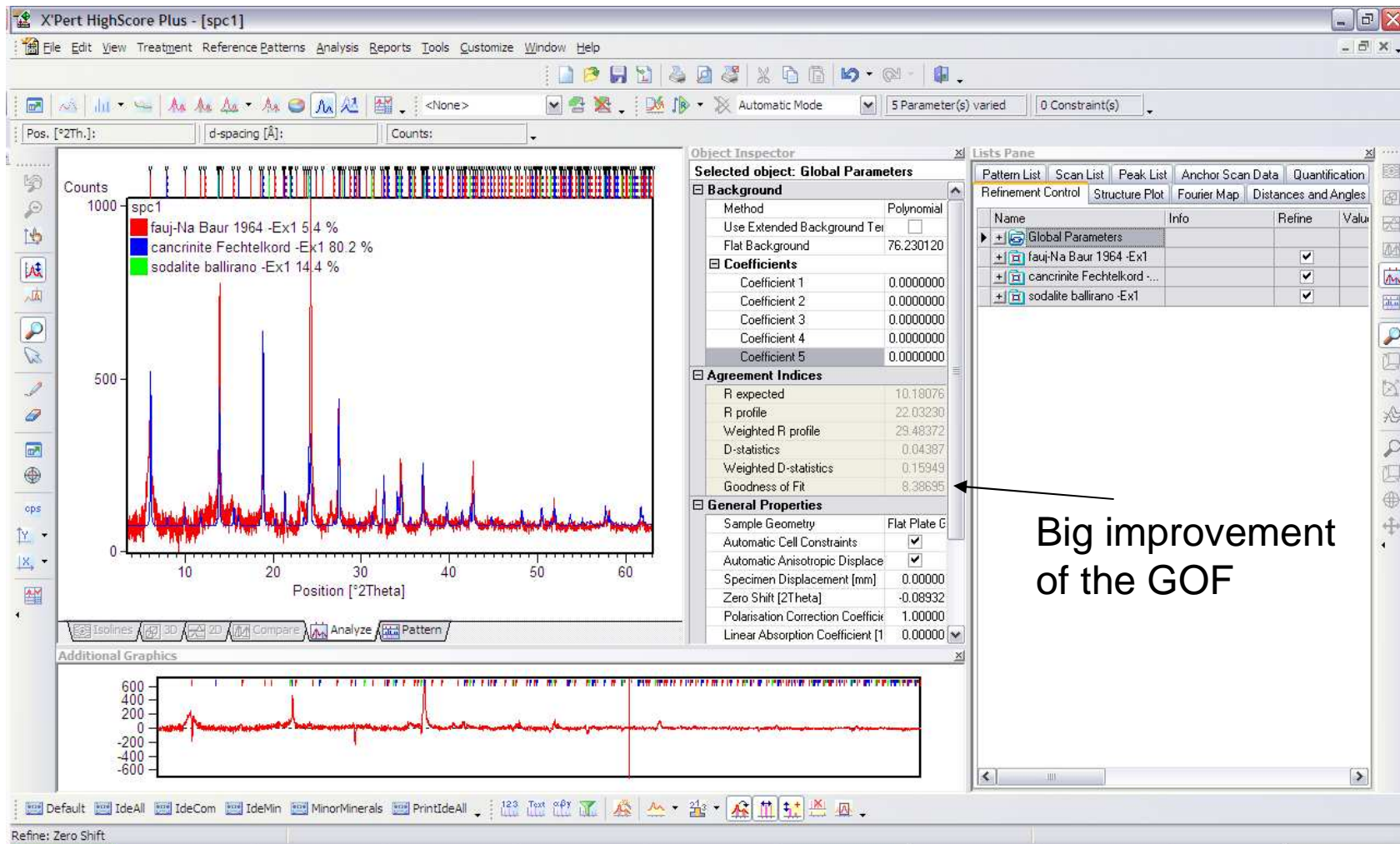


Refine: Scale Factor

Cycle: 6; Rp: 87.9309 Rwp: 103.1608 Rexp: 10.1924 GOF: 102.4414; Max.Shift: cancrinite Fechtelkord -Ex1 Scale Factor: -0.0149227

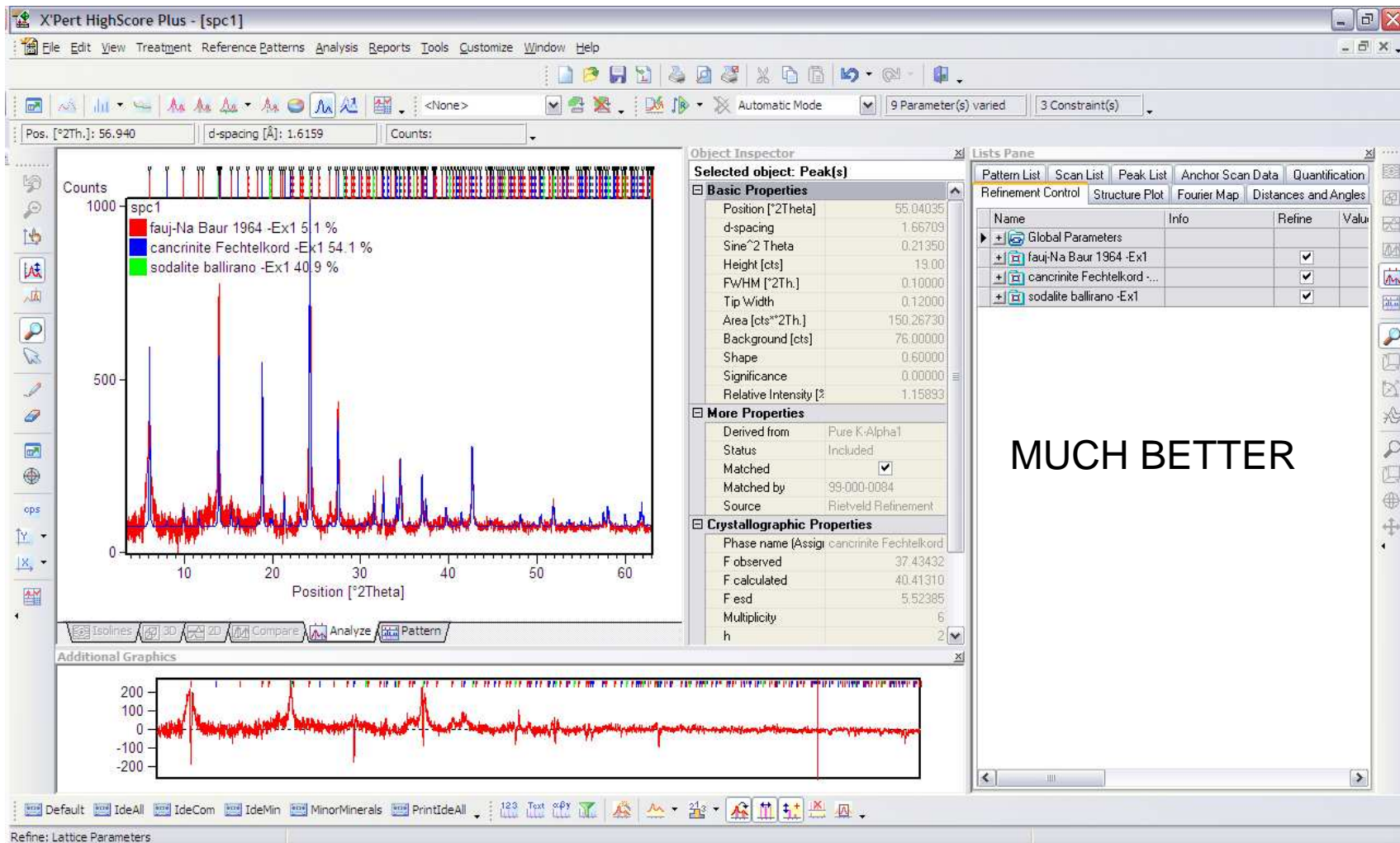
Exercise 1

1. We are testing the effect of adding bkgd and zero shift
2. Edit → undo Rietveld (or Ctrl+Z)
3. Edit autom. Rietveld steps, add flat bkgd and zero shift



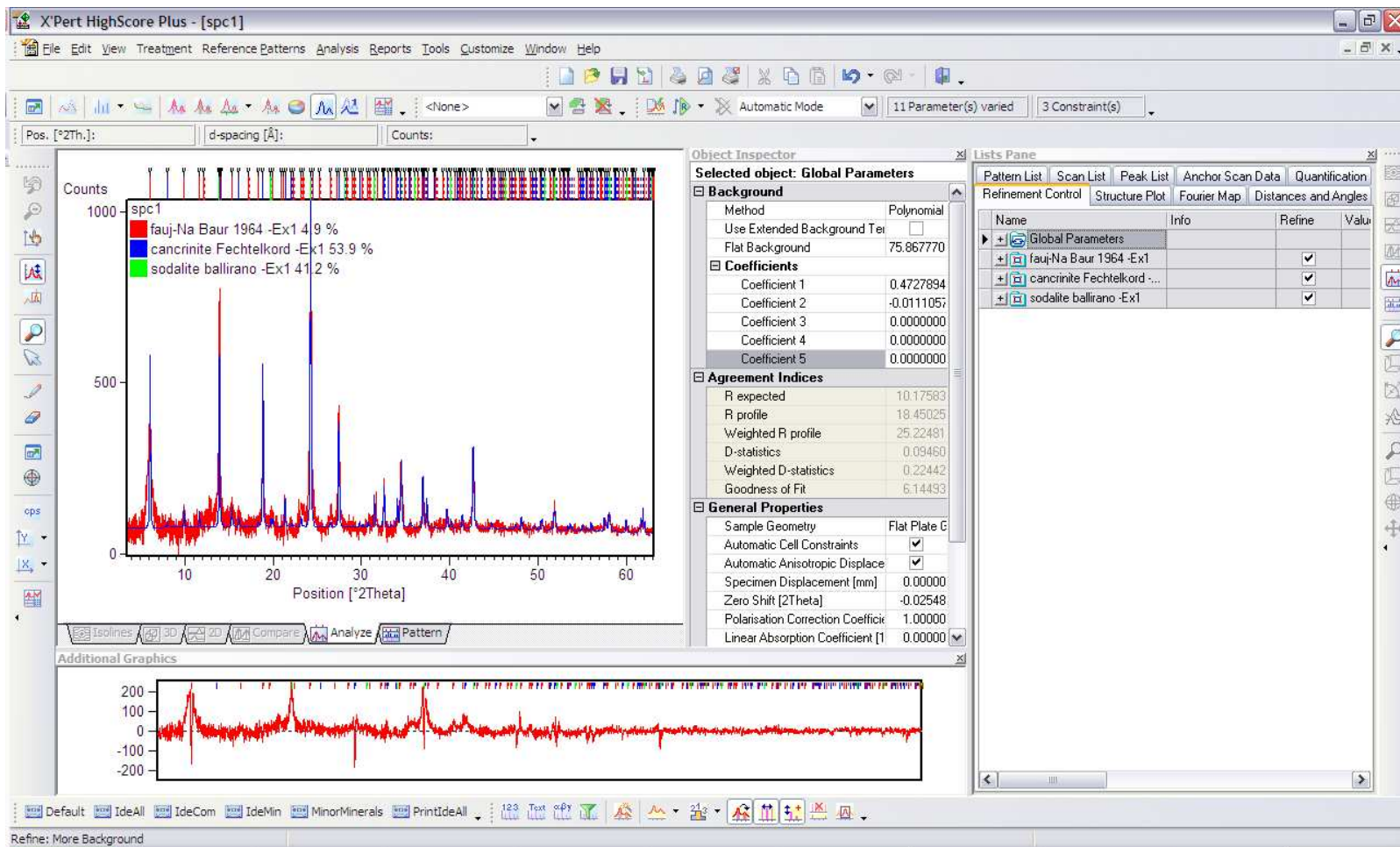
Exercise 1

1. Now the most important: the lattice param
2. Edit → undo Rietveld (or Ctrl+Z)
3. Edit autom. Rietveld steps, add lattice parameter



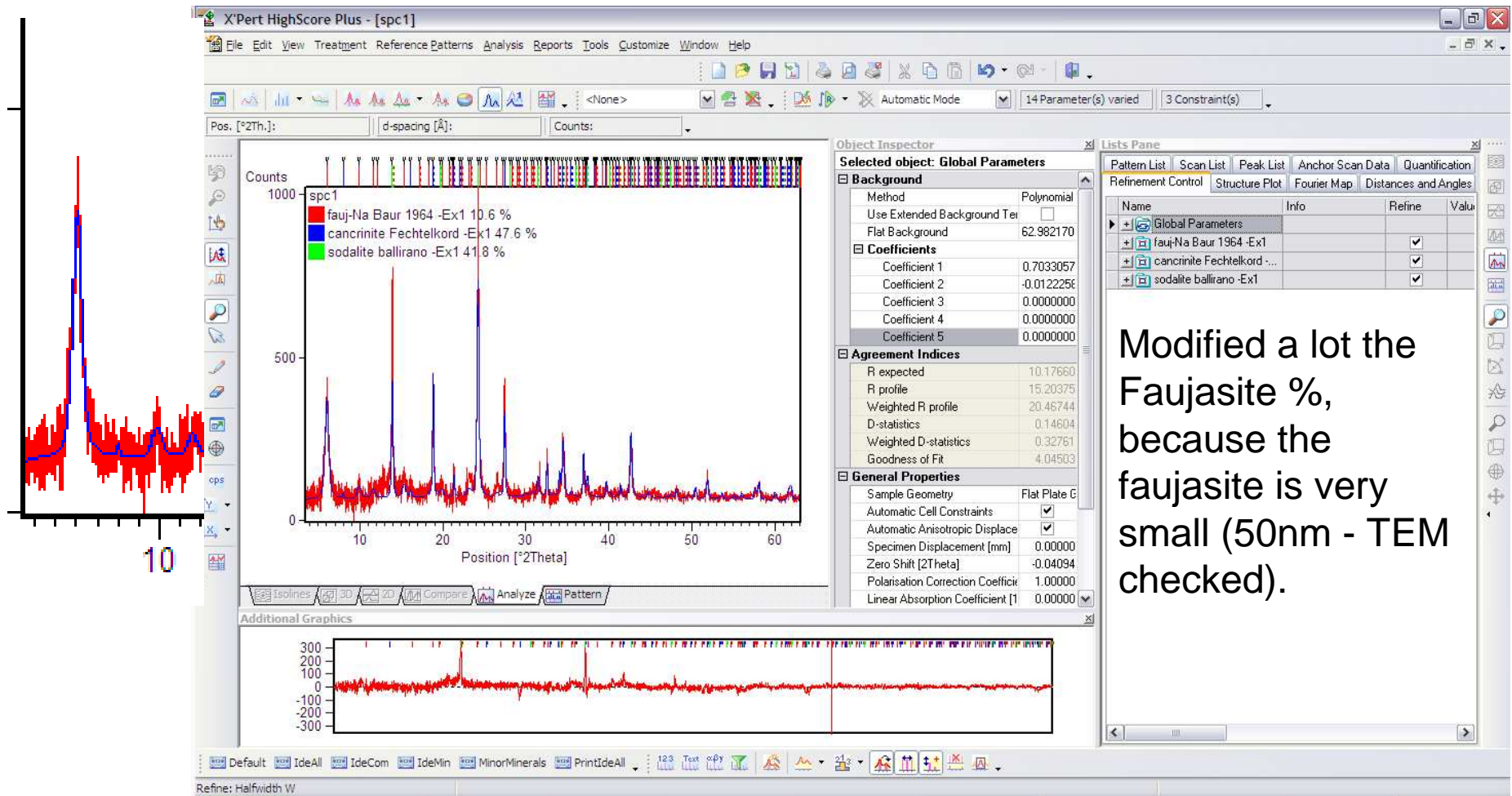
Exercise 1

1. Adding more bkgd doesn't improve much cause we already have a flat bkgd
2. Edit → undo Rietveld (or Ctrl+Z)
3. Edit autom. Rietveld steps, add more background



Exercise 1

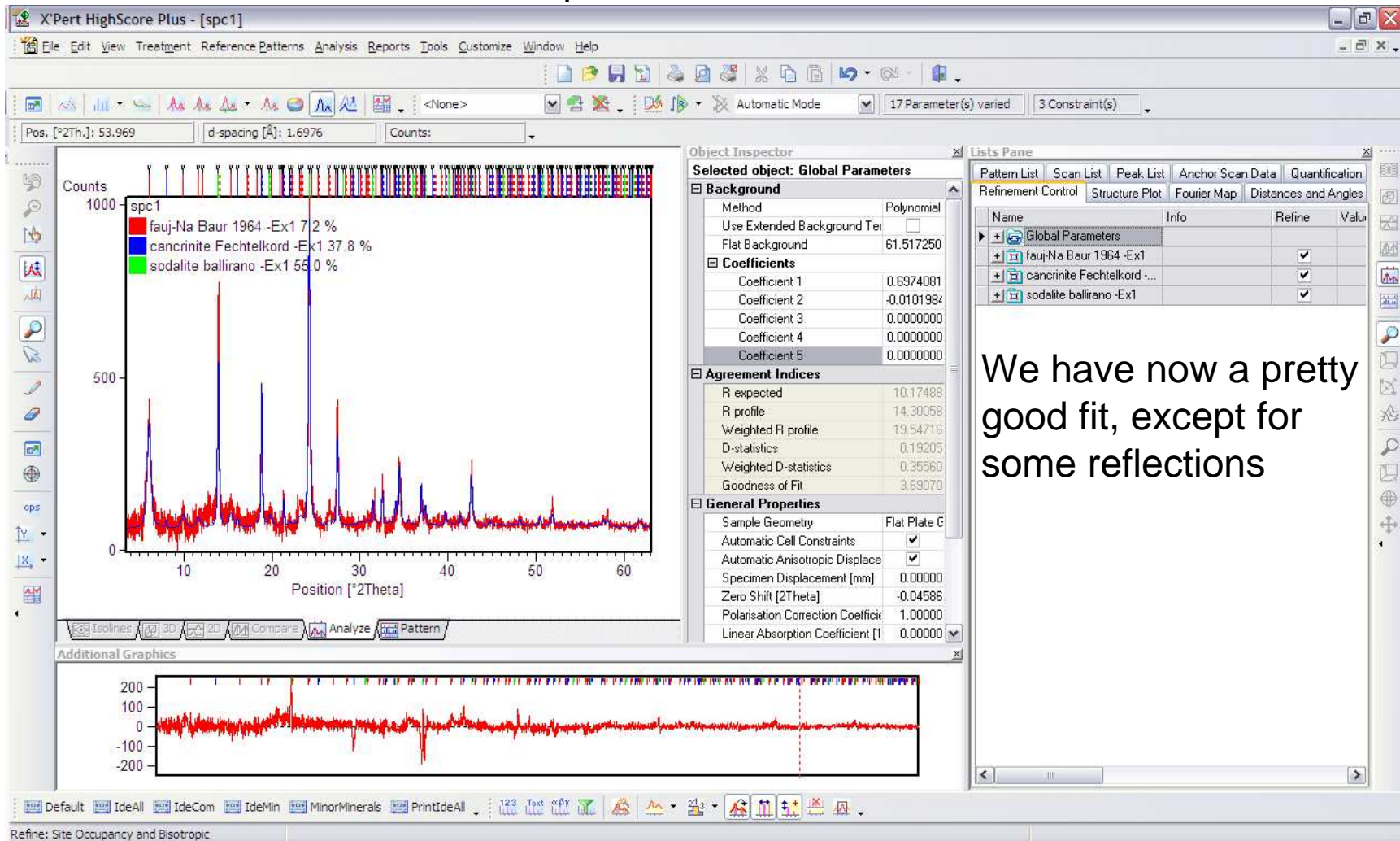
1. The halfwidth parameter account geometrically for the width of the peaks, in reality it represents the size of the crystallites (on a coherent domain).
2. Edit → undo Rietveld (or Ctrl+Z)
3. Edit autom. Rietveld steps, add W halfwidth



Modified a lot the Faujasite %, because the faujasite is very small (50nm - TEM checked).

Exercise 1

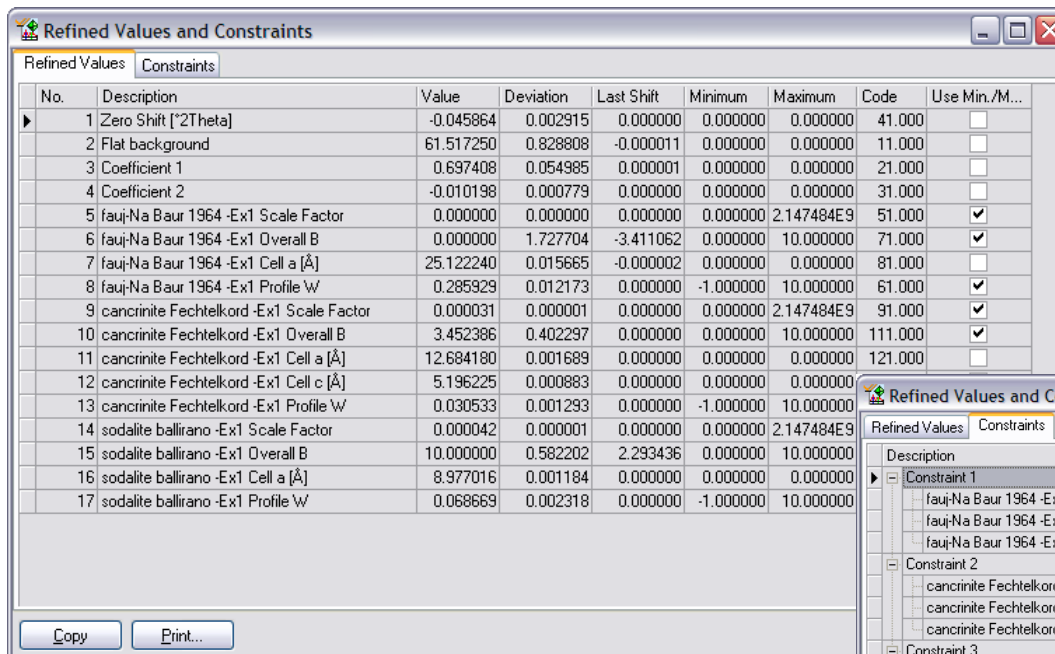
1. Will the variation of site occupancies and Biso modify the quanti
2. Edit → undo Rietveld (or Ctrl+Z)
3. Edit autom. Rietveld steps, add site occ and Biso



Exercise 1

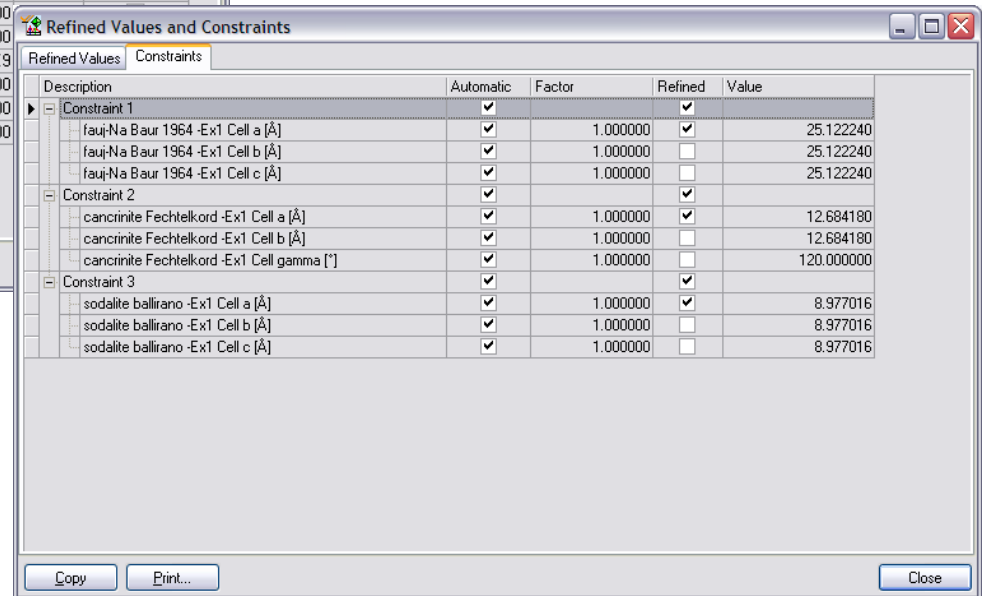
What did we do?

1. Right click on mineral list → show refined values/constraints
2. This gives the deviations operated on the phases for each parameter.



No.	Description	Value	Deviation	Last Shift	Minimum	Maximum	Code	Use Min./M...
1	Zero Shift [*2Theta]	-0.045864	0.002915	0.000000	0.000000	0.000000	41.000	<input type="checkbox"/>
2	Flat background	61.517250	0.828808	-0.000011	0.000000	0.000000	11.000	<input type="checkbox"/>
3	Coefficient 1	0.697408	0.054985	0.000001	0.000000	0.000000	21.000	<input type="checkbox"/>
4	Coefficient 2	-0.010198	0.000779	0.000000	0.000000	0.000000	31.000	<input type="checkbox"/>
5	fauj-Na Baur 1964 -Ex1 Scale Factor	0.000000	0.000000	0.000000	0.000000	2.147484E9	51.000	<input checked="" type="checkbox"/>
6	fauj-Na Baur 1964 -Ex1 Overall B	0.000000	1.727704	-3.411062	0.000000	10.000000	71.000	<input checked="" type="checkbox"/>
7	fauj-Na Baur 1964 -Ex1 Cell a [Å]	25.122240	0.015665	-0.000002	0.000000	0.000000	81.000	<input type="checkbox"/>
8	fauj-Na Baur 1964 -Ex1 Profile W	0.285929	0.012173	0.000000	-1.000000	10.000000	61.000	<input checked="" type="checkbox"/>
9	cancrinite Fechtelkord -Ex1 Scale Factor	0.000031	0.000001	0.000000	0.000000	2.147484E9	91.000	<input checked="" type="checkbox"/>
10	cancrinite Fechtelkord -Ex1 Overall B	3.452386	0.402297	0.000000	0.000000	10.000000	111.000	<input checked="" type="checkbox"/>
11	cancrinite Fechtelkord -Ex1 Cell a [Å]	12.684180	0.001689	0.000000	0.000000	0.000000	121.000	<input type="checkbox"/>
12	cancrinite Fechtelkord -Ex1 Cell c [Å]	5.196225	0.000883	0.000000	0.000000	0.000000		<input type="checkbox"/>
13	cancrinite Fechtelkord -Ex1 Profile W	0.030533	0.001293	0.000000	-1.000000	10.000000		<input type="checkbox"/>
14	sodalite ballirano -Ex1 Scale Factor	0.000042	0.000001	0.000000	0.000000	2.147484E9		<input type="checkbox"/>
15	sodalite ballirano -Ex1 Overall B	10.000000	0.582202	2.293436	0.000000	10.000000		<input type="checkbox"/>
16	sodalite ballirano -Ex1 Cell a [Å]	8.977016	0.001184	0.000000	0.000000	0.000000		<input type="checkbox"/>
17	sodalite ballirano -Ex1 Profile W	0.068669	0.002318	0.000000	-1.000000	10.000000		<input type="checkbox"/>

And the constraints

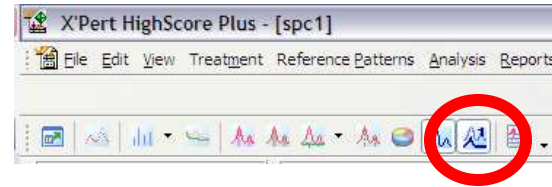


Description	Automatic	Factor	Refined	Value
[-] Constraint 1	<input checked="" type="checkbox"/>		<input checked="" type="checkbox"/>	
fauj-Na Baur 1964 -Ex1 Cell a [Å]	<input checked="" type="checkbox"/>	1.000000	<input checked="" type="checkbox"/>	25.122240
fauj-Na Baur 1964 -Ex1 Cell b [Å]	<input checked="" type="checkbox"/>	1.000000	<input type="checkbox"/>	25.122240
fauj-Na Baur 1964 -Ex1 Cell c [Å]	<input checked="" type="checkbox"/>	1.000000	<input type="checkbox"/>	25.122240
[-] Constraint 2	<input checked="" type="checkbox"/>		<input checked="" type="checkbox"/>	
cancrinite Fechtelkord -Ex1 Cell a [Å]	<input checked="" type="checkbox"/>	1.000000	<input checked="" type="checkbox"/>	12.684180
cancrinite Fechtelkord -Ex1 Cell b [Å]	<input checked="" type="checkbox"/>	1.000000	<input type="checkbox"/>	12.684180
cancrinite Fechtelkord -Ex1 Cell gamma [°]	<input checked="" type="checkbox"/>	1.000000	<input type="checkbox"/>	120.000000
[-] Constraint 3	<input checked="" type="checkbox"/>		<input checked="" type="checkbox"/>	
sodalite ballirano -Ex1 Cell a [Å]	<input checked="" type="checkbox"/>	1.000000	<input checked="" type="checkbox"/>	8.977016
sodalite ballirano -Ex1 Cell b [Å]	<input checked="" type="checkbox"/>	1.000000	<input type="checkbox"/>	8.977016
sodalite ballirano -Ex1 Cell c [Å]	<input checked="" type="checkbox"/>	1.000000	<input type="checkbox"/>	8.977016

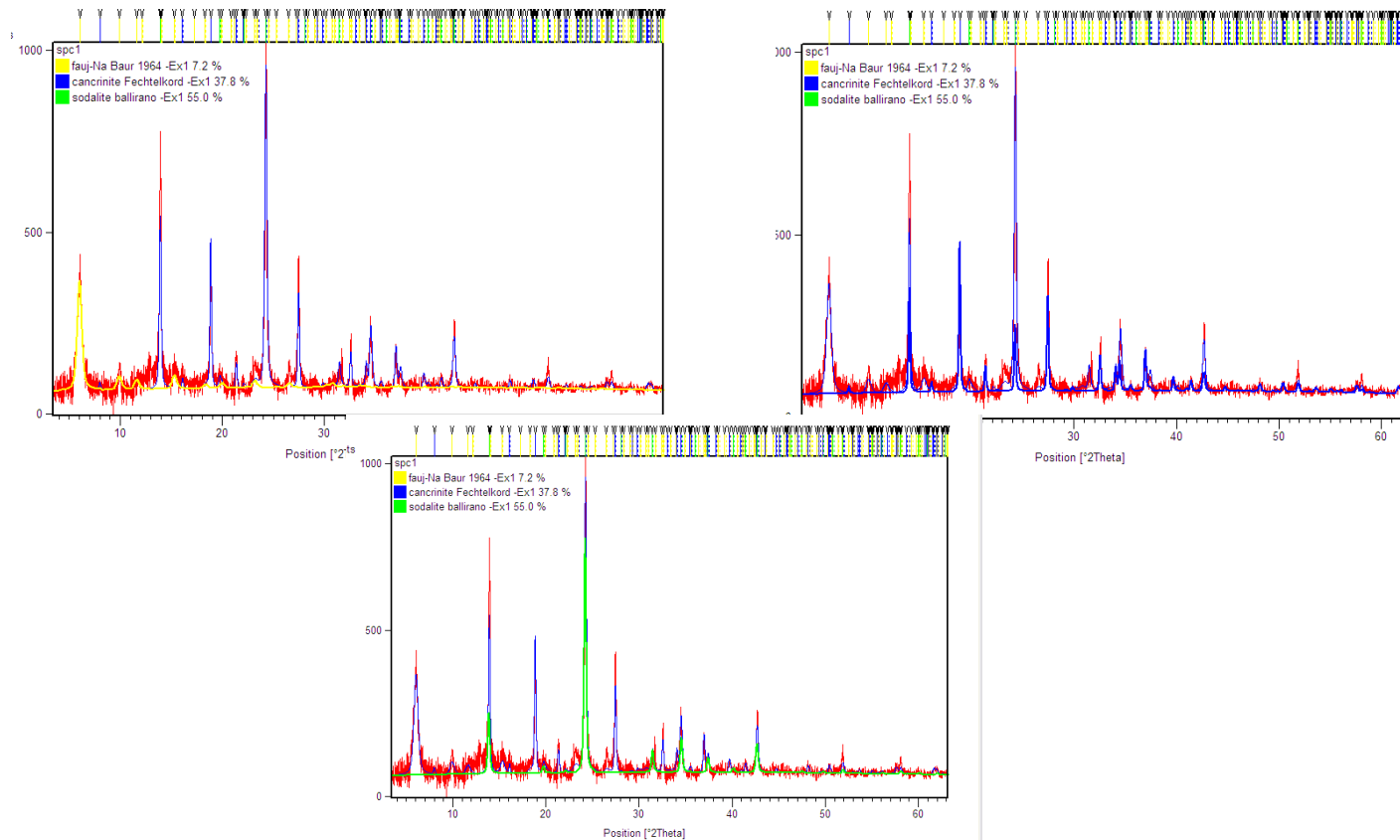
Exercise 1

What did we do?

1. Click on show selected phase profile icon



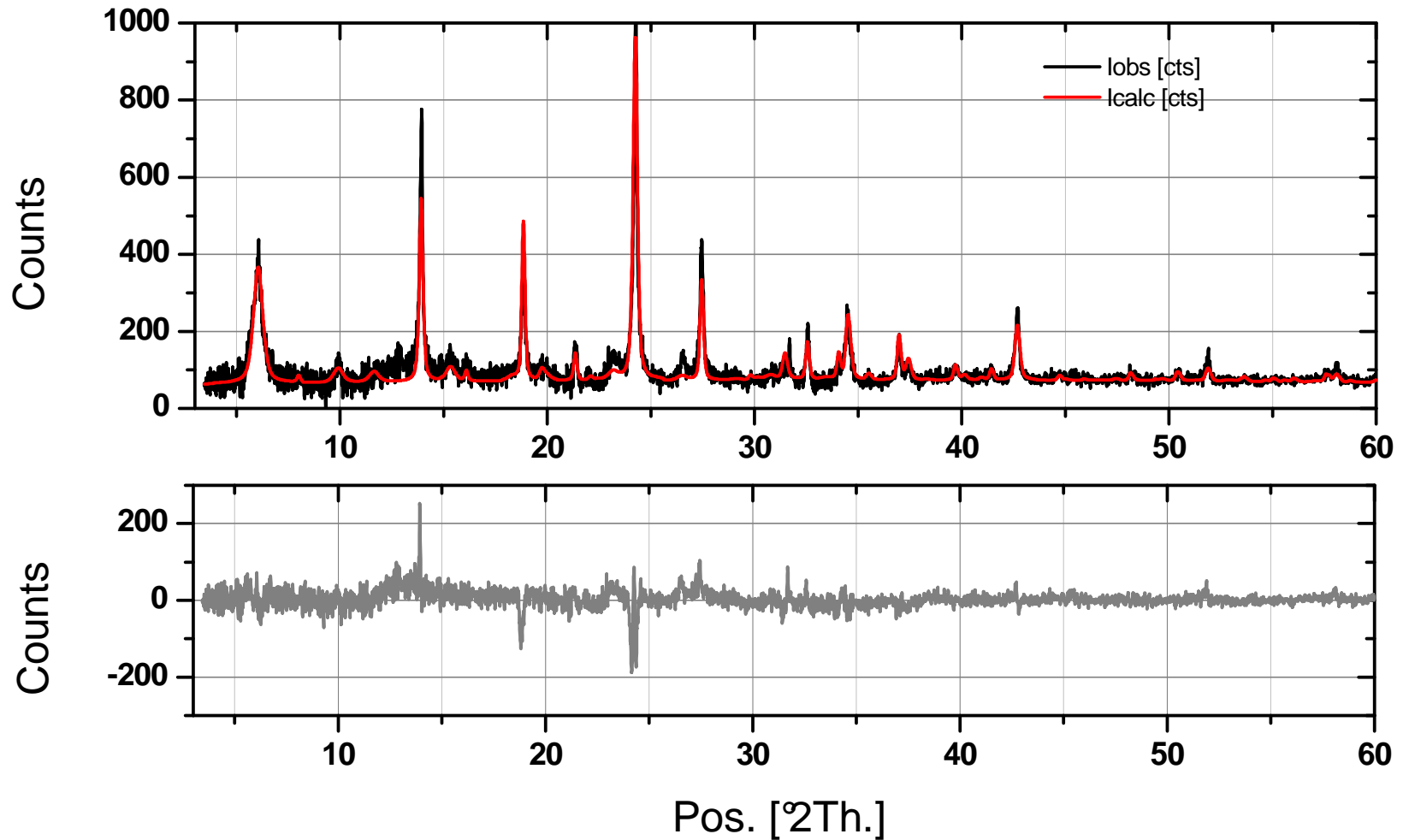
2. Select the phases. We can see the part of each phase in the calculated profile



Exercise 1

What did we do?

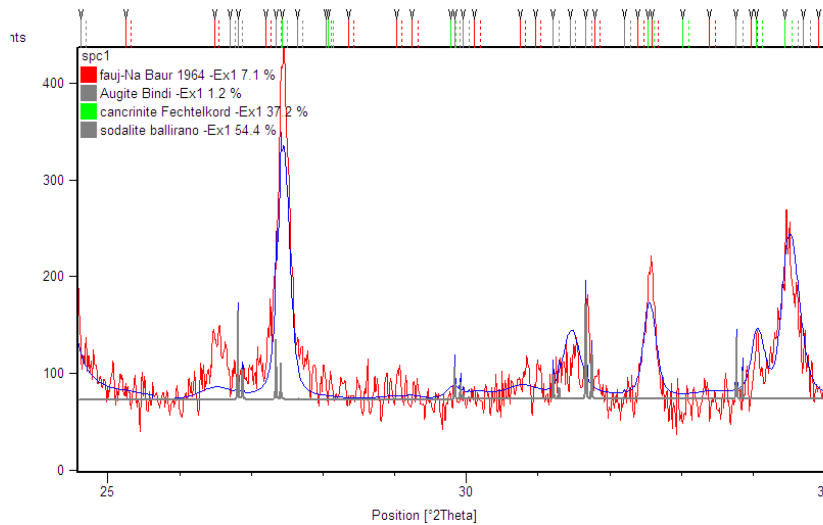
1. In the anchor scan data tab appear the numerical values of the scan.
2. Right click → copy list → past in excel or origin



Exercise 1

How to check ?

1. Close and open spc1 again
2. Insert sod, canc fau + augite structure
3. Run Rietveld
4. Look at the individual phase



Too much deviation in B

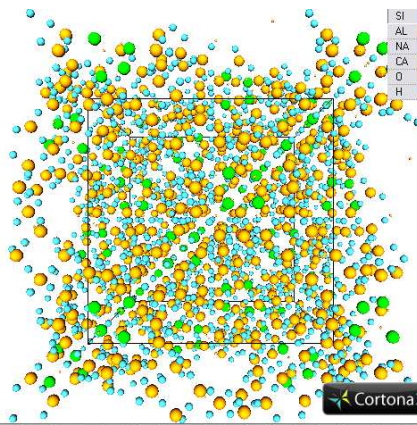
No.	Description	Value	Deviation	Last Shift	Minimum	Maximum	Code	Use Min./M...
7	fauj-Na Baur 1964 -Ex1 Cell a [Å]	25.122830	0.015256	-0.000008	0.000000	0.000000	81.000	<input type="checkbox"/>
8	fauj-Na Baur 1964 -Ex1 Profile W	0.284668	0.012133	-0.000001	-1.000000	10.000000	61.000	<input checked="" type="checkbox"/>
9	Augite Bindi -Ex1 Scale Factor	0.000002	0.000001	0.000000	0.000000	2.147484E9	91.000	<input checked="" type="checkbox"/>
10	Augite Bindi -Ex1 Overall B	10.000000	6.000724	3.804851	0.000000	10.000000	111.000	<input checked="" type="checkbox"/>
11	Augite Bindi -Ex1 Cell a [Å]	11.209450	0.001156	0.000007	0.000000	0.000000	121.000	<input type="checkbox"/>
12	Augite Bindi -Ex1 Cell b [Å]	6.658890	0.000691	0.000000	0.000000	0.000000	131.000	<input type="checkbox"/>
13	Augite Bindi -Ex1 Cell c [Å]	15.966710	0.001691	-0.000004	0.000000	0.000000	141.000	<input type="checkbox"/>
14	Augite Bindi -Ex1 Cell beta [°]	155.452800	0.002111	0.000015	0.000000	0.000000	151.000	<input type="checkbox"/>
15	Augite Bindi -Ex1 Profile W	-0.008153	0.000032	0.000073	-1.000000	10.000000	101.000	<input checked="" type="checkbox"/>
16	cancrinite Fechtelkord -Ex1 Scale Factor	0.000030	0.000001	0.000000	0.000000	2.147484E9	161.000	<input checked="" type="checkbox"/>
17	cancrinite Fechtelkord -Ex1 Overall B	3.460865	0.404351	-0.000069	0.000000	10.000000	181.000	<input checked="" type="checkbox"/>

Exercise 1

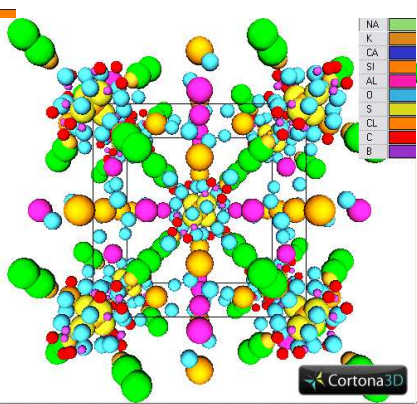
If we look at the structures before and after

Before

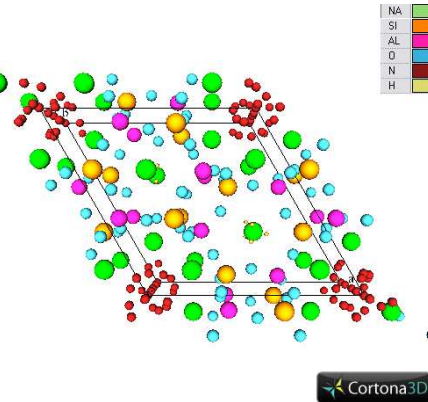
FAU



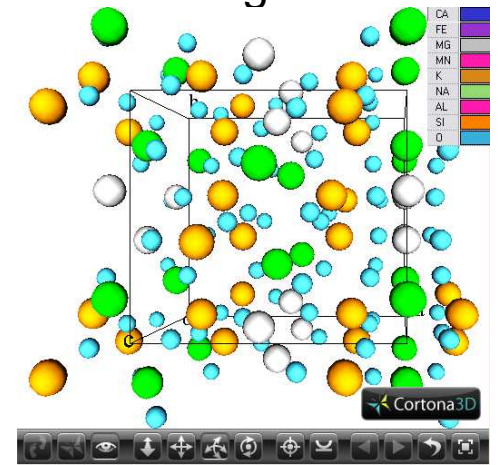
SOD



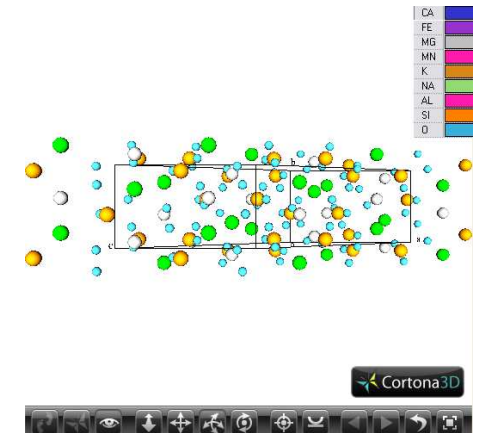
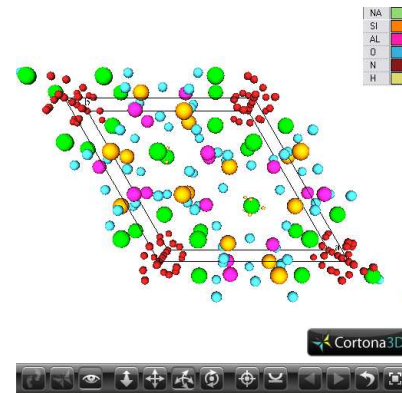
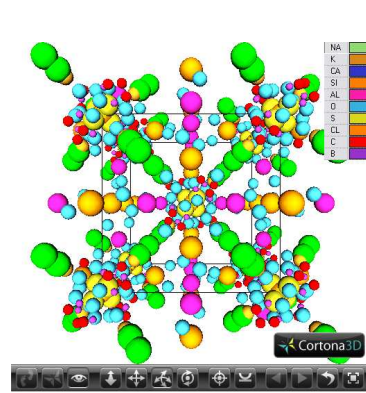
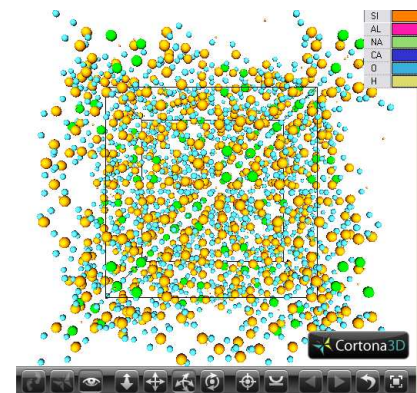
CAN



augite



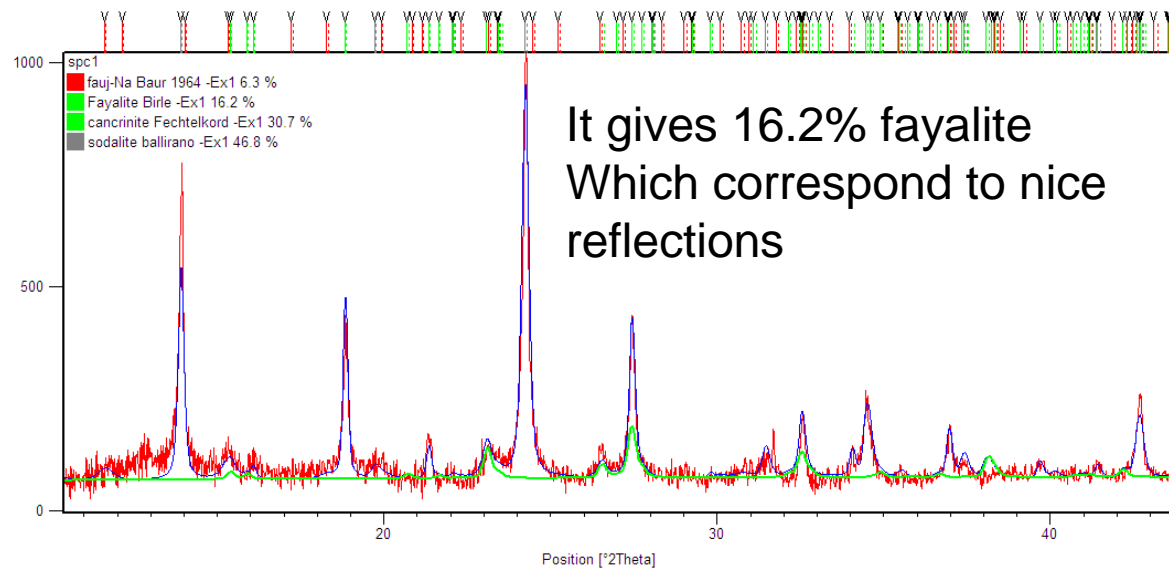
after



Exercise 1

How to check ?

1. Close and open spc1 again
2. Insert sod, canc fau + fayalite structure
3. Run Rietveld
4. Look at the individual phase



The refine values are fairly good

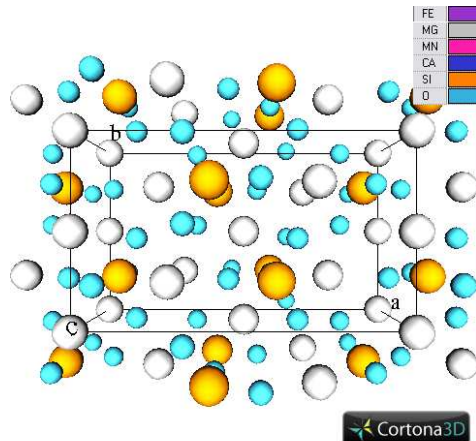
No.	Description	Value	Deviation	Last Shift	Minimum	Maximum	Code	Use Min./M...
1	Zero Shift [$^{\circ}2\theta$]	-0.041905	0.003168	0.000390	0.000000	0.000000	41.000	<input type="checkbox"/>
2	Flat background	61.668970	0.878603	-0.013476	0.000000	0.000000	11.000	<input type="checkbox"/>
3	Coefficient 1	0.617753	0.062118	0.002190	0.000000	0.000000	21.000	<input type="checkbox"/>
4	Coefficient 2	-0.007791	0.000876	-0.000023	0.000000	0.000000	31.000	<input type="checkbox"/>
5	fauj-Na Baur 1964 -Ex1 Scale Factor	0.000000	0.000000	0.000000	0.000000	2.147484E9	51.000	<input checked="" type="checkbox"/>
6	fauj-Na Baur 1964 -Ex1 Overall B	5.449069	2.715352	0.648939	0.000000	10.000000	71.000	<input checked="" type="checkbox"/>
7	fauj-Na Baur 1964 -Ex1 Cell a [Å]	25.146550	0.018362	0.004772	0.000000	0.000000	81.000	<input type="checkbox"/>
8	fauj-Na Baur 1964 -Ex1 Profile W	0.296919	0.013020	0.001335	-1.000000	10.000000	61.000	<input checked="" type="checkbox"/>
9	Fayalite Birle -Ex1 Scale Factor	0.000036	0.000002	0.000000	0.000000	2.147484E9	91.000	<input checked="" type="checkbox"/>
10	Fayalite Birle -Ex1 Overall B	10.000000	0.926359	7.976365	0.000000	10.000000	111.000	<input checked="" type="checkbox"/>
11	Fayalite Birle -Ex1 Cell a [Å]	11.123330	0.004991	0.003526	0.000000	0.000000	121.000	<input type="checkbox"/>
12	Fayalite Birle -Ex1 Cell b [Å]	5.167479	0.002146	-0.007446	0.000000	0.000000	131.000	<input type="checkbox"/>
13	Fayalite Birle -Ex1 Cell c [Å]	6.702837	0.004560	0.000446	0.000000	0.000000	141.000	<input type="checkbox"/>
14	Fayalite Birle -Ex1 Profile W	0.075161	0.009018	-0.009326	-1.000000	10.000000	101.000	<input checked="" type="checkbox"/>

Exercise 1

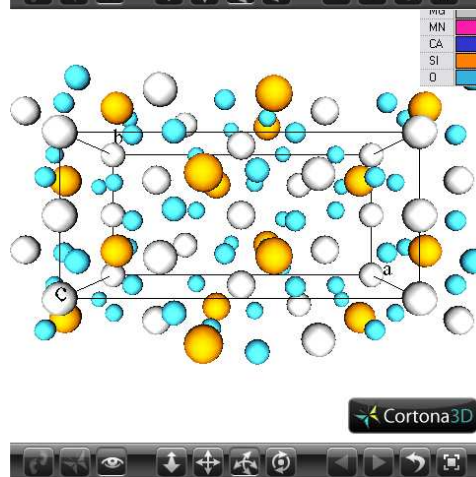
If we look at the structures before and after

fayalite

Before



after



That look good!

HOWEVER, the sample we analyzed is the product of the precipitation at room temperature of Si, Al, Na, Cs and Sr.

There is **not a single chance** that fayalite would:

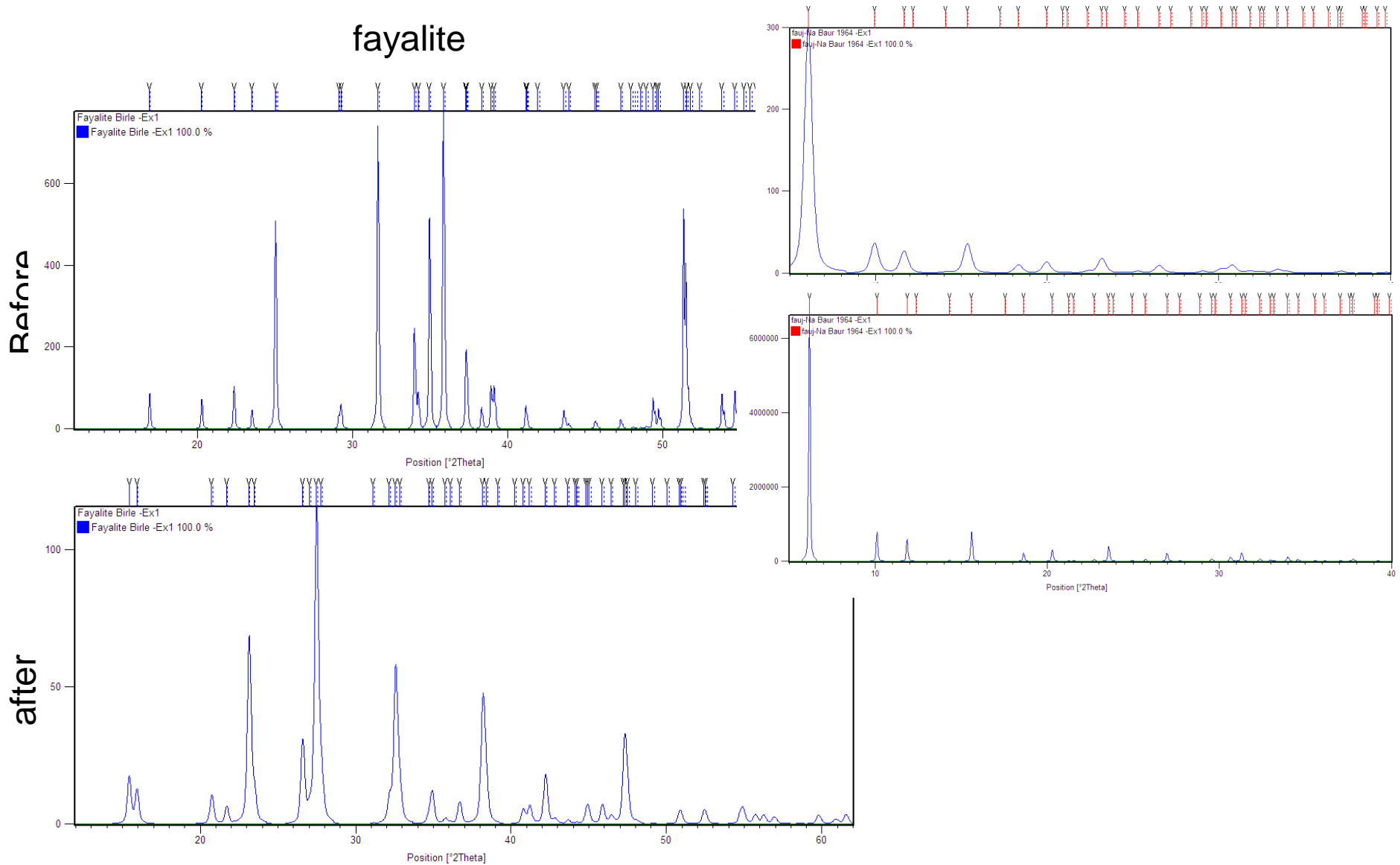
1. Precipitate at room temperature
2. Form in the absence of Fe.

In any case, Rietveld is a mathematical module that **requires YOU to do the perfect work** of peak characterization. Rietveld wants to fit anything you feed it with.

Exercise 1

If we look at the spectrum before and after

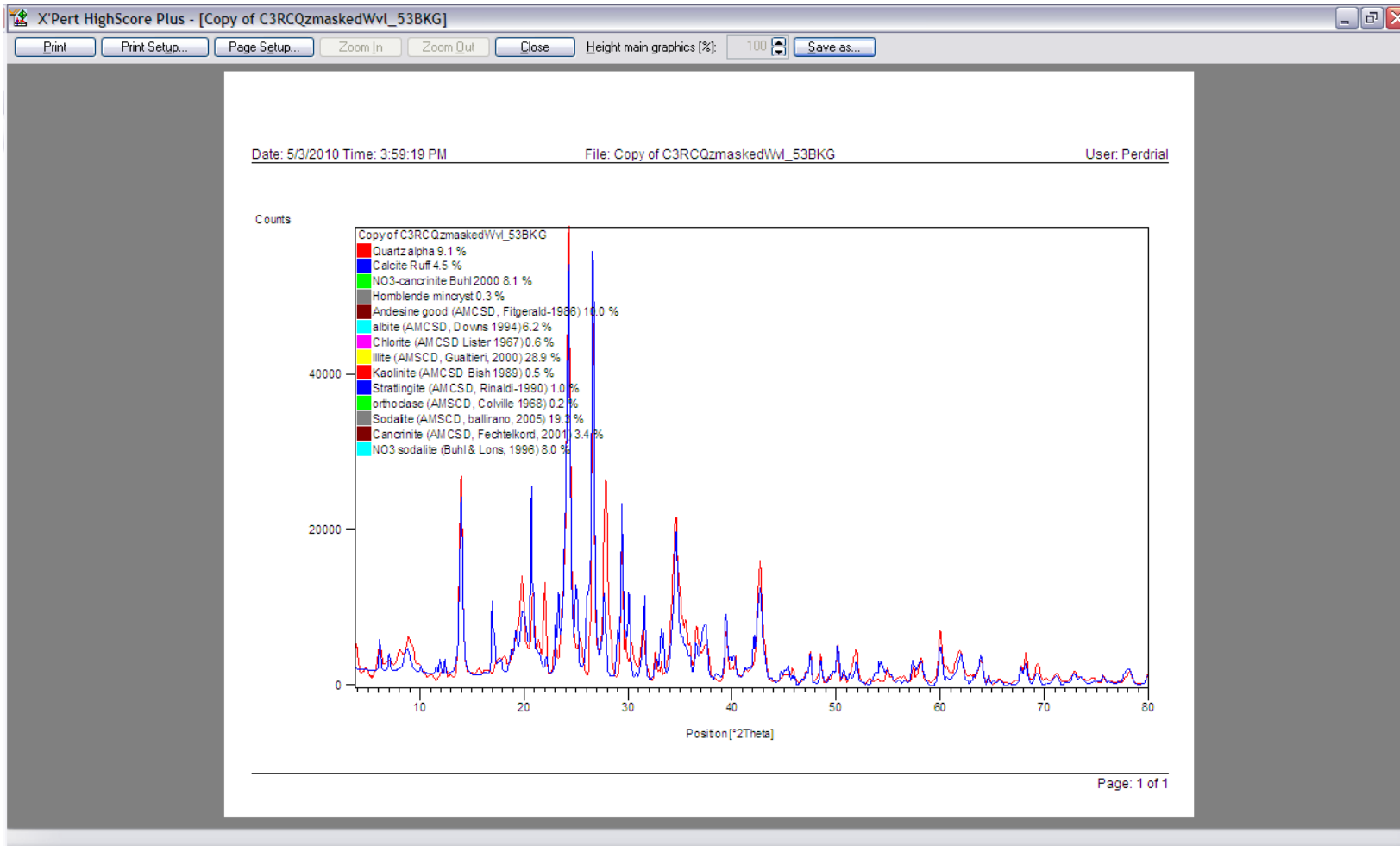
fayalite



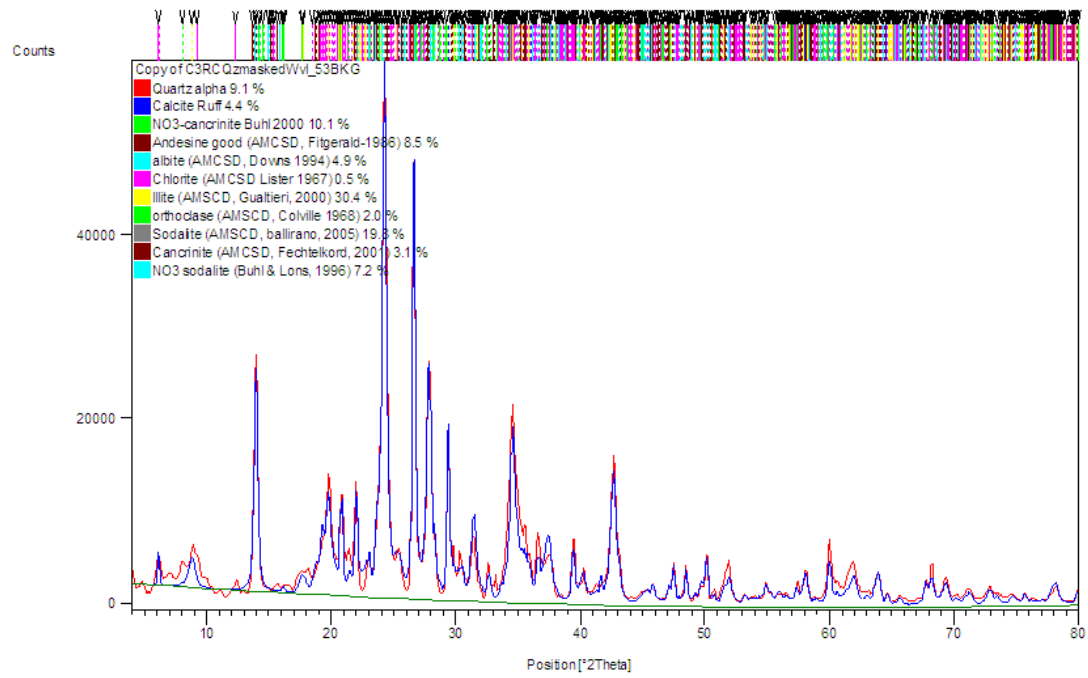
Exercise 2

Open spc2

Insert structure 2 and.. try to make it good...



Date: 5/3/2010 Time: 4:05:51 PM File: Copy of C3RCQzmaskedWvl_53BKG User: Perdrial



Misc. tips

- Removing background.
 - Highscore plus not very good, use manual removing for better quality.

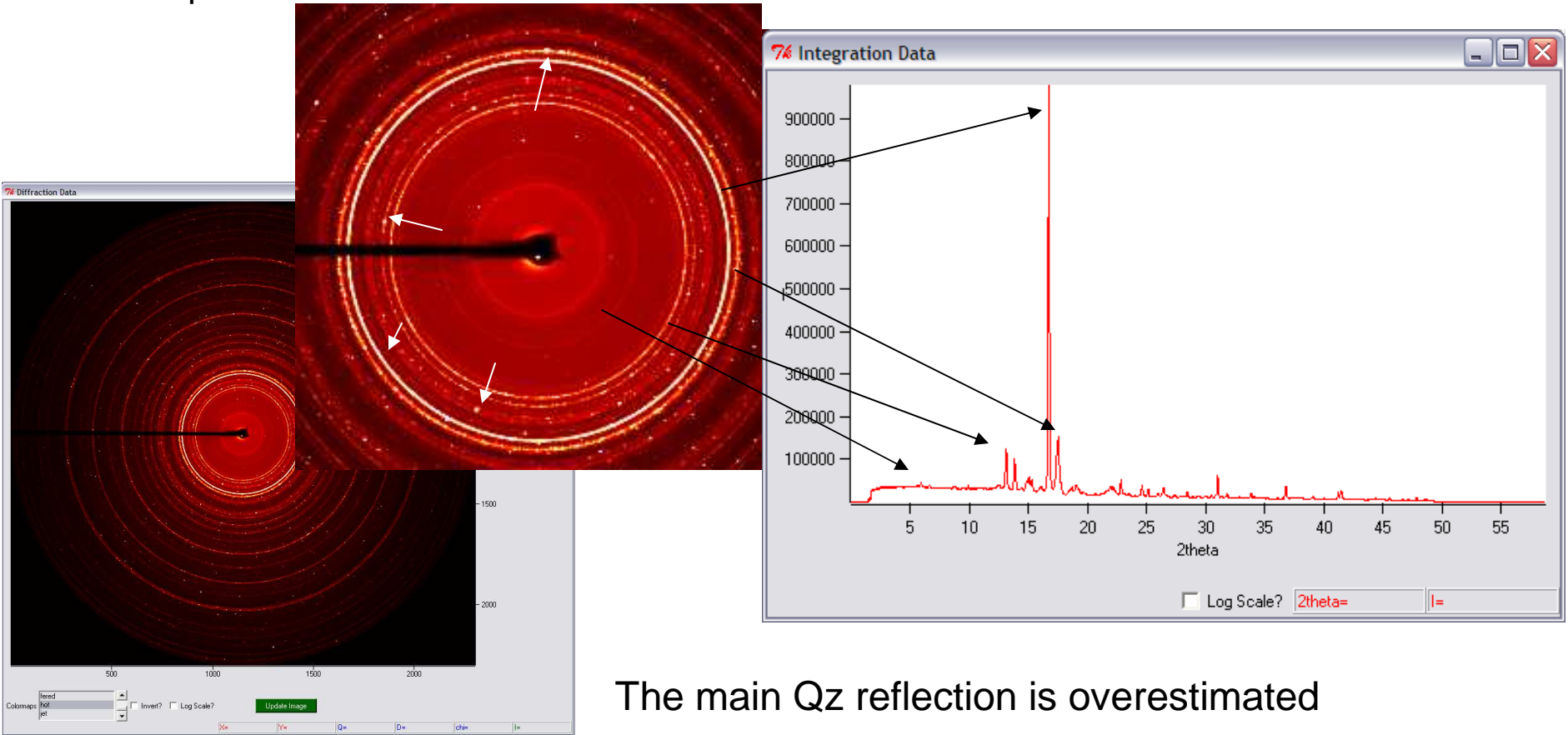
Be careful, Rietveld doesn't like negative values.

 - Possible to remove in excel or origin if bkgd acquired separately.
 - Other softwares

Misc. Tips

If spectra acquired at the synchrotron, there is often a particle size effect. It produces overflows (pixel saturation in the detector). Using masks allows to get rid of such overflows.

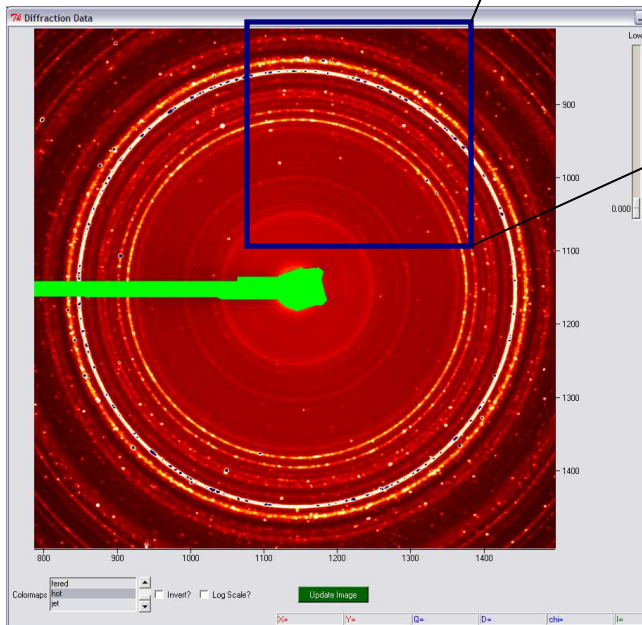
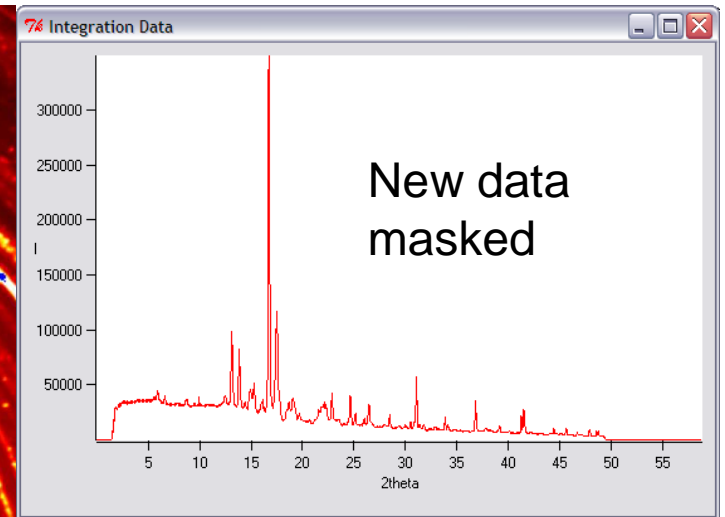
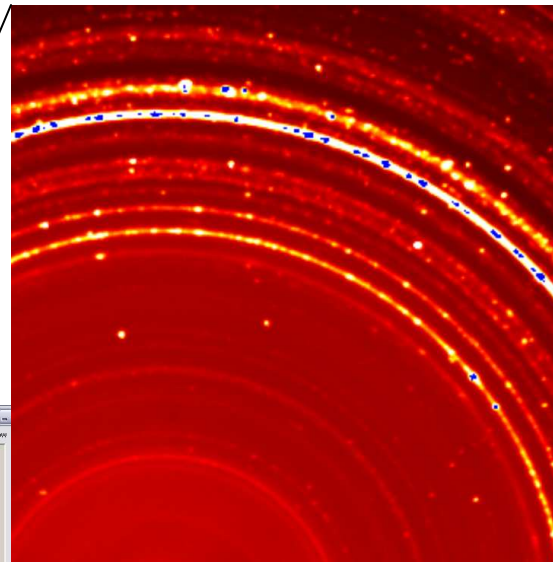
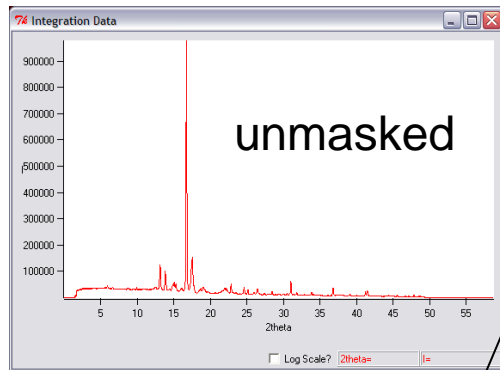
Example.



The main Qz reflection is overestimated

Misc. Tips

In order to correct from that I assumed my quartz to standard, i.e. having a constant 100/011 peak intensity ratio equal to 4.67. With the raw file we have $I_{100/011} = 9.91$



The Area Diffraction Machine

File Calibration Masking Cake Integrate Macro Help

Calibration Masking Cake Integrate

Masking Options

Value reflects counts

Threshold Masking

Do Greater Than Mask?

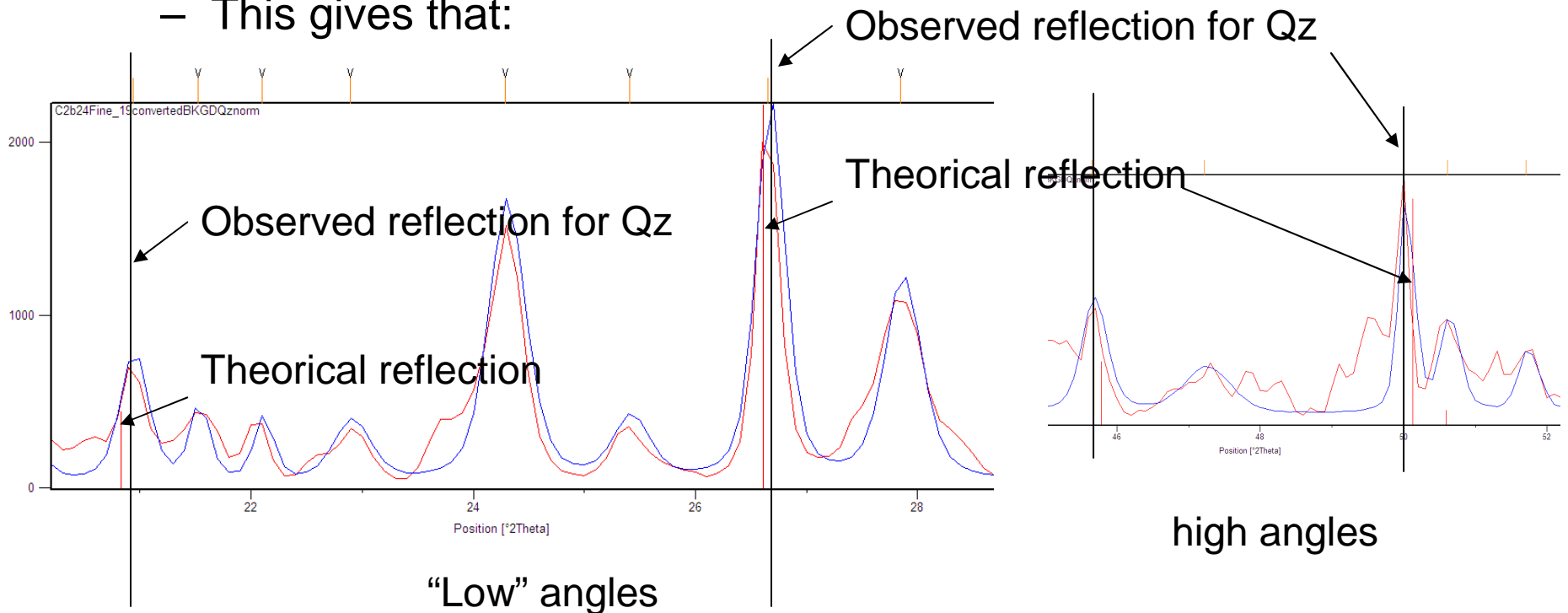
(Pixels Can't Be) Greater Than Mask: 1340000

Polygon Masking

Do Polygon Masking

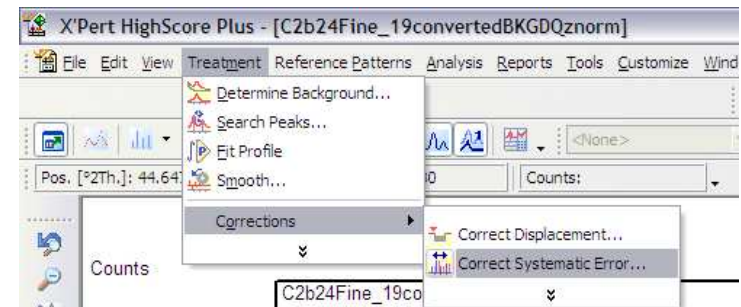
Misc. tips

- Correcting from systematic displacement
 - Particularly useful (needed) when using synchrotron-XRD.
 - Sometimes the LaB6 is bad leading to a bad calibration (as it was the case last time).
 - This gives that:



Misc. tips

- X'Pert has a function for that.
- Open spc 3
- Do peak search and search and match.
- Assign Quartz
- See the unmatching
- Go to correction systematic error. In select standard choose SiO₂ and accept polynomials.
- Go back to select stds, select none and hit recall polynomials, select SiO₂- ok, then correct, check with Quartz standard



Misc. tips

- To add your own std
- Open the Qz Antao file and simulate pattern, then search peaks, then fit profile (both in treatments)
- Go to correction systematic error. In select standard choose add new stad, name it and OK