Quantitative X-Ray Diffraction

X’Pert Highscore Plus

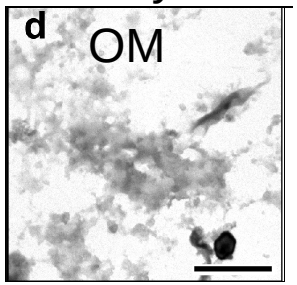
Rietveld Module

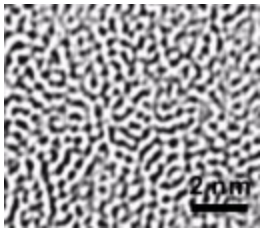
05/28/2010 Nico Perdrial

Principles of X-Ray diffraction

There is two types of solid material:

- Amorphous: Atoms are randomly arranged in a define volume

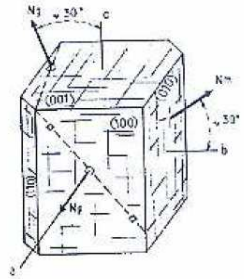


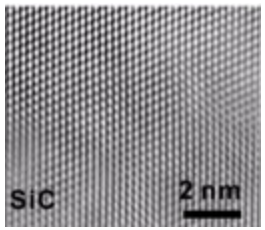


HRTEM

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”



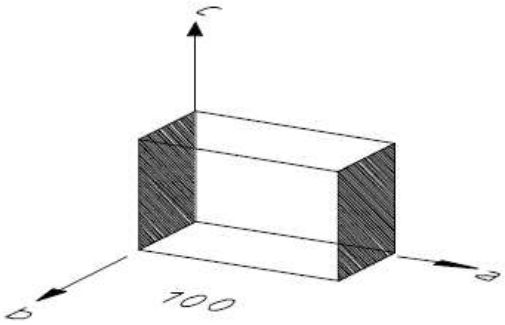


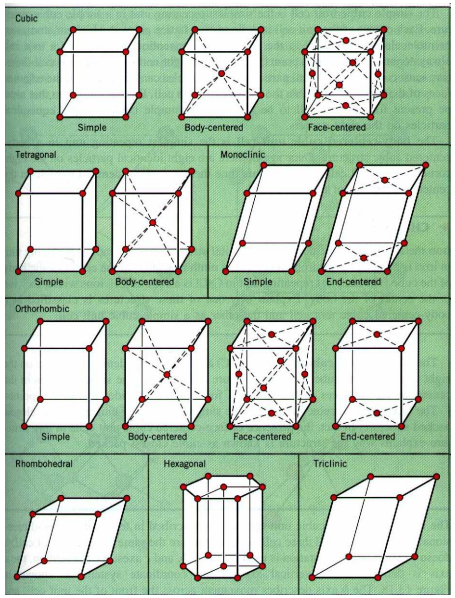
http://www.nano.drexel.edu/research/projects/cdc

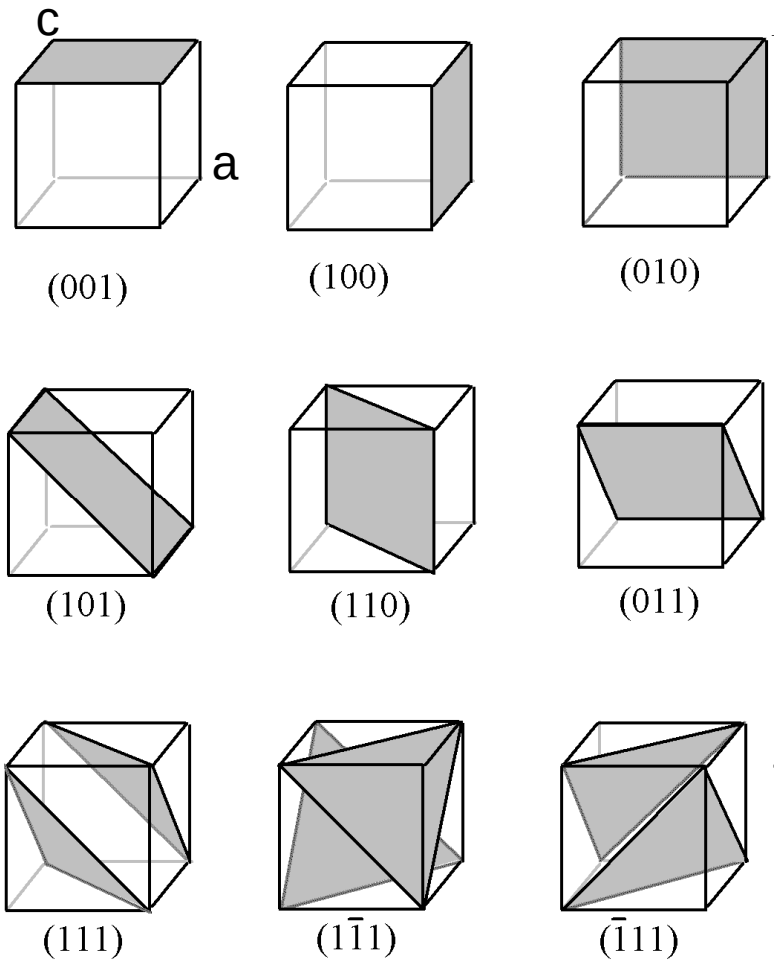
http://www.scielo.org.ve/scielo.php?pid=S0255-69522001000200009&script=sci_arttext

The unit cell

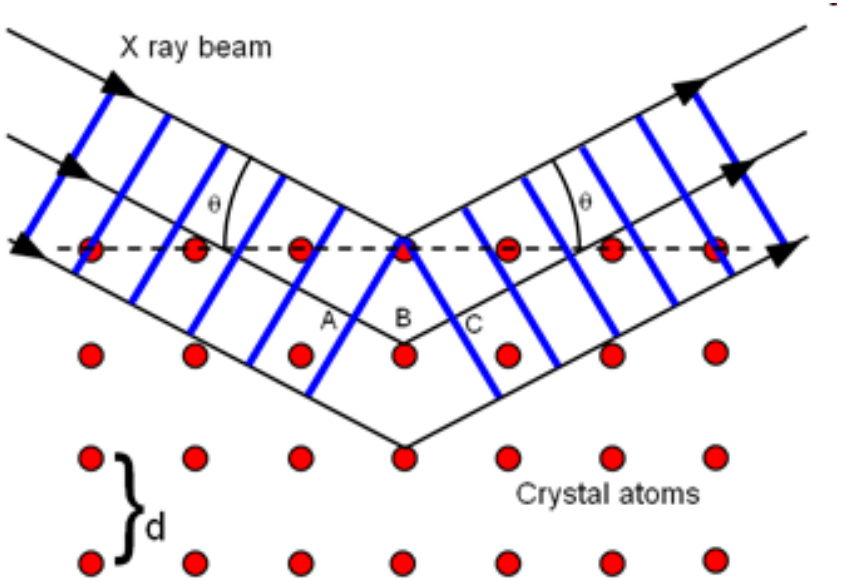
Always defined by three axes: a, b & c which help defining the h, k ,l plans







X-Ray diffraction



BRAGG LAW

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

where:

d = lattice interplanar spacing of the crystal

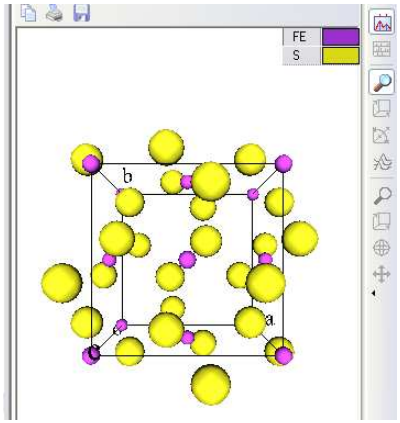
θ = x-ray incidence angle (Bragg angle)

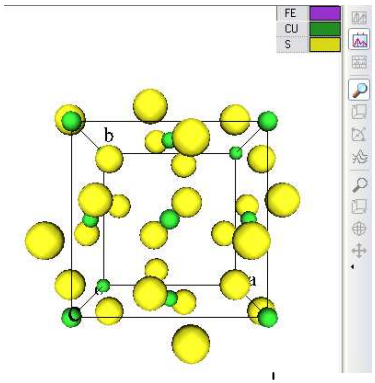
λ = wavelength of the characteristic x-rays

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

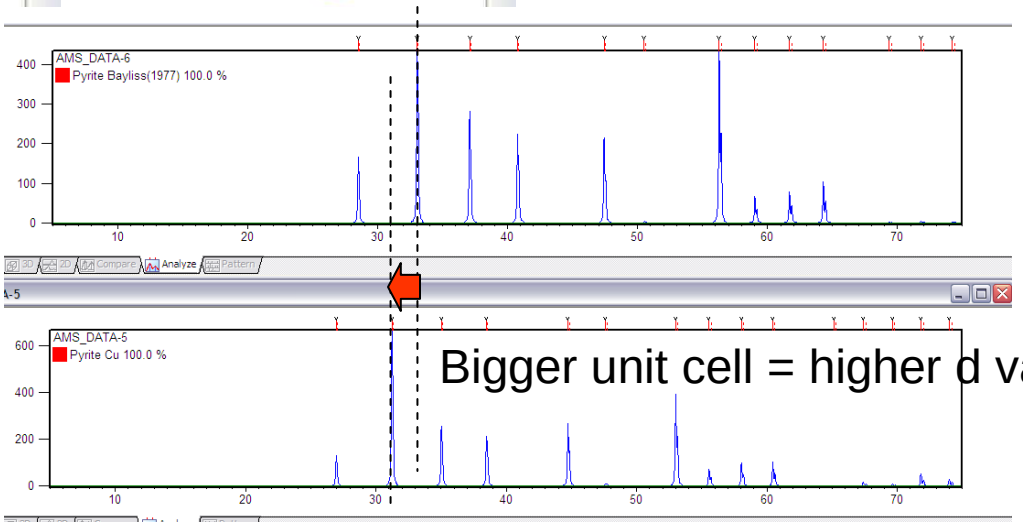
X-Ray diffraction

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



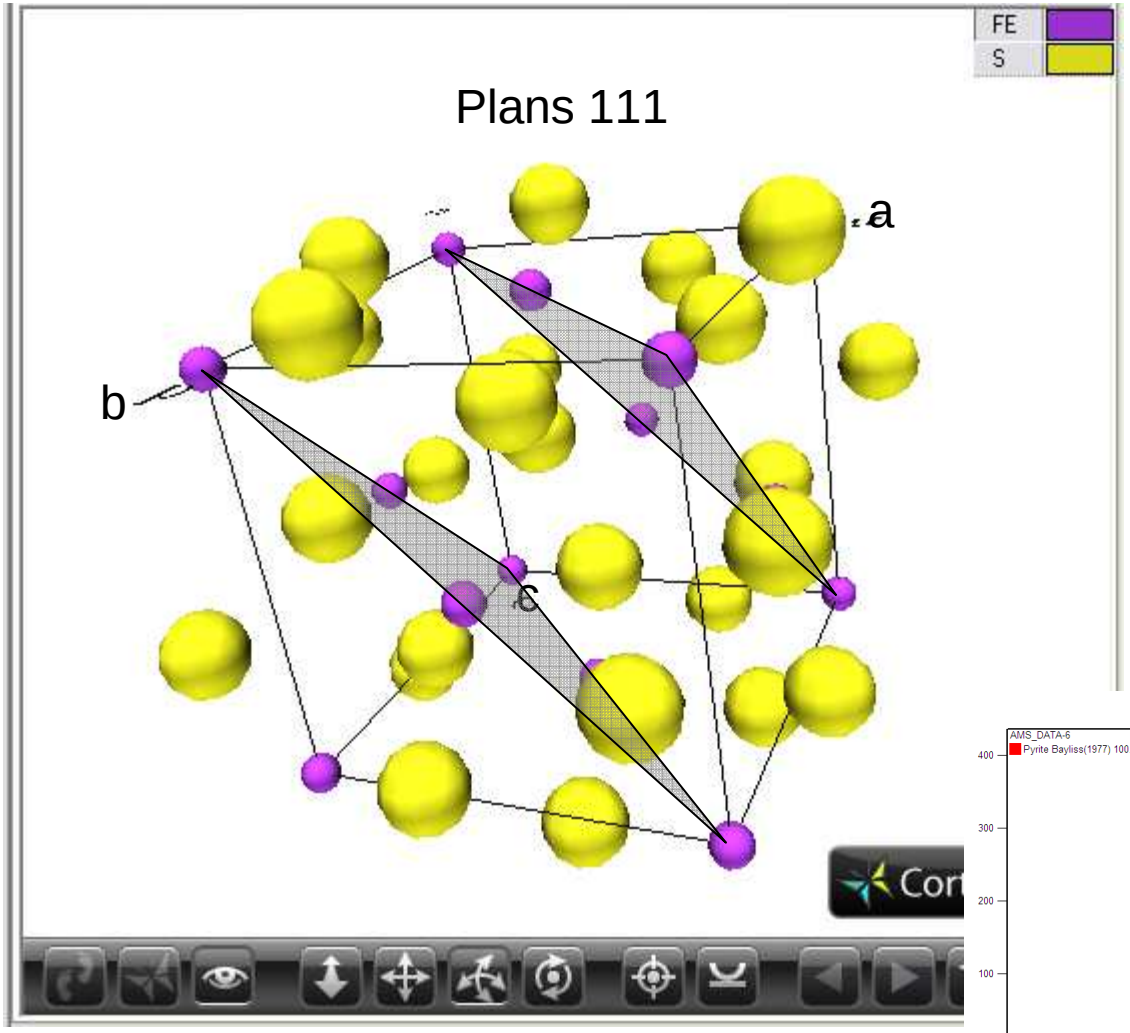


Pyrite	Pyrite Cu
a [Å],5.41700	a [Å],5.72500
b [Å],5.41700	b [Å],5.72500
c [Å],5.41700	c [Å],5.72500
alpha [°],90.00000	alpha [°],90.00000
beta [°],90.00000	beta [°],90.00000
gamma [°],90.00000	gamma [°],90.00000
Volume [Å^3],158.95580	Volume [Å^3],187.640
Assumed Crystal System,Cubic	Assumed Crystal Syste
Crystal System,Cubic	Crystal System,Cubic



Bigger unit cell = higher d values

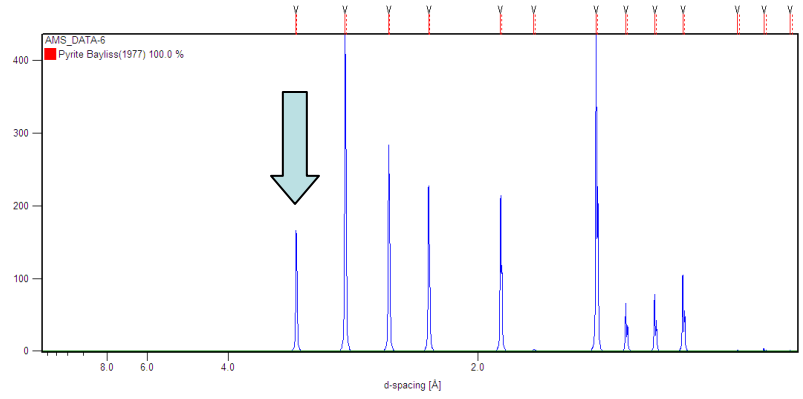
X-Ray diffraction



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

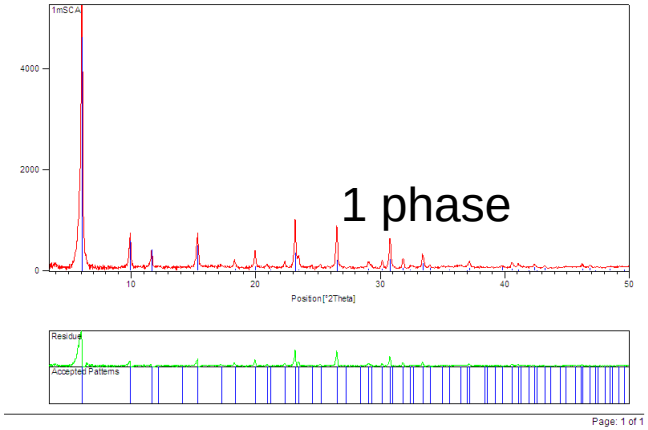
d = 3.83 A

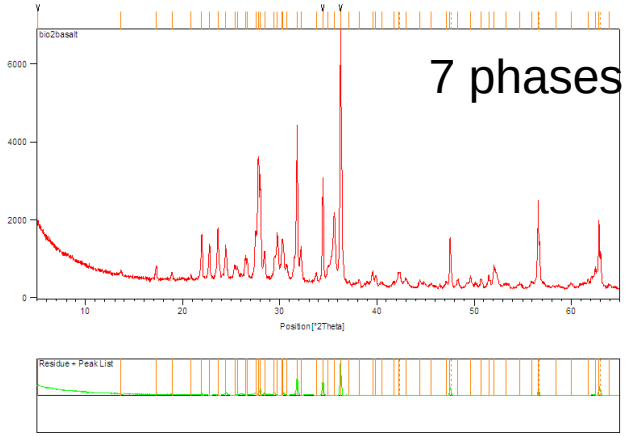
Minus the atomic radius of Fe (0.64A)
d = 3.19 (approx)

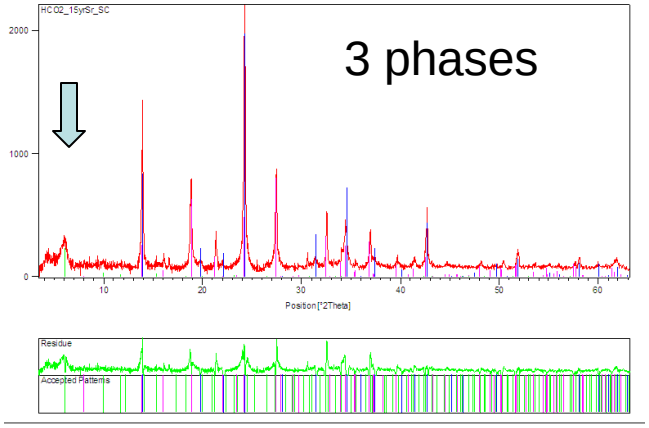


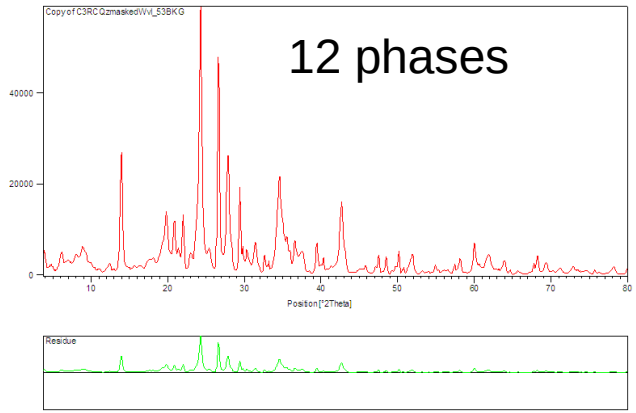
X-Ray diffraction

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









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

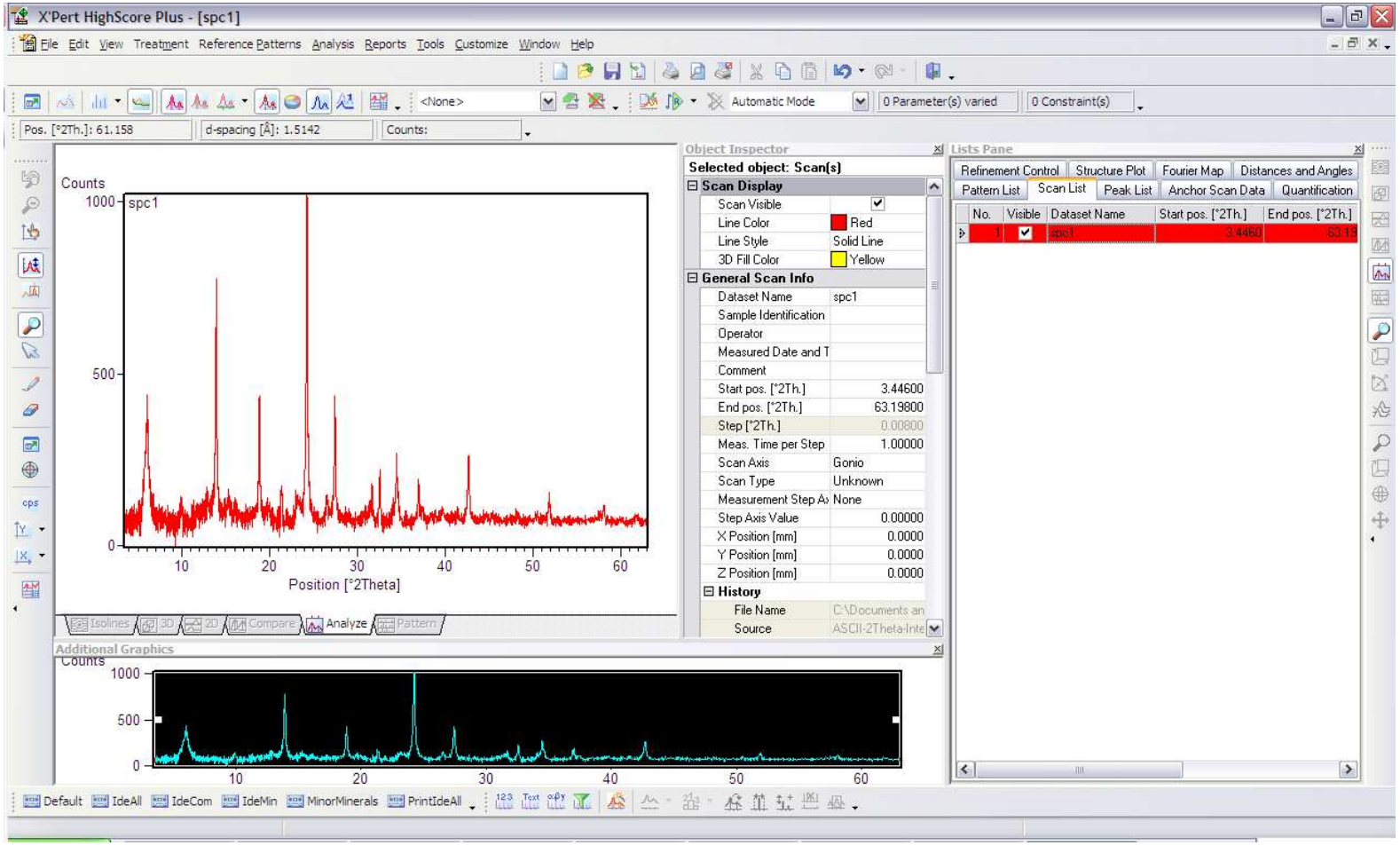
The initial publi can be found here:

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

Rietveld refinement in highscore

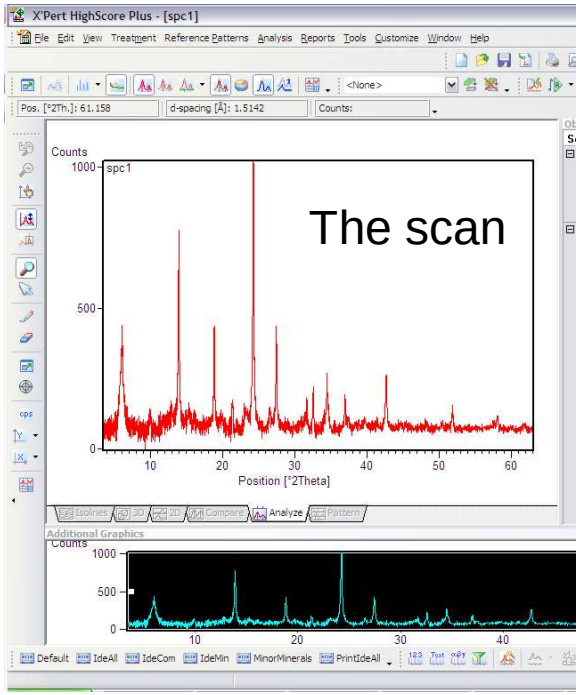
The Highscore plus interface

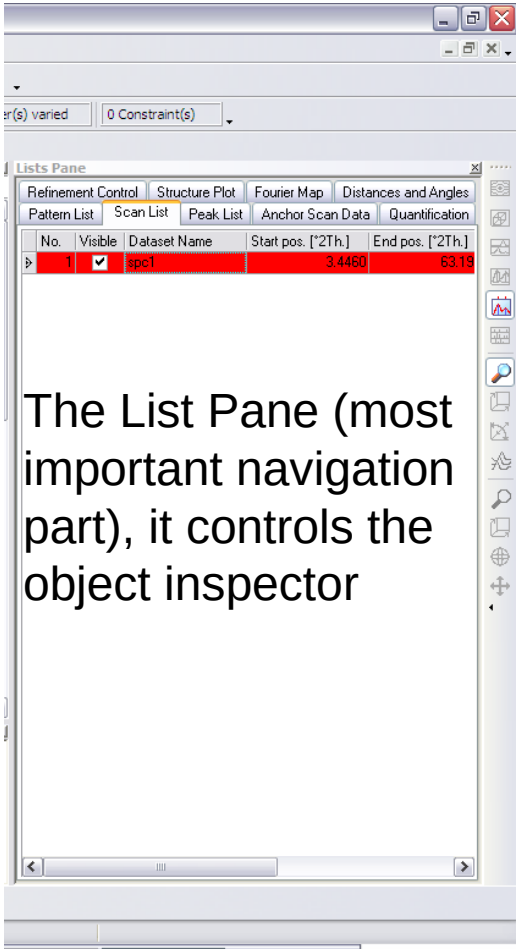
1. Open Highscore
2. Open spc1.asc
3. Select spc1 in Scan list tab

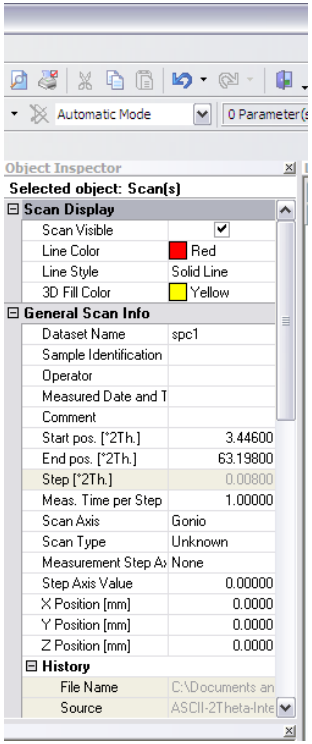


Rietveld refinement in highscore

The Highscore plus interface



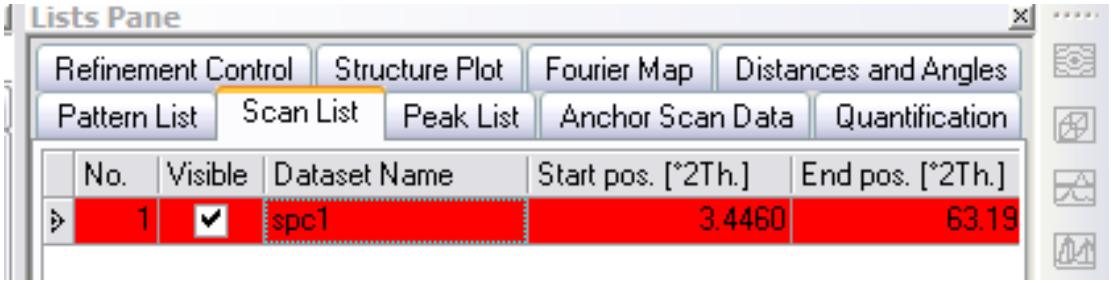


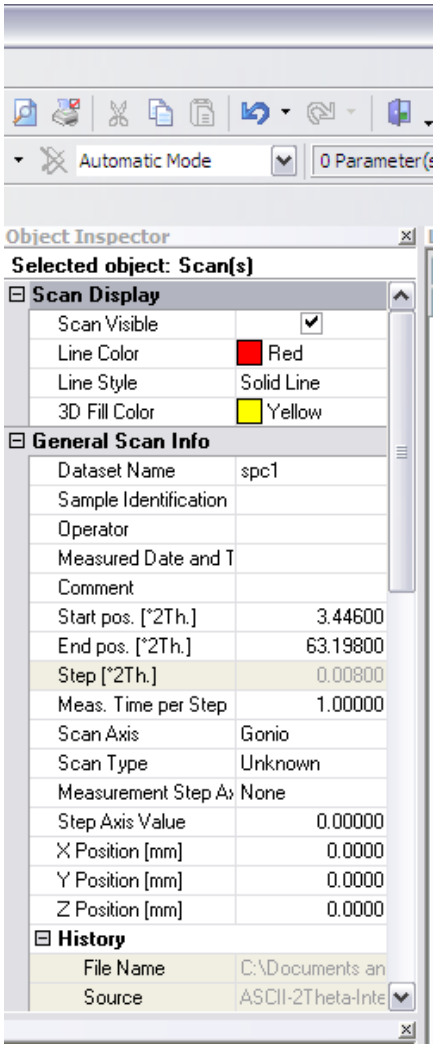


The object inspector provide important informations

Rietveld refinement in highscore

The Highscore plus interface

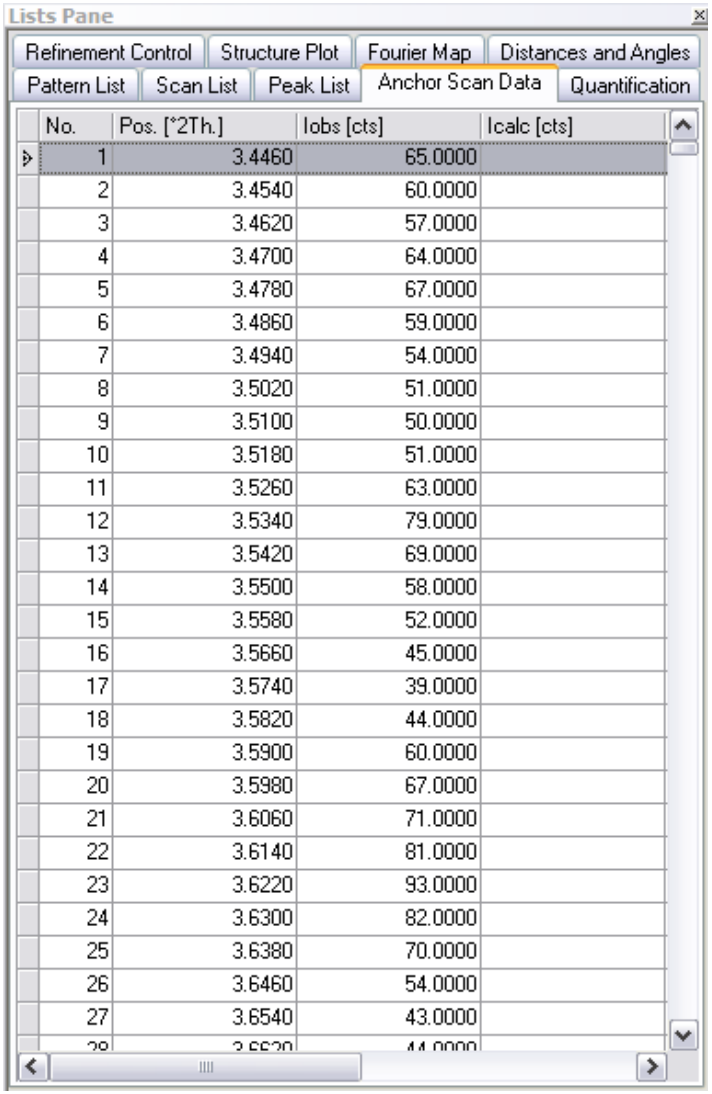




The scan tab allow to select the spectrum.
In the corresponding object inspector, you can modify the name, the color the starting/ending positions of the scan.

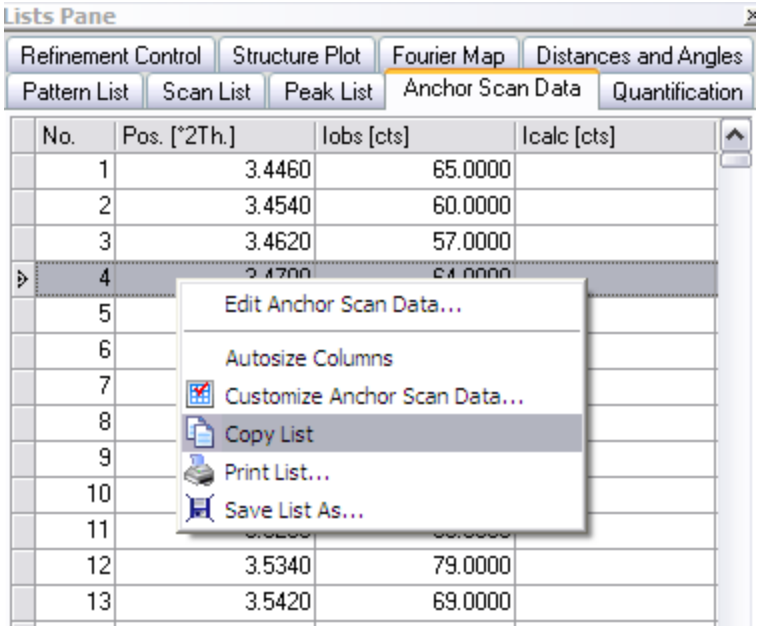
Rietveld refinement in highscore

The Highscore plus interface



No.	Pos. [°2Th.]	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	

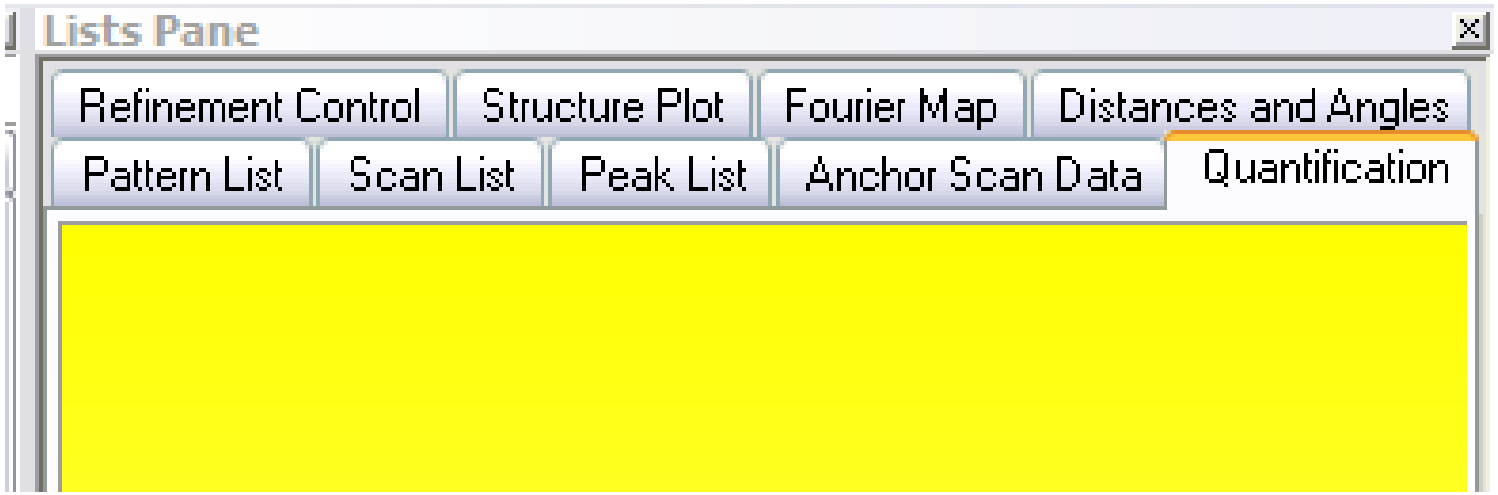
The Anchor scan data tab (very important) provides the actual numerical data of the displayed graph.
Right click on the list allows to copy the data that you can paste in excel



Rietveld refinement in highscore

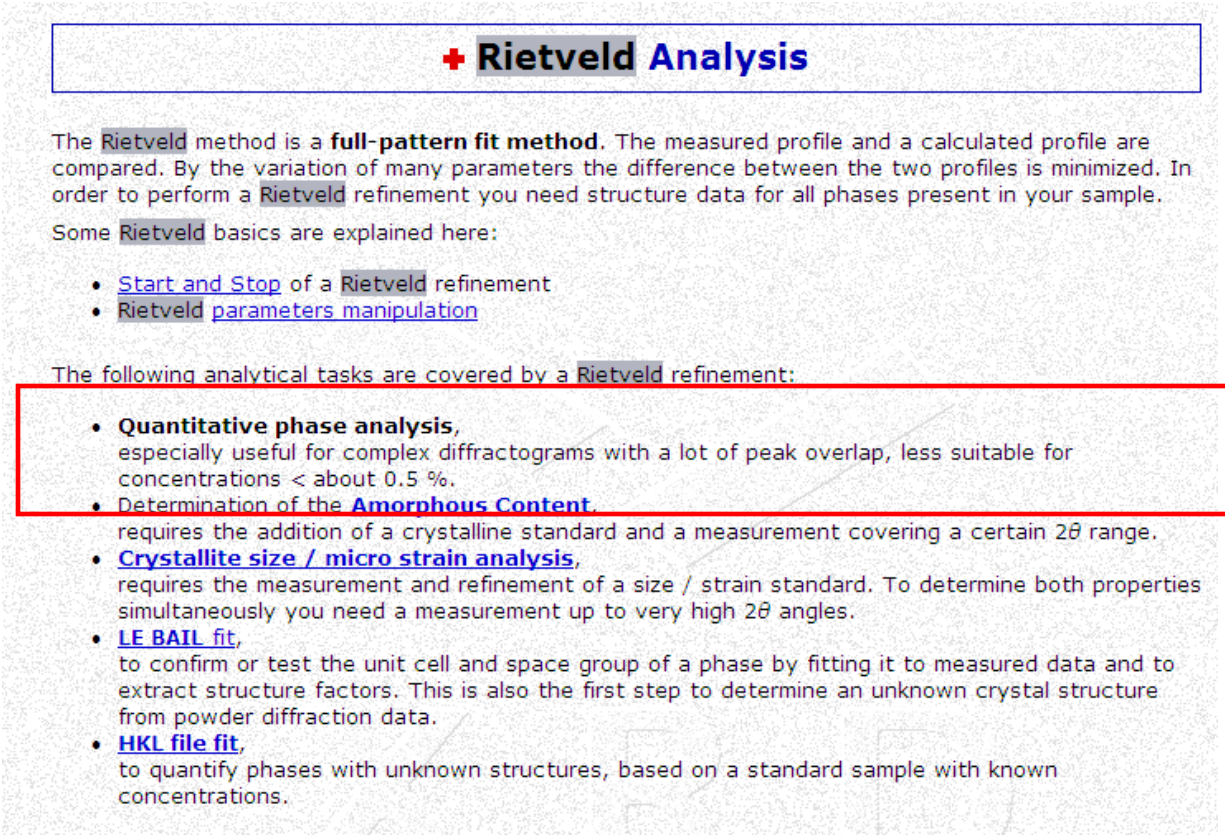
The Highscore plus interface

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:

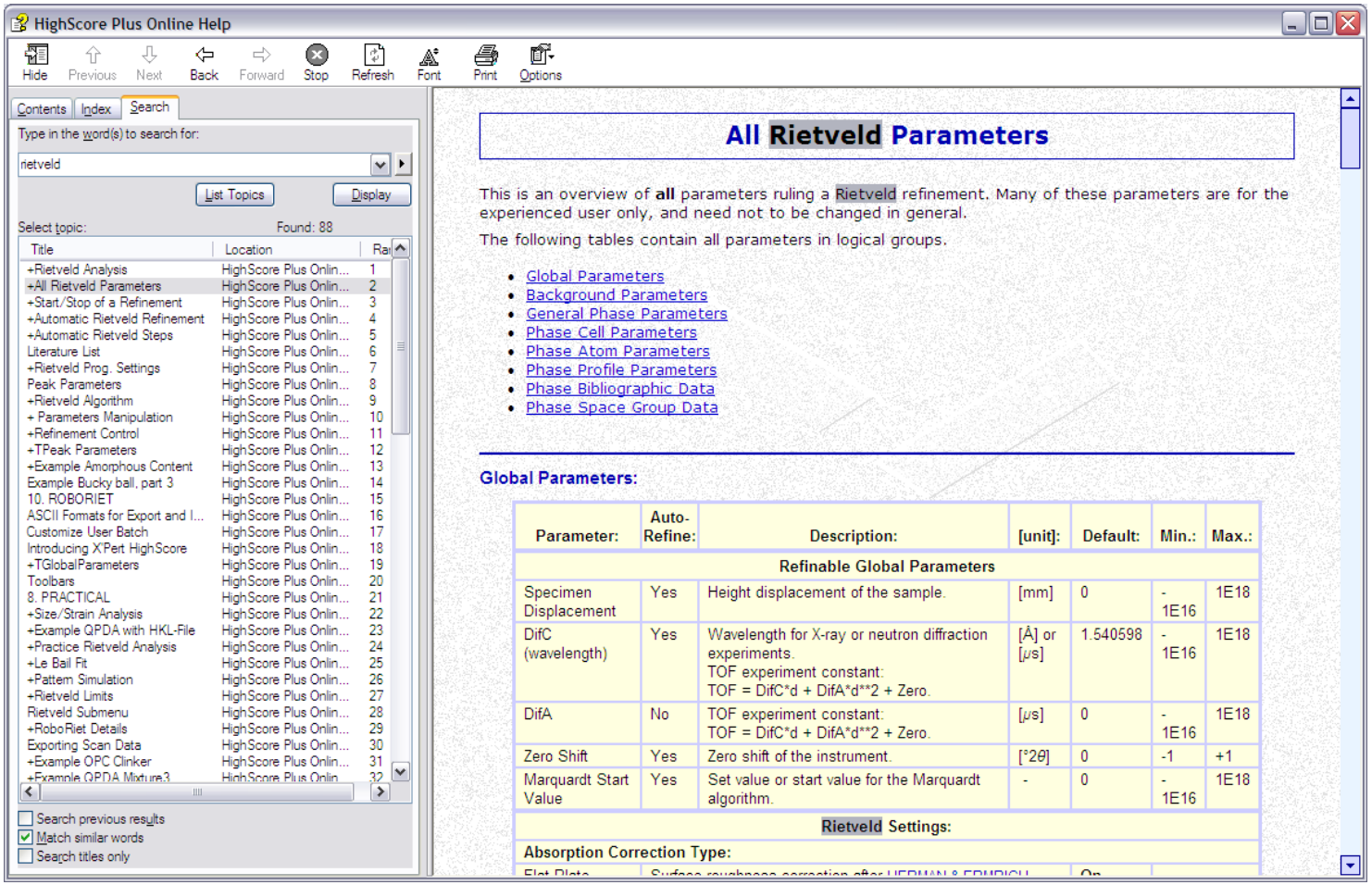
- Start and Stop of a Rietveld refinement
- Rietveld parameters manipulation

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



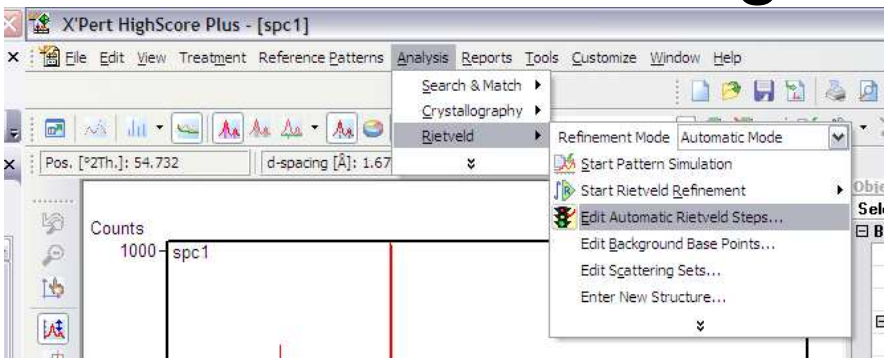
Rietveld refinement in highscore

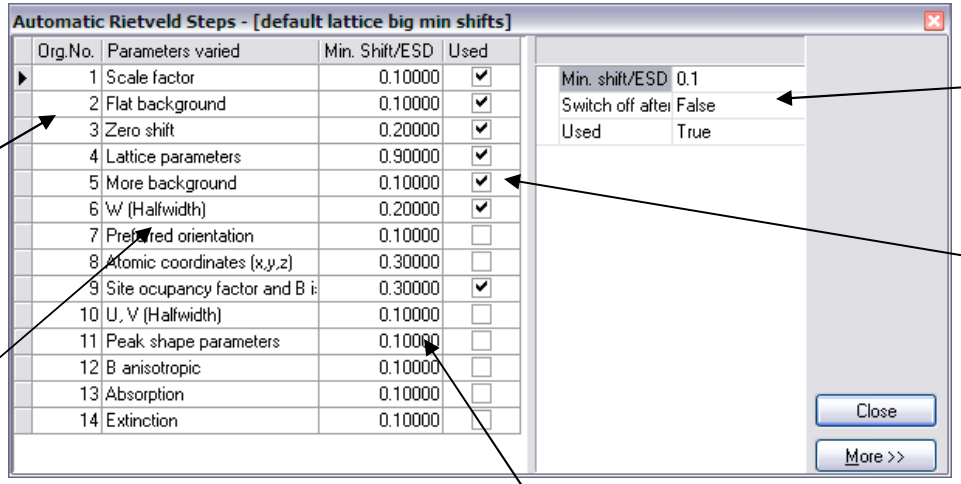
- We can change a lot of parameters but many of them MUST not be change.

- 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:





Switch/unswitch after used.

Order of steps

Activation box

parameter

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	☑	Modify the scale of each phase to better fit
2	Flat background	0.10000	☑	Flatten the background to get rid of amorphous
3	Zero shift	0.20000	☑	Shift the spectrum to correct systematic error
4	Lattice parameters	0.90000	☑	Modify the lattice parameters
5	More background	0.10000	☑	Add background to correct small angle uncertainties
6	W (Halfwidth)	0.20000	☑	Variation of the principal halfwidth coefficient
7	Preferred orientation	0.10000	☐	Modify peaks intensity to allow pref orient of plates
8	Atomic coordinates (x,y,z)	0.30000	☐	Modify atom positions
9	Site ocupancy factor and B i:	0.30000	☑	Modify site occupancy and general displacement
10	U, V (Halfwidth)	0.10000	☐	Variation of the 2 other halfwidth coefficients
11	Peak shape parameters	0.10000	☐	Modify the “gaussianity” of the peaks
12	B anisotropic	0.10000	☐	Vary degree of freedom of atoms in the structure
13	Absorption	0.10000	☐	Unvolontary absorption of radiations (e.g. from Cu)
14	Extinction	0.10000	☐	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 Mincryst 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

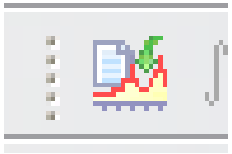
Also any published structure can be added to your reference library

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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6. Go back
7. Click on **Download CIF data**
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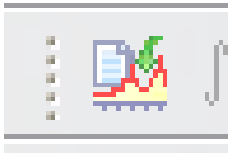
By simulating pattern



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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

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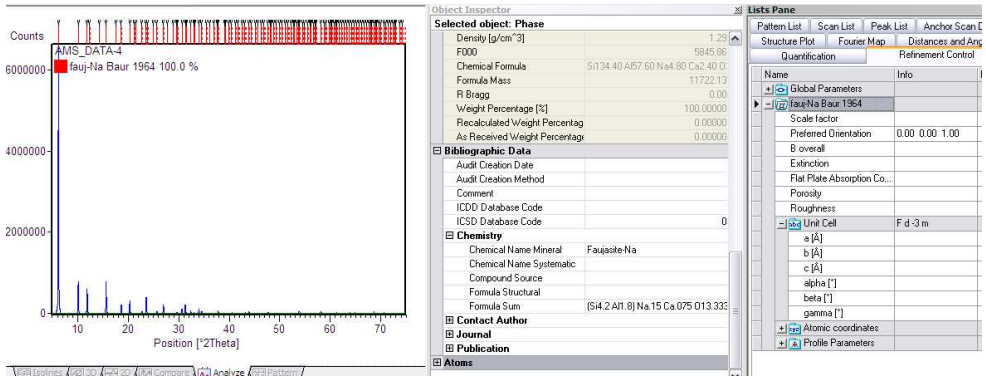
Download CIF data (View Text File)
Download diffraction data (View Text File)
View JMOL 3-D Structure

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.

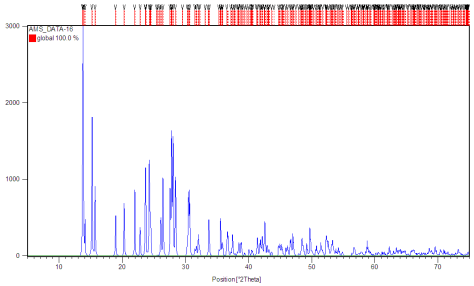
12. Lets add more minerals in the dbs.
Sodalite from ballirano (last in the list)
Cancrinite from Fechtelkord (first in the list)
Fayalite from Birle et al (first)
Augite from Bindi (first)

Do not close the widow

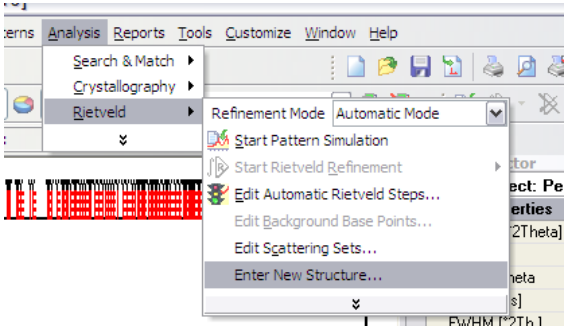
Building a reference library

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 !!



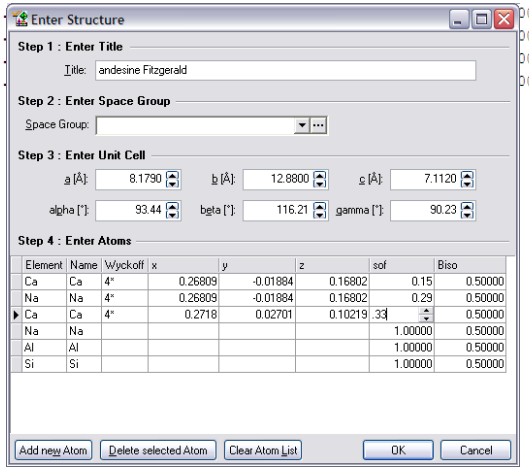
3. we need to enter the data manually.



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
OA1	.00387	.13025	.98101		.01141	.00352	.00750	.00086	.00582	.00103
OA2	.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									00411	.00040
OCm									00194	-.00009
ODo									00127	.00069
ODm									00004	-.00069



5. Add file to references

Do not close the widow

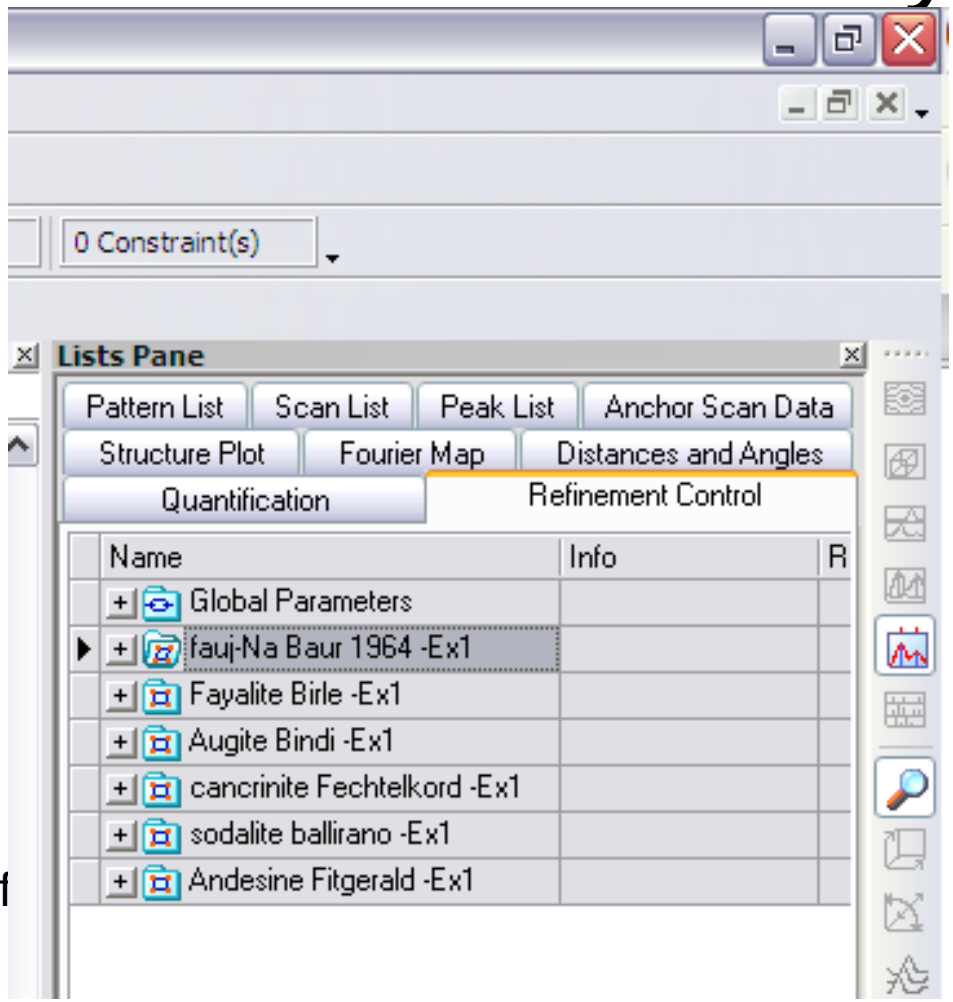
Building a crystal structure library

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”



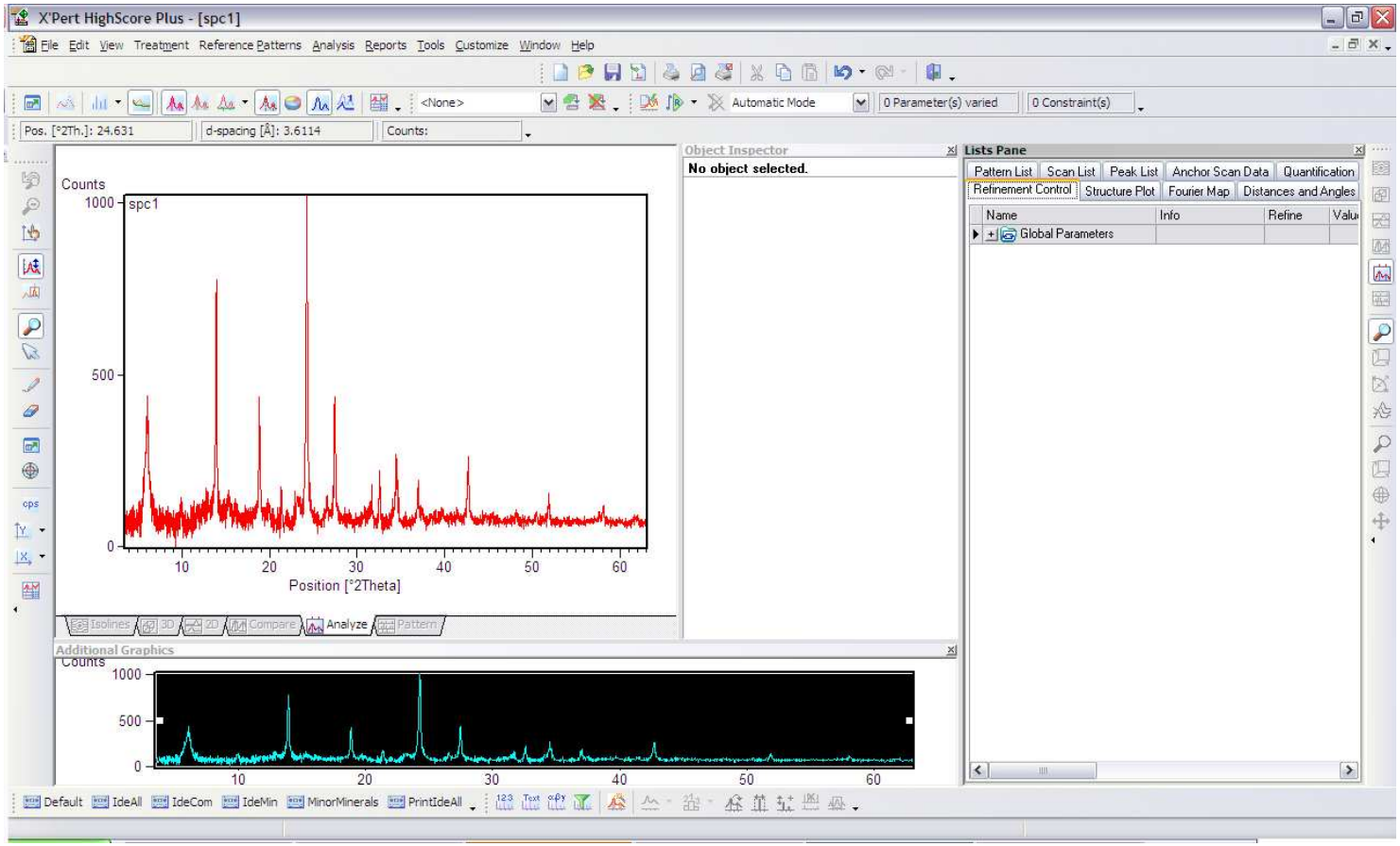
Rietveld refinement in highscore:

EXERCICE 1

Quantification of homogeneous nucleation of hyper alkaline solution

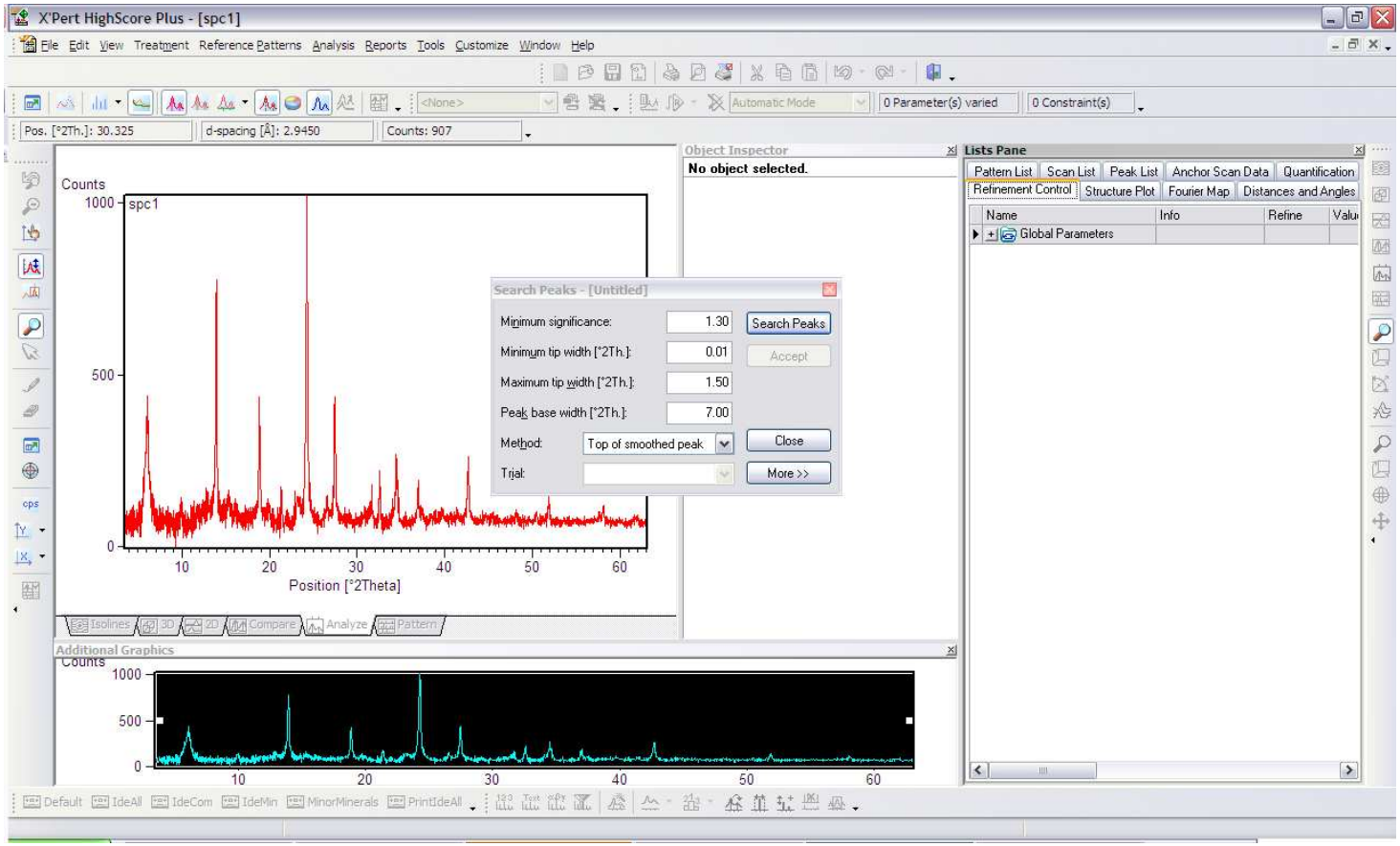
EXERCICE 1

1. Open spc1



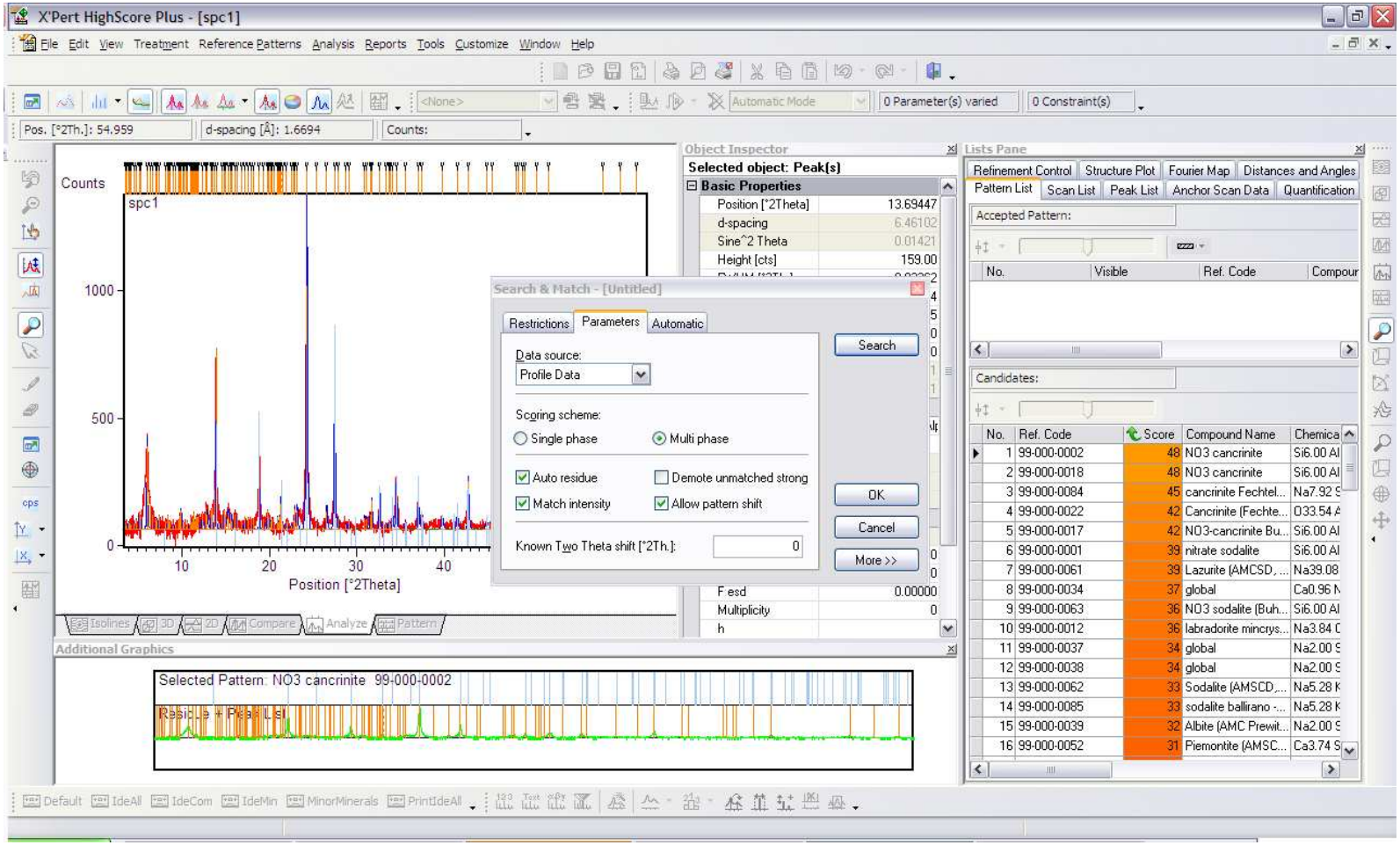
EXERCICE 1

1. Go toTreatment → Search Peaks → Accept



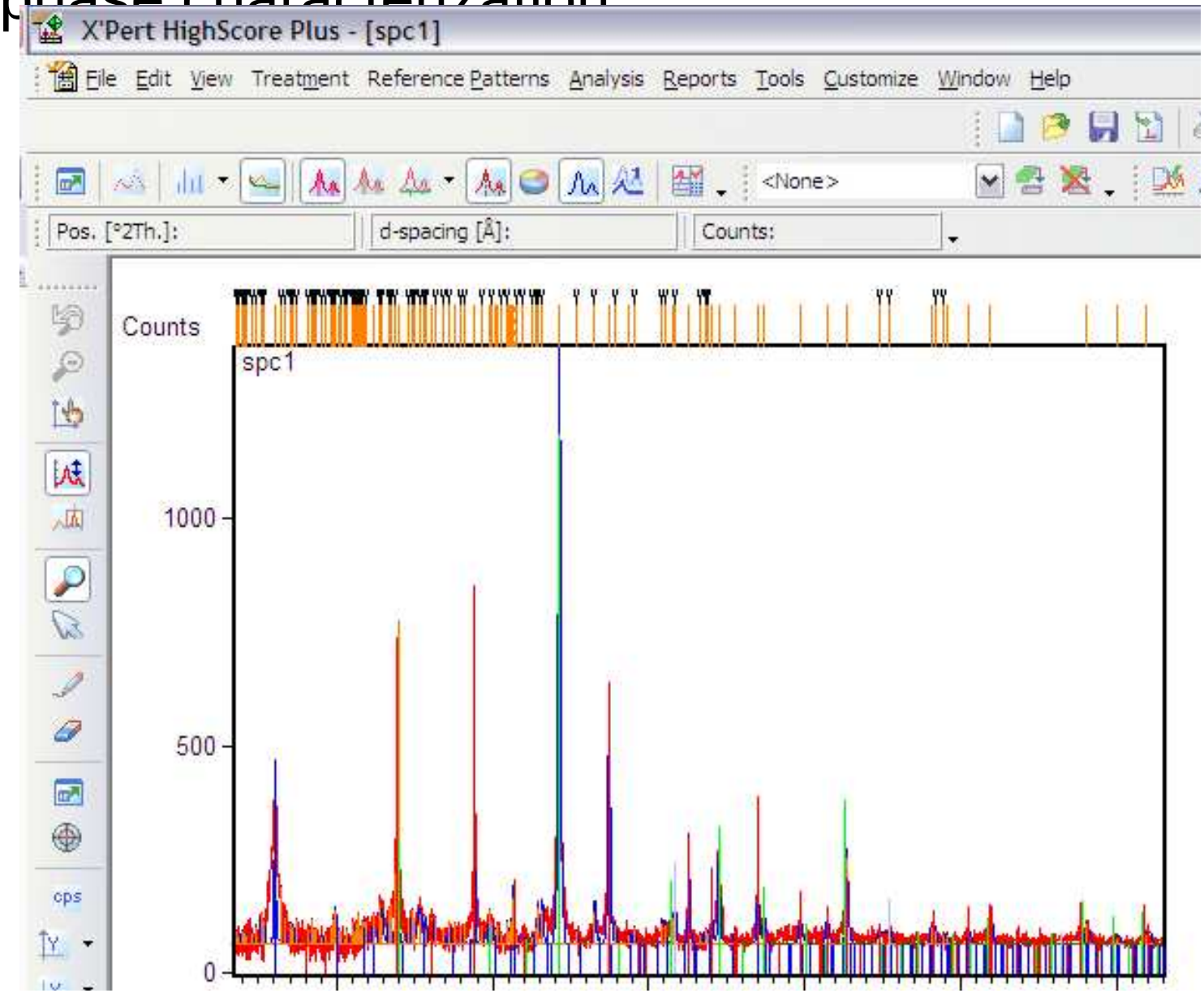
EXERCICE 1

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



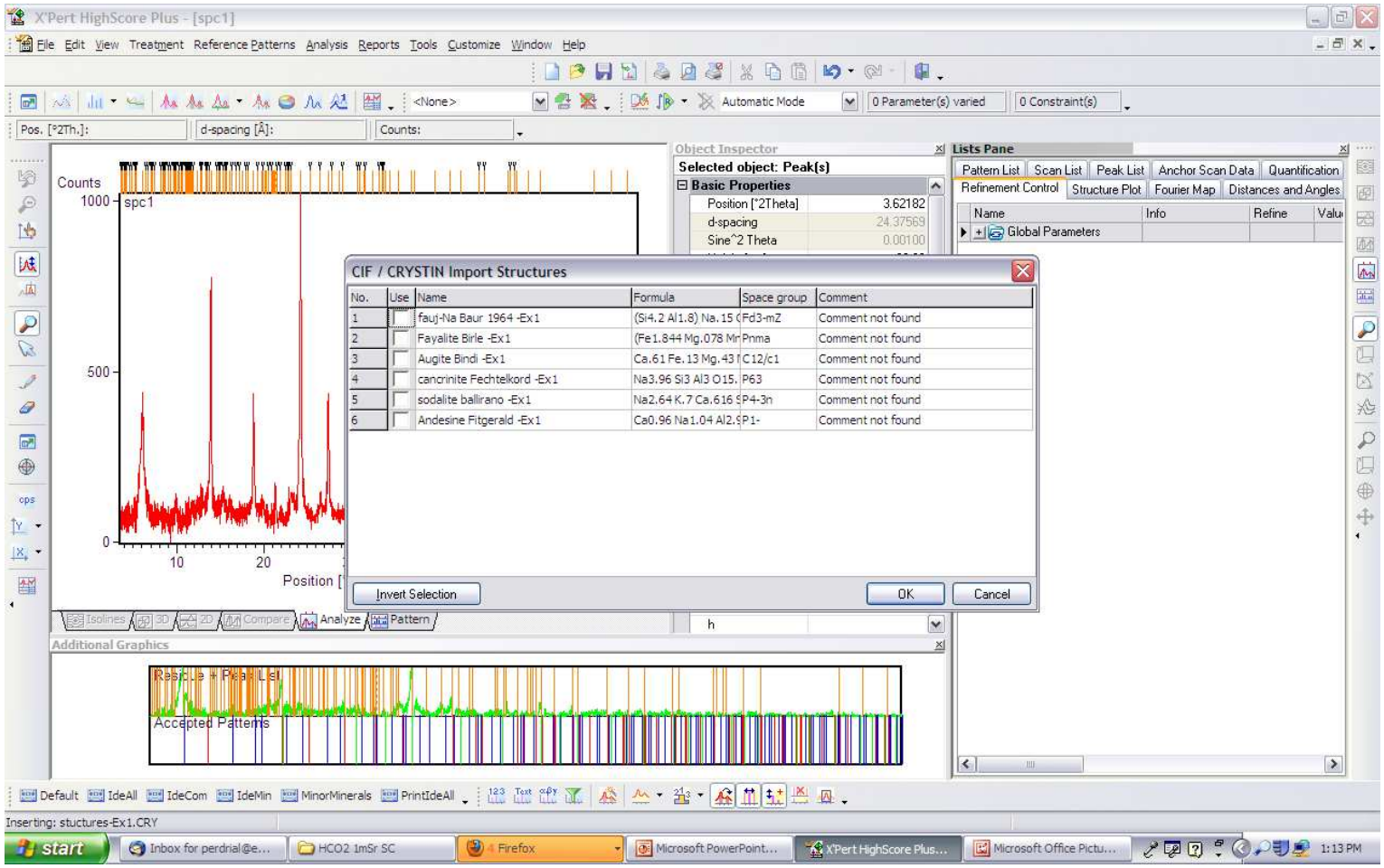
EXERCICE 1

1. Do the phase characterization



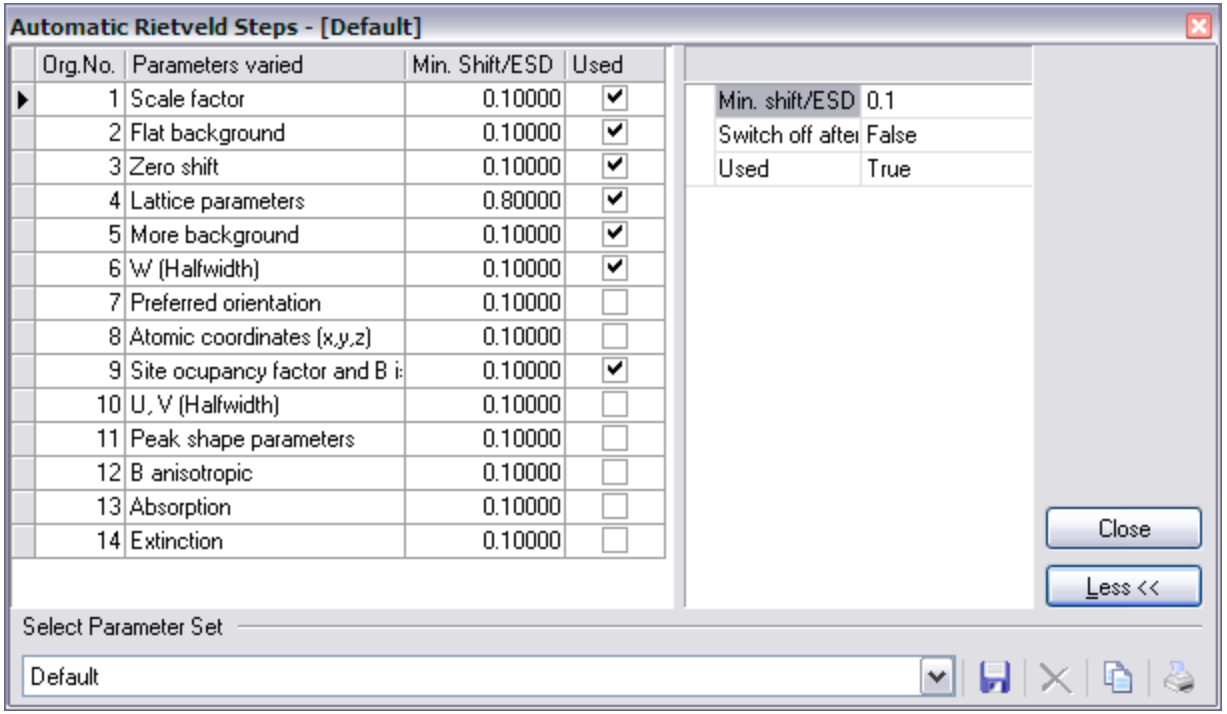
EXERCICE 1

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



EXERCICE 1

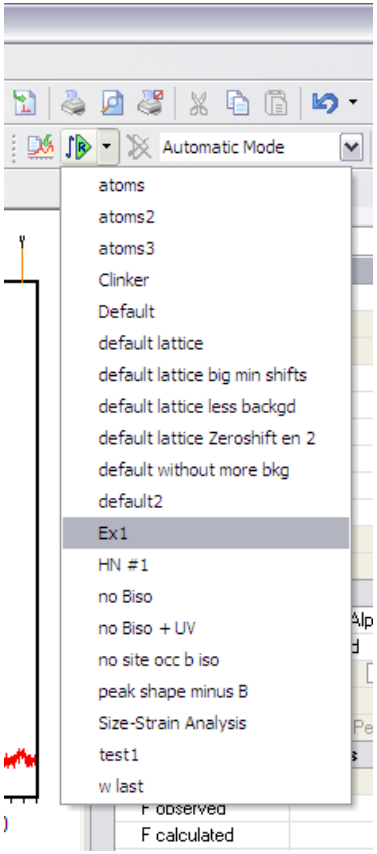
1. Phases are now in the Refinement Control Tab
2. Let's look at the parameters. Open the automatic Rietveld steps, deselect all except the first one. Then click more, disc icon and name Ex1

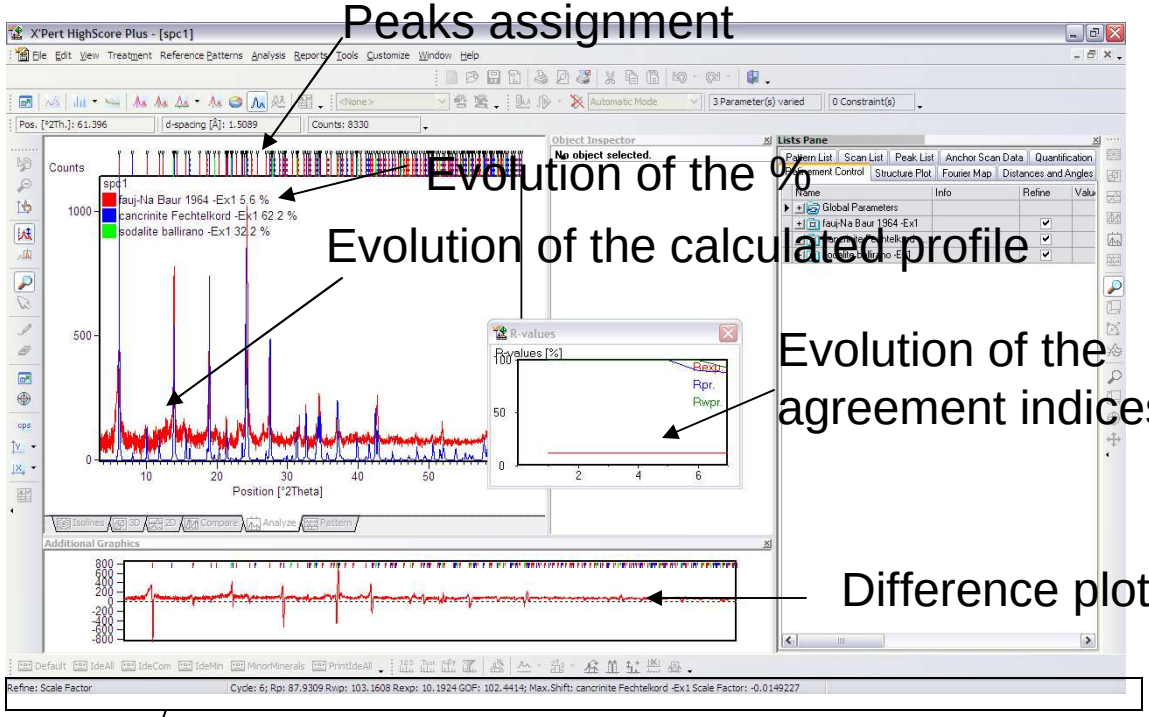


Exercise 1

1. We are testing the effect of the first param
2. Run rietveld:

That modified the peak intensities

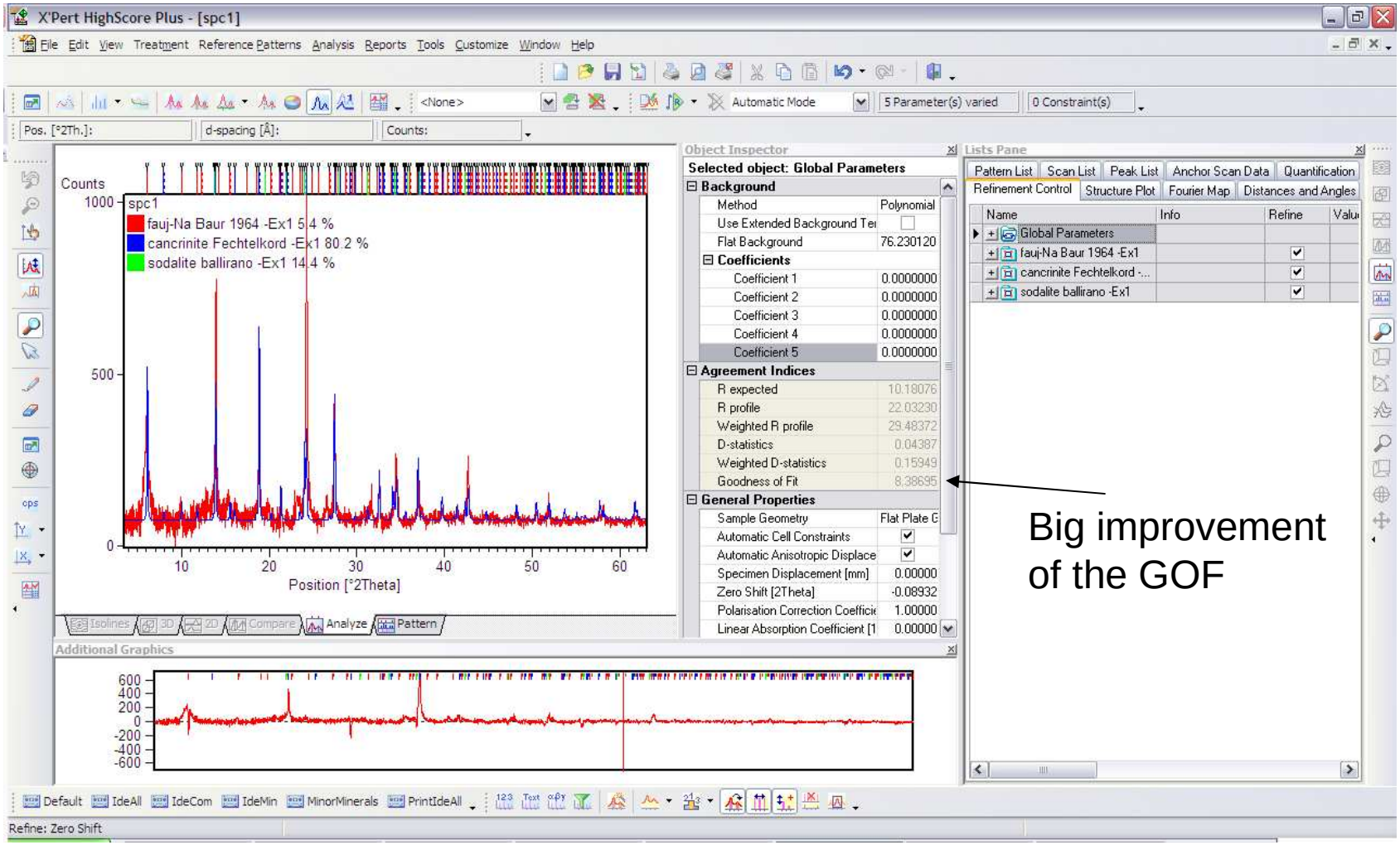




Refine: Scale Factor
Cycle: 6; Rp: 87.9309 Rwp: 103.1608 Rexp: 10.1924 GOF: 102.4414; Max.Shift: cancrinite Fechtelkord -Ex1 Scale Factor: -0.0149227

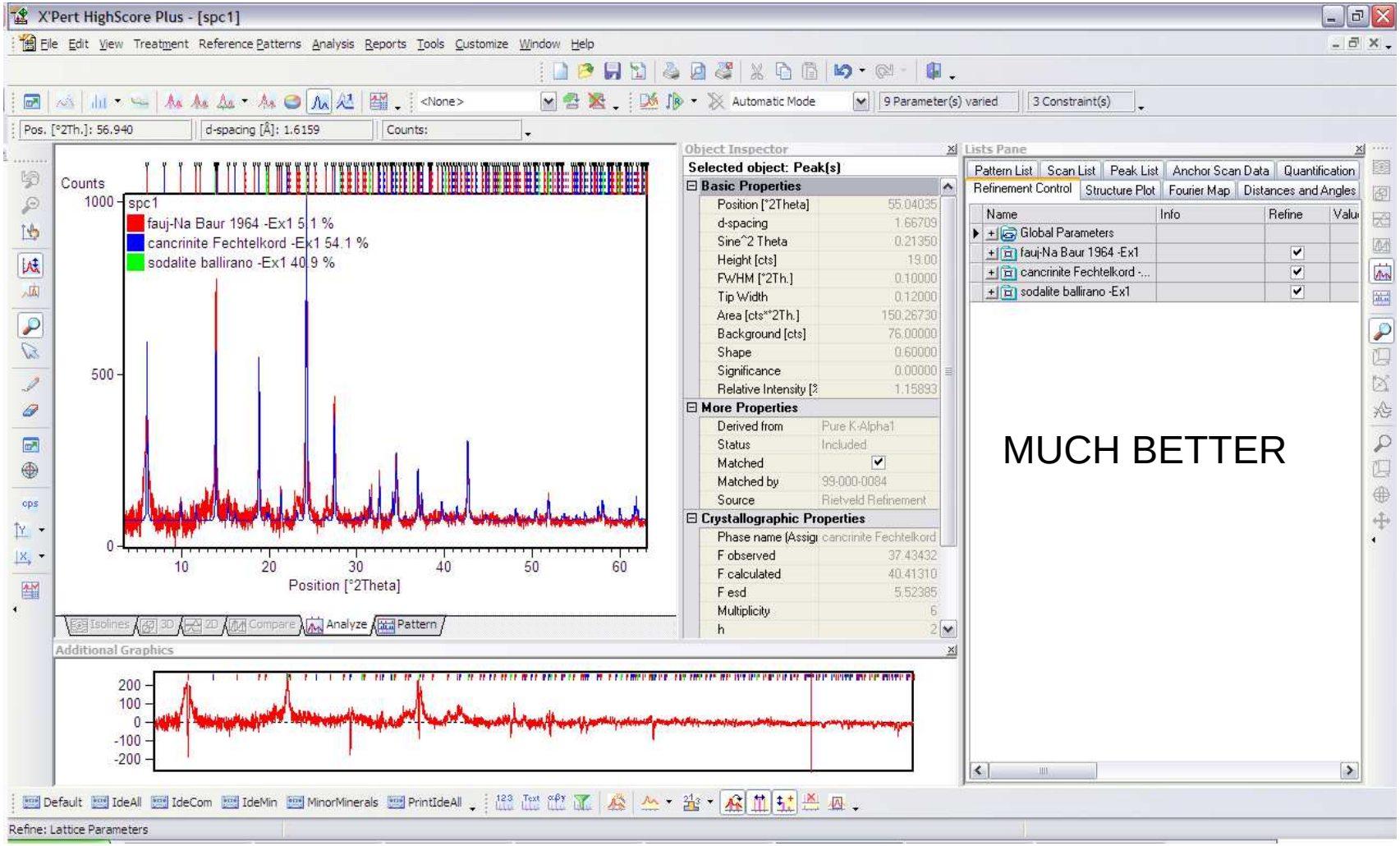
Exercise 1

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



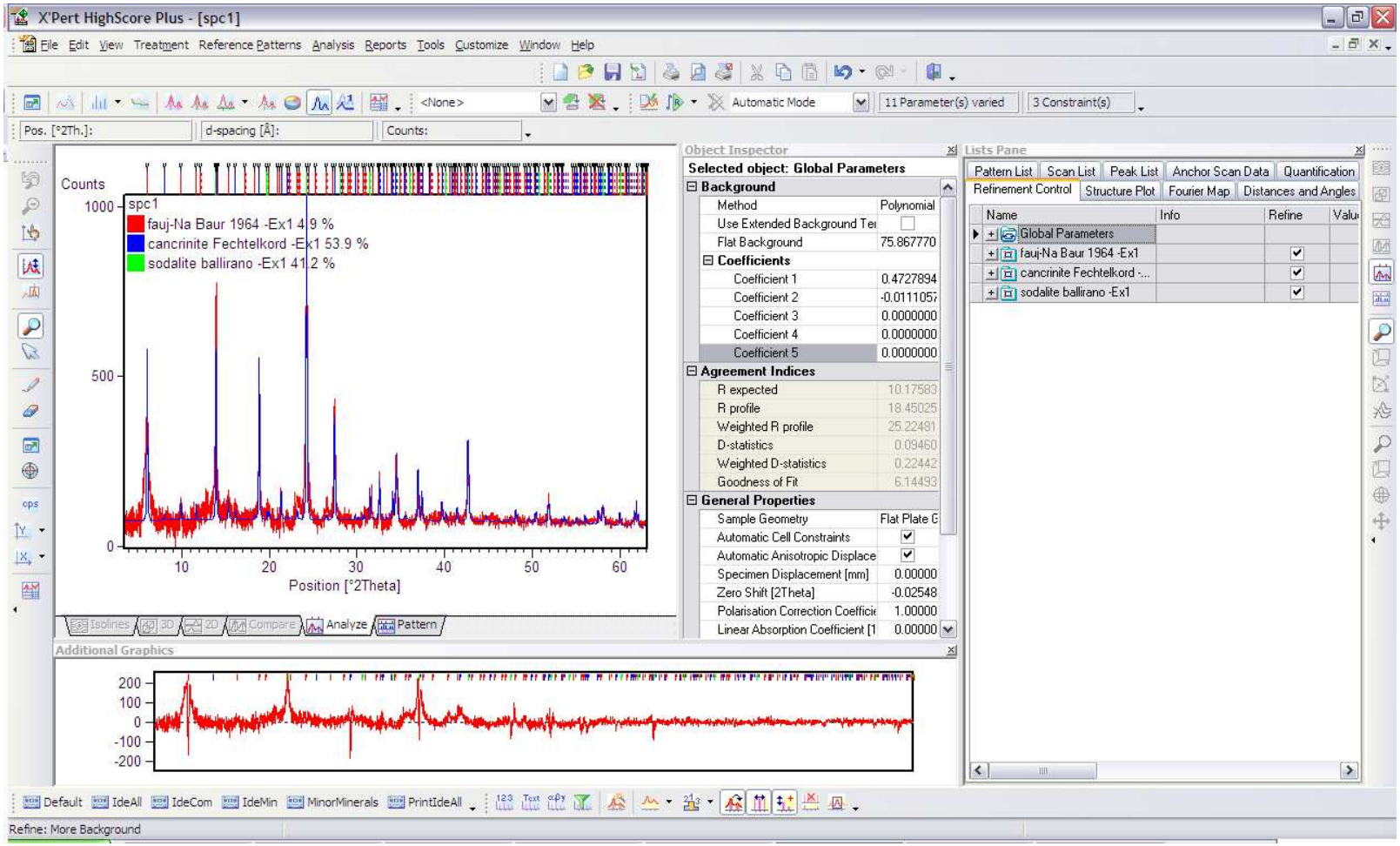
Exercise 1

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



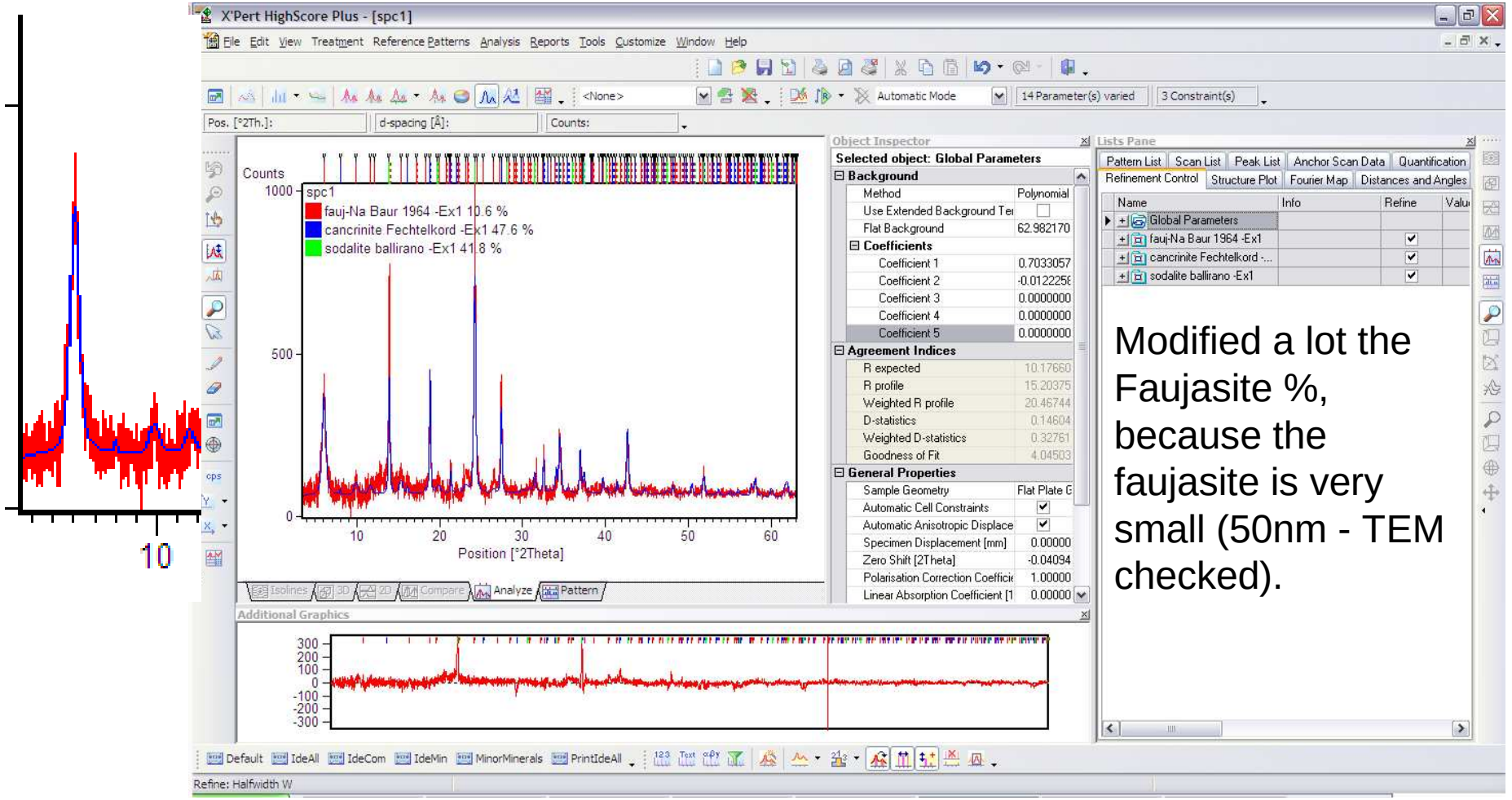
Exercise 1

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



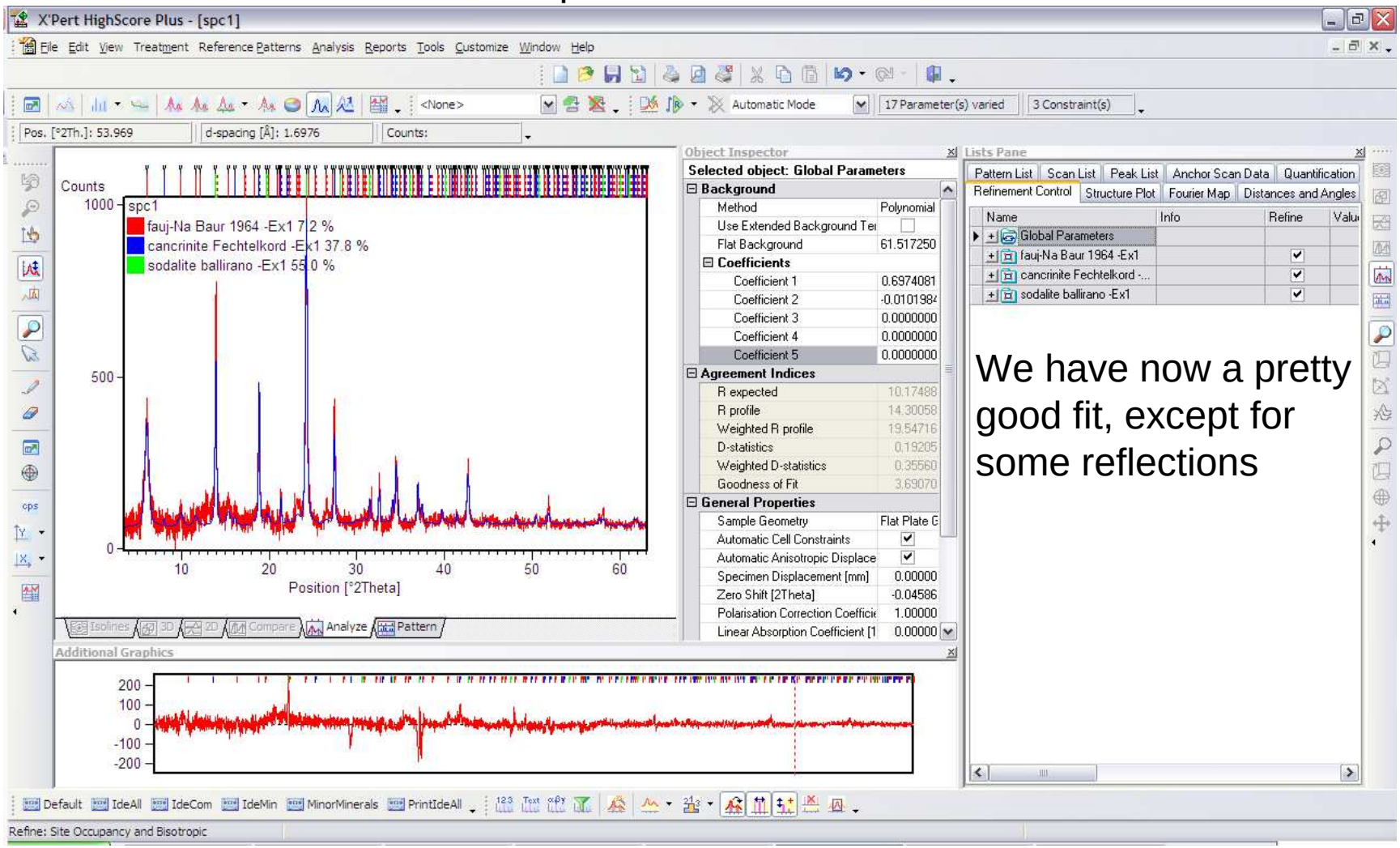
Exercise 1

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 Crtl+Z)
3. Edit autom. Rietveld steps, add W halfwidth



Exercise 1

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

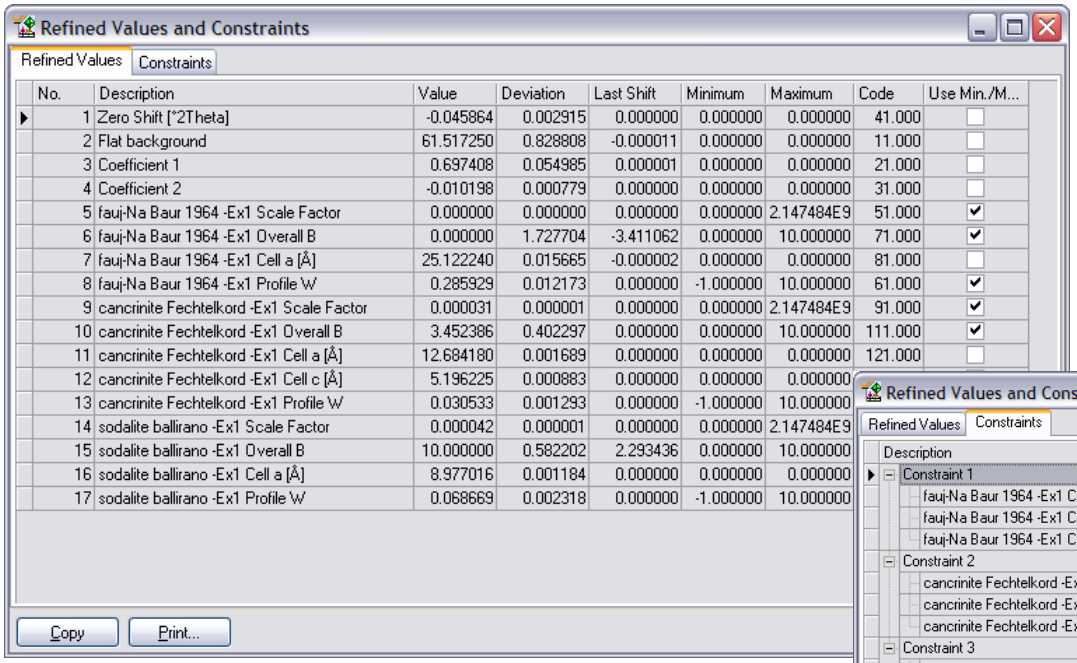


Exercise 1

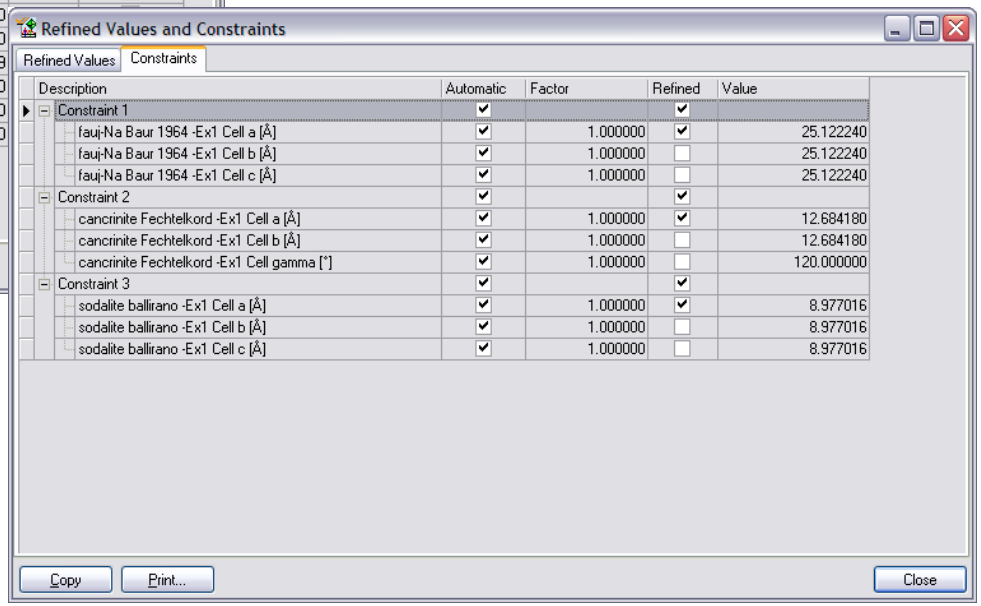
What did we do?

1. Right click on mineral list → show refined values/constraints

2. This gives the deviations operated on the phases for each parameter.



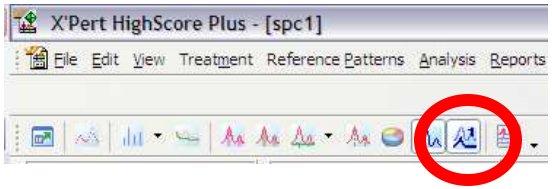
And the constraints



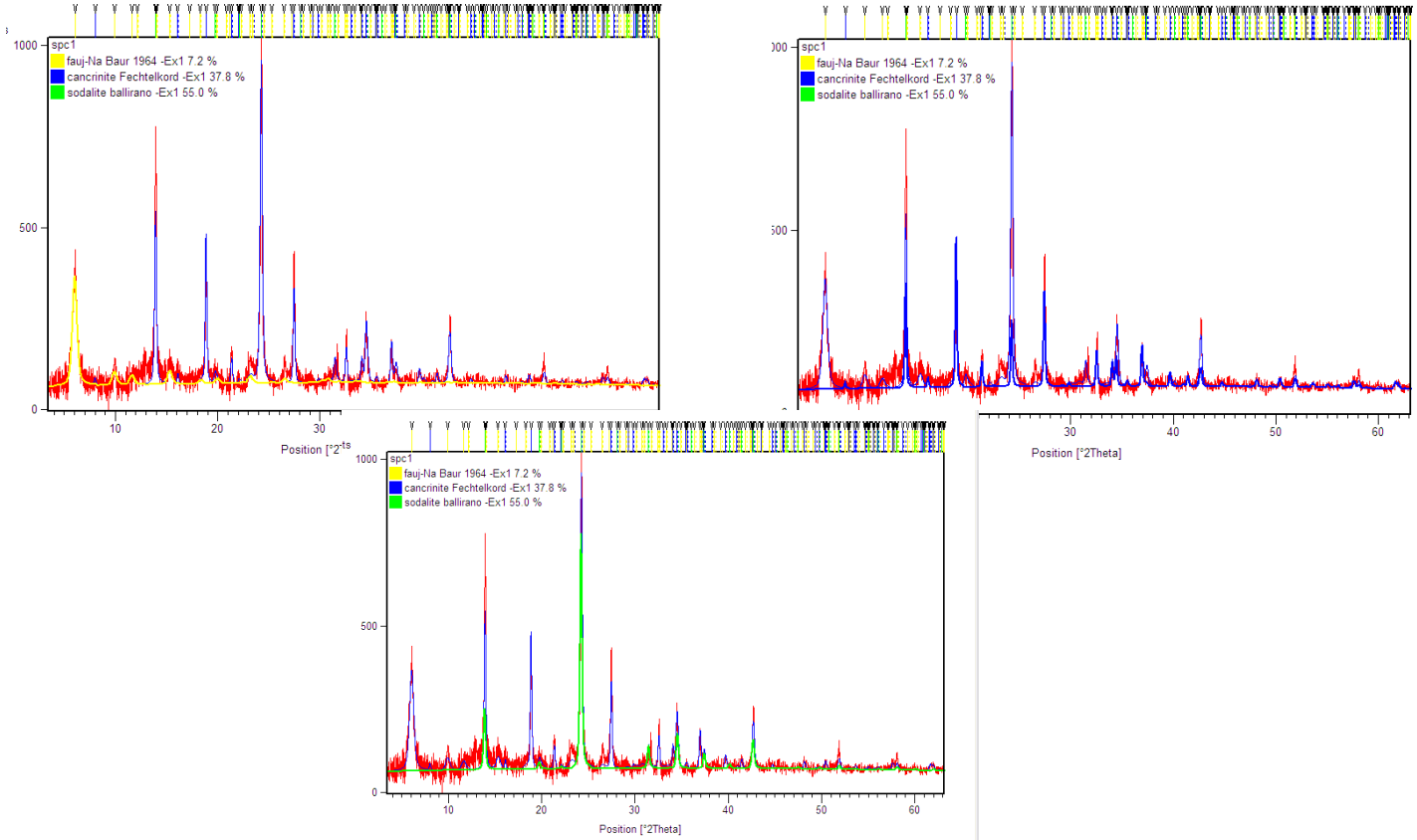
Exercise 1

What did we do?

1. Click on show selected phase profile icon



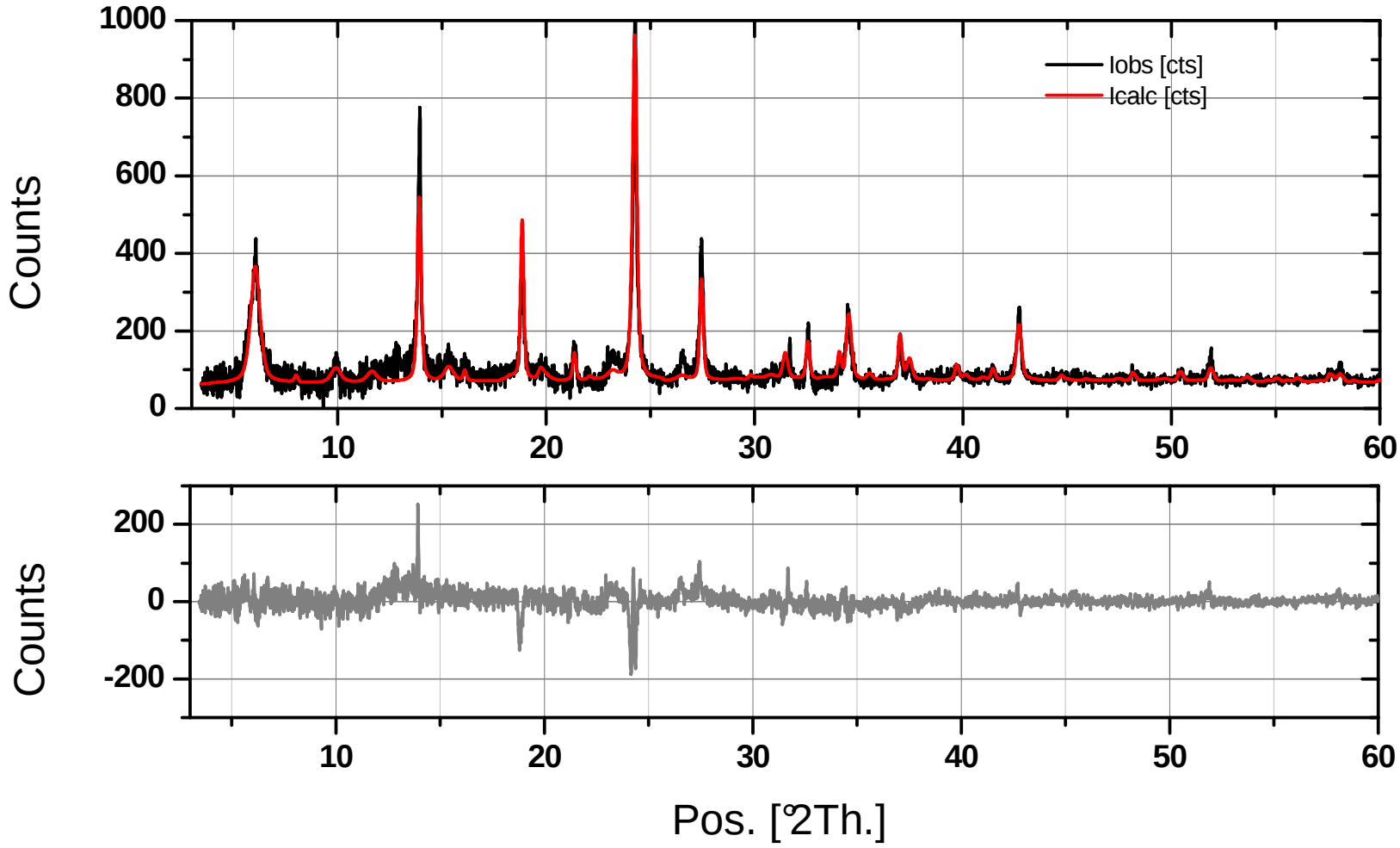
2. Select the phases. We can see the part of each phase in the calculated profile



Exercise 1

What did we do?

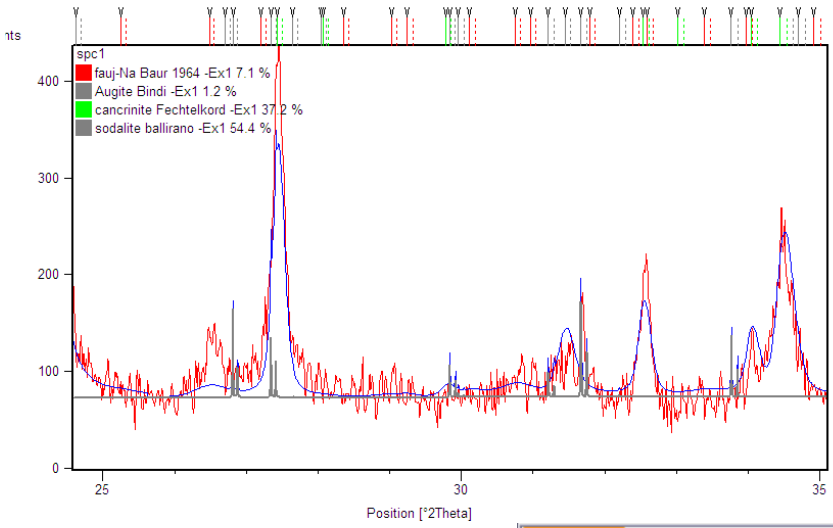
1. In the anchor scan data tab appear the numerical values of the scan.
2. Right click → copy list → past in excel or origin

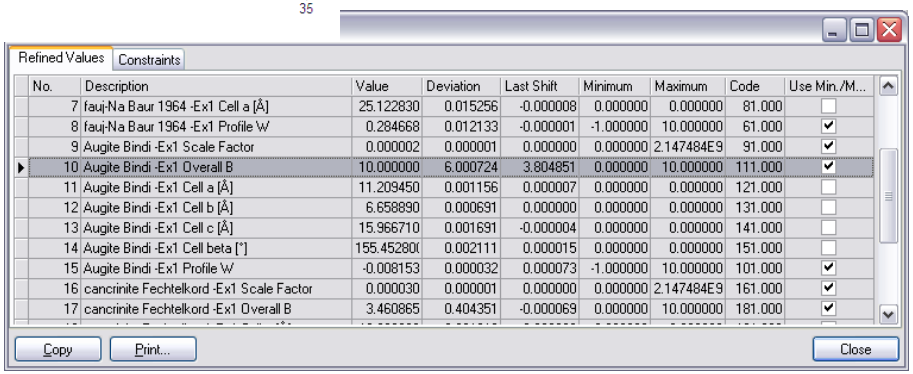


Exercise 1

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

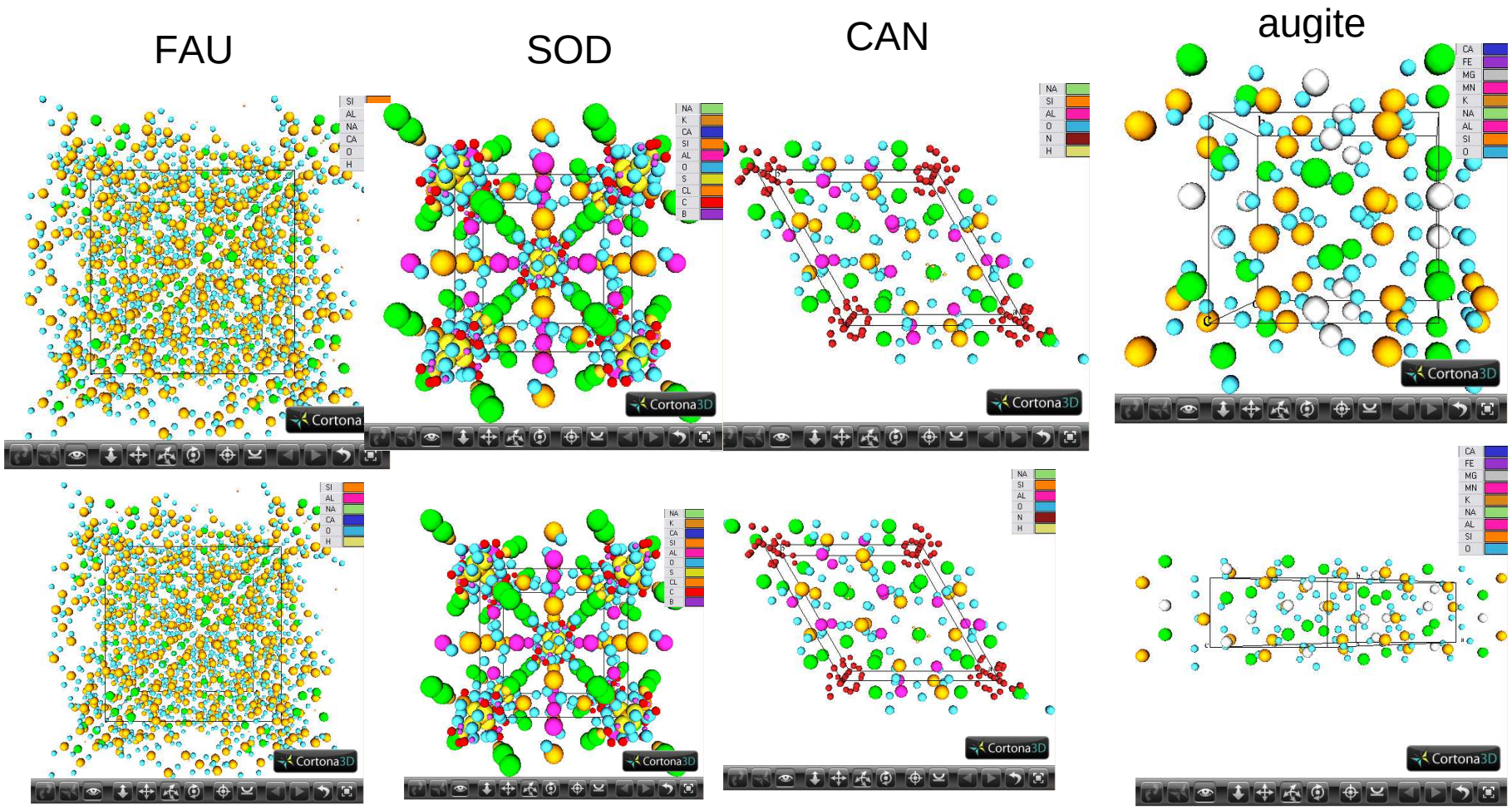




Too much deviation in B

Exercise 1

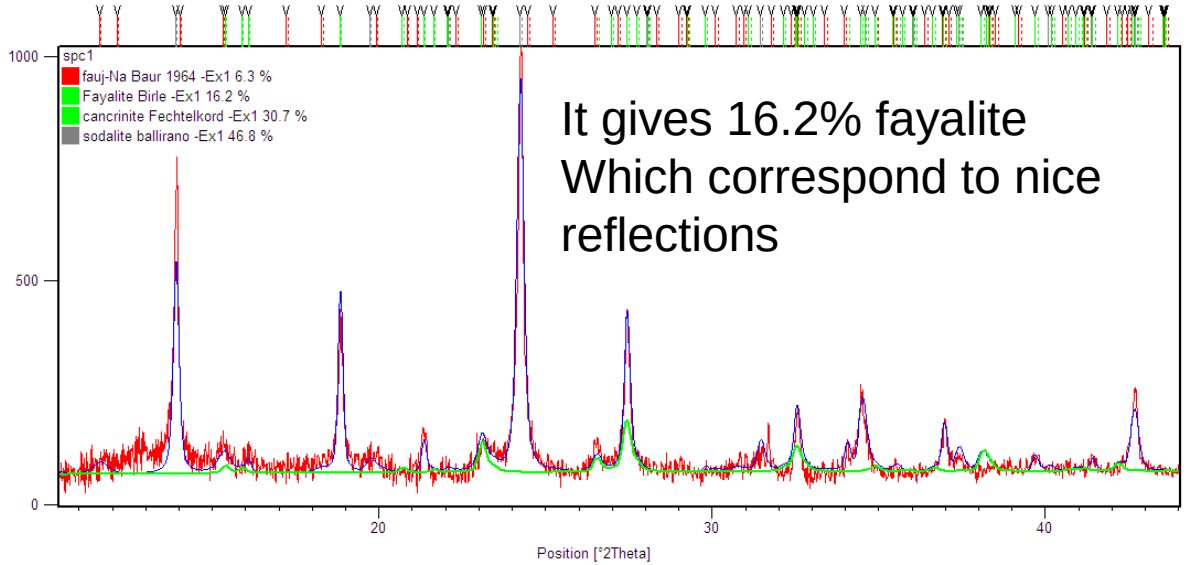
If we look at the structures before and after



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



It gives 16.2% fayalite
Which correspond to nice reflections

The refine values are fairly good

Refined Values and Constraints

Refined Values | Constraints

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

Copy | Print... | Close

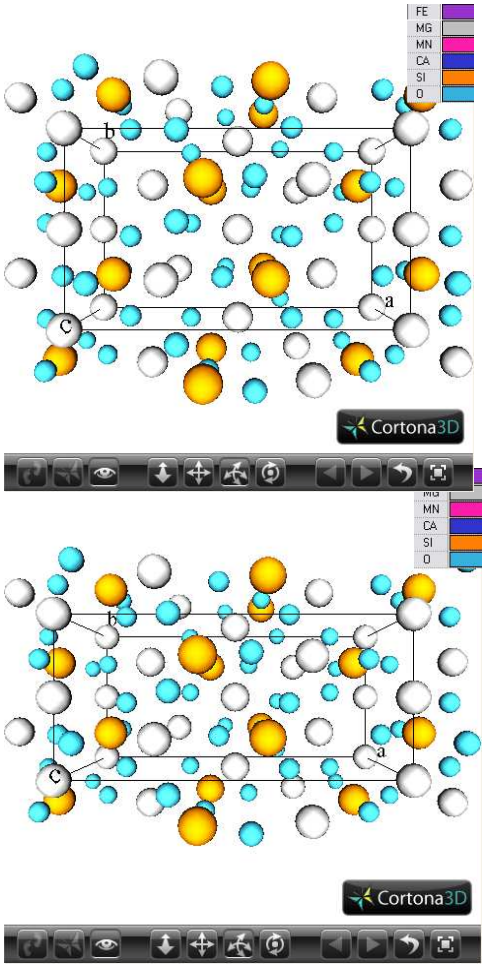
Exercise 1

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.

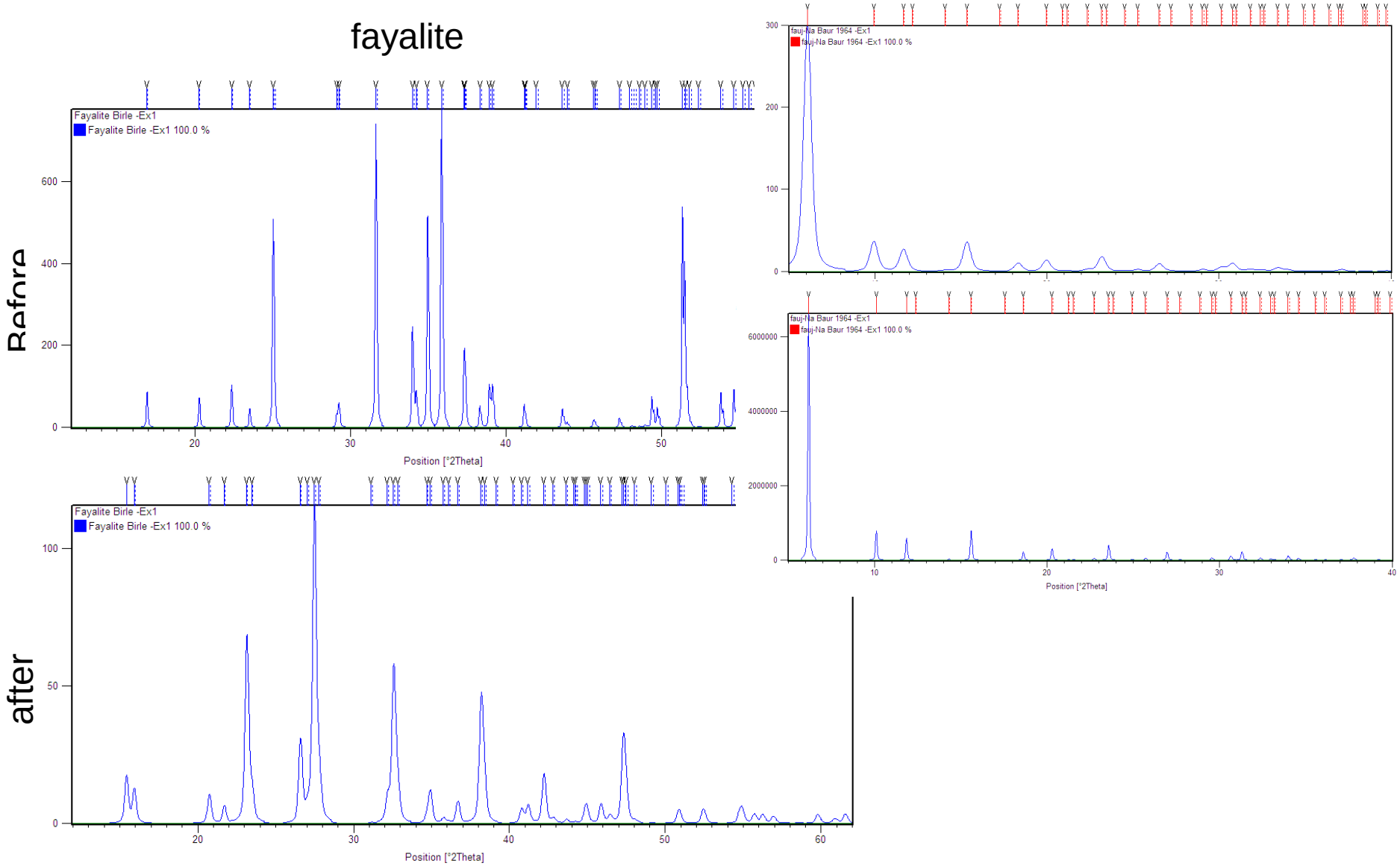
There is not a single chance that fayalite would:

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

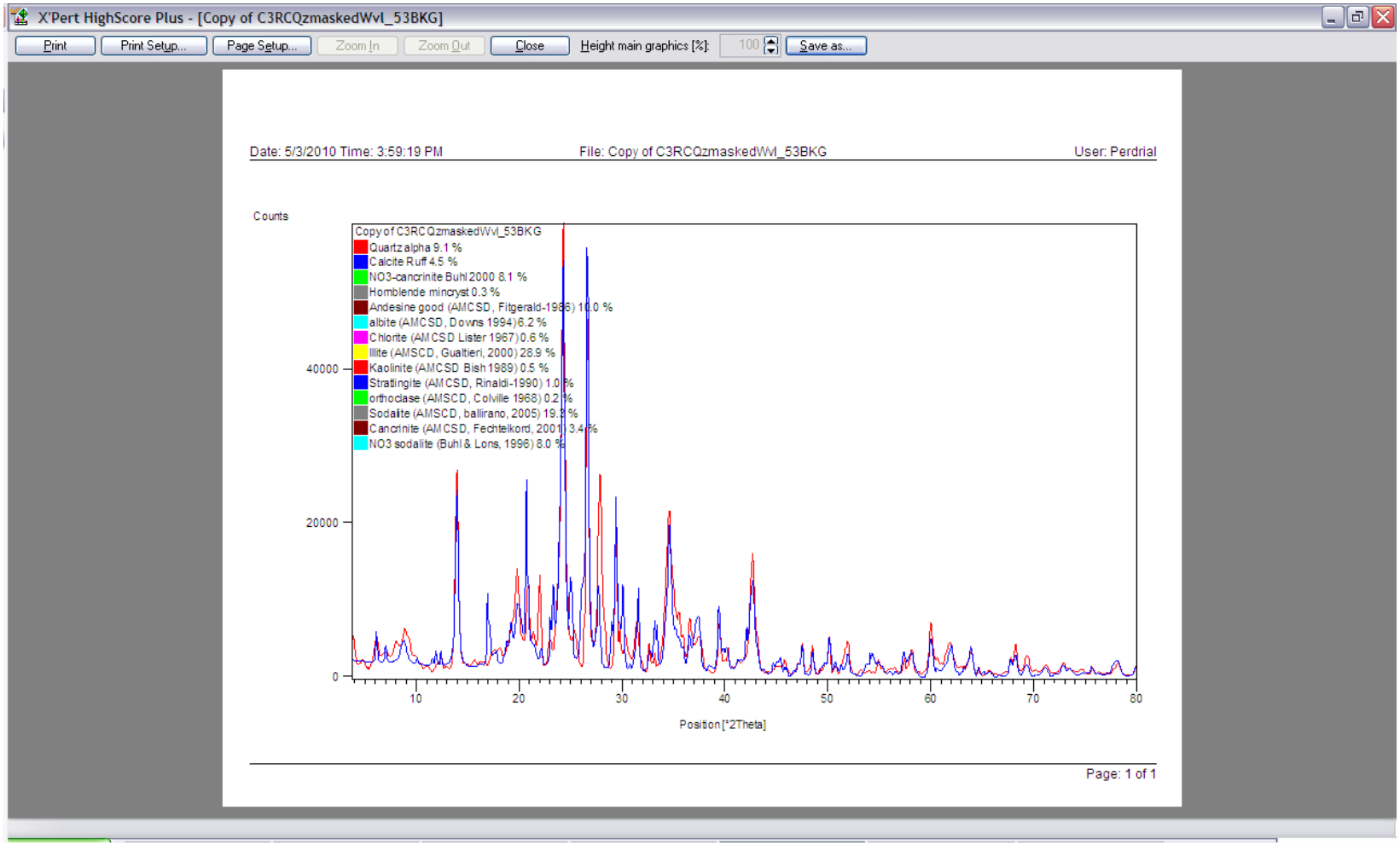
If we look at the spectrum before and after



Exercise 2

Open spc2

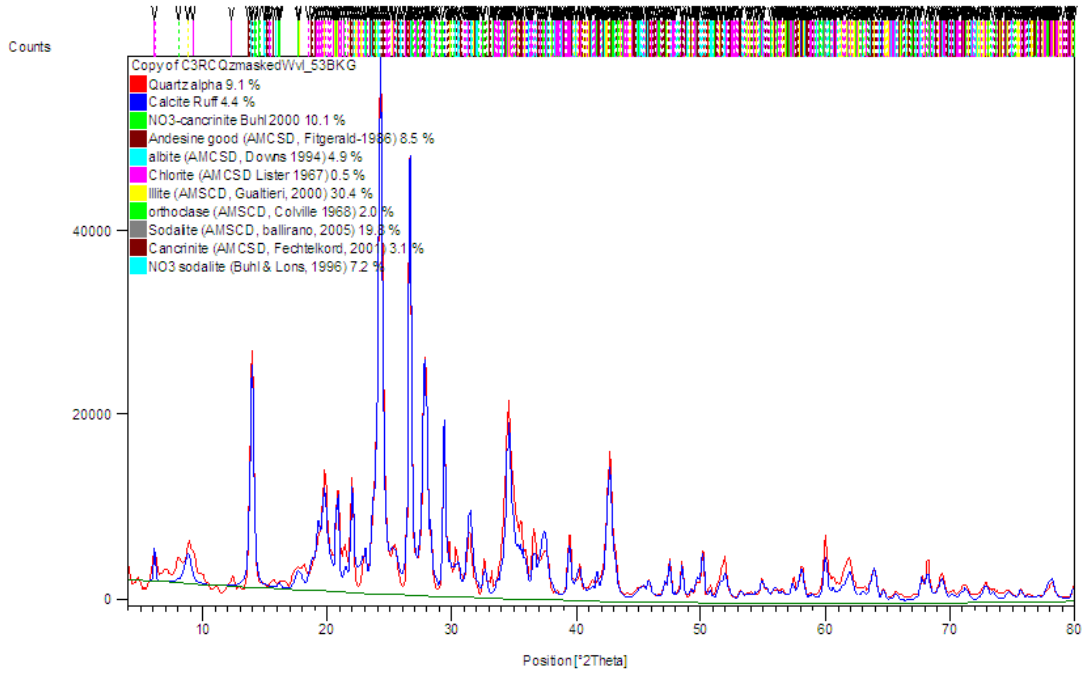
Insert structure 2 and.. try to make it good…



X'Pert HighScore Plus - [Copy of C3RCQzmaskedWvl_53BKG]

Print | Print Setup... | Page Setup... | Zoom In | Zoom Out | Close | Height main graphics [%]: 100 | Save as...

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



Page: 1 of 1

Misc. tips

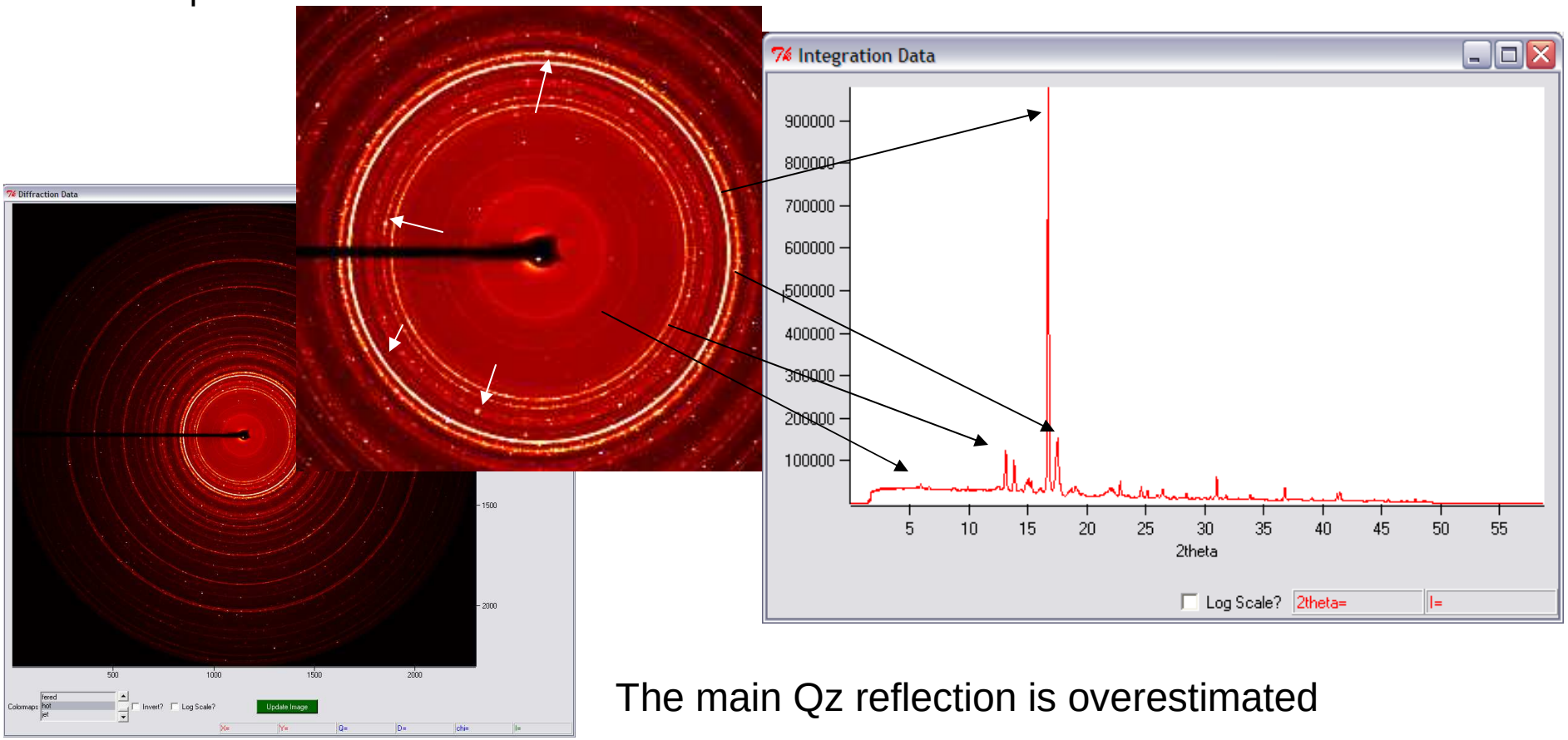
- Removing background.
  - Highscore plus not very good, use manual removing for better quality.

  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.

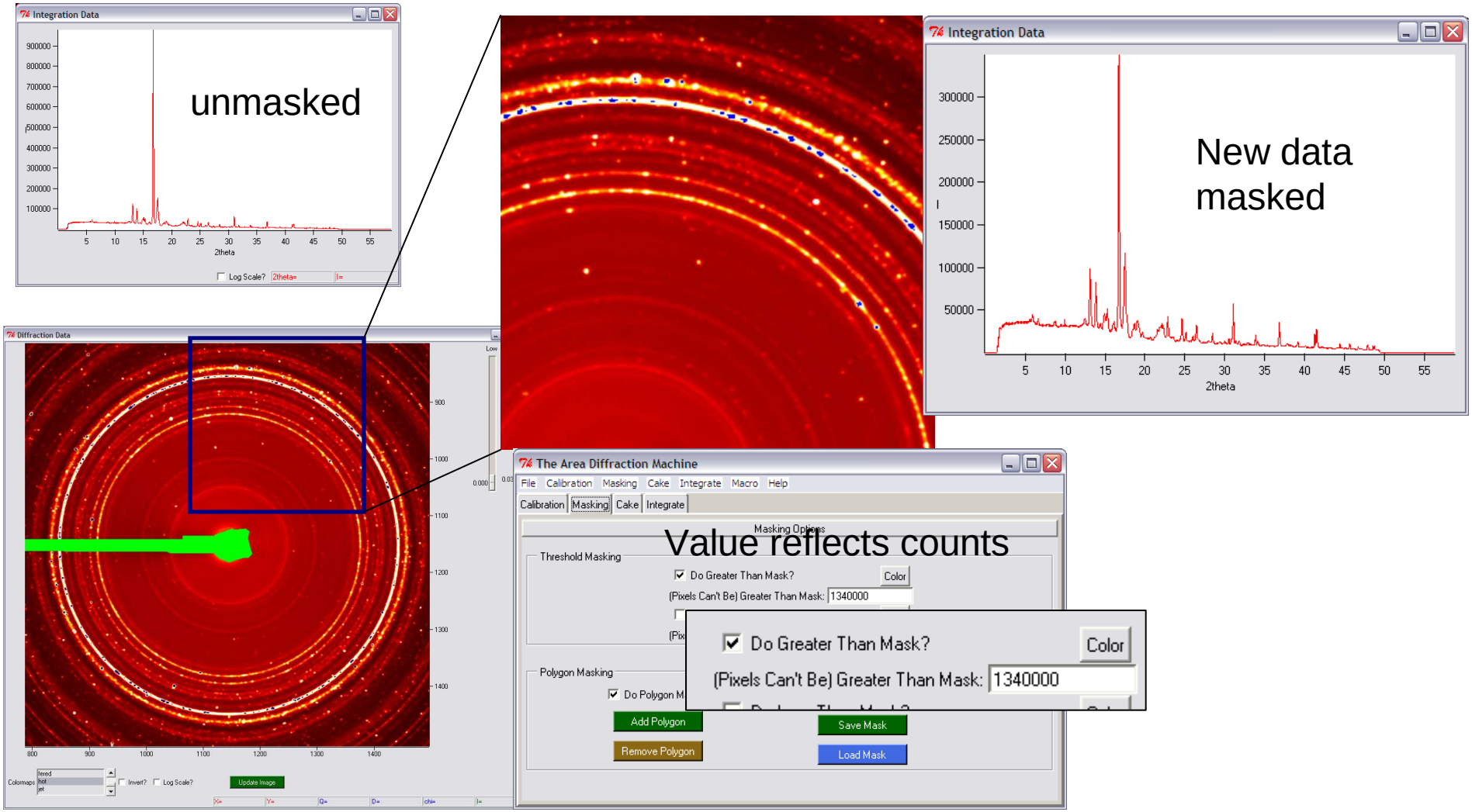
Example.



The main Qz reflection is overestimated

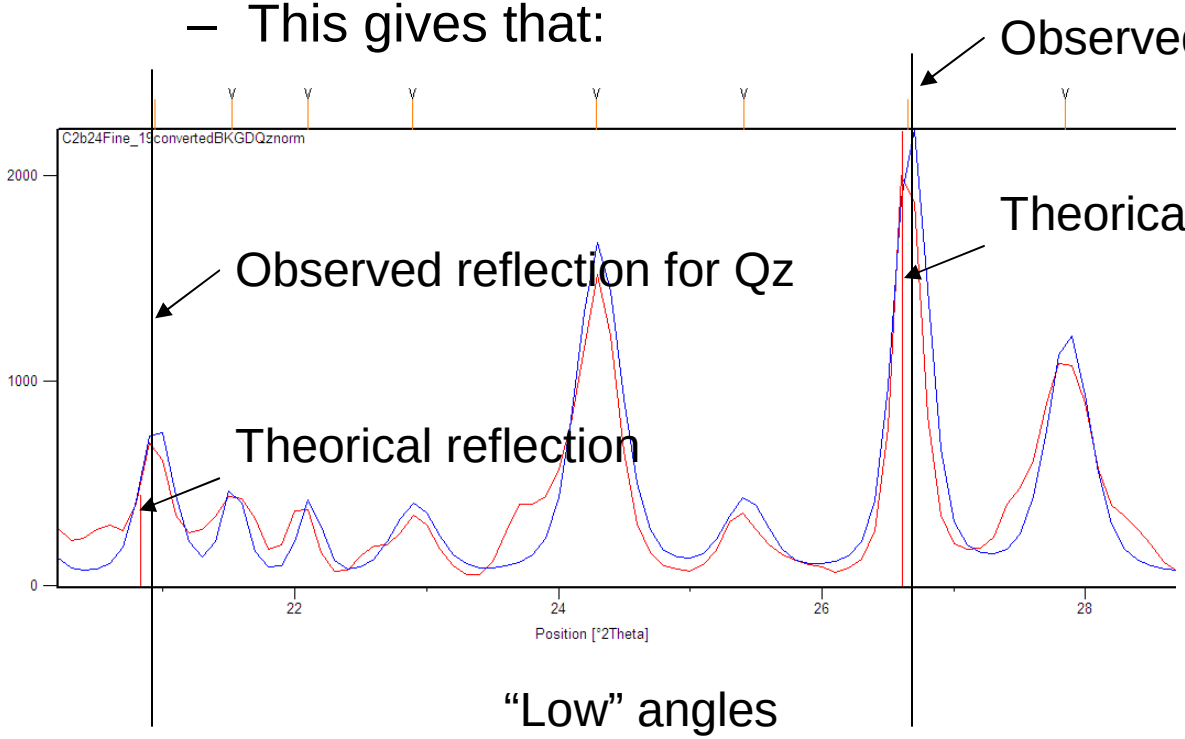
Misc. Tips

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

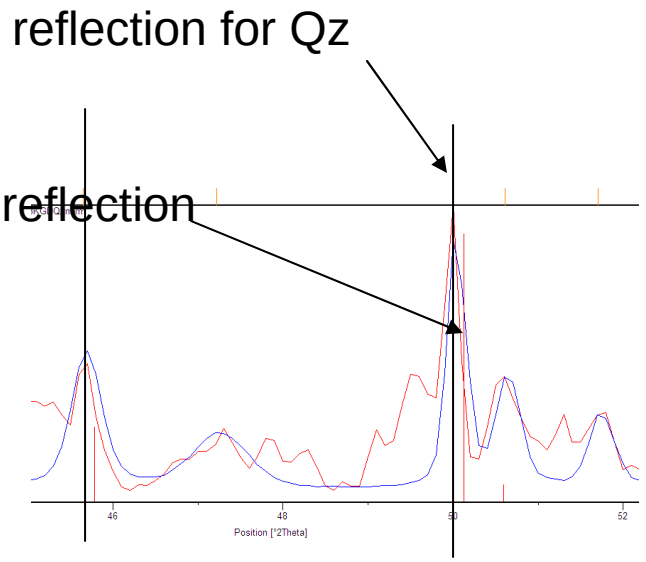


Misc. tips

- 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:

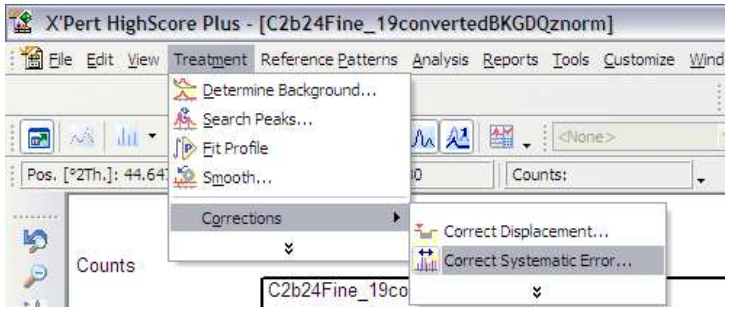


"Low" angles



high angles

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 slect stds, slect 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