PROYECTO DE INNOVACIÓN Y BUENAS PRÁCTICAS DOCENTES BÁSICOS 2020-2021

Identification and quantification of mineral phases commonly found in building materials using the software HighScore available at the Department of Mineralogy and Petrology (UGR)

Introduction

Generally, building materials contain several different minerals. More than 4000 minerals are officially recognized. Fortunately, the number of minerals that we normally find in materials such as earth, stone, bricks, mortars, alteration products, etc. is more limited. The following table shows the most common minerals in these materials and their most intense (identifying) d_{hkl} reflection. Mineral names are included in English because XRD-analysis programs use English names.

Mineral Phases

- Earth

  (quartz 3.34 Å, phyllosilicates ~4.50 Å; calcite 3.03 Å, dolomite 2.88 Å, gypsum 7.59 Å; feldspars ~3.20 Å, hematite, goethite, rutile)

- Clay fraction (<2µm)

  (smectite (montmorillonite, beidellite, nontronite, saponite ~13-15Å), mica/illite 10.0 Å, paragonite 9.6 Å, kaolinite 7.15 Å, chlorite ~7.15 Å, quartz, calcite)

- Bricks

  (quartz, mica/illite, feldspars (orthoclase, plagioclase, etc.), calcite, dolomite, hematite, mullite, gehlenite, diopside, wollastonite)

- Mortars/Plasters

  (quartz, lime (CaO), calcite, vaterite, aragonite, dolomite, portlandite, periclase, brucite, hydromagnesite, calcium silicate hydrate (cemento Portland), gypsum, bassanite, anhydrite, phyllosilicates (mica/illite))

- Stone

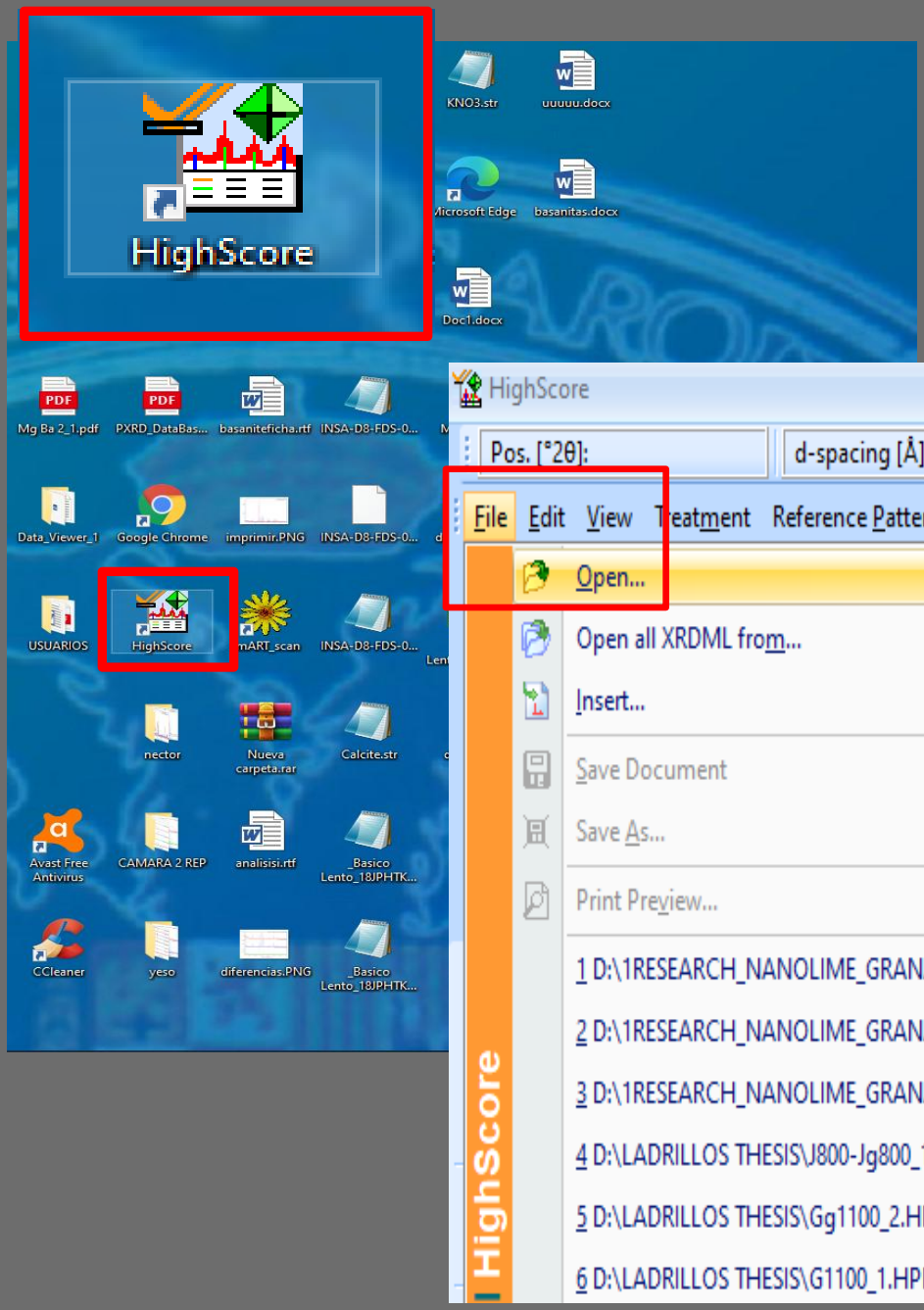
  (quartz, calcite, dolomite, gypsum, feldspars, pyroxene, amphibole, olivine, phyllosilicates, phyllosilicates (mica), magnetite, hematite, goethite, pyrite, rutile)

- Alteration Products

  (bassanite, calcite, hexahydrite, anhidrite, gypsum, epsomite, halite, kalicinite, mirabilite, natron, niter, thenardite, trona, weddellite, whewellite)

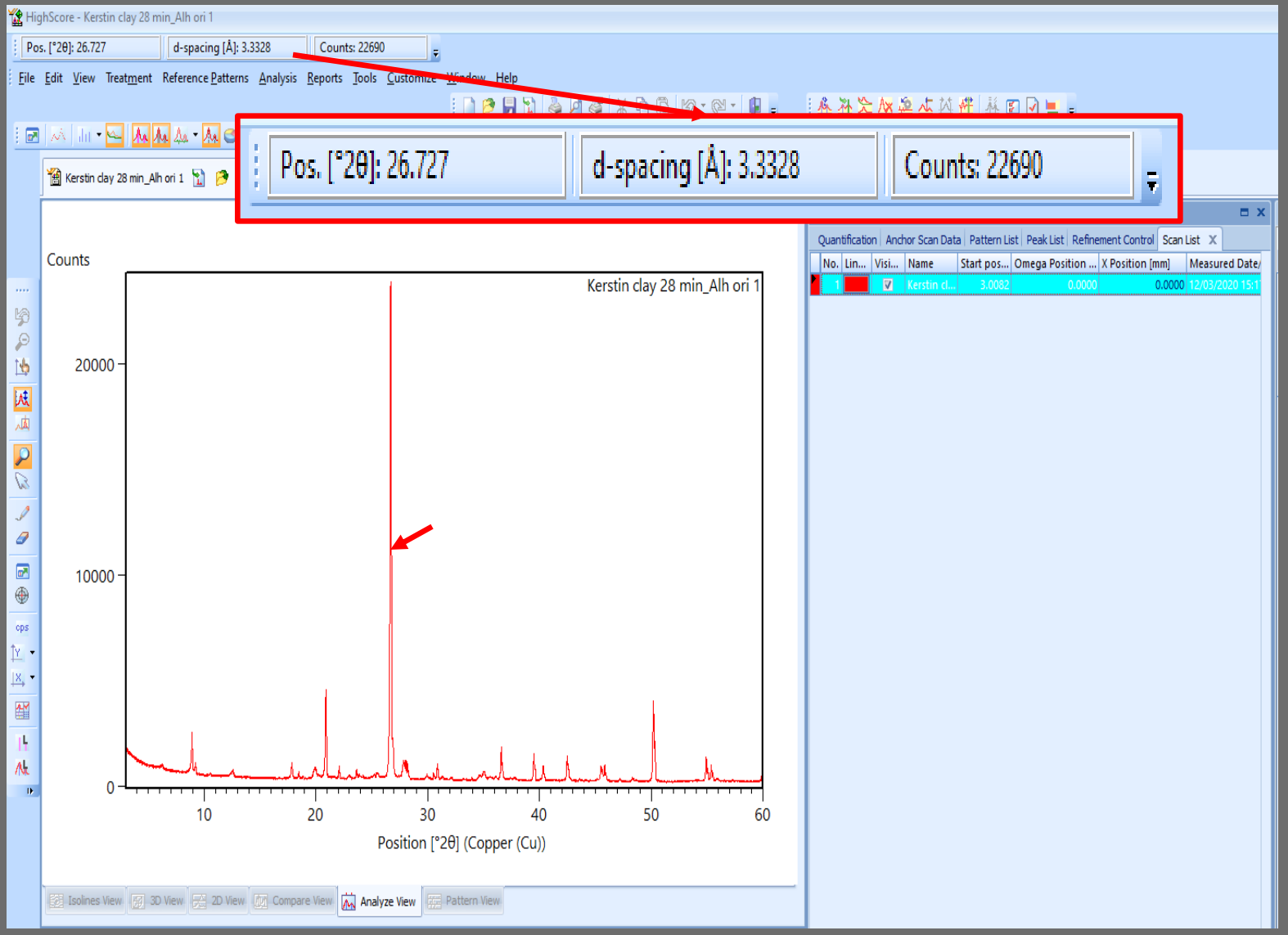
Additional information about minerals: http://www.webmineral.com y https://www.mindat.org

Use of the software «HighScore»

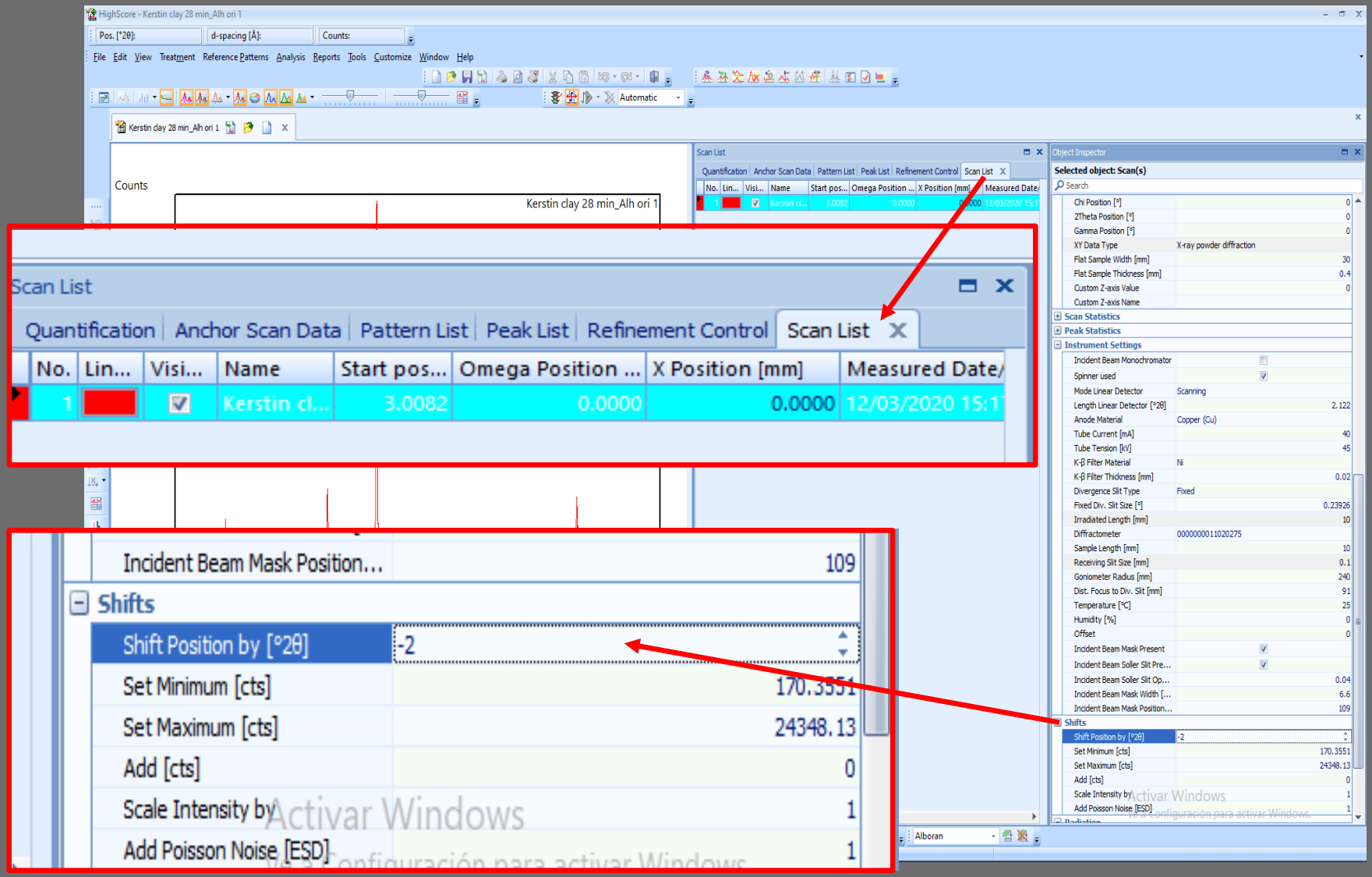


1. We open the HighScore software and a diffractogram using «File» and «Open».

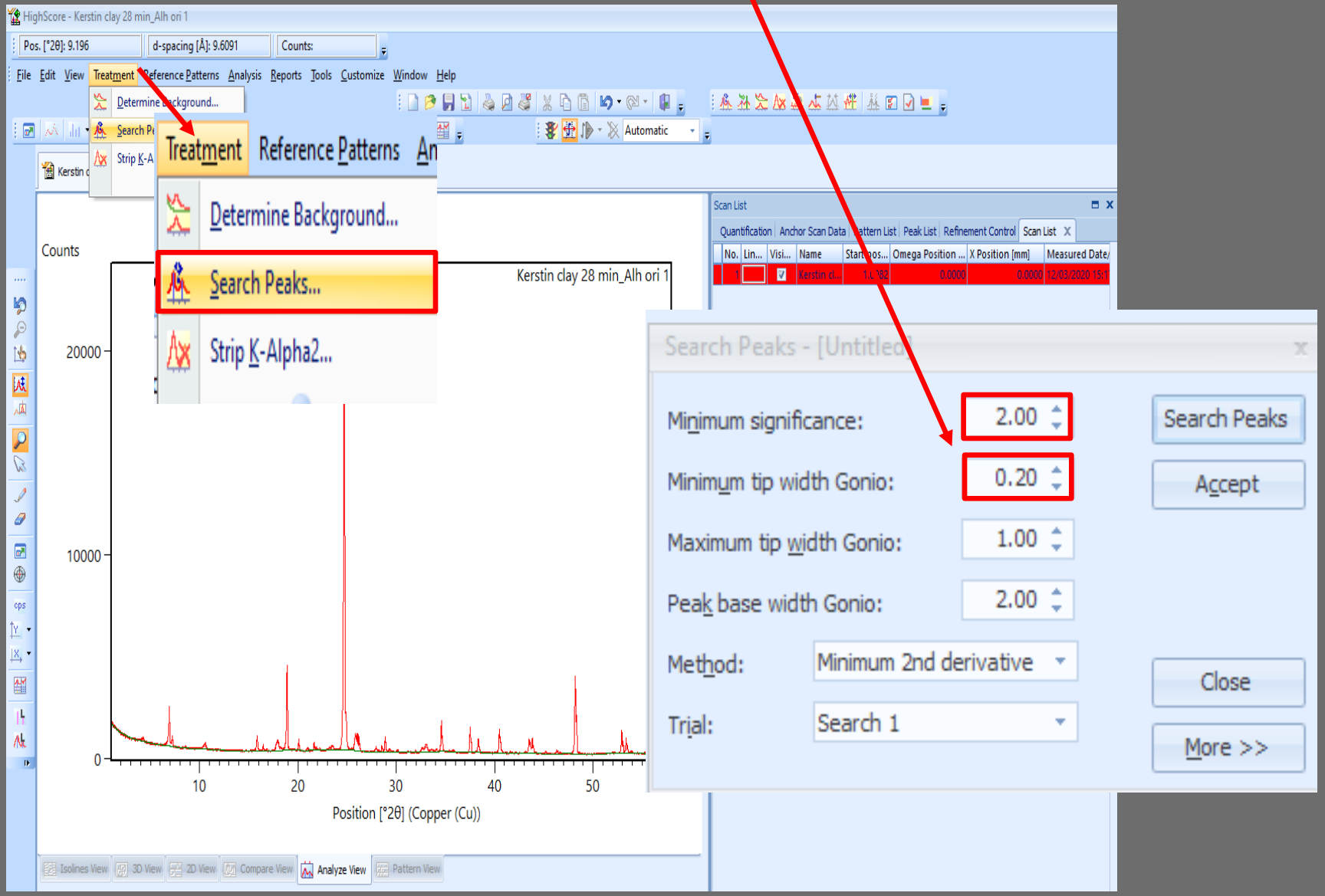
2. We verify that the diffractogram is not shifted, preferably using the most intense peak of quartz at 3.34 Å or another mayor phase (due to small variations in the height of the sample during analysis the peaks may be shifted). Place the mouse above the peak and check the value.



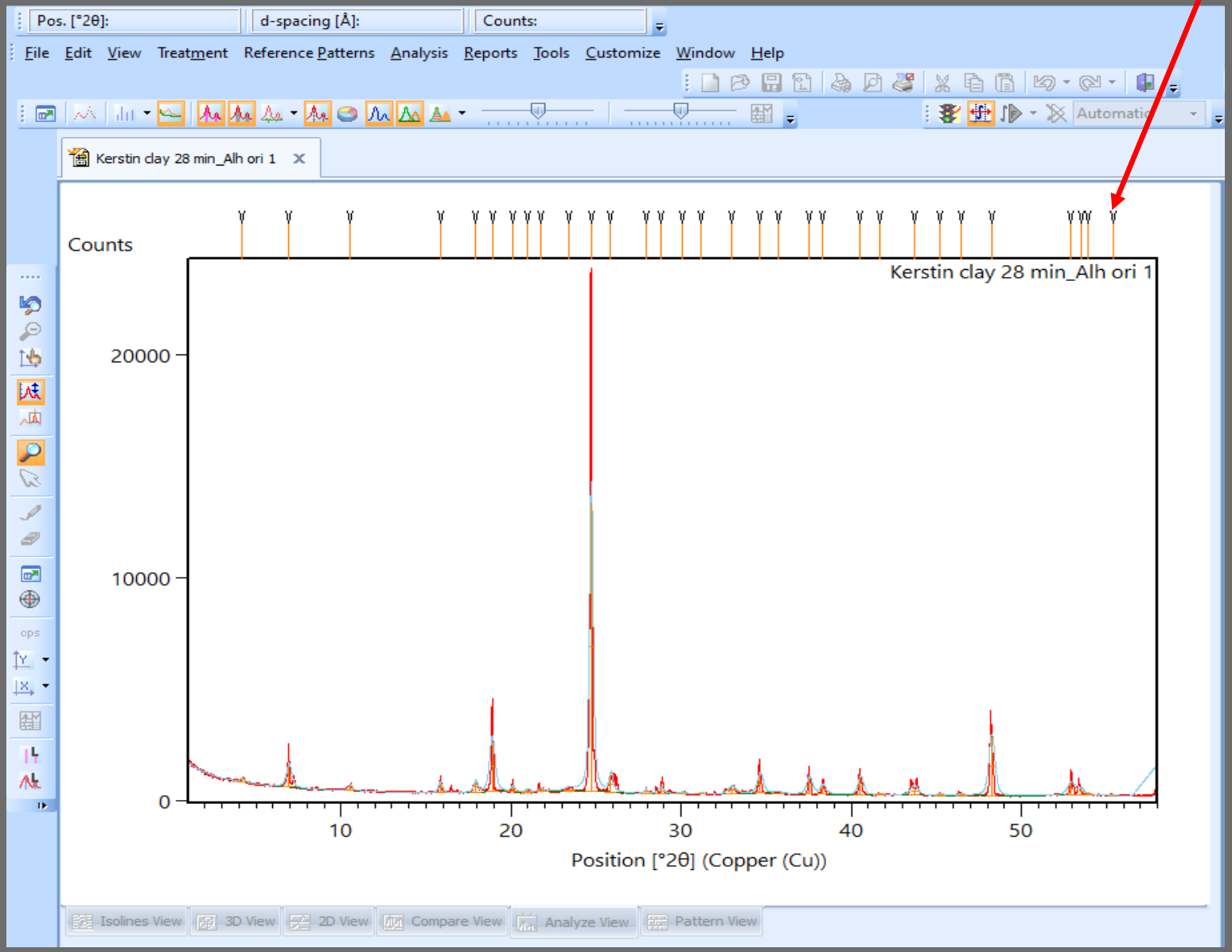
3. If the value does not coincide with 3.34 Å, select «Scan List» and «Shifts» and enter a negative value to shift the diffractogram to the left or positive value to shift it to the right so that the value of the quartz peak of our sample is equal to 3.34 Å.



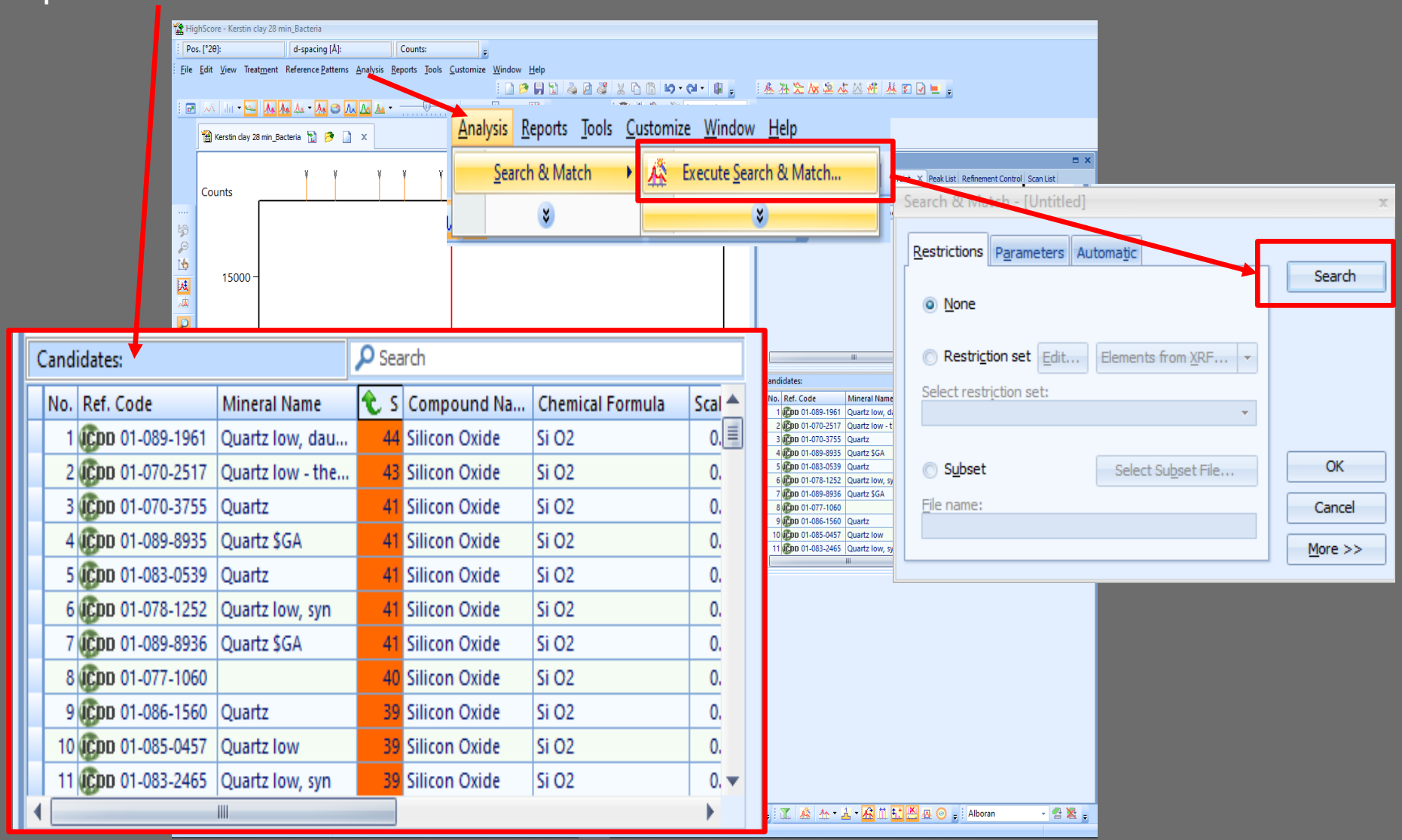
4. For the analysis of our diffractogram we have to select the peaks using «Treatment» and «Search Peaks» and «Accept». If the values of «Minumum significance» and «Minimum tip width Gonio» are too high, only the highest intensity peaks are marked (if we decrease the values the program will also select the smaller peaks).



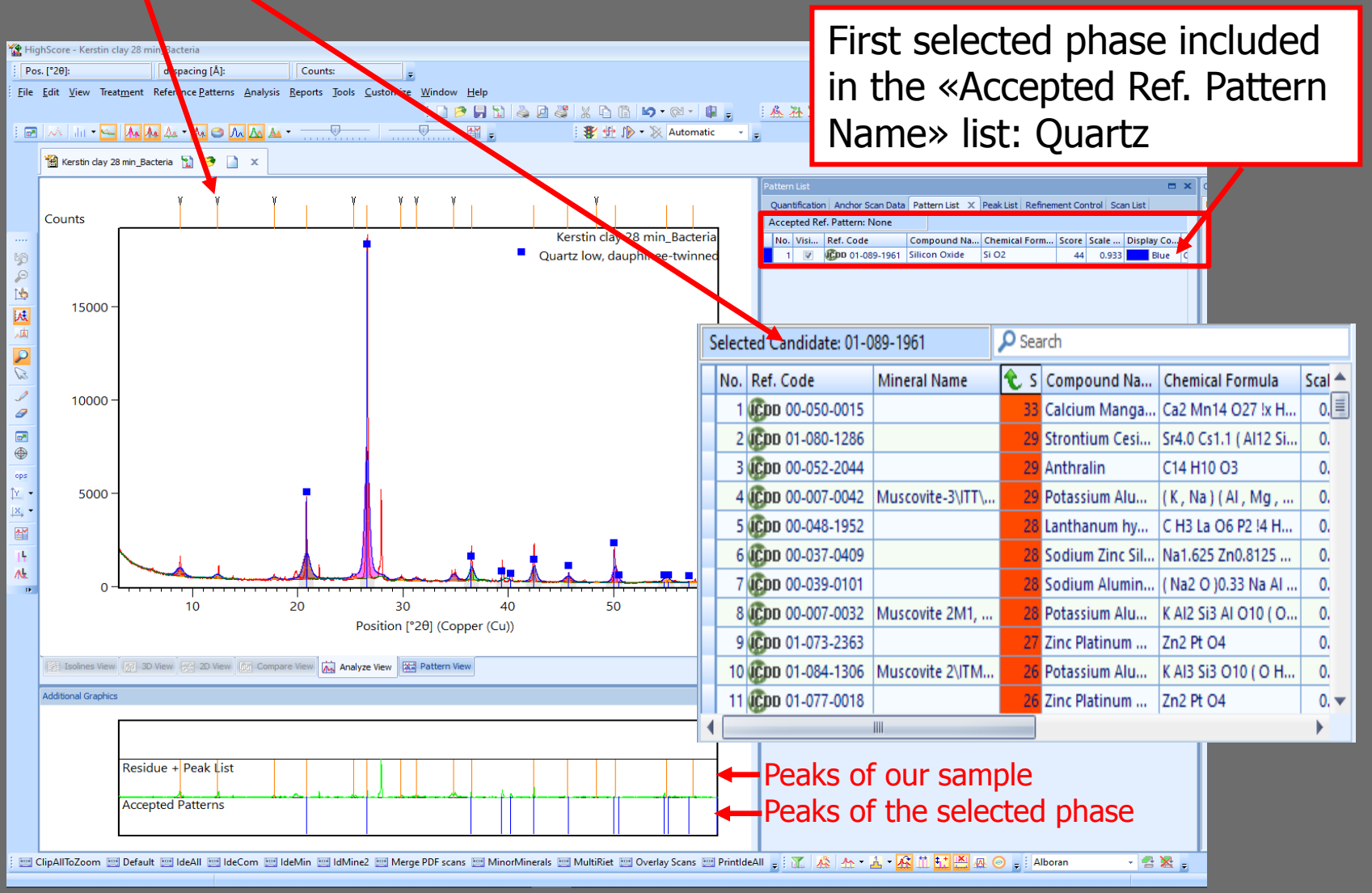
Example of a diffractogram with selected peaks (marked by a line and a «V»).



5. For the «automatic» analysis of our diffractogram by comparison with reference data files included in the software database, we choose «Analysis» and «Execute Search & Match» and click «Search» and "OK". The program gives us a list of possible candidates, indicating the match (Score, orange column) of the peaks of each candidate with our sample.



6. Once the reference mineral with the positions and intensities of peaks that fit best those of our sample (generally the phase with the highest «Score», orange column) has been selected, we drag it to the list of «Accepted Ref. Pattern Name». The program indicates the peaks of our sample that still need to be assigned (V) and automatically selects the next phase in the list whose peaks coincide with unidentified peaks.



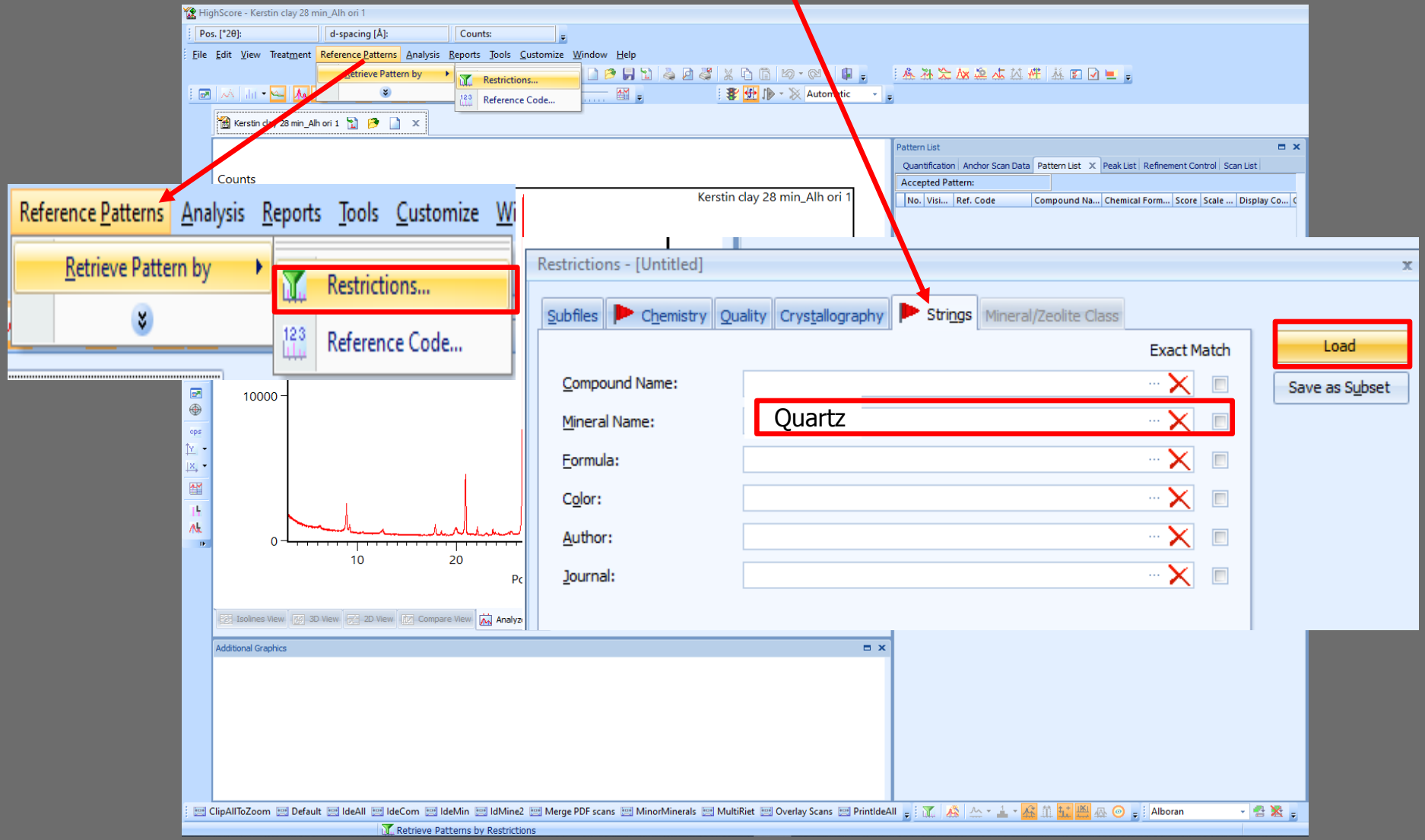
«Manual» analysis

In many cases the automatic analysis gives satisfactory results. However, we have to consider that the software chooses candidate minerals based on similarity of the position and intensity of their peaks. We have to use common sense to select the «true» minerals from the list and exclude those with «exotic» compositions. In the case of more complex diffractograms, it may be necessary to do an additional «manual» analysis, looking for specific mineral phases. In the case of construction materials, it is useful to first look for the maximum intensity peaks of the most common minerals (see below) using their d_{hkl} and mark all peaks of the identified phase. Then you would search for phases that match the peaks that have not been assigned to any of the «common» minerals.

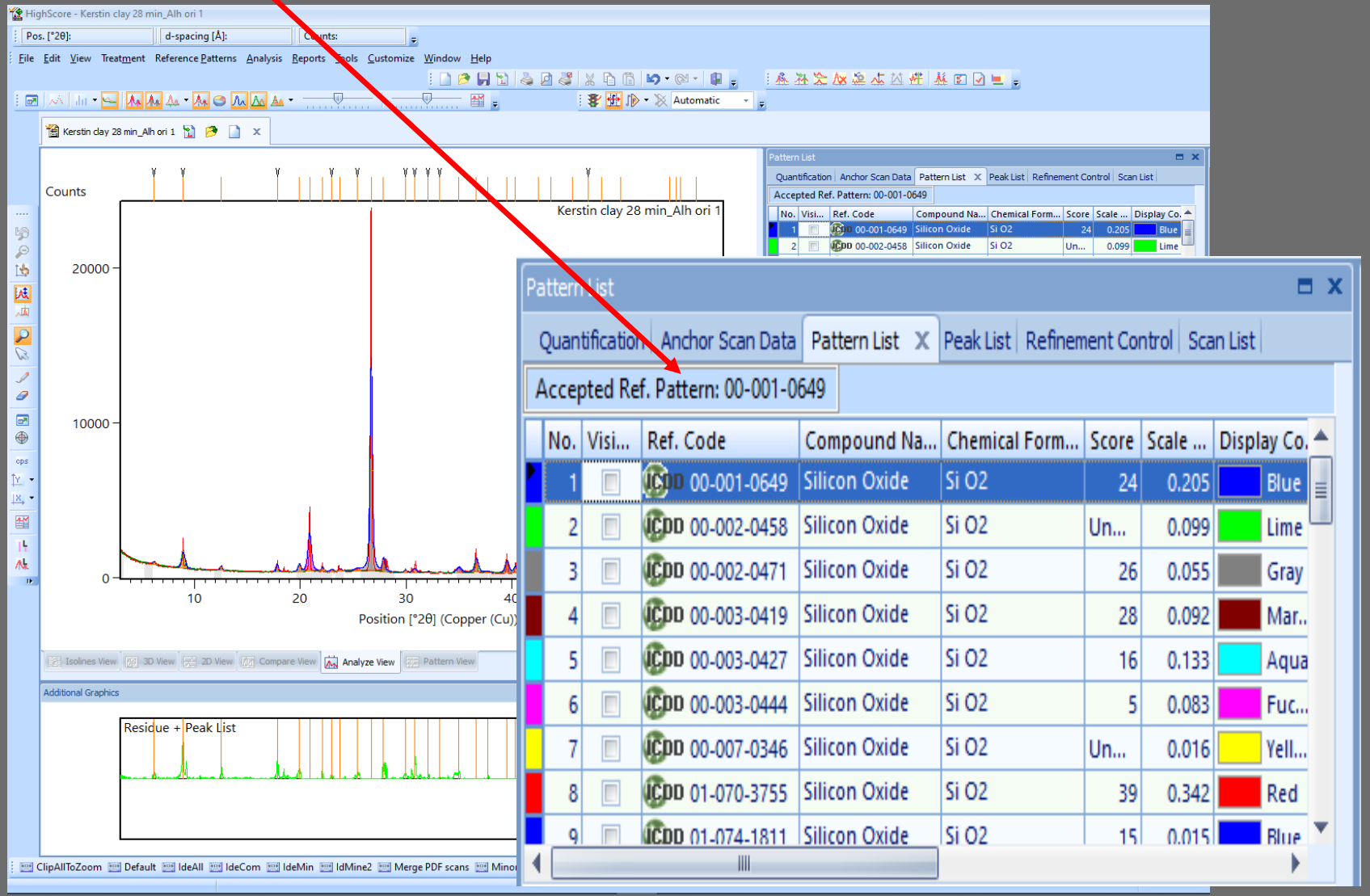
Quartz (3.34 Å)
Calcite (3.03 Å)
Dolomite (2.88 Å)
Feldspars (~3.20 Å)
Gypsum (~7.60 Å)
Clays (~4.50 Å), including smectites, illite, kaolinite etc.

«Manual» analysis

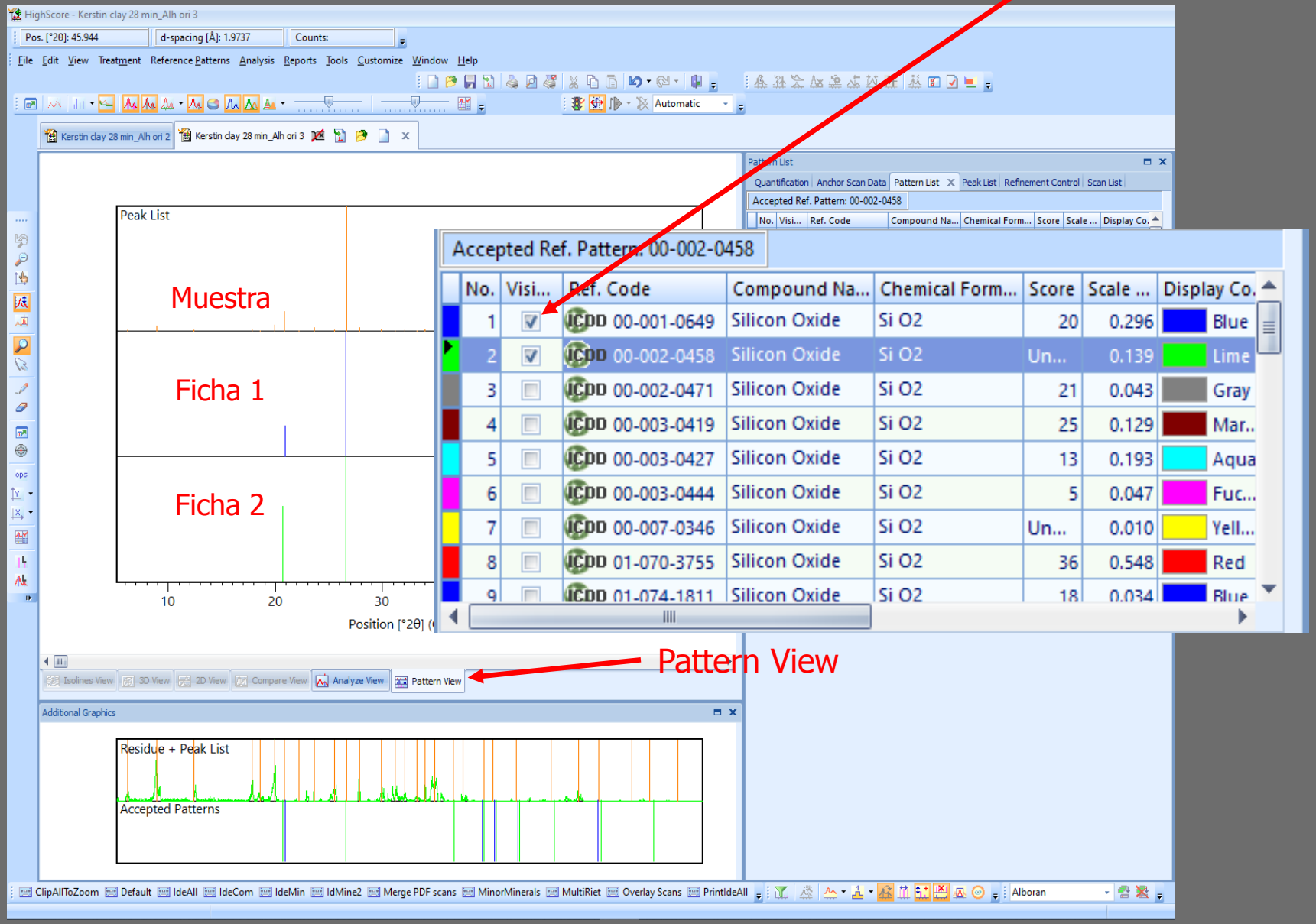
7. There is also the possibility to search for a specific phase by choosing «Reference Patterns» and «Restrictions». We select «Strings» and we introduce the name of the mineral phase (Quartz) and press «Load».



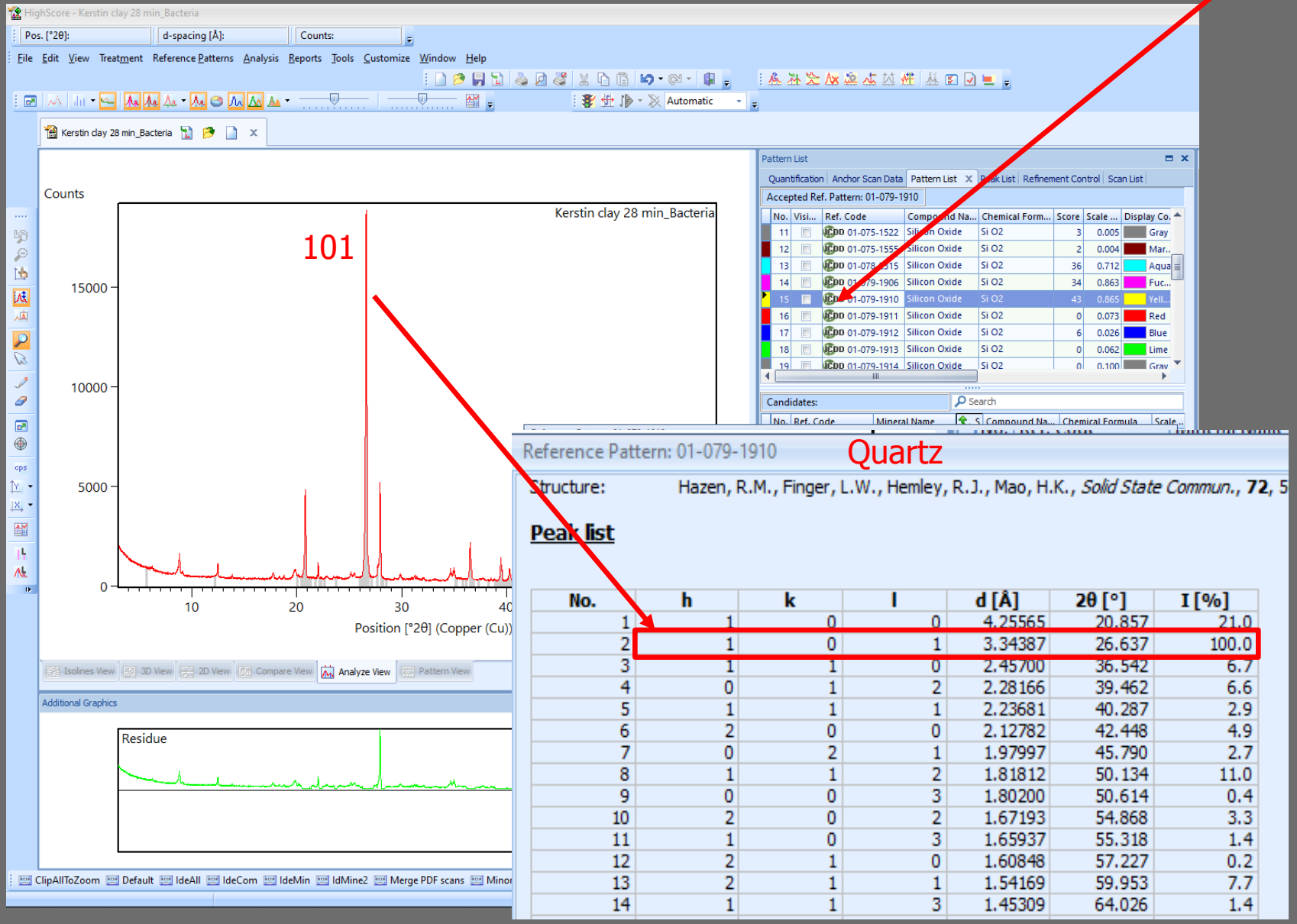
8. All the files of the particular mineral in the database appear in the list «Accepted Ref. Pattern Name». We should choose the most «suitable» candidate. Duplicates can be removed by selecting them and pressing «Delete».



9. The program allows the comparison of the similarity of the peaks of our sample with several reference mineral files at the same time by choosing the reference files from the list «Accepted Ref. Pattern Name» and selecting «Pattern View».

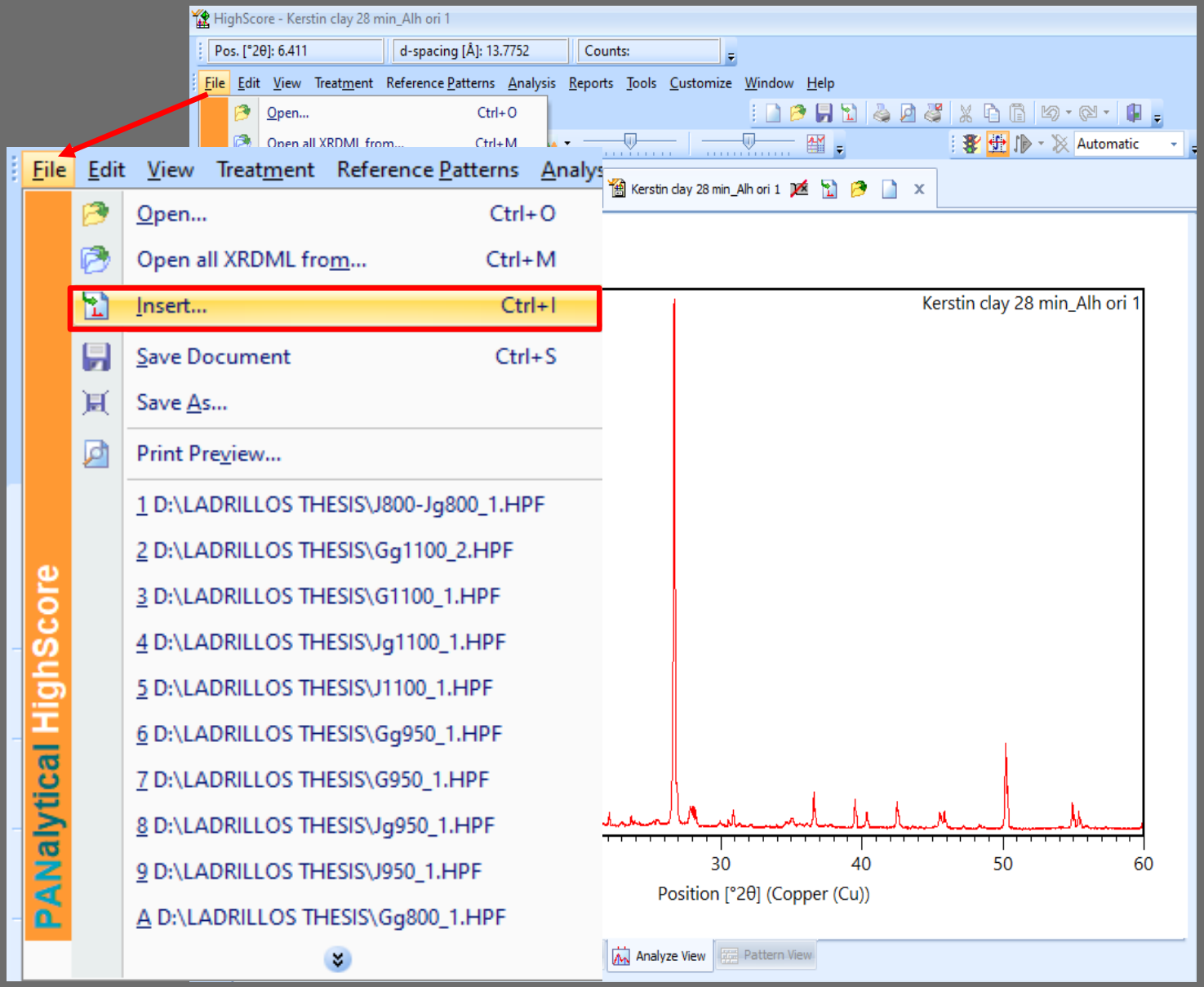


10. The program allows to view the information of the reference mineral files (including the d_{hkl} of each peak), by double clicking with the right mouse button on the Ref. Code of the selected mineral file.

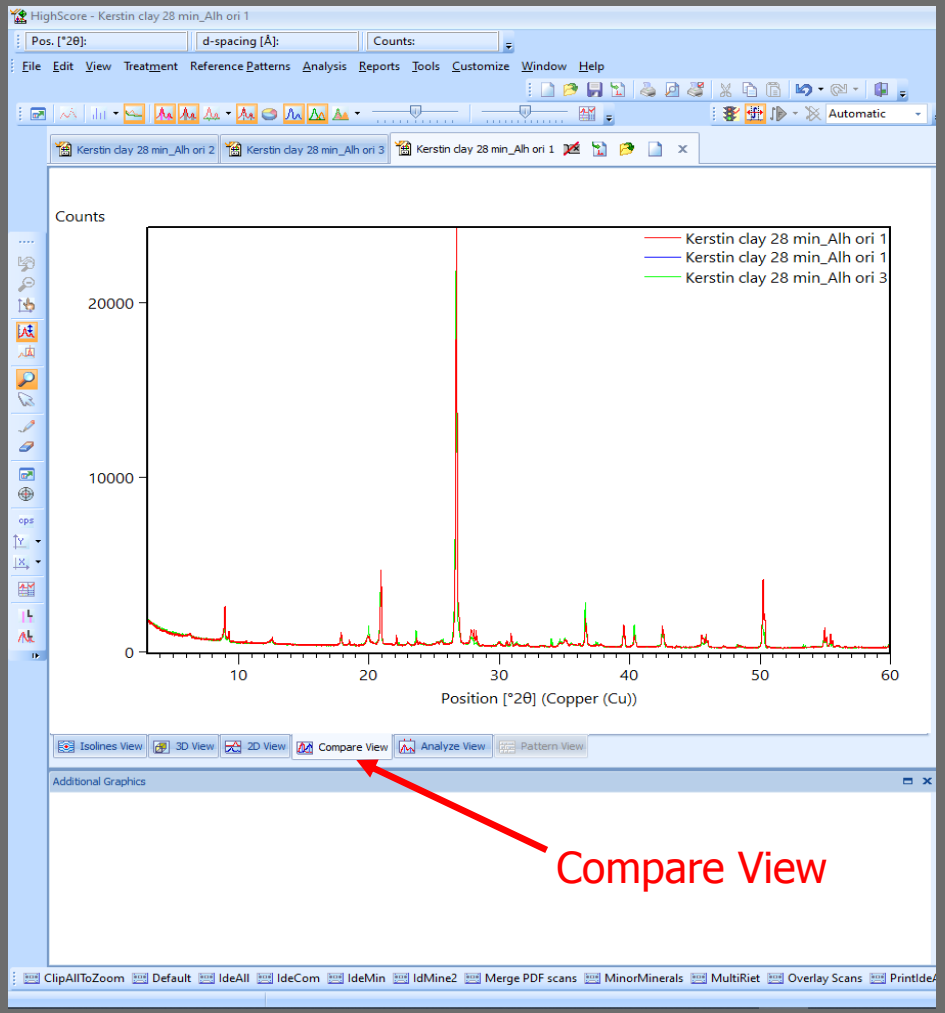


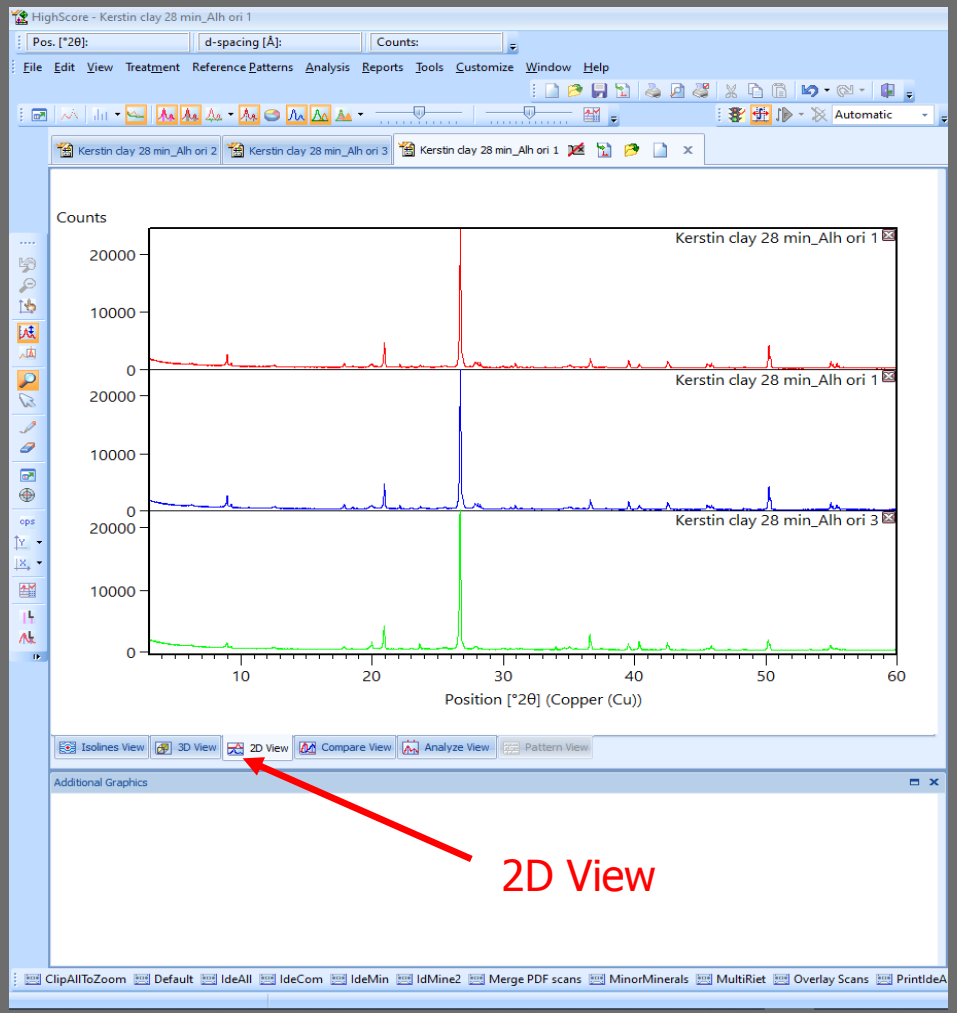
No.	h	k	l	d [Å]	2θ [°]	I [%]
1	1	0	0	4.25565	20.857	21.0
2	1	0	1	3.34387	26.637	100.0
3	1	1	0	2.45700	36.542	6.7
4	0	1	2	2.28166	39.462	6.6
5	1	1	1	2.23681	40.287	2.9
6	2	0	0	2.12782	42.448	4.9
7	0	2	1	1.97997	45.790	2.7
8	1	1	2	1.81812	50.134	11.0
9	0	0	3	1.80200	50.614	0.4
10	2	0	2	1.67193	54.868	3.3
11	1	0	3	1.65937	55.318	1.4
12	2	1	0	1.60848	57.227	0.2
13	2	1	1	1.54169	59.953	7.7
14	1	1	3	1.45309	64.026	1.4

11. To analyze several samples at the same time use «File» and «Insert» to open additional sample files.

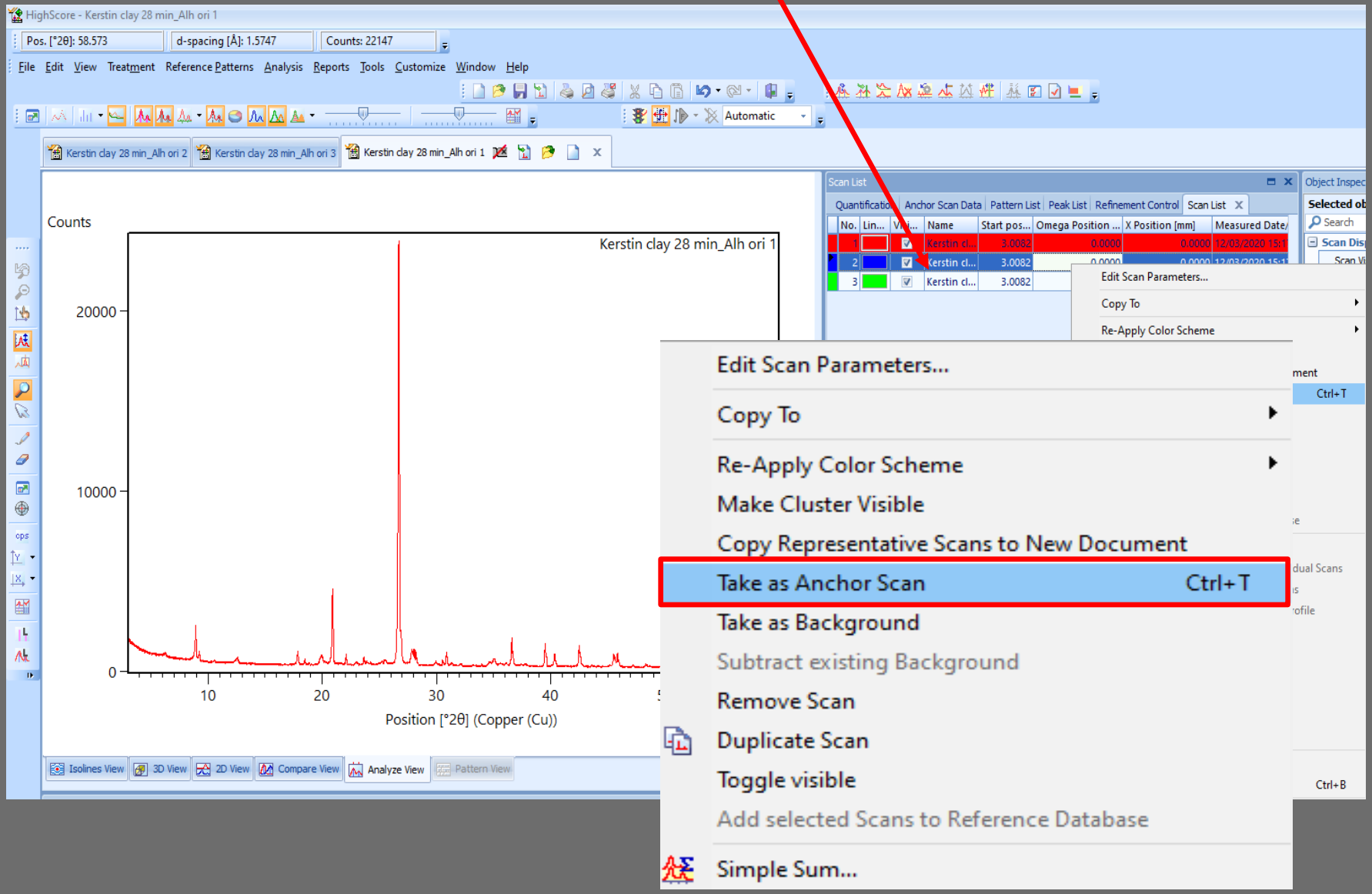


12. There are several options to compare different samples, for example: «Compare View» (you see the diffractograms stacked on top of each other) or «2D View» (you see the diffractograms separately, one above the other).

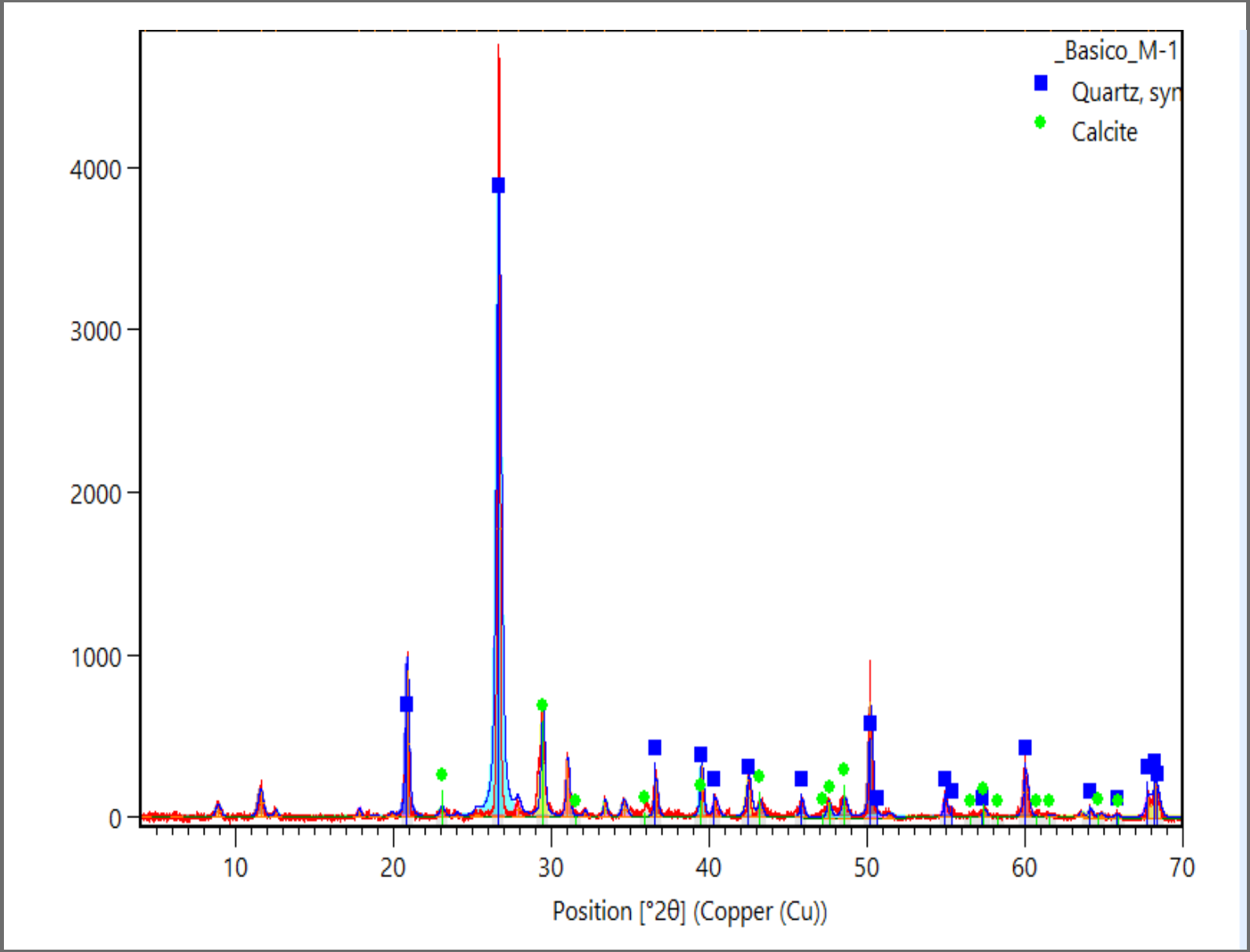




13. By default the program analyzes the first sample. If you want to analyze a different sample, you have to select it with a double «clic» of the right mouse button and choose «Take as Anchor Scan».

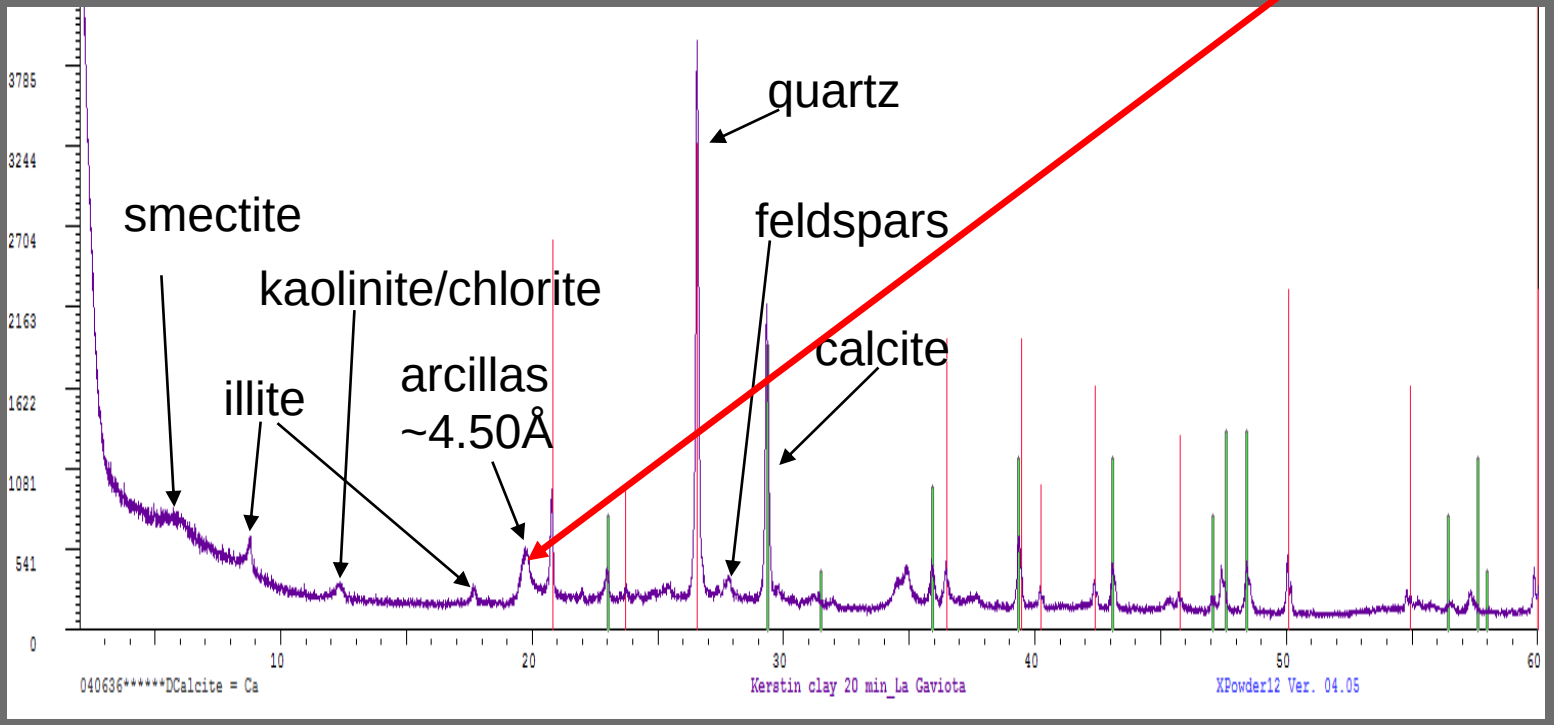


The analyzed diffractogram can be stored as a pdf file.

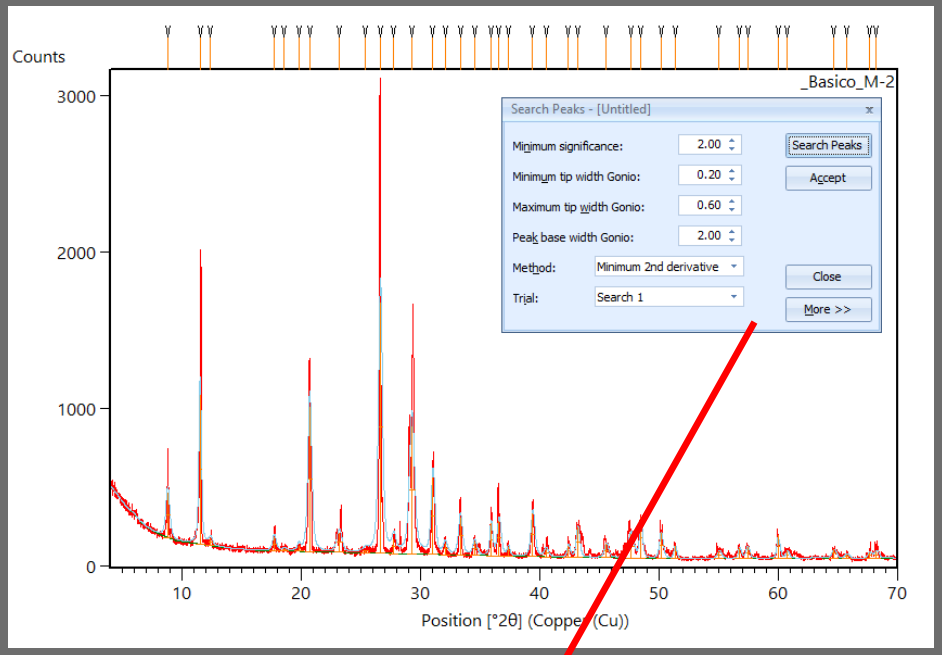


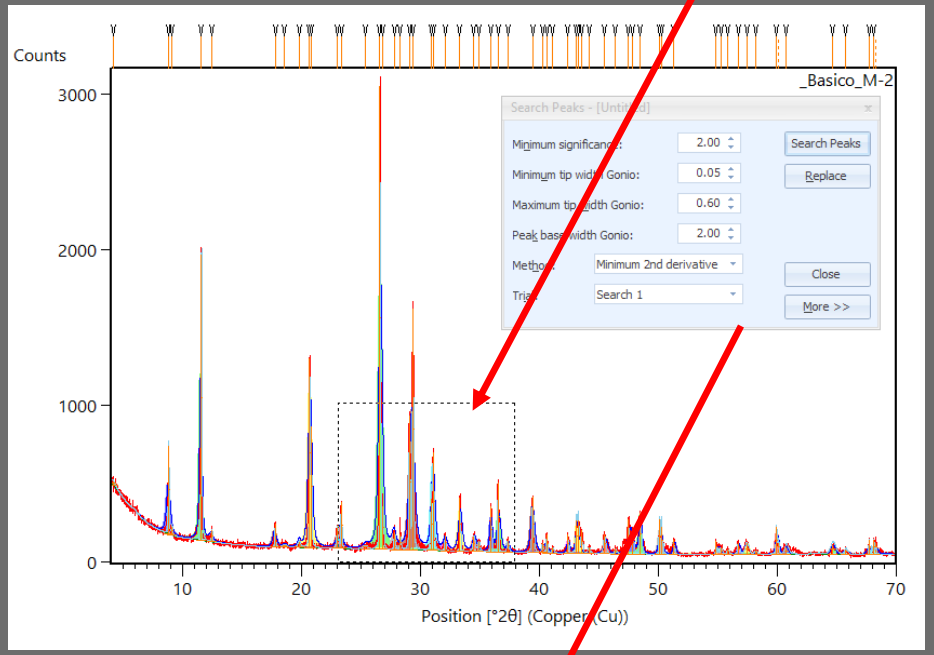
Quantification of mineral phases using XRD

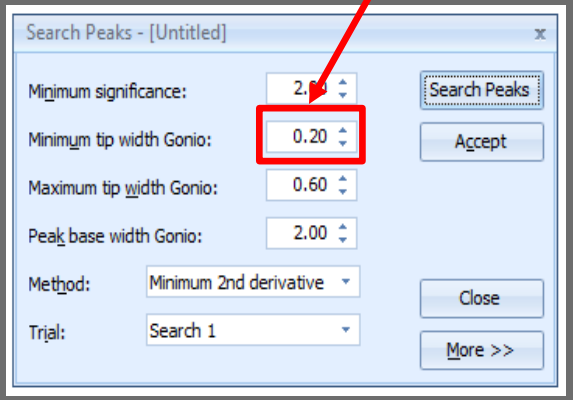
Generally, commercial software allows a more or less reliable automatic quantification. A high precision quantitative analysis requires the application of the Rietveld method (advanced XRD analysis). In general, the XRD analysis is semiquantitative and in many cases we have to assume an error of approximately ±5 wt% (in the case of clay minerals up to ±10 wt%). Considering that many building materials are quite complex and contain several mineral phases including clays, a «semimanual» quantification is recommended. The automatic and semimanual methods are described below, using experimental reflective power values and the general peak of clays at ~4.50 Å (if the sample contains clay minerals) in the case of the latter.

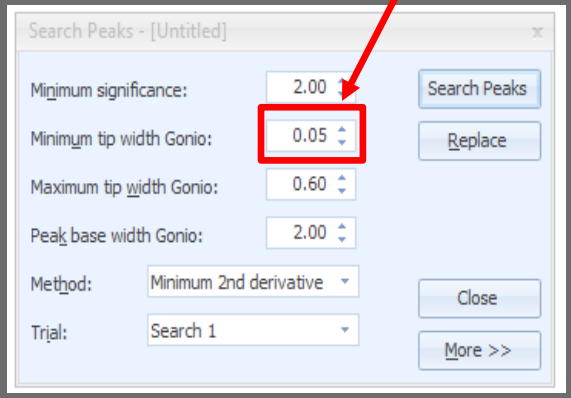


14. For a correct quantification we have to ensure that all peaks are selected and separated adequately. This can be verified by selecting a specific zone using the left mouse button.

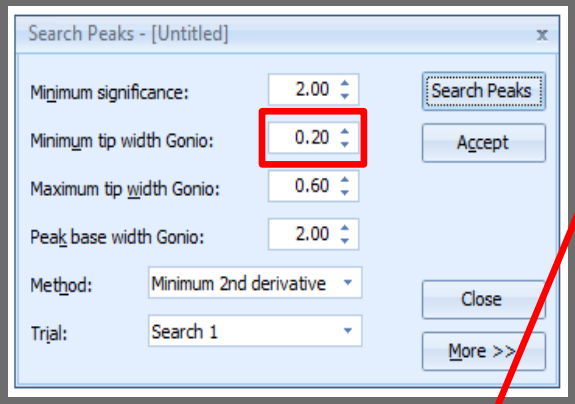


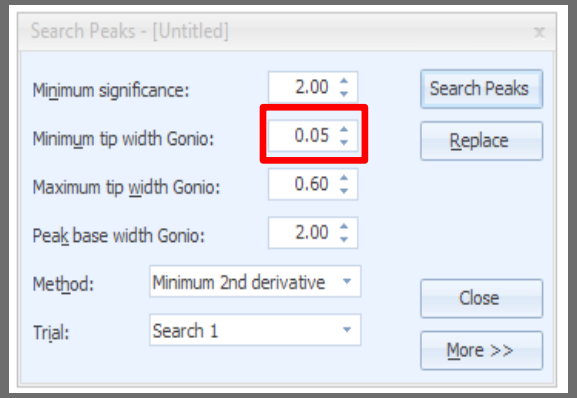


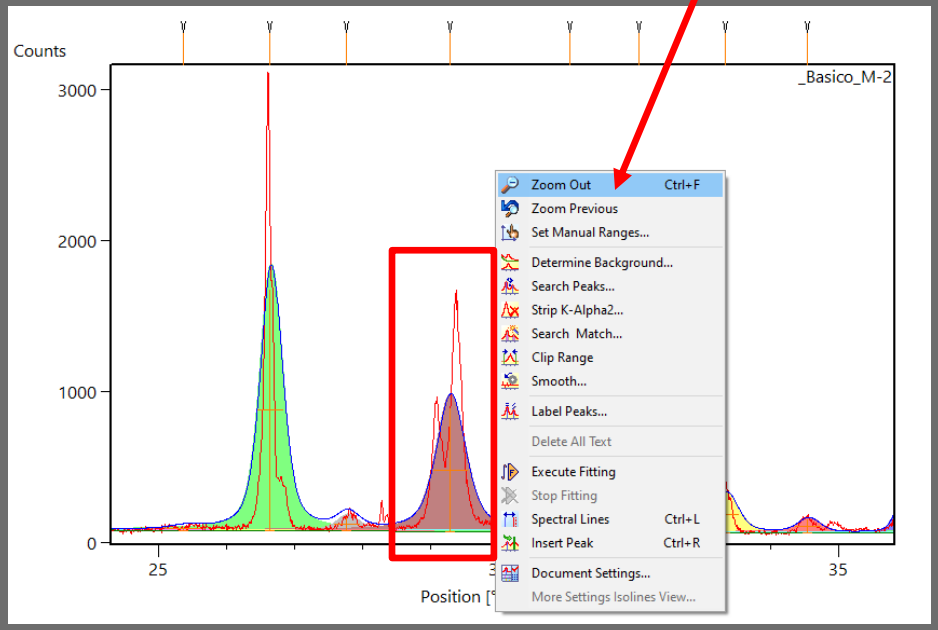


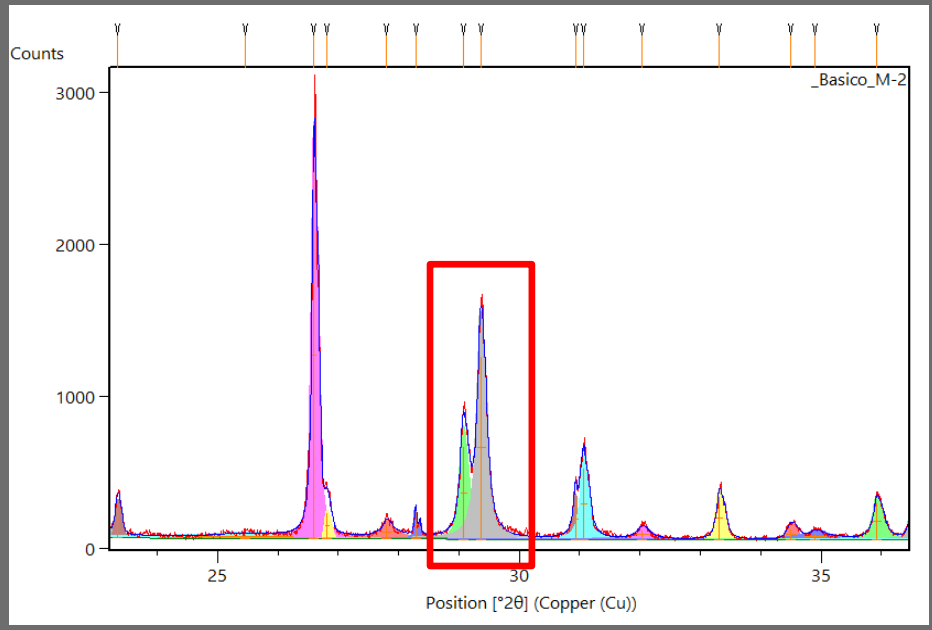


Here we see the effect of a reduction in the «Minimum tip width Gonio» on the peak separation. To obtain the full view of the diffractogram again we use the right mouse button and select «Zoom Out».

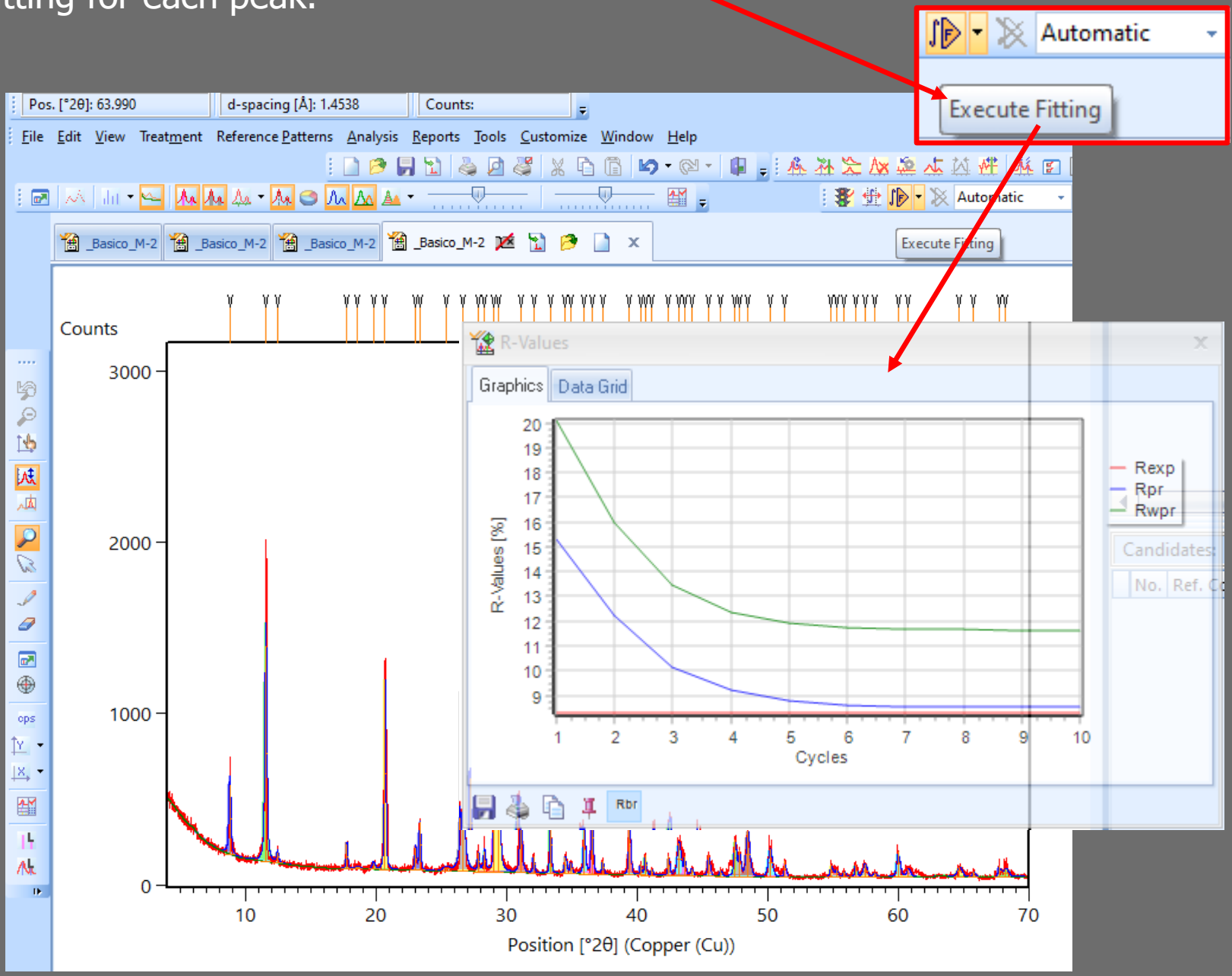




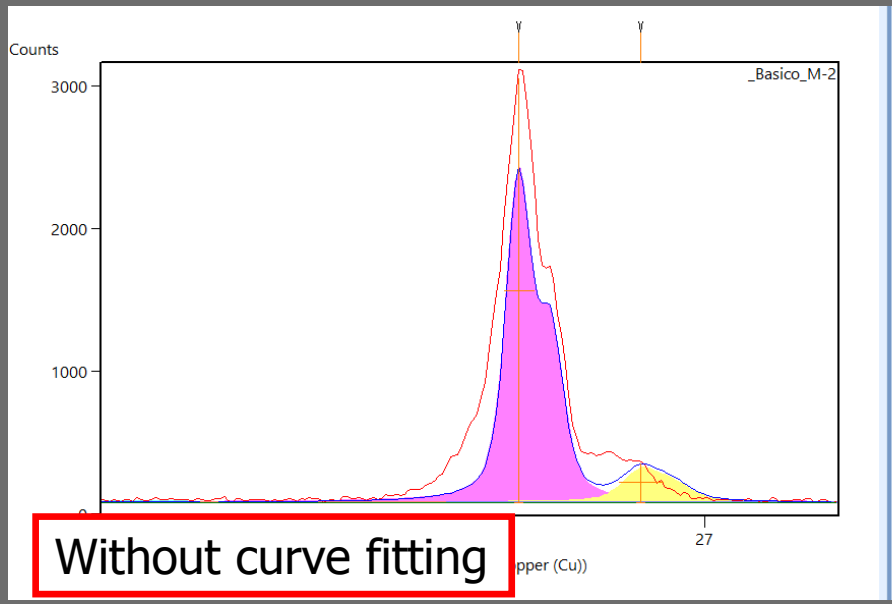




15. Once we have selected all peaks, we click on «Execute Fitting» in order to improve the curve fitting for each peak.



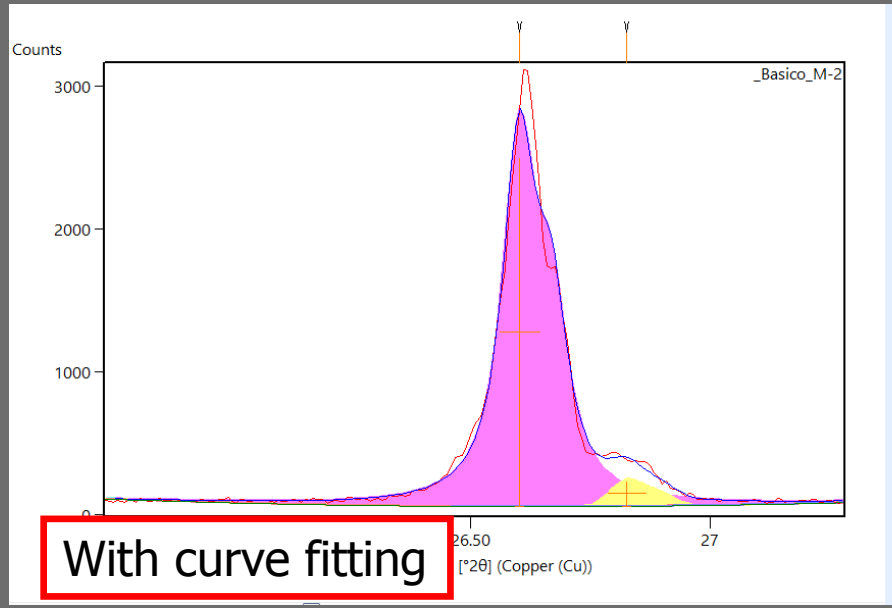
Below we see how the curve fitting influences the value of the peak area (counts). This information can be obtained by selecting «Peak List».



Peak List

Quantification | Anchor Scan Data | Pattern List | Peak List | Refinement Control | Scan List

No.	Pos. [°2θ]	d-spacing ...	Height [c...	Sha...	Area [cts*°2θ]	Status	Crystallite Size only [Å
1	4.2042	21.01773	146.17	0.600	54.48	Incl...	24
2	8.8595	9.98151	575.72	0.600	44.71	Incl...	210
3	9.1360	9.68002	57.13	0.600	5.32	Incl...	133
4	11.6197	7.61587	1872.05	0.600	145.37	Incl...	207
5	12.5004	7.08126	78.12	0.600	7.28	Incl...	132
6	17.8077	4.98097	154.38	0.600	9.59	Incl...	2827
7	18.5897	4.77315	15.21	0.600	5.67	Incl...	24
8	19.8153	4.48061	38.59	0.600	9.59	Incl...	37
9	20.7000	4.29106	1242.01	0.600	96.45	Incl...	201
10	20.8393	4.26271	800.38	0.600	49.72	Incl...	2840
11	23.0329	3.86146	139.34	0.600	21.64	Incl...	63
12	23.3584	3.80839	305.34	0.600	23.71	Incl...	200
13	25.3734	3.51033	21.07	0.600	10.47	Incl...	18
14	26.6098	3.34996	3035.81	0.600	188.59	Incl...	2870

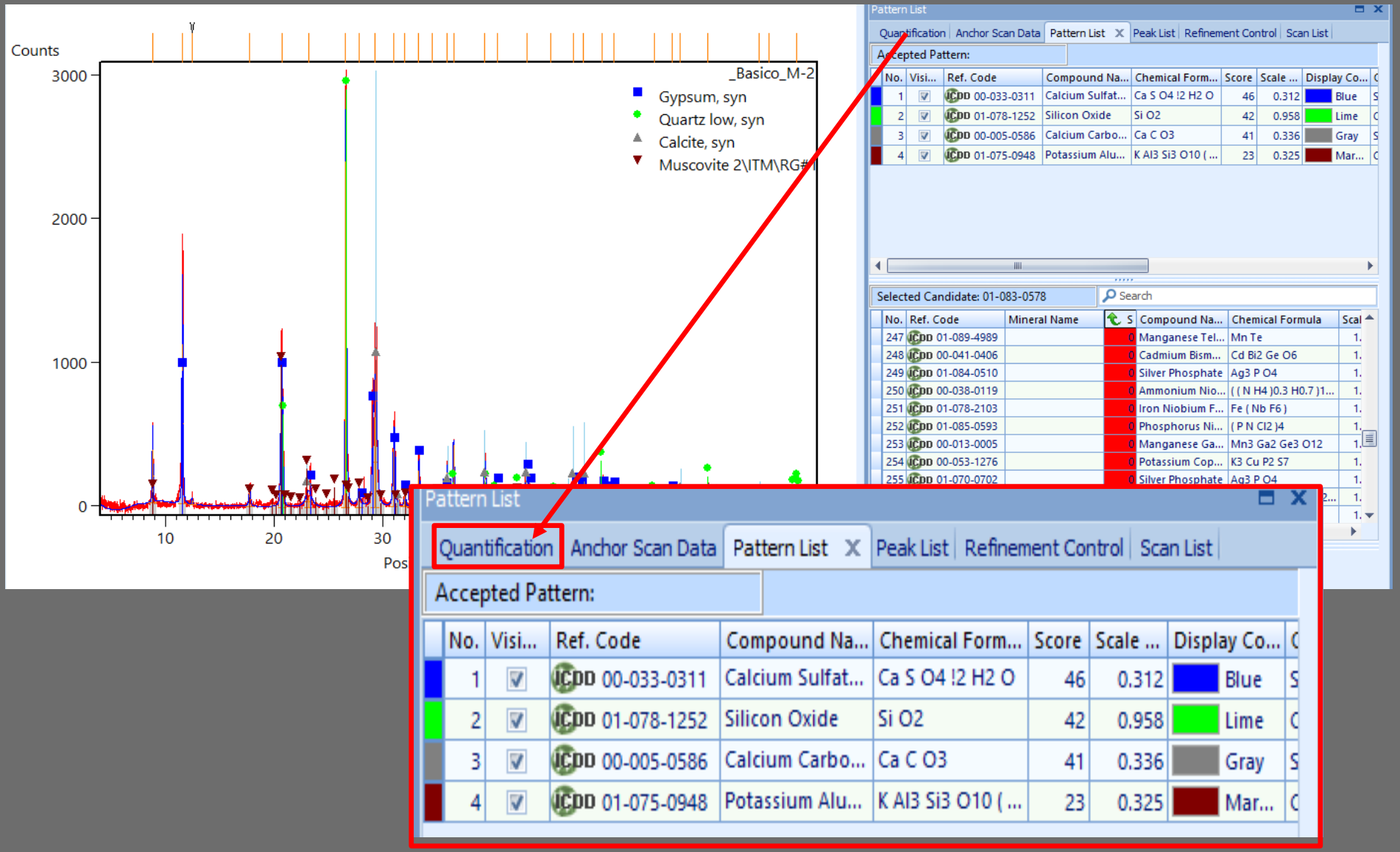


Peak List

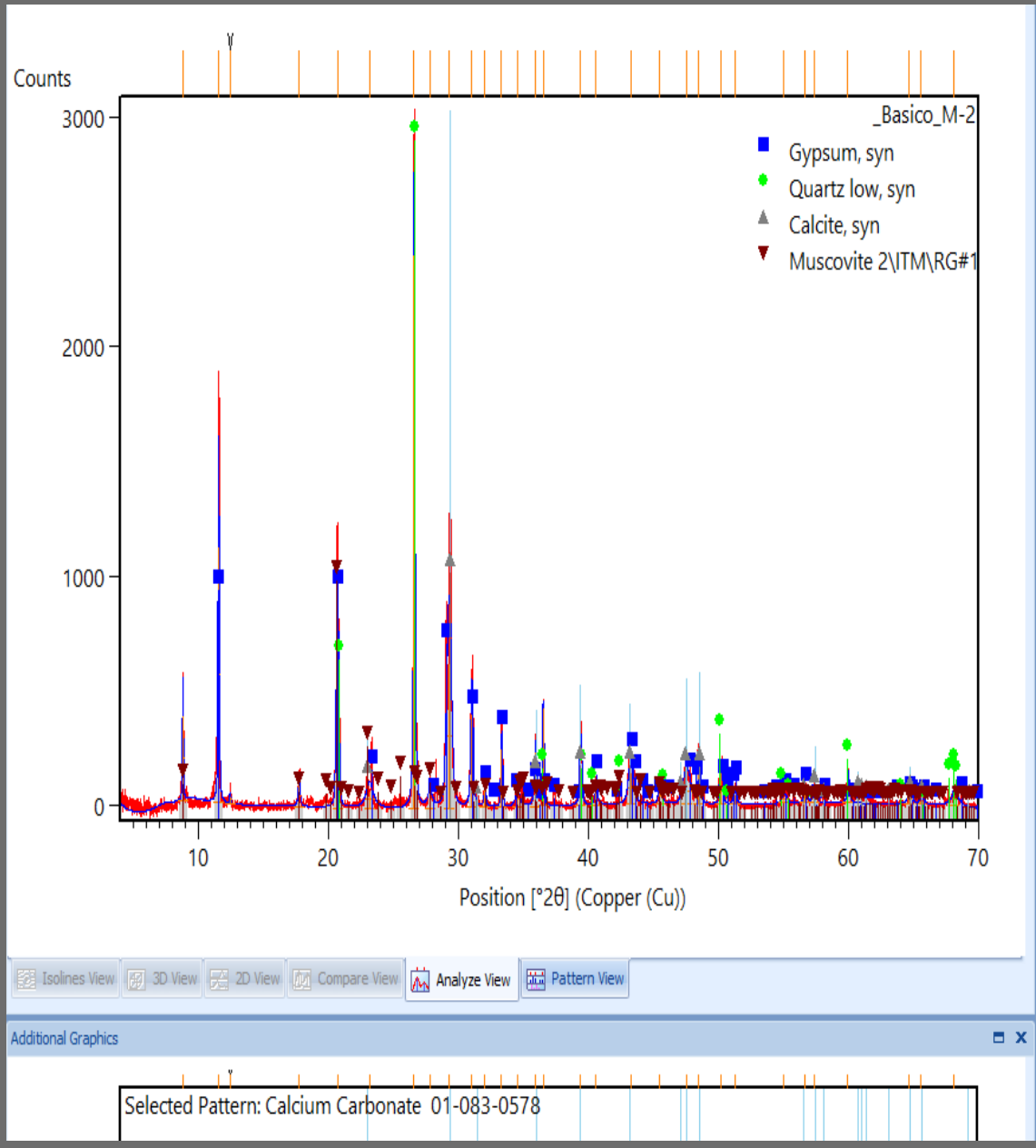
Quantification | Anchor Scan Data | Pattern List | Peak List | Refinement Control | Scan List

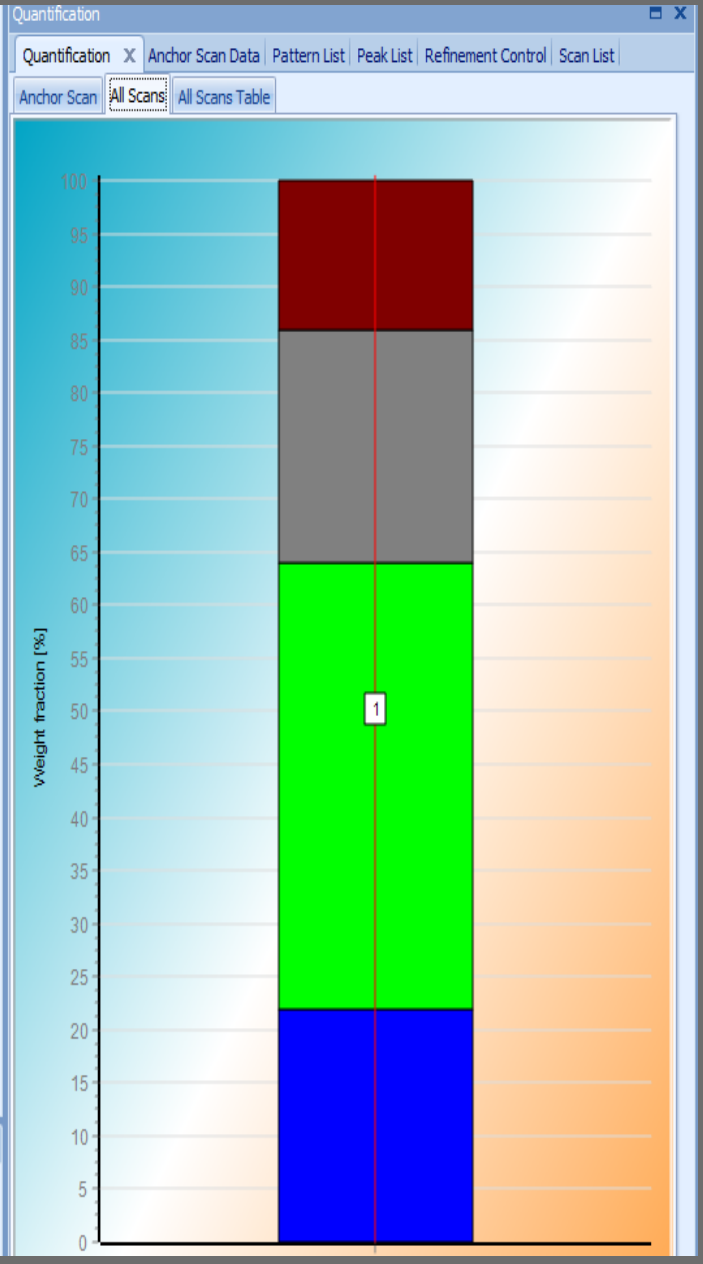
No.	Pos. [°2θ]	d-spacing ...	Height [c...	Sha...	Area [cts*°2θ]	Status	Crystallite Size only [Å
1	4.2042	21.01773	146.17	0.600	54.48	Incl...	24
2	8.8595	9.98151	575.72	0.600	44.71	Incl...	210
3	9.1360	9.68002	57.13	0.600	5.32	Incl...	133
4	11.6197	7.61587	1872.05	0.600	145.37	Incl...	207
5	12.5004	7.08126	78.12	0.600	7.28	Incl...	132
6	17.8077	4.98097	154.38	0.600	9.59	Incl...	2827
7	18.5897	4.77315	15.21	0.600	5.67	Incl...	24
8	19.8153	4.48061	38.59	0.600	9.59	Incl...	37
9	20.7000	4.29106	1242.01	0.600	96.45	Incl...	201
10	20.8393	4.26271	800.38	0.600	49.72	Incl...	2840
11	23.0329	3.86146	139.34	0.600	21.64	Incl...	63
12	23.3584	3.80839	305.34	0.600	23.71	Incl...	200
13	25.3734	3.51033	21.07	0.600	10.47	Incl...	18
14	26.6007	3.34831	2488.77	0.959	322.34	Incl...	180

16. The program HighScore allows an automatic quantification considering all fases included in «Accepted Pattern».

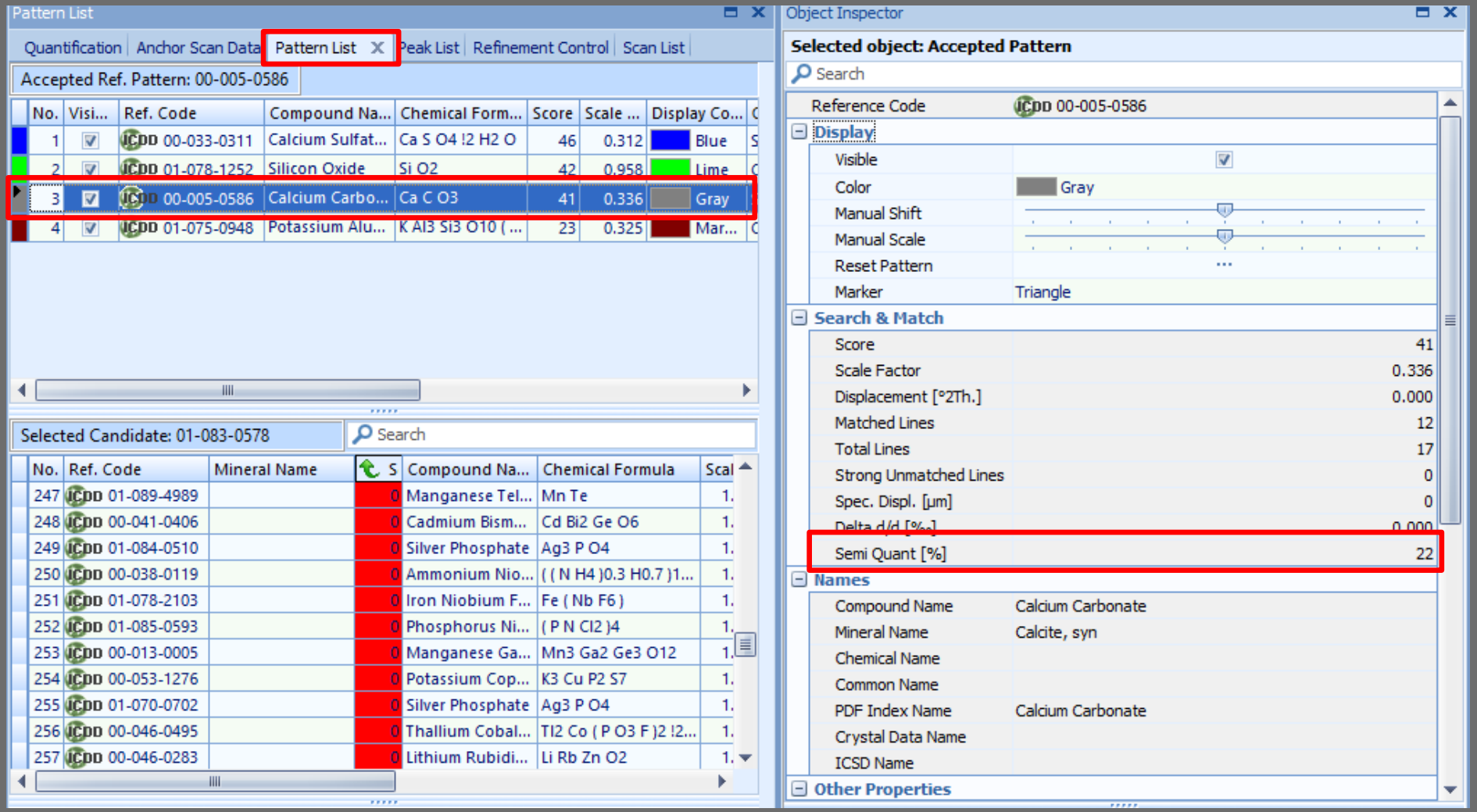


Example of an automatic quantification considering all phases included in «Accepted Pattern».

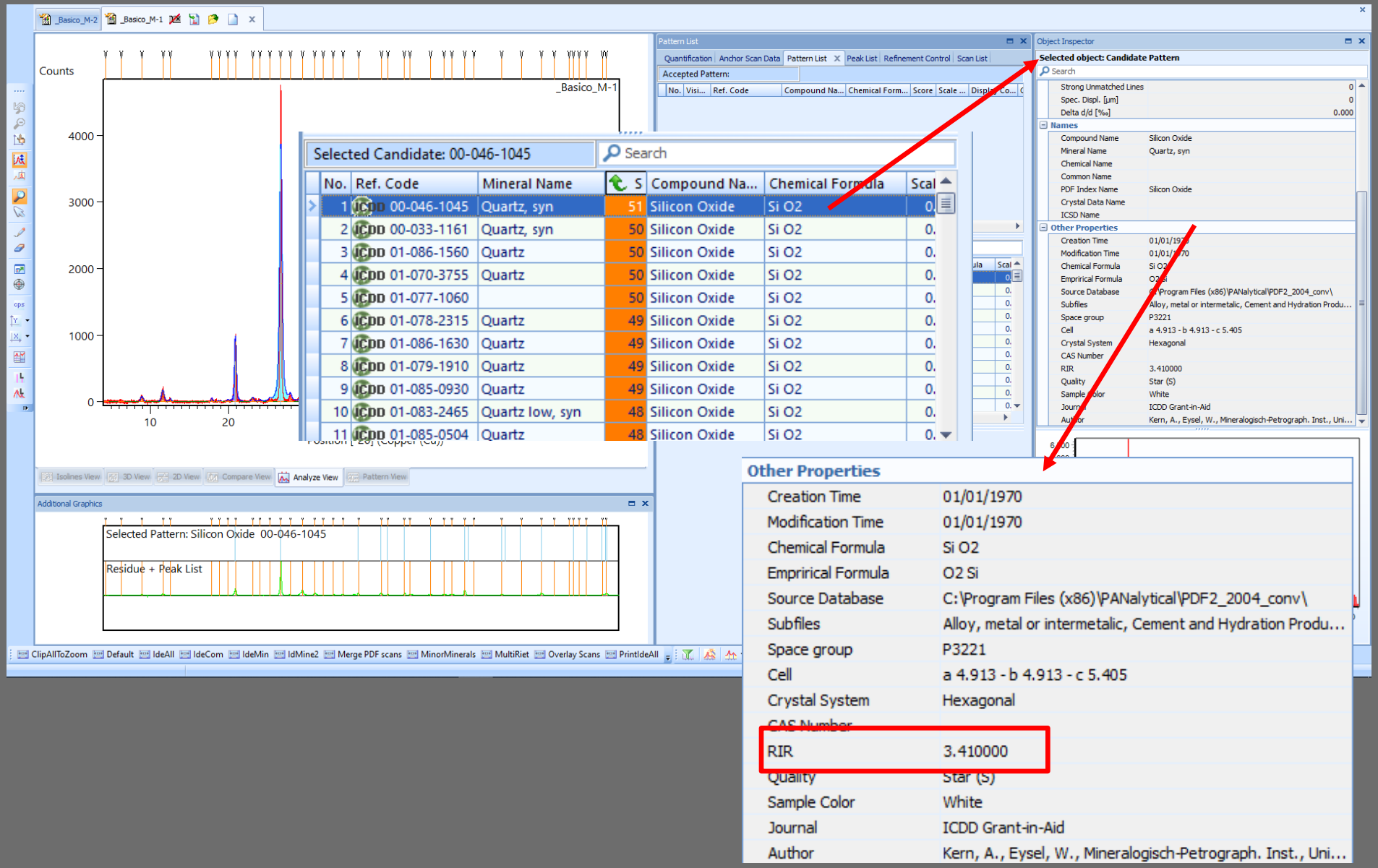




In order to obtain the values (weight percent) of the semiquantification of each phase, we have to select «Pattern List» and the file of the corresponding phase. Below we see the semiquantification for calcium carbonate (calcite).



We have to ensure that all selected files contain the RIR values in order to obtain an automatic quantification. We can obtain this information by selecting «Pattern List» and clicking on the selected file.



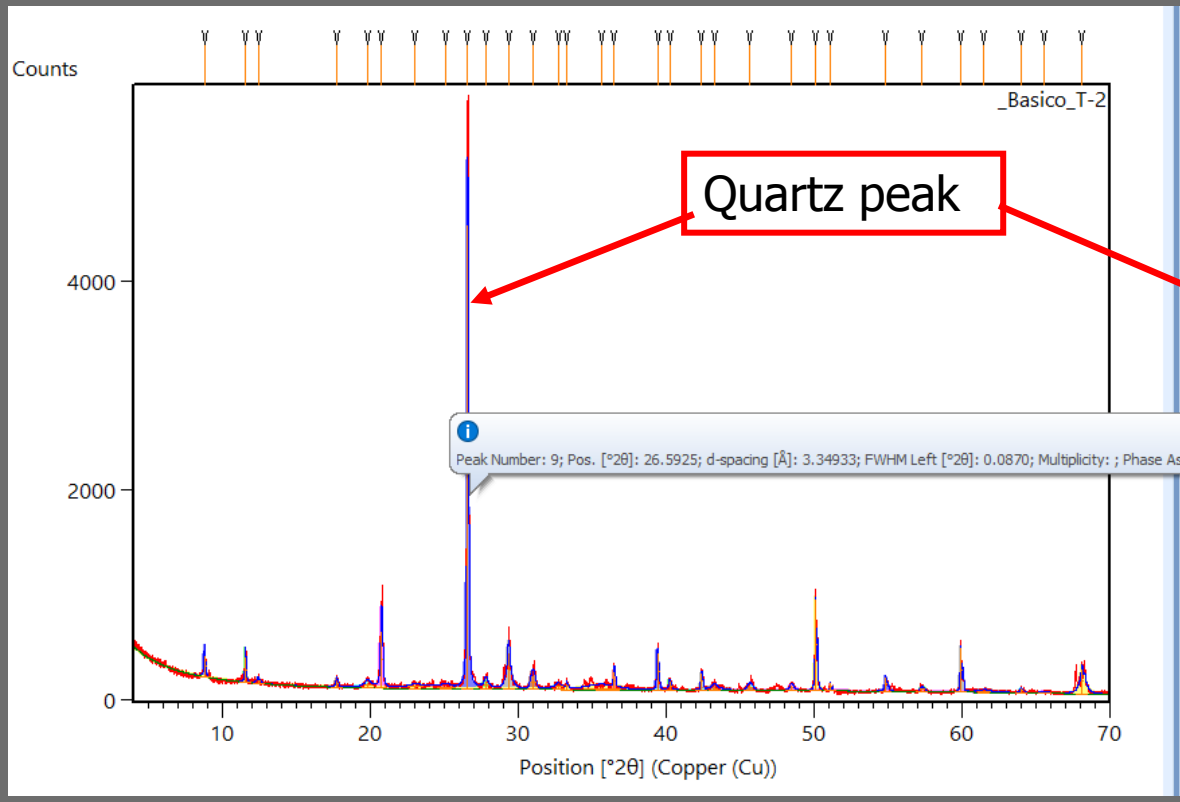

Counts
_Basico_M-1
Quartz, syn
Calcite
4000
3000
2000
1000
0
10
20
30
40
50
60
70
Position [°2θ] (Copper (Cu))
In this case one or more of the selected files do not contain the RIR value in order to allow the automatic quantification.
Isolines View
3D View
2D View
Compare View
Analyze View
Pattern View
Additional Graphics
Residue + Peak List
Accepted Patterns
Quantification
Quantification
Anchor Scan Data
Pattern List
Peak List
Refinement Control
Scan List
Anchor Scan
All Scans
All Scans Table
No quantification data available
Weight fraction [%]
0
1
1
Scan number

The values of the «Reference Intensity Ratio» (RIR, similar to the reflective power), which are used by the program in order to perform the automatic quantification might vary for each file. Consequently, the quantification will vary depending on the selected files.

Gypsum Patterns 9 Offset ☑ Max offset 0.15 Convergence 0

Set-Fil	Phase name	Q	Fract	RIR.	% W Unc Ab	m/rho	% W Xtal	% W Xtal+A	min %
700982	Gypsum	1	0.683	1.90	14.5(0.3)	60.8	14.6(0.3)	14.1(0.3)	000.0
700983	Gypsum	1	0.415	1.70	09.8(0.5)	60.8	09.9(0.5)	09.6(0.4)	000.0
700984	Gypsum	1	0.682	1.70	16.2(0.3)	60.8	16.3(0.3)	15.8(0.3)	000.0
720596	Gypsum	1	0.250	1.90	05.3(0.5)	60.8	05.3(0.5)	05.2(0.5)	000.0
741433	Gypsum	1	0.682	1.60	17.2(0.3)	60.8	17.3(0.3)	16.8(0.3)	000.0
741904	Gypsum	1	0.415	1.70	09.8(0.5)	60.8	09.9(0.5)	09.6(0.4)	000.0
741905	Gypsum	1	0.415	1.90	08.8(0.5)	60.8	08.9(0.5)	08.6(0.4)	000.0
761746	Gypsum	1	1.000	5.00	08.1(0.2)	60.8	07.5(0.2)	07.3(0.2)	000.0

17. For a «semimanual» quantification, instead of measuring the height and calculating the absolute intensity as we have done in the case of the XRD exercises, we are going to use the number of counts corresponding to the area of the peak with the maximum intensity of each phase. If we place the mouse on top of the peak the program will mark the corresponding data in the «Peak List».



Peak List

Quantification | Anchor Scan Data | Pattern List | Peak List | Refinement Control | Scan List

No.	Pos. [°2θ]	d-spacing ...	Height [c...	Sha...	Area [cts*°2θ]	Status	Crystallite Size only [Å]
1	8.8312	10.00517	215.83	0.829	33.83	Incl...	1577
2	11.5885	7.62999	256.04	1.097	31.07	Incl...	1993
3	12.4458	7.10630	40.77	1.410	15.58	Incl...	292
4	17.7522	4.99227	67.98	1.024	15.08	Incl...	615
5	19.8372	4.47201	50.67	1.303	47.45	Incl...	105
6	20.7748	4.27226	560.13	0.445	121.77	Incl...	603
7	23.0632	3.85326	32.08	1.500	77.47	Incl...	39
8	25.1464	3.53857	30.07	1.313	72.19	Incl...	39
9	26.5925	3.34933	4534.63	0.794	564.31	Incl...	3286
10	27.8074	3.20570	81.90	1.297	48.10	Incl...	178
11	29.3555	3.04007	353.12	1.338	135.49	Incl...	297
12	30.9945	2.88294	132.88	0.293	54.68	Incl...	259
13	32.6985	2.73649	44.24	1.500	47.36	Incl...	93
14	33.3039	2.68812	62.67	1.500	4.05	Incl...	29132
15	35.6543	2.51611	35.53	0.415	110.55	Incl...	30
16	36.4918	2.46027	173.85	-0.100	20.54	Incl...	928
17	39.4196	2.28402	368.76	0.761	55.39	Incl...	2100
18	40.2385	2.23941	90.83	1.151	16.81	Incl...	852
19	42.3947	2.13036	162.07	-0.081	20.77	Incl...	847
20	43.2376	2.09076	43.63	1.500	40.63	Incl...	111
21	45.6458	1.98590	50.38	-0.100	21.94	Incl...	222
22	48.4558	1.87710	57.17	1.062	23.75	Incl...	285
23	50.1036	1.81916	592.83	0.747	104.43	Incl...	5815
24	51.0938	1.78620	80.93	1.500	5.65	Incl...	30935
25	54.8357	1.67283	141.34	1.162	27.46	Incl...	841
26	57.2737	1.60728	36.82	-0.097	11.01	Incl...	344
27	59.9114	1.54266	443.38	0.683	57.72	Incl...	5765
28	61.4783	1.50709	20.94	1.500	35.39	Incl...	64
29	63.9848	1.45312	47.31	0.660	8.24	Incl...	1211

9	26.5925	3.34933	4534.63	0.794	564.31	Incl...

Semimanual quantification

For the quantification, we divide the number of counts corresponding to the area of each phase (peak of max. intensity) by the corresponding reflective power (R.P.). Note: Mineral names are included in English because identification programs use English names.

Phase	R.P.	d_{hkl} (Å)
Quartz	1.43	3.34
Calcite	1.05	3.03
Dolomite	1.03	2.88
Gypsum	0.70	7.56
Feldspars	0.98	~3.20
Strontianite	0.60	3.53
Celestite	0.52	2.97
Fluorite	2.00	3.16
Galena	1.50	2.96
Clays (mica, illite, kaolinite, smectite, ect.)	0.09	~4.50

18. For a semiquantitative analysis we create an EXCEL (or other spreadsheet software) document with the following columns: mineral name, d_{hkl}, reflective power, area counts, area counts divided by reflective power (AC/RP), weight percentage (wt%) and semiquantitative percentage (± 5 wt%). We simply have to enter the number of counts corresponding to the area of each mineral (red column), add all AC/RP values (green column), divide the AC/RP value of each mineral by the sum of AC/RP (blue column), and adjust the semiquantitative values by rounding to multiples of five.

Mineral	d_{hkl}	Reflective Power	Area Counts	AC/RP	Percentage (wt%)	Percentage semicuant. (wt%)
Phyllosilicates	4.49	0.09	512	(512/0.09 =) 5689	(5689/14039 =) 40	40
Quartz	3.34	1.43	11011	7700	55	55
Calcite	3.03	1.05	0	0	0	0
Dolomite	2.88	1.08	279	258	2	<5
Gypsum	7.05	0.70	0	0	0	0
Feldspars	3.21	1.03	404	392	3	<5
				Sum 14039		

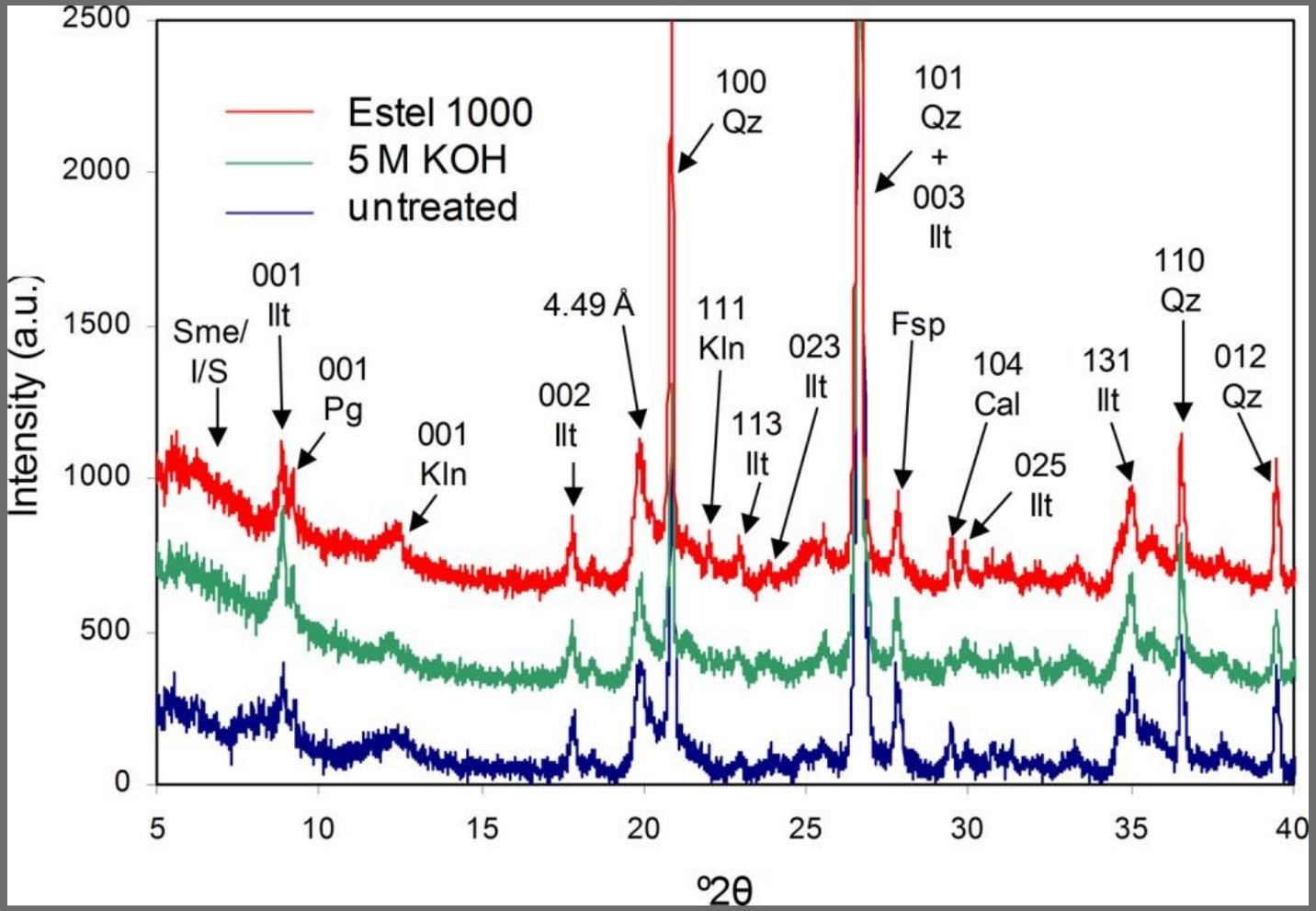
19. We also have the possibility to present the results of an XRD analysis in a table, describing the abundance of each phase using the following terms: very abundant, abundant, less abundant and trace (see table). We have to consider that some minerals have very low reflective power, resulting in a relatively small peak despite a considerable amount of this mineral in the sample (for example smectites) or that the position of peaks of two minerals overlap (for example the 003 reflection of illite and 101 reflection of quartz), which may cause an underestimation of smectite or an overestimation of quartz if quantification is done by a «visual» estimate.

Example

Sample	Phyllosilicates	Quartz	Calcite	Dolomite	Gypsum	Feldspars
Alhambra 1	+	+++	+	+	-	+
Alhambra 2	tr	++	++	+	-	+
Alhambra 3	+	+++	+	tr	tr	tr
Alhambra 4	++	++	+	tr	tr	tr
Alhambra 5	tr	++	++	+	+	-
Alhambra 6	-	++	++	-	tr	-

+++ = very abundant
++ = abundant
+ = less abundant
tr = trace
- = not detected

20. For the presentation of the XRD data it is recommended to use a spreadsheet program such as EXCEL or ORIGIN and include the names of the minerals (official abbreviation *) and their d_{hkl} (see reference mineral files). To be able to open the files in these programs, you must convert them to text or xy using programs such as POWDLL.



*D.L. Whitney y B.W. Evans, Abbreviations of names of rock-forming minerals, Amer. Miner. 95 (2010) 185–187.