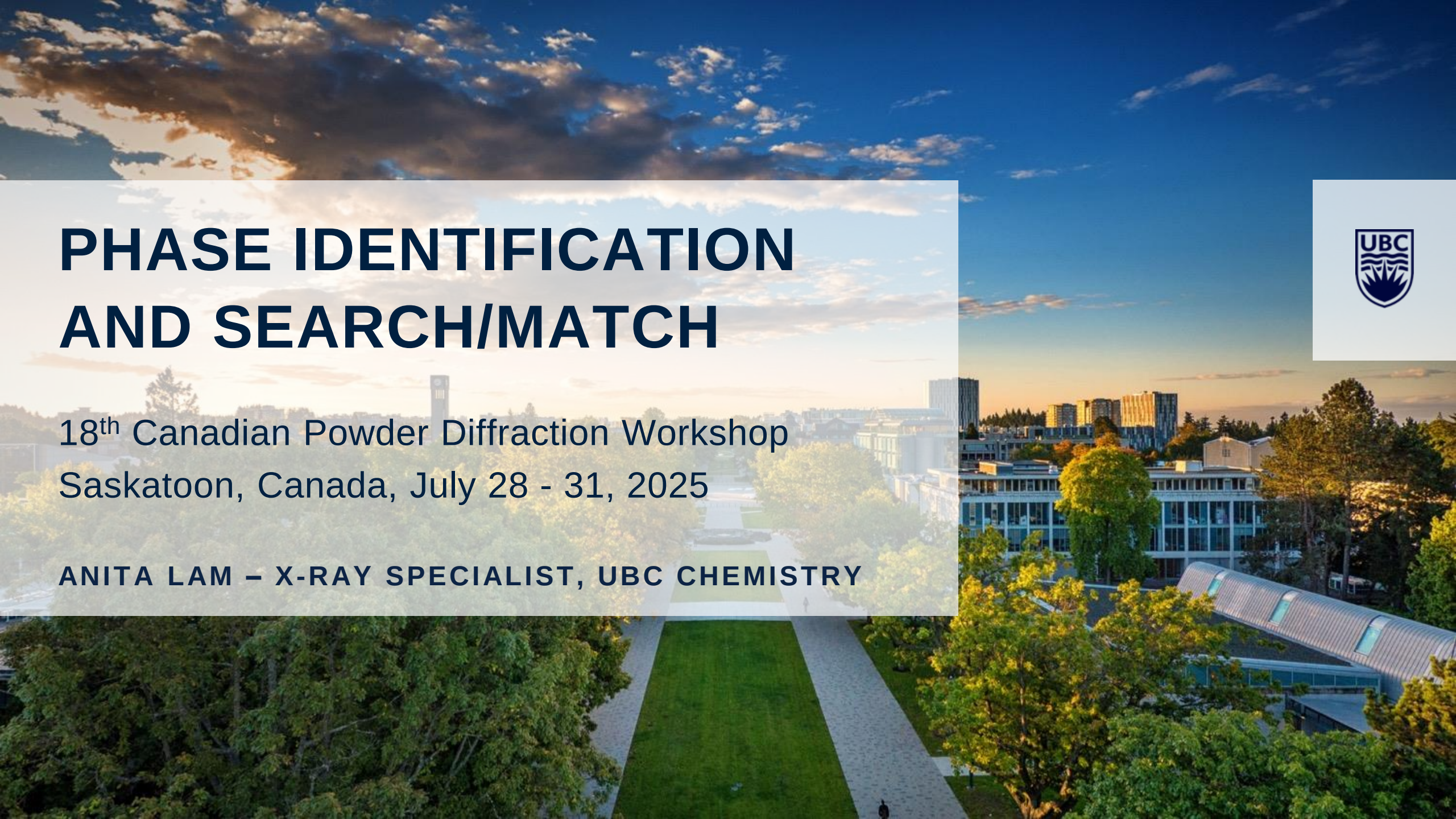


PHASE IDENTIFICATION AND SEARCH/MATCH

18th Canadian Powder Diffraction Workshop

Saskatoon, Canada, July 28 - 31, 2025

ANITA LAM – X-RAY SPECIALIST, UBC CHEMISTRY

ACKNOWLEDGMENTS

Parts of this presentation were inspired from previous PXRD Phase ID presentations by:

- Lachlan Cranswick
- Pamela Whitfield
- Nicola Döbelin
- Bussaraporn Patarachao

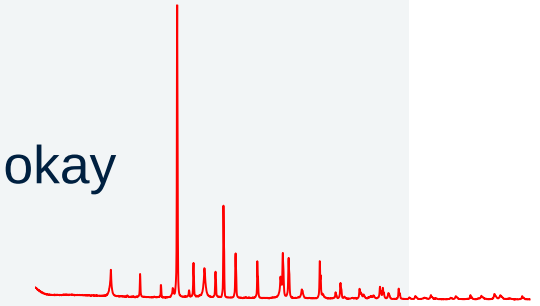
Special acknowledgments to:

- Mati Raudsepp
- Lee Groat and Julie (Melluish) McIntosh who started me on this XRD journey

INTRODUCTION

THE PROCESS OF PHASE IDENTIFICATION

What do we need?



- **Data**: acquire data for the purpose of phase ID – qualitative quality is okay
  - What do you do with it? How do you look at it?

- **Software for phase ID**: commercial, freeware; spreadsheet plot
  - Not absolutely necessary but it definitely helps

- **Database** (‘fingerprints’): commercial database, free database, books, individual files
  - Historically, phase identification was done manually (Hanawalt, Fink methods)

SEARCH/MATCH

- From the DIFFRAC.EVA User Manual (DOC-M88-EXX200 V2 – 09.2011)

“The Aim of EVA Search/Match

The purpose of EVA Search/Match is to search the current scan of an **unknown** material and then identify **reference patterns** that are likely to explain the unknown scan. A Search algorithm is applied, comparing the reference patterns of a database to the scan. The algorithm gives a rank to the Patterns and lists the "best candidates". The user must compare the pattern to the scan and accept or reject the found pattern. This is called the match procedure.”

BEFORE WE CONTINUE

Software and Databases shown and used in this presentation:

Software:

- EVA and Apex (Bruker)
- HighScorePlus (Malvern-Panalytical)
- QualX (Institute of Crystallography-CNR) – free for academic and non-profit

Databases:

- PDF-2 from the International Centre for Diffraction Data (ICDD)
- Crystallography Open Database (COD)
- American Mineralogist Crystal Structure Database (AMCSD)

DATABASES

- Inorganic and organic **databases** and crystal structure **resources**:
  - **PDF-5+**, **PDF-4 Minerals**, **PDF-4 Axiom** and **PDF-2** (Powder Diffraction File) from the **ICDD** (International Center for Diffraction Data) – commercial
  - **ICSD** (Inorganic Crystal Structure Database) – commercial
  - **COD** (Crystallography Open Database) – open access
  - **AMCSD** (American Mineralogist Crystal Structure Database) – open access
  - **CSD** (Cambridge Structural Database; organic and organometallic) – commercial
  - Published papers
  - Unpublished data: your files; research group files – create your own database; personal communication

- for phase identification
- no atomic positions given so can't use for Rietveld work

➢ CIF file → convert to diffraction pattern then bring it into the phase ID software to try to **match**

- For more information on databases: see International Tables for Crystallography (2019). Vol. H Chapter 3.7, pp. 304-324 (Crystallographic databases and powder diffraction by James Kaduk)

DATABASE EXAMPLE

You can search databases to find crystal structures and their information – but this is not the matching process...

... what do you need for matching?

American Mineralogist Crystal Structure Database

This site is an interface to a crystal structure database that includes every structure published in the American Mineralogist, The Canadia Mineralogist, European Journal of Mineralogy and Physics and Chemistry of Minerals, as well as selected datasets from other journals. Th database is maintained under the care of the Mineralogical Society of America and the Mineralogical Association of Canada, and financed the National Science Foundation.

pyrite — Mineral

Author

(Fe,S) — Chemistry Search

Cell Parameters and Symmetry

Diffraction Search

General Search

Search Tips

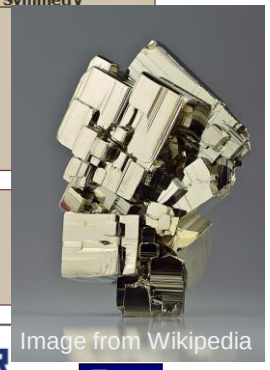
Search | Reset

Logic interface ● AND ○ OR

Viewing (About File Formats) ● amc long form ○ amc short form ○ cif

Download ● amc ○ cif ○ diffraction data

People | Extra



9 matching records for this search.

Pyrite
Ramsdell L S
American Mineralogist 10
The crystal structures o
Locality: natural, unkno
_database_code_amcsd 000
5.38 5.38 5.38 90 90 90

atom	x	y	z
Fe	0	0	0
S	.338	.338	.338

Download AMC data (View Text
Download CIF data (View Text
Download diffraction data (Vie
View JMOL 3-D Structure (perm

Pyrite
Bayliss P
American Mineralogist 62
Crystal structure refine
cubic model
_database_code_amcsd 0000605
5.4166 5.4166 5.4166 90 90 90 P a3

atom	x	y	z	Biso
Fe	0	0	0	.28
S	.3851	.3851	.3851	.33

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

Pyrite
Bayliss P
American Mineralogist 62 (1977) 1168-1172
Crystal structure refinement of a weakly anisotropic pyrite
_database_code_amcsd 0000606
5.4166 5.4166 5.4166 90 90 90 P1

atom	x	y	z	B(1,1)	B(2,2)	B(3,3)	B(1,2)	B(1,3)	B(2,3)
Fe1	.0010	.0020	.0030	.0023	.0024	.0017	.0000	.0000	.0004
Fe2	.4966	.0001	.5036	.0026	.0026	.0019	.0002	-.0003	-.0001
Fe3	.5001	.5020	.0011	.0026	.0021	.0022	.0007	-.0002	-.0003
Fe4	-.0006	.5013	.5038	.0026	.0026	.0016	.0001	-.0002	-.0001
S1	.3857	.3832	.3840	.0020	.0018	.0004	-.0007	-.0003	-.0004
S2	.1149	.6114	.8846	.0038	.0069	.0050	.0002	-.0001	-.0007
S3	.8854	.1157	.6143	.0034	.0001	-.0002	-.0001	-.0004	-.0004
S4	.6153	.8865	.1141	.0039	.0075	.0039	-.0003	-.0008	-.0010
S5	.6151	.6132	.6137	.0035	.0046	.0049	.0002	-.0002	.0000
S6	.8854	.3818	.1149	.0026	-.0005	-.0002	.0000	-.0003	.0002
S7	.1147	.8856	.3841	.0035	.0057	.0054	.0001	-.0003	-.0001
S8	.3857	.1161	.8842	.0014	-.0004	.0011	.0004	.0001	.0004

Download AMC data (View Text File)
Download CIF data (View Text File)

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Pyrite
Bayliss P
American Mineralogist 62 (1977) 1168-1172
Crystal structure refinement of a weakly anisotropic pyrite
cubic model
_database_code_amcsd 0000605

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X-RAY WAVELENGTH:     1.541838
Cell Volume:    158.921
Density (g/cm3):      5.014
MAX. ABS. INTENSITY / VOLUME**2:      47.22399758
RIR:      3.067
RIR based on corundum from Acta Crystallographica A38 (1982) 733-739
         2-THETA      INTENSITY    D-SPACING   H   K   L   Multiplicity
           28.54          39.18        3.1273   1   1   1          8
           33.08          95.52        2.7083   2   0   0          6
           37.11          54.86        2.4224   2   1   0         12
           40.81          45.47        2.2113   2   1   1         24
           47.48          51.01        1.9151   2   2   0         12
           56.33         100.00        1.6332   3   1   1         24
           59.08          15.84        1.5636   2   2   2          8
           61.75          16.11        1.5023   3   0   2         12
           64.35          15.90        1.4476   3   2   1         24
           64.35           5.65        1.4476   3   1   2         24
           76.69          10.49        1.2427   3   3   1         24
           79.06           6.56        1.2112   4   2   0         12
           79.06           6.56        1.2112   4   0   2         12
           81.42           8.55        1.1820   4   2   1         24
           83.76           4.21        1.1548   3   3   2         24
           88.41          12.51        1.1057   4   2   2         24

 XPOW Copyright 1993 Bob Downs, Ranjini Swaminathan and Kurt Bartelmehs
reference, see Downs et al. (1993) American Mineralogist 78, 1104-1107.
```

Crystallographic information file (CIF)

```
lobal
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author_name
ss P'
al_name_full 'American Mineralogist'
al_volume 62
al_year 1977
al_page_first 1168
al_page_last 1172
section_title

al structure refinement of a weakly anisotropic pyrite
 model

ase_code_amcsd 0000605
cal_formula_sum 'Fe S2'
length_a 5.4166
length_b 5.4166
length_c 5.4166
angle_alpha 90
angle_beta 90
angle_gamma 90
volume 158.921
_crystal_density_diffrn      5.015
_symmetry_space_group_name_H-M 'P a 3'
loop_
_space_group_symop_operation_xyz
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  '1/2+z,x,1/2-y'
  'z,1/2-x,1/2+y'
  '1/2-z,1/2+x,y'
  '-z,-x,-y'
  '1/2+y,1/2-z,-x'
  '1/2-y,-z,1/2+x'
  '-y,1/2+z,1/2-x'
  'y,z,x'
  'x,1/2-y,1/2+z'
  '1/2-x,1/2+y,z'
  '1/2+x,y,1/2-z'
  '-x,-y,-z'
  '1/2-z,-x,1/2+y'
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  'y,1/2-z,1/2+x'
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  '-x,1/2+y,1/2-z'
  '1/2+x,1/2-y,-z'
  '1/2-x,-y,1/2+z'
loop_
_atom_site_label
_atom_site_fract_x
_atom_site_fract_y
_atom_site_fract_z
_atom_site_U_iso_or_equiv
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S   0.38510   0.38510   0.38510   0.00418
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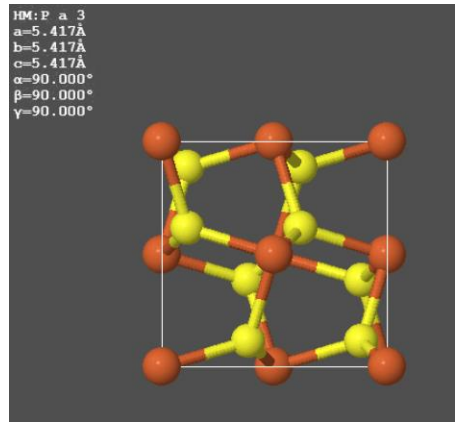

REMEMBER DIFFRACTION

Crystalline materials have long range periodicity. Once you know the crystal structure of a material you can generate a list of expected diffraction peaks (peak positions/d-spacings with relative intensities) and this is like a **fingerprint** of the material. It is unique to the material although there may be similar diffraction patterns across similarly structured materials.

X-ray diffraction experiment: An X-ray beam interacts with a crystalline substance and diffraction occurs when the Bragg equation is satisfied resulting in a set of diffraction peaks. These peaks are characterized by peak positions (related to d-spacings), intensities, and peak shape.

$$n\lambda = 2d\sin\theta \quad \text{Bragg equation}$$

```
Pyrite
Bayliss P
American Mineralogist 62 (1977) 1168-1172
Crystal structure refinement of a weakly anisotropic pyrite
cubic model
_database_code_amcsd 0000605

CELL PARAMETERS:    5.4166   5.4166   5.4166   90.000   90.000   90.000
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          56.33        100.00        1.6332    3   1   1        24
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          61.75         16.11        1.5023    3   0   2        12
          64.35         15.90        1.4476    3   2   1        24
          64.35          5.65        1.4476    3   1   2        24
          76.69         10.49        1.2427    3   3   1        24
          79.06          6.56        1.2112    4   2   0        12
          79.06          6.56        1.2112    4   0   2        12
          81.42          8.55        1.1820    4   2   1        24
          83.76          4.21        1.1548    3   3   2        24
          88.41         12.51        1.1057    4   2   2        24
================================================================================
 XPOW Copyright 1993 Bob Downs, Ranjini Swaminathan and Kurt Bartelmehs
reference, see Downs et al. (1993) American Mineralogist 78, 1104-1107.
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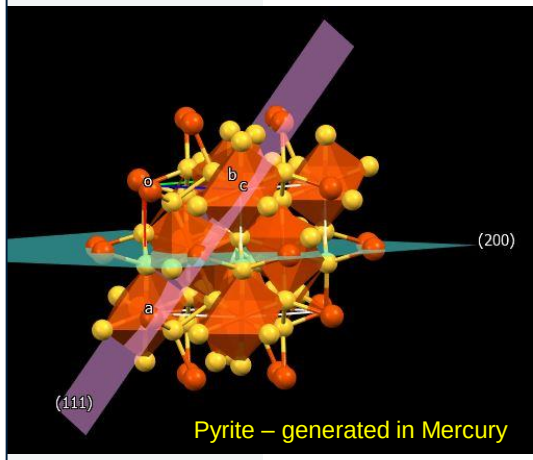

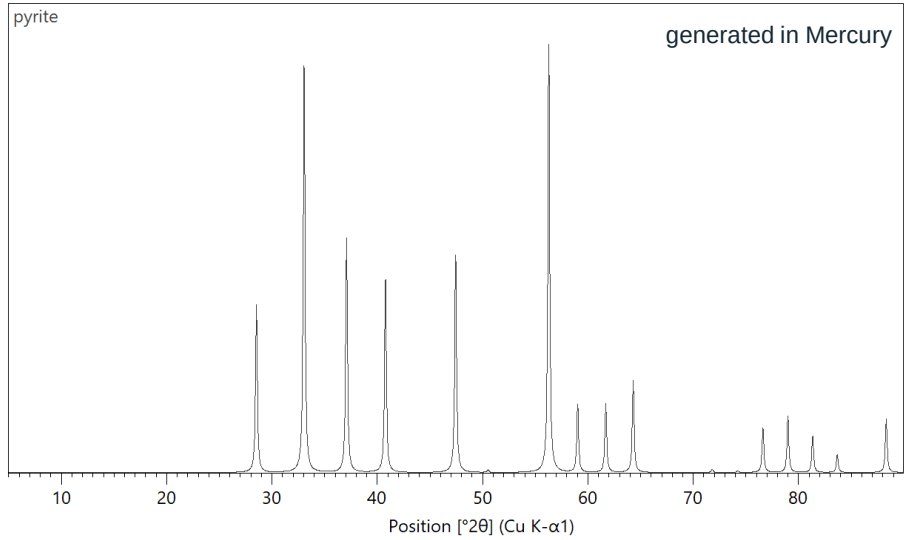

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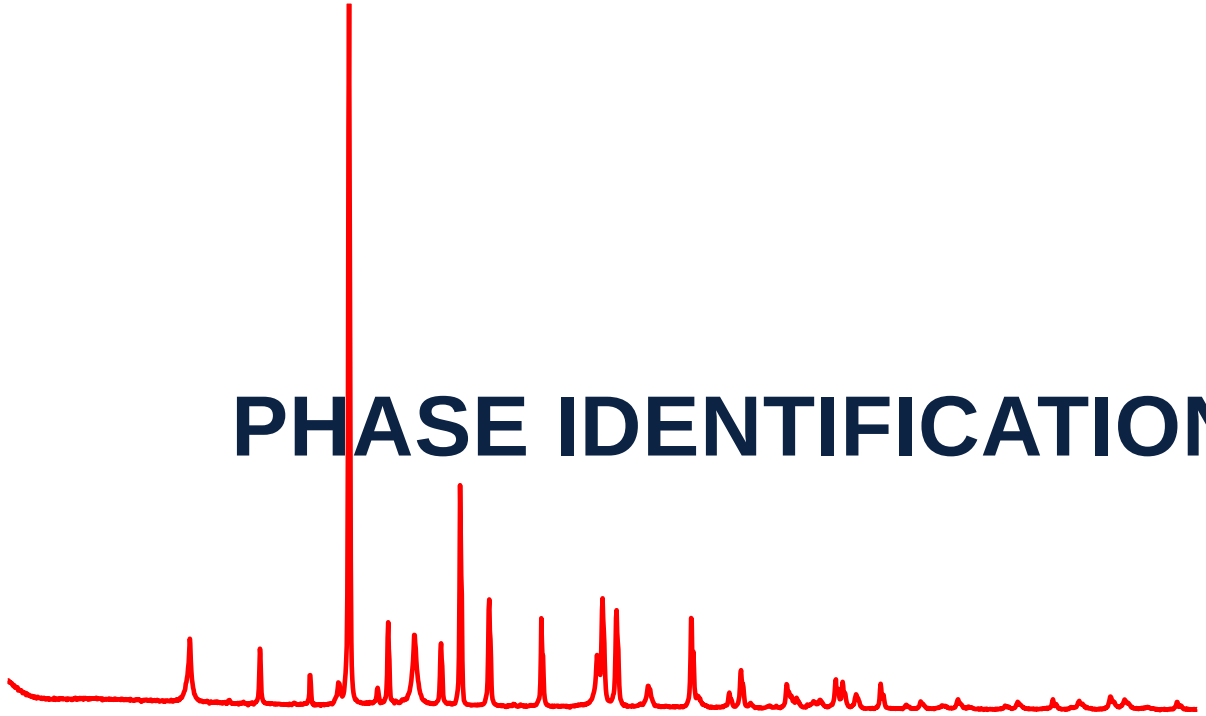

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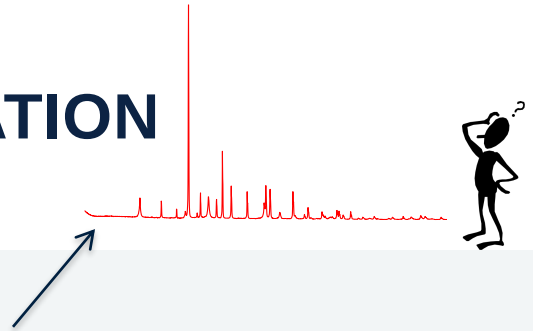
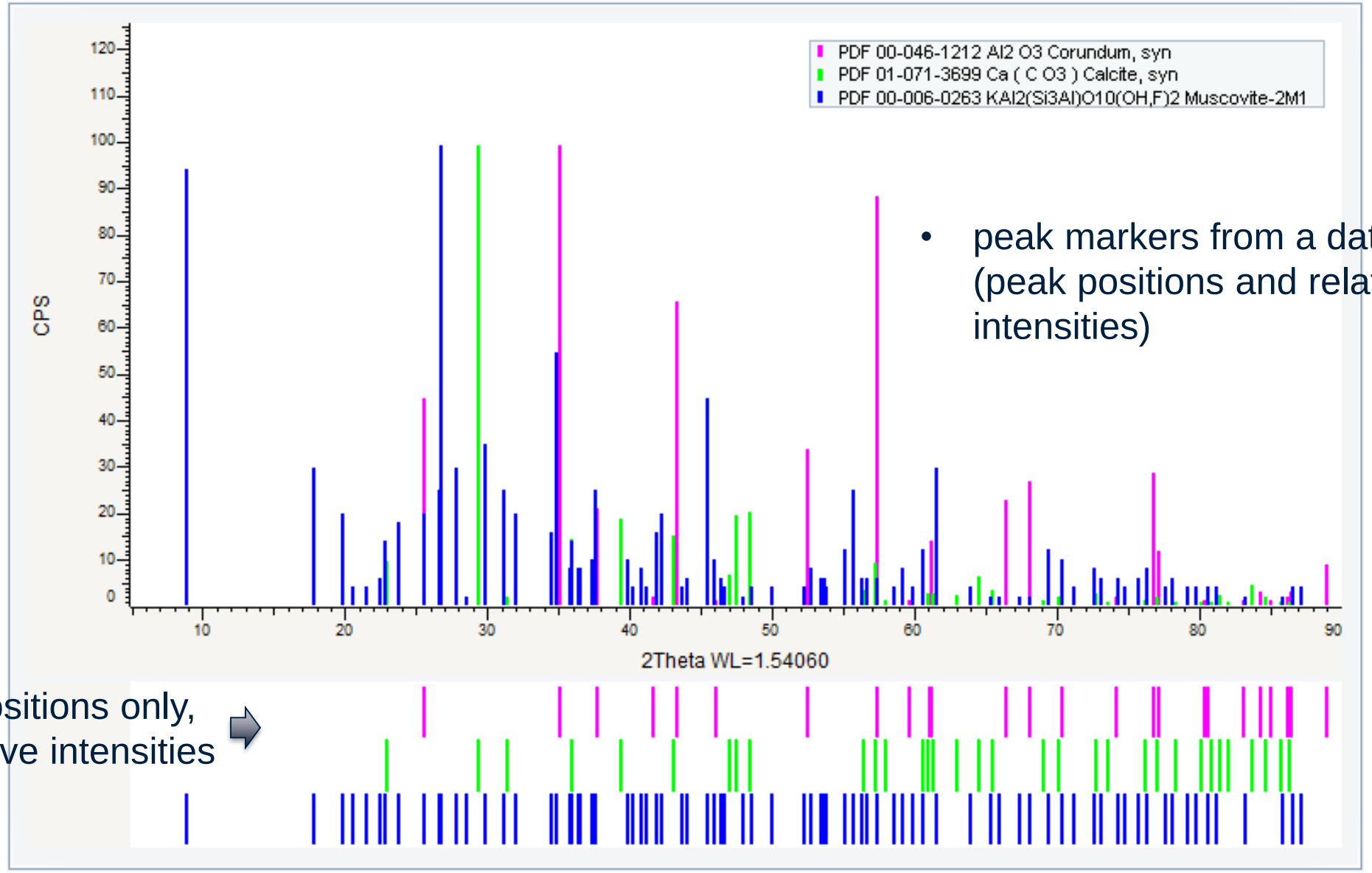


- It’s like matching a fingerprint to known patterns in a database
- Peak positions are key for phase identification
  - Relative intensities are helpful but we know that the peak intensities may differ from ideal
- XRD is sensitive to structural differences; if you only have qualitative XRD data, you should be careful of drawing conclusions about the chemistry of the phases
  - chemical analyses and sample information help with phase identification
- Note: you need to do phase identification before you attempt to try quantitative phase analysis (QPA)

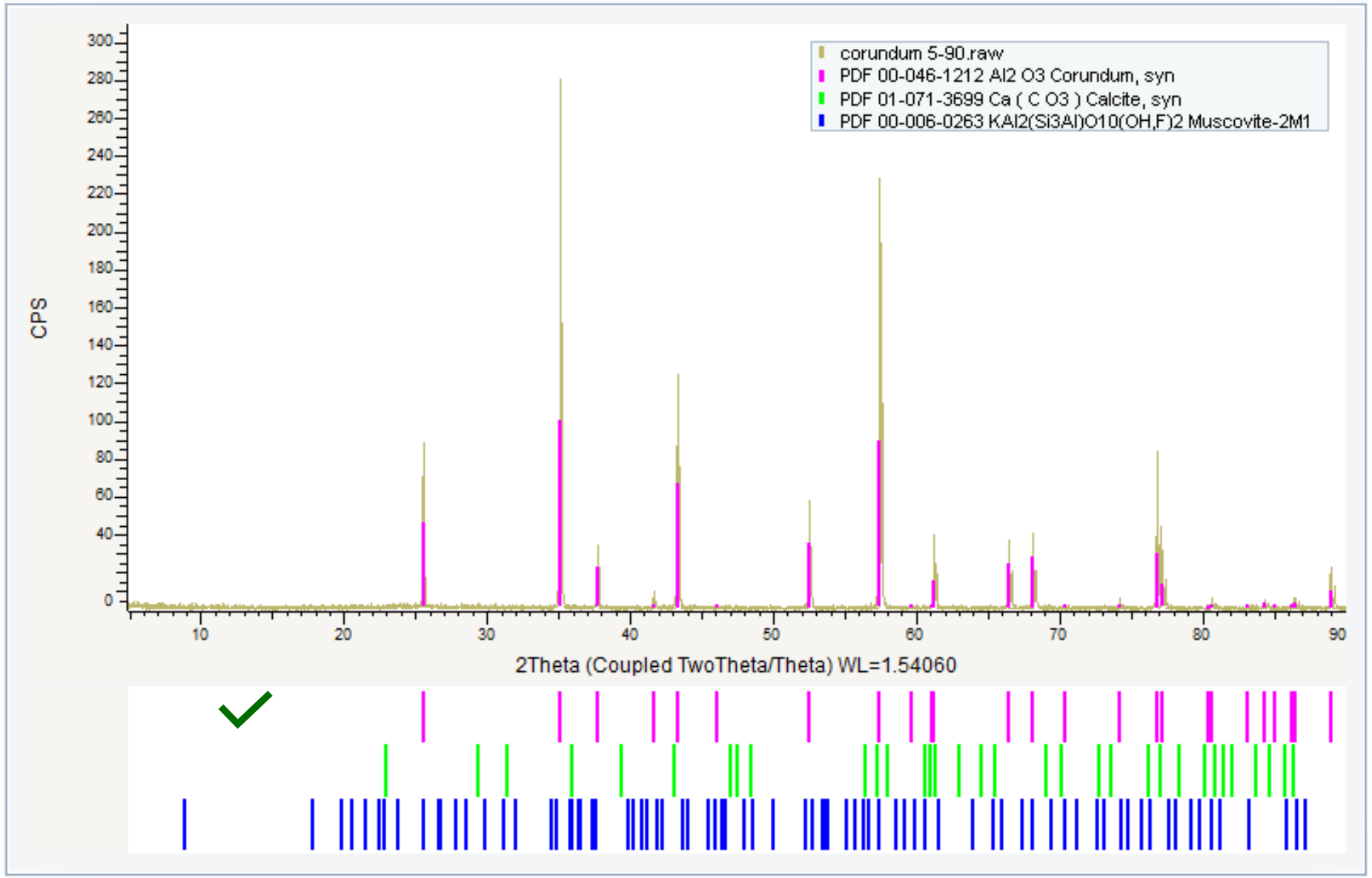
FINGERPRINT



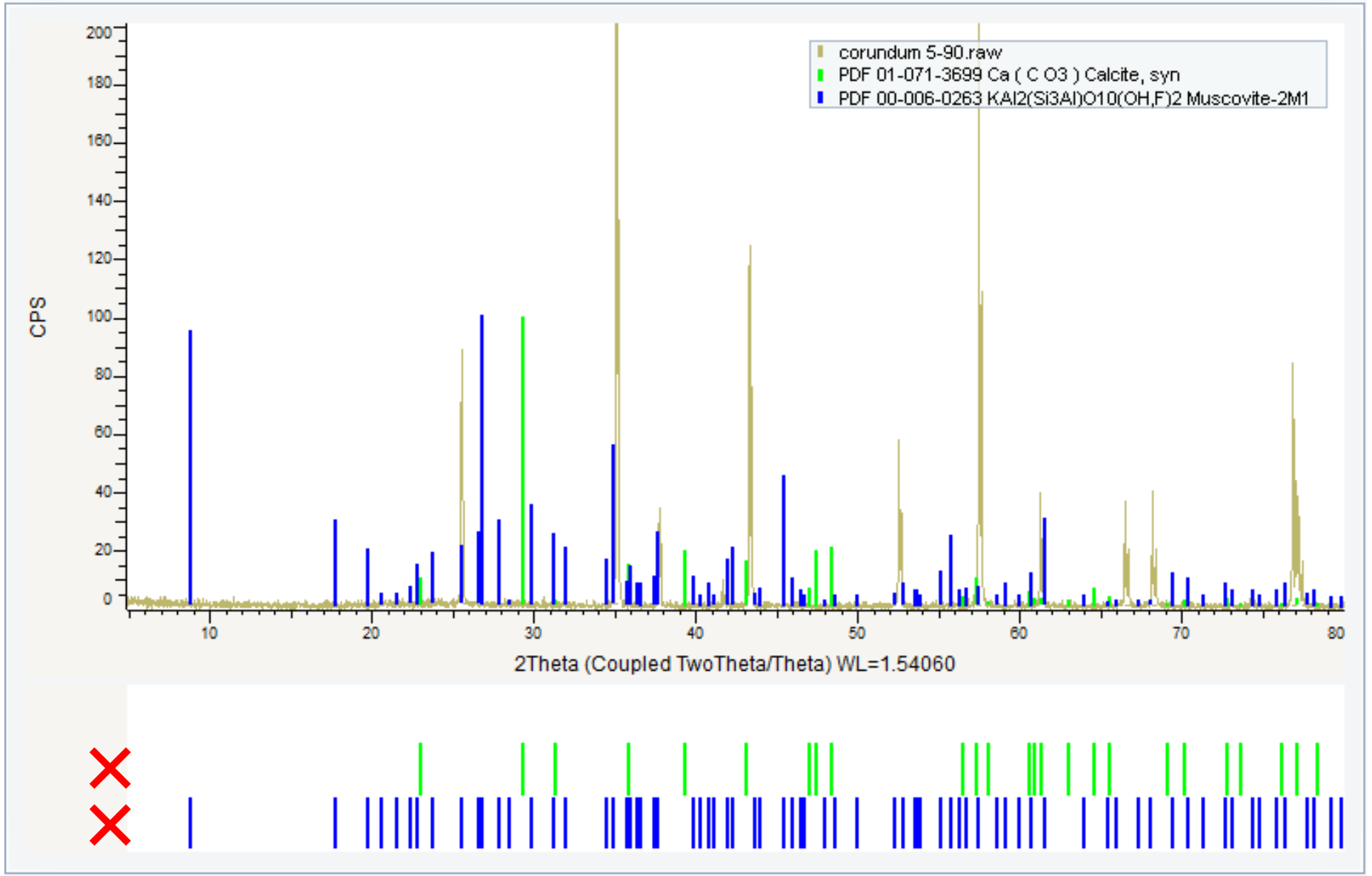
- peak markers from a database (peak positions and relative intensities)

Peak positions only, no relative intensities

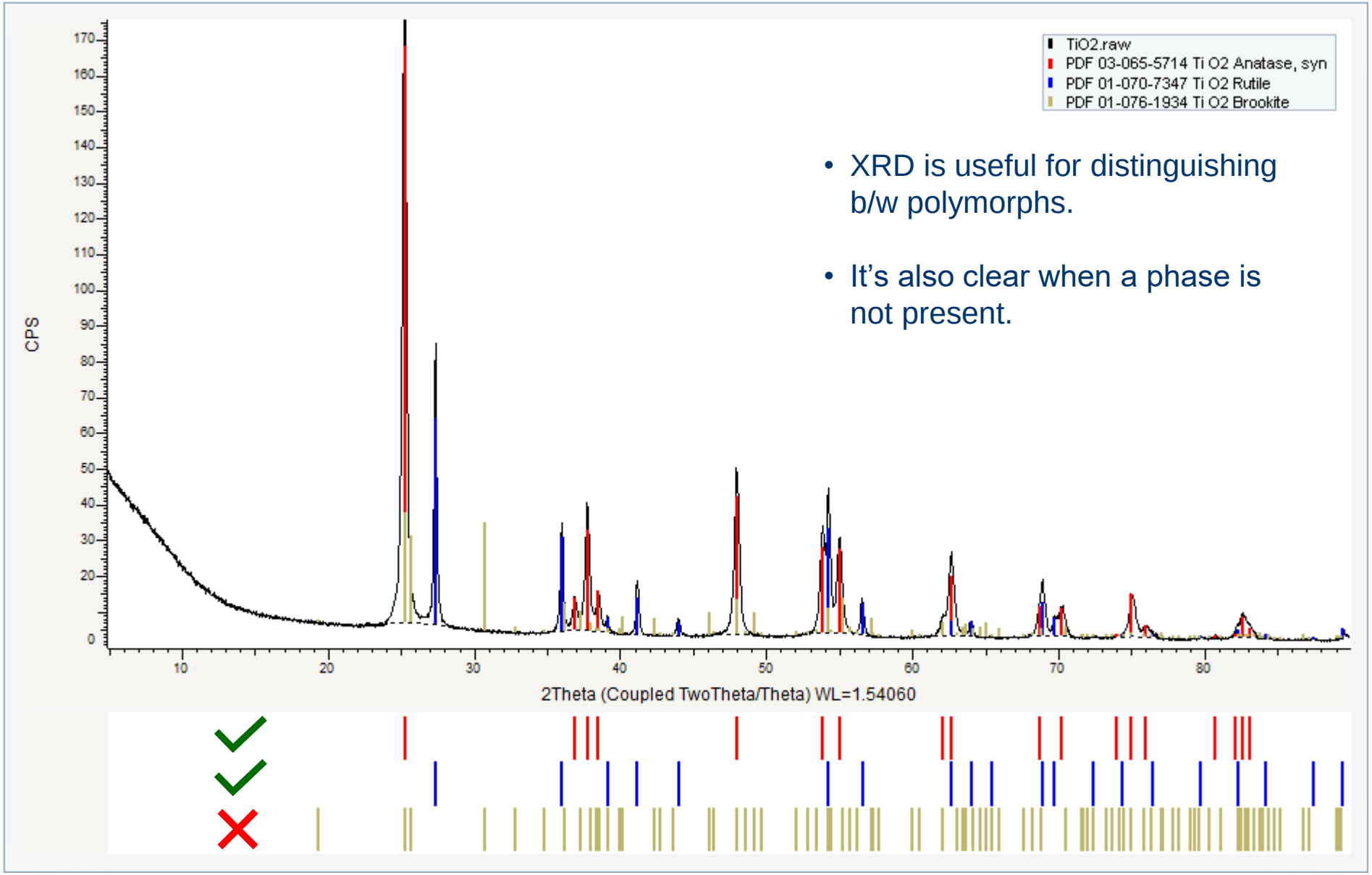
Match! – it is the set of peaks that make up the fingerprint of the pattern. You need to match the set not just one peak.



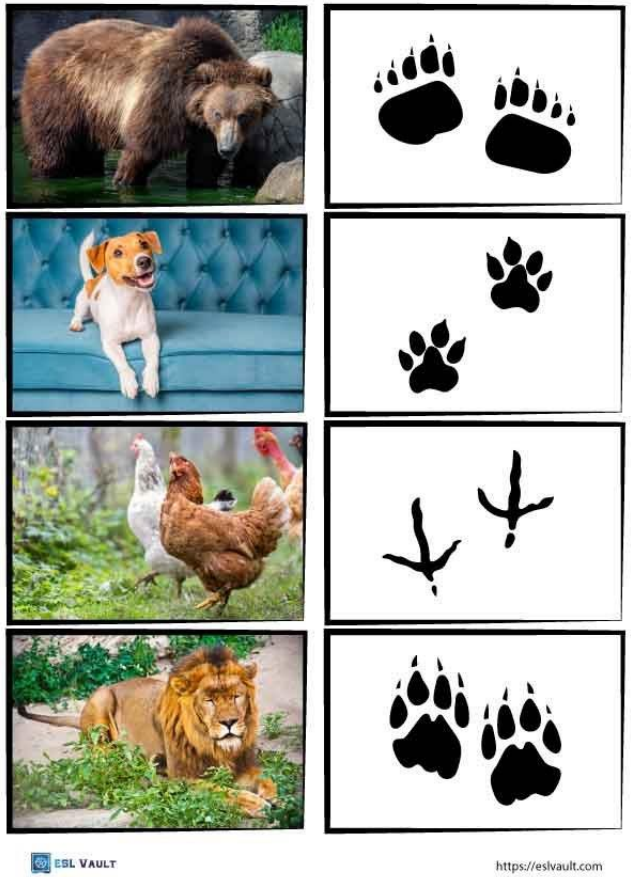
NOT a match! – it is the set of peaks that make up the fingerprint of the pattern. You need to match the set not just one peak. <u>The absence of peaks should also match.</u>



POLYMORPH EXAMPLE



- XRD is useful for distinguishing b/w polymorphs.
- It's also clear when a phase is not present.



MATCH

SEARCH/MATCH

- Search results are dependant on criteria input by the user

- Search results are suggestions or candidates
  - It is up to the researcher to select the most likely matches
  - Automatic match function in the software can be helpful but the software has no idea if the match that it selected is correct or not – that is up to you!

- An interactive process between the user and the software + database
  - User knowledge, experience, and intuition are valuable to the process

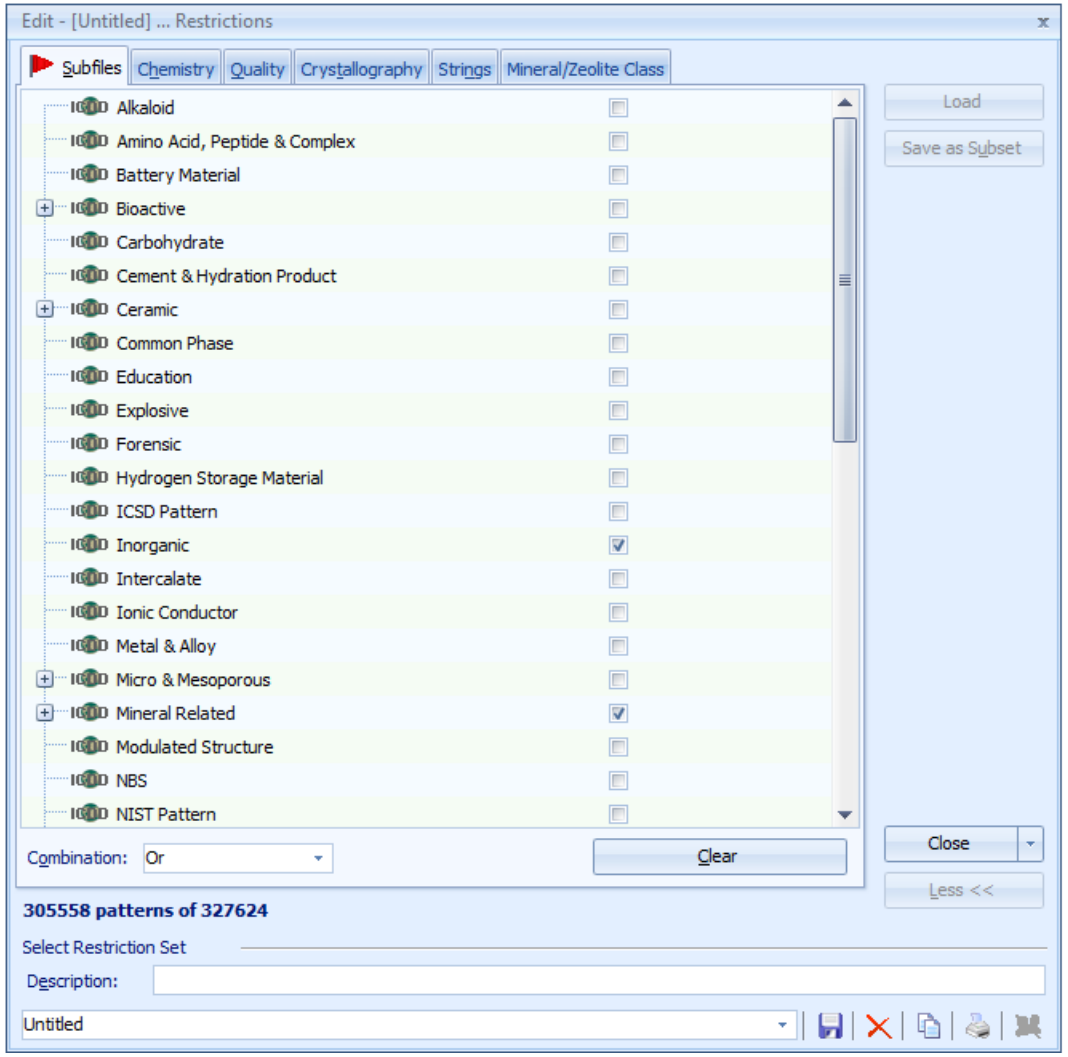
Get to work! Start practising and gaining experience!

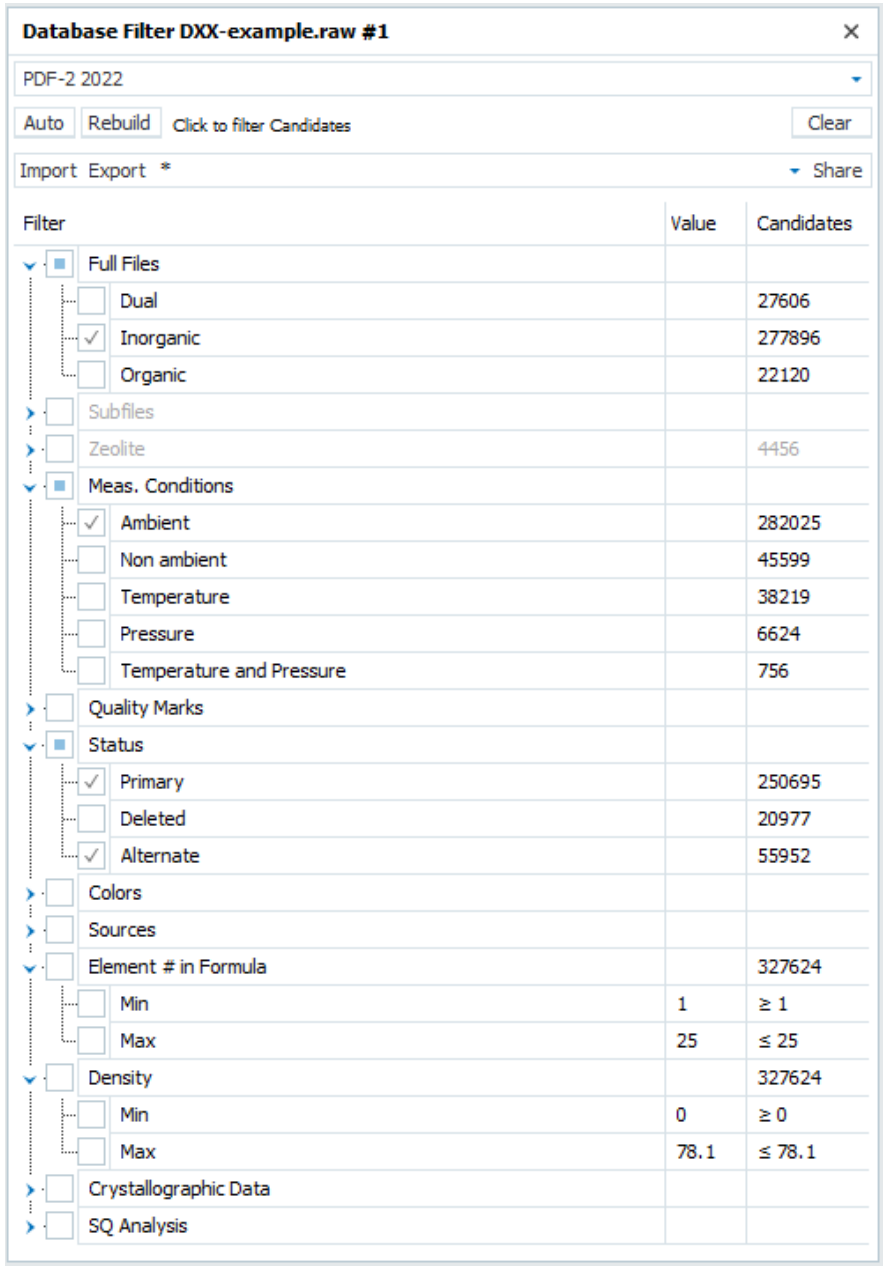
SEARCH/MATCH – SAMPLE INFORMATION

- Obtain as much information as possible about the sample
  - Where did it come from? What is likely to be in it? What are the reaction conditions? etc.
    - What industry is it from? – geological, cement, pharmaceutical, battery, etc.
      - Tip: useful to learn the language of the industry
  - Are there any chemical analyses available?
  - I usually ask the client to list **every possible element** in the system including anything the sample came into contact with such as the reaction vessel, atmosphere, wash solution, etc.
  - Have a sample with no information? – start with a light/common element search with the mineral database in the hope that it is a common substance
    - Minerals are naturally occurring crystalline materials and many are common substances (with a common name that's easy to recognize)
  - If you get stuck, go back to the client and ask for more information.

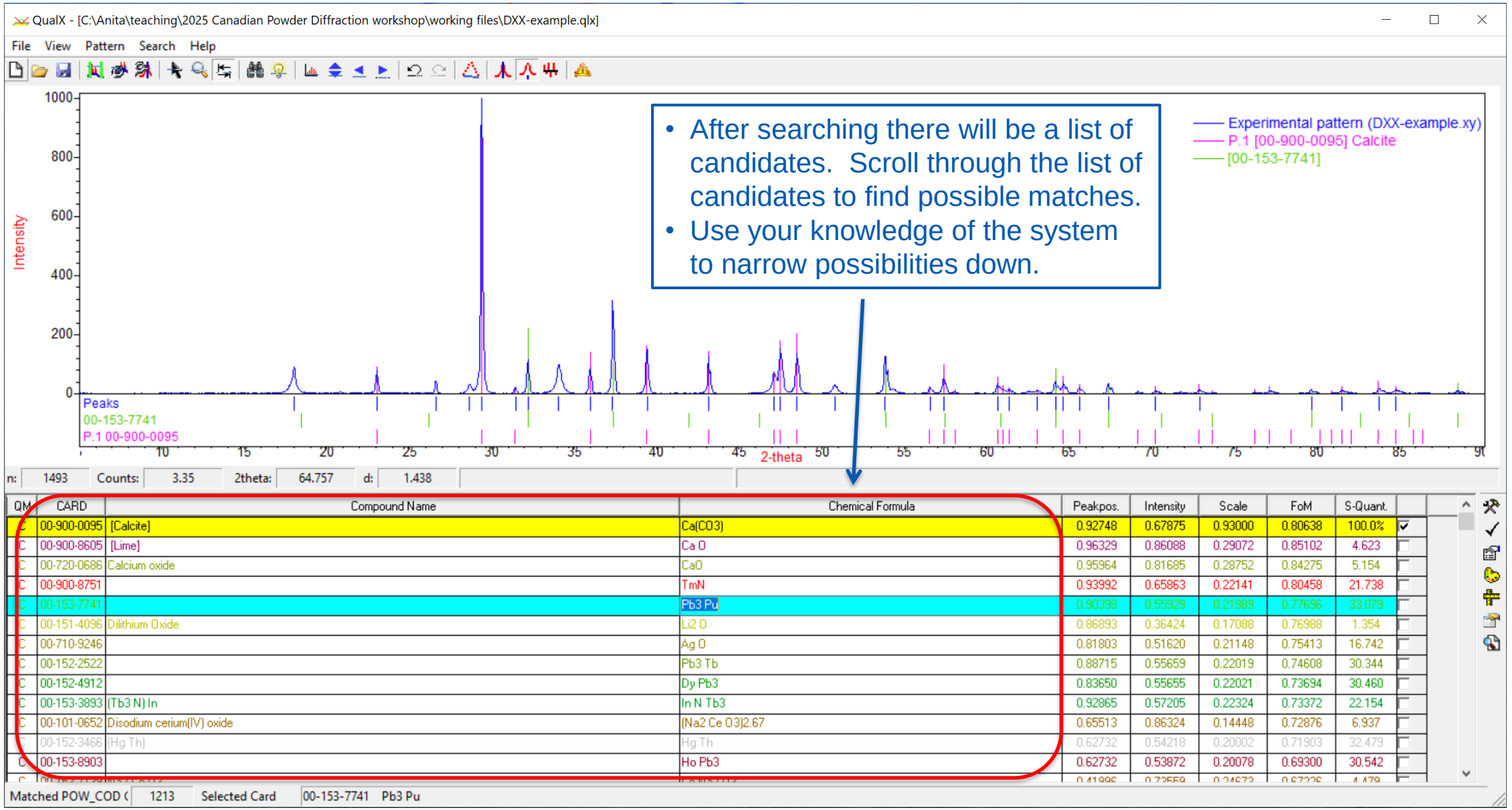
SEARCH – NARROWING THE FIELD

Database Subfiles:





MATCHING



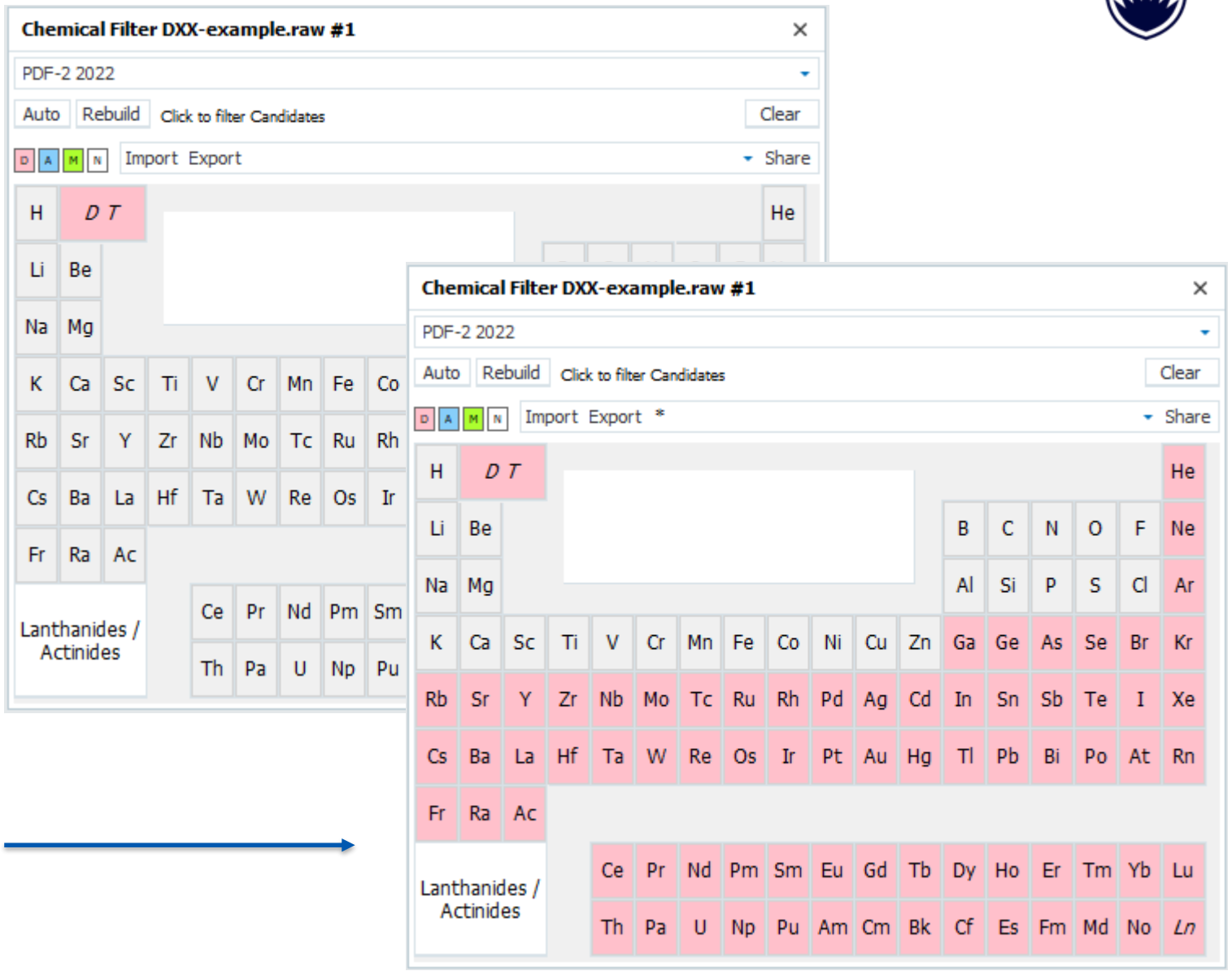
- After searching there will be a list of candidates. Scroll through the list of candidates to find possible matches.
- Use your knowledge of the system to narrow possibilities down.

QM	CARD	Compound Name	Chemical Formula	Peakpos.	Intensity	Scale	FoM	S-Quant.
C	00-900-0095	[Calcite]	Ca(CO3)	0.92748	0.67875	0.93000	0.80638	100.0%
C	00-900-8605	[Lime]	Ca O	0.96329	0.86088	0.29072	0.85102	4.623
C	00-720-0686	Calcium oxide	CaO	0.95964	0.81685	0.28752	0.84275	5.154
C	00-900-8751		TmN	0.93992	0.65863	0.22141	0.80458	21.738
C	00-153-7741		Pb3 Pu	0.90398	0.55929	0.21989	0.77696	33.079
C	00-151-4096	Dilithium Oxide	Li2 O	0.86893	0.36424	0.17088	0.76988	1.354
C	00-710-9246		Ag O	0.81803	0.51620	0.21148	0.75413	16.742
C	00-152-2522		Pb3 Tb	0.88715	0.55659	0.22019	0.74608	30.344
C	00-152-4912		Dy Pb3	0.83650	0.55655	0.22021	0.73694	30.460
C	00-153-3893	(Tb3 N) In	In N Tb3	0.92865	0.57205	0.22324	0.73372	22.154
C	00-101-0652	Disodium cerium(IV) oxide	(Na2 Ce O3)2.67	0.65513	0.86324	0.14448	0.72876	6.937
C	00-152-3466	(Hg Th)	Hg Th	0.62732	0.54218	0.20002	0.71903	32.479
C	00-153-8903		Ho Pb3	0.62732	0.53872	0.20078	0.69300	30.542

SEARCHING – POSSIBLE ELEMENTS

Periodic Table

- Grey – possible elements
- Red – excluded elements
- Green – has to be there
- Blue – one of the elements has to be there

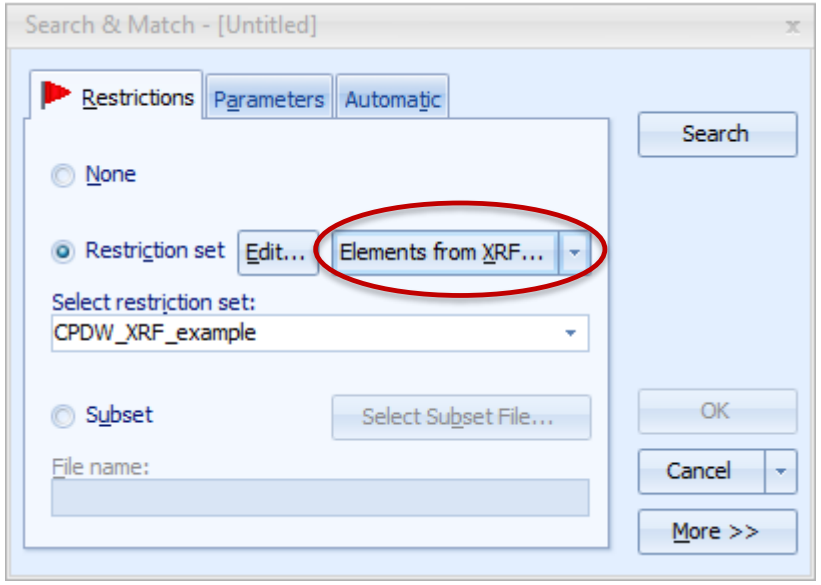


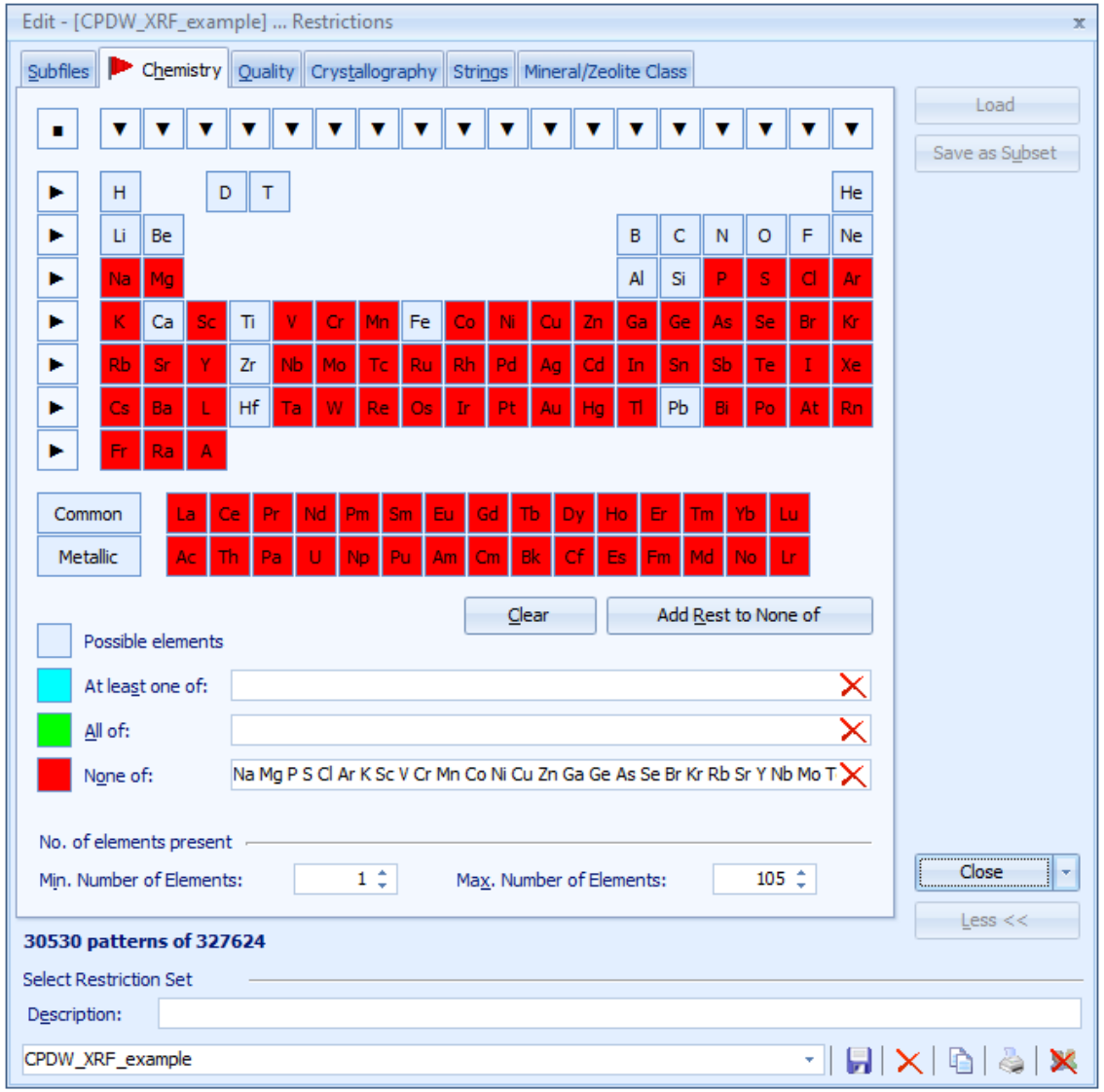
- A light element search

SEARCHING – CHEMICAL ANALYSES

XRF results

- Grey – possible elements
- Red – excluded elements





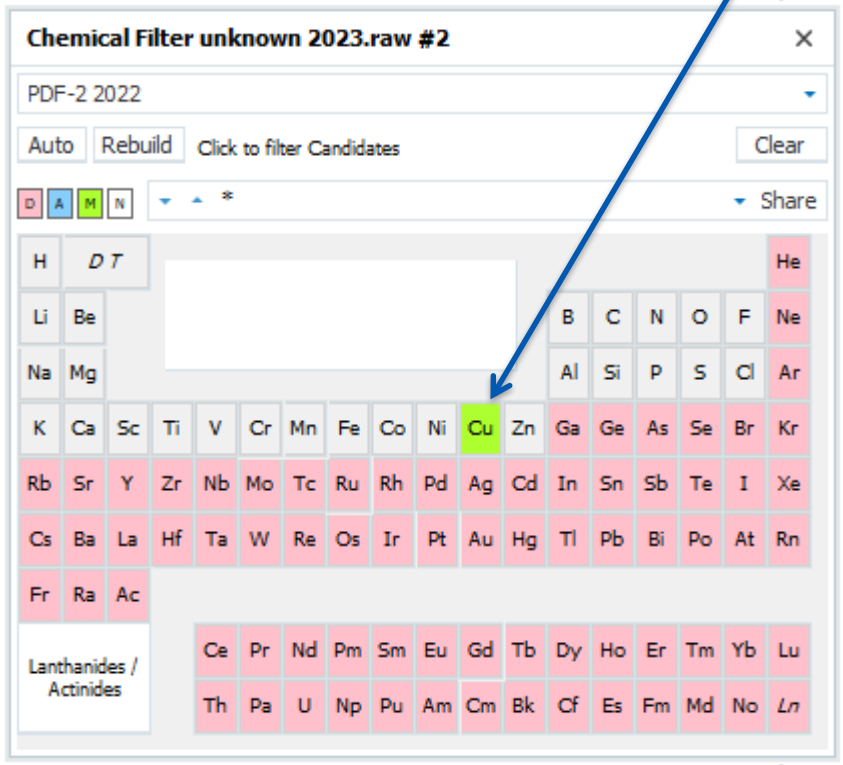
- This allows you to search only the elements known to be in your system.

SEARCHING – ELEMENT SPECIFIC

Element focussed

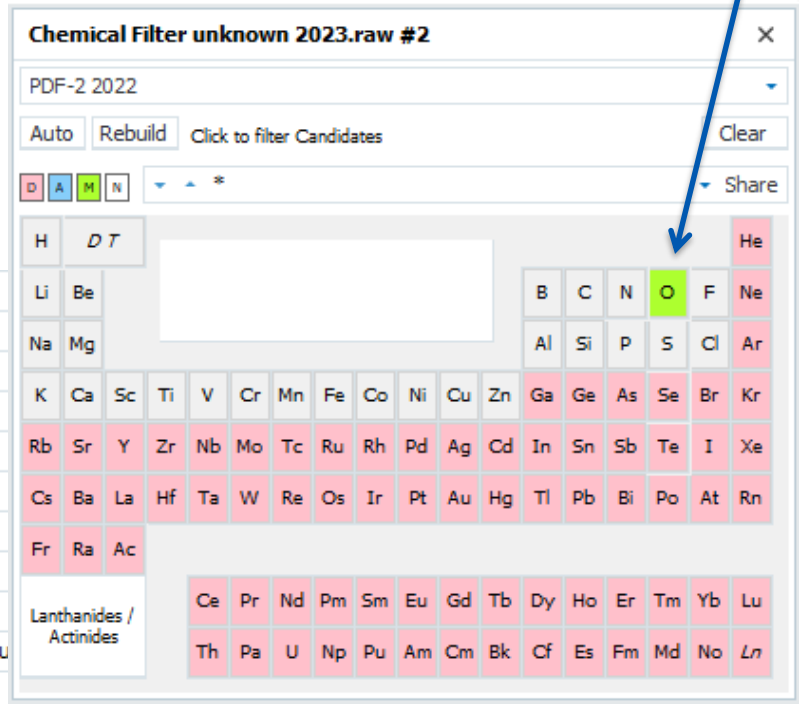
- Grey – possible elements
- Red – excluded elements
- Green – has to be there

Searching for a copper phase



1	Cu2(OH)3NO3
	CuO·3H2O
	Cu0.4V2O5
	C52H56Cl8CoCuN12
	C8H8Cu3Na2O16
	Cu4SO4(OH)6·H2O
	Cu6Al(SO4)(OH)12Cl(H2O)3
	C15H14CuN4O2S2·2H2O
	Cu4(OH)6SO4·H2O
	Na4(Cu4O2(SO4)4)((Na0.26Cu
	C4H10Cu3O14P4·6H2O
	C38H38CuN8O2
	((N(CH3)4)(CuZn(CN)4))(CCl4)0.9
	Cu1.3V9O22
	C21H24CuF12N2O6
	C28H22CuN2O4
	3CuO·2(P2O5)
	Cu2(NO3)(OH)3
	Zn7Cu(O4H7)0.3(OH)13((SiO(OH)3)0.7(SO4))
	Na2Cu(C2O4)2(H2O)2
21	Cu6(Al0.94Fe0.06)(SO4)(OH)12Cl(H2O)3
22	Na2(Cu3(CHO2)8)

Searching for an oxide

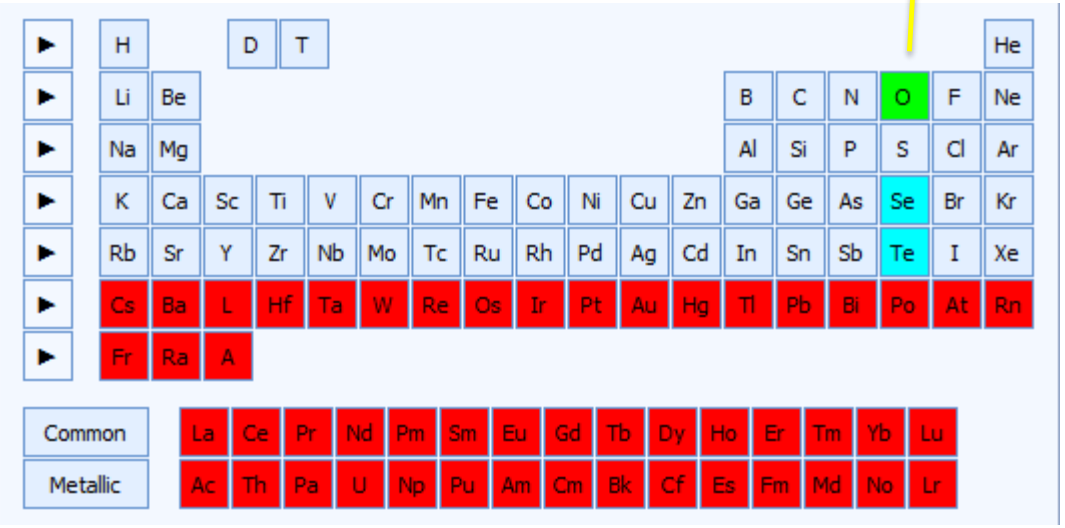


	Na2(CO3)
	Na7.4Al6.4Si25.6O64·O20
	Na2CO3
	Na2(CO3)
	Na2(CO3)H2O
	C48H74O14·0.5H2O·0.82(C2H5OH)
	Cu2(OH)3NO3
	C20H19N5O6Na2·7H2O
	C3H4CoO5·H2O
	C2H5N5O3·H2O
	CoLi1.865(P2O7)
	C3H3N3O2
13	Na2(CO3)
14	CuO·3H2O
15	Na4Ti5O12
16	C40H50N4O4
17	K(OH)
18	O2NC6H4CONHNCHC6H4N(C6H4CH3)2·H2O
19	C26H23N5O2S
20	C6H9O6Sc
21	Na2(CO3)(H2O)
22	Zn2V2O7

SEARCHING – ELEMENT SPECIFIC

Element focussed

- Grey – possible elements
- Red – excluded elements
- Green – has to be there
- Blue – one of the elements has to be there



No.	Ref. Code	Chemical Formula
1	ICDD 01-082-1460	Rb Fe (Se O4)2
2	ICDD 00-068-0618	Sr Ca Ni Te O6
3	ICDD 01-085-7056	Sr3 Fe2 Te O9
4	ICDD 01-084-8465	Sr Ca Ni Te O6
5	ICDD 01-075-8547	Sr2 Fe1.33 Te0.67 O6
6	ICDD 01-075-8546	Sr2 Fe1.33 Te0.67 O6
7	ICDD 01-075-8548	Sr2 Fe1.33 Te0.67 O6
8	ICDD 01-075-8549	Sr2 Fe1.33 Te0.67 O6
9	ICDD 01-089-8379	Sr2 Cu (Te O6)
10	ICDD 01-072-4327	Cd2 (Te2 O7)
11	ICDD 00-050-0401	Cu Sr2 Te O6
12	ICDD 01-075-9489	Sr2 ((Fe1.33 Te0.67) O6)
13	ICDD 00-047-0010	Sc2 Te4 O11
14	ICDD 01-080-8053	Sr4 (V O2)2 (Se O3)4 (Se2 O5)
15	ICDD 01-083-3020	Se Mn O3
16	ICDD 01-076-3289	Sr2 Fe1.47 Te0.53 O6
17	ICDD 01-077-5338	Ag4 (Mo2 O5) (Se O4)2 (Se O3)
18	ICDD 00-055-0529	Cd2 Te2 O7
19	ICDD 01-077-5586	Cd4 V2 Te3 O15
20	ICDD 01-070-0241	Mn (Se O3)
21	ICDD 00-031-0830	Mn Se O3
22	ICDD 00-036-0881	Ca Te O3
23	ICDD 01-072-7832	Mn (Se O3)
24	ICDD 01-085-2142	Ca3 Fe2 (Se O3)6
25	ICDD 01-086-9658	Cu2 (Se O3) F2
26	ICDD 01-076-9766	Sr (Te3 O8)
27	ICDD 00-053-0208	Sr2 Fe1.33 Te0.67 O6
28	ICDD 00-029-0897	Sr2 Mn Te O6
29	ICDD 01-082-3425	Y6 Te O12
30	ICDD 01-072-7831	(Cu0.25 Mn0.75) (Se O3)

These are just a few examples – the search criteria should be tailored to your samples.

SEARCHING – CHEMICAL FILTER

Element focussed

- Grey – possible elements
- Red – excluded elements
- Green – has to be there
- Blue – one of the elements has to be there

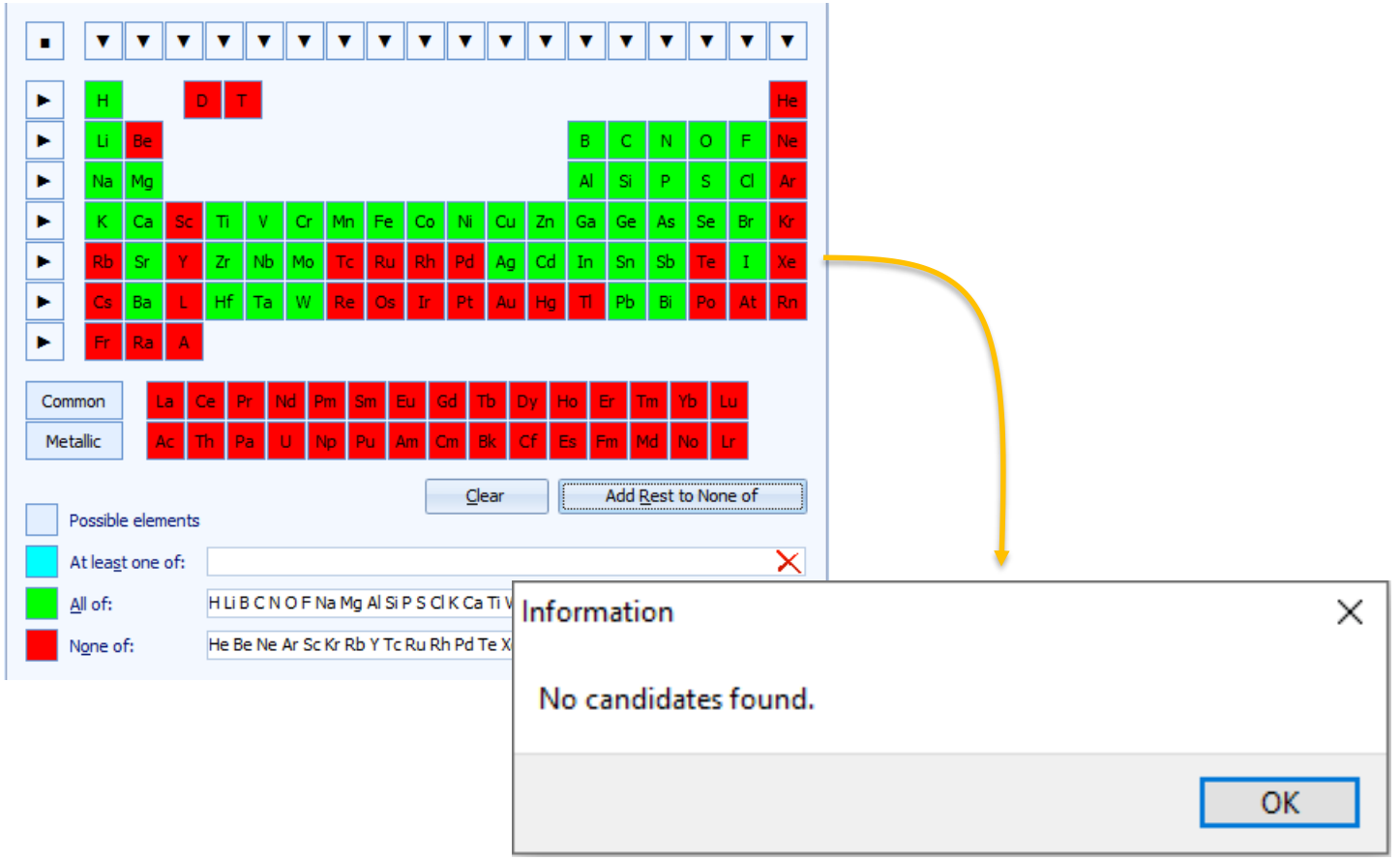
Search using common elements – all blue is okay

SEARCHING – CHEMICAL FILTER

Element focussed

- Grey – possible elements
- Red – excluded elements
- Green – has to be there
- Blue – one of the elements has to be there

Don't do this.....Why?

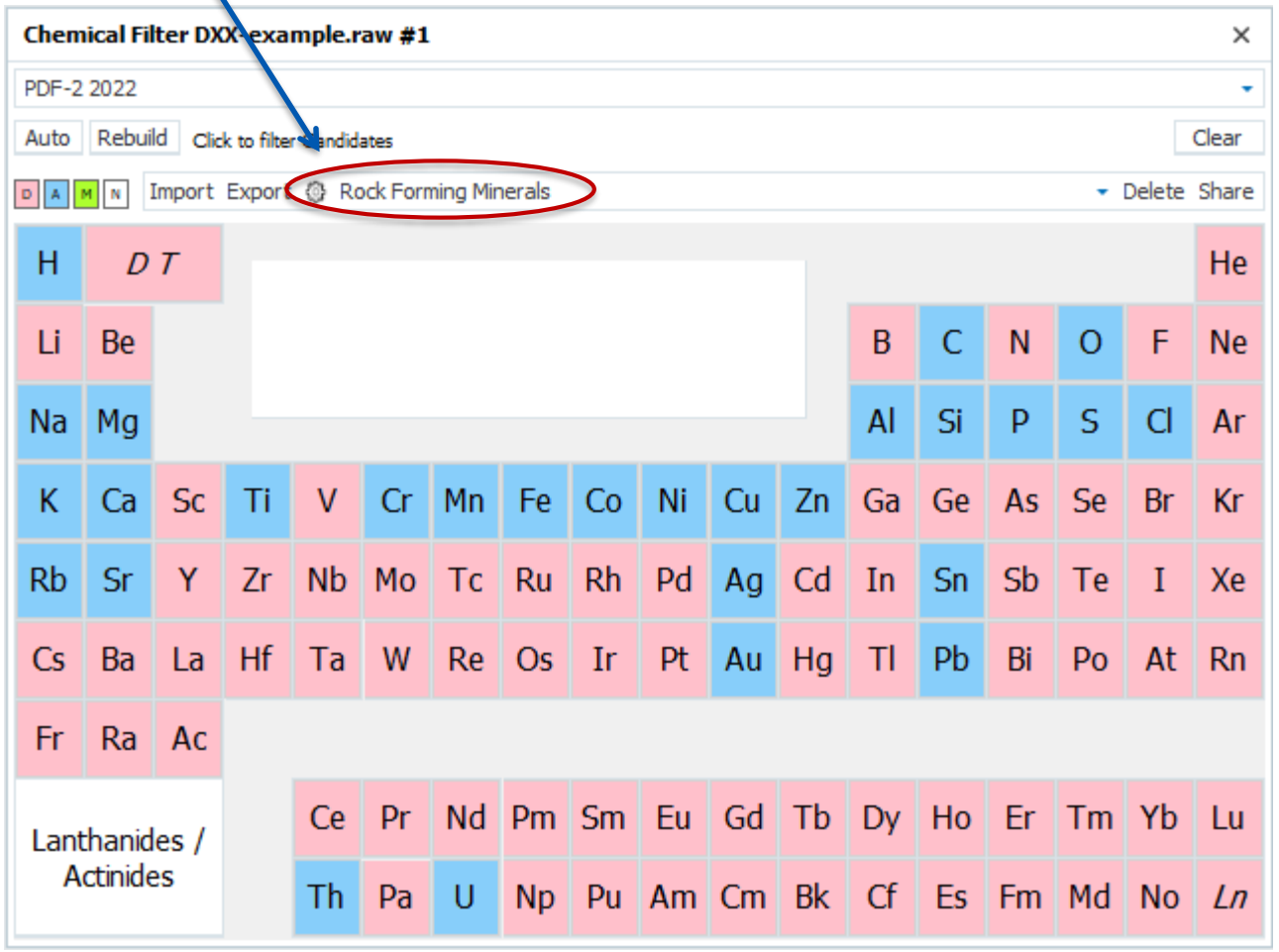


SEARCHING – CHEMICAL FILTERS

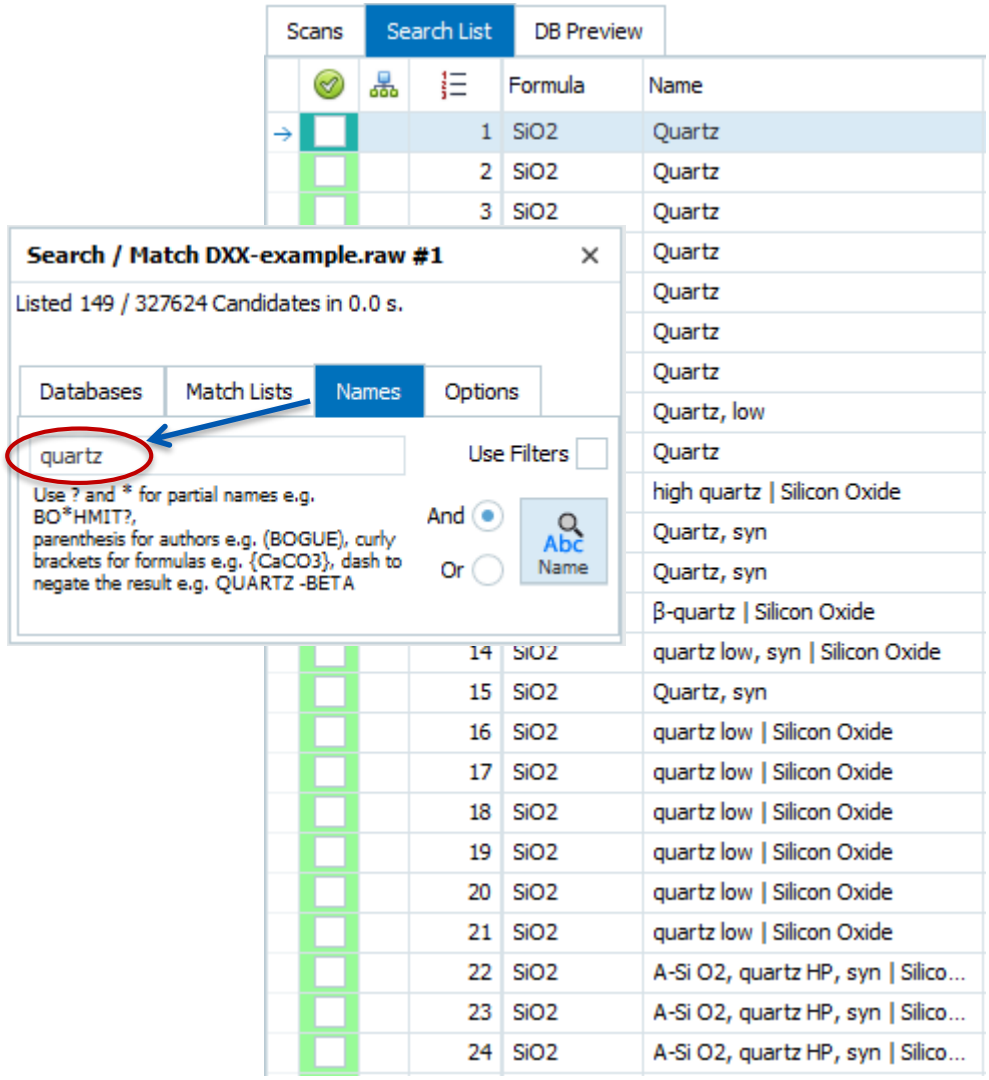
Element focussed

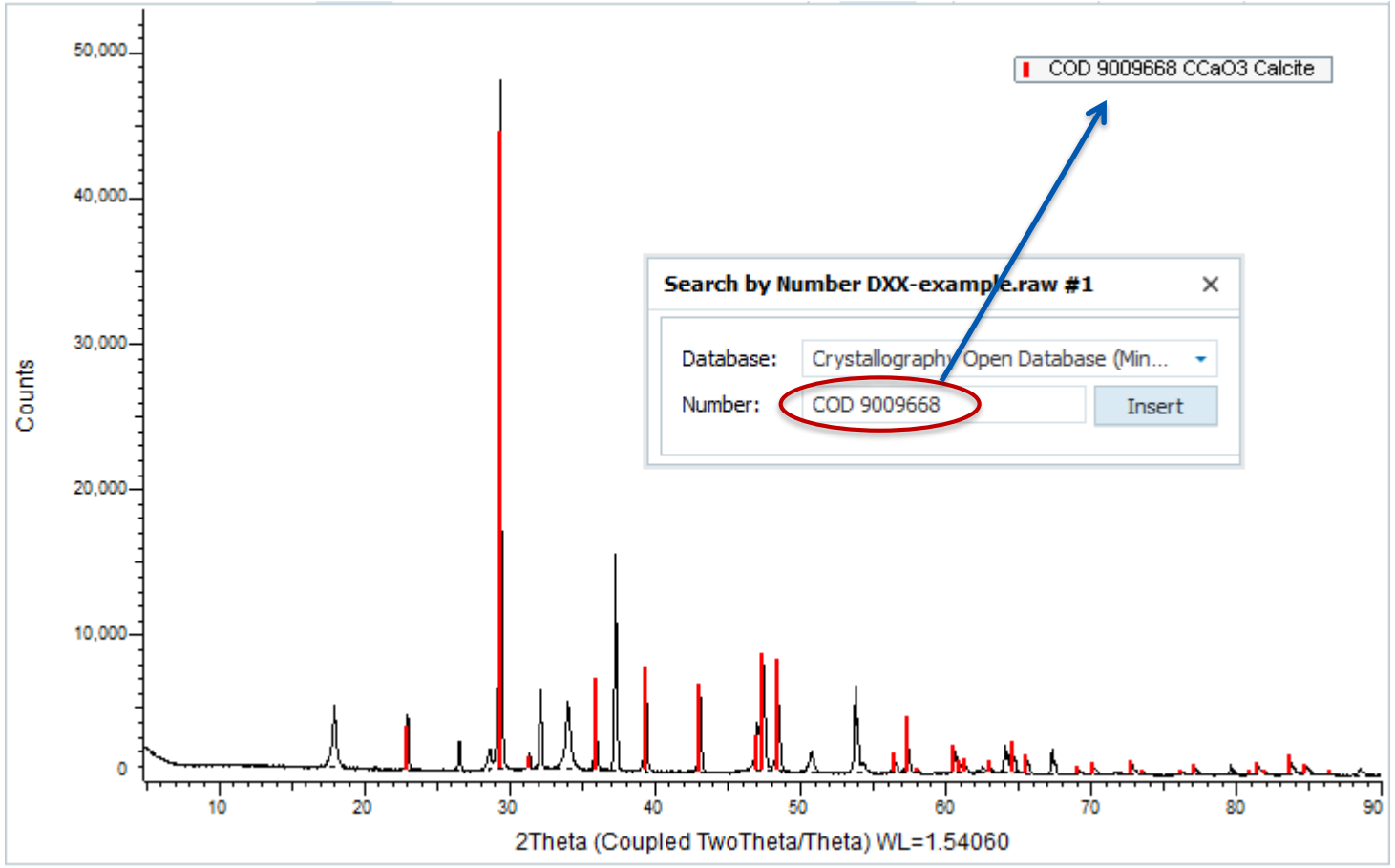
- Grey – possible elements
- Red – excluded elements
- Green – has to be there
- Blue – one of the elements has to be there

Some built-in filters are available or you can create your own.

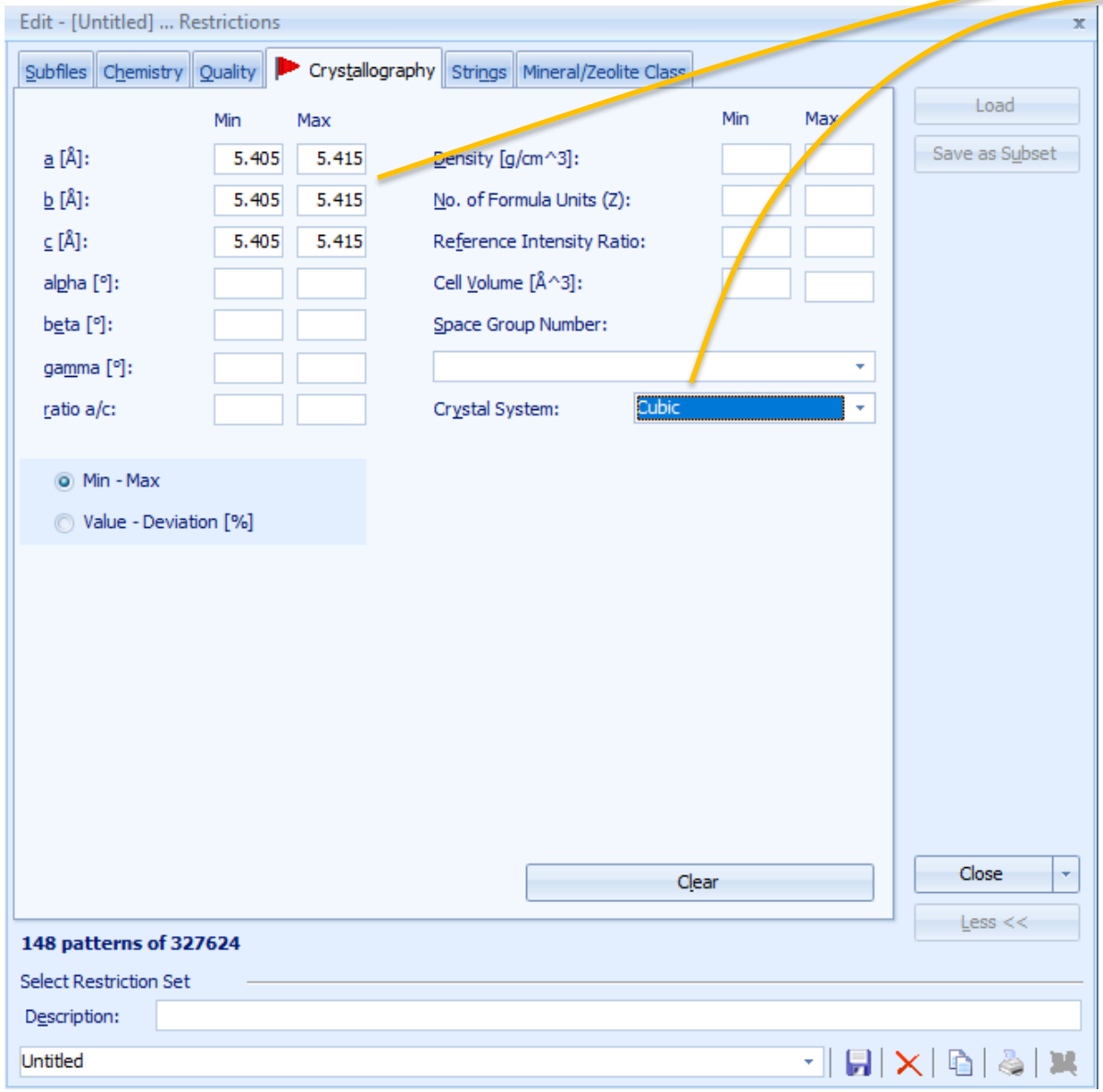


SEARCHING – BY NAME OR FILE NUMBER





SEARCHING – BY CRYSTALLOGRAPHY



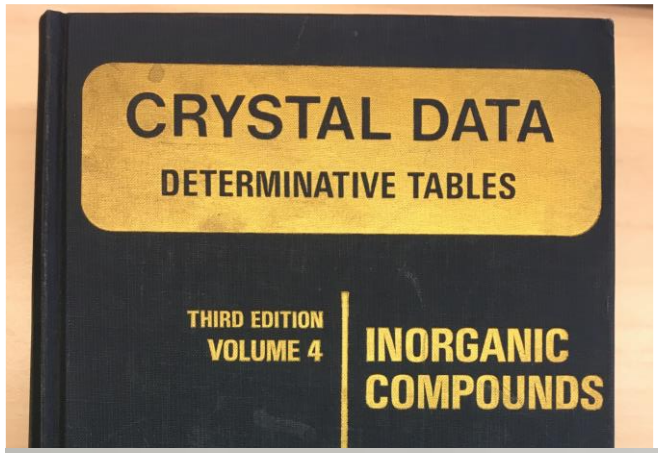
Candidates:

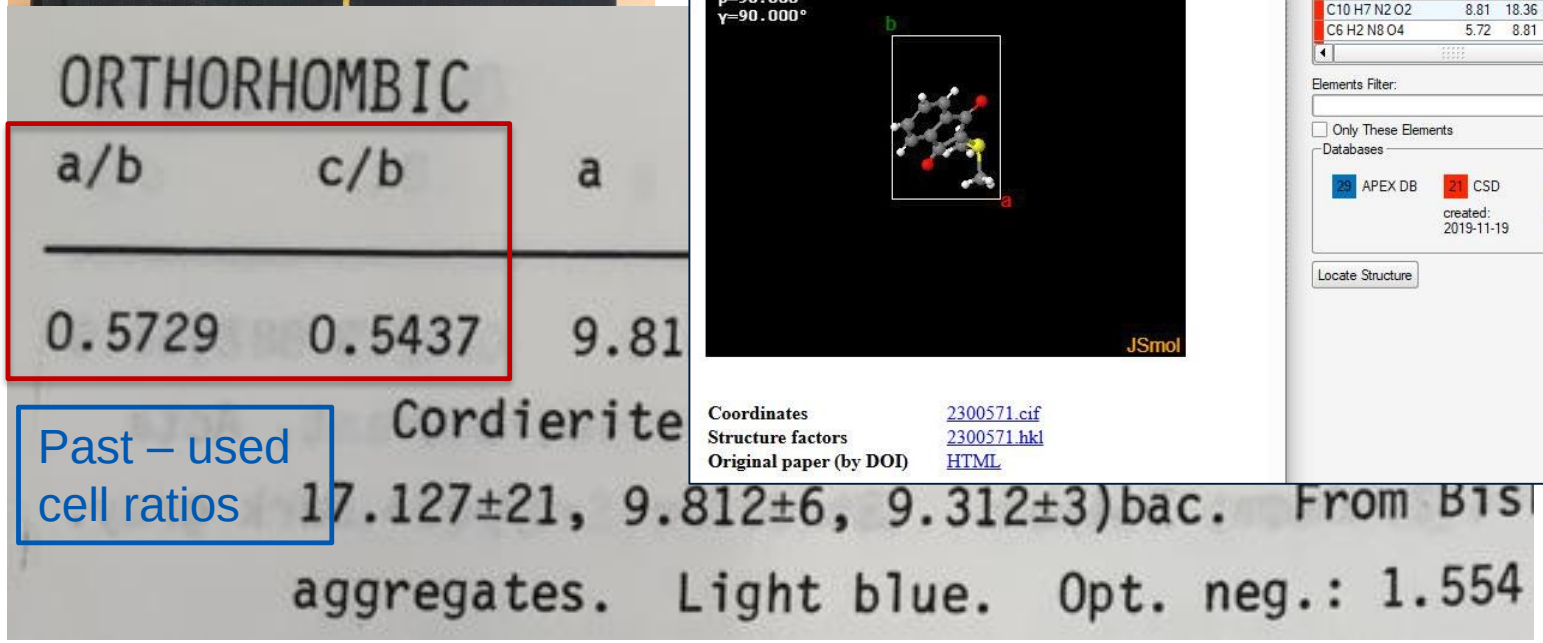
Search...

No.	Ref. Code	Cryst. Syst.	Space Gr...	Cell	Compound Name
1	ICDD 03-065-2974	Cubic	Fm-3m	a 5.406 - b 5.406 - c 5.406	Nickel Silicon
2	ICDD 00-047-1655	Cubic	F-43m	a 5.407 - b 5.407 - c 5.407	Cobalt Zinc Sulfide
3	ICDD 00-016-0576	Cubic	F-43m	a 5.405 - b 5.405 - c 5.405	Strontium Arsenic Sulfide
4	ICDD 01-085-8588	Cubic	F-43m	a 5.406 - b 5.406 - c 5.406	Zinc Sulfide
5	ICDD 01-081-5205	Cubic	F-43m	a 5.410 - b 5.410 - c 5.410	Copper Sulfide
6	ICDD 01-071-5971	Cubic	F-43m	a 5.409 - b 5.409 - c 5.409	Zinc Sulfide
7	ICDD 01-073-8755	Cubic	F-43m	a 5.409 - b 5.409 - c 5.409	Nickel Zinc Sulfide
8	ICDD 03-065-4586	Cubic	F-43m	a 5.409 - b 5.409 - c 5.409	Nickel Zinc Sulfide
9	ICDD 03-065-9585	Cubic	F-43m	a 5.409 - b 5.409 - c 5.409	Zinc Sulfide
10	ICDD 01-071-4258	Cubic	F-43m	a 5.407 - b 5.407 - c 5.407	Cobalt Iron Zinc Sulfide
11	ICDD 01-078-2500	Cubic	Fd-3m	a 5.406 - b 5.406 - c 5.406	Silicon
12	ICDD 01-072-2669	Cubic	F-43m	a 5.411 - b 5.411 - c 5.411	Nickel Zinc
13	ICDD 03-065-9470	Cubic	F-43m	a 5.411 - b 5.411 - c 5.411	Nickel Zinc
14	ICDD 00-050-0202	Cubic	Fm-3m	a 5.413 - b 5.413 - c 5.413	Cerium Gadolinium Yttrium ...
15	ICDD 01-080-6505	Cubic	Fm-3m	a 5.405 - b 5.405 - c 5.405	Calcium Cerium Oxide
16	ICDD 03-065-7441	Cubic	F-43m	a 5.411 - b 5.411 - c 5.411	Manganese Zinc Sulfide
17	ICDD 00-027-0843	Cubic		a 5.410 - b 5.410 - c 5.410	Neodymium Antimony Oxide
18	ICDD 01-081-9692	Cubic	Fm-3m	a 5.406 - b 5.406 - c 5.406	Cerium Yttrium Oxide
19	ICDD 01-080-6915	Cubic	Fm-3m	a 5.405 - b 5.405 - c 5.405	Cerium Oxide
20	ICDD 01-080-5532	Cubic	Fm-3m	a 5.406 - b 5.406 - c 5.406	Cerium Yttrium Oxide
21	ICDD 01-073-2568	Cubic	F-43m	a 5.406 - b 5.406 - c 5.406	Zinc Sulfide
22	ICDD 01-082-9831	Cubic	Fm-3m	a 5.406 - b 5.406 - c 5.406	Cerium Oxide
23	ICDD 01-075-0167	Cubic	Fm-3m	a 5.405 - b 5.405 - c 5.405	Dysprosium Cerium Oxide
24	ICDD 01-089-4958	Cubic	F-43m	a 5.411 - b 5.411 - c 5.411	Manganese Zinc Sulfide
25	ICDD 01-074-6110	Cubic	F-43m	a 5.411 - b 5.411 - c 5.411	Zinc Sulfide
26	ICDD 03-065-1691	Cubic	F-43m	a 5.411 - b 5.411 - c 5.411	Zinc Sulfide
27	ICDD 01-081-9649	Cubic	F-43m	a 5.409 - b 5.409 - c 5.409	Molybdenum Phosphide
28	ICDD 01-071-6544	Cubic	F-43m	a 5.412 - b 5.412 - c 5.412	Zinc Iron Sulfide
29	ICDD 01-083-5829	Cubic	Fm-3m	a 5.406 - b 5.406 - c 5.406	Cerium Praseodymium Oxide
30	ICDD 01-080-4831	Cubic	Fm-3m	a 5.406 - b 5.406 - c 5.406	Cerium Praseodymium Oxide

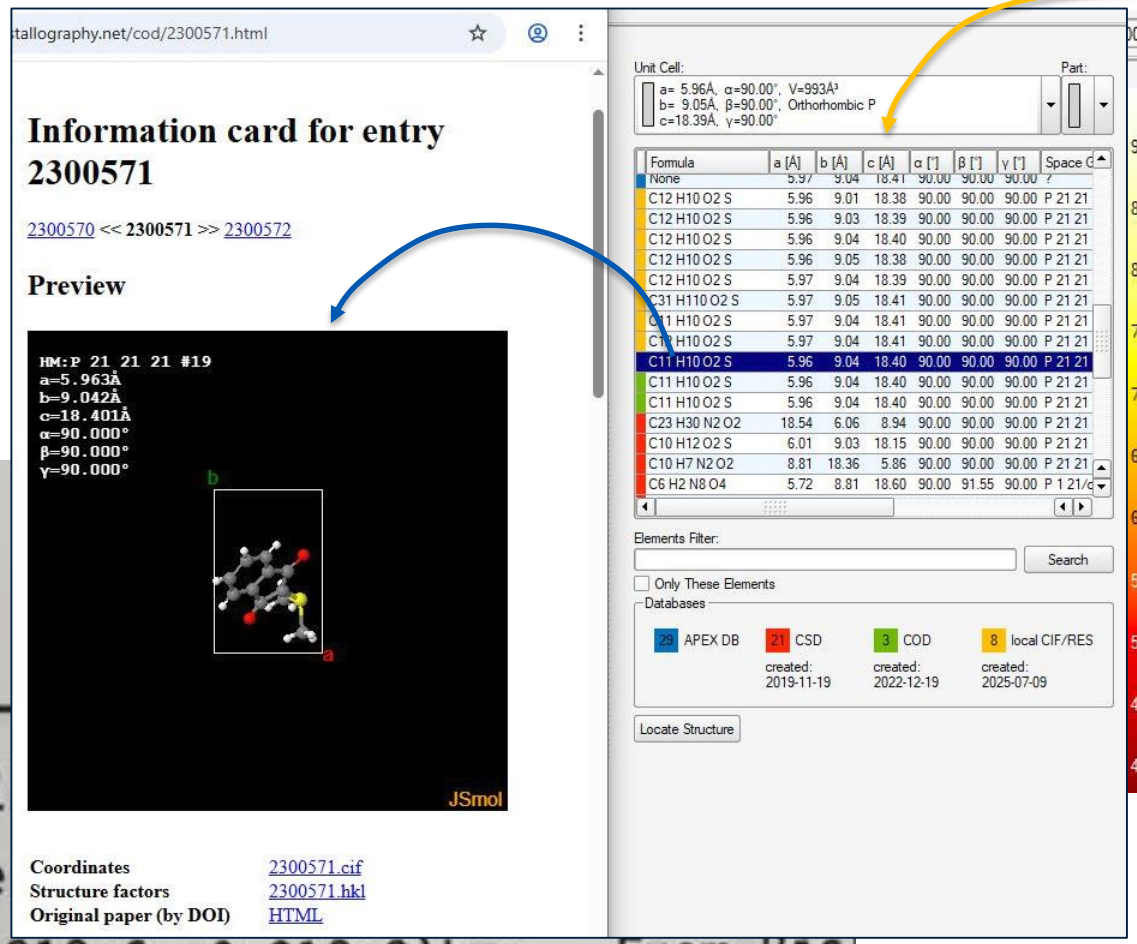
SEARCHING – BY UNIT CELL

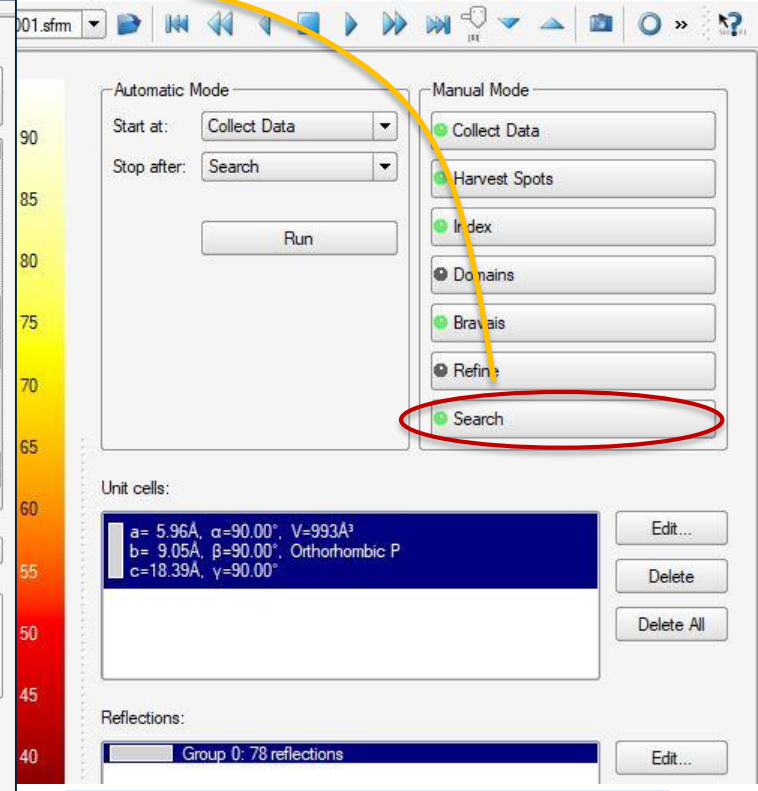
- an aside: (single crystal) users sometimes do phase ID by checking the unit cell





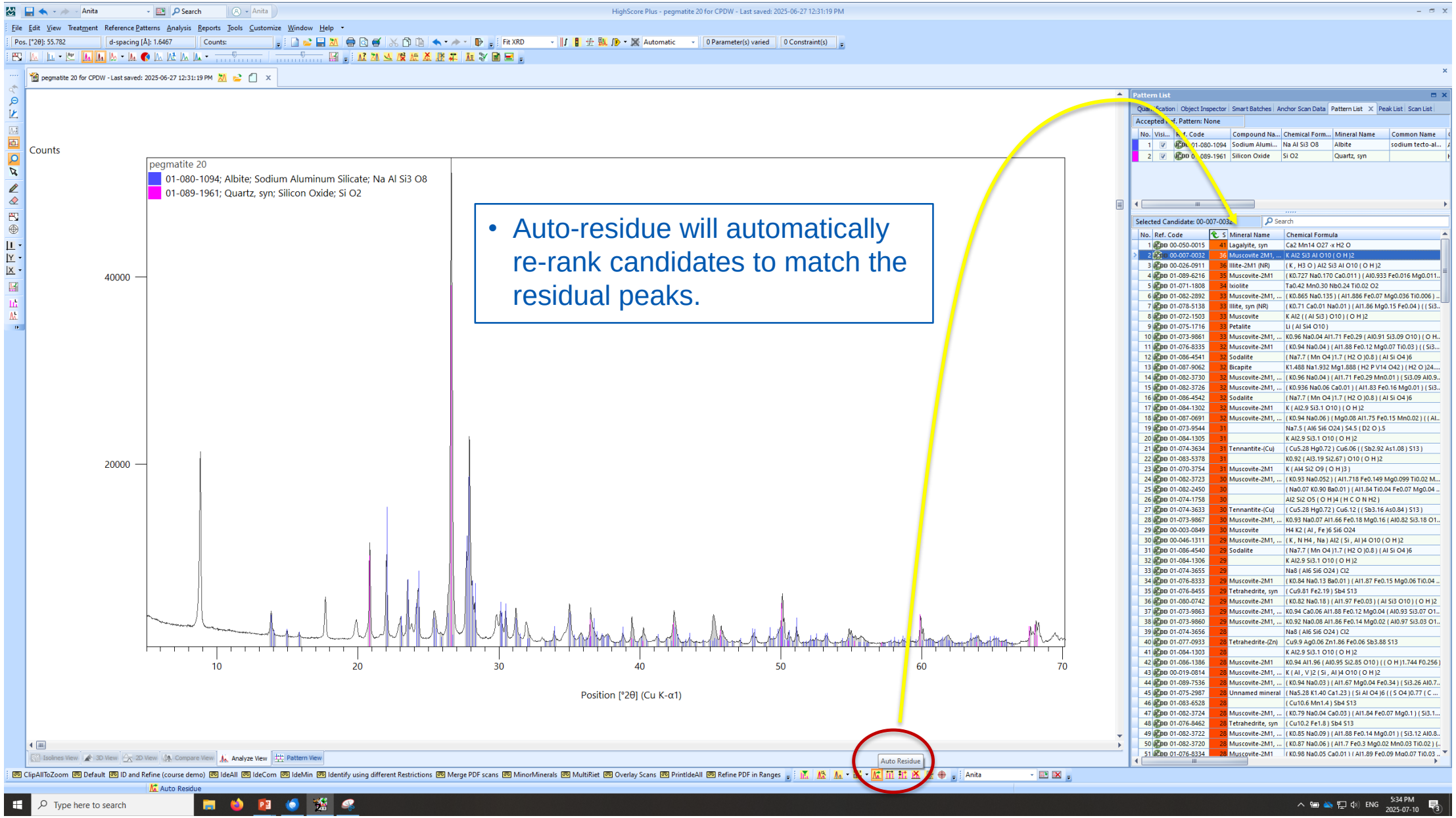
Past – used cell ratios



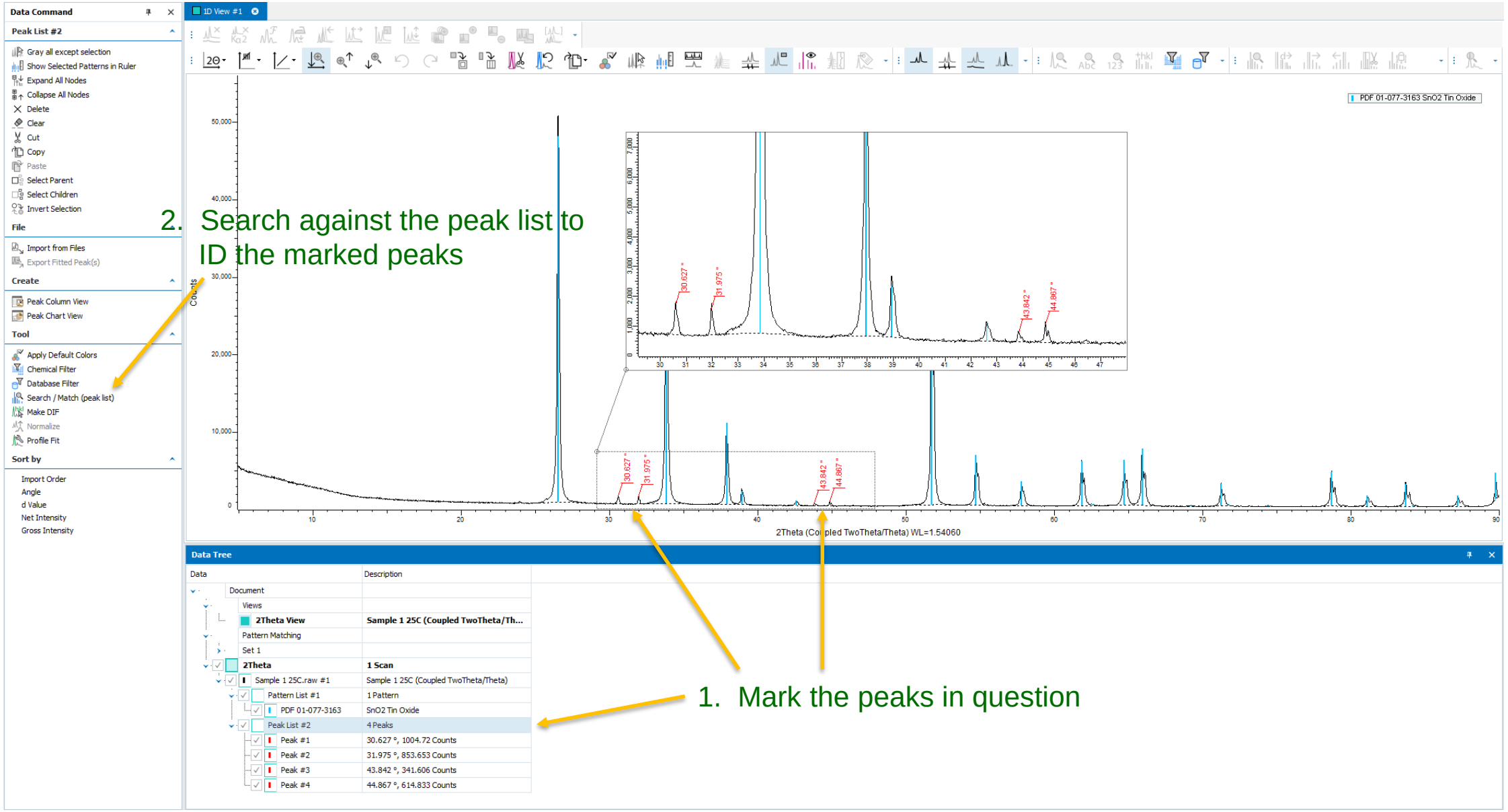


Present – search unit cell

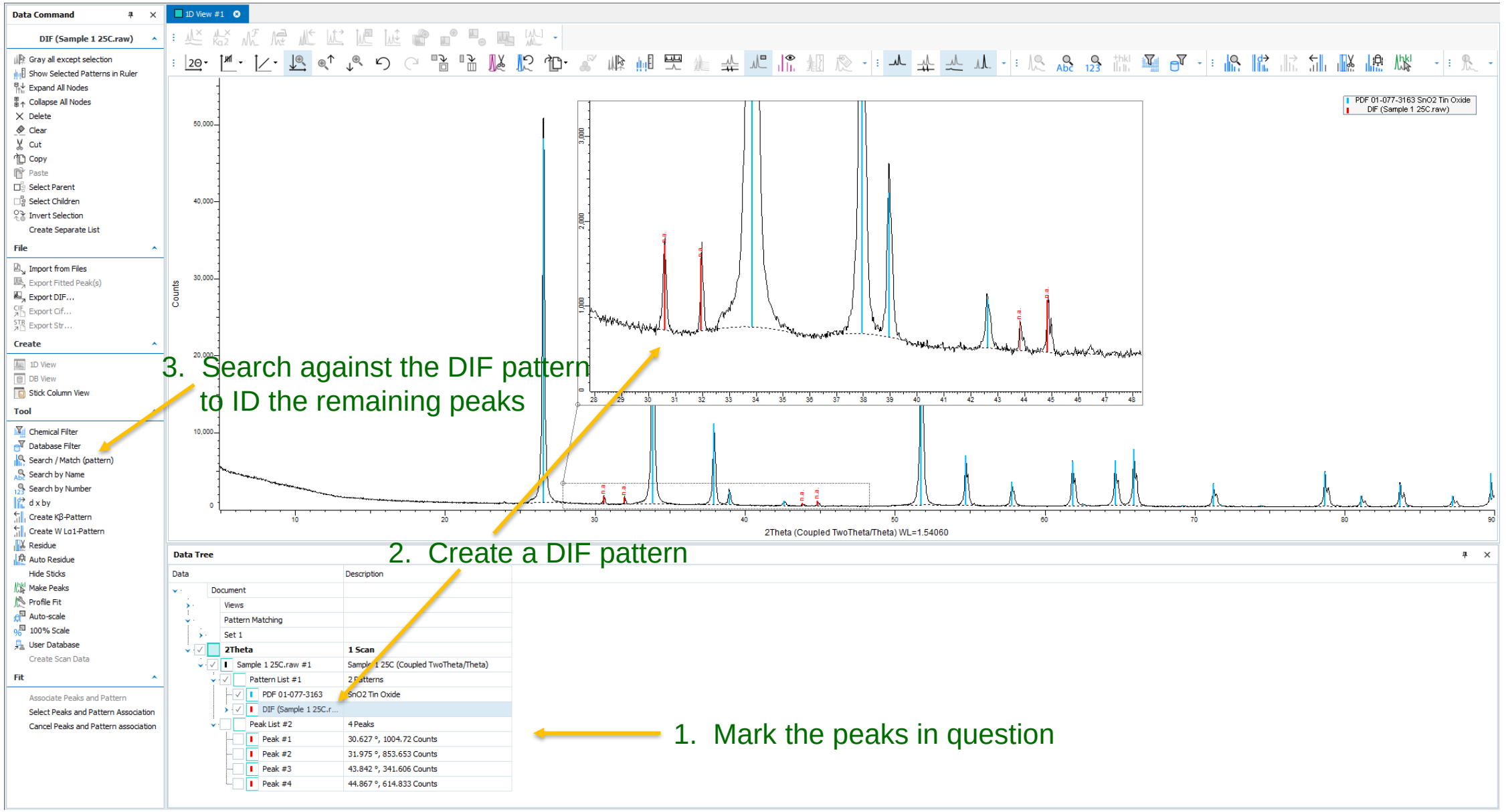
SEARCHING – RESIDUAL PEAKS



SEARCHING – SPECIFIED PEAKS



SEARCHING – SPECIFIED PEAKS, DIF PATTERN

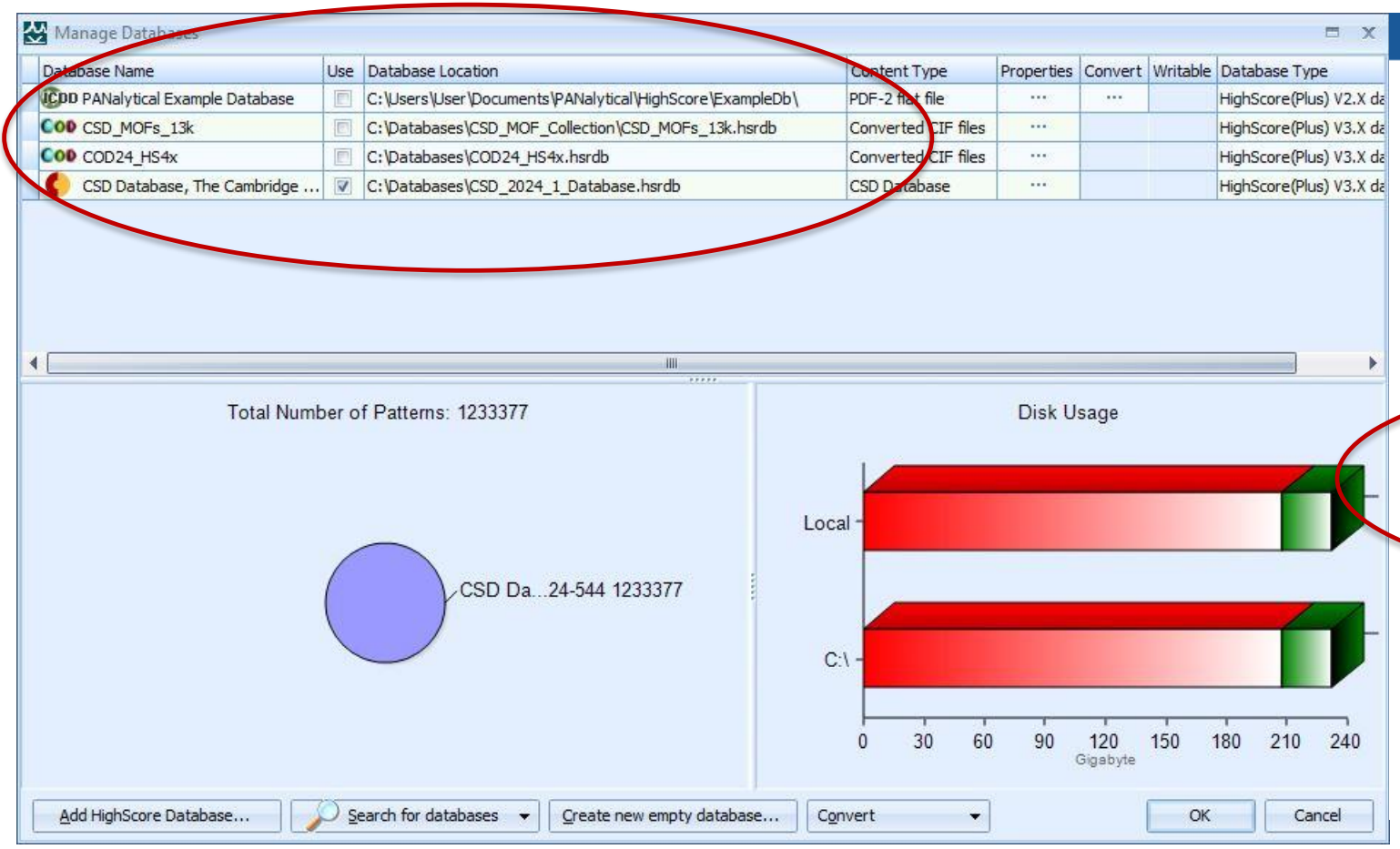


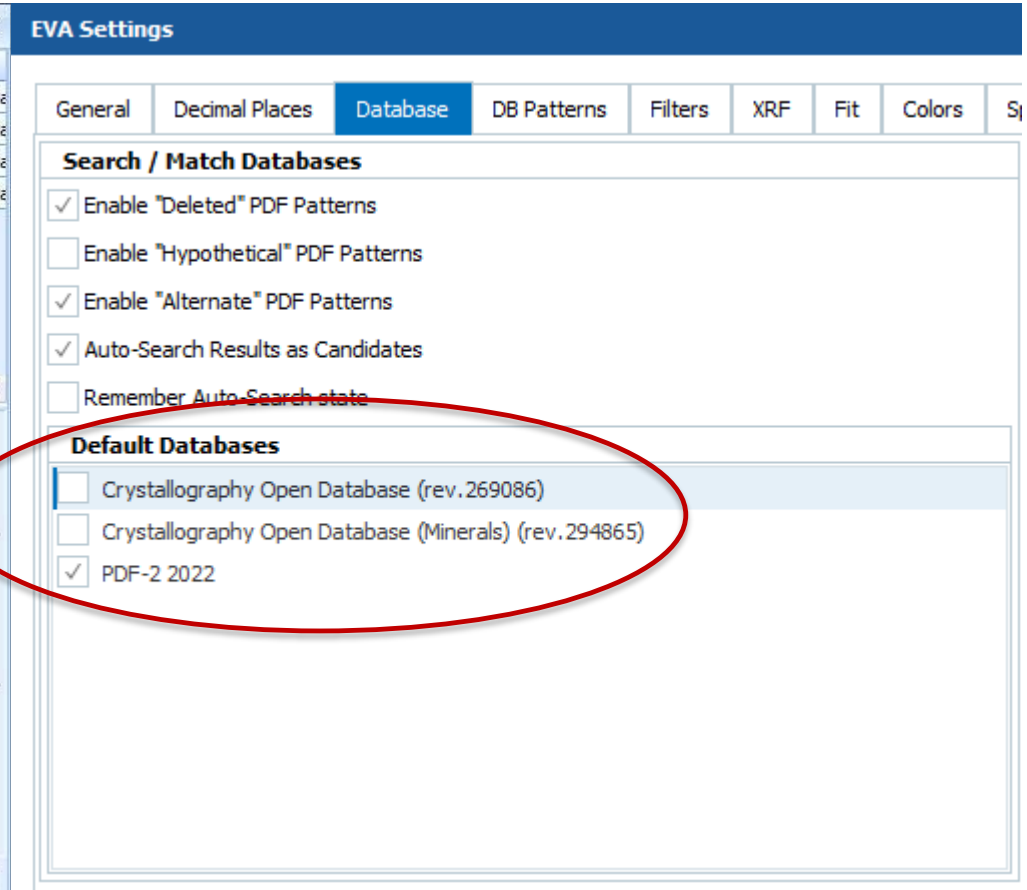
Still having Trouble?

Other Tips and Tricks

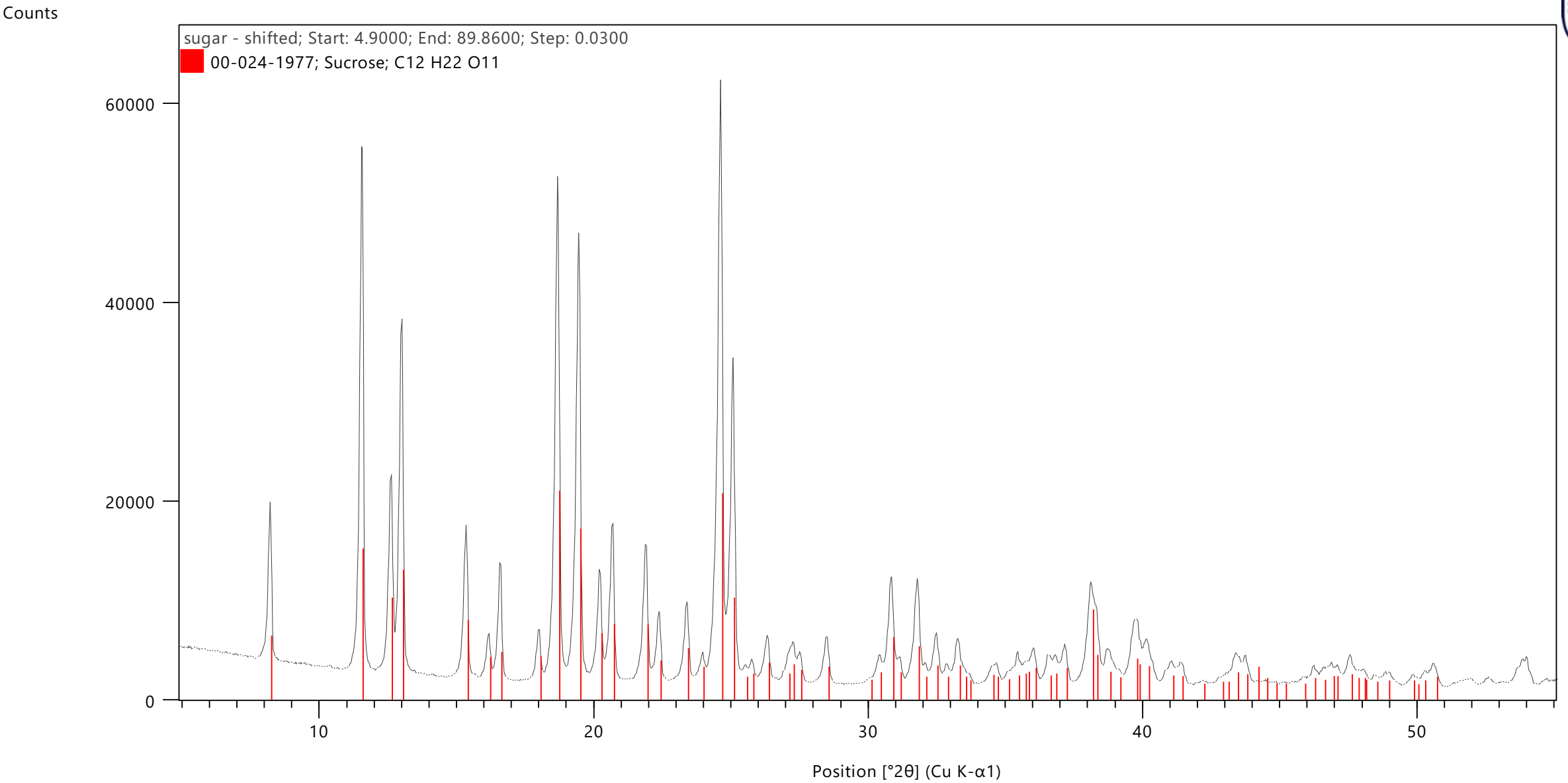
CHANGE DATABASES

- Sometimes a pattern or clue to the unidentified phase might be in a different database

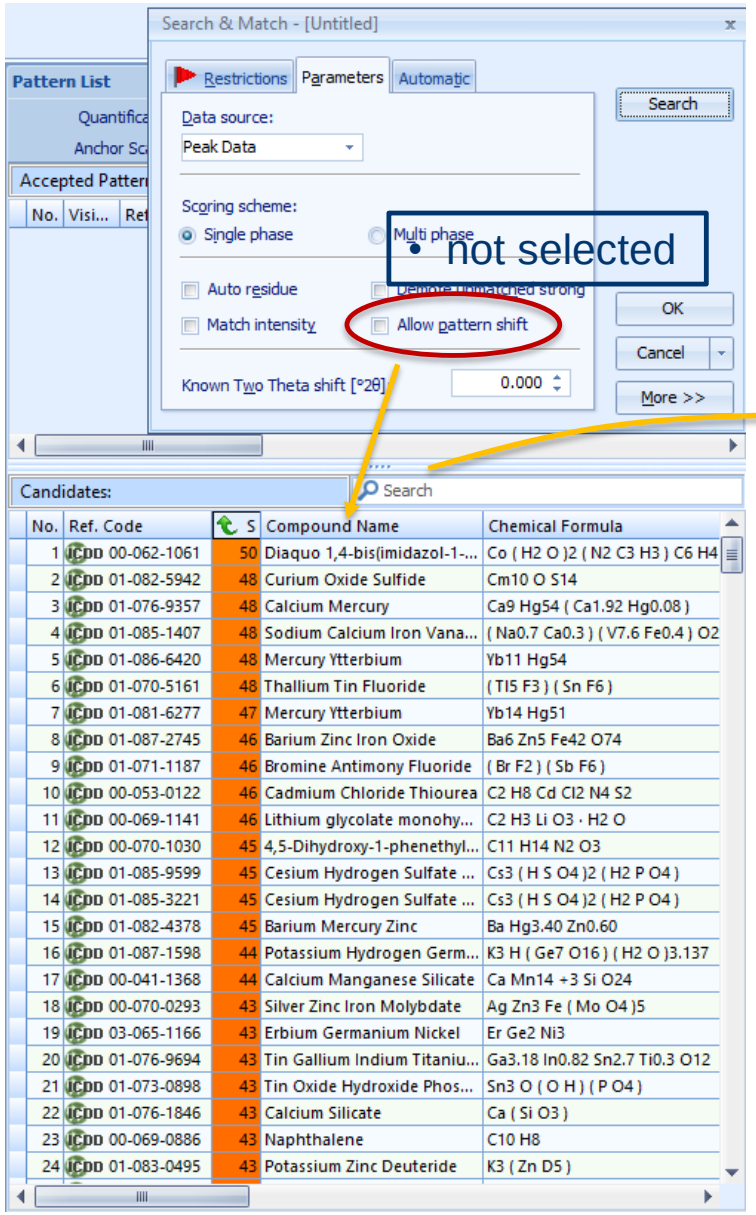


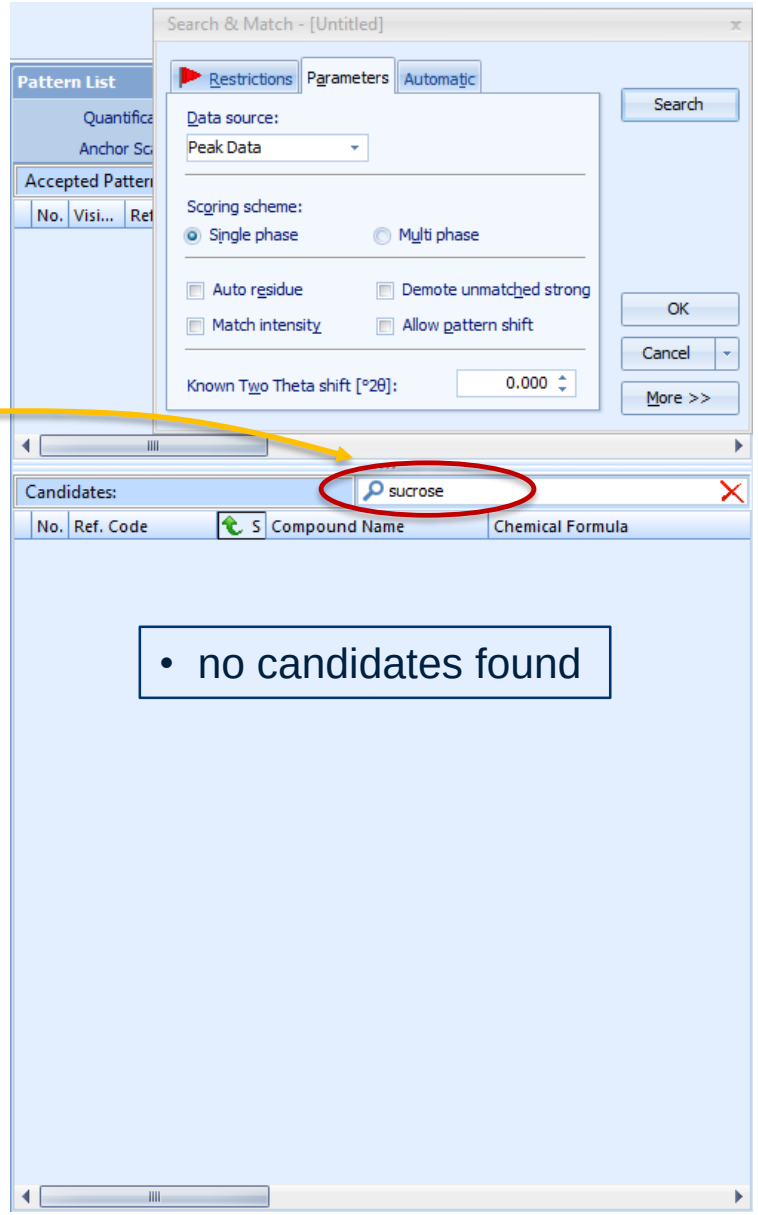


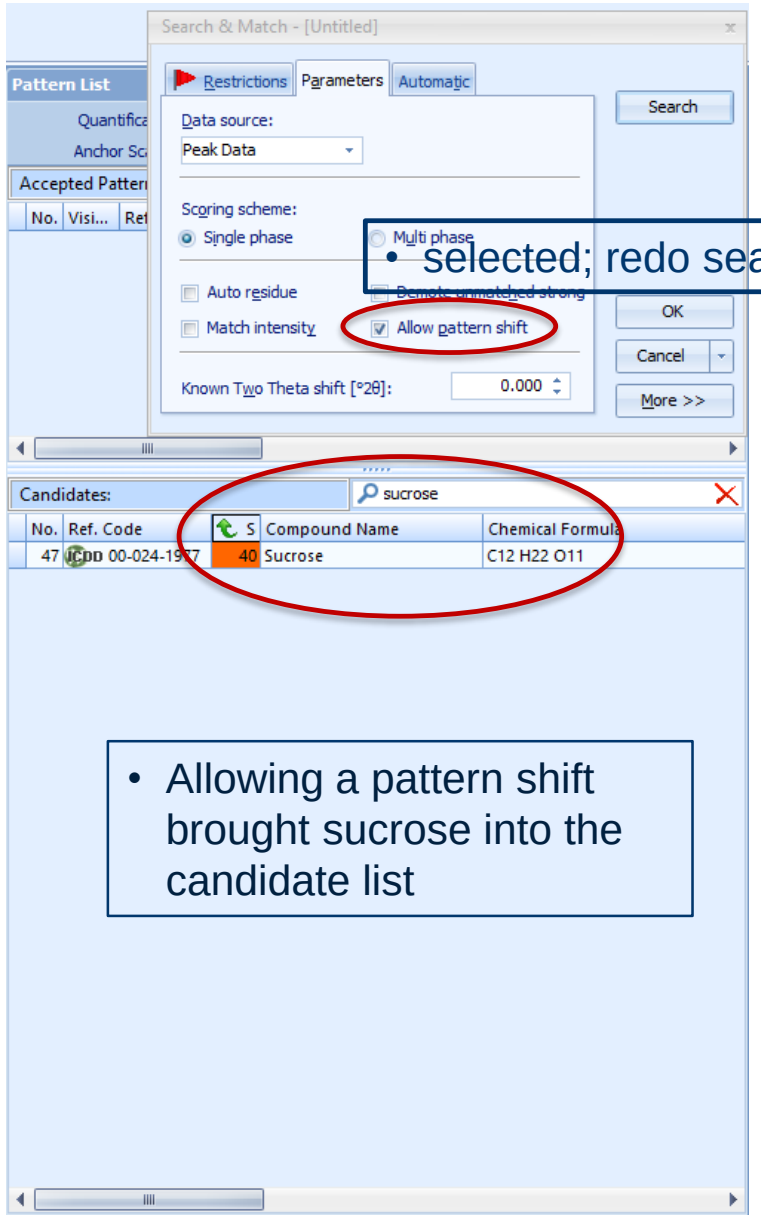
PEAK SHIFTS (see next slide)



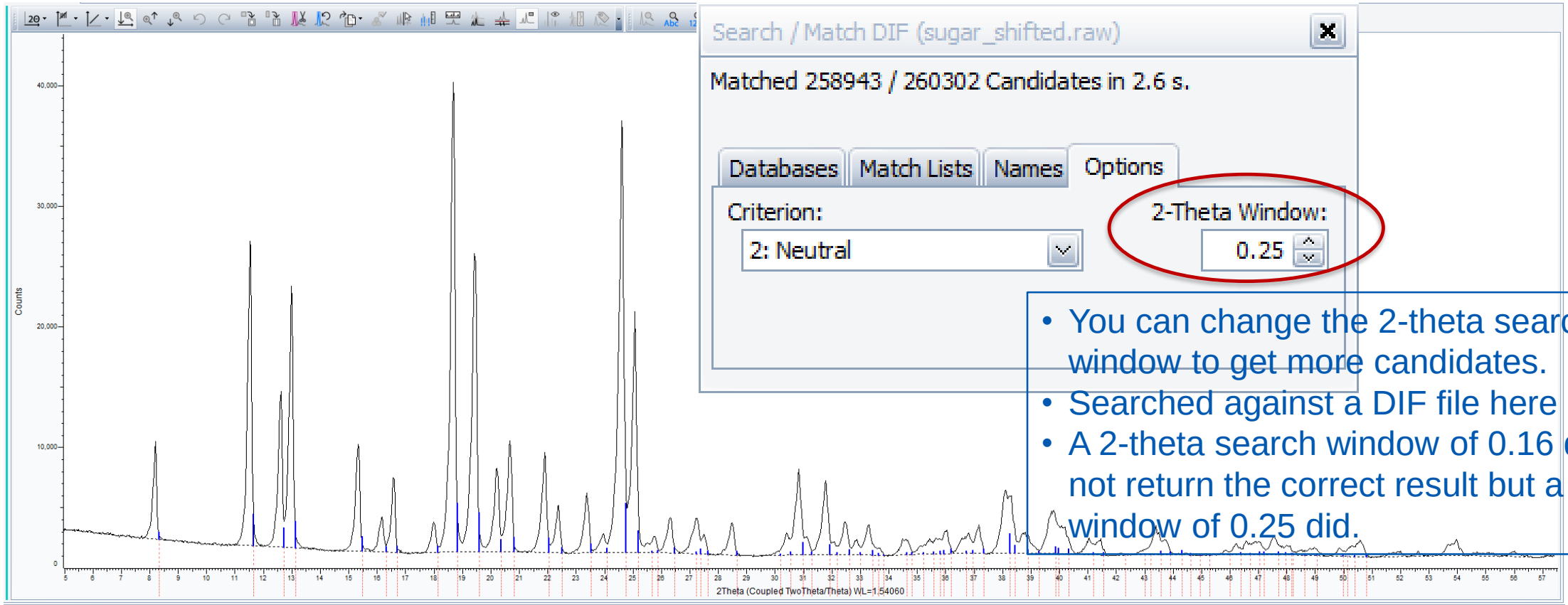
PEAK SHIFTS (see previous slide)



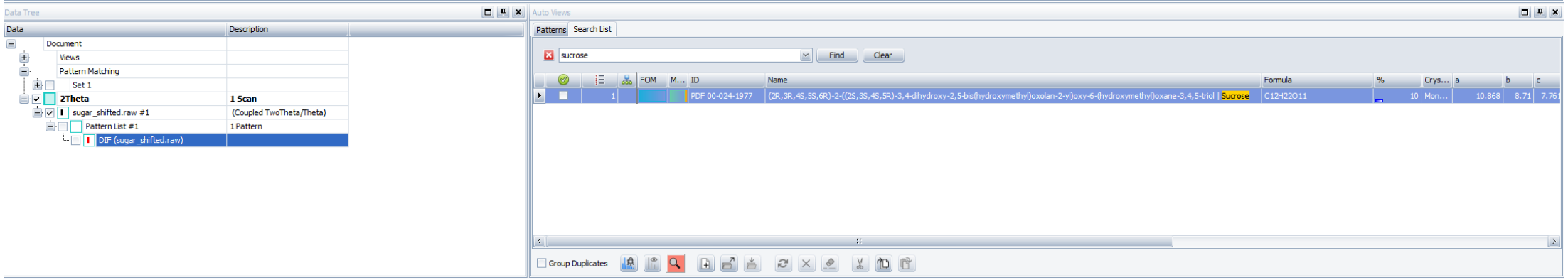




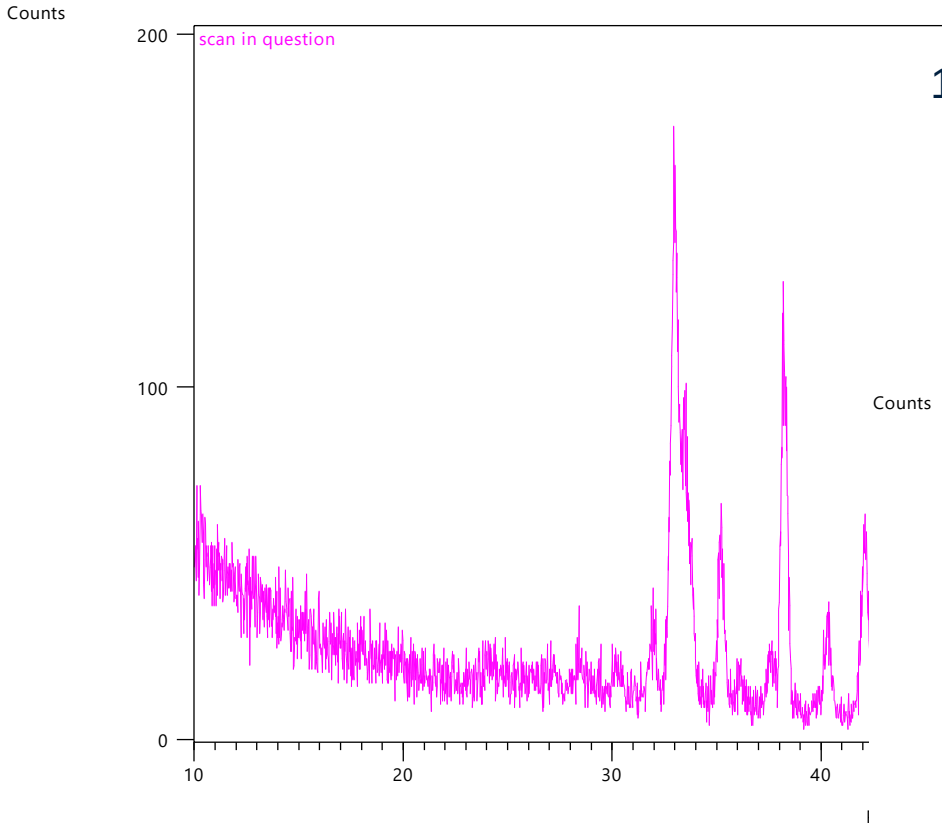
PEAK SHIFTS (see previous slide)



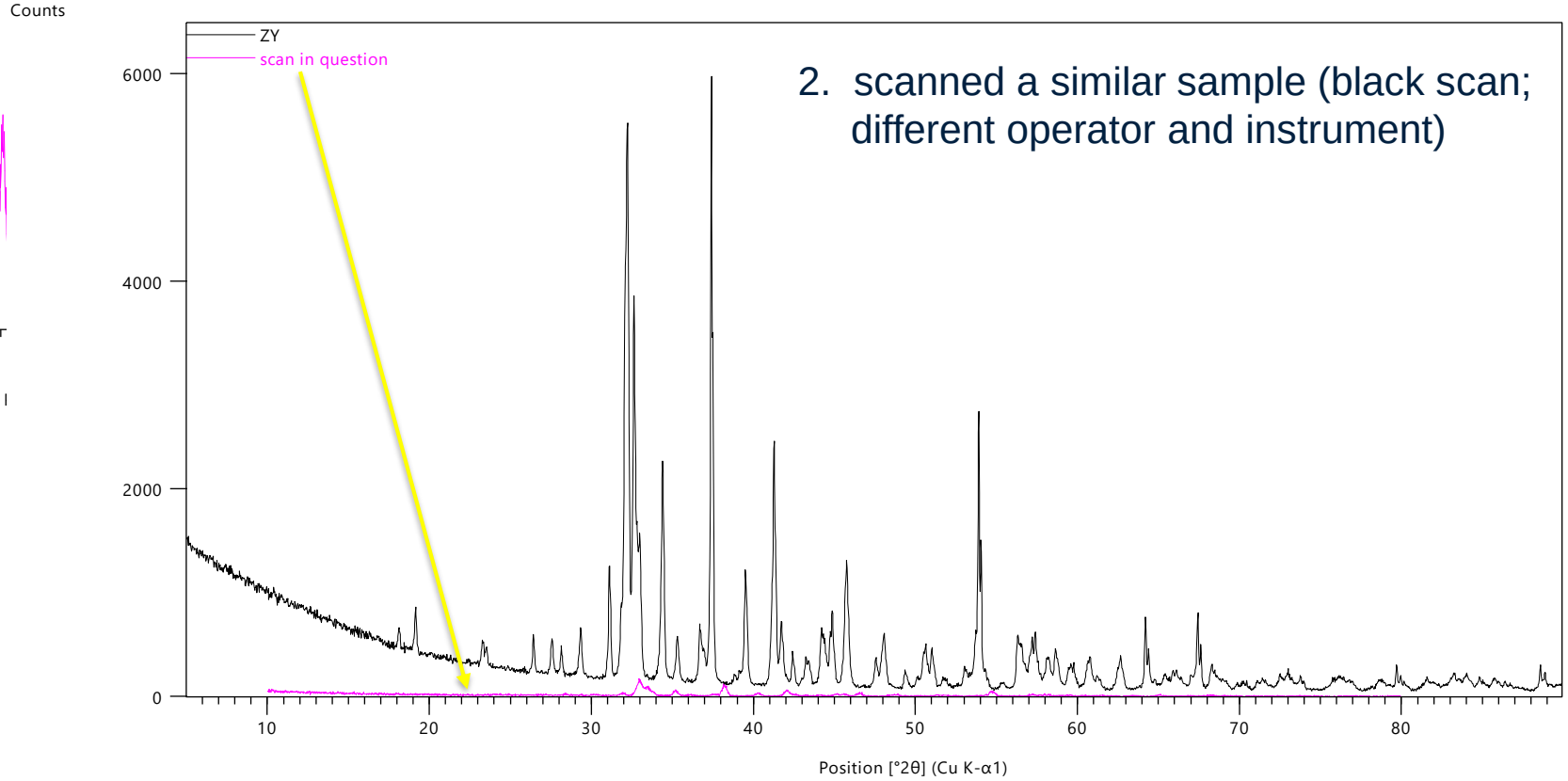
- You can change the 2-theta search window to get more candidates.
- Searched against a DIF file here
- A 2-theta search window of 0.16 did not return the correct result but a window of 0.25 did.



PEAK SHIFTS – SOMETIMES YOU HAVE TO SQUINT, part 1

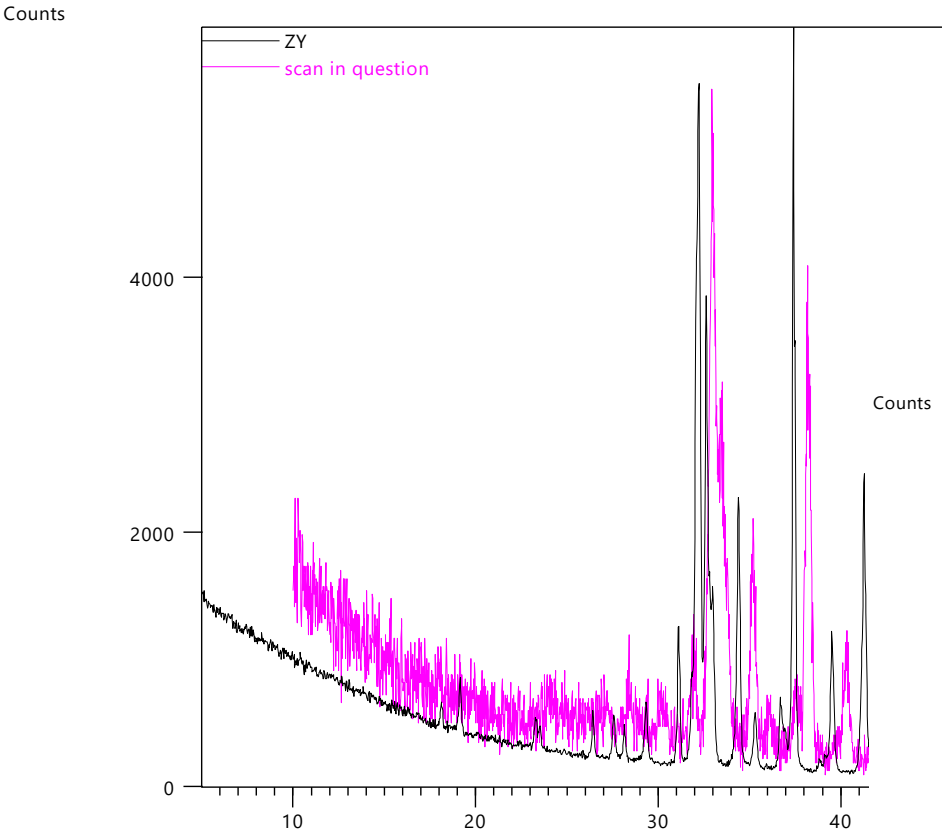


1. student run sample; had trouble identifying phase(s)

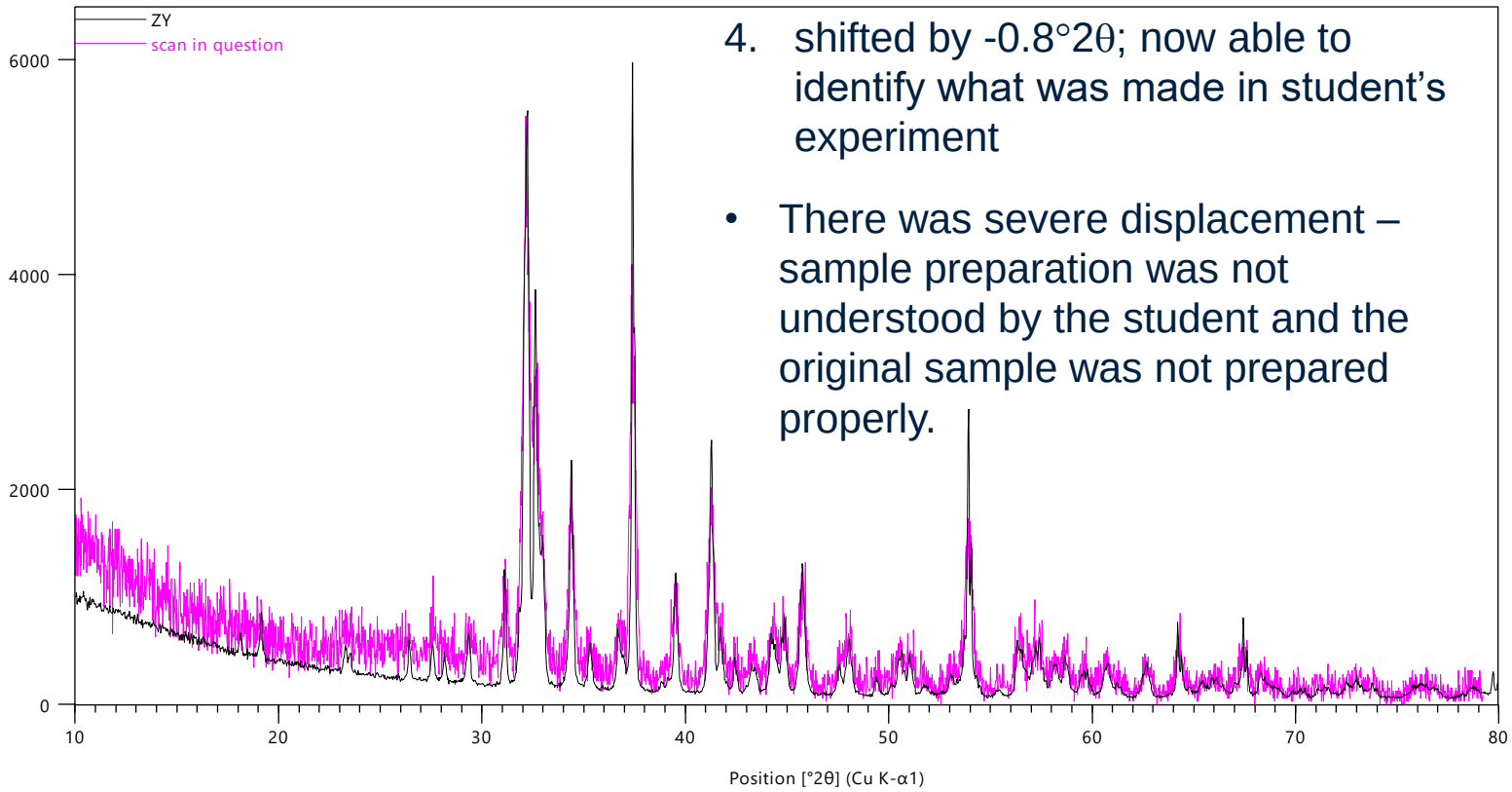


2. scanned a similar sample (black scan; different operator and instrument)

PEAK SHIFTS – SOMETIMES YOU HAVE TO SQUINT, part 2



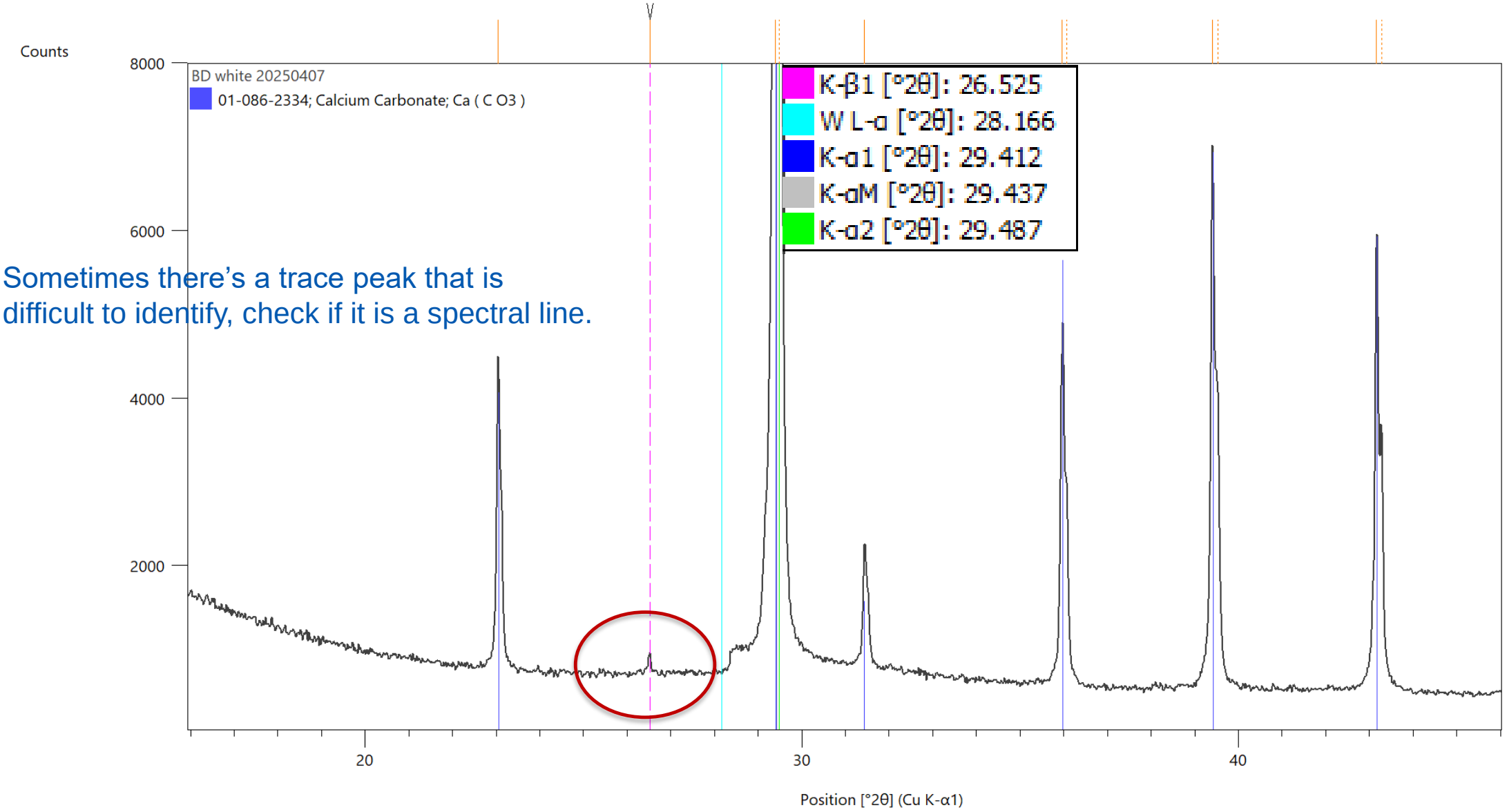
3. scaled up; if you squint you can sort of see similarities



4. shifted by -0.8°2θ; now able to identify what was made in student's experiment

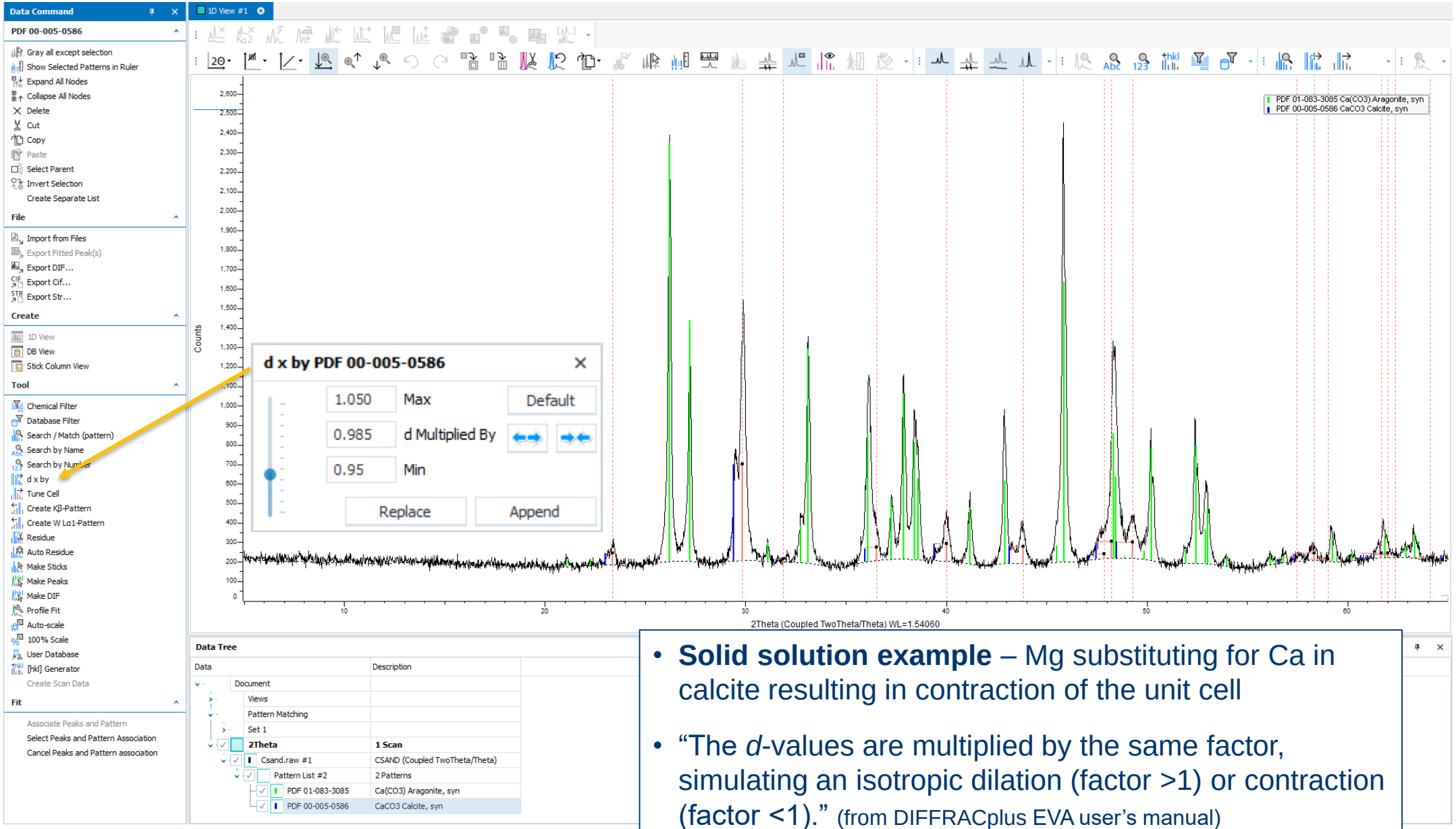
- There was severe displacement – sample preparation was not understood by the student and the original sample was not prepared properly.

MINOR PEAKS – Check for Kβ or WLα_1 lines



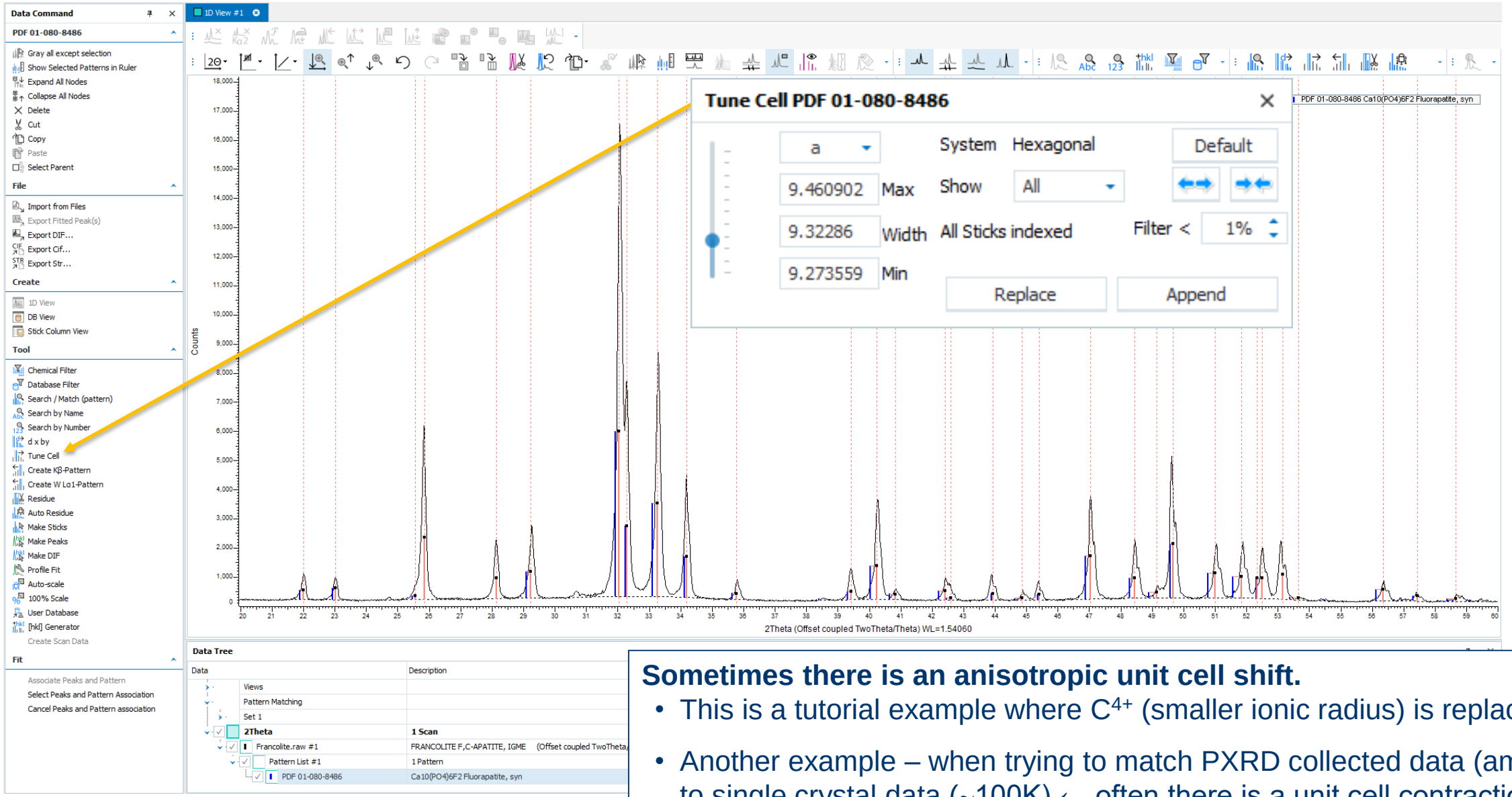
- Sometimes there's a trace peak that is difficult to identify, check if it is a spectral line.

SOLID SOLUTION – d x by (d multiplied by)



- **Solid solution example** – Mg substituting for Ca in calcite resulting in contraction of the unit cell
- "The *d*-values are multiplied by the same factor, simulating an isotropic dilation (factor >1) or contraction (factor <1)." (from DIFFRACplus EVA user's manual)

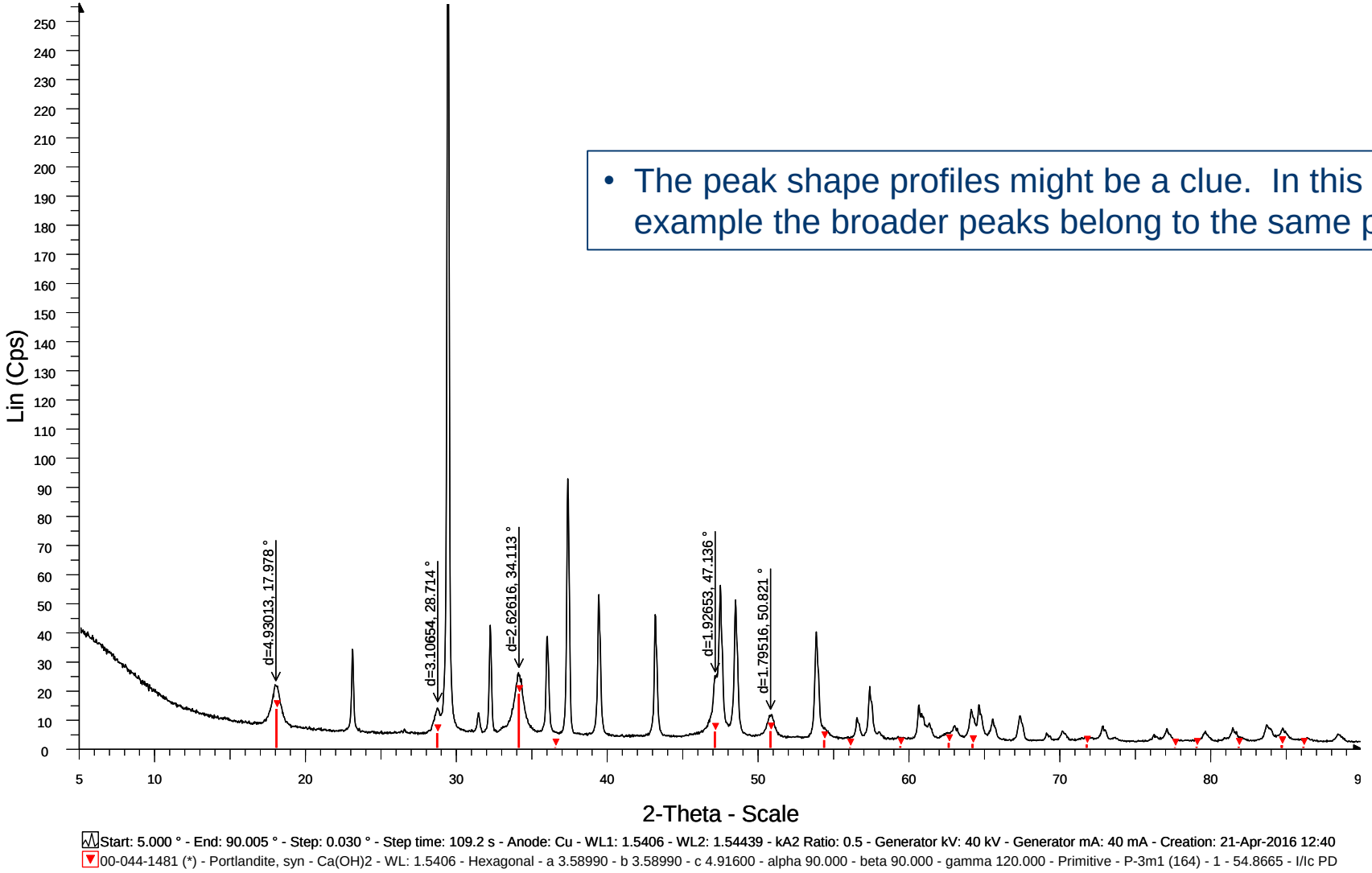
TUNE CELL – check for anisotropic unit cell shift



Sometimes there is an anisotropic unit cell shift.

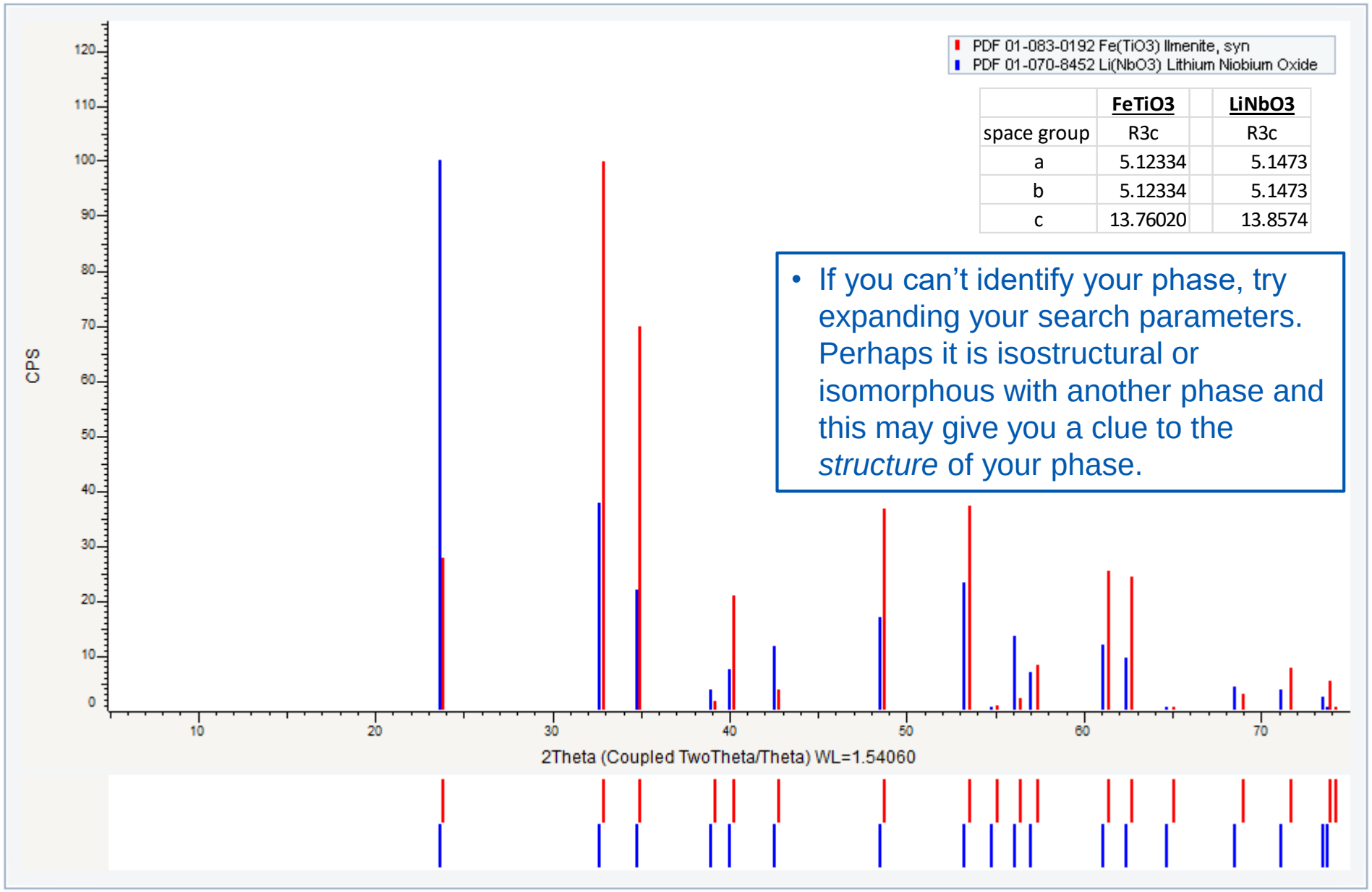
- This is a tutorial example where C^{4+} (smaller ionic radius) is replacing P^{5+}
- Another example – when trying to match PXRD collected data (ambient T) to single crystal data (~100K) ← often there is a unit cell contraction

SIMILAR PEAK SHAPES



- The peak shape profiles might be a clue. In this example the broader peaks belong to the same phase.

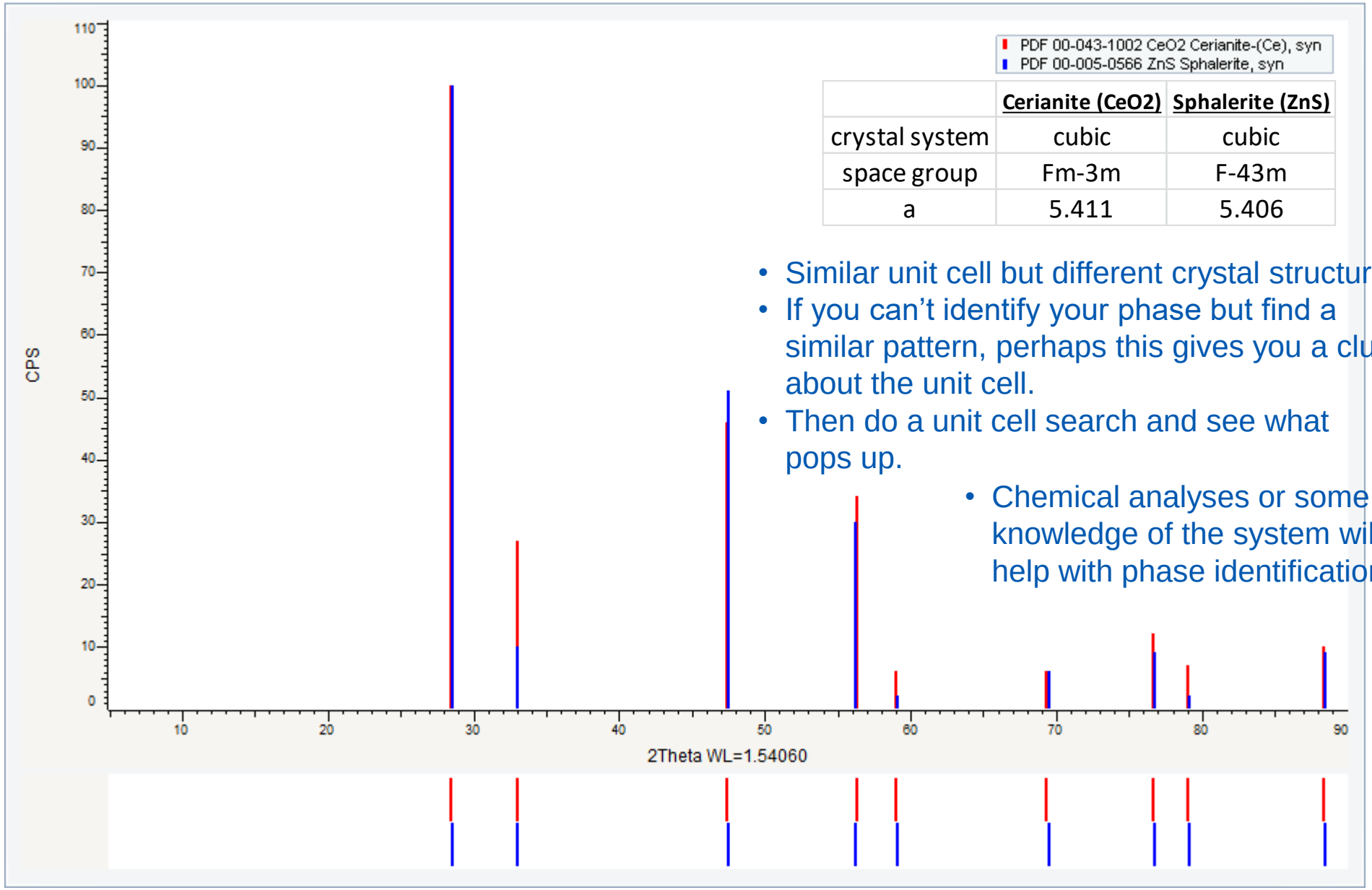
ISOSTRUCTURAL



	FeTiO3		LiNbO3
space group	R3c		R3c
a	5.12334		5.1473
b	5.12334		5.1473
c	13.76020		13.8574

- If you can't identify your phase, try expanding your search parameters. Perhaps it is isostructural or isomorphous with another phase and this may give you a clue to the *structure* of your phase.

SIMILAR PATTERN (but not isostructural)



	Cerianite (CeO2)	Sphalerite (ZnS)
crystal system	cubic	cubic
space group	Fm-3m	F-43m
a	5.411	5.406

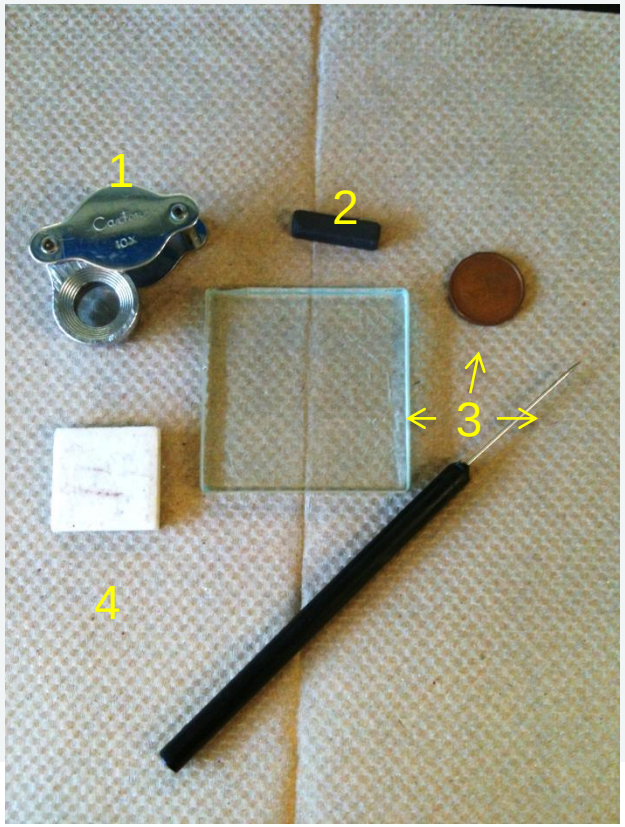
- Similar unit cell but different crystal structure.
- If you can't identify your phase but find a similar pattern, perhaps this gives you a clue about the unit cell.
- Then do a unit cell search and see what pops up.
  - Chemical analyses or some knowledge of the system will help with phase identification.

PHYSICAL PROPERTIES

- Physical properties can be useful to help with identification
  - Geologists use a basic mineral ID kit in the field

1. Visual properties – hand lens
2. Magnetism – easily tested
3. Hardness – Moh's scale
   - steel > glass > copper
4. Streak
5. Carbonate – dilute acid (not shown)

- Example



MINDSET – TIPS

Don’t miss the forest for the trees

- Don’t focus on specific elements too quickly
- I’ve had more than one student who has wasted hours trying to identify a phase when it was something simple like NaCl

Be open to possibilities

- Perhaps it is a contaminant from sample preparation or an unclean reaction vessel
- If it’s a minor phase – is there a way to concentrate it or use selective dissolution?
- Maybe it’s something new

Ask for help

- Staff at X-ray diffraction facilities
- Researchers working on the same or similar system
- Someone with fresh eyes

WHEN YOU'VE DONE ALL THAT YOU CAN

Sometimes no matter what you do:

- you are unable to identify a peak
  - it's okay to mark the peak as unidentified
- or several peaks remain unidentified
  - perhaps the phase is not in the database
- or sometimes two or more 'possibilities' exist (for example if you don't have much information about the system and more than one pattern may fit)
  - when I've done all that I can, I'll just give a list of reasonable possibilities to the client

Generally, it's good practice to not conclude beyond what the evidence is giving you.

SUMMARY

- Phase identification is like matching fingerprints – comparing your scan to a database of known phases
- The search/match process is an interactive process between the user and software + database
- XRD is sensitive to structural differences; if you have qualitative data, you should take care in drawing conclusions about the chemistry of the phases
  - chemical analyses and sample information help with phase identification
- User knowledge and experience is valuable to the process

THANK YOU

- UBC Chemistry Department
- Dr. Brian Patrick and Fahd Murad
- Dr. Beatriz Diaz Moreno
- And to you the audience ☺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